JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 6, 47–53 (1993)

PRECIPITATION OF STRONG UNCHARGED ORGANIC ACIDS WITH VARIOUS CROWN ETHERS OR WITH ACYCLIC POLYETHERS FROM AQUEOUS MEDIUM. CHARACTERIZATION OF ADDUCTS IN THE SOLID STATE

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It was found that substituted picric acids form slightly soluble 1 : 2 : 2 adducts with several simple crown ethers or with tri-, tetra-, or pentaethylene glycol dimethyl ether (glymes 4, 5 and 6) in water, whereas 2,4,6-trinitrobenzenesulfonic acid forms a 1 : 1 : 1 adduct with dicyclohexano-18-crown-6 (*cis-syn-cis*). The ability of a crown ether to precipitate a given acid follows the order dicyclohexano-18-crown-6 (*cis-syn-cis*) > benzo-15-crown-5 > dicyclohexano-24-crown-8 > 18-crown-6 > 21-crown-7, 15-crown-5 ≫ 12-crown-4, roughly in the order of its base strength. Precipitation can occur even when the concentration(s) of one or more of the components are $<10^{-4}$ M. The solubility products of the 18-crown-6 complexes with dichloro- or dimethylpicric acids were estimated. In the solid state the 1 : 2 : 2 dicyclohexano-18-crown-6 (*cis-anti-cis*)–dichloropicric acid–water complex, which reportedly has two pseudohydronium ions lacking C_{3v} symmetry of H_3O^+, exhibits an IR spectrum in the OH stretching region characteristic of an aqua complex.

INTRODUCTION

Many weak uncharged organic acids, HX, that are good hydrogen bond donors, such as substituted phenols[1-3] or aliphatic carboxylic acids,[4] can form 1 : 1 : 1 or 1 : 2 : 2 (crown: HX : H_2O) adducts with macrocyclic polyethers, e.g. 18-crown-6. The water molecule(s) function as a hydrogen bond donor to the crown ether oxygens and a hydrogen bond acceptor toward the acid functional group. An excellent review on this subject has appeared.[5] Generally, the above adducts have been crystallized from a low- or medium-polarity solvent containing water, such as tetrahydrofuran or toluene, but not from water itself. When the organic acid is sufficiently strong ($pK_a < 0$), complexes can form with a crown ether binding a hydronium or one or two pseudohydronium ion(s) (see below). An example of a hydronium ion complex is 18-crown-6·$H_3O^+CF_3SO_3^-$,[6] which was characterized from its IR and Raman spectra.

In order to obtain further information as to the nature of the bound water, the conformation of the polyether ring and the polarity of the hydronium and pseudohydronium ion adducts, IR, differential scanning calorimetric (DSC), D_2O–H_2O vapor exchange and melting point experiments were performed in this study. The complexes investigated were 18-crown-6·H_3O^+·dichloropicrate (**1**),[7] dicyclohexano-18-crown-6 (*cis-anti*-cis)(H_3O^+·dichloropicrate)$_2$ (**4**)[8] and dicyclohexano-18-crown-6·H_3O^+·picrylsulfonate, the last two being slightly water soluble.

It was concluded from single-crystal x-ray diffraction studies that 18-crown-6(dichloropicric acid·H_2O)$_2$ (**2**)[9] is non-ionic whereas **4** is ionic.[8]

In addition, a survey was conducted to ascertain which strong uncharged acids (i.e. nitrophenols, nitrobenzenesulfonic and nitrobenzoic acids) are precipitated from water by simple water-soluble crown ethers or acyclic polyethers. The solubility products in water of **2**, 18-crown-6(HPiMe$_2$·H_2O)$_2$ (**2a**) and glyme-6(HPiCl$_2$·H_2O)$_2$ were also determined. The following abbreviations are used in this paper: 18-crown-6 = 18C-6, dicyclohexano-18-crown-6 = DCC-18C-6, benzo-15-crown-5 = B-15C-5, dichloropicric acid = HPiCl$_2$, dimethylpicric acid = HPiMe$_2$, picrylsulfonic acid = HPiSA and DCE = dichloroethane.

Knowledge of formation of the above water-insoluble adducts could aid in designing liquid membrane carrier systems for exchange of X^- (e.g. picrate) with OH^-.

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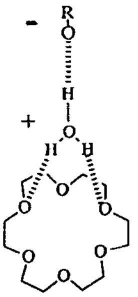
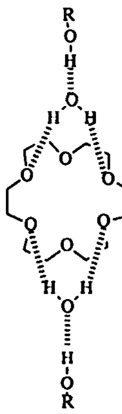
0894–3230/93/010047–07$08.50

Received 20 March 1992
Revised 14 July 1992

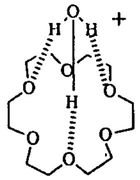


1



2

$R\text{-}OH\cdots O\text{—}R^{-}$



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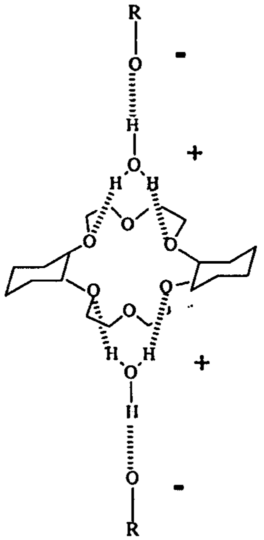

4

1,2,3,4 R = 2,4,6-$(NO_2)_3$ - 3,5 Cl_2 - phenyl

The water-immiscible phase can contain DCC-18C-6 and the aqueous phases picric acid and $Mg(OH)_2$ separately. A monesin Na^+–H^+ liquid exchange membrane has been described by Cussler and Evans.[10] Precipitation from aqueous medium as crown ether adducts can effect separations of trinitro-aromatic sulfonic or aromatic hydroxy compounds from their mono- or dinitro analogues. Conversely, water-soluble crown ethers can be separated from their mixtures by precipitation with substituted picric acids.

RESULTS

Precipitation from water of aquo complexes of crown ethers and uncharged acids

Results of a preliminary survey of the precipitation of phenols and sulfonic and benzoic acids ($pK_a < 4$) from aqueous medium with six water-soluble crown ethers are summarized in Table 1. It was found that glyme-6,[7] glyme-5 and glyme-4 (this work) form slightly soluble 1:2:2 adducts with $HPiCl_2$. Neither 0·05 M $HPiCl_2$ nor 0·005 M $HPiMe_2$ is precipitated by 1 M 12-crown-4. The ability of a crown ether to precipitate a given acid generally follows the order DCC-18C-6 (isomer A) > B-15C-5, DCC-24C-8 > 18C-6 > 21C-7,15C-5 ⋙ 12C-4. This is approximately the order of decreasing base strength of the crown ether toward the solvated proton in acetonitrile,[12] DCC-18C-6 (isomer A) > 18C-6 > 21C-7,15C-5 ⋙ 12C-4, and that of decreasing lipophilicity of the crown ether, B-15C-5 > 15C-5, 12C-4 > 18C-6. The relative lipophilicity of the crown ethers had been deduced from partitioning of the crown ether between benzene and water.[13] It is of interest that, in spite of the presence of a hydrophobic tail in *n*-octylphosphonic and bis(2-ethylhexyl)phosphoric acids, precipitation does not occur from a 0·01 M aqueous solution of these acids in the presence of 0·01 M DCC-18C-6 (isomer A). This is attributed to the strong hydration of the phosphonate group (see Discussion).

Chloranilic acid, $C_6(OH)_2(=O)_2Cl_2$, is a strong lipophilic acid in water ($pK_1 = 0{\cdot}7, pK_2 = 2{\cdot}5$)[14,15] whose monoanion, and particularly the dianion, bear a delocalized charge. In 0·005 M solution (purple) this acid is not precipitated by 0·02 M DCC-18C-6 (isomer A), presumably as a result of a lack of a strong electrostatic interaction of DCC-18C-6·H_3O^+ with the monoanion.

Solubility product of $L(HX \cdot H_2O)_2$

Table 2 gives the concentrations of the ligand (L), X^- and H^+ in saturated aqueous solutions of **2** (both polymorphs), **2a**, 15C-5$(HPHiMe_2{\cdot}H_2O)_2$ and glyme-6$(HX \cdot H_2O)_2$ (square plates) along with the corresponding solubility product. In addition, [L], $[X^-]$ and $[H^+]$ were obained in saturated solutions of **2** with 0·008–0·03 M added 18C-6, 0·0049–0·035 M LiX, 0·006–0·017 M added HX and 0·012–0·053 M HCl. Data are available on request from the authors. In the presence of added L or HCl it was found that $[L] \approx [X^-]/2 + C_L$ (added), whereas in the presence of LiX, $[X^-] \approx 2[L] + C(X^-)_{\text{added}}$. The electrolytes $L(HPiCl_2{\cdot}H_2O)_2$, $LiPiCl_2$, $LiPiMe_2$ and $HPiCl_2$ were considered to be completely dissociated, whereas association of $HPiMe_2$ ($pK_a = 1{\cdot}57$[16]) was taken into account. Complexation of 18C-6 by Li^+ or H^+ in water ($\log K_{LH^+} = 1{\cdot}46$,[17a] $-0{\cdot}40$[17b]) can be considered to be negligible here. Using the solubility product expression for a 1:2:2 adduct:

$$K^{sp} = [L]a^2(H^+)[X^-]^2y^2(X^-) \qquad (1)$$

where, $[L] = a_L$ the average values K^{sp} found were $(4{\cdot}18 \pm 1{\cdot}01) \times 10^{-11}$ mol^5 l^{-5} for **2** and $(1{\cdot}53 \pm 0{\cdot}24) \times 10^{-13}$ mol^5 l^{-5} for **2a**. For calculation of the solution

Table 1. Occurrence of precipitation of uncharged acids with crown ethers from aqueous solution[a]

Acid and concentration	pK_a (H_2O)	Ligand[b] and concentration[c]					
		15C-5	B-15C-5	18C-6	DCC-18C-6(A)	21C-7	DCC-24C-8
2,4-Dinitrophenol, 0·0026 M (satd)	4·09[d]		(−) 0·02 M	(−) 0·02 M	(−) 0·02 M		
2,6-Dinitrophenol, 0·0071 M (satd)	3·71[d]	(−) 0·1 M	(−) 0·02 M	(−) 0·02 M	(−) 0·02 M		
2,4,6-Trinitrophenol, 0·058 M (satd)	0·40[d]	(−) 0·4 M	(+)[f] 0·02 M	(−) 0·1 M	(+) 0·005 M	(−) 1 M	(+) 0·01 M
2,4,6-Trinitro-3,5-dimethylphenol, 0·0066 M (satd)	1·57[e]	(−) 0·1 M	(+) 0·004 M	(+) 0·01 M	(+) 0·005 M	(−) 0·1 M	(+) 0·01 M
2,4,6-Trinitro-3,5-dichlorophenol, 0·02 M	−0·7[e]	(+) 0·1 M	(+) 0·007 M	(+) 0·05 M	(+) 0·005 M	(+) 0·1 M	(+) 0·005 M
2,4,6-Trinitrobenzenesulfonic acid, 0·04 M		(−) 0·1 M	(−) 0·02 M	(−) 0·02 M	(+)[f] 0·02 M	(−) 0·02 M	(−) 0·02 M
2,4,6-Trinitrobenzoic acid, 0·015 M (satd)				(−) 0·02 M	(−) 0·02 M		

[a] (+) Denotes precipitation, (−) denotes no precipitation and no symbol denotes not investigated.

[b] Abbreviations: 15C-5 = 15-crown-5; B-15C-5 = benzo-15-crown-5; 18C-6 = 18-crown-6; DCC-18C-6(A) = dicyclohexano-18-crown-6 (*cis*-syn-*cis*); 21C-7 = 21-crown-7; DCC-24C-8 = dicyclohexano-24-crown-8.

[c] Concentration of ligand taken.

[d] Ref. 11.

[e] Ref. 16.

[f] Slow precipitation (12 h).

Table 2. Solubility of 1 : 2 : 2 adducts in water at 25 °C

Adduct	Solubility				K^{sp}
	[L] (M × 10^3)	[X^-] (M × 10^2)	[H^+] (M × 10^2)	paH[a]	
2 (polymorph II)	5·43	1·08	1·15	2·11	$5{\cdot}7 \times 10^{-11}$[c] $3{\cdot}1 \times 10^{-11}$[a]
2 (polymorph II)[b]	57·1[b]	11·8[b]	–	–	–
2 (polymorph I)	5·40	1·06	1·13	2·17	$5{\cdot}3 \times 10^{-11}$[c] $2{\cdot}3 \times 10^{-11}$[a]
2a	1·89	0·339	0·341	2·54	$1{\cdot}3 \times 10^{-13}$[c] $1{\cdot}3 \times 10^{-13}$[a]
15C-5($HPiMe_2{\cdot}H_2O)_2$	–	0·499	–	–	$6{\cdot}8 \times 10^{-13}$[d]
Glyme-6($HPiCl_2{\cdot}H_2O)_2$	–	5·05	–	–	–

[a] Potentiometric value, using the glass electrode.

[b] Recrystallized from $CHCl_3$; solubility in $CHCl_3$.

[c] From alkalimetric titration of saturated solution.

[d] Calculated assuming [L] = [X^-]/2.

activity coefficient, y, in water, the Debye–Hückel expression $-\log y = 0{\cdot}515\,\mu^{1/2}/(1 + 0{\cdot}329 b\mu^{1/2})$ was used, taking $b = 9$ and 7 for H^+ and $PiCl_2^-$ (or $PiMe_2^-$), respectively. When the solubility data in the presence of excess of L, X^- or HCl are introduced into the solubility product expression for a 1 : 1 : 1 adduct,

$$K^{sp\prime} = [L]a(H^+)[X^-]y(X^-) \qquad (2)$$

a large increase in values of $K^{sp\prime}$ with increasing amount of L is encountered, whereas those in presence of LiX or HX are constant. This attests to a 1 : 2 crown : acid stoichiometry in **2**, consistent with the x-ray crystallographic structure and assay of the solid. Solubility data in a solution saturated both with **2** and with 18C-6 · $KPiCl_2$ are presented in the Appendix.

Addition of organic cosolvents to water results in a marked increase in the solubility of **2**, which is 0·0108 M in pure water (Table 2), 0·0159 and 0·0438 M in the presence of 0·030 and 0·0787 mole fraction, X, of acetonitrile, respectively, and 0·0171, 0·0178 and 0·0310 M when $X = 0{\cdot}0293$, 0·0357 and 0·0740, respectively, of dimethyl sulfoxide.

Characterization of adducts in the solid state

IR spectra from 3800 to 1600 cm^{-1} of **4** and DCC-18C-6·H_3O^+PiSA$^-$ are compared in Figure 1 with those of **1** and **2**, reported previously.[7] Characteristic ν_1/ν_3 (OH stretching), $2\nu_2$ (symm. OH bending) and ν_4 (asymm. OH bending) bands of H_3O^+ occur in DCC-18C-6·H_3O^+PiSA$^-$ at 2300–3200, 2137 and 1715 cm^{-1}, respectively (Figure 1). They resemble those found in 18C-6·$H_3O^+BF_4^-$[18] or in 18C-6·$H_3O^+CF_3SO_3^-$.[6] Further, the bands at 1544, 1358, 1249, 1119, 1070, 1033, 897, 750, 721 and 634 cm^{-1} (not shown) match those of picrylsulfonic acid trihydrate.[19] Adducts containing the pseudohydronium ion, however, display OH ν_1/ν_3 bands of water and phenolic OH (these occur at 3358 and 1722 cm^{-1}, respectively in **4**; see Discussion).

Owing to the ionic nature of **1**, **4** and DCC-18C-6·H_3O^+PiSA$^-$, the pseudohydronium (or hydronium) entity does not exchange with D_2O vapor. These adducts tend to be brightly colored, have relatively high melting points and lack a DSC endotherm before fusion (see Table 3).

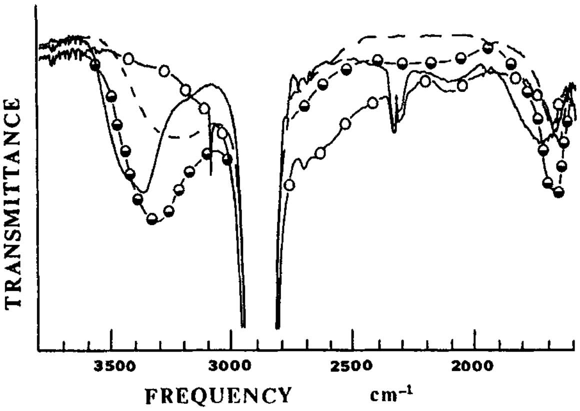

Figure 1. Fourier transform IR spectra of adducts in the region 3800–1600 cm^{-1} (Nujol mull, NaCl discs). Dashed lines, **1**; solid lines, **2**; ●, **4**; and ○, 18C-6·H_3O^+PiSA$^-$

DISCUSSION

Polyether–hydronium complexes

Formation of the crown–hydronium–anion complex, L·$H_3O^+X^-$, in solution (as an ion pair) or in the solid state requires (i) transfer of the proton from HX to water to produce H_3O^+, (ii) virtually complete desolvation of solvated H_3O^+ (in aqueous solution the crown ether and bulk water compete for H_3O^+[17a]), (iii) subsequent binding of H_3O^+ to the polyether[12,18] and (iv) strong electrostatic interaction between L·H_3O^+ and X^- (which can be minimized when X^- is strongly solvated).

An example of factor (i) is that 4-nitro- and 2,6-dinitrophenol are too weak to precipitate any of the crown ethers in Table 1 from water, whereas HPiSA is precipitated by DCC-18C-6 (isomer A). In methyl isobutyl ketone (MIBK) the pK_a values are 21·2,[20] 17·6[21] and 5·55,[21] respectively. Although CF_3SO_3H (pK_a = 4·68 in MIBK)[22] and HPiSA are of comparable acid strength, CF_3SO_3H is too hydrophilic to allow precipitation of the 18C-6 adduct from water. To illustrate factor (ii), precipitation of 18C-6·$H_3O^+ClO_4^-$ occurs from tetrahydrofuran (THF) containing diethyl ether,[18] but not from water. The difference in the enthalpy of solvation of H_3O^+ by bulk water and bulk acetonitrile (AN) was estimated by Benoit and Lam[23] to be −16·8 kJ mol^{-1}. The basic strength of AN and the THF–Et_2O mixtures should be comparable. Factor (iii) is exemplified by precipitation of glyme-4·H_3O^+ [Mo(O)$Br_4(H_2O)$]$^-$ in 1,2-dichloroethane,[24] facilitated by the flexible polyether adapting a favorable conformation in the complex (despite an unfavorable entropy effect). Factor (iv) is borne out by the fact that although naked Cl^- has a high charge density, the electrostatic interaction between the hydrated chloride ion and 18C-6·H_3O^+ is attenuated to such an extent that 18C-6·$H_3O^+Cl^-$ does not precipitate, even from wet THF. On the other hand, the BF_4^- adduct readily does,[18] as BF_4^- is likely to be poorly hydrated. The above accounts, at least in part, for the failure of the alkylphosphoric acids to precipitate from water with DCC-18C-6.

Polyether–pseudohydronium ion complexes

The 1:2:1 adduct, probably 18C-6·H_3O^+ [$H(PiCl_2)_2$]$^-$ (**3**), had been prepared previously[7] by heating **2** to 117 °C. It is proposed that the charge density on the homoconjugate anion $H(PiCl_2)_2^-$ is sufficiently low that the homoconjugate acts as a very poor H-bond acceptor toward the complexed hydronium ion, 18C-6·H_3O^+. Coulombic interaction between the cation and anion is minimized [e.g. the association constants of Et_4NPiCl_2 and of $Et_4NH(PiCl_2)_2$ are $3{\cdot}8 \times 10^3$ and $4{\cdot}5 \times 10^2$, respectively, in DCE saturated with water[25]]. On the other hand, a pseudohydronium ion[26] could bridge a simple phenoxide ion (with its high charge density) with two alternate oxygens of the crown ether. Disruption of the D_{3d} symmetry of the crown is minimal; this was found in the crystal structure of **4** by Wang *et al.*[8] and is inferred in **1**,[7] whose crystal structure has not been determined. High-frequency IR spectra of both **1** and **4** in Figure 1 possess ν_1/ν_3 stret-

Table 3. Characteristics of crown–acid–water adducts

	IR spectrum						
Adduct[a]	OH stretching or bending	Crown conformation, C—O—C stretching	H_2O exchange with D_2O vapor	M.p. (°C)	DSC[b]	Color	State of water in complex
2[c,d]	ν_1/ν_3	Very slightly split, $\sim D_{3d}$	Exchanges	That of 3	+	Light yellow	H_2O
4[c,e]	ν_1/ν_3	Slightly split, $\sim D_{3d}$	No exchange	70–73		Bright yellow	Pseudo-H_3O^+
1[f]	ν_1/ν_3	Not split, $\sim D_{3d}$	Hygroscopic	98–99	–	Bright yellow	Postulated pseudo-H_3O^+
3[f,g]	$2\nu_2$, ν_4	Split	No exchange	123–124	–	Bright yellow	Postulated H_3O^+
DCC-18C-6(A)·$H_3O^+PiSA^-$	$2\nu_2$, ν_4	Split		144–145 (decom.)	–	Light yellow	H_3O^+
L·$H_3O^+BF_4^-$[h]	$2\nu_2$, ν_4		No exchange (DCC-18C-6·$H_3O^+ClO_4^-$)	141	–	Colorless	H_3O^+

[a] L = 18-crown-6.

[b] + Denotes endotherm due to release of H_2O; – denotes endoetherm absent.

[c] Crystal structure determined by single-crystal x-ray diffraction.

[d] Ref. 9.

[e] Ref. 8.

[f] Postulated ionic form.

[g] 18C-6·$H_3O^+[H(PiCl_2)_2]^-$; Ref. 7.

[h] Ref. 27.

ching OH frequencies of phenol to water and water to crown as in **2**. It is concluded that the pseudohydronium ion, lacking C_{3v} symmetry (in the total hydrogen-bonded environment) of the pyramidal H_3O^+ species, has essentially the same spectrum in the high-frequency IR region as incorporated, uncharged H_2O. The phenolic OH–water and water–crown vibrations are decoupled.

Characteristics of the various crown–acid–water adducts are summarized in Table 3.

Precipitation of polyether–water–acid complexes

Even though two different adducts conceivably could precipitate from the same crown–acid–water solution, the concentrations of the constituents favoring both, only one adduct may precipitate. This is the case of crystallization of **2**, and not **3**, from 1,2-dichloroethane saturated with water, DCE(W)$_s$.[7] Uncharged species in solution would be expected to precipitate as **2** and charged forms as **3**. In DCE(W)$_s^{25}$ when $C(HPiCl_2) = C(18C\text{-}6) = 2{\cdot}97 \times 10^{-3}$ M; $[HPiCl_2] = 2{\cdot}86 \times 10^{-4}$ M, $[LH_3OPiCl_2] = 4{\cdot}35 \times 10^{-4}$ M, $[LH_3O^+] = [PiCl_2^-] = 3{\cdot}86 \times 10^{-4}$ M, $[LH_3OPiCl_2] = 4{\cdot}35 \times 10^{-4}$ M, $[H(PiCl_2)_2^-] = 9{\cdot}32 \times 10^{-4}$ M and $[L] = 1{\cdot}22 \times 10^{-3}$ M. We can assess qualitatively the factors contributing to the lattice free energy of **2** in the solid state. One factor involves binding of H_2O to the crown ether. Ranghino *et al.*[28] deduced from Monte Carlo calculations on 18C-6 surrounded by a cluster of 100 water molecules that the crown ether adopts primarily the D_{3d} conformation. The crown ether then has a good solvent-accessible surface, while the water molecules display extensive cooperativity. Indeed, they attributed the stability of 18C-6(4-nitrophenol·$H_2O)_2$ in the solid state to the above features. Another factor is the packing in the crystal lattice. Not mentioned in a previous paper,[7] but a factor which can contribute to the stability of **2**, is the relatively short N—O distance between an *ortho*-nitro group nitrogen and water oxygen, 2·90 and 2·88 Å, in polymorphs II and I, respectively.

Precipitation of **2** from aqueous solution occurs despite the extensive dissociation of $HPiCl_2$ (*ca* 97% in 0·01 M solution). Protonation of the crown and $H(PiCl_2)_2^-$ formation are negligible.

EXPERIMENTAL

Chemicals. Dichloropicric[29] and picric[30] acids were products used previously and dimethylpicric acid was a gift from Marion McLean Davis, National Institute of Standards and Technology (Gaithersburg, MD, USA). 2,4-Dinitrophenol, 2,6-dinitrophenol and 2,4,6-trinitrobenzenesulfonic acid trihydrate were obtained from Aldrich (Milwaukee, WI, USA) and used as received. Ligands 12-crown-4, 15-crown-5, 18-crown-6, dicyclohexano-18-crown-6 (*cis-syn-cis*), glyme-4, glyme-5 and glyme-6 were used previously;[29] benzo-15-crown-5 and dicyclohexano-24 crown-8 were purchased from Parish (Orem, UT, USA) and used as received. The adducts cited below generally were prepared from aqueous solution by mixing the polyether and 0·02 M $HPiCl_2$ or 0·003 M $HPiMe_2$ in a 1 : 2 mole ratio. The suspension was stirred overnight, filtered and recrystallized from water by slow evaporation at room temperature. They were dried over $CaCl_2$ or dry N_2 at room temperature and atmospheric pressure. Adducts glyme-4$(HPiCl_2 \cdot H_2O)_2$ (m.p. 103–104 °C) and glyme-5$(HPiCl_2 \cdot H_2O)_2$ (m.p. 66·5–67·5 °C) were assayed in the same way as the corresponding glyme-6 adduct;[7] assay 1 : 2·09 : 2·26 and 1 : 2·14 : 1·69 (L : $HPiCl_2$: H_2O), respectively.

Employing a ^1H NMR procedure in $CDCl_3$ that utilizes the CH_3 signal of $HPiMe_2$ at 2·34–2·37 ppm, the dimethylpicric acid adducts containing 15-crown-5 or 18-crown-6 were found to have a mole ratio of 1 : 1·92 : 1·49 and 1 : 1·97 : 1·41, respectively. Apparently, some water is lost in the latter two on drying. It is noteworthy that the 15-crown-5 ring is sufficiently large that its oxygens function as H-bond acceptors toward two water molecules. Other adducts prepared were B-15C-5 · $nHPiCl_2 \cdot mH_2O$ (m.p. 49–52 °C) and 18C-6 · H_3O · picrylsulfonate [m.p. 144 °C (decomp.)]. Assay by ^1H NMR in $CDCl_3$: 1 : 0·85 : 0·863 (L : H_3O^+ : $PiSA^-$).

Aqueous solutions 0·03 M in lithium dichloropicrate or dimethylpicrate were prepared by neutralizing the acid with LiOH (Alpha-Ventron). The latter was recrystallized from water to remove traces of alkali metal impurities.

Solubility determination. A suspension of *ca* 100 mg of adduct was made in 1 ml of aqueous solution of ligand, HCl, $LiPiCl_2$ or $LiPiMe_2$, stirred for 5 min and then decanted. Then 15–20 ml of fresh solution were introduced and the suspension was stirred at 25 °C for 24 h. The filtrate was analyzed spectrophotometrically for $PiCl_2^-$ in 0·001 M aqueous NaOH as described previously[7] at λ_{max} 380 nm ($\varepsilon = 4{\cdot}18 \times 10^3$) or for $PiMe_2^-$ at λ_{max} 383 nm ($\varepsilon = 4{\cdot}85 \times 10^3$). The content of 18C-6 in the saturated solutions of the dichloropicrate adducts was found by exhaustive extraction with $KPiCl_2$ into CH_2Cl_2,[7,31] while $KPiMe_2$ was used in the extraction of solutions of the dimethylpicrate adduct [λ_{max} 404 nm ($\varepsilon = 5{\cdot}71 \times 10^3$)]. Alkalimetric titrations and pH measurements were performed using an Orion Model 701A potentiometer with a Fisher combination pH glass electrode. The presence of 0·085 M $LiPiCl_2$ introduced a negligible Li^+ ion error since the paH of a $2{\cdot}91 \times 10^{-3}$ M $HClO_4$–0·035 M Et_4NClO_4 mixture was 2·53, compared with 2·56 in $2{\cdot}91 \times 10^{-3}$ M $HClO_4$–0·035 M $LiPiCl_2$ solution.

Instrumentation. ^1H NMR, Fourier transform IR, differential scanning calorimetry, capillary melting point equipment and techniques have been described previously.[7]

ACKNOWLEDGMENTS

The authors thank Professor Wen-Ji Wang (Fudan University, Shanghai, China) for the IR spectrum of DCC-18C-6$(H_3O \cdot PiCl_2)_2$ and Professors. D. Britton and M. C. Etter (University of Minnesota) for helpful suggestions. Grateful acknowledgment is made to the National Science Foundation for financial support by grant CHE-8401840.

REFERENCES

1. F. Vögtle and W. Müller, *Chem. Ber.* **114**, 3179 (1981).
2. B. Belrami and C. Bavoux, *Acta. Crystallogr., Sect. C* **44**, 2173 (1988).
3. B. Belrami, C. Bavoux and M. Perrin, *J. Crystallogr. Spectrosc. Res.* **17**, 177 (1987).
4. R. Savoie, A. Rodrigue, M. Pigeon-Gosselin and R. Chênevert, *Can. J. Chem.* **63**, 1457 (1985).
5. F. Vögtle, W. Müller and W. Watson, *Top. Curr. Chem.* **125**, 131 (1985).
6. R. Chênevert, A. Rodrigue, P. Beauchesne and R. Savoie, *Can. J. Chem.* **62**, 2293 (1984).
7. I. M. Kolthoff and M. K. Chantooni, Jr, *Can. J. Chem.* **70**, 177 (1992).
8. Z. Peiju, W. Ming and W.-J. Wang, *Acta. Crystallogr, Sect. C* **46**, 1522 (1990).
9. D. Britton, M. K. Chantooni, Jr and I. M. Kolthoff, *Acta. Crystallogr., Sect. C* **44**, 303 (1988).
10. E. L. Cussler and D. F. Evans, *Sep. Purif. Methods* **3**, 399 (1974).
11. G. Kortum, W. Vogel and K. Andrussow, *Dissociation Constants of Organic Acids in Aqueous Solution*, Butterworths, London (1961).
12. I. M. Kolthoff, W.-J. Wang and M. K. Chantooni, Jr, *Anal. Chem.* **55**, 202 (1983).
13. (a) Y. Takeda, Y. Wada and S. Fujiwara, *Bull. Chem. Soc. Jpn.* **54**, 3727 (1981); (b) Y. Takeda and H. Goto, *Bull. Chem. Soc. Jpn.* **52**, 1027 (1979); (c) Y. Takeda, *Bull. Chem. Soc. Jpn.* **53**, 2393 (1980).
14. A. Beauchamp and R. Benoit, *Can. J. Chem.* **42**, 2161 (1964).
15. E. Patton and P. West, *J. Phys. Chem.* **74**, 2512 (1970).
16. P. J. Pearce and R. J. Simkins, *Can. J. Chem.* **46**, 241 (1968).
17. (a) A. A. Majumdar and A. R. Gupta, *Indian J. Chem.* **25A**, 861 (1986); (b) A. G. Gaikwad, H. Noguchi and M. Yoshio, *Anal. Sci.* **3**, 217 (1987).

18. G. S. Heo and R. A. Bartsch, *J. Org. Chem.* **47**, 3557 (1982).
19. *Grating Spectra*, Spectrum 31349K. Sadler Research Laboratories, Philadelphia (1974).
20. V. Dostal, Z. Stransky and J. Slouka, *Collect. Czech. Chem. Commun.* **47**, 1203 (1982).
21. J. Juillard and I. M. Kolthoff, *J. Phys. Chem.* **75**, 2496 (1971).
22. T. Fujinaga and I. Sakamoto, *J. Electroanal. Chem.* **85**, 185 (1977).
23. R. L. Benoit and S. Y. Lam, *J. Am. Chem. Soc.* **96**, 7385 (1974).
24. R. Neumann and I. Assael, *J. Chem. Soc., Chem. Commun.* 547 (1989).
25. M. K. Chantooni, Jr and I. M. Kolthoff, *J. Solution Chem.* **21**, 683 (1992).
26. R. Chênevert, A. Rodigue, D. Chamberland, J. Ouellet and R. Savoie, *J. Mol. Struct.* **131**, 187 (1985).
27. R. Chênevert, A. Rodigue, M. Pigeon-Gosselin and R. Savoie, *Can. J. Chem.* **60**, 853 (1982).
28. G. Raghino, S. Romano, J. M. Lehn and G. Wipff, *J. Am. Chem. Soc.* **107**, 7873 (1985).
29. W.-J. Wang, M. K. Chantooni, Jr and I. M. Kolthoff, *J. Coord. Chem.* **22**, 43 (1990).
30. I. M. Kolthoff and M. K. Chantooni, Jr, *J. Am. Chem. Soc.* **87**, 4428 (1965).
31. I. M. Kolthoff, *Can. J. Chem.* **59**, 1548 (1981).
32. R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet and J. J. Christensen, *J. Am. Chem. Soc.* **98**, 7620 (1976).

APPENDIX

When water is saturated both with respect to **2** and 18C-6·KPiCl$_2$, PiCl$_2^-$ (X$^-$) functions as the common ion. Therefore,

$$[\mathrm{LK}^+] + [\mathrm{K}^+] + [\mathrm{H}^+] = [\mathrm{X}^-] \tag{3}$$

Substituting the equations

$$K(\mathrm{LK}^+) = [\mathrm{LK}^+]y(\mathrm{LK}^+)/[\mathrm{L}]\,[\mathrm{K}^+]y(\mathrm{K}^+) \tag{4}$$

and

$$K^{\mathrm{sp}}(\mathrm{LKX}) = [\mathrm{LK}^+]\,[\mathrm{X}^-]y(\mathrm{LK}^+)y(\mathrm{X}^-) \tag{5}$$

and equation (1) into equation (3) gives

$$\begin{aligned} K^{\mathrm{sp}}(\mathrm{LKX}) = \{1 + y(\mathrm{LK}^+)/K(\mathrm{LK}^+)[\mathrm{L}]y(\mathrm{K}^+)\} \\ + K^{\mathrm{sp}1/2}[\mathrm{L}(\mathrm{HX}\cdot\mathrm{H_2O})_2]y(\mathrm{LK}^+)/[\mathrm{L}]^{1/2} \\ y(\mathrm{H}^+) = [\mathrm{X}^-]^2 y(\mathrm{LK}^+)y(\mathrm{X}^-) \end{aligned} \tag{6}$$

Using values of $K(\mathrm{LK}^+) = 10^{2\cdot03}$,[32] $K^{\mathrm{sp}}(\mathrm{LKX}) = 1\cdot44 \times 10^{-7}$,[29] $K^{\mathrm{sp}}[\mathrm{L}(\mathrm{HX}\cdot\mathrm{H_2O})_2] = 4\cdot18 \times 10^{-11}$ (this work) and the experimental value of [L], $5\cdot29 \times 10^{-3}$ M, in equation (6), $[\mathrm{X}^-]_{\mathrm{calc.}} = 0\cdot0104$ M, compared with the experimental value of 0·0106 M. To a good approximation, [L] is the concentration of free ligand, calculated to be $5\cdot27 \times 10^{-3}$ M. From the above, it is concluded that mixed complexes $\mathrm{LK}^+(\mathrm{HX}\cdot\mathrm{H_2O})_2\mathrm{X}^-$ and $\mathrm{LK}^+(\mathrm{HX}\cdot\mathrm{H_2O})\mathrm{HX_2}^-$ are essentially absent, both in solution and in the solid state.