

Preparation and Characterization of some P-Quaternary Compounds

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The preparation of phosphonium salts of the type $[R'_3R''P^+]_2X^{2-}$ with $R' = C_6H_5$, $R'' = C_6H_5CH_2$ or C_2H_4OH and $X = CdCl_4$, $CdBr_4$ and Cd_2Cl_6 is reported. Their far-infrared spectra have been investigated and band assignments are proposed for the metal-halogen frequencies in the tetrahedral $CdCl_4^{2-}$, $CdBr_4^{2-}$ and bitetrahedral $Cd_2Cl_6^{2-}$ anionic species, which are present according to X-ray diffraction studies.

Introduction

The purpose of the study reported here is to prepare and characterize some new phosphonium compounds of interest as catalysts in phase transfer nucleophilic substitutions [1–3], as flame retardants for a variety of thermoplastic polymers [4], and in some peculiar bulk reactions such as the crosslinking of vinylidene fluoride elastomers, as previously reported for other phosphorous compounds [5–8]. The compounds described here have been

previously studied by single crystal X-ray diffraction [9–12].

Experimental

Preparation of Compounds

Bistriphenylbenzylphosphonium tetrachlorocadmiate bis-1,2-dichloroethane, $[(C_6H_5)_3PCH_2C_6H_5]_2CdCl_4 \cdot 2Cl_2C_2H_4$ (I), was obtained in 90% yield by treating 1 mole of bistriphenylphosphinedichlorocadmium, prepared by established methods [13], with 2 moles of benzylchloride in methylglycol for 2 h at reflux temperature. After cooling and filtering, the product was recrystallized from 1,2-dichloroethane, filtered and dried at room temperature. The white product thus obtained is a bis-1,2-dichloroethane solvate, as indicated by a DSC spectrum which shows the peak due to weight loss of dichloroethane at 85 °C.

Bistriphenylbenzylphosphonium tetrabromocadmiate, $[(C_6H_5)_3PCH_2C_6H_5]_2CdBr_4$ (II), was synthe-

TABLE I. Analytical Data.

Compound	C%		H%		Halogen %		M.p. (°C)
	Calc.	Found	Calcd.	Found	Calcd.	Found	
$[(C_6H_5)_3PCH_2C_6H_5]_2CdCl_4 \cdot 2Cl_2C_2H_4$	55.98	55.92	4.49	4.50	24.46	24.50	218
$[(C_6H_5)_3PCH_2C_6H_5]_2CdBr_4$	52.71	52.73	3.86	3.83	28.11	28.13	226
$[(C_6H_5)_3PCH_2C_6H_5]_2Cd_2Cl_6$	52.48	52.45	3.85	3.87	18.58	18.51	225
$[(C_6H_5)_3PC_2H_4OH]_2CdCl_4$	55.30	55.25	4.61	4.63	16.31	16.27	164

TABLE II. Crystal Data of P-Quaternary Compounds.

Compound	Space group	Z	Unit cell parameters					
			a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
$[(C_6H_5)_3P(C_6H_5CH_2)]_2CdCl_4 \cdot 2Cl_2C_2H_4$	$P2_1/c$	4	14.73(2)	24.88(3)	16.37(2)	—	112.61(10)	—
$[(C_6H_5)_3P(C_6H_5CH_2)]_2CdBr_4$	$P\bar{1}$	2	12.506(6)	10.471(5)	18.396(13)	93.07(4)	105.75(5)	92.58(4)
$[(C_6H_5)_3P(C_6H_5CH_2)]_2Cd_2Cl_6$	$P\bar{1}$	2	20.593(20)	12.832(15)	12.730(18)	120.84(5)	117.84(6)	83.97(5)
$[(C_6H_5)_3P(C_2H_4OH)]_2CdCl_4$	$P\bar{2}_1/n$	4	18.010(8)	18.574(8)	12.178(6)	—	93.03(6)	—
	Cc	4	16.054(9)	14.741(10)	16.964(9)	—	93.91(5)	—

sized in 92% yield by treating 1 mole of bistrphenylphosphinedibromocadmium, obtained according to Evans *et al.* [14], with 2 moles of benzylbromide in methylglycol for 0.5 h at reflux temperature. After cooling and filtering, the white product was recrystallized from 1,2-dichloroethane.

Bistrphenylbenzylphosphonium hexachlorodcadmate, $[(C_6H_5)_3PCH_2C_6H_5]_2Cd_2Cl_6$ (*III*), was obtained in low yield by treatment of triphenylphosphine (1 mole) with anhydrous cadmium chloride (2 moles) in diglyme at room temperature followed by addition of 1 mole of benzylchloride (to the non-isolated intermediate $[(CdCl_2 \cdot P(C_6H_5)_3)_2]$) with heating for 2 h at reflux temperature. After filtering the hot mixture and cooling, a white product precipitated which was filtered, washed with ethyl ether and dried at room temperature. Attempts to prepare this product by treatment of equimolecular quantities of triphenylphosphine and anhydrous cadmium chloride were unsuccessful, as was the use of hydroxyl containing solvents.

Bistrphenyl(2-hydroxyethyl) phosphonium tetrachlorocadmiate, $[(C_6H_5)_3PC_2H_4OH]_2CdCl_4$ (*IV*), was prepared in 85% yield from 1 mole of bistrphenylphosphinedichlorocadmium and 2 moles of 2-chloroethanol in ethylglycol at reflux temperature for 3 h. After cooling, the white crystals were filtered, washed with ethanol, and recrystallized with 1,2-dichloroethane.

Elemental analyses of the complexes were in agreement with the theoretical values. The analysis data and melting points of the complexes are given in Table I.

Far infrared spectra were recorded with a Perkin-Elmer FIS 3 spectrophotometer using Nujol mulls supported between Polythene discs. Adsorption due to Polythene is weak (it occurs only below 230 cm^{-1} and could be compensated) and did not interfere with the assignment of the metal-halogen stretching frequencies.

Results and Discussion

The molecular and crystal structures of the compounds have previously been determined by X-ray diffraction techniques. As the results have been reported in full elsewhere [9–12], we limit ourselves here to an evaluation of the main structural aspects of each compound and of common features within the series. The crystal data are collected in Table II.

The crystal structure of *I* is built up by juxtaposition of well separated $CdCl_4^{2-}$ anions and phosphonium cations in the presence of solvent molecules. The phosphonium ions are far apart with few interactions with the $CdCl_4^{2-}$ ions. Similarly, the structures of *II* and *III* are composed of well separated

TABLE III. Far-infrared Active Vibrational Frequencies (cm^{-1}) for CdX_4^{2-} Anions and Their Assignments.

Compound	$\nu_3(\text{F}_2)$	$\nu_4(\text{F}_2)$
$[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{C}_6\text{H}_5]_2\text{CdCl}_4 \cdot 2\text{Cl}_2\text{C}_2\text{H}_4$	240 vs, br	110 s, br
$[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{C}_6\text{H}_5]_2\text{CdBr}_4$	181 vs	70 s
$[(\text{C}_6\text{H}_5)_3\text{PC}_2\text{H}_4\text{OH}]_2\text{CdCl}_4$	268 vs, br	106 s

s = strong; v = very; br = broad.

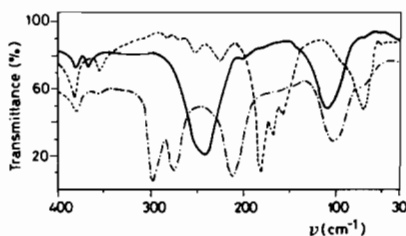


Fig. 1. Far-infrared spectra in nujol mull of $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{C}_6\text{H}_5]_2\text{CdCl}_4 \cdot 2\text{Cl}_2\text{C}_2\text{H}_4$ (—), $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{C}_6\text{H}_5]_2\text{Cd}_2\text{Cl}_6$ (---), $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{C}_6\text{H}_5]_2\text{CdBr}_4$ (- - -).

CdBr_4^{2-} and $\text{Cd}_2\text{Cl}_6^{2-}$ ions and phosphonium cations. Compound *IV* shows a more pronounced cation-anion interaction in the solid state with each anion being linked through two Cl-H-O hydrogen bonds to two different phosphonium cations, thus establishing a well-defined 1:2 complex. At variance to the cadmium complexes $(\text{R}_3\text{P})\text{CdX}_2$ and $(\text{R}_3\text{P})_2\text{CdX}_2$ no metal-phosphorous bonding [14–18] is present in compounds *I–IV*.

Anionic Structures

The CdCl_4^{2-} ions of *I* and *IV* have a quasi-perfect tetrahedral symmetry with average Cd-Cl bond lengths of 2.441(5) Å (range 2.433–2.455 Å) and 2.448(4) Å (range 2.439–2.453 Å), respectively and an average value of the Cl-Cd-Cl angles of 109.5(1)° (range: 105.8–112.5° in *I* and 104.5–114.4° in *IV*). The fairly weak secondary bonding effects in *IV* (hydrogen bond Cl-H-O) or the solvation by two dichloroethane molecules in *I* do not greatly influence the Cd-Cl bond lengths.

The CdBr_4^{2-} ion in *II* has also a quasi-perfect tetrahedral symmetry with an average Cd-Br bond length of 2.588(2) Å (range 2.566–2.635 Å) and an average value of the Br-Cd-Br angles of 109.9(9)° (range 105.6–111.8°). The dimensions of the anion conform to the expected values compared to CdCl_4^{2-} on the basis of the 0.17 Å difference in the ionic radii of the chloride and bromide ions.

Assignments of the $\nu(\text{M-X})$ and $\delta(\text{X-M-X})$ modes for *I*, *II*, and *IV* are reported in Table III. For MX_4^{2-} ions with T_d symmetry only the $\nu_3(\text{F}_2)$

stretching and $\nu_4(\text{F}_2)$ bending vibrations are expected to be infrared active [19]. The spectrum of the CdCl_4^{2-} anion of compound *I* is characterized by a broad band at 240 cm^{-1} (Fig. 1), which is assigned to the ν_3 stretching vibration. On the basis of the mean Cd-Cl bond distances (2.441(5) Å in *I* and 2.448(4) Å in *IV*) it is not immediately obvious that the ν_3 stretching vibration of the CdCl_4^{2-} anion in *IV* is at 268 cm^{-1} . The corresponding value for CdBr_4^{2-} in *II* is shifted down at 181 cm^{-1} (Fig. 1), as expected on the basis of the mass ratio. The values for the ν_3 and ν_4 frequencies are in accordance with those found for other compounds containing the CdX_4^{2-} anion [15, 20]. The average $\nu(\text{Cd-Br})/\nu(\text{Cd-Cl})$ frequency ratio of 0.68 is close to that reported elsewhere (0.68–0.71) [15, 16].

The binuclear $\text{Cd}_2\text{Cl}_6^{2-}$ anion of *III* is composed of a slightly distorted edge-condensed bitetrahedron with approximate D_{2h} (*mmm*) symmetry [11]. X-ray structural data for $\text{Cd}_2\text{X}_6^{2-}$ anions are scarce and are limited to compound *III* and $[\text{Cu}_3(\text{Bu}_2\text{dtc})_6][\text{Cd}_2\text{Br}_6]$, where $\text{Bu}_2\text{dtc} = \text{N,N}$ -di-*n*-butyl-dithiocarbamate anion [21]. In *III*, the cadmium atoms are thus joined by a double chlorine atom bridge in such a way that two cadmium atoms and two bridging chlorine atoms (Cl_b) are in a slightly distorted square-planar arrangement with the four terminal chlorine atoms (Cl_t) being above and below the bridging plane. The bond angles of the $\text{Cd}_2\text{Cl}_6^{2-}$ anion deviate considerably from tetrahedral values and range from 118.5(1) to 91.0(1)° with the following average bond angles: $\text{Cl}_b\text{-Cd-Cl}_b$, 91.3(1)°; $\text{Cl}_t\text{-Cd-Cl}_t$, 118.1(1)°; $\text{Cl}_t\text{-Cd-Cl}_b$, 111.0(1)°; $\text{Cd-Cl}_b\text{-Cd}$, 88.5(1)°. As expected, Cd- Cl_t bond lengths (average 2.391(5) Å) are shorter than the Cd-Cl distances in the tetrachlorocadmiate ions.

The molecular vibrations in the $\text{Cd}_2\text{Cl}_6^{2-}$ anion of *III* are more complex than in the simpler CdCl_4^{2-} anion (Fig. 1). According to the literature [22], for ions of the type M_2X_6 with D_{2h} symmetry we expect two infrared active vibrations, $\nu_8(\text{B}_{1u})$ and $\nu_{16}(\text{B}_{3u})$, for the terminal MX_2 stretching motions and two infrared active vibrations, $\nu_{13}(\text{B}_{2u})$ and $\nu_{17}(\text{B}_{3u})$, for the bridging MX_2 stretching motions. In agreement with the assignment proposed for the $\nu(\text{Ga-Cl})$ stretching vibrations of Ga_2Cl_6 [23], a molecule

TABLE IV. Far-infrared Active Vibrational Stretching Frequencies (cm^{-1})^a for the $\text{Cd}_2\text{Cl}_6^{2-}$ Anion and Their Assignments.

Compound	ν_8 (CdCl_t)	ν_{16} (CdCl_t)	ν_{13} (CdCl_b)	ν_{17} (CdCl_b)
$[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{C}_6\text{H}_5]_2\text{Cd}_2\text{Cl}_6$	297 s	276 s	212 s	208 sh

^a CdCl_t and CdCl_b denote terminal and bridging CdCl stretching modes, respectively. s = strong, sh = shoulder.

with D_{2h} symmetry in the solid state [24], and in accordance with the interpretation of the infrared spectrum of gaseous Al_2Cl_6 [25, 26], also of D_{2h} symmetry [27], the terminal and bridging $\nu(\text{Cd}-\text{Cl})$ stretching frequencies are assigned as reported in Table IV. As no infrared data are available with regard to the $\text{Cd}-\text{Br}$ stretching vibrations of the hexabromodicadmate complex this work is consequently the first to report on the assignment of the stretching vibration frequencies due to the terminal and bridging $\text{Cd}-\text{Cl}$ bonds of the $\text{Cd}_2\text{X}_6^{2-}$ anion ($\text{X} = \text{Cl}$).

It has not been possible to assign the bending vibrations of the $\text{Cd}_2\text{Cl}_6^{2-}$ anion. Namely, in the spectral range examined (Fig. 1) only the broad band at 102 cm^{-1} and a shoulder at about 70 cm^{-1} are possible candidates for such vibrations, whereas according to expectation [22], five infrared bands should have been active.

Cationic Structures

The two independent $(\text{C}_6\text{H}_5)_3\text{P}^+\text{CH}_2\text{C}_6\text{H}_5$ cations in each of the structures *I-III* and the two $(\text{C}_6\text{H}_5)_3\text{P}^+\text{C}_2\text{H}_4\text{OH}$ cations of *IV* all show a *quasi*-perfect tetrahedral symmetry around the five-valent phosphorus atoms. This also holds for the related compounds benzyl(2-methoxyphenyl)-diphenylphosphonium bromide (*V*) [28] and triphenylbenzylphosphonium chloride (*VI*) [29]. As to the conformation of the triphenylbenzylphosphonium cations in *I-III*, the $\text{P}-\text{C}(sp^2)$ bonds are nearly *staggered* (*gauche* +, *gauche* - and *trans*) in respect of the $\text{CH}_2-\text{C}(sp^2)$ bond of the benzyl residues. The orientations of the phenyl groups, expressed by the torsion angles around the $\text{P}-\text{C}(sp^2)$ bonds in respect of the $\text{P}-\text{CH}_2$ bonds, indicate conformations intermediate between *staggered* and *eclipsed*, with the exception of the cations of *III*, centred on P(1), where the coordination is *staggered* and *eclipsed*. Mean values for $\text{C}(sp^2)-\text{C}(sp^3)-\text{P}-\text{C}(sp^2)$ torsion angles are 64.8° , -56.6° and 184.1° in the six independent triphenylbenzylphosphonium cations of *I-III*, with $\text{P}-\text{C}(sp^3)-\text{C}(sp^2)-\text{C}(sp^2)$ being -94.8° and 88.5° on average. Rotations around the $\text{P}-\text{C}(sp^2)$ bonds in triphenylbenzylphosphonium cations are likely to be on account of packing requirements. However, as may be seen from Fig. 2, some rather well-defined conformations of these cations in the solid state, as in the case of *V*, *I* (P(1) cation, original atom nota-

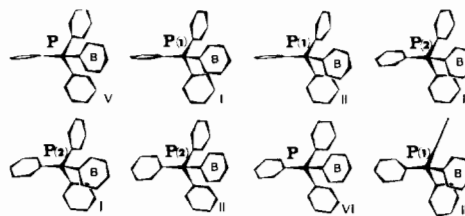


Fig. 2. Conformation of triphenylbenzylphosphonium cations of bistriphenylbenzylphosphonium tetrachlorocadmate bis-1,2-dichloroethane (*I*), bistriphenylbenzylphosphonium tetrabromocadmate (*II*), bistriphenylbenzylphosphonium hexachlorodicadmate (*III*), benzyl(2-methoxyphenyl)-diphenylphosphonium bromide (*V*) and triphenylbenzylphosphonium chloride (*VI*). The projection axis is along the $\text{P}-\text{CH}_2$ bond. Original atom notation; B, benzyl.

tion), *II* (P(1)); *III* (P(2)), *I* (P(2)) and *II* (P(2)), *VI* (see Fig. 2) suggest that packing requirements are often of secondary importance in regulating molecular geometries.

In agreement with the triphenylbenzylphosphonium cations also in the β -hydroxyethyl residues the $\text{P}-\text{C}(sp^2)$ bonds are in a nearly *staggered* conformation (*gauche* +, *gauche* - and *trans*) in respect of the $\text{C}-\text{C}$ bond. As above, the orientations of the phenyl groups are intermediate between *staggered* and *eclipsed*.

No attempt was made to assign the modes of the weak phosphonium cation frequencies.

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