Inorganica Chimica Acta, *187* (1991) 141–147

Piperazinium and *N*-methyl-piperazinium tetrahalocadmates(II) containing discrete $[CdX_4]^{2-}$ units

Luigi Pietro Battaglia, Anna Bonamartini Corradi*
Istituto di Chimica Generale e Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., University of Parma, 43100 Parma (Italy)

Silvia Bruni, Franco Cariati
Dipartimento di Chimica Inorganica e Metallorganica, University of Milan, via Venezian 21, 20133 Milan (Italy)

and Marian Koman
Department of Inorganic Chemistry, Slovak Technical University, 812 37 Bratislava (Czechoslovakia)

(Received March 22, 1991)

Abstract

Compounds of formula $[CdX_4]$ $LH_2 \cdot nH_2O$ (LH_2 = piperazinium dication; X = Cl, Br, I; $n = 1$ for Cl and Br. LH_2 = *N*-methylpiperazinium dication; X = Cl, Br, I; $n = 0$) were prepared and characterized. The crystal structure of the piperazinium tetrabromocadmate(II) monohydrated complex was also determined by means of X-ray analysis. The $[CdBr_4] \cdot (pipzn) \cdot (H_2O)$ (pipzn = piperazinium dication) salt is monoclinic (space group and lattice constants: $P2_1/c$, $a = 6.887(4)$, $b = 13.429(8)$, $c = 14.260(9)$ Å, $\beta = 92.82(5)°$, $Z = 4$, $R = 0.072$, $R_w = 0.073$). Its structure consists of discrete monomeric $[CdBr_4]^{2-}$ anions, piperazinium dications and water molecules. Coordination around the cadmium ion is a very slightly distorted tetrahedron. All the compounds were also investigated by means of IR and Raman spectroscopic measurements and in particular the Cd–X stretching vibrations were discussed and unambiguously assigned on the basis of calculations performed on the spectra of the structurally known piperazinium tetrabromocadmate(II) monohydrate compound and of literature data.

Introduction

Halocadmates(II) have recently received a great deal of attention from both theoretical and experimental points of view for their peculiar properties (related to their polymorphic behavior), impurity electronic configurations and lattice locations, which are the key problems in semiconductors physics [1–3].

Being particularly interested in this field, we have focused our attention on the synthesis and characterization of polymeric one-dimensional linear chain halocadmates [4–6], since very little is known about their properties. This type of structure appears to be more unusual than the polymeric two-dimensional one for Cd(II) ion [7,8]. In particular, in previous papers the correlations between structure, thermal and electrical characteristics of some monodimensional halocadmates, having as counterions the piperazinium and *N*-methylpiperazinium dications (hereafter abbreviated as pipzn and mepipzn, respectively) [8], have been investigated with the aim of evidencing the factors controlling the stereochemistry and polymeric nature of halocadmates(II).

In this paper we report the structural and spectroscopic results performed on some discrete monomeric $[CdX_4]^{2-}$ anions having as counterions the pipzn and mepipzn dications to be compared with those obtained for the polymeric halocadmates(II) of the same dications. This seems very appropriate in order to extend our knowledge of the factors controlling the polymeric natures of halocadmates(II) and to make possible the design of new solid inorganic/organic composites presenting unusual properties.

Furthermore the Cd ion, being a d^{10}, represents an ideal system for our tests, since it shows a variety of coordination numbers and geometries, depending on many factors, prevalent among which are crystal packing, hydrogen bonding and halide dimensions [7, 9].

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*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

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Experimental

Preparation of the complexes

The crystalline compounds were precipitated by mixing concentrated hydrogen halide solutions of the appropriate amine and cadmium(II) halide salt in 1:1 molar ratios, and standing the solutions for some hours. Recrystallizations were obtained from concentrated hydrogen halide solutions.

Elemental analyses

$CdCl_4 \cdot pipzn \cdot H_2O$: Found: C, 13.41; H, 4.02; N, 7.75. Calc. for $C_4H_{14}N_2OCdCl_4$: C, 13.32; H, 3.92; N, 7.77%.

$CdBr_4 \cdot pipzn \cdot H_2O$: Found: C, 8.90; H, 2.71; N, 5.24. Calc. for $C_4H_{14}N_2OCdBr_4$: C, 8.92; H, 2.62; N, 5.21%.

$CdI_4 \cdot pipzn$: Found: C, 6.74; H, 1.77; N, 3.90. Calc. for $C_4H_{14}N_2OCdI_4$: C, 6.78; H, 1.71; N, 3.96%.

$CdCl_4 \cdot mepipzn$: Found: C, 16.89; H, 4.05; N, 7.90. Calc. for $C_5H_{14}N_2CdCl_4$: C, 16.84; H, 3.96; N, 7.86%.

TABLE 1. Experimental data for the crystallographic analysis of the $[CdBr_4] \cdot (pipzn) \cdot (H_2O)$ compound

Formula	$C_4H_{14}Br_4CdN_2O$
Molecular weight	538.2
Space group	$P2_1/c$
a (Å)	6.887(4)
b (Å)	13.429(8)
c (Å)	14.260(9)
β (°)	92.82(5)
V (Å^3)	1317(1)
Z	4
D_{calcd} (g cm^{-3})	2.71
D_{obs} (by flotation (g cm^{-3})	2.70
$F(000)$	992
Temperature (K)	293
Crystal size (mm)	0.35×0.47×0.55
Diffractometer	Siemens AED
μ (Mo Kα) (cm^{-1})	136.4
Scan speed (° min^{-1})	2.4
Scan width (°)	1.60
Radiation (Å)	Mo Kα $\lambda = 0.7107$
θ range (°)	2.5×25.0
h range	0.7
k range	0.14
l range	−14.15
Standard reflections	203
Max intensity variation (%)	3.5
Scan mode	ω–2θ
Measure reflections	1848
Conditions for observed reflections	$I > 3\sigma(I)$
No. reflections used in the refinement	977
Min. max. height in final $\Delta\rho$ (e Å^{-3})	−2.7, 2.0
No. of Ref. Parameters	74
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.072
$R_w = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{1/2}$	0.073
$s = [\Sigma w(\Delta F)^2/(N-P)]^{1/2}$	0.75
k, g ($w = k[\sigma^2(F_o) + gF_o^2]$)	1, 0.01338

TABLE 2. Fractional atomic coordinates (×10^4) for non-hydrogen atoms in the $[CdBr_4] \cdot (pipzn) \cdot (H_2O)$ compound (e.s.d.s. in parentheses)

Atom	x/a	y/b	z/c
Cd	215(3)	13(2)	2353(1)
Br(1)	−3561(4)	−192(2)	2282(2)
Br(2)	648(4)	1928(2)	2254(2)
Br(3)	1319(4)	−952(2)	921(2)
Br(4)	1706(4)	−591(2)	3943(2)
O(1)	−5811(35)	7137(18)	1796(15)
N(1)	−2906(35)	7105(19)	5624(16)
N(2)	−4480(30)	7928(17)	3884(14)
C(1)	−1931(37)	7969(19)	5188(17)
C(2)	−3432(37)	8550(19)	4588(17)
C(3)	−5366(38)	7105(21)	4302(17)
C(4)	−3985(39)	6512(19)	4916(17)

$CdBr_4 \cdot mepipzn$: Found: C, 11.19; H, 2.65; N, 5.25. Calcd. for $C_5H_{14}N_2CdBr_4$: C, 11.23; H, 2.64; N, 5.25%.

$CdI_4 \cdot mepipzn$: Found: C, 8.37; H, 2.00; N, 3.95. Calcd. for $C_5H_{14}N_2CdI_4$: C, 8.31; H, 1.95; N, 3.88%.

Physical measurements

IR spectra were recorded with a Digilab FTS 40 spectrophotometer as Nujol mulls on KBr pellets or as powder dispersed in alkali metals halides pellets in the 4000–500 cm^{-1} range at room temperature (no differences were observed among spectra obtained by these two different methods), and as powder in polythene pellets in the 500–50 cm^{-1} range at liquid nitrogen temperature. Raman spectra at room temperature were recorded on solid samples with a Coderg PHO spectrophotometer equipped with an argon laser. Nitrogen, carbon and hydrogen were analyzed with a Carlo Erba model 1106 elemental analyzer.

X-ray crystallographic data

The structure was solved by the heavy-atom method and refined anisotropically for Cd and Br atoms and isotropically for C, N and O atoms. Hydrogen atoms were placed in the calculated positions and introduced in the calculations of the final structure factors. The hydrogen atoms belonging to the water molecule were not calculated. Intensity data were corrected for Lorentz and polarization effects and put on absolute scale by least-squares. Correction for absorption was not applied because of the irregular shape of the crystals. The atomic scattering factors for the neutral atoms were taken from ref. 10. Crystal data and parameters associated with data collection are summarized in Table 1. The final atomic coordinates for non-hydrogen atoms are listed in Table 2. See also 'Supplementary material'. All calculations were performed on the GOULD 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR of the University of Parma with SHELX76 [11], PARST [12] and ORTEP [13] programs.

Results and discussion

All the compounds are stable in air and strongly soluble in organic polar solvents. The hydrated compounds completely lose the water molecule at temperatures around 100 °C. Their spectroscopic properties demonstrate that there is close correspondence among chloride, bromide and iodide complexes. In order to clarify unambiguously their stereochemistry the bromide complex of the pipzn dication was structurally characterized, as it presents the most suitable crystals.

Description of the structure of the $[CdBr_4]\cdot(pipzn)\cdot(H_2O)$ compound

The structure of the salt consists of discrete $[CdBr_4]^{2-}$ anions, piperazinium dications and water molecules, as shown in Fig. 1, where the numbering system employed is also displayed.

The geometry about the cadmium atom in the anion is that of a very slightly distorted tetrahedron due to the formation of hydrogen bonds with the cations and the water molecules. In fact, although all the Cd–Br bond lengths (Table 3) agree well with the sum of the covalent radii [14] and are in the range normally observed in other tetrabromocadmates [15], two of them (Cd–Br(1) 2.612(4) Å, Cd–Br(2) 2.597(4) Å) are slightly, but significantly, longer than the others (Cd–Br(3) 2.565(4) Å, Cd–Br(4) 2.574(4) Å). This distortion affects the Br–Cd–Br bond angles (Table 3) in the way expected when two of the ligands move out.

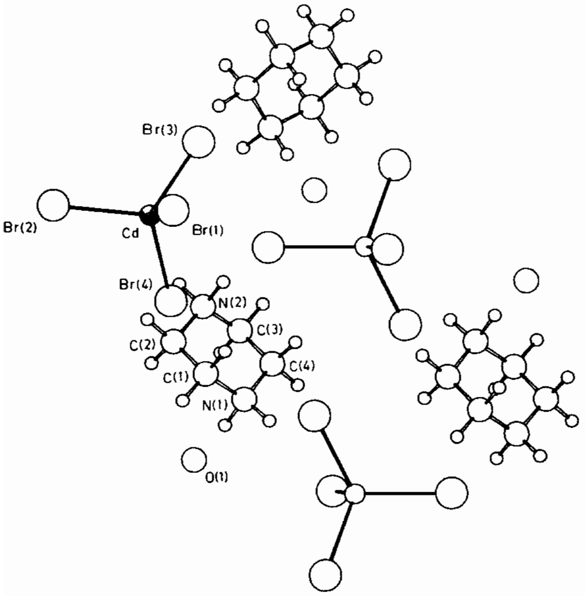

Fig. 1. ORTEP drawing of the structure of the $[CdBr_4]\cdot(pipzn)\cdot(H_2O)$ compound.

TABLE 3. Selected bond distances (Å) and angles (°) for the $[CdBr_4]\cdot(pipzn)\cdot(H_2O)$ compound (e.s.d.s in parentheses)

Cd–Br(1)	2.612(2)	Cd–Br(3)	2.565(4)
Cd–Br(2)	2.597(4)	Cd–Br(4)	2.574(4)
Br(3)–Cd–Br(4)	114.9(1)	Br(1)–Cd–Br(4)	110.8(1)
Br(2)–Cd–Br(4)	108.3(1)	Br(1)–Cd–Br(3)	104.4(1)
Br(2)–Cd–Br(3)	114.5(1)	Br(1)–Cd–Br(2)	103.2(1)

TABLE 4. Possible hydrogen bonds in the $[CdBr_4]\cdot(pipzn)\cdot(H_2O)$ compound (distances (Å) and angles (°))

$N(1)\cdots O(1^{i})$	2.86(3)	$N(1)–H(1)\cdots O(1^{i})$	<173
$N(1)\cdots Br(3^{ii})$	3.31(2)	$N(1)–H(2)\cdots Br(3^{ii})$	<140
$N(2)\cdots Br(2^{iii})$	3.42(2)	$N(2)–H(3)\cdots Br(2^{iii})$	<166
$N(2)\cdots Br(4^{iv})$	3.30(2)	$N(2)–H(4)\cdots Br(4^{iv})$	<131
$O(1)\cdots Br(1^{v})$	3.43(2)		
$O(1)\cdots Br(3^{iv})$	3.44(2)		

$i = x, \frac{3}{2}-y, \frac{1}{2}+z$, $ii = x, \frac{1}{2}-y, \frac{1}{2}+z$; $iii = -x, \frac{1}{2}+y, \frac{1}{2}-z$; $iv = x-1, 1+y, z$; $v = -x-1, \frac{1}{2}+y, \frac{1}{2}-z$.

The crystal lattice is stabilized by hydrogen bonding interactions among tetrabromocadmates, countercations and water molecules (Table 4). It is interesting to note that each pipzn dication, in the usual 'chair' conformation, as indicated by the puckering parameters ($q_2 = 0.033$, $q_3 = -0.562$, $\phi_2 = -97.1°$, $Q = 0.53$ Å) [16]), joins three $[CdBr_4]^{2-}$ anions and a water molecule, both N atoms being involved in bifurcated hydrogen bonding interactions. In particular, N(2) atoms 'bridges' two bromine atoms (Br(4) and Br(2)) of two adjacent $[CdBr_4]^{2-}$ units and the N(1) atom splits its interactions between the Br(3) atom of a third $[CdBr_4]^{2-}$ anion and one water molecule. Since the water molecules strongly interact with the N(1) atom of the pipzn dications, their hydrogen bonding capabilities toward the Br atoms of the $[CdBr_4]^{2-}$ anions are considerably weakened, the $O\cdots Br$ bonds being weaker than the $N\cdots Br$ ones, despite their electronegativities. In the structure of the previously examined $[Cd_2Cl_6(H_2O)]_n\cdot n(pipzn)$ salt [6], which consists of pipzn dications and 1-D endless inorganic chains of distorted octahedral $[CdCl_5\cdot H_2O]^{3-}$ ions, joined via two centrosymmetrically related bridging chlorine atoms, the strong hydrogen bonding capabilities of the pipzn dications are evidenced by the formation of a network of strongly directional interactions between countercations and chains, which firmly anchors adjacent chains one to another.

Infrared data

Spectral range 4000–2000 cm^{-1}

The IR spectra in the range of 4000–2000 cm^{-1} are recorded in order to evidence the H_2O and NH_2^+ and NH^+ stretching vibrations (the last one only present in mepipzn complexes). The experimental results are reported in Table 5. The two predictable bands due to the symmetric and asymmetric vibrations of the H_2O molecule are observed in the 3550–3400 spectral range, those corresponding to the symmetric and antisymmetric stretching vibrations of the NH_2^+ group in the 3150–3000 cm^{-1} spectral range and the expected band for the NH^+ group at about 2750 cm^{-1}, in perfect agreement with the literature data [17, 18].

Spectral range 500–50 cm^{-1}

An appropriate discussion of the IR and Raman stretching modes of the CdX_4^{2-} groups must start from examination of the spectra of the structurally known piperazinium tetrabromocadmate(II) compound. This compound presents a $P2_1/c$ space group with four CdX_4^{2-} groups in the Bravais cell. Although the factor group, being C_{2h}, can present site symmetries of type $4C_i(2)$, $C_1(4)$, the $CdBr_4^{2-}$ groups in the Bravais cell obviously occupy four sites of C_1 symmetry. In fact the $CdBr_4^{2-}$ anion, having four different Cd–Br bond lengths, does not present symmetry elements beyond the identity operation and therefore it has C_1 symmetry.

For the $CdBr_4^{2-}$ group based on the factor group (*i.e.* space symmetry), eight IR and Raman active stretching vibrations are calculated, whereas on the basis of the site symmetry only four IR and Raman active bands are expected (Table 6). The experimental results (Table 7 and Fig. 2) show the presence of four IR bands (192, 183, 176, 162.4 cm^{-1}) assignable to the $CdBr_4^{2-}$ anion, agreeing with the C_1 symmetry. Of these bands only the less energetic and intense one finds correspondence in the Raman spectrum, which presents a strong band at 161.5 cm^{-1} (Fig. 3). This trend suggests that the first three strong bands may originate from the F_2(IR, R) vibration, which is transformed into the 3A (IR, R) vibration by descent in symmetry of the T_d group ($T_d \rightarrow C_1$), and that the lonely fourth band is derived from the A_1 vibration, only Raman active in the T_d group, but becoming IR active too (A(IR, R)) by the descent in symmetry. It is worthy of note that the less intense IR band corresponds to the most intense Raman band, which is practically the only band certainly assignable to the Cd–Br vibration. The absence in the Raman spectrum of the $CdBr_4^{2-}$ anion of the three correspondent strong F_2 IR bands depends on the fact that they are probably very weak and therefore are not normally observed [19].

TABLE 5. More relevant infrared frequencies of the pipzn and mepipzn compounds (cm^{-1})^a

Compound	H_2O stretching	NH_2^+ stretching	NH^+ stretching
$[CdCl_4]\cdot$(pipzn)$\cdot(H_2O)$	3522s, 3454s	3084s, 3038s	
$[CdBr_4]\cdot$(pipzn)$\cdot(H_2O)$	3520s, 3458s	3084s, 3044s	
$[CdI_4]\cdot$(pipzn)		3084s, 3008s	
$[CdCl_4]\cdot$(mepipzn)		3126m, 2998s	2756s
$[CdBr_4]\cdot$(mepipzn)		3122m, 3000s	2756s
$[CdI_4]\cdot$(mepipzn)		3110m, 2998s	2744s

^{a}Abbreviations: s = strong; m = medium.

TABLE 6. Correlation diagram and selection rules of the Cd–Br stretching vibrations of the $[CdBr_4]^{2-}$ unit in the $[CdBr_4]\cdot$(pipzn)$\cdot(H_2O)$ compound^a

Point group T_d	Site group C_1	Factor group C_{2h}
A_1(R)		4 A_g(R)
F_2(IR, R)	4 A(IR, R)	4 B_g(R)
		4 A_u(IR)
		4 B_u(IR)

^{a}Abbreviations: IR = infrared; R = Raman.

TABLE 7. Metal–halogen stretching frequencies (cm^{-1}) in the pipzn and mepipzn compounds^a

Compound		ν(Cd–X)			
$[CdCl_4]\cdot$(pipzn)$\cdot(H_2O)$	R	263s			
	IR	254s	286s	270s	
$[CdBr_4]\cdot$(pipzn)$\cdot(H_2O)$	R	161.5s			
	IR	162.4s	192s	183s	176s
$[CdI_4]\cdot$(pipzn)	R	118.5s			
	IR	114.5s	156s	149s	141s
$[CdCl_4]\cdot$(mepipzn)	R	258.5s			
	IR	252s	282s		
$[CdBr_4]\cdot$(mepipzn)	R	164s			
	IR	168s	201s		
$[CdI_4]\cdot$(mepipzn)	R	116s			
	IR	117sh	134s		

^{a}Abbreviations: s = strong; sh = shoulder.

Furthermore, as described above, the $CdBr_4^{2-}$ group shows four different Cd–Br bond lengths, the longest observed for the bromine atom involved in hydrogen bonding interactions with the water molecule. Based on C_1 symmetry, four vibrational symmetry coordinates (A symmetry), corresponding to the four Cd–Br bonds can be built up for the $CdBr_4^{2-}$ group. By neglecting the interactions among the symmetry coordinates four Cd–Br vibrations, in every one of which a Cd–Br bond vibrates each time, can be predicted. This model, although approximate,

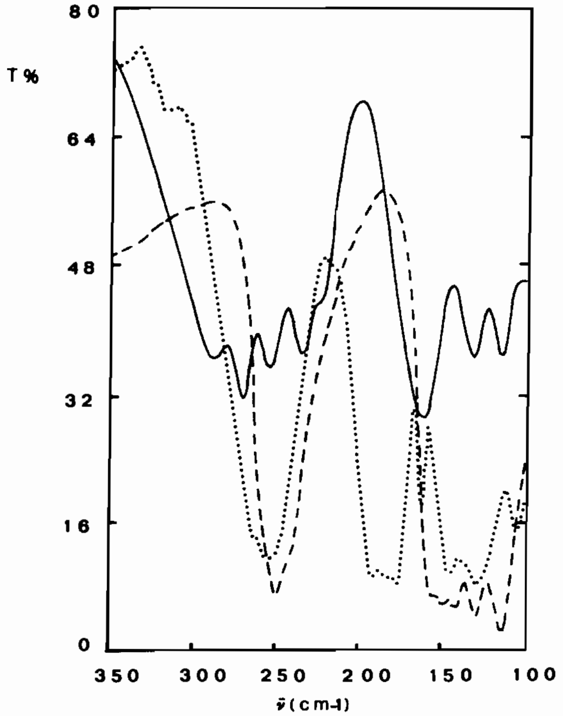

Fig. 2. Far-IR spectra of $[CdCl_4]\cdot(pipzn)\cdot(H_2O)$ (——), $[CdBr_4]\cdot(pipzn)\cdot(H_2O)$ (·····) and $[CdI_4]\cdot(pipzn)$ (– – –).

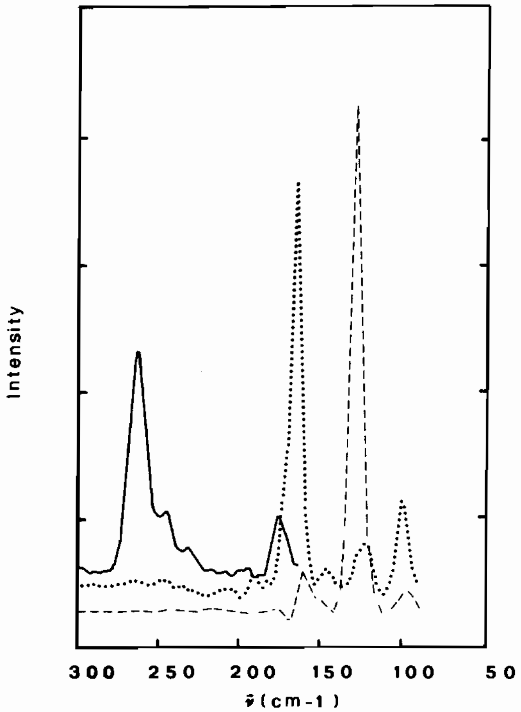

Fig. 3. Raman spectra of $[CdCl_4]\cdot(pipzn)\cdot H_2O)$ (——), $[CdBr_4]\cdot(pipzn)\cdot(H_2O)$ (·····) and $[CdI_4]\cdot(pipzn)$ (– – –).

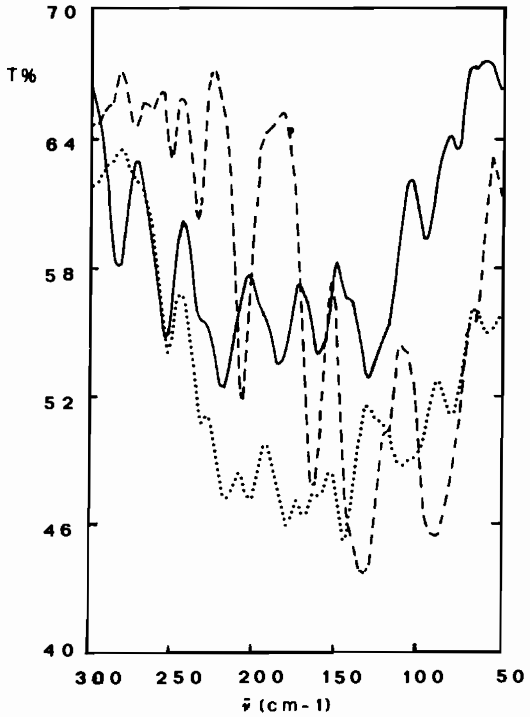

Fig. 4. Far-IR spectra of $[CdCl_4]\cdot(mepipzn)$ (——), $[CdBr_4]\cdot(mepipzn)$ (·····) and $[CdI_4]\cdot(mepipzn)$ (– – –).

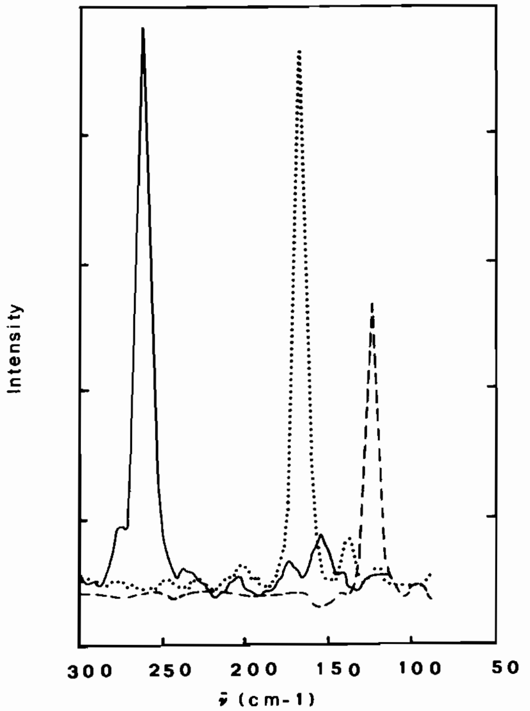

Fig. 5. Raman spectra of $[CdCl_4]\cdot(mepipzn)$ (——), $[CdBr_4]\cdot(mepipzn)$ (·····) and $[CdI_4]\cdot(mepipzn)$ (– – –).

TABLE 8. Halogen stretching frequencies ratios for the pipzn and mepipzn compounds

pipzn compounds				
Br/Cl	161.5/263 = 0.61	192/286 = 0.67	183/270 = 0.67	
I/Cl	118.5/263 = 0.45	156/286 = 0.54	149/270 = 0.55	
I/Br	118.5/161.5 = 0.73	156/192 = 0.81	149/183 = 0.81	149/176 = 0.8
mepipzn compounds				
Br/Cl	164/258.5 = 0.63		201/282 = 0.71	168/252 = 0.66
I/Cl	116/258.5 = 0.45		134/282 = 0.47	117/252 = 0.46
I/Br	116/164 = 0.71		134/201 = 0.67	117/168 = 0.70

suggests for a system of such a low symmetry the following correlation among the Cd–Br stretching frequencies and the bond lengths.

ν(Cd–Br) (cm^{-1})	(Cd–Br) Å
192	
183	2.596, 2.565, 2.574
176	
162.4	2.612

The trend of the Cd–I stretching frequencies in the IR and Raman spectra of the $[CdI_4]\cdot(pipzn)$ compound (Table 7 and Figs. 2 and 3) closely resembles that of the bromide one, and therefore it is possible to suggest for the $[CdI_4]^{2-}$ anion a C_{2v} (or lower) symmetry too.

The IR spectrum of the $[CdCl_4]\cdot(pipzn)\cdot(H_20)$ compound (Table 7 and Fig. 2) shows only three bands and the Raman spectrum (Fig. 3) only one strong band assignable to the Cd–Cl stretching vibrations, with a correspondence between the Raman band and the lowest energy IR band. This suggests for the $[CdCl_4]^{2-}$ anion a C_{3v} site symmetry, which predicts three IR and Raman active bands ($2A_1+E$), since the F_2 asymmetric stretching vibration of the T_d group by descent in symmetry originates only two bands.

Compared with the above described far-IR spectra, those of the $[CdX_4]\cdot(mepipzn)$ salts (Table 7 and Fig. 4), although more complex than those of analogous pipzn compounds, show only two strong IR bands assignable to the Cd–X stretching modes. On the contrary the Raman spectra of the mepipzn salts (Fig. 5) are identical to those of the pipzn ones presenting only one strong Raman band, unambiguously assignable to a Cd–X stretching vibration. The Raman band, nearly coincident with the lowest energy IR band and normally present in the Raman spectra of tetrahedral or distorted tetrahedral $[CdX_4]^{2-}$ anions, is assigned to the Cd–X total symmetric vibration [20]. Therefore also for the mepipzn compounds it is possible to suggest the presence of discrete $[CdX_4]^{2-}$ anions having distorted tetrahedral geometry, similarly to the pipzn ones; but in the former the splitting of the F_2 band of T_d type is too small to be revealed with low temperature far-IR spectroscopy.

Our assignments for the pipzn and mepipzn complexes (Table 7) are also ratified by the stretching frequency ratios (Table 8), which strongly resemble those reported in the literature [19].

Conclusions

The coordinative flexibility of the halocadmates(II) is demonstrated by their ability to form monomeric and/or polymeric species, which can be designed by playing, in the presence of appropriate countercations, with some factors among which the countercation hydrogen bonding abilities, the preparative media and the molar and size dimension ratios of the reagents are particularly important.

Analysis of the properties of different halometallate systems from several points of view (structural, spectroscopic, thermal, magnetic, electrical, etc.) outlines a consistent picture of the behavior of these compounds, which could be very useful for future application as engineering materials. These systems furthermore allow the practice of what has been called 'crystal lattice engineering' on a specific class of mixed organic–inorganic materials that exhibit a wide variety of interesting properties.

Supplementary material

Anisotropic and isotropic thermal parameters, atomic coordinates for hydrogen atoms and a list of observed and calculated structure factors are available from the authors on request.

Acknowledgements

The authors are grateful to Consiglio Nazionale delle Ricerche (C.N.R.) of Italy for financial support and to the Centro C.N.R. di Studio sulla Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione for the use of the Codeg PHO spectrophotometer.

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