Preparation and Characterisation of Solid Ditetra-alkylammonium Tetrahalogenocadmates $(R_4N)_2CdX_4$ (R = Me, Et, or Bu^n; X = I or Br) and Tetra-n-butylammonium Tri-iodocadmate $Bu^n{}_4NCdI_3$, and an Interpretation of their Vibrational Spectra

By **S. D. Ross, I. W. Siddiqi, and H. J. V. Tyrrell,*** Department of Chemistry, Chelsea College, Manresa Road, London SW3 6LX

A new and simple method of preparing these salts by mixing hot ethanolic solutions of the components and subsequent precipitation is described. They were characterised by chemical analysis, *X*-ray powder photographs, and vibrational spectroscopy. The i.r. and Raman spectra indicate that in the tetrahalogenocadmates the cadmium atoms are tetrahedrally co-ordinated to the halogen, and that this co-ordination persists in $Bu^n{}_4NCdI_3$ where the anions appear to be dimeric, *i.e.*, this salt should be formulated as $(Bu^n{}_4N)_2Cd_2I_6$. The vibrational spectrum of solid cadmium iodide is also reported in detail. A limited *X*-ray structural study showed $(Et_4N)_2CdI_4$ to be tetragonal with 8 molecules per unit cell.

A NUMBER of salts of the general formulae $MCdX_3$ and M_2CdX_4 (M, univalent cation, X = Cl, Br, or I) are described in the older literature.[1,2] These were usually prepared by careful evaporation of aqueous solutions of the component salts in the appropriate proportions, or from melts. They often contained water of crystallisation when prepared from aqueous media. Adams

---

[1] J. W. Mellor, 'Treatise on Inorganic and Theoretical Chemistry,' vol. IV, Longmans, London, 1923.

[2] N. V. Sidgwick, 'The Chemical Elements and Their Compounds,' Oxford University Press, 1950.

et al.[3] prepared a number of complex anhydrous tetraethylammonium salts, including $(Et_4N)_2CdCl_4$, by mixing solutions of the component salts in thionyl chloride. The method was less successful for preparing the analogous bromides, with thionyl bromide as solvent, and these authors did not report the formation of $(Et_4N)_2CdBr_4$. During studies on the spectra of tetrahalogenocadmates in solution it was discovered that anhydrous tetrabromo- and tetraiodo-cadmates could be prepared very simply by mixing hot ethanolic solutions of cadmium bromide or cadmium iodide with a similar solution of a tetra-alkylammonium halide R_4NX ($R = Me$, Et, or Bu^n; $X = Br$ or I). In almost all cases, the product, which precipitated on cooling, analysed as the tetrahalogenocadmate whatever ratio of cadmium halide to alkylammonium halide was used. However, a precipitate analysing as tetrabutylammonium tri-iodocadmate ($Bu^n_4NCdI_3$) was obtained when tetrabutylammonium iodide in ethanol was added to ethanolic cadmium iodide in equimolar ratio. Chloro-complexes could not be prepared in this way and the method therefore complements the thionyl chloride technique. The compounds were characterised by *X*-ray and vibrational spectroscopy, and by elemental analysis.

TABLE 1

Elemental analysis (%) of tetra-alkylammonium halogenocadmate complexes. Calculated values for anhydrous salts are shown in parentheses

Compound	Carbon	Hydrogen	Nitrogen	Halide	Cadmium
$(Me_4N)_2CdI_4$	12·0 (12·5)	3·32 (3·15)	3·75 (3·65)	66·19 (66·07)	14·50 (14·63)
$(Et_4N)_2CdI_4$	21·86 (21·82)	4·40 (4·58)	3·28 (3·18)	57·87 (57·65)	12·82 (12·76)
$(Et_4N)_2CdBr_4$	27·92 (27·75)	5·67 (5·82)	4·21 (4·04)	46·27 (46·15)	16·22 (16·23)
$(Bu^n_4N)_2CdI_4$	34·82 (34·78)	6·46 (6·56)	2·49 (2·53)	45·65 (45·94)	10·21 (10·17)
$Bu^n_4NCdI_3$	27·85 (26·12)	5·14 (4·93)	1·94 (1·90)	50·56 (51·76)	15·20 (15·28)

TABLE 2

Assignment of vibrational frequencies observed for solid tetrahalogenocadmates on the assumption of tetrahedral symmetry, and comparison with solution spectra [6]

Assignments	CdI_4^{2-} [a]	$(Me_4N)_2CdI_4$		$(Et_4N)_2CdI_4$		$(Bu_4N)_2CdI_4$		$CdBr_4^{2-}$ [a]	$(Et_4N)_2CdBr_4$	
	R	R	I.r.	R	I.r.	R	I.r.	R	R	I.r.
$\nu_1 A_1$	116	120		120		119		166	164	
$\nu_2 E$	36	51		46		50		53	48	
$\nu_3 F_2$	144	146	145	146	145	138	143, 138	181	182	180
$\nu_4 F_2$	44	*b*	75, 69	*b*	64	*b*	60	62	80	77

[a] Ref. 6. [b] Not observed owing to ghost peak.

RESULTS AND DISCUSSION

Five compounds were prepared. They are listed, together with their elemental analyses, in Table 1. The experimental analyses fit the suggested formulae well, and the identity of each compound was proved by the *X*-ray powder photographs. Each had its own characteristic diffraction pattern which differed from those of the constituent salts. In particular, the *d*-spacings found for the salts analysing as $(Bu^n_4N)_2CdI_4$ and $Bu^n_4NCdI_3$ were quite different. In the first case, they were as follows (relative intensity is represented by vs = very strong, s = strong, m = medium, w = weak, vw = very weak): **13·05m, 11·29m, 8·71vs, 6·38m, 4·96w, 3·88s, 3·24m, 3·12w, 2·58w, 2·32m, 2·13m, 1·89**, and **1·85** (doublet, s) Å. $Bu^n_4NCdI_3$ on the other hand gave the *d*-spacings **11·22vs, 8·96vs, 7·50w, 6·51w, 5·61m, 3·85vs, 3·65vw, 3·39vw, 2·95vw, 2·60w, 2·09**, and **2·04** (doublet, vs).

The compound $(Et_4N)_2CdI_4$ crystallised as square layered plates which, under the microscope, appeared as flat, distorted octahedra. It was possible to pick out suitable crystals for rotation and Weissenberg photographs and, from these the crystals were found to be tetragonal with $a = b = 19·75$ Å, $c = 14·68$ Å. The *d*-spacings recorded above for this salt were satisfactorily indexed by use of these cell dimensions.[4] The density was *ca.* 2, and calculation showed eight molecules in the unit cell. A study of the systematic absences showed that the crystals belonged to one of three space groups $P4/mbm$, $P\bar{4}bm$, or $P4b2$.

I.r. and Raman spectra were obtained for all five compounds and provided further evidence for their separate identity. The low-frequency tetrahalogenocadmate spectra showed close similarities with the spectra of similar compounds in solution,[5-8] and the observed frequencies have therefore been assigned on the same basis, namely that tetrahedral CdX_4^{2-} anions (point-group T_d) are present (Table 2). Rolfe *et al.*,[6] calculated stretching force constants from Raman spectral data on aqueous solutions of $CdBr_4^{2-}$ and CdI_4^{2-}, and found values of 1·25 and 1·02 mdyn Å^{-1} respectively. Similar calculations on the data in Table 2 for the tetraethylammonium salts gave respectively 1·25 and 1·10 mdyn Å^{-1}. The solid-state

---

[3] D. M. Adams, J. Chatt, J. M. Davidson, and J. Garrett, *J. Chem. Soc.*, 1963, 2189.

[4] I. W. Siddiqi, Ph.D. Thesis, London, 1971.

[5] M. Delwaulle, F. François, and J. Wieman, *Compt. rend.*, 1939, **208**, 184, 1818; *Bull. Soc. chim. France*, 1955, 1294.

[6] J. A. Rolfe, D. E. Sheppard, and L. A. Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1275.

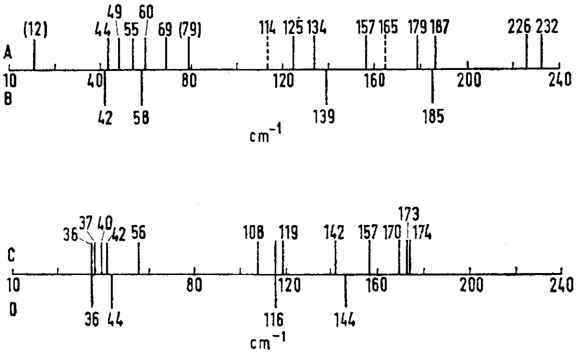
[7] J. E. D. Davies and D. A. Long, *J. Chem. Soc.* (*A*), 1968, 2054.

[8] I. A. Jagtiani, I. W. Siddiqi, and H. J. V. Tyrrell, unpublished work.

vibrational spectra of the tetrabromo- and tetraiodocadmates are therefore consistent with the view that discrete tetrahalogenocadmate ions, with T_d symmetry, exist in the lattice, though not, of course, an unequivocal proof of this. The vibrational spectrum of crystalline $(Et_4N)_2CdCl_4$ has also been analysed in terms of T_d symmetry.[7,9]

The Raman and i.r. spectra of the compound analysing as $Bu^n{}_4NCdI_3$ are less simple to interpret. The principal bands observed are as follows: Raman-active 37, 40, 42, 116, 157, and 173 cm^{-1}; and i.r.-active 36, 56, 108, 119, 142, 170, and 174 cm^{-1}.

The Raman spectrum of the CdI_3^- species in tributyl phosphate has been reported by Davies and Long.[7] Three bands (50, 124, and 163 cm^{-1}) were observed and interpreted in terms of a planar ion with D_{3h} symmetry. Clearly the more complex spectrum of the solid tetrabutylammonium tri-iodocadmate is unlikely to arise from the presence of CdI_3^- as a monomer of D_{3h} symmetry. If the structure were known it might be possible to account for this increased complexity in terms of factor-group splitting but in the absence of any structural information this possibility cannot be further discussed.



Vibrational spectra for A, In_2I_6; B, InI_4^{2-}; C, $Bu^n{}_4NCdI_3$; and D, $(Bu^n{}_4N)_2CdI_4$. Numbers in parentheses refer to calculated frequencies with no observed counterpart. The broken lines represent alternative assignments of the B_{1g} bridge stretching mode

Comparison of the tetraiodocadmate spectra (Table 2) with that of $Bu^n{}_4CdI_3$ on the one hand, and the Raman spectrum[10] of InI_4^- and the vibrational spectrum of indium tri-iodide[11] on the other, may be useful (Figure). Indium tri-iodide is known[12] from a single-crystal X-ray study to exist as the dimer In_2I_6, this being formed by two tetrahedra sharing an edge with the indium atoms in tetrahedral co-ordination, as in InI_4^-. The effect on the spectrum is to split the four bands characteristic of InI_4^- into a number of bands grouped recognisably around the original set. The spectra of Bu_4NCdI_3 and of the tetraiodocadmates are related in a similar manner and we therefore suggest that this salt may contain dimeric anions with cadmium in tetrahedral co-ordination, the pairs of tetrahedra sharing an edge. Its formula should, on this view, be written $(Bu^n{}_4N)_2Cd_2I_6$.

During this work the spectrum of solid cadmium iodide was also studied, since the complexes were characterised by their vibrational spectra, among other properties. Cadmium iodide has a layer lattice structure in which the cadmium is octahedrally co-ordinated, and, as might be expected, the vibrational spectrum is significantly different from those already described, the highest frequency being at 114 cm^{-1} (Raman-active). Another Raman-active band was seen at 44 cm^{-1}, and i.r. bands at 80 and 95 cm^{-1}, with another feature at 110 cm^{-1} and a weak, sharp, band near 40 cm^{-1}, were found. The only other reported spectroscopic work on the solid was that of Randi[13] who found an i.r. band at 88 cm^{-1}. The shift in the Raman-active symmetric stretching frequency of cadmium iodide from the (calculated) value of 149·5 cm^{-1} in the vapour phase,[14] and 144 and 138 cm^{-1} in solutions of tributyl phosphate[7] and tetrahydrofuran[15] to 114 cm^{-1} in the solid reflects the change in co-ordination number of cadmium from two (vapour) to six (solid).

EXPERIMENTAL

Ditetra-alkylammonium tetraiodocadmates $(R_4N)_2CdI_4$ (R = Me, Et, or Bu^n) were prepared by mixing hot ethanolic solutions of cadmium iodide and R_4NI in the proportions 1 : 2. The mixture was boiled to dissolve the solid product, and allowed to cool slowly, whereupon a precipitate formed. The product was filtered off and recrystallised from hot ethanol. The recrystallised salt was separated, washed with cold ethanol, and dried at 60 °C. The anhydrous salt $(Et_4N)_2CdBr_4$ was prepared similarly from $CdBr_2,4H_2O$ and Et_4NBr, but the separate solutions were boiling when mixed, and the mixed solution was then cooled slowly. A solid product separated which did not redissolve at a measurable rate even in boiling ethanol. It could not therefore be recrystallised from ethanol, but was simply washed with cold ethanol and dried at 60 °C before analysis.

Except when the tetra-n-butylammonium iodide was used, the tetraiodocadmate was always formed irrespective of the ratio of cadmium iodide to alkylammonium iodide. When however tetra-n-butylammonium iodide in hot ethanol was added to a hot ethanolic solution of cadmium iodide in a 1 : 1 ratio, a thick white precipitate analysing as $Bu^n{}_4NCdI_3$ was formed, which was isolated and purified as for the tetraiodocadmates. Its analysis is shown in Table 1 together with those of the tetrahalogenocadmates.

The iodide content of these salts was determined titrimetrically by the usual iodate method, and bromide by silver nitrate with dichlorofluorescein as indicator. The metal content was determined complexometrically with edta.[4] The carbon, hydrogen, and halide contents were

---

[9] J. E. D. Davies and D. A. Long, *J. Chem. Soc.* (*A*), 1971, 1273.

[10] L. A. Woodward and G. A. Singer, *J. Chem. Soc.*, 1958, 716.

[11] I. R. Beattie, T. Gibson, and G. A. Ozin, *J. Chem. Soc.* (*A*), 1968, 813.

[12] J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 1964, **3**, 63.

[13] G. Randi, *Atti. Accad. naz Lincei, Rend. Classe Sci. fis. mat. nat.*, 1966, **41**, 197.

[14] A. Loewenschuss, A. Ron, and O. Schnepp, *J. Chem. Phys.*, 1969, **50**, 2502.

[15] K. Cavanagh and D. F. Evans, *J. Chem. Soc.* (*A*), 1969, 2890.

determined commercially; in all cases, the two independent halide analyses agreed very well.

Raman spectra in the solid phase were measured with a Cary 81 spectrometer and a helium–neon laser source (London Inter-Collegiate Research Service at Imperial College). The far-i.r. spectra were measured (PCMU Harwell, R11C FS-720-EL with analogue computer FTC-100) by use of 15—50 mg of complex in 300 mg of wax matrix pressed into a thin disc. Polythene optics were removed for these measurements.

X-Ray spectra were done with Cu-K_α radiation.

We thank Dr. J. Donaldson for help and advice in connection with the *X*-ray work, and Chelsea College for a studentship (to I. W. S.).

[2/149 *Received, 24th January,* 1972]