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Reactions of mercuric acetate with pentacarbonyliron in alcohols. Crystal and molecular structures of $Hg[Fe(COOR)(CO)_4]_2$ ($R = CH_3, C_2H_5$)

Antonio Eduardo Mauro [a,*], Vicente Alexandre De Lucca Neto [a], José Roberto Zamian [a], Regina Helena de Almeida Santos [b], Maria Teresa do Prado Gambardella [b], Johannes Rüdiger Lechat [b], Hercílio Rodolfo Rechenberg [c]

[a] *Instituto de Química de Araraquara, UNESP, CP 355, 14800-900 Araraquara SP, Brazil*
[b] *Instituto de Física e Química de São Carlos, USP, CP 369, 13560-250 São Carlos SP, Brazil*
[c] *Instituto de Física, USP, CP 20516, 05508-900 São Paulo SP, Brazil*

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Abstract

Reactions of $Hg(CH_3COO)_2$ with $[Fe(CO)_5]$ in MeOH and EtOH lead to the compounds $Hg[Fe(COOR)(CO)_4]_2$ (I for $R = CH_3$ and II for $R = C_2H_5$). Crystals of I are triclinic, $P\bar{1}$, with $a = 6.272(2)$, $b = 6.441(3)$, $c = 11.703(4)$ Å, $\alpha = 92.94(3)°$, $\beta = 103.77(3)°$, $\gamma = 96.10(2)°$, and $Z = 1$. Crystals of II are tetragonal, $I4_1/a$, with $a = 17.906(3)$ Å, $c = 12.756(2)$ Å, and $Z = 8$. The geometry around Hg is linear for compound I and approximately linear for compound II. The Hg–Fe distances are 2.5716(8) and 2.575(4) Å for compounds I and II, respectively. The geometry around the Fe in both compounds is approximately octahedral. The carboalkoxy group is *cis* to Hg in both compounds with Fe–C distances equal to 2.034(6) and 2.05(4) Å for compounds I and II, respectively.

Keywords: Iron; Mercury; Carbonyl; Crystal structure; Infrared spectroscopy; Mössbauer spectroscopy

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1. Introduction

Bimetallic compounds are now widely studied for their improved properties when compared with homometallic compounds [1]. The reasons for carrying out the present work include our interest in the physical and chemical properties of bimetallic and mixed-metal polynuclear transition metal complexes, which render possible applications in catalysis and in electron transport.

In our previous publications [2,3] the synthesis and X-ray analysis of $[Fe(CO)_4(HgSCN)_2]$ and $[Fe(CO)_4(HgSCN)_2(phen)_2]$ have been reported. In the present paper we report data concerning the structures of $Hg[Fe(COOR)(CO)_4]_2$ (I, $R = CH_3$ and II, $R = C_2H_5$), which were prepared by allowing $Hg(CH_3COO)_2$ to react with $[Fe(CO)_5]$ in MeOH and EtOH. Actually, these compounds were first described in 1929 [4]. At that time they were formulated as $2Fe(CO)_5, Hg(OR)_2$.

A relevant aspect observed in the present investigation was a nucleophilic activation of a carbonyl group attached to iron by alkoxide anions. In fact, considerable interest has been demonstrated during the past few years in alkoxycarbonyl complexes [5], since there is increasing evidence that these species are intermediates in several important catalytic reactions, challenging the carbon monoxide insertion route.

2. Results and discussion

Reactions of transition-metal complexes with mercury salts have yielded compounds in which metal–mercury bonds occur [6,7]. Amongst the first ones described were those complexes containing Fe–Hg bonds, like $[HgFe(CO)_4]$, a typical example of a cluster [8,9], prepared by reacting $HgSO_4$ with $[Fe(CO)_5]$ in

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* Corresponding author.

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water. Acetone also may be used to obtain the same compound when $Hg(CH_3COO)_2$ is taken as starting material.

However, quite different compounds were obtained when the solvents used were MeOH or EtOH. In order to explain the role of the above alcohols in the formation of the final products a previously proposed [4] this equation may be considered as the most appropriate.

$$\mathrm{Hg(CH_3COO)_2 + 2ROH + 2[Fe(CO)_5] \longrightarrow Hg[Fe(COOR)(CO)_4]_2 + 2CH_3COOH}$$ [1]

$(I, R = CH_3; II, R = C_2H_5)$

Some important points emerged from the analysis of the IR spectra of compounds I and II. First, four ν(CO) stretching bands were observed at 2078m, 2050sh, 2025m and 1990m cm^{-1} for I and at 2088m, 2060sh, 2030m and 1955m cm^{-1} for II. Secondly, a band assignable to ν(CO) of an ester function [10] was detected at 1630m cm^{-1} for I and at 1632m cm^{-1} for II. These facts allowed us to conclude that only terminal CO groups are present [11] and furthermore suggested the presence of an alkoxycarbonyl ligand coordinated to iron.

In order to clarify those aspects related to the geometry around the iron atom and the metal oxidation state, use was made of Mössbauer spectroscopy. The spectra of the two compounds are very similar, displaying a quadrupole doublet. The small quadrupole splittings observed, 0.392 for I and 0.379 mm s^{-1} for II, are typical of iron complexes with an octahedral structure [12]. In addition, the isomer shift values, 0.121 for I and 0.122 mm s^{-1} for II, are similar to those of iron(0) carbonyl compounds [13].

The monomeric nature of the compounds and the structural features suggested by IR and Mössbauer spectroscopies were definitely proved by X-ray analysis.

Selected bond lengths and angles are listed in Tables 1 and 2 for compounds I and II, respectively. The molecular structures and the adopted numbering schemes are shown in Figs. 1 and 2 for compounds I and II respectively.

The X-ray analysis confirms the monomeric nature of compounds I and II. The geometry around the mercury atom is linear for compound I and approximately linear for compound II. The Hg-Fe distances are 2.5716(8) and 2.575(4) Å for compounds I and II respectively and are in good agreement with the observed values of 2.549(3) and 2.564(3) Å for compound $[Fe(CO)_4(HgSCN)_2(phen)_2]$ [3]. The geometry around the iron atom in both compounds is approximately octahedral. The carboalkoxy groups are planar and the geometry around C(5) clearly indicates an sp^2 hybridization. These groups are *cis* to Hg in both compounds with the metal-ester bond length, Fe-C(5), equal to 2.034(6) and 2.05(4) Å for compounds I and II, respectively.

Table 1
Bond distances (Å) and angles (°) for compound I; e.s.d. values in parentheses

Hg-Fe	2.5716(8)	Fe-C(1)	1.828(6)
Fe-C(2)	1.793(6)	Fe-C(3)	1.810(7)
Fe-C(4)	1.833(6)	Fe-C(5)	2.034(6)
C(1)-O(1)	1.111(8)	C(2)-O(2)	1.160(8)
C(3)-O(3)	1.128(8)	C(4)-O(4)	1.132(8)
C(5)-O(5)	1.180(9)	C(5)-O(6)	1.322(9)
O(6)-C(6)	1.46(2)		
Fe-Hg-Fe *	180	He-Fe-C(1)	176.4(3)
Hg-Fe-C(2)	81.2(2)	Hg-Fe-C(3)	83.9(2)
Hg-Fe-C(4)	87.3(2)	Hg-Fe-C(5)	85.2(2)
Fe-C(1)-O(1)	179.5(7)	Fe-C(4)-O(4)	178.8(5)
Fe-C(2)-O(2)	178.2(5)	Fe-C(5)-O(5)	127.8(6)
Fe-C(3)-O(3)	177.9(5)	Fe-C(5)-O(6)	112.3(4)
C(1)-Fe-C(2)	97.9(3)	C(2)-Fe-C(5)	87.4(3)
C(1)-Fe-C(3)	96.7(3)	C(3)-Fe-C(4)	92.7(3)
C(1)-Fe-C(4)	96.3(3)	C(3)-Fe-C(5)	85.6(3)
C(1)-Fe-C(5)	91.3(3)	C(4)-Fe-C(5)	172.4(2)
C(2)-Fe-C(3)	164.0(3)	O(5)-C(5)-O(6)	120.0(7)
C(2)-Fe-C(4)	92.4(3)	C(5)-O(6)-C(6)	116.8(6)

* −x, −y, −z

Current studies are under way to induce coupling of the two alkoxycarboxylate ligands present in compounds I and II in order to produce dialkyl oxalates.

Table 2
Bond distances (Å) and angles (°) for compound II; e.s.d. values in parentheses

Hg-Fe	2.575(4)	Fe-C(1)	1.74(3)
Fe-C(2)	1.82(3)	Fe-C(3)	1.81(4)
Fe-C(4)	1.85(3)	Fe-C(5)	2.05(4)
C(1)-O(1)	1.22(4)	C(2)-O(2)	1.16(5)
C(3)-O(3)	1.13(4)	C(4)-O(4)	1.12(4)
C(5)-O(5)	1.19(4)	C(5)-O(6)	1.33(4)
O(6)-C(6)	1.42(4)	C(6)-C(7)	1.45(5)
Fe-Hg-Fe *	177.0(2)	Hg-Fe-C(1)	81.6(9)
Hg-Fe-C(2)	87(1)	Hg-Fe-C(3)	177(1)
Hg-Fe-C(4)	81(1)	Hg-Fe-C(5)	85.9(9)
C(1)-Fe-C(2)	95(1)	C(1)-Fe-C(3)	97(1)
C(1)-Fe-C(4)	161(1)	C(1)-Fe-C(5)	82(1)
C(2)-Fe-C(3)	96(1)	C(2)-Fe-C(4)	92(1)
C(2)-Fe-C(5)	172(1)	C(3)-Fe-C(4)	101(1)
C(3)-Fe-C(5)	91(1)	C(4)-Fe-C(5)	90(1)
Fe-C(1)-O(1)	175(2)	Fe-C(2)-O(2)	172(3)
Fe-C(3)-O(3)	174(3)	Fe-C(4)-O(4)	175(3)
Fe-C(5)-O(5)	125(3)	Fe-C(5)-O(6)	115(3)
O(6)-C(6)-C(7)	111(3)	O(5)-C(5)-O(6)	120(3)
C(5)-O(6)-C(6)	119(2)		

* −x, 1/2−y, z.

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[1] Spectroscopic data (NMR) consistent with the formation of CH_3COOR are also available. They will be published elsewhere.

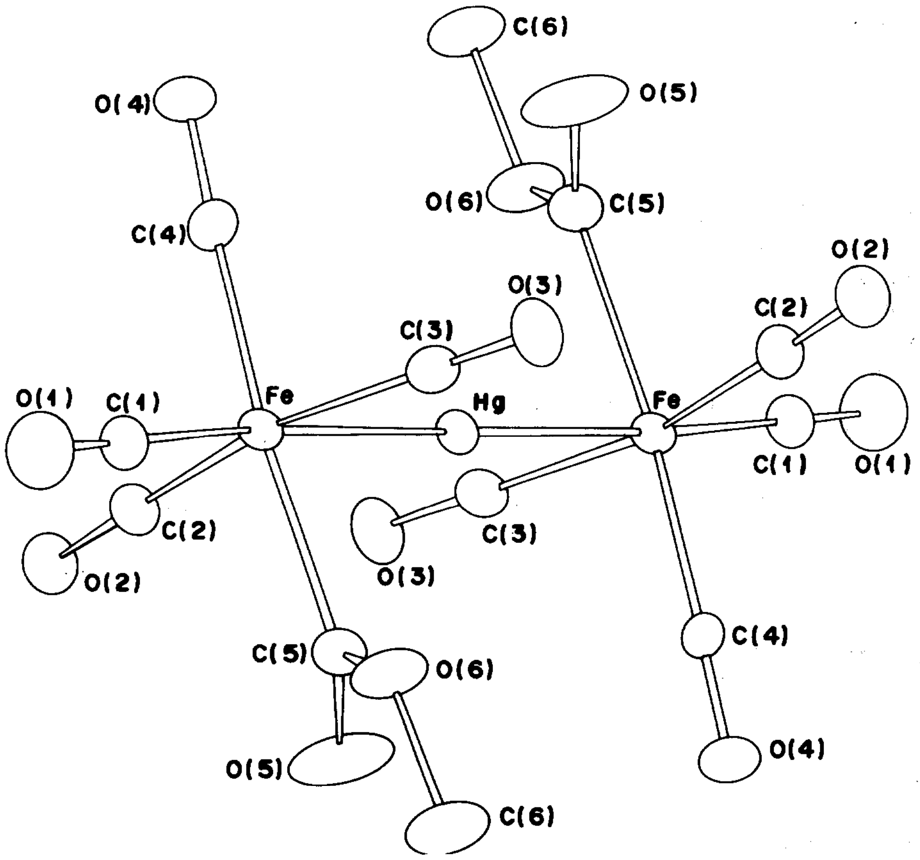

Fig. 1. Molecular structure and adopted numbering scheme for I.

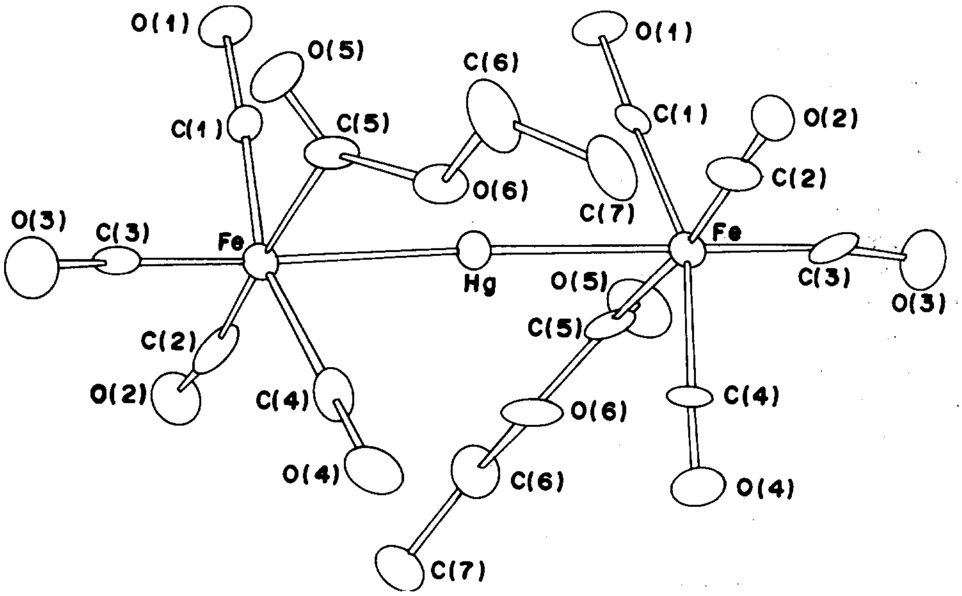

Fig. 2. Molecular structure and adopted numbering scheme for II.

3. Experimental section

3.1. Synthesis of $Hg[Fe(COOR)(CO)_4]_2$ (I, $R = CH_3$ and II, $R = C_2H_5$)

To a solution of 0.238 g (0.75 mmol) of $Hg(CH_3CO\text{-}O)_2$ in 10 ml of CH_3OH or 18 ml of C_2H_5OH, clarified by adding a few drops of glacial acetic acid, was added 0.2 ml (1.49 mmol) of $[Fe(CO)_5]$. The mixture was gently heated and stirred for 15 min. The solids formed were filtered off, washed thoroughly with the respective alcohols and diethyl ether and then dried in vacuo. Recrystallization from MeOH for I and EtOH for II gave orange crystals suitable for X-ray analysis. Anal. for I. Found: C, 21.85; H, 0.90; Fe, 17.32. Calc: C, 22.02; H, 0.92; Fe, 17.07%. Anal. for II: C, 24.65; H, 1.40; Fe, 16.65. Calc: C, 24.64; H, 1.48; Fe, 16.45%.

3.2. IR spectra

The IR spectra were recorded as Nujol mull between CsI plates on a Carl Zeiss Specord 75 IR spectrophotometer.

3.3. Mössbauer spectra

The Mössbauer spectra were obtained at room temperature in the standard transmission geometry with a Wiss-El transducer and a ^{57}Co in Rh source. The samples were kept in vacuo in order to avoid oxidation during the measurements. The lines were fitted with Lorentzians without constraining any parameter and the isomer shift was made relative to sodium nitroprusside.

3.4. X-ray crystal structure

Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Table 3 summarizes the crystal data, data collection and refinement parameters. Unit-cell parameters were refined by a least-squares fit to the setting angles of 25 reflections ($14 \leq 2\theta \leq 22°$ for I and $12 \leq 2\theta \leq 20°$ for II). Intensity measurements were carried out by employing the ω-2θ scan technique. Three standard reflections were remeasured every hour of X-ray exposure and did not suffer appreciable intensity variation. Lorentz and polarization corrections were applied and an empirical absorption correction was also applied to both sets of data [14]. The structures were solved by means of the Patterson and Fourier methods. Refinements were carried out by full-matrix least-squares method minimizing $\Sigma\omega_i(k\,|F_o| - |F_c|)^2$ with $\omega_1^{-1} = \sigma(F)^2 + gF^2$ for observed and $\omega_1 = 0$ for unobserved reflections until all atomic parameter shifts were smaller than each standard deviation [15]. The atomic scattering factors were taken from Cromer and Mann [16], and the dispersion correction factors from Ref. [17].

Table 3
Crystallographic data for $Hg[Fe(COOR)(CO)_4]_2$ with $R = CH_3$ for compound I and $R = C_2H_5$ for compound II

	I	II
Formula	$HgFe_2O_{12}C_{12}H_6$	$HgFe_2O_{12}C_{14}H_{10}$
Formula weight	654.45	682.50
Crystal system	triclinic	tetragonal
Crystal size (mm)	0.05×0.05×0.10	0.075×0.05×0.10
Space group, Z	$p\bar{1}$, 1	$I4_1$, 8
Unit-cell parameters		
a, Å	6.272(2)	17.906(3)
b, Å	6.441(3)	17.906(3)
c, Å	11.703(4)	12.756(2)
α, °	92.94(3)	90
β, °	103.77(3)	90
γ, °	96.10(2)	90
V, Å^3	455.1(5)	4089(2)
D_C, g cm^{-3}	2.388	2.217
μ(Mo Kα), cm^{-1}	100.4	89.5
F(000)	306	2576
λ(Mo Kα), Å	0.70930	0.70930
θ range, °	0-25	0-23
Range in hkl, min.	−7, −7, 0	−13, 0, 0
Range in hkl, max.	7, 7, 13	13, 19, 13
Measured reflections	1691	1612
Unique reflections	1603	1381
Observed reflections $[I \geq 3\sigma(I)]$	1564	603
Transmission factors min. and max.	0.76, 1.27	0.86, 1.36
Number of parameters	127	136
Value of g in w	0.00072	0.000042
Final R' and R_w	0.028, 0.030	0.053, 0.047
Goodness of fit	1.13	1.36

Final atomic coordinates and equivalent isotropic temperature factors [18] are given in Tables 4 and 5 for compounds I and II respectively.

Table 4
Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) for compound I; e.s.d. values in parentheses

Atom	x	y	z	B_{eq} [a]
Hg	0	0	0	2.72(1)
Fe	0.2218(1)	−0.1292(1)	0.1917(1)	2.52(2)
C(1)	0.379(1)	−0.205(1)	0.3326(6)	3.8(2)
O(1)	0.474(1)	−0.250(1)	0.4187(5)	6.4(2)
C(2)	0.4402(9)	0.0369(9)	0.1554(5)	3.3(1)
O(2)	0.5828(8)	0.1470(8)	0.1348(5)	5.3(2)
C(3)	−0.046(1)	−0.2513(9)	0.2018(5)	3.3(1)
O(3)	−0.2101(7)	−0.3283(8)	0.2116(5)	4.8(1)
C(4)	0.2663(9)	−0.3534(9)	0.1010(5)	3.2(1)
O(4)	0.2897(8)	−0.4922(7)	0.0439(4)	4.6(1)
C(5)	0.145(1)	0.1301(9)	0.2724(5)	3.6(2)
O(5)	0.179(1)	0.3061(8)	0.2515(7)	8.5(3)
O(6)	0.049(1)	0.0843(7)	0.3585(5)	5.6(2)
C(6)	−0.013(2)	0.259(1)	0.4222(7)	6.2(3)

[a] $B_{eq} = 8\pi^2/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i.a_j$.

Table 5
Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) for compound II; e.s.d values in parentheses

Atom	x	y	z	B_{eq} [a]
Hg	0	0.2500	0.4192(2)	3.29(8)
Fe	0.0827(2)	0.1324(2)	0.4139(3)	3.2(2)
C(1)	0.079(1)	0.144(1)	0.549(3)	2.0(1)
C(2)	−0.003(2)	0.079(2)	0.407(2)	5.0(1)
O(1)	0.081(1)	0.149(1)	0.644(2)	6.0(1)
O(2)	−0.054(1)	0.040(1)	0.411(2)	5.1(9)
O(3)	0.187(1)	0.006(1)	0.406(2)	7.0(1)
O(4)	0.080(1)	0.164(1)	0.186(2)	6.0(1)
O(5)	0.227(1)	0.191(1)	0.477(2)	7.0(1)
O(6)	−0.168(1)	0.236(1)	0.370(2)	4.3(8)
C(3)	0.145(2)	0.053(2)	0.414(2)	4.0(1)
C(4)	0.078(2)	0.153(2)	0.272(3)	5.0(1)
C(5)	0.171(2)	0.204(2)	0.430(3)	4.0(1)
C(6)	−0.228(2)	0.184(2)	0.374(3)	8.0(1)
C(7)	−0.217(2)	0.124(2)	0.299(3)	7.0(1)

[a] $B_{eq} = 8\pi^2/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i . a_j$.

Supplementary material

Tables of hydrogen coordinates, thermal parameters, and structure factors have been deposited with the Cambridge Crystallograph Data Centre or are available from the authors.

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