only a small fraction of the entire reaction utilizes an outer-sphere path. Where differences exist, the trends have been somewhat sharpened. Adjustment for the outer-sphere components is most substantial in the case of the U^{3+} reduction of the α-aminoisobutyrato complex (VI), for which this treatment sets the inner-sphere specific rate as 3.9 M^{-1} s^{-1}. Here the combination of electrostatic and steric effects appears to have reduced the inner-sphere component to about 75% of the entire reaction.[11]

Registry No. I, 19173-62-7; II, 68582-30-9; III, 80327-80-6; IV, 45127-13-7; V, 33887-25-1; VI, 31133-42-3; VII, 40544-43-2; VIII, 69421-16-5; IX, 30931-78-3; X, 31133-44-5; $Ru(NH_3)_6^{2+}$, 19052-44-9; U, 7440-61-1; Cr, 7440-47-3; V, 7440-62-2; Eu, 7440-53-1.

---

[11] A reviewer has pointed out that our argument may be strengthened by showing that the 3+/2+ outer-sphere ratio for each pair in Table II is greater than 1. Although we have not listed these ratios, the Ru^{II} data in Table I demonstrate that this is so since outer-sphere components of each reaction may be estimated by multiplying k_{Ru} by a constant characteristic of the reductant (as indicated in the text). Thus the calculated 3+/2+ outer-sphere ratio for each pair corresponds to the ratio of observed k_{Ru}'s; this ratio exceeds 1 in each case.

Communications

Characterization of a Mixed-Metal Bimetallic with an Unusual Set of Carbonyl Distortions: $[Na(THF)_2]^+{}_2[Zn(Fe(CO)_4)_2]^{2-}$

Sir:

Our recent disclosure of the synthesis[1] of $[Fe(CO)_4(SnR_2)]^{2-}$, coupled with a theoretical study[2] postulating an unusual $CO_{(eq)\pi^*}$ interaction, has suggested that careful study of other reduced mixed-metal bimetallic organometallic compounds may reveal subtle bonding patterns that may ultimately aid in the understanding of promotional effects induced by the M–L bond. We have examined the reduction of $[ZnFe(CO)_4]$ in Lewis bases yielding $[Na(THF)_2]^+{}_2[Zn(Fe(CO)_4)_2]^{2-}$. Its characterization and single-crystal X-ray diffraction structure determination serve as a basis for this report. The structure of the dianion (Figure 1) is highly novel as it represents an example of a zinc-capped iron tetrahedron that is intermediate between face capping and edge capping. Bonding in the dianion may be described as a near-ionic form. The sodium counterion has an unusual dimeric bridged structure.

The compound $[ZnFe(CO)_4]$, prepared in the form[3] $[(NH_3)_3ZnFe(CO)_4]$ (1.0 g, 3.53 mmol), was added to a solution of 1% Na/Hg amalgam in THF (50 mL) and stirred for $^1/_2$ h before being filtered through Celite to yield a yellow-orange solution of $[Na(THF)_2]^+{}_2[Zn(Fe(CO)_4)_2]^{2-}$. This complex may be isolated as very air-sensitive colorless crystals (0.82 g, 63%) with a light pink tint from a standing toluene/THF solution.[4] Crystals obtained from this solution were found to form in the monoclinic crystal system, space group *I*2/*m*, with two formula units per cell. The results of a molecular structure determination[5] show that the zinc atom is located at a site of 2/*m* symmetry with the iron atom and two carbonyl ligands of the independent $Fe(CO)_4$ fragment lying on a crystallographic mirror plane. A view of the $[Zn(Fe(CO)_4)_2]^{2-}$ anion is shown in Figure 1. The coordination geometry about the iron atoms resembles an intermediate case between a distorted tetrahedron with the Zn–Fe bond at an axial or face/edge capping site. A reasonable Fe–Zn single bond length, estimated from half the Fe–Fe length in $[Fe_2(CO)_8]^{2-}$ and the Zn–C length of $Zn(CH_3)_2$, would be approximately 2.56 Å.[6] This agrees well with an average value of 2.559 Å found[7] for $[(bpy)ZnFe(CO)_4]_2$ but is nearly 0.25 Å longer than the value of 2.317 (1) Å found for $[Zn(Fe(CO)_4)_2]^{2-}$. The sum of the zinc and carbon covalent radii is 2.08 Å, although zinc–carbon bond lengths in alkyl complexes are generally found to be less than 2.0 Å. The major distortion from a regular TBP geometry is found for the axial carbonyl ligand CO(1) and two equatorial carbonyl ligands CO(3) and CO(3′), which are bent toward the zinc atom. The trans Zn–Fe–C(1) angle was found to be 162.3 (2)° and the cis Zn–Fe–Cn(3) angle is 74.8°. The carbonyl carbon atom C(3) and the three symmetrically related carbonyl carbons form a square-planar geometry about the Zn with a Zn–C interatomic contact distance of 2.502 (5) Å. We have found in other studies a marked tendency for carbonyl ligands of complexes containing polar heterobimetallic metal–metal bonds to be oriented toward the M–M′ bond for either electronic or steric reasons.[8] Initial theoretical studies suggest little or no bonding of the $CO_\pi \rightarrow Zn_{p\pi}$ type. In the neutral cobalt analogue of the anion, $[Zn(Co(CO)_4)_2]$, the coordination spheres about the cobalt

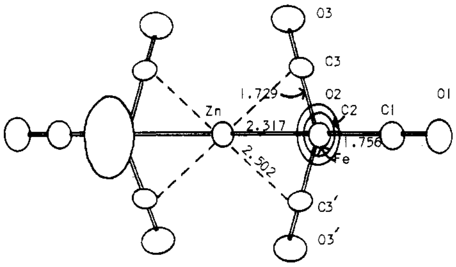

Figure 1. View of the $[Zn(Fe(CO)_4)_2]^{2-}$ anion. The Zn atom is located at a site of 2/*m* crystallographic symmetry with the Fe and carbonyl ligands CO(1) and CO(2) lying on the mirror plane. This results in overall C_{2h} symmetry for the ion.

---

(1) Sosinsky, B. A.; Shelly, J.; Shong, R. *Inorg. Chem.* **1981**, *20*, 1370.

(2) Silvestre, J.; Albright, T. A.; Sosinsky, B. A. *Inorg. Chem.* **1981**, *20*, 3937.

(3) Hsieh, A. T. T.; Mays, M. J.; Platt, R. H. *J. Chem. Soc. A* **1971**, 3296. Hsieh, A. T. T.; Mays, M. J. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *6*, 43.

(4) Data for the complex $[Na(THF)_2]^+{}_2[ZnFe(CO)_4)_2]^{2-}$: mp 175 °C (in vacuo); IR (KBr) 1990 (sh), 1952 (m), 1894 (w), 1809 (vs) cm^{-1}; IR (THF) 1990 (sh), 1970 (sh), 1941 (s), 1868 (vs), 1852 (vs), 1817 (vs) cm^{-1}; conductivity (CH_3CN) 463.18 Ω (mhos L cm^{-1} mol^{-1}) for mol wt 735.6; ^{57}Fe Mössbauer $\delta = 0.416$ mm/s, $\Delta = 1.429$ mm/s (relative to SNP). Anal. Calcd for $Na_2Fe_2ZnC_{24}H_{32}O_{12}$: C, 39.18; H, 4.35; Zn, 8.89; Fe, 15.18. Found: C, 39.35; H, 4.51; Zn, 8.52; Fe, 14.90.

(5) X-ray data for $[Na(THF)_2]^+{}_2[Zn(Fe(CO)_4)_2]^{2-}$: space group *I*2/*m*, monoclinic; 1092 unique reflections $[F_o^2 > 3\sigma(F_o^2)]$; $a = 10.654$ (3) Å, $b = 9.848$ (3) Å, $c = 15.333$ (3) Å, $\beta = 100.79$ (2)°, $V = 1580$ Å^3; $Z = 2$; $R_F = 0.048$, $R_{wF} = 0.057$; bond lengths Fe–Zn = 2.317 (1), Fe–C(1) = 1.756 (8), Fe–C(2) = 1.743 (9), Fe–C(3) = 1.729 (5), ZnC(3) = 2.502 (5), C(1)–O(1) = 1.147 (9), C(2)–O(2) = 1.128 (10), C(3)–O(3) = 1.172 (6), O(3)–Na = 2.308 (4), O(1)–Na = 2.584 (7) Å; bond angles Zn–Fe–C(1) = 162.3 (2), Zn–Fe–C(2) = 90.5 (3), Zn–Fe–C(3) = 74.8 (1), C(1)–Fe–C(2) = 107.2 (4), C(1)–Fe–C(3) = 98.2 (2), C(2)–Fe–C(3) = 110.8 (2), C(3)–Fe–C(3)′ = 127.9 (3), Fe–C(1)–O(1) = 177.5 (7), Fe–C(2)–O(2) = 178.9(9), Fe–C(3)–O(3) = 177.7 (7), C(3)–Zn–C(3)′ = 76.7 (2)°.

(6) Chin, H. B.; Smith, M. B.; Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1974**, *96*, 528. Rundle, R. W. *Surv. Prog. Chem.* **1963**, *1*.

(7) Neustadt, R. J.; Cymbaluk, T. H.; Ernst, R. D.; Cagle, F. W. *Inorg. Chem.* **1980**, *19*, 2375.

(8) (a) Finke, R. G.; Gaughan, G.; Pierpont, C. G.; Cass, M. E. *J. Am. Chem. Soc.* **1981**, *103*, 1394. (b) Roberts, D. A.; Zahorak, S.; Geoffrey, G. L.; Cass, M. E.; Pierpont, C. G., submitted for publication in *J. Am. Chem. Soc.*

0020-1669/82/1321-3247$01.25/0 © 1982 American Chemical Society

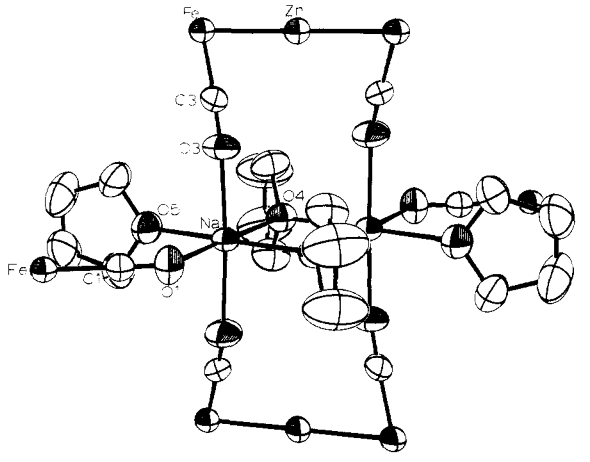

Figure 2. View of the dimeric $[Na_2(THF)_4]^{2+}$ cation, which is located about a site of $2/m$ crystallographic symmetry. Each Na^+ ion is coordinated by two bridging THF molecules, one terminal THF, and the carbonyl oxygens of three different complex molecules. Adjacent Na^+ ions are bridged by complex 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.

Department of Chemistry
The University of Colorado
Boulder, Colorado 80309
Cortlandt G. Pierpont*

Department of Chemistry
William Marsh Rice University
Houston, Texas 77251
Barrie A. Sosinsky*
Robert G. Shong

Received November 10, 1981

---

[9] Lee, B.; Burlitch, J. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1967**, *89*, 6362.

[10] St. Denis, J.; Butler, W.; Glick, M. D.; Oliver, J. B. *J. Am. Chem. Soc.* **1974**, *96*, 5427.

[11] Ernst, R. D.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2090, 2098.

[12] Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 2434.

[13] Greenwood, N. N.; Gibb, T. C. "Mossbauer Spectroscopy;" Chapman and Hall: London, 1971.

[14] Collins, R. L.; Pettit, R. *J. Chem. Phys.* **1963**, *34*, 3433.

[15] Carrol, W. E.; Deeney, F. A.; Delaney, J. A.; Lalor, F. J. *J. Chem. Soc., Dalton Trans.* **1973**, 718.

[16] Sosinsky, B. A.; Shong, R.; Norem, N. *Inorg. Chem.*, in press.

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

---

[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.

0020-1669/82/1321-3248$01.25/0 © 1982 American Chemical Society