$(F_3CSO_2)_2O$ was rationalized as a reflection of kinetic inertness to water substitution rather than thermodynamic stability, because **1** does not dehydrate HTFMS to make **3** and $(F_3CSO_2)_2O$. Our failure to dehydrate **3** has caused us considerable concern as to whether it is correctly formulated. In light of this, we were again surprised to find that the water is readily expelled when acetonitrile is added to **3**, as shown by eq 2. We believe this to be the first isolated tetracation of binuclear molybdenum(II) with a unidentate ligand.

$$\underset{\mathbf{3}}{[Mo_2(H_2O)_4(TFMS)_2](TFMS)_2} + 8CH_3CN \rightarrow \underset{\mathbf{4}}{[Mo_2(CH_3CN)_8](TFMS)_4} \quad (2)$$

The deep blue compound **4** is formed instantly when **3** is dissolved in acetonitrile and precipitates as large crystals upon cooling. It is very air sensitive and loses acetonitrile on exposure to vacuum or other solvents—the low stability relative to other Mo_2^{4+} complexes may be due to the 4+ charge. San Filippo and co-workers have reported the preparation of $Mo_2(CH_3CN)_4Cl_4$ from acetonitrile and $Mo_2[S(CH_3)_2]Cl_4$;[8] there is no evidence for further substitution to a cationic species.

In the course of studying these complexes of TFMS, we carried out the reaction of $Mo(CO)_6$ with HTFMS. The product is the Mo(III) complex $Mo(TFMS)_3$. In view of the poor coordinating ability of TFMS, this complex may be of value as a precursor to the synthesis of other Mo(III) complexes. Complexes of this valence state are generally quite unstable to oxidation except in the presence of rather special ligands.[9]

In conclusion, we have prepared two new cationic complexes of Mo_2^{4+}, and they seem somewhat less stable than the neutral or anionic derivatives. Their formation raises questions about the poorly understood substitution behavior of the binuclear ion. The acetonitrile complex **4** is the first isolated example of a quadruple-bonded dimer coordinated only to monodentate neutral ligands. The trifluoromethanesulfonate derivative **3** is a very labile and reactive compound, and it seems to be a good starting material to prepare new complexes of binuclear molybdenum(II). However, it should be noted that solutions that we believe contain **3** were used by DeSimone in reactions with macrocycles. Both Mo(II) and Mo(IV) complexes were formed, but the Mo(II) complex no longer had a quadruple metal–metal bond.[10]

Registry No. 2, 51329-49-8; **3**, 86527-40-4; **4**, 86527-42-6; $Mo(TFMS)_3$, 86527-43-7; $Mo(CO)_6$, 13939-06-5.

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Carbon-13 Line Width Criterion for the *lel* Conformation of Chelated Diamine Ligands

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In 1976, Baggar and Bang[1] discovered a dramatic ^{13}C NMR line width difference between diastereotopic methyl groups in (±)-2,3-butanediamine chelated to cobalt(III). While unable to explain the phenomenon, they recognized a convenient method for distinguishing the *lel* from the *ob* conformation of a five-member chelate ring, and since then a methyl ^{13}C line width in the range 15–25 Hz has become the accepted criterion[2] for recognizing an *lel* conformation. It is highly probable that the observed broadening has its origin not in nuclear shielding as has been suggested[2] but in nuclear relaxation and that scalar coupling of the second kind[3] to ^{59}Co is the source.

When chelated in a tris(diamine) complex, the five-member ring can adopt either the *lel* conformation in which the HC–CH axis is paral*lel* to the pseudo-C_3 molecular axis or the *ob* conformation in which the HC–CH axis is *ob*lique to the pseudo-C_3 axis by about 60°. The 15–25-Hz line width observed for the *lel* conformation distinguishes it from the *ob* conformation with a 5–10-Hz line width showing little if any anomalous broadening. By comparison, methyl or methine ^{13}C chemical shift differences between *lel* and *ob* conformations of 1 ppm or less[2] provide only a tenuous criterion for making the distinction.

In the absence of fluxional motion or chemical exchange that can limit the lifetime of a nuclear spin state, the natural ^{13}C line width is determined by the rate of transverse relaxation, R_2, according to the equation $\Delta\nu_{1/2} = R_2/\pi$. Most ^{13}C relaxation occurs through magnetic dipole–dipole coupling to bonded protons, modulated by molecular rotation; and this relatively inefficient relaxation mechanism places an upper limit of about 1 Hz on the line width in situations where the molecular motion is normal. If ^{13}C is scalar coupled to a nucleus with spin I whose relaxation rate is less than the coupling constant, a $2I + 1$ multiplet is observed. If, however, the other nucleus is undergoing rapid relaxation at a rate that exceeds the coupling constant, the multiplet is collapsed and the coupling is manifest only as a relaxation mechanism for ^{13}C, the efficiency of which can be considerably greater than that of the dipole–dipole mechanism. The scalar coupling contribution to the rate of ^{13}C relaxation is given by[4]

$$R_2^{SC}(^{13}C) = 21\pi^2[J(^{59}Co-^{13}C)]^2[R_1(^{59}Co)]^{-1}$$

^{59}Co is 100% abundant and has a spin $I = {}^7/_2$ and an electric quadrupole moment of 0.5 b. In sites having symmetry lower than O_h, the cobalt nucleus can experience a significant electric field gradient that promotes quadrupolar relaxation, and ^{59}Co relaxation rates in tris(diamine) complexes as high as 280 s^{-1} have been observed.[3]

Two- and three-bond coupling constants are highly sensitive to dihedral angle, and $^{205}Tl-^{13}C$ couplings[5] in a thallium adduct of bicyclo[3.2.1]octadiene are known to obey a Karplus-type[6] relationship. As a result, not only can $^3J(^{205}Tl-^{13}C)$ vary by a factor of 20 depending upon dihedral angle but $^3J(^{205}Tl-^{13}C)$ can exceed $^2J(^{205}Tl-^{13}C)$ by a factor of 3. These two facts taken together and placed in the context of tris(diamine)cobalt(III) complexes provide an angle-dependent relaxation mechanism that is of the correct magnitude to explain the atypically broad ^{13}C lines observed in some tris((±)-2,3-butanediamine)cobalt(III) isomers.

Where it is to be used as a diagnostic test for the presence of an *lel* conformation, several features of this relaxation-induced broadening are worth noting.

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1. Scalar coupling relaxation contributes primarily to transverse relaxation and line width and not to longitudinal relaxation. In most instances, an independently measured R_1 significantly slower than R_2 confirms the presence of scalar coupling relaxation.

2. Because it enters the ^{13}C relaxation equation as a squared term, a large coupling constant can broaden a resonance beyond recognition, removing much of the mystery from missing peaks whose absence is otherwise unexplainable.

3. Tris(diamine) complexes of metals such as chromium with few magnetically active nuclei or of rhodium that is not quadrupole relaxed will *not* contain a scalar coupling contribution to ^{13}C relaxation, and this convenient criterion for identifying *lel* ring conformations will not be available for analyzing the stereochemistry of complexes containing these materials.

Registry No. Tris((±)-2,3-butanediamine)cobalt(3+), 30768-19-5.

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Thin-Layer Spectroelectrochemical Studies of Copper and Nickel Unsymmetrical Schiff Base Complexes

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The metal binding sites in proteins are highly developed for the purpose of efficiently performing very specific function(s). At least for copper- and zinc-binding proteins, the metal ion is often found in a site of low symmetry comprised of a mixed set of donor atoms (Table I). Moreover, the three-dimensional arrangement of the ligands in the resting state may be somewhat strained so as to facilitate the formation of some kinetically important state in a reaction sequence.[1] Of the variety of ligands utilized, the imidazole moiety of histidine is frequently involved thanks in part to the fact that its p*K* value occurs in the physiologically important range.[2]

Chelates derived from Schiff base condensation reactions form a convenient vehicle for preparing related small molecules, including, ultimately, synthetic representations of important protein centers. Ligands can be designed to incorporate mixed donor sets[3,4] as well as relevant geometrical constraints,[4–6] and their characteristic imine nitrogens can be viewed as analogues of histidine nitrogen. The ease with which these ligands form complexes with a variety of metals is also an advantage since the metal replacement technique has been so useful in the characterization of the protein systems.[7–9] Here we show that electrochemical methods can be a useful probe in systematic studies of low-symmetry complexes of this type.

Experimental Section

Materials and Nomenclature. Ligand abbreviations are based on the starting materials for the 1:1:1 condensations; sl, py, and pl denote the terminal ligands salicylaldehyde, pyridine-2-carbaldehyde, and pyrrole-2-carbaldehyde, respectively, and e, p, and t, in order, denote the bridging diamines ethylenediamine, propylenediamine, and 2,5-diamino-2,5-dimethylhexane. Thus plppl denotes the symmetrical Schiff base adduct of propylenediamine with 2 equiv of pyrrole-2-carbaldehyde. The syntheses of all complexes except [Ni(slppy)]BF_4 have been described.[3] The BF_4^- salt, synthesized in a fashion analogous to the preparation of the previously reported NO_3^- salt, was characterized by UV–vis and IR absorption spectroscopy. Except for the absence of bands at 1340 and 825 cm^{-1} attributable to NO_3^- and the presence of bands at 1070, 770, and 520 cm^{-1} attributable to BF_4^-,[10] the complex gave the same IR spectrum as [Ni(slppy)]NO_3.

Table I. Properties of the Binding Sites of Selected Copper- and Zinc-Containing Proteins

protein	metal	ligating atoms	no. of histidine ligands	approximate symmetry	ref
superoxide dismutase	Cu	N_4O	4	distorted square pyramidal	*a*
laccase[b]	Cu	N_3O_2?	3?	distorted square pyramidal	*c*
plastocyanin	Cu	N_2SS^*	2	distorted tetrahedral	*d*
alcohol dehydrogenase	Zn	NS_2O	1	distorted tetrahedral	*e*
carbonic anhydrase	Zn	N_3O	3	distorted tetrahedral	*f*

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Instrumentation. UV–visible spectra were recorded with a Harrick Rapid Scanning spectrophotometer (RSS-B) with data acquisition and display controlled by a microprocessor-based computer system.[11] The sample compartment contained an optically transparent thin-layer electrode (OTTLE) and Lucite cell holder, both of which were maintained in an argon atmosphere with an enclosed Lucite box. Two opposing 1-in.-diameter holes were drilled into the box and two quartz plates inserted to provide a gas-tight container with a quartz optical path. Electrochemistry was performed with a 173 potentiostat/galvanostat (Princeton Applied Research Corp.) driven either by a 175 Universal Programmer for cyclic voltammetry or by the microprocessor system for spectropotentiostatic experiments. The OTTLE was constructed from 500 lines/in. gold minigrid and quartz plates as described elsewhere.[12] The OTTLE was immersed in a sample cup containing a coiled-platinum-wire auxiliary electrode and an aqueous saturated sodium chloride calomel electrode (SSCE) of the H-cell type. The SSCE was separated from the sample solution via a salt bridge that was constructed from heat-shrink Teflon tubing with a Vycor plug. The salt bridge contained 0.4 M supporting electrolyte

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