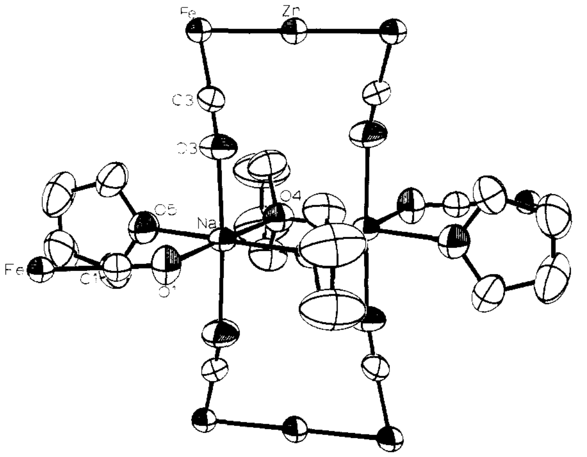

Figure 2. View of the dimeric $[Na_2(THF)_4]^{2+}$ cation, which is located about a site of $2/m$ crystallographic symmetry. Each Na^+ ion is coordinated by two bridging THF molecules, one terminal THF, and the carbonyl oxygens of three different complex molecules. Adjacent Na^+ ions are bridged by complex anions by virtue of coordination to carbonyl ligands CO(3). Bond lengths to the Na^+ ion for oxygens O(1), O(3), O(4), O(4′), and O(5) are 2.584 (7), 2.308 (4), 2.456 (5), 2.572 (6), and 2.315 (6) Å, respectively.

atoms have a more regular TBP geometry, but a slight umbrella bending of three equatorial carbonyl ligands occurs toward the zinc atom with an average Zn–Co–C_{eq} angle of 81.1°.[9] Carbonyl ligands of $[\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2Zn]$ and related complexes are directed along the Mo–Zn bond and form Zn–C contacts of 2.522–2.561 Å. The interaction is viewed to be nonbonding and to be a consequence of the general structural features of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3X]$ species.[10] Structural studies carried out on base adducts of complexes related as precursors to the present compound, $[B_2M'(Fe(CO)_4)]_n$ (M′ = Zn, Cd, Hg), also show carbonyl ligands bent toward the M′–Fe bond, but M′–C contacts for these compounds are in the 2.70-Å range.[10,11] While most of these compounds show quite low carbonyl stretching bands, the M–C–O bond angles remain essentially linear. This is true also of $[Zn(Fe(CO)_4)_2]^{2-}$, where the Fe–C(3)–O(3) angle is 177.7 (7)°.

The crystal structure of $[Na(THF)_2]^+{}_2[Zn(Fe(CO)_4)_2]^{2-}$ shows strong ion pairing between dimeric $[Na_2(THF)_4]^{2+}{}_2$ cations and the carbonyl oxygen of the anions. Adjacent sodium ions are bridged by the oxygen atoms of THF ligands as shown in Figure 2. The strongest bonds to the sodium are for the oxygen atoms of carbonyl ligands CO(3) with Na–O(3) lengths of 2.308 (4) Å. This value is slightly shorter than values of 2.318 (5) and 2.324 (5) Å found for $Na_2Fe(CO)_4{\cdot}1.5C_4H_8O_2$.[12]

It is pertinent that distortion of the normal d^8-Fe^0 TBP appears related to electronic effects within the dianion rather than rigid geometrical preferences of the iron or strong intermolecular forces. The electronic occupancy of iron increases due to ionicity in the Zn–Fe bond toward a d^{10}-Fe^{2-} T_d description. An alternative description of the electronic distortion in the dianion is that a small highly charged cation (Zn^{2+}) will alter the field of a larger polarizable anion ($Fe(CO)_4{}^{2-}$) as required by Fajan's rules. The bridging sodium interaction is indicative of the tight ion pairing suggested by the structure (see Figure 2). Ion pairing is maintained in solution as evidenced by the ν_{CO} stretching pattern, which contains a doublet centered around 1860 cm^{-1} that collapses for the analogous cadmium and mercury compounds. A reviewer has suggested that the structure is like an infinite ionic polymeric array, and this analogy strikes us as apt.

The charge or oxidation state about iron has been assessed by ^{57}Fe Mössbauer spectroscopy, and for a series[13] of iron carbonyl and carbonyl anions a value of $\delta = 0.416$ mm/s for $[Zn(Fe(CO)_4)_2]^{2-}$ (relative to SNP, or 0.156 mm/s relative to iron foil) corresponds nicely to a charge of –I as is found for $[Fe_2(CO)_8]^{2-}$, where $\delta = 0.16$ mm/s (relative to iron foil). We note that $[Zn(Fe(CO)_4)_2]^{2-}$ violates the Collins–Pettit plot (δ vs. Δ) for equatorially substituted trigonal-bipyramidal $[Fe(CO)_4L]$ complexes[14] and a similar plot for axially substituted $[Fe(CO)_4L]$ complexes,[15] all suggesting a non-d^8-Fe^0 description.[16]

Acknowledgment. Research at Rice University was supported by The Robert A. Welch Foundation and is gratefully acknowledged. Related support (B.A.S.) by the Research Corp. and the Dow Corp. is also appreciated. Research at the University of Colorado was supported by the Department of Energy through the Solar Energy Research Institute.

Registry No. $[Na(THF)_2]^+{}_2[Zn(Fe(CO)_4)_2]^{2-}$, 82110-39-2; $(NH_3)_3ZnFe(CO)_4$, 34720-06-4.

Supplementary Material Available: A listing of the positional and thermal parameters derived from the crystallographic analysis (1 page). Ordering information is given on any current masthead page.

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A Direct Method for Determining the Structure of Chromium(III) Complexes in Solution by Deuteron Nuclear Magnetic Resonance

Sir:

We report here the use of deuteron nuclear magnetic resonance (^2H NMR) as a structural probe of Cr(III) complexes in solution. By comparison of ^2H NMR spectra obtained for $[Cr(mal\text{-}d_2)_3]^{3-}$,[1] $[Cr(mal\text{-}d_2)_2(bpy)]^-$, $[Cr(mal\text{-}d_2)_2(py)_2]^-$, $[Cr(mal)_2(py\text{-}d_5)_2]^-$, $[Cr(edda)(mal\text{-}d_2)]^-$, and $[Cr(edda\text{-}\alpha\text{-}d_4)(mal)]^-$, the complexes $[Cr(mal)_2(py)_2]^-$ and $[Cr(edda)(mal)]^-$ are assigned the trans and sym-cis[2] configurations, respectively. To our knowledge, this is the first demonstration of the use of NMR as a broadly applicable technique to study the structure of Cr(III) complexes in solution.

Proton nuclear magnetic resonance (^1H NMR) spectroscopy has been used to establish conclusively the stereochemistry of

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[1] Abbreviations: mal = malonate, bpy = 2,2′-bipyridine, py = pyridine, edda = ethylenediamine-*N*,*N*′-diacetate, or 2,5-diazahexanedionate, edda-α-d_4 = 2,5–diazahexanedionate-*1*,*1*,*6*,*6*-d_4.

[2] A complex of the linear tetradentate ligand edda, [M(edda)(bidentate)], has two possible isomers, sym-cis (symmetrical cis), where the edda carboxylates are trans, and uns-cis (unsymmetricl cis), where the edda carboxylates are cis. See: Brubaker, G. R.; Schaefer, D. P.; Worrell, J. H.; Legg, J. I. *Coord. Chem. Rev.* **1971**, *7*, 161.

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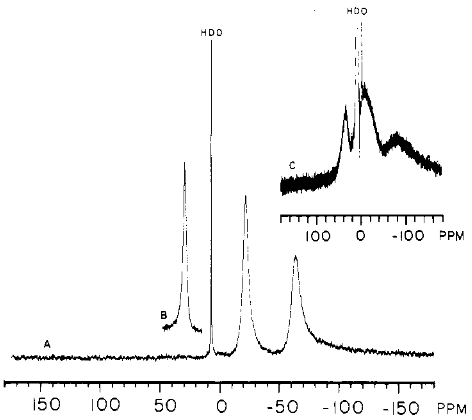

Figure 1. ^{2}H NMR spectra of [Cr(edda-α-d_4)(mal)]$^-$ (A) and [Cr(edda)(mal-d_2)]$^-$ (B) in 10^{-3} M HClO$_4$ solution and the 200-MHz ^{1}H NMR spectrum of [Cr(edda)(mal)]$^-$ in D$_2$O (C).

Table I. Deuteron NMR Spectral Data for Cr(III) Complexes[a]

complex	δ (ω)[b]	rel integration
[Cr(mal-d_2)$_3$]$^{3-}$ [c]	29 (150)	
[Cr(mal-d_2)$_2$(bpy)]$^-$ [d]	57 (270), −4 (70)	1:1
trans-[Cr(mal-d_2)$_2$(py)$_2$]$^-$ [d]	21 (90)	
trans-[Cr(mal)$_2$(py-d_5)$_2$]$^-$ [d]	11 (30), −24 (55), −71 (480)	2:1:2
sym-cis-[Cr(edda)(mal-d_2)]$^-$ [c]	30 (100)	
sym-cis-[Cr(edda-α-d_4)(mal)]$^-$ [c]	−21 (120), −63 (250)	1:1

[a] A typical spectrum required about 5000 scans. The acquisition time was about 0.5 h/spectrum. [b] δ = chemical shift in ppm with respect to Me$_4$Si; downfield >0. ω = width at half-height in Hz. [c] In 10^{-3} M HClO$_4$. [d] In MeOH.

diamagnetic Co(III) complexes. For Cr(III) complexes, however, ^{1}H NMR is of little use due to the extreme broadening of the resonances arising from the long electron-spin relaxation times associated with paramagnetic Cr(III) ions.[3] Thus, a great deal of frustration developed over the structural assignments for Cr(III) complexes, as the emphasis in this laboratory shifted from Co(III) to Cr(III) chemistry. A number of years ago, Everett and Johnson demonstrated that deuteron substitution for protons produces significant line narrowing (by a factor of about 40) for chromium(III) acetylacetonate complexes. An enhancement in resolution of about 6.5 should also occur; but since no compounds of Cr(III) with detectable multiple resonances were reported, this could not be demonstrated.[4] This technique was not developed further for the characterization of Cr(III) complexes, perhaps due to the inconvenience of producing isotopically labeled ligands and the lack of instrumentation that could conveniently detect the deuteron. The increasing availability of deuterated ligands[5] and improvements in NMR instrumentation have facilitated our exploration of ^{2}H NMR for the structural study of Cr(III) complexes in solution.

The complexes K$_3$[Cr(mal)$_3$]·3H$_2$O and K[Cr(edda)(mal)]·3H$_2$O were prepared by literature methods.[6,7] The new complex Na[Cr(mal)$_2$(py)$_2$]·2H$_2$O was obtained by heating *cis*-Na[Cr(mal)$_2$(H$_2$O)$_2$]·3H$_2$O[8] in a solution of water and pyridine (1:1) for about 4 h. Red crystals were isolated by treatment with ether. The product was recrystallized from water and acetone. Chromatography on QAE-Sephadex A-25 (Cl$^-$ form) showed only one band. This suggests that the complex obtained is one of two geometrical isomers. Li[Cr(mal)$_2$(bpy)]·2.5H$_2$O was newly prepared by heating an equimolar mixture of *cis*-Na[Cr(mal)$_2$(H$_2$O)$_2$]·3H$_2$O and 2,2′-bipyridine in dimethyl sulfoxide. This was converted to the lithium salt by cation-exchange chromatography on Dowex 50W-X4 (Li$^+$ form). The malonate methylenes were deuterated directly on the Cr(III) complexes by dissolution in D$_2$O for several hours at room temperature (a small amount of pyridine was added to the pyridine and bpy complexes) followed by either removal of solvent or precipitation. Deuteration was checked by IR spectroscopy. Deuterated H$_2$edda (H$_2$edda-α-d_4) was prepared by a method similar to that previously described.[5] Deuteration was confirmed by the ^{2}H NMR spectrum.[9a] Fully deuterated pyridine (99 atom % ^{2}H) was purchased from Sigma.[9b]

The 31-MHz ^{2}H NMR spectra were recorded on a Nicolet NT-200 spectrometer with a field of 4.7 T at ambient temperature. Data were collected in 12-mm tubes containing 5 mL of a ~30–100 mM aqueous (1 mM HClO$_4$) or methanol solution of the complex. The spectral region isolated was ±200 ppm with respect to Me$_4$Si. An external standard of CDCl$_3$ was assigned to a chemical shift of 7.24 ppm.[10]

In comparison with the 200-MHz ^{1}H NMR spectrum of [Cr(edda)(mal)]$^-$, the ^{2}H NMR spectra of the corresponding deuterated complex are found to give much narrower (by a factor of ~30) and better resolved resonance signals (Figure 1). As summarized in Table I the complexes show simple zero-order ^{2}H NMR spectra similar to the ^{2}H NMR spectra observed for diamagnetic compounds. This behavior is predicted from the small homonuclear coupling constants for deuterons.[11] Thus, it is reasonable to expect that each magnetically inequivalent deuteron will give rise to one resonance signal.

For [Cr(mal-d_2)$_3$]$^{3-}$, only one signal is observed (Table I), indicating equivalence of all the methylene deuterons. This fact suggests that the malonate chelate rings in solution are in an environment leading to effective D_3 symmetry. Malonate chelated to both Cr(III) and Co(III) has been studied in the solid[12] and solution (Co(III) only)[13] states. Proton NMR studies of Co(III) complexes support dynamic conformational equilibrium for chelated malonate.[13]

In the case of [Cr(mal-d_2)$_2$(bpy)]$^-$ the two malonate rings are equivalent but the two geminal deuterons on a given malonate ring are inequivalent. For this type of complex, an AB pattern is expected as is observed for the ^{1}H NMR of [Co(mal)$_2$(en)]$^-$.[13a,b] Two well-separated (61 ppm), zero-order resonance signals with equal intensity are in fact observed (Table I). Since the isolated [Cr(mal-d_2)$_2$(py)$_2$]$^-$ isomer gives only one ^{2}H NMR signal (Table I), this complex is a trans isomer. In this isomer all four deuterons of the two malonates

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are equivalent. The ^{2}H NMR spectrum of this complex with deuteron-substituted pyridines shows three resonance signals with relative integration values of 2:1:2 (Table I).[14] The observation of only one set of resonances for the three types of deuterons indicates the equivalence of the two pyridines, supporting the assignment based on the malonate deuteron NMR spectrum.

In the [Cr(edda)X_2] system (X_2 = two monodentates or one bidentate ligand), both the sym-cis and uns-cis isomers have been reported.[7,15] With the assumption that [Cr(edda)(mal-d_2)]$^-$ has the sym-cis configuration as proposed on the basis of visible spectra by Radanovic et al.,[7] one resonance is predicted due to the equivalent malonate deuterons, which are related by the 2-fold axis through the malonate ring. In the sym-cis geometry the glycinate rings are also equivalent but the geminal hydrogens are inequivalent. Thus for *sym-cis*-[Cr(edda-α-d_4)(mal)]$^-$ two resonance signals with equal integration should be observed. These expectations are borne out as shown in Figure 1A,B and summarized in Table I. The corresponding Co(III) isomer behaves in an analogous manner as demonstrated by the ^{1}H NMR spectra obtained for the sym-cis and uns-cis isomers.[13b] Thus, [Cr(edda)(mal)]$^-$ can be assigned unambiguously as the sym-cis isomer.

We have demonstrated that deuteron nuclear magnetic resonance is a potentially valuable technique for studying Cr(III) complexes in solution. The simple zero-order spectra obtained show that even inequivalent geminal deuterons are strongly affected to different extents by paramagnetic Cr(III). It should now be possible to determine directly, and in many cases unambiguously, stereochemistries of Cr(III) complexes in solution whenever deuterated ligands can be included in the coordination sphere of the complex.

Acknowledgment. We express our deep thanks to Donald Appel for training W.D.W. in the use of the Nicolet NT-200, the critical "Christmas Even Spectrum", and his valuable input. Support of this study by the National Institutes of Health (Grant GM 23081) is gratefully acknowledged. The Nicolet 200-MHz spectrometer was acquired with the assistance of the Boeing Co.

Registry No. [Cr(mal)$_3$]$^{3-}$, 19203-86-2; [Cr(mal)$_2$(bpy)]$^-$, 82065-75-6; [Cr(mal)$_2$(py)$_2$]$^-$, 82065-74-5; [Cr(edda)(mal)]$^-$, 82080-06-6; deuterium, 7782-39-0.

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(16) On leave from the Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630, Japan.

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Received May 10, 1982

Synthesis, Structure, and Reactivity of a Binuclear Three-Coordinate Copper(I) Complex

Sir:

Corequisite with pursuing the goal to model the binuclear copper proteins hemocyanin[1] and tyrosinase[2] is the need to study and understand the coordination chemistry of Cu(I) ligated by nitrogenous donors.[3] Historically, such complexes have resisted careful scrutiny because of the absence of spectroscopic "handles" for the spin-paired d^{10} Cu(I) ion as well as their tendency to disproportionate (especially in aqueous solution)[4] and to undergo facile autoxidation in the presence of air.[5] As part of a project aimed at a systematic study of coordinatively unsaturated (two- and three-coordinate) mono- and binuclear Cu(I) complexes,[6] we report here the preparation, structural characterization, and reactions of a binuclear Cu(I) complex having the rare (N)$_3$ donor set.[7] Furthermore, we show that because small differences in structure can create significant yet unpredictable changes in reactivity, the relationship between a biological system and its alleged "model" may be obscured.

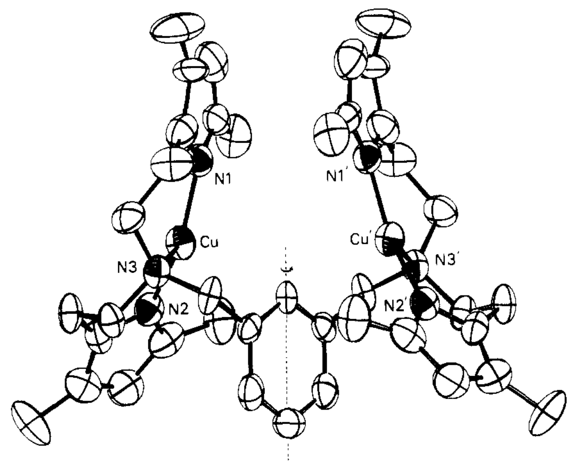

Figure 1. Full structure of the [Cu$_2$(mxyN$_6$)]$^{2+}$ cation showing 40% probability thermal elipsoids. The Cu···Cu distance is 5.100 (1) Å and the molecule sits on a 2-fold axis as indicated by the dashed lines.

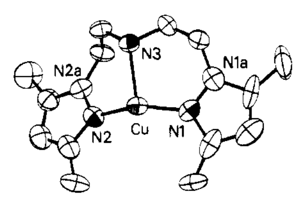

Figure 2. Coordination sphere about copper. Selected distances (Å): Cu–N1 = 1.916 (4); Cu–N2 = 1.895 (4); Cu–N3 = 2.195 (3). Bond angles (deg): N1–Cu–N2 = 156.0 (2); N1–Cu–N3 = 99.2 (2); N2–Cu–N3 = 100.0 (2).

The reaction of bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine[8] with α,α'-dibromo-*m*-xylene in 1:1 tetrahydrofuran–benzene gave the binucleating ligand **1** as a colorless oil after flash chromatography.[9] Slow evaporation of a solution of **1** and [Cu(CH$_3$CN)$_4$]BF$_4$[6a] in ethanol–benzene under an inert at-

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(11) Crystal data for **2**: monoclinic; a = 23.788 (11), b = 13.901 (3), c = 16.688 (4) Å; β = 129.22 (3)°; Z = 4; space group $C2/c$; Mo Kα radiation; 1973 independent nonzero [$I > 3\sigma(I)$] reflections with 2θ between 2 and 50°; R = 5.4%; R_w = 6.0%. The copper atom position was located by the Patterson function, and all non-hydrogen atoms were located on difference Fourier maps. Full details will be presented in a future paper.

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