Research Article

Synthesis and Structural Study of the (N,N,N',N'-Tetraethylethylenediamine)CdFe(CO)₄ Dimer

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The new [(teeda)CdFe(CO)₄]₂ complex has been isolated from the reaction of [(NH₃)₂CdFe(CO)₄]_n with tetraethylethylenediamine. Unlike previous structural reports of ligand adducts of [L₂CdFe(CO)₄]_x complexes, which have all been trimeric species composed of six-membered Cd₃Fe₃ rings, the teeda complex crystallized as a dimer, analogous to [(2,2-bpy)ZnFe(CO)₄]₂. As in the zinc dimer, significant distortion arises from steric interactions between the axial carbonyl ligands on opposing iron centers. The complex sits on an inversion center, leading to two independent Cd–Fe distances, 2.7244(6) and 2.7433(6) Å, and crystallizes in the monoclinic space group *P*2₁/*a* with *a* = 14.8546(2) Å, *b* = 15.1647(3) Å, *c* = 15.5252(3) Å, β = 90.9517(12)°, and *D*_{calc} = 1.719 g/cm³ at 150(1) K.

1. Introduction

While cadmium iron carbonyl complexes have been known since at least 1933 [1, 2], only a few of these [L_nCdFe(CO)₄]_x complexes have been structurally characterized, with L being THF or a variety of aromatic amines. For L being pyridine or THF [3] or L₂ being 2,2'-bipyridine (bpy) [4], trimeric species, having *x* = 3, have been observed, though [(bpy)ZnFe(CO)₄]₂ adopts a dimeric (four-membered ring) structure [5] (Figure 1). In addition, some more complicated species such as Cd[Fe₂(CO)₈]₂²⁻ [6], Cd[Fe₃(CO)₁₁]₂²⁻ [7], [(Cd₄Cl₆)Fe(CO)₄(THF)₅], and {[CdFe(CO)₄]₆Cl₂(DME)₂]₂²⁻ [8] have been reported. A clear question that these studies have tried to address is what factors control the extent of oligomerization, and potentially polymerization, of these species. In order to better understand these factors, it appears necessary to expand upon the types of molecules being studied. As structural data for alkyl amine complexes have thus far not been reported, it was of interest to examine such species. While an L_n = en (ethylenediamine) complex has been reported [2], its low solubility in noncoordinating solvents does not make this compound conducive to crystallization. The use of tetramethylethylenediamine also did not lead to a particularly soluble species, and,

as a result, use was made of tetraethylethylenediamine, (C₂H₅)₂NC₂H₄N(C₂H₅)₂ (teeda), which did lead to a nicely soluble species that could be readily crystallized.

2. Materials and Methods

2.1. Synthesis. All reactions were carried out in Schlenk apparatus under a nitrogen atmosphere. THF was dried by distillation from sodium benzophenone ketyl under nitrogen. All nonmetallic reagents were obtained commercially.

A Schlenk flask was charged in a glove box with 0.50 g (1.6 mmol) of [(NH₃)₂CdFe(CO)₄]_x [2]. After the flask was brought out, 15 mL of THF and 0.50 g (3.2 mmol) of N,N,N',N'-tetraethylethylenediamine were added under nitrogen. The suspension was stirred while being gently warmed by a water bath for a few minutes, yielding a yellow solution. The solvent was evaporated, producing a yellow solid. Approximately 4 mL of THF was used to redissolve the solid. The resulting solution was cooled overnight to –30°C after adding 2 more mL of THF. This produced a nicely crystalline product. After the THF was syringed out, the crystals were dried first with a nitrogen flow and then under vacuum.

Anal. Calc. for C₂₈H₄₈O₈N₄Cd₂Fe₂: C, 37.15; H, 5.34. Found: C, 37.73; H, 5.54.

FIGURE 1: Structural arrangements in dimeric and trimeric $[L_nMFe(CO)_4]_x$ complexes ($x = 2, 3$).

FIGURE 2: Molecular structure of the $[(teeda)CdFe(CO)_4]_2$ complex, showing the 30% probability ellipsoids.

FIGURE 3: Alternative view of the $[(teeda)CdFe(CO)_4]_2$ complex, showing the 30% probability ellipsoids.

2.2. X-Ray Crystallography. Single crystals of the compound were examined under Paratone oil, and a suitable crystal was selected for data collection. It was transferred to a Nonius Kappa CCD diffractometer where it was held in place on a glass fiber through the use of a cold nitrogen stream. The programs COLLECT, DENZO-SMN, and SCALEPAC [9] were used for unit cell determination and data collection and processing. SIR97 [10] was used for the initial structure solution, while SHELXL-97 [11] was used for subsequent refinements, which utilized published scattering factors [12]. All nonhydrogen atoms were refined anisotropically, while the hydrogen atoms were allowed to ride on their attached carbon atoms, and the former were assigned isotropic thermal parameters based upon those of the latter. Two independent half dimers are present in the asymmetric unit, with each resulting dimer then being located on a center of inversion. The teeda ligands both are subject to significant disorder, particularly for the second dimer, in which the disorder even

involves at least one nitrogen atom. Key experimental details are given in Table 1, while pertinent bonding parameters are listed in Table 2. ORTEP representations of the molecule are given in Figures 2 and 3.

The CCDC deposition 978824 contains the full crystallographic information for this structure. 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; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

3. Results and Discussion

3.1. Synthesis. The complex $[(en)CdFe(CO)_4]_x$ has been known for some time [2], but its structure has not been reported, quite likely due to its insolubility in noncoordinating organic solvents. Attempts to convert this complex to a tmeda (tetramethylethylenediamine) analog, by direct

TABLE 1: Crystal and experimental data.

Empirical formula	C ₂₈ H ₄₈ Cd ₂ Fe ₂ N ₄ O ₈
Formula weight	905.20
Temperature (K)	150(1) K
Wavelength (Å)	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> ₂ ₁ / <i>a</i>
Unit cell dimensions	
<i>a</i>	14.8546(2)
<i>b</i>	15.1647(3)
<i>c</i>	15.5252(3)
β (°)	90.9517(12)
Volume (Å ³)	3496.81(11)
<i>Z</i>	4
<i>D</i> _{calcd} (g cm ⁻³)	1.719
μ (MoKα) (mm ⁻¹)	2.062
<i>F</i> (000)	1824
θ range (°)	2.62–27.46
	−19 ≤ <i>h</i> ≤ 19
Limiting indices	−19 ≤ <i>k</i> ≤ 18
	−20 ≤ <i>l</i> ≤ 20
Reflections collected/unique	13001/7974
Completeness (%)	99.6%
Goodness of fit on <i>F</i> ²	1.034
<i>R</i> indices [<i>I</i> > 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0380, <i>wR</i> ₂ = 0.0899
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0530, <i>wR</i> ₂ = 0.0988
(Δρ) _{max, min}	1.847, −1.238
<i>R</i> (int)	0.0198

interaction with an excess of tmeda, appeared successful, though the product was still not reasonably soluble in noncoordinating organic solvents. However, the use of teeda (tetraethylethylenediamine) did lead to a complex that was quite soluble in a variety of solvents and also was found to crystallize very readily (see Section 2). In addition to providing an opportunity to assess the likely structures of its en and tmeda analogues, this species should make for a useful starting material for further chemistry. One potential application could be for the crystallization of nearly insoluble complexes, such as the en and tmeda complexes, whose formations from [(teeda)CdFe(CO)₄]₂ could be driven by Le Chatelier's principle. Such use has in fact already been made for the crystallization of related neocuproine complexes [13].

3.2. Structural Description. Although the presence of the ethyl substituents in [(teeda)CdFe(CO)₄]₂ was crucial in allowing for its isolation and crystallization, these substituents also resulted in significant structural disorder, though not of sufficient magnitude to prevent the determination of key structural parameters, which will be the focus of the ensuing discussion. As can be seen from Figures 2 and 3, the complex is dimeric, and two crystallographically independent half dimers are found in the asymmetric unit, each generating its own dimer which is located on a center

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

Bond distances			
Cd1–Fe1	2.7433(6)	Cd1–Fe1'	2.7244(6)
Cd1–N1	2.421(4)	Cd1–N2	2.451(3)
Fe1–C1	1.765(4)	C1–O1	1.163(5)
Fe1–C2	1.768(4)	C2–O2	1.146(5)
Fe1–C3	1.776(4)	C3–O3	1.157(5)
Fe1–C4	1.786(4)	C4–O4	1.158(5)
Cd1–Fe1	2.7139(7)	Cd1–Fe1'	2.7340(7)
Cd1–N1	2.441(5)	Cd1–N2	2.470(11)
Fe1–C1	1.767(6)	C1–O1	1.144(7)
Fe1–C2	1.766(6)	C2–O2	1.152(7)
Fe1–C3	1.757(6)	C3–O3	1.183(7)
Fe1–C4	1.763(5)	C4–O4	1.162(6)
Bond angles			
Fe1–Cd1–Fe1'	106.050(15)	Cd1–Fe1–Cd1'	73.950(15)
C1–Fe1–C2	99.5(2)	Fe1–C1–O1	177.2(4)
C1–Fe1–C3	100.9(2)	Fe1–C2–O2	177.1(4)
C1–Fe1–C4	103.9(2)	Fe1–C3–O3	174.1(3)
C2–Fe1–C3	101.2(2)	Fe1–C4–O4	172.9(3)
C2–Fe1–C4	97.6(2)	Cd1–Fe1–C1	86.98(13)
C3–Fe1–C4	145.8(2)	Cd1'–Fe1–C2	99.66(15)
N1–Cd1–N2	77.15(13)		
Fe1–Cd1–Fe1'	107.02(2)	Cd1–Fe1–Cd1'	72.98(2)
C1–Fe1–C2	100.8(3)	Fe1–C1–O1	177.8(6)
C1–Fe1–C3	103.5(3)	Fe1–C2–O2	178.8(7)
C1–Fe1–C4	101.1(3)	Fe1–C3–O3	175.9(4)
C2–Fe1–C3	99.2(3)	Fe1–C4–O4	173.8(4)
C2–Fe1–C4	96.6(3)	Cd1–Fe1–C1	87.8(2)
C3–Fe1–C4	147.6(2)	Cd1'–Fe1–C2	98.4(2)

of inversion. As a result, the Cd₂Fe₂ rings are rigorously planar. This result provides the first example in which a dimeric form is clearly favored for a [L_nCdFe(CO)₄]_x species. While a dimeric structure has also been observed for L_n = neocuproine (2,9-dimethylphenanthroline), the complex has also been observed to crystallize as a trimer [13]. As noted above, the other reported [L_nCdFe(CO)₄]_x complexes were also trimeric (*x* = 3), having THF, pyridine, or 2,2'-bipyridine as the coordinated ligands, and the existence of dimeric species should offer an opportunity to better understand the factors that control the extent of oligomerization in these species. One factor that has been uncovered is the steric interaction that takes place between the axial carbonyl ligands (C3, O3; C4, O4) on opposing iron atoms. These interactions can be quite significant, especially for the smaller dimers, due to a substantial tilting that occurs between these ligands on a given iron center, which can lead to a coordination environment approaching (Cd-)bicapped tetrahedral, instead of octahedral. Aside from having a system transform to a larger ring structure, a system could alleviate the problem through a twisting of the opposing Fe(CO)₄ tetrahedra away from each other. One measure

that can be used to compare these twists is the difference between the (cis) Cd–Fe–C (equatorial) angles. In [(2,2'-bpy)ZnFe(CO)₄]₂, this difference was quite significant at 22°, arising from angles of 84.4° and 106.4°. An even larger difference of 27.6° was found for [(neocuproine)CdFe(CO)₄]₂ [13]. For [(teeda)CdFe(CO)₄]₂, however, the difference is only about 12° (Table 2). Given that the greater basicity of an alkyl, as opposed to aryl, amine should tend to increase the contribution of a more ionic biccapped tetrahedral resonance form, one might have expected an even greater twisting for the teeda complex. Notably, other distortions that accompany the twisting are also not enhanced for the teeda complex. Thus, for the dimeric form of the neocuproine compound, one observes a significant difference between the Cd–Fe bond lengths, 2.6532(3) versus 2.8125(3) Å, while in the present case the lengths for the two dimers are almost equivalent at 2.7244(6) versus 2.7433(6) and 2.7139(7) versus 2.7340(7) Å. Additionally, the angles between the axial carbonyl ligands are also quite similar for the two compounds. For the neocuproine structure, a value of 146.6° was observed, as compared to values of 145.8(2)° and 147.6(2)° for the two teeda dimers. Hence, the greater basicity of the alkyl amines is not having the expected influence on these parameters.

From the above discussion, one can conclude that there must be another factor influencing the extent of oligomerization. While an earlier proposal was that the repulsions between opposing axial carbonyls could lead to the observed distortions and/or the adoption of larger ring systems, it seems evident that additional repulsions involving the cadmium ligands may also be important. In particular, the aromatic ligands could interact with each other, as well as with the axial carbonyls, whereas the alkyl substituents in the teeda complex have orientations that do not give rise to severe repulsions, at least not with the axial carbonyls. Conceivably, the use of nonchelating alkyl amines could generate such repulsions and lead to greater distortions. However, the alkyl amines, whether chelating or not, could generate lateral repulsions, whose effects could be substantial in some cases, and are in need of investigation. In fact, the observation of a large Fe–Cd–Fe angle of 157.27(2)° about a mono(THF)-coordinated cadmium center might provide an indication that mono(ligand) complexes could be more amenable to chain formation than the more common bis(ligand) complexes.

There are some other bonding parameters that merit comparison. Concerning the steric interactions in these rings, one can note that the contacts between opposing axial carbonyl oxygen atoms are actually shorter than in the dimeric neocuproine complex, 2.97 and 3.04 versus 3.33 and 3.79 Å. However, one finds a more severe Cd–Cd contact in the neocuproine complex, 3.085 versus 3.24 and 3.29 Å in the teeda dimers. Additionally, the Cd–N distances for the teeda complex are significantly longer than those in the neocuproine complex dimer, 2.42 and 2.48 versus 2.3635(17) and 2.3621(17) Å, as would be expected based on their respective sp³ and sp² hybridizations.

The use of alkyl amines as ligands in these cadmium-iron complexes can be seen to lead to interesting and marked structural differences and provide additional insight into

the factors affecting the extent of their oligomerizations. These species should be readily amenable to changes that will allow for desired solubilities and interring repulsive interactions and thus can be expected to offer much promise for subsequent studies. Further results with other alkyl amine complexes will be reported in the future.

4. Conclusions

The use of the teeda ligand has led to a nicely soluble and readily crystallized complex that could be useful for future synthetic applications. It is possible that this species could even be used to lead to the slow formation and crystallization of its en and tmeda analogs. The complex itself displays substantial distortion associated with the teeda ligand, but the primary metal-related parameters are fairly well defined. Although the more basic nature of alkyl versus aryl amines might lead one to expect a greater contribution of ionic resonance hybrids involving formal cadmium-biccapped [Fe(CO)₄]²⁻ species, this was not observed, though it is possible that the structurally compact nature of the dimeric species may have repressed these distortions. The fact that the aryl amine species could not readily exist as dimers suggests the presence of an additional repulsive interaction, which appears to be interactions between pyridine rings and either with other pyridine rings or with the axial carbonyl ligands.

Conflict of Interests

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

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