

Preparation and characterization of some P-quaternary salts of tetracoordinate halogenozincate(II) and halogenocadmiate(II) anions

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Abstract

The synthesis and characterization of the following phosphonium salts L_2MX_4 , L'_2MX_4 ($X = \text{Cl, Br, I; M = Zn, Cd}$), $L_2MX_2Y_2$, $L'_2MX_2Y_2$ ($X = \text{Cl, Y = Br, I}$ or $X = \text{Br, Y = I; M = Zn, Cd}$), $L_2Cd_2Cl_6$ and $L_2Cd_2Br_6$ are reported ($L = [(C_6H_5)_2P(CH_2C_6H_5)-N(C_2H_5)_2]^+$; $L' = [(C_6H_5)_3P(CH_2C_6H_5)]^+$). Far-IR spectra have been investigated and bands assignments are proposed for the metal–halogen stretching frequencies. Positive and negative FAB mass spectrometry data in different matrices are also reported.

Introduction

In a previous paper [1] we reported the synthesis and characterization of some complexes of the type L'_2CdX_4 ($X = \text{Cl, Br}$) and $L_2Cd_2Cl_6$. These compounds are of interest as catalysts in phase transfer nucleophilic substitutions, as flame retardants for a variety of thermoplastic polymers, and cross-linking of fluopolymers, such as vinylidene fluoride elastomers. Compounds L'_2MX_4 and L_2MX_4 have been claimed to improve adhesion to metals of the cured vinylidene fluoride fluoroelastomers [2].

In this paper we report the synthesis and characterization of the salts of the cations $L = [(C_6H_5)_2P(CH_2C_6H_5)-N(C_2H_5)_2]^+$ and $L' = [(C_6H_5)_3P(CH_2C_6H_5)]^+$ with the halogenocadmiate(II) and halogenozincate(II) anions shown in Table 1.

Experimental

Preparation of compounds

L_2MX_4 compounds were prepared by the reaction of LX (2 mol) with MX_2 (1 mol) in methyl glycol at reflux temperature for 1 h. After cooling, filtering and washing with ethyl alcohol, the products were dried at

room temperature. LX intermediates were prepared from diphenyldiethylaminophosphine and benzyl halide in 1,1,1-trichloroethane at reflux temperature.

L'_2MX_4 compounds were prepared using the procedure described previously [1].

$L_2Cd_2Br_6$ and $L_2Cd_2Cl_6$ compounds were obtained by treatment of triphenylphosphine (1 mol) or diphenyldiethylaminophosphine (1 mol) with anhydrous cadmium halide (2 mol) in diglyme at room temperature, followed by addition of benzyl halide (1 mol) and heating for 2 h at reflux temperature. After filtering the hot mixture and cooling, white compounds were isolated.

Analytical data are reported in Table 1 and are in agreement with the theoretical values.

Instrumentation

Carbon, hydrogen and nitrogen were analysed with a Perkin-Elmer elemental analyser instrument model 2400, while zinc and cadmium metals were determined with a Perkin-Elmer atomic absorption spectrophotometer model 4000.

IR spectra were obtained at *c.* 77 K on polythene pellets of the samples with the aid of a Digilab FTS-40 spectrometer.

Mass spectrometry determinations were obtained on a double focusing, reverse geometry VG 7070 EQ instrument; FAB spectra were carried out in different

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TABLE 1. Analytical data (calculated values in parentheses)

Compound	C	H	N	M	Melting point (°C)
L ₂ ZnCl ₄	60.91(61.1)	5.90(6.0)	3.16(3.10)	7.30(7.23)	153
L ₂ ZnBr ₄	49.86(51.10)	4.72(5.0)	2.35(2.60)	6.20(6.04)	131
L ₂ ZnI ₄	43.34(43.50)	4.07(4.30)	2.06(2.20)	5.09(5.15)	193
L ₂ CdCl ₄	58.20(58.10)	5.63(5.70)	2.92(2.90)	11.76(11.82)	142
L ₂ CdBr ₄	48.94(48.90)	4.65(4.80)	2.56(2.50)	9.92(9.96)	159
L ₂ CdI ₄	42.02(41.90)	3.91(4.10)	2.03(2.10)	8.51(8.54)	199
L ₂ ZnCl ₄	65.56(65.70)	4.81(4.80)		6.98(7.15)	230
L ₂ ZnBr ₄	54.89(55.00)	4.21(4.10)		5.95(5.98)	211
L ₂ ZnI ₄	47.01(46.90)	3.54(3.50)		5.16(5.11)	217
L ₂ ZnCl ₂ Br ₂	55.72(55.60)	5.25(5.50)	2.52(2.80)	6.48(6.58)	194
L ₂ ZnBr ₂ I ₂	46.79(47.00)	4.39(4.60)	2.20(2.40)	5.51(5.56)	165
L ₂ CdCl ₂ Br ₂	53.13(53.10)	5.11(5.20)	2.43(2.70)	10.75(10.81)	142
L ₂ CdCl ₂ I ₂	47.83(48.7)	4.62(4.80)	2.40(2.50)	9.87(9.91)	167
L ₂ CdBr ₂ I ₂	45.12(45.20)	4.29(4.40)	2.24(2.30)	9.17(9.19)	183
L ₂ ZnCl ₂ I ₂	54.65(54.70)	3.85(4.00)		5.94(5.96)	175
L ₂ ZnBr ₂ I ₂	50.47(50.60)	3.66(3.70)		5.48(5.51)	191
L ₂ Cd ₂ Cl ₆	48.72(48.70)	4.63(4.80)	2.47(2.50)	20.03(19.8)	175
L ₂ Cd ₂ Br ₆	42.36(42.60)	2.86(3.10)		16.84(17.40)	222

matrices (glycerol, thioglycerol, sulfolane, nitrobenzyl alcohol) using a Xe atom beam with a translational energy of 8 KeV.

Results and discussion

The IR spectra of the L₂MX₄ and L₂'MX₄ compounds show three metal-halogen stretching bands at frequencies similar to those reported in the literature [1, 3–8]. These are shown in Table 2.

From an analysis of these data it is possible to assign to the MX₄²⁻ anions a site symmetry lower than T_d. In fact, while in T_d symmetry only one IR active triply degenerate F₂ metal-halogen stretching vibration is expected, in C_{3v} three stretching vibrations are expected,

TABLE 2. IR metal-halogen stretching frequencies (cm⁻¹) of MX₄²⁻ anions

Compound	$\nu(\text{MX}_4)$
L ₂ ZnCl ₄	286s, 270sh, 266vs
L ₂ ZnBr ₄	211s, 200s, 188vs
L ₂ ZnI ₄	174sh, 169vs, 159vs
L ₂ CdCl ₄	262vs, 250sh, 242vs
L ₂ CdBr ₄	181s, 173s, 164vs
L ₂ CdI ₄	150sh, 145vs, 137vs
L ₂ ZnCl ₄	286vs, 272vs, 266vs
L ₂ ZnBr ₄	211vs, 208sh, 186s
L ₂ ZnI ₄	177s, 168vs, 162vs

s = strong, vs = very strong, sh = shoulder.

two of which (A₁+E) are due to the splitting of the triply degenerate vibration, while the third vibration (A₁) originates from the only Raman active A₁ vibration of the T_d group.

Similar conclusions have been reached by Contreras and Meyer [8], who have assigned the C_{3v} symmetry to the CdCl₄²⁻ anion of (Pr₄N)₂CdCl₄.

The metal-halogen bending vibration of the compounds of this study have not been analysed because the modes occur in a region where the lattice modes can also be observed. For this reason these vibrations are of little use to elucidate the structure of these compounds.

The IR spectra of the mixed halide complexes L₂MX₂Y₂ and L₂'MX₂Y₂ show four metal-halogen stretching bands (2A₁+B₁+B₂), which is as expected for C_{2v} symmetry (see Table 3).

It is worth noting that the values of the cadmium-halogen stretching frequencies of our com-

TABLE 3. IR metal-halogen stretching frequencies (cm⁻¹) of MX₂Y₂²⁻

Compound	$\nu(\text{MX}_2)$	$\nu(\text{MY}_2)$
L ₂ ZnCl ₂ Br ₂	285sh, 277vs	217sh, 205vs
L ₂ ZnBr ₂ I ₂	208m, 190vs	171s, 162s
L ₂ CdCl ₂ Br ₂	250sh, 240vs	178sh, 171vs
L ₂ CdCl ₂ I ₂	255sh, 232vs	148s, 138s
L ₂ CdBr ₂ I ₂	180m, 166vs	150s, 142m
L ₂ ZnCl ₂ I ₂	287vs, 276vs	166sh, 160s
L ₂ ZnBr ₂ I ₂	208vs, 194vs	170sh, 165vs

m = medium, s = strong, vs = very strong.

TABLE 4. IR metal-halogen stretching frequencies (cm^{-1}) of $\text{Cd}_2\text{X}_6^{2-}$ anions^a

Compound	$\nu(\text{CdX}_t)$	$\nu(\text{CdX}_t)$	$\nu(\text{CdX}_b)$	$\nu(\text{CdX}_b)$
$\text{L}_2\text{Cd}_2\text{Cl}_6$	296s	280s	225s	212s
$\text{L}'_2\text{Cd}_2\text{Br}_6$	215s	180s	156s	145s

^a CdX_t and CdX_b denote terminal and bridging CdX stretching modes respectively; s = strong.

pounds are very similar to those reported in the literature for similar compounds [6].

Finally the IR spectra of L_2CdCl_6 and $\text{L}'_2\text{Cd}_2\text{Br}_6$ compounds show four cadmium-halogen stretching bands: two are due to bridged halogens and the other two are attributed to terminal halogens (see Table 4). Accordingly, we assign D_{2h} symmetry to the $\text{Cd}_2\text{X}_6^{2-}$ anions [1]. In fact, for this symmetry one can expect two IR vibrations ($B_{1u} + B_{3u}$) for the terminal CdX_2 stretching motions and two IR vibrations ($B_{2u} + B_{3u}$) for the bridging CdX_2 stretching motions.

The fast atom ionization technique makes it possible to obtain information on the molecular weight of the studied complexes by investigating both positive and negative ion spectra [9, 10].

The positive FAB spectra of the compounds of formula L_2MX_4 showed a trivial behaviour and the parent peak, which is almost the only observable peak, corresponds to that of $[\text{L}]^+$. The only exception was the complex L_2ZnI_4 which gave a parent ion at m/z 603 corresponding to $[\text{L}_2\text{H}]^+$. The negative FAB spectra did not show appreciable differences in the matrices used; the higher sensitivities were obtained however using nitrobenzyl alcohol. The complexes L_2ZnX_4 and L_2CdX_4 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) showed very similar spectra; the most abundant ion was $[\text{MX}_3]^-$, arising from a one

electron reduction or a dissociative resonance capture process of the doubly charged monomer $[\text{MX}_4]^{2-}$. All the compounds also showed a small intensity peak (less than 5% of the parent ion $[\text{MX}_3]^-$) corresponding to the fragment $[\text{M}_2\text{X}_5]^-$. As an example, in Fig. 1(a) is reported the FAB⁻ spectrum of the complex $[\text{CdCl}_4]^{2-}$ and in Fig. 1(b) are shown the calculated relative intensities of the fragments $[\text{CdCl}_3]^-$ and $[\text{Cd}_2\text{Cl}_5]^-$. The presence of dimeric species in all the matrices and always in the same ratio to the parent ion $[\text{MX}_3]^-$ could be due to rearrangements generated by ionization conditions rather than to the presence in solution of dimeric species. In fact the IR spectra for L_2MX_4 solutions in solvents of different chemical properties, such as CH_2Cl_2 , CH_3CN and DMSO, always show only one band for the metal-halogen stretching motions, as expected for MX_4^{2-} anions.

In the FAB⁻ spectra of the complexes of formula $\text{L}_2\text{MX}_2\text{Y}_2$ the only detectable ions were the fragments corresponding to the species $[\text{MX}_3]^-$, $[\text{MX}_2\text{Y}]^-$, $[\text{MXY}_2]^-$ and $[\text{MY}_3]^-$, almost in the same intensity. As an example, Fig. 2 shows the FAB⁻ spectra of the complex $\text{L}_2\text{CdCl}_2\text{Br}_2$ (a) together with the calculated relative intensities of the fragments $[\text{CdCl}_3]^-$, $[\text{CdCl}_2\text{Br}]^-$, $[\text{CdClBr}_2]^-$ and $[\text{CdBr}_3]^-$ (b). The species $[\text{MX}_2\text{Y}]^-$ and $[\text{MXY}_2]^-$ could be generated from a one electron reduction or from a dissociative resonance capture process of the doubly charged monomer $[\text{MX}_2\text{Y}_2]^{2-}$ with a resulting loss either of a chloride or a bromide ion. The other two negative ions $[\text{MX}_3]^-$ and $[\text{MY}_3]^-$, in the absence of dimeric species, would arise only from a fast rearrangement due to the reaction between the parent ions $[\text{MX}_2\text{Y}]^-$ and $[\text{MXY}_2]^-$ with highly energetic Br^- or Cl^- ions. These conclusions are supported by the results of two further experiments. The FAB⁻ spectra of L_2CdCl_4 and of L_2CdBr_4 in the presence of a slight excess of NaCl and NaBr, re-

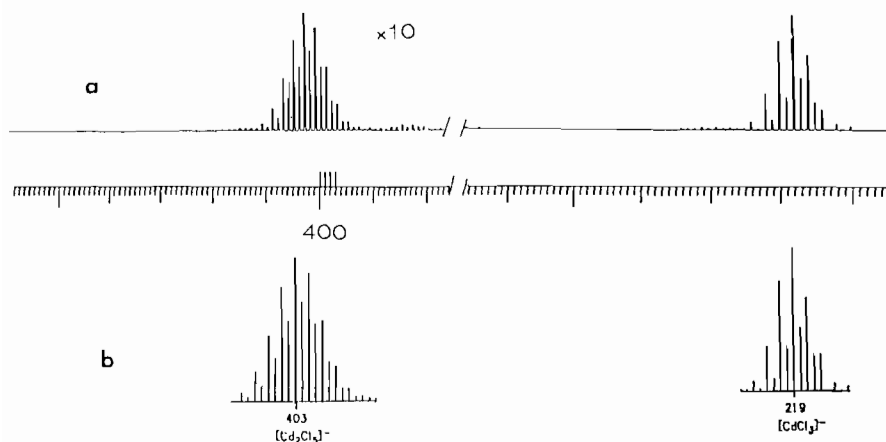


Fig. 1. Mass spectrum of L_2CdCl_4 (a); calculated relative intensities of the $[\text{Cd}_2\text{Cl}_5]^-$ and $[\text{CdCl}_3]^-$ ions (b).

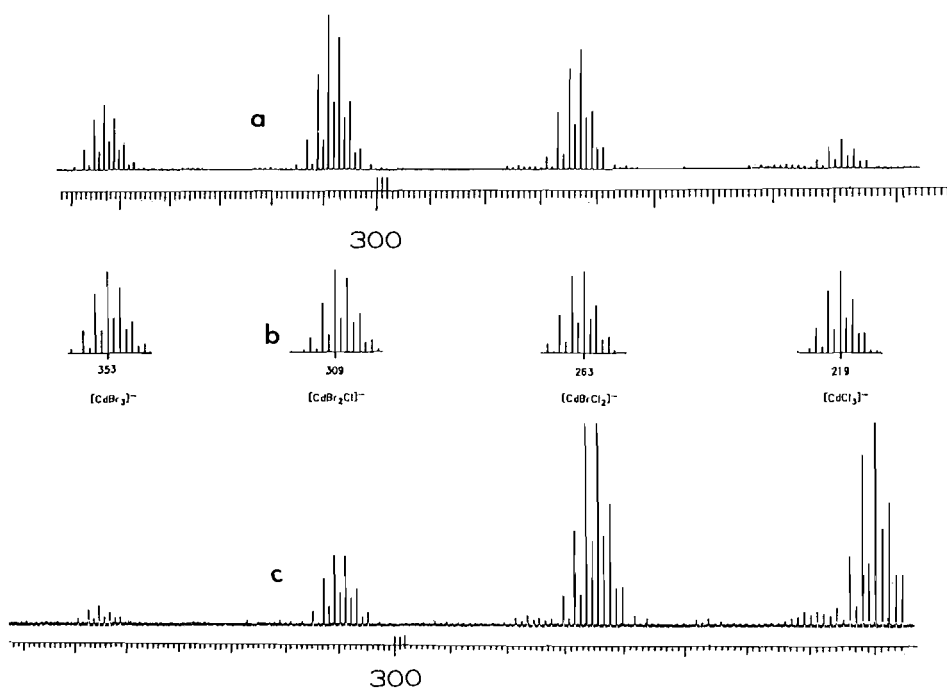


Fig. 2. Mass spectrum of $L_2CdCl_2Br_2$ (a); calculated relative intensities of the $[CdCl_nBr_{3-n}]^-$ ($n=0,1,2,3$) ions (b); mass spectrum of the 1:1 mixture of L_2CdCl_4 and L_2CdBr_4 (c).

spectively, give no detectable ions corresponding to cadmium containing species, thus indicating that the presence of highly reacting ions gives rise to irreversible transformations of the complexes.

The FAB⁻ spectrum (Fig. 2(c)) of an equimolar mixture of L_2CdCl_4 and L_2CdBr_4 in glycerol gives, together with the ions $[CdCl_3]^-$ and $[CdBr_3]^-$ which are typical of the complexes L_2CdCl_4 and L_2CdBr_4 , the ions corresponding to the species $[MCl_2Br]^-$ and $[MClBr_2]^-$. In this case any ambiguity is removed, in the sense that the anions $[MCl_2Br]^-$ and $[MClBr_2]^-$ can be generated only from a rearrangement of the parent compounds by chloride or bromide negative ions.

Conclusions

The main conclusions of this work can be summarized as follows.

(i) MX_4^{2-} anions in the solid state show a symmetry lower than T_d .

(ii) From IR spectra it is possible to exclude the dimerization of MX_4^{2-} in solution.

(iii) X^- and Y^- anions are very reactive toward MX_4^{2-} , MY_4^{2-} and $MX_2Y_2^{2-}$. By fast atomic bombardment, these anions generate $MX_nY_m^-$ ($n+m=3$) species, whose formation can be explained only by taking into account the preliminary formation of X^- and Y^- anions.

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