QUÍMICA EXPERIMENTAL III

PROGRAMA DE QUÍMICA INORGÁNICA

ÍNDICE

Página

Presentación

4. Experimentos en química del estado sólido:

5. Catálisis homogénea:

7. Efecto plantilla:

Presentación

En este cuadernillo de prácticas se resume la información necesaria para la realización de los experimentos de Química Inorgánica de la asignatura Química Experimental III. Los objetivos de esta parte de la asignatura son:

- Conocer las técnicas y métodos de síntesis y caracterización de compuestos inorgánicos con especial énfasis en compuestos de coordinación y organometálicos y ser capaces de llevarlas a cabo.
- Asignar y determinar la estructura de los distintos tipos de compuestos inorgánicos utilizando las técnicas instrumentales de caracterización adecuadas.
- Predecir y analizar las propiedades de los compuestos inorgánicos.
- Interpretar los datos procedentes de las reacciones químicas en el laboratorio en términos de su significación y de las teorías que la sustentan.
- Adquirir destreza en el manejo de las principales técnicas instrumentales empleadas en química y poder determinar a través del trabajo experimental las propiedades estructurales, termodinámicas, y el comportamiento cinético de los sistemas químicos.

En las páginas siguientes encontrarás instrucciones para sintetizar algunos compuestos de coordinación y organometálicos, que deberás caracterizar con los medios más habituales en química. No se trata de realizar los experimentos deprisa, ni de obtener muy altos rendimientos, sino de comprender los principios químicos asociados a cada experimento. No todos los alumnos harán los mismos experimentos; con frecuencia distintos alumnos realizarán experimentos complementarios, de forma que para discutir algunos resultados necesitarás usar datos o compuestos obtenidos por otros compañeros de laboratorio. El trabajo en equipo requiere cuidado y atención, los resultados de otros dependen de ti.

A continuación de cada guión se han recogido algunos artículos y fragmentos de libros que te pueden ayudar a realizar los experimentos y a interpretar los resultados, así como otra bibliografía recomendada. Lee este material adicional atentamente antes de realizar los experimentos. Tu profesor te instruirá en el manejo de aquellos instrumentos disponibles para la caracterización estructural y te dará las indicaciones básicas para la interpretación de los resultados. Manipular un equipo sin saber exactamente lo que se está haciendo no tiene ninguna justificación. Si no sabes usar una aparato, pregunta a tu profesor antes de hacer nada.

Como parte de tu formación, debes habituarte a identificar los riesgos inherentes a la manipulación de productos químicos y a actuar en consecuencia. No se trata solo de cumplir con las normas de seguridad básicas, sino de ser capaz de hacer una previsión de riesgos y medidas de precaución que es necesario adoptar. También te debes habituar a elaborar un cuaderno de laboratorio inteligible, detallado y ordenado. En las páginas siguientes se te dan instrucciones para ambas cosas, que deben quedar recogidas en el cuaderno de la asignatura.

Finalmente, recuerda que la asignatura está constituida por dos partes:

a) El trabajo experimental, que se desarrolla en el laboratorio.

b) La preparación de la práctica y el estudio de los temas relacionados, que se desarrolla fuera del laboratorio.

La superación de los créditos de la asignatura requiere el aprovechamiento de ambas.

1. EL CUADERNO DE LA ASIGNATURA

La realización de la asignatura lleva aparejada la elaboración de un cuaderno con las siguientes características:

a) Debe estar formado por hojas inseparables.
b) Un grupo de hojas contiguas se reservarán como "cuaderno de laboratorio". Otro grupo se reservará para escribir las notas previas a los experimentos y responder a las cuestiones y problemas asociados a cada práctica.

En el cuaderno de la asignatura no se deben incluir los cálculos matemáticos elementales ni se debe usar como "papel en sucio".

Notas previas a los experimentos.

La realización de un experimento químico requiere cierta preparación previa. Antes de hacerlo se debe tener una mínima idea de las propiedades químicas de los reactivos y productos de la reacción. Para ello lo más recomendable es acudir a los libros de Química Inorgánica básica (pueden ser el de Greenwood y Earnshaw "Chemistry of the Elements", el de Holleman y Wiberg "Inorganic Chemistry" o cualquier otro de química descriptiva) y leer las propiedades generales del elemento principal del experimento: En particular la estabilidad de los distintos estados de oxidación, reactividad y propiedades ácido-base. Eso permitirá entender el resultado del experimento y prever sus dificultades.

Además, antes de realizar el experimento es necesario preparar el material necesario y los reactivos, y evaluar los posibles riesgos que conlleva. También, si es necesario, hay que calcular las cantidades necesarias de reactivos y disolventes a usar manteniendo las proporciones molares del guión.

En las hojas reservadas para las cuestiones y problemas se deben resumir las <u>notas previas</u> a cada experimento:

Listado de material y reactivos necesario. Comprobar su disponibilidad y estado.

Posibles riesgos y precauciones que es necesario adoptar. Se debe indicar si las reacciones son fuertemente exotérmicas o si se produce desprendimiento de gases. También si en alguna de las manipulaciones hay riesgo de incendio, explosión, inundación, rotura de vidrio etc., así como si alguno de los reactivos o disolventes es particularmente tóxico o nocivo por cualquier razón y las medidas de precaución que se deben tomar para su manipulación. Se puede encontrar información acerca de las características de cada compuesto en la página de cualquier suministrador de productos químicos, así como en la página del Ministerio de Empleo y Seguridad Social: http://www.insht.es/portal/site/Insht/menuitem.a82abc159115c8090128ca10060961ca/?vgnextoid=4458908b51593110VgnVCM100000dc0ca8c0RCRD

Cuestiones y problemas.

Una vez realizado el experimento, se escribirán a continuación de las “notas previas” las respuestas a las cuestiones y problemas que aparecen al final de cada guión de prácticas.

Cuaderno de laboratorio.

En las hojas reservadas como **cuaderno de laboratorio** se escribirán los experimentos realizados de acuerdo con el siguiente esquema general:

Cada síntesis de laboratorio se escribe en una hoja par del cuaderno, y los datos experimentales de caracterización en la hoja impar siguiente, de forma que al abrir el cuaderno se pueda ver toda la información relativa a ese compuesto.

(*Código del experimento*) **AAA-01**	Fecha (opcional)
(*Nombre del experimento*)	
Ecuación química ajustada, condiciones de reacción Peso molecular o peso de la unidad fórmula de los reactivos Valores de las magnitudes experimentales medidas Moles Descripción del experimento Cantidad obtenida % rendimiento	

En la hoja siguiente se da un ejemplo.

AAA-01 **25-12-2001**

Síntesis de trans-$[Pd(C_6F_5)(SbPh_3)_2(NCMe)]BF_4$

$$[Pd(C_6F_5)Br(SbPh_3)_2] + AgBF4 \xrightarrow{CH3CN} [Pd(C_6F_5)(CH3CN)(SbPh_3)_2]BF4 + \downarrow AgBr$$

P_M = 1059.54	PM = 194,67
1.5484 g	0.2845 g
1.461 mmol	1.461 mmol

Sobre una disolución de $AgBF_4$ (0.2845 g, 1.461 mmol) en acetonitrilo (15 ml) se añadió $[Pd(C_6F_5)Br(SbPh_3)_2]$ (1.5484 g, 1.461 mmol). Se mantuvo con agitación a oscuras durante una hora y se filtró en kieselgur para eliminar el AgBr formado en la reacción. Se eliminó el disolvente a vacío hasta un volumen de 5 ml, se añadió Et_2O (15 ml), se filtró en placa lavando con Et_2O (3 x 5 ml) y se secó a vacío. El compuesto se recristalizó disolviéndolo en 50 mL de CH_2Cl_2, filtrando un residuo blanco insoluble y añadiendo n-hexano (25 mL). Al concentrar en el rotavapor la disolución cristaliza el compuesto amarillo claro.
Se obtienen 1.2129 g.

Rendimiento: 75%.

Análisis elemental calculado para $C_{44}H_{33}NSb_2BF_9Pd$: C 47.72, H 3.00, N 1.26 encontrado: C 46.71, H 3.14, N 1.15.

Conductividad: medido en acetona.

20 mg en 25 mL , disol $7 \cdot 10^{-4}$ M(supuesto Pm = 1107.49 g/mol)

κ = 101 μScm^{-1}. Acetona pura κ = 3.1 μScm^{-1}

Λ_M = 140 $\mu Scm^2 mol^{-1}$ (electrolito 1:1)

IR (en Nujol-polietileno) zona de tensión CN: 2326 y 2296 cm^{-1}

RMN (ARX-300), 6 mg en 0.6 mL de $CDCl_3$. Registrado a temperatura ambiente.
^1H RMN: δ = 7.6-7.3 (m, 30H, Ph), 2.11 (s, 3H, $CH3_CN$).

^{13}C RMN DEPT δ = 135.36 (Ph), 131.43 ($Cp_{ara,}$ Ph), 130.10 (Ph), 127.65 ($Ci_{pso,}$ Ph), 3.09 (CH3 de $CH3_CN$).

^{19}F RMN δ = -112.66 (m, 2F, Fo_{rto}), -153.07 (BF4), -153.12 (BF4), -157.54 (t, J = 19 Hz, 1F, Fp), -160.51 (m, 2F, F_{meta}).

Todos los experimentos han de *codificarse* con un grupo de dos o tres letras (preferentemente las iniciales del alumno), y numerarse consecutivamente. Ejemplo, el alumno Arturo Arellano Álvarez usaría como código para su primer experimento: AAA-01.

Este código debe utilizarse para rotular los distintos documentos asociados al experimento, espectros, análisis, etc. Ha de figurar también en las etiquetas de todos los productos obtenidos.

A continuación se debe escribir el *nombre del experimento*, que debe reflejar el propósito del mismo. (Si es una síntesis, qué producto se sintetiza, si un experimento de otra naturaleza, en qué consiste o qué se pretende demostrar o comprobar).

Las reacciones químicas deben escribirse de forma que quien lea el cuaderno tenga una visión inmediata de lo que se ha hecho: cantidades y proporción relativa de reactivos, y condiciones de reacción. Para ello se debe escribir la reacción química ajustada, y sobre la flecha las condiciones de reacción: disolvente, temperatura (si no es temperatura ambiente). Bajo cada reactivo de debe escribir su peso molecular o de la unidad fórmula, y si se trata de una disolución, su concentración molar y el disolvente en que está preparada. En una tercera línea hay que especificar la cantidad que se ha empleado en las unidades en que se ha medido (si es un sólido su peso, si un líquido o una disolución su volumen). En la cuarta línea se debe escribir la cantidad en moles a la que corresponde la cantidad medida de cada reactivo, de esta forma se puede comprobar inmediatamente si los reactivos están o no en proporciones estequiométricas.

La *descripción del experimento* debe incluir la descripción detallada de todas las operaciones que se efectúan para llevar a cabo el experimento. Esta parte, probablemente será muy semejante a la que aparece en el guión de la práctica. No se trata de ser creativo, sino de adquirir el hábito de redactar correctamente los procedimientos experimentales para poder hacerlo cuando no exista guión de apoyo. Además de la descripción de la síntesis o del experimento, ha de incluirse cualquier incidente, variación, o modificación del guión, así como cualquier observación experimental adicional.

A continuación se debe indicar el resultado del experimento, si se trata de una síntesis, el peso y el rendimiento expresado en tanto por ciento.

En la hoja siguiente (normalmente la hoja impar) se deben incluir los datos espectroscópicos y analíticos asociados a la muestra:

- *Datos de conductividad*: disolvente empleado, temperatura, concentración de la muestra utilizada, conductividad específica medida de la disolución y del disolvente puro y conductividad molar.
- *Datos de espectroscopia uv/vis*: Disolvente y concentración de la muestra. Longitud de onda y intensidad de las bandas de absorción.
- *Datos de espectroscopia IR*: Disolvente o agente dispersante utilizado. Número de onda de las absorciones más significativas.
- *Datos de espectroscopia RMN*: Disolvente y concentración aproximada de la muestra. Temperatura a la que se ha adquirido el espectro. Equipo en el que se ha registrado la muestra y núcleos registrados. Para cada espectro, desplazamiento químico, multiplicidad y intensidad integrada de todas las señales y valor de las constantes de acoplamiento.
- *Datos analíticos*. Ensayos analíticos realizados cuantitativos y cualitativos y su resultado.

Normas de seguridad:

Ver la normativa y los consejos del Servicio de Prevención de Riesgos Laborales de la UVa:

http://www.uva.es/opencms/contenidos/serviciosAdministrativos/recursosHumanos/prevencionRiesgosLaborales/consejosPreventivos/Enlaces_Listados_Quimicos/Borrador_normas_usuario.

Bibliografía:

Al final de cada práctica se señala la bibliografía que se debe consultar.

Otras fuentes de interés:

Dodd, R.E. y Robinson, P.L. “Química Inorgánica Experimental”. Reverté, 1981.

Schlessinger, G.G. “Preparación de Compuestos Inorgánicos en el Laboratorio”. Ed. Continental, 1986.

Szafran, Z.; Pike, R.M.; Singh, M.M. “Microscale Inorganic Chemistry: A Comprehensive Laboratory Experience”. Wiley, 1991.

Woollins, J.D. Ed. “Inorganic Experiments” VCH, Weinheim, 1994

Angelici, R.J. “Técnicas y Síntesis en Química Inorgánica”. Reverté, 1979.

Brauer, G. “Química Inorgánica Preparativa”. Reverté, 1958.

2. PREPARACIÓN Y CARACTERIZACIÓN DE COMPLEJOS DE NÍQUEL.

Los complejos mononucleares de níquel(II) presentan una amplia variedad de estructuras, siendo las más habituales la octaédrica, la tetraédrica y la planocuadrada. Los complejos octaédricos y tetraédricos tienen generalmente dos electrones desapareados mientras que los planocuadrados son diamagnéticos.

Muchos ligandos utilizados en química de la coordinación pueden actuar únicamente como monodentados (por ejemplo PPh_3), sin embargo hay otros que pueden enlazarse de diferentes formas. El ión NO_3^- puede encontrarse libre sin coordinarse (simetría D_{3h}) pero también puede actuar como ligando monodentado (coordinándose a través de uno de sus oxígenos) o bidentado (coordinándose a través de dos de sus oxígenos) en complejos mononucleares. Por otro lado hay ligandos que pueden coordinarse a través de átomos diferentes. Éste es el caso del ión NCS^- que puede coordinarse a través del azufre, del nitrógeno, o a través de ambos actuando como puente entre dos metales.

Esta práctica propone la síntesis y la caracterización estructural de dos complejos de níquel(II). La determinación de las geometrías de los complejos y el modo de coordinación de los ligandos se realizará sobre la base de los resultados experimentales de espectroscopia vibracional IR.

Procedimiento experimental

Preparación de $[Ni(NCS)_2(PPh_3)_2]$.

Una mezcla de nitrato de níquel hexahidratado (1.4 g), tiocianato potásico pulverizado (1.4 g) y butanol (75 mL) se calienta a reflujo durante dos horas. La mezcla amarillenta resultante se enfría y se filtra obteniéndose una disolución verde. Esta se calienta a ebullición y se añade sobre una disolución, también a ebullición, de trifenilfosfina (2.623 g) en butanol (25 mL). Por enfriamiento lento se obtiene el producto buscado en forma cristalina que se filtra, se lava y se seca por succión.

Preparación de $Ni(NO_3)_2(PPh_3)_2$.

Sobre una disolución de nitrato de níquel hexahidratado (1.4 g) en 1.5 mL de agua se añaden 25 mL de ácido acético glacial, se añade otra caliente de trifenilfosfina (2.6 g) también en ácido acético glacial (25 mL). La disolución resultante se mantiene templada por calentamiento suave y con agitación, apareciendo paulatinamente el producto como un sólido verde. La mezcla se deja en reposo 24 horas y se filtra el producto obtenido que se lava dos veces con acetona y se seca por succión.

Cuestiones y experimentos adicionales.

1) Describir las reacciones globales que tienen lugar en cada una de las síntesis realizadas y calcular los rendimientos de los productos sintetizados.

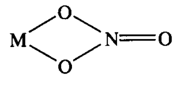
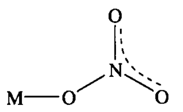
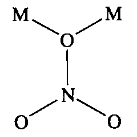
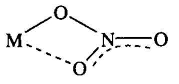
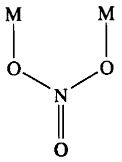
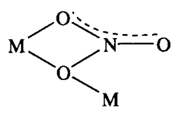
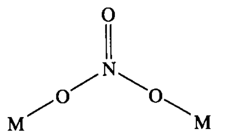
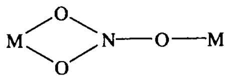
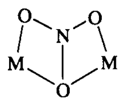
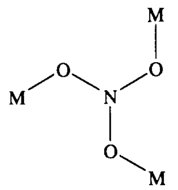
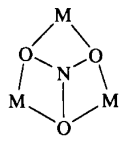
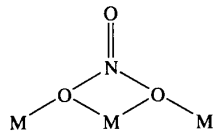
2) Indicar todos los posibles isómeros de los compuestos preparados sabiendo que los dos grupos nitrato están enlazados al níquel.

3) Registrar e Interpretar los espectros IR (en KBr) de los compuestos preparados.

Bibliografía: Nakamoto, K., Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part A, Theory and Applications in Inorganic Chemistry, Wiley, 1997. **Ver páginas siguientes.** (Extraidas del texto de K. Nakamoto, *Infrared and raman spectra of inorganic and coordination compounds*, 4th edition, John Wiley and Sons: New York, 1986).

The Nitrate Ion

This ion has several structural roles,[134] as follows:

The most common forms of the nitrate ion are symmetrical bidentate followed by η^1. The free NO_3^- ion has relatively high symmetry (D_{3h}); thus its ir spectrum is fairly simple. The totally symmetric N—O stretching mode is not ir active, but the doubly degenerate N—O stretching mode gives rise to a strong band at ~1390 cm^{-1}. There are also two ir-active deformation modes, one of which is doubly degenerate, at 830 and 720 cm^{-1}. When NO_3^- is coordinated, its effective symmetry is reduced, causing the degeneracies to split and all modes (six) to be ir active. Hence, it is possible to distinguish between ionic and coordinated NO_3 groups.

Because the two commonest forms of coordinated NO_3^- have the same effective symmetry, hence the same number of ir-active vibrational modes, criteria for distinguishing between them must be based on the positions of the bands rather than their number. In practice, the situation is quite complex and there are no entirely straightforward criteria. This is because the array of frequencies depends on both the geometry and strength of coordination.

---

[134] C. Orvig *et al., Inorg. Chem.* **1995,** *34,* 4921; P. N. V. P. Kumar and D. S. Marynick, *Inorg. Chem.* **1993,** *32,* 1857; R. Han and G. Parkin, *J. Am. Chem. Soc.* **1991,** *113,* 9707; O. Yamauchi *et al., Inorg. Chem.* **1996,** *35,* 7148.

III-6. THIOCYANATO AND OTHER PSEUDOHALOGENO COMPLEXES

The CN^-, OCN^-, SCN^-, $SeCN^-$, CNO^-, and N_3^- ions are called "pseudohalide ions," since they resemble halide ions in their chemical properties. These ions may coordinate to a metal through either one of the end atoms. As a result, the following linkage isomers are possible:

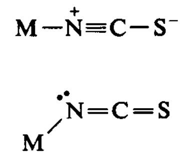
M—CN, cyano complex	M—NC, isocyano complex
M—OCN, cyanato complex	M—NCO, isocyanato complex
M—SCN, thiocyanato complex	M—NCS, isothiocyanato complex
M—SeCN, selenocyanato complex	M—NCSe, isoselenocyanato complex
M—CNO, fulminato complex	M—ONC, isofulminato complex

Two compounds are called true linkage isomers if they have exactly the same composition and different linkages mentioned above. A well-known example is nitro (and nitrito) pentammine Co(III) chloride discussed in Sec. III-2. A pair of true linkage isomers is difficult to obtain since, in general, one form is much more stable than the other. As will be shown later, several pairs of new linkage isomers have been isolated, and infrared spectroscopy has proved to be very useful in distinguishing them.

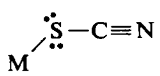
(1) Thiocyanato (SCN) Complexes

The SCN group may coordinate to a metal through the nitrogen or the sulfur or both (M—NCS—M′). In general, Class A metals (first transition series such as Cr, Mn, Fe, Co, Ni, Cu, and Zn) form the M—N bonds, whereas Class B metals (second half of the second and third transition series such as Rh, Pd, Ag, Cd, Ir, Pt, Au, and Hg) form the M—S Bonds.[191] However, other factors such as the oxidation state of the metal, the nature of other ligands in a complex, and steric consideration also influence the mode of coordination. Mitchell and Williams[192] have shown that the CN stretching frequencies are generally lower in the M—NCS complexes than in the M—SCN complexes. The C—S stretching frequency is more useful in distinguishing these two isomers: 780–860 cm^{-1} for the M—NCS and 690–720 cm^{-1} for the M—SCN group.[193-195] The NCS bending frequency is also different between two isomers; 450–490 cm^{-1} for the M—NCS and 400–440 cm^{-1} (often accompanied by weaker bands at higher frequency side) for the M—SCN group.[194,195] Table III-24 lists some results obtained by Sabatini and Bertini.[195] The M—NCS group is linear or bent, while the M—SCN group is always bent. This seems to suggest that the following resonance structures are predominant in each case:

M—NCS Group



M—SCN Group



Pecile[196] has noted that the integrated intensity of the CN stretching band can also be used to distinguish two linkage isomers.

Clark and Williams[197] have obtained the infrared spectra of tetrahedral $[M(NCS)_2L_2]$ and octahedral $[M(NCS)_2L_4]$-type complexes (M = Fe, Co, Ni, etc.; L = pyridine, etc.) and discussed stereochemistry from infrared spectra. A similar study has been made by Nelson and Shepherd.[198] Bennett et al.[199] have obtained the infrared spectra of $[Cr(NCS)_4L_2]^-$, where L is an amine or phosphine, and have assigned the Cr—N and Cr—L stretching bands in addition to the NCS group vibrations. In $[M(NCS)_2L_2]$-type complexes in which M is Pt(II) or Pd(II), the NCS group is S-bonded if L is an amine and N-bonded if L is a phosphine.[193] This is because a strong π-acceptor such as a tertiary phosphine makes the *d*-orbitals of the metal less available for bonding with the π-orbitals of sulfur. Jennings and Wojcicki[200] obtained the infrared spectra of square-planar $[Rh(CO)(NCS)L_2]$, $[Rh(NCS)L_3]$, $[Rh(CO)_2(NCS)_2]^-$, and $[Rh_2(NCS)_2L_4]$-type complexes in

TABLE III-24. VIBRATIONAL FREQUENCIES OF ISOTHIOCYANATO AND THIOCYANATO COMPLEXES (CM^{-1})[195]

Compound[a]	ν(CN)	ν(CS)[b]	δ(NCS)
K[NCS]	2053	748	486, 471
$(Et_4N)_3[Cr(—NCS)_6]$	2078	–	483
$(Et_4N)_2[Co(—NCS)_4]$	2065	844 838	481
$(Et_4N)_4[Ni(—NCS)_6]$	2112 2103	828	470
$(Et_4N)_2[Zn(—NCS)_4]$	2072	837	482
$(Et_4N)_2[Pd(—SCN)_4]$	2112 2109	698 694	465, 433 429, 418
$(Et_4N)[Au(—SCN)_4]$	2127	695	454, 415
$(Et_4N)_2[Pt(—SCN)_6]$	2120	692	461, 457 418, 415

[a] Et, C_2H_5.

[b] The S-bonded complex may exhibit a band at 880–810 cm^{-1} which is the first overtone of δ(NCS). Care must be taken, therefore, in distinguishing this band from ν(CS).[205]

which L is a phosphine, an arsine, a stibine, or a phosphite. Infrared spectra show that all these Rh(I) complexes are N-bonded. The *cis* and *trans* isomers of Co(III)-NCS complexes can be distinguished from infrared spectra.[201,202]

As stated before, the distinction of true linkage isomers by infrared spectroscopy has been made for $[Co(NH_3)_5(-NO_2$ or $-ONO)]Cl_2$[10] and $[KFeCr(CN)_6]$[184]. Basolo et al.[203] succeeded in isolating true linkage isomers of

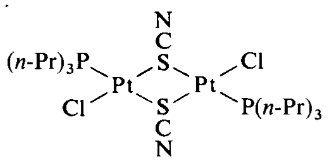
trans-$[Pd(As(Ph)_3)_2(NCS)_2]$:

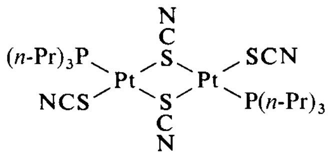
The bright-yellow, N-bonded complex absorbs at 2089 (CN stretching) and 854 cm^{-1} (CS stretching); the yellow-orange, S-bonded complex absorbs at 2119 cm^{-1} (CN stretching), although the phenyl absorption near 700 cm^{-1} obscures its C—S stretching band. Infrared spectra of linkage isomers have also been reported for $[Pd(bipy)(NCS/SCN)_2]$[204,205] and $[Pd(As(n\text{-}C_4H_9)_3)_2(NCS/SCN)_2]$.[205] A complex of the composition $[Cu(tren)(NCS)_2]$ (tren, triaminotriethylamine) exhibits two CN stretching (2094 and 2060 cm^{-1}) and two CS stretching (818 and 745 cm^{-1}) bands. Based on this and other data, Raymond and Basolo[206] suggested that this complex may contain both Cu—NCS and Cu—SCN linkages. Later, Jain and Lingafelter[207] have shown from x-ray analysis that one NCS group is bonded to the metal through nitrogen and the other group is not coordinated with it. Bertini and Sabatini[208] suggest that

$[Pd(4,4'\text{-dimethyl-bipy})(NCS)_2]$

may contain both types of coordination, since it exhibits two CN stretchings at 2120 and 2090 cm^{-1}.

The NCS group also forms a bridge between two metal atoms. The CN stretching frequency of a bridging group is generally higher than that of a terminal group. For example, $HgCo(NCS)_4$(Co—NCS—Hg) absorbs at 2137 cm^{-1}, whereas $(Et_4N)_2$ $[Co(—NCS)_4]$ absorbs at 2065 cm^{-1}. According to Chatt and Duncanson,[209] the CN stretching frequencies of Pt(II) complexes are 2182–2150 cm^{-1} for the bridging and 2120–2100 cm^{-1} for the terminal NCS group. $[(P(n\text{-}Pr)_3)_2Pt_2(SCN)_2Cl_2]$ (compound I) exhibits one bridging CN stretching, whereas $[(P(n\text{-}Pr)_3)_2Pt_2(SCN)_4]$ (compound II) exhibits both bridging and terminal CN stretching bands. Thus the infrared spectra suggest the structure of each compound to be:


I


II

(*n*-Pr, *n*-Propyl)

3.- PREPARACIÓN DE ACETILACETONATOS DE METALES DE TRANSICIÓN.

Los acetilacetonatos forman con los elementos metálicos una importante clase de complejos. El ligando acetilacetonato forma un quelato muy estable capaz de coordinarse a prácticamente todos los átomos metálicos de la tabla peródica. A continuación se propone la síntesis de cuatro de esos complejos, que responden a la fórmula general M(acac)$_3$, octaédricos, cuyas diferentes propiedades se deben únicamente al diferente centro metálico.

3.A. Síntesis de Co(acac)$_3$.

Add approximately 1.0 g of powdered Co(II) carbonate into a 50-mL Erlenmeyer flask and add 8 mL of acetylacetone. Drop in a small magnetic stir bar and cover with a small watch glass. Place the reaction vessel into a water bath on a stirring hot plate.
(Note: do not set the flask directly on the bottom of the water bath; instead, clamp it so that the flask is suspended within the water bath with its contents below the water line; refill the bath as needed as the water evaporates during heating).

Stir the reaction using the magnetic stirring bar and heat the reaction to about 80°C , maintaining it at this temperature for approximately 5 minutes. Slowly add 6 mL of 10% hydrogen peroxide (H_2O_2) drop-wise at a rate of 1-2 mL/min using a disposable pipette while continuing to stir the reaction mixture. **(CAUTION: 10% H_2O_2 will damage the surface of the skin! Wear gloves or be extra careful! The reaction will bubble vigorously.)** Reheat the mixture to 80°C after the addition of H_2O_2 is complete, then add an additional 6 mL of H_2O_2 in the same manner. After the second addition of H_2O_2 is complete, remove the water bath, place the flask directly on the hotplate surface and briefly bring the flask to boiling. Cool the mixture to room temperature and then place it in an ice bath for about 15 minutes or until crystallization appears to be complete. Filter the product using a Büchner funnel, washing remnants out of the flask with deionized water (2 x 5 mL). Wash with several small (2-3 mL) volumes of cold ethanol (make sure you chill it first or it will dissolve your compound!). Allow the compound to dry until the next lab period and then weigh the compound to get the yield of dry product.

3.B. Síntesis de $Cr(acac)_3$.

Heat a water bath on a stirring hotplate. Add approximately 1.30 g of $CrCl_3•6H_2O$ into a 50-mL Erlenmeyer flask. Drop in a small magnetic stirring bar, add 20.0 mL of distilled water and stir briefly. When the chromium compound has dissolved into solution, add 5.0 g of urea and 4.0 mL of acetylacetone. Clamp the flask in place in the water bath (see note in part A) and heat the water bath to a temperature greater than 90°C. Heat the mixture, uncovered and with vigorous stirring, and deep maroon crystals will begin to form. After one hour, allow the reaction to cool to room temperature, and then place it in an ice-bath to complete crystallization (Note: if you do not see solid after 1 h, continue to heat and stir until you do: sometimes it takes a bit longer!). Collect the product by vacuum filtration using a Büchner funnel. Wash out the flask and the crystals on the filter with plenty of deionized water (about 3 x 10 mL). Allow the product to dry until the next lab period and then weigh the dry final product to determine the yield of dry product.

3.C. Preparation of $Mn(acac)_3$.

Add approximately 1.0 g of $MnCl_2•4H_2O$ and 2.6 g of sodium acetate trihydrate into a 100-mL Erlenmeyer flask. Add a stirring bar, and dissolve the solids in a minimal amount of distilled water (add very small amounts at a time until the solids dissolve completely). When the solids are dissolved, add 4.0 mL of acetylacetone with continued stirring. Prepare another solution containing 200 mg of $KMnO_4$ in 10 mL of deionized water. Make sure you stir this for quite a while - $KMnO_4$ is difficult to dissolve and it color makes it hard to see if it has dissolved!- Add the $KMnO_4$ solution slowly and drop-wise, with stirring, to the above mixture. After addition is complete, a small portion of distilled water (1-2 mL) should be pipetted (using a disposable pipet) into the flask or beaker originally containing the $KMnO_4$ solution and then used to rinse the walls of the reaction flask to remove any permanganate that is sticking to the side. After stirring the mixture for about five minutes, add drop-wise a second 2.6 g portion of sodium acetate trihydrate dissolved in a minimal amount of water. Heat the resulting mixture directly on a hotplate for 10 minutes at about 70°C (put a thermometer directly in the reaction flask) and then set aside to cool to room temperature. Collect the dark brown precipitate on a Büchner funnel. Use small portions of deionized water (2 x 5 mL) to wash any remaining crystals out of the flask. Allow the product to dry until the next lab period and then weigh the dry final product to determine the yield of dry product.

3.D. Preparación de $Fe(acac)_3$.

Add approximately 1.3 g of $Fe(NO_3)_3•9H_2O$ into a 50-mL Erlenmeyer flask and dissolve in 7 mL of distilled water. Drop in a magnetic stir bar, stir the solution, and add a mixture of 1.0 mL of acetylacetone in 7 mL of methanol. Next, add a solution containing 1.3 g of sodium acetate trihydrate in 7 mL of distilled water, and briefly heat the mixture on a hotplate until some of the methanol has boiled away (you should see the volume of the reaction mixture go down). Cool to room temperature, and then place in an ice bath for about 15 minutes. Filter the red crystalline solid using a Büchner funnel, wash the flask and crystals, using 2 x 5 mL) of deionized water. Allow the product to dry until the next lab period and then weigh the dry final product to determine the yield of dry product.

Cuestiones y experimentos adicionales.

1) Ajustar las reacciones que tienen lugar en cada una de las síntesis realizadas y calcular los rendimientos de los productos sintetizados.

2) Determinar el Δ_O de los compuestos sintetizados a partir de sus espectros visible-ultravioleta.

3) Hacer un espectro IR de los compuestos preparados y compararlos con el de la 2,4-pentanodiona. (Las bandas de tensión C=C y C=O aparecen entre 1500 y 1700 cm^{-1}).

4) Discutir las principales diferencias y semejanzas de los procedimientos de síntesis. Para que la 2,4-pentanodiona se coordine como acetilacetonato es necesario que se deprotone. Indicar qué especie química acúa como base en cada una de las reacciones.

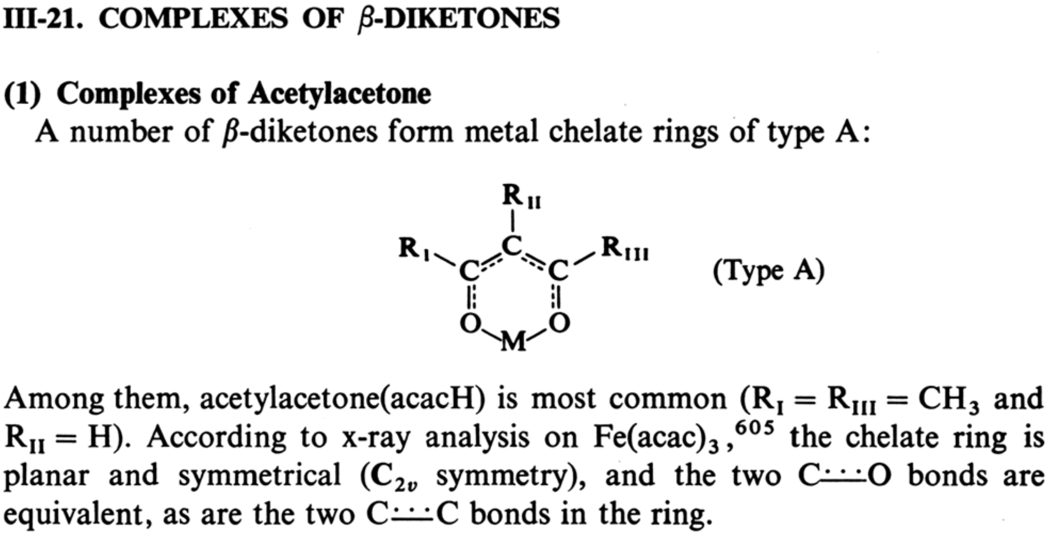
Bibliografía

1. Bryant, B. E.; Fernelius, W. C. Inorg. Synth. 1957, 5, 188.
2. Charles, R. G.; Pawlikowski, M. A. J. Phys. Chem. 1958, 62, 440.

3. Fernelius, W. C., Blanch, J. E. Inorg. Synth. 1957, 5, 130.

4. Charles, R. G. Inorg. Synth. 1963, 7, 183.

Ver también páginas siguientes. (Extraidas del texto de K. Nakamoto, *Infrared and raman spectra of inorganic and coordination compounds*, 4th edition, John Wiley and Sons: New York, 1986).



III-21. COMPLEXES OF β-DIKETONES

(1) Complexes of Acetylacetone

A number of β-diketones form metal chelate rings of type A:

(Type A)

Among them, acetylacetone(acacH) is most common ($R_I = R_{III} = CH_3$ and $R_{II} = H$). According to x-ray analysis on Fe(acac)$_3$,[605] the chelate ring is planar and symmetrical (C_{2v} symmetry), and the two C$\cdots$O bonds are equivalent, as are the two C$\cdots$C bonds in the ring.

The infrared spectra of metal acetylacetonate complexes have been studied extensively. In 1956, Mecke and Funck[606] assigned the infrared spectra of acetylacetone (keto and enol forms) and its metal complexes on an empirical basis. In 1960, Nakamoto and Martell[607] carried out an approximate normal coordinate analysis on $Cu(acac)_2$. At the time of this earlier research, no spectral data were available below 400 cm^{-1} and no isotopically substituted acetylacetonato complexes were studied. Since then, a number of investigators[608–610a] have extended their measurements to the far-infrared region. The spectra of metal complexes containing C^{13}- and O^{18}-labeled acetyacetones have been obtained.[611,612] A rigorous normal coordinate analysis considering all the atoms in the molecule has been made for $M(acac)_2$ and $M(acac)_3$-type complexes.[613] Table III-49a lists the observed frequencies, band assignments, and M—O stretching force constants obtained by Mikami et al.[613] Figure III-33a shows the infrared spectra of six acetylacetonato complexes.

The nature of the 1577 and 1529 cm^{-1} bands of $Cu(acac)_2$ has been a subject of controversy. Originally, Nakamoto and Martell[607] assigned the former to a $C\overset{\cdots}{-}C$ stretching and the latter to a $C\overset{\cdots}{-}O$ stretching mode. Mikami et al.[613] also gave similar assignments although they showed that these two modes are coupled slightly with each other. However, the results of the C^{13} and O^{18} experiments [611,612] suggest that the former is a pure $C\overset{\cdots}{-}O$ stretching and the latter is a pure $C\overset{\cdots}{-}C$ stretching. A further theoretical study is needed to solve this discrepancy.

The M—O stretching vibrations of acetylacetonato complexes are most important since they provide direct information about the strength of the M—O bonds. Thus far, they have been assigned from normal coordinate analyses[607,613] without experimental evidence. As stated in Sec. III-9, the metal isotope technique[389] provides a unique method to detect the metal-ligand vibrations. Nakamoto et al.[614a], therefore, applied this technique to acetylacetonato complexes of Fe(III), Cr(III), Pd(II), Cu(II), and Ni(II). Their results indicate that previous band assignments on the M—O stretching vibrations are essentially correct. As an example, Table III-49b gives the observed frequencies, isotopic shifts, and band assignments for $Cr(acac)_3$. Figure III-33b shows an actual tracing of the infrared spectra of $Cr^{50}(acac)_3$ and its Cr^{53} analog. Two bands at 463 and 358 cm^{-1} of the former must be assigned to the Cr—O stretching modes since they give large shifts relative to others. On the other hand, Pinchas et al.[611] assigned the 592 cm^{-1} band to a pure Cr—O stretching since it gives the largest isotopic shift (19 cm^{-1}) by the O^{16}—O^{18} substitution of $Cr(acac)_3$. However, this band is shifted by only 0.7 cm^{-1} by the Cr^{50}—Cr^{53} substitution, and cannot be assigned to a pure Cr—O stretching mode. It may be due to a ligand vibration in which the oxygen atom moves appreciably (e.g., $C\overset{\cdots}{-}O$ out-of-plane bending). It

TABLE III-49a. OBSERVED FREQUENCIES AND BAND ASSIGNMENTS OF ACETYLACETONATO COMPLEXES[613] (cm^{-1})

$Cu(acac)_2$	$Pd(acac)_2$	$Fe(acac)_3$	Predominant Mode
3072	3070	3062	$\nu(\mathrm{CH})$
2987 2969 2920	2990 2965 2920	2895 2965 2920	$\nu(\mathrm{CH_3})$
1577	1569	1570	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$
1552	1549		combination
1529	1524	1525	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
1461	(1425)	1445	$\delta(\mathrm{CH}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
1413	1394	1425	$\delta_d(\mathrm{CH_3})$
1353	1358	1385 1360	$\delta_s(\mathrm{CH_3})$
1274	1272	1274	$\nu(\mathrm{C{-}CH_3}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
1189	1199	1188	$\delta(\mathrm{CH}) + \nu(\mathrm{C{-}CH_3})$
1019	1022	1022	$\rho_r(\mathrm{CH_3})$
936	937	930	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$
780	786 779	801 780 771	$\pi(\mathrm{CH})$
684	700	671 667 [a]	$\nu(\mathrm{C{-}CH_3})$ + ring def. $+ \nu(\mathrm{M{-}O})$
653	678	656	 $\pi\left(\mathrm{CH_3{-}C}\begin{smallmatrix}\diagup\mathrm{C}\\ \diagdown\mathrm{O}\end{smallmatrix}\right)$
612	661	559 548 [a]	ring def. $+ \nu(\mathrm{M{-}O})$
451	463	433	$\nu(\mathrm{M{-}O}) + \nu(\mathrm{C{-}CH_3})$
431	441	415 408	ring def.
291	294	298	$\nu(\mathrm{M{-}O})$
1.45	1.85	1.30	K(M—O), mdyn/A (UBF)

[a] Pure ring deformation.

should be noted that an isotopic substitution of the α-atom of the ligand (atom bonded directly to a metal) shifts the metal-ligand as well as ligand vibrations involving the motion of the α-atom. Thus, the metal-ligand vibrations cannot be uniquely assigned by this method.

Behnke and Nakamoto[615] prepared three deutero analogs of K[Pt(acac) Cl_2], and calculated a set of UBF force constants to fit the observed frequencies of four isotopically substituted species. Table III-50 lists the observed

4. EXPERIMENTOS EN QUÍMICA DEL ESTADO SÓLIDO.

4.A.- Preparación del granate $Y_xGd_{3-x}Fe_5O_{12}$.

Los granates son minerales de fórmula general $M_3M'_2(SiO_4)_3$, (M y M' pueden ser el mismo elemento). Por extensión se denomina "granate" a aquellos sólidos de fórmula general $M_3M'_2M''_3O_{12}$ y que tienen la misma estructura: Octaedros $M'O_6$ y tetraedros $M''O_4$ formando una red en la que cada octaedro está unido por cada vértice a un tetraedro y viceversa. En esa red los cationes M ocupan posiciones dodecaédricas (número de coordinación 8). El granate que se va a preparar contiene dos tipos de cationes M (Y(III) y Gd(III)) que forman una disolución sólida, de tal forma que ambos metales pueden sustituirse en la red cristalina para dar cualquier composición intermedia ($0 \leq x \leq 3$). El resto de los cationes son Fe(III) algunos de los cuales tienen un entorno octaédrico (M') y otros tetraédrico (M'').

Una de las propiedades interesantes de los granates es que son materiales magnéticos. En este caso, el comportamiento es ferrimagnético y se deriva de la presencia de átomos de gadolino (III) (IC = 8, [Xe] $4f^7$, 7 electrones desemparejados) y hierro(III) (en los entornos de coordinación del granate IC = 6 o IC = 4, [Ar] $3d^5$, tiene 5 electrones desemparejados). El Y(III) tiene configuración electrónica de gas noble ([Kr]), por lo que no contribuye al magnetismo de la muestra. Los dominios magnéticos del hierro en entorno octaédrico y del gadolinio son paralelos (sus momentos magnéticos individuales se suman), y el del hierro en entorno tetraédrico es antiparalelo a ellos. Por lo tanto la magnetización total será proporcional a la cantidad de átomos que hay de cada clase (Ga, Fe_{Oh} y Fe_{td}) por la cantidad de electrones desemparejados de cada uno y contribuirá positiva o negativamente según su orientación relativa:

$(3-x) \times 7 + 2 \times 5 - 3 \times 5$.

El experimento se realizará coordinadamente en grupos de cuatro alumnos, de forma que cada uno de los cuatro sintetice una muestra con un valor diferente de "x" (0.4; 1.2 1.8 y 2.7) para obtener granates con distinto comportamiento magnético.

La síntesis se efectúa mediante el "método del precursor". Se forma un hidróxido mixto conteniendo los tres metales, con lo que se obtiene una sustancia homogénea, que luego se transforma en el granate por calefacción.

Procedimiento experimental:

You will prepare one member of the $Y_xGd_{3-x}Fe_5O_{12}$ ($0 \leq x \leq 3$) family, that is, you will be assigned a particular value of x. A description of the synthesis of $Y_{1.5}Gd_{1.5}Fe_5O_{12}$ via a mixed metal hydroxide precursor follows. Other compositions in the series can be prepared by varying the volumes of $Gd(NO_3)_3$ and $Y(NO_3)_3$ used, in such a way that the amount of $Gd(NO_3)_3$ plus the amount of $Y(NO_3)_3$ totals 6 mL.

Place 10 mL of 0.3 M $FeCl_3$ in a beaker. Add 3 mL of 0.3 M $Gd(NO_3)_3$ solution and 3 mL of 0.3 M $Y(NO_3)_3$ solution. Add 5-10 mL of 2 M NaOH dropwise to the metal ion solution in order to precipitate a reddish-brown solid. Decant the solution, and wash the remaining solid repeatedly with water until the wash is no longer basic (test with pH paper). Filter and dry the solid in a drying oven (120 ˚C) overnight.

Press the powder into 1/2-inch-diameter pellets using a standard pellet press, and fire in a furnace at 900 ˚C for 18-24 hours. A visible color change from reddish-brown to olive green after firing indicates that a reaction has taken place.

Determine the strength of the attraction of your pellet of garnet to a strong magnet at room temperature, dry-ice temperature, and liquid-nitrogen temperature. Discuss your procedure with other students in the class and agree on a method that will allow comparison of the magnetic effects as a function of the garnet composition.

Cuestiones:

1.- Identificar en el granate sintetizado los iones M, M' y M" que ocupan posiciones dodecaédricas, octaédricas y tetraédricas respectivamente.

3.- Indicar las cantidades que ha empleado de cada reactivo y qué composición de granate se obtiene con ellas.

2.- Explicar, a partir de las variaciones en composición, la variación en el magnetismo observado cualitativamente para cada una de las cuatro muestras de su grupo de trabajo.

Bibliografía

A. F. Wells, "Química Inorgánica Estructural" Ed. Reverté, Barcelona 1978.

W. D. Calister, "Introducción a la ciencia e ingeniería de los materiales", Vol II, Ed. Reverté, Barcelona 2000.

M. J. Geselbracht, A. M. Cappellari, A. B. Ellis, M. A. Rzeznik, B. J. Johnson, *J. Chem. Ed*. **1994**, *71(8)*, 696-703. (**ver páginas siguientes**)

Rare Earth Iron Garnets

Their Synthesis and Magnetic Properties

Margret J. Geselbracht, Ann M. Cappellari, and Arthur B. Ellis[1]
University of Wisconsin–Madison, Madison, WI 53706

Maria A. Rzeznik
University of California Berkeley, Berkeley, CA 94720

Brian J. Johnson
St. John's University, St. Joseph, MN 56374

The interaction of solids with magnetic fields is a topic that is discussed rarely in introductory chemistry courses. This occurs in spite of the proliferation of magnetic materials in today's society, including magnetic recording media and data storage. We believe that a presentation of the magnetic properties of solids fits well into the general chemistry course, because it provides a vehicle for discussing the existence of electrons, the electronic configurations of ions, and the role of solid state structure. Our experiment involving the preparation and study of a series of magnetic garnets with the composition $Y_xGd_{3-x}Fe_5O_{12}$ ($0 \leq x \leq 3$) that illustrates these topics follows. In addition, this experiment provides the opportunity to discuss the different types of magnetism in solids, to perform some chemistry using rare earth elements, and to learn about solid solutions and the tunability of properties by varying the composition of a solid solution. Furthermore, it can be performed in such a way that each student has a unique compound to prepare. The class data can then be compiled to obtain a picture of the magnetic properties of the entire range of composition of $Y_xGd_{3-x}Fe_5O_{12}$.

The majority of molecules and solids that we encounter are nonmagnetic. All of the electrons in these materials are paired, and the molecule or solid is said to be diamagnetic. The simplest type of magnetism, paramagnetism, often is demonstrated in introductory chemistry courses by observing the behavior of liquid oxygen in a magnetic field. Due to the presence of unpaired electrons in O_2, the liquid is attracted to a strong magnet, and if a large horseshoe magnet is used, the liquid oxygen appears to hover, trapped between the poles of the magnet (*1*).

Many solids exhibit interesting magnetic behavior as well, often more complex than simple paramagnetism, due to the cooperative effect of many electrons in the solid acting in concert. Ferromagnetism is a property of solids that is technologically important and exploited in the use of permanent magnets, magnetic recording media, and

Addendum

Description of the March 1994 Cover

The cover of the March 1994 issue needs further amplification to be useful for teachers. It shows a sample of zinc rod on the left-hand side of the page. The bottom portion of the rod was etched by human handling (this portion of the rod was exposed as the rod was passed around classes over a period of several semesters; the top portion of the rod had a protective cover) and reveals the boundaries between different grains. As discussed in the accompanying paper (Geselbracht, M. J.; Ellis, A. B.; Penn, R. L.; Lisensky, G. C.; and Stone., D. S. *J. Chem. Educ.* **1994,** *71,* 254) the bubble raft on the right-hand side of the cover (also shown schematically in Figs. 2 and 3 in the paper) provides a model for the grains, which are close-packed arrays of atoms having different relative orientations.

---

[1] Author to whom correspondence should be addressed.

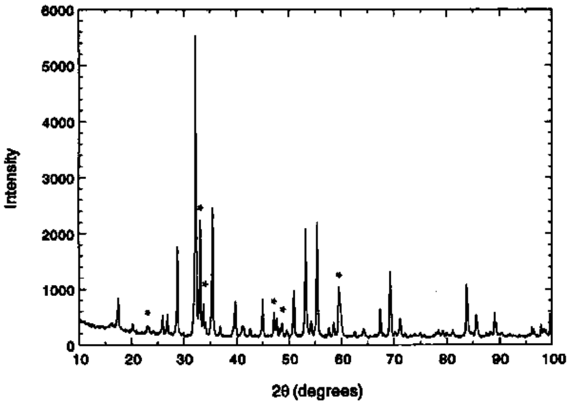


Figure 1. X-ray powder diffraction pattern of a sample of $Y_{1.5}Gd_{1.5}Fe_5O_{12}$ prepared via a mixed metal hydroxide precursor. Diffraction peaks that are marked with an asterisk correspond to the impurity $RFeO_3$ (R = Y or Gd).

transformers. We believe that a discussion of the chemistry of magnetic solids in introductory chemistry courses not only illustrates the effect of unpaired electrons, but also introduces the concept that electrons in a solid can communicate with one another, leading to properties that are vastly different from those stemming from isolated, localized electrons.

What do we mean by the chemistry of magnetic solids? The magnetic properties of a solid depend on composition (the presence of magnetic ions), on the underlying crystal structure (the geometrical arrangement of the ions in three dimensions), and on temperature. In order to eliminate the influence of structure and to isolate the effects of composition and temperature on magnetic properties, ideally, we would like to change the composition of a magnetic solid without disrupting the crystal structure. In other words, we would like to study the magnetic properties of a solid solution.

In this paper, we will describe a general synthesis for compositions in the solid solution series $Y_xGd_{3-x}Fe_5O_{12}$ ($0 \leq x \leq 3$), and a simple demonstration that illustrates the differing magnetic properties of these materials. This experiment serves several purposes. Students gain experience in synthetic techniques commonly used to prepare many solid state oxides that are important in materials chemistry today. If X-ray powder diffraction is available, the X-ray diffraction patterns can be analyzed to discuss the structural characterization of solid solutions and illustrate the evolution of the lattice parameter with composition. Finally, these materials display some unique magnetic properties, that open the discussion to cooperative effects in solids and the applications of magnetic materials to technology.

Experimental

Synthesis

Compounds in the $Y_xGd_{3-x}Fe_5O_{12}$ ($0 \leq x \leq 3$) solid solution series were synthesized via a mixed metal hydroxide precursor (*2*). A 1 M stock solution containing yttrium nitrate was prepared by dissolving $Y(NO_3)_3 \cdot 5H_2O$ (Aldrich, 99.9%) in deionized water. Likewise, 1 M stock solutions were prepared from $Gd(NO_3)_3 \cdot 6H_2O$ (Aldrich, 99.9%) and $FeCl_3 \cdot 6H_2O$ (Alfa, ACS grade). A description of the synthesis of $Y_{1.5}Gd_{1.5}Fe_5O_{12}$ follows. Other compositions in the series can be prepared by varying the volumes of $Gd(NO_3)_3$ and $Y(NO_3)_3$ used.

A 3-mL aliquot of 1 M $Gd(NO_3)_3$ solution and a 3-mL aliquot of 1 M $Y(NO_3)_3$ solution were added to 10 mL of 1 M $FeCl_3$ in a beaker. Excess 6 M NaOH (5–10 mL) was then added dropwise to the metal ion solution in order to precipitate a reddish-brown solid. After precipitation was complete, the solution was decanted, and the remaining solid was washed repeatedly with water until the supernatant solution no longer tested basic using standard pH paper. Then the reddish-brown solid was filtered and dried in a drying oven (120 °C) overnight. The resultant powder was pressed into 1/2-in. diameter pellets using a standard pellet press and fired in a furnace at 900 °C for 18–24 h. A visible color change from reddish-brown to olive green after firing indicated that a reaction had taken place.

Preparing the material in the form of a pellet is necessary to carry out the magnetic tests described below. If a pellet press is not available, we have found that the loose powder can be packed into an empty gelatin capsule (available at a pharmacy counter) before carrying out the magnetic tests. Note that if a press is not available, the loose powder may require longer or repeated firings in order to complete the reaction.

X-Ray Powder Diffraction (optional)

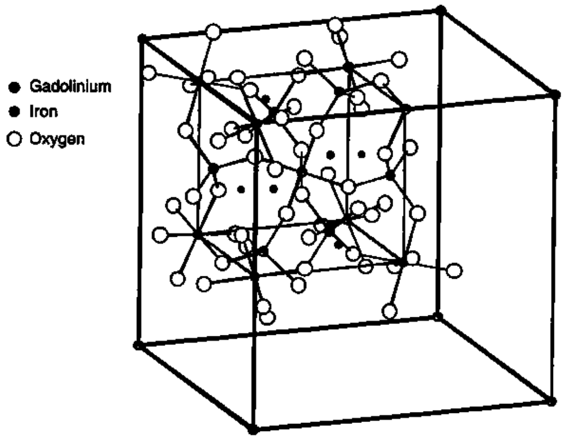
Some instructors may wish to have their students verify the identity of the olive-green solid by X-ray powder diffraction. X-ray powder diffraction patterns of the samples were recorded from 10–100° 2θ on a *Nicolet* X-ray powder diffractometer. The powder diffraction pattern of the sample with the nominal composition $Y_{1.5}Gd_{1.5}Fe_5O_{12}$ is shown in Figure 1. The major product of the reaction was the garnet phase, $R_3Fe_5O_{12}$ (R = rare earth element). The peaks indicated with an asterisk in Figure 1 are due to $RFeO_3$ (R = rare earth element), which is a common impurity in samples of $R_3Fe_5O_{12}$. Grinding the olive-green solid, repelletizing, and firing a second time at 900 °C (or higher temperatures) for 24 h led to a noticeable decrease in the intensities of the peaks of the impurity phase in the diffraction pattern. It should be noted that the presence of a small amount of the $RFeO_3$ phase in the samples does not adversely affect the investigation of the magnetic properties in this experiment.

To obtain the lattice parameters for the samples, silicon was added as an internal standard prior to collecting the diffraction data, and the line positions were corrected for systematic errors by applying a linear correction, derived from the Si data, to the observed angles. Lattice parameters were refined from 15–18 reflections using standard least-squares refinement techniques. Using line positions that have not been corrected led to the same overall trend in lattice parameter with composition, although there was more scatter in the data (see Fig. 4).

Studies of Magnetic Properties

To demonstrate the magnetic properties of these materials we have used a qualitative test of the strength of the magnetism: the strength of the attraction of a pellet of garnet to a cow magnet (Edmund Scientific). Pellets that exhibit strong magnetism can be picked up by the cow magnet, while pellets that are only weakly magnetic cannot be picked up by the cow magnet. The temperature dependence of the magnetic properties can be demonstrated by studying the magnetic behavior of the pellets of the different compositions at room temperature, and after cooling the pellets in dry ice or liquid nitrogen. For more data points, students can prepare and use other low temperature baths (*3*).

More detailed investigations of the magnetism were carried out at the University of California, Berkeley with a *Quantum Design* SQUID magnetometer. The magnetiza-



Metal ion location within one octant of the unit cell:

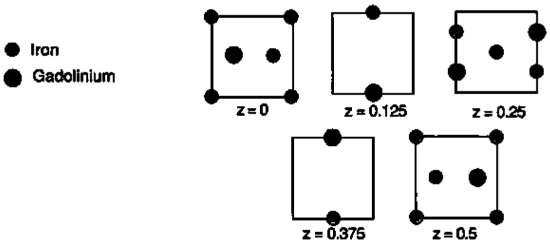


Figure 2. Portion of the unit cell of the garnet structure of $Gd_3Fe_5O_{12}$ is shown at the top. All of the metal ions in one-eighth of the unit cell are drawn along with the oxygen ions that complete the octahedral or tetrahedral coordination around the iron atoms. The rest of the atoms have been deleted for clarity. At the bottom, horizontal sections perpendicular to the *z* direction are shown to indicate the precise positions of the iron and gadolinium ions within this octant of the unit cell. Note that in this figure, the $z = 0$ section corresponds to the top face of the cube and *z* increases in the downward direction.

tion was measured as a function of temperature in an applied magnetic field of 40 kGauss.

Suggested Use in Lab

Due to the need to fire these samples in a high temperature furnace for 18–24 h, we would suggest that the instructor allow two to three laboratory periods for this experiment, perhaps running concurrently with another experiment. One period is necessary for the preparation of the hydroxide precursor, and depending on the availability of furnaces, the firing can be done in the week between two meetings. In the second laboratory period, students can ascertain whether a second firing is necessary to complete the reaction. The magnetic studies then can be carried out in a second or third laboratory period. If the instructor includes X-ray powder diffraction in this experiment, the time must be adjusted accordingly.

The students can be given individual projects by asking them to synthesize a particular member of the $Y_xGd_{3-x}Fe_5O_{12}$ family of compounds. This might be done by giving each student the formula (or *x* value) for their target compound and informing them that 1 M solutions of $Y(NO_3)_3$, $Gd(NO_3)_3$, and $FeCl_3$ are available in the lab and that everyone should use 10 mL of 1M $FeCl_3$ so that approximately the same amount of material is prepared by each student.

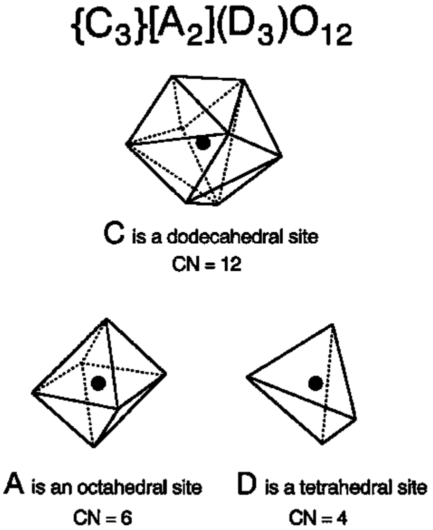


Figure 3. The three polyhedral coordination environments that are present in the garnet structure. In $Gd_3Fe_5O_{12}$, gadolinium ions are in the dodecahedral sites, and iron atoms are in both the octahedral and the tetrahedral sites.

After the synthesis, the students can perform the magnetic studies on their own compounds. Students may be asked to design their own tests of magnetic strength to get a more quantitative measurement of the relative magnetization of two different samples at a given temperature. This might be done by measuring the distance between the magnet and the sample when an interaction is first noticed. Finally, the results of the class can be tabulated to get an overall picture of the magnetic properties of these compounds.

Results and Discussion

The magnetic properties of rare earth iron garnets have been of great interest for the past two decades. Rare earth iron garnets, $R_3Fe_5O_{12}$, can be prepared with all of the rare earth ions except R = La, Ce, Pr, or Nd. Detailed reviews of the crystal chemistry and the physical properties of rare earth iron garnets abound in the literature (*4*).

Structure

Gadolinium iron garnet (GIG) and yttrium iron garnet (YIG) are members of the garnet structural family of complex oxides. The general formula for a garnet is $\{C_3\}[A_2](D_3)O_{12}$ where the C cations occupy dodecahedral sites, the A cations occupy octahedral sites, and the D cat-

Table 1. Variation in Cubic Lattice Parameter, *a*, with Composition for $Y_xGd_{3-x}Fe_5O_{12}$

Composition	Lattice Parameter (Å)
$Y_3Fe_5O_{12}$	12.370 (1)
$Y_{2.5}Gd_{0.5}Fe_5O_{12}$	12.382 (2)
$Y_2Gd_1Fe_5O_{12}$	12.402 (2)
$Y_{1.5}Gd_{1.5}Fe_5O_{12}$	12.423 (2)
$Y_1Gd_2Fe_5O_{12}$	12.437 (2)
$Y_{0.5}Gd_{2.5}Fe_5O_{12}$	12.450 (1)
$Gd_3Fe_5O_{12}$	12.468 (2)

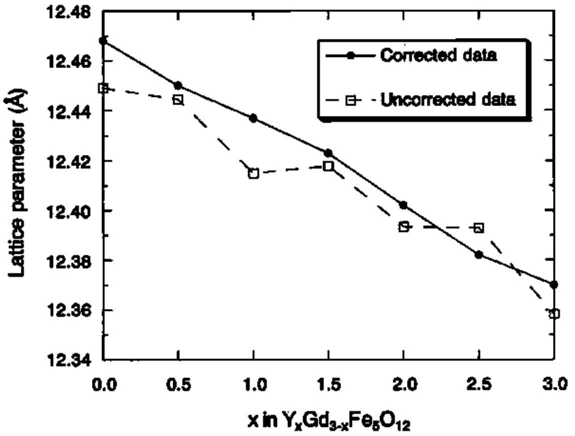


Figure 4. The variation in the cubic lattice parameter, *a*, with composition in $Y_xGd_{3-x}Fe_5O_{12}$. The corrected data were obtained by adding silicon as an internal standard prior to collecting the diffraction data. The line positions of $Y_xGd_{3-x}Fe_5O_{12}$ were corrected for systematic errors by applying a linear correction, derived from the Si data, to the observed angles.

ions occupy tetrahedral sites in the crystal structure. The unit cell of the garnet structure has cubic symmetry and contains eight formula units for a total of 160 atoms (*5*). A portion of the unit cell of $Gd_3Fe_5O_{12}$ is drawn in Figure 2 with only the cations and selected oxygens shown for clarity. The three different polyhedral coordination environments for the cations in the garnet structure are drawn in Figure 3. In the case of $Gd_3Fe_5O_{12}$, Gd^{3+} occupies dodecahedral sites and Fe^{3+} occupies both octahedral and tetrahedral sites in the structure. However, a wide variety of cations in different valence states can reside in the cation sites. The primary consideration for site occupancy is ionic size. This leads to many compositions that form the garnet structure.

Because of the similarity in ionic radii of the rare earth ions, many rare earth iron garnets will form solid solution phases. In the case of yttrium (ionic radius = 0.900 Å) and gadolinium (ionic radius = 0.938 Å), the complete solid solution is stable:

$$Y_xGd_{3-x}Fe_5O_{12}\ (0 \le x \le 3)$$

Substitution of yttrium for gadolinium occurs on the dodecahedral site. Because Gd^{3+} is slightly larger than Y^{3+}, we would expect that the lattice parameter, *a* (the length of the side of the cubic unit cell), would increase with increasing gadolinium content. This trend is clearly seen in the data presented in Table 1 and graphically depicted in Figure 4.[2]

Many students have difficulty understanding the difference between a single-phase solid solution compound, such as $Y_{1.5}Gd_{1.5}Fe_5O_{12}$, where there is a 50% probability that the atom on the rare earth site is Y or Gd, and a physical two-phase mixture containing equal amounts of $Y_3Fe_5O_{12}$ and $Gd_3Fe_5O_{12}$. The X-ray powder patterns illustrate beautifully the difference between these two cases. Because the lattice parameters of $Y_3Fe_5O_{12}$ and $Gd_3Fe_5O_{12}$ differ, the positions of the diffraction peaks also should differ. Thus, in a two-phase mixture, formed for this purpose by physically mixing equal amounts of $Y_3Fe_5O_{12}$ and $Gd_3Fe_5O_{12}$, the diffraction pattern consists of two distinct patterns superimposed as shown in Figure 5a. However, the solid solution compound, $Y_{1.5}Gd_{1.5}Fe_5O_{12}$, should have a single lattice parameter that is intermediate between the pure yttrium-containing material and the pure gadolinium-containing material. The diffraction pattern of the solid solution compound should consist of one set of peaks that are midway between the two sets for the pure materials. This is shown in Figure 5b. The point should be made to students that a two-phase mixture, such as that described in Figure 5a, could be physically separated into the two components provided that one had "tweezers" small enough to pick out the particles of pure $Y_3Fe_5O_{12}$ and leave the pure $Gd_3Fe_5O_{12}$ behind. However, in practice, this physical separation is impossible to carry out in most cases, so we must design the syntheses to lead to a single-phase product.

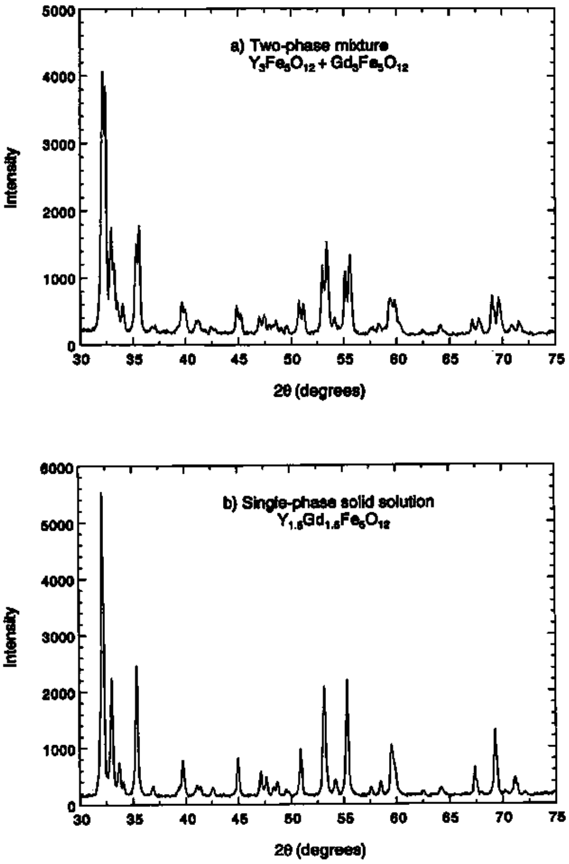


Figure 5. A portion of the X-ray powder diffraction pattern of a) a two-phase mixture of $Y_3Fe_5O_{12} + Gd_3Fe_5O_{12}$ and b) a single-phase solid solution compound $Y_{1.5}Gd_{1.5}Fe_5O_{12}$.

Magnetic Properties

Electrons in a solid can behave cooperatively, leading to different properties from those observed in the gas or liquid states. An excellent example of cooperative behavior in solids is ferromagnetism.[3] The difference between simple paramagnetism and ferromagnetism is shown in Figure 6. Unpaired electrons or spins are depicted in this figure by

---

[2] The shifts in the positions of the lines in the X-ray powder diffraction pattern are not clearly visible to the eye. However, by accurately determining the position of the lines and refining the lattice parameter, the shifts in the lattice parameters are significant.

[3] Theoretically, ferromagnetism is feasible in a liquid, although a liquid ferromagnet has not, to our knowledge, been reported. Ferrofluids have been made that are colloidal suspensions of tiny solid ferromagnetic particles (~100 Å in diameter) suspended in a liquid medium.

arrows. There are unpaired spins in a simple paramagnet (Fig. 6a), but in the absence of a magnetic field, the spins are oriented randomly relative to one another due to thermal motion. In a ferromagnet, the unpaired electrons communicate with one another and align in large regions known as magnetic domains[4] (Fig. 6b). The sizes of the domains vary with the material but are typically on the order of hundreds of angstroms. In the absence of a magnetic field, the composite spins of individual domains are ordered randomly so that the net magnetization of a macroscopic piece of ferromagnet is zero. The application of a magnetic field (Fig. 6c) aligns all of the spins in the direction of the magnetic field, leading to an overall net magnetization. The application of a magnetic field to a paramagnet also would align the spins in the direction of the magnetic field, but the overall magnetization is less than in the case of a ferromagnet, because there is no communication or magnetic ordering between the spins.

The observed temperature-dependent magnetic behavior of a ferromagnet is derived from the interplay of thermal energy, which randomizes the spins, and the energy stabilization gained by aligning the spins in the ferromagnetic state. Ferromagnetism is an example of a solid-state phase transition with a characteristic transition temperature. Above an ordering temperature, known as the Curie temperature (T_c), thermal energy is sufficient to break the alignment of the spins, and the material exhibits simple paramagnetism. But below T_c, the aligning forces overcome thermal randomization, the spins are locked in alignment, and the material becomes ferromagnetic.

Another type of magnetic ordering that can occur in solids is antiferromagnetism. In this type of magnetic behavior, the spins align opposite to each other below the ordering temperature[5] to lessen the overall magnetism.

Ferrimagnetism, the type of magnetic ordering that occurs in the garnets, differs from ferromagnetism in that ions with different local moments are present in ferrimagnets. These unequal spins align antiparallel (antiferromagnetically) below the Curie temperature (T_c), but because the spins have different magnitudes, the cancellation is not complete. A simple schematic representing the differences between the magnetic ordering in ferromagnetism, antiferromagnetism, and ferrimagnetism is shown in Figure 7.

The magnetic properties of the rare earth iron garnets can be understood by considering that each type of coordination site in the crystal structure leads to a separate magnetic sublattice. Thus, for $Gd_3Fe_5O_{12}$, there are three magnetic sublattices comprised of the unpaired spins of the

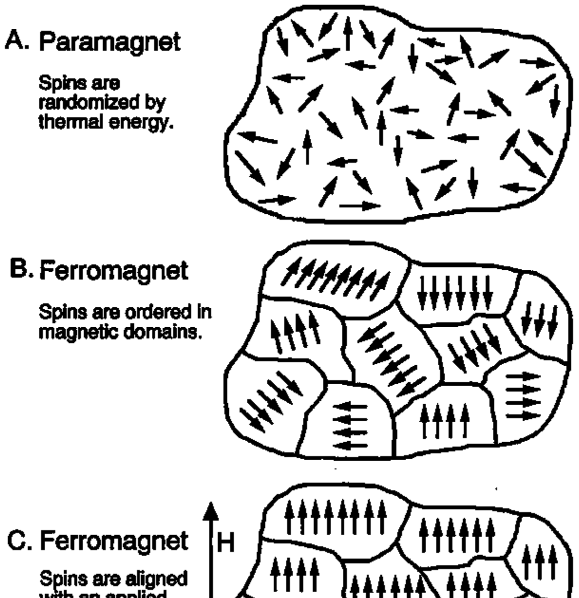


Figure 6. (a) In the absence of an applied magnetic field, the unpaired electrons (or spins) of a paramagnet are randomly oriented due to thermal energy. In contrast, the spins of a ferromagnet (b) spontaneously align with each other within regions known as magnetic domains. (c) In an applied magnetic field, the individual magnetic domains all align with the field, resulting in a large, overall magnetization.

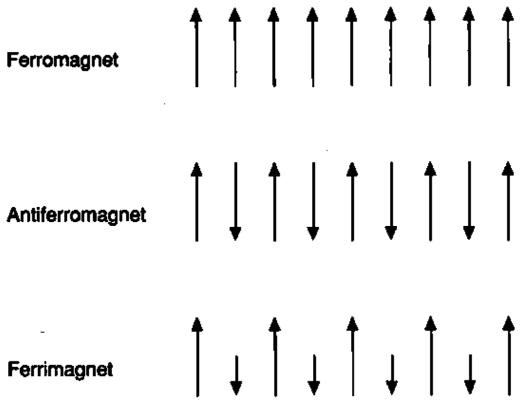


Figure 7. The magnetic ordering of linear arrays of spins (unpaired electrons) in a ferromagnet, antiferromagnet, and a ferrimagnet. Ferrimagnetism is the type of magnetic ordering that occurs in the rare earth iron garnets.

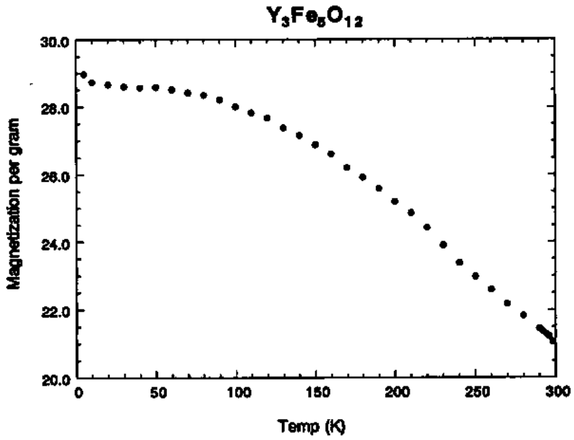


Figure 8. The temperature dependence of the magnetization per gram for $Y_3Fe_5O_{12}$.

---

[4] The application of magnetic properties in technology relies on the existence of domain walls and the ability to control the movement of the domain walls. For example, in permanent magnets, the domain walls are not moved easily. However, in the promising technology of magnetic bubble domain memory storage, the ability to move the domain walls underlies the writing capabilities in the read/write mode.

[5] The ordering temperature of an antiferromagnet is called the Neel temperature, T_N.

different cations: the gadolinium sublattice, the octahedral iron sublattice, and the tetrahedral iron sublattice. The total magnetic moment can be represented by eq 1:

$$M(T) = M_d(T) - M_a(T) - M_c(T) \qquad (1)$$

where $M_d(T)$ represents the temperature-dependent magnetization of the tetrahedral sublattice, $M_a(T)$ represents the temperature-dependent magnetization of the octahedral sublattice, and $M_c(T)$ represents the temperature-dependent magnetization of the dodecahedral sublattice.[6] Each term, such as $M_d(T)$, represents a sum of the magnetic moments at that particular crystallographic site (i.e., There are three tetrahedral sites in each formula unit.). The negative signs in eq 1 result from the fact that the spins in the octahedral sublattice (M_a) and the spins in the dodecahedral sublattice (M_c) align parallel to each other but antiparallel to the spins in the tetrahedral sublattice (M_d). The different magnetic sublattices can have different temperature dependencies for their magnetization that may lead to $M(T) = 0$ at a specific temperature below T_c. This temperature is the compensation temperature, T_{comp}.

For the material $Y_3Fe_5O_{12}$, the Fe^{3+} ions (with five unpaired electrons) in the octahedral holes order antiferromagnetically (spins aligned antiparallel) with the Fe^{3+} ions (also with five unpaired electrons) in the tetrahedral holes. However, because there are three tetrahedral sites and two octahedral sites in the garnet formula, there is a net magnetic moment of five unpaired electrons. There is no magnetic contribution from the closed shell yttrium ion. Thus, $Y_3Fe_5O_{12}$ is strongly magnetic at all temperatures. This behavior can be demonstrated by the fact that the pellet of $Y_3Fe_5O_{12}$ can be picked up by the cow magnet at room temperature, dry ice temperature, and liquid nitrogen temperature. A plot of the magnetization of $Y_3Fe_5O_{12}$ versus temperature, shown in Figure 8, agrees with this qualitative behavior.

At the other extreme in the solid solution, $Gd_3Fe_5O_{12}$ has the same net five unpaired electrons from the two iron sublattices. But, in addition, each Gd^{3+} ion (there are three in the garnet formula) has seven unpaired electrons. The electrons in the gadolinium sublattice order antiferromagnetically (antiparallel) to the net five unpaired electrons of the tetrahedral iron. This suggests that the magnetic moment of $Gd_3Fe_5O_{12}$ should be 16 ($3 \times 7 - 5$) unpaired electrons. This is true if the moment is measured at very low temperatures. However, the gadolinium sublattice and the iron sublattice thermally randomize at different temperature dependencies. The result is a compensation temperature, T_{comp}, where the net magnetization is zero. In $Gd_3Fe_5O_{12}$, the compensation temperature is just below

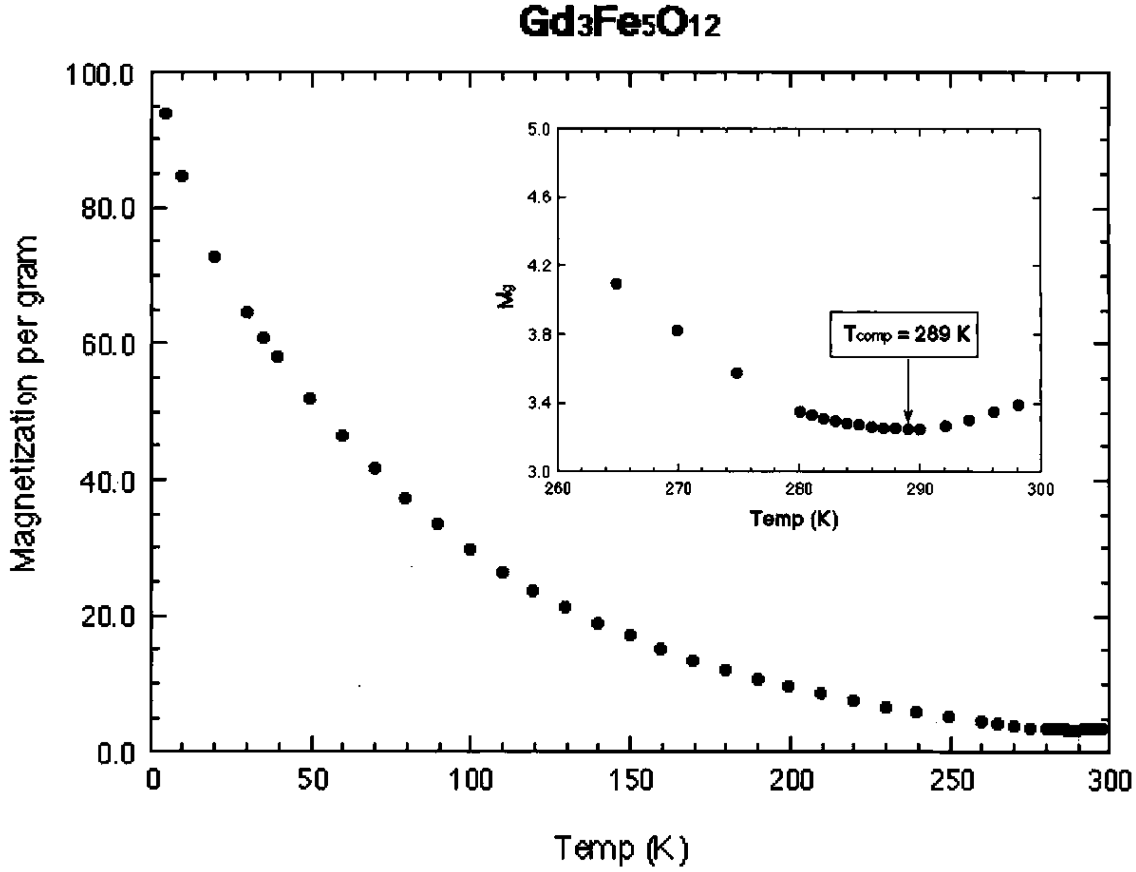


Figure 9. The temperature dependence of the magnetization per gram for $Gd_3Fe_5O_{12}$. The inset contains an enlargement of the region from 260 to 300 K in order to identify the compensation temperature (T_{comp} = 289 K).

---

[6] The identity of the subscripts is derived from the standard notation for the garnet formula, $C_3A_2D_3O_{12}$, where C represents the dodecahedral site, A represents the octahedral site, and D represents the tetrahedral site.

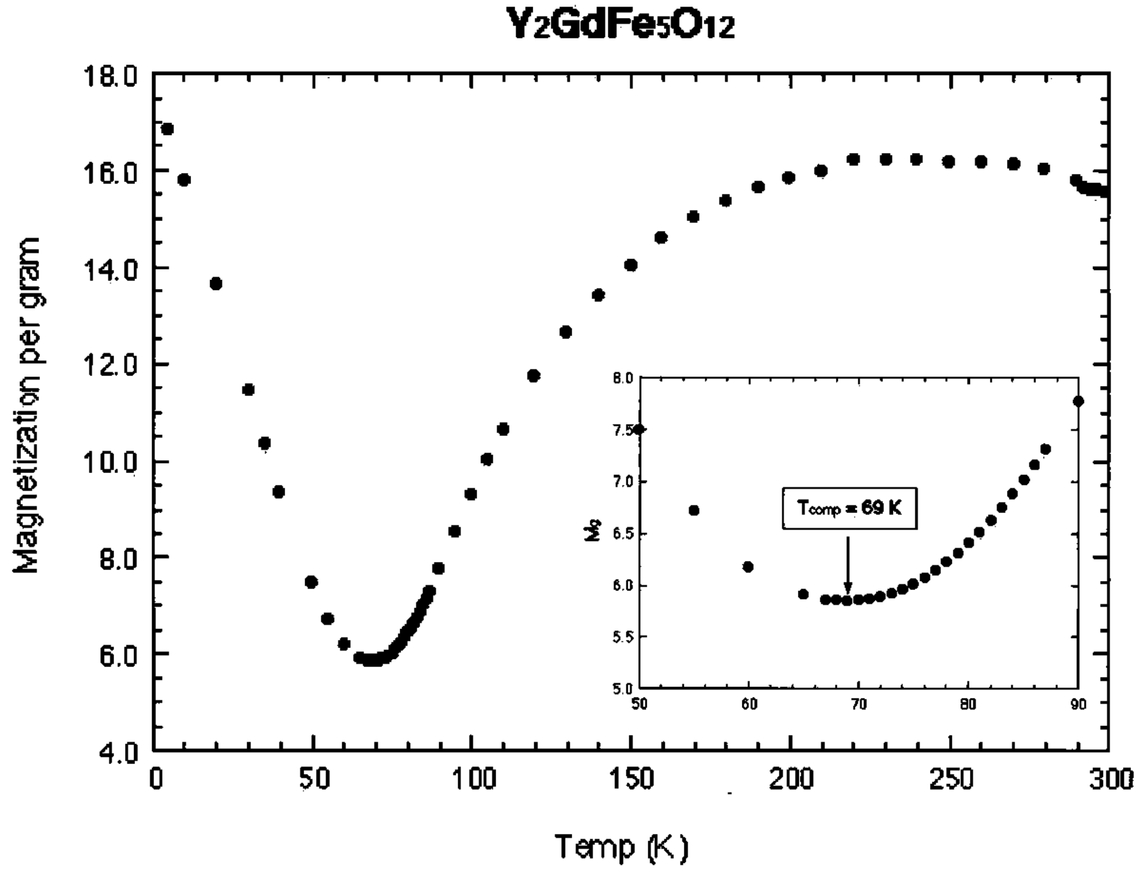


Figure 10. The temperature dependence of the magnetization per gram for $Y_2Gd_1Fe_5O_{12}$. The inset contains an enlargement of the region from 50 to 90 K in order to identify the compensation temperature (T_{comp} = 69 K).

room temperature. This can be verified qualitatively by the observation that the $Gd_3Fe_5O_{12}$ pellet is not attracted to the cow magnet at room temperature. However, if this pellet is cooled in dry ice or liquid nitrogen, for example, the pellet becomes strongly magnetic and can be picked up with the cow magnet.[7] The corresponding plot of magnetization versus temperature for this material is shown in Figure 9. Note that at the compensation temperature (289 K) and at room temperature, the magnetization is very small,[8] but it increases dramatically as the temperature is lowered. Also note that at low temperatures, the magnetization of $Gd_3Fe_5O_{12}$ is roughly three times larger than the magnetization of $Y_3Fe_5O_{12}$, as is predicted from the described simple calculation of the number of unpaired electrons.

The effect of combining both yttrium and gadolinium in the garnet structure in the solid solution compounds is that the compensation temperature becomes a strong function of composition (*6*). This is obvious from the magneti-

Table 2. Variation in Compensation Temperature, T_{comp}, with Composition for $Y_xGd_{3-x}Fe_5O_{12}$

Composition	T_{comp} (K)	Reference
$Y_3Fe_5O_{12}$	—[a]	This work
$Y_{2.7}Gd_{0.3}Fe_5O_{12}$	— (only measured above 73 K)	*6*
$Y_{2.1}Gd_{0.9}Fe_5O_{12}$	— (only measured above 73 K)	*6*
$Y_2Gd_1Fe_5O_{12}$	69	This work
$Y_{1.8}Gd_{1.2}Fe_5O_{12}$	93	*6*
$Y_{1.2}Gd_{1.8}Fe_5O_{12}$	158	*6*
$Y_1Gd_2Fe_5O_{12}$	175	This work
$Y_{0.6}Gd_{2.4}Fe_5O_{12}$	218	*6*
$Gd_3Fe_5O_{12}$	289	This work

[a] No compensation temperature was observed down to 5 K.

---

[7] This unusual magnetic behavior suggests an interesting experiment: If a magnet is secured at the proper distance above a cooling bath, upon cooling, the pellet will automatically jump up to the magnet. As the pellet warms, it should fall back into the cooling bath, where upon cooling again, the pellet will repeat this motion cycle. This behavior should continue indefinitely, provided that the cooling bath is replenished periodically and provided that the pellet does not fall out of the range of the magnet.

[8] In this particular measurement, the magnetization is not exactly zero, probably due to the presence of a small amount of $GdFeO_3$ in the sample.

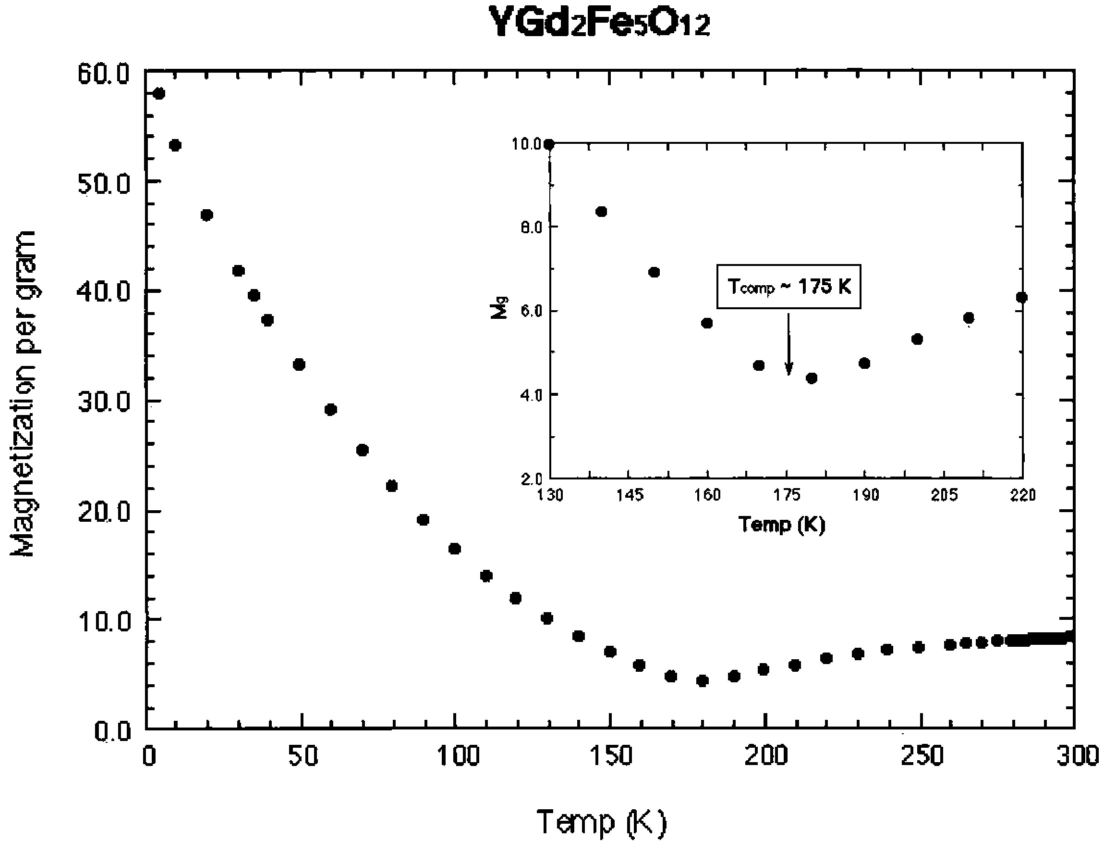


Figure 11. The temperature dependence of the magnetization per gram for $Y_1Gd_2Fe_5O_{12}$. The inset contains an enlargement of the region from 130 to 220 K in order to identify the compensation temperature (T_{comp} = 175 K).

zation behavior plotted in Figures 10 and 11 for the two intermediate compositions $Y_2Gd_1Fe_5O_{12}$ and $Y_1Gd_2Fe_5O_{12}$. From the data, it is clear that the compensation point for $Y_2Gd_1Fe_5O_{12}$ is~70 K (Fig. 10) and for $Y_1Gd_2Fe_5O_{12}$ is ~175 K (Fig. 11). Again, these can be verified qualitatively with the cow magnet. If $Y_2Gd_1Fe_5O_{12}$ is cooled in liquid nitrogen, the pellet cannot be picked up with the cow magnet. Likewise, if $Y_1Gd_2Fe_5O_{12}$ is cooled in dry ice, the pellet only weakly responds to the cow magnet. This information is summarized in Table 2, which lists the compensation temperatures for various compositions in the solid solution series, $Y_xGd_{3-x}Fe_5O_{12}$.

Conclusions

This laboratory presents an opportunity to introduce solid-state chemistry into the introductory chemistry course. The synthesis and qualitative magnetic measurements described above are not difficult, yet they provide insight into preparative chemistry and the magnetic properties of solids. In addition, the experiment is such that the students have their "own" individual compound to prepare in order to contribute to the overall understanding of the system. We believe that this team approach generates a more positive laboratory experience.

Acknowledgment

The authors would like to thank Frank DiSalvo at Cornell University for providing the inital suggestion for this experiment, Debbie Stafslien for early experimental investigations, and the Dreyfus Foundation and the National Science Foundation (grant USE-9150484) for financial support.

Literature Cited

1. Shakhashiri, B. Z.; Dirreen, G. E.; Williams, L. G. *J. Chem. Educ.* **1980**, *57*, 373–374.
2. (a) Vidyasagar, K.; Gopalakrishnan, J.; Rao, C. N. R. *J. Solid State Chem.* **1985**, *58*, 29–37. (b) Robbins, M.; Wertheim, G. K.; Storm, A. R.; Buchanan, D. N. E. *Mat. Res. Bull.* **1972**, *7*, 233–239.
3. Gordon, A. J.; Ford, R. A. *The Chemist's Companion*;Wiley: New York, 1972; pp 451–452.
4. (a) Wang, F. F. Y. In *Treatise on Materials Science and Technology*, Vol. 2; Herman, H., Ed.; Academic Press: New York, 1973; pp 279–384. (b) Geller, S. In *Physics of Magnetic Garnets*; Paoletti, A., Ed.; North–Holland Publishing Co.: Amsterdam, 1978; pp 1–55. (c) Khattak, C. P.; Wang, F. F. Y. In *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 3; Gschneidner, K. A., Jr.; Eyring, L., Eds.; North–Holland Publishing Co.: Amsterdam, 1979; pp 525–607.
5. Weidenborner, J. E. *Acta Cryst.* **1961**, *14*, 1051–1056.
6. Harrison, G. R.; Hodges, L. R., Jr. *J. Appl. Phys.*, **1962**, *33*, 1375–1376.

4.B.– Inserción de hidrógeno en trióxido de wolframio.

El trióxido de wolframio tiene una estructura formada por octaedros "WO_6" que comparten vértices. En los huecos de esa estructura se pueden alojar distintos cationes para dar lugar a especies no estiquiométricas de fórmula M_xWO_3 con $0 < x < 1$ (conocidos como bronces de wolframio cuando M es un metal alcalino), donde M puede ser H, Li, Na, K, Rb, Ca, Sr, Ba, Al, In, Tl, Sn, Pb, Cu, Ag, Cd, un metal del bloque f o el catión amonio.

$$(x/2)H_2 + WO_3 \rightarrow H_xWO_3$$

La reacción que se va a efectuar conduce a un compuesto de esta clase, y supone la inserción de hidrógeno en los huecos de la estructura del sólido, produciéndose formalmente la reducción parcial de W y la oxidación de H a H^+. Los electrones añadidos a la red se alojan la banda de conducción lo que da lugar a cambio en el color del compuesto y a comportarse como conductor eléctrico.

Procedimiento experimental.

Place 500 mg of WO_3 into a 250 mL beaker. Carefully pour about 50 mL dilute hydrochloric acid (3 molar) onto the WO_3. Does anything happen? Now very carefully drop some zinc filings (*ca.* 3 g) into the acid. After all reaction has ceased filter off the solid product. After washing, place it on a filter paper and observe what happens when you leave it exposed to the air. Write balanced equations for both the reduction of WO_3 and its subsequent re-oxidation.

Make pellets of WO_3 and H_xWO_3 in a pellet press and measure the electrical resistance using an ohmmeter. Is there any difference?

Cuestiones y experimentos adicionales.

1. Escribir y ajustar todas las reacciones que tienen lugar
2. Construir con modelos la estructura del trióxido de wolframio y identificar las posiciones que puede ocupar el hidrógeno. (Trabajo en grupo)

3. Calentar una pequeña muestra en la estufa (a unos 100 ˚C) durante unos días, anotar cualquier cambio de aspecto y explicar a qué se debe. Tomar otra pequeña muestra y agitarla en un tubo de ensayo con un par de mL de H_2O_2 diluida. Anotar y explicar los cambios observados.

Bibliografía

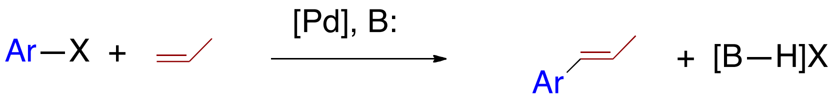
A. F. Wells, “Química Inorgánica Estructural” Ed. Reverté, Barcelona 1978.

E. Kikuchi; N. Hirota; A. Fujishima, K. Itoh; M. Murabayashi, *J. Electr. Chem.* **1995**, *381*, 15 - 19. DOI: http://dx.doi.org/10.1016/0022-0728(94)03649-N.

5. CATÁLISIS HOMOGÉNEA.

5.A.- La arilación del ácido acrílico.

La reacción de Heck, conocida también como Mizoroki- Heck,[123] es un método eficiente y muy usado para la formación de enlaces carbono-carbono en el que un alqueno y, usualmente un haluro de arilo o vinilo se acoplan en presencia de un catalizador de paladio (Esquema 1). La reacción es frecuentemente regio y estereoselectiva, formándose predominantemente el alqueno *trans*. La adición de una base es necesaria para eliminar el haluro de hidrógeno formado.



Esquema 1

Cuando se usa un disolvente orgánico se suele emplear trietilamina como base, pero si los reactivos son solubles en agua se puede sustituir la trietilamina por bases más comunes como hidróxido o carbonato de sodio.

Procedimiento experimental.

En un matraz de fondo redondo de 50 mL de una boca se adiciona el yoduro de arilo correspondiente (3.00 mmol), ácido acrílico (0.25 mL, 3.60 mmol), acetato de paladio (entre 0.1 y 0.5 % mol) y una disolución 0.5 M de hidróxido de sodio en agua. La mezcla se agita vigorosamente a temperatura ambiente con un agitador magnético hasta que se observa la disolución completa de los reactivos (unos 5 min). Tras acoplar un refrigerante, la disolución se refluye con agitación vigorosa durante 1 h. Finalizado este tiempo, la mezcla se deja enfriar a temperatura ambiente y se filtra para eliminar los posibles restos sólidos. El filtrado se acidifica con una disolución acuosa 3.0 M de HCl, precipitando un sólido blanco que se filtra con un embudo Büchner, lavándose a continuación con abundante agua fría con el fin de eliminar el cloruro de sodio y el exceso de ácido acrílico que no hubiera reaccionado. El sólido blanco obtenido se seca en una estufa a 100 °C durante una noche y se pesa.

Ácido (E)-3-(4-acetilfenil)acrílico.

Siguiendo el procedimiento anterior, se utilizaron 0.753 g de 1-(4-yodofenil)etanona, 0.7 mg de acetato de paladio (3 µmol) y 15 mL de la disolución de hidróxido de sodio. El compuesto se obtuvo como un sólido blanco cristalino. Si es necesario, el producto se puede recristalizar de etanol.

Ácido (E)-4-(2-carboxivinil)benzoico.

Siguiendo el procedimiento anterior, se utilizaron 0.759 g de ácido 4-yodobenzoico, 2 mg de acetato de paladio (9 µmol) y 21 mL de la disolución acuosa de hidróxido de sodio. El compuesto se obtuvo como un sólido blanco cristalino.

Cuestiones:

1.- Discutir el papel del acetato de paladio en la reacción. Buscar en la bibliografía recomendada un ciclo catalítico que permita explicar el mecanismo de la reacción.

2.- Buscar un ejemplo de aplicación de la reacción de Heck a la síntesis de un producto natural o a un producto de importancia industrial.

Bibliografía:

---

[1] T. Mizoroki, K. Mori, A. Ozaki, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581. (b) R. F. Heck, J. P. Nolley, Jr., *J. Org. Chem.* **1972**, *14*, 2320-2322.

[2] Ver revisiones en: (a) S. Bräse, A. de Meijere en Metal-Catalyzed Cross-Coupling Reactons, (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, New York, 2004, capítulo 5. (b) I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009-3066.

[3] Una descripción de estos experimentos se puede encontrar en *An. Quim.* **2009**, *105(2)*, 126-129. Accesible a través de dialnet: http://dialnet.unirioja.es/servlet/listaarticulos?tipo_busqueda=EJEMPLAR&revista_busqueda=2860&clave_busqueda=225728.

5. B.- Oxidación catalítica de trifenilfosfina por un dioxocomplejo de molibdeno (VI).

La oxidación de ciertos sustratos catalizada por oxocomplejos de molibdeno(VI) tiene mucho interés por estar involucrada en procesos biológicos importantes.

La práctica consiste en la preparación de dos complejos de molibdeno (VI), $[MoO_2Cl_2(DMSO)_2]$ y $[MoO_2(acac)_2]$. Posteriormente se analiza su capacidad como catalizadores en la oxidación de trifenilfosfina.

Experimental

Preparación de $[MoO_2Cl_2(DMSO)_2]$.

En un tubo de ensayo se colocan 0.25 g de $(NH_4)_6Mo_7O_{24}.4H_2O$, 1 g de agua y 2 g de HCl del 37%. La mezcla se calienta con agitación durante 10 minutos a 100 ˚C en un baño de agua, y la disolución resultante se enfría a temperatura ambiente. Posteriormente se añaden con agitación 0.5 g de dimetilsulfóxido y la mezcla se enfría de nuevo. El precipitado blanco se filtra, se lava con acetona (2 x 1 mL) y posteriormente con éter etílico (2 x 1 mL) y finalmente se seca por succión.

Preparación de $[MoO_2(acac)_2]$.

En un tubo de ensayo se colocan 0.25 g de MoO_3, 0.4 g de agua y 0.4 g (5.5 mmol) de NH_3 del 24%. La mezcla se agita hasta obtener una disolución incolora, produciéndose una reacción exotérmica. A continuación, se añaden 0.75 g de 2,4-pentanodiona, y aunque la mezcla se agita se mantienen dos fases. Finalmente, se adiciona 1 g de ácido nítrico al 63% produciéndose un proceso exotérmico. La mezcla se enfría a temperatura ambiente, manteniendo la agitación, precipitando el producto como un polvo amarillo. Se recoge por filtración y se lava sucesivamente con agua (4 x 2 mL), etanol (2 x 2 mL) y dietil éter (2 x 2 mL). Finalmente se seca por succión.

Ensayos de oxidación catalítica de la trifenilfosfina.

En un tubo de ensayo se colocan 50 mg de $[MoO_2Cl_2(DMSO)_2]$, 0.5 g de trifenilfosfina y 2.5 g de dimetilsulfóxido. La mezcla se calienta a 100 ˚C durante 15 minutos en una campana. La disolución obtenida se añade sobre 12 mL de NaOH 1 M. El precipitado se filtra, se lava con agua (3 x 2 mL) y se seca bien por succión.

Se procede de forma similar a la indicada en el apartado anterior utilizando como catalizador [$MoO_2(acac)_2$].

Cuestiones y experimentos adicionales.

1) Indicar la ecuación del proceso que conduce a la obtención de los dos complejos metálicos y calcular los rendimientos obtenidos.
2) Registrar un IR de cada uno de los sólidos obtenidos y asignar las absorciones ν(Mo=O) y ν(P=O). Basándose en los datos de IR, discutir la oxidación de trifenilfosfina en función del catalizador utilizado.
3) Discutir la información que puede obtenerse por IR y ^{1}H RMN para elucidar la estructura de los complejos de molibdeno preparados.
4) ¿Por qué se utiliza una disolución de NaOH en los ensayos de la oxidación catalítica? ¿Podría utilizarse sólo agua?

Bibliografía: ver páginas siguientes.

F. J. Arnaiz y R. Aguado, J. Chem. Ed. 1995, A7- A8, asi como las páginas extraidas del texto de K. Nakamoto, *Infrared and raman spectra of inorganic and coordination compounds*, 4th edition, John Wiley and Sons: New York, 1986.

the microscale laboratory

edited by
Arden P. Zipp
SUNY–Cortland
Cortland, NY 13045

The Conversion of Triphenylphosphine to the Oxide: A Simple Experiment to Illustrate Catalytic Oxotransfer

Francisco J. Arnáiz and Rafael Aguado
Laboratorio de Química Inorgánica
Universidad de Burgos
09001 Burgos, Spain

Oxygen atom transfer reactions involving dioxomolybdenum(VI) complexes are of current interest because of their relevance in some important biological processes (*1*). Most synthetic complexes that mimic oxotransferases contain sterically demanding sulfur ligands because two of the criteria for relevant models are the sulfur environment and hindrance to irreversible µ-oxo dimer formation. However, some molybdenum complexes lacking these requisites show a remarkable ability to act as oxotransfer agents (*2*).

Here we describe the facile synthesis of a simple, very active, catalyst ($MoO_2Cl_2(DMSO)_2$, (DMSO = dimethylsulfoxide)) and its application in the oxidation of triphenylphosphine (PPh_3) to triphenylphosphine oxide ($OPPh_3$) by DMSO.

This oxidation of PPh_3 provides a good example of the catalytic oxotransfer process because PPh_3 is inexpensive, resistant to aerial oxidation, widely used in oxotransfer studies, and has a low volatility. Conducting the experiment in an aprotic medium with simple reagents minimizes the number of species involved in the overall process, which facilitates the interpretation of the results at the time that dramatically evidences the role of the catalyst (cleavage of strong multiple X–O bonds).

Preparing the Catalyst

The procedure presented here is related to that recently reported for the multigram scale synthesis of $MoO_2Cl_2(DMSO)_2$ from aqueous hydrochloric solutions of MoO_3 (*3*) although the use of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, in place of MoO_3, saves time and gives a product that is not contaminated appreciably with NH_4Cl. A typical run is described:

In a 5-mL vial are placed 0.25 g (0.2 mmole) of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 1 g H_2O and 2 g (20 mmole) 37% HCl. The mixture is heated for 10 min at ~100 °C (e.g., boiling water bath) with stirring, and the resulting solution is cooled to room temperature. Then, 0.5 g (6.4 mmole) DMSO is added with stirring and the mixture is cooled again. The white precipitate is filtered, washed with acetone (2 × 1 mL) and peroxide-free diethyl ether (2 × 1 mL), and dried in air. 0.37 g (~75% yield) of $MoO_2Cl_2(DMSO)_2$ is obtained as a white microcrystalline powder.

The compound melts at 172±1 °C and is very stable at ambient conditions. The IR spectrum is characterized by two strong bands at 921 and 892 cm^{-1} corresponding to the stretching vibrations of the *cis*-MoO_2 arrangement (*3, 4*).

Preparing $OPPh_3$ via Catalytic Oxotransfer

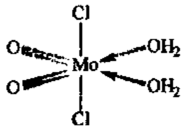
In a medium-size test tube (e.g., 100 × 15 mm) is placed 50 mg (0.14 mmole) of $MoO_2Cl_2(DMSO)_2$, 500 mg (1.9 mmole) PPh_3 and 2.5 g (32 mmole) DMSO. The mixture is heated at ~100 °C for 15 min in a well-ventilated hood because the foul-smelling dimethylsulfide (DMS) is released. The resulting colorless solution is poured into a 25-mL vessel containing 12 mL of ~1 M NaOH solution (this solution can be prepared by dissolving 0.5 g of NaOH in 12 mL of water). The precipitate is filtered, washed with water (3 × 2 mL), and dried in an oven at ~120 °C for 30 min. One obtains 0.49 g (92% yield) of white $OPPh_3$. This product melts at 157±1 °C and displays an IR spectrum characteristic of $OPPh_3$ (e.g., a strong ν(P=O) band at 1182 cm^{-1}) (*4*).

Discussion

The above procedures can be explained, in a simplified manner, as follows.

With regard to the preparation of the catalyst:

1. Ammonium heptamolybdate reacts with warm hydrochloric acid to form NH_4Cl, H_2O, and *cis, trans, cis*-$MoO_2Cl_2(H_2O)_2$.

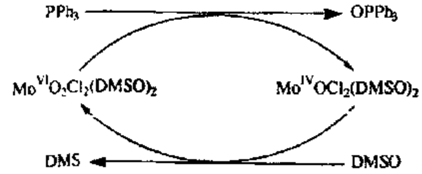


This species has been detected in solution (*5*), isolated as $MoO_2Cl_2(H_2O)_2 \cdot H_2O \cdot [(C_2H_5)_4N]Cl$ (*6*) and, more recently, as the outer-sphere diglyme adduct $[MoO_2Cl_2(H_2O)_2]{\cdot}(diglyme)_2$ (*7*). Molybdenum trioxide, previously dissolved in the minimum amount of ~12% NH_3, can be used in place of ammonium molybdate in this preparation.

2. DMSO is able to displace H_2O from the coordination sphere of many metallic centers producing a more hydrophobic environment around the metal. Thus, the HCl-NH_4Cl-$MoO_2Cl_2(H_2O)_2$ aqueous solution reacts with excess DMSO, and the resulting *cis, trans, cis*-$MoO_2Cl_2(DMSO)_2$ precipitates while NH_4Cl remains dissolved.

With regard to the preparation of $OPPh_3$:

1. PPh_3 reacts with DMSO in the presence of $Mo^{VI}O_2Cl_2(DMSO)_2$ to give $OPPh_3$ and DMS as represented in the catalytic cycle:



2. The lack of color in the resulting DMSO solution, which contains mainly $OPPh_3$, the catalyst, and some DMS, suggests that Mo(V) or Mo(IV) species are not present in significant amounts (*8*).

3. The DMSO solution is poured into sufficient aqueous NaOH so that $OPPh_3$ precipitates as the $MoO_2Cl_2(DMSO)_2$ is converted into soluble sodium chloride and molybdate, thus avoiding contamination of the $OPPh_3$.

Final Considerations

To highlight the role of the molybdenum complex it is advisable to conduct a blank experiment. To minimize waste, the procedure for the preparation of $OPPh_3$ can be modified so that a solution of PPh_3 in DMSO is prepared and heated while the catalyst is prepared. Then, a sample of ~0.5 mL is taken off and treated with water to precipitate the unreacted PPh_3, which may be further characterized (mp 80 °C). Finally, the catalyst is added, and the solution is worked up as described.

These experiments can be performed in a three-hour laboratory period, although this catalyzed oxotransfer reaction also proceeds at room temperature over a longer period. If necessary, significant time can be saved by washing the wet $OPPh_3$ with small portions of ethanol (e.g., 2 × 1 mL) and diethyl ether (e.g., 2 × 1 mL), followed by drying at room temperature, although this reduces the yield considerably.

Acknowledgment

To the editor for helpful comments and to DGICYT (Grant PS90-0134) for financial support.

Literature Cited

1. (a) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401, and references therein. (b) Holm, R. H. *Coord. Chem. Rev.* **1990**, *100*, 183, and references therein. (c) Enemark, J. H.; Young, C. G. *Adv. Inorg. Chem.* **1994**, *40*, 1, and references therein.
2. (a) Roberts, S. A.; Young, C. G.; Kipke, C. A.; Cleland, W. E., Jr.; Yamanouchi, K.; Carducci, M. D.; Enemark, J. H. *Inorg. Chem.* **1990**, *29*, 3650. (b) Arzoumanian, H.; López, R.; Agrifoglio, G. *Inorg. Chem.* **1994**, *33*, 3177. (c) Arnáiz, F. J.; Aguado, R.; Martínez de Ilarduya, J. M. *Polyhedron* **1994**, *13*, 3515.
3. Arnáiz, F. J. *Inorg. Synth.*, in press.
4. Butcher, R. J.; Gunz, H. P.; MacLagan, R. G. A. R.; Kipton, H.; Powell, J.; Wilkins, C. J.; Hian, Y. S. *J. Chem. Soc., Dalton Trans.* **1975**, 1223.
5. Coddington, J. M.; Taylor, M. J. *J. Chem. Soc., Dalton Trans.* **1990**, *1*, 41
6. Taylor, M. J.; Jirong W.; Rickard, C. E. F. *Polyhedron* **1993**, *12*, 1433.
7. Arnáiz, F. J.; Aguado, R.; Sanz-Aparicio, J.; Martínez-Ripoll, M. *Polyhedron* **1994**, *13*, 2745.
8. Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, 1984.

Reprinted from Journal of Chemical Education, Vol. 72, Page A7-A8, January 1995.

Microscale Synthesis of $MoO_2(acac)_2$

Francisco J. Arnáiz
Laboratorio de Química Inorgánica
Universidad de Burgos
09001 Burgos (Spain)

$MoO_2(acac)_2$ (acac = 2,4–pentanedionate) is one of the most important starting materials for preparing other dioxomolybdenum compounds of current interest (*1*) because:

- acac can be displaced from the coordination sphere of molybdenum by numerous ligands
- acacH is volatile
- acacH is soluble in many organic solvents and can be removed from the product
- $MoO_2(acac)_2$ works well in fundamental IR and ^1H NMR experiments

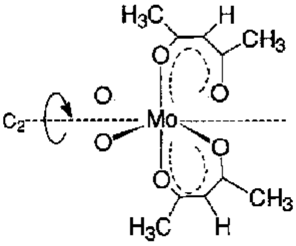
The synthesis described here is a modification of that recently reported (*2*). The main alterations are (in addition to the scale and molar ratio of reactants):

- starting from MoO_3 powder, which is cheaper than the conventional $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$.
- using the common 24% (13 M) instead of 15% (8 M) NH_3 solution.
- adding the reagents sequentially by weighing, which facilitates the work up.
- ending the washings with diethyl ether so that drying the product is more rapid.

A Typical Run

In a 5-mL conical vial (on an electronic balance) is placed 0.25 g (1.7 mmole) of MoO_3 powder, 0.40 g H_2O and 0.40 g (5.5 mmole) 24% NH_3 (Pasteur pipet). The mixture is stirred with a glass rod for about one min to obtain a clear colorless solution (exothermic reaction). Then, 0.75 g (7.5 mmole) of 2,4-pentanedione is added, and the mixture is stirred; however, two phases remain. Finally, 1 g (10 mmole) of 63% HNO_3 is added dropwise (exothermic reaction). The mixture is cooled to room temperature while stirring and the solid formed is ground until a yellow powder results. (Powdering the initially lumpy precipitate improves the purity of the product and requires less than 5 min.) The product is filtered through a Hirsch funnel, washed consecutively with distilled water (4 × 2 mL), ethanol (2 × 2 mL) and peroxide-free diethyl ether (2 × 2 mL), and dried in air. Washings also may be done by decanting. The powder settles sufficiently in less than 1 min so that more than 75% of the liquid can be removed. Using a Pasteur pipet is advisable in this case to reduce product losses because $MoO_2(acac)_2$ forms a supernatant skin every time water is added.

The entire process requires about 30 min. About 0.19 g of a light yellow finely powdered product melting at 179 ± 1 °C (the reported value) is obtained. The IR spectrum of the compound shows two strong bands at 900 and 930 cm^{-1} corresponding to the stretching vibrations characteristic of the *cis*-MoO_2 arrangement. Singlets at 2.12 and 2.14 δ (CD_2Cl_2, room temperature), assignable to the two sets of inequivalent methyl groups (see drawing), are observable in the ^1H NMR spectrum.



Acknowledgement

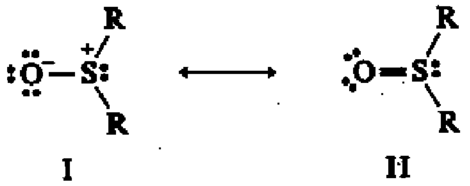
I am grateful to the editor for helpful comments.

Literature Cited

1. See, e. g.: (a) Srivastava, A.; Ma, Y.; Pankayatselvan, R.; Dinges, W.; Nicholas, K. M. *J Chem. Soc., Chem. Commun.* **1992**, 853. (b) Bustos, C.; Manzur, C.; Carrillo, D.; Robert, F.; Gouzerh, P. *Inorg. Chem.* **1994**, *33*, 1427.
2. Chakravorti, M. C.; Bandyopadhyay, D. *Inorg Synth.* **1992**, 29, 129.

(2) Complexes of Sulfoxides and Related Compounds

Cotton et al.[410] studied the infrared spectra of sulfoxide complexes to see whether coordination occurs through oxygen or sulfur. The electronic structure of sulfoxides may be represented by a resonance hybrid of the structures:



If coordination occurs through oxygen, contribution of structure II will decrease and result in a decrease of the SO stretching frequency. If coordination occurs through sulfur, contribution of structure I will decrease and may result in an increase of the SO stretching frequency.

TABLE III-34. SHIFTS OF SO STRETCHING BANDS IN DPSO AND DMSO COMPLEXES (CM^{-1})[412]

	DPSO Complex		DMSO Complex
Metal	ν(SO)	Shift	Shift
Ca(II)	1012–1035	0 – (−23)	–
Mg(II)	1012	−23	–
Mn(II)	983–991	−45	−41
Zn(II)	987–988	−47	–
Fe(II)	987	−48	–
Ni(II)	979–982	−55	−45
Co(II)	978–980	−56	−51
Cu(II)	1012, 948	−23, −87	−58
Al(III)	942	−93	–
Fe(III)	931	−104	–

The far-infrared spectra of DMSO complexes have been studied by Johnson and Walton,[413] who assigned the M—O stretching bands at 500–400 cm^{-1}. The S-bonded DMSO complexes (Pt(II) and Pd(II)) also exhibit a strong band in the same region. Hence it is difficult to differentiate the O-

6. ESTUDIO DE LA REACTIVIDAD DE UN LIGANDO COORDINADO: PREPARACIÓN DE FERROCENO Y ACETILFERROCENO

El descubrimiento en 1951 de bis(ciclopentadienil)hierro, con una estructura tipo "sandwich" en la que los dos anillos ciclopentadieno tienen carácter aromático, dio lugar a un desarrollo importante de la química organometálica.

La práctica consiste en la preparación de ferroceno para después realizar una sustitución electrofílica sobre uno de los anillos ciclopentadieno, aislando acetilferroceno.

Procedimiento experimental

6.A. Obtención de ferroceno.

En un matraz de 100 mL equipado con un refrigerante se ponen bajo atmósfera de nitrógeno 5.2 g de NaOH (triturado) y 50 mL de éter etílico. A la suspensión bien agitada, se añaden 5.6 mL de ciclopentadieno recién destilado, y después de 20 minutos. una disolución formada por 6.6 g de $FeCl_2{\cdot}4H_2O$ en 25 mL de dimetilsulfóxido, gota a gota. La reacción que se produce es exotérmica y se pone espontáneamente a reflujo. Finalizada la adición, se mantiene la agitación durante 30 minutos más. La fase líquida contenida en el matraz se decanta y el residuo negro se trata con 30 mL de éter. La fase líquida decantada se junta con la fase etérea y el combinado se trata, primero, con HCl 2M (2 x 40 mL) y después con agua (2 x 40 mL). La fase orgánica, después de secarse con sulfato magnésico, se concentra y cristaliza el ferroceno como cristales de color naranja. Se pueden recristalizar en hexano.

6.B. Preparación de acetilferroceno

A una mezcla de 10 mL de anhídrido acético y 3 g de ferroceno, contenida en un matraz provisto de un tubo de cloruro cálcico, se añaden gota a gota 2 mL de ácido ortofosfórico. La mezcla se calienta en baño de agua a 100 ºC durante 30 minutos y a continuación se vierte sobre 80 g de hielo picado con agitación. Cuando todo el hielo se haya fundido, la disolución se neutraliza con hidrogeno carbonato sódico sólido. La mezcla se enfría en baño de hielo durante 20 minutos y se recoge por filtración el producto como un sólido amarillento, que posteriormente se seca en un desecador de vacío.

Cuestiones y experimentos adicionales.

1) Describir las ecuaciones de todas las reacciones que tienen lugar en cada una de las síntesis realizadas. Calcular los rendimientos obtenidos en la preparación del ferroceno y acetilferroceno.

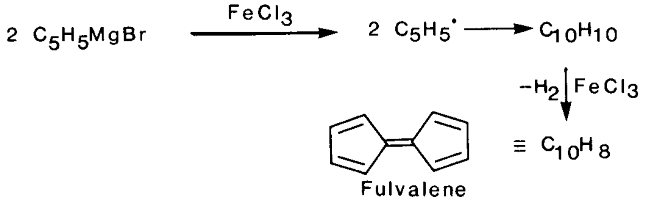
2) Describir detalladamente la estructura del ferroceno y discutir brevemente el enlace.

3) En un tubo de ensayo, añadir 0.02 g de ferroceno a 2 mL de agua y después 2 mL de ácido nítrico concentrado. Posteriormente agitar el tubo durante unos dos minutos. 4) Observar e interpretar el resultado obtenido.

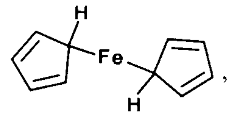
5) Discutir los espectros de IR y de ^{1}H NMR, tanto del ferroceno como del acetilferroceno.

Bibliografía: ver en páginas siguientes (a) C. Elschembroich, “Organometallics” Wiley-VCH, Weinheim, 2006. (b) H. McKone, J. Chem. Ed. 1980, 57(5), 380-381.

Their actual goal was the synthesis of fulvalene:



Structures which were originally proposed:

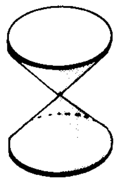


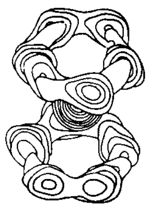
, $[C_5H_5^- Fe^{2+} C_5H_5^-]$

1952 E. O. Fischer: "**Double-cone structure**"

based on:

- *X-ray structural analysis (compare the electron density contour lines)*
- *diamagnetism*
- *chemical behavior*

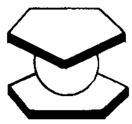




1952 G. Wilkinson, R. B. Woodward: "**Sandwich structure**"

based on:

- *IR spectroscopy*
- *diamagnetism*
- *dipole moment* = 0



Woodward: The cyclopentadienyl rings of $Fe(C_5H_5)_2$ *are amenable to electrophilic substitutions. This similarity to the aromatic behavior of benzene led to the trivial name* ***ferrocene****, later being extended to the designation* ***metallocenes*** *for compounds* $M(\eta^5\text{-}C_5H_5)_2$ *in general.*

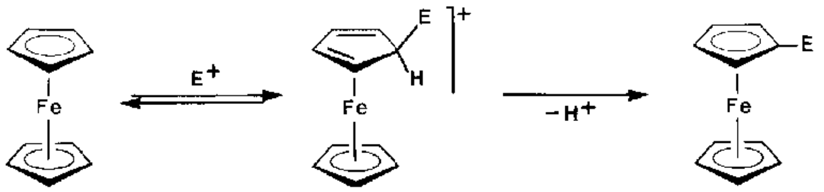
15.4.3.1 Binary Cyclopentadienyl Transition-Metal Complexes

PREPARATION

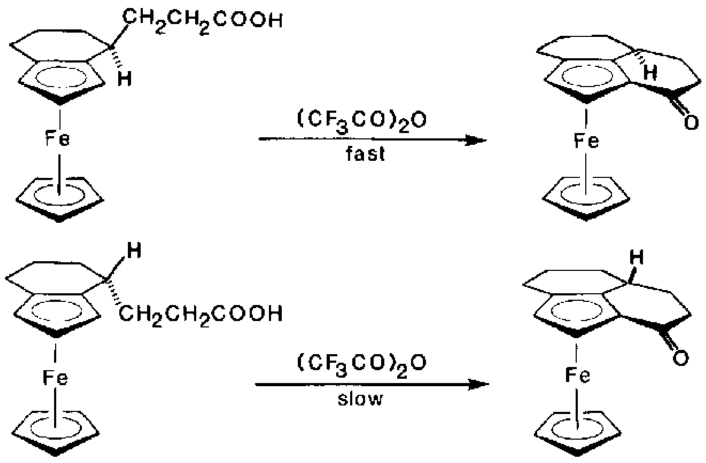
1. Metal Salt + Cyclopentadienyl Reagent

Dicyclopentadiene has first to be "cracked" in a retro-Diels-Alder reaction to give monomeric C_5H_6. Cyclopentadiene is a weak acid, $pK_a \approx 15$; it can be deprotonated by strong bases or by alkali metals. Cyclopentadienylsodium (NaCp) is the most common reagent for the introduction of cyclopentadienyl ligands.

Ferrocene, ruthenocene and osmocene are susceptible to **electrophilic substitution.** Compared to benzene, ferrocene reacts 3 x 10^6 times faster.



The electrophile should not be an oxidizing agent, as substitution would then be suppressed by oxidation to the ferricinium ion $[FeCp_2]^+$ which is inert to attack by electrophiles. That electrophilic substitution of ferrocene does not involve direct participation of the metal has been established by the intramolecular acylation of two isomeric ferrocene carboxylic acids. It was found that the *exo*-isomer, in which the acylium ion cannot directly interact with the metal, cyclizes faster than the *endo*-isomer (Rosenblum, 1966):



This result suggests that electrophilic attack occurs from the *exo*-direction.

Harold T. McKone
St. Joseph College
West Hartford, CT 06117

Acylation of Ferrocene

Effect of temperature on reactivity as measured by reverse phase high performance liquid chromatography

The Friedel-Crafts Reaction, a widely used synthetic tool, is an integral part of most organic laboratory courses. Formally, benzene was the preferred substrate for this electrophilic substitution reaction. However, recent reports confirming benzene's carcinogenicity necessitate using a safer aromatic compound. Ferrocene (I) is a reasonable alternative since it is relatively non-toxic, stable, more reactive than benzene, inexpensive in the quantities needed per student, and affords an interesting array of acylation products (*1–2*). In fact, the Friedel-Crafts acylation of ferrocene with product identification by thin layer and open column chromatography is currently a popular undergraduate experiment (*3–10*). Haworth and Liu recently reported a high performance liquid chromatographic (lc) separation of acylated ferrocenes using "normal-phase" conditions of silica packing and an ether: methanol mobile phase (*11–12*). The increasing use of lc in separating components in organic reaction mixtures encouraged us to investigate incorporating this lc separation of ferrocenes into our undergraduate laboratory. However, "normal-phase" lc has several disadvantages over the more versatile "reverse-phase" chromatography. The former requires relatively long column equilibration times and generally necessitates using non-aqueous mobile phases. We have developed a reverse-phase separation of these ferrocenes using a C_{18} bonded to silica column (μBONDAPAK/C_{18}-Waters Associates) and a far less bothersome mobile phase of methanol:water. A complete introduction to reverse phase lc may be found in references (*13*) and (*14*)

Instrumentation

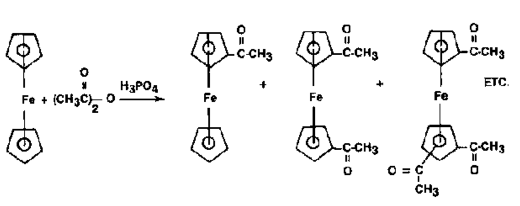
A Waters ALC/GPC-204 Liquid Chromatographic with a Model U6K Injector and a Houston Omni-Scribe Model 5211-1 Recorder were used. The prepacked analytical column consisted of C_{18} bonded to 10 μm silica particles (Waters Associates, Inc., Milford, MA 01757), and the mobile phase was a mixture of methanol:water in a ratio of 3:1. The flow rate was 0.9 ml/min and the absorbance detector was at 254 nm.

Experimental Conditions

Since ferrocene acylates readily, the reaction may be investigated at a variety of temperatures from 45°–100°C. A styrofoam cup serves as an excellent individual constant temperature bath. The results described here were obtained at 100°C with each student assigned a different reaction time.

Procedure

Place 0.2 g (~0.001 mole) of ferrocene, 1.0 ml of acetic anhydride and 0.1 ml of 85% phosphoric acid into a small test tube, cork, shake, and immediately place in a constant temperature bath. At designated intervals (15 sec, 30 sec, etc.) quench the reaction by pouring onto about 5 g of crushed ice. Allow the red-brown mixture to stand (with occasional stirring) for 15 min. Filter, wash the solid with 5 ml of cold water, and air-dry. Dissolve a small amount of the dry solid in 5 ml of methanol, filter[1], and separate by tlc and lc.



II III IV

Figure 1. Acylation of ferrocene.

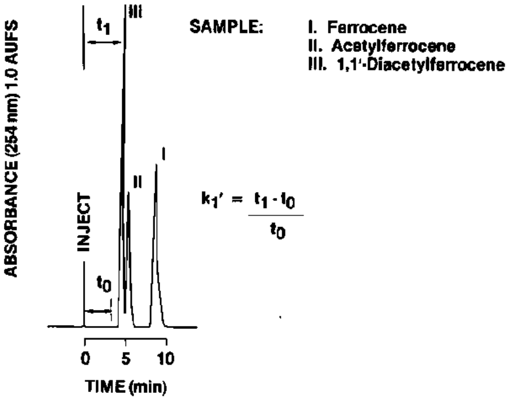


Figure 2. Liquid Chromatogram of the Separation of Standards of Ferrocene (I), Acetylferrocene (II), and 1, 1-Diacetylferrocene (III).

Table 1. k' and R_f Values for Ferrocene and Some Acylated Derivatives

Compound	k'	R_f
Ferrocene (I)	2.14	0.9
Acetylferrocene (II)	1.00	0.6
1,1-Diacetylferrocene (III)	0.64	0.3

Table 2. LC Analysis of Products of Acylation of Ferrocene at 100°C

	Product Composition			
Reaction Time	Ferrocene	Acetyl-Ferrocene	Diacetyl-Ferrocene	Other
0.1 min	(+)	trace	(−)	(−)
0.5 min	(+)	(+)	(−)	(−)
1.5 min	trace	(+)	trace	(−)
10 min	(−)	(+)	(+)	trace
25 min	(−)	(+)	(+)	(+)

Results and Discussion

Ferrocene acylates readily, yielding a variety of products as is indicated in Figure 1. A typical chromatogram, depicting the separation of ferrocene (I) and two major acylation products (acetylferrocene, II, and 1,1-diacetylferrocene, III) is shown in Figure 2. Under reverse phase conditions, the most polar compound, III, elutes first while the relatively non-polar ferrocene (I), which is adsorbed more strongly on the non-polar packing, elutes last. The separation is complete in less than 10 min allowing many injections during a single laboratory session. Table 1 summarizes the results of the lc analysis of reactions quenched at different times and Table 2 lists k' and R_f values for

---

[1] To extend column life, all samples should be filtered prior to lc separation.

[2] *k'*, the capacity factor, may be defined in terms of the difference between the time (t_1) required for a component to travel the length of the column and the time (t_0) required for solvent (or other non-retained molecules) to traverse the column, divided by t_0. See Figure 2.

ferrocene and its mono and diacylated products[2]. Thin layer chromatograms were run on silica using a developing solution of toluene:methanol in proportions of 20:1.

Conclusions

Monitoring the ferrocene acylation reaction by reverse phase lc is an excellent method of integrating this important separations technique into the undergraduate organic laboratory and of providing students with hands-on experience with lc. Because of the short reaction time, simple product work-up, and rapid lc separation, many students have the opportunity to complete this experiment in one laboratory session.

Acknowledgment

The author wishes to thank the National Science Foundation (Undergraduate Research Participation Grants #GY5892 and GY7241) and Ms. Gerry Granda, Ms. Helen Grzybowski, and Ms. Diane Sommerer for their work in tlc analysis. Thanks are also extended to Waters Associates, Milford, MA, for providing materials and financial support.

Literature Cited

(1) Rosenblum, M., "Chemistry of the Iron Group Metallocenes: Ferrocene, Ruthenocene and Osmocene," John Wiley and Sons, Inc., New York, 1965.
(2) Dauben, W. G., "Organic Reactions," 17, John Wiley and Sons, Inc., New York, 1969.
(3) Clark, A. K. and Bell, C. E., "Laboratory Experience in Organic Chemistry," Charles E. Merrill Publishing Co., Columbus, Ohio, 1972, p. 55.
(4) Fieser, L. F., and Williamson, K. L., "Organic Experiments," 4th Ed., D.C. Heath and Co., Lexington, MA, 1979, p. 169.
(5) Adams, R., *et al.*, "Laboratory Experiments in Organic Chemistry," 7th Ed. Macmillan Publishing Co., New York, 1979, p. 452.
(6) Wade, L. G., J. CHEM. EDUC., **55,** 208 (1978).
(7) Bozak, R. E., J. CHEM. EDUC., **43,** 73 (1966).
(8) Herz, J. E., J. CHEM. EDUC., **43,** 599 (1966).
(9) Bohen, J. M., *et al.*, J. CHEM. EDUC., **50,** 367 (1973).
(10) Gilbert, J. C., and Monti, S. A., J. CHEM. EDUC., **50,** 369 (1973).
(11) Haworth, D. T., and Liu, T. J., J. CHEM. EDUC., **53,** 730 (1976).
(12) Haworth, D. T. and Liu, T. J., *J. Chromatogr.* **14,** 519 (1976).
(13) Colin, H., and Guiochon, G., *J. Chromatogr.* **141,** 289 (1977).
(14) Gloor, R., and Johnson, E. L., *J. Chromatogr.* **15,** 419 (1977).

7.- EFECTO PLANTILLA.

La coordinación de ligandos a metales de transición permite dirigir estereoquímicamente su reactividad, dando lugar a productos diferentes a los que se obtendrían sin la participación del metal. Un buen ejemplo de esto es el conocido “efecto plantilla”. Los ligandos coordinados a un metal reaccionan dando lugar a un nuevo ligando que se adapta a la geometría definida por el metal.

7.A.- Síntesis de complejos macrocíclicos de níquel y cobre.

En el ejemplo que se va a realizar, la condensación de una diamina y una dicetona en presencia de acetato de níquel da lugar a un macrociclo que actúa como ligando quelato en torno a átomo de níquel. Si la reacción se hiciera en ausencia del metal se obtendría el ciclo 3 de la Figura 1.

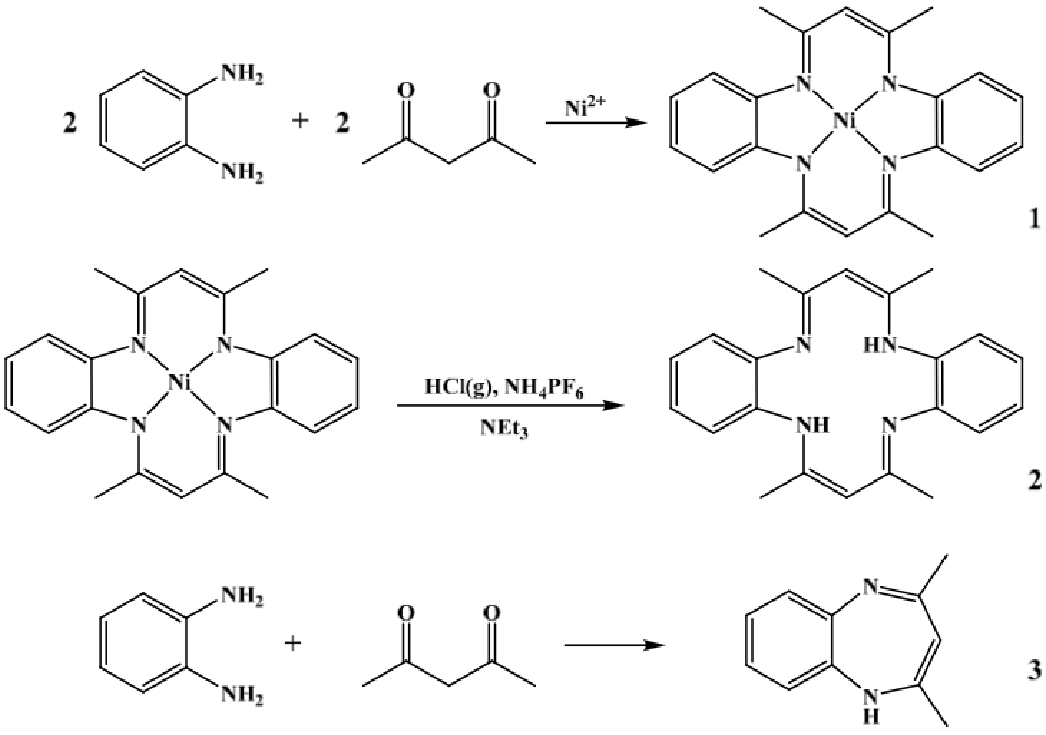


Figura 1

Una vez sintetizado el macrociclo es posible aislar el ligando destruyendo el complejo haciéndolo reaccionar con HCl, para lo que es necesario generar una corriente de

HCl(gas). Una vez aislado el macrociclo, puede ser utilizado para sintetizar complejos con otros metales.

Procedimiento experimental

All reagents and solvents are used as supplied except 1,2-diaminobenzene (*o*-phenylenediamine) that should be purified by a single recrystallization from EtOH in the presence of decolorizing charcoal or by sublimation. Dry the *n*-butanol over 4 Å molecular sieves.

Complejo macrocíclico de níquel.

Place 2.00 g of $Ni(OAc)_2{\cdot}4H_2O$ (8.03 mmol), 1.73 g of *o*-phenylenediamine (1.60 mmol), 35 mL of **dry** butan-1-ol, 1.7 mL of 2,4-pentanedione (~1.66 mmole), and a stirring bar in a 100-mL round-bottom flask. Adapt a reflux condenser to the flask and set it in a heating mantle. Bring the mixture to a brisk reflux and stir for 1.5 hours, noting any color changes. Then, concentrate the solution (by slow distillation of the BuOH at ordinary pressure) to aprox. 20 mL and reflux it 35 minutes more.

Remove the flask from the heat source and allow it to cool until it is just warm to the touch. Add 30 mL of methanol and cool the mixture in an ice-salt bath for at least 15 min to precipitate the nonpolar macrocyclic complex. Filter the solid and wash it with methanol (about 2 x 10 mL; the washings should be colorless to pale green). The dark purple microcrystalline macrocycle is generally obtained in a 37-40% yield. Retain a small sample of product for IR analysis. Use the remaining product to synthesize the free macrocycle as described below.

Preparación de $[H_4(Macrocycle)][NiCl_4]$

Prepare a suspensión of 1.0 g of the nickel complex in 30 mL of ethanol in a 100-mL round-bottom flask. Bubble HCl gas through the suspension at a moderate flow and stir it from time to time. (See note at the end of the experimental part). **Caution: the**

mixture gets quite warm. Once a copious turquoise precipitate forms, filter it off and wash it with ethanol (2 × 5 mL) and ether to obtain about ~95% yield of product.

Aislamiento de la sal del macrociclo (Mac) $[H_4(Mac)][BF_4]_2$

Dissolve the turquoise $[H_4(Mac)][NiCl_4]$ salt in 10 mL water. Occasionally white, water insoluble, impurities are present at this stage and can be removed by filtration. Add 1.0 g of solid NH_4BF_4 to the filtrate and swirl until a large amount of white precipitate forms. Filter the $[H_4(Mac)][BF_4]_2$ in a sintered glass filter and wash with water until the product is pale green. (In this step the $(NH_4)_2NiCl_4$ byproduct needs to be washed away to prevent nickel from re-coordinating into the macrocycle upon basification). Transfer the sticky solid to a 25 mL Erlenmeyer flask, rinsing the sintered glass filter with methanol several times. Enough methanol should be present in the flask to cover the salt. Add triethylamine dropwise to the suspension and swirl. Filter the free yellow macrocycle, wash with 5 mL of methanol, and air dry. Record the IR spectrum.

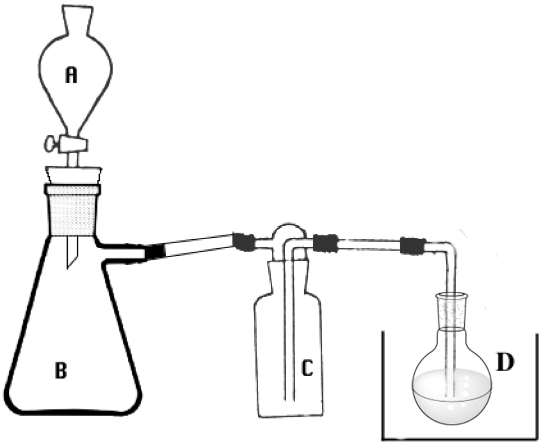
Reacción de $Cu(O_2CMe)_2 \cdot H_2O$ con el macrociclo.

Charge a 10-mL round-bottom flask with $Cu(OAc)_2 \cdot H_2O$ (0.1 g, 0.6 mmol), a stirring bar, and acetonitrile (4 mL). Attach a condenser and reflux the suspension until all the $Cu(OAc)_2 \cdot H_2O$ dissolves. Remove the heater and, with a micropipete add slowly a mixture of the macrocycle (0.1 g, 0.56 mmol), acetonitrile (2 mL), and triethylamine (0.20 mL). Reflux the resulting dark-green solution for about 10 min, then cool to room temperature, and finally keep it in an ice bath for 20 min. Filter the dark green microcrystalline solid and wash it with a 2 mL of acetonitrile and then 2 mL of ether.

NOTA. Procedimiento para generar una corriente de HCl.

Debe prepararse en la vitrina el montaje que se describe a continuación y que puede verse en la figura adjunta. El mismo montaje puede servir para dos alumnos. El embudo de adición **A** se coloca perfectamente ajustado sobre el kitasato **B**, cuyo tubo de desprendimiento conduce a un frasco lavador de seguridad **C**, que a su vez conduce a un matraz **D** sumergido en un baño de hielo. Hay que asegurarse que las uniones estén perfectamente ajustadas para que no se produzcan fugas de gases.

A debe contener 20 mL de H_2SO_4 concentrado y en **B** se colocan 20 g de NaCl cubiertos de ácido clorhídrico concentrado. El tubo de ensayo **D** debe contener el complejo de níquel que se pretende destruir.



Cuestiones.

1.- Indicar la geometría de todos los compuestos de níquel y cobre empleados como reactivos y obtenidos como productos.

2.- ¿Porqué es necesario añadir una disolución de HCl en el matraz B para generar HCl?

3.- Se usa una sal amónica para separar el macrociclo de la sal de níquel. ¿Podría usarse una sal potásica? Razonar la respuesta.

References

1. Lindoy, L. F. The Chemistry of Macrocyclic Ligand Complexes; Cambridge University Press: Cambridge, 1989.
2. Sacconi, L.; Mani, F.; Bencini, A. In Comprehensive Coordination Chemistry; Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 5, Chapter 5, Sect. 50.5.9.
3. Merrell, P. H.; Urbach, F. L.; Arnold, M. *J. Chem. Educ.* **1977**, 54, 580-582.
4. Goedken, V. L.; Weiss, M. C.; Place, D.; Dabrowiak J. *Inorg. Synth.* **1980**, 20, 115-119.
5. Tait, A. M.; Busch, D. H.; Curtis, N. F. *Inorg. Synth.* **1978**, 18, 2-9.

8. Woodruff, W. H.; Pastor, R. W.; Dabrowiak, J. C. *J. Am. Chem. Soc*. **1976**, 98, 7999-8006.

7.B. Síntesis de un complejo encapsulado de cobalto.

En este experimento el metal dirige la reactividad de los ligandos para formar un biciclo que actúa como ligando *criptando* en torno a él (L_1 en Figura 2).

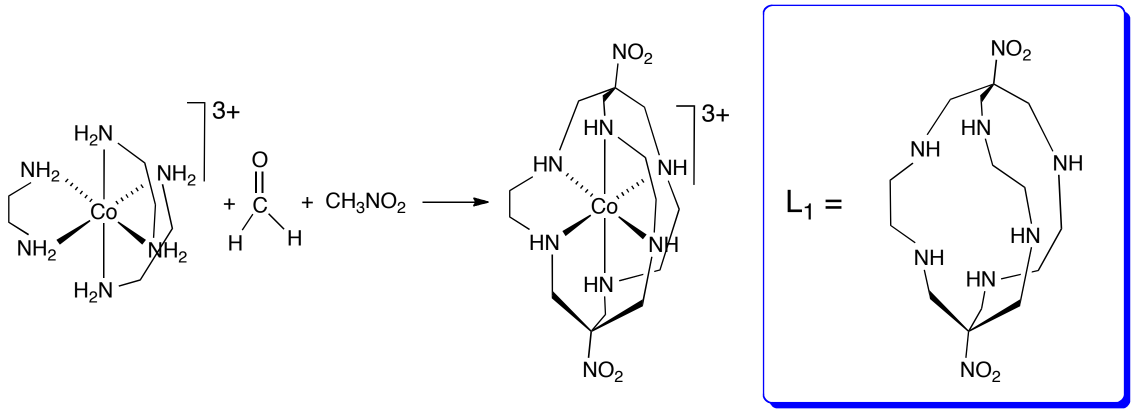


Figura 2

Procedimiento experimental

Cosideraciones generales. Todos los reactivos usados son higroscópicos, mantener los recipientes que los contienen abiertos el tiempo imprescindible para tomar la cantidad necesaria para el experimento.

1. Síntesis del cloruro de tris(etilenodiamina)cobalto(III), $[Co(en)_3]Cl_3 \cdot 1/2NaCl \cdot 3H_2O$.

(Adaptado de "*Synthesis and Technique in Inorganic Chemistry*", Girolami, Rauchfuss, Angelici, 1999).

En un vaso de precipitados de 100 mL, se disuelven 7,0 mL de etilenodiamina en 8 mL de agua. Aparte, en un Erlenmeyer de 250 mL, provisto de una varilla imantada se disuelven 6 g de $CoCl_2 \cdot 6H_2O$ previamente pulverizado en 16,5 mL de HCl concentrado (37%) y se pone a agitar. A esta disolución agitada se añade con una micropipeta, gota a gota, muy despacio, la disolución de etilenodiamina previamente preparada. **ATENCIÓN**: esta reacción es muy exotérmica. Una vez terminada la adición se agita la disolución resultante diez minutos más. En este punto la disolución debe tener un color muy oscuro, rosa grisáceo.

A esta disolución se añaden, en pequeñas porciones, 8.0 g (200 mmol) de hidróxido sódico sólido. **ATENCIÓN**: esta reacción es exotérmica. La disolución toma un color azulado. Cuando toda la sosa se ha disuelto se añaden 20 ml (20 mmol) de peróxido de hidrógeno al 3%. La disolución toma un color salmón oscuro. Si durante este proceso se ha evaporado agua, diluir la disolución hasta 50 mL. Se debe obtener una disolución homogénea. Se transfiere la disolución y la varilla imantada a un vaso de 250 mL, filtrando si permanece algún sólido sin disolver, y se lleva a ebullición durante diez minutos con agitación. El volumen final debe ser ligeramente inferior a 50 mL. Se retira la varilla imantada y se deja enfriar la disolucón, primero hasta temperatura ambiente, y luego en un baño de hielo y sal durante media hora. Durante este tiempo el compuesto cristaliza en pequeñas agujas de color salmón. El sólido se filtra en placa. Se retiran las aguas madres (concentrándolas se puede obtener más compuesto), se lava el sólido con etanol (2 veces con 5 mL) y se seca pasando aire. Concentrando las aguas madres se puede obtener una segunda fracción cristalina (¡cuidado! si se concentra demasiado cristaliza NaCl con el producto). Se obtienen unos seis gramos de producto.

2. Synthesis of cobalt complex of encapsulating ligand L_1

Procedure

Dissolve 2.45 g of $[Co(en)_3]Cl_3$ and 1.2 g of Na_2CO_3 in 25 cm^3 water and add 18 cm^3 of 40% aqueous formaldehyde (with CAUTION!) and 2.5 cm^3 of nitromethane. Allow the mixture to stand at room temperature for 4 hours and add 5 cm^3 ethanol to induce crystallization. Filter the resulting solid off using suction and wash it with ethanol (10 cm^3) and diethyl ether (10 cm^3). Dry the solid in air and store it.

Cuestiones:

1. Explicar brevemente los factores que contribuyen a la estabilidad de los complejos con ligandos macrociclo.
2. Comparar los espectros vis-uv de los dos complejos preparados.
3. Proponer un mecanismo para la formación del complejo$[CoL_1]^{3+}$.

Referencias

E.C. Constable, *Coordination chemistry of macrocyclic compounds*, Oxford Chemistry Primers, 1999

K. Nakamoto, *Infrared and raman spectra of inorganic and coordination compounds*, 4th edition, John Wiley and Sons: New York, 1986.

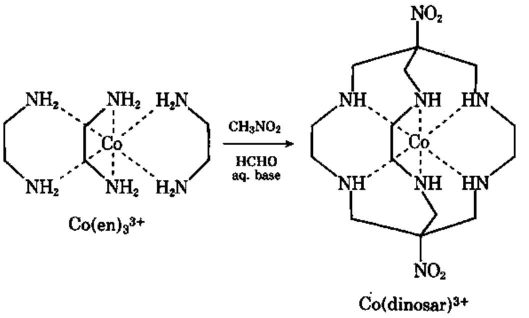
A. Gordon, *The chemist's companion: A handbook of practical data, techniques, and references*, John Wiley and Sons: New York, 1972.

Facile Synthesis of a Macrobicyclic Hexaamine Cobalt(III) Complex Based on Tris(Ethylenediamine)Cobalt(III)

An Advanced Undergraduate Inorganic Laboratory Experiment

Jack MacB. Harrowfield
The University of Western Australia, Nedlands 6009, Western Australia
Geoffrey A. Lawrance
The University of Newcastle, New South Wales 2308, Australia
Alan M. Sargeson
The Australian National University, Canberra 2601, Australia

The synthesis and resolution of tris(ethylenediamine)-cobalt(III) is a classical undergraduate experiment in coordination chemistry, which had been described in THIS JOURNAL and elsewhere (*1–4*). Chelation of cobalt(III) by multidentate ligands has been extended in recent years to include many examples of macromonocyclic ligands (*5*), and recently examples of saturated macrobicyclic ligands (*6*). The latter complexes totally encapsulate the metal ion, and are prepared by an organic template reaction about the inert $Co(en)_3^{3+}$ precursor (en = ethylenediamine = $H_2NCH_2CH_2NH_2$), e.g.



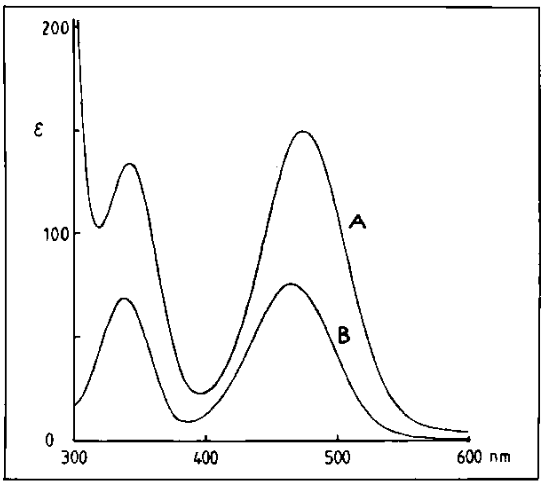
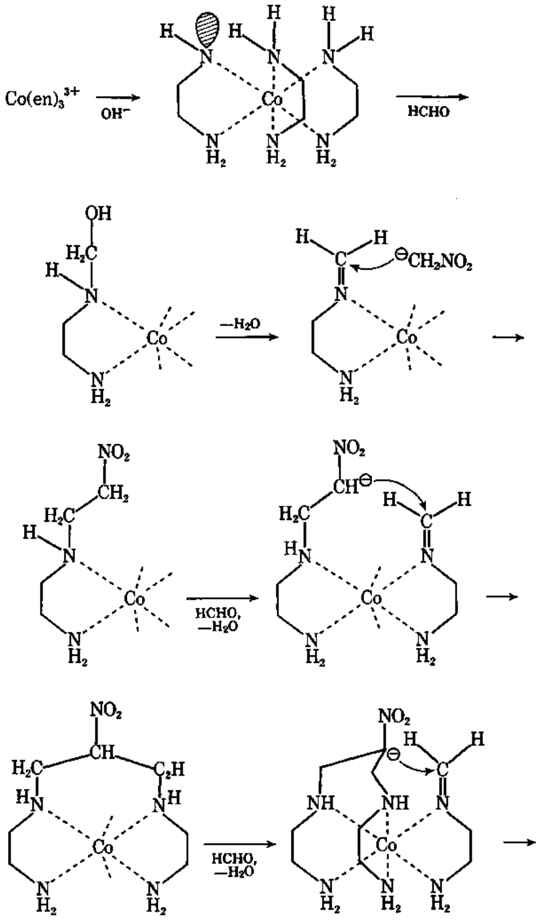
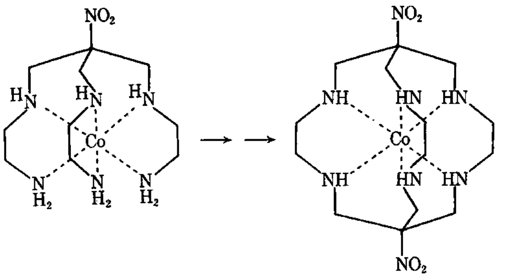


Figure 1. Visible absorption spectra of (A) [Co(dinosar)]Br_3 and (B) [$Co(en)_3$]Br_3.

The encapsulation of the cobalt ion in the macrobicyclic ligand renders it substitution inert, even in the normally labile cobalt(II) state. The synthesis is a good example of reactions of coordinated ligands, and it proceeds in a stepwise fashion, most likely as illustrated in the reaction scheme below. The constraint and ordering of reactants about the metal ion and the small ring closures involved make the template synthesis entropically favorable.





This type of synthesis introduces a new class of coordination compounds as direct descendants from classical complexes. The synthesis of an aza-capped analog of Co(dinosar)$^{3+}$ has been described (*7*), but that synthesis involves an isolation procedure less facile, and less suitable for subsequent experiments, than is the case of Co(dinosar)$^{3+}$ (dinosar = 1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo-(6.6.6)icosane). The described synthesis from Co(en)$_3^{3+}$ can be completed within 2 to 3 h, and is inexpensive and safe. Various aspects of visible, infrared and nuclear magnetic resonance spectroscopy, and of electrochemistry and optical activity can be incorporated into the program as desired.

Synthesis of the Macrobicyclic Complex

(Co(en)$_3$)Br$_3$ (2.5 g) and anhydrous Na_2CO_3 (1.5 g) are dissolved in water (90 mL) in a 200-mL beaker, and nitromethane (5 mL) and 37% aqueous formaldehyde (40 mL) added. (**Caution:** Reaction should be performed in a fume hood.) After stirring briefly to mix reagents, the solution is placed (not stirred) in a waterbath and maintained at 35°→40°C for approximately 1 to 1½ h. The color rapidly darkens from yellow to brown, and after ~1 h an appreciable amount of yellow crystals form. The solution is stirred briefly and occasionally with a glass rod to help induce crystallization. The solution is removed from the waterbath after the 1→1½ h period, and cooled immediately to ~5°C in an ice bath. The crystals are collected on a sintered frit, under suction. The filtrate is discarded (fume hood sink). If crystallization upon cooling is not substantial, addition of up to an equal volume of ethanol to induce precipitation may be employed but is normally not required.

The collected solid is dissolved on the frit using portions of hot dilute acetic acid (a total of ~30 mL of ~1 *M*). The hot yellow filtrate is treated immediately with 15 mL of concentrated HBr. A copious fine yellow crystalline precipitate forms. After cooling to room temperature, this is collected on a frit under suction, washed with cold 1:1 methanol:water, methanol, then ether, and dried at the pump and, if required, in a vacuum desiccator (yield 1.95g, 55%).

Characterization of the Macrobicyclic Complex

Electronic Spectrum: The Co(dinosar)$^{3+}$ complex has absorption maxima in the visible region at 475 nm (ϵ 148 M^{-1} cm^{-1}) and 342 nm (ϵ 133), typical of an octahedral saturated CoN$_6^{3+}$ chromophore, and similar to the Co(en)$_3^{3+}$ precursor (466 nm (ϵ 75), 338 nm (ϵ 68)), Figure 1.

Infrared Spectra: The "fingerprint" pattern of the macrobicyclic ligand is quite different from that of the (Co(en)$_3$)Br$_3$ precursor. The characteristically strong absorbance of -NO$_2$ can be seen at ~1560 cm^{-1} in a KBr disc spectrum of the macrobicyclic complex.

NMR Spectra: The ^{13}C NMR spectrum (JEOL FX-60 spectrometer, D_2O, shifts relative to dioxan, +ve downfield) illustrates the essentially D_3 symmetry in the macrobicyclic complex. Three signals are observed at −11.3 ppm (due to -CH$_2$- groups of the en ring residues), −15.1 ppm (due to -CH$_2$- groups of the capping units), and a resonance at +21.4 ppm (due to the tertiary $\geq$C-NO$_2$ of the caps). For Co(en)$_3^{3+}$, a single resonance occurs at −21.8 ppm. The high symmetry of the macrobicycle is also evident from the ^{1}H NMR spectrum (200 MHz spectrometer, D_2O, N-deuterated, shifts relative to DSS); mainly two overlapping quartets are observed, associated with AB (or AA′BB′) patterns of the cap and en methylene groups, Figure 2.

Electrochemistry: In water, a reversible 1 e$^-$ couple at −0.20 V (versus SCE, mercury electrode, 0.1 *M* NaClO$_4$ electrolyte) is observed for Co(dinosar)$^{3+}$ in both dc (at DME) and cyclic (at HMDE) voltammetry. Further, an irreversible 8 e$^-$ reduction occurs in neutral solution at −0.7 V, due to reduction of both -NO$_2$ capping groups to -NHOH (4 e$^-$ each). Cyclic voltammetry at a hanging mercury drop electrode clearly defines the reversible nature of the first (Co(III)/Co(II)) reduction, and the irreversible nature of the second (-NO$_2$ → -NHOH) reduction. By comparison, Co(en)$_3^{3+}$ exhibits only a single wave at −0.41 V, and this reduction is not fully reversible. Detailed electrochemical studies of a range of such macrobicycles have appeared (*8*).

Further Experiments: Reduction of the Co(dinosar)$^{3+}$ complex chemically with Zn/HCl and air oxidation subsequently yields the (Co(diamsarH$_2$))Cl$_5$ complex from HCl solution with fully reduced (-NH$_3^+$) groups on the apical caps (*9*). The absence of the -NO$_2$ groups can be readily established by IR spectroscopy and electrochemistry. The original synthesis can be performed with optically active Co(en)$_3^{3+}$, whence the product is optically active. Reduction with Zn/HCl and subsequent reoxidation with air (the cobalt(II) salts are air sensitive but can be isolated and their properties studied) yields a complex which retains its chirality. In fact, reduction/reoxidation of the Co(diamsarH$_2$)$^{5+}$ ($E_{1/2}$ −0.18 V) or Co(diamsar)$^{3+}$ ($E_{1/2}$ −0.54 V versus SCE) product can be performed at room temperature with total retention of ligation and chirality; the same experiment performed with chiral Co(en)$_3^{3+}$ leads to complete loss of chirality. This is a simple test of the unusual stability of the cobalt(II) macrobicycles which arises as a consequence of the encapsulation of the metal ion within the ligand cavity.

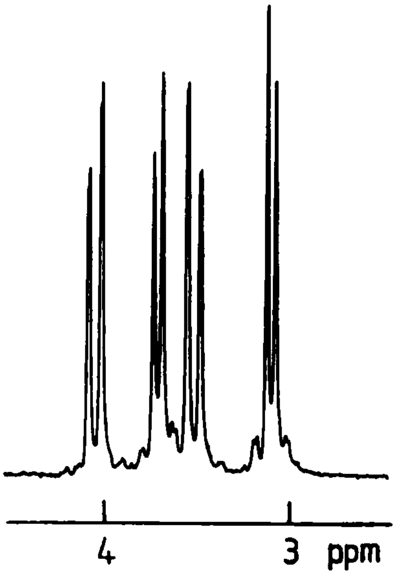


Figure 2. ^{1}H NMR spectrum in D_2O (N-deuterated) of Co(dinosar)$^{3+}$.

Literature Cited

(1) Pass, G., and Sutcliff, H., "Practical Inorganic Chemistry," 2nd ed., Chapman and Hall, London, **1974**.
(2) Angelici, R. J., "Synthesis and Technique in Inorganic Chemistry," W. B. Saunders Co., Philadelphia, **1969**.
(3) Bell, C. J., "Synthesis and Physical Studies of Inorganic Compounds," Pergamon, Oxford, **1972**.
(4) Krause, R. A., and Magargle, E. A., J. CHEM. EDUC., **53**, 667 (1976).
(5) Curtis, N. F., *Coord. Chem. Rev.*, **3**, 3 (1968); Lindoy, L. F., and Busch, D. H., *Preparative Inorg. React.*, **6**, 1 (1971).
(6) Sargeson, A. M., *Chem. Brit.*, **15**, 23 (1979).
(7) Harrowfield, J. MacB., Herlt, A. J., and Sargeson, A. M., *Inorg. Synth.*, **20**, 85 (1980).
(8) Bond, A. M., Lawrance, G. A., Lay, P. A., and Sargeson, A. M., *Inorg. Chem.*, **22**, 2010 (1983).
(9) Geve, R. J., Hambley, T. W., Harrowfield, J. MacB., Sargeson, A. M., and Snow, M. R., *Inorg. Chem.*, **23**, *J. Amer. Chem. Soc.*, **106**, 5478 (1984).

APÉNDICE 1

NORMAS GENERALES DE SEGURIDAD E HIGIENE EN UN LABORATORIO QUÍMICO

En un laboratorio de Química se manipulan sustancias y se realizan operaciones que pueden resultar peligrosas si no se realizan adecuadamente. Es necesario, por consiguiente, extremar las precauciones y actuar conociendo los riesgos de las operaciones que se realizan para prevenir y evitar los pequeños accidentes que pueden producirse. Conocer el contenido de este apartado es por ello fundamental antes de iniciar el trabajo en un laboratorio. A continuación se indican algunas normas y recomendaciones a tener en cuenta.

NORMAS GENERALES

1- El alumno seguirá minuciosamente el guión de prácticas y, en su caso, los consejos del profesor al llevar a cabo un experimento.

2- El alumno no debe realizar nunca experimentos diferentes a los señalados en el guión de prácticas, salvo consulta previa con el profesor y consentimiento de éste.

3- Ante cualquier percance o accidente avisar *inmediatamente* al profesor.

4.- Durante la jornada de trabajo las puertas de acceso a los edificios deben permanecer abiertas y libres de obstáculos. Mantenga despejadas las zonas de entrada, salida y circulación en el laboratorio.

5- Antes de iniciar un experimento, los que participen en él deben hacer una evaluación de todos los riesgos y tomar las medidas necesarias para la prevención de accidentes. Así mismo, deben conocer las instrucciones de operación de los equipos y las propiedades de los materiales que vayan a usarse.

6- El laboratorio cuenta con: Duchas y lavaojos, extintores de incendios, botiquín de primeros auxilios, recipientes metálicos conteniendo arena u otro material inerte. Antes de empezar a trabajar todos deben conocer la ubicación de los elementos y dispositivos de seguridad.

Indumentaria y precauciones personales

7- *Las gafas de seguridad han de usarse en el laboratorio en todo momento*. Protegen los ojos de proyecciones y salpicaduras. Nunca deben usarse lentes de contacto; éstas pueden ser muy peligrosas en caso de accidente porque no pueden quitarse con rapidez; las sustancias corrosivas pueden situarse por debajo de la lentilla y permanecer junto al tejido que dañan más tiempo.

8- Es obligatorio el uso de una bata de laboratorio que debe llevarse siempre abrochada, y que protege el resto de la ropa y la piel.

9- No es recomendable el uso de sandalias o zapatos abiertos, que no protegen los pies.

10- El pelo largo debe estar siempre recogido.

11- No está permitido comer, beber o fumar en el laboratorio, por el peligro de contaminación o incendio que supone.

12- Nunca se debe trabajar solo en un laboratorio, con objeto de poder recibir ayuda en caso de accidente.

Manipulación de reactivos y residuos

10- Antes de utilizar un producto el alumno debe leer atentamente la etiqueta, advertir los riesgos específicos que comporta su uso y seguir en su manipulación las normas o consejos de seguridad que se le indiquen.

11- Los productos inflamables o explosivos deben mantenerse siempre alejados de puntos o focos calientes (mecheros, estufas, radiadores, placas y mantas calefactoras, hornillos, etc.). Una sustancia inflamable o explosiva no debe calentarse nunca a fuego directo (mechero Bunsen).

12- Debe evitarse la contaminación de los productos o reactivos que se utilicen. Para ello se extremarán las condiciones de limpieza en su manipulación no utilizando espátulas, vasos, matraces, etc., que no estén perfectamente limpios. Se tomará del envase original la cantidad de producto necesaria y no se devolverá al mismo el exceso empleado.

13- Los productos o reactivos que puedan verterse accidentalmente sobre la mesa de trabajo deben neutralizarse antes de proceder a su eliminación. Por ejemplo, si se trata de una disolución de base, se neutralizará con hidrogenocarbonato sódico o ácido acético diluido; si de un ácido, con hidróxido cálcico en polvo; si de un oxidante con sulfito sódico sólido, etc.

14- No debe arrojarse a las pilas o fregaderos material o producto alguno que pueda obstruir los desagües.

15- El alumno debe tener sumo cuidado en verter los residuos o productos desechados de las reacciones en los correspondientes recipientes dispuestos a tal efecto en el laboratorio. Para ello ha de seguir las instrucciones del profesor y evitar mezclar productos.

Manipulación de material y operaciones en el laboratorio

16- El puesto de trabajo debe mantenerse en todo momento limpio y ordenado. Finalizada la sesión práctica se procederá al lavado de todo el material y a la limpieza de la mesa y/o la vitrina.

17- Está prohibido acumular o almacenar en las vitrinas de trabajo reactivos o disolventes de cualquier tipo.

18- Todas las operaciones que comporten el uso de disolventes nocivos, o desprendimiento de gases tóxicos, inflamables, o simplemente con mal olor, deben realizarse en el interior de una vitrina.

19- Después del montaje de un aparato de reacción debe comprobarse que sus uniones están perfectamente ajustadas. En caso contrario podría producirse la emisión de gases o vapores tóxicos o inflamables, con el riesgo de accidentes que ello comportaría

19- El trasvase de líquidos con pipetas no debe realizarse nunca por succión directa, sino con la correspondiente pera o goma de succión, a fin de evitar cualquier ingestión accidental del líquido y el riesgo que ello llevaría consigo.

20- Debe evitarse el contacto de las manos con objetos calientes y la proximidad de la ropa a mecheros encendidos; en caso contrario pueden producirse quemaduras, incluso graves.

21- Las substancias inflamables nunca se deben calentar a la llama directa, sino usando un calefactor eléctrico o una manta calefactora. Ha de disponerse además el correspondiente dispositivo de recogida o condensación de vapores. No se debe calentar un sistema cerrado pues el aumento de presión por evaporación del disolvente puede producir una explosión.

22- Los vapores emitidos por las sustancias no deben olerse directamente. Si es necesario comprobar su olor basta acercar el rostro a 10-20 cm. del recipiente y pasar la mano sobre él en dirección a las fosas nasales: los vapores así arrastrados llegan fácilmente a la nariz.

23- La mayoría de los cortes en el laboratorio se producen en el manejo de tubos de vidrio (cortado, introducción en tapones, etc.), por lo que éste debe realizarse siempre con el auxilio de una bayeta.

24- Antes de abandonar el lugar de trabajo se debe comprobar que las llaves de gases y los grifos de agua están cerrados, y que se encuentran desconectados todos los aparatos eléctricos utilizados en la práctica.

Mientras se trabaje o se permanezca en los laboratorios, queda prohibido: maquillarse, fumar, ingerir bebidas o alimentos y usar material de laboratorio para comer o beber.

PROCEDIMIENTO PARA CASOS DE EMERGENCIA Y/O ACCIDENTES

1) **PROTEGER**: Haga el lugar seguro para usted y el accidentado, eliminando cualquier riesgo.

2) **AVISAR**: Comunique la urgencia inmediatamente.

- Al profesor responsable del laboratorio. Si no estuiviera accesible o localizado en ese momento:
- Servicio de emergencias **112** desde cualquier teléfono.

En cualquiera de los casos se deberá indicar: Ubicación de la emergencia (edificio, piso, sala) - Tipo de emergencia - Si hay personas accidentadas

3) **SOCORRER**: - Actúe sin precipitación. - Si hay alguna persona accidentada no la mueva sin conocer antes las posibles lesiones. - Permanezca sereno y tranquilice al lesionado hasta que llegue la ayuda de un profesional médico.

PRIMEROS AUXILIOS

Para poder reaccionar con rapidez en caso de accidente, hay que conocer en primer lugar la localización exacta de extintores, duchas y lavaojos. En todos los casos hay que avisar *inmediatamente* al profesor.

A continuación se enumeran algunas contingencias ante las que debe procederse con toda rapidez como se indica:

1. Proyección de compuestos a los ojos. Enjuáguense éstos, inmediatamente, con mucha agua (ducha lavaojos) durante al menos diez minutos e informe al profesor de lo sucedido. Si las molestias persisten o existe evidencia de daños es necesario consultar a un oftalmólogo.
2. Vertido de productos sobre la piel. Retirar la ropa contaminada y proceder al lavado inmediato con mucha agua de la zona afectada. Cuando se produzcan contactos irritantes de ácidos con la piel, seque la zona afectada y luego lave rápidamente con solución de bicarbonato sódico al 5-10% y posteriormente con abundante agua. Si la irritación fue causada por un álcali, lave rápidamente las zonas afectadas con una solución saturada de ácido bórico o una solución al 1% de ácido acético y posteriormente con abundante agua.

3. Quemaduras por calor. Enfriar la zona afectada con agua abundante. Aplicar la pomada idónea que encontrará en el botiquín del laboratorio.

4. Cortes. Si son pequeños, la herida se lavará con agua, se desinfectará (alcohol o agua oxigenada) y se cubrirá con gasa. Si el corte es grande o profundo puede precisar de asistencia médica: Informar de ello al profesor, que adoptará las medidas pertinentes.

5. Incendio del vestido. Si algún líquido inflamable se proyecta ardiendo sobre la bata, las llamas han de extinguirse mediante la oportuna ducha o cubriendo las llamas con una manta, bata o ropa de algodón. Avisar al profesor y, en su caso, desvestirse y examinar las quemaduras: si son leves, proceder como en 3; si revisten importancia, es necesaria la atención médica.