

Octahedral Complexes of Fe(III) with Phosphorylic Ligands Closely Related to β -Diketones

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Iron(III) coordination compounds of the general formula FeL_3 (where $\text{L}^1 = \{\text{CCl}_3\text{C}(\text{O})\text{NP}(\text{O})[\text{N}(\text{C}_2\text{H}_5)_2]_2\}^-$ -N,N'-tetraethyl-N''-trichloroacetylphosphoric triamide anion, and $\text{L}^2 = \{\text{CCl}_3\text{C}(\text{O})\text{NP}(\text{O})[\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}]_2\}^-$ -dimorpholido-N-trichloroacetylphosphoricamide anion) have been synthesized and characterized by means of IR, UV-VIS, ESR spectroscopy, and X-ray analysis. The complexes have a molecular structure with the phosphoryl ligands coordinated to the metal ion in a bidentate manner *via* phosphoryl and carbonyl oxygen atoms with formation of six membered chelate rings. The coordination around the Fe(III) atoms is distorted octahedral, to give *fac*-isomers in both structures.

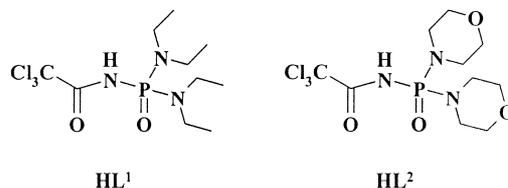
Introduction

Metal acetylacetonate complexes which can be used as phase precursors in alkoxo syntheses of esters, continue to attract considerable attention [1 - 4]. In previous studies [5], the synthesis of chiral manganese(III) and iron(III) binaphthyl Schiff-base complexes of the general formula $[\text{M}^{\text{III}}\text{L}(\text{acac})]$ were investigated in asymmetric catalysis. A new reducing system trialkylsilane - transition metal acetylacetonate used in organic synthesis was reported by Russian authors in a series of publications [6 - 8].

Carbacylamidophosphates of the general formula $\text{R}^n\text{C}(\text{O})\text{NHP}(\text{O})\text{R}'_2$ are P,N-substituted analogues of β -diketones and potential O,O'-donor ligands. They may be regarded as powerful chelating systems for various metal ions [9]. Contrary to the extensively studied β -diketonate complexes and their derivatives with one or both O atoms substituted by NH, S or Se [10], the coordination chemistry of heterosubstituent phosphorylic analogues remains relatively poorly elaborated.

The first studies of the coordination chemistry of transition metals with N,N'-tetraethyl-N''-benzoylphosphoric triamide and the dimethyl ester of trichloroacetylamidophosphoric acid were reported

earlier [11, 12]. Following these investigations we were successful in preparing stable molecular $[\text{M}\{\text{L}\}_3]$ species with N,N'-tetraethyl-N''-trichloroacetylphosphoric triamide (**HL**¹) and dimorpholido-N-trichloroacetylphosphoricamide (**HL**²) ligands.



Here we report the synthesis and results of spectral and X-ray studies of the Fe(III) complexes.

Experimental Section

Synthesis

The phosphorylic ligands **HL**¹ and **HL**² and their sodium salts were prepared according to the literature [13, 14]. The coordination compounds $[\text{Fe}\{\text{L}^1\}_3]$ (**1**) and $[\text{Fe}\{\text{L}^2\}_3]$ (**2**) were synthesized according to the following scheme:



For the synthesis of **1**, dry acetone was used as a solvent. Iron(III) nitrate nonahydrate [0.2104 g (0.5 mmol)]

was dissolved in 15 ml of the solvent and triethylorthoformate [0.66 ml (dehydration agent)] was added. The resulting solution was combined with a solution of NaL¹ [0.5650 g (1.5 mmol)]. The precipitate of NaNO₃ was filtered off and the clear solution obtained was evaporated slowly in a vacuum desiccator over dry CaCl₂. The crystals precipitated from the solution after standing for 3 d, and were filtered, washed with a few drops of 2-propanol and dried over CaCl₂. The yield was 0.361 g (65 %).

For the synthesis of **2**, a solution of the complex was prepared starting with 0.1935 g (0.46 mmol) of Fe(NO₃)₃·9H₂O and 0.5252 g (1.38 mmol) of NaL² in absolute methanol and evaporated until dry. The residue was dissolved in a methanol / 2-propanol mixture (1:9, v/v), the precipitate of NaNO₃ was filtered off and the solution of the complex was allowed to stand in a vacuum desiccator over CaCl₂. The orange prismatic crystals of the complex were filtered, washed with cold 2-propanol and dried in air. The yield was 0.324 g (55 %).

The compounds are stable in air. **1** is soluble in CCl₄, benzene, but insoluble in alcohols; **2** is soluble in acetone and insoluble in CCl₄ and alcohols.

The composition of the complexes {FeL₃} as confirmed by microanalysis: **1**, C₃₀H₆₀N₉Cl₉O₆P₃Fe (1110,68 g·mol⁻¹): calcd. C 32.44, H 5.45, N 11.35; found C 32.25; H 5.36; N 11.35. **2**, C₃₀H₄₈N₉Cl₉O₁₂-P₃Fe (1178,46 g·mol⁻¹): calcd. C 30.16, H 4.05, N 10.56; found C 30.19, H 4.05, N 10.45.

Measurements

IR-spectra were recorded using an UR-10 spectrometer (Carl Zeiss, Jena) in the region 4000 to 400 cm⁻¹ (KBr pellets, nujol mulls and solutions in chloroform).

Electronic diffuse reflectance and absorption spectra of the complexes were recorded on a SPECORD M40 (Carl Zeiss, Jena) UV-VIS spectrometer and on a KSVU-23 (LOMO, USSR) IBM PC adapted spectrophotometer, respectively.

ESR spectra were recorded on powdered polycrystalline samples at X-frequency (ca. 9,4 GHz) under non-saturating conditions with a PS 100.X spectrometer (ADANI) at room temperature and at 77 K (liquid nitrogen).

The structures were solved by direct methods and refined by the least-squares method using the program SHELXS-86 and SHELXL-97 [15, 16]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of ethyl groups and morpholine rings were included in the refinement as fixed contributions with their isotropic *U* values set invariant at 0.08 Å².

Data collection for **1** were carried out at 100 K using a KM4CCD (Mo-radiation, graphite monochromator, λ =

0.71073 Å) area detector diffractometer. In the final difference map, the highest peak of 1.077 e·Å⁻³ was near atoms Cl(8A) (0.48 Å) and C(31) (2.04 Å). The chlorine atoms of one CCl₃ group in the structure were found to be disordered over two positions, and refinement of the isotropic *U* values suggested partial occupancies of the corresponding sites of 0.61 and 0.39.

Data collection of **2** were carried out at 223 K using a SMART CCD area detector diffractometer (Siemens) (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å). The trichloromethyl group shows positional disorder. The site occupancies of the disordered atoms were 0.57 and 0.43, and the C-Cl separations were constrained at 1.75(1) Å. In the area of morpholine rings [N(12), C(16), C(17), O(13), C(19), C(18)] some intense peaks of electronic density were disposed of. This fact can be explained by disordering of the morpholine groups over two positions. The disorderings were refined with site occupancy factors of 0.68 and 0.32. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Center and are available on request quoting the depository numbers CCDC-174761 for **1** and CCDC-174762 for **2** [17].

Results and Discussion

IR spectroscopy

The organic ligands are bidentate *via* the oxygen atoms of phosphoryl and carbonyl groups. This is confirmed by the IR-spectroscopic study. The valence vibration shifts of ν(P=O) and ν(C=O) in the low frequency region have the values: for complex **1** - Δ((P=O)) = 65 cm⁻¹ and Δ((C=O)) = 15 cm⁻¹; for complex **2** - Δ((P=O)) = 43 cm⁻¹ and Δ((C=O)) = 18 and 31 cm⁻¹ (with respect to the spectra of the sodium salts).

In the spectrum of complex **1** as a solid (KBr pellet), in the region of 1610 - 1625 cm⁻¹ two absorption bands ν(C=O) are observed, whereas in the spectrum of a chloroform solution only one band is observed at 1610 cm⁻¹. The presence of two bands ν(C=O) in the spectrum of the solid complex can be explained by Davydov splitting.

In the area 1330 - 1480 cm⁻¹ the intensive amide II absorption band is observed. This frequency is increased with respect to the sodium salts (~1340 cm⁻¹) by 105 - 145 cm⁻¹. The value of this shift exceeds that for ν(C=O) by 100 - 115 cm⁻¹. With the formation of six-membered rings the C=O bond order decreases and therefore the absorption band ν(C=O) shifts to lower frequencies. The mul-

	1	2
Empirical formula	C ₃₀ H ₆₀ C ₁₉ FeN ₉ O ₆ P ₃	C ₃₀ H ₄₈ C ₁₉ FeN ₉ O ₁₂ P ₃
Formula weight	1110.68	1178.46
Temperature (K)	100(2)	223(2)
Crystal system	orthorhombic	monoclinic
Space group	<i>Pbca</i>	<i>P2_{1/n}</i>
<i>a</i> (Å)	20.534(4)	22.809(1)
<i>b</i> (Å)	18.417(4)	10.1131(5)
<i>c</i> (Å)	26.727(5)	23.009(1)
β (°)		107.362(1)
Volume (Å ³)	10107(4)	5065.4(4)
Z	8	4
D _{calc} (g/cm ³)	1.460	1.545
Crystal size (mm)	0.4×0.4×0.25	0.2×0.3×0.3
Absorption coefficient (mm ⁻¹)	0.916	0.928
Radiation, λ (Å)	Mo-K α = 0.71073	Mo-K α = 0.71073
θ_{\max} for data reduction (°)	28.87	25.52
Reflections collected	67988	27787
Independent reflections	12514 [<i>R</i> (int) = 0.0483]	9421 [<i>R</i> (int) = 0.0629]
Observed reflections	8809	7875
Data / restraints / parameters	12514 / 0 / 560	7875 / 12 / 651
Goodness-of-fit on <i>F</i> ²	1.077	0.804
<i>R</i> 1, <i>wR</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0684, 0.1657	0.0482, 0.0800
<i>R</i> 1, <i>wR</i> (all data)	0.1001, 0.1758	0.1203, 0.1261
Largest diff. peak/hole (e ⁻ Å ⁻³)	1.077 / -1.084	0.585 / -0.368

Table 1. Crystal data and structure refinement for **1** and **2**.

tiplicity of the amide II band (with a participation of the C-N bond) increases. The displacement amounts to 25 - 35 cm⁻¹ in the spectrum of complexes (with respect spectra to the of the sodium salts), an additional confirmation for ligand coordination *via* the carbonyl group. The spectra of the title compounds do not exhibit bands in the characteristic region of ν (N-H) (*ca.* 3070 cm⁻¹) suggesting deprotonation of the ligand.

The UV-VIS absorption data are proof of an octahedral environment of the metal atoms. Thus, in the spectra of solutions in toluene (**1**) and acetone (**2**) the low intensity bands at 9330 cm⁻¹ correspond to ⁶A_{1g}→⁴T_{2g} transitions. The transition ⁶A_{1g}→⁴T_{1g} for the acetone solution of complex **2** (11800 cm⁻¹) is also observed with low intensity in the diffusion reflectance spectra (for **1** and **2** near 12000 cm⁻¹). The very intense absorptions at (22000 - 24000 cm⁻¹) correspond to charge transfer bands.

The ESR spectra of **1** and **2** are presented in Fig. 1. The form of the spectra is typical for high-spin iron(III) complexes. They are unchanged on cooling of the sample to 77 K. It has been shown that ESR spectra of "FeO₆" complexes are crucially dependent on very small changes in geometry about

the Fe center caused by lattice distortion, solvent molecules or counterions.

The most exhaustive ESR investigation of high-spin FeO₆ complexes has been carried out for a series of tris-chelate complexes of iron(III) [18]. These spectra were interpreted by using a spectrum simulation program based on matrix diagonalization methods for a general spin Hamiltonian, and a library of spectral types for high-spin ferric systems has been presented in a pictorial manner. The interpretation of the present ESR spectra was made by comparison with this model FeO₆ complexes.

The data can be described by means of a rhombic spin Hamiltonian:

$$\mathbf{H} = \beta \cdot \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + [S_z^2 - S(S+1)] + E(S_x^2 - S_y^2),$$

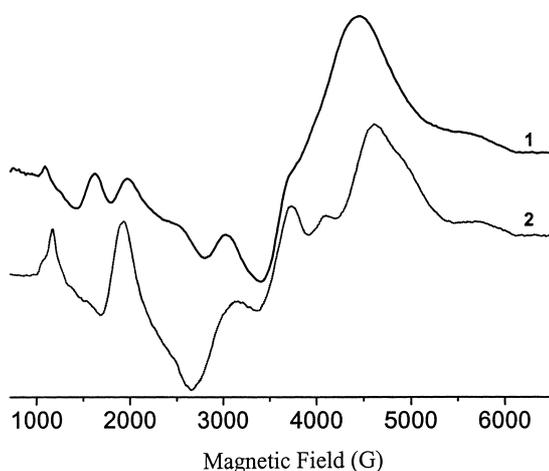
where β is the electronic Bohr's magneton, and \mathbf{H} is the applied magnetic field. The degree of rhombic distortion is indicated by the value of $\lambda = E/D$. Estimated parameters are $D = 0,1 \text{ cm}^{-1}$, $E = 0,03 \text{ cm}^{-1}$, $\lambda = 0,3$.

These results are in good agreement with a trigonally distorted octahedral array of oxygen atoms.

Table 1 lists the cell parameters and details of the data acquisition and structure refinement. The

Table 2. Average bond lengths (Å) and angles (°) for **1** and **2**.

Fe-O(P)	1.971(3)	1.979(3)
Fe-O(C)	2.027(3)	2.010(3)
P-O	1.516(3)	1.512(3)
O(Fe)-C	1.263(5)	1.263(5)
P-N	1.638(4)	1.631(4)
P-N(R)	1.632(4)	1.626(5)
N-C	1.289(5)	1.286(5)
C(O)-C(Cl)	1.557(6)	1.555(6)
O-Fe-O	89.5(1)	89.0(1)
C-O-Fe	129.27(3)	127.4(3)
P-O-Fe	130.0(1)	128.1(2)
O-C-N	131.9(4)	131.9(4)
C-N-P	123.07(3)	121.9(3)
N-P-O	114.3(1)	114.53(3)
O-P-N(R)	110.4(1)	110.17(2)
N(R)-P-N(R)	106.6(1)	105.4(2)

Fig. 1. ESR spectra of polycrystalline powders of $[\text{Fe}\{\text{L}^1\}_3]$ (**1**) and $[\text{Fe}\{\text{L}^2\}_3]$ (**2**) at 77 K.

principal interatomic distances and angles are listed in Table 2.

The complexes have a molecular structure (Fig. 1). There are no short contacts between neighboring molecules in the crystal. The phosphoramidic ligands are coordinated in a bidentate manner *via* the oxygen atoms of the phosphoryl and carbonyl groups. The coordination sphere of the central atoms may be characterized as a slightly distorted octahedron (FeO_6), and the coordination polyhedra represent the *fac*-isomers.

The six-membered metallacycles of **1** are planar within 0.1 Å, and are situated on three interperpendicular planes (the corresponding angles are 85.52, 85.55 and 97.7°). For comparison, complex **2** has

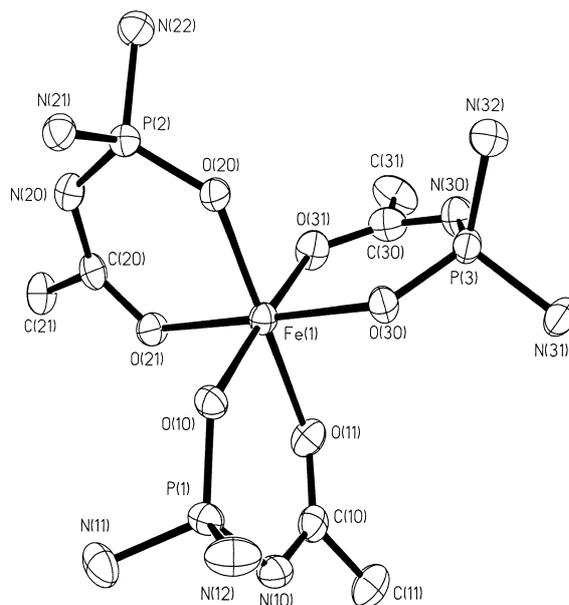


Fig. 2. The structure of complex **1**. (Non-hydrogen atoms represented with thermal ellipsoids at the 50% probability level. The chlorine atoms of the CCl_3 - and of the ethyl-groups in NEt_2 are omitted for clarity). The structure of the complex **2** is very similar.

angles 86.8, 81.2 and 75.1°. The three chelate O-Fe-O angles average to 89.5(1)° for **1** and 89.0(1)° for **2**, to be compared with angles in $\{\text{Fe}[(\text{OPPh}_2)_2\text{N}]_3\}$ of 89.3(2)° [19].

The phosphorus atoms have a slightly distorted tetrahedral configuration.

The average bond lengths for Fe-O(C) [2,027(3) for **1** and 2.010(3) Å for **2**] are larger than in $\{\text{Fe}_4(\text{OCH}_3)_6(\text{acac})_4(\text{N}_3)_2\}$ [1.991(6) Å], (where *acac* = acetylacetonate) [20]. The average Fe-O(P) bond lengths for **1** [1,971(3) Å] and for **2** [1.979(3) Å] are shorter than Fe-O(P) in $\{\text{Fe}[(\text{OPPh}_2)_2\text{N}]_3\}$ [19]. The changes of the bond lengths in the chelate rings indicate the presence of π -conjugation in the coordinated anion. Thus, the mean distances $\text{C}=\text{O}$ and $\text{P}=\text{O}$ in the complexes (compared with the free ligand) are increased [$d(\text{C}=\text{O})_{\text{complex}} = 1.263(5)$ Å for both structures; $d(\text{C}=\text{O})_{\text{HL}^1} = 1.207(2)$ Å and $d(\text{C}=\text{O})_{\text{HL}^2} = 1.202(4)$ Å; $d(\text{P}=\text{O})_{\text{complex}} = 1.516(3)$ and 1.512(3) Å for **1** and **2** respectively; $d(\text{P}=\text{O})_{\text{HL}^1} = 1.475(1)$ and $d(\text{P}=\text{O})_{\text{HL}^2} = 1.477(2)$ Å] [13]. On the other hand, the π -conjugation causes the increase of bond orders P-N and N-C in the chelate frame. As a result, a shortening of P-N and N-C distances with respect of those

in the free ligands is observed: $[d(\text{P-N})_{\text{complex}} = d(\text{N-C})_{\text{complex}} = 1.289(5)$ for **1** and $1.286(5)$ Å $1.638(4)$ for **1** and $1.631(4)$ Å for **2**; $d(\text{P-N})_{\text{HL}^1} =$ for **2**; $d(\text{N-C})_{\text{HL}^1} = 1.338(3)$ Å and $d(\text{N-C})_{\text{HL}^2} = 1.696(2)$ Å and $d(\text{P-N})_{\text{HL}^2} = 1.697(3)$ Å; $1.346(4)$ Å].

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