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Complexes of the Proton and Its Hydrates with Carbamoylphosphine Oxide in Wet Dichloroethane Solutions

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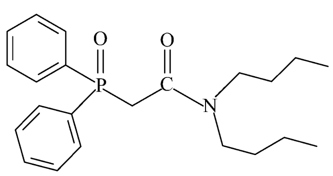
To better understand the complex equilibria involved in the UNEX process for acidic solvent extraction of radionuclides, the interaction of a carbamoylphosphine oxide ligand (L) with the proton of hydrated chlorinated cobalt(III)dicarbollide acid, $H[Co(C_2B_9H_8Cl_3)_2]$, has been studied in wet 1,2-dichlorethane (DCE) solution using IR and NMR (^{13}C and ^{31}P) spectroscopy. The formation of two groups of complexes has been determined. The first group contains three complexes with 1:1 composition of acid to ligand (Scheme 1). The second group of complexes has 1:2 composition in the equilibrium, shown in Scheme 2. Within each group, the complexes differ in composition only by the number of incorporated water molecules. The equilibria (Schemes 1 and 2) are both very sensitive to the content of self-associated water in solution and are driven by its concentration, which is unsteady and depends on the solution preparation history. The simultaneous presence of both anhydrous (**I**, **II**) and hydrated (**III**, **IIIa**, **IV**) proton solvates indicates that the enthalpies of carbamoylphosphine oxide complex formation with H^+, H_3O^+, and $H_5O_2^+$ are very close to each other.

Introduction

Modern methods for the separation of radioactive wastes are based on classic solvent extraction technologies. At present, two such extraction technologies have been developed: the transuranic extraction (TRUEX) process and the universal extraction (UNEX) process. Both processes are based on the use of (*N*,*N*-di-*n*-butylcarbamoylmethyl)diphenylphosphine oxide (CMPO) as the active actinide extractant. The UNEX process is based on metal cation exchange for the proton in a unique acidic mixture of CMPO, poly(ethylene glycol), and the chlorinated cobalt(III) dicarbollide anion (CCD).[1] Its main advantage is the simultaneous recovery of all major radionuclides in a single process. However, the extraction characteristics of the solution are dependent on the preparation history, suggesting that UNEX solutions are complex mixtures with many intermolecular interactions. For example, while preparing the UNEX solutions for tests,[2] it was found that three separately prepared fresh portions with the same composition (0.08 M CCD, 0.02 M CMPO, 0.6% PEG) extracted europium(III) with distribution coefficients differing by more than a factor of 2. If solutions are first heated to 80 °C for 5 min and then cooled, their extractability becomes reproducible and even improves. Thus, further development of the UNEX process is constrained by an insufficient understanding of the mechanism associated with the complicated extraction process at the molecular level. Complexation of poly(ethylene glycol) with hydrated chlorinated cobalt(III) dicarbollide acid (hydrated HCCD) is known to be reproducible and has been studied in detail.[3,4] That is why the investigation of CMPO interactions with hydrated HCCD in wet organic solutions, as well as the dependence of the structure and composition of species formed on the preparation conditions, is of key importance. The large, hydrophobic CCD^- anion, $[Co(C_2B_9H_8Cl_3)_2]^-$, is an interesting conjugate base for study, because the anhydrous acid (HCCD) has recently been deduced to be a superacid.[5]

The study of the molecular state of proton solvates and hydratosolvates is also of fundamental importance in solution-phase chemistry and biology.[6,7] Many of these studies involve compounds with very strong H-bonds, and most use vibrational (IR and Raman) spectroscopy, which is the most efficient technique for elucidation of the nature of $H^+\cdot nH_2O\cdot mL$ species with strong H-bonds.[6,8,9] Stepwise formation of proton hydratosolvates formed in tributyl phosphate (TBP) solutions of strong acids (hydrated $HFeCl_4$, $HClO_4$, and HCl) has been studied in detail.[10−12] The proton is in the form of the $H_5O_2^+$ cation, which is located in the water core of reverse micelles near the water/TBP interface and bound with two TBP molecules of the core solvation shell via H-bonds. Diphosphine dioxides, which are more basic than TBP, form two types of complexes with hydrated HCCD acid in wet DCE solutions: anhydrous complexes containing a symmetric $(P{=})O{-}H^+{-}O({=}P)$ group with very strong H-bonds and complexes containing $H_5O_2^+$ cation.[13] Under the same conditions, crown ethers and poly(ethylene glycol)s form $H_3O^+\cdot L$ and $H_5O_2^+\cdot L$ type complexes[3] with specific bifurcated and cooperative H-bonds.[4] CMPO is a more complex reagent, because it contains three functional proton acceptor groups of different types: P=O, C=O, and $R'R_2N$.



CMPO

Its interaction with hydrated $HClO_4$ acid in water-saturated DCE solutions is distinguished by enhanced sensitivity to

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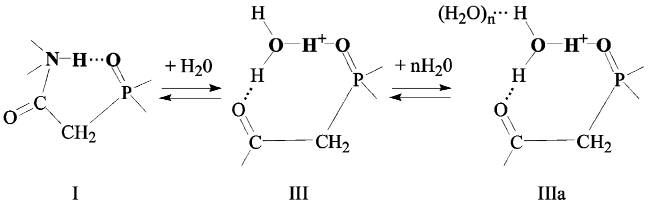
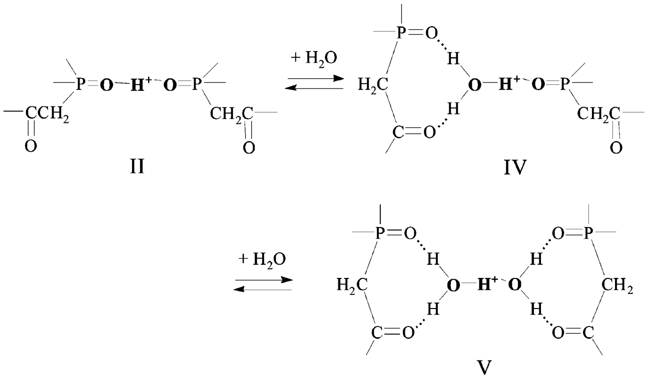
SCHEME 1



SCHEME 2



temperature and other solution preparation conditions.[14] This strengthens the assumption that there is a relationship between extraction nonreproducibility of freshly prepared UNEX solutions and the peculiarities of CMPO complexation with hydrated HCCD.

We propose that these peculiarities arise from a self-association of $[\mathrm{H}\cdot n\mathrm{H_2O}\cdot m\mathrm{L}^+]\mathrm{An}^-$ ion pairs that is very sensitive to the conditions of solution preparation. For example,[15] studies of benzene solutions of $\mathrm{H_3O^+(Carb^-)}$, where $\mathrm{Carb^-}$ = carborane ion ($\mathrm{CCD^-}$ is a carborane), show that the dual presence of both hydronium ion and benzenium salts leads to solubility of the latter, $\mathrm{C_6H_7^+(Carb^-)}$, despite its insolubility as a single component. This can be explained if aggregates of polar ion pairs of $\mathrm{H_3O^+(Carb^-)}$ incorporate polar ion pairs of $\mathrm{C_6H_7^+(Carb^-)}$. In a related example, the aging of benzene solutions of $\mathrm{H_3O^+(Carb^-)}$ in contact with its solid phase leads to a subtle transformation of the tribenzene solvate $\mathrm{[H_3O^+\cdot 3C_6H_6]Carb^-}$ to the more tightly ion-paired monosolvate $\mathrm{[H_3O^+\cdot C_6H_6\cdot Carb^-]}$. This can only be explained by an accompanying disproportion reaction which produces insoluble benzenium ion salt, a minor quantity of the soluble $\mathrm{H_5O_2^+}$ salt which, in aggregates, favors the change in $\mathrm{H_3O^+}$ ion pairing.[15] In the case of UNEX solutions, the aggregation of polar IPs may also be responsible for the peculiarities of its behavior.

In the present work, we report our IR and NMR study of the complexes which CMPO forms with hydrated HCCD acid in wet DCE solutions, prepared at different conditions.

Experimental Section

1,2-Dichloroethane (DCE) of chemical purity grade was purified using standard methods. Chlorinated cobalt(III) dicarbollide CCD (90% in H-form and 10% in Na-form) from KatChem (Czech Republic), and (*N,N*-di-*n*-butylcarbamoylmethyl)diphenylphosphine oxide (CMPO) from VEKTON (St. Petersburg, Russia) were used without any additional purification. CCD was converted into 100% H-form (HCCD) by mixing its DCE solution with 3 M $\mathrm{H_2SO_4}$ aqueous solution for 5 min.

Four series of solutions with constant 0.02 M HCCD concentration and 0.01 to 0.06 M CMPO concentrations in 0.01 M increments (solutions 1 through 6, Table 1) were prepared by mixing calculated volumes of standard HCCD and CMPO solutions prepared using weighed portions of the reagents.

TABLE 1: Composition of Series A Solutions 1 Day after Their Preparation[a]

solution	$C^{\mathrm{o}}_{\mathrm{CMPO}}$	$C^{\mathrm{I-III}}_{\mathrm{HCCD}}$	$C^{\mathrm{bound}}_{\mathrm{CMPO}}$	$C^{\mathrm{mono}}_{\mathrm{CMPO}}$	$C^{\mathrm{bi}}_{\mathrm{CMPO}}$
1	0.01	0.0090	0.01	0.0028	0.0072
2	0.02	0.0174	0.02	0.0054	0.0146
3	0.03	0.02	0.0294	0.0122	0.0172
4	0.04	0.02	0.0336	0.0155	0.0181
5	0.05	0.02	0.038	0.0196	0.0184
6	0.06	0.02	0.0395	0.0195	0.02

[a] Values in mol/L. The HCCD concentration in all solutions is constant and equal to 0.02 mol/L

IR spectra were recorded using a BOMEM MB-102 FTIR spectrometer (30 scans, 4 $\mathrm{cm^{-1}}$ resolution). Liquid solutions were recorded using a cell with $\mathrm{CaF_2}$ windows with 0.04 mm spacing in the frequency range 4000−920 $\mathrm{cm^{-1}}$. Solid compounds were recorded as thin films of amorphous products prepared by evaporating several drops of the solution on the surface of Si windows (frequency range 4000−220 $\mathrm{cm^{-1}}$).

NMR data (^{31}P, ^{13}C) were acquired using SXP-300 (^{31}P) and MSL-400 Bruker (^{13}C) spectrometers with operating frequencies of 121.47 and 104.61 MHz, respectively, at 20 °C. Chemical shifts were calculated from external 85% $\mathrm{H_3PO_4}$ and tetramethylsilane.

Determination of the Concentration of Free and Proton-Bound CMPO Molecules. IR spectra of solutions 1−6 consist of overlapping spectra of the following components: (i) DCE solvent, (ii) water dissolved in it, (iii) "free" CMPO molecules (i.e., not bound to HCCD), and (iv) compounds with a general formula $[\mathrm{H}^+\cdot n\mathrm{H_2O}\cdot m\mathrm{L}]\mathrm{CCD}^-$, where L = CMPO, $n \geq 0$, $m \geq 1$, which are the subject of our study. To isolate their IR spectra, it is necessary to subtract spectra (i)−(iii) successively from the initial spectra. The concentrations of "free" and H-bonded CMPO can be determined during this procedure. Thus, upon subtraction of the spectrum of DCE saturated with water from the IR spectra of the solutions, the bands ν_{as} 3677, ν_{s} 3592, and δ 1607 $\mathrm{cm^{-1}}$ of dissolved water are also subtracted along with the spectrum of the solvent. If the spectrum of uncomplexed CMPO molecules, which are the equilibrium mixture of anhydrous and hydrated molecules (eq 1)

$$\mathrm{CMPO} + n\mathrm{H_2O} \leftrightarrow \mathrm{CMPO}\cdot n\mathrm{H_2O} \qquad (1)$$

is subtracted with a subtraction factor f that allows for complete compensation of the bands of $\mathrm{H_2O}$ molecules in $\mathrm{CMPO}\cdot n\mathrm{H_2O}$ hydrates, then the ν(P═O) band at 1200 $\mathrm{cm^{-1}}$ of "free" P═O groups (Figure 1b) as well as all other bands of excess CMPO are also simultaneously subtracted. The resulting spectra belong to the complexes $[\mathrm{H}^+\cdot n\mathrm{H_2O}\cdot m\mathrm{L}]\mathrm{CCD}^-$ under investigation, and only such spectra will be considered hereinafter.

The concentration of uncomplexed (anhydrous and hydrated) CMPO molecules is determined using the equation $C^{\mathrm{free}}_{\mathrm{CMPO}} = C^{\mathrm{st}}_{\mathrm{CMPO}} \times f$, where $C^{\mathrm{st}}_{\mathrm{CMPO}}$ is the CMPO concentration in its standard water-saturated DCE solution. The spectrum of the latter is used for subtraction. The concentration of CMPO bound with the cation via the P═O group is evaluated as $C^{\mathrm{bound}}_{\mathrm{CMPO}} = C^{\mathrm{o}}_{\mathrm{CMPO}} - C^{\mathrm{free}}_{\mathrm{CMPO}}$. The results obtained are reported in Table 1.

The IR spectra of solids isolated from solutions 4−6 developed a band of free P═O group at 1200 $\mathrm{cm^{-1}}$. Subtraction of this band using the spectrum of solid CMPO (thin amorphous film on Si window surface) made it possible to isolate the spectra of the complexes under study and determine the molar fraction of free CMPO. Hence, the molar fraction of CMPO H-bonded

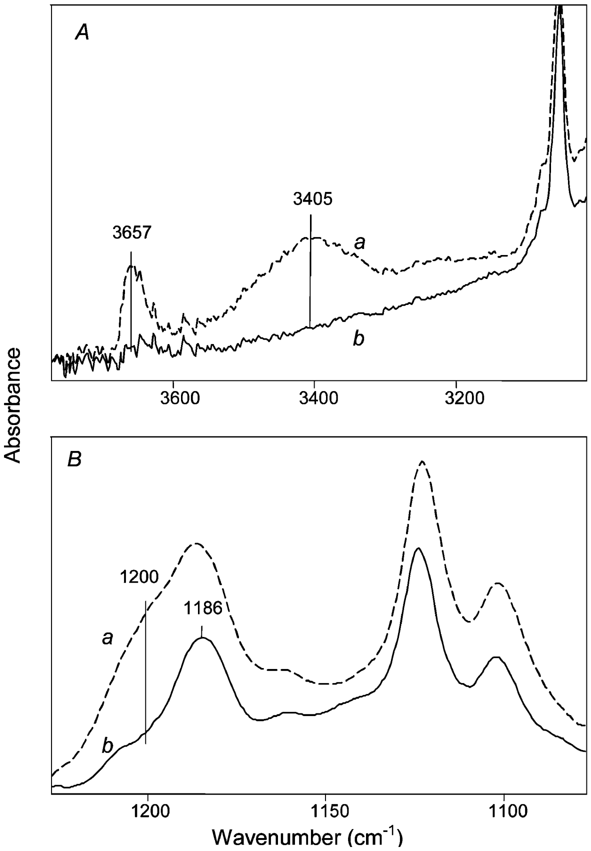


Figure 1. IR spectrum of a DCE solution of 0.02 M HCCD + 0.06 M CMPO (solution 6 from series A; see Table 1) in the O−H (A) and P=O (B) frequency range after subtracting the spectrum of solvent and dissolved monomer water (spectrum *a*). Spectrum *b* is obtained by subtracting from *a* the spectrum of "free" CMPO up to complete compensation of the bands of H_2O molecules in $CMPO{\cdot}nH_2O$ hydrates (A) and the band $\nu(P{=}O) = 1200$ cm^{-1} of "free" P=O groups (B). Spectrum *b* belongs to complex **IV**.

TABLE 2: Composition of Solid Products Isolated from Solutions 1−6 (see Table 1)

sample	α_{CMPO}^{free} [a]	$CMPO_{bound}/HCCD$ [b]
1	~0	0.5
2	~0	1.0
3	0.085	1.373
4	0.162	1.675
5	0.26	1.85
6	0.32	2.04

[a] Ratio of free CMPO relative to total amount of CMPO. [b] Molar ratio of coordinated CMPO relative to HCCD.

via the P=O group was determined, and the average statistical stoichiometry of complexes $C_{CMPO}^{bound}/C_{HCCD}$ was calculated (Table 2).

Results and Discussion

The IR spectrum of the $[Co(C_2B_9H_8Cl_3)_2]^-$ anion in the ion pairs $[H^+{\cdot}nH_2O{\cdot}mL]CCD^-$ under study is always the same and does not depend on the cation composition or the solution preparation conditions. This indicates that the interaction of the large, weakly basic $[Co(C_2B_9H_8Cl_3)_2]^-$ anion with different cations is so weak that it is not reflected in their IR spectra and may be neglected. That is why hereafter we shall consider only the IR spectra of cationic complexes of the ion pairs.

The IR spectra of water-saturated DCE solutions of 0.02 M HCCD and 0.01−0.06 M CMPO (i.e., solutions 1−6) are dependent on the preparation temperature and the time of aging. Therefore, we have studied a set of solutions prepared at 15 °C (series A and B) and 20−22 °C (series C and D). The IR spectra of these series changed during the first several hours after their preparation but after 24 h attained a constant state. That is why we recorded the IR spectra of freshly prepared solutions (series B and C) and the same solutions after 24 h (Series A and C). If solutions from series A−D with the same CMPO/HCCD ratio are evaporated on the surface of Si window, the IR spectra of these four solid films coincide, irrespective of the solution preparation history. Hence, first we shall discuss the IR spectra of the solids isolated from solutions under consideration.

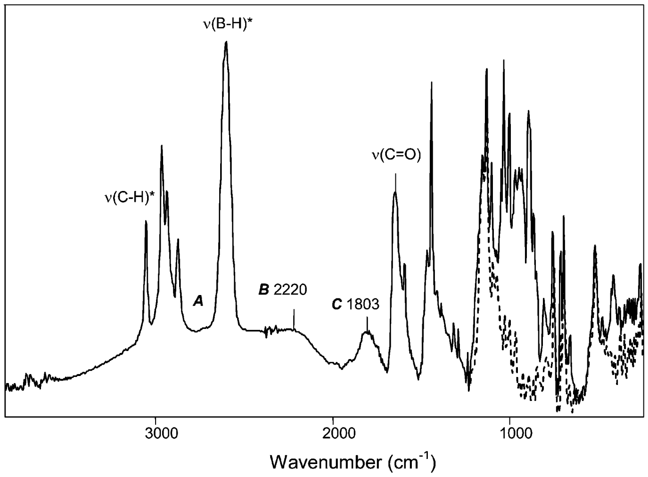
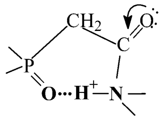


Figure 2. IR spectrum of the solid phase isolated from solution 2. It belongs mostly to complex **I**. The bands of the CCD^- anion are marked by asterisks or subtracted in the region 1200−400 cm^{-1} (dashed line).

Solids. A complex with 1:1 composition should be formed in sample 1 (see Table 2), because HCCD is in excess relative to CMPO. Its IR spectrum contains bands $\nu(C{=}O) = 1653$ cm^{-1} and $\nu(P{=}O) = 1150$ cm^{-1} which are different from those of free CMPO and characterize CMPO molecules bound to a cation. These bands of the formed complex, hereinafter denoted as **I**, are more intense in the spectrum of sample 2 where the molar ratio $CMPO_{bound}/HCCD = 1$. The IR spectrum of complex **I** (Figure 2) does not contain bands from water but does show a broad absorption in the frequency range 1600−3200 cm^{-1}, with the so-called A (~2700), B (2230), and C (1805 cm^{-1}) Fermi resonance structures,[16−18] that characterizes H-complexes with O···H−O, O···H−N, or N···H−O fragments having strong asymmetric hydrogen bonds. The shift of the $\nu(P{=}O)$ band to lower frequency by 50 cm^{-1} indicates that the oxygen atom of the P=O group forms an H-bond of moderate strength. The C=O group cannot be involved in H-bonding, because the $\nu(C{=}O)$ frequency actually increases (by 16 cm^{-1}) compared to the free ligand. This increase can occur only if complex **I** includes protonation on nitrogen forming an O···H−N fragment with a strong H-bond. Nitrogen protonation increases participation of the O atom lone pairs in the carbonyl double bond, increasing the bond order and $\nu(C{=}O)$. Therefore, the structure of **I** is represented as



(I)

The IR spectrum of **I** is identical to that of a similar complex formed in extracts from concentrated perchloric acid by CMPO solutions in DCE.[13]

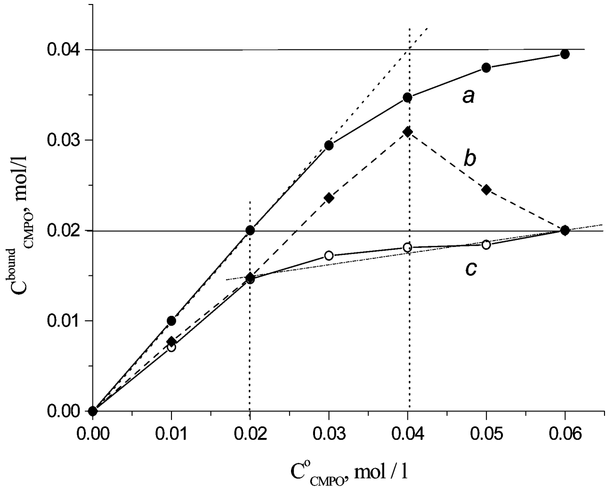
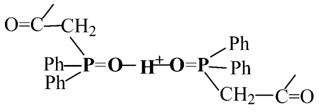


Figure 3. Dependencies on the total CMPO concentration of: the concentration of all types (mono- and bidentate) of CMPO molecules bound with proton via the P=O group for series A and B (line *a*); the concentration of bidentate-bound CMPO molecules (with C=O group) for series A (line *c*) and for series B (line *b*).

When the CMPO/acid molar ratio grows above 1, bands of a second complex (**II**) appear in the IR spectra. Their intensity reaches a maximum in samples 5 and 6 where the molar ratio CMPO$_{bound}$/acid = 2 (Table 2). Hence, complex **II** formed in molar excess of CMPO has the composition CMPO/HCCD = 2:1. The spectrum of this complex is typical of a proton disolvate [L−H$^+$−L], in our case with the following structure



II

Its spectrum has very wide and intense bands, δ(OHO) at 1440 cm^{-1} and ν_{as}(OHO) at 880 cm^{-1}, from the O−H$^+$−O group having a very strong H-bond and a single-well proton potential with a flat bottom (so-called short, strong, low-barrier (SSLB) H-bonds).[19−22] The ν(C=O) frequency coincides exactly with the corresponding frequency of the free ligand (1637 cm^{-1}). The ν(P=O) frequency is not observed in the spectra due to its abnormal broadening in proton disolvates.[23,24]

Solutions. The concentrations of CMPO molecules bound to cationic complexes via the P=O groups relative to the total CMPO concentration are practically the same for different solution series (Figure 3a). However, the spectra of the resulting compounds are different. This means that they depend on the solution preparation conditions.

Series A Solutions (24 h after preparation at 15°C). The IR spectra of complexes formed in solutions 1 and 2 have three ν(C=O) bands: a weak band of complex **I** at 1653 cm^{-1}, a more intense band of complex **II** at 1637 cm^{-1}, and a strong band at 1607 cm^{-1} belonging to a new complex that will be hereafter denoted as **III** (Figure 4). Since the 1637 cm^{-1} band of complex **II** belongs to an unperturbed C=O group, it can be easily subtracted using the spectrum of free CMPO. (Note: The ν(C=O) = 1637 cm^{-1} band does not overlap with the δ(H$_2$O) band, because no stretching vibration bands of water molecules in the frequency range above 3000 cm^{-1} are observed.) This allows for better isolation of the C=O vibration band in complexes **I** and **III** (Figure 6b) and the determination of the concentration of CMPO molecules in monodentate fashion in complex **II** (via the P=O group): $C^{mono}_{CMPO} = C^{st}_{CMPO} \times f_1$, where C^{st}_{CMPO} is the CMPO concentration in a standard solution, and f_1 is the subtraction coefficient. Then, the total concentration of bidentate CMPO molecules in complexes **I** and **III** can be calculated as $C^{bi}_{CMPO} = C^{bound}_{CMPO} - C^{mono}_{CMPO}$ (Table 1).

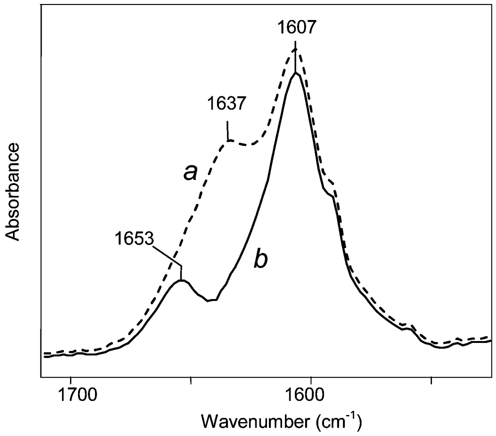
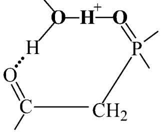


Figure 4. IR spectrum in the frequency range of the C=O vibrations of the complexes, formed in solution 2 (series A) before (spectrum *a*) and after (spectrum *b*) subtraction the ν(C=O) band at 1634 cm^{-1} of the monodentate-bound CMPO molecules.

The spectra of solutions 1 and 2 also contain bands ν_{as} 3637 and ν_s 3582 cm^{-1} belonging to [$H_5O_2^+ \cdot 4H_2O$] cations arising from excess HCCD (i.e., not complexed by CMPO).[3] The intensity of these bands can be used (using the spectrum subtraction procedure) to determine the concentration of these HCCD molecules (C^{free}_{HCCD}) and HCCD molecules forming complexes **I**−**III**: $C^{\mathbf{I-III}}_{HCCD} = C_{HCCD} - C^{free}_{HCCD}$ (see Table 1). Then, the averaged CMPO/HCCD composition of complexes **I** and **III** can be determined as $C^{bi}_{CMPO}/(C^{\mathbf{I-III}}_{HCCD} - {}^1/_2 C^{mono}_{CMPO})$. Using the data in Table 1, one can find that this ratio is equal to 1 for both solutions. Therefore, the CMPO/HCCD molar ratio is equal to 1 in both complexes **I** and **III**.

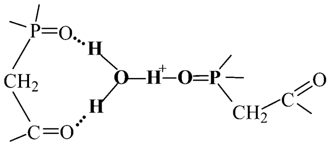
The best spectrum of complex **III** is observed for solution 2, because overlapping by the spectrum of complex **II** is minor, and one can neglect a very weak spectrum of complex **I**. The spectrum of complex **III** is satisfied by the following structure



III

The ν(P=O) band is not observed in the spectrum due to its abnormal broadening resulting from adjacency of the P=O group to an O−H$^+$−O group with an almost single-well proton potential.[23,24] The small shift of ν(C=O) to lower frequency by 30 cm^{-1} corresponds well to a C=O group bound to a hydrated proton with a medium strength H-bond. The extended absorption of the asymmetric H$_3$O$^+$ ion in the 3000−1500 cm^{-1} range[10] and a narrow band ν(OH) = 3672 cm^{-1} of one free OH group are also observed.

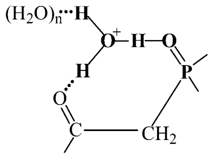
The dependence of the concentration of CMPO$_{bound}$ on its total concentration in solution reaches a plateau at 0.04 M (Figure 3a, Table 1). This means that complexes with CMPO/HCCD ratios equal to 2 are formed at high C^{o}_{CMPO}. Two intense ν(C=O) bands are observed in the IR spectra: a band at 1637 cm^{-1} from the free C=O group of CMPO molecules with monodentate coordination (via the P=O group) and a band of a bound C=O group of CMPO molecules with bidentate coordination. The frequency of the latter is decreased to 1612 cm^{-1}. In excess of free CMPO (solutions 5 and 6), the concentrations of the C═O groups of both types become equal reaching 0.02 M and coinciding with the HCCD concentration (Table 1, Figure 3c). Therefore, only one new complex with molar ratio CMPO/HCCD = 2:1 having one CMPO molecule with monodentate coordination and a second one with bidentate coordination is formed in these solutions (**IV**).



IV

The ν(P═O) frequency of bidentate CMPO is at 1186 cm^{-1}, indicating a medium strength H-bond linking the P═O group with the hydrated proton (Figure 1b). The H-bond formed with the C═O group is somewhat weaker than in complex **III** ($\Delta\nu$ decreases by 25 cm^{-1}). The spectrum of the monodentate CMPO molecule in complex **IV** is similar to that in complex **II**. The extended absorption of the asymmetric hydroxonium ion in the 3200−1500 cm^{-1} frequency range is similar to that observed in the spectrum of complex **III**, except that the ν(OH) band of a free OH group is not observed.

Series B Solutions (freshly prepared at 15°C). The easiest way to see the differences between the spectrum of a solution recorded immediately after preparation and the spectrum of the same solution recorded the next day is to take their difference. The complexes having higher concentrations in the freshly prepared solution will give positive differences in absorption bands, whereas those having higher concentrations in the aged solution will have negative intensities in the difference spectrum. The difference spectrum for solutions 1 as well as for solutions 2 show positive bands for (i) self-associated water molecules (3400 and 1630 cm^{-1}); (ii) a very weak ν(C═O) 1647 cm^{-1} band of complex **I** (the band of the C═O group of complex **II** is practically compensated); and (iii) a spectrum similar to that of complex **III** with slightly decreased ν(C═O) frequency (to 1601 cm^{-1}) and a more intense absorption in the range of ν(P═O) 1150−1060 cm^{-1}. The spectrum of complex **III** with the ν(C═O) band at 1607 cm^{-1} had negative intensity. Therefore, fresh solutions 1 and 2 contain self-associated water. This is known to form when DCE solutions of oxygenated compounds are saturated with water, and it gradually dissipates with time.[3] The presence of such water molecules has practically no effect on the concentrations of complexes **I** and **II**. However, it hydrates complex **III** to form complex **IIIa**



IIIa

Addition of water molecules to the OH group of hydrated proton results in redistribution of the positive charge toward the oxygen atom of H_3O^+. This results in a strengthening of the CO···H_3O^+ bond, decreasing the ν(C═O) frequency. On the other hand, the bond of the P═O···H_3O^+ bond weakens, and the $(H_2)O^+$—H—O(P) group becomes less symmetric. This narrows the ν(P═O) band, such that it becomes observable as wide absorption in the 1150−1060 cm^{-1} range.

The concentration of CMPO molecules with bidentate coordination is the same in both series of solution 1 and 2 (Figure 3a). However, when excess of free CMPO appears in solutions, the $C^{\mathrm{bi}}_{\mathrm{CMPO}}$ dependence on $C^{\mathrm{o}}_{\mathrm{CMPO}}$ for series B becomes significantly different from that of series A (Figure 3b and c). It continues to grow linearly and has a sharp bend at $C^{\mathrm{o}}_{\mathrm{CMPO}}$ = 0.04 M (solution 4), which corresponds to the formation of a new complex **V** with molar ratio CMPO/HCCD = 2.

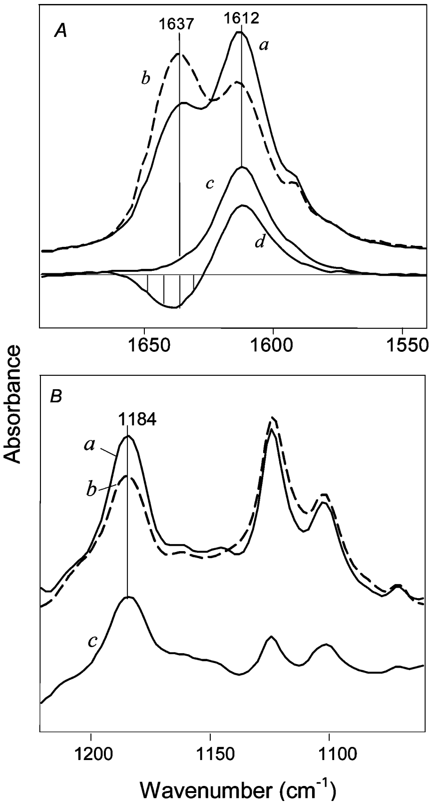
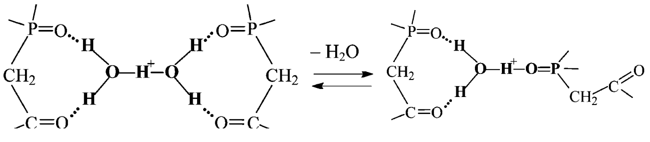


Figure 5. IR spectra of solution 4 (series B) in the frequency range of C═O (A) and P═O groups (B): (*a*) registered at once after preparation; (*b*) after 1 day; (*c*) difference (*a*) − *f* × (*b*), where *f* is a subtraction factor that allows for complete compensation of the band ν(C═O) 1637 cm^{-1} of monodentate CMPO; (*d*) the difference (*a*) − *f* × (*b*) with *f* = 1.

The difference spectrum of fresh and aged solution 4 shows positive intensity bands from bidentate CMPO molecules, ν-(C═O) 1612 cm^{-1} and ν(P═O) 1184 cm^{-1}, in addition to those of self-associated water molecules. The ν(C═O) 1637 cm^{-1} band of monodentate CMPO molecules has negative intensity (Figure 5). This observation may be explained by the fact that complex **V**, which is gradually transformed into complex **IV**, is formed in the fresh solution

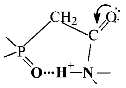
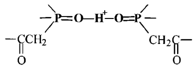
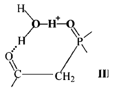
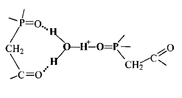
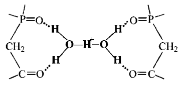


V IV

The bands of bidentate CMPO molecules practically coincide in the spectra of complexes **IV** and **V**. The mostly characteristic ν(P═O) and ν(C═O) frequencies of CMPO molecules forming complexes **I**−**V** are presented in Table 3.

Series C Solutions (freshly prepared at 20−22°C). The IR spectra of this series are similar to those of series A. Unlike the spectra of series B, they have practically no signals from self-associated water, whereas changes in the absorption band

TABLE 3: The ν(P═O) and ν(C═O) Frequencies of CMPO Molecules in Complexes I−V

Compound		ν(P=O) (Δν) cm^{-1}	ν(C=O) (Δν) cm^{-1}
"Free" CMPO		1200	1637
I		1150 (-50)	1653 (+16)
II		*	1637 (0)
III		*	1607 (-30)
IV		* 1186 (-14)	1637 (0) 1612 (-25)
V		1184 (-16)	1612 (-25)

*The ν(P═O) band of P═O groups forming very strong O−H$^+$−O bonds is too broad to identify.

intensities of formed compounds indicate that the equilibria are shifted toward less hydrated complexes **I**, **II**, and **IV**.

Series D Solutions (1 day after preparation at 20−22°C). The IR spectra of series D are significantly different from all those discussed above. In fact, they are similar to the spectra of the solid phases isolated from the extracts and have practically no absorption bands of hydrated complexes **III**−**V**. Nevertheless, the intensities of bands of monomeric water molecules dissolved in DCE (3677, 3591, and 1607 cm^{-1}) are the same as in the spectra of series A−C discussed above, confirming that solutions of series D are indeed saturated with water.

The spectra of solutions 1 and 2 contain overlapping spectra of only two complexes, **I** and **II**. On passing to solution 3, the intensity of the spectrum of complex **I** decreases, and in solution 4, it disappears. On the other hand, the intensities of the most characteristic for complex **II**, the broad bands δ(OHO) ≈ 1400 cm^{-1} and ν_{as}(OHO) = 910 cm^{-1} of its central fragment O−H$^+$−O, reach a maximum for solution 4, when the molar ratio $\mathrm{CMPO_{bound}/HCCD} = 2$. After that, they do not change with the further increase of the CMPO concentration.

NMR was used for the investigation of these solutions because the absence of hydrated compounds means that fast exchange processes mediated by water will not be occurring.

Figure 6 presents the ^{13}C NMR spectrum of CMPO in DCE solution (in the absence of HCCD) and the peak attribution. The peaks of nuclei C1 and C5, and to a lesser extent nuclei C2 and C3, are split by spin−spin coupling with the ^{31}P nucleus. The peaks from C7 and C8 are observed as doublets, because the butyl groups are nonequivalent relative to the O atom. This is typical for dialkyl amide groups. However, this difference is not resolved for atoms C9 and C10.

Exchange-averaged peaks from different type of CMPO molecules, those that are free and those forming complexes **I** and **II**, are observed in the ^{13}C and ^{31}P NMR spectra of solutions 2, 3, 5, and 6. Therefore, let us discuss in detail the NMR spectra of solution 1, where CMPO molecules are predominantly in the form of complex **I**, and solution 4, containing only one complex **II** in the presence of a negligibly small excess of free CMPO (Table 4).

The interaction of CMPO in complex **II** with H$^+$ via the P═O group mostly shifts the NMR peaks of the P atom and C atoms nearest to it: C5 of the (P)CH$_2$ group and C1 (and C4) of the phenyl groups donating electron density to the P═O bond. The peaks of the more remote C6 and C7 nuclei experience smaller shifts. In general, the changes of the chemical shifts of ^{13}C and ^{31}P nuclei in complex **II** are in accord with the electron density redistribution after bonding of the CMPO molecule with H$^+$ according to the structure of complex **II**.

The chemical shifts of the ^{13}C and ^{31}P nuclei in complex **I** are also in good agreement with its structure. Protonation of the N atom together with a simultaneous formation of a strong H-bond to the P═O group leads to a considerable downfield shift of the C5 line, opposite to that observed for complex **II**. Also significantly changed are the positions of the peaks of nuclei C7 and even C8. Electron density shifts from the phenyl groups (C1 moves upfield) to the P atom and (P)CH$_2$ group, and further to C6 and the N atom.

Summary and Conclusions

The results indicate that both anhydrous complexes **I** and **II** and hydrated complexes **III**−**V** with different numbers of water molecules can be formed in water-saturated CMPO + HCCD solutions containing a constant concentration of monomeric water dissolved in DCE (0.1 M).

Self-associated water plays a key role in the formation of the different cationic complexes because of ion pair self-

TABLE 4: ^{13}C and ^{31}P NMR Spectra of Complexes I (solution 1) and II (solution 4)

		complex **I**		complex **II**		
nucleus	atom	δ ppm {J(P−C), Hz}	$\Delta\delta^a$ ppm	δ ppm {J(P−C), Hz}	$\Delta\delta^a$ ppm	CMPO in DCE; δ, ppm {J(P−C), Hz}
^{13}C	C1	125.4 {92}	−4.8	127.3 {108}	−2.9	130.2 {106}
	C2	131.2	1.4	130.5	0.7	129.8
	C3	132.2	0.1	132.2	0.1	132.1
	C4	136.6	2.6	136.5	2.5	134.0
	C5 (P)CH$_2$	42.6	5.9	34.2 {66.1}	−2.5	36.7 {71.2}
	C6 C═O	169.8	4.9	166.8	1.9	164.9
	C7 CH$_2$(N)	52.6; 50.6	3.0	50.5; 48.4	0.9	49.6; 46.9
	C8	30.8; 29.8	−1	31.4; 30.1	−0.4	31.8; 30.4
	C9	20.7	−0.2	20.9	0	20.9
	C10	14.2		14.2		14.4
^{31}P	P	40.8	15.7	39.0	13.9	25.1

[a] Shift relative to the corresponding peak in free CMPO.

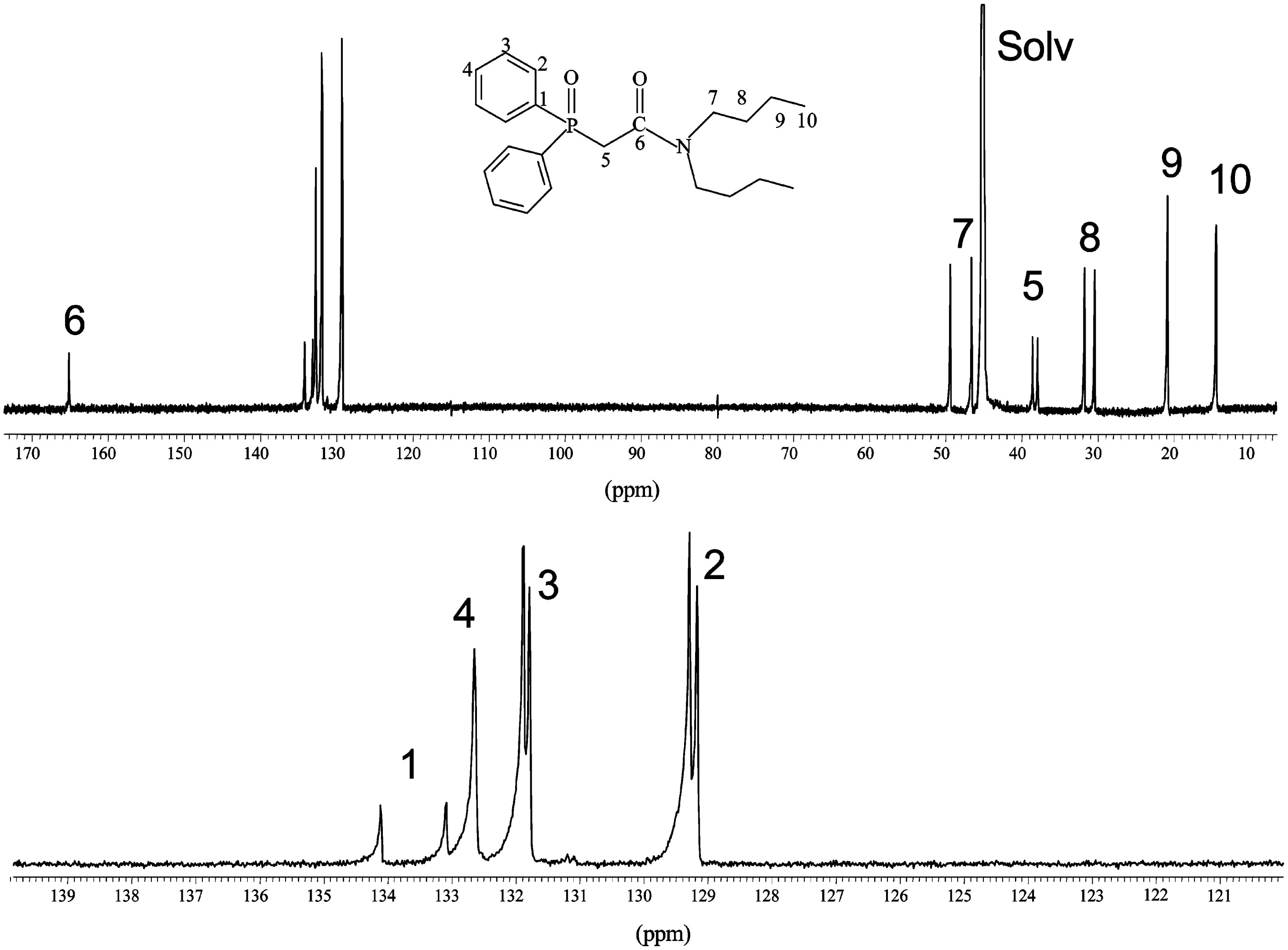
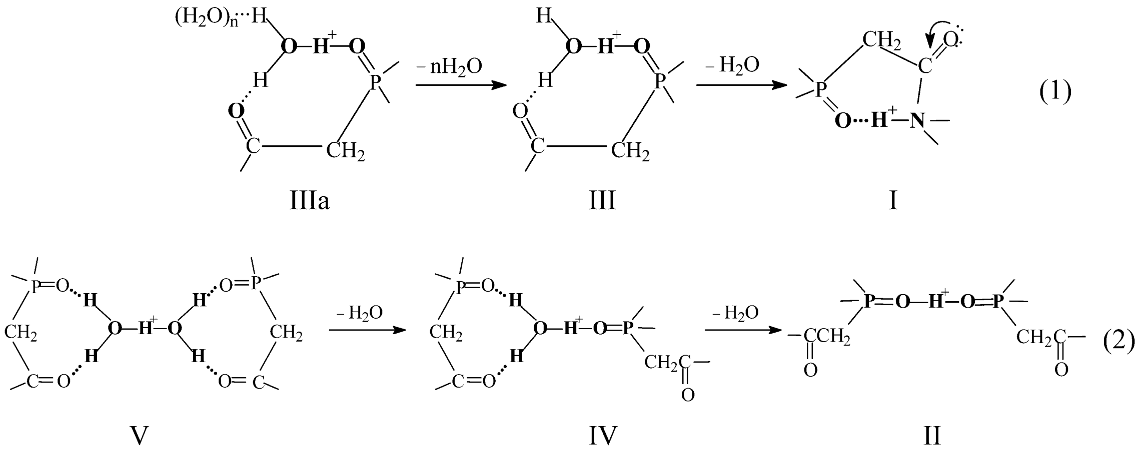


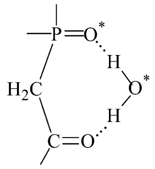
Figure 6. ^{13}C NMR spectrum of CMPO in DCE solution (the spectrum of the phenyl groups is presented in expanded scale). Peaks are labeled according to the numbering scheme shown for CMPO. Solv denotes the signal of DCE solvent.

SCHEME 3



association. This self-association is similar to micelle formation and is seen in solutions of strong acids in organic solvents.[11,15] In the benzene solutions of $H_3O^+Carb^-$, it is responsible for variability in neighboring environment of the H_3O^+ cation, changing the IR spectrum of the hydronium ion.[15] In associates of tetrachloroferrate acid, $H^+(H_2O)_xFeCl_4^-$, formed in tributyl phosphate solutions, it is responsible for the incorporation HCl in reverse nanomicelles of definite composition.[11] We have also identified self-associated water in DCE solutions of poly(ethylene glycol) and crown ethers with HCCD, and its behavior and properties are similar to that of micellar water.[3] When the temperature is increased or the solutions are aged, the micelles are destroyed, and water is isolated in the form of a separate phase without change in the concentration of monomer water dissolved in DCE. The present investigation shows that self-associated water significantly affects related processes involving CMPO.

The stepwise shift of equilibria (1) and (2) (Scheme 3) from left to right occurs in solution as self-associated water is taken from them. This is possible only if the formation enthalpies of complexes **I**, **III**, and **IIIa** in equilibrium (1) or complexes **II**, **IV**, and **V** in equilibrium (2) are close to each other. For complexes in equilibrium (2), this means that the proton acceptor properties (basicity) of oxygen atoms in the P═O group of CMPO and water molecule bound to CMPO are comparable. This is one of the reasons for the sensitivity of eq 2 to hydration levels and contributes to the nonreproducibility of the extraction process. The similarity of the basicity of these two oxygen atoms (see asterisks below)



is not too surprising, because a significant increase in the basicity of a water molecule forming two H-bonds with basic molecules is well-known. For example, the C═O group of butyl acetate is more basic than a monomer water molecule.[25] However, the basicity of a double-solvated water molecule (C═O···H─O─H···O═C) increases to such an extent that it surpasses the basicity and proton acceptor properties of the butyl acetate C═O group. Evidently, this feature of a water molecule leads to the formation of the variety of proton hydratosolvates in solutions, and their concentrations will be dependent on the presence of "excess" micellar water in solutions. The unsteady and not always reproducible concentration of this type of water leads to corresponding variability in the position of equilibria (1) and (2).

If complexes **I**, **III**, and **IIIa** (or **II**, **IV**, and **V**) have different abilities to exchange a proton for a metal cation, this may be one of the reasons why the extraction properties of HCCD/CMPO solutions in DCE depend on their preparation history.

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