

# Syntheses and spectroscopic properties of halocadmates(II): crystal and molecular structure of a new tribromo[*N*-benzylpiperazinium]cadmium(II) compound

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## Abstract

Compounds of formula  $[\text{CdX}_4] \cdot (\text{LH}_2) \cdot (\text{H}_2\text{O})$  ( $\text{LH}_2 = N$ -benzylpiperazinium dication;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and one of formula  $[\text{CdBr}_3(\text{LH})]$  ( $\text{LH} = N$ -benzylpiperazinium monocation) were prepared and characterized. The crystal structure of the monoprotonated *N*-benzylpiperazinium tribromocadmiate(II) complex was determined by means of X-ray analysis. The  $[\text{CdBr}_3 \cdot (\text{LH})]$  salt is triclinic (space group and lattice constants:  $P\bar{1}$ ,  $a = 9.500(3)$ ,  $b = 13.145(7)$ ,  $c = 6.801(1)$  Å,  $\alpha = 103.79(2)$ ,  $\beta = 96.24(2)$ ,  $\gamma = 96.17(5)^\circ$ ,  $Z = 2$ ,  $R = 0.0392$ ,  $R_w = 0.0394$ ). Its structure consists of discrete monomeric  $[\text{CdBr}_3(\text{LH})]$  units, in which the coordination polyhedron around the cadmium ion is a distorted tetrahedron. The coordination sphere is comprised of the three anionic bromide ligands and one terminal N atom of the *N*-benzylpiperazinium monocation. All the compounds were also investigated by means of IR and Raman spectroscopic measurements. The Cd–Br stretching vibrations of the structurally known  $[\text{CdBr}_3 \cdot (\text{LH})]$  salt were unambiguously assigned on the basis of calculations performed on its spectra and by comparison with literature data. The Cd–X stretching vibrations of the  $[\text{CdX}_4] \cdot (\text{LH}_2) \cdot (\text{H}_2\text{O})$  compounds, assigned by comparing their spectra with those of the monoprotonated *N*-benzylpiperazinium tribromocadmiate and on the basis of literature data, strongly suggest the presence of discrete  $[\text{CdX}_4]^{2-}$  anions.

## Introduction

Interest in the chemical behavior of halocadmates(II) derives from their unique structural, thermal, catalytic and electrical properties [1–3]. In particular, we were attracted by their peculiar coordinative and structural flexibility which enables the researcher to design materials, presenting very distinct structures, opportunely playing, in the presence of appropriate counterations, with some factors predominant among which seem to be the counteration hydrogen bonding abilities, the preparative media and the molar and size dimension ratios of the reagents. Furthermore these systems enable 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.

Being particularly engaged in this field we have previously focused our attention on the synthesis and characterization of monomeric and polymeric one-dimensional linear chain halocadmates(II) using as counterions mono and diprotonated saturated cyclic amines [4–7], with the final aim of evidencing the factors controlling their polymeric nature. Extending our studies in this paper, we discuss the spectroscopic results performed on some discrete monomeric  $[\text{CdX}_4]^{2-}$  anions having as counterions the *N*-benzylpiperazinium dications (abbreviated as  $\text{LH}_2$ ), and the structural and spectroscopic results performed on a compound of formula  $[\text{CdBr}_3(\text{LH})]$ , in which the diamine, in the monoprotonated form (abbreviated as  $\text{LH}$ ), is forced to act as monodenate ligand toward cadmium(II) bromide.

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This study seems to be very appropriate both in order to extend our knowledge on the factors controlling the wide structural abilities of halocadmates(II) and to verify the influence of the positive charge on the donor properties of the amino group.

Further interest derives from the fact that although zwitterionic  $\text{MX}_3\text{LH}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ;  $\text{LH} =$  monoprotonated diamine) species are common for some divalent metal ions, such as manganese(II), iron(II), cobalt(II), nickel(II), copper(II), zinc(II) [8–10], to our knowledge the one reported in this paper is the first to be isolated for the cadmium(II) ion.

## Experimental

### Preparation of the $[\text{CdBr}_3(\text{LH})]$ complex

The compound was prepared by mixing  $\text{CdBr}_2 \cdot 2\text{H}_2\text{O}$  salt, *N*-benzylpiperazine and hydrogen bromide [4] in a 1/1/1 ratio in methanolic solution. By slow evaporation of the solution for some days white crystals separated. *Anal.* Found: C, 24.90; H, 3.28; N, 5.25. Calc. for  $\text{C}_{11}\text{H}_{17}\text{N}_2\text{CdBr}_3$ : C, 24.93; H, 3.24; N, 5.29%.

Attempts to prepare the analogue chloride and iodide salts were a failure.

### Preparation of the $[\text{CdX}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$ complexes

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 are obtained from concentrated hydrogen halide solutions.

*Anal.*  $\text{CdCl}_4 \cdot (\text{LH}_2) \cdot \text{H}_2\text{O}$ : Found: C, 29.25; H, 4.56; N, 6.16. Calc. for  $\text{C}_{11}\text{H}_{20}\text{N}_2\text{OCdCl}_4$ : C, 29.31; H, 4.48; N, 6.22%.

$\text{CdBr}_4 \cdot (\text{LH}_2) \cdot \text{H}_2\text{O}$ : Found: C, 20.98; H, 3.28; N, 4.40. Calc. for  $\text{C}_{11}\text{H}_{20}\text{N}_2\text{OCdBr}_4$ : C, 21.01; H, 3.21; N, 4.48%.

$\text{CdI}_4 \cdot (\text{LH}_2) \cdot \text{H}_2\text{O}$ : Found: C, 16.00; H, 2.58; N, 3.34. Calc. for  $\text{C}_{11}\text{H}_{20}\text{N}_2\text{OCdI}_4$ : C, 16.17; H, 2.47; N, 3.43%.

### Physical measurements

IR spectra recorded with a Digilab FTS 40 spectrophotometer as Nujol mulls on KBr pellets or as powder dispersed in alkali metals halides pellets in the  $4000\text{--}500\text{ cm}^{-1}$  range at room temperature (no differences were observed among spectra obtained by these two different methods), and as powder dispersed in polythene pellets in the  $500\text{--}50\text{ cm}^{-1}$  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

Crystal data and parameters associated with data collection are summarized in Table 1. The X-ray measurements were carried out as described in Table 1. The lattice parameters were determined from least-squares refinement of  $\theta$  values for 15 reflections accurately centered on the diffractometer. The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was also applied [11]. The structure was solved by the Patterson and Fourier methods and refined isotropically ( $R = 0.093$ ), then anisotropically by least-squares. The hydrogen atoms, located in the final  $\Delta F$  map, were included in the last refinement cycle with isotropic thermal parameters. The atomic scattering factors for the neutral atoms were taken from the International Tables [12]. The final atomic coordinates for non-hydrogen atoms are reported in Table 2 and selected bond distances and angles in Table 3. All calculations were performed on a GOULD 32/77 computer of the 'Centro di Studio per la Strutturistica Diffrattometrica del CNR' of the

TABLE 1. Experimental data for the crystallographic analysis of  $[\text{CdBr}_3(\text{LH})]$  compound

Formula	$\text{C}_{11}\text{H}_{17}\text{Br}_3\text{CdN}_2$
Molecular weight	529.4
Space-group	$P\bar{1}$ (No. 2)
$a$ (Å)	9.500(3)
$b$ (Å)	13.145(7)
$c$ (Å)	6.801(1)
$\alpha$ (°)	103.79(2)
$\beta$ (°)	96.24(2)
$\gamma$ (°)	96.17(5)
$V$ (Å <sup>3</sup> )	812.1(5)
$Z$	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	2.17
$D_{\text{obs}}$ (by flotation) (g cm <sup>-3</sup> )	2.20
$F(000)$	500
Temperature (K)	273
Crystal size (mm)	0.16 × 0.42 × 0.84
Diffractometer	Philips PW1100
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	86.37
Absorption correction (min.–max.)	1.00–2.12
Scan speed (° min <sup>-1</sup> )	4.5
Scan width (°)	1.80
Radiation (Å)	Mo K $\alpha$ , $\lambda$ = 0.7107
$\theta$ -range (°)	2.5–25.0
Scan mode	$\omega$ -2 $\theta$
Measured reflections	2858
Condition for observed reflections	$I > 3\sigma(I)$
No. reflections used in refinement	2018
Min., max. height in final $\Delta F$ (e Å <sup>-3</sup> )	2.7, 2.0
No. refined parameters	222
$R = \sum \Delta F /\sum F_o $	0.0392
$R_w = [\sum w(\Delta F)^2/\sum w F_o^2]^{1/2}$	0.0394
$k, g$ ( $w = k/[\sigma^2(F_o) + gF_o^2]$ )	1.000, 0.000516

Table 2. Fractional atomic coordinates ( $\times 10^5$ ) for non-hydrogen atoms in the  $[\text{CdBr}_3(\text{LH})]$  compound with e.s.d.s in parentheses

Atom	$x/a$	$y/b$	$z/c$
Cd	29106(7)	15616(5)	15936(9)
Br(1)	6319(10)	23221(8)	26505(13)
Br(2)	28013(10)	9941(9)	-23280(12)
Br(3)	53339(10)	24914(9)	34648(14)
N(1)	26630(70)	-690(50)	24100(100)
N(2)	16410(80)	-23210(60)	15850(110)
C(1)	11640(90)	-4680(70)	25430(150)
C(2)	10250(110)	-15080(70)	-15080(140)
C(3)	31750(90)	-19350(70)	15120(150)
C(4)	32840(100)	-8760(70)	9890(140)
C(5)	14120(130)	-33900(80)	20290(170)
C(6)	19610(90)	-42440(70)	5690(140)
C(7)	28820(120)	-48600(90)	13130(200)
C(8)	33630(150)	-56890(100)	20(250)
C(9)	29720(150)	-59010(100)	-20830(240)
C(10)	20550(150)	-52860(90)	-28200(200)
C(11)	15430(120)	-44820(90)	-15220(150)

TABLE 3. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the  $[\text{CdBr}_3(\text{LH})]$  compound with e.s.d.s in parentheses

In the coordination polyhedron			
Cd-Br(1)	2.581(2)	Cd-Br(3)	2.536(2)
Cd-Br(2)	2.580(1)	Cd-N(1)	2.334(7)
Br(3)-Cd-N(1)	104.8(2)	Br(1)-Cd-N(1)	102.7(2)
Br(2)-Cd-N(1)	101.8(2)	Br(1)-Cd-Br(3)	119.3(1)
Br(2)-Cd-Br(3)	114.0(1)	Br(1)-Cd-Br(2)	111.6(1)
In the <i>N</i> -benzylpiperazinium monocation			
N(1)-C(1)	1.48(1)	C(5)-C(6)	1.49(1)
N(1)-C(4)	1.47(1)	C(6)-C(7)	1.39(2)
N(2)-C(2)	1.50(1)	C(7)-C(8)	1.39(2)
N(2)-C(3)	1.50(1)	C(8)-C(9)	1.38(2)
N(2)-C(5)	1.50(1)	C(9)-C(10)	1.38(2)
C(1)-C(2)	1.49(1)	C(10)-C(11)	1.37(2)
C(3)-C(4)	1.51(1)		
Cd-N(1)-C(4)	112.1(5)	N(2)-C(5)-C(6)	114.3(9)
Cd-N(1)-C(1)	113.3(5)	C(5)-C(6)-C(11)	112.5(9)
C(1)-N(1)-C(4)	110.1(7)	C(5)-C(6)-C(7)	119.6(9)
C(3)-N(2)-C(5)	113.9(8)	C(7)-C(6)-C(11)	117.9(10)
C(2)-N(2)-C(5)	111.4(7)	C(6)-C(7)-C(8)	121.0(1.2)
C(2)-N(2)-C(3)	110.0(7)	C(7)-C(8)-C(9)	120.7(1.3)
N(2)-C(2)-C(1)	111.2(8)	C(8)-C(9)-C(10)	118.2(1.4)
N(2)-C(3)-C(4)	109.8(7)	C(9)-C(10)-C(11)	121.3(1.2)
N(1)-C(4)-C(3)	113.3(8)	C(6)-C(11)-C(10)	120.9(1.0)

University of Parma with SHELX76 [13], PARST [14] and ORTEP [15] 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  $100^\circ\text{C}$ . The spectroscopic properties of the  $[\text{CdX}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$  compounds demonstrate that there are

close correspondences among chloride, bromide and iodide complexes. Since among all compounds the  $[\text{CdBr}_3(\text{LH})]$  one seems to be the most interesting presenting an unusual stoichiometry for the cadmium(II) ion, its structure was determined.

### Description of the structure of the $[\text{CdBr}_3(\text{LH})]$ compound

The structure of the salt consists of discrete neutral  $[\text{CdBr}_3(\text{LH})]$  units, as shown in Fig. 1, where the numbering system employed is also displayed. The compound is formally a zwitterion with a positive charge on the N(2) atom and a negative charge on the  $\text{CdBr}_3$  group. Coordination around the cadmium(II) atom involves three bromine atoms and one nitrogen atom of the organic ligand in a distorted tetrahedral arrangement.

The Cd-Br(1) and Cd-Br(2) bond distances are nearly identical (2.581(2), 2.580(1)  $\text{\AA}$ ) and significantly longer than the Cd-Br(3) bond length (2.536(2)  $\text{\AA}$ ). These longer bond lengths are due to the fact that both the Br(1) and Br(2) atoms are involved in intermolecular hydrogen bonding interactions. In particular the Br(1) atom, directed towards the cationic nitrogen atom, forms a contact  $(\text{N}(2)-\text{H}(6)\cdots(\text{Br}(1) (-x, -y, -z) = 3.407(8) \text{\AA}; \text{N}(2)-\text{H}(6)\cdots\text{Br}(1) (-x, -y, -z) = 162.4(9)^\circ)$  which connects two centrosymmetric complex molecules. The Br(2) directed towards the neutral N(1) atoms forms a contact  $(\text{N}(1)-\text{H}(1)\cdots\text{Br}(2) (x, y, z + 1) = 3.500(6) \text{\AA}; \text{N}(1)-\text{H}(1)\cdots\text{Br}(2) = 131(1)^\circ)$  which connects the structure along the  $[001]$  axis.

The Cd-Br distances average 2.566  $\text{\AA}$  and are significantly shorter than those found in the  $[\text{CdBr}_4]^{2-}$  ion (2.600  $\text{\AA}$ ) [7]. The increase of the Cd-Br distances on increasing the numbers of Br atoms bonded to the cadmium ions can be explained by invoking the s-character arguments of Bent [16], also previously preferred to electro-neutrality arguments for the interpretation of similar trends observed in Zn-Cl distances [9]. In fact as additional X (X = Cl, Br, I) atoms are added, the amount of s-character per M-X (M = Zn, Cd) bond decreases as the limiting tetrahedral  $\text{sp}^3$  case is reached in the  $[\text{MX}_4]^{2-}$  ions.

The Cd-N(1) distance (2.334(7)  $\text{\AA}$ ), very similar to the literature data for Cd-N bond lengths, suggests that the positive charge on the N(2) atom does not influence the donor properties of the ligand [17].

The *N*-benzylpiperazinium moiety presents bond distances and angles within the generally accepted values and the usual chair conformation with the following puckering parameters:  $q_2 = 0.027$ ,  $q_3 = -0.556$ ,  $\phi = 10.6^\circ$ ,  $Q = 0.57 \text{\AA}$

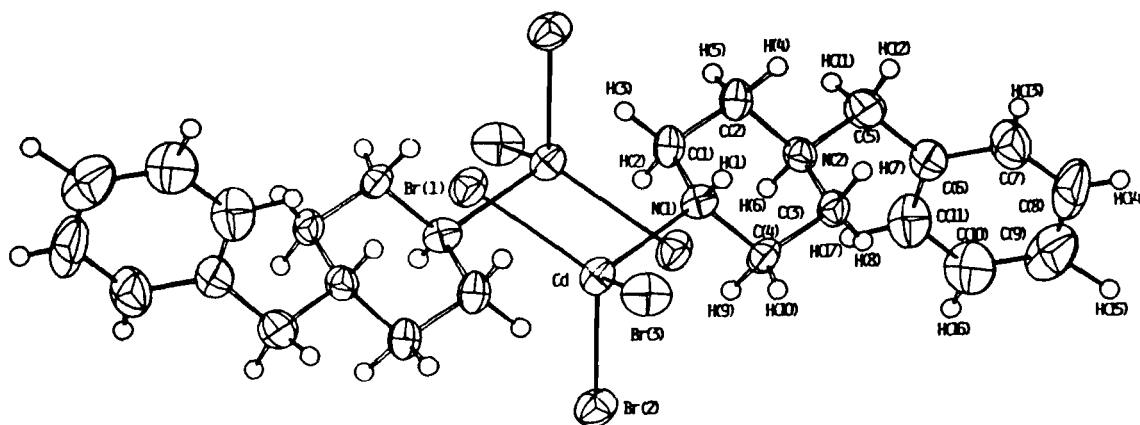


Fig. 1. ORTEP drawing of two centrosymmetrically related  $[\text{CdBr}_3(\text{LH})]$  molecules.

[18]. The phenyl ring is planar and the orientation between the phenyl ring and piperazinium moiety can be described by using the torsion angles around the  $\text{N}(2)\text{-C}(5)$  and  $\text{C}(5)\text{-C}(6)$  bonds:  $\text{C}(3)\text{-N}(2)\text{-C}(5)\text{-C}(6) = -57(1)^\circ$ ;  $\text{C}(2)\text{-N}(2)\text{-C}(5)\text{-C}(6) = 178(1)^\circ$ ;  $\text{N}(2)\text{-C}(5)\text{-C}(6)\text{-C}(11) = -56(1)^\circ$ ;  $\text{N}(2)\text{-C}(5)\text{-C}(6)\text{-C}(7) = 127(3)^\circ$ .

On the overall solid state packing only one contact less than  $3.5 \text{ \AA}$  is observed to involve the  $\text{C}(8)\cdots\text{C}(8)$  ( $1-x, -y-1, -z$ ) ( $3.43(2) \text{ \AA}$ ) atoms of adjacent zwitterions. The presence of the cationic nitrogen atom on the ligand may hinder the formation of intermolecular stacking interactions among the phenyl rings.

#### Spectroscopic results for the $[\text{CdBr}_3(\text{LH})]$ compound

##### Spectral range $4000\text{--}2000 \text{ cm}^{-1}$

The IR spectra in the range of  $4000\text{--}2000 \text{ cm}^{-1}$  show two bands at  $3244\text{s}$  and  $2776 \text{ cm}^{-1}$  assignable to the  $\text{NH}$  and  $\text{NH}^+$  stretching vibrations, respectively, in perfect agreement with the literature data [19].

##### Spectral range $500\text{--}50 \text{ cm}^{-1}$

The structurally known  $[\text{CdBr}_3(\text{LH})]$  compound presents a  $P\bar{1}$  space group, corresponding to a  $C_i$  factor group, with 2 molecules in the Bravais cell. The Cd atom occupies a  $C_1$  site symmetry, but by considering the two  $\text{Cd}\text{-Br}(1)$  and  $\text{Cd}\text{-Br}(2)$  bond lengths identical a  $C_{2v}$  type site symmetry could also be considered. The calculated number of predictable  $\text{Cd}\text{-Br}$  stretching bands (Table 4) results in 3 IR ( $A_u$ ) and 3 ( $A_g$ ) Raman active bands when considering the Bravais cell symmetry, and 3 IR and 3 Raman active bands, energetically coincident, on the basis of  $C_1$  site symmetry. Referring to the idealized  $C_{2v}$  site symmetry 3 bands ( $2A_1 + B_2$ ), IR and Raman active, are still calculated.

TABLE 4. Calculated stretching vibration modes of  $\text{Cd}\text{-Br}$  in the  $[\text{CdBr}_3(\text{LH})]$  compound

$f$	$C_{3v}$	$C_1$	$C_{2h}$
2	$A_1$		$3A_g$
4	$E$	$3A$	$3A_u$
Total 6			

The IR and Raman spectra of the compound (Table 5 and Fig. 2) show two very strong IR and two weak Raman bands, nearly coincident in position, and one medium IR and one strong Raman band, having nearly identical frequency values. On the basis of the anticipations of Table 4 one can suggest that the experimental results confirm the expected band number both for the  $C_1$  site and the Bravais cell symmetry. In our opinion it seems more reasonable to proceed in the assignments of bands arising from the  $\text{Cd}\text{-Br}$  stretching vibrations on the basis of the site symmetry only. It is worth observing that the  $\text{Cd}\text{-Br}$  frequency values in the  $[\text{CdBr}_3(\text{LH})]$  compound are very similar to those of the  $\text{Cd}\text{-Br}$  stretching modes in the  $[\text{CdBr}_4]^{2-}$  anions [20].

In the literature the IR and Raman spectra of a series of compounds containing the  $-\text{MX}_3$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ;  $M = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ ) group, having a structure quite similar to that of the  $-\text{CdBr}_3$

TABLE 5. Vibrational  $\text{Cd}\text{-Br}$  stretching frequencies ( $\text{cm}^{-1}$ ) in the  $[\text{CdBr}_3(\text{LH})]$  compound, according to  $C_1$  site symmetry<sup>a</sup>

Species	IR	Raman
A	205vs	200w
A	188vs	184w
A	170m	168vs

<sup>a</sup>Abbreviations: vs = very strong; m = medium; w = weak.

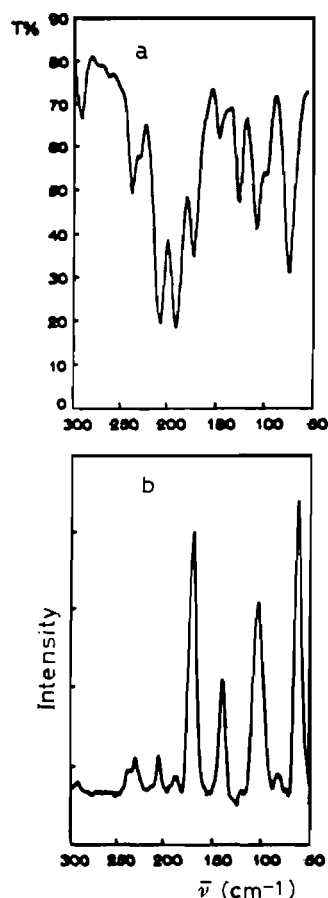


Fig. 2. Vibrational spectra of the  $[\text{CdBr}_3(\text{LH})]$  compound: (a) IR spectrum; (b) Raman spectrum.

unit under examination, are reported [21]. The spectra of the literature compounds present only two bands assignable to the Cd–Br stretching modes, suggesting a  $C_{3v}$  coordination geometry around the metal atom. On this basis for the  $\text{HgBr}_3(\text{LH})$  compound a metal atom  $C_{3v}$  symmetry has also previously been suggested [19c].

#### Spectroscopic results for the $[\text{CdX}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$ compounds

##### Spectral range $4000\text{--}2000\text{ cm}^{-1}$

The assignments of the IR bands of the  $[\text{CdX}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$  compounds in the range of  $4000\text{--}2000\text{ cm}^{-1}$ , as reported in Table 6, are made by comparison with the spectra of the analogous deuterated compounds and with literature data [19, 22]. It is interesting to note that both  $\text{H}_2\text{O}$  and  $\text{NH}_2^+$  groups show the symmetric and asymmetric stretching vibrations and that the  $\nu(\text{H}_2\text{O})$  modes increase in energy on passing from Cl, to Br and I, inversely to their electronegativity values, as a consequence of the weakness of their hydrogen bonding abilities in the same order.

TABLE 6. More relevant vibrational stretching frequencies ( $\text{cm}^{-1}$ ) in the  $[\text{CdX}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$  compounds<sup>a</sup>

Compound	( $\text{H}_2\text{O}$ )	( $\text{NH}_2^+$ )	( $\text{NH}^+$ )
$[\text{CdCl}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$	3414s, 3388s	3134s, 2988s	2792m
$[\text{CdBr}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$	3452s, 3392s	3134s, 2990s	2788m
$[\text{CdI}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$	3504s, 3412s	3124s, 3002s	2780m

<sup>a</sup>Abbreviations: s = strong; m = medium.

##### Spectral range $500\text{--}50\text{ cm}^{-1}$

The Raman spectra of all the compounds (Table 7 and Fig. 3) show only one band assignable to the Cd–X stretching vibration, while the IR spectra (Table 7 and Fig. 4) show one strong Cd–Br mode, at higher frequency than the Raman band, and a second band, well resolved for the chloride compound or as a shoulder for the bromide and iodide ones, at frequency values very similar to those of the Raman band.

These spectral trends suggest that the coincident IR and Raman bands should be assigned to the total symmetric stretching frequency, and the second band, only present in the IR spectra, to the non-symmetric stretching frequency. This and the band positions strongly

TABLE 7. Metal–halogen stretching frequencies ( $\text{cm}^{-1}$ ) in the  $[\text{CdX}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$  compound<sup>a</sup>

Compound		$A_1$	$F_2$
$[\text{CdCl}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$	R	255s	
	IR	257s	272s
$[\text{CdBr}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$	R	164.5s	
	IR	167sh	196s
$[\text{CdI}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$	R	123s	
	IR	129sh	142s

<sup>a</sup>Abbreviations: s = strong; sh = shoulder.

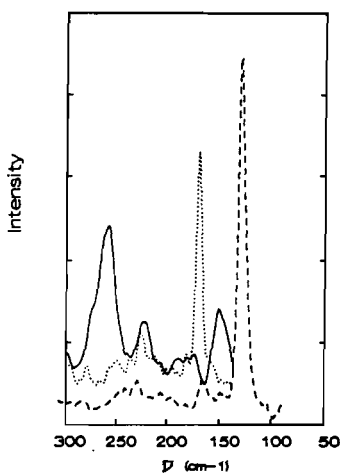


Fig. 3. Raman spectra of  $[\text{CdCl}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$  (—),  $[\text{CdBr}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$  (···) and  $[\text{CdI}_4](\text{LH}_2) \cdot (\text{H}_2\text{O})$  (---).

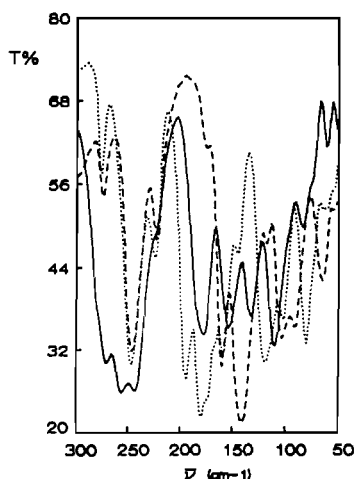


Fig. 4. Far IR spectra of  $[\text{CdCl}_4]\cdot(\text{LH}_2)\cdot(\text{H}_2\text{O})$  (—),  $[\text{CdBr}_4]\cdot(\text{LH}_2)\cdot(\text{H}_2\text{O})$  (···) and  $[\text{CdI}_4]\cdot(\text{LH}_2)\cdot(\text{H}_2\text{O})$  (---).

suggest the presence of discrete  $[\text{CdX}_4]^{2-}$  anions in the  $[\text{CdX}_4]\cdot(\text{LH}_2)\cdot(\text{H}_2\text{O})$  compounds which must have a lower symmetry than  $T_d$ . The expected splitting, due to the lowering symmetry of the  $F_2$  type mode, is probably too small to be revealed by the IR spectra even at the temperature of liquid nitrogen. Therefore the bands arising from  $F_2$  vibration may be masked in the broad IR band appearing at the highest energy value compatible with the  $\nu(\text{Cd-X})$  frequency [20]. In the assignment of the  $\nu(\text{Cd-X})$  stretching vibrations, reported in Table 7, the  $T_d$  symmetry symbology has been used.

## Conclusions

The coordinative flexibility of the halocadmates(II) is further demonstrated in this paper in which a new type of compound, hitherto unknown for the cadmium(II) ions, has been designed, isolated and characterized. The results clearly show the zwitterionic nature of the  $[\text{CdBr}_3(\text{LH})]$  complex. The overall solid state structure of the compound can be visualized as being comprised of dimers joined by one directional intermolecular hydrogen bonding between the proton of the cationic nitrogen and one bromine atom. The positive charge on the protonated nitrogen atom does not seem to influence the donor properties of the ligand, but it affects the phenyl ring orientation, for which stacking interactions are not observed.

## Supplementary material

Anisotropic thermal parameters, atomic coordinates for hydrogen atoms and list of observed

and calculated structure factors are available from the authors on request.

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