# Complexes of Some Alkali-metal and Silver Salts with 1,4-Dioxan

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The 1,4-dioxan (dx) complexes $NaClO_4$,3dx, $NaBF_4$,3dx, and NaI,3dx have the cubic structure of $AgClO_4$,3dx. The metal ion is octahedrally co-ordinated by oxygen atoms from dioxan with Na–O distance 2·43—2·46 Å, identical to those found in $Na(OH_2)_6$ octahedral Size and shape requirements limit the anions found in complexes of this structure. The heavier alkali-metal ions are too large for the structure to be stable. The lattice energy of the parent salt is not important in selecting which alkali-metal ions form complexes with dioxan. The lattice energy of the complex is dominated by metal–dioxan ion–dipole interaction. Temperatures, enthalpies, and entopies of decomposition are reported. $AgClO_4$,3dx decomposes to $AgClO_4$,dx and thence to $AgClO_4$, $NaClO_4$,dx, and $NaBF_4$,3dx decompose directly to the parent salt. NaI,3dx decomposes to NaI at atmospheric pressure but NaI,2dx and NaI,dx have been characterised *in vacuo*. Temperatures and enthalpies of phase changes in $AgClO_4$, $NaClO_4$, $NaBF_4$, and $NaClO_4$,3dx are reported.

THERE has been a revival of interest in the complexes formed by alkali metals.[1] Work on the polyether complexes has shown that ether groups are good ligands for these metals.[2] A number of complexes of alkali metal salts with 1,4-dioxan (dx) have been reported (Table 1).

TABLE 1

Dioxan complexes of alkali metal salts [a]

| | $Cl^-$ [b] | $Br^-$ [b] | $I^-$ [b] | $ClO_4^-$ [c] | $BF_4^-$ [d] | $SCN^-$ |
|---|---|---|---|---|---|---|
| $Li^+$ | 1 | 1 | 2 | – | – | 1 |
| $Na^+$ | 0 | 0 | 2,3 | 3 | 3 | 3 |
| $K^+$ | 0 | 0 | 1 | 0 | 0 | 2 |
| $Rb^+$ | 0 [d] | 0 [d] | 0 [d] | 0 | – | 0 |
| $Cs^+$ | 0 [d] | 0 [d] | 0 [d] | 0 | – | 0 |

[a] The Table lists values of $n$ in MX,$n$dx. A zero entry indicates a system for which no complex was obtained, a dash indicates a system which has not been investigated. [b] H. Rheinboldt, A. Luyken, and H. Schmittman, *J. prakt. Chem.*, 1937, **148**, 81; **149**, 30. [c] T. Gruhn and M. Gorman, *J. Inorg. Nuclear Chem.*, 1965, **27**, 482. [d] Present work. [e] M. Gorman, D. DeMattio, D. Doonan, and G. McDonald, *J. Chem. Educ.*, 1970, **47**, 466.

These complexes are of very low thermal stability, exerting significant vapour pressures of dioxan at 300 K. Although some can be prepared from aqueous solution, the crystalline complexes react with atmospheric moisture, usually with loss of dioxan. Only the system LiCl–dx–$H_2O$ has been investigated in detail; LiCl,dx,$H_2O$ occurred over much of the phase diagram but this compound was stable only in contact with its mother-liquor.[3]

Table 1 shows that a number of complexes have the stoichiometry NaX,3dx. There have been no previous studies of these compounds beyond reports of their preparation. Analogous sodium and silver(I) salts are often isostructural and the structure of $AgClO_4$,3dx is known,[4] and shown in Figure 1. The unit cell is cubic, with $a = 7{\cdot}67$ Å. Vapour pressure measurements[5] showed that $AgClO_4$,3dx decomposed to $AgClO_4$,dx and thence to $AgClO_4$. The values of $\Delta H_{298}$ and $\Delta S_{298}$ obtained from these measurements have been criticised.[6]

## RESULTS

$NaClO_4$,3dx, $NaBF_3$,3dx, and NaI,3dx are all cubic with unit cell parameters very close to that of $AgClO_4$,3dx (Table 2). It seems safe to assume that all these compounds are isostructural.

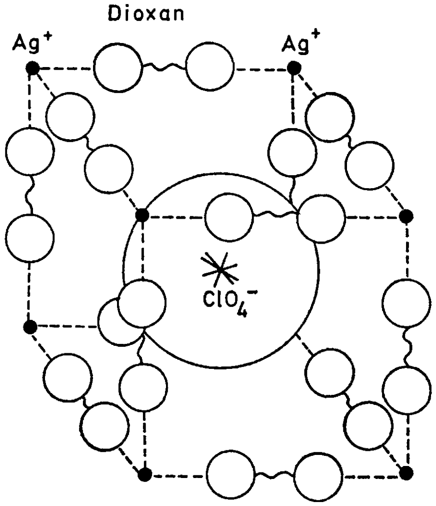

FIGURE 1 Unit-cell of $AgClO_4$,3(1,4-dioxan). The anion rotates freely and the dioxan molecules rotate about the O–O axes (Prosen and Trueblood, *Acta Cryst.*, 1956, **9**, 741)

The decomposition of these 1 : 3 complexes has been studied by differential enthalpic analysis (d.e.a.), by thermogravimetry and by vapour pressure measurements.

TABLE 2

Unit cell parameters of cubic MX,3dx compounds

| | $a$, Å |
|---|---|
| $AgClO_4$,3dx | 7·66 ± 0·02 (7·67 ± 0·01) * |
| NaI,3dx | 7·59 ± 0·03 |
| $NaBF_4$,3dx | 7·66 ± 0·01 |
| $NaClO_4$,3dx | 7·66 ± 0·02 |

* Single-crystal data from R. J. Prosen and K. N. Trueblood, *Acta Cryst.*, 1956, **9**, 741.

The latter offer a more reliable route than d.e.a. to the enthalpies of decomposition of compounds which exert a finite vapour pressure at ambient temperature since a partially decomposed sample will exert the same vapour pressure as a stoichiometric sample but will give a peak area in d.e.a. which is too small by an uncertain amount. This point is illustrated in Table 3 in which the decomposition data is summarised.

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[1] M. R. Truter, *Chemistry in Britain*, 1971, 203.

[2] D. Bright and M. R. Truter, *Nature*, 1970, **225**, 176.

[3] C. C. Lynch, *J. Phys. Chem.*, 1942, **46**, 366.

[4] R. J. Prosen and K. N. Trueblood, *Acta Cryst.*, 1956, **9**, 741.

[5] L. W. Baasch, *Spectrochim. Acta*, 1959, **17**, 726.

[6] J. C. Barnes, *Inorg. Chem.*, 1972, in the press.

$AgClO_4$,3dx.—Two endothermic decomposition reactions corresponded to the formation of $AgClO_4$,dx and $AgClO_4$. $AgClO_4$ shows phase changes at 371, 398·6, and 423 K (Table 4). The last represents the change to the cubic modification. Only the last phase change is seen in $AgClO_4$ freshly decomposed from $AgClO_4$,3dx.

TABLE 3

Thermal decomposition reactions [a]

| Reagent | $T_1$/K | $T_2$/K | $\Delta W_{expt}$% | $\Delta W_{Th}$% | $\Delta H$/kJ mol$^{-1}$ (d.e.a.) | $\Delta H_{298}$/kJ mol$^{-1}$ (v.p.) | $\Delta S_{298}$/J K$^{-1}$ mol$^{-1}$ (v.p. | $-\Delta G_{298}$/kJ mol$^{-1}$ (v.p.) |
|---|---|---|---|---|---|---|---|---|
| $AgClO_4$,3dx | 358 | 397 | 55·6 ± 0·5 | 56·04 | 39·2 ± 0·9 | 58·96 ± 0·61 | 246 ± 10 | 14·24 ± 0·21 |
| $AgClO_4$,dx | 400 | 420 | 28·1 ± 1·0 | 29·82 | 59·2 ± 2·1 | 92·09 ± 1·10 | 399 ± 12 | 26·87 ± 0·40 |
| $NaClO_4$,3dx | 343 | 398 | 67·3 ± 0·7 | 68·35 | 54·9 ± 1·6 | 62·42 ± 0·57 | 260 ± 12 | 14·90 ± 0·20 |
| NaI,3dx | 321 | 383 | 62·4 ± 0·5 | 63·81 | 54·5 ± 1·3 [b] | 41·93 ± 0·42 [c] | 174 ± 10 [c] | 9·90 ± 0·15 [c] |
| $NaBF_4$,3dx | 283 | 356 | 71·9 ± 0·9 | 70·65 | 35·6 ± 0·7 | 44·00 ± 0·51 | 176 ± 12 | 8·59 ± 0·15 |
| NaI,2dx | <301 | 365 | 54·9 ± 0·3 | 54·04 | 67·7 ± 1·0 [b] | 61·84 ± 0·61 [d] | 313 ± 10 | 12·33 ± 0·15 |
| | e | 381 | | | | | | |

[a] D.e.a. experiments were carried out at atmospheric pressure under nitrogen flowing at 30 cm$^3$ min$^{-1}$, heating at 8·33 K min$^{-1}$. $T_1$ was the minimum temperature at which the endotherm was detected. $T_2$ was the peak temperature of the endotherm. All thermodynamic quantities are expressed 'per mole of dioxan released'. $\Delta W$ represents weights loss to MX. [b] Decomposition to NaI. [c] Decomposition to NaI,2dx. [d] Decomposition to NaI,dx. [e] Obscured by previous endotherm.

$NaBF_4$,3dx and $NaClO_4$,3dx.—D.e.a., t.g., and v.p. measurements with analysis, agree that these compounds decompose directly into $NaBF_4$ and $NaClO_4$ in one step.

Two endothermic phase changes occur during the decomposition of $NaClO_4$,3dx (Table 4). Both were readily reversible. The areas of these endotherms were proportional to the fraction ($1 - \alpha$) of the sample remaining undecomposed when the phase change occurred, indicating that both phase changes are associated with $NaClO_4$,3dx and not with the decomposition products. (Some control of the relationship between $\alpha$ and $T$ can be obtained by varying the heating rate in d.e.a.) Phase changes in $NaBF_4$,dx occur between 273 and 293 K and appeared to be unreproducible, possibly for instrumental reasons. $NaBF_4$ and $NaClO_4$ change from the anhydrite structure to cubic at 516 and 576 K respectively. These phase changes also occur in samples decomposed from the dioxan complexes (Table 4).

TABLE 4

Phase transitions observed by d.e.a.

| Compound | $T_1$/K | $T_2$/K | $\Delta H$/kJ mol$^{-1}$ |
|---|---|---|---|
| NaI,2dx | 321 | 325·3 | 5·91 ± 0·11 |
| $NaClO_4$,3dx | 316·3 | 317·6 | 70·0 ± 0·04 |
| | 368·6 | 369·2 | 0·92 ± 0·21 |
| $NaClO_4$ | 576·3 | 579·1 | 1·46 ± 0·05 |
| $NaBF_4$ | 515·6 | 520·7 | 5·56 ± 0·25 |
| $AgClO_4$ | 371·4 | 373·1 | 1·22 ± 0·02 |
| | 398·6 | 402·1 | 0·51 ± 0·01 |
| | 423·5 | 429·5 | 3·70 ± 0·02 |

Experimental conditions as in Table 3.

NaI,3dx.—This compound behaved differently under different experimental conditions. D.e.a. measurements showed only a single decomposition endotherm, with no phase changes. The product was found to be NaI. V.p. measurements showed an initial reaction

$$NaI,3dx_s \longrightarrow NaI,2dx_s + dx_g \qquad (1)$$

This reaction is followed by

$$NaI,2dx_s \longrightarrow NaI,dx_s + dx_g \qquad (2)$$

for which $\Delta H$ is greater than for reaction (1), leading to a transition temperature at 340 K (Figure 2). D.e.a. measurement on NaI,2dx showed a phase change and two endothermic decomposition steps to NaI. V.p. measurements on samples of NaI,dx prepared by driving reaction (2) to completion in the v.p. apparatus, were unsatisfactory. Non-linear Arrhenius plots were obtained. No convincing explanation for this behaviour is available at present.

DISCUSSION

In the $AgClO_4$,3dx structure the size of the unit-cell is determined by the silver–dioxan contacts. The Ag–O distance is 2·46 Å, which is typical of non-covalent Ag–O bonds. From the unit-cell parameters and the O–O distance in dioxan the Na–O distances in NaX,3dx range between 2·43 and 2·46 Å. These are in good agreement with the values of 2·37—2·47 and 2·40—2·45 Å found in $Na_2SO_4,10H_2O$ and in borax respectively.[7] In both these compounds the sodium ions are at the centres of irregular octahedra of water molecules and thus in a similar environment to the octahedron of oxygen atoms in $NaClO_4$,3dx. The Ag–Cl distance in $AgClO_4$,3dx is 6·63 Å compared with 3·46 Å in cubic $AgClO_4$.[7]

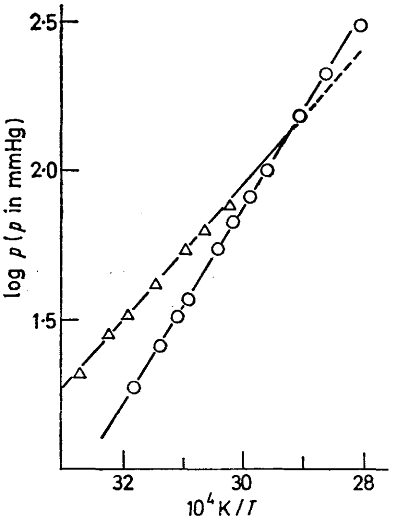

FIGURE 2 Vapour pressure data for the decomposition of NaI,$n$dx; Triangles NaI·3dx; Circles NaI·2dx

The anion, situated at the body centre of a cubic array of metal ions, must be at least pseudo-spherical to allow the rotational freedom observed in $AgClO_4$,3dx.[4]

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[7] R. W. G. Wyckoff, 'Crystal Structures,' Interscience, New York, 1964, vols. 2 and 3.

$NaNO_3$ and $NaBrO_3$ do not form compounds of this structure. The effective radius of the anion must be large enough to prevent rattling but small enough to allow rotation unimpeded by the rotating methylene groups of the dioxan. The limits, in terms of ionic radii, are shown by NaBr and $NaIO_4$, neither of which have been found to form compounds of this series. The values are

| $Br^-$ | $I^-$ | $BF_4^-$ | $ClO_4^-$ | $IO_4^-$ |
|---|---|---|---|---|
| 1·96 | 2·16 | 2·28 | 2·33 | 2·48 Å |

using Kaputinskii's thermochemical radii [8] for the polyatomic ions.

None of the corresponding potassium salts form complexes of this type. Substitution of $K^+$ for $Na^+$ would give a unit-cell parameter of 8·40 Å, increasing the radius of the anion site by 0·5 Å. This would allow even $IO_4^-$ to rattle. Ionic radii show that LiCl could form LiCl-3dx but only a phase reported as LiCl,dx is known and that is of very low thermal stability.[3] The formation of $AgBF_4$,dx and $AgClO_4$,dx, for which sodium analogues have not been prepared may represent $Ag^+$ adopting the familiar linear two-co-ordinate geometry.

The contrast between the alkali metal complexes formed by 1,4-dioxan and those formed by thiourea can be explored by lattice energy arguments. Boeyens and co-workers [9,10] have shown that thiourea complexes are formed only for salts with lattice energies below 670 kJ $mol^{-1}$. These complexes have lattice energies *ca.* 750 kJ $mol^{-1}$. Metal–thiourea interactions make a relatively small contribution to the overall lattice energy of the complex.

The enthalpy cycle shows that dioxan complexes are favoured only if the lattice energy of the complex exceeds the sum of the lattice energy of the parent salt and the heat of vaporisation of dioxan, that is if the heat of decomposition of the complex exceeds $\Delta H_{vap}$ (37·5 kJ $mol^{-1}$).[11] This condition is only satisfied for the MX,3dx structure in the few cases where the packing is very efficient. Comparison of the lattice energies of MX,3dx

$$\begin{tikzcd}
 & MX_s + 3dx_l \arrow[dl, "\Delta H_f"'] & \\
MX{,}3dx & & MX_s + 3dx_g \arrow[ul, "-3\Delta H_{vap}"'] \arrow[ll, "-3\Delta H_d"'] \\
 & M_g^+ + X_g^- + 3dx_g \arrow[ul, "-\Delta H_{L(MX,3dx)}"] \arrow[ur, "-\Delta H_{L(MX)}"'] &
\end{tikzcd}$$

obtained by use of the enthalpy cycle with the calculated cohesive Madelung energies for $M^+$ and $X^-$ arranged in the position which these ions occupy in MX,3dx shows that this Madelung energy (*ca.* 370 kJ $mol^{-1}$) is only about 40% of the total lattice energy (Table 5). Allowing for Born repulsion the contribution from ion–dipole interactions must be about 670 kJ $mol^{-1}$. The relative positions of dioxan, $M^+$ and $X^-$ in the structure show that the dioxan will be strongly polarised by $M^+$ so as to increase the two opposed dipoles in the molecule (a similar effect is found in thiourea [10]).

TABLE 5

Lattice energies and Madelung energies [a]

| | Lattice energy (MX), kJ $mol^{-1}$ | Lattice energy (MX,3dx), kJ $mol^{-1}$ | Madelung energy (MX,3dx), kJ $mol^{-1}$ |
|---|---|---|---|
| $AgClO_4$,3dx | 798 [b] | 1008 | 369 |
| $NaClO_4$,3dx | 732 [b] | 918 | 369 |
| NaI,3dx | 699 [c] | 865 | 372 |
| $NaBF_4$,3dx | | | 369 |

[a] Madelung energy is used here for the attraction between anions and cations, spaced as required by the $AgClO_4$,3dx structure, in the absence of the dioxan molecules. [b] D. F. C. Morris, *J. Inorg. Nuclear Chem.*, 1958, **6**, 295. [c] D. F. C. Morris, *Acta Cryst.*, 1956, **9**, 197.

The decrease in the cohesive energy for the ions and the ion–dipole interaction as $r_m^+$ increases must be sufficient to compensate for the decreasing lattice energy of MX and to prevent the formation of dioxan complexes of the heavier alkali metals.

Comparison with data for other dioxan complexes indicates that the low thermal stability of the MX,3dx series arises largely from unfavourable entropy terms. The enthalpies of decomposition reported for dioxan complexes lie between 50 and 85 kJ $mol^{-1}$ per dioxan lost [11-13] so that the values reported in Table **3** are not unduly low.

## EXPERIMENTAL

The adducts were precipitated by the addition of freshly distilled dioxan to aqueous solutions of the salts at room temperature. The dry adducts were kept in an atmosphere saturated with dioxan vapour. They were characterised by thermogravimetry and by determination of the anion content by ion-exchange. Attempts were made to obtain the corresponding potassium complexes and complexes of other sodium salts, without success.

D.e.a. measurements were made with the Perkin-Elmer DSC 1B scanning calorimeter used previously.[12,13] I.r. spectra were recorded on Nujol mulls on a Perkin-Elmer 521 instrument, but showed no features of interest. *X*-Ray photographs were obtained using Cu-$K_\alpha$ radiation either photographically using a 5·71 cm diameter camera calibrated with NaCl or using a recording diffractometer. Since no low temperature or controlled atmosphere *X*-ray facilities were available it was necessary to obtain successive powder patterns and extrapolate to zero time to eliminate reflections due to decomposition products.

Vapour pressure measurements were made using an apparatus based on that used by earlier workers,[11] maintained in a thermostatted oil bath.

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[13] J. C. Barnes and C. S. Duncan, *J. Chem. Soc.* (*A*), 1970, 1442.