Infrared and Raman Spectra of Di-μ-halogeno-bis[dihalogenocadmate(II)] Anions

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The salts $[NR_4]_x[(CdX_3)_x]$ (R = Pr^n or longer n-alkyl; X = Cl, Br, or I) are shown by i.r. and Raman spectroscopy to contain the halide-bridged dimeric anions $[Cd_2X_6]^{2-}$ both in the solid state and when dissolved in non-complexing solvents. Recent conclusions on the nature of the mixed-halide systems $[NPr^n{}_4]_x[(CdX_2Y)_x]$ are shown to be questionable. Previous assignments for the anions $[CdX_4]^{2-}$ have been augmented from studies on $[NR_4]_2[CdX_4]$.

COMPLEX cadmium(II) halide salts are known with cadmium to halide proportions of 1 : 3, 1 : 4, 1 : 5, and 1 : 6. Those of empirical formulae M_4CdCl_6 (M = K, NH_4, or Rb) have been shown by crystallographic means to contain identifiable $[CdCl_6]^{4-}$ octahedra in the solid state,[1] whilst $[Co(NH_3)_6][CdCl_5]$ contains trigonal-bipyramidal $[CdCl_5]^{3-}$ anions.[2] Infrared and Raman spectra of solid $[NMe_4]_2[CdI_4]$, $[NEt_4]_2[CdBr_4]$, $[NEt_4]_2[CdI_4]$, and $[NBu^n{}_4]_2[CdI_4]$ have been interpreted on the basis of tetrahedral $[CdX_4]^{2-}$ anions[3] as have those of $[NEt_4]_2[CdCl_4]$ in the solid state and in acetonitrile solution.[4]

In contrast, salts with empirical formula $MCdCl_3$ show a much more varied behaviour. Where M = K, Rb, or NH_4, the CdX_3 units are aggregated into double chains of linked $CdCl_6$ octahedra,[5,6] whilst $[NMe_4]_x[(CdCl_3)_x]$ is isomorphous[7] with $[NMe_4]_x[(NiCl_3)_x]$ which has chains of octahedra linked by opposite faces.[8] The i.r. and Raman spectra of these crystal forms have been studied in detail.[7,9] Ross *et al.*[3] pointed out a resemblance between the complicated vibrational spectra of $[NBu^n{}_4]_x[(CdI_3)_x]$ and those of In_2I_6[10] and tentatively suggested that it might indicate the presence of $[Cd_2I_6]^{2-}$ anions. Recently, however, Contreras and Tuck have reported[11] the solid-state Raman spectra of salts $[NPr^n{}_4]_x[(CdX_3)_x]$ (X = Cl, Br, and I) and concluded that these contain monomeric anions with, somewhat amazingly, C_{2v} symmetry.

There have been spectroscopic studies of $[(CdX_3)_x]^{x-}$ species in solution in tributyl phosphate[12] and in water[13] which have been variously interpreted in terms of planar D_{3h} and pyramidal C_{3v} monomeric anions. However, because these solvents are capable of co-ordination to cadmium they may have a decisive influence on the structure of the complex. In order to clarify the structural nature of the $[NR_4]_x[(CdX_3)_x]$ salts with the larger tetra-alkylammonium cations (*i.e.* those with R = Pr^n or longer), we have investigated both the i.r. and Raman spectra of the solids and their solutions in solvents of very low complexing ability, *e.g.* dichloromethane. We have also carried out similar measurements with the salts $[NR_4]_2[CdX_4]$.

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RESULTS AND DISCUSSION

The i.r. and Raman spectra of salts of composition $[NR_4]_x[(CdX_3)_x]$ (R = Pr^n or Bu^n; X = Cl, Br, or I), $[N(n\text{-}C_6H_{13})_4]_x[(CdI_3)_x]$, and $[N(n\text{-}C_7H_{15})_4]_x[(CdCl_3)_x]$ as solids are reported in Table 1. Only features at <300 cm^{-1} are listed since it was clear that no fundamentals of the anions occurred above this wavenumber. It should be noted, however, that the Raman spectra of $[NPr^n_4]_x[(CdX_3)_x]$ all showed bands at *ca.* 314 and 340 cm^{-1} which are absent from the salts with other cations but occur for other tetrapropylammonium salts, *e.g.* $[NPr^n_4]I$. Neither of these were reported by Contreras and Tuck in their study of $[NPr^n_4]_x[(CdX_3)_x]$ except in the case of $[NPr^n_4]_x[(CdCl_3)_x]$ where the band near 314 cm^{-1} is wrongly assigned as a fundamental of $[CdCl_3]^-$. The true fundamentals of the chloro-anion are rather broad and of lower Raman intensity than those of the bromide or iodide, possibly explaining this confusion. It will be seen that, at >100 cm^{-1}, the effect of changing the cation has only a marginal effect on the wavenumbers and the appearance of the spectra of the anions, and the chemical form of the species in the solid must clearly be the same in all the cases for a given halide.

Both the i.r. and the Raman spectra of the salts of $[(CdI_3)_x]^{x-}$ as solids show four bands in the region appropriate to CdX stretching; for the most part they are not coincident between the two. The same applies to the bromides. This number of stretching vibrations is, of course, much greater than that to be expected for a $[CdX_3]^-$ ion of any shape, but is in accordance with predictions for a D_{2h} dimeric anion $[Cd_2X_6]^{2-}$ which, based on tetrahedral geometry around the metal, should show four Raman-active ($2A_g + B_{1g} + B_{2g}$) and four i.r.-active ($B_{1u} + B_{2u} + 2B_{3u}$) modes.

To make sure that the multiplicity of bands is not simply the result of factor-group effects in the solid, we measured the spectra in solution where possible (Table 1). In most cases the solvents used were $CDCl_3$, CH_2Cl_2, or mixtures of $CDCl_3$ and CD_2Cl_2. Some spectra were obtained from acetone solutions and closely resembled those in the other solvents which have no significant complexing ability towards metals. The striking similarity between i.r. spectra of the solids and solutions leaves no doubt that the form of the complex cadmium species is the same in both states. The Raman spectra of solutions are not as rich as those of the solids, the weaker features probably being masked by the stronger ones which are broader for the solutions. However, the fact that two of the three bands for the bromo- and iodo-anions are polarised is strong support for the D_{2h} structure.

The solid-state Raman spectrum of the chloride showed only two CdCl stretching bands which are rather broad, and the solution spectrum was virtually identical with both bands being polarised. The i.r. spectra of the different solids showed three or four bands for the 200—300 cm^{-1} region, and the solution of the tetraheptylammonium salt exhibited four features. Thus, although the total predicted number of stretching vibrations has not been observed, there can be little doubt that the chloro-complex is of similar structure to the bromo- and iodo-anions.

With the polarisation data, the assignment of the Raman bands is straightforward. In terms of the motion about the metal atom, there is a fairly close resemblance between A_g and B_{3u} modes, B_{1g} and B_{2u} modes, and between B_{2g} and B_{1u} modes. The first set can be of mixed terminal and bridging bond-stretching nature but the second pair refer specifically to terminal bonds and the third set to bridging bonds. The i.r. assignments assume that the i.r.-active members of these pairs will occur in the same wavenumber order as their Raman-active counterparts as indeed was the case for the planar D_{2h} anions $[M_2X_6]^{2-}$.[14]

Very recently, Contreras and Tuck[15] published a further paper concerning this topic in which they report the Raman spectra of $[NPr^n_4]_x[(CdX_2Y)_x]$ (X, Y = Cl, Br, or I). They interpreted their observations on the same structural basis as they have wrongly concluded for the $[NPr^n_4]_x[(CdX_3)_x]$ systems, and assumed that the complexes contain only one anionic species in the crystal state. We repeated some of this work. In general, we observe most of the Raman features they report at >100 cm^{-1} but not always with the relative intensities given. However, we invariably observe additional bands and in some systems these are extremely intense. We note that: (*i*) bands at *ca.* 320 cm^{-1} assigned as CdCl vibrations are in fact due to the cation; (*ii*) whilst the simplicity of some of the Raman spectra may suggest a simple anion $[CdX_2Y]^-$, the i.r. spectra immediately refute such conclusions and highlight the dangers of relying on a single vibrational-spectroscopic technique; (*iii*) detailed consideration of all the peaks observed in the spectra suggests, not surprisingly, that the solids contain a mixture of the various possible mixed halogeno-anions; and (*iv*) the characterisation of mixed-halide complexes should include analyses for individual halides since C, H, N, and Cd percentages are relatively insensitive to the halide composition.

We will give one example of such a system, $[NPr^n_4]_x[(CdCl_2I)_x]$ prepared as in ref. 14. Analysis [found (calc.)]: C, 29.3 (29.0); H, 5.8 (5.7); Cl, 14.75 (14.3); I, 25.9 (25.55); N, 2.8 (2.8%). Raman spectrum (25—400 cm^{-1},* cation feature,† feature at similar wavenumber to that given in ref. 14): 377w,* *ca.* 346vw,* 333w,* 312wm,*† 286wm,† 250w,br, 166s, *ca.* 155 (sh), 125wm,† 74 (sh), 56s, and 38s cm^{-1}. Infrared spectrum: 285vs, 213vs, 173 (sh), 163wm, 146vw, 93m,br, and *ca.* 70 (sh) br cm^{-1}.

As an adjunct to this work we examined the salts $[NR_4]_2[CdX_4]$ (R = Pr^n or Bu^n) (Table 2). Results for $[NBu^n_4]_2[CdI_4]$ have been reported before,[3] as have those for $[NEt_4]_2[CdX_4]$ (X = Cl, Br, or I).[3,4] Our observations for the bromo- and iodo-complexes are a little

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TABLE 1

Infrared and Raman spectra below 300 cm^{-1} of salts of $[Cd_2X_6]^{2-}$ (X = Cl, Br, or I)

	$[NPr^n_4]_2$-$[Cd_2Cl_6]$	$[NBu^n_4]_2[Cd_2Cl_6]$			$[N(n\text{-}C_7H_{15})_4]_2$-$[Cd_2Cl_6]$		$[NPr^n_4]_2$-$[Cd_2Br_6]$	$[NBu^n_4]_2[Cd_2Br_6]$		$[NBu^n_4]_2$-$[Cd_2I_6]$	$[NPr^n_4]_2[Cd_2I_6]$			$[N(n\text{-}C_6H_{13})_4]_2$-$[Cd_2I_6]$	
Infrared	(mull)	(mull)			(mull)	$(CDCl_3)$	(mull)	(mull)	$(CDCl_3$–$CD_2Cl_2)$	(mull)	(mull)	$(CDCl_3$–$CD_2Cl_2)$		(mull)	$(CDCl_3$–$CD_2Cl_2)$
CdX str. (terminal) B_{2u} [a]	287s	290s			288s	289m	210s	210 206 ms	209s	168s	170s	170s		164s	171s
CdX str. (terminal) B_{3u}	280s	278s			276 (sh)	276wm	186s	183s	182ms	144s	141s	141ms		140s	141ms
CdX str. (bridge) B_{1u}	214s	213s			213s	211m	155m	151ms	150 (sh)	125m	119m	123m		127m	124m
CdX str. (bridge) B_{3u}	214s	203 (sh)			213s	204 (sh)	149m	142m	145ms	109wm	107wm			109wm	107wm
Bending and lattice modes	90m, br	97m, br			109 (sh) 80w		62w, br	64wm, br		56wm				62w, br	
Limit of study	(50)	(40)			(40)	(100)	(50)	(50)	(100)	(50)	(60)	(110)		(40)	(100)
Raman	(solid)	(solid)	(acetone)	(CH_2Br_2)	(solid)	(CH_2Br_2)	(solid)	(solid)	(acetone)	(solid)	(solid)	(CH_2Cl_2)	(acetone)	(solid)	
CdX str. (terminal) B_{1g}				285 [b]			209w (sh)	206w (sh)		167wm	170w	170vw, dp	170vw, dp	*ca.* 165 (sh) [c]	
CdX str. (terminal) A_g	288m	287m	282m, p	282m, p	283m, br	283m, br, p	200m	197m	195m, p	158wm	154wm	157w, p	154w, p	159wm	
CdX str. (bridge) B_{2g}							178vw	175vw	172vw	138vw	135vw				
CdX str. (bridge) A_g	249wm	245wm [c]	257m, p [c]	257m, p [c]	245wm, br	250wm, br, p	161s	157s	161s, p	116vs	115s	117vs, p	117vs, p	119vs	
Bending and lattice modes	98wm 79s, br 68wm 43vw 31wm	117m 74s 41m			121m		74m 56s, br 45m 23w	77m 55s 27wm		56wm 43w 32s	55w 43 (sh) 38s			63s 46vs 38m (sh)	
Other band (cation)								258w	258w, p		260w	257vw, p	258vw, p		
Limit of study	(10)	(10)	(120)	(200)	(10)	(200)	(10)	(20)	(100)	(20)	(30)	(70)	(60)	(20)	

[a] The Cd · · · Cd axis is taken as x and X · · · X (bridging) as z. [b] $\nu_{max.}$ of residual band under crossed-polarisation condition. [c] Position may be influenced by contribution from cation band.

TABLE 2

Infrared and Raman spectra below 300 cm^{-1} of salts of $[CdX_4]^{2-}$ (X = Cl, Br, or I)

	$[NPr^n_4]_2[CdCl_4]$		$[NBu^n_4]_2[CdCl_4]$			$[NPr^n_4]_2[CdBr_4]$		$[NBu^n_4]_2[CdBr_4]$				$[NPr_4{}^n]_2[CdI_4]$		$[NBu^n_4]_2[CdI_4]$			
				Raman													
	I.r. (mull)	Raman (solid)	I.r. (mull)	(solid)	(Me_2CO)	I.r. (mull)	Raman (solid)	I.r. (mull)	Raman (solid)	I.r. $(CDCl_3)$ [a]	Raman (CH_2Cl_2)	I.r. (mull)	Raman (solid)	I.r. (mull)	Raman (solid)	I.r. $(CDCl_3)$ [a]	Raman (Me_2CO)
ν_1 str. A_1	260wm	261m		255m [c]	257m, p [c]	159 (sh)	159s		161s		161s, p		117vs		116vs		114vs, p
ν_3 str. T_2	236s	249w 240w	239vs	236 (sh)	243vw [b]	179 (sh) 172s	180 (sh) 174wm	177s	177vw	179s		141s	142m	142s 138s	138m	142ms	141w, dp
ν_4 bend T_2	98m	98m	103wm	95wm		74wm 68wm	81 (sh) 68s		75 (sh) 61s			57w	52ms	62w	50w		
ν_2 bend E		84wm		82wm			52m		49m				42m		39w		
Lattice modes		42w 39w 29w		58wm			35w 23w		24vw				30vw 20m				
Other band (cation)									252w, bd		258w, p				260w, bd		259vw, p
Limit of study	(50)	(20)	(50)	(40)	(100)	(50)	(10)	(80)	(15)	(60)	(110)	(50)	(10)	(50)	(25)	(60)	(90)

[a] With added $[N(n\text{-}C_6H_{13})_4]X$. [b] and [c] as in Table 1.

more complete. We have been able to obtain all the stretching wavenumbers from solutions in organic solvents; the values are just a little less than for aqueous solutions.[16] In order to obtain the i.r. spectra in $CDCl_3$ it was necessary to add a little $[N(n\text{-}C_6H_{13})_4]X$ to suppress separation into two liquid phases, but there was no indication from the spectra that the added halide had affected the chemical form of the anion. In some of the solid-state spectra there is evidence of splitting of degenerate vibrations and environmentally induced i.r. activity of the symmetric breathing mode.

The spectra of the solid chloro-complexes corroborate the stretching assignments of Davies and Long [4] in their later report. We have identified an additional Raman band in the skeletal-deformation region which then places ν_2 below ν_4 as is usual, instead of them being coincident.

Comparison between the spectra of $[CdX_4]^{2-}$ and $[Cd_2X_6]^{2-}$ shows a striking similarity in wavenumber between ν_1 of the former and the lower A_g stretching vibration of the latter, but the possibility of our $[(CdX_3)_x]^{x-}$ systems being mixtures can be ruled out on the grounds that they do not systematically show bands at the same wavenumbers as the other vibrations of $[NR_4]_2[CdX_4]$. From our studies on the planar anions $[MX_4]^{2-}$ and $[M_2X_6]^{2-}$, a similar close correspondence between ν_1 of the former and ν_2 of the latter is apparent.[13,17]

Conclusion.—The salts $[NR_4]_x[(CdX_3)_x]$ ($R = Pr^n$ or a longer n-alkyl group) contain the dimeric halide-bridged anions $[Cd_2X_6]^{2-}$ in the solid state and when dissolved in chloroform, dichloromethane, or acetone.

EXPERIMENTAL

Infrared spectra were recorded using a Perkin-Elmer model 225 double-beam spectrophotometer and a Grubb-Parsons I.R.I.S. far-i.r. interferometer, as detailed previously.[18] Raman spectra were recorded with Coderg PHO double and T800 triple monochromators using Coherent Radiation Laboratories model 52 krypton-ion and argon-ion lasers.[18]

Preparation of the Salts.—The iodides $[NR_4]_2[Cd_2I_6]$ and $[NR_4]_2[CdI_4]$ ($R = Pr^n$, Bu^n, or $n\text{-}C_6H_{13}$) were prepared by dissolving CdI_2 in the minimum volume of acetone and adding to a stirred solution of 1 or 2 equivalents respectively of $[NR_4]I$ dissolved in the minimum volume of acetone. The tetra-n-propylammonium salts crystallised out during the addition, but the salts of the larger cations remained in solution and were precipitated by adding diethyl ether. The salts of the bromo-anions were prepared by stirring $CdBr_2$ (0.5 g) with the appropriate weight of $[NR_4]Br$ dissolved in acetone (150 cm³ for $[NPr^n_4]^+$ and 50 cm³ for $[NBu^n_4]^+$). When all the $CdBr_2$ had dissolved (*ca.* 10 min), diethyl ether was added to crystallise the product. The chloro-complexes were prepared in a similar way from $CdCl_2 \cdot 2.5H_2O$ (0.5 g) and $[NR_4]Cl$ dissolved in acetone–methanol (10 : 1, 40 cm³).

Analytical results are given in Table 3.

TABLE 3

Characterisation of salts

		Analysis (%) *		
Salt	M.p. (θ_c/°C)	C	H	N
$[NPr^n_4]_2[CdCl_4]$	163—164	46.0	9.0	4.45
		(45.95)	(9.0)	(4.45)
$[NPr^n_4]_2[CdBr_4]$	278	36.0	2.1	3.7
		(35.8)	(2.0)	(3.5)
$[NPr^n_4]_2[CdI_4]$	297—298	29.1	5.85	2.8
		(29.05)	(5.7)	(2.8)
$[NBu^n_4]_2[CdCl_4]$	90—91	52.15	10.05	3.85
		(52.0)	(9.85)	(3.8)
$[NBu^n_4]_2[CdBr_4]$	92—99	41.35	7.95	3.05
		(41.9)	(7.95)	(3.05)
$[NBu^n_4]_2[CdI_4]$	147	34.7	6.5	2.5
		(34.8)	(6.55)	(2.55)
$[NPr^n_4]_2[Cd_2Cl_6]$	198—200	35.3	6.95	3.35
		(35.55)	(7.0)	(3.4 5)
$[NPr^n_4]_2[Cd_2Br_6]$	225—228	26.6	5.4	2.65
		(26.75)	(5.25)	(2.6)
$[NPr^n_4]_2[Cd_2I_6]$	241	21.75	4.35	2.15
		(21.2)	(4.15)	(2.05)
$[NBu^n_4]_2[Cd_2Cl_6]$	127—128	41.9	7.8	3.2
		(41.65)	(7.9)	(3.05)
$[NBu^n_4]_2[Cd_2Br_6]$	117—121	31.85	6.15	2.3
		(32.3)	(6.1)	(2.35)
$[NBu^n_4]_2[Cd_2I_6]$	184—186	26.2	5.0	1.9
		(26.1)	(4.95)	(1.9)
$[N(n\text{-}C_6H_{13})_4]_2[Cd_2I_6]$	130—131	34.0	6.45	1.7
		(34.0)	(6.1)	(1.7)
$[N(n\text{-}C_7H_{15})_4]_2[Cd_2Cl_6]$	130—138	53.3	9.8	2.05
		(53.4)	(9.6)	(2.25)

* Calculated values are given in parentheses.

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