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

BY

F. G. MOERS and J. P. LANGHOUT

(Inorganic Chemistry Laboratory, University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands)

The preparations of the complexes $M(PCy_3)_2X_2$ and $M(PCy_3)X_2$ with $M=\text{Zn}, \text{Cd or Hg}$, $X=\text{Cl, Br, I or SCN}$, $PCy_3=\text{tricyclohexylphosphine and some of their adducts with acetone, methanol or carbon disulfide are reported. Their infrared spectra in the range 4000–200 cm}^{-1}$ and their Raman spectra between 4000–100 cm$^{-1}$ have been investigated. From these data we conclude for the dimeric complexes $M(PCy_3)X_2$ with $M=\text{Cd or Hg}$ and $X=\text{Cl, Br or I}$, a distorted tetrahedral coordination around mercury or cadmium. For the complex $\text{Hg(PCy}_3)(\text{SCN})_2$ 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 $M=\text{Zn, Cd or Hg}$ and $X=\text{Cl, Br or I}$, are considered to have tetrahedral coordination of the central metal atom. The X-ray structure of the complex $[\text{HgBr}_2(\text{AsPh}_3)]_2 \cdot \text{HgBr}_2$ 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 $\text{Hg(pyridine oxide)X}_2$ that the halide bridge is weak and the covalent X-Hg-X linkage is nearly linear.

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Complexes with $\text{PCy}_3$ 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 complexes$^5$. 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 $\text{M(PCy}_3)_2\text{X}_2$ with $\text{M}=\text{Zn, Cd or Hg}, \text{X}=\text{Cl, Br or I}$ 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 $\text{M—X}$ frequencies shift to lower frequency as the mass of the halogen increases. It is found for the zinc series that $\nu_{\text{Zn—Br}}/\nu_{\text{Zn—Cl}}$ is 0.72 and $\nu_{\text{Zn—I}}/\nu_{\text{Zn—Cl}}$ is 0.53. For the cadmium compounds these ratios are $\nu_{\text{Cd—Br}}/\nu_{\text{Cd—Cl}}$ 0.69, $\nu_{\text{Cd—I}}/\nu_{\text{Cd—Cl}}$ 0.50 and for the mercury compounds $\nu_{\text{Hg—Br}}/\nu_{\text{Hg—Cl}}$ 0.70 and $\nu_{\text{Hg—I}}/\nu_{\text{Hg—Cl}}$ 0.50. The $\text{M—P}$ 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 $\text{P}_2\text{MX}_2$ skeleton. Recently the X-ray structure determination of $\text{CdCl}_2(\text{PPh}_3)_2$ 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 $\text{trans}$ 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

in the 700–200 cm\(^{-1}\) range we found, in fact, two strong bands assigned to metal-chlorine stretching vibrations for \(\text{Zn(PCy}_3\text{)}_2\text{Cl}_2\) and \(\text{Cd(PCy}_3\text{)}_2\text{Cl}_2\) 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 \(v_{\text{sym}}(M–X)\) \((a_1)\), \(v_{\text{asym}}(M–X)\) \((b_1)\), \(v_{\text{sym}}(M–P)\) \((a_1)\) and \(v_{\text{asym}}(M–P)\) \((b_1)\). The assignments are given in Table I.

**Table I**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>(v_{\text{M–X}}) Infrared</th>
<th>(v_{\text{M–X}}) Raman</th>
<th>(v_{\text{M–P}}) Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Zn(PCy}_3\text{)}_2\text{Cl}_2)</td>
<td>292 (vs), 277 (s)</td>
<td>288 (sh), 276</td>
<td>182</td>
</tr>
<tr>
<td>(\text{Zn(PCy}_3\text{)}_2\text{Br}_2)</td>
<td>210 (s), &lt;200 (s)</td>
<td>218, 188</td>
<td>188</td>
</tr>
<tr>
<td>(\text{Zn(PCy}_3\text{)}_2\text{I}_2)</td>
<td></td>
<td>152</td>
<td>208, 168</td>
</tr>
<tr>
<td>(\text{Cd(PCy}_3\text{)}_2\text{Cl}_2)</td>
<td>260 (sh), 248 (vs)</td>
<td>256, 250</td>
<td>176</td>
</tr>
<tr>
<td>(\text{Cd(PCy}_3\text{)}_2\text{Br}_2)</td>
<td>182 (sh), 168</td>
<td>168</td>
<td></td>
</tr>
<tr>
<td>(\text{Cd(PCy}_3\text{)}_2\text{I}_2)</td>
<td>125</td>
<td>170, 162</td>
<td></td>
</tr>
<tr>
<td>(\text{Hg(PCy}_3\text{)}_2\text{Cl}_2)</td>
<td>200 (vs)</td>
<td>208, 187</td>
<td>134</td>
</tr>
<tr>
<td>(\text{Hg(PCy}_3\text{)}_2\text{Br}_2)</td>
<td>144, 132</td>
<td>132</td>
<td></td>
</tr>
<tr>
<td>(\text{Hg(PCy}_3\text{)}_2\text{I}_2)</td>
<td>103</td>
<td>132, 128 (sh)</td>
<td></td>
</tr>
<tr>
<td>(\text{Cd(PCy}_3\text{)}_2\text{Cl}_2\cdot2\text{CH}_3\text{OH})</td>
<td>260 (sh), 248 (vs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Cd(PCy}_3\text{)}_2\text{Br}_2\cdot\text{CH}_3\text{COCH}_3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

We prepared for two of the complexes the adducts Cd(PCy₃)₂Cl₂ • 2CH₃OH and Cd(PCy₃)₂Br₂ • 1CH₃COCH₃. An X-ray structure determination showed for the adduct HgCl₂ • 2CH₃OH a weak interaction between the alcohol and mercury. In the infrared spectrum of the adduct Cd(PCy₃)₂Cl₂ • 2CH₃OH we found no shift of the cadmium-halogen stretching frequency in comparison with Cd(PCy₃)₂Cl₂. In the acetone adduct the vCO frequency was found at 1705 cm⁻¹ and shows no shift to lower frequency in comparison with the vCO 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(PCy₃)₂X₂ with M = Cd or Hg, X = Cl, Br or I and their adducts with carbon disulfide

These complexes were found to be slightly soluble in benzene and chloroform. The compounds Cd(PCy₃)I₂ and Hg(PCy₃)Cl₂ were sufficiently soluble to obtain their molecular weights in benzene. These compounds were dimeric in benzene solution. The chloro complex Cd(PCy₃)Cl₂ 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 ligands. For some of these complexes there is crystallographic evidence 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 study has been made of the triphenylphosphine complexes of mercury, assuming that the PXHgX₂HgXP skeleton has C₂ᵥ symmetry.

In the infrared spectra of MCl₂(PCy₃) with M = Cd or Hg and HgCl₂(PPh₃), we found bands in the 200–300 cm⁻¹ range, assignable to νM–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 C₂ᵥ 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.

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Table II

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

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Raman bands</th>
<th>Infrared bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-Cd(PCy(_3))Cl(_2)</td>
<td>277 (s), 273 (s), 252 (s), 248 (s)</td>
<td>184, 170, 148, 83</td>
</tr>
<tr>
<td>(\beta)-Cd(PCy(_3))Cl(_2)</td>
<td>293 (s)</td>
<td>228, 183, 85, 83 (sh)</td>
</tr>
<tr>
<td>Cd(PCy(_3))Br(_2)</td>
<td>212 (s), 183 (s)</td>
<td>166, 143, 73</td>
</tr>
<tr>
<td>Cd(PCy(_3))I(_2)</td>
<td>172 (s), 164 (sh)</td>
<td>121, 43?</td>
</tr>
<tr>
<td>Hg(PCy(_3))Cl(_2)</td>
<td>282 (s), 270 (s)</td>
<td>186, 146, 76</td>
</tr>
<tr>
<td>Hg(PCy(_3))Br(_2)</td>
<td>180(s)</td>
<td>141, 44</td>
</tr>
<tr>
<td>Hg(PCy(_3))I(_2)</td>
<td>154 (s)</td>
<td>137, 104, 34?</td>
</tr>
<tr>
<td>Hg(PPh(_3))Cl(_2)</td>
<td>287 (s), 274 (s)</td>
<td>191, 156, 87, 66</td>
</tr>
</tbody>
</table>

Table III

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

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(\nu_{CN})</th>
<th>(\delta_{NCS})</th>
<th>Hg-ligand vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raman</td>
<td>Infrared</td>
<td>Raman</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(nujol mull)</td>
<td>(benzene soln.)</td>
</tr>
<tr>
<td>Hg(PCy(_3))(_2)(SCN)(_2)</td>
<td>2097 (s)</td>
<td>2090 (s), 2058 (m)</td>
<td>2105 (s), 2035 (s)</td>
</tr>
<tr>
<td></td>
<td>2020–2050(wv)</td>
<td>2025 (s)</td>
<td></td>
</tr>
<tr>
<td>Hg(PCy(_3))(SCN)(_2)</td>
<td>2125 (s), 2113 (s)</td>
<td>2125 (sh), 2100 (s)</td>
<td>2110 (a)(s)</td>
</tr>
<tr>
<td></td>
<td>2105 (s), 2040 (v)</td>
<td>2065 (sh)</td>
<td></td>
</tr>
<tr>
<td>Hg(SCN)(_2)</td>
<td>2111 (vs), 2093 (sh)</td>
<td>2105 (s), 2060 (sh)</td>
<td>459 (s)</td>
</tr>
<tr>
<td></td>
<td>2069 (m), 2045 (sh)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 CdX₂(PCy₃)(CS₂) with X= Br or I. The infrared spectrum of CdBr₂(PCy₃)(CS₂) showed no Cd–Br stretching
bands above 200 cm⁻¹. On heating CdBr₂(PCy₃)(CS₂) at 180° the
complex CdBr₂(PCy₃) was formed as indicated by the vCd–Br fre-
quencies at 206 and 204 cm⁻¹ in the infrared spectrum. The compound
Cd(PCy₃)I₂(CS₂) decomposed at about 40°. These data indicate a weak
interaction of the carbon disulfide molecule with the complexes CdX₂(PCy₃).

(c) Thiocyanate complexes with the composition Hg(PCy₃)₂(SCN)₂
and Hg(PCy₃)(SCN)₂

These compounds were prepared by the reaction of tricyclohexyl-
phosphine with mercury thiocyanate in a 2:1 or 1:1 molar ratio.
Molecular weight measurements performed in benzene indicated a
monomeric structure for Hg(PCy₃)₂(SCN)₂. Because of the insolubility
of Hg(PCy₃)(SCN)₂ the molecular weight in solution could not be
determined.

The complex Hg(PCy₃)₂(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 com-
ponds, suggesting coordination of the mercury to the sulphur atom¹⁰.
The SSCN in Hg(PCy₃)₂(SCN)₂ and Hg(PCy₃)(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 vCN has been found in the 2020–2125 cm⁻¹ range. For a
bridging SCN group we expect metal-nitrogen stretching vibrations in
the 280–320 cm⁻¹ range¹⁰ and the vCN in the 2135–2180 cm⁻¹
range¹²,¹³.

From these data we conclude that these compounds are coordinated
through sulfur of the SCN ligand. In Hg(PCy₃)₂(SCN)₂ the mercury
atom has a four coordination. The structure of Hg(PCy₃)(SCN)₂ may

be described as a trigonal configuration around mercury, comparable with \(\text{Hg(SCN)}_2(\text{AsPh}_3)\), in which an X-ray study\(^{14}\) 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 \(\text{M(PCy}_3)_2\text{X}_2\), \(\text{M(PCy}_3)\text{X}_2\) with \(\text{X}=\text{Cl, Br, I or SCN, M=}\text{Zn, Cd or Hg}\) and some of their adducts with acetone, methanol or carbon disulfide, were prepared by the reaction of \(\text{PCy}_3\) and the corresponding \(\text{MX}_2\) compound in stoichiometric amounts. Methanol was used as preparation solvent for \(\text{Cd(PCy}_3)\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}\); methanol/acetone for \(\text{Cd(PCy}_3)_2\text{Br}_2 \cdot \text{CH}_3\text{COCH}_3\) and \(\text{Cd(PCy}_3)\text{Cl}_2\); methanol/carbon disulfide for \(\text{Cd(PCy}_3)_2\text{Br}_2(\text{CS}_2)\); ethanol/carbon disulfide for \(\text{Cd(PCy}_3)\text{I}_2(\text{CS}_2)\); 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\(^\circ\).

The compounds \(\text{Hg(SCN)}_2\) and \(\text{Hg(PPh}_3)\text{Cl}_2\) 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 4000–700 cm\(^{-1}\) range and a Hitachi EPI-L for the 700–200 cm\(^{-1}\) region. The spectra were taken using the nujol mull technique. For Raman spectra in the 4000–1000 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\(^\circ\) in benzene solution, using the vapour pressure osmometer Hewlett-Packard model 302 B. Found (calc.): \(\text{Cd(PCy}_3)_2\text{Br}_2\) 781, (833); \(\text{Cd(PCy}_3)_2\text{I}_2\) 846, (927); \(\text{Hg(PCy}_3)_2(\text{SCN})_2\) 954, (878); \(\text{Cd(PCy}_3)_2\text{I}_2\) 1243, (647); \(\text{Hg(PCy}_3)\text{Cl}_2\) 1085, (552).

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\(^{16}\) W. Peters, ibid. 77, 157 (1912).
