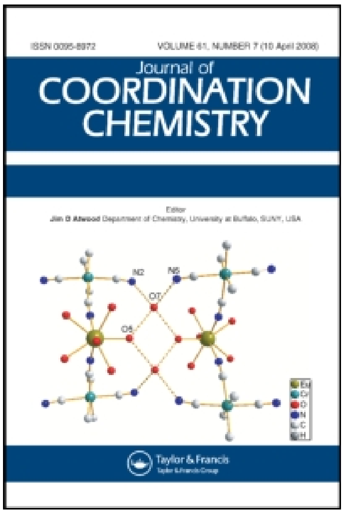

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Precipitation of Inorganic Cations and Ammonium Complexed with Crown Ethers or Acyclic Polyethers from Aqueous Solution as Dichloropicrates

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PRECIPITATION OF INORGANIC CATIONS AND AMMONIUM COMPLEXED WITH CROWN ETHERS OR ACYCLIC POLYETHERS FROM AQUEOUS SOLUTION AS DICHLOROPICRATES

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Alkali, alkaline earth, Group IB, IIB, IIIA, IVA, VIIB, VIII, lanthanide and ammonium 2,4,6-trinitro-3,5-dichlorophenoxides (dichloropicrates, $PiCl_2^-$) although quite soluble in water, can precipitate in the presence of the ligands 12-crown-4, 15-crown-5, 18-crown-6, dicyclohexano-18-crown-6 (*cis-syn-cis* isomer) and 21-crown-7. Open chain polyether analogues of the above are much less effective precipitants. Solubility products, K^{sp}, of 18-crown-6 $M(PiCl_2)_n(M^{n+} = NH_4^+, Na^+, K^+, Cs^+, Ag^+, Tl^+, Ca^{2+}, Sr^{2+}, Ba^{2+}$ and $Pb^{2+})$ were estimated in water; log K^{sp} values of the complexed univalent metal dichloropicrates are a linear function of the free energy of hydration of M^+. The difference in lattice energies of 18-crown-6 $MPiCl_2$ and 18-crown-6 $AgPiCl_2$ (as reference) amounts to only $\sim$4 kcal mol^{-1} less than that between $MPiCl_2$ and $AgPiCl_2$. Apparently, the crown metal ion binding has little effect on the strong electrostatic M^+ $PiCl_2^-$ interaction. Comparison of lattice energies of 18-crown-6 $MPiCl_2$ and $MPiCl_2$ reveals that the crown-metal ion binding further stabilizes 18-crown-6 $MPiCl_2$ in the solid state.

Keywords: Solubility product, complexation, lattice energy, precipitation, crown ether

INTRODUCTION

Pedersen,[1] the originator of crown ethers, crystallized 1:1 and 1:2 alkali or alkaline earth metal ion–crown ether complexes as iodides or thiocyanates from methanol. Picrates of these complexed cations were shown by Frensdorff[2] to be readily extractable from water into dichloromethane. Inorganic cations are hydrophilic, but when embedded in a crown ether cavity they become more or less lipophilic.[3] Thus, it can be expected that salts of these complexed cations with a lipophilic anion will be slightly soluble in water. Qualitative observations, therefore, were made in this study on the precipitation of Group 1A, 1B, IIA, IIB, IIIA, IVA, VIIB, VIII, lanthanides and ammonium dichloropicrates, picrates or sodium tetraphenylborate from aqueous solution with 12-crown-4 (12-cr-4), 15-crown-5 (15-cr-5), 18-crown-6 (18-cr-6), dicyclohexano-18-crown-6 (*cis,syn,cis* isomer (DCC-18-cr-6(A))) or 21-crown-7 (21-cr-7). Also included are the open chain polyethers, tri-, tetra- and pentaethyleneglycol dimethyl ether (EO-4, EO-5, and EO-6, respectively). An attempt has been made to correlate the solubility with the free energy of hydration of M^{n+}, nature of the anion and of the complexing ligand.

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In the present paper are presented solubility products in water of dichloropicrates of several uni- and divalent ions complexed with 18-cr-6. Combining the values of K^{sp}(18-cr-6MPiCl$_2$), K^{sp}(18-cr-6AgPiCl$_2$) with literature values of the stability constants of 18-cr-6M$^+$, 18-cr-6Ag$^+$ in water and the hydration energies of M$^+$ and Ag$^+$, the difference in lattice energies of 18-cr-6MPiCl$_2$ and that of 18-cr-6AgPiCl$_2$ (as a reference) is computed. This difference is then compared with that between uncomplexed MPiCl$_2$ and AgPiCl$_2$. From this, the strength of the M$^+$-PiCl$_2^-$ interaction in solid 18-crown-6MPiCl$_2$ is inferred. A similar comparison between lattice energies of the complexed and corresponding uncomplexed metal dichloropicrates allows an assessment of the strength of the metal ion–crown interactions in solid 18-crown-6MPiCl$_2$.

The term "complex" is loosely defined in this paper to include aquo complexes, particularly of transition metal cations, as well as those in which M^{n+} is bonded directly to the crown ether oxygens by ion–dipole interaction. In the former, water molecules in the inner coordination sphere of M^{n+} are hydrogen bonded to the crown ether oxygens, as in Co(H$_2$O)$_6$·18-cr-6·acetone·CoCl$_4$.[4]

EXPERIMENTAL

Chemicals

18-Crown-6 (Fluka) was purified from its acetonitrile complex, according to the method of Gokel *et al.*[5] The ligands 12-crown-4, 15-crown-5, 21-crown-7, penta- and tetraethylene glycol dimethyl ether (Parish, Orem, UT) were distilled *in vacuo* (0.5 torr), while triethyleneglycol-dimethyl ether (Aldrich) was used as received. The *cis-syn-cis* isomer of dicyclohexano-18-crown-6 was isolated from the mixture of isomers (Aldrich) according to the procedure of Izatt *et al.*[6] Cryptands 222 and 221 (Merck, Darmstadt, F.R.G.) were used without further purification. Dichloropicric acid was prepared by the procedure of Willstätter and Schudel.[7] Sodium, potassium, cesium, silver, thallium(I), calcium, strontium and barium dichloropicrates were obtained by neutralizing the hydroxide (or Ag$_2$O) with dichloropicric acid in water at 60°, cooling, crystallizing, and drying the salt at 80° at atmospheric pressure. For preparation of 18-cr-6M (PiCl$_2$)$_n$, 0.010 M aqueous 18-cr-6 solution was added slowly to 10–50 cm^3 of a filtered saturated solution of M(PiCl$_2$)$_n$ until precipitation was complete. The precipitate was washed with five 1 cm^3 portions of ice water, then dried *in vacuo* at 50°C. Melting points of the sodium, potassium, cesium, silver and thallium(I) dichloropicrate 1:1 complexes with 18-cr-6 were 234–6°, 200–2°, 210–12°, 181–2° and 183–5°C, respectively.

Hydrates of picrates and dichloropicrates

Lithium and sodium picrates crystallize from water as the monohydrate, while the other alkali picrates are anhydrous.[8] In this study, 1 g dried silver, thallium, and alkali dichloropicrates were kept in a sealed jar over water until constant weight was attained (2–4 weeks). The following values of x in MPiCl$_2$·xH$_2$O were found: Ag$^+$, 0.015 (virtually anhydrous); Tl$^+$, 0.32; Na$^+$, 6.53; K$^+$, 5.09; Rb$^+$, 1.95; and Cs$^+$, 2.02. The above procedure was applied to 18-cr-6 NaPiCl$_2$ and to 18-cr-6KPiCl$_2$; x was found to be only 0.0009 and 0.028, respectively. Differential scanning calorimetry from 40–130° indicates the absence of bound water in TlPiCl$_2$ and the two complexed metal dichloropicrates.

Solubility product determination

About 50 mg of 18-cr-6 M $(PiCl_2)_n$ were added to 25 cm^3 aqueous 0.010 M 18-cr-6 solution, or to pure water, stirred for 12 hours, allowed to stand overnight at 25° and then filtered. Dichloropicrate in the filtrate was determined spectrophotometrically at 420 nm ($\varepsilon_{420} = 2.15 \times 10^3\ M^{-1}\ cm^{-1}$). The total concentration of 18-cr-6, C(L), was determined by diluting 3–30 cm^3 saturated solution with 50 cm^3 water, adding 10 cm^3 0.010 M $KPiCl_2$, extracting with 50 cm^3 portions of dichloromethane until the organic phase was colourless, and measuring the absorbance of extracted 18-cr-6 $KPiCl_2$ at 395 nm ($\varepsilon_{395} = 5.40 \times 10^3\ M^{-1}\ cm^{-1}$).

RESULTS AND DISCUSSION

Qualitative observation of precipitation from aqueous medium of salts of complexed metal ions and complexed ammonium with lipophilic anions

Table I summarizes qualitative observations on whether or not precipitation of metal and ammonium dichloropicrates occurs in aqueous medium with the four different simple crown ethers and with tri- tetra- and pentaethylene glycol dimethyl ether.

TABLE I

Occurrence of precipitation as dichloropicrates of various cations complexed with crown ethers and glymes in aqueous medium.[a]

Group in periodic table	Ion	log K^f ($M(OH)^{(n-1)+}$)	12-cr-4	15-cr-5	18-cr-6	21-cr-7	EO-4	EO-5	EO-6
	NH_4^+	4.75	−	+	+	+		−	−
IA	Li^+	0.2	−	−	−	−	−	−	−
IA	Na^+	strong	(+)	+	+	(+)		−	−
IA	K^+	strong	−	+[b]	+	+		−	−
IA	Rb^+	strong	−	+[b]	+	+			
IA	Cs^+	strong	−	(+)[b]	+	+		−	−
IB	Cu^{2+}	6.0	−	+	+	+		−	−
IB	Ag^+	2.3	(+)	+[b]	+	+		−	−
IIA	Mg^{2+}	2.6	(+)	−	−	−	−	−	−
IIA	Ca^{2+}	1.2	−	+	+	+	−	+	+
IIA	Sr^{2+}	0.7	−	+	+	+	−	+	+
IIA	Ba^{2+}	2.1	−	+	+	+	−	+	+
IIB	Zn^{2+}	4.4	−	+	+	−		−	−
IIB	Cd^{2+}	7.9	−	+	+	+		−	−
IIIA	Tl^+		−	+[b]	+	+		−	−
IVA	Pb^{2+}	6.2	−	+[b]	+	+	−	+	+
VIIB	Mn^{2+}		−	+	+	−		−	−
VIII	Fe^{2+}	4.5	−	+	(+)	−		−	−
VIII	Co^{2+}	4.2	−	(+)	+	+		−	−
VIII	Ni^{2+}	4.2	−	−	+	−		−	−
4f series	La^{3+}	3.9	−	(+)	+	−		−	−
5f series	UO_2^{2+}	~8.6	−	−	+	+	−	−	−

[a] "+" denotes precipitation, "(+)" slow precipitation, usually after 1/2 hour and requiring >0.2 M ligand, "−" denotes no precipitation, and no symbol, not investigated. [b] formation of slightly soluble $(15\text{-cr-}5)_2\ M(PiCl_2)_n$ possible, based on crown cavity hole size and unsolvated ionic radius.

Similar observations are summarized in Table II for the corresponding picrates and in Table III for sodium tetraphenylborate. Other uncomplexed alkali and alkaline earth tetraphenylborates are too slightly soluble in water. The ligand DCC-18-cr-6 is also included in Table II. Ammonium, alkali, silver, thallium(I) and alkaline earth ions were introduced as picrates ([Pi$^-$)] ~ 0.04 M) or dichloropicrates ([PiCl$_2^-$] = 0.02 to 0.09 M); the others as chlorides or nitrates (0.01 M) with 0.02 M lithium picrate or dichloropicrate. Ligand concentrations varied from 0.01 to 0.1 M. For cations that undergo moderate acid hydrolysis (log $K^f(M(OH)^{n-1}) > 4$), the pH was maintained at ~3.8 by means of a 0.02 M lithium acetate −0.02 M acetic acid buffer. Hydrolysis constants (1:1) from the literature[9] are included in Table I. Below pH 3 the slightly soluble crystalline adduct[10] 18-cr-6 ($H_2O{\cdot}HPiCl_2)_2$ separates out. Metal ions in Groups IIIB, IVB, VB and VIB are excluded from this study, as they hydrolyze readily.

TABLE II

Precipitation of picrates of various cations complexed with crown ethers.

Ion	15-cr-5	18-cr-6	DCC-18-cr-6(A)[a]
Li^+	−	−	−
Na^+	+	−	+
K^+	−	+	+
Cs^+	−	−	+
Tl^+	+	+	+
Ca^{2+}	+	+	+
Ba^{2+}	−	−	+

[a] saturated solution of DCC-18-cr-6(A).

TABLE III

Precipitation from water of sodium tetraphenylborate complexed with crown ethers or glymes.

Ligand	Occurrence of precipitation[a]
12-cr-4	−
15-cr-5	+
18-cr-6	+
21-cr-7	+
EO-4	−
EO-5	(+)
EO-6	(+)

[a] solutions 0.01–0.02 M in $NaBPh_4$ and 0.05 M in ligand.

With the exception of Li^+, the univalent metal and ammonium dichloropicrates precipitate with 15-cr-5, 18-cr-6 and 21-cr-7. It is of interest to note that Ba^{2+}, Sr^{2+}, Pb^{2+} and Ca^{2+}, having the lowest electrostatic hydration energies of the divalent ions listed in Noyes' compilation[11] readily precipitate as dichloropicrates with 15-cr-5, 18-cr-6, 21-cr-7 and even with EO-5, EO-6 and carbowax 1500. Lattice energies of these complexes must be considerably negative. Other divalent and the univalent ions tested did not precipitate with the open chain polyethers. In fact, the hydration energies[11] of Li^+ (−510.9) and Mg^{2+} (−1900.4 kJ mol^{-1}) are so great that precipitation as the complexed metal dichloropicrate does not occur with any of the ligands (Table I). A notable exception is that of 12-cr-4 with Mg^{2+}. Its crystal structure may resemble that of B-15-cr-5·$Ca(Pi)_2$. $3H_2O$, reported by Poonia *et al.*,[12,13] in which water bridges the central metal atom and crown ether oxygens.

It is concluded from Tables I and II that 18-cr-6 and DCC-18-cr-6(A) are the most effective precipitants of the five crown ethers examined. The lipophilic ligand, benzo-15-crown-5, described as a "good cation discriminating ligand" by Poonia *et al.*[13] may be an even better precipitant. As expected from consideration of the "macrocyclic effect"[14] on the stability constant of LM^+ in methanol, the open chain polyethers are much less efficient precipitants than the corresponding crown ethers.

A cursory survey has been carried out on precipitation of metal ion cryptate dichloropicrates from water. Cryptand 211 (0.01 M), a good complexer of Li^+, does precipitate 0.1 M Li^+ or 0.1 M Na^+, but not 0.02 M K^+, while cryptand 222 (0.01 M) which preferentially complexes K^+, precipitates 0.01 M Na^+ or 3.4×10^{-3}M K^+, but not 4×10^{-3}M Li^+.

We next consider the effect of the anion on the precipitation of LMX_n. From a comparison of Tables I and II it is apparant that the picrate of a given complexed metal ion is considerably more soluble than the dichloropicrate or tetraphenylborate. This is attributed to the lesser lipophilicity of picrate and possibly also to differences in lattice energy of LMX_n. As a measure of lipophilicity, the following values of the free energy of transfer from propylene carbonate (a poorly structured dipolar aprotic solvent) to water have been reported, BPh_4^- 39.3,[15] $PiCl_2^-$ 19.7[16] and Pi^- 6.3[16] kJ mol^{-1}. Other lipophilic anions, such as dipicrylaminate or 2,4,6 trinitrobenzene sulfonate could be promising candidates for precipitation of 18-cr-6 MX_n from water.

Solubility product of 18-cr-6M$(PiCl_2)_n$ in water

From the total concentration of dichloropicrate, C($PiCl_2^-$), and of 18-cr-6, C(L), found experimentally in saturated solutions of $LM(PiCl_2)_n$ in pure water or in 0.010 M aqueous 18-cr-6, values of the solubility product

$$K^{sp}(LM(PiCl_2)_n) = [LM^{n+}][PiCl_2^-]^n y^{n+1} \qquad (1)$$

have been calculated using the following well known relations

$$C(M^{n+}) = C(PiCl_2^-)/n = [M^{n+}] + [LM^{n+}] \qquad (2)$$

$$C(L) = [L] + [LM^{n+}] \qquad (3)$$

$$K^f(LM^{n+}) = [LM^{n+}]/[L][M^{n+}] \quad y(LM^{n+}) = y(M^{n+}) \qquad (4)$$

Eqn. (*4*) is the stability constant of LM^{n+} in water. Complete dissociation of $M(PiCl_2)_n$ and of 18-cr-6M$(PiCl_2)_n$[17] has been assumed. The symbol y denotes the limiting Debye–Hückel mean ionic activity coefficient.

Experimental values of C($PiCl_2^-$) and C(L) together with the resulting values of the solubility products of dichloropicrates of alkali, alkaline earth, silver, thallium(I), lead(II) and ammonium complexed with 18-cr-6 are entered in Table IV. Hydrolysis of M^{n+} in solutions of the latter two salts was taken into account. It is found that the total dichloropicrate and ligand concentrations in saturated 18-cr-6 $KPiCl_2$ or 18-cr-6 $Ba(PiCl_2)_2$ solutions without added ligand correspond to a 1:1 crown:metal mole ratio (Table IV). Moreover, values of the solubility products of these salts, calculated on the basis of 1:1 stoichiometry are independent of ligand concentration. This precludes the presence of L_2M^+ "sandwich" complexes in solution. As observed by Poonia *et al.*,[13] sandwich complexes in the solid state can be formed when the cation–anion electrostatic attraction is weak and M^{n+} is too large to fit in the cavity of the crown, as in $(B\text{-}15\text{-cr-}5)_2KPi$.

TABLE IV
Solubility products in water at 25° of dichloropicrates of metal ions and ammonium complexed with 18-crown-6.

salt	$C(PiCl_2^-)$ $M \times 10^4$	C(L) $M \times 10^2$	$[L]_{calc}$ $M \times 10^2$	$[LM^+]_{calc}$ $M \times 10^4$	$\log K^f(LM^{n+})$[c]	$y^\pm$	K^{sp}
$LNaPiCl_2$	42.8	1.46	1.42	3.53	0.8	0.926	$1.2_9 \times 10^{-6}$
$LKPiCl_2$	12.8	0.129[a]	0.114	1.42	2.03	0.921	$1.6_7 \times 10^{-7}$
$LKPiCl_2$	5.35	1.08	1.05	2.82	2.03	0.973	$1.4_4 \times 10^{-7}$
$LCsPiCl_2$	5.95	1.09	1.08	0.568	0.99	0.972	$3.1_9 \times 10^{-8}$
$LAgPiCl_2$	30.5	1.33	1.24	8.61	1.50	0.937	$2.3_0 \times 10^{-6}$
$LTlPiCl_2$	4.23	1.07	1.04	2.79	2.27	0.976	$1.1_2 \times 10^{-7}$
LNH_4PiCl_2	6.37	1.09	1.03	0.821[b]	1.23	0.971	$4.9_3 \times 10^{-8}$
$LCa(PiCl_2)_2$	1.27	1.03	1.03	0.020	0.48[d]	0.968	2.9×10^{-14}
$LSr(PiCl_2)_2$	1.25	1.03	1.02	0.525	2.72	0.968	$7.4_4 \times 10^{-13}$
$LBa(PiCl_2)_2$	1.19	1.03	1.02	0.595	3.87	0.969	$7.5_6 \times 10^{-13}$
$LBa(PiCl_2)_2$	2.06	0.0116[a]	0.0068_3	0.34_5	3.87	0.958	$1.3_4 \times 10^{-12}$
$LPb(PiCl_2)_2$	0.884	1.04	1.03	0.43_9[e]	4.27	0.973	$3.1_6 \times 10^{-13}$
$LCu(PiCl_2)_2$	28.1	1.31					
$LZn(PiCl_2)_2$	110.0	2.13					

[a] no 18-cr-6 added; all others 0.010 M 18-cr-6 added. [b] hydrolysis of NH_4^+ taken into account; $[NH_3] = [H^+] = 0.90 \times 10^{-4}M$, $[NH_4^+] = 4.65 \times 10^{-4}M$. [c] ref. 19. [d] H. Høiland, J.A. Ringseth and T.S. Brun, *J. Solution Chem.*, **8**, 779 (1979). [e] hydrolysis of Pb^{2+} taken into account; $[PbOH^+] \sim 1.4 \times 10^{-8}$, $[Pb^{2+}] = 2.3 \times 10^{-4}$, $[H^+] = 2.0 \times 10^{-7}M$; $LPbOH^+$, $LPbPiCl_2^+$ formation neglected.

An *empirical* linear relation between $\log K^{sp}(18\text{-cr-}6MPiCl_2)$ *vs* Solomon's[18] values of the free energy of hydration of the uncomplexed univalent cation, $\Delta G°(M^+)_h$, has been found in this study and is graphically depicted in Figure 1. A similar plot, not shown, with intercept −14.3 and slope −0.0605, is obtained using Noyes' values of $\Delta G°(M^+)_h$. These linear relations incorporate the effects of K^f (LM^+) and lattice energy of $LMPiCl_2$ on $K^{sp}(LMPiCl_2)$ in addition to that of $\Delta G°$ $(M^+)_h$, (*9*). There appears to be no relation between $K^{sp}(18\text{-cr-}6M(PiCl_2)_2)$ in Table IV and Noyes' values of the electrostatic hydration energy of the alkaline earth and Pb^{2+} ions.

Solubility product of $CsPiCl_2 \cdot 2H_2O$ in water

This is needed for calculation of the difference in lattice free energies of $CsPiCl_2$ and $AgPiCl_2$ in Table V. In water, a saturated solution of $CsPiCl_2 \cdot 2H_2O$ is 0.0125 M (spectrophotometric value) yielding* $RT\ln K^{sp}$ $(CsPiCl_2 \cdot 2H_2O) = -5.33$ kcal mol^{-1}. Complete dissociation was assumed.

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* Here and throughout, 1 cal = 4.184 J.

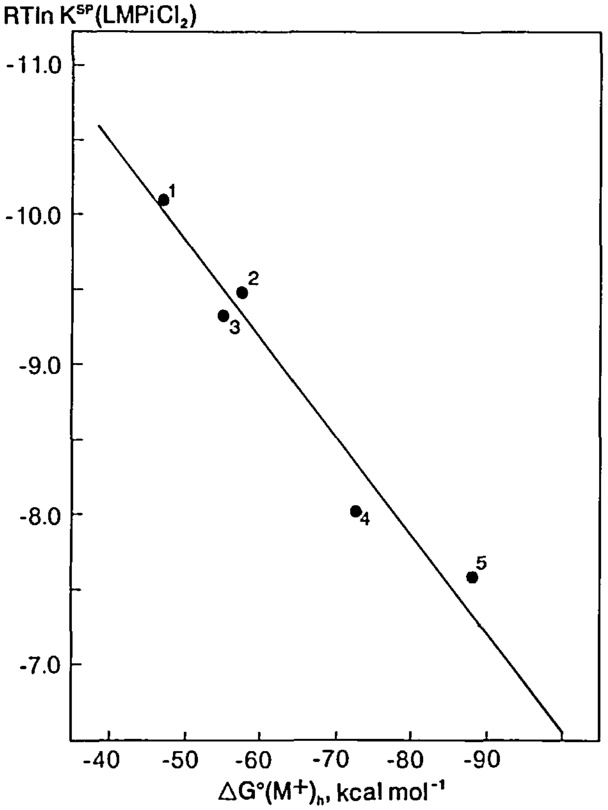

FIGURE 1 Plot of $RT\ln K^{sp}$(18-cr-6MPiCl$_2$)(kcal mol^{-1}) in water at 25°C versus free energy of hydration of M^+, $\Delta G°(M^+)_h$. Values of $\Delta G°(M^+)_h$ from ref. 18, 1. LCsPiCl$_2$, 2. LTlPiCl$_2$, 3. LKPiCl$_2$, 4. LNaPiCl$_2$, 5. LAgPiCl$_2$. Intercept -13.0_4, slope -0.064.

Lattice free energies of complexed univalent metal dichloropicrates

In the following treatment we consider the anhydrous complexes of Ag^+, Tl^+ and the alkali ions (excepting Li^+) with 18-cr-6 in the solid state, dichloropicrate being the counter ion. The possible presence of water in the structures of alkaline earth complexes, like B-15-cr-5$\cdot$Ca(Pi)$_2\cdot$3H$_2$O, makes the interpretation of their lattice free energies involved.

The thermodynamic steps involved in formation of anhydrous crystalline LMX are

$M^+_g \rightleftarrows M^+_{aq}$ hydration energy of M^+ (*5*)

$X^-_g \rightleftarrows X^-_{aq}$ hydration energy of X^- (*6*)

$M^+_{aq} \rightleftarrows L_{aq} = LM^+_{aq}$ stability constant of LM^+ (*4*)

$LMX_S \rightleftarrows LM^+_{aq} + X^-_{aq}$ solubility product of LMX (*1*)

$L_S \rightleftarrows L_{aq}$ free energy solution of L in water (*7*)

$L_g \rightleftarrows L_S$ minus free energy of sublimation of L (*8*)

The standard state is one atmosphere. The subscripts g, aq, and s denote gas phase, aqueous solution and solid, respectively. The free energy change accompanying the overall reaction (*5–8*)

$$M^+_g + L_g + X^-_g \rightleftarrows LMX_S$$

corresponds to the lattice energy of LMX, U(LMX). The ionization potential of M and electron affinity of X in the gas phase has been omitted.
Thus,

$$U(LMX) = \Delta G^\circ(M^+)_h + \Delta G^\circ(X^-)_h - RT\ln K^f(LM^+) + RT\ln K^{sp}(LMX) + \Delta G^\circ(L)_h \quad (9)$$

By taking the difference in lattice energies of LMX and the reference LAgX, the unknown hydration energy of X$^-$ cancels, in addition to that of L, leaving

$$\Delta G^\circ(M^+)_h - \Delta G^\circ(Ag^+)_h - RT\ln[K^f(LM^+)/K^f(LAg^+)] + RT\ln[K^{sp}(LMX)/K^{sp}(LAgX)] = U(LMX) - U(LAgX) \quad (10)$$

Using Solomon's hydration energies of M$^+$ and Ag$^+$ (Table V), complexation constants of 18-cr-6 with M$^+$ and Ag$^+$ in water reported by Izatt *et al.*,[19] and the solubility products of 18-cr-6 $MPiCl_2$ and 18-cr-6 $AgPiCl_2$ in Table IV, values of U(18-cr-6 $MPiCl_2$) − U(18-cr-6 $AgPiCl_2$) have been calculated by means of (*10*) and are entered in the last column of Table V.

TABLE V

Difference in lattice energies of dichloropicrates of univalent metal ions complexed with 18-cr-6, U($LMPiCl_2$), and that of U($LAgPiCl_2$), at 25°C.

M^+	$\Delta G^\circ(M^+)_h$[a] /k cal mol^{-1}	RTlnK^{sp}(MPi)[b] /k cal mol^{-1}	U(MPi) − U(AgPi)[e] /k cal mol^{-1}	U($LMPiCl_2$) − U($LAgPiCl_2$)[f] /k cal mol^{-1}
Ag^+	−87.9	-3.8_1[c]	0.00	0.00
		-3.5_8[g]		
Na^+	−72.4	(−2.1)[d]	(13.7)	16.1
K^+	−54.9	−4.65[c]	33.8_4	30.7
Cs^+	−46.7	-5.6_8[c]	43.1	39.4
		-4.5_2[g,h]	42.1[g]	
Tl^+	−56.9	-5.5_1[c]	32.7_4	28.2
		-5.4_0[g]	29.2[g]	

[a] ref. 18. [b] RTlnK = 1.36 log K. [c] average of values of picrates from several authors from compilation by I.M. Kolthoff and M.K. Chantooni, Jr., *J. Phys. Chem.*, 76, 2024 (1972). [d] calculated from RTlnK^{sp}(NaPi) in acetonitrile, −4.91 and $\Delta G^\circ_{tr}(Na^+) = 3.3$, $\Delta G^\circ_{tr}(Pi^-) = -0.4$ k cal mol^{-1} from water into acetonitrile; ref. in footnote c. The value of RTlnK^{sp}(NaPi) in water, −2.1, was evaluated from acetonitrile, which, was derived in this study from the conductivity of a saturated solution of NaPi, 2.57×10^{-3} S cm^{-1} and Λ_0 (NaPi) = 154.6 (C.H. Springer, R.L. Kay, *J. Phys. Chem.*, 73, 471 (1969)). [e] calculated from solubility products in third column of this Table, and using (*11*). [f] calculated using (*10*). [g] denotes dichloropicrate. [h] from RTlnK^{sp}($CsPiCl_2 \cdot 2H_2O$) = −5.33 in water (see text) and adding 0.82 k cal mol^{-1} for the formation of the dihydrate from the anhydrous salt. The value of 0.82 kcal mol^{-1} was derived by comparing the sum of the free energies of transfer of Cs^+ and $PiCl_2^-$ from 1,2-dichloroethane to water with the ratio of K^{sp} of $CsPiCl_2$ in $C_2H_4Cl_2$ and K^{sp} of $CsPiCl_2 \cdot 2H_2O$ in water (ref. 16).

The lattice energy of 18-cr-6 $MPiCl_2$ is found to decrease in the order $LAgPiCl_2 > LNaPiCl_2 > LKPiCl_2$, $LTlPiCl_2 > LCsPiCl_2$. This not only is the same order as that of the uncomplexed metal picrates (or dichloropicrates) in Table V, 4th column, but the values of $U(LMPiCl_2)-U(LAgPiCl_2)$ themselves are only ~ 4 kcal mol^{-1} less positive than those of U(MPi)−U(AgPi). It is inferred from this that the presence of the crown has little influence on the strong electrostatic cation–anion interaction in the complexed salt in the solid state. In this context, it would be desirable to have crystallographic M^+-phenoxide oxygen distances in the anhydrous complexed and uncomplexed univalent metal dichloropicrates.

It has been documented in the literature that in LM^+ picrate complexes in the solid state, *e.g.* benzo-15-cr-5 Na^+Pi^-,[20] M^+ is displaced from the cavity of the crown toward the picrate, as a result of such strong cation–anion interaction.

The difference in lattice energies of a given anhydrous complexed univalent metal dichloropicrate and its corresponding uncomplexed salt yields information regarding the strength of the metal ion–crown interaction in solid $LMPiCl_2$. The lattice energy of MX, U(MX), customarily is given by

$$U(MX) = \Delta G^\circ(M^+)_h + \Delta G^\circ(X^-)_h + RT\ln K^{sp}(MX) \qquad (11)$$

As a rough approximation, U(AgPi) ~ −131 kcal mol^{-1} from eqn (*11*) using the estimated value of $\Delta G^\circ(Pi^-)_h = -39$ kcal mol^{21} and those of $RT\ln K^{sp}(AgPi)$ and $\Delta G^\circ(Ag^+)_h$ in Table V.
Subtracting (*11*) from (*9*) gives (*12*)

$$-RT\ln K^f(LM^+) + RT\ln [K^{sp}(LMX)/K^{sp}(MX)] + \Delta G^\circ(L)_h = U(LMX) - U(MX) \qquad (12)$$

Again, introducing Izatt's values of K^f (18-cr-6M^+), those of $RT\ln K^{sp}(MPiCl_2)$ from Table V and $K^{sp}(LMPiCl_2)$ from Table IV into (*12*) we have for silver, cesium and thallium dichloropicrates

$$U(\text{18-cr-6 } AgPiCl_2) - U(AgPiCl_2) = -6.13 + \Delta G^\circ(\text{18-cr-6})_h \qquad (12a)$$

$$U(\text{18-cr-6 } CsPiCl_2) - U(CsPiCl_2) = -5.39 + \Delta G^\circ(\text{18-cr-6})_h \qquad (12b)$$

$$U(\text{18-cr-6 } TlPiCl_2) - U(TlPiCl_2) = -7.14 + \Delta G^\circ(\text{18-cr-6})_h \qquad (12c)$$

in kcal mol^{-1}. Unfortunately, values of U(18-cr-6 $MPiCl_2$) − $U(MPiCl_2)$ could not be calculated from (*12*) for $M^+ = Na^+$, K^+ and NH_4^+ as values of $K^{sp}(MPiCl_2)$ are not available for the anhydrous dichloropicrates. Thallium dichloropicrate has been regarded as being anhydrous (Experimental). The hydration energy of 18-cr-6, $\Delta G^\circ(\text{18-cr-6})_h$, in (*12a, 12b, 12c*) is expected to be negative; the crown-metal ion interaction contributes to the lattice free energy of $LMPiCl_2$ in addition to that of M^+-$PiCl_2^-$. Interestingly, this contribution is only 5–6 kcal mol^{-1} larger than that of the hydration energy of 18-cr-6 and is practically independent of the metal ion. One should recognize, however, that minor changes in the crystal packing pattern of LMX can exert a considerable effect on the lattice energy.

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