Available online at www.sciencedirect.com

Journal of Molecular Structure 740 (2005) 9–16

Journal of MOLECULAR STRUCTURE

www.elsevier.com/locate/molstruc

Proton solvates, $H^+ \cdot nH_2O \cdot mL$, formed by diphosphine dioxides with chlorinated cobalt(III) dicarbollide acid

Evgenii S. Stoyanov[a,*], Igor' V. Smirnov[b]

[a]Boreskov Institute of Catalysis, Prospekt Lavrentieva 5, 630090 Novosibirsk, Russian Federation
[b]Khlopin Radium Institute, 28 2nd Murinsky Av., 194021, St Petersburg, Russia Federation

Received 15 October 2004; revised 15 December 2004; accepted 21 December 2004

Abstract

Interaction of hydrated proton, $H_5O_2^+ \cdot (H_2O)_4$, in dichloroethane solutions with diphosphine dioxides (L) having methyl (Ph_4Me), ethyl (Ph_4Et) and polyoxyethylene chains (Ph_4PEG) linking two diphenyl phosphine oxide groups has been investigated. A bulky counter ion: chlorinated cobalt(III) bis(dicarbollide), $[Co(C_2B_9H_8Cl_3)_2]^-$, minimizes perturbation of the cation. At low concentrations, Ph_4Et and Ph_4PEG form anhydrous 1:1 complexes with (P=)O–H^+–O(=P) fragment having very strong symmetrical H-bonds. At these conditions Ph_4Me form another compound, $H_5O_2^+ \cdot L(H_2O)_2$, due to lower P=O basicity and optimal geometry of the chelate cycle. At higher concentrations, Ph_4Me and Ph_4Et form isostructural complexes $H_5O_2^+ \cdot L_2$, whereas Ph_4PEG forms only a 1:1 complex with proton dihydrate, $H_3O^+ \cdot H_2O$. In excess of free Ph_4Me and Ph_4Et a water molecule is introduced to the first coordination sphere of $H_5O_2^+$ and the average molar ratio $L/H_5O_2^+$ of the complexes exceeds 2. The composition of these complexes as a function of L and its concentration is discussed.

Keywords: IR spectroscopy; Strong H-bonds; Proton hydrates and solvates; Diphosphine dioxides

1. Introduction

Bidentate neutral organophosphorus compounds—diphosphine dioxides and carbamoyl phosphine oxides are known to be very effective complexing agents for actinides and lanthanides. They are the most effective extractants for elimination of these metals from the high-level waste of the nuclear fuel cycle [1,2]. The complexation capacity of diphosphine dioxides (DPDO) significantly depends on the length of the aliphatic chain—$(CH_2)_n$—connecting two phosphine oxide groups. For example, the extraction ability of methylene DPDO derivatives towards lanthanides and actinides is three orders of magnitude higher than that of the ethylene derivatives [3]. A strong synergistic effect has been observed upon addition of chlorinated cobalt(III) dicarbollide acid (HCCD) to organic solutions of bidentate neutral organophosphorus compounds: Am and Eu are extracted in several orders of magnitude more efficiently [4,5]. At that the extractability of DPDO as a function of the length of their aliphatic chain is even essentially intensify. It is supposed to be caused not only by specific complexation with metal cations, but also by the peculiarities of their interaction with proton hydrates, which are exchanged with the metal cations during extraction [5]. Because of this, the study of DPDO interaction with HCCD is important to understand the peculiarities of extraction processes. Moreover, it has a specific interest since the molecular state of proton hydratosolvates $H^+ \cdot nH_2O \cdot mL$ in solutions as a whole is of key importance for the chemistry of solutions [6] and is closely related to studies of compounds with very strong H-bonds.

The interaction of hydrated protons with tributylphosphate that is less basic than DPDO results in the formation a set of compounds: $H_3O^+ \cdot L_3$; $H_5O_2^+ \cdot L_4$ and others [7,8], up to micelle formation [9], as a function of the preparation conditions. Cycle and linear polyethers (crown-ethers, polyethylene glycols) that are even less basic selectively form complexes with hydronium ions, H_3O^+ [10], $H_5O_2^+$, $H_7O_3^+$ [11,12] and are distinguished by the formation of

---

* Corresponding author. Tel.: +7 3832 30 84 88; fax: +7 383 2 34 30 56.
E-mail address: stoyanov_e@mail.ru (E.S. Stoyanov).

0022-2860/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2004.12.037

cooperative H-bonds [13,14]. Highly basic phosphine oxides in water saturated organic solutions can form both anhydrous disolvates L–H^+–L and mixed hydrate-solvates [15].

In the present work we report on the interaction of hydrated proton of chlorinated cobalt(III) bis(dicarbollide) acid, $H^+[Co(C_2B_9H_8Cl_3)_2]^-$ (H-CCD), which is known to be a superacid [16], with diphosphine dioxides having methylene, ethylene and polyoxyethylene chains connecting two diphenyl phosphine oxide groups in water saturated dichlorethane solutions. DPDO with long polyoxyethylene chain was chosen because, in the mixture with HCCD it shows synergism in the extraction of Am and Eu [17], and it is an analog of polyethylene glycol, which is proposed in the mixture with HCCD as extractant for reprocessing of radioactive waste [18]. The bulky CCD^- anion minimizes perturbation of the cation via ion-pairing effects.

2. Experimental

The cesium salt of chlorinated cobalt dicarbollide, CsCCD, with an analysis of 9.35% Co, and 29.05% Cl was received from KatChem (Czech Republic) and used without additional purification. Stock solutions of CsCCD salt were prepared by dissolution of a known mass in the dichloroethane and converting from the Cs salt to the acid form, H^+CCD-, by multiple (4–5) batch contacts with fresh aliquots of 3 M H_2SO_4. 1,2-Dichloroethane (DCE) of chemical purity grade was purified using standard methods. Diphosphine dioxides were synthesized at Institute of Reagents (Moscow). Their structure and abbreviated designation are given in Table 1.

Ph_4PEG contains a mixtures of linear $Ph_2P(O)CH_2(OCH_2CH_2)_nOCH_2P(O)Ph_2$ molecules with average $n=5$. These compounds can be represented as polyethylene glycols with peripheral OH groups substituted by diphenyl phosphine oxide groups.

Dichloroethane solutions with constant 0.02 M concentration of HCCD and variable 0.01–0.06 M concentration of DPDO = Ph_4Me, Ph_4Et and Ph_4PEG were prepared by mixing DCE solutions of HCCD and DPDO prepared by dissolving weighed amounts of CsCCD or DPDO. The resulting solutions were then equilibrated with water.

Table 1
The structure and designation of the Diphosphine dioxides used in present work

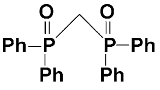
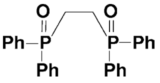
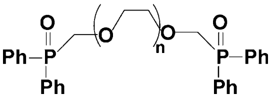
Structure	Name	Designation
	Tetraphenylmethyl diphosphine dioxide	Ph_4Me
	Tetraphenylethyl diphosphine dioxide	Ph_4Et
	Tetraphenyl polyoxyethylene diphosphine dioxide with $n\approx5$	Ph_4PEG

Table 2
Composition of 0.02 M HCCD solutions in DCE containing 0.01–0.06 M DPDO (L)

C^o_L, M	C^0_L/C_{HCCD}	Ph_4Me	Ph_4Et			Ph_4PEG
		C^{bound}_L, M	C^{bound}_L, M	C_{II}, M	C_{III}, M	C^{bound}_L, M
0.01	0.5	0.01	0.01	0.01	0	0.01
0.02	1.0	0.02	0.02	0.02	0	0.017
0.03	1.5	0.03	0.03	0.014	0.016	0.0182
0.04	2.0	0.04	0.0378	0.0032	0.0346	0.019
0.05	2.5	0.041	0.0429	0	0.0429	0.0197
0.06	3.0	0.0424	0.0475	0	0.0475	0.02

The IR spectra were recorded using a Bomem M-102 FTIR spectrometer (40 scans, resolution 4 cm^{-1}) in the 380–4000 cm^{-1} range. A cell with silicon windows and a 0.036 mm layer at the beam passage point was used. To avoid interference, the layer was wedge-shaped. The spectra were recorded within 2–3 h after preparation of solutions.

The IR spectra of the $H^+\cdot nH_2O\cdot mL$ species under study were obtained from measured data by sequential digital subtraction of the spectra of the solvent (DCE), water dissolved in DCE, and excess of free L molecules (if any) simultaneously with water molecules bound with them using the spectrum of standard DPDO solution in water saturated DCE. This allowed us to determine the concentration of free P=O groups of L molecules: $C^{free}_{P=O}=f_i\cdot C^{st}_{P=O}$, where $C^{st}_{P=O}$ is the concentration of P=O groups in standard DPDO solution; f_i is the selected subtraction coefficient that provides complete compensation of the ν(P=O) band of free DPDO. This method of spectrum subtraction and $C^{free}_{P=O}$ determination was previously described in detail in [7–9,13,14]. The concentration of P=O groups bound with proton species was evaluated as $C^{bound}_{P=O}=2C^o_L-C^{free}_{P=O}$, where C^o_L is the total DPDO concentration in solutions. The concentration of bound L molecules is equal to $1/2C^{bound}_{P=O}$. The results obtained are presented in Table 2.

3. Results and discussion

In water saturated DCE solutions HCCD forms ion pairs $[H_5O_2^+\cdot4H_2O]CCD^-$. Their IR spectra contain very broad and characteristic bands of $H_5O_2^+$ cation at ~1000 and 1738 cm^{-1} together with intense absorption in the whole frequency region below 3000 cm^{-1}, as well as the bands ν_{as} 3629, ν_s 3566 and δ 1610 cm^{-1} of H_2O molecules in its first coordination sphere [13]. The DPDO addition to these solution leads to the formation of a number of proton