A SPECTROSCOPIC STUDY OF ZINC(II), CADMIUM(II) AND MERCURY(II) COMPLEXES WITH TRICYCLOHEXYLPHOSPHINE AS LIGAND

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The preparations of the complexes $M(PCy_3)_2X_2$ and $M(PCy_3)X_2$ with $M = Zn, Cd$ or Hg , $X = Cl, Br, I$ or SCN , $PCy_3 =$ tricyclohexylphosphine and some of their adducts with acetone, methanol or carbon disulfide are reported. Their infrared spectra in the range $4000\text{--}200\text{ cm}^{-1}$ and their Raman spectra between $4000\text{--}100\text{ cm}^{-1}$ have been investigated. From these data we conclude for the dimeric complexes $M(PCy_3)_2X_2$ with $M = Cd$ or Hg and $X = Cl, Br$ or I , a distorted tetrahedral coordination around mercury or cadmium. For the complex $Hg(PCy_3)(SCN)_2$ we suggest a trigonal coordination around mercury. Assignments are proposed for the metal-halogen and metal-phosphorus frequencies.

Introduction

The infrared spectra of triphenylphosphine and its compounds with zinc, cadmium and mercury have been intensively studied by *Deacon* and *Green*¹. However Raman spectra of these complexes have not been reported. These complexes with the formula $M(PPh_3)_2X_2$ and $M(PPh_3)X_2$, with $M = Zn, Cd$ or Hg and $X = Cl, Br$ or I , are considered to have tetrahedral coordination of the central metal atom. The X-ray structure of the complex $[HgBr_2(AsPh_3)]_2 \cdot HgBr_2$ has been determined by *Evans* et al.² who showed that the mercury-bromine distances in the bridge are considerably greater than the terminal mercury-bromine distances. Recently *Brill* and *Wertz*^{3,4} suggested for the dimeric complexes $Hg(\text{pyridine oxide})X_2$ that the halide bridge is weak and the covalent $X\text{--}Hg\text{--}X$ linkage is nearly linear.

¹ G. B. Deacon, J. H. S. Green and D. J. Harrison, *Spectrochim. Acta* **24A**, 1921 (1968).

² R. C. Evans, F. G. Mann, H. S. Peiser and D. Purdie, *J. Chem. Soc.* 1209 (1940).

³ T. B. Brill and D. W. Wertz, *Inorg. Chem.* **9**, 2692 (1970).

⁴ T. B. Brill, *J. Inorg. Nucl. Chem.* **32**, 1869 (1970); *Inorg. Chem.* **9**, 984 (1970).

Complexes with PCy_3 as ligand are of particular interest because the bulky cyclohexyl groups and the strongly basic nature of this ligand cause a different behaviour of these complexes in comparison with other phosphine complexes⁵. The present study was therefore undertaken to investigate the Raman and infrared spectra of tricyclohexylphosphine complexes of mercury, cadmium and zinc and their adducts with methanol, acetone and carbon disulphide.

Results and discussion

(a) *Complexes with the composition $M(\text{PCy}_3)_2\text{X}_2$ with $M = \text{Zn}, \text{Cd}$ or Hg , $\text{X} = \text{Cl}, \text{Br}$ or I and their adducts with acetone and methanol*

These complexes were formed by adding an alcoholic solution of the metal halide to a solution of tricyclohexylphosphine with a metal to ligand ratio of 1 : 2. The complexes were soluble in benzene and chloroform and they were slightly soluble in ethanol. Osmometric molecular weight measurements on some of these complexes (experimental part) indicated that they are monomeric in benzene solution.

Infrared and Raman data are reported in Table I. The $M-X$ frequencies shift to lower frequency as the mass of the halogen increases. It is found for the zinc series that $\nu\text{Zn}-\text{Br}/\text{Zn}-\text{Cl}$ is 0.72 and $\nu\text{Zn}-\text{I}/\text{Zn}-\text{Cl}$ is 0.53. For the cadmium compounds these ratios are $\nu\text{Cd}-\text{Br}/\text{Cd}-\text{Cl}$ 0.69, $\nu\text{Cd}-\text{I}/\text{Cd}-\text{Cl}$ 0.50 and for the mercury compounds $\nu\text{Hg}-\text{Br}/\text{Hg}-\text{Cl}$ 0.70 and $\nu\text{Hg}-\text{I}/\text{Hg}-\text{Cl}$ 0.50. The $M-P$ stretching vibrations are approximately independent of the mass of the halogen atom and they are assigned for the zinc compounds to the band at about 180 cm^{-1} , for the cadmium compounds to 170 cm^{-1} and for the mercury complexes to 130 cm^{-1} .

For the four coordinate complexes a pseudo tetrahedral configuration with molecular symmetry C_{2v} is most probable for the P_2MX_2 skeleton. Recently the X-ray structure determination of $\text{CdCl}_2(\text{PPh}_3)_2$ ⁶ showed a pseudotetrahedral four coordination of the central cadmium atom. For the complexes with the bulky tricyclohexylphosphine molecule it may also be possible that the central atom is in a planar configuration coordinated with *trans* phosphines, as has been found in the nickel complex $\text{NiCl}_2(\text{PCy}_3)_2$ with the molecular symmetry D_{2h} ⁷. In the infrared spectra

⁵ F. G. Moers and J. P. Langhout, Recl. Trav. Chim. Pays-Bas **91**, 591 (1972).

⁶ A. F. Cameron, J. Chem. Soc. [A], 1286 (1971).

⁷ P. L. Bellon, V. Albano, V. D. Bianco, F. Pompa and V. Scatturin, Ric. Sci., Rend. Ser. A3 (8), 1213 (1963), cf. Chem. Abstr. **60**, 14106a (1964).

in the 700–200 cm^{-1} range we found, in fact, two strong bands assigned to metal-chlorine stretching vibrations for $\text{Zn}(\text{PCy}_3)_2\text{Cl}_2$ and $\text{Cd}(\text{PCy}_3)_2\text{Cl}_2$ at the same frequency as in the Raman spectra, indicating C_{2v} symmetry for these complexes. For the other complexes the M–X stretching frequencies and the ratios are close to the corresponding data reported for tetrahedral zinc, cadmium and mercury complexes^{1,8}, suggesting that these compounds also have the C_{2v} symmetry. For this symmetry we have eight infrared active fundamentals $4a_1 + 2b_1 + 2b_2$ and nine Raman active fundamentals $4a_1 + a_2 + 2b_1 + 2b_2$. The most important bands can, as an approximation, be described as $\nu_{\text{sym}}(\text{M}-\text{X}) (a_1)$, $\nu_{\text{asym}}(\text{M}-\text{X})(b_1)$, $\nu_{\text{sym}}(\text{M}-\text{P}) (a_1)$ and $\nu_{\text{asym}}(\text{M}-\text{P}) (b_1)$. The assignments are given in Table I.

Table I

The fundamental vibrations of the complexes $\text{M}(\text{PCy}_3)_2\text{X}_2$ in the 300–100 cm^{-1} region of the Raman spectrum and the 300–200 cm^{-1} region of the infrared spectrum [cm^{-1}].

Complexes	$\nu_{\text{M-X}}$		$\nu_{\text{M-P}}$
	Infrared	Raman	Raman
$\text{Zn}(\text{PCy}_3)_2\text{Cl}_2$	292 (vs), 277 (s)	288 (sh), 276	182
$\text{Zn}(\text{PCy}_3)_2\text{Br}_2$	210 (s), <200 (s)	218, 188	188
$\text{Zn}(\text{PCy}_3)_2\text{I}_2$		152	208, 168
$\text{Cd}(\text{PCy}_3)_2\text{Cl}_2$	260 (sh), 248 (vs)	256, 250	176
$\text{Cd}(\text{PCy}_3)_2\text{Br}_2$		182 (sh), 168	168
$\text{Cd}(\text{PCy}_3)_2\text{I}_2$		125	170, 162
$\text{Hg}(\text{PCy}_3)_2\text{Cl}_2$	200 (vs)	208, 187	134
$\text{Hg}(\text{PCy}_3)_2\text{Br}_2$		144, 132	132
$\text{Hg}(\text{PCy}_3)_2\text{I}_2$		103	132, 128 (sh)
$\text{Cd}(\text{PCy}_3)_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$	260 (sh), 248 (vs)		
$\text{Cd}(\text{PCy}_3)_2\text{Br}_2 \cdot \text{CH}_3\text{COCH}_3$			

⁸ R. J. H. Clark, *Spectrochim. Acta* 21, 955 (1965).

We prepared for two of the complexes the adducts $\text{Cd}(\text{PCy}_3)_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$ and $\text{Cd}(\text{PCy}_3)_2\text{Br}_2 \cdot 1\text{CH}_3\text{COCH}_3$. An X-ray structure determination showed for the adduct $\text{HgCl}_2 \cdot 2\text{CH}_3\text{OH}$ ⁹ a weak interaction between the alcohol and mercury. In the infrared spectrum of the adduct $\text{Cd}(\text{PCy}_3)_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$ we found no shift of the cadmium-halogen stretching frequency in comparison with $\text{Cd}(\text{PCy}_3)_2\text{Cl}_2$. In the acetone adduct the νCO frequency was found at 1705 cm^{-1} and shows no shift to lower frequency in comparison with the νCO in acetone. These data indicate a negligible interaction between the solvent molecule and the cadmium atom in these tricyclohexylphosphine complexes.

(b) *Complexes with the composition $M(\text{PCy}_3)_2\text{X}_2$ with $M = \text{Cd}$ or Hg , $X = \text{Cl}$, Br or I and their adducts with carbon disulfide*

These complexes were found to be slightly soluble in benzene and chloroform. The compounds $\text{Cd}(\text{PCy}_3)_2\text{I}_2$ and $\text{Hg}(\text{PCy}_3)_2\text{Cl}_2$ were sufficiently soluble to obtain their molecular weights in benzene. These compounds were dimeric in benzene solution. The chloro complex $\text{Cd}(\text{PCy}_3)_2\text{Cl}_2$ exists in two modifications, as indicated by the infrared and Raman spectra (Table II). The α -modification was obtained in methanol/acetone as preparation solvent at 0° and the other, the β -modification, at 60° .

Dimeric complexes of this type have also been described with other phosphine ligands². For some of these complexes there is crystallographic evidence² for a centre of symmetry and a tetrahedral arrangement around the metal atom in the dimeric structure. However, precise data for the structure have not been given. An infrared study¹ has been made of the triphenylphosphine complexes of mercury, assuming that the $\text{PXHgX}_2\text{HgXP}$ skeleton has C_{2h} symmetry.

In the infrared spectra of $\text{MCl}_2(\text{PCy}_3)_2$ with $M = \text{Cd}$ or Hg and $\text{HgCl}_2(\text{PPh}_3)_2$, we found bands in the $200\text{--}300\text{ cm}^{-1}$ range, assignable to $\nu\text{M--Cl}$, at the same frequencies as in the Raman spectra (Table II). These data indicate a non-centrosymmetric molecular structure and are not compatible with the C_{2h} symmetry. The Raman spectra show three sets of bands dependent on the mass of the halogen and they may be assigned to metal-halogen frequencies. Assuming a dimeric distorted tetrahedral structure in which the X--M--X covalent linkage is not linear and the metal-halogen distances in the bridged ring are considerably greater than the distances between the metal and an unbridged halogen atom, the first set of metal-halogen frequencies may be assigned

⁹ H. Brusset and F. Madaule-Aubry, Bull. Soc. Chim. France 3121 (1966).

Table II

Metal-halogen vibrational frequencies [cm^{-1}] of the complexes $\text{M}(\text{PR}_3)_2\text{X}_2$ with $\text{R}=\text{Cy}$ or Ph .

Complexes	Raman bands			Infrared bands	
$\alpha\text{-Cd}(\text{PCy}_3)_2\text{Cl}_2$	277 (s), 273 (s), 252 (s), 248 (s)	184, 170, 148	83	273 (s), 249 (s)	205–220 (s)
$\beta\text{-Cd}(\text{PCy}_3)_2\text{Cl}_2$	293 (s)	228, 183	85, 83 (sh)	294 (s), 290 (sh)	210 (sh), 202 (s)
$\text{Cd}(\text{PCy}_3)_2\text{Br}_2$	212 (s), 183 (s)	166, 143	73	206 (s), 204 (s)	
$\text{Cd}(\text{PCy}_3)_2\text{I}_2$	172 (s), 164 (sh)	121	43?		
$\text{Hg}(\text{PCy}_3)_2\text{Cl}_2$	282 (s), 270 (s)	186, 146	76	283 (sh), 273 (s)	
$\text{Hg}(\text{PCy}_3)_2\text{Br}_2$	180(s)	141	44		
$\text{Hg}(\text{PCy}_3)_2\text{I}_2$	154 (s)	137, 104	34?		
$\text{Hg}(\text{PPh}_3)_2\text{Cl}_2$	287 (s), 274 (s)	191, 156	87, 66	287 (s)	

Table III

Infrared vibrational frequencies of the thiocyanates complexes (in cm^{-1})

Compounds	ν_{CN}			δ_{NCS}		Hg-ligand vibrations	
	Raman	Infrared (nujol mull)	Infrared (benzene soln.)	Raman	Infrared (nujol mull)	Raman	Infrared (nujol mull)
$\text{Hg}(\text{PCy}_3)_2(\text{SCN})_2$	2097 (s) 2020–2050 ^b (vww)	2090 (s), 2058 (m) 2025 (s)	2105 (s), 2035 (s)	460	463 (sh), 427 (sh)	175, 136, 74	
$\text{Hg}(\text{PCy}_3)(\text{SCN})_2$	2125 (s), 2113 (s) 2105 (s), 2040 (vw)	2125 (sh), 2100 (s) 2065 (sh)	2110 ^b (s)	460, 430?	459 (m), 423 (m)	246, 180, 152 124, 72, 44	247 (s), 208 (s)
$\text{Hg}(\text{SCN})_2$	2111 (vs), 2093 (sh) 2069 (m), 2045 (sh)	2105 (s), 2060 (sh)		459 (s)	460 (m), 448 (s)	268, 147, 98, 33	310 (s), 220 ^b (s)

mainly to metal-halogen terminal stretching, the second set to the metal-halogen bridging with some involvement of the M—P link and the third set to the metal-halogen bending vibrations.

On reaction of an alcoholic solution of cadmium bromide or cadmium iodide with tricyclohexylphosphine and carbon disulfide we isolated the yellow brown compounds $\text{CdX}_2(\text{PCy}_3)(\text{CS}_2)$ with $\text{X} = \text{Br}$ or I . The infrared spectrum of $\text{CdBr}_2(\text{PCy}_3)(\text{CS}_2)$ showed no Cd—Br stretching bands above 200 cm^{-1} . On heating $\text{CdBr}_2(\text{PCy}_3)(\text{CS}_2)$ at 180° the complex $\text{CdBr}_2(\text{PCy}_3)$ was formed as indicated by the $\nu\text{Cd—Br}$ frequencies at 206 and 204 cm^{-1} in the infrared spectrum. The compound $\text{Cd}(\text{PCy}_3)\text{I}_2(\text{CS}_2)$ decomposed at about 40° . These data indicate a weak interaction of the carbon disulfide molecule with the complexes $\text{CdX}_2(\text{PCy}_3)$.

(c) *Thiocyanate complexes with the composition $\text{Hg}(\text{PCy}_3)_2(\text{SCN})_2$ and $\text{Hg}(\text{PCy}_3)(\text{SCN})_2$*

These compounds were prepared by the reaction of tricyclohexylphosphine with mercury thiocyanate in a 2:1 or 1:1 molar ratio. Molecular weight measurements performed in benzene indicated a monomeric structure for $\text{Hg}(\text{PCy}_3)_2(\text{SCN})_2$. Because of the insolubility of $\text{Hg}(\text{PCy}_3)(\text{SCN})_2$ the molecular weight in solution could not be determined.

The complex $\text{Hg}(\text{PCy}_3)_2(\text{SCN})_2$ showed bands in the infrared and Raman spectrum (Table III), which lie between the metal-halogen stretching frequencies of the corresponding chloro and bromo compounds, suggesting coordination of the mercury to the sulphur atom¹⁰. The δSCN in $\text{Hg}(\text{PCy}_3)_2(\text{SCN})_2$ and $\text{Hg}(\text{PCy}_3)(\text{SCN})_2$ are in the same region as found for mercury thiocyanate complexes¹¹. A strong bridging SCN group may be excluded for these compounds because of the absence of metal-nitrogen stretching vibrations in the 300 cm^{-1} region, and the fact that the νCN has been found in the $2020\text{--}2125\text{ cm}^{-1}$ range. For a bridging SCN group we expect metal-nitrogen stretching vibrations in the $280\text{--}320\text{ cm}^{-1}$ range¹⁰ and the νCN in the $2135\text{--}2180\text{ cm}^{-1}$ range^{12,13}.

From these data we conclude that these compounds are coordinated through sulfur of the SCN ligand. In $\text{Hg}(\text{PCy}_3)_2(\text{SCN})_2$ the mercury atom has a four coordination. The structure of $\text{Hg}(\text{PCy}_3)(\text{SCN})_2$ may

¹⁰ F. Forster and D. M. L. Goodgame, *Inorg. Chem.* **4**, 715 (1965).

¹¹ H. P. Fritz and J. Manchot, *Chem. Ber.* **96**, 1891 (1963).

¹² H. L. Burmeister and M. U. Al-Janabi, *Inorg. Chem.* **4**, 962 (1965).

¹³ P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.* 1912 (1960).

be described as a trigonal configuration around mercury, comparable with $\text{Hg}(\text{SCN})_2(\text{AsPh}_3)_3$, in which an X-ray study¹⁴ has shown coordination of the mercury atom with two thiocyanate groups and one arsenic atom; in addition there are weak intermolecular interactions with nitrogen.

Experimental section

Tricyclohexylphosphine was prepared as described by *Issleib* et al.¹⁵

All other chemicals and solvents were of reagent grade.

The complexes of formula $\text{M}(\text{PCy}_3)_2\text{X}_2$, $\text{M}(\text{PCy}_3)\text{X}_2$ with $\text{X} = \text{Cl}, \text{Br}, \text{I}$ or SCN , $\text{M} = \text{Zn}, \text{Cd}$ or Hg and some of their adducts with acetone, methanol or carbon disulfide, were prepared by the reaction of PCy_3 and the corresponding MX_2 compound in stoichiometric amounts. Methanol was used as preparation solvent for $\text{Cd}(\text{PCy}_3)\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$; methanol/acetone for $\text{Cd}(\text{PCy}_3)_2\text{Br}_2 \cdot \text{CH}_3\text{COCH}_3$ and $\text{Cd}(\text{PCy}_3)\text{Cl}_2$; methanol/carbon disulphide for $\text{Cd}(\text{PCy}_3)\text{Br}_2(\text{CS}_2)$; ethanol/carbon disulfide for $\text{Cd}(\text{PCy}_3)\text{I}_2(\text{CS}_2)$; ethanol for the other complexes. The solution was heated for about half an hour. After cooling to room temperature the crystals were filtered off, washed with the solvent and air dried. The $\alpha\text{-CdCl}_2(\text{PCy}_3)$ was obtained after cooling the solution to 0° .

The compounds $\text{Hg}(\text{SCN})_2$ and $\text{Hg}(\text{PPh}_3)\text{Cl}_2$ were prepared by reported methods^{16,17}.

The elemental analyses of the complexes were in agreement with the theoretical values. The analysis data and melting points of the complexes are available from the editorial office.

Infrared spectra were obtained with a Perkin-Elmer 257 spectrophotometer for the $4000\text{--}700\text{ cm}^{-1}$ range and a Hitachi EPI-L for the $700\text{--}200\text{ cm}^{-1}$ region. The spectra were taken using the nujol mull technique. For Raman spectra in the $4000\text{--}1000\text{ cm}^{-1}$ range a Cary-81 spectrophotometer (He-Ne laser) and in the range below 700 cm^{-1} a Jeol JRS-SI spectrophotometer (Ar-laser) was used. The spectra were obtained from the solid compounds. The molecular weights of the complexes were determined at 37° in benzene solution, using the vapour pressure osmometer Hewlett-Packard model 302 B. Found (calc.): $\text{Cd}(\text{PCy}_3)_2\text{Br}_2$ 781,(833); $\text{Cd}(\text{PCy}_3)_2\text{I}_2$ 846,(927); $\text{Hg}(\text{PCy}_3)_2(\text{SCN})_2$ 954,(878); $\text{Cd}(\text{PCy}_3)\text{I}_2$ 1243,(647); $\text{Hg}(\text{PCy}_3)\text{Cl}_2$ 1085,(552).

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¹⁴ R. C. *Makhija*, A. L. *Beauchamp* and R. *Rivest*, J. Chem. Soc. D, Chem. Commun. 1043 (1972).

¹⁵ K. *Issleib* and A. *Brack*, Z. Anorg. Allgem. Chem. 227, 258 (1954).

¹⁶ W. *Peters*, *ibid.* 77, 157 (1912).

¹⁷ A. R. *Davies*, C. J. *Murphy* and R. A. *Plane*, Inorg. Chem. 9, 423 (1970).