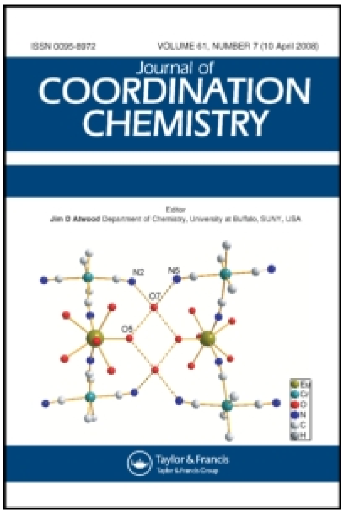

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SYNTHESIS AND STRUCTURE OF IRON(III) AND CHROMIUM(III) COMPLEXES OF 2-DIETHOXYPHOSPHONYL-2-PHENYLETHEN-1-OL

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SYNTHESIS AND STRUCTURE OF IRON(III) AND CHROMIUM(III) COMPLEXES OF 2-DIETHOXYPHOSPHONYL-2-PHENYLETHEN-1-OL

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Iron(III) and chromium(III) complexes of 2-diethoxyphosphonyl-2-phenylethen-1-ol (**2** and **3** respectively) have been synthesized and characterized by IR and electronic spectroscopic data. IR spectra have shown that **2** and **3** exist in (Z)-chelate and (E)-enolate forms. The crystal structure of **2** has been solved by X-ray methods. Crystal data: $M = 821.54$, monoclinic, $P2_1/c$, $a = 19.249(5)$, $b = 8.211(3)$, $c = 25.313(5)$Å, $\beta = 98.10(2)°$, $V = 4106(4)$Å, $Z = 4$, $D_x = 1.328$ g.cm^{-3}, $R = 0.081$, $R_w = 0.086$ for 3012 reflections with $I > 2\sigma(I)$. The structure consists of discrete ML_3 units in which the Fe cation is octahedrically coordinated by the three chelating ligands. The electronic spectrum of **3** indicated an octahedral structure as well.

KEYWORDS: iron, chromium, 2-diethoxyphosphonyl-2-phenylethen-1-ol, crystal structure

INTRODUCTION

In previous papers[1-3] we have explored the reactivtity of esters of 2-oxoalkyl- and 2-oxophenylalkylphosphonic acids in salt and complex formation. It has been shown that the lithium salt of 2-diethoxyphosphonyl-2-methylethen-1-ol exists as a mixture of (Z)- and (E)-forms, while the lithium salt and zinc complex of 2-diethoxyphosphonyl-2-phenylethen-1-ol, **1**, have the (Z)-chelate structure.[2] Experimental data indicate that the cobalt(II) and nickel(II) complexes of **1**, obtained from the corresponding metal acetates, are octahedrically coordinated by the bidendate phosphonyl and acetate ligands.[3] EPR evidence of formation of two different copper(II) complex species (square-planar and octahedral) in solution has been obtained.[3]

In the present paper we report the synthesis and characterization of the iron(III) complex of 2-diethoxyphosphonyl-2-phenylethen-1-ol,**2**, and the chromium(III)

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complex of 2-diethoxyphosphonyl-2-phenylethen-1-ol,**3**, as well as the crystal structure of complex **2**.

EXPERIMENTAL

Reagents and measurements

The ligand **1** was obtained by literature methods.[4] $CrCl_3.3THF$ was synthesized by a method described in ref. 5. The solvents tetrahydrofuran (THF), diethyl ether and hexane were dried by distillation from sodium benzophenone. Methanol was destilled from CaH_2. Analytical data were obtained from the Microanalytical Laboratory of the Department of Chemistry, University of Sofia. Electronic and IR spectra were recorded on Specord UV-vis (VEB Carl Zeiss, Jena) and Specord IR-71 spectrophotometers. The crystal data and intensities were collected on an Enraf-Nonius CAD-4 difractometer (Enraf-Nonius Software 1988).[6]

Synthesis of the complexes

Tris(2-diethoxyphosphonyl-2-phenylethen-1-olato)iron, 2

NaOH (0.129 g, 3 mmol) was added to a solution of **1** (0.770 g, 3 mmol) in 4 cm^3 of anhydrous methanol and immediately was added a solution of anhydrous $FeCl_3$ (0.160 g, 1 mmol) in 4 cm^3 of methanol. The red reaction mixture was stirred for 6 hours at room temperature and left overnight. The precipitate of sodium chloride was filtered off*, the solvent was removed in vacuum and the resulting oil stirred with 5 cm^3 of ether/hexane (3:2) for 30 min. The precipitate was filtered off, washed with 2 cm^3 of hexane and dried in vacuum. The yield of crude tris-(2-diethoxyphosphonyl-2-phenylethen-1-olato)iron, **2**, is 0.520 g (63.3%); m.p. 111–119°C. After recrystallisation from ether/hexane (2:1) dark red needles of complex **2** were isolated (0.350 g, 42.5%), m.p. 116–118°C. The complex is soluble in ether, hexane, $CHCl_3$, THF, DMF, benzene, toluene, isopropanol, ethanol and methanol and insoluble in water. Anal.; calcd. for $C_{36}H_{48}O_{12}P_3Fe$ (821.369): C, 52.64; H, 5.88; Fe, 6.79%. Found: C, 52.40; H, 5.83; Fe, 6.45%. Ebullioscopic molecular weight (in THF) 780 ± 39 D. Crystals for the structure determination were grown by slow evaporation from a toluene solution.

Tris(2-diethoxyphosphonyl-2-phenylethen-1-olato)chromium, 3

a) To a solution of the ligand **1** (1.14 g, 4.5 mmol + 10% excess) in 6 cm^3 of anhydrous THF, sodium hydroxide (0.180 g, 4.5 mmol) was added under argon and immediately a solution of $CrCl_3.3THF$ (0.540 g, 1.5 mmol) in 6 cm^3 of THF was added. The dark green reaction mixture was stirred for two hours at room temperature, the precipitate of sodium chloride was filtered off and washed with THF. The solvent was removed in vacuum and the residue (1.20 g) was treated with a mixtue of ether/H_2O (3:2). The ether solution was dried with anhydrous $MgSO_4$. After removing the solvent, the oil (0.72 g, 57.6%) was dissolved in ether/hexane(2:1). Crystals of complex **3**, precipitated from the solution after a long time at − 20°C, were filtered off and washed with hexane. The dark green crystals of **3**

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*Separation of sodium chloride is possible by washing the dried reaction mixture with 5 cm^3 of water.

(0.25 g) have m.p. 148–150°C and are soluble in ether, $CHCl_3$, THF, methanol, but poorly soluble in hexane. Anal.; calcd. for $C_{36}H_{48}O_{12}P_3Cr.H_2O$ (835.52): C, 51.75; H, 6.02; Cr, 6.22%. Found: C, 51.80; H, 5.90; Cr, 6.33%.

b) A solution of 2-diethoxyphosphonyl-2-phenylethen-1-olato-sodium (0.584 g, 2.1 mmol)[7] in 17 cm^3 of THF was added dropwise over 30 min to a solution of $CrCl_3$.3THF (0.262 g, 0.7 mmol) in 25 cm^3 of THF under argon. The green solution was stirred for 2.5 hours at room temperature, filtered off and evaporated in vacuum. After addition of a benzene/hexane mixture (8 cm^3, 1:1) the precipitated sodium chloride (0.100 g, 83%) was filtered off and the solvents were evaporated in vacuum to a dark green oil (0.450 g, 78.7%). This oil was dissolved in 3 cm^3 of ether and 1.5 cm^3 of the solution placed on alumina column (30 cm x 1 cm) packed under argon as a slurry in hexane. Elution with a pentane-acetone mixture (from 99:1 to 80:20) and collection of the dark green fractions with $R_f = 0.60$ (tlc in toluene/$CHCl_3$/CH_3OH 8:3:1.5) gave after evaporation 0.080 g of a dark green oil of complex **3** which could not crystallize. Anal.; calcd. for $C_{36}H_{48}O_{12}P_3Cr$ (817.518): C, 52.89; H, 5.91%. Found: C, 53.84; H, 6.44%.

X-ray data collection

Experimental details and relevant crystallographic data for **2** are summarized in Table 1. Cell constants for **2** were determined from a least-squares refinement of

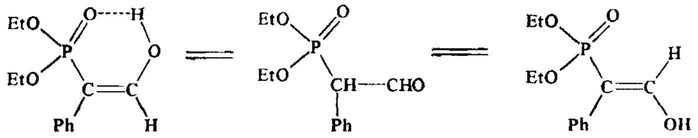
Table 1 Crystal data and experiment details for **2**.

formula	$C_{36}H_{48}FeO_{12}P_3$
molecular weight	821.54
crystal dimensions, mm	0.53 × 0.43 × 0.09
crystal system	monoclinic
space group	$P2_1/n$
a, Å	19.249(5)
b, Å	8.511(3)
c, Å	25.313(5)
β,°	98.10(2)
V, Å^3	4106(4)
Z	4
D_x, g.cm^{-1}	1.328
temperature, K	292
μ, cm^{-1}	0.53
F(000)	821.55
radiation	MoKα(λ = 0.71073)
monochromator	graphite crystal
scan method	ω/2θ
scan width/deg	0.80±0.35 tg(θ)
θ max/deg	24
hkl range	$+h, +k, l$
total reflections	6637
unique feflections	6423
$R_{int}(F)$	0.017
reflections used, I >2 σ(I)	3012
R	0.081
R_W	0.086
final GOF	3.581
weighting scheme	unit weights
maxΔ/σ	0.35

difractometer angles for 22 automatically centred reflections with 20.0 < θ< 21.0°. Three standard reflections were monitored every two hours (1.9% gain of intensity). The structure was solved by MULTAN/82[8] followed by normal heavy atom procedures. It was refined by full-matrix least-squares methods with isotropic non-hydrogen atoms and subsequent restrained least-square refinement with geometrical restraints on phenyl and ethoxy groups, all atoms being anisotropic. Most H-atoms were calculated and refined with fixed overall U_{eq} = 0.1013Å^2. Unit weights for all observed reflections were used. After the convergence reached to R = 0.152 and R_H = 0.178, empirical absorption correction based on F[9] with two sets of starting thermal parameters was performed (max., min. correction factors = 1.272, 0.553). The first one with lower U_{eq} (0.038 for Fe and P, 0.0507 for O and C_{phenyl} and 0.063Å^2 for C_{ethoxy} and H) gave R = 0.099 and R_H = 0.089. The second model with higher U_{eq} (0.063 for Fe and P, 0.082 for O and C_{phenyl}, 0.114 for C_{ethoxy} and 0.101Å^2 for H) converged to a final R = 0.081 and R_W = 0.086. Atomic scattering data were as given in SDP/PDP V3.O.[10] Fractional coordinates and equivalent thermal parameters for the non-hydrogen atoms are given in Table 2.

RESULTS AND DISCUSSION

The ligand **1** was obtained according to reference 4, using ethyl formate as formylating agent. It was a mixture of aldehyde, (Z)- and (E)-enol forms, which indicates that, unlike β-dicarbonyl compounds, the (E)-tautomer appears to have similar stabilisation by intermolecular H- bonding as the intramolecular bonding in the (Z)-tautomer.[2] Elemental analyses of the complexes **2** and **3** proved the ligand:metal ratio to be 3:1, the structure of the complexes being L_3Fe and L_3Cr (L = $(EtO)_2P(O)CHPh$ = CH-O)$^-$. The solubility and the experimental value of the molecular weight (780±39 D, THF, 45°C) showed that the iron (III) complex **2** exists in monomeric form.



(Z)-1

(E)-1

Scheme 1 Keto-enol equilibrium of ligand **1**.

Spectroscopic data

IR data, given in Table 3, prove that the crystalline precipitates of **2** and **3** contain two kinds of complexes: (Z)- and (E)- enolates. In (Z)- enolates the complexation leads to a shifts of 30–35 cm^{-1} for P=O and 65–70 cm^{-1} for C=C stretching vibrations with respect to the starting ligand (Z- enol), indicating its chelate structure. A similar shift of 30 cm^{-1} for P=O and 75 cm^{-1} for C=C stretching vibrations was observed for (E)- enolate forms of **2** and **3** (towards to the starting (E)- enol),

Table 2 Positional and equivalent isotropic displacement parameters ($Å^2$) for the non-hydrogen atoms in **2**.

Atom	*x/a*	*y/b*	*z/c*	*Ueq*
Fe	0.21278(8)	0.1047(2)	0.15902(6)	0.0632(4)
Pa	0.3448(2)	0.1312(4)	0.0926(1)	0.0680(9)
Pb	0.0902(2)	0.3151(5)	0.0928(1)	0.081(1)
Pc	0.2765(2)	0.3054(4)	0.2618(1)	0.072(1)
O1a	0.2098(4)	- 0.0618(9)	0.1061(3)	0.080(2)
O2a	0.3053(4)	0.1735(9)	0.1377(3)	0.076(2)
O3a	0.3601(4)	0.2753(9)	0.0574(3)	0.079(3)
O4a	0.4231(4)	0.088(1)	0.1137(3)	0.086(3)
O1b	0.1209(4)	0.0523(9)	0.1778(3)	0.082(3)
O2b	0.1649(4)	0.261(1)	0.1049(3)	0.079(3)
O3b	0.0553(5)	0.266(2)	0.0364(4)	0.140(4)
O4b	0.0848(4)	0.499(1)	0.0891(4)	0.103(3)
O1c	0.2576(4)	- 0.0319(9)	0.2161(3)	0.081(3)
O2c	0.2237(4)	0.2827(9)	0.2119(3)	0.074(2)
O3c	0.2392(4)	0.383(1)	0.3048(3)	0.100(3)
O4c	0.3350(4)	0.428(1)	0.2550(4)	0.100(3)
C1a	0.2446(6)	- 0.086(1)	0.0662(4)	0.071(4)
C2a	0.3016(5)	- 0.017(1)	0.0525(4)	0.061(3)
C3a	0.4373(8)	- 0.025(2)	0.1542(7)	0.150(7)
C4a	0.496(1)	0.025(3)	0.1949(7)	0.22(1)
C5a	0.3017(7)	0.352(2)	0.0264(6)	0.114(5)
C6a	0.3215(9)	0.522(2)	0.0179(7)	0.150(7)
C11a	0.3300(5)	- 0.064(1)	0.0033(4)	0.061(3)
C12a	0.3991(6)	- 0.100(1)	0.0019(5)	0.082(4)
C13a	0.4232(6)	- 0.151(2)	- 0.0450(5)	0.098(5)
C14a	0.3773(7)	- 0.171(2)	- 0.0906(5)	0.097(5)
C15a	0.3087(7)	- 0.137(2)	- 0.0909(5)	0.088(4)
C16a	0.2846(6)	- 0.083(1)	- 0.0447(5)	0.079(4)
C1b	0.0615(6)	0.123(2)	0.1707(5)	0.083(4)
C2b	0.0376(5)	0.243(1)	0.1390(4)	0.074(4)
C3b	0.1218(9)	0.599(2)	0.1290(8)	0.156(8)
C4b	0.075(1)	0.666(3)	0.1657(8)	0.22(1)
C5b	0.079(1)	0.291(3)	- 0.0123(8)	0.22(1)
C6b	0.095(2)	0.129(4)	- 0.032(1)	0.32(2)
C11b	- 0.0343(6)	0.307(1)	0.1389(5)	0.078(4)
C12b	- 0.0596(6)	0.338(2)	0.1878(5)	0.093(5)
C13b	- 0.1264(7)	0.393(2)	0.1885(6)	0.111(5)
C14b	- 0.1689(7)	0.417(2)	0.1422(5)	0.096(5)
C15b	- 0.1459(7)	0.390(2)	0.0948(5)	0.096(5)
C16b	- 0.0793(6)	0.334(2)	0.0937(5)	0.112(5)
C1c	0.3007(6)	- 0.003(1)	0.2593(4)	0.070(4)
C2c	0.3205(5)	0.132(1)	0.2848(4)	0.064(3)
C3c	0.3186(8)	0.582(2)	0.2353(7)	0.146(7)
C4c	0.335(1)	0.595(2)	0.1791(8)	0.185(8)
C5c	0.1776(8)	0.318(2)	0.3206(6)	0.168(7)
C6c	0.118(1)	0.428(3)	0.3124(9)	0.23(1)
C11c	0.3749(5)	0.129(1)	0.3325(4)	0.068(3)
C12c	0.4315(6)	0.029(2)	0.3338(5)	0.081(4)
C13c	0.4818(6)	0.019(2)	0.3779(5)	0.095(5)
C14c	0.4755(7)	0.111(2)	0.4230(5)	0.099(5)
C15c	0.4215(7)	0.214(2)	0.4205(5)	0.100(5)
C16c	0.3708(6)	0.223(2)	0.3772(5)	0.085(4)

Table 3 Selected IR data (nujol; ν/cm^{-1}) for ligand **1**, the iron (III) complex **2** and the chromium (III) complex **3**.

Ligand **1**	Iron complex **2**	Chromium complex **3**	Ass
1020	1015	1015	$\nu_{P\text{-}O\text{-}C}$
1050	1040	1014	
1165^a	1130	1135	$\nu_{P=O}$
1200^b	1170	1170	
1250^c			
1600^a	1530	1535	$\nu_{C=C}$
1635^b	1560	1560(infl.)	
2700^b			$\nu_{O\text{-}H}$

^{a}In (Z)- enol. ^{b}In (E)- enol. ^{c}In aldehyde form.

due to a possible intermolecular coordination in dimeric or oligomeric structures. The decrease of the P=O stretch in respect to the starting aldehyde form of **1**[2] is 115–120 cm^{-1} for the (Z)- enolate form of **2** and **3** and 80 cm^{-1} for the (E)- enolate **2** and **3** (see Table 3). These data are in agreement with the literature for complexes with neutral or ionic ligands (dcrease of 80–100 cm^{-1} compared to the starting ketone).[11–13] The observed data show considerable differences in shifts of P=O stretch in the ligands (Z)- **1** and (E)- **1** towards to the aldehyde form of **1**, while the decrease of frequences, due to the complexation in (Z)- and (E)- complexes **2** and **3** with respect to the corresponding enols are almost equal.

In order to obtain some information on the stereochemistry of the complexes **2** and **3** experiments were performed to prepare suitable crystals for X-ray investigations. Attempts were successful only in the case of the iron(III) complex, **2**. For that reason the supposition of an octahedral structure for the chromium (III) complex, **3**, is based only on electronic spectroscopic data. A solution of **3** in chloroform (conc. 1×10^{-2} M; $1 = 2$ cm) shows a maximum at $\lambda = 620$ nm, corresponding to the transition $^4A_2 \rightarrow {}^4T_2$. The location of this maximum, as well as the value of ε (47 l mol^{-1} cm^{-1}) is in agreement with literature data[11,14] for chromium (III) complexes with octahedral stereochemistry.

Crystal structure

The crystal structure of tris(2-diethoxyphosphonyl-2-phenylethen-1-olato)iron, **2**, consists of discrete ML_3 units in which the Fe cation is octahedrically coordinated by the three chelating ligands (Fig. 1). The twist angle φ between the 'basal' triangular faces[15] is 56.6°. The $Fe\text{-}O_{(phosphonyl)}$ average bond length [1.950(8) Å] is shorter by 9σ than the $Fe\text{-}O_{(carrbonyl)}$ average [2.223(8) Å]. The intra-chelate O1-Fe-O2 angle is 88.2(3)°. This value is similar to the angle in the previously studied[13] complex tris(di-O-ethyl-1-cyano-2-oxoprophylphosphonato)-zincate(II), $Zn(CNpaac)_3^-$, 87.3(2)°. The chelate O...O bite distances vary in the range 2.754(11)–2.778(11) Å, while the inter-chelate O...O distances vary in the much wider range 2.768(10)–2.889(11) Å. The fold angles along the O...O are 10.1(9), 11.4(9) and 20.0(5)° for a-, b- and c- ligands respectively. These values are smaller than those in $Zn(CNpaac)_3^-$ [26.0(4)°], the latter representing the greatest deviation known for such complexes.[13] The chelate parts of the ligands are planar to within ±0.036(3), ±0.076(7) and ±0.025(9)Å respectively. The Fe atom deviates from the corresponding planes by 0.252(2), −0.285(2) and

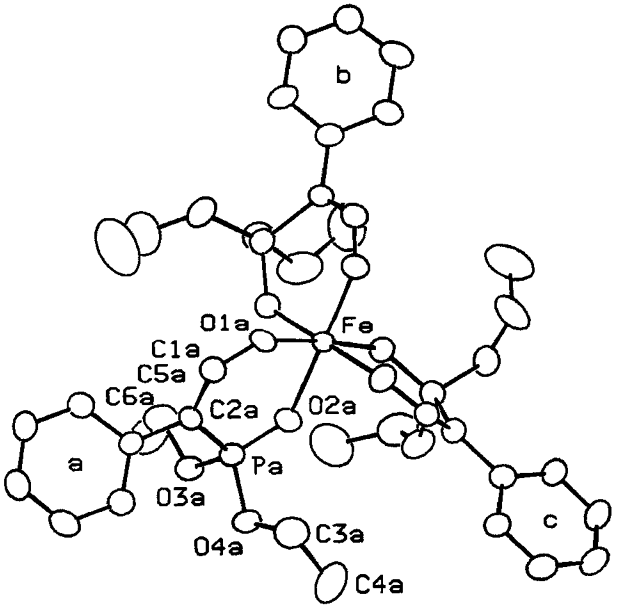


Figure 1 The molecule 2 (ORTEP II, Johnson, 1976) with the atom numbering scheme; 20% probability thermal ellipsoids. H atoms are omitted for clarity.

0.497(2)Å. Phenyl rings are rotated with respect to the chelate planes by 47.9(3), 46.3(4) and 36.3(5)°, respectively. Bond lengths and angles in the chelating parts of the ligands (Table 4) indicate a delocalization including the phosphorus atom. Strong support for that conclusion is the average length of the P-C bonds [1.758(11) Å] which seems to be strongly influenced by coordination. Literature data for phsphonates show that the range of variation of this bond length (1.812–1.832 Å) for non-coordinated phosphonates reduces to 1.784–1.792 Å for neutral β-ketophosphonate ligands and further to 1.695–1.734 Å for ionic ligands.[13] As seen from Table 4 the length of the P=O group in **2** [average length 1.506(8)Å] is significantly changed by complexation (irrespective of the P=O groups in phosphonate ligands (1.451–1.471Å).[13,16] The length of the P=O bond in **2** is the greatest observed for phosphonate complexes with neutral and ionic ligands (1.464–1.490Å; compare with ref. 13). The C1–C2 bond in **2** [average length 1.338(16)Å] is shortened in comparison with the C–C bond in β-hydroxyethane- phosphonic ester [1.552(5) Å].[16] These data prove a π-electron distribution, including P=O, as shown below

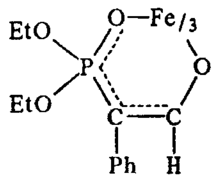


Table 4 Interatomic distances (Å) and angles (°) for **2**.

Fe-O1a	1.946(8)	O1a-C1a	1.303(14)	C1b-C2b	1.338(17)
Fe-O2a	2.019(8)	O3a-C5a	1.435(15)	C2b-C11b	1.490(16)
Fe-O1b	1.947(8)	O4a-C3a	1.407(20)	C3b-C4b	1.499(31)
Fe-O2b	2.034(8)	O1b-C1b	1.282(14)	C5b-C6b	1.512(43)
Fe-O1c	1.957(8)	O3b-C5b	1.395(25)	C11b-C12b	1.418(19)
Fe-O2c	2.014(8)	O4b-C3b	1.432(20)	C11b-C16b	1.351(17)
Pa-O2a	1.502(9)	O1c-C1c	1.299(13)	C12b-C13b	1.372(18)
Pa-O3a	1.568(9)	O3c-C5c	1.415(19)	C13b-C14b	1.347(18)
Pa-O4a	1.570(8)	O4c-C3c	1.425(18)	C14b-C15b	1.356(19)
Pa-C2a	1.752(11)	C1a-C2a	1.332(16)	C15b-C16b	1.373(19)
Pb-O2b	1.500(8)	C2a-C11a	1.485(16)	C1c-C2c	1.345(15)
Pb-O3b	1.547(10)	C3a-C4a	1.490(25)	C2c-C11c	1.483(14)
Pb-O4b	1.569(10)	C5a-C6a	1.517(23)	C3c-C4c	1.507(28)
Pb-C2b	1.761(12)	C11a-C12a	1.371(16)	C5c-C6c	1.461(29)
Pc-O2c	1.516(8)	C11a-C16a	1.402(15)	C11c-C12c	1.380(16)
Pc-O3c	1.537(9)	C12a-C13a	1.404(19)	C11c-C16c	1.394(17)
Pc-O4c	1.561(9)	C13a-C14a	1.361(17)	C12c-C13c	1.373(16)
Pc-C2c	1.762(11)	C14a-C15a	1.351(19)	C13c-C14c	1.405(19)
		C15a-C16a	1.393(18)	C14c-C15c	1.353(20)
				C15c-C16c	1.363(16)
O1a-Fe-O2a	88.2(3)	O1a-C1a-C2a	131.6(1.0)		
O1a-Fe-O1b	93.6(3)	Pa-C2a-C1a	120.5(9)		
O1a-Fe-O2b	92.6(3)	Pa-C2a-C11a	118.8(8)		
O1a-Fe-O1c	92.5(3)	C1a-C2a-C11a	120.7(1.0)		
O1a-Fe-O2c	175.1(3)	O4a-C3a-C4a	110.8(1.6)		
O2a-Fe-O1b	176.0(3)	O3a-C5a-C6a	108.9(1.1)		
O2a-Fe-O2b	87.9(3)	C2a-C11a-C12a	123.8(9)		
O2a-Fe-O1c	93.2(3)	C2a-C11a-C16a	120.0(9)		
O2a-Fe-O2c	86.9(3)	C12a-C11a-C16a	116.1(1.1)		
O1b-Fe-O2b	88.4(3)	C11a-C12a-C13a	121.9(1.0)		
O1b-Fe-O1c	90.3(3)	C12a-C13a-C14a	120.2(1.2)		
O1b-Fe-O2c	91.3(3)	C13a-C14a-C15a	119.7(1.2)		
O2b-Fe-O1c	174.9(3)	C14a-C15a-C16a	120.4(1.1)		
O2b-Fe-O2c	87.2(3)	C11a-C16a-C15a	121.6(1.1)		
O1c-Fe-O2c	87.8(3)	O1b-C1b-C2b	131.8(1.2)		
O2a-Pa-O3a	113.6(5)	Pb-C2b-C1b	118.9(9)		
O2a-Pa-O4a	111.2(4)	Pb-C2b-C11b	119.4(9)		
O2a-Pa-C2a	111.3(5)	C1b-C2b-C11b	121.5(1.1)		
O3a-Pa-O4a	97.4(4)	O4b-C3b-C4b	112.2(1.4)		
O3a-Pa-C2a	110.2(5)	O3b-C5b-C6b	105.2(2.1)		
O4a-Pa-C2a	112.5(5)	C2b-C11b-C12b	120.0(1.0)		
O2b-Pb-O3b	112.6(5)	C2b-C11b-C16b	123.2(1.2)		
O2b-Pb-O4b	111.9(5)	C12b-C11b-C16b	116.8(1.1)		
O2b-Pb-C2b	112.4(5)	C11b-C12b-C13b	120.9(1.1)		
O3b-Pb-O4b	101.3(6)	C12b-C13b-C14b	119.6(1.4)		
O3b-Pb-C2b	107.6(6)	C13b-C14b-C15b	120.9(1.3)		
O4b-Pb-C2b	110.4(6)	C14b-C15b-C16b	119.8(1.2)		
O2c-Pc-O3c	108.7(5)	C11b-C16b-C15b	122.1(1.3)		
O2c-Pc-O4c	113.8(5)	O1c-C1c-C2c	132.1(1.0)		
O2c-Pc-C2c	113.8(5)	Pc-C2c-C1c	117.8(8)		
O3c-Pc-O4c	101.9(5)	Pc-C2c-C11c	122.2(8)		
O3c-Pc-C2c	112.1(5)	C1c-C2c-C11c	120.0(9)		
O4c-Pc-C2c	106.0(5)	O4c-C3c-C4c	109.4(1.3)		
Pa-O3a-C5a	118.2(8)	O3c-C5c-C6c	112.3(1.7)		
Pa-O4a-C3a	119.1(9)	C2c-C11c-C12c	119.5(1.0)		
Pb-O3b-C5b	128.3(1.2)	C2c-C11c-C16c	122.5(1.0)		
Pb-O4b-C3b	121.7(9)	C12c-C11c-C16c	117.9(1.0)		
Pc-O3c-C5c	121.7(1.0)	C11c-C12c-C13c	121.5(1.2)		
Pc-O4c-C3c	121.7(9)	C12c-C13c-C14c	119.5(1.2)		
		C13c-C14c-C15c	118.5(1.1)		
		C14c-C15c-C16c	122.2(1.3)		
		C11c-C16c-C15c	120.2(1.2)		

The molecules in the complex **2** are held together by van der Waals forces only.

SUPPLEMENTARY DATA

Lists of H atom coordinate, anisotropic thermal parameters and observed and calculated structure factors are available from JP upon request.

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