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 FeL₂ (where L₁ = [CCl₃C(O)NP(O)N(CH₂)₃]⁻·N,N'-tetraethyl-N'-trichloroacetylphosphoric triamide anion, and L₂ = [CCl₃C(O)NP(O)N(CH₂)₃]⁻·dimorpholido-N-trichloroacetylphosphoricamidate 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 alkoxide 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 [MIII(acac)] were investigated in asymmetric catalysis. A new reducing system trialkylsilane - transition metal acetylacetone used in organic synthesis was reported by Russian authors in a series of publications [6 - 8].

Carbacylamidophosphates of the general formula R'OCl(NH₂)PO₂(NH₂)₃ 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-diketone 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 trichloroacetylaminophosphoric acid were reported earlier [11, 12]. Following these investigations we were successful in preparing stable molecular [M(L₃)₃] species with N,N'-tetraethyl-N'-trichloroacetylphosphoric triamide (HL₁) and dimorpholido-N-trichloroacetylphosphoricamidate (HL₂) ligands.

[Chemical structure images are not transcribed.]

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

Experimental Section

Synthesis

The phosphorylic ligands HL₁ and HL₂ and their sodium salts were prepared according to the literature [13, 14]. The coordination compounds [FeL₁]₃ (1) and [FeL₂]₃ (2) were synthesized according to the following scheme:

Fe(NO₃)₃·9H₂O + 3NaL → FeL₃ + 3NaNO₃ + 9H₂.

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 triethylthio- 
formate [0.66 ml (dehydration agent)] was added. The 
resulting solution was combined with a solution of NaI 
[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 crys-
tals 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 NaI₃ in 
absolute methanol and evaporated until dry. The residue 
was dissolved in a methanol / 2-propanol mixture (1:9, 
ν/ν), 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, C₂₀H₂₆N₆Cl₂O₇P₂Fe 
(1110.68 g mol⁻¹): calc. C 32.44, H 5.45, N 11.35; 
found C 32.25, H 5.36, N 11.35. 2, C₂₀H₂₆N₆Cl₂O₇P₂ 
Fe(1178.46 g mol⁻¹): calc. 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 polycrys-
talline samples at X-frequency (ca. 9.4 GHz) under 
non-saturating conditions with a PS 100 X spectrome-
ter (ADAN1) 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 isotopic 
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 dif-
dference 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-Kα, radiation, 
λ = 0.71073 Å). The trichloromethyl group shows po-
ositional 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 disordered of the morpholine groups 
on two positions. The disorderings were refined with 
site occupancy factors of 0.68 and 0.32. Full crystallo-
graphic 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 va-

cence vibration shifts of υ(P=O) and υ(C=O) in the 
low frequency region have the values: for complex 1 
- Δυ(P=O) = 65 cm⁻¹ and Δυ(C=O) = 15 cm⁻¹; for 
complex 2 - Δυ(P=O) = 43 cm⁻¹ and Δυ(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 ab-
sorption bands υ(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 
υ(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 υ(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 υ(C=O) shifts to lower frequencies. The mul-

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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 ⁶A₁g − ⁴T₂g transitions. The transition ⁶A₁g − ⁴T₁g 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:

\[ H = \beta \cdot H \cdot g \cdot S + S \cdot (S + 1) + E(S_x^2 - S_y^2) \]

where \( \beta \) is the electronic Bohr’s magneton, and \( H \) 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
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 phosphoramic ligands are coordinated in a bidentate manner via the oxygen atoms of the phosphoryl and carboxyl groups. The coordination sphere of the central atoms may be characterized as a slightly distorted octahedron (FeO₅), 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

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 {Fe[(OPPh₂)₂N]₂} 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 {Fe₄-(OCH₃)₆(acac)₄(N₃)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 {Fe[(OPPh₂)₂N]₂} [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 C=O and P=O in the complexes (compared with the free ligand) are increased [d(C-O)complex = 1.26(3) Å for both structures; d(C-O)H₃.L₁ = 1.207(2) Å and d(C-O)H₃.L₂ = 1.202(4) Å; d(P-O)complex = 1.516(3) and 1.512(3) Å for 1 and 2 respectively; d(P-O)H₃.L₁ = 1.475(1) and d(P-O)H₃.L₂ = 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: \[d(P-N)_{\text{complex}} = 1.638(4) \text{ Å for 1 and 1.631(4) Å for 2}; d(P-N)_{\text{HL}} = 1.696(2) \text{ Å and } d(P-N)_{\text{HL}^2} = 1.697(3) \text{ Å;} \] \( d(N-C)_{\text{complex}} = 1.289(5) \) for 1 and 1.286(5) \( \text{Å} \) for 2; \( d(N-C)_{\text{HL}} = 1.338(3) \text{ Å and } d(N-C)_{\text{HL}^2} = 1.346(4) \text{ Å}. \]

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