room-temperature magnetic moment and the exchange integral for values of $\mu_{\text{eff}}(\text{RT})$ in the range 0.3–1.6 $\mu_B$ and $-2J$ in the range 190–1000 cm$^{-1}$. However, if one includes a larger selection of spin-coupled complexes involving a variety of ligand bridges and covering an extended range of $-2J$ and $\mu_{\text{eff}}(\text{RT})$ it becomes apparent that the relationship is not linear. Figure 1 contains $-2J$ vs. $\mu_{\text{eff}}(\text{RT})$ data for a varied selection of binuclear copper(II) complexes involving unrelated ligands, which have been synthesized and studied in a variety of different laboratories, where variable-temperature magnetic measurements have been carried out on a variety of different susceptometers with room-temperature magnetic moments quoted at different room temperatures.

Substitution of the Van Vleck equation (eq 1) into the expression (eq 3) (TIP, temperature-independent paramagnetism,

$$\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2} \qquad (3)$$

not included in the corrected molar susceptibility term) for the effective magnetic moment gives (eq 4) an expression, in which

$$-2J = kT \ln \left( \frac{3.0003 g^2}{\mu_{\text{eff}}^2} - 3 \right) \qquad (4)$$

the exchange integral ($-2J$) and the effective magnetic moment at temperature $T$ are variables ($N\beta^2/3k = 0.12505$). A nonlinear regression analysis of the 36 data (Figure 1) using this two-parameter expression (eq 4) and using a weighting scheme in between a constant and proportional standard deviation[16] gave the theoretical line (Figure 1) and a two-parameter fit of $g = 2.198 \pm 0.008$ and $T = 295.6 \pm 4.5$ K.

The very reasonable fit of the data with a sensible mean $g$ value and mean room-temperature indicates, quite clearly, that realistic estimates of exchange integrals can be obtained for antiferromagnetically coupled binuclear copper(II) complexes by the use of this graphical fit or by substituting known values of $g$, $T$, and $\chi_M$ into the Van Vleck equation itself. The errors from this estimation are not likely to be unreasonable, and, in fact, for very strongly coupled systems, where variable temperature susceptibility measurements may involve large errors because of the weak paramagnetism involved, especially at low temperatures, measurements of $-2J$ values are likely to provide very reasonable results.

The upsurge of interest in spin-coupled copper compounds, which are relevant as models for spin-coupled binuclear copper protein active sites, has led to the synthesis and study of a large number of binuclear copper complexes, many of which have not been investigated by variable-temperature susceptibility studies because of the lack of suitable equipment. However, since most chemistry departments have room-temperature susceptibility equipment, which can be purchased or constructed at a modest cost, the results of room-temperature magnetic moment measurements can be used to provide reasonable estimates of exchange integrals. Of the simple techniques suitable for such measurements the Faraday method, using a sensitive microbalance with resolution at the microgram level, would be favored, especially for weakly paramagnetic, strongly coupled complexes.

(8) Dooley, D. M.; Scott, R. A.; Ellinghaus, J.; Solomon, E. I.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 3019.
(9) Morgenstern-Badarau, I.; Cocco, D.; Desideri, A.; Rotilio, G.; Jardonov, J.; Dupre, N. *J. Am. Chem. Soc.* **1986**, *108*, 300.
(10) Thompson, L. K.; Hanson, A. W.; Ramaswamy, B. S. *Inorg. Chem.* **1984**, *23*, 2459.
(11) Thompson, L. K.; Hartstock, F. W.; Robichaud, P.; Hanson, A. W. *Can. J. Chem.* **1984**, *62*, 2755.
(12) Mandal, S. K.; Woon, T. C.; Thompson, L. K.; Newlands, M. J.; Gabe, E. J. *Aust. J. Chem.*, in press.
(13) Thompson, L. K.; Woon, T. C.; Murphy, D. B.; Gabe, E. J.; Lee, F. L.; Le Page, Y. *Inorg. Chem.* **1985**, *24*, 4719.
(14) Robichaud, P.; Thompson, L. K. *Inorg. Chim. Acta* **1984**, *85*, 137.
(15) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.
(16) Duggleby, R. G. *Anal. Biochem.* **1981**, *110*, 9.

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## Crystal Structure of Bis(*p*-toluidine)bis(acetonitrile)tetraiodotetracopper: Correction of Space Group

William P. Schaefer

The crystal structure of the tetrameric copper cluster bis(*p*-toluidine)bis(acetonitrile)tetraiodotetracopper has recently been described.[1] It was reported in the triclinic space group $P\bar{1}$ with two formula weights in the unit cell. In fact it should be formulated in the monoclinic space group $C2/c$, with $Z = 4$.

The reported cell dimensions are $a = 14.274$ (5) Å, $b = 7.587$ (2) Å, $c = 14.239$ (5) Å, $\alpha = 88.61$ (2)°, $\beta = 110.07$ (2)°, and $\gamma = 88.70$ (2)°. The vectors $\mathbf{c} + \mathbf{a}$, $\mathbf{c} - \mathbf{a}$ and $-\mathbf{b}$ describe an effectively monoclinic cell with $a = 16.340$ Å, $b = 23.366$ Å, $c = 7.587$ Å, $\alpha = 90.05$, $\beta = 92.35°$, and $\gamma = 90.15°$. The atomic coordinates, transformed according to the relations $x_m = \frac{1}{2}x_t + \frac{1}{2}z_t + \frac{1}{4}$, $y_m = -\frac{1}{2}x_t + \frac{1}{2}z_t - \frac{1}{4}$, and $z_m = -y_t$, yield values that are compatible with the space group $C2/c^2$ within the reported esd's (Table I, supplementary material). Since the coordinate shifts necessary to achieve the higher symmetry are no greater than the esd's, the change in space group does not change the description of the structure, other than to introduce an exact crystallographic twofold axis in place of the approximate one. Further confirmation of the correctness of this description is obtained from the structure factors, which show the appropriate absences (triclinic $hkh$, $k = 2n + 1$)[3] for space group $C2/c$.

(1) Rath, N. P.; Holt, E. M.; Tanimura, K. *Inorg. Chem.* **1985**, *24*, 3934–3938.
(2) The translational components of $^1/_4$ are needed to put the origin at the conventional center of symmetry.
(3) Of the 250 reflections of this type listed in the supplementary data, 119 had $k$ odd and 118 of these were marked with an asterisk, presumably indicating unobserved. The sole exception, 14,1,14, had $F_o = 208$ where some unobserved reflections had $F_o = 164^*$. Of the 131 such reflections with $k$ even, 59 were not marked and were presumably considered observed.

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## Synthesis and Characterization of a Ruthenium(II) Clathrochelate Complex

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Metal clathrochelates consist of a metal ion encapsulated by a bicyclic macrocyclic ligand.[2] These complexes often possess greater thermodynamic and kinetic stability than that found in analogous open-chain complexes, because of their greatly reduced

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capacity for ligand exchange. Thus, complexes of this type can lead to studies involving limited-pathway racemizations, metal ion analysis, ion-transport phenomena, and outer-sphere electron-transfer reactions.[3-9] Many examples of iron and cobalt clathrochelates containing dioxime bidentate ligands and various boron capping agents have been investigated,[9-14] with the observation that cobalt clathrochelate complexes are stable as neutral (cobalt(II)) and 1+ (cobalt(III)) species, while the analogous iron complexes are stable only as the neutral (iron(II)) species. Other types of cage complexes encapsulating cobalt, rhodium, iridium, and platinum have been developed and studied, primarily by Sargeson.[15-19] Presently, the only encapsulated ruthenium(II) complex to be reported involved the insertion of a ruthenium(II) center into a preformed hexadentate bicyclic macrocyclic ligand.[20] This synthetic route was taken due to the difficulties encountered on attempting to cap the tris(1,2-ethylenediamine)ruthenium(III) ion. We wish to report the first in situ template synthesis of a clathrochelate complex containing ruthenium(II), $[Ru(NOX)_3(BC_6H_5)_2]$ (1) (NOX = deprotonated cyclohexanedione dioxime).

**1**
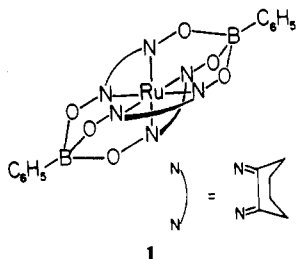
In addition, by reporting the electrochemistry of this ruthenium(II) complex, we will comment on the stability of complex 1 upon electrochemical oxidation.

## Experimental Section

All chemicals were obtained commercially: ruthenium(III) chloride trihydrate (AESAR), cyclohexanedione dioxime (Aldrich), and phenylboric acid (Aldrich). The elemental analyses were performed by Galbraith Laboratories, Inc. Infrared spectra were measured with a Perkin-Elmer Model 457 spectrometer, the NMR spectra were measured with a JEOL FX90Q spectrometer, and the UV spectra were measured with a Bausch and Lomb 2000 spectrometer. Cyclic voltammetry data was collected with the use of a IBM-EC 225 polarographic analyzer, employing a saturated sodium chloride calomel reference electrode (SSCE), a polished-platinum-disk working electrode (Bioanalytical Systems Inc), and a platinum-wire counter electrode. Electrolyses were performed in a three-compartment cell utilizing a platinum-gauze working electrode, a SSCE reference electrode and a platinum-wire
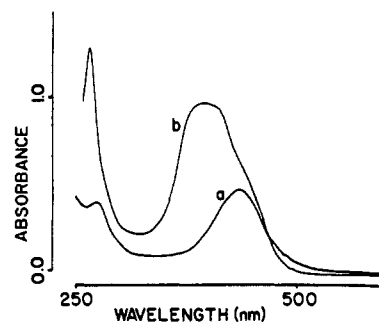
(3) Dietrich, B.; Lehn, J. M.; Sauvage, J. P. *Tetrahedron Lett.* **1964**, *34*, 2889.
(4) Lehn, J. M.; Sauvage, J. P.; Dietrich, B. *J. Am. Chem. Soc.* **1970**, *92*, 2916.
(5) Zakerzewski, G. A.; Ghilardi, C. A.; Lingafelter, E. C. *J. Am. Chem. Soc.* **1971**, *93*, 4411.
(6) Borchardt, D.; Pool, K.; Wherland, S. *Inorg. Chem.* **1982**, *21*, 93.
(7) Borchardt, D.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 2542.
(8) Herron, N.; Grzybowski, J. J.; Matsumoto, N.; Zimmer, L. L.; Christoph, G. G.; Busch, D. H. *J. Am. Chem.Soc.* **1982**, *104*, 1999.
(9) Jackels, S. C.; Dierdorf, D. S.; Zektzer, J.; Rose, N. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1291.
(10) Boston, D. R.; Rose, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 4163.
(11) Johnson, J. N.; Rose, N. J. *Inorg. Synth.* **1982**, *21*, 112.
(12) Jackels, S. C.; Rose, N. J. *Inorg. Chem.* **1973**, *12*, 1232.
(13) Robbins, M. K.; Naser, D. K.; Heiland, J. L.; Grzybowski, J. J. *Inorg. Chem.* **1985**, *24*, 3381.
(14) Grzybowski, J. J. *Inorg. Chem.* **1985**, *24*, 1125.
(15) Boucher, H. A.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M., Bond, A. M.; Sangster, D. F.; Sullivan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 4652.
(16) Harrowfield, J. Macb.; Herlt, A. J.; Lay, P. A.; Sargeson, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 5503.
(17) Bond, A. M.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 2010.
(18) Creaser, I. I.; Sargeson, A. M.; Zanella, A. W. *Inorg. Chem.* **1983**, *22*, 4022.
(19) Creaser, I. I.; Lydon, J. D.; Sargeson, A. M. *J. Am. Chem. Soc.* **1984**, *106*, 5729.
(20) Bernhard, P.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1985**, 1516.

**Figure 1.** UV–visible spectra of (a) $[Fe(NOX)_3(BC_6H_5)_2]$ ($2.86 \times 10^{-5}$ M) and (b) $[Ru(NOX)_3(BC_6H_5)_2]$ ($5.55 \times 10^{-5}$ M) in methylene chloride.
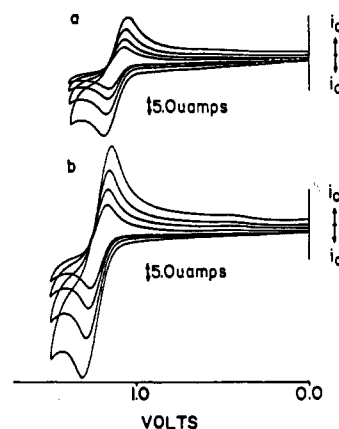
**Figure 2.** Cyclic voltammograms of (a) $[Fe(NOX)_3(BC_6H_5)_2]$ and (b) $[Ru(NOX)_3(BC_6H_5)_2]$. Scan rates: 50, 100, 200, and 400 mV/s.

counter electrode. Coulombs were measured by using an Electrosynthesis Company, Inc., Digital coulometer, Model No. 630. Methylene chloride, distilled from calcium hydride, was used as the spectrophotometric solvent and the electrochemical solvent. Tetrabutylammonium tetrafluoroborate, recrystallized twice from methanol, was used as the supporting electrolyte for all electrochemical experiments. Chloroform-$d_3$ was used as the solvent for all NMR experiments.

**Preparation of [Tris($\mu$-1,2-cyclohexanedione dioximato-$O$:$O'$)diphenyldiborato(2-)-$N$,$N'$,$N''$,$N'''$,$N''''$,$N'''''$]ruthenium(II), [Ru(NOX)$_3$(BC$_6$H$_5$)$_2$].** Under argon, 7.0 mL of dry ethanol (distilled from magnesium metal) and 0.1 g (0.382 mol) of Ru$^{III}$Cl$_3$·3H$_2$O were combined in a 50-mL round-bottom flask and refluxed until the brown solution turned green. Then 0.163 g (1.15 mmol) of cyclohexanedione dioxime (NOXH$_2$) was added, and the solution was refluxed for 1 h, yielding a dark brown solution, which was cooled to room temperature and treated with 0.093 g (0.765 mmol) of phenylboric acid. The mixture was stirred for 1 h and then cooled in an ice bath, resulting in the precipitation of a brown solid. Under atmospheric conditions, the crude brown product was collected by suction filtration and washed with diethyl ether. The brown filtrate was reduced to dryness by rotary evaporation. The brown residue and the filtered solid was combined, dissolved in a minimum amount of methylene chloride, and passed down a column containing neutral alumina (CH$_2$Cl$_2$ eluant). The purified [Ru(NOX)$_3$(BC$_6$H$_5$)$_2$] was recovered as a yellow fraction and was recrystallized from diethyl ether/ethanol following removal of the methylene chloride by rotary evaporation. The yield was 33.1 mg (12.5%). Anal. Calcd for C$_{30}$H$_{34}$N$_6$O$_6$B$_2$Ru: C, 51.67; H, 4.91. Found: C, 51.40; H, 4.83.

## Results

The preparation of a clathrochelate can involve a template reaction between the three bidenate ligands and the two capping agents.[10] The use of cyclohexanedione dioxime as the bidentate ligand and phenylboric acid as the capping agent was first used in the preparation of an iron(II) clathrochelate by Johnson and Rose.[11] A modification of this procedure, involving a different metal ion sources and a different solvent, was used for the preparation of the complex reported.

The infrared spectrum of the ruthenium complex (C=N stretch, 1545 cm$^{-1}$; N—O stretches, 1230 and 1085 cm$^{-1}$) is consistent with the spectrum reported for the analogous iron

**Figure 3.** Nuclear magnetic resonance spectra of [Ru(NOX)₃(BC₆H₅)₂]: (a) ¹³C NMR (proton decoupled); (b) ¹H NMR.

complex.[11] The electronic spectrum of the ruthenium clathrochelate reveals a complex charge-transfer band centered at 25 100 cm⁻¹ ($\epsilon$ = 18 000 L/(mol cm); CH₂Cl₂) (Figure 1). The analogous iron complex generates a qualitatively similar spectrum with a band centered at 22 300 cm⁻¹ ($\epsilon$ = 17 000 L/(mol cm)).

Cyclic voltammetric studies of [Ru(NOX)₃(BC₆H₅)₂] reveal a quasi-reversible couple with $E_{1/2}$ = +1.28 V ($\Delta E_p$ = 70 mV; $I_{p,c}/I_{p,a}$ = 0.89; scan rate = 100 mV/s)[21] (Figure 2). In comparison, cyclic voltammetric studies of the iron clathrochelate complex in methylene chloride revealed a quasi-reversible couple with $E_{1/2}$ = +1.12 V ($\Delta E_p$ = 80 mV; $I_{p,c}/I_{p,a}$ = 0.92; scan rate = 100 mV/s). Oxidative electrolysis of a methylene chloride solution of [Ru(NOX)₃(BC₆H₅)₂], where a platinum-mesh electrode was held at a potential value of +1.43 V, resulted in a transfer of >>1 electron/molecule. Cyclic voltammetry of the electrolyzed solution illustrated that the original clathrochelate complex had undergone extensive decomposition, most likely occuring via an ECE mechanism involving rupture of the ligand superstructure. This is comparable to the behavior of the analogous iron complexes reported previously.[13]

The ¹H NMR spectrum of [Ru(NOX)₃(BC₆H₅)₂] shows two broad methylene resonances (1.71 and 2.88 ppm vs TMS), both of which integrate to account for 12 hydrogen atoms (Figure 3). These resonances were assigned to the hydrogen atoms bonded to the γ- and β-carbons of the oxime. Two multiplets at chemical shift values of 7.36 and 7.89 ppm were assigned to the phenyl hydrogen atoms. These resonances integrate to values of four and six hydrogen atoms, respectively. The proton-decoupled ¹³C NMR spectrum of the ruthenium clathrochelate revealed six peaks. The two peaks that appeared at chemical shift values of 21.54 and 25.41 ppm were assigned to the γ- and β-carbons of the oximes. Examination of the proton-coupled ¹³C NMR spectrum allowed assignment of the peaks at 127.37, 127.90, and 131.77 ppm to phenyl carbon atoms bonded to hydrogen atoms. The remaining peak at 147.86 ppm is assigned to the azomethine carbon. The ¹³C resonance for the carbon atom bonded directly to the boron atom was not observed. This is most likely due to quadrupole broadening caused by the adjacent boron atom.[22]

**Conclusions**

In order to further explore the chemistry of transition-metal clathrochelate complexes based on dioxime/boron bicyclic macrocyclic ligands, the first example of an in situ template synthesis of a ruthenium(II) clathrochelate was successfully conducted. Since ruthenium complexes are generally much more substitutionally inert than analogous iron complexes,[23] it was anticipated that the electrochemical generation of a ruthenium(III) clathrochelate complex might be a possibility, if the mechanism of

the analogous iron(III) clathrochelate complex decomposition involves a simple ligand dissociation subsequent to complex oxidation. However, the exhaustive oxidative electrolysis of a ruthenium(II) clathrochelate complex solution resulted in the decomposition of the complex, in a manner very similar to that observed for analogous iron(II) clathrochelate complexes.[13] These observations, coupled with the fact that an analogous cobalt(III) clathrochelate complex is stable,[10] indicate that, for the iron and ruthenium complexes, the clathrochelate ligand probably undergoes decomposition subsequent to complex oxidation, possibly due to the substantially more positive oxidation potentials associated with ruthenium and iron clathrochelate complexes relative to the analogous cobalt clathrochelate complex. For the generation of stable ruthenium(III/II) redox couples, clathrochelate ligands that lower the redox potential of the ruthenium(III/II) couples to values closer to the vales for cobalt(III/II) couples will be investigated.

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**Reaction of Nitrosoarenes with Trinuclear Metal Carbonyl Clusters of Iron, Ruthenium, and Osmium**

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Bridging ligands play an important role in cluster chemistry often by adding stability to the particular group of metals to which they are attached. Certain four-electron-donor ligands such as PR,[3] S,[4-8] and other group 16 elements[9] have found many such applications. Organoimido ligands (RN) on metal carbonyl clusters have been less well studied, in part, because of the low yields that typically characterize their synthesis.[10-26] We report

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(3) (a) Huttner, G.; Schneider, J.; Müller, H. D.; Mohr, G.; von Sereyl, J.; Wohlfahrt, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 46. (b) Pittman, C. U.; Wilemon, G. M.; Wilson, W. D.; Ryan, R. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 478. (c) Vahrenkamp, H.; Wucherer, E. J.; Wolters, D. *Chem. Ber.* **1983**, *116*, 1219. (d) Burkhardt, E. W.; Mercer, W. C.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1251. (e) Mays, M. J.; Raithby, P. R.; Taylor, P. L.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1984**, 959. (f) Lunniss, J.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J.; Sappa, E. *Organometallics* **1985**, *4*, 2066.
(4) Adams, R. D.; Horváth, I. T.; Mathur, P. *J. Am. Chem. Soc.* **1984**, *106*, 6296 and references therein.
(5) Adams, R. D.; Horváth, I. T.; Kim, H. S. *Organometallics* **1984**, *3*, 548.
(6) Adams, R. D.; Horváth, I. T.; Segmüller, B. E.; Yang, L. W. *Organometallics* **1983**, *2*, 144.
(7) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322.
(8) Cresswell, T. A.; Howard, J. A. K.; Kennedy, F. G.; Knox, S. A. R.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1981**, 2220.
(9) Bogan, E. L.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 3843 and references therein.
(10) Dekker, M.; Knox, G. R. *J. Chem. Soc., Chem. Commun.* **1967**, 1243.
(11) Stanghellini, P. L.; Rossetti, R. *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Nat.* **1970**, *105*, 391.
(12) von Gustorf, E. K.; Wagner, R. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 910.
(13) Alper, H. *Inorg. Chem.* **1972**, *11*, 976.
(14) Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 387.
(15) Aime, S.; Gervasio, G.; Milone, L.; Rossetti, R.; Stanghellini, P. L. *J. Chem. Soc., Dalton Trans.* **1978**, 534.

(21) Evans, D. H.; O'Connell, K. M.; Peterson, R. A.; Kelly, M. J. *J. Chem. Educ.* **1983**, *60*, 290.
(22) Eaton, G. R.; Lipscomb, W. N. *NMR Studies of Boron Hydrides and Related Compounds*; W. A. Benjamin: New York, 1969.
(23) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. In *Coordination Chemistry*; Martell, A. E., Ed.; ACS Monograph 174; American Chemical Society: Washington, DC, 1978; Vol. 2, Chapter 1.