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(48) Metal pentafluorides are also known in which flexing of the M-F-M bridges leads to tetrameters of D_{2d} symmetry (MF_5, M = Ru, Os, Rh, Ir, Pt).[46]

Metal-Metal Bond Cleavage Reactions. The Crystal and Molecular Structure of (2,2′-Bipyridyl)cadmium Tetracarbonyliron, (bpy)CdFe(CO)$_4$

Richard D. Ernst,[1] Tobin J. Marks,*[2] and James A. Ibers*

Contribution from the Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201. *Received June 25, 1976*

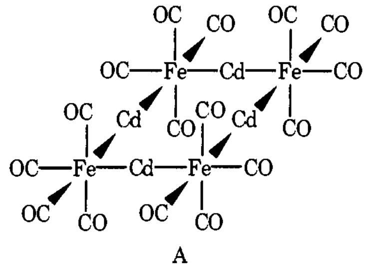
Abstract: The complex (bpy)CdFe(CO)$_4$ crystallizes from hot 1,2,4-trichlorobenzene as a trimer with the stoichiometry $[(bpy)CdFe(CO)_4]_3\cdot\frac{3}{4}C_6H_3Cl_3$. The crystals belong to the tetragonal space group S_4^1-$P\bar{4}$ with eight six-membered metal-metal bonded rings and six solvent molecules in a unit cell of dimensions $a = b = 29.049$ (10), $c = 13.241$ (5) Å, $V = 11\ 170$ Å^3. Full-matrix least-squares refinement yielded a final value of the conventional R index (on F) of 0.066 for 5643 reflections having $F_o^2 > 3\sigma(F_o^2)$. The molecular structure consists of nearly planar rings of alternating *cis*-Fe(CO)$_4$ and (bpy)Cd units. The ring is distorted from ideal D_{3h} to approximate C_2 symmetry by compression along a C_2 axis in the plane of the ring. All Fe-Cd distances are equal within experimental error [2.640 (7) Å]. The Cd-Fe-Cd angles vary from 138.81 (15) to 148.40 (15)°, and the Fe-Cd-Fe angles from 94.78 (14) to 102.04 (16)°. The iron coordination geometry is significantly distorted from an octahedral one toward a tetrahedral one in which cadmium atoms cap two of the faces. There is evidence for a weak semibridging interaction between carbonyl carbon and cadmium atoms. The Cd-Fe bonding in $[(bpy)CdFe(CO)_4]_3$ appears to be more ionic than in $[CdFe(CO)_4]_4$. The trimeric compound dissociates in benzene solution.

In an accompanying article[3] we discussed means to purify and to crystallize certain classes of oligomeric metal-metal bonded materials by employing reversible base-induced cleavage reactions. This allowed the crystallization of CdFe(CO)$_4$[4]

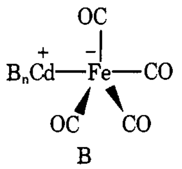
$$[CdFe(CO)_4]_4 + 4nB \rightleftharpoons 4B_nCd^+{-}{}^-Fe(CO)_4 \quad (1)$$

$$B = \text{acetone, THF, } NH_3$$

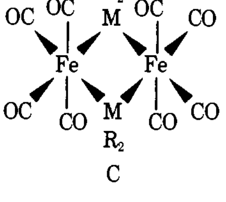
and unambiguous definition of the molecular structure by x-ray diffraction.[3] The molecule was found to possess an unusual tetrameric structure consisting of nearly square-planar centrosymmetric eight-membered ring of alternating Cd and *cis*-Fe(CO)$_4$ units (A). The nature of the base-induced cleavage products in solution was proposed on the basis of cryoscopic molecular weight and infrared spectral studies to be B. These measurements, of course, provided no quantitative structural details and no information on the solid state geometry. They also yielded little information on what features of B might provide a driving force for the metal-metal bond breaking process. For $n = 2$ it was not clear why a dimeric structure could not exist, as found in the isoelectronic, structurally well-characterized group IV metal-iron dimers $[R_2MFe(CO)_4]_2$[5] (C), M = Si, Ge, Sn, Pb. These show little tendency to undergo unassisted dissociation.[6] The $n = 3$ species are isoelectronic with the group IV cleavage products, $B\cdot R_2MFe(CO)_4$,[7] the structural details of which have not been obtained and can only be inferred from spectral studies[7] and by comparison with the $B\cdot R_2MCr(CO)_5$ derivatives.[7b,8] For these reasons we have undertaken an x-ray diffraction study of the $B_nCdFe(CO)_4$ adduct where B_n = 2,2′-bipyridyl.[9] In this compound the base is sufficiently strong and nonvolatile so that stable crystals can be grown. Mössbauer data[9] suggested that the coordination about iron was probably cis octahedral, but provided no further structural information. Dimeric and polymeric states of (bpy)CdFe(CO)$_4$ aggregation were recognized as possibilities.[9] We discuss here our results on the rather complex crystal structure of this molecule. Our data reveal the presence of unusual six-membered metal-metal bonded rings and somewhat different Cd-Fe interactions than were found in the base-free eight-membered ring of $[CdFe(CO)_4]_4$.



A



B



C

Experimental Section

X-Ray Diffraction Study of (bpy)CdFe(CO)$_4$. The compound was synthesized as described previously.[3] Attempts at crystallization (by slow cooling) from a number of solvents (benzene, toluene, CH_2Cl_2/hexane) yielded well-formed single crystals which became opaque and crumbled on isolation owing to loss of occluded solvent. However, stable crystals could be obtained from less volatile solvents, such as 1,2,4-trichlorobenzene, by very slow cooling of hot saturated solutions. In this case, very slow cooling was achieved by enclosing the hot solution (under nitrogen in a Schlenk tube) in a covered Dewar flask containing oil at the same temperature. This procedure resulted in the formation of large, well-formed, orange-red needles in a size suitable for x-ray diffraction. Even larger crystals could be obtained by further insulating the Dewar, or by controlling the rate of cooling with a heating element connected to a variable ac voltage regulator. When the cooling process was completed, the supernatant liquid was removed by syringe, and the crystals allowed to dry on filter paper in the air. The product so obtained contains 1,2,4-trichlorobenzene of crystallization.

Anal. Calcd for $C_{14}H_8CdFeN_2O_4 \cdot \frac{1}{4}C_6H_3Cl_3$: C, 38.64; H, 1.83; N, 5.81; Cl, 5.52. Found: C, 38.95; H, 1.80; N, 5.30; Cl, 5.61.

IR data (Nujol mull): 1970 vs, 1905 vs, 1875 vs, 1590 mw, 1565 w, 1320 w, 1250 vw, 1175 vw, 1160 w, 1100 w, 1035 w, 1015 mw, 895 w, 870 w, 818 m, 810 m, 755 s, 738 m, 725 w cm^{-1}. The bands at 1035, 810, and 722 cm^{-1} are assigned to 1,2,4-trichlorobenzene by comparison with a spectrum of the pure compound.

A crystal of approximate dimensions 0.15 × 0.25 × 0.70 mm was mounted on a glass fiber, with [001] coincident with the spindle axis. Preliminary film data exhibited primitive $4/m$ symmetry in the tetragonal system with no true extinctions, although the $00l$ reflections were very weak for l odd. No unambiguous assignment of space group was possible at this time.

Intensity measurements were made with Mo Kα_1 radiation using a Picker FACS-I computer-controlled four circle x-ray diffractometer equipped with a scintillation counter and pulse height analyzer. Cell constants and their standard deviations were derived from a least-squares refinement of 19 hand-centered reflections, using the Mo Kα_1 peak at 0.709 300 Å. The unit cell parameters are $a = b = 29.049$ (10), $c = 13.241$ (5) Å, $V = 11\,170$ Å^3. The calculated density for $24[(bpy)CdFe(CO)_4 \cdot \frac{1}{4}(C_6H_3Cl_3)]$ is 1.72 g/cm^3, which agrees with the experimental value of 1.74 g/cm^3 measured by flotation in aqueous zinc chloride solution.

The data crystal displayed acceptable mosaicity for the θ–2θ scan technique. Mo Kα_1 radiation was monochromatized using the 002 face of mosaic graphite. In order to avoid multiple diffraction, the crystal orientation was adjusted so that the [001] direction was approximately 12° from the spindle axis. Scans were from 0.7° below to 0.7° above the Mo Kα_1 peak at a rate of 2°/min. The takeoff angle was 2.3°, the aperture was set at 4.5-mm high by 1.5-mm wide, and the counter was positioned 32 cm from the crystal. Data were collected in the range $3° \leq 2\theta \leq 42°$ with background counts of 10 s for $2\theta \leq 32°$ and of 20 s thereafter. The intensities of six standard reflections were monitored every 100 reflections and showed only slight monotonic increases or decreases, which are assumed to result from slow loss of solvent of crystallization.

All data were processed as described previously;[10] a value of 0.04 was used for p in the estimation of $\sigma(F_o^2)$. A total of 8036 reflections was processed, yielding 6372 unique reflections, of which 5643 had $F_o^2 > 3\sigma(F_o^2)$, and were used in subsequent calculations.

With 24 cadmium atoms and 24 iron atoms in the unit cell, resort was made to direct methods for a structure solution. Trial solutions were first sought in space group $P4/m$ using the LSAM[11] programs. All of the 16 solutions produced had nearly identical signs for the majority of reflections. Fourier syntheses of the more likely solutions (those with the highest figures of merit) yielded unreasonable, nearly identical, structures.

A Patterson synthesis revealed that no mirror plane was present perpendicular to the z axis, and that the metal atoms were not present in high symmetry positions, both contradicting the solutions in $P4/m$. The next most likely space group was considered to be $P\bar{4}$. Using the MULTAN[11] programs, eight trial solutions were produced. However, the figures of merit among the solutions were nearly identical, and no correct solution could be readily found, although the highest electron density was now present in general positions. On the basis of the nearly extinct $00l$, l odd reflections, we considered that there could be psuedo 4_2 symmetry present. Solutions were then sought in space group $P4$ using MULTAN, as it is known that translational symmetry greatly aids in obtaining a correct solution by direct methods.

Four trial solutions were obtained, and the correct one was clearly indicated by the figures of merit. A Fourier synthesis revealed the positions of the six independent cadmium atoms. The six independent iron atoms were also located, although some of them were of relatively low intensity in the Fourier map. The solution consisted of two independent, nearly planar six-membered metal–metal bonded rings. Two cycles of isotropic refinement resulted in $R = 0.42$, $R_w = 0.55$.

Throughout these and subsequent refinements, full-matrix least-squares techniques were employed. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and the weight, w, is $4F_o^2/\sigma(F_o^2)$. The agreement indices R and R_w are defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$. The atomic scattering factors were taken from the new tabulation,[12] as were the anomalous dispersion terms[12] for iron, cadmium, and chlorine.

A difference Fourier synthesis indicated the positions of eight unresolved peaks for the 24 independent carbonyl ligands. Attempts to refine these positions proved fruitless. Moreover, the metal–metal distances also varied in a random fashion, from ca. 2.2 to 3.1 Å. Examination of the two independent trimers showed that they were nearly related by $\bar{4}$ symmetry. The metal positions were averaged to give transformed coordinates in the space group $P\bar{4}$, and then slightly distorted to break the 4_2 symmetry. Two cycles of isotropic refinement yielded agreement indices of $R = 0.44$, $R_w = 0.52$, and it was observed that the metal–metal distances were much more uniform, varying from ca. 2.4 to 2.7 Å. A difference Fourier map yielded positions of 22 of the 24 independent carbonyl ligands, again each carbonyl appearing as a single unresolved peak. Parts of the bipyridyl groups seemed to appear, although they were poorly resolved. The 12-membered planar bipyridyl ligands were assumed to be rigid bodies and were placed in idealized positions on each cadmium atom. The carbonyl carbon and oxygen atom positions were extrapolated from the single carbonyl peaks. The final two carbonyl groups were found on a subsequent difference Fourier map. With these atoms in place values of R and R_w of 0.38 and 0.46 were obtained. One cycle of isotropic refinement of the metals and the six bipyridyl units (with one temperature factor per group) brought these indices down to 0.34 and 0.42, respectively. The bipyridyl ligands were next assumed to consist of rigid six-membered rings, and two cycles of full isotropic refinement (including the carbonyl positions) led to values of $R = 0.18$ and $R_w = 0.25$. A major characteristic of the early refinements was the tendency of some of the atoms to become ill-defined, and considerable difficulty was experienced in the replacement of these atoms. The problems probably arose from the presence of pseudosymmetry.

A difference Fourier synthesis revealed that the largest remaining electron density was present near the metal atoms, and on the twofold rotation axis. Six chlorine atoms were found about this axis, each chlorine being disordered between two positions. The carbon atom positions in the solvent molecules could not be discerned, presumably owing to complications arising from the deviation of the ortho chlorine atoms from the plane of the benzene ring. The hydrogen atoms of the bipyridyl groups were included in calculated positions, and anisotropic thermal parameters were assigned to the metal atoms. Two cycles of refinement led to values of $R = 0.098$ and $R_w = 0.14$. A difference Fourier map revealed a number of peaks on the two $\bar{4}$ symmetry axes. From these, the most likely chlorine atom positions, with occupancy factors of 0.25, were chosen. With the cell composition now specified, an absorption correction was applied ($\mu = 20.44$ cm^{-1}, transmission factors ranged from 0.69 to 0.75). Two more cycles of refinement led to convergence at $R = 0.066$ and $R_w = 0.099$ and to an error in an observation of unit weight of 3.19 e for the 433 variables and 5643 observations. Two of the chlorine atoms on the $\bar{4}$ axes had very large thermal parameters. A difference Fourier map revealed that the true positions of the two chlorine atoms were essentially underneath two of the other chlorine atoms (that is, they both occupied symmetry related disordered positions). Redefinition of these two atoms led to satisfactory thermal parameters, but owing to their relative unimportance in the structure, final refinement resulted in no significant changes except for the chlorine atoms in question. A final difference Fourier map contained a number of significant peaks on the high-symmetry axes (all, however, less than 1.4 e/Å^3). As no meaningful model for the carbon atom disorder was recognized, no further attempts were made at improving the description of the structure.

The final positional and thermal parameters appear in Tables I and II, and the root-mean-square amplitudes of vibration are given in Table III. A listing of $10|F_o|$ vs. $10|F_c|$ for those reflections used in the calculations and a listing of bipyridyl hydrogen atom positions will appear in the microfilm edition.[13]

Results

In our hands, crystals of (2,2′-bipyridyl)cadmium tetracarbonyliron, $(bpy)CdFe(CO)_4$, suitable for diffraction studies

Table I. Positional and Thermal Parameters for the Nongroup Atoms of $[(C_{10}N_2H_8)CdFe(CO)_4]_3 \cdot \frac{3}{4}C_6H_3Cl_3$

ATOM	X^A	Y	Z	B11^B	B22	B33	B12	B13	B23
CO(1)	0.214305(68)	0.036312(67)	-0.39710(16)	12.90(30)	10.66(28)	45.4(14)	0.63(23)	0.37(54)	-0.58(52)
CO(2)	0.037349(68)	0.264313(67)	0.17614(17)	13.22(30)	12.57(29)	44.1(14)	-0.29(23)	-0.43(56)	-0.30(56)
CO(3)	0.267933(70)	0.104041(70)	-0.17374(17)	13.74(30)	13.59(30)	50.0(14)	-0.48(24)	1.73(59)	-4.17(60)
CO(4)	0.282591(70)	0.484660(67)	-0.10348(16)	12.90(29)	10.75(27)	46.5(14)	0.66(22)	1.32(54)	0.12(53)
CO(5)	0.432537(68)	0.243139(67)	0.31909(16)	12.79(29)	12.80(29)	44.3(14)	0.72(23)	2.66(56)	-1.09(55)
CO(6)	0.220955(68)	0.427423(69)	-0.33194(17)	13.24(30)	13.10(30)	46.4(14)	-0.72(23)	2.14(58)	-2.37(57)
FE(1)	0.29784(15)	0.03263(15)	-0.07045(31)	15.30(64)	15.45(64)	40.1(28)	-1.24(51)	0.0(11)	-2.0(11)
FE(2)	0.22323(13)	0.12290(13)	-0.34230(31)	13.27(56)	10.70(51)	50.6(28)	0.34(42)	2.7(11)	-0.4(10)
FE(3)	0.05193(12)	0.22247(13)	0.35008(29)	10.40(51)	12.84(56)	44.8(27)	-0.28(42)	0.3(10)	-0.1(10)
FE(4)	0.20106(14)	0.50420(14)	-0.42972(31)	14.34(62)	14.06(61)	42.6(27)	-0.84(49)	-0.6(10)	1.2(10)
FE(5)	0.25981(13)	0.40079(13)	-0.16169(34)	13.58(57)	10.42(52)	58.1(29)	-0.11(43)	0.9(11)	1.0(11)
FE(6)	0.42723(12)	0.28889(13)	0.14703(29)	10.99(52)	11.89(55)	46.1(28)	-0.20(42)	-0.8(10)	-1.8(10)

ATOM	X	Y	Z	B,A^2	ATOM	X	Y	Z	B,A^2
O(1)	0.33779(90)	0.10554(92)	0.0512(22)	8.33(66)	C(1)	0.3209(12)	0.0767(12)	0.0090(29)	6.28(80)
O(2)	0.32950(86)	-0.04031(88)	0.0656(21)	8.01(65)	C(2)	0.3174(10)	-0.0107(11)	0.0072(26)	5.21(69)
O(3)	0.20058(82)	0.03390(81)	-0.0272(19)	6.81(56)	C(3)	0.2388(11)	0.0362(10)	-0.0513(25)	5.05(68)
O(4)	0.35796(77)	0.03001(76)	-0.2474(20)	6.86(55)	C(4)	0.33507(95)	0.0316(10)	-0.1773(26)	4.77(60)
O(5)	0.23873(96)	0.2185(10)	-0.2774(23)	9.56(75)	C(5)	0.2321(10)	0.1770(10)	-0.3062(25)	5.29(67)
O(6)	0.17403(73)	0.14811(72)	-0.5254(18)	6.23(50)	C(6)	0.1923(10)	0.1377(10)	-0.4522(25)	4.73(65)
O(7)	0.14881(75)	0.09437(72)	-0.2138(18)	6.08(52)	C(7)	0.1795(11)	0.1048(10)	-0.2644(26)	5.16(68)
O(8)	0.31272(77)	0.09779(75)	-0.4249(19)	6.64(53)	C(8)	0.27732(95)	0.10467(92)	-0.3898(23)	4.35(58)
O(9)	0.15195(78)	0.23068(78)	0.2972(19)	6.97(57)	C(9)	0.2268(10)	-0.1073(10)	-0.3163(26)	4.96(65)
O(10)	0.18122(73)	-0.06711(73)	-0.5471(18)	6.06(50)	C(10)	0.1967(10)	-0.0610(10)	-0.4724(25)	4.30(63)
O(11)	0.14914(86)	-0.02383(84)	-0.2221(21)	7.74(62)	C(11)	0.1816(10)	-0.03344(96)	-0.2720(23)	4.34(60)
O(12)	0.03106(77)	0.31600(83)	0.4169(19)	7.00(56)	C(12)	0.0382(10)	0.2781(10)	0.3860(24)	4.90(64)
O(13)	0.56274(87)	0.16267(85)	0.5682(20)	7.49(62)	C(13)	0.5341(11)	0.1759(10)	0.5123(26)	5.23(69)
O(14)	0.17403(90)	0.58290(92)	-0.5497(22)	8.62(67)	C(14)	0.1850(12)	0.5514(12)	-0.4994(29)	6.43(80)
O(15)	0.48873(71)	0.14040(70)	0.2525(19)	6.08(50)	C(15)	0.4923(10)	0.1642(10)	0.3260(28)	4.95(65)
O(16)	0.50828(74)	0.29731(77)	0.4733(19)	6.37(53)	C(16)	0.50083(88)	0.26107(93)	0.4506(22)	3.91(56)
O(17)	0.22970(88)	0.31091(89)	-0.2216(21)	8.39(66)	C(17)	0.2407(10)	0.3494(11)	-0.2033(26)	5.68(73)
O(18)	0.30401(96)	0.36879(97)	0.0260(24)	9.10(74)	C(18)	0.2836(12)	0.3838(12)	-0.0463(30)	6.05(83)
O(19)	0.17502(31)	0.43854(86)	-0.0888(20)	7.69(61)	C(19)	0.2079(10)	0.4246(10)	-0.1173(24)	4.88(64)
O(20)	0.58140(77)	0.33834(79)	0.2891(19)	6.98(56)	C(20)	0.5872(11)	0.3053(11)	0.2368(27)	5.66(75)
O(21)	0.33135(79)	0.29473(77)	0.1994(19)	7.02(56)	C(21)	0.37144(84)	0.29222(80)	0.1807(22)	3.52(50)
O(22)	0.42134(71)	0.33503(69)	-0.0445(18)	5.67(48)	C(22)	0.4251(10)	0.31856(95)	0.0348(23)	4.20(60)
O(23)	0.43465(69)	0.19603(73)	0.0786(17)	5.85(48)	C(23)	0.43229(91)	0.23279(93)	0.1060(22)	4.10(56)
O(24)	0.46825(78)	0.35698(78)	0.2770(19)	6.71(56)	C(24)	0.4521(10)	0.3272(10)	0.2255(23)	4.45(61)
CL(1)	0.43229(81)	-0.06845(79)	-0.0255(20)	9.58(60)	CL(7)	0.0076(20)	0.0256(16)	0.2131(44)	10.6(15)
CL(2)	-0.4557(11)	0.0949(12)	-0.0311(31)	14.6(10)	CL(8)	0.0785(19)	0.0501(19)	0.0542(47)	16.1(15)
CL(3)	0.4562(10)	-0.0493(10)	-0.3182(26)	12.43(78)	CL(9)	0.0909(20)	0.0929(21)	0.0844(49)	12.8(17)
CL(4)	0.4271(12)	-0.0453(12)	0.4794(29)	15.1(10)	CL(10)	0.4944(19)	0.4724(15)	0.2781(40)	10.3(13)
CL(5)	0.4015(12)	0.0598(11)	0.4010(29)	14.4(10)	CL(11)	0.4124(19)	0.4557(19)	0.4412(46)	13.7(15)
CL(6)	0.4427(10)	-0.0305(10)	0.2013(23)	11.41(79)	CL(12)	0.4005(19)	0.4296(19)	0.4125(46)	9.7(15)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficients × 10^4.

could only be grown with solvent included in the cell. The structure determination was undertaken on a crystalline sample grown from and containing 1,2,4-trichlorobenzene. This crystal featured a very large unit cell and a number of other crystallographic problems which were overcome only with great difficulty (see Experimental Section). The solid state structure of $(bpy)CdFe(CO)_4$ was found to consist of two independent, planar six-membered rings of alternating iron and cadmium atoms. In contrast, molecular weight measurements[3] show both $(bpy)CdFe(CO)_4$ and $(py)_2CdFe(CO)_4$ to be unassociated in benzene solution. Figure 1 presents a packing diagram of the six-membered rings. The disordered solvent molecules fill channels along the twofold rotation axes ($\frac{1}{2}, 0, z$ and $0, \frac{1}{2}, z$), as well as pockets between bipyridyl ligands on the $\bar{4}$ axes ($0, 0, z$ for $0.20 \gtrsim z \gtrsim -0.20$ and $\frac{1}{2}, \frac{1}{2}, z$ for $0.70 \gtrsim z \gtrsim 0.30$). There are no unusually short intermolecular contacts in the unit cell.

A perspective view of an individual $[(bpy)CdFe(CO)_4]_3$ molecule with the atom numbering scheme is shown in Figure 2. Within each six-membered ring, the cadmium atoms are pseudotetrahedrally coordinated by a bidentate 2,2′-bipyridyl moiety, and by two iron atoms. The iron atoms are coordinated by four carbonyl groups and two cadmium atoms, in what can be described as either a highly distorted octahedral geometry or, perhaps more appropriately, as a tetrahedral disposition of the four carbonyl groups, with the cadmium atoms capping two tetrahedral faces. For reasons of clarity, each carbonyl group in Figure 2 has been identified by a single number. Thus, carbonyl 11 is composed of C(11) and O(11). Similarly, each bipyridyl ligand is defined by two rigid groups, which are identified by letter. The numbering scheme for the atoms in these groups is given in Figures 2 and 4. For the second, crystallographically independent six-membered ring in the unit cell, the numbering system continues sequentially. Thus, Fe(4) takes the place of Fe(1), C(13) takes the place of C(1), BPYR(G) takes the place of BPYR(A), etc.

Pertinent bond distances and angles are set out in Tables IV and V; a summary of structural parameters within the metal–metal bonded framework is shown in Figure 3. Within experimental error, the two independent six-membered rings

Table II. Derived Parameters for the Rigid Group Atoms of [(C$_{10}$N$_2$H$_8$)CdFe(CO)$_4$]$_3$·¾C$_6$H$_3$Cl$_3$

ATOM	X	Y	Z	B,A^2	ATOM	X	Y	Z	B,A^2
N(1A)	0.14466(58)	0.04225(63)	-0.4882(16)	6.48(31)	N(1G)	0.26836(76)	0.48336(77)	0.0700(13)	6.78(32)
C(1A)	0.14727(55)	0.04920(69)	-0.5892(16)	6.48(31)	C(1G)	0.30425(54)	0.47527(70)	0.1328(18)	6.78(32)
C(2A)	0.10980(76)	0.06435(76)	-0.6442(12)	6.48(31)	C(2G)	0.29895(64)	0.47549(74)	0.2365(17)	6.78(32)
C(3A)	0.06877(59)	0.07248(67)	-0.5937(17)	6.48(31)	C(3G)	0.25561(79)	0.48427(80)	0.2760(13)	6.78(32)
C(4A)	0.06637(57)	0.06534(68)	-0.4911(17)	6.48(31)	C(4G)	0.21930(56)	0.49246(70)	0.2117(18)	6.78(32)
C(5A)	0.10482(75)	0.05020(71)	-0.4400(12)	6.48(31)	C(5G)	0.22655(62)	0.49183(70)	0.1089(16)	6.78(32)
N(1B)	0.22768(77)	0.03980(74)	-0.5725(13)	6.76(33)	N(1H)	0.34974(56)	0.46736(63)	-0.0154(16)	6.33(30)
C(1B)	0.19114(56)	0.04114(70)	-0.6360(18)	6.76(33)	C(1H)	0.34828(56)	0.46366(68)	0.0865(16)	6.33(30)
C(2B)	0.19633(64)	0.03560(75)	-0.7390(17)	6.76(33)	C(2H)	0.38629(78)	0.44997(78)	0.1415(12)	6.33(30)
C(3B)	0.24024(79)	0.02854(79)	-0.7772(13)	6.76(33)	C(3H)	0.42665(59)	0.43990(68)	0.0901(17)	6.33(30)
C(4B)	0.27720(57)	0.02722(72)	-0.7122(18)	6.76(33)	C(4H)	0.42788(56)	0.44374(70)	-0.0135(17)	6.33(30)
C(5B)	0.27003(62)	0.03295(70)	-0.6101(16)	6.76(33)	C(5H)	0.38893(74)	0.45755(74)	-0.0646(12)	6.33(30)
N(1C)	0.23602(70)	-0.08817(65)	-0.0480(13)	6.32(32)	N(1I)	0.20194(69)	0.63840(53)	-0.3321(18)	6.55(32)
C(1C)	0.26466(60)	-0.12235(72)	-0.0182(15)	6.32(32)	C(1I)	0.21740(62)	0.66967(73)	-0.4000(16)	6.55(32)
C(2C)	0.25781(68)	-0.14594(64)	0.0713(17)	6.32(32)	C(2I)	0.19782(76)	0.71286(66)	-0.4080(15)	6.55(32)
C(3C)	0.22055(74)	-0.13371(69)	0.1312(13)	6.32(32)	C(3I)	0.16149(74)	0.72394(55)	-0.3445(18)	6.55(32)
C(4C)	0.19159(61)	-0.09894(72)	0.1003(15)	6.32(32)	C(4I)	0.14596(63)	0.69195(75)	-0.2758(16)	6.55(32)
C(5C)	0.20006(64)	-0.07667(60)	0.0104(16)	6.32(32)	C(5I)	0.16677(71)	0.64941(64)	-0.2710(15)	6.55(32)
N(1D)	0.31512(61)	-0.10119(53)	-0.1513(15)	5.64(29)	N(1J)	0.27591(73)	0.61532(70)	-0.4487(14)	6.88(34)
C(1D)	0.30611(57)	-0.13187(67)	-0.0769(14)	5.64(29)	C(1J)	0.25361(64)	0.65500(76)	-0.4708(16)	6.88(34)
C(2D)	0.33240(70)	-0.17108(60)	-0.0643(13)	5.64(29)	C(2J)	0.26555(76)	0.68139(62)	-0.5536(18)	6.88(34)
C(3D)	0.36877(64)	-0.17872(55)	-0.1301(16)	5.64(29)	C(3J)	0.30131(78)	0.66641(73)	-0.6147(14)	6.88(34)
C(4D)	0.37771(58)	-0.14739(69)	-0.2055(14)	5.64(29)	C(4J)	0.32381(66)	0.62605(78)	-0.5918(16)	6.88(34)
C(5D)	0.35037(66)	-0.10846(59)	-0.2146(13)	5.64(29)	C(5J)	0.31046(72)	0.60109(60)	-0.5083(18)	6.88(34)
N(1E)	0.24597(67)	0.15630(62)	-0.0427(13)	6.08(30)	N(1K)	0.16216(58)	0.37300(55)	-0.3543(15)	5.58(29)
C(1E)	0.27260(57)	0.19378(71)	-0.0259(15)	6.08(30)	C(1K)	0.16797(56)	0.33885(68)	-0.4228(14)	5.58(29)
C(2E)	0.26254(66)	0.22483(60)	0.0500(17)	6.08(30)	C(2K)	0.13774(69)	0.30224(59)	-0.4289(14)	5.58(29)
C(3E)	0.22412(72)	0.21693(65)	0.1098(14)	6.08(30)	C(3K)	0.10073(61)	0.30092(58)	-0.3627(15)	5.58(29)
C(4E)	0.19721(60)	0.17876(73)	0.0922(15)	6.08(30)	C(4K)	0.09505(57)	0.33574(69)	-0.2934(14)	5.58(29)
C(5E)	0.20886(64)	0.14893(58)	0.0154(16)	6.08(30)	C(5K)	0.12626(66)	0.37144(57)	-0.2906(13)	5.58(29)
N(1F)	0.32221(67)	0.16622(57)	-0.1564(17)	6.54(33)	N(1L)	0.23826(64)	0.37709(58)	-0.4668(12)	5.48(28)
C(1F)	0.31118(62)	0.20141(74)	-0.0938(16)	6.54(33)	C(1L)	0.20595(52)	0.34538(66)	-0.4913(14)	5.48(28)
C(2F)	0.33686(77)	0.24142(63)	-0.0910(16)	6.54(33)	C(2L)	0.21072(58)	0.31726(60)	-0.5748(15)	5.48(28)
C(3F)	0.37475(70)	0.24510(60)	-0.1543(18)	6.54(33)	C(3L)	0.24973(67)	0.32204(61)	-0.6343(12)	5.48(28)
C(4F)	0.38575(62)	0.22920(76)	-0.2177(16)	6.54(33)	C(4L)	0.28243(53)	0.35433(67)	-0.6090(14)	5.48(28)
C(5F)	0.35892(73)	0.17008(62)	-0.2173(15)	6.54(33)	C(5L)	0.27590(56)	0.38147(56)	-0.5248(15)	5.48(28)

RIGID GROUP PARAMETERS

GROUP	X_C^A	Y_C	Z_C	DELTA^B	EPSILON	ETA
BPYR 1	0.10696(47)	0.05730(38)	-0.5410(12)	-2.139(25)	1.050(13)	1.896(27)
BPYR 2	0.23377(51)	0.03421(40)	-0.6745(13)	-1.441(35)	1.171(13)	-1.839(36)
BPYR 3	0.22845(47)	-0.11094(45)	0.0411(11)	0.366(16)	-0.719(12)	0.879(16)
BPYR 4	0.34174(44)	-0.13984(44)	-0.1405(10)	0.238(13)	-0.507(11)	-2.350(14)
BPYR 5	0.23522(46)	0.18658(47)	0.0331(11)	-0.242(14)	-2.605(12)	-0.735(14)
BPYR 6	0.34827(48)	0.20556(49)	-0.1551(11)	-0.188(13)	-2.767(13)	2.442(15)
BPYR 7	0.26217(43)	0.48378(37)	0.1726(13)	1.319(37)	-1.171(13)	1.523(38)
BPYR 8	0.38795(47)	0.45370(37)	0.0374(12)	1.125(27)	-1.061(13)	-1.746(29)
BPYR 9	0.18190(47)	0.68103(48)	-0.3386(12)	3.192(14)	0.438(13)	2.416(15)
BPYR10	0.28844(48)	0.64087(50)	-0.5313(12)	0.160(16)	2.525(13)	2.331(16)
BPYR11	0.13166(44)	0.33704(45)	-0.3588(10)	-0.328(12)	0.430(11)	0.760(13)
BPYR12	0.24383(43)	0.34960(41)	-0.5501(10)	2.705(14)	2.504(11)	0.798(14)

[a] x_c, y_c, and z_c are the fractional coordinates of the origin of the rigid group. [b] The rigid group orientation angles delta, epsilon, and eta (radians) have been defined previously: S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965).

have essentially identical structures. The Fe-Cd distances are nearly equal and fall in the range 2.631 (4)-2.653 (5) Å. This is markedly longer than found in [CdFe(CO)$_4$]$_4$,[3] 2.562 (3) Å. The distance is comparable to Fe-Sn distances in isoelectronic species such as [(CH$_3$)$_2$SnFe(CO)$_4$]$_2$ (2.631 (11) and 2.647 (8) Å].[5a] The ring defined by the iron and cadmium atoms in [(bpy)CdFe(CO)$_4$]$_3$ is very nearly planar, and as can be seen in Table VI no metal atom deviates from the mean-square plane by more than 0.158 (39) Å. In spite of the planarity there is considerable distortion of the ring system from D_{3h} symmetry. There appears to be significant compression along the z direction of the unit cell and the angle Cd(2)-Fe(1)-Cd(3) (102.04 (16)°) is considerably greater than ∠Cd(1)-Fe(2)-Cd(3) (94.78 (14)°) and ∠Cd(1)-Fe(3)-Cd(2) (95.22 (13)°). Similarly, the angle about Cd(1), ∠Fe(2)-Cd(1)-Fe(3) (148.40 (15)°), has opened in comparison with ∠Fe(1)-Cd(2)-Fe(3) (138.81 (15)°) and ∠Fe(1)-Cd(3)-Fe(2) (139.93 (15)°). Besides describing the ring geometry, these parameters reveal the changes, in comparison with [CdFe(CO)$_4$]$_4$,[3] which coordination of 2,2′-bipyridyl has brought about at the individual metal atoms. First, the valence angles about iron have increased from the original,[3] nearly octahedral values of 87.76 (5) and 89.31 (4)°. The present metal-iron-metal valence angles of 94.78 (14) -102.04 (16)° are still smaller than found in the acyclic system [((CH$_3$)$_3$Si]$_2$Fe(CO)$_4$,[14] 111.8 (2)°, but larger than in the five-membered ring of [(η^5-C$_5$H$_5$)Co(CO)]$_2$(GeCl$_2$)$_2$-Fe(CO)$_4$[15] (88.2 (2)°) and in the acyclic complex [(C$_6$H$_5$)$_3$-

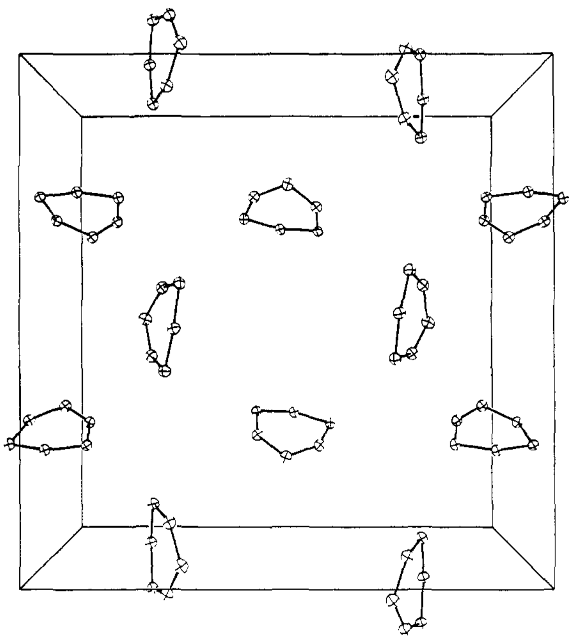


Figure 1. Packing of the $[(bpy)CdFe(CO)_4]_3$ Cd-Fe rings in the unit cell. The x axis is horizontal to the right, the y axis is vertical, and the z axis points out of the plane of the page. The rings arranged in vertical columns are centered near $z = 0.75$, while those arranged in horizontal rows are centered near $z = 0.25$.

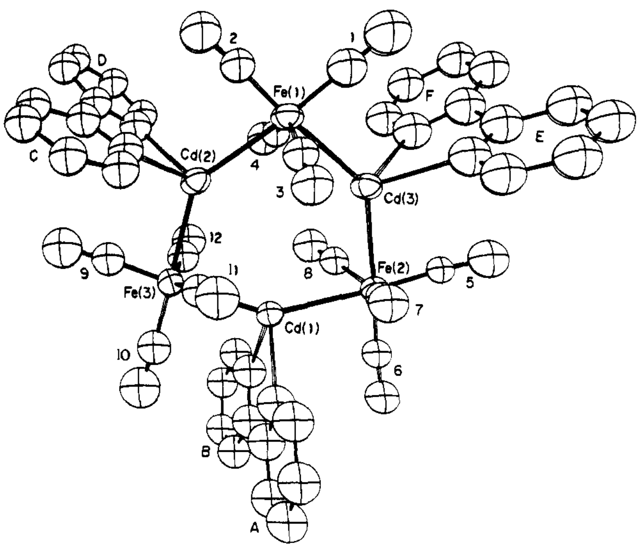


Figure 2. Perspective view of $[(bpy)CdFe(CO)_4]_3$ showing atom numbering scheme. The 50% probability vibrational ellipsoids are shown.

$Sn]_2Fe(CO)_4$ (96.0°).[16] The bipyridyl coordination has also altered the geometry about cadmium, which was only slightly distorted from linearity in $[CdFe(CO)_4]_4$ (∠Fe-Cd-Fe = 170.25 (5) and 189.85 (5)°). The present Fe-Cd-Fe angles are 138.81 (15)-148.40 (15)°, somewhat larger than values reported for ∠Mn-Cd-Mn in $BCd[Mn(CO)_5]_2$ derivatives where B is diglyme[17] (135.9 (1)°), 2,2′-bipyridyl[18] (127.7 (2)°), 1,10-phenanthroline[18] (131.4 (2)°), or 2,2′:6′2″-terpyridyl[19] (132.4 (2)°). The average Cd-N distance that we find (2.373 (18) Å) is comparable with those found in the above-mentioned bipyridyl[18] [2.358(10) and 2.349 (9) Å] and phenanthroline[18] (2.382 (14) and 2.342 (14) Å) derivatives, but shorter than in the terpyridyl complex[19] (2.475 (14), 2.405 (12), 2.493 (14) Å).

The disposition of the nonmetallic ligands about iron in $[(bpy)CdFe(CO)_4]_3$ also deviates appreciably from an octahedral configuration. We define the equatorial carbonyl ligands as the six CO groups which lie essentially in the plane of the ring (e.g., CO(1)) and the axial carbonyls as the six which are out of the plane (e.g., CO(3)). The average C(axial)-Fe-C(axial) angle is 139.5 (14)°, compared with 154.7 (3)° in $[CdFe(CO)_4]_4$[3] and 180° for an ideal octahedron (Table VII). This angle is frequently somewhat less than 180° in related systems, viz $[(CH_3)_2SnFe(CO)_4]_2$ (156 (4) and 165 (4)°);[5a] $[(\eta^5\text{-}C_5H_5)Co(CO)]_2(GeCl_2)_2Fe(CO)_4$ (172.0 (1)°);[15] and $(CH_3)_4Sn_3[Fe(CO)_4]_4$ (158 (2)-165 (2)°),[20] but seldom in this range. Only in $[(CH_3)_3Si]_2Fe(CO)_4$[14] is a comparably small C(axial)-Fe-C(axial) angle observed: 141.2 (2)°. In $[(bpy)CdFe(CO)_4]_3$, the average C(axial)-Fe-C(equatorial) angle expands to 103.4 (14)°. This can be compared with an average value of 99.4 (4)° in $[CdFe(CO)_4]_4$.[3] In the present case, the C(equatorial)-Fe-C(equatorial) angles average 96.3 (15)°, the expansion, at first glance, appearing to be constrained by the cadmium atoms which occupy the same plane. However, the average C(equatorial)-Fe-Cd angle is surprisingly small, 83.2 (17)°. The average C(axial)-Fe-Cd angle is even smaller, 76.8 (20)°, and suggests possible Cd-C interaction (vide infra). The Fe-C(equatorial) and Fe-C(axial) distances in $[(bpy)CdFe(CO)_4]_3$ are essentially identical and average 1.727 (7) Å, while the average C-O distance is 1.178 (9) Å. In $[CdFe(CO)_4]_4$, the average Fe-C and C-O distances of 1.779 (3) and 1.152 (3) Å are slightly longer and shorter, respectively, than those found in the present complex. These differences are in accord with infrared spectroscopic data which indicate lower C-O force constants for the base adduct in solution[3] and in the solid state (see Experimental Section). The average Fe-C-O angle is 175.2 (28)° (176.3 (9)° in $[CdFe(CO)_4]_4$[3]). Table VIII presents a comparison of average bond distances and angles in these two compounds.

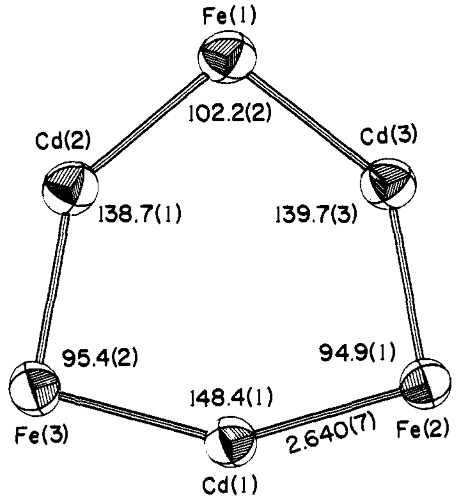


Figure 3. Important structural parameters in the Fe-Cd ring of $[(bpy)CdFe(CO)_4]_3$. Within experimental error, all Fe-Cd distances are equal.

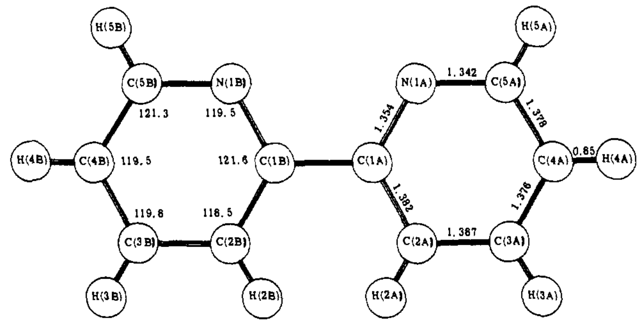


Figure 4. Numbering scheme and assumed (rigid body refinement model) bond distances and angles in 2,2′-bipyridyl ligands.

Table IV. Selected Bond Distances in $[(bpy)CdFe(CO)_4]_3 \cdot \frac{3}{4}C_6H_3Cl_3$

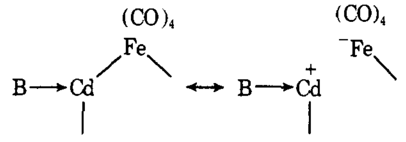
Cd(1)-Fe(2)	2.631 (4)	Fe(1)-C(1)	1.79 (4)	C(1)-O(1)	1.12 (4)	C(1A)-C(1B)	1.44 (2)
Cd(1)-Fe(3)	2.649 (4)	Fe(1)-C(2)	1.72 (3)	C(2)-O(2)	1.21 (4)	C(1C)-C(1D)	1.46 (3)
Cd(2)-Fe(1)	2.653 (5)	Fe(1)-C(3)	1.74 (3)	C(3)-O(3)	1.16 (4)	C(1E)-C(1F)	1.45 (3)
Cd(2)-Fe(3)	2.638 (5)	Fe(1)-C(4)	1.78 (3)	C(4)-O(4)	1.14 (4)	C(1G)-C(1H)	1.46 (3)
Cd(3)-Fe(1)	2.632 (5)	Fe(2)-C(5)	1.66 (3)	C(5)-O(5)	1.28 (4)	C(1I)-C(1J)	1.47 (3)
Cd(3)-Fe(2)	2.640 (5)	Fe(2)-C(6)	1.76 (3)	C(6)-O(6)	1.15 (4)	C(1K)-C(1L)	1.44 (2)
Cd(4)-Fe(5)	2.640 (4)	Fe(2)-C(7)	1.72 (3)	C(7)-O(7)	1.15 (4)	Cl(1)-Cl(2)	3.34 (4)
Cd(4)-Fe(6)	2.630 (4)	Fe(2)-C(8)	1.77 (3)	C(8)-O(8)	1.15 (4)	Cl(1)-Cl(3)	6.10 (4)
Cd(5)-Fe(4)	2.648 (5)	Fe(3)-C(9)	1.67 (3)	C(9)-O(9)	1.33 (4)	Cl(2)-Cl(3)	5.66 (5)
Cd(5)-Fe(6)	2.642 (4)	Fe(3)-C(10)	1.80 (3)	C(10)-O(10)	1.10 (4)	Cl(4)-Cl(5)	3.31 (5)
Cd(6)-Fe(4)	2.643 (5)	Fe(3)-C(11)	1.66 (3)	C(11)-O(11)	1.18 (4)	Cl(4)-Cl(6)	5.72 (5)
Cd(6)-Fe(5)	2.637 (5)	Fe(3)-C(12)	1.73 (3)	C(12)-O(12)	1.19 (4)	Cl(5)-Cl(6)	5.31 (5)
Cd(1)-N(1A)	2.362 (18)	Fe(4)-C(13)	1.72 (3)	C(13)-O(13)	1.18 (4)	Cl(7)-Cl(8)	3.03 (8)
Cd(1)-N(1B)	2.358 (18)	Fe(4)-C(14)	1.72 (4)	C(14)-O(14)	1.17 (5)	Cl(7)-Cl(9)	5.64 (8)
Cd(2)-N(1C)	2.394 (18)	Fe(4)-C(15)	1.75 (3)	C(15)-O(15)	1.20 (4)	Cl(8)-Cl(9)	5.17 (8)
Cd(2)-N(1D)	2.393 (17)	Fe(4)-C(16)	1.77 (3)	C(16)-O(16)	1.13 (4)	Cl(10)-Cl(11)	3.25 (8)
Cd(3)-N(1E)	2.392 (18)	Fe(5)-C(17)	1.69 (3)	C(17)-O(17)	1.19 (4)	Cl(10)-Cl(12)	5.83 (8)
Cd(3)-N(1F)	2.409 (18)	Fe(5)-C(18)	1.75 (4)	C(18)-O(18)	1.21 (5)	Cl(11)-Cl(12)	5.23 (8)
Cd(4)-N(1G)	2.334 (18)	Fe(5)-C(19)	1.76 (3)	C(19)-O(19)	1.10 (4)		
Cd(4)-N(1H)	2.327 (18)	Fe(5)-C(20)	1.69 (3)	C(20)-O(20)	1.21 (4)		
Cd(5)-N(1I)	2.391 (17)	Fe(6)-C(21)	1.68 (3)	C(21)-O(21)	1.19 (3)		
Cd(5)-N(1J)	2.406 (20)	Fe(6)-C(22)	1.72 (3)	C(22)-O(22)	1.16 (4)		
Cd(6)-N(1K)	2.346 (17)	Fe(6)-C(23)	1.72 (3)	C(23)-O(23)	1.13 (3)		
Cd(6)-N(1L)	2.363 (17)	Fe(6)-C(24)	1.69 (3)	C(24)-O(24)	1.20 (4)		

As mentioned in the Experimental Section, each 2,2′-bipyridyl ligand was treated as two rigid six-membered rings in refinement. The dimensions of each ring were taken from structural studies of other 2,2′-bipyridyl complexes.[21a] This approach still yields three independent parameters which can be defined by reference to Figure 4. The average C(1)-C(1) distance (Table IV) was found to be 1.453 (13) Å, which is in good agreement with published values in the neighborhood of 1.460 (15) Å[18,21] and supports the validity of the rigid body refinement model. The dihedral angle between the two rings in the bipyridyl ligands varies from 6.2 (10) to 17.8 (10)° and probably results from repulsions between the C(2) hydrogen atoms[21] and from packing forces. Such distortions of 6-12° are not uncommon for this ligand,[18,21] but 17.8 (10)° is the largest twisting observed to date. Another distortion which is found in the present case is a 4.2 (9)-7.0 (9)° deviation from collinearity of the two C(1)-C(4) vectors in each bipyridyl ligand. The bending is in the direction which increases the Cd-N overlap and flexing of this magnitude has been reported in other structures.[18,21] The bending and twisting parameters are summarized in Table IX.

The disorder in the trichlorobenzene molecules has hampered accurate location of the carbon and hydrogen atoms. It was possible to locate the chlorine atoms, and the interatomic distances (Table IV) are in good agreement with distances obtained by electron diffraction[22] on other polychlorobenzenes.

Discussion

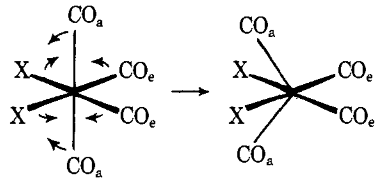
This study has afforded the first opportunity to examine the molecular structure of a $B_2CdFe(CO)_4$ molecule in the solid state and to compare it with the base-free, square $[CdFe(CO)_4]_4$ structure.[3] In the present case of B_2 = 2,2′-bipyridyl the molecule is a trimer, with smaller (by ca. 30°) Fe-Cd-Fe bond angles, longer (by ca. 0.08 Å) Fe-Cd bond distances, and a marked distortion of the iron coordination sphere from an octahedral configuration. The coordination by the 2,2′-bipyridyl unit no doubt has caused the decrease in the Fe-Cd-Fe bond angles. This is in accord with simple valence bond hybridization arguments.[23] A similar, though slightly larger bending (ca. 45-60°) is observed in the analogous $B_2Cd[Mn(CO)_5]_2$ derivatives.[17-19] The lengthening of the Fe-Cd bonds over those in $[CdFe(CO)_4]_4$ can also be explained by hybridization considerations, since cadmium changes approximately from an sp to an sp^3 configuration. Related to the present case is the lengthening of the Sn-Cr bond observed in $[(py)(t\text{-}C_4H_9)_2Sn]\text{-}Cr(CO)_5$ (Sn-Cr = 2.654 (3) Å)[8b] over that in the complex where no base is coordinated to tin, $([((CH_3)_3Si)_2CH]_2Sn)\text{-}Cr(CO)_5$(Sn-Cr = 2.562 (5) Å).[24] In this compound and in $[(bpy)CdFe(CO)_4]_3$ it is also possible that the Lewis base stabilizes an ionic resonance hybrid such as E involving less metal-metal interaction.



D E

The importance of this contribution was noted in infrared spectral results in the C-O stretching region.[3] It may also help to explain the distortion of the iron coordination sphere observed in the diffraction study.

As was noted above, the geometry adopted by the $Cd_2Fe(CO)_4$ moiety deviates appreciably from octahedral symmetry. The distortion is toward a bicapped tetrahedral configuration with the cadmium ions occupying the capping vertices X, as pictured in eq 2. The extent to which the distortion in $[(bpy)CdFe(CO)_4]_3$ reaches an idealized bicapped tetrahedron is summarized in Table VII. The observed geometry is approximately midway along the potential energy surface connecting the two extremes. The reasons for such distortions in octahedral complexes such as $X_2Fe(CO)_4$ have recently been discussed by Hoffmann, Howell, and Rossi.[25] It appears that strongly σ-electron releasing X substituents will stabilize the $Fe(CO)_4$ tetrahedral array. This can be pictured as forcing the iron electronic configuration toward d^{10}. The



(2)

Table V. Selected Bond Angles in $[(\mathrm{bpy})\mathrm{CdFe(CO)_4}]_3\text{-}{}^3\!/_4\mathrm{C_3H_3Cl_3}$

Cd(2)-Fe(1)-Cd(3)	102.04 (16)	Cd(1)-Fe(2)-C(5)	176.7 (10)	N(1I)-Cd(5)-N(1J)	69.4 (7)	Fe(2)-C(7)-O(7)	176.0 (28)
Cd(1)-Fe(2)-Cd(3)	94.78 (14)	Cd(1)-Fe(2)-C(6)	87.4 (10)	N(1K)-Cd(6)-N(1L)	69.0 (6)	Fe(2)-C(8)-O(8)	172.2 (25)
Cd(1)-Fe(3)-Cd(2)	95.22 (13)	Cd(1)-Fe(2)-C(7)	78.5 (10)	C(1)-Fe(1)-C(2)	92.8 (16)	Fe(3)-C(9)-O(9)	175.5 (29)
Cd(5)-Fe(4)-Cd(6)	102.31 (15)	Cd(1)-Fe(2)-C(8)	72.8 (9)	C(1)-Fe(1)-C(3)	104.0 (15)	Fe(3)-C(10)-O(10)	179.2 (26)
Cd(4)-Fe(5)-Cd(6)	94.94 (14)	Cd(3)-Fe(2)-C(5)	83.0 (11)	C(1)-Fe(1)-C(4)	104.6 (15)	Fe(3)-C(11)-O(11)	172.3 (27)
Cd(4)-Fe(6)-Cd(5)	95.54 (13)	Cd(3)-Fe(2)-C(6)	177.5 (10)	C(2)-Fe(1)-C(3)	106.4 (15)	Fe(3)-C(12)-O(12)	174.9 (27)
Fe(2)-Cd(1)-Fe(3)	148.40 (15)	Cd(3)-Fe(2)-C(7)	78.0 (11)	C(2)-Fe(1)-C(4)	105.2 (14)	Fe(4)-C(13)-O(13)	173.4 (28)
Fe(1)-Cd(2)-Fe(3)	138.81 (15)	Cd(3)-Fe(2)-C(8)	78.6 (10)	C(3)-Fe(1)-C(4)	135.8 (15)	Fe(4)-C(14)-O(14)	178.5 (34)
Fe(1)-Cd(3)-Fe(2)	139.93 (15)	Cd(1)-Fe(3)-C(9)	177.9 (12)	C(5)-Fe(2)-C(6)	94.9 (15)	Fe(4)-C(15)-O(15)	177.0 (27)
Fe(5)-Cd(4)-Fe(6)	148.39 (15)	Cd(1)-Fe(3)-C(10)	83.9 (9)	C(5)-Fe(2)-C(7)	103.3 (15)	Fe(4)-C(16)-O(16)	170.8 (26)
Fe(4)-Cd(5)-Fe(6)	138.61 (14)	Cd(1)-Fe(3)-C(11)	76.7 (10)	C(5)-Fe(2)-C(8)	104.4 (14)	Fe(5)-C(17)-O(17)	171.6 (30)
Fe(4)-Cd(6)-Fe(5)	139.46 (15)	Cd(1)-Fe(3)-C(12)	78.3 (10)	C(6)-Fe(2)-C(7)	101.2 (15)	Fe(5)-C(18)-O(18)	171.4 (33)
Fe(2)-Cd(1)-N(1A)	99.0 (5)	Cd(2)-Fe(3)-C(9)	83.5 (11)	C(6)-Fe(2)-C(8)	103.4 (14)	Fe(5)-C(19)-O(19)	178.4 (28)
Fe(2)-Cd(1)-N(1B)	102.4 (5)	Cd(2)-Fe(3)-C(10)	176.9 (10)	C(7)-Fe(2)-C(8)	140.9 (14)	Fe(5)-C(20)-O(20)	175.7 (28)
Fe(3)-Cd(1)-N(1A)	105.5 (5)	Cd(2)-Fe(3)-C(11)	74.6 (10)	C(9)-Fe(3)-C(10)	97.5 (15)	Fe(6)-C(21)-O(21)	176.6 (26)
Fe(3)-Cd(1)-N(1B)	105.0 (5)	Cd(2)-Fe(3)-C(12)	76.9 (11)	C(9)-Fe(3)-C(11)	101.4 (15)	Fe(6)-C(22)-O(22)	173.4 (25)
Fe(1)-Cd(2)-N(1C)	103.0 (5)	Cd(5)-Fe(4)-C(13)	174.2 (11)	C(9)-Fe(3)-C(12)	103.0 (14)	Fe(6)-C(23)-O(23)	178.6 (25)
Fe(1)-Cd(2)-N(1D)	107.2 (4)	Cd(5)-Fe(4)-C(14)	82.5 (12)	C(10)-Fe(3)-C(11)	108.0 (14)	Fe(6)-C(24)-O(24)	175.2 (26)
Fe(3)-Cd(2)-N(1C)	111.2 (5)	Cd(5)-Fe(4)-C(15)	78.9 (10)	C(10)-Fe(3)-C(12)	100.0 (14)	C(2A)-C(1A)-C(1B)	121.6 (19)
Fe(3)-Cd(2)-N(1D)	106.2 (5)	Cd(5)-Fe(4)-C(16)	71.9 (9)	C(11)-Fe(3)-C(12)	139.7 (14)	C(2B)-C(1B)-C(1A)	122.8 (18)
Fe(1)-Cd(3)-N(1E)	102.2 (4)	Cd(6)-Fe(4)-C(13)	81.9 (11)	C(13)-Fe(4)-C(14)	93.4 (16)	C(2C)-C(1C)-C(1D)	118.8 (17)
Fe(1)-Cd(3)-N(1F)	109.0 (5)	Cd(6)-Fe(4)-C(14)	175.2 (12)	C(13)-Fe(4)-C(15)	106.1 (15)	C(2D)-C(1D)-C(1C)	123.2 (17)
Fe(2)-Cd(3)-N(1E)	110.5 (5)	Cd(6)-Fe(4)-C(15)	78.4 (10)	C(13)-Fe(4)-C(16)	105.4 (14)	C(2E)-C(1E)-C(1F)	120.9 (18)
Fe(2)-Cd(3)-N(1F)	104.3 (5)	Cd(6)-Fe(4)-C(16)	78.0 (9)	C(14)-Fe(4)-C(15)	102.1 (16)	C(2F)-C(1F)-C(1E)	121.9 (19)
Fe(5)-Cd(4)-N(1G)	103.2 (6)	Cd(4)-Fe(5)-C(17)	174.6 (11)	C(14)-Fe(4)-C(16)	104.4 (15)	C(2G)-C(1G)-C(1H)	121.1 (17)
Fe(5)-Cd(4)-N(1H)	99.0 (5)	Cd(4)-Fe(5)-C(18)	84.6 (12)	C(15)-Fe(4)-C(16)	137.1 (14)	C(2H)-C(1H)-C(1G)	123.1 (19)
Fe(6)-Cd(4)-N(1G)	104.1 (6)	Cd(4)-Fe(5)-C(19)	75.8 (10)	C(17)-Fe(5)-C(18)	99.6 (16)	C(2I)-C(1I)-C(1J)	120.5 (19)
Fe(6)-Cd(4)-N(1H)	105.2 (5)	Cd(4)-Fe(5)-C(20)	77.6 (11)	C(17)-Fe(5)-C(19)	100.1 (14)	C(2J)-C(1J)-C(1I)	121.6 (19)
Fe(4)-Cd(5)-N(1I)	109.1 (5)	Cd(6)-Fe(5)-C(17)	80.8 (11)	C(17)-Fe(5)-C(20)	104.4 (16)	C(2K)-C(1K)-C(1L)	123.5 (17)
Fe(4)-Cd(5)-N(1J)	100.9 (5)	Cd(6)-Fe(5)-C(18)	177.7 (12)	C(18)-Fe(5)-C(19)	99.1 (16)	C(2L)-C(1L)-C(1K)	120.2 (16)
Fe(6)-Cd(5)-N(1I)	105.3 (5)	Cd(6)-Fe(5)-C(19)	78.7 (10)	C(18)-Fe(5)-C(20)	105.3 (17)	N(1A)-C(1A)-C(1B)	116.8 (17)
Fe(6)-Cd(5)-N(1J)	112.4 (5)	Cd(6)-Fe(5)-C(20)	76.8 (12)	C(19)-Fe(5)-C(20)	141.8 (15)	N(1B)-C(1B)-C(1A)	115.6 (20)
Fe(4)-Cd(6)-N(1K)	110.3 (4)	Cd(4)-Fe(6)-C(21)	177.2 (10)	C(21)-Fe(6)-C(22)	99.6 (13)	N(1C)-C(1C)-C(1D)	119.4 (18)
Fe(4)-Cd(6)-N(1L)	101.5 (4)	Cd(4)-Fe(6)-C(22)	83.1 (9)	C(21)-Fe(6)-C(23)	102.7 (12)	N(1D)-C(1D)-C(1C)	115.0 (17)
Fe(5)-Cd(6)-N(1K)	102.8 (5)	Cd(4)-Fe(6)-C(23)	77.4 (9)	C(21)-Fe(6)-C(24)	102.2 (13)	N(1E)-C(1E)-C(1F)	117.5 (18)
Fe(5)-Cd(6)-N(1L)	111.9 (4)	Cd(4)-Fe(6)-C(24)	76.3 (10)	C(22)-Fe(6)-C(23)	101.8 (14)	N(1F)-C(1F)-C(1E)	116.5 (18)
Cd(2)-Fe(1)-C(1)	175.4 (12)	Cd(5)-Fe(6)-C(21)	81.8 (9)	C(22)-Fe(6)-C(24)	102.5 (14)	N(1G)-C(1G)-C(1H)	117.2 (20)
Cd(2)-Fe(1)-C(2)	82.9 (11)	Cd(5)-Fe(6)-C(22)	178.6 (10)	C(23)-Fe(6)-C(24)	141.5 (13)	N(1H)-C(1H)-C(1G)	115.4 (17)
Cd(2)-Fe(1)-C(3)	76.1 (10)	Cd(5)-Fe(6)-C(23)	78.0 (10)	Fe(1)-C(1)-O(1)	173.4 (34)	N(1I)-C(1I)-C(1J)	117.7 (19)
Cd(2)-Fe(1)-C(4)	77.9 (9)	Cd(5)-Fe(6)-C(24)	77.0 (10)	Fe(1)-C(2)-O(2)	176.5 (29)	N(1J)-C(1J)-C(1I)	116.8 (19)
Cd(3)-Fe(1)-C(1)	82.2 (12)	N(1A)-Cd(1)-N(1B)	68.6 (7)	Fe(1)-C(3)-O(3)	169.9 (29)	N(1K)-C(1K)-C(1L)	114.9 (17)
Cd(3)-Fe(1)-C(2)	174.5 (11)	N(1C)-Cd(2)-N(1D)	68.7 (7)	Fe(1)-C(4)-O(4)	177.8 (27)	N(1L)-C(1L)-C(1K)	118.0 (17)
Cd(3)-Fe(1)-C(3)	72.7 (10)	N(1E)-Cd(3)-N(1F)	68.3 (7)	Fe(2)-C(5)-O(5)	179.3 (29)		
Cd(3)-Fe(1)-C(4)	78.5 (9)	N(1G)-Cd(4)-N(1H)	69.6 (7)	Fe(2)-C(6)-O(6)	176.9 (27)		

Table VI. Best Weighted Least-Squares Planes for $[(C_{10}N_2H_8)CdFe(CO)_4]_3$

(a) Defining Parameters of the Planes

Plane	Atoms defining plane	Equation (tetragonal coordinates)
1	Cd(1)-Cd(3), Fe(1)-Fe(3)	$25.274x + 0.498y - 6.523z = 7.969$
2	Cd(4)-Cd(6), Fe(4)-Fe(6)	$25.171x - 2.994y - 6.467z = 6.381$

The dihedral angle between planes 1 and 2 = 6.9°

(b) Deviations of Atoms from Best Planes, Å

Atom	Plane 1	Atom	Plane 2
Cd(1)	0.056 (17)	Cd(4)	−0.050 (18)
Cd(2)	−0.158 (39)	Cd(5)	0.104 (39)
Cd(3)	−0.012 (17)	Cd(6)	0.048 (18)
Fe(1)	0.035 (17)	Fe(4)	−0.051 (18)
Fe(2)	−0.032 (17)	Fe(5)	0.005 (18)
Fe(3)	−0.088 (39)	Fe(6)	0.127 (39)
C(1)	0.121	C(13)	−0.034
C(2)	0.002	C(14)	−0.145
C(5)	−0.018	C(17)	−0.054
C(6)	−0.089	C(18)	−0.092
C(9)	−0.227	C(21)	0.262
C(10)	0.055	C(22)	0.142
O(1)	0.288	O(13)	0.079
O(2)	−0.089	O(14)	−0.197
O(5)	−0.017	O(17)	−0.097
O(6)	−0.069	O(18)	−0.001
O(9)	−0.275	O(21)	0.326
O(10)	0.147	O(22)	0.032

Table VII. Comparison of the Average Bond Angles about Iron with Ideal Octahedral and Tetrahedral Coordination

Angle	Frequency	T_d	O_h	Obsd
C_{ax}-Fe-C_{ax}	1	109.5	180	139.5
C_{eq}-Fe-C_{eq}	1	109.5	90	96.3
C_{eq}-Fe-C_{ax}	4	109.5	90	103.4
Cd-Fe-Cd	1	109.5	90	97.5
Cd-Fe-C_{eq}(trans)	2	180.0	180	176.4
Cd-Fe-C_{eq}(cis)	2	70.5	90	83.2
Cd-Fe-C_{ax}	4	70.5	90	76.8

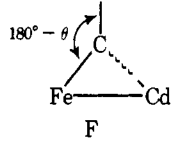
extreme would be the ionic structure $X_2^{2+}Fe(CO)_4^{2-}$ in which the isolated d^{10} $Fe(CO)_4^{2-}$ moiety is tetrahedral. The structure of $Na_2Fe(CO)_4 \cdot 1.5C_4H_8O_2$[26] provides an interesting comparison with $[(bpy)CdFe(CO)_4]_3$ since it no doubt represents a case very close to the ionic extreme. The geometry of the $Fe(CO)_4^{2-}$ ion is distorted from ideal tetrahedral ligation by the presence of two sodium ions, which can be viewed as capping two of the faces of the tetrahedron. The result is a C(axial)-Fe-C(axial) angle of 129.7 (2)° and an Fe-Na distance of 3.086 (2) Å. These observations indicate that the iron coordination geometry in $[(bpy)CdFe(CO)_4]_3$ is not incommensurate with considerable ionic character in the Fe-Cd bonding. As already noted, both the short Fe-C bond lengths and the low C-O stretching frequencies are evidence for the buildup of negative charge on the $Fe(CO)_4$ moiety resulting in higher Fe-C and lower C-O bond orders. The appreciable variation in Cd-Fe-Cd bond angles found within the molecule also suggests that the Cd-Fe interaction may be less directed than in $[CdFe(CO)_4]_4$. An alternative explanation for this variability derives from observations[6,27,28] that a number of $X_2Fe(CO)_4$ molecules are stereochemically nonrigid: relatively little energy is required for molecular deformation along certain normal coordinates.

Table VIII. Average Bonding Parameters for $[(C_{10}N_2H_8)CdFe(CO)_4]_3 \cdot \frac{3}{4}C_6H_3Cl_3]$ and $[CdFe(CO)_4]_4 \cdot 2C_3H_{16}O$[a]

	Trimer	Tetramer
	Distances, Å	
Fe-Cd	2.640 (7, 5, 12)	2.562 (3, 2, 4)
Fe-C	1.73 (4, 3, 24)	1.779 (8, 10, 8)
C-O	1.18 (5, 4, 24)	1.152 (6, 10, 8)
Cd-N	2.37 (3, 2, 12)	
C(1)-C(1) (bpy)	1.453 (13, 26, 6)	
Cl—Cl (ortho)	3.29 (14)	
Cl—Cl (meta)	5.40 (22)	
Cl—Cl (para)	5.89 (20)	
	Angles, deg	
Cd-Fe-Cd[b]	102.2 (2), 95.4 (2), 94.9 (1)	88.6 (11)
Fe-Cd-Fe[b]	148.4 (1), 139.7 (3), 138.7 (1)	170.20 (7)
Fe-C-O	175.2 (28, 28, 24)	176.3 (9, 8, 8)
Cd-Fe-C_{eq} (cis)	83.2 (17, 11, 12)	86.8 (15, 3, 4)
Cd-Fe-C_{eq} (trans)	176.4 (15, 11, 12)	174.9 (18, 3, 4)
Cd-Fe-C_{ax}	76.8 (20, 10, 24)	81.1 (15, 3, 8)
C_{ax}-Fe-C_{ax}	139.5 (15, 14, 6)	154.7 (3, 4, 2)
C_{eq}-Fe-C_{eq}	96.3 (30, 15, 6)	97.8 (5, 4, 2)
C_{ax}-Fe-C_{eq}	103.4 (22, 15, 24)	98.3 (19, 4, 8)
Fe-Cd-N	102.7 (24, 5, 12), 108.3 (34, 5, 12)	
N-Cd-N	68.9 (5, 7. 6)	
N(1)-C(1)-C(1)′ (bpy)	116.7 (14, 18, 12)	
C(2)-C(1)-C(1)′ (bpy)	121.6 (14, 18, 12)	

[a] The first number in parentheses is the standard deviation of a single observation as estimated on the assumption that the *n* values averaged are from the same population. The second and third numbers, when given, are the average standard deviation (as estimated from the final least-squares refinement) and the number *n* of observations, respectively. The standard deviation of the mean may be obtained by dividing the first deviation by $\sqrt{n}$. [b] For the trimeric ring, the three angles refer to average values of the pseudo-related bond angles. See Figure 3.

Another feature of note in the $[(bpy)CdFe(CO)_4]_3$ molecular structure and one that may influence the iron coordination geometry is the evidence for weak attractive interaction between the carbonyl carbon atoms and cadmium atoms. Distances for Cd-C as short as 2.69 (3) Å are observed (Table X), slightly beyond the range of 2.1-2.55 Å assigned to semibridging[29,30] interactions in a number of polynuclear first-row transition-metal carbonyl complexes. This effect can also be seen in the Cd-Fe-C bond angles (Tables V and VIII) which are in the range 71.9 (9)-87.4 (10)°. Bending of the carbonyl ligands toward cadmium was also noted in the $B_2Cd[Mn(CO)_5]_2$ complexes[17-19] and was ascribed to an attractive interaction. Here the minimum Cd-C distance was 2.822 Å[18] and the minimum Cd-Mn-C angle 78.9 (6)°.[18] The deviation, θ, of the Fe-C-O angles from 180° in $[(bpy)CdFe(CO)_4]_3$ is in the range 0-10 (2.9)°. The bend invariably displaces the oxygen atom away from the cadmium atom (F),



F

as commonly observed for a semibridging interaction.[29] For $MnY(CO)_5$ compounds, Y = a halogen, a slight bending of the equatorial carbonyl groups toward Y[17,31] could be attributed to electron donation from filled halogen p orbitals to the carbonyl 2π (π*) orbital.[32] Similarly, the attraction in polynuclear complexes has been ascribed[29] to an intermetal charge com-

Table IX. Bipyridyl Ligand Distortions

Rings	Ring-ring dihedral angles, deg	Noncollinearity of C(1)-C(4) vectors, deg
AB	17.8 (10)	7.0 (9)
CD	12.6 (9)	5.6 (8)
EF	8.9 (10)	4.7 (9)
GH	6.2 (10)	6.9 (9)
IJ	11.3 (10)	4.2 (9)
KL	12.3 (9)	5.3 (8)

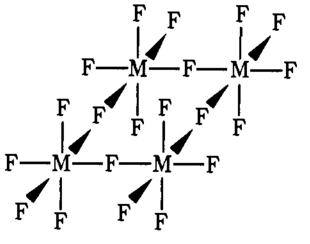
Table X. Intramolecular Contacts between Cadmium Atoms and Neighboring Carbonyl Carbon Atoms.

Contact	Distance, Å	Contact	Distance, Å
Cd(1)-C(6)	3.10 (3)	Cd(4)-C(18)	3.03 (4)
Cd(1)-C(7)	2.84 (3)	Cd(4)-C(19)	2.79 (3)
Cd(1)-C(8)	2.70 (3)	Cd(4)-C(20)	2.81 (3)
Cd(1)-C(10)	3.04 (3)	Cd(4)-C(22)	2.96 (3)
Cd(1)-C(11)	2.78 (3)	Cd(4)-C(23)	2.81 (3)
Cd(1)-C(12)	2.85 (3)	Cd(4)-C(24)	2.77 (3)
Cd(2)-C(2)	2.98 (3)	Cd(5)-C(14)	2.96 (4)
Cd(2)-C(3)	2.80 (3)	Cd(5)-C(15)	2.88 (3)
Cd(2)-C(4)	2.87 (3)	Cd(5)-C(16)	2.69 (3)
Cd(2)-C(9)	2.96 (3)	Cd(5)-C(21)	2.92 (3)
Cd(2)-C(11)	2.72 (3)	Cd(5)-C(23)	2.84 (3)
Cd(2)-C(12)	2.81 (3)	Cd(5)-C(24)	2.80 (3)
Cd(3)-C(1)	2.98 (4)	Cd(6)-C(13)	2.94 (3)
Cd(3)-C(3)	2.69 (3)	Cd(6)-C(15)	2.86 (3)
Cd(3)-C(4)	2.87 (3)	Cd(6)-C(16)	2.86 (3)
Cd(3)-C(5)	2.94 (3)	Cd(6)-C(17)	2.89 (3)
Cd(3)-C(7)	2.83 (3)	Cd(6)-C(19)	2.87 (3)
Cd(3)-C(8)	2.87 (3)	Cd(6)-C(20)	2.79 (3)

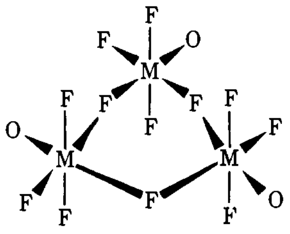
pensation process employing the electron acceptor properties of the carbonyl ligand. It is unlikely that cadmium functions as an electron donor in the present system. However, in a complex with such high ionic character, π back-bonding will place considerable electron density in the carbonyl 2π orbital (localized principally on carbon[33]) which could interact with the dipositively charged cadmium ion. Again the driving force for semibridge formation is intermetal charge compensation.

In accord with the trimeric solid state structure, the solution molecular weight data[3] indicate that $[(bpy)CdFe(CO)_4]_3$ is trimeric in benzene. The related base adduct $(py)_2CdFe(CO)_4$ was found to be dissociated (monomeric) in benzene solution,[3] while $(phen)CdFe(CO)_4$[3] was insufficiently soluble for molecular weight measurements.

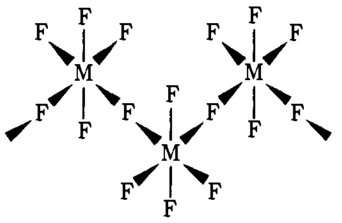
The size and shape of the heterometallic ring in $[(bpy)CdFe(CO)_4]_3$ compared with the eight-membered square in $[CdFe(CO)_4]_4$[3] no doubt reflects the changes in bond angles at iron and especially at cadmium. Neither structure has been previously observed in metal-metal bonded systems involving transition metals.[34] An interesting analogy does exist between these structural results and those for transition metal pentafluorides and oxytetrafluorides where the metal is six coordinate and where fluoride bridges can be linear or bent. The compounds MF_5, M = Nb, Ta, Mo, and W adopt the $[CdFe(CO)_4]_4$-type structure, G, as do $NbCl_4F$, $TaCl_4F$, $SbCl_4F$, and WOF_4.[35] Several others are tetrameric with bent (∠M-F-M ≈ 130-145°) bridges (MF_5, M = Ru, Os, Rh, Ir, Pt;[35] $[Ru(CO)_3F_2]_4$[36]). On the other hand, the hexagonal forms of $TcOF_4$ and $MoOF_4$ adopt the planar $[(bpy)CdFe(CO)_4]_3$ structure, H.[35,37] Polymeric structures with the metal atom in the cis-octahedral configuration and with slightly bent bridges (e. g., ∠V-F-V = 150° [38]) are found for MF_5, M = V, Cr, Tc, Re, $ReOF_4$, and the monoclinic forms of $TcOF_4$ and $MoOF_4$.[35] This structure is idealized as I. Interestingly, α-UF_5 appears to have the polymeric trans-octahedral structure J.[39] Those factors which dictate the molecular geometries of these compounds are not well understood and may involve subtle combinations of ligand → metal π bonding,[40] electrostatic considerations,[35a] and packing forces.[35a]



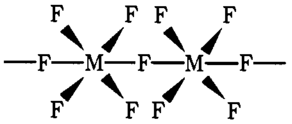
G



H



I



J

For the present metal-metal bonded systems, given the choice of a ring rather than a polymer, the gross structural features can be easily rationalized. The nearly linear Fe-Cd-Fe bond angles in $[CdFe(CO)_4]_4$ ensure, for any physically reasonable Cd-Fe-Cd angle, that the smallest possible ring will be a tetramer. In $[(bpy)CdFe(CO)_4]_3$, the Fe-Cd-Fe angles of ca. 140° and Cd-Fe-Cd angles of ca. 100° are well-suited for a trimer, but contractions of these angles by ca. 35 and 20°, respectively, would be required for a dimer of the $[(CH_3)_2SnFe(CO)_4]_2$[5] type. The small bipyridyl "bite" angle of 68° (Table V) probably prohibits this by requiring greater p character in the Cd-N bonding, and correspondingly less in the Cd-Fe bonds. Thus, for $CdFe(CO)_4$ and its derivatives it seems unlikely that various oligomeric structures are stabilized or destabilized to any degree by overriding collective electronic factors, but rather by local bond angles and distances, as well as by more intricate effects such as crystallization conditions and packing forces. Further work to learn how to manipulate these factors is in progress.[41]

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Supplementary Material Available: a listing of root-mean-square amplitudes of vibration (Table III), bipyridyl hydrogen atom positions, and structure amplitudes (40 pages). Ordering information is given on any current masthead page.

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