Research Article

Structural Studies of $[(\text{py})_2\text{CdFe}(\text{CO})_4]_3$ and $\{(\text{THF})_5[\text{CdFe}(\text{CO})_4]_3\}$

Bryce Anderson, Atta M. Arif, and Richard D. Ernst

Department of Chemistry, University of Utah, 315 South 1400 East, Room 2020, Salt Lake City, UT 84112-0850, USA

Correspondence should be addressed to Richard D. Ernst; ernst@chem.utah.edu

Received 19 October 2013; Accepted 21 December 2013; Published 13 February 2014

Academic Editor: Dong Qiu

Copyright © 2014 Bryce Anderson et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The structures of $[(\text{py})_2\text{CdFe}(\text{CO})_4]_3$ and $\{(\text{THF})_5[\text{CdFe}(\text{CO})_4]_3\}$ have been determined (py = pyridine; THF = tetrahydrofuran). Each is composed of a six-membered ring having alternating cadmium and iron centers. The presence of the more strongly basic amine ligands in the former led to a greater contribution of an ionic resonance form, which resulted in overall longer Cd–Fe bonds and a greater contribution of a bicapped tetrahedral coordination geometry about iron. Thus, the Cd–Fe distances range from 2.5679(4) to 2.6501(1) Å for the THF complex versus 2.6445(8) to 2.6833(7) Å for the py complex. Similarly, the Fe–Cd–Fe and Cd–Fe–Cd angles for the THF complex fell in respective ranges of 139.03(2)–157.27(2)° and 84.41(1)–99.79(1)°, as compared to 135.31(3)–139.51(4)° and 102.52(3)–104.62(4)° for the py complex. The space group for the former compound is *Pbcn*, with $a = 12.2678(2)$, $b = 22.4601(5)$, and $c = 17.0039(4)$ Å, while for the THF complex, the space group is $P2_1/c$, with $a = 10.7297(2)$, $b = 20.4961(2)$, $c = 18.7464(3)$ Å, and $\beta = 94.2715(6)^\circ$.

1. Introduction

The complex $\text{HgFe}(\text{CO})_4$ was first reported in 1929, and due to its insolubility, it was proposed to be a polymeric species [1]. Subsequent studies of its cadmium analogue revealed the cadmium complex to be tetrameric, composed of a square, eight-membered ring having alternating cadmium and iron atoms [2]. The respective metal coordination geometries were shown to be linear and cis-disubstituted octahedral, and powder pattern data demonstrated that the mercury compound was isomorphous [3]. The crystallization of the cadmium compound was made possible by the fact that some ether, ketone, and amine ligands readily coordinate, while that does not happen for the mercury compound, and in at least some of these cases, the coordination is readily reversible.

The base-coordinated cadmium compounds typically exist as $[\text{L}_2\text{CdFe}(\text{CO})_4]_n$ species (L = an ether, ketone, or amine; L_2 = a bidentate amine) [2–4], and they would generally be expected to be dimeric or trimeric (i.e., $n = 2$ or 3, Figure 1) though at least one $[\text{LCdFe}(\text{CO})]_n$ species (L = 4-phenylpyridine) is known, as well as monomeric $\text{L}_x\text{CdFe}(\text{CO})_4$ complexes, in which L_x represents

a combination of at least three donor sites [3, 5]. The isolations of such species appear to have been promoted by the use of chelating ligands, or via the use of coordinating solvents for crystallization. In comparison, analogous complexes with the harder zinc ion are typically isolated as such monomeric species, whether chelating ligands are employed or not.

To date, the only $[\text{L}_2\text{CdFe}(\text{CO})_4]_n$ species to have been crystallographically characterized has been the $\text{L}_2 = 2,2'$ -bipyridine species [6], which was found to exist as a trimeric complex. Notably, its zinc analogue has been found to exist as a dimer [7]. In order to attempt to gain a better understanding of the factors that control the extent of oligomerization in these complexes, we have determined the structures of $[\text{L}_x\text{CdFe}(\text{CO})_4]_n$ complexes in which the coordinated ligands are pyridine or THF.

2. Materials and Methods

All reactions were carried out in Schlenk apparatus under a nitrogen atmosphere. The pyridine (1) and THF (2) complexes were prepared and crystallized as previously described [2]. Single crystals of each compound were mounted on glass

TABLE 1: Crystal and experimental data.

Empirical formula	C ₄₂ H ₃₀ Cd ₃ Fe ₃ N ₆ O ₁₂	C ₃₂ H ₄₀ Cd ₃ Fe ₃ O ₁₇
Formula weight	1315.47	1201.39
Temperature (K)	150(1)	150(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbcn</i>	<i>P2₁/c</i>
Unit cell dimensions		
<i>a</i>	12.2678(2)	10.7297(2)
<i>b</i>	22.4601(5)	20.4961(2)
<i>c</i>	17.0039(4)	18.7464(3)
α (°)	90	90
β (°)	90	94.2715(6)
γ (°)	90	90
Volume (Å ³)	4685.19(17)	4111.20(11)
<i>Z</i>	4	4
<i>D</i> _{calcd} (g cm ⁻³)	1.865	1.941
μ (MoK α) (mm ⁻¹)	2.307	2.623
<i>F</i> (000)	2,568	2,360
θ range (°)	2.17–27.48	1.47–27.49
	$-15 \leq h \leq 15$	$-13 \leq h \leq 13$
Limiting indices	$-29 \leq k \leq 29$	$-26 \leq k \leq 21$
	$-22 \leq l \leq 22$	$-24 \leq l \leq 24$
Reflections collected/unique	10130/5365	16074/9418
Completeness (%)	99.8	99.8
Goodness of fit on <i>F</i> ²	1.041	1.104
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0462, <i>wR</i> ₂ = 0.1007	<i>R</i> ₁ = 0.0275, <i>wR</i> ₂ = 0.0583
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0845, <i>wR</i> ₂ = 0.1162	<i>R</i> ₁ = 0.0357, <i>wR</i> ₂ = 0.0614
($\Delta\rho$) _{max, min}	0.891, -0.715	0.836, -0.623
<i>R</i> (int)	0.0422	0.0180

fibers with Paratone oil, and transferred to a Nonius Kappa CCD diffractometer. Systematic absences uniquely identified the two space groups. Data collection and processing utilized the programs COLLECT, DENZO-SMN, and SCALEPAC [8]. The structures were solved using heavy atom and direct methods with SIR97 [9] and SHELXL97 [10]. Final refinements were carried out with anisotropic thermal parameters for all nonhydrogen atoms, while the hydrogen atoms were given isotropic thermal parameters and were allowed to ride on their attached carbon atoms. For the pyridine complex, the pyridine ligand on Cd2 was found to be disordered over two sites, in a ratio of ca. 1.36 : 1. Scattering factors were taken from the literature [11, 12]. Pertinent experimental parameters are provided in Table 1, selected bonding parameters are given in Tables 2 and 3, and ORTEP representations of the molecules are given in Figures 2 and 3.

The CCDC depositions 966874 and 966875 contain the full crystallographic information for the pyridine and THF

TABLE 2: Selected bond lengths (Å) and angles (°) for [(py)₂CdFe(CO)₄]₃.

Bond distances			
Cd1–Fe1	2.6645(8)	Cd2–N3	2.441(4)
Cd1–Fe2	2.6833(7)	Cd2–N3A	2.429(10)
Fe1–C1	1.747(7)	C1–O1	1.158(7)
Fe1–C2	1.767(6)	C2–O2	1.151(7)
Fe1–C3	1.784(7)	C3–O3	1.156(7)
Fe1–C4	1.767(6)	C4–O4	1.164(7)
Fe2–C5	1.765(6)	C5–O5	1.162(7)
Fe2–C6	1.779(7)	C6–O6	1.163(7)
Cd1–N1	2.424(4)	Cd2–Fe1	2.6429(8)
Cd1–N2	2.444(5)		
Bond angles			
Fe1–Cd1–Fe2	135.31(3)	Fe1–Cd2–Fe1'	139.51(4)
Cd1–Fe1–Cd2	102.52(3)	Cd1–Fe2–Cd1'	104.62(4)
C1–Fe1–C2	93.2(3)	C5–Fe2–C5'	92.7(4)
C3–Fe1–C4	138.2(3)	C6–Fe2–C6'	135.8(4)
Cd1–Fe1–C2	79.8(2)	N1–Cd1–N2	87.39(16)
Cd2–Fe1–C1	84.7(2)	N3–Cd2–N3'	88.2(4)
Cd1–Fe2–C5'	81.6(2)	N3'–Cd2–N3A	86.7(2)

structures, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, UK.

3. Results and Discussion

The previously reported complex [(py)₂CdFe(CO)₄]_n (**1**) was found to be trimeric and located on a two-fold rotational axis, in agreement with previous suggestions [2]. The axis passes through Cd2 and Fe2. The six-membered ring is nearly planar, with the Fe1 atoms deviating by 0.038 Å while the Cd1 atoms deviate by 0.044 Å. The two independent metals of each type possess similar, but not quite identical, environments. This can be seen from the angles within the ring, Fe1–Cd1–Fe2, 135.31(3)° versus Fe1–Cd2–Fe1', 139.51(4)°, and Cd1–Fe1–Cd2, 102.52(3)° versus Cd1–Fe2–Cd1', 104.62(4)°. In the related [(2,2'-bpy)CdFe(CO)₄]₃ complex (**3**), the differences are actually several times greater [3]. Slight differences are also seen in the Cd–Fe bond distances, with those around Fe1 (2.6645(8) and 2.6429(8) Å) being shorter than that around Fe2 (2.6833(7) Å). The value for Cd2 (2.6429(8) Å) is likewise shorter than those around Cd1, 2.6645(8) and 2.6833(7) Å. The values in **3** were more consistent, ranging only about 0.02 Å, while also being slightly shorter, averaging 2.640(2) Å.

The chelating nature of the 2,2-bpy ligand led to N–Cd–N' angles averaging 68.9(2)°, as compared to ca. 87° in **1**. This naturally leads to larger overall Fe–Cd–Fe' angles in **3**, which range from 138.6(1) to 148.4(2)°, and then also to smaller overall Cd–Fe–Cd' angles, which range from 94.8(1) to 102.3(2)°. The larger Cd–Fe–Cd' angles in **1** then lead to smaller C(ax)–Fe–C(ax)' and C(eq)–Fe–C(eq)' angles

FIGURE 1: Representations of dimeric (a) and trimeric (b) $[L_xMFe(CO)_4]_n$ structural arrangements. FIGURE 2: The structure of $[(py)_2CdFe(CO)_4]_3$. FIGURE 3: The structure of $\{(THF)_5[CdFe(CO)_4]_3\}$.TABLE 3: Selected bond lengths (Å) and angles (°) for $\{(THF)_5[CdFe(CO)_4]_3\}$.

Bond distances			
Fe1–C1	1.788(3)	C1–O1	1.146(4)
Fe1–C2	1.776(3)	C2–O2	1.152(4)
Fe1–C3	1.781(3)	C3–O3	1.156(4)
Fe1–C4	1.786(3)	C4–O4	1.162(4)
Fe2–C5	1.781(3)	C5–O5	1.150(4)
Fe2–C6	1.789(3)	C6–O6	1.144(4)
Fe2–C7	1.787(3)	C7–O7	1.157(4)
Fe2–C8	1.793(3)	C8–O8	1.157(4)
Fe3–C9	1.783(3)	C9–O9	1.148(4)
Fe3–C10	1.781(3)	C10–O10	1.147(4)
Fe3–C11	1.785(3)	C11–O11	1.157(4)
Fe3–C12	1.782(3)	C12–O12	1.155(4)
Cd1–Fe2	2.5679(4)	Cd1–O13	2.475(2)
Cd1–Fe3	2.5803(4)	Cd2–O14	2.476(2)
Cd2–Fe1	2.6201(4)	Cd2–O15	2.415(2)
Cd2–Fe3	2.6350(4)	Cd3–O16	2.406(2)
Cd3–Fe1	2.6466(5)	Cd3–O17	2.372(2)
Cd3–Fe2	2.6501(5)		
Bond angles			
Fe1–Cd2–Fe3	143.34(2)	C1–Fe1–C2	93.94(14)
Fe1–Cd3–Fe2	139.03(2)	C3–Fe1–C4	139.09(15)
Fe2–Cd1–Fe3	157.27(2)	C5–Fe2–C6	98.22(14)
Cd1–Fe2–Cd3	87.13(1)	C7–Fe2–C8	146.31(14)
Cd1–Fe3–Cd2	84.41(1)	C9–Fe3–C10	98.94(14)
Cd2–Fe1–Cd3	99.79(1)	C11–Fe3–C12	147.61(14)
Cd1–Fe2–C6	84.22(10)	Cd2–Fe3–C9	86.73(10)
Cd1–Fe3–C10	98.93(10)	Cd3–Fe1–C1	88.22(11)
Cd2–Fe1–C2	78.15(9)	Cd3–Fe2–C5	90.41(11)
O14–Cd2–O15	87.35(8)	O16–Cd3–O17	83.27(8)
O13–Cd1–Fe2	99.80(6)	O13–Cd1–Fe3	102.83(6)

in **1** (138.2(3) and 135.8(4)° versus 93.2(3) and 92.7(4)°). As found for complex **3**, the iron coordination geometry in **1** is nearly midway between octahedral and bicapped tetrahedral. The latter geometry is promoted by the presence of basic donor ligands on the cadmium center, which leads to a

greater contribution of an ionic resonance hybrid involving a coordinated Cd(II) center and $\text{Fe}(\text{CO})_4^{2-}$.

It was also desired to compare the above nitrogen-based ligand complexes with an oxygen-based one. The complex $[(\text{THF})_2\text{CdFe}(\text{CO})_4]_n$ has been previously reported [2], and it was selected for this purpose. A trimer was again adopted, which quite unexpectedly possessed one three-coordinate cadmium center, and two of the expected four-coordinate cadmium centers, as a result of the constitution actually being $\{(\text{THF})_5[\text{CdFe}(\text{CO})_4]_3\}$, at least for the crystal under study. As would be expected, the three-coordinate cadmium center, Cd1, has Cd–Fe bonds (2.5679(4) and 2.5803(4) Å) that are shorter than those for Cd2 and Cd3, which ranged from 2.6201(4) to 2.6501(5) Å. The presence of the less basic THF as compared to amine ligands can be seen to have led to a lesser contribution of the ionic resonance form, and thus to shorter Cd–Fe bonds. Surprisingly, the Cd1–O13 distance of 2.475(2) Å is longer overall than the corresponding distances for the four coordinate Cd2 (2.476(2), 2.415(2) Å) and Cd3 (2.406(2) and 2.372(2) Å) centers. This would seem to be related to the significantly larger Fe–Cd–Fe' angle about Cd1 (157.27(2)°) compared to those for Cd2 (143.34(2)°) and Cd3 (139.03(2)°). The presence of just one THF does not seem to be able to bring about much bending of the Fe2–Cd1–Fe3 angle, in accordance with the observation that cadmium has a greater preference for bonding to iron as opposed to even amine ligands, in contrast to zinc. The situation is reminiscent of a $[\text{CdFe}(\text{CO})_4]_4$ structural result, in which two acetone molecules were found engaging in weak interactions with two opposing cadmium centers (2.688(9) Å, Fe–Cd–Fe' = 170.25(5)°). Somewhat analogous situations exist in $[(4\text{-phenylpyridine})_2\text{CdFe}(\text{CO})_4]_2$ [3] and in a square planar cadmium complex [13].

The presence of the weakly basic THF ligands in **2** also results in iron coordination geometries that lie more towards the octahedral than biccapped tetrahedral extreme, as reflected by C(ax)–Fe–C(ax)' angles of 139.09(15)°, 146.31(14)°, and 147.61(14)°, and C(eq)–Fe–C(eq)' angles of 93.94(14)°, 98.22(14)°, and 98.94(14)°.

Some comparisons may also be made to various other interesting complexes. The $\{\text{Cd}[\text{Fe}_2(\text{CO})_8]_2\}^{2-}$ ion has pseudotetrahedral coordination about cadmium as the result of the formation of four Cd–Fe bonds, two of which have a length of 2.721(1) Å, the other two being 2.727(1) Å [14]. A similar coordination environment is found in the related $\{\text{Cd}[\text{Fe}_3(\text{CO})_{11}]_2\}^{2-}$ ion, whose four Cd–Fe bonds average 2.743(3) Å [15]. The more complicated cluster $[(\text{Cd}_4\text{Cl}_6)\text{Fe}(\text{CO})_4(\text{THF})_5]$ has a Cd–Fe distance of 2.575(1) Å, while the $\{[\text{CdFe}(\text{CO})_4]_6\text{Cl}_2(\text{DME})_2\}^{2-}$ ion has Cd–Fe distances ranging from 2.578(2) to 2.680(2) Å [16].

4. Conclusions

The complexes $[(\text{py})_2\text{CdFe}(\text{CO})_4]_3$ and $\{(\text{THF})_5[\text{CdFe}(\text{CO})_4]_3\}$ have both been found to exist as trimers, analogous to the 2,2'-bipyridine complex. More recent studies have found both other examples of related trimeric species, as well as some that are dimeric, and even tetrameric. In the present

complexes, the replacement of THF by the more basic pyridine ligands was found to lead to a greater contribution of an ionic resonance form, as indicated by the Cd–Fe bond lengthening and a coordination geometry about iron that had a greater resemblance to a cis-disubstituted octahedral iron coordination geometry.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

- [1] H. Hock and H. Stuhlmann, "Über die einwirkung von quecksilbersalzen auf eisenpentacarbonyl (II Mitteil)," *Berichte der Deutschen Chemischen Gesellschaft*, vol. 62, no. 2, pp. 431–437, 1929.
- [2] R. D. Ernst, T. J. Marks, and J. A. Ibers, "Metal-metal bond cleavage reactions. The crystallization and solid state structural characterization of cadmium tetracarbonyliron, $\text{CdFe}(\text{CO})_4$," *Journal of the American Chemical Society*, vol. 99, no. 7, pp. 2090–2098, 1977.
- [3] R. D. Ernst and T. J. Marks, "Chemical and structural relationships among the oligomeric compounds $\text{MFe}(\text{CO})_4$ (M = Zn, Cd, Hg), $\text{PbFe}(\text{CO})_4$, $\text{AgCo}(\text{CO})_4$, and their base adducts," *Inorganic Chemistry*, vol. 17, no. 6, pp. 1477–1484, 1978.
- [4] A. T. T. Hsieh, M. J. Mays, and R. H. Platt, "Infrared and mössbauer spectra of tetracarbonylcadmioiron and related complexes," *Journal of the Chemical Society A*, pp. 3296–3300, 1971.
- [5] B. E. Zaugg, T. Kolb, A. M. Arif, and R. D. Ernst, "Structural studies of $(\text{Pyridine})_3\text{ZnFe}(\text{CO})_4$ and $(\text{Pyridine})(\text{Neocuproin})\text{CdFe}(\text{CO})_4$," *Journal of Chemical Crystallography*, vol. 40, no. 9, pp. 778–782, 2010.
- [6] R. D. Ernst, T. J. Marks, and J. A. Ibers, "Metal-metal bond cleavage reactions. The crystal and molecular structure of $(2,2'\text{-Bipyridyl})\text{cadmium Tetracarbonyliron}$, $(\text{bpy})\text{CdFe}(\text{CO})_4$," *Journal of the American Chemical Society*, vol. 99, no. 7, pp. 2098–2107, 1977.
- [7] R. J. Neustadt, T. H. Cymbaluk, R. D. Ernst, and F. W. Cagle Jr., "Crystallization and solid-state structural characterization of $(2,2'\text{-Bipyridyl})\text{zinc Tetracarbonyliron}$, $(\text{bpy})\text{ZnFe}(\text{CO})_4$," *Inorganic Chemistry*, vol. 19, no. 8, pp. 2375–2381, 1980.
- [8] Z. Otwinowski and W. Minor, "Processing of X-ray diffraction data collected in oscillation mode," *Methods in Enzymology*, vol. 276, pp. 307–326, 1997.
- [9] A. Altomare, M. C. Burla, M. Camalli et al., "SIR97: a new tool for crystal structure determination and refinement," *Journal of Applied Crystallography*, vol. 32, no. 1, pp. 115–119, 1999.
- [10] G. M. Sheldrick, "SHELXL97, programs for crystal structure analysis," University of Göttingen, Göttingen, Germany, 1997.
- [11] D. C. Creagh and W. J. McDauley, "Production and properties of radiations," in *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*, A. J. C. Wilson, Ed., vol. C, chapter 4, pp. 206–222, Kluwer Academic, Dordrecht, The Netherlands, 1992.
- [12] E. N. Maslen, A. G. Fox, and M. A. O'Keefe, "Interpretation of diffracted intensities," in *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*, A. J. C.

- Wilson, Ed., vol. C, chapter 6, pp. 476–516, Kluwer Academic, Dordrecht, The Netherlands, 1992.
- [13] S. C. Goel, M. Y. Chlang, and W. E. Buhro, "The first square-planar complex of Cd(II): $\text{Cd}(\text{OAr})_2(\text{THF})_2$ where OAr = 2,6-Di-tert-butylphenoxide. A structure governed by two strong covalent and two weak dative bonds," *Journal of the American Chemical Society*, vol. 112, no. 18, pp. 6724–6725, 1990.
- [14] V. G. Albano, M. Monari, F. Demartin et al., "Synthesis and chemical behavior of $[\text{MFe}_4(\text{CO})_{16}]^{n-}$ (M=Au, Zn, Cd, Hg) clusters: X ray structure of $[\text{NMe}_3\text{CH}_2\text{Ph}]_2[\text{Au}\{\text{Fe}_2(\text{CO})_8\}_2]\text{Cl}$ and $[\text{PPh}_4]_2[\text{Cd}\{\text{Fe}_2(\text{CO})_6(\mu\text{-CO})_2\}_2\text{CH}_3\text{CN}]$," *Solid State Sciences*, vol. 1, no. 7-8, pp. 597–606, 1999.
- [15] W. Deck, A. K. Powell, and H. Vahrenkamp, "Cluster mit Fe_6Cd - and Fe_6Hg -Baueinheiten," *Journal of Organometallic Chemistry*, vol. 428, no. 3, pp. 353–362, 1992.
- [16] O. Fuhr and D. Fenske, "Syntheses and structure elucidations of novel (Ironcarbonyl)zinc and -cadmium chloride derivatives," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 626, no. 8, pp. 1822–1830, 2000.