

Properties of Iron(II) and Iron(III) Perchlorate Complexes with Triphenylphosphine Oxide

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α - $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ was prepared by the reaction of solution of iron(II) perchlorate hydrate and triphenylphosphine oxide in ethyl alcohol. β - $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ was prepared by the reaction of iron(III) perchlorate hydrate in acetonitrile solution with triphenylphosphine (PPh_3) and dioxygen. $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$ was prepared by the reaction of ethanolic solution of iron(III) perchlorate hydrate with triphenylphosphine oxide.

On the basis of spectral and magnetic properties of α - and β - $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ tetrahedral arrangement of ligands OPPh_3 around Fe(II) atom is suggested. The degree of distortion is different for the α and β forms and this allows to characterize these complexes as distortion isomers. For $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$ we propose a square-planar arrangement of ligands around the Fe(III) atom. In all studied complexes the ClO_4 groups are attached by ionic bonding.

Fe(II) perchlorate complexes with triphenylphosphine oxide (OPPh_3) can be prepared either by a direct synthesis of the starting compounds in ethanol [1] or by an indirect reaction of triphenylphosphine (PPh_3) with oxygen and $\text{Fe}(\text{ClO}_4)_3$ at about 50 °C in acetonitrile. The amount of substance ratio of $\text{Fe}(\text{ClO}_4)_3$ and PPh_3 equals 1:4 [2]. In both cases a purple coloured complex of stoichiometric composition $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ was obtained.

On the other hand, the Fe(III) perchlorate complex with OPPh_3 can be prepared only by the direct reaction of starting compounds [3] and it is a yellow powder of the composition $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$.

Despite of the fact that these complexes have been studied rather extensively their stereochemical arrangement is not quite clear. Yellow Fe(III) perchlorate complex with OPPh_3 of the composition $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$ was prepared for the first time in 1959 by Cotton *et al.* [4] by the reaction of iron(III) perchlorate hydrate and OPPh_3 (the mole ratio of substances was 1:4). On the basis of indirect methods the cited authors came to the conclusion that the complex cation $[\text{Fe}(\text{OPPh}_3)_4]^{3+}$ had a shape of a regular tetrahedron. One year later Bannister [5] expressed the opinion that the space configuration around Fe(III) in $[\text{Fe}(\text{OPPh}_3)_4]^{3+}$ had not to be necessarily a tetrahedral one. Karayannis *et al.* [6, 7] studied $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$ by infrared spectroscopy. They considered that the two bands at $\tilde{\nu} = 429 \text{ cm}^{-1}$ and 344 cm^{-1} belonging to the vibration $\nu(\text{Fe}-\text{O}(\text{ligand}))$ were especially important. They assumed that this can be explained by the existence

of pentacoordinated binuclear cation. The OPPh_3 groups play the role both as bridging and terminal ligands. Absorption bands at $\tilde{\nu} = 1080 \text{ cm}^{-1}$ and 620 cm^{-1} corresponding to the $\nu_3(\text{ClO}_4)$ and $\nu_4(\text{ClO}_4)$ vibrations characterize the existence of ion-bonded perchlorate group with the symmetry T_d . In contradiction to the above mentioned, Cotton [3] came on the basis of IR, Raman, and EPR spectroscopy to the conclusion that the complex compound $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$ contains a square-planar cation $[\text{Fe}(\text{OPPh}_3)_4]^{3+}$.

Similarly, the structure of the complex $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ is not clear as well. Karayannis *et al.* [6, 7] claim that this violet complex (which has been probably contaminated with a small amount of Fe(III)) contains tetracoordinated cation $[\text{Fe}(\text{OPPh}_3)_4]^{2+}$. IR spectrum of the complex showed one band at $\tilde{\nu} = 426 \text{ cm}^{-1} \nu(\text{Fe}-\text{O}(\text{ligand}))$ and two bands at $\tilde{\nu} = 1080 \text{ cm}^{-1} \nu_3(\text{ClO}_4)$ and $620 \text{ cm}^{-1} \nu_4(\text{ClO}_4)$ characterizing ion-bonded ClO_4 group. The electronic spectrum of solid Fe(II) complex showed a simple broad band with the maximum at $\lambda = 950 \text{ nm}$. The cited authors judge that the symmetry of $[\text{Fe}(\text{OPPh}_3)_4]^{2+}$ lies between T_d and D_{4h} . However, in the case of white $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ [6, 7] (probably pure, non-contaminated with Fe(III)) it follows from the values of $\tilde{\nu}(\nu(\text{Fe}-\text{O}(\text{ligand}))) = 414 \text{ cm}^{-1}$ and 336 cm^{-1} that this is a binuclear pentacoordinated Fe(II) complex with terminal as well as bridging OPPh_3 molecules and noncoordinated ClO_4 groups.

Hunter *et al.* [1] are of another opinion. They assumed that only one ClO_4 group is coordinated on Fe(II) (this follows from the existence of two

bands at $\tilde{\nu}(\nu(\text{Fe—O})) = 414 \text{ cm}^{-1}$ and 336 cm^{-1} . They assumed that in the complex compound $[\text{Fe}(\text{OPPh}_3)_4\text{OClO}_3]\text{ClO}_4$ the cation has a square-pyramidal structure.

These contradictions regarding the structure of the Fe(II) and Fe(III) perchlorate complexes with OPPh_3 ligands, as well as the fact that we prepared a new β form of $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ stimulated our interest in a more detailed investigation of these complexes.

EXPERIMENTAL

$\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was prepared by dissolution of powder iron in perchloric acid [8]; it crystallized in the form of green needles. Elemental analysis: $w_{\text{Fe}}(\text{calc.}) = 15.39 \%$, $w_{\text{Fe}}(\text{found}) = 15.13 \%$. $\text{Fe}(\text{ClO}_4)_3 \cdot 12\text{H}_2\text{O}$ was prepared by the reaction of $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ with perchloric acid. The substance crystallized as yellowish crystals. Elemental analysis: $w_{\text{Fe}}(\text{calc.}) = 9.79 \%$, $w_{\text{Fe}}(\text{found}) = 9.81 \%$. OPPh_3 was prepared by catalytic oxidation of PPh_3 with O_2 in the presence of $[\text{Fe}(\text{OPPh}_3)_4](\text{I}_3)_2$ [9]. Acetonitrile, anal. grade (Apolda, Germany) was used without any further treatment.

Content of Fe(II) in the prepared samples was determined spectrophotometrically using 2,2'-bipyridine. The content of Fe(III) was determined after dissolution of the sample in ethanol complexometrically with chelator 3 and salicylic acid. Content of carbon and hydrogen was determined by elemental analysis.

The complex compound $\alpha\text{-Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ (violet) was prepared by a direct reaction of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with OPPh_3 in ethanol [1]. The ratio of $n(\text{OPPh}_3) : n(\text{Fe})$ was 4 : 1.

$\beta\text{-Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ (violet) was prepared indirectly from $\text{Fe}(\text{ClO}_4)_3 \cdot 12\text{H}_2\text{O}$, PPh_3 , and O_2 at about 50°C in acetonitrile [2]. Analytical composition of α and β forms is identical and it corresponds to the calculated formula composition [1].

The complex compound $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$ (yellow) was prepared by the reaction of $\text{Fe}(\text{ClO}_4)_3 \cdot 12\text{H}_2\text{O}$ with OPPh_3 ($n(\text{OPPh}_3) : n(\text{Fe}) = 4 : 1$) in ethanol. The results of analysis correspond to the calculated values [3, 10].

Apparatuses Used for the Study of Properties

Infrared spectra of the complex compounds were measured in the region of $\tilde{\nu} = 200\text{—}4000 \text{ cm}^{-1}$ in nujol suspension by a Specord M-80 apparatus. Also electronic spectra were measured in nujol suspension in the region of $\lambda = 300\text{—}800 \text{ nm}$ by apparatus Beckman 12. Magnetic susceptibility of investigated polycrystalline com-

plexes was measured by Gouy method using electronic balances of the type Cahn RM-2 in the temperature range from 77 to 293 K. Intensity of magnetic field was 787.8 kA m^{-1} . $\text{HgCo}(\text{SCN})_4$ was used as a standard [11]. Correction on diamagnetism of studied complexes was calculated by using Pascal constants [12]. The values of magnetic moments were calculated according to the equation

$$\mu_{\text{eff}} = 2.83(\chi_m^{\text{corr}} T)^{1/2}$$

RESULTS AND DISCUSSION

Complexes $\alpha\text{-}$, $\beta\text{-Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ and $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$ were investigated by IR and electronic spectroscopy. Temperature dependence of their magnetic susceptibility was measured as well. IR spectra of $\alpha\text{-}$ and $\beta\text{-Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ showed bands corresponding to an ion-bonded ClO_4 group, viz. asymmetric stretching vibration at $\tilde{\nu}(\nu_3) = 1080 \text{ cm}^{-1}$ and symmetric bending vibration at $\tilde{\nu}(\nu_4) = 618 \text{ cm}^{-1}$. Also in the IR spectrum of $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$ are the bands at $\tilde{\nu}(\nu_3) = 1088 \text{ cm}^{-1}$ and $\tilde{\nu}(\nu_4) = 620 \text{ cm}^{-1}$, which points to ionic bond of perchlorate group. Vibrations ν_3 and ν_4 for the free ClO_4 anion have the values of wavenumbers 1120 cm^{-1} and 625 cm^{-1} , respectively [13]. Vibration $\nu(\text{P—O})$ is shifted towards lower energies, as a result of OPPh_3 coordination with respect to the central atom Fe(II) or Fe(III) (through oxygen atom), about 34 and 36 cm^{-1} , respectively, i.e. to the value of $\tilde{\nu}(\nu(\text{P—O})) = 1148 \text{ cm}^{-1}$ for iron(II) complexes and to $\tilde{\nu}(\nu(\text{P—O})) = 1146 \text{ cm}^{-1}$ for iron(III) complexes.

The bands lying in the region of $\tilde{\nu}/\text{cm}^{-1}$: 1436, 1120, 996—993, and 722—720, correspond to the vibrations of triphenylphosphine as well and they are not influenced by coordination on Fe(II) or Fe(III). Their attachment is in good agreement with the literature [14]. Stretching vibrations $\nu(\text{Fe(II)—O})$ and $\nu(\text{Fe(III)—O})$ are in the region of wavenumbers 433 and 340 cm^{-1} and 426 and 350 cm^{-1} , respectively.

Magnetic susceptibility of investigated complexes was measured in the temperature range $77\text{—}293 \text{ K}$. Dependences of molar magnetic susceptibility χ_m and its reciprocal value on temperature for all studied complexes are shown in Figs. 1a, b, and c. It follows that in all three cases the temperature dependence behaves according to the Curie—Weiss law

$$\chi_m^{\text{corr}} = \frac{C}{T - \Theta}$$

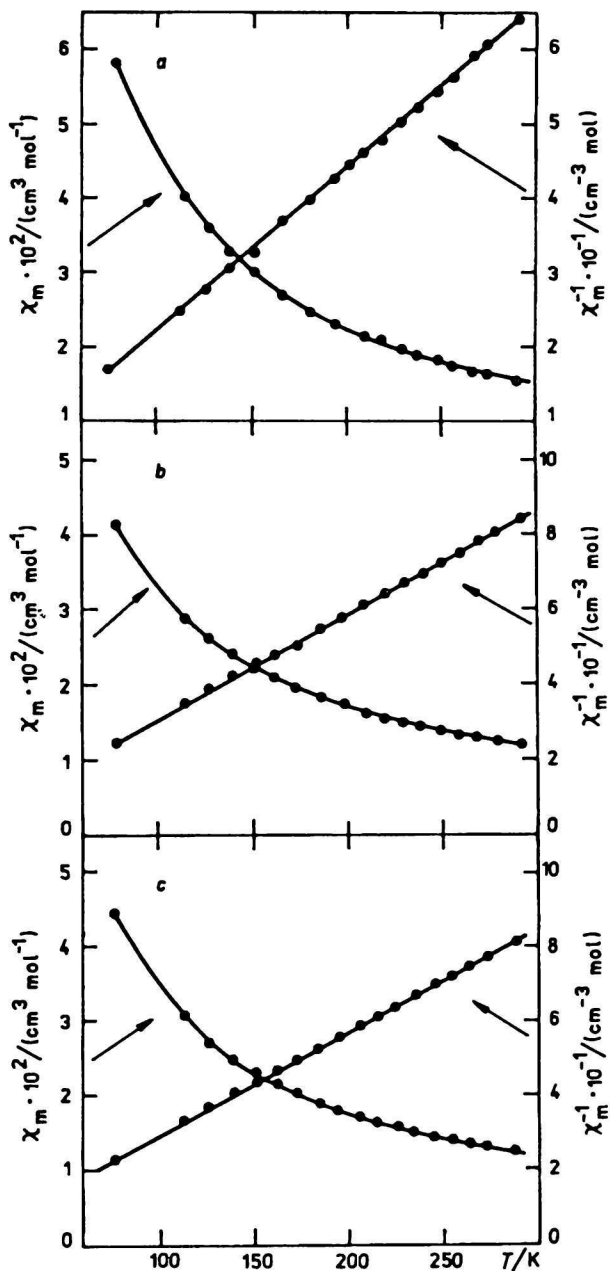


Fig. 1. Dependence of molar magnetic susceptibility χ_m and of its reciprocal value on temperature.

a) $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$; $C = 4.52 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, $\Theta = 0.1 \text{ K}$. b) $\alpha\text{-Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$; $C = 3.64 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, $\Theta = -13.4 \text{ K}$. c) $\beta\text{-Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$; $C = 3.66 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, $\Theta = -8.1 \text{ K}$.

Table 1. Magnetic Data of Complexes

Complex	Magnetic moment μ_{eff}/μ_B (at T/K)	Curie	Weiss	Diamagnetic
		constant C	constant Θ	correction
		$\text{cm}^3 \text{ mol}^{-1} \text{ K}$	K	$\text{m}^3 \text{ mol}^{-1}$
$\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$	6.02 ± 0.02 (291)	4.52	0.1	-739
	6.00 ± 0.02 (77)			
$\alpha\text{-Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$	5.27 ± 0.02 (293)	3.64	-13.4	-708
	5.05 ± 0.02 (77)			
$\beta\text{-Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$	5.33 ± 0.02 (289)	3.66	-8.1	-708
	5.24 ± 0.02 (77)			

where C and Θ are the Curie and Weiss constant, respectively. The values of magnetic moments at ambient temperature (Table 1) show that the investigated complexes belong to the class of the high-spin substances. The values $5.92 \mu_B$ for five and $4.90 \mu_B$ for four uncoupled electrons point at spin-orbital contributions. While the value of magnetic moment $6.02 \mu_B$ at 291 K observed for $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$ practically does not change with temperature ($6.00 \mu_B$ at 77 K), in the case of iron(II) complexes α - and β - $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$, it slowly decreases (Table 1). Of course the behaviour is reflected also in the numerical values of the Weiss constants. It can be seen that the value of Weiss constant for the α complex is slightly higher than for the β one, which suggests a somewhat greater antiferromagnetic interaction in the case of α form in comparison with β form. Comparison of the values of magnetic moment of these two isomeric iron(II) complexes (Table 1) shows that in the whole investigated temperature range this value is lower for α form, which can be explained by a greater distortion around the Fe(II) atom in α - than in β - $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$. At higher degree of distortion the energy difference between two cooperating forms increases and this results in decreasing of the value of magnetic moment.

Electronic spectrum of $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$ in UV region shows one remarkable maximum at $\lambda = 335 \text{ nm}$. There is no band in the visible region of spectrum.

On the basis of spectral and magnetic properties of $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_3$ we assume a planar coordination in the vicinity of Fe(III) atom. On the structure of this coordination four molecules of OPPh_3 bonded to the Fe(III) atom through oxygen donor atoms take part. ClO_4^- ions are probably attached to the complex cation $[\text{Fe}(\text{OPPh}_3)_4]^{3+}$ only by hydrogen bonds.

Electronic spectra of α - and β - $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ are different. While the electronic spectrum of β form shows two bands, one at $\lambda = 335 \text{ nm}$ and the second, very broad and asymmetrically centred around 520 nm, α form gives three bands: one at $\lambda = 335 \text{ nm}$, the second with higher maxi-

num at $\lambda = 570$ nm and the third one at $\lambda = 925$ nm. Conspicuous band in the visible part of spectrum, with maximum at about 520 and 570 nm observed for Fe(II) complexes can be characterized as charge-transfer [15]. Presence of another band with a maximum at $\lambda = 925$ nm (α form) characterizes the symmetry of the $\text{Fe}(\text{OPPh}_3)_4^{2+}$ cation between T_d and D_{4h} with negligible axial interaction [16, 17]. Absence of this band in the spectrum of β form is caused probably by "higher symmetry" than in the α form. This corresponds quite well with magnetic properties of these isomeric Fe(II) complexes.

On the basis of spectral and magnetic properties of α - and β - $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ we assume a tetrahedral arrangement around Fe(II) atoms. This arrangement has a different degree of distortion and is formed by OPPh_3 molecules which are bonded to the iron(II) through oxygen donor atoms. ClO_4^- ions are probably attached by hydrogen bonds. α - and β - $\text{Fe}(\text{OPPh}_3)_4(\text{ClO}_4)_2$ forms differ by the degree of distortion of tetrahedron. Thus they belong to the distortion isomers which are typical e.g. for Cu(II) complexes [18]. However, they are not rare, they have been found also for another central atoms like gold [19], titanium [20], niobium [21], and tantalum [22] complexes.

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