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Crystallization and Solid-State Structural Characterization of (2,2′-Bipyridyl)zinc Tetracarbonyliron, (bpy)ZnFe(CO)$_4$

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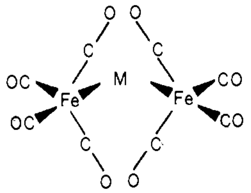
Infrared studies of the known compound $(NH_3)_3ZnFe(CO)_4$ indicate its nature to be monomeric. From this compound, $[ZnFe(CO)_4]_4$ has been prepared and characterized. By very slow diffusion of 2,2′-bipyridine (bpy) into $[ZnFe(CO)_4]_4$ in acetone, crystals of the insoluble (2,2′-bpy)ZnFe(CO)$_4$ compound have been obtained and shown to consist of a highly distorted and crowded planar, dimeric, four-membered metal–metal bonded ring containing alternating zinc and iron atoms. Crystal data: triclinic space group 2-C_i^1-$P\bar{1}$, a = 8.541 (2) Å, b = 8.712 (2) Å, c = 10.518 (2) Å, α = 69.66 (1)°, β = 79.33 (2)°, γ = 77.83 (2)°, Z = 2. The structure has been refined by block-diagonal least-squares refinement to a conventional R index on F of 0.030 and a weighted index of 0.040 for 2815 unique reflections for which $I > 3\sigma(I)$. Two noticeably different Zn–Fe distances are observed: 2.532 (1) and 2.585 (1) Å. On the basis of a comparison of this structure with other related oligomers, it is suggested that the factors controlling the type of structure adopted in these systems depend on a subtle combination of axial carbonyl distortion and a given system's ability to adapt to the distortion. This conclusion allows the prediction of the extent of association to be expected in most other related systems.

Recently, various metal–metal bonded compounds have proven of interest in the long-range goal of preparing infinite metal–metal bonded chains, which ultimately could prove to possess interesting electronic properties.[1] One class of such materials is based upon compounds such as $[CdFe(CO)_4]_4$,[1] $[R_2SnFe(CO)_4]_2$,[2] and their various base adducts. Except in cases where the main group metal would be more than four-coordinate (e.g., $(py)_3ZnFe(CO)_4$, in which case a monomeric complex generally results), these species could exist either as rings (planar dimers, trimers, and tetramers presently being known with idealized cis octahedral iron geometries)[1a–c] or as infinite (linear or bent) chains. Perhaps due to the ability of such metals to readily hybridize and assume a wide range of bond angles,[3] these systems have thus far displayed a singular tendency to exist as rings rather than chains. It has also not been completely clear why some species formed dimeric rings while others formed trimeric rings. It was therefore of interest to seek out other, perhaps more subtle, factors which could be of importance in these ring systems in the hope that a better understanding would emerge. One such factor which may have been partly responsible for the trimeric nature of $[(bpy)CdFe(CO)_4]_3$ as compared to its isoelectronic, dimeric $[R_2SnFe(CO)_4]_2$ analogues[2] (R = alkyl or aryl group) is the pronounced bending of the axial carbonyl ligands in the cadmium system where ionic resonance structures involving $Fe(CO)_4^{\delta-}$ fragments contribute substantially to the bonding.[4] This bending, depicted in A, tends to bring opposing axial carbonyl oxygen atoms closer together which should tend to destabilize ring structures. (In A, only one of the metals bonded to a given iron atom is shown.) To maximize the axial oxygen–oxygen contacts, it should be beneficial to employ a smaller, more electropositive metal (e.g., zinc). A smaller metal would serve to contract the ring while a more electropositive metal should induce more negative charges on the $Fe(CO)_4$ fragment and therefore tend to bring about more bending. In order to probe the possible structure influences of such intramolecular contacts, we undertook the crystallization and X-ray crystallographic characterization of the known insoluble (bpy)ZnFe(CO)$_4$[2c] compound. The structure of this compound is actually revealed to be that of a dimer in which some extremely pronounced and unusual distortions have taken place.



A

Experimental Section

All operations involving metal carbonyls were carried out under an atmosphere of prepurified nitrogen in a Schlenk apparatus or in a glovebox. Nonaqueous solvents were thoroughly dried and deoxygenated in a manner appropriate to each and were distilled immediately prior to use. Aqueous solutions were deoxygenated under a nitrogen stream. Elemental analyses were performed by Dornis and Kolbe Analytical Laboratories.

Spectroscopic Studies. Infrared spectra were recorded with a Beckman IR-20 spectrophotometer. Mulls were prepared in a glovebox with dry, degassed Nujol. All spectra were calibrated with polystyrene.

X-ray Powder Diffraction Studies. X-ray powder diffraction patterns were recorded photographically on a Debye-Scherrer camera using Ni-filtered Cu Kα radiation. Samples were sealed in 0.5-mm glass capillaries under nitrogen and rotated during exposure to ensure average random orientation of the crystallites.

Triamminezinc Tetracarbonyliron, $(NH_3)_3ZnFe(CO)_4$. This air-sensitive compound was prepared as previously described[5,6] from $HFe(CO)_4^-$ and ammoniacal aqueous zinc acetate. The two previously reported C–O stretching bands[5] were observed as minor components of the infrared spectrum. A third, very broad and predominant peak had apparently been overlooked. Complete infrared data (Nujol mull): 3345 m, 3262 mw, 3167 w, 1989 w, 1948 m, 1823 br, sh, 1805 vs, 1604 m, 1223 m, 629 s cm^{-1}.

Zinc Tetracarbonyliron, $ZnFe(CO)_4$. Approximately 0.3 g of $(NH_3)_3ZnFe(CO)_4$ was finely ground with a mortar and pestle in a glovebox. The powder was then spread out into a very thin layer on the bottom of a flask and heated at 80 °C under vacuum for 3–10 days, by which time no N–H stretching modes could be observed in the infrared spectrum. During the heating period, the powder was redistributed daily to expose unconverted material and care was taken to avoid overheating, which can readily result in extensive decom-

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(1) (a) R. D. Ernst, T. J. Marks, and J. A. Ibers, *J. Am. Chem. Soc.*, **99**, 2090 (1977); (b) R. D. Ernst, T. J. Marks, and J. A. Ibers, *ibid.*, **99**, 2098 (1977); (c) R. D. Ernst and T. J. Marks, *Inorg. Chem.*, **17**, 1477 (1978); (d) J. P. Collman, D. W. Murphy, E. B. Fleischer, and D. Swift, *ibid.*, **13**, 1 (1974).

(2) (a) W. Hieber and R. Breu, *Chem. Ber.*, **90**, 1270 (1957); (b) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 3833 (1960); (c) O. Kahn and M. Bigorgne, *C. R. Hebd. Seances Acad. Sci., Ser. B*, **262**, 906 (1966); (d) E. H. Brooks and R. J. Cross, *Organomet. Chem. Rev., Sect. A*, **6**, 227 (1970).

(3) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Interscience, New York, 1972, Chapter 3.

(4) In (bpy)CdFe(CO)$_4$ for example,[1b] the iron coordination angles are actually closer to a bicapped tetrahedral geometry than to a cis octahedral one. For example, the C_{ax}–Fe–C_{ax} angles averaged 139.5 (6)°.

(5) A. T. T. Hsieh, M. J. Mays, and R. H. Platt, *J. Chem. Soc. A*, 3296 (1971).

(6) A. T. T. Hsieh and M. J. Mays, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, **6**, 43 (1972).

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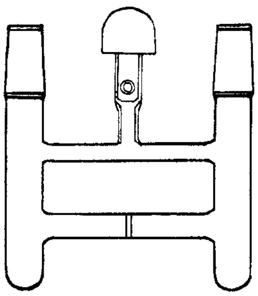

Figure 1. Apparatus used for the crystallization of $[(bpy)ZnFe(CO)_4]_2$. Actual size is approximately $4^1/_2$ in. wide by 5 in. tall.

position. The resulting light tannish, air-sensitive compound is soluble in acetone and other coordinating solvents and is isomorphous with $[CdFe(CO)_4]_4$: complete infrared data (Nujol mull) 2039 s, 2008 ms, 1990 s, 1974 s, 1944 s, 1904 s, 1869 sh, 603 s cm^{-1}. Anal. Calcd for C_4FeO_4Zn: C, 20.60; H, 0.00; N, 0.00. Found: C, 20.44; H, 0.00; N, 0.00.

X-ray Diffraction Study of (2,2′-Bipyridyl)zinc Tetracarbonyliron, $(bpy)ZnFe(CO)_4$. Crystals of $(bpy)ZnFe(CO)_4$ suitable for diffraction studies were grown by slow diffusion of 2,2′-bipyridine and zinc tetracarbonyliron in acetone under a nitrogen atmosphere. Approximately 0.1–0.2 g of each reactant was separately dissolved in ca. 15 mL of acetone. Each solution was then transferred simultaneously to one of two vertical tubes, which were connected near the bottom by a smaller horizontal tube having a coarse frit located in its center. A second horizontal tube, located above the liquid levels, connected the two vertical tubes to a stopcock. This stopcock was used for evacuating and purging the system. Each of the two vertical tubes was fitted with standard taper joints near the top to allow capping of the system (see Figure 1). Once the solutions were introduced, the system was capped and shut under a nitrogen atmosphere. During a period of 5–6 months, the two reacting solutions slowly diffused through the frit, producing a mixture of reddish powder and some well-formed deep purple crystals. The edges on a given crystal possessed similar lengths, and the crystals obtained had edge lengths varying from ca. 0.2 to 1.5 mm. Several infrared spectra, both on individual single crystals and on the powder sample, were identical with the spectrum reported for the known compound.[1c]. A number of the poorer crystals were loaded under nitrogen in thin-walled glass capillaries and sealed. Oscillation and Weissenberg photographs of several of these indicated an identical triclinic space group, which was assumed to be No. 2 (C_i^1-$P\bar{1}$). At this point a somewhat higher quality crystal was mounted and transferred to a Syntex $P\bar{1}$ autodiffractometer equipped with a scintillation counter and pulse height analyzer. Using standard software programs, we readily located the appropriate reduced cell. Accurate cell constants and their standard deviations were derived from a least-squares refinement of 15 centered reflections for which $25° < 2\theta < 40°$, by using the Mo $K\bar{\alpha}$ peak at 0.710730 Å. The unit cell parameters are $a = 8.541$ (2) Å, $b = 8.712$ (2) Å, $c = 10.518$ (2) Å, $\alpha = 69.66$ (1)°, $\beta = 79.33$ (2)°, $\gamma = 77.83$ (2)°, and $V = 712.1$ Å^3. The observed density is 1.81 g/cm^3, measured in iodobenzene/heptane, which compares well with a calculated density of 1.82 g/cm^3 for $Z = 2$.

The data crystal displayed acceptable mosaicity for the θ–2θ scan technique. Mo radiation was monochromatized by using the 002 face of mosaic graphite. Scans were from 1.3° below the Mo $K\alpha_1$ peak to 1.1° above the Mo $K\alpha_2$ peak at a rate of 2°/min. A collimator with a diameter of 1.0 mm was used as the crystal edges varied from 0.4 to 0.6 mm. Data were collected in two concentric shells of 2θ, 0–45° and 45–55° with background time equal to half the total scan time. The intensities of five standard reflections were monitored for every 95 reflections and showed during data collection an average 3.3% decomposition for which correction was made. Coincidence corrections were made for intense reflections. However six reflections ((100), (010), $(0\bar{1}0)$, (001), $(00\bar{1})$, (222)) were so intense that they were recollected later at lowered current along with several sets of the standards.

All data were processed by using the X-RAY 70 program package.[7]

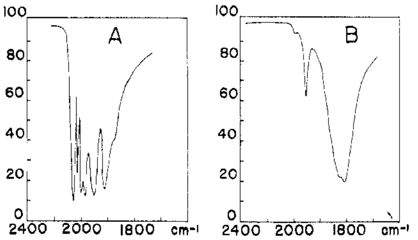

Figure 2. Nujol mull infrared spectra in the C–O stretching region for (A) $[ZnFe(CO)_4]_4$ and (B) $(NH_3)_3ZnFe(CO)_4$.

An absorption correction (μ(Mo $K\alpha$) = 27.65 cm^{-1}) was applied for a spherical crystal. A total of 3727 reflections were processed, yielding 3290 unique reflections, of which 2815 had intensities judged to be above background ($I > 3\sigma(I)$). These were used in subsequent calculations. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with empirical weights assigned by the method of Cruikshank.[8] The atomic scattering factors were taken from the new tabulation,[9] as were the anomalous dispersion terms for zinc and iron.

The positions of the single zinc and iron atoms were each uniquely discerned from a Patterson map. All remaining nonhydrogen atoms were located on a subsequent difference Fourier synthesis. Block-diagonal least-squares refinement led to an anisotropic agreement index ($R = \sum||F_o| - |F_c||/\sum|F_o|$) of 0.038 and a weighted index ($R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$) of 0.053. A difference Fourier indicated that all expected hydrogen atoms were in regions of positive electron density. All eight were placed in their calculated positions. Final refinement led to agreement indices of $R = 0.030$ and $R_w = 0.040$. A final difference Fourier map revealed no peaks greater than 0.35 e/Å^3. The standard deviation for the map was 0.06 e/Å^3. The final positional and thermal parameters obtained from the last cycle of least-squares refinement are presented in Table I, along with their estimated standard deviations. Root-mean-square amplitudes of vibration are given in Table II. The final values of $10|F_o|$ and $10|F_c|$ in electrons are available as supplementary material.[10] Reflections for which the measured intensity was less than zero were assigned zero values of F_o. Other than those mentioned later, intermolecular contacts are normal.

Synthetic and Spectroscopic Results and Discussion

In contrast to its cadmium and mercury analogues, zinc tetracarbonyliron was previously only known in the form of various base adducts,[1c,5] $B_nZnFe(CO)_4$ (B = Lewis base), where $n = 2$ or 3. Reported attempts of the preparation of $ZnFe(CO)_4$ had met with no success.[5] We have found, however, that the base-free zinc compound can readily be isolated by carefully controlled removal of NH_3 from $(NH_3)_3ZnFe(CO)_4$ in vacuo. The resulting product was characterized unambiguously by elemental analysis, infrared spectroscopy, and X-ray powder diffraction. The infrared spectrum (Figure 2) lacks any N–H stretching frequencies,[11] and the C–O vibrational band pattern is nearly identical with that of $[CdFe(CO)_4]_4$ and $[HgFe(CO)_4]_4$.[1,12] X-ray powder diffraction shows the compound to be isomorphous with its cadmium and mercury analogues,[1c,12] thereby demonstrating the tetrameric nature of $[ZnFe(CO)_4]_4$ (planar ring, approximately D_{4h} symmetry).

It is interesting to note that the C–O stretching bands in the zinc complex actually occur at higher frequency than those of the cadmium analogue. In general, a more electropositive

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(7) J. A. Stewart, F. A. Kundell, and J. C. Baldwin, "The X-Ray System of Crystallographic Programs", Computer Science Center, University of Maryland, College Park, Md., 1970.

(8) (a) D. W. J. Cruickshank in "Crystallographic Computing", F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, pp 187–196. (b) The function used in this case was $w = (12.0 + |F_o| + 0.006|F_o|^2 + 0.00025|F_o|^3)^{-1}$.

(9) D. T. Cromer and J. T. Waber in "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Tables 2.2A and 2.3.1.

(10) See paragraph at end of paper regarding supplementary material.

(11) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed., Interscience, New York, 1970, pp 150–158.

(12) T. Takano and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 44, 431 (1971).

metal such as zinc would be expected to donate more electron density to the $Fe(CO)_4$ moiety, some of which would populate the empty C–O π^* orbitals, resulting in *lower* C–O stretching frequencies. Such an effect is indeed observed in corresponding $B_2MFe(CO)_4$ and $B_3MFe(CO)_4$ complexes[1c] where M (Zn or Cd) is four-coordinate (formal sp^3 hybridization). In the base-free compounds, however, the two-coordinate main-group metal (formal sp hybridization) has available two empty p orbitals, which can serve as $d\pi$–$p\pi$ electron acceptors from the filled d orbitals on the adjacent iron atoms. Presumably, for the smaller zinc atom the metal–metal orbital overlap is more effective, resulting in more transfer of electron density from iron to zinc as compared with iron to cadmium transfer such that the C–O stretching frequencies for $[ZnFe(CO)_4]_4$ occur actually higher than in $[CdFe(CO)_4]_4$. A similar observation has been made concerning the monomeric $Zn[Co(CO)_4]_2$ and $Cd[Co(CO)_4]_2$ compounds.[13]

The infrared spectrum of $(NH_3)_3ZnFe(CO)_4$ is also of interest. When first reported, this compound was formulated as a monomer.[14] Subsequently, however, other workers reformulated it as an oligomer, possibly dimeric, on the basis of their reported infrared spectrum.[5,6] Reference to Figure 2, however, demonstrates that the major C–O stretching bands at 1805 and 1823 cm^{-1} had been overlooked. The spectrum of Figure 1 shows C–O stretching modes at lower frequencies than those in the known monomeric complex $(py)_3ZnFe(CO)_4$[1c]. Thus, $(NH_3)_3ZnFe(CO)_4$ is clearly monomeric, as originally formulated.

Crystallographic Results

A perspective view of an individual $[(bpy)ZnFe(CO)_4]_2$ molecule is presented in Figure 3, along with the atom numbering scheme. The hydrogen atoms are deleted for clarity, and each has been assigned the same number as the carbon atom to which it is bonded. Due to the presence of a crystallographic center of symmetry, the four-membered metal–metal bonded ring is rigorously planar. Each zinc atom is pseudotetrahedrally bonded to the two nitrogen atoms in a bidentate 2,2′-bipyridyl ligand and to two adjacent iron atoms. The iron atoms are each bonded to the two adjacent zinc atoms and to four carbonyl groups in what can be described as an extremely distorted cis octahedral geometry. These and other molecular distortions and the packing along the *b* axis can be seen more clearly in Figure 4 and will be discussed subsequently. Pertinent bond distances and angles are presented in Table III, and several best weighted least-squares planes are given in Table IV

Quite unusually, the two Zn–Fe bond distances differ significantly, being 2.532 (1) and 2.585 (1) Å. The difference might be related to the close proximity of the two zinc atoms, 2.788 (1) Å, which are essentially at their estimated van der Waals radii,[15] or it may simply reflect general molecular crowding. It is clearly of some concern to determine what brought the zinc atoms so close in the first place. For this to happen, the Zn–Fe–Zn angle had to decrease dramatically, to 66.02 (2)°, as compared to other related dimeric species such as $[R_2MFe(CO)_4]_2$ (R = alkyl group; M = Ge, Sn, Pb) where M–Fe–M angles in the range 75–78° are commonly observed.[16] This distortion, resulting in an increased Fe–Fe separation as well as the decreased Zn–Zn separation, seems to have taken place to relieve another unfavorable intramolecular contact, that between opposite axial carbonyl oxygen atoms, which even so are only 3.048 (4) Å apart, a value probably within that expected from the normal van der Waals radius of oxygen.[17-19]

Several other distortions have possibly been induced by the short O···O contacts. First, when the Zn–Fe distances of 2.532 (1) and 2.585 (1) Å are compared with other metal–metal bonded distances, it appears that the present Zn–Fe bonds may have been somewhat stretched, again perhaps to relieve zinc–zinc and axial oxygen–oxygen repulsions. Thus, by an examination of various single-bond metallic radii[20] (Zn, 1.249 Å; Cd, 1.413 Å; Ge, 1.223 Å; Fe, 1.165 Å), one might expect from the respective Ge–Fe and Cd–Fe bond lengths of 2.492 (6) Å in $[(C_2H_5)_2GeFe(CO)_4]_2$[16] and 2.640 (2) Å in $[(bpy)CdFe(CO)_4]_3$[1b] a Zn–Fe bond length of no more than 2.47–2.52 Å. As a further comparison, the Zn–Co and Zn–Mo bond distances of 2.305 (2) and 2.538 (1) Å in the base-free $Zn[Co(CO)_4]_2$ and $Zn((C_5H_5)Mo(CO)_3)_2$ complexes can be cited.[21] Second, reference to Figure 4 illustrates that the axial carbonyls are not symmetrically bent toward the metal ring center. Had they been, the O···O separation would be even shorter, assuming no other changes took place in the system. The bending itself (∠C(3)–Fe–C(4) = 150.05 (14)°) has been shown in other systems to be due to stabilization of ionic resonance hybrids which tend to induce a nearly tetrahedral $Fe(CO)_4^{\delta-}$ species which has two metal ions capping tetrahedral faces.[1a-c] In the present case, however, with the small Zn–Fe–Zn′ angle of 66.02 (2)°, it is not possible for the two zinc atoms to each cap a tetrahedral face. What is observed instead is that one zinc atom nearly caps a tetrahedral face (∠Zn–Fe–C(2) = 171.86 (9)°) while the other comes closer to capping a tetrahedral edge (the angle between the Zn′–Fe vector and the Fe–C(3)–C(4) plane being 16.17° while the Zn′–Fe–C(1) angle is 150.32 (13)°). Put in other words, the apparent unsymmetric orientation of zinc atoms arises from the short O···O contacts which cause a twisting of the entire $Fe(CO)_4$ fragments to opposite sides (see Figure 4). Perhaps the most dramatic illustration of this distortion can be observed in the Zn–Fe–C_{eq} angles, where the Zn–Fe–C(1) angle of 84.40 (14)° differs markedly from the Zn–Fe–C(2) angle of 106.42 (9)°. That the distortion is not primarily related to an unsymmetric carbonyl disposition is evidenced by the axial carbonyl plane coming within 6° of bisecting the C_{eq}–Fe–C_{eq} angle. (The respective angles between the Fe–C(3)–C(4) plane and the Fe–C(1) and Fe–C(2) vectors are 45.81 and 57.40°. As a result, while the equatorial carbonyls have twisted 11.01°, the axial carbonyls have twisted to a slightly greater extent, some 16.80°.) Thus, it appears that it is the Fe–Zn (metal–metal) bonds rather than the Fe–CO bonds which are more

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(13) R. J. Ziegler, J. M. Burlitch, S. E. Hayes, and W. M. Risen, Jr., *Inorg. Chem.*, **11**, 702 (1972).

(14) W. Hieber and E. Fack, *Z. Anorg. Allg. Chem.*, **236**, 83 (1938).

(15) (a) An approximate van der Waals radius for zinc has been determined as 1.39 Å.[15b] It can be noted that the Zn–Zn contact distance is not that much greater than the Zn–Fe bond distances. (b) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(16) (a) C. J. Gilmore and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1387 (1972); (b) P. G. Harrison, T. J. King, and J. A. Richards, *ibid.*, 2097 (1975); (c) J. C. Zimmer and M. Huber, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **267**, 1685 (1968).

(17) (a) A value of 1.6 Å has been given on the basis of various oxygen allotropes in which the shortest contact observed is 3.18 Å.[18,19] However, it appears that the van der Waals radius of oxygen, as well as that for other elements, varies dramatically with orientation.[15b,19] A "compromise" value of 1.50 Å has been adopted, but perpendicular to multiple bond axes this distance may be as large as 1.7 Å.[15b] It may be noted that in several other locations in this structure where oxygen–oxygen constants are observed, a minimum value of 3.385 (5) Å was noted. The greater bending of the $(Fe–C–O)_{ax}$ angles with respect to the Fe–C–O_{eq} angles may be due in part to this interaction. Even shorter O_{ax}–O_{ax} contacts have been observed, but they do not involve configurations in which the π clouds are interacting.[17b] (b) H. J. Haupt, W. Wolfes, and H. Preut, *Inorg. Chem.*, **15**, 2920 (1976).

(18) J. Donohue, "The Structures of the Elements", Interscience, New York, 1974.

(19) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, Chapter 7.

(20) Reference 19, p 256.

(21) (a) B. Lee, J. M. Burlitch, and J. L. Hoard, *J. Am. Chem. Soc.*, **89**, 6362 (1967); (b) J. St. Denis, W. Butter, M. D. Glick, and J. P. Oliver, *ibid.*, **96**, 5427 (1974).

Table I. Positional and Thermal Parameters for the Atoms of $[(bpy)ZnFe(CO)_4]_2$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	0.048 70 (3)	−0.032 25 (3)	0.376 52 (3)	0.008 45 (4)	0.010 16 (4)	0.006 01 (3)	−0.000 16 (3)	−0.000 07 (3)	−0.002 48 (3)
Fe	0.211 01 (4)	0.109 16 (4)	0.475 84 (4)	0.007 24 (5)	0.011 17 (6)	0.006 94 (4)	−0.001 30 (4)	−0.000 10 (3)	−0.002 86 (4)
O(1)	0.428 46 (36)	0.136 69 (45)	0.224 00 (28)	0.019 99 (28)	0.041 03 (83)	0.011 45 (30)	−0.010 44 (53)	0.005 75 (31)	−0.011 31 (42)
O(2)	0.372 65 (37)	0.247 51 (39)	0.621 21 (28)	0.024 20 (56)	0.031 44 (66)	0.013 29 (33)	−0.010 86 (50)	−0.001 58 (34)	−0.010 97 (39)
O(3)	0.302 52 (29)	−0.238 98 (29)	0.632 03 (29)	0.013 44 (37)	0.014 88 (38)	0.017 58 (36)	0.002 41 (30)	−0.002 76 (29)	−0.001 36 (30)
O(4)	−0.020 14 (33)	0.404 01 (31)	0.365 06 (30)	0.016 89 (43)	0.014 72 (39)	0.018 25 (40)	0.000 91 (33)	−0.002 96 (33)	0.001 83 (32)
C(1)	0.343 44 (37)	0.124 05 (43)	0.323 57 (32)	0.011 71 (42)	0.020 21 (59)	0.009 55 (32)	−0.004 51 (40)	0.000 57 (29)	−0.005 65 (35)
C(2)	0.307 22 (36)	0.192 52 (39)	0.566 69 (30)	0.012 35 (43)	0.016 93 (51)	0.008 30 (28)	−0.003 88 (38)	0.000 42 (28)	−0.004 32 (31)
C(3)	0.260 83 (33)	−0.100 79 (38)	0.570 98 (33)	0.008 24 (36)	0.014 99 (48)	0.011 99 (36)	−0.000 43 (33)	−0.001 16 (28)	−0.003 84 (33)
C(4)	0.064 81 (36)	0.282 85 (37)	0.413 55 (31)	0.011 77 (42)	0.013 15 (44)	0.010 22 (32)	−0.003 25 (34)	−0.001 00 (29)	−0.001 00 (30)
C(5)	0.257 42 (32)	−0.136 74 (34)	0.156 18 (27)	0.010 37 (37)	0.013 03 (42)	0.007 97 (27)	−0.001 80 (32)	0.000 25 (25)	−0.004 33 (27)
C(6)	0.379 69 (43)	−0.222 82 (46)	0.088 39 (34)	0.015 55 (53)	0.020 28 (62)	0.010 16 (35)	−0.000 45 (46)	0.002 43 (34)	−0.006 49 (38)
C(7)	0.453 14 (43)	−0.378 44 (46)	0.161 27 (39)	0.014 61 (53)	0.019 08 (62)	0.014 61 (46)	0.001 91 (45)	0.002 09 (39)	−0.008 49 (45)
C(8)	0.404 55 (39)	−0.443 90 (39)	0.296 57 (37)	0.013 50 (48)	0.013 26 (47)	0.013 91 (41)	0.000 92 (38)	−0.000 33 (35)	−0.005 37 (36)
C(9)	0.284 54 (37)	−0.351 01 (35)	0.358 83 (32)	0.013 11 (44)	0.011 34 (41)	0.011 04 (34)	0.000 07 (34)	−0.000 25 (30)	−0.003 89 (30)
C(10)	0.167 59 (34)	0.026 41 (34)	0.085 02 (27)	0.012 17 (40)	0.013 37 (42)	0.007 21 (25)	−0.003 43 (33)	−0.000 12 (25)	−0.003 65 (27)
C(11)	0.195 66 (45)	0.103 04 (43)	−0.054 56 (31)	0.018 81 (59)	0.018 28 (58)	0.007 48 (29)	−0.002 94 (47)	0.000 29 (33)	−0.003 02 (33)
C(12)	0.101 41 (51)	0.253 21 (44)	−0.115 06 (31)	0.024 77 (74)	0.017 52 (58)	0.006 61 (29)	−0.003 62 (53)	−0.000 43 (36)	−0.001 49 (33)
C(13)	−0.014 83 (46)	0.322 29 (39)	−0.033 72 (33)	0.020 88 (63)	0.012 92 (47)	0.009 92 (34)	−0.001 58 (43)	−0.004 55 (37)	−0.001 69 (32)
C(14)	−0.035 60 (42)	0.241 26 (37)	0.104 97 (31)	0.017 61 (54)	0.013 03 (46)	0.009 08 (31)	0.000 10 (39)	−0.002 49 (33)	−0.003 50 (31)
N(1)	0.211 95 (26)	−0.199 94 (27)	0.290 82 (22)	0.010 23 (32)	0.010 99 (32)	0.007 83 (22)	−0.001 24 (26)	0.000 36 (21)	−0.003 36 (22)
N(2)	0.053 39 (29)	0.095 95 (27)	0.164 44 (22)	0.012 55 (34)	0.011 26 (33)	0.007 13 (22)	−0.001 37 (27)	−0.000 94 (22)	−0.003 00 (22)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(6)	0.41245	−0.175 70	−0.006 50	5.48	H(11)	0.278 65	0.053 48	−0.108 58	5.15
H(7)	0.537 17	−0.439 09	0.116 68	5.85	H(12)	0.117 43	0.306 76	−0.211 05	5.35
H(8)	0.452 18	−0.551 68	0.347 50	5.15	H(13)	−0.080 64	0.425 17	−0.072 49	5.25
H(9)	0.252 06	−0.396 16	0.453 90	4.60	H(14)	−0.116 32	0.290 50	0.160 55	4.90

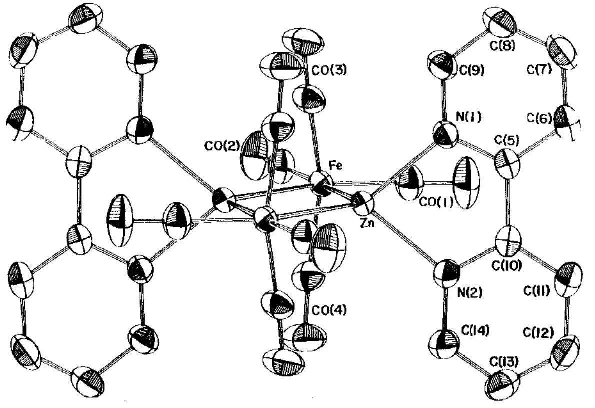

Figure 3. Perspective view and numbering scheme for the centrosymmetric $[(bpy)ZnFe(CO)_4]_2$. The 40% probability vibrational ellipsoids are shown.

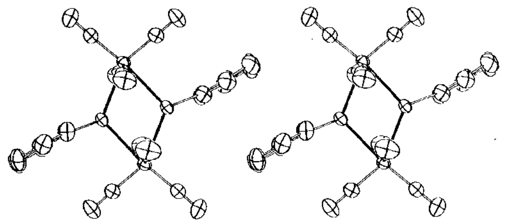

Figure 4. Perspective view of two adjacent $[(bpy)ZnFe(CO)_4]_2$ molecules approximately normal to the metal atom plane illustrating the packing along the horizontal *b* axis. The 50% probability vibrational ellipsoids are shown.

Table III. Selected Bond Distances (Å) and Angles (Deg) in $[(bpy)ZnFe(CO)_4]_2$

Bond Distances

Fe–Zn	2.585 (1)	Fe–C(1)	1.763 (3)	C(1)–O(1)	1.144 (4)	C(7)–C(8)	1.356 (5)
Fe–Zn′	2.532 (1)	Fe–C(2)	1.772 (4)	C(2)–O(2)	1.137 (6)	C(8)–C(9)	1.380 (5)
Zn–N(1)	2.117 (2)	Fe–C(3)	1.757 (3)	C(3)–O(3)	1.164 (4)	C(10)–C(11)	1.384 (4)
Zn–N(2)	2.116 (2)	Fe–C(4)	1.759 (3)	C(4)–O(4)	1.158 (4)	C(11)–C(12)	1.390 (5)
C(5)–N(1)	1.343 (3)	C(10)–N(2)	1.348 (4)	C(5)–C(6)	1.388 (5)	C(12)–C(13)	1.368 (5)
C(9)–N(1)	1.340 (3)	C(14)–N(2)	1.338 (3)	C(6)–C(7)	1.384 (5)	C(13)–C(14)	1.378 (4)
						C(5)–C(10)	1.477 (3)

Bond Angles

Zn–Fe–Zn′	66.02 (2)	Fe–C(1)–O(1)	178.8 (3)	N(1)–C(5)–C(10)	116.2 (2)
Fe–Zn–Fe′	113.98 (2)	Fe–C(2)–O(2)	177.7 (3)	C(6)–C(5)–C(10)	122.4 (2)
Fe–Zn–N(1)	108.67 (7)	Fe–C(3)–O(3)	176.3 (3)	N(2)–C(10)–C(5)	115.8 (2)
Fe–Zn–N(2)	107.84 (8)	Fe–C(4)–O(4)	173.9 (3)	C(11)–C(10)–C(5)	122.7 (3)
Fe′–Zn–N(1)	121.94 (6)	C(1)–Fe–C(2)	103.25 (16)	C(5)–C(6)–C(7)	118.9 (3)
Fe′–Zn–N(2)	121.25 (7)	C(1)–Fe–C(3)	101.86 (15)	C(6)–C(7)–C(8)	119.7 (3)
N(1)–Zn–N(2)	77.75 (8)	C(1)–Fe–C(4)	98.88 (14)	C(7)–C(8)–C(9)	118.7 (3)
Zn–Fe–C(1)	84.40 (14)	C(2)–Fe–C(3)	97.41 (16)	C(8)–C(9)–N(1)	122.8 (3)
Zn–Fe–C(2)	171.86 (9)	C(2)–Fe–C(4)	98.59 (16)	C(9)–N(1)–C(5)	118.5 (2)
Zn–Fe–C(3)	78.07 (13)	C(3)–Fe–C(4)	150.05 (14)	C(10)–C(11)–C(12)	119.4 (3)
Zn–Fe–C(4)	82.75 (13)	Zn–N(1)–C(5)	114.35 (16)	C(11)–C(12)–C(13)	118.7 (3)
Zn′–Fe–C(1)	150.32 (13)	Zn–N(2)–C(10)	114.58 (16)	C(12)–C(13)–C(14)	119.3 (3)
Zn′–Fe–C(2)	106.42 (9)	Zn–N(1)–C(9)	126.71 (20)	C(13)–C(14)–N(2)	122.7 (3)
Zn′–Fe–C(3)	75.39 (9)	Zn–N(2)–C(14)	126.77 (20)	C(14)–N(2)–C(10)	118.5 (2)
Zn′–Fe–C(4)	75.88 (9)	N(1)–C(5)–C(6)	121.4 (2)	N(2)–C(10)–C(11)	121.5 (3)

Table IV. Deviations (Å) of Atoms from Best Weighted Least-Squares Planes[a]

(a) Plane Defined by the Metal Atoms[b]

atom[a]	dist	atom	dist
Zn	0.000 (0)	Fe	0.000 (0)
C(1)	0.078	O(1)	0.152
C(2)	−0.095	O(2)	−0.149

(b) Planes Defined by the Bipyridyl Ligand[c]

atom	dist (plane 1)	atom	dist (plane 2)
N(1)	0.007	N(2)	0.002
C(5)	−0.010	C(10)	−0.007
C(6)	0.004	C(11)	0.007
C(7)	0.006	C(12)	−0.003
C(8)	−0.009	C(13)	−0.002
C(9)	0.003	C(14)	0.003

[a] The symmetry-related atoms have deviations equal but opposite to those given here. [b] Equation (triclinic coordinates): $3.396x - 5.925y + 2.887z = 1.443$. [c] Equations (triclinic coordinates: first plane, $7.164x + 5.846y + 5.290z = 1.881$; second plane, $7.013x + 6.239y + 4.732z = 1.749$. The dihedral angle between these two planes is 5.05°.

deformable in this and other systems.[22]

A third effect to be attributed to the relatively close O···O contacts has to do with the bending of the C_{ax}–Fe–C_{ax} angle. As already described, this results from negative charge buildup on the $Fe(CO)_4$ moiety. However, it appears by comparison with the $[(bpy)CdFe(CO)_4]_3$ structure that the extent of bending has been significantly reduced from what might have been expected in the present system. In two similar sp^3 systems, the more electropositive zinc atoms would be expected to contribute more electron density to the iron atoms than cadmium atoms could. This leads to the expectation that the zinc system should cause more bending of the axial carbonyl ligands, when in fact less is observed (150.05 (14)° vs. 139.5 (6)°). This can readily be attributed to the O···O contacts presently observed in the dimer. However, it is interesting to note that the average Fe–C and C–O distances in the zinc complex are respectively *longer* and *shorter* than in the cadmium analogue (1.763 (2) and 1.151 (2) Å vs. 1.727 (7) and 1.178 (9) Å, respectively), indicating that the cadmium atoms actually seem to be transferring more electron density to iron atoms than do the zinc atoms,[23] contrary to what is generally observed (e.g., $(py)_3M^+Fe^-(CO)_4$ species).[1c] In the present system it is also interesting to note that the Fe–C_{ax} and C_{ax}–O_{ax} distances of 1.758 (2) and 1.161 (3) Å appear to be respectively shorter and longer than the Fe–C_{eq} and C_{eq}–O_{eq} distances of 1.768 (3) and 1.141 (4) Å, seemingly indicating more negative charge being placed on the axial carbonyls. The Fe–C_{ax}–O_{ax} angles are also somewhat more bent than the Fe–C_{eq}–O_{eq} angles (see Table III).

Several other metal coordination parameters are also of some interest. Likely in response to the small Zn–Fe–Zn angle and the negative charge on the $Fe(CO)_4$ group, the C(1)–Fe–C(2) angle is observed to be 103.25 (16)°, near an ideal tetrahedral value of 109.5°. The average C_{ax}–Fe–C_{eq} angle of ca. 99.19 (8)° is approximately midway between tetrahedral and octahedral extremes. Zn–Fe–C_{ax} angles as small as 75.39 (9)° are observed with Zn–C_{ax} contacts being shortest at 2.693 (3) and 2.708 (3) Å for Zn′–C(3) and Zn′–C(4), respectively. These distances are considered too long to result in any major interaction.[1b,24] The average Zn–N bond length of 2.116 (1) Å is somewhat longer than in other four-coordinate complexes such as $(phen)ZnCl_2$[25,26] (Zn–N = 2.061 (5) Å, ∠N–Zn–N = 80.4 (3)°) resulting in the slightly smaller N(1)–Zn–N(2) bite angle of 77.75 (8)°. The Zn–N distance is actually more comparable to those observed in various five- or six-coordinate complexes such as $Zn(F_6acac)_2(C_5H_5N)_2$,[27] for which Zn–N = 2.116 (7) Å.

Bond distances and angles within the bipyridyl ligand are rather normal.[28] The atoms in the separate six-membered

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[22] (a) T. J. Marks and G. W. Grynkewich, *J. Organomet. Chem.*, **91**, C9 (1978); (b) G. W. Grynkewich and T. J. Marks, *Inorg. Chem.*, **15**, 1307 (1976); (c) L. Vancea, R. K. Pomeroy, and W. A. G. Graham, *J. Am. Chem. Soc.*, **98**, 1407 (1976).

[23] It may be speculated that the close proximity of the two zinc atoms prevents them from building up more substantial charges, which would increase ionic repulsions. It can also be noted that the C–O stretching frequencies for the zinc compound came lower than those of the cadmium compound.[1] The difference, however, was small and could possibly be a solvent effect as the zinc compound was recorded as a mull while the cadmium compound was in benzene solution.[1a–c]

[24] (a) F. A. Cotton, *Prog. Inorg. Chem.*, **21**, 1 (1976); (b) G. Dettlaf and E. Weiss, *J. Organomet. Chem.*, **108**, 213 (1976).

[25] C. W. Reimann, S. Block, and A. Perloff, *Inorg. Chem.*, **5**, 1185 (1966).

[26] (a) W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, **16**, 1119 (1977); (b) W. R. Scheidt, M. E. Kastner, and K. Hatano, *ibid.*, **17**, 706 (1978).

[27] J. Pradilla-Sorzano and J. P. Fackler, Jr., *Inorg. Chem.*, **12**, 1174 (1973).

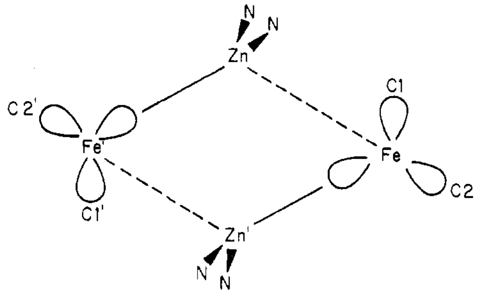
rings are planar within 0.010 and 0.007 Å, respectively (Table IV). An angle of 7.40° is found between the C(5)–C(8) and C(10)–C(13) vectors. It can be noted here that the enlarging of one Zn–Fe–C_{eq} angle at the expense of the other Zn–Fe–C_{eq} angle has apparently been taken advantage of by a bipyridyl ligand in an adjacent dimer (see Figure 4), resulting in more efficient packing along the *b* axis in which the adjacent bipyridyl ligands become sandwiched together. Two features can be attributed to this packing. First, the bipyridyl ligands are tilted with respect to the Zn–Fe and Zn–Fe′ vectors (the best plane for the entire 12-membered ligand makes an angle of 104.34° with the Zn–Fe vector and an angle of 141.69° with the Zn–Fe′ vector). Second, a relatively low value[28] of 5.05° is observed for the noncoplanarity between the two six-membered pyridine rings in a given ligand (see Table IV), possibly as a result of squashing taking place between the adjacent ligands, favoring a more planar orientation.

Crystallographic Discussion

The present structural investigation has established the constitution of the insoluble (bpy)ZnFe$(CO)_4$ species as a dimer and pointed out a heretofore unrecognized factor influencing the extent of oligomerization or polymerization observed in these systems. Rather than their geometries depending only on the extent of axial carbonyl bending, it appears that it might be a combination of this bending and the systems ability to accommodate and relieve the unfavorable axial O···O interactions, which arise as a result of this bending, which seems to determine the type of structure formed. On this basis, it is possible to explain the structures observed for related known systems. In the present $[B_2ZnFe(CO)_4]_2$ system, the metal ring was able to relieve the O···O interactions somewhat by decreasing the Zn–Fe–Zn angle while increasing the Fe–Zn–Fe angle, during which the iron atoms became further separated, while the zinc atoms came into close proximity (at ca. van der Waals radii). Apparently for the analogous nitrogenous $B_2CdFe(CO)_4$ systems,[1a–c] where the cadmium atom is somewhat larger than the zinc atom, the system could not distort itself sufficiently to relieve O···O interactions enough while retaining a dimeric structure without the cadmium atoms becoming severely close, so that an entropically less favorable trimeric structure was adopted. Complexes of the type $R_2MFe(CO)_4$ (M = Ge, Sn, Pb) are dimeric[16,29] for large or small atoms due to their greater covalent character (observed in infrared spectra), which results in less bending of the axial carbonyls ($\angle C_{ax}$–Fe–$C_{ax} \approx$ 160–165°)[16] and therefore no appreciable O···O repulsions. The dimeric nature of $[BCdFe(CO)_4]_2$,[1c] B = 4-$C_6H_5C_5H_4N$, can likewise be explained. Two mechanisms allow reduction of iron negative charge density, one being the existence of one less (electron donating) base than present in $B_2CdFe(CO)_4$ complexes. Second, the three-coordinate (sp^2) cadmium atom has an empty p orbital available to absorb electron density from the filled iron d orbitals. As noted previously, this type of interaction was observed both in the present studies for the $[MFe(CO)_4]_4$ complexes and in previous studies on $M[Co(CO)_4]_2$ complexes (M = Zn, Cd).[13] Again, the reduced electron density on the $Fe(CO)_4$ fragment results in less bending and a dimeric structure.

In this light, the structure of other related species may be considered. First, the insoluble PbFe$(CO)_4$ compound[1c,30] may well be dimeric (with a stereochemically active lone pair on lead),[31] similar to the insoluble (bpy)ZnFe$(CO)_4$ dimer.[32] Second, it must be expected that previously unreported BRGaFe$(CO)_4$ complexes (as well as base-free RMFe$(CO)_4$ (M = Ga, In, Tl) species or BZnFe$(CO)_4$) should be dimeric, with less severe distortions than those observed in the present study,[33] while hypothetical BRInFe$(CO)_4$ species could be either dimeric or trimeric as they lie between isoelectronic $[B_2CdFe(CO)_4]_3$ and $[R_2SnFe(CO)_4]_2$ species and should possess an intermediate degree of ionic character.[35]

It is interesting that some of the observed distortions actually are consistent with a simple valence-bond interpretation in which two monomeric (bpy)Zn^+–$Fe^-(CO)_4$ species are brought into proximity such that the iron coordination geometry is viewed as monocapped trigonal-bipyramidal (it can be noted that ZnFe$(CO)_4$ base adducts are generally monomers with a trigonal-bipyramidal iron coordination environment). The diagram



illustrates the principal features of this model (axial carbonyls omitted).

First, as the Fe–Zn′ bond is shorter than the Fe–Zn bond, Zn′ is denoted as the fifth ligand on the Fe coordination sphere.[36] Zn is thus seen to nearly cap a trigonal edge on Fe and the Zn′–Fe–C(2) angle is larger than the Zn–Fe–C(1) angle, as observed. An ideal Zn–Fe–Zn′ angle of 60° would be predicted, compared to the observed 66.02°. In addition, the two nitrogen atoms on Zn′ would be expected to tilt to one side (toward Fe′) so that N(1), N(2), Zn′, and Fe would lie roughly in the same plane (approximate sp^2 hybridization with Fe′ interacting with the empty p orbital or an orbital of high p character, in Zn′). This distortion is also observed, in the predicted direction. While this hybrid model accounts for several features of this molecule, it cannot be determined, of course, whether the contribution of such a resonance form is responsible for the observed distortions or whether an initial distortion (e.g., packing and tilting of the bipyridyl ligands) has simply initiated the other features by forcing the system to some extent to adopt the given resonance structures, although the latter seems more likely.

It is of final interest to compare some of the more unusual features observed for $[(bpy)ZnFe(CO)_4]_2$ with other related systems. In at least two other cases, similar O···O interactions have been observed, which may have brought about appre-

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(28) (a) C. W. Reimann, M. Zocchi, A. D. Mighell, and A. Santoro, *Acta Crystallogr., Sect. B*, **27**, 2211 (1971); (b) W. Clegg and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, 511 (1974); (c) I. M. Procter and F. S. Stephens, *J. Chem. Soc. A*, 1248 (1969).

(29) F. Hein and W. Jehn, *Justus Liebigs Ann. Chem.*, **684**, 5 (1965).

(30) P. Krumholz and S. Bril, *Proc. Chem. Soc. London*, 116 (1960).

(31) P. G. Harrison, *Coord. Chem. Rev.*, **20**, 1 (1976).

(32) The infrared C–O stretching frequencies were observed at relatively high frequency,[1c] indicating that little bending of the axial carbonyl ligand should have taken place, so that a much less distorted structure is expected.

(33) We have recently prepared and characterized several such gallium compounds, including a mono(tetrahydrofuran) adduct which has been crystallized and is presently undergoing structural determination.[34]

(34) R. D. Ernst, T. H. Cymbaluk, J. Vanderhooft, R. J. Neustadt, and F. W. Cagle, Jr., experiments in progress. See companion paper in this issue.

(35) J. Vanderhooft and R. D. Ernst, experiments in progress.

(36) While the difference in the two Zn–Fe bond distances is not great, it is highly significant statistically, and to our knowledge such differences have not been observed in any related oligomers. In the model given, it is not intended that there is a great difference between these bonds, just that the Zn′ atom is using more p character in the orbital bonding to Fe than in the orbital bonding to Fe′.

ciable structural influences. In (2,2′:6′,2″-terpyridyl)Cd-$[Mn(CO)_5]_2$,[37] O···O contacts of 3.035 Å were observed. The two Cd–Mn distances differed and were perhaps a bit long at 2.760 (4) and 2.799 (5) Å. In the rather more ionic $Na_2Fe(CO)_4\cdot{}^3/_2$(dioxane) structure,[38] one can observe an essentially dimeric, planar $[NaFe(CO)_4^-]_2$ cluster (see Figure 5, ref 37). In this cluster, both short O···O contacts (3.02 Å) and long Na–Fe bond distances (3.086 Å) were reported, somewhat analogous to the present situation.

The present study indicates that the axial carbonyl oxygen–oxygen repulsions present in these ring systems are apparently not capable of destabilizing ring structures sufficiently to result in chain formation. The very severe distortions which are found in this structure seemingly point out a marked reluctance of these species to form polymers. Hence, the prospects of preparing such polymers, in the present systems at least, may be expected to be a difficult task. It is, however, somewhat encouraging that virtually insoluble species such as $[(bpy)ZnFe(CO)_4]_2$ can be crystallized and characterized by proper manipulations.

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Registry No. $(NH_3)_3ZnFe(CO)_4$, 45048-25-7; $[ZnFe(CO)_4]_4$, 73513-02-7; $[(bpy)ZnFe(CO)_4]_2$, 66027-70-1.

Supplementary Material Available: A listing of root-mean-square amplitudes of vibration (Table II) and the structure amplitude table (19 pages.) Ordering information is given on any current masthead page.

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[37] W. Clegg and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, 90 (1973).

[38] H. B. Chin and R. Bau, *J. Am. Chem. Soc.*, **98**, 2434 (1976).

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Synthesis and Characterization of Lewis Base Adducts of Ethylgallium Tetracarbonyliron, $B_n(C_2H_5)GaFe(CO)_4$ (B = Lewis Base)

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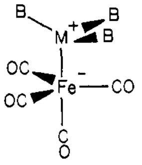
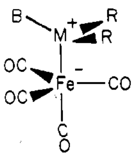
The syntheses and complete characterization of various base adducts of ethylgallium tetracarbonyliron are reported. With nitrogenous bases, monomeric complexes incorporating two base molecules are isolated, while with THF (tetrahydrofuran), a dimeric complex incorporating one donor THF molecule for each gallium atom is obtained. Infrared spectral evidence is also presented which indicates a similar associated base-free complex also exists. The nature of these compounds is discussed and compared with other related metal–metal bonded complexes.

A number of metal–metal bonded compounds have been reported which can be looked upon as being derived from $Fe(CO)_4^{2-}$ interacting with either a B_nM^{2+} (B = Lewis base; n = 0–3 and M = Zn, Cd or n = 0 and M = Hg)[1] or $B_nR_2M^{2+}$ (R = alkyl; n = 0, 1; M = Ge, Sn, Pb)[2] species. In general, the $B_3MFe(CO)_4$ (M = Zn, Cd) and $(B)R_2MFe(CO)_4$ (M = Ge, Sn, Pb) complexes are monomeric, with four-coordinate metal M and a five-coordinate (TBP) iron, as in I and II. In the other cases, a monomeric complex would impose a coordination number less than 4 on the metal M, and as a result, each metal M and each iron atom form a second metal–metal bond, resulting in each case so far in the formation of a cyclic ring structure containing cis-disubstituted octahedrally coordinated iron (e.g., $[(C_2H_5)_2GeFe(CO)_4]_2$, $[(bpy)CdFe(CO)_4]_3$, $[CdFe(CO)_4]_4$ (bpy = 2,2′-bipyridyl)), although a chain structure is also possible.


I (M = Zn, Cd)


II (M = Ge, Sn, Pb)

It can be noted that the group 4B metals Ge, Sn, and Pb do not differ very substantially in their preference for base adduct molecules, generally the preferred value of n being 0.[2d] However, in the group 2B series, a value of n = 3 is favored for zinc, n = 2 for cadmium, and n = 0 for mercury (where the Lewis base generally contains a nitrogen donor atom).[1h–j] To date, no intermediate group 3B species of the general type $B_nRMFe(CO)_4$ (M = Ga, In, Tl) have been reported, although various other complexes are known in which these metals form typical single bonds to $Co(CO)_4$,[3] $Mn(CO)_5$,[4] $(C_5H_5)Fe(CO)_2$,[5] etc.[6] It was therefore of interest to attempt the

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