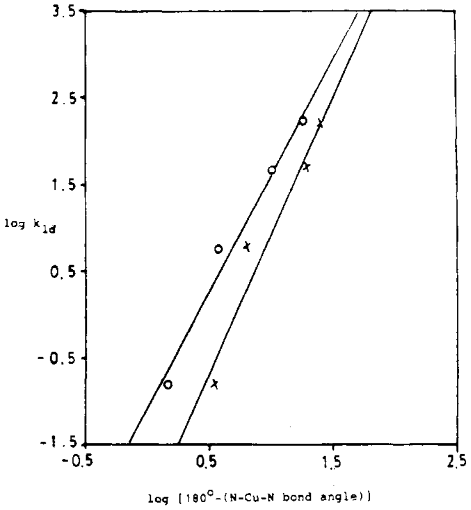

Figure 3. log k_{1d} as a function of log (180° – the N–Cu–N bond angle): (O) large trans N–Cu–N bond angle; (X) small trans N–Cu–N bond angle.

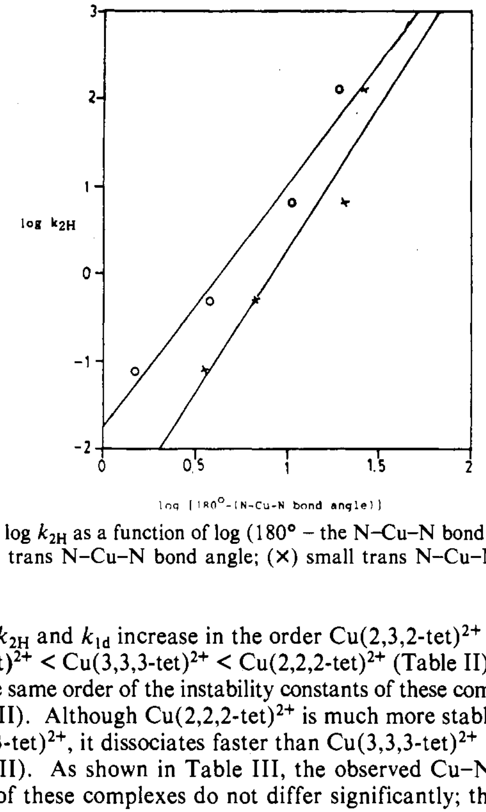

Figure 4. log k_{2H} as a function of log (180° – the N–Cu–N bond angle): (O) large trans N–Cu–N bond angle; (X) small trans N–Cu–N bond angle.

Both k_{2H} and k_{1d} increase in the order Cu(2,3,2-tet)$^{2+}$ < Cu(3,2,3-tet)$^{2+}$ < Cu(3,3,3-tet)$^{2+}$ < Cu(2,2,2-tet)$^{2+}$ (Table II). This is not the same order of the instability constants of these complexes (Table III). Although Cu(2,2,2-tet)$^{2+}$ is much more stable than Cu(3,3,3-tet)$^{2+}$, it dissociates faster than Cu(3,3,3-tet)$^{2+}$ (Table II and III). As shown in Table III, the observed Cu–N bond lengths of these complexes do not differ significantly; the conformations of the chelate rings are the most stable six-membered chair and five-membered gauche forms.

As shown in Figure 2, the initial phase of the chelate ring-opening step involves some angular distortion of the bond angles in the chelate rings. This led us to think that there must be a relation between the bond angles and the kinetic properties of these complexes. Within the Cu(2,3,2-tet)$^{2+}$ unit, the N–Cu–N bond angles (178.5 and 176.4) are very close to 180°.[8] Consequently, the N_4 donor set in this complex nearly matches the symmetry properties of the Cu(II) orbital; on this basis, a relatively inert complex is expected (and found). Deviations of the homologous, crystallographically characterized Cu(3,2,3-tet)$^{2+}$, Cu(3,3,3-tet)$^{2+}$, and Cu(2,2,2-tet)$^{2+}$ complexes from this idealized bonding arrangement are reflected by the kinetic data.[7,8] As shown in Table III the N–Cu–N bond angles vary in the order Cu(2,3,2-tet)$^{2+}$ > Cu(3,2,3-tet)$^{2+}$ > Cu(3,3,3-tet)$^{2+}$ > Cu(2,2,2-tet)$^{2+}$; thus, the rate constants k_{2H} and k_{1d} are expected to vary in the order Cu(2,3,2-tet)$^{2+}$ < Cu(3,2,3-tet)$^{2+}$ < Cu(3,3,3-tet)$^{2+}$ < Cu(2,2,2-tet)$^{2+}$. This sequence is found experimentally (Table II).

There are two trans N–Cu–N bond angles for each of these copper(II)-tetraamine complexes (Table III). Plots of log k_{1d} vs log (180° – the large N-Cu-N bond angle) and log k_{1d} vs log (180° – the small N-Cu-N bond angle) are shown in Figure 3. Analogous plots for log k_{2H} are shown in Figure 4. On the basis of these results, we are able to conclude that it is not the instability constant but the trans N–Cu–N bond angle that affects the dissociation rate constant of the copper(II)–tetraamine complex, and the linear correlation between log k_{1d} (or log k_{2H}) and log (180° – the N–Cu–N bond angle) could serve as a basis for predictions.

Acknowledgment. The support of the Chemistry Research Center, National Science Council of the Republic of China, under Grants NSC 75-0208-M007-04 and NSC 76-0208-M007-66 is gratefully acknowledged.

Registry No. Cu(2,2,2-tet)$^{2+}$, 45840-81-1; Cu(2,3,2-tet)$^{2+}$, 45980-55-0; Cu(3,3,3-tet)$^{2+}$, 46242-92-6.

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Spectroscopic and Solution Properties of the Cobalt(III) Hexaimidazole Ion

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The imidazole side chain of histidine is a very common ligand of metal ions in metalloproteins. Some well-known examples are the enzymes such as carboxypeptidase A, carbonic anhydrase, thermolysin, superoxide dismutase, and alkaline phosphatase, metal-carrying proteins such as transferrin and conalbumin, and redox proteins such as hemerythrin.[1] It was shown[2] that the optical spectra of cobalt(III)-substituted metalloproteins can be employed in identifying the ligands of the metals in the native enzymes. The study described herein led to the spectroscopic characterization of the parent cobalt(III) hexaimidazole compound $Co(ImH)_6{}^{3+}$.

Experimental Section

The synthesis of $Co(ImH)_6(ClO_4)_3$ was done by H_2O_2 oxidation of $Co(ImH)_6(ClO_4)_2$. The conditions of the oxidation reactions were optimized by following in situ the sharp ^{59}Co NMR spectra of the $Co(ImH)_6(ClO_4)_3$ ion with the chemical shift of 8940 ppm relative to $K_3Co(CN)_6$.

For the oxidation of a reaction mixture containing $Co(ClO_4)_2 \cdot 6H_2O$ (3.8×10^{-3} mol), imidazole (0.27 mol), and $HClO_4$ (0.09 mol) in 30 mL of water 0.02 mol of H_2O_2 was added within a period of 1 h at room temperature. $Co(ImH)_6(ClO_4)_3$ was purified by using chromatography on an SE-Sephadex G50 column, eluted with a linear gradient of $Ba(ClO_4)_2$ (0.05–0.1 M). The Ba^{2+} ions were removed by careful addition of H_2SO_4, and the $BaSO_4$ precipitate was removed by filtering. $Co(ImH)_6(ClO_4)_3$ was crystallized by slow evaporation of its aqueous solution. The crystals were filtered and washed with cold dilute $HClO_4$.

Anal. Found (calcd) for $Co(ImH)_6(ClO_4)_3$: C, 27.7 (28.2); H, 3.09 (3.16); N, 21.0 (21.95); Cl, 14.5 (13.9); Co, 8.8 (7.7). The yield of the oxidation reaction (in situ) was 40%, and the final yield of the synthesis was 25%. Solutions of $Co(ImH)_6Cl_3$ were prepared by dissolving $Co(ImH)_6(ClO_4)_3$ in KCl, cooling the solution, and filtering the precipitated $KClO_4$.

Caution! Although we have experienced no difficulties with the perchlorate salts described here, these should be regarded as potentially explosive and handled accordingly.

NMR measurements were done by using a Bruker AM-360 WB NMR spectrometer. All spectra were taken at ambient temperature, which was about 20 °C. Proton NMR spectra were obtained from D_2O solutions of $Co(ImH)_6$ with 3-(trimethylsilyl)propionic-*2,2,3,3-d$_4$* acid

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[1] Sundberg, R. J.; Martin, R. B. *Chem. Rev.* **1974**, *74*, 471.
[2] Navon, G.; Shinar, H. *Inorg. Chim. Acta* **1980**, *46*, 51.

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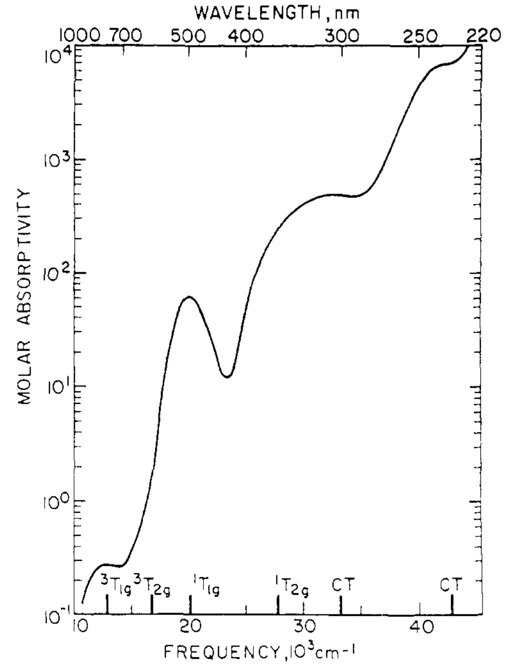


Figure 1. Optical spectrum of $Co(ImH)_6^{3+}$. The spectrum is a combination of the spectra of $Co(ImH)_6(ClO_4)_3$, which was run in the region between 220 and 700 nm, and $Co(ImH)_6Cl_3$, which was run in the region of 400–1000 nm. The labeled vertical lines correspond to the values of the transition energies given in Table I.

Table I

	optical band					
	I	II	III	IV	V	VI
assignment	$^3T_{2g}$	$^3T_{1g}$	$^1T_{2g}$	$^1T_{1g}$	CT	CT
λ_{max}, nm	771	595	497	359	302	234
ν_{max}, 10^3 cm^{-1}	13.0	16.8	20.1	27.8	33.2	42.8
ϵ_{max}, M^{-1} cm^{-1}	0.28	0.64	60	101	489	6970
$\Delta\lambda_{1/2}$, nm	340	100	81	58	88	37

(TSP) as a chemical shift reference, taking into account its pH dependence corresponding to δ(acid) = 0.000, δ(base) = 0.019, and pK = 5.0.[3] ^{13}C NMR spectra were obtained from D_2O solutions of $Co(ImH)_6Cl_3$ with dioxane as a reference, assuming δ_C(dioxane) = 67.8 ppm.

Results

1. **pH titration** of the $Co(ImH)_6^{3+}$ ion was performed at 24 ± 1 °C on a 0.01 M $Co(ImH)_6(ClO_4)_3$ aqueous solution, with HCl or NaOH at a pH range of 2.0–10.8. Above pH 10.8, some decomposition and slight precipitation were detected. The following pK values were obtained by a nonlinear least-squares fitting procedure: pK_1 = 8.65 ± 0.02; pK_2 = 9.88 ± 0.04; pK_3 = 10.63 ± 0.12. The errors reflect the scatter of results obtained in three separate experiments.

2. **The optical spectrum** of the $Co(ImH)_6^{3+}$ ion is given in Figure 1. Because of the limited solubility of $Co(ImH)_6(ClO_4)_3$, the low-absorption part of the spectrum was measured by using the corresponding chloride salt, and the result in Figure 1 is a combination of both measurements. In order to obtain accurate values for the transition energies, Gaussian fitting was performed to both wavenumber and wavelength scales. Both fitting procedures yielded essentially the same results. However, since the wavelength-scale fit was associated with a somewhat smaller standard deviation, the latter results are listed in Table I. The assignment of the transitions is based on the observed relative intensities and by analogy with other cobalt(III) complexes. We have derived the crystal field parameters B and C by fitting them to the four transition energies. Instead of diagonalizing the Tanabe and Sugano determinants, we have used the polynomials given by Boxall et al.[4] The values obtained are listed in Table II, together with the corresponding parameters for $Co(NH_3)_6^{3+}$ obtained by Boxall et al.[4] Another estimation of Δ and B based on the two spin-allowed transitions, and assuming C/B = 4.0,[5] is also given in the table.

Table II

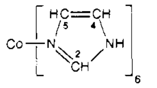
	Δ^a	B^a	C^a	Δ^b	B^b
$Co(ImH)_6^{3+}$	22 250	617	3380	21 640	566
$Co(NH_3)_6^{3+}$	23 500	707	3540	22 870	617

[a] Parameters, in cm^{-1}, obtained by fitting to the four transition energies, with use of the procedure of Boxall et al.[4] [b] Parameters obtained by assuming C/B = 4.0 and using only the two spin-allowed d–d transitions.[5]

Table III. ^{1}H NMR Spectra[a,b]

	C_2	C_4	C_5
$Co(ImH)_6^{3+}$[c]	6.87 [0.19, 0.34]	7.45 [0.11, 0.20]	6.05 [0.07, 0.12]
α-Co(trien)-$(ImH)_2^{3+}$	7.99 (0.49)	7.51 (0.21)	7.02 (0.12)
β-Co(trien)-$(ImH)_2^{3+}$	7.95 (0.74)	7.45 (0.30)	6.98 (0.23)
$Co(NH_3)_5ImH^{3+}$	8.05 (0.61)	7.46 (0.22)	7.07 (0.16)
N-CH_3-ImH	8.66 (1.07)	7.43 (0.43)	7.43 (0.35)
ImH_2^+	8.75 (0.99)	7.56 (0.41)	

[a] The numbering of the ring carbons is as shown:



All values are given in ppm. [b] The numbers in parentheses are δ(acid) − δ(base) values. [c] The numbers in brackets are the differences in δ between neutral pH and pH meter readings of 9.6 and 10.7, corresponding approximately to deprotonation of one and two protons, respectively.

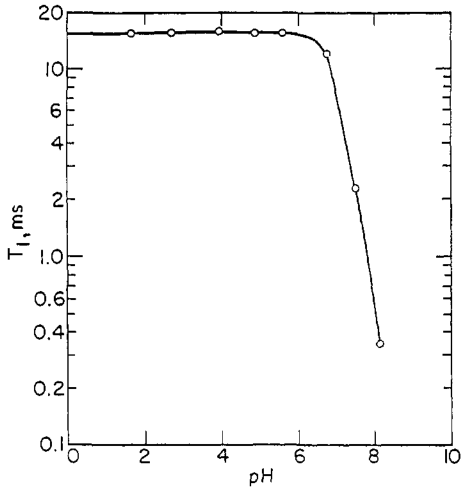


Figure 2. ^{59}Co longitudinal relaxation of $Co(ImH)_6^{3+}$ as a function of pH.

3. **The proton NMR spectrum** of $Co(ImH)_6^{3+}$ consists of three signals of the same integrated intensity: chemical shifts of 6.05, 6.87, and 7.45 ppm relative to internal TSP. The two signals at the higher field are relatively broad, while the low-field signal is narrow. At basic pH values all three lines shift to higher fields and their line widths narrow. The chemical shifts and their variations in alkaline pH are compared with those of other imidazole derivatives in Table III. The assignment of the spectra was not based on the values of the chemical shifts but rather on their change at basic pH. In analogy with other complexes, the peak that shifts the most at high pH was assigned to C_2, the one that shifts about half as much is C_4, and the one with the smallest shift at basic pH—the farthest from the ionizable NH—is C_5.

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(3) De Marco, A. *J. Magn. Reson.* **1977**, *26*, 527.

(4) Boxall, L. G.; Fung, K. W.; Johnson, K. E. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3523.

(5) Bramley, R.; Brorson, M.; Sargeson, A. M.; Schaffer, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 2780.

Table IV. ^{13}C NMR Spectra[a]

	C_2	C_4	C_5
$Co(ImH)_6^{3+}$	140.58 (−0.45)[b]	122.80 (−0.37)[b]	129.11 (0.04)[b]
$Co(NH_3)_5ImH^{3+}$ [c]	139.64 (−6.00)	121.84 (−8.50)	128.04 (1.71)
N-CH_3-ImH^+ [c]	136.24 (−3.10)	120.54 (−8.20)	124.24 (1.95)
ImH_2^+ [d]	134.59 (−1.64)	120.10 (−2.23)	

[a] The numbers in parentheses are the differences between the acidic and the basic forms, δ(acid) − δ(base). All values are given in ppm. [b] The difference in δ between neutral pH and pH = 9.0. [c] Reference 7. [d] Reference 8.

The absolute values of the pH shift of $Co(ImH)_6^{3+}$ are smaller than for the other imidazole complexes since the shift is a weighted average for the six imidazole groups. Thus, the first ionization corresponds to one-sixth ionization for each one of the imizadole groups. A further confirmation of this assignment comes from the line width data. The signals assigned to C_2 and C_5 are the broad ones. We attribute this broadening to unresolved *J* coupling with the ^{59}Co nucleus. We tested this hypothesis by measuring the ^{59}Co NMR spin–lattice relaxation time as a function of pH. The result, given in Figure 2, shows a sharp drop in the T_1 value of the ^{59}Co nucleus, at pH values of about 6.5, while the first pK_a is pK_1 = 8.65. It is in this pH range where the proton resonances become sharp. The decrease in the ^{59}Co T_1 value at basic pH values is likely to originate from the dissociation of a proton from one of the imidazole ligands. This makes the complex more asymmetric and gives rise to quadrupolar relaxation. Fast proton exchange between the protonated and the deprotonated complexes is responsible for the averaging of T_1, which consequently starts to decrease at a pH where only a small fraction of the complex molecules is ionized.

4. The ^{13}C NMR spectrum of $Co(ImH)_6^{3+}$ is summarized in Table IV. The chemical shifts are similar to those of analogous imidazole compounds. Again, the absolute values of the pH shifts are small since they are averages of one ionized imidazole and five unionized ones. ^{13}C spectra without proton broad-band decoupling resulted in $^1J_{CH}$ values of 216, 198, and 197 Hz for the C_2, C_4, and C_5 carbons, respectively. These values may be compared to $^1J_{CH}$ values of 225 and 203 Hz for C_2 and $C_{4,5}$ of ImH_2^+ and 207 and 191 Hz for the same carbons of ImH.

Discussion

In this paper we report for the first time the preparation of the $Co(ImH)_6^{3+}$ ion and the measurement of some of its properties. As could be expected on the basis of its high symmetry, the ^{59}Co NMR signal of $Co(ImH)_6^{3+}$ is sharp relative to those of other cobalt complexes. Still, since its symmetry is not strictly octahedral, it is not surprising that its T_1 relaxation time is substantially shorter than that of $Co(CN)_6^{3-}$. An immediate use of the sharp ^{59}Co NMR signal of $Co(ImH)_6^{3+}$ was done in the present work, where we optimized the yield of its synthesis by following the concentration of the compound in the reaction mixture in situ. Another application of this signal was the determination of intracellular and extracellular water space in biological systems.[6]

The measurement of the properties of $Co(ImH)_6^{3+}$ enables us to examine the properties of imidazole as a ligand.

1. p*K* Value. The first pK_a value of $Co(ImH)_6^{3+}$, pK_a = 8.65 ± 0.02, is significantly lower than those obtained for $Co(NH_3)_5ImH^{3+}$, α-$Co(trien)(ImH)_2^{3+}$, and β-$Co(trien)(ImH)_2^{3+}$, which are 10.0,[7] 10.1, and about 9.6, respectively[8] (trien = triethylenetetramine). This discrepancy is due in part to the difference in probability of ionization in relation to the number of imidazole ligands in the complex. On this basis alone we expect the first pK_a of $Co(ImH)_6^{3+}$ to be lower than that of $Co(NH_3)_5ImH^{3+}$ by log 6 = 0.78 and those of α- and β-$Co(trien)(ImH)_2^{3+}$ by log 3 = 0.48. Part of the further reduction of the pK_a from the expected value of about 9.2 to the experimental value 8.65 is due to the differences between $Co(ImH)_5^{3+}$ and $Co(NH_3)_5^{3+}$ or $Co(trien)ImH^{3+}$ as ligands of the ionizable imidazole. Another important difference between $Co(ImH)_6^{3+}$ and the other cobalt–imidazole complexes is seen in the proton chemical shifts of the C_2 and C_5 CH groups (see Table II). We suggest this difference results from the magnetic field anisotropies of the neighboring imidazole groups. In the $Co(trien)(ImH)_2^{3+}$ ion, which also contains adjacent imidazole groups, this field anisotropy is averaged out by free rotation of these imidazole groups. We expect this free rotation to be largely restricted in the $Co(ImH)_6^{3+}$ ion.

2. Position in the Spectrochemical Series. The ligand field splitting for $Co(ImH)_6^{3+}$, which was calculated on the basis of its optical spectrum, was found to be lower by 5.4% as compared to that of $Co(NH_3)_6^{3+}$ (see Table II). This difference is the same for two calculation procedures. Thus, imidazole falls below NH_3 in the spectrochemical series. Assuming a value of f_{ligand} = 1.25 for NH_3,[9,10] one can estimate f_{ligand} = 1.18 for imidazole. The values of the Racah parameters *B* and *C* are smaller than those of $Co(NH_3)_6^{3+}$ by 13% and 5%, respectively, indicating higher covalency for the imidazole as a ligand. In another procedure of calculation, which assumes $C/B = 4.0$, the Racah parameter *B* of $Co(ImH)_6^{3+}$ is smaller than that of $Co(NH_3)_6^{3+}$ by 8.3%. Since the nephelauxetic series is based on such an assumption, we shall use this value for estimating h_{ligand} for imidazole. Thus, since h_{ligand} = 1.4 for NH_3,[9] the corresponding value for imidazole is h_{ligand} = 1.53. These values position imidazole as a ligand in the spectrochemical and in the nephelauxetic series.

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Registry No. $Co(ImH)_6(ClO_4)_3$, 119414-02-7; $Co(ImH_6)^{3+}$, 99774-48-8; $Co(ImH)_6Cl_3$, 119414-03-8; ^{59}Co, 7440-48-4; α-$Co(trien)(ImH)_2^{3+}$, 77341-40-3; β-$Co(trien)(ImH)_2^{3+}$, 77299-00-4; $Co(NH_3)_5ImH^{3+}$, 38716-02-8; *N*-CH_3-ImH^+, 17009-89-1; ImH_2^+, 17009-90-4.

---

(6) Shinar, H.; Navon, G. *FEBS Lett.* **1985**, *193*, 75.

(7) Harrowfield, J. M.; Norris, V.; Sargeson, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 7282.

(8) Rowan, N. S.; Storm, C. B.; Rowan, R. *J. Inorg. Biochem.* **1981**, *14*, 59.

(9) Jørgensen, C. K. *Oxidation Numbers and Oxidation States*; Springer-Verlag: Berlin, Heidelberg, New York, 1969; p 84.

(10) Figgis, B. N. *Introduction to Ligand Fields*; Interscience: New York, 1967; p 244.

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New Classes of Monomeric and Dimeric Square-Planar Chromium(II) Aryloxides: Syntheses and Structures

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The chemistry of low- and medium-valent transition-metal alkoxides has experienced a spectacular growth of interest during the last decade.[3] In contrast to the versatile chemistry discovered for the trivalent molybdenum and tungsten alkoxides,[4] the

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(2) Rijksuniversiteit Utrecht.

(3) (a) Mehrotra, R. C. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 269. (b) Chisholm, M. H.; Huffman, J. C.; Van Der Sluys, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 2514 and references cited therein. (c) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 3509 and references cited therein.

(4) Chisholm, M. H.; Folting, K.; Hammond, C. E.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 3314 and references cited therein.

0020-1669/89/1328-1407$01.50/0