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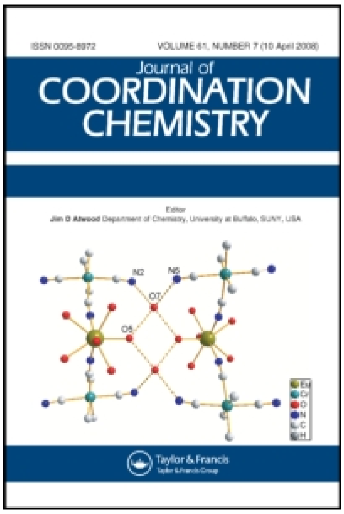

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SYNTHESIS, STRUCTURE AND CHARACTERIZATION OF TRINITRATOTRI (*N*-BUTYLCAPROLACTAM) SAMARIUM (III)

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SYNTHESIS, STRUCTURE AND CHARACTERIZATION OF TRINITRATOTRI(*N*-BUTYLCAPROLACTAM)SAMARIUM(III)

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The synthesis, characterization and structure of a trinitratotri(*N*-butylcaprolactam)samarium(III) complex (**1**) is reported. The Sm(III) ion is coordinated by nine oxygen atoms, three from NBCLM (*N*-butylcaprolactam) ligands, which are monodentates, and six from three bidentate nitrate groups. The geometry around the Sm(III) ion is a distorted tricapped trigonal prism. Spectroscopic and thermal decomposition data for **1** are reported. Magnetic susceptibilities of **1** were measured (80-300 K) and non-linear temperature dependence of magnetic susceptibility and effective magnetic moments were found. The effective moment is 1.8 B.M. at room temperature.

Keywords: samarium(III) complex; *N*-butylcaprolactam; structure; magnetic properties

INTRODUCTION

In the nuclear industry, it is desirable to select extractants which will generate smaller amounts of wastes than the organophosphorus molecules now in current use [1]. It has been reported that *N,N*-dialkylamides were effective for the extraction and separation of lanthanides [2]. We have recently found *N*-alkylcaprolactams even more effective for this purpose and also reported the crystal structure of a uranyl nitrate complex with this extractant [3]. Knowledge

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of the structural chemistry of the corresponding extractant is useful for investigating the extraction mechanism. Since *N*-alkylcaprolactams are potential extractants for lanthanides and actinides it was of interest to investigate the structure of its complexes. Questions concerned the nature of binding sites (O or N), whether the ligand was a chelate, and if counter ions played any significant role in bonding. Here, the synthesis, characterization and structure of the samarium(III) complex is reported. We were also interested in the samarium complex because of its unusual magnetic properties.

EXPERIMENTAL

Preparation of the Complex

$$Sm[CH_2(CH_2)_4CONC_4H_9]_3(NO_3)_3 \qquad (1)$$

N-Butylcaprolactam (NBCLM) was synthesized according to a method described in the literature [4]. Thus, 1 mmol of $Sm(NO_3)_3{\cdot}6H_2O$ was dissolved in 3 cm^3 of ethylorthoformate and 1 cm^3 of absolute alcohol. The mixture was refluxed for about four hours, then 3 mmol of NBCLM was added with stirring for about two hours at 60°C. The solution was distilled *in vacuo* until it became sticky and then toluene was added. The mixture was filtered, cooled and allowed to crystallize. Single crystals suitable for X-ray diffraction studies were obtained by recrystallization from toluene. *Anal.* calcd. for $C_{30}H_{57}N_6O_{12}Sm$ (%): C, 42.69; H, 6.76; N, 9.96. Found: C, 42.40; H, 7.07; N, 9.97.

Measurements

Carbon, nitrogen and hydrogen contents were determined using an MOD 1106 element analyzer. Infrared spectra were measured with a Jasco infrared spectrophotometer (model IR700) in the 400-4000 cm^{-1} region in KBr disk. Solid state electronic spectra were measured with a Shimadzu spectrophotometer (model UV-3100). Magnetic susceptibilities were measured over the 80-300 K range by the Faraday method. Susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants. TG-DTG runs were carried out on a Perkin Elmer TGA-7 Data series thermogravimetrie analyzer equipped with a 3700 Data station.

X-ray Crystal Structure Analysis

A colourless prism (0.64 × 0.63 × 0.52 mm) of **1** was mounted on an Enraf Nonius CAD4 diffractometer. The unit cell parameters and intensities was

TABLE I Atomic coordinates of non-H atoms and equivalent isotropic thermal parameters.

Atom	*x/a*	*y/b*	*z/c*	*B* (Å^2)
Sm	0.75296(2)	0.18441(3)	0.75687(1)	4.639(6)
O1	0.7724(3)	0.2135(5)	0.6536(2)	6.9(1)
O2	0.8143(2)	0.3899(5)	0.7734(2)	6.4(1)
O3	0.6526(2)	0.3204(5)	0.7289(2)	6.3(1)
O4	0.7552(2)	−0.0633(5)	0.7305(2)	6.5(1)
O5	0.6557(3)	0.0362(5)	0.7017(2)	6.8(1)
O6	0.6645(4)	−0.1837(6)	0.6942(3)	10.1(2)
O7	0.8429(3)	0.0915(6)	0.8380(2)	7.1(1)
O8	0.8830(3)	0.1204(6)	0.7508(2)	7.4(1)
O9	0.9524(3)	0.0377(7)	0.8275(3)	10.5(2)
O10	0.6825(2)	0.0717(5)	0.8332(2)	6.5(1)
O11	0.7228(3)	0.2689(5)	0.8620(2)	6.4(1)
O12	0.6684(3)	0.1449(7)	0.9242(2)	8.8(2)
N1	0.7966(3)	0.1949(7)	0.5565(2)	7.0(1)
N2	0.8805(3)	0.5732(6)	0.8031(3)	7.1(2)
N3	0.5347(3)	0.3625(6)	0.7118(2)	5.9(1)
N4	0.6904(3)	−0.0740(6)	0.7079(3)	6.9(1)
N5	0.8956(3)	0.0833(6)	0.8053(3)	7.0(2)
N6	0.6913(3)	0.1623(6)	0.8744(2)	5.8(1)
C1	0.8130(4)	0.2400(9)	0.6125(3)	7.0(2)
C2	0.8829(5)	0.323(1)	0.6285(4)	9.3(3)
C3	0.8784(6)	0.454(1)	0.6001(5)	11.0(3)
C4	0.9005(6)	0.449(1)	0.5338(5)	15.2(4)
C5	0.8475(7)	0.361(1)	0.4923(4)	14.5(4)
C6	0.8428(6)	0.224(1)	0.5069(4)	11.5(3)
C7	0.7333(4)	0.1041(9)	0.5421(3)	7.3(2)
C8	0.7512(4)	−0.0416(9)	0.5491(3)	7.5(2)
C9	0.6880(5)	−0.136(1)	0.5353(4)	9.3(3)
C10	0.7033(8)	−0.281(1)	0.5470(5)	12.6(4)
C11	0.8183(4)	0.5127(7)	0.7897(3)	6.0(2)
C12	0.7515(5)	0.5929(9)	0.7952(5)	8.9(3)
C13	0.7414(6)	0.632(1)	0.8601(5)	12.6(3)
C14	0.7808(7)	0.755(1)	0.8830(5)	12.9(4)
C15	0.8611(7)	0.745(1)	0.8847(4)	11.4(3)
C16	0.8870(5)	0.7158(8)	0.8228(5)	9.4(3)
C17	0.9450(5)	0.496(1)	0.7997(5)	9.6(3)
C18	0.9732(6)	0.444(1)	0.8618(6)	14.9(4)
C19	1.033(1)	0.370(2)	0.8667(9)	23.3(7)
C20	1.052(1)	0.321(2)	0.931(1)	23.3(7)
C21	0.6005(4)	0.3637(6)	0.6946(3)	5.4(1)
C22	0.6111(4)	0.4209(8)	0.6319(3)	7.3(2)
C23	0.5729(5)	0.343(1)	0.5784(3)	8.9(2)
C24	0.4927(5)	0.374(1)	0.5651(4)	9.7(3)
C25	0.4488(4)	0.342(1)	0.6165(4)	8.4(2)
C26	0.4720(4)	0.4198(8)	0.6745(4)	7.5(2)
C27	0.5224(4)	0.2996(9)	0.7705(3)	7.3(2)
C28	0.5287(4)	0.402(1)	0.8205(3)	8.3(2)
C29	0.5128(5)	0.333(1)	0.8816(4)	9.2(3)
C30	0.5225(8)	0.428(1)	0.9313(5)	13.8(4)

TABLE II Selected bondlengths (Å) and angles (°) for complex **1**.

Sm-O(1)	2.343(4)	Sm-O(2)	2.335(5)
Sm-O(3)	2.334(4)	Sm-O(4)	2.506(5)
Sm-O(5)	2.534(5)	Sm-O(7)	2.484(5)
Sm-O(8)	2.534(5)	Sm-O(10)	2.498(5)
Sm-O(11)	2.566(4)	O(1)-C(1)	1.268(9)
O(2)-C(11)	1.259(8)	O(3)-C(21)	1.240(7)
O(1)-Sm-O(2)	85.3(2)	O(1)-Sm-O(3)	83.2(2)
O(1)-Sm-O(4)	83.6(2)	O(1)-Sm-O(5)	77.9(2)
O(1)-Sm-O(7)	124.7(2)	O(1)-Sm-O(8)	74.3(2)
O(1)-Sm-O(10)	147.9(2)	O(1)-Sm-O(11)	153.7(2)
O(2)-Sm-O(3)	85.0(2)	O(2)-Sm-O(4)	149.1(2)
O(2)-Sm-O(5)	152.7(2)	O(2)-Sm-O(7)	85.6(2)
O(2)-Sm-O(8)	76.3(2)	O(2)-Sm-O(10)	124.6(2)
O(2)-Sm-O(11)	74.5(2)	O(3)-Sm-O(4)	122.0(2)
O(3)-Sm-O(5)	71.8(2)	O(3)-Sm-O(7)	149.6(2)
O(3)-Sm-O(8)	151.7(2)	O(3)-Sm-O(10)	87.7(2)
O(3)-Sm-O(11)	78.4(1)	O(4)-Sm-O(5)	50.2(1)
O(4)-Sm-O(7)	77.3(2)	O(4)-Sm-O(8)	72.9(2)
O(4)-Sm-O(10)	75.3(2)	O(4)-Sm-O(11)	122.2(2)
O(5)-Sm-O(7)	121.7(2)	O(5)-Sm-O(8)	118.5(2)
O(5)-Sm-O(10)	70.0(1)	O(5)-Sm-O(11)	113.4(2)
O(7)-Sm-O(8)	50.5(2)	O(7)-Sm-O(10)	74.1(2)
O(7)-Sm-O(11)	71.1(2)	O(8)-Sm-O(10)	120.4(2)
O(8)-Sm-O(11)	115.7(2)	O(10)-Sm-O(11)	50.3(1)

measured using graphite-monochromated Mo$K\alpha$ radiation based on 25 reflections with $20 \leq 2\theta \leq 30°$ at 25 ± 1°C. Intensity data were collected by the scan technique and corrected for Lorentz polarization effects. A total of 6682 reflections were measured in the range $2 \leq 2\theta \leq 48°$ and 4848 reflections with $I \geq 3\sigma(I)$ were assumed as being observed. The structure was solved by direct methods and refined by full-matrix least-squares methods.

Crystal data for **1**: $C_{30}H_{57}N_6O_{12}Sm$, F.W. = 844.18, monoclinic, $P2_1/n$, a = 18.729(7), b = 9.838(2), c = 21.875(3) Å, β = 96.26(2)°, V = 4007(2) Å^3, Z = 4, Dm = 1.41 g cm^{-3}, Dc = 1.40 g cm^{-3}, μ(MoKα) = 15.27 cm^{-1}, R = 0.042, R_w = 0.049.

All calculations were carried out on a VAX station 4000 (90A) computer using the MolEN program package [5]. Atomic coordinates and thermal parameters of the non-hydrogen atoms are listed in Table I. Selected bond distances and angles are listed in Table II. Lists of anisotropic thermal parameters, H atom positions and observed and calculated structure factors are available from the authors on request.

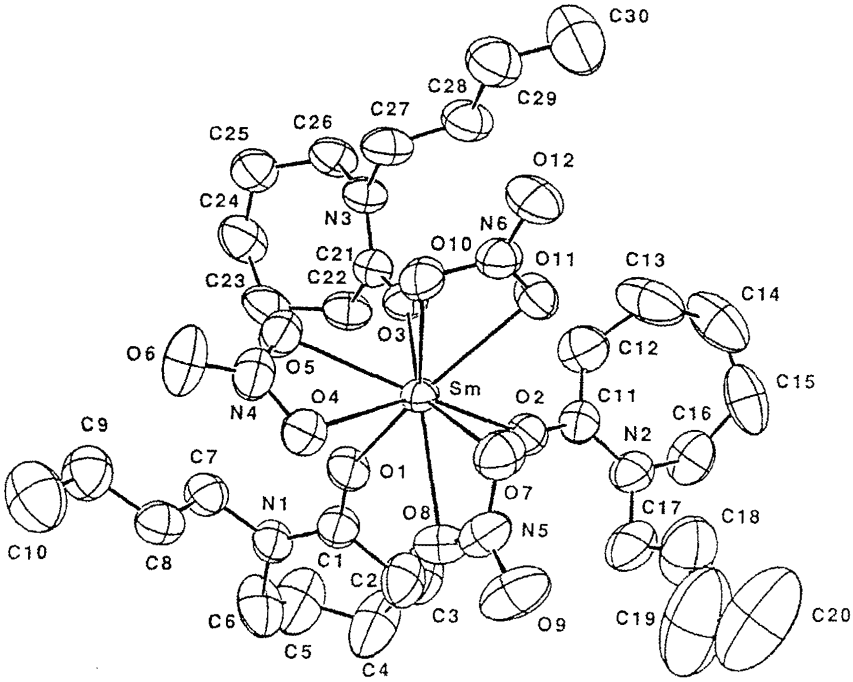

FIGURE 1 Structure of the complex showing the atom numbering scheme.

RESULTS AND DISCUSSION

Crystal Structure of the Sm(III) Complex, 1

Figure 1 shows the molecular structure of the complex. The Sm(III) ion is coordinated by nine oxygen atoms, three from NBCLM ligands, which are monodentates, and six from three bidentate nitrate groups. The average Sm-O distance of 2.337 Å for carbonyl oxygen of NBCLM ligands is shorter than that of 2.520 Å for the nitrate groups.

Lanthanide nitrate complexes of γ-butylolactam $[Ln(BuL)_8](NO_3)_3$ (Ln = La, Nd, Gd) have been reported [6], in which the metal complexes contain uncoordinated ionic nitrate and eight coordinated butylolactams. In this work all three nitrate anions are present as bidentates and the coordination number is increased to nine. It could be expected that nitrate anion is cooperative in the extraction and separation of lanthanides by NBCLM.

The geometry around the Sm(III) ion is a distorted tricapped trigonal prism (Figure 2). The three oxygen atoms O(1), O(2) and O(3) of the organic ligands form one triangular face, while nitrate oxygen atoms O(7), O(4) and O(10) form

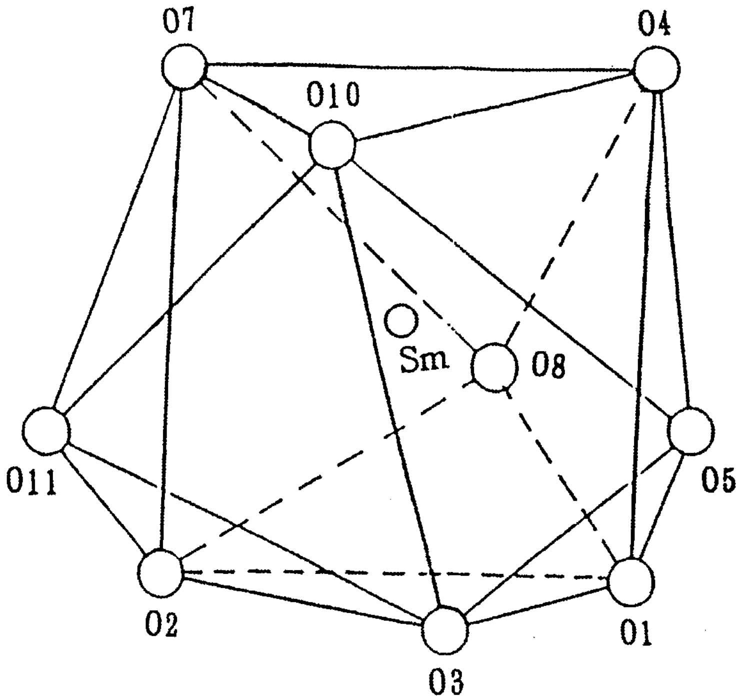

FIGURE 2 Details of the Sm(III) coordination sphere.

the other triangular face. These faces are nearly parallel with a dihedral angle of 18.37°. In addition, the apices O(5), O(8) and O(11) of the three caps are occupied by nitrate oxygen atoms. Distances from the caps to the corners of the trigonal prism are not equivalent. For example, O(11)-O(2), O(11)-O(3), O(11)-O(7) and O(11)-O(10) are 2.977, 3.104, 2.950 and 2.169Å respectively.

Other Physical Measurements

In the IR spectra of **1**, the strong carbonyl absorption is located at 1585 cm^{-1}, with a remarkable shift compared with the free ligand (1642 cm^{-1}), indicating that samarium(III) ion is coordinated through the carbonyl oxygen atom. The difference between the two strongest characteristic frequencies of coordinating nitrate groups (1486 and 1291 cm^{-1}) is nearly 200 cm^{-1}, indicating the nitrate groups are coordinated as bidentates [7].

The solid state electronic-NIR reflectance spectrum of **1** is shown in Figure 3. Because the *f* orbitals are so well shielded, the *f*-*f* transition bands from one *J*

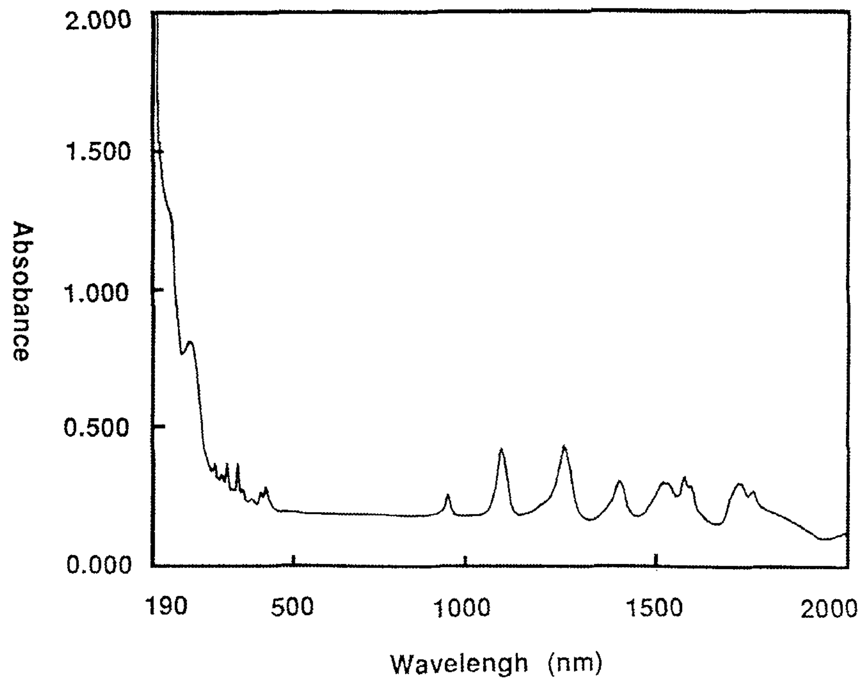

FIGURE 3 Electronic spectrum of the complex.

state to another are extremely sharp and similar to those for samarium(III) nitrate. Both **1** and the nitrate show two groups of *f-f* transitions, one in the near-UV and the other in the near-IR. We have not found any data about near-IR spectra of Sm(III) and consider that they occur for the first excited *J* state transition (see below). Although the spectra of the Sm(III) complex and nitrate are similar, changes in the intensity and shifts in position of the bands are noted. These shifts have been ascribed to a nephelauxetic effect [8, 9].

Magnetic susceptibilities of **1** were measured over 80-300 K (Figure 4). The results for the Sm(III) complex are similar to the free ion (1.5 B.M.), giving a higher effective moment of 1.8 BM. It has been noted that experimental values of susceptibilities and magnetic moments for Sm^{3+} and Eu^{3+}, unlike other Ln^{3+} ion, can not be calculated straightforwardly by considering only one well-defined *J* state [8, 9]. Non-linear temperature dependences of the magnetic susceptibility and effective magnetic moment data are observed. The first excited *J* state is sufficiently close to the ground state to be populated at ordinary temperatures. At low temperatures, the effective magnetic moment data relate to the ground state only.

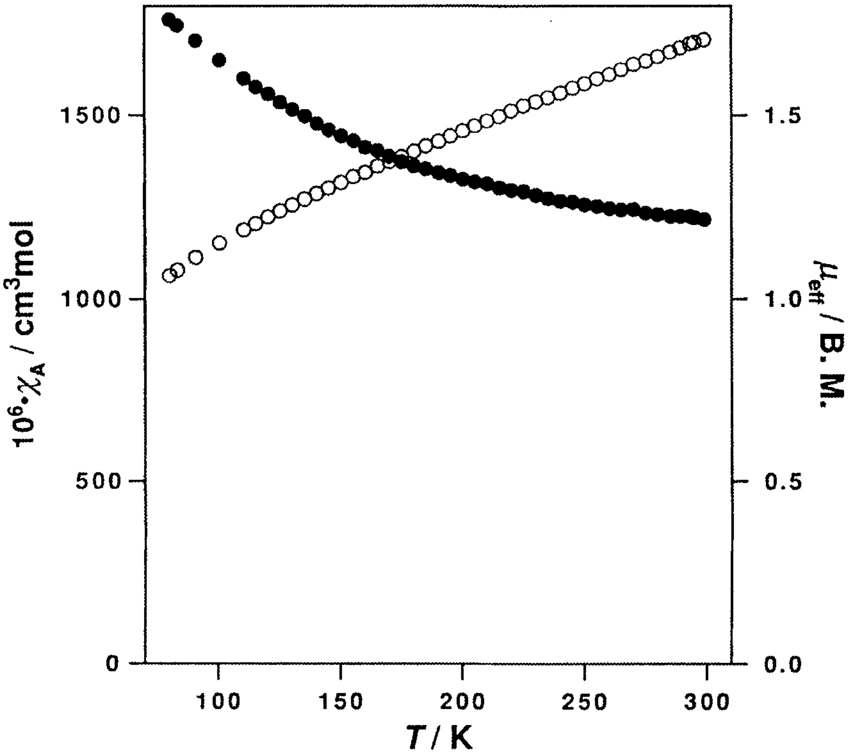

FIGURE 4 Magnetic data for the complex. Open circles refer to effective moments.

The thermal decomposition of **1** was studied by TG-DTG. The complex first releases organic ligands in the range of 190-260°C, then nitrate decomposes *via* two steps to 670°C, giving the residue Sm_2O_3.

References

[1] C. Musikas, *Inorg. Chim. Acta*, **140**, 197 (1987).
[2] G.M. Graparint and G. Grossi, *Solvent Extraction and Ion Exchange*, **4**, 1233 (1986).
[3] Z.B. Cao, H.Z. Wang, L.M. Zhu, J.S. Gu, Z.R. Lu and K.B. Yu, *J. Chinese Uni. Chem.*, **14**, 1051 (1993).
[4] C.S. Marvel and W.W. Moyer, *J. Org. Chem.*, **22**, 1065 (1957).
[5] C.K. Fair, *MolEn Structure Determination System* (Delft Instruments, Delft, The Netherlands 1990).
[6] W.V. Miller and S.K. Madan, *J. Inorg. Nucl. Chem.*, **30**, 2785 (1968).
[7] N.F. Curtis and Y.M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).
[8] S.A. Cotton, *Encyclopedia of Inorganic Chemistry*, Vol. 7, Ed. R.B. King, (J. Wiley and Sons, New York, 1994), pp. 3601-3602.
[9] F.A. Hart, *Comprehensive Coordination Chemistry*, Vol. 5, Eds. G. Wilkinson, R.D. Gillard, and J.A. McCleverty, (Pergamon Press, New York, 1987), pp. 1059-1127.