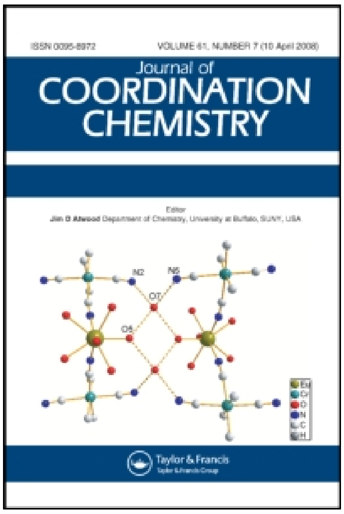

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, Crystal Structure and Thermal Properties of a Novel Ferrocenecarboxylato-Bridged Zinc(II) Dimer [Zn_2(μ-OOCFc)$_4$(3-PyCOOCH$_3$)$_2$]

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To cite this Article Li, Gang , Chen, Bing-Yi , Li, Lin-Ke , Hou, Hong-Wei , Zhu, Yu and Fan, Yao-Ting(2003) 'Synthesis, Crystal Structure and Thermal Properties of a Novel Ferrocenecarboxylato-Bridged Zinc(II) Dimer [Zn_2(μ-OOCFc)$_4$(3-PyCOOCH$_3$)$_2$]', Journal of Coordination Chemistry, 56: 10, 877 — 884
To link to this Article: DOI: 10.1080/0095897031000135252
URL: http://dx.doi.org/10.1080/0095897031000135252

J. Coord. Chem., Vol. 56, No. 10, 10 July 2003, pp. 877–884

SYNTHESIS, CRYSTAL STRUCTURE AND THERMAL PROPERTIES OF A NOVEL FERROCENECARBOXYLATO-BRIDGED ZINC(II) DIMER [$Zn_2(\mu\text{-}OOCFc)_4(3\text{-}PyCOOCH_3)_2$]

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(Received 28 May 2002; Revised 25 September 2002; In final form 3 April 2003)

A novel ferrocenyl dimer [$Zn_2(\mu\text{-}OOCFc)_4(3\text{-}PyCOOCH_3)_2$] (Fc=($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)), **1**, was obtained by the reaction of $Zn(OAc)_2 \cdot 2H_2O$ with sodium ferrocenecarboxylate and 1,4-butanediol dinicotinate in methanol solution. X-ray structural analysis reveals that the compound contains two zinc(II) centers symmetrically bridged by four ferrocenecarboxylate anions as O,O′-bridging ligands, leading to a dimeric tetrabridged [$Zn_2(\mu\text{-}OOCFc)_4$] core. The zinc(II) ion is in a distorted octahedral environment with four oxygen atoms from four distinct ferrocenecarboxylates, a nitrogen atom from the ligand $NC_5H_4CO_2CH_3$, and another zinc atom. The symmetry of the complex in the paddle-wheel structure brings the metal centers close, the Zn⋯Zn intradimer distance being 2.934(11) Å. It is the first example of a zinc(II) dimer with ferrocenecarboxylate anion ligands. Its thermal properties were measured in air.

Keywords: Dimer; Zinc(II); Sodium ferrocenecarboxylate; Crystal structure; Thermal properties

INTRODUCTION

Ferrocenyl compounds continue to attract interest as components in homogeneous catalysts [1] and have potential applications in materials science as, for example, molecular sensors [2], and molecular magnetic [3] and non-linear optical materials [4]. Several groups have used ferrocenecarboxylic acid or its sodium salt as a multifunctional ligand, exploiting its size and the strong inductive effect of the ferrocene unit [5]. Depending on the mode of coordination of this group to one or more metals, a wide variety of transition metal complexes containing the ferrocenecarboxylato ligand have been prepared [6]. Although ferrocenecarboxylate anions commonly act as terminal monodentate or bidentate ligands, reports of their use as O,O′-bridging ligands are limited. Only five such compounds contain dimeric [$M_2(\mu\text{-}OOCFc)_n$] cores (Fc = (η^5-C_5H_5)Fe(η^5-C_5H_4), $n = 2$ or 4 and $M = Cu^{2+}$ or Mo^{2+}) [6e–h].

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ISSN 0095-8972 print: ISSN 1029-0389 online, © 2003 Taylor & Francis Ltd
DOI: 10.1080/0095897031000135252

Moreover, to the best of our knowledge, there are no reports of a zinc(II) dimer containing the ferrocenecarboxylate ligand. In this contribution, we utilized the reaction of sodium ferrocenecarboxylate and 1,4-butanediol dinicotinate (BDDT) with $Zn(OAc)_2 \cdot 2H_2O$ to afford a novel zinc(II) dimer, $[Zn_2(\mu\text{-}OOCFc)_4(3\text{-}PyCOOCH_3)_2]$, **1**. Here we report the synthesis, crystal structure and thermal analysis of Compound **1**.

EXPERIMENTAL

Materials and Physical Techniques

Ferrocenecarboxylic acid and other starting materials were obtained from commercial sources and used without further purification. Sodium ferrocenecarboxylate was prepared as described previously [7].

IR data were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. ^1H NMR spectra were recorded in $CDCl_3$ at room temperature on Bruker DPX 400 spectrometers. Elemental analyses (C, H and N) were carried out on a Carlo-Erbal 106 Elemental analyzer. TGA-DTA measurements were performed by heating the sample from 20 to 600°C at a rate of $10°C\,min^{-1}$ in air on a Perkin-Elmer DTA-7 differential thermal analyzer.

Preparation of 1,4-Butanediol Dinicotinate, BDDT

To a solution of 1,4-dibromobutane (2.2 g, 10 mmol) and 3-pyridinecarboxylic acid (3.7 g, 30 mmol) in 30 mL DMSO, K_2CO_3 (5 g, 35 mmol) was added with constant stirring. The reaction mixture was heated at 70°C for 10 h, and then cooled with an ice-water bath. The yellow precipitate was filtered, and washed with water until $pH \approx 7$, and dried in vacuo. Yield: 84%; m.p. 88–89°C. Anal. Calcd. for $C_{16}H_{16}N_2O_4$: C, 64.01; H, 5.33; N, 9.33%. Found: C, 63.89; H, 5.49; N, 9.39%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.4–9.2 (m, C_5H_4N, 8H), 4.45 (s, CH_2, 4H), 1.98 (s, CH_2, 4H). IR (cm^{-1}, KBr): 1714 (s), 1590 (s), 1422 (m), 1297 (s), 1127 (s), 1109 (m), 955 (m), 741 (m), 701 (m).

Synthesis of Dimer 1

$Zn(OAc)_2 \cdot 2H_2O$ (0.0118 g; 0.05 mmol) and NaOOCFc (0.025 g; 0.1 mmol) were dissolved in 7 mL of CH_3OH. BDDT (0.015 g; 0.05 mmol) in 3 mL of CH_3OH was added dropwise to the mixture. The resulting pale-yellow solution was allowed to stand at room temperature in the dark. Good quality red single crystals were obtained after several weeks. Yield: 74%. Anal. Calcd. for $C_{58}H_{50}Fe_4N_2O_{12}Zn_2$: C, 52.68; H, 3.78; N, 2.12%. Found: C, 52.47; H, 3.75; N, 2.03%. IR (cm^{-1}, KBr): 1725 (s), 1621 (s), 1588 (s), 1477 (s), 1390 (s), 1358 (m), 1291 (m), 514 (m).

Crystallography

Crystal data and experimental details for **1** are contained in Table I. A crystal having approximate dimensions of $0.28 \times 0.25 \times 0.20\,mm^3$ was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and expanded using the Fourier technique. The

TABLE I Crystal data and structure refinement parameters for **1**

Formula	$C_{58}H_{50}O_{12}N_2Fe_4Zn_2$
Formula weight	1321.14
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	13.425(3)
b (Å)	20.425(4)
c (Å)	9.435(2)
α (°)	90
β (°)	92.06(3)
γ (°)	90
V (°)	2585.5(9)
D_{calc} ($\mathrm{mg\,m^{-3}}$)	1.697
Z	2
μ ($\mathrm{mm^{-1}}$)	2.074
Reflections collected/unique	8740/4963 [$R_{\mathrm{in}} = 0.0506$]
Data/restraints/parameters	4963/0/353
Goodness-of-fit on F^2	1.072
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0522$; $wR_2 = 0.1079$
R indices (all data)	$R_1 = 0.0923$; $wR_2 = 0.1191$
$\Delta\rho_{\mathrm{min}}$, $\Delta\rho_{\mathrm{max}}$ ($\mathrm{e\,Å^{-3}}$)	-0.482, 0.493

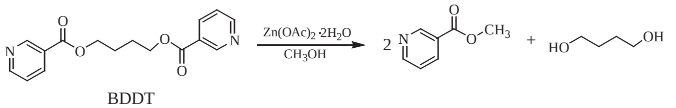
non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Crystal data: monoclinic, space group $P2_1/c$, with $a = 13.425(3)$, $b = 20.425(4)$, $c = 9.435(2)$ Å; $\alpha = 90$, $\beta = 92.06(3)$, $\gamma = 90°$; $Z = 2$; $D_{\mathrm{calc}} = 1.697\ \mathrm{Mg/m^3}$; final $R = 0.0522$, $wR_2 = 0.1079$ for 4963 independent reflections.

All data were collected at a temperature of 291(2) K using the ω–2θ scan technique and correction was applied for Lorenz–polarization effects. A correction for secondary extinction was applied. The final cycle of the full-matrix least-squares refinement was based on 3638 observed reflections ($I > 2.00\,\sigma(I)$) and 353 variable parameters. All calculations were performed using the SHELXL-97 crystallographic software package [8]. Selected bond lengths and bond angles are listed in Table II, and final atomic coordinates in Table III.

RESULTS AND DISCUSSION

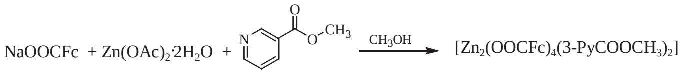
Syntheses

On the basis of the structural analysis of the product and determinations of BDDT, we propose that there are two steps in the preparation of $[Zn_2(\mu\text{-}OOCFc)_4(3\text{-}PyCOOCH_3)_2]$. The first is cleavage of BDDT. BDDT is unstable under acidic or basic conditions or in the presence of metal ions (Lewis acid), undergoing alcoholysis to yield methyl nicotinate, $3\text{-}PyCOOCH_3$. The second step is zinc(II) ions reacting with NaOOCFc and $3\text{-}PyCOOCH_3$ obtaining a novel zinc dimer (Eq. (2)).



BDDT

(1)



(2)

TABLE II Selected bond distances (Å) and angles (°) for **1**

Zn(1)–O(1)	2.017(3)	Zn(1)–O(2)	2.055(3)
Zn(1)–O(3)	2.025(3)	Zn(1)–O(4)	2.116(3)
Zn(1)–N(1)	2.059(4)	Zn(1)–Zn(1)#1	2.9340(11)
Fe(1)–C(1)	2.049(5)	Fe(2)–C(12)	2.026(6)
Fe(1)–C(2)	2.054(5)	Fe(2)–C(13)	2.053(5)
Fe(1)–C(3)	2.055(5)	Fe(2)–C(14)	2.060(5)
Fe(1)–C(4)	2.050(5)	Fe(2)–C(15)	2.038(7)
Fe(1)–C(5)	2.042(5)	Fe(2)–(C16)	2.020(7)
Fe(1)–C(6)	2.056(5)	Fe(2)–(C17)	2.048(5)
Fe(1)–C(7)	2.076(5)	Fe(2)–(C18)	2.061(6)
Fe(1)–C(8)	2.041(4)	Fe(2)–(C19)	2.055(5)
Fe(1)–C(9)	2.035(5)	Fe(2)–(C20)	2.043(5)
Fe(1)–C(10)	2.040(4)	Fe(2)–(C21)	2.039(4)
C(10)–C(11)	1.481(6)	C(11)–O(1)	1.269(5)
C(21)–C(22)	1.489(6)	C(11)–O(3)#1	1.257(6)
C(22)–O(4)	1.260(5)	C(22)–O(2)#1	1.271(5)
C(28)–C(26)	1.484(7)	C(28)–O(5)	1.196(6)
C(28)–O(6)	1.317(6)	O(6)–C(29)	1.450(7)
O(1)–Zn(1)–O(3)	160.17(14)	O(1)–Zn(1)–O(2)	89.61(14)
O(3)–Zn(1)–O(2)	89.55(13)	O(1)–Zn(1)–N(1)	98.24(14)
O(3)–Zn(1)–N(1)	101.19(14)	O(2)–Zn(1)–N(1)	103.89(14)
O(1)–Zn(1)–O(4)	87.50(14)	O(4)–Zn(1)–O(3)	86.80(13)
O(2)–Zn(1)–O(4)	160.75(12)	N(1)–Zn(1)–O(4)	95.37(14)
O(1)–Zn(1)–Zn(1)#1	76.86(10)	O(2)–Zn(1)–Zn(1)#1	91.89(9)
O(3)–Zn(1)–Zn(1)#1	83.38(10)	N(1)–Zn(1)–Zn(1)#1	163.53(11)
O(4)–Zn(1)–Zn(1)#1	68.92(9)	O(1)–C(11)–O(3)#1	125.2(4)
O(4)–C(22)–O(2)#1	124.8(4)	C(10)–C(11)–O(1)	116.0(4)
C(21)–C(22)–O(4)	117.4(4)	C(10)–C(11)–O(3)#1	118.8(4)
C(21)–C(22)–O(2)#1	117.8(4)	C(28)–O(6)–C(29)	117.8(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x+3$, $-y$, $-z+2$.

On the other hand, we should note that self-assembly of Zn(OAc)$_2$ with sodium ferrocenecarboxylate in the dark is an effective route for preparation of novel zinc(II) complexes containing ferrocene. It is well known [9] that ferrocene derivatives that contain a photo-active carbonyl group on the Cp ring, such as diacylferrocenes [9b,d] and ferrocenylacetylacetone [9e], are more photolabile, and can undergo photolysis in some solvents to cause both ring–metal and ring–carbonyl cleavage, giving free Fe^{2+} cations and free radicals. These active intermediates are sensitive to oxygen, water, heat and light, and make the secondary reactions complicated. For example, the mixture of zinc(II) ion, BDDT and ferrocenecarboxylato ligand in methanol solution in the presence of light, turned from pale yellow to dark-brown and then produced brown precipitation products, whose composition cannot be readily defined. We believe that the ferrocenecarboxylato ligand undergoes photolysis, so that our target compounds, ferrocene-containing zinc(II) complexes, could not be obtained.

Structure of [Zn$_2$(μ-OOCFc)$_4$(3-PyCOOCH$_3$)$_2$], 1

Solution of the single crystal structure shows that Compound **1** crystallizes in space group $P2_1/c$. The lattice is composed of dimers, the monomeric units of which are related by a crystallographically imposed center of inversion. That is to say, this compound contains two zinc(II) centers symmetrically bridged by four ferrocenecarboxylate anions, leading to a dimeric tetrabridged [Zn$_2$(μ-OOCFc)$_4$] core.

TABLE III Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters (Å × 10^3)

	x	y	z	$U_{(eq)}$
Zn(1)	15371(1)	519(1)	10956(1)	32(1)
Fe(1)	13009(1)	1706(1)	6717(1)	35(1)
Fe(2)	18231(1)	201(1)	6830(1)	41(1)
O(1)	15022(2)	1006(2)	9146(3)	46(1)
O(2)	13966(2)	702(2)	11653(3)	42(1)
O(3)	15514(2)	−225(2)	12367(3)	42(1)
O(4)	16551(2)	79(2)	9874(3)	41(1)
O(5)	19428(4)	2232(3)	12271(6)	104(2)
O(6)	18985(3)	1588(2)	10459(4)	61(1)
N(1)	16240(3)	1229(2)	11935(4)	35(1)
C(1)	12192(4)	1804(3)	8499(6)	61(2)
C(2)	11803(4)	2221(3)	7405(7)	61(2)
C(3)	11516(4)	1828(3)	6236(6)	53(1)
C(4)	11719(4)	1170(3)	6603(5)	47(1)
C(5)	12137(4)	1154(3)	7984(5)	54(1)
C(6)	14443(3)	2010(2)	7195(5)	38(1)
C(7)	14064(4)	2350(2)	5966(5)	43(1)
C(8)	13787(4)	1864(2)	4930(5)	42(1)
C(9)	14005(3)	1238(2)	5497(4)	39(1)
C(10)	14414(3)	1329(2)	6905(4)	33(1)
C(11)	14651(3)	812(3)	7964(4)	36(1)
C(12)	17063(6)	769(4)	6184(8)	86(3)
C(13)	17440(5)	443(3)	5002(6)	64(2)
C(14)	18428(5)	624(3)	4879(6)	70(2)
C(15)	18691(7)	1051(4)	5931(8)	89(2)
C(16)	17871(9)	1161(3)	6775(7)	102(3)
C(17)	18045(4)	−776(2)	7229(4)	41(1)
C(18)	19068(4)	−642(3)	7031(5)	48(1)
C(19)	19393(4)	−173(3)	8056(5)	53(1)
C(20)	18571(4)	−19(3)	8903(5)	44(1)
C(21)	17732(3)	−390(2)	8396(4)	35(1)
C(22)	16700(3)	−334(2)	8912(4)	35(1)
C(23)	15940(4)	1544(3)	13081(5)	44(1)
C(24)	16532(4)	2002(3)	13792(5)	54(1)
C(25)	17478(4)	2120(3)	13329(5)	49(1)
C(26)	17801(4)	1790(2)	12155(5)	40(1)
C(27)	17152(3)	1348(2)	11472(4)	37(1)
C(28)	18822(4)	1899(3)	11651(6)	52(1)
C(29)	19966(4)	1646(3)	9875(7)	71(2)

$U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

All ferrocenecarboxylate bridges in this complex exhibit *syn–syn* geometry. Figure 1 gives a view of $[Zn_2(\mu\text{-}OOCFc)_4(3\text{-}PyCOOCH_3)_2]$ with the numbering scheme.

Each zinc(II) ion is in a distorted-octahedral environment with the four oxygen atoms from four distinct ferrocenecarboxylato groups occupying the equatorial plane. Nitrogen atoms from 3-PyCOOCH$_3$ and the neighboring zinc atom occupy the axial positions. The Zn–O bond lengths range from 2.017(3) to 2.116(3) Å, while Zn(1)–N(1) and Zn(1)–Zn(1A) distances are 2.059(4) and 2.934(11) Å respectively. Bond angles around the central Zn ion range from 68.92(9) to 163.53(11)° compared to 90 or 180° for an ideal octahedral structure. The O(A)–C(22)–O(2A) and O(1)–C(11)–O(3A) angles of the ferrocenecarboxylate bridges were found to be 124.8(4) and 125.2(4)°, respectively. Interestingly, the Zn···Zn

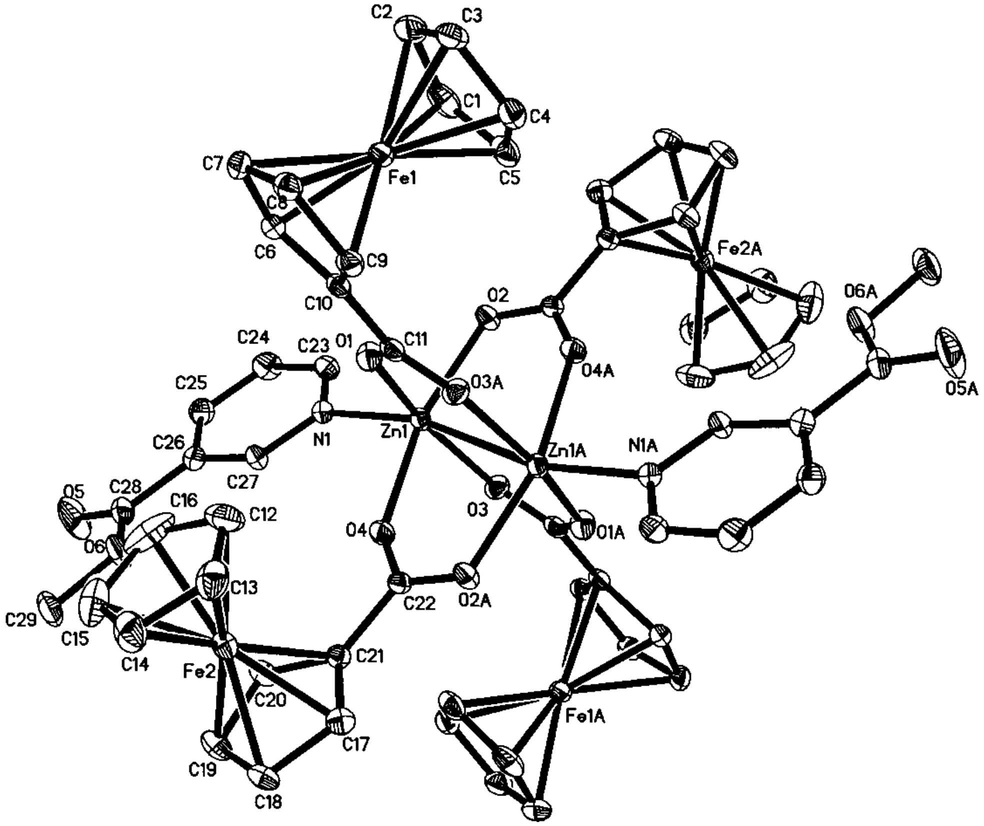


FIGURE 1 Molecular structure of $[\text{Zn}_2(\mu\text{-OOCFc})_4(3\text{-PyCOOCH}_3)_2]$, **1**. Hydrogen atoms are omitted for clarity.

intradimer distance is significantly shorter than that of reported zinc(II) dimers $[(\eta^1\text{-Me}_2\text{NC}_2\text{H}_4\text{C}_5\text{H}^1\,\text{Pr}_3)\text{Zn}(\mu\text{-Cl})]_2$ ($\text{Zn}\cdots\text{Zn} = 3.245\,\text{A}$), $[(\eta^1\text{-cyclo-C}_4\text{H}_8\text{C}_2\text{H}_4\text{C}_5\text{Me}_4)\text{Zn}(\mu\text{-OAc})]_2$ ($\text{Zn}\cdots\text{Zn} = 3.821\,\text{Å}$) and $[(\eta^1\text{-cyclo-C}_4\text{H}_8\text{C}_2\text{H}_4\text{C}_5\text{Me}_4)\text{Zn}(\mu\text{-OAc})(\mu\text{-OEt})]_2$ ($\text{Zn}\cdots\text{Zn} = 3.397\,\text{Å}$) [10]. The two Zn ions are brought into close proximity by the four double-bridging ferrocenecarboxylate ligands. The symmetry of the resultant paddle-wheel structure is a consequence of this bonding arrangement.

Cotton and coworkers have demonstrated that dimeric transition metal complexes containing four bridging groups could have strong metal–metal bonds [11]. For example, the Mo–Mo distance (2.105(1) Å) of the cluster $[\text{Mo}_2(\mu\text{-OOCFc})_4(\text{CH}_3\text{CN})_2\text{-}(\text{DMSO})](\text{DMSO})_2$ is indicative of the presence of a strong quadruple molybdenum–molybdenum bond [6e]; the simple MO treatment developed by Cotton rationalizes the quadruple Mo–Mo bond in the $\text{Mo}_2\text{Cl}_8^{2-}$ dianion and the related dinuclear complexes: one σ bond, two π bonds and one δ bond. The bonding (σ, π, δ) and antibonding (σ^*, π^*, δ^*) orbitals associated with the metal–metal bonding description in Complex **1** are completely full for d^{10}, Zn^{2+}. Thus, the net bond order between the two Zn atoms is zero. The $\text{Zn}\cdots\text{Zn}$ separation of 2.934 Å of **1** is substantially longer than twice the covalent radius of Zn (1.33 Å), indicating the lack of a significant bonding interaction.

The carboxylate groups, with bite angles ranging from 124.8(4) to 125.2(4)°, are nearly coplanar with the C_5H_4 rings (angles varying from 11.2 to 9.6°) and close to those of reported compounds [6f]. The C–C distances (1.415(8) Å, av.), Fe–C_{ring} distances (2.047(5) Å, av.) and C–C–C angles (108.0(5)°, av.) of the ferrocenyl units are all similar to those reported in the literature [6e, 12]. In each ferrocenyl moiety, the cyclopentadienyl rings are planar and nearly parallel, with a dihedral angle of 2.6° or 3.2°. The two sets of mutually-trans ferrocenyl moieties of $[Zn_2(\mu\text{-OOCFc})_4(3\text{-PyCO}_2CH_3)_2]$ exhibit both eclipsed and staggered configurations, as has been observed for the analogous dimolybdenum complex [6e].

TGA of $[Zn_2(\mu\text{-OOCFc})_4(3\text{-PyCOOCH}_3)_2]$

The compound $[Zn_2(\mu\text{-OOCFc})_4(3\text{-PyCOOCH}_3)_2]$ was heated to 600°C in air. TGA data show that the dimeric structure is stable up to 181°C. The compound goes through complicated multiple weight-loss steps in the temperature range 181–344°C. The total weight loss corresponds to loss of two 3-$PyCOOCH_3$ ligands (observed 20.24%, calculated 20.74%). The final process is accompanied by decomposition of the organic units of ferrocenecarboxylate anions. A brown amorphous residue of 2ZnO + 4FeO (observed 35.11%, calculated 34.10%) remained. These results are in reasonable agreement with the crystal structure analysis.

Acknowledgments

We gratefully acknowledge the financial support of the National Natural Science Foundation of China, the Outstanding Young Teacher Foundation of Ministry of Education of China, and Innovation Engineering Foundation of Henan Province.

Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 178860. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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