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Kinetic studies of complexation reaction of polyoxaalkyl phosphates with Fe(III) in ethanol

Bogusława Łęska, Iwona Kałużna, Błażej Gierczyk, Grzegorz Schroeder, Piotr Przybylski, Bogumił Brzezinski^{*}

Faculty of Chemistry, Adam Mickiewicz University, ul Grunwaldzka 6, 60-780 Poznan, Poland

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Abstract

Complexation reactions of the Fe(III) cation by seven oxaalkyl phosphate esters and ethyl phosphate in ethanol were studied by kinetic methods, as well as ³¹P NMR and semi-empirical methods. The ΔG^{\neq} values for almost all phosphates were in the range of 53–56 kJ mol⁻¹. The greatest differences were observed for the ΔS^{\neq} values of the systems studied, whereas the enthalpies of activation ΔH^{\neq} were compensated by the entropy of activation. The structures of the complexes formed between the Fe(III) cation and the oxaalkyl phosphate esters and the mechanisms of these reactions are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics; Complexation; Iron(III); Podandes; Phosphates; ³¹P NMR; ¹⁷O NMR; Semiempirical calculation

1. Introduction

The formation of complexes between the crown ethers or cryptands (macrocyclic and macrobicyclic ligands) and protons or the monovalent cations is discussed in detail in Refs. [1-4]. Particularly interesting are the open-chained, polyoxaalkyl ligands complexating with a variety of organic and metallic cations (mostly of I and II group) [5-9]. In our previous papers, the behaviour of such ligands complexed by protons and various metal cations was studied by spectroscopic methods [10-15]. We have demonstrated that proton and monovalent metal cations undergo fast fluctuations in a multiminima

cation potential along the O-atoms in the channels formed by the polyoxaalkyl chains, whereas the size of the cation and the length of the polyoxaalkyl ligands influence the properties of these complexes. Due to the fast fluctuations of the cations, the proton and cation polarisabilities, the so-called Zundel's polarisabilities [16–19], appeared and were manifested in the infrared spectra by a continuous absorption in MIR and FIR regions. In the case of complexes with CoCl₂, NiCl₂ and CuCl₂ the respective cations are coordinated by oxygen atoms of three polyoxaalkyl chains and also by one chlorine atom.

The Fe(II) and Fe(III) cations and their complexes are interesting because of their important role in biological systems. The recent interest in iron complexes derives from the importance of such compounds in controlled solubilisation, transport and release of iron by various organism [20]. Iron(III)

^{*} Corresponding author. Tel.: +48-61-8291330; fax: +48-61-865-8008.

E-mail address: bbrzez@main.amu.edu.pl (B. Brzezinski).

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chloride and other simple salts react with a range of organic ligands, such as alcohols, ethers, aldehydes, ketones, amides, sulphoxides, phosphine oxides, etc. The structures of many of these complexes are unknown, some appear to be simple addition compounds, while they have salt structures [21]. The complexes of FeCl₃ with alcohols ROH (R = Me, Et, etc.) have been isolated from solutions of FeCl₃ in benzene containing the appropriate alcohol [22]. The anhydrous binary FeCl₃ has nearly regular octahedral coordination, but the hexahydrate of FeCl₃ has a trans octahedral arrangement [Fe(H₂O)₄Cl₂)Cl·2H₂O and exhibits pronounced quadrupole splitting [23,24]. With Ph₃PO, Ph₃AsO and analogous ligands, the complexes of the stoichiometry as in FeL₄(ClO₄)₃ and FeL_2Cl_3 are common [25,26].

In this paper, we present kinetic results of the complexation reaction of some bis- and tris-(oxaalkyl) phosphates, as well as tetrakis(oxaalkyl) phosphates with Fe(III) cation in the ethanol solvent. These new compounds are characterised by different number of oxygen atoms in the oxaalkyl chains. The obtained results are compared with those of simple triethyl phosphate with non-podand-like character.

2. Experimental

Ethanol and anhydrous $FeCl_3$ were used as a commercial product (Fluka). Triethyl phosphate (PO3Et) was used as a commercial product (BDH Chemicals Ltd.).

2.1. Syntheses of polyoxaalkyl phosphates

Tris(oxaalkyl) phosphates (OP3.2, OP3.7 and OP3.12) were obtained by the dropping of phosphorus oxychloride (0.33 mol) under reduced pressure (200 mmHg) to the respective mixtures of anhydrous glycolmonomethyl ethers (1.3 mol) in 250 cm³ xylene) at temperature -10 °C. Afterwards, the mixture was heated to temperature 50 °C for 1 h and the solvent was evaporated. The OP3.2 product (yield = 80%) was distilled under reduced pressure. bp = 160–163 °C/0.04 mmHg. OP3.7 and OP3.12 compounds were purified by the chromatographic method (SiO₂–ethyl acetate). Yield = 80%.

Bis(oxaalkyl) phosphates (OPH2.2 and OPH2.3)

were synthesised by mixing respective anhydrous glycolmonomethyl ether (0.1 mol) and phosphorus trichloride (0.33 mol) in 250 cm³ benzene at temperature 0 °C during 3 h. After this time, the mixture was heated under reflux for 2 h. The solvent was evaporated under reduced pressure. The obtained product OPH2.2 (yield = 85%) was distilled under reduced pressure bp = 130-132 °C/0.1 mmHg. OPH2.3 was purified by the chromatographic method (SiO₂-ethyl acetate). Yield = 80%.

Tetrakis(oxaalkyl) pyrophosphates $[(R^{3}O)_{2}PO-O-PO(OR^{3})_{2}$ and $(R^{7}O)_{2}OP-O-PO(OR^{7})_{2}]$ were obtained by dropping to the mixture of pyrophosphoric tetrachloride (0.1 mol) in xylene the corresponding glycolmonomethyl ether (0.4 mol) in 50 cm³ xylene. The mixture was stirred all time. Afterwards the mixture was heated to temperature 80 °C for 3 h. Xylene was evaporated under reduced pressure and the residue was purified by the chromatographic method (SiO₂-ethyl acetate). Yield = 82%.

2.2. NMR measurements

The ³¹P NMR spectra were recorded in CD₃CN using a Varian Gemini 300 MHz spectrometer using the following parameters: sfrq = 121.472, pw = 60°, sw = 50,000 Hz, at = 2 s, T = 293 K and 85% H₃PO₄ as external standard. All spectra were locked to deuterium resonance of CD₃CN. The error in ppm values is 0.1.

³¹P chemical shifts for the synthesised compounds are: -2.2 ppm (septet, $J_{HP}^3 = 8.1$ Hz) for PO3Et, -0.1 ppm (septet, septet, $J_{HP}^3 = 7.5$ Hz, $J_{HP}^4 = 1.6$ Hz) for OP3.2, 1.72 ppm (septet, septet, $J_{HP}^3 = 7.5$ Hz, $J_{HP}^4 = 1.6$ Hz) for OP3.7, 1.93 ppm (septet, septet, $J_{HP}^3 = 7.5$ Hz, $J_{HP}^4 = 1.6$ Hz) for OP3.12, 9.3 ppm (dq, $J_{HP}^1 = 7.2$ Hz, $J_{HP}^3 = 9.2$ Hz) for OPH2.2, 9.0 ppm (dq, $J_{HP}^1 = 7.5$ Hz, $J_{HP}^3 = 9.0$ Hz) for OPH2.3, -0.3 ppm for (R³O)₂OP-O-PO(OR³)₂ and (R⁷O)₂OP-O-PO(OR⁷)₂.

2.3. Kinetic study

The complexation of the iron cation (Fe^{3+}) , by a ligand (L) in ethanol (Sol) can be represented by the

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following equilibrium:

$$n(L)_{Sol} + (Fe^{3+})_{Sol} \stackrel{k}{\underset{k_{-}}{\rightleftharpoons}} (L, Fe^{3+})_{Sol} \rightleftharpoons (L_n Fe^{3+})_{Sol}$$

where *k* and *k*₋ are the rate constants for complexation and decomplexation process, respectively. The formation of 1:1 complexes is the rate-determining step. The kinetic runs were carried out using a stopped-flow spectrophotometer (Applied Photophysics) with the cellblock thermostated to ± 0.1 °C. The kinetic runs were completed under pseudo-first-order conditions with the ligands concentration in large excess. The observed rate constants were calculated from the traces of absorbance versus time. The observed rate constant *k*_{obs} depends on the initial ligands concentration [L] and is given by the equation: $k_{obs} = k[L] + k_{-}$.

Rate constants for forward (k) reaction were calculated by linear least-squares fit of the variation of k_{obs} versus the base concentration. The activation parameters were calculated by the linear least-square fit of ln *k* versus 1/T.

2.4. AM1d calculations

AM1d semi-empirical calculations were performed using the Win Mopac 2002 program [27]. In all cases, full geometry optimisation was carried out without any symmetry constraints [28,29].

3. Results and discussion

The structures of ethyl phosphate (OP3Et) and oxaalkyl phosphate esters are shown in Scheme 1. These compounds belong to three groups distinguished on the basis of the number of oxaalkyl chains. The first group, of the so-called tripodands (OP3Et, OP3.2, OP3.7, OP3.12) forms complexes with the metal cation preferably via the oxygen atoms of the oxaalkyl chains. The compounds of the second group (OPH2.2 and OPH2.3) are dipodands. The complexation of the cation by these compounds can occur via oxygen atoms of the oxaalkyl chains or oxygen atoms of the (O=P) groups. The coordination by the oxygen atoms of (O=P) groups is more favourable if the concentration of ligands is high enough. The third group is represented by two pyrophosphates

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Table 1 Kinetics parameters (\pm standard deviation) for the reaction of OP3Et with FeCl₃ in ethanol

Temperature (°C)	$k_{\rm obs}~({\rm s}^{-1})~{\rm f}$	or ligands co	oncentration		$k (M^{-1} s^{-1})$	$k_{-}(s^{-1})$	ΔH^{\neq} (kJ mol ⁻¹)	ΔS^{\neq} (J mol ⁻¹ deg ⁻¹)	ΔG^{\neq} (kI mol ⁻¹)
	0.062 (M)	0.085 (M)	0.100 (M)	0.125 (M)		(-)	((**************************************	(
25							42.1 ± 3.8	-84 ± 12	67.0 ± 3.8
30	0.3 ± 0.1	0.6 ± 0.2	1.0 ± 0.1	1.3 ± 0.2	16 ± 2	-0.7 ± 0.2			
40	0.8 ± 0.1	1.3 ± 0.1	1.8 ± 0.1	2.4 ± 0.1	26 ± 1	-0.8 ± 0.1			
50	1.5 ± 0.1	2.4 ± 0.1	3.5 ± 0.1	4.4 ± 0.1	47 ± 4	-1.5 ± 0.4			

 $(R^{3}O)_{2}OP-O-PO(OR^{3})_{2}$ and $(R^{7}O)_{2}OP-O-PO(OR^{7})_{2}$ the so-called two-core ligands, which can form complexes through O-P-O-P-O bonds or oxygen atoms of oxaalkyl chains. Thus, these compounds differ not only in the number of oxaalkyl chains, but also in the chain length.

The obtained ΔH^{\neq} , ΔS^{\neq} and ΔG^{\neq} values for the reactions studied are shown in Tables 1–8.

It is well known that the activation entropy (ΔS^{\neq}) is a measure of the difference in the solvation degree of the substrates and the transition product. Low (ΔS^{\neq}) values are observed when in the transition state the complex motions are restricted as a result of the solvation process. The lowest values of (ΔS^{\neq}) are found for complexes of Fe(III) cation with OP3.2 and OPH2.3 esters $(-156 \text{ and } -138 \text{ J mol}^{-1} \text{ deg}^{-1})$, respectively), which become stereochemically ordered. This situation is a result of a substantial restriction of the complex motions in transition state, while in the complexes obtained with a small steric hindrance, ΔS^{\neq} values are, relatively, large (the highest values are for OP3.7, where $\Delta S^{\neq} = -5 \text{ J mol}^{-1} \text{ deg}^{-1} \text{ and } (R^3O)_2OP-O-OP(OR^3)_2, \text{ where } \Delta S^{\neq} = -4 \text{ J mol}^{-1} \text{ deg}^{-1}). \text{ The }$ enthalpies of activation ΔH^{\neq} are compensated by the entropy of activation, ΔS^{\neq} . The values of ΔG^{\neq} in Tables 1-8 are comparable and they are in the range of $53-56 \text{ kJ mol}^{-1}$ except for the complex formation by the simple ethyl phosphate and OP3.12 ester, i.e. with the longest oxaalkyl chains. For them, the ΔG^{\neq} values are slightly higher (67) and 64 kJ mol⁻¹).

The data calculated for some exemplary complexes formed between phosphate esters and Fe(III) cation are shown in Tables 9-11 and the respective structures are shown in Figs. 1–4. The kinetic studies were performed in ethanol and for this reason the complexes with this solvent are also calculated and discussed. From literature data, it is well known that the P=O phosphate group is a strong proton acceptor [30-32]. A comparison of the total energy values given in Table 9 for hydrogen-bonded complexes with one ethanol molecule and without this hydrogen bond,



Fig. 1. Structures of 1:1:1 complexes of phosphate esters with Fe(III) cation and one ethanol molecule calculated by AM1d method. (a) OP2.3 and (b) OP3.2.

Table 2 Kinetics parameters (\pm standard deviation) for the reaction of OP3.2 with FeCl₃ in ethanol

Temperature (°C)	$k_{\rm obs}$ (s ⁻¹) for ligands concentration			$k (M^{-1} s^{-1})$	$k_{-} (s^{-1})$	$\Delta H^{\neq} (\text{kJ mol}^{-1})$	$\Delta S^{\neq} (\mathrm{J} \mathrm{mol}^{-1} \mathrm{deg}^{-1})$	$\Delta G^{\neq} (\text{kJ mol}^{-1})$	
	0.005 (M)	0.010 (M)	0.015 (M)	0.020 (M)					
15	18.2 ± 1.0	32.5 ± 1.7	48.4 ± 3.0	62.2 ± 1.5	2958 ± 55	3.4 ± 0.8			
25	23.9 ± 1.2	42.8 ± 2.1	57.8 ± 2.3	74.9 ± 2.1	3360 ± 102	7.9 ± 1.4	6.6 ± 0.2	-156 ± 1	52.9 ± 0.3
35	30.2 ± 2.4	52.6 ± 2.7	68.1 ± 1.0	87.4 ± 1.2	3742 ± 180	2.5 ± 2.0			
45	38.7 ± 3.3	61.8 ± 0.9	80.7 ± 2.3	103.1 ± 2.0	4242 ± 111	18.1 ± 1.5			

Table 3 Kinetics parameters (\pm standard deviation) for the reaction of OP3.7 with FeCl₃ in ethanol

Temperature (°C)	$k_{\rm obs}~({\rm s}^{-1})$ for	r ligands concen	tration			$k (M^{-1} s^{-1})$	$k_{-}(s^{-1})$	ΔH^{\neq} (kJ mol ⁻¹)	ΔS^{\neq} (J mol ⁻¹ deg ⁻¹)	ΔG^{\neq} (kJ mol ⁻¹)	
	0.0031 (M)	0.0063 (M)	0.0125 (M)	0.0250 (M)	0.0375 (M)	· · ·		× /	、	. ,	
15	0.5 ± 0.1	1.4 ± 0.1	3.1 ± 0.1	8.2 ± 0.1	12.9 ± 0.3	366 ± 13	-1.0 ± 0.3				
25	2.7 ± 0.1	4.3 ± 0.2	8.4 ± 0.4	17.3 ± 0.6	27.2 ± 0.7	716 ± 20	-0.1 ± 0.4	55.0 ± 2.4	-5 ± 8	56.6 ± 2.4	
35	5.6 ± 0.2	10.2 ± 0.3	14.5 ± 0.6	40.9 ± 1.3	61.1 ± 2.0	1654 ± 109	-1.5 ± 2.3				
45	14.9 ± 0.5	22.9 ± 0.7	43.8 ± 1.3	85.7 ± 2.4	132.3 ± 4.3	3429 ± 75	2.0 ± 1.6				

Table 4 Kinetics parameters (\pm standard deviation) for the reaction of OP3.12 with FeCl₃ in ethanol

Temperature (°C)	$k_{\rm obs}~({\rm s}^{-1})$ for	ligands concent	ration		$k (M^{-1} s^{-1})$	$k_{-} (s^{-1})$	$\Delta H^{\neq} (\text{kJ mol}^{-1})$	$\Delta S^{\neq} (\mathrm{J} \mathrm{mol}^{-1} \mathrm{deg}^{-1})$	$\Delta G^{\neq} (\text{kJ mol}^{-1})$
	0.0025 (M)	0.0070 (M)	0.0150 (M)	0.0250 (M)					
15	0.08 ± 0.02	0.14 ± 0.02	0.26 ± 0.05	0.41 ± 0.02	14.7 ± 0.2	0.1 ± 0.1			
25	0.29 ± 0.01	0.46 ± 0.02	0.72 ± 0.03	1.17 ± 0.02	38.7 ± 2.0	0.2 ± 0.1	62.8 ± 4.7	-4 ± 16	64.1 ± 4.7
35	0.56 ± 0.20	0.96 ± 0.29	1.72 ± 0.21	2.84 ± 0.08	101.5 ± 3.7	0.3 ± 0.1			
45	1.01 ± 0.05	2.83 ± 0.06	3.64 ± 1.30	5.29 ± 0.09	174.8 ± 30.7	1.1 ± 0.5			

Table 5	
Kinetics parameters (\pm standard deviation) for the reaction of OPH2.2 with FeCl ₃ in ethanol	

Temperature (°C)	$k_{\rm obs}~({\rm s}^{-1})$ for	r ligands conce	ntration		$k (M^{-1} s^{-1})$	$k_{-} (s^{-1})$	$\Delta H^{\neq} (\text{kJ mol}^{-1})$	$\Delta S^{\neq} (\mathrm{J} \ \mathrm{mol}^{-1} \ \mathrm{deg}^{-1})$	$\Delta G^{\neq} (\text{kJ mol}^{-1})$
	0.005 (M)	0.010 (M)	0.015 (M)	0.020 (M)					
15	3.8 ± 1.5	6.7 ± 1.0	8.4 ± 2.0	12.4 ± 2.5	550 ± 60	1.0 ± 0.8			
25	9.1 ± 2.0	13.4 ± 2.0	17.5 ± 2.0	22.6 ± 1.5	892 ± 31	4.5 ± 0.4	38.2 ± 1.8	-60 ± 6	56.1 ± 1.8
35	15.1 ± 2.5	24.8 ± 3.0	32.4 ± 1.5	40.5 ± 1.5	1676 ± 63	7.3 ± 0.9			
45	23.0 ± 2.0	37.4 ± 2.5	50.1 ± 1.0	62.8 ± 1.0	2642 ± 59	10.3 ± 0.8			

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Table 6 Kinetics parameters (\pm standard deviation) for the reaction of OPH2.3 with FeCl₃ in ethanol

Temperature (°C)	$k_{\rm obs}$ (s ⁻¹) for ligands concentration			$k (M^{-1} s^{-1})$	$k_{-} (s^{-1})$	$\Delta H^{\neq} (\text{kJ mol}^{-1})$	$\Delta S^{\neq} (\mathrm{J} \ \mathrm{mol}^{-1} \ \mathrm{deg}^{-1})$	$\Delta G^{\neq} (\text{kJ mol}^{-1})$	
	0.005 (M)	0.010 (M)	0.015 (M)	0.020 (M)					
15	12.0 ± 0.3	25.4 ± 0.5	37.7 ± 0.4	51.4 ± 0.8	2610 ± 37	-1.0 ± 0.5			
25	18.3 ± 0.4	33.9 ± 0.7	49.6 ± 1.0	66.1 ± 1.0	3182 ± 30	2.2 ± 0.4	12.0 ± 0.1	-138 ± 1	53.1 ± 0.1
35	26.1 ± 0.3	43.5 ± 0.7	64.3 ± 0.9	83.5 ± 1.5	3860 ± 91	6.1 ± 1.2			
45	29.6 ± 0.9	54.8 ± 0.7	77.3 ± 1.2	99.1 ± 1.0	4620 ± 111	7.5 ± 1.5			

Table 7					
Kinetics parameters	(± standard deviation)) for the reaction of	$(R^{3}O)_{2}OP - O - PC$	$O(OR^3)_2$ with FeCl ₃	in ethanol

Temperature (°C)	$k_{\rm obs}~({\rm s}^{-1})$ for	r ligands concer	ntration			$k (M^{-1} s^{-1})$	$k_{-}(s^{-1})$	ΔH^{\neq} (kJ mol ⁻¹)	ΔS^{\neq} (J mol ⁻¹ deg ⁻¹)	ΔG^{\neq} (kJ mol ⁻¹)
	0.0031 (M)	0.0063 0.0125 0.0250 0.0375 (M) (M) (M) (M) (M)			`	、				
15 25 35	1.1 ± 0.1 3.0 ± 0.1 8.2 ± 0.2 28.6 ± 0.8	1.5 ± 0.1 8.6 ± 0.2 20.6 ± 0.6 50.2 ± 1.2	6.1 ± 0.2 17.6 ± 0.4 40.1 ± 0.8 80.7 ± 2.1	13.3 ± 0.3 34.0 ± 0.8 76.9 ± 1.8 155.4 ± 2.0	20.6 ± 0.4 49.2 ± 0.8 106.4 ± 1.8 214.6 ± 2.1	585 ± 22 1331 ± 37 2847 ± 115 5270 ± 100	-1.4 ± 0.5 0.0 ± 0.8 2.4 ± 2.4 16.0 ± 4.0	54.1 ± 1.2	-4 ± 4	55.3 ± 1.2

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Temperature (°C)	$k_{\rm obs}$ (s ⁻¹) for	r ligands concer	tration			$k (M^{-1} s^{-1})$	$k_{-}(s^{-1})$	ΔH^{\neq} (kJ mol ⁻¹)	$\frac{\Delta S}{(\text{J mol}^{-1} \text{ deg}^{-1})}$	ΔG^{\neq} (kJ mol ⁻¹)
	0.0031 (M)	0.0063 (M)	0.0125 (M)	0.0250 (M)	0.0375 (M)					
15	8.9 ± 0.2	15.8 ± 0.3	22.4 ± 0.5	38.5 ± 0.9	58.7 ± 1.4	1398 ± 56	5.3 ± 1.2			
25	15.3 ± 0.4	29.4 ± 0.7	55.2 ± 1.4	92.4 ± 2.4	130.7 ± 3.7	3302 ± 136	8.9 ± 2.9	44.9 ± 4.0	-28 ± 13	53.3 ± 4.0
35	22.7 ± 0.6	44.5 ± 0.6	85.2 ± 1.6	152.5 ± 3.0	223.8 ± 4.1	5783 ± 121	8.1 ± 2.6			
45	36.3 ± 0.7	61.9 ± 0.8	124.3 ± 1.8	237.1 ± 3.1	348.9 ± 4.8	9137 ± 90	7.5 ± 1.9			

Table 8 Kinetics parameters (\pm standard deviation) for the reaction of $(R^7O)_2OP-O-PO(OR^7)_2$ with FeCl₃ in ethanol

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Fig. 2. Structure of 1:1 complex of OP3.7 with Fe(III) cation calculated by AM1d method.

indicates that this bond influences the coordination strength of the cation. The same is indicated by the partial charge (Table 10) and the distances (Table 11) between the cation and the oxygen atoms of the oxaalkyl chains. The OP2.3 and OP3.2 esters formed the simplest octahedral 1:1 complexes with Fe(III)



Fig. 3. Possible structures of complexes formed between $(R^{3}O)_{2}OP-O-PO(OR^{3})_{2}$ with Fe(III) cation (a) stoichiometry 2:1 and (b) stoichiometry 1:1 calculated by AM1d method.



Fig. 4. Structure of 6:1 complex of OP2.3 with Fe(III) cation calculated by AM1d method.

cation, whose structures are shown in Fig. 1(a) and (b), respectively. In these complexes, all oxygen atoms of the oxaalkyl chains are involved in the coordination process of Fe(III) cation. With increasing number of the oxygen atoms in the oxaalkyl chains, different octahedral structures, in which various oxygen atoms are involved in the coordination of cation, are possible. One such structure for the 1:1 complex of OP3.7 with Fe(III) cation is shown in Fig. 2.

Table 9

Values of HOF (heat of formation) and total energy of the complexes formed between phosphate esters and Fe^{3+} calculated by AM1d method

Compound	HOF (kcal mol ⁻¹)	Total energy (eV)
OP3.2	394.75	-4120.22
OP3.2/Fe ³⁺ (1:1)	408.37	-4208.34
OP3.2/Fe ³⁺ /EtOH (1:1:1)	447.23	-4264.98
OP2.3	127.45	- 3956.84
OP2.3/Fe ³⁺ (1:1)	371.34	-4365.48
OP2.3/Fe ³⁺ /EtOH (1:1:1)	394.78	-4393.27
OP2.3/Fe ³⁺ (6:1)	-243.27	- 5794.32
OP3.7	111.20	-6154.46
OP3.7/Fe ³⁺ (1:1)	132.24	-6326.54
$(R^{3}O)_{2}OP-O-PO(OR^{3})_{2}$	203.12	-10,073.85
$(R^{3}O)_{2}OP-O-PO(OR^{3})_{2}/Fe^{3+}$ (1:1)	255.39	-10,781.01
$(R^{3}O)_{2}OP - O - PO(OR^{3})_{2}/Fe^{3+}$ (2:1)	-302.27	- 12,496.23

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Table 10

Values of partial charge for O-atoms, which coordinate with Fe^{3+} cation in the complexes formed between phosphate esters and Fe^{3+} calculated by AM1d method

Compound	Fe	0	0	0	0	0	0	O=P	O=P
OP3 2	_	-0.728	-0.717	-0.714	-0.295	-0.285	-0.292	-1.086	_
$OP3.2/Fe^{3+}$ (1:1)	0.701	-0.677	-0.676	-0.683	-0.270	-0.272	-0.274	-0.807	_
OP3.2/Fe ³⁺ /EtOH (1:1:1)	0.763	-0.703	-0.704	-0.687	-0.262	-0.269	-0.269	-0.772	_
OP2.3	_	-0.755	-0.724	-0.284	-0.286	-0.301	-0.302	-1.064	_
OP2.3/Fe ³⁺ (1:1)	0.693	-0.664	-0.666	-0.279	-0.269	-0.287	-0.288	-0.881	_
OP2.3/Fe ³⁺ /EtOH (1:1:1)	0.706	-0.676	-0.681	-0.251	-0.247	-0.254	-0.253	-0.789	_
OP2.3/Fe ³⁺ (6:1)	0.402		_	-	_	_	_	-0.596	-
OP3.7	_	-0.727	-0.715	-0.714	-0.293	-0.284	-0.292	-1.092	_
OP3.7/Fe ³⁺ (1:1)	0.601	-0.674	-0.675	-0.691	-0.269	-0.270	-0.281	-1.091	
$(R^{3}O)_{2}OP - O - PO(OR^{3})_{2}$	_	-0.722	-0.709	-0.712	-0.372	-0.338	-0.394	-1.111	-1.132
$(R^{3}O)_{2}OP - O - PO(OR^{3})_{2}/Fe^{3+}$ (1:1)	0.391	-0.544	-0.545	-0.444	-0.332	-0.325	-0.336	-1.111	- 1.329
$(R^{3}O)_{2}OP-O-PO(OR^{3})_{2}/Fe^{3+}$ (2:1)	0.372	-0.535	-0.539	-0.437	-0.329	-	-	-0.438	- 0.434

Table 11

Distances (Å) between O-atoms and Fe³⁺ cation in the complexes formed between phosphate esters and Fe³⁺ calculated by AM1d method

Compound	FeO	FeO	FeO	FeO	FeO	FeO	FeO=P	FeO=P
OP3 $2/\text{Fe}^{3+}(1.1)$	2.01	2.02	2.05	1.91	1.93	1.94	_	_
$OP3.2/Fe^{3+}/EtOH (1:1:1)$	2.09	2.11	2.09	1.95	1.93	1.92	_	_
OP2.3/Fe ³⁺ (1:1)	1.98	1.97	1.95	2.01	1.98	1.98	_	_
OP2.3/Fe ³⁺ /EtOH (1:1:1)	2.12	2.10	1.92	1.97	1.95	1.93	_	_
OP2.3/Fe ³⁺ (6:1)	_	_	_	_	_	_	1.90	_
OP3.7/Fe ³⁺ (1:1)	1.91	1.93	1.95	1.95	1.92	1.93	_	_
$(R^{3}O)_{2}OP - O - PO(OR^{3})_{2}/Fe^{3+}$ (1:1)	1.92	1.94	1.92	1.90	1.92	1.92	-	-
$(R^{3}O)_{2}OP-O-PO(OR^{3})_{2}/Fe^{3+}$ (2:1)	-	-	1.92	1.92	1.90	1.90	1.89	1.86

In the case of pyrophosphate esters with four oxaalkyl chains, two types of structures, i.e. structures including the coordination with P=O oxygen atoms and structures in which the cation is coordinated only by oxygen atoms of oxaalkyl chains, are probable (Fig. 3).

For the stereochemical reasons the OP2.3 ester, including only two oxaalkyl chains, can form a complex with the Fe(III) cation in which it is coordinated by six P=O oxygen atoms (Fig. 4). This complex is much more stable than that with the 1:1 stoichiometry, discussed earlier.

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