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# Coordination Complexes of Trichlorovinylmercury Chloride and Bromide

NORMAN A. BELL*, IAN W. NOWELL and DAVID J. STARKEY

*Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield, S1 1WB, U.K.*

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*The formation of complexes between trichlorovinylmercury chloride and bromide with selected nitrogen, phosphorus and sulphur bases has been studied. Adducts $C_2Cl_3HgX \cdot L$ ($X = Cl, Br$; $L$ = phen, dmp, tmp, bipy, tmed)** have been isolated in the solid state whereas reactions of the organomercury halides with triphenylphosphane or diphos** result in symmetrisation to form the mercury(II)halide–phosphane adducts. No complex could be isolated with 2,5-dithiahexane. Thermal and spectral characteristics ($^1H$ NMR, infrared and mass spectra) have been examined for the isolated complexes. The organomercury halides appear to be slightly stronger acceptors than bis(trichlorovinyl)mercury.*

## Introduction

In marked contrast to mercury(II) halides [1], dialkylmercurials do not form stable addition complexes. Substitution in $R_2Hg$ by electron-withdrawing substituents in R, increase the formal charge on mercury thereby enhancing the formation of stable complexes, such that bis(trinitromethyl)mercury [2] and bis(fluoroalkyl) mercurials [3] form isolable complexes. Similarly, though diphenylmercury forms only weak complexes [4], bis(pentafluorophenyl)-mercury complexes are more numerous and stable [5]. We have previously shown that the acceptor behaviour of bis(trichlorovinyl)mercury appears to be intermediate between that of diphenylmercury and that of bis(pentafluorophenyl)mercury [6]. The X-ray structure of $(C_2Cl_3)_2Hg(tmp)$ shows that there is a weak yet significant donor–acceptor interaction between mercury and the ligand [7].

The replacement of an organic group in $R_2Hg$ by more electronegative groups, such as the halogens to form RHgX, also enhances stable complex formation so that a wide range of complexes, particularly with nitrogenous bases have been isolated for a range of R and X [8, 9]. The replacement of a $C_2Cl_3$ group by a halogen might not be expected to markedly change the acceptor character of the mercury. Herein we report the results of our studies of the coordination behaviour of $C_2Cl_3HgX$ (X = Cl, Br).

## Results and Discussion

Trichlorovinylmercury chloride and bromide form isolable 1:1 complexes with phen, dmp, tmp, bipy and tmed but no complexes could be isolated with 2,5-dithiahexane. In terms of the number of complexes formed, $C_2Cl_3HgX$ (X = Cl, Br) appear to be slightly stronger acceptors than $(C_2Cl_3)_2Hg$ for while the latter did form isolable complexes with the other nitrogen donors no complexes were isolated with tmed [6]. Both triphenylphosphane and diphos caused symmetrisation of $C_2Cl_3HgX$ and the phosphane complexes of $HgX_2$ were isolated and identified by their analytical data, melting points and low frequency infrared spectra [10]. Such symmetrisation of RHgX by phosphanes has previously been noted [11]. No significant differences in the acceptor character of the chloride and bromide could be detected. Both are weaker acceptors than $(C(NO_2)_3)_2Hg$ [2] and $(C_6F_5)_2Hg$ [5] which form complexes with a wide variety of ligands but stronger acceptors than PhHgX (X = Cl, Br): PhHgCl only forms complexes with phen and tmp but not bipy whereas the bromide does not form complexes with any of these ligands [9].

Mass spectral examination of the complexes showed that all dissociated even at low bombarding voltage (20 eV) and the spectra were similar to those of the free organomercury halides in that the ion of highest molecular mass corresponded to that of $RHg^+$. Comparison of the infrared spectra of the complexes (Table I) with that of the parent mercurial shows that strong absorptions due to the free mercurials at 1542 and 850 $cm^{-1}$ are moved significantly to lower frequencies on complexation, as expected for an increase in coordination number. Most of

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*Author to whom correspondence should be addressed.

**phen, dmp, tmp, bipy, tmed, diphos represent abbreviations for 1,10-phenanthroline; 2,9-dimethyl-1,10-phenanthroline; 3,4,7,8-tetramethyl-1,10-phenanthroline; 2,2′-bipyridyl; N,N,N′,N′-tetramethylethane-1,2-diamine and bis(1,2-diphenylphosphano)ethane respectively.

TABLE I. Infrared Absorptions (2000–400 $cm^{-1}$) for Complexes of Trichlorovinylmercury Halides.

| | |
|---|---|
| $C_2Cl_3HgCl$(phen) | 1997w, 1922w, 1810w, 1618m, 1588m, 1572m, 1516s, 1490w, 1422vs, 1412m, 1340m, 1237m, 1210w, 1160mw, 1152w, 1112m, 1102w, 1044w, 1003mw, 869m, 851vs, 776m, 730vs, 643m, 514w, 473w, 420mw, $cm^{-1}$. |
| $C_2Cl_3HgCl$(dmp) | 1620w, 1592m, 1560w, 1540m, 1502s, 1438w, 1414w, 1375w, 1292w, 1228m, 1157w, 1150w, 1030w, 937w, 920m, 873s, 846w, 824s, 808msh, 775m, 731m, 686m, 657m, 550m, 431w, 405w, $cm^{-1}$. |
| $C_2Cl_3HgCl$(tmp) | 1610w, 1580m, 1540m, 1520s, 1425s, 1380m, 1300w, 1270w, 1244m, 1198w, 1176w, 1088w, 1075w, 1015m, 952w, 922s, 878m, 857m, 833s, 816s, 727vs, 690m, 638m, 616m, 567w, 547w, 520m, 477w, 457w, $cm^{-1}$. |
| $C_2Cl_3HgCl$(bipy) | 1587s, 1575m, 1480w, 1470m, 1438s, 1330m, 1260m, 1228w, 1183m, 1168m, 1127w, 1120w, 1065w, 1048w, 1020s, 1015s sh, 976w, 772vs, 737s, 653m, 630mw, $cm^{-1}$. |
| $C_2Cl_3HgCl$(tmed) | 1625w, 1614w, 1532s, 1460s, 1420w, 1378w, 1350w, 1318m, 1272w, 1204w, 1180m, 1147m, 1125w, 1115w, 1086m, 1048s, 1038m, 1026m, 1018w, 976s, 940msh, 929s, 921s, 832s, 796s, 780m, 686m, 585w, 478w, 464m, 430m, 481w, $cm^{-1}$. |
| $C_2Cl_3HgBr$(phen) | 1618w, 1582w, 1568w, 1508m, 1490m, 1421s, 1405w, 1340w, 1312w, 1226w, 1145m, 1101m, 1088w, 997w, 865m, 852s, 785m, 729s, 722s, 638m, 470w, 410 w, $cm^{-1}$. |
| $C_2Cl_3HgBr$(dmp) | 1618w, 1588m, 1560w, 1504s, 1424w, 1408w, 1378m, 1294w, 1252w, 1227m, 1154m, 1108w, 1040w, 998w, 940w, 871s, 847w, 812w, 777m, 730s, 683w, 655m, 552m, 432w, $cm^{-1}$. |
| $C_2Cl_3HgBr$(tmp) | 1608m, 1582m, 1538s, 1520s, 1428s, 1380ms, 1300w, 1271w, 1246s, 1200w, 1179w, 1089w, 1078w, 1018m, 975w, 955w, 922s, 881m, 860m, 830s, 819s, 728s, 688m, 640m, 618m, 569w, 549w, 522m, 479w, 460w, 420w, $cm^{-1}$. |
| $C_2Cl_3HgBr$(bipy) | 1588s, 1578m, 1484w, 1471m, 1468s, 1310m, 1263m, 1230w, 1188m, 1168m, 1130w, 1112w, 1083w, 1071w, 1050w, 1025s, 1020msh, 984w, 911w, 775vs, 738s, 654m, 630m, $cm^{-1}$. |
| $C_2Cl_3HgBr$(tmed) | 1618w, 1532m, 1479s, 1380w, 1347w, 1290s, 1246m, 1212w, 1182w, 1156mw, 1128s, 1100w, 1065m, 1044w, 1028s, 1012s, 952s, 927m, 915m, 820m, 787s, 768m, 677mw, 580w, 465m, 432m, 417w, $cm^{-1}$. |

the ligand bands in the 1300–1600 $cm^{-1}$ region in the phen, dmp, tmp complexes are shifted to higher frequencies on coordination. The $\nu$(CC) mode of 2,2′-bipyridyl at 1582 and 1560 $cm^{-1}$ and the ring breathing mode at 992 $cm^{-1}$ and the very intense broad band at 756 $cm^{-1}$ are shifted to higher frequencies as expected for the coordinated ligand. The most notable features of the spectra of the tmed spectra are the displacement to higher frequencies of the band at 1265 $cm^{-1}$ and the increase in intensities of the bands in the 850–1000 $cm^{-1}$ region on complexation.

The $^1H$ NMR spectral data are reported in Table II. The complexes of $C_2Cl_3HgX \cdot L$ (X = Cl, Br, L = phen; X = Cl, L = bipy) were too insoluble for their spectra to be obtained. Small downfield shifts of resonance bands on complexation due to the ligands of the order of 0.1–0.2 ppm are observed. This is in keeping with the withdrawal of electron density from the ligands. For $C_2Cl_3HgX$(tmp) (X = Cl, Br) shifts on complexation of the bands due to the ligands were very similar to those found for $(C_2Cl_3)_2Hg$(tmp) and also the onset of mass loss occurred at similar temperature suggesting that these complexes have similar stability. However, for the other complexes examined the shifts are slightly larger than those found for comparable complexes with $(C_2Cl_3)_3Hg$ and indicate the greater acceptor character of $C_2Cl_3HgX$ as compared to $(C_2Cl_3)_2Hg$. This is confirmed by our thermal work (Table III) where onset of mass loss occurred at higher temperatures than for corresponding $(C_2Cl_3)_2Hg$ complexes [6]. The complexes of $C_2Cl_3HgX$ with phen and bipy and $C_2Cl_3HgCl$ (tmed) volatilised in a single step, in some cases leaving a slight residue doubtless from thermal degradation of the complexes. For $C_2Cl_3HgBr$ (tmed) and both tmp complexes, the TG traces showed evidence for the formation of intermediates but it was not possible to predict the nature of these which may result from the breakdown of the $C_2Cl_3$ moiety. The complex, $C_2Cl_3HgCl$(dmp) decomposes from 190–240 °C with loss of ligand (mass loss found 34.0%; calcd. 33.8%) and from 240–450 °C with loss of $HgCl_2$ (found 44.7%: calcd. 47.2%) leaving a residue of $(C_2Cl_2)_n$ which vaporises slowly up to 700 °C.

## Experimental

Microanalyses were carried out by the Oxford Microanalytical Laboratories of Dr. F. B. Strauss.

TABLE II. $^1$H NMR Spectral Data for Ligands and their Complexes with $C_2Cl_3HgX$ (X = Cl, Br) in $CDCl_3$ Solutions[a] ($\delta$(TMS) = 0 ppm).

| | L | $C_2Cl_3HgCl \cdot L$ | $C_2Cl_3HgBr \cdot L$ |
|---|---|---|---|
| dmp | 2.98, 7.47, 7.61 7.75, 8.12, 8.25 | 3.10, 7.66, 7.78 7.87, 8.31, 8.45 | 3.15, 7.71, 7.86 7.93, 8.38, 8.52 |
| tmp | 2.56, 2.69, 8.07, 8.99 | 2.59, 2.76, 8.15, 8.85 | 2.59, 2.76, 8.15, 8.84 |
| bipy | 7.41, 7.48, 7.51, 7.54, 7.63, 7.88, 7.90, 8.00, 8.13, 8.15, 8.41, 8.43, 8.54, 8.73, 8.82 | | 7.31, 7.60, 7.71, 7.80, 8.05, 8.07, 8.19, 8.20, 8.29, 8.31, 8.54, 8.68, 8.81 |
| tmed | 2.27, 2.41 | 2.48, 2.58 | 2.48, 2.58 |

[a] Deuteriodimethylsulphoxide for 2,2′-bipyridyl and its complex.

TABLE III. Thermal Characteristics of $C_2Cl_3HgX$ and $C_2Cl_3HgX \cdot L$ (X = Cl, Br; L = phen, dmp, tmp, bipy, tmed).

| Compound | Temperature/°C | Thermal Behaviour* |
|---|---|---|
| $C_2Cl_3HgCl$ | 90–180 | total mass loss in single step |
| $C_2Cl_3HgBr$ | 90–185 | total mass loss in single step |
| $C_2Cl_3HgCl$(phen) | 160–355 | mass loss in single step, leaving ~4% residue |
| $C_2Cl_3HgBr$(phen) | 210–350 | major mass loss (residue 4.3%) |
| | 350–500 | steady decrease in mass to ~0.7% residue |
| $C_2Cl_3HgCl$(dmp) | 190–240 (inflexion) | mass loss 34.0%, attributed to dmp (required 33.8%) |
| | 240–450 | mass loss 44.7%, attributed to $HgCl_2$ (required 47.2%) |
| | 450–>700 | slow continuous loss of mass, attributed to loss of $(C_2Cl_2)_n$ |
| $C_2Cl_3HgBr$(dmp) | 180–500 | mass loss 68.1% with an indication of an inflexion at ~320 °C |
| | 500–>700 | slow continuous mass loss |
| $C_2Cl_3HgCl$(tmp) | 190–230 | mass loss 20.0% |
| | 230–350 | mass loss 60.0% |
| | 350–500 | steady mass loss leaving 10.0% residue |
| $C_2Cl_3HgBr$(tmp) | 205–230 | mass loss 20.0% |
| | 230–340 | mass loss 58.7% |
| | 340–600 | slow mass loss leaving ~2% residue |
| $C_2Cl_3HgCl$(bipy) | 140–260 | single step mass loss, leaving 2.3% residue |
| $C_2Cl_3HgBr$(bipy) | 155–255 | single step mass loss, leaving 5.2% residue |
| $C_2Cl_3HgCl$(tmed) | 75–450 | single step mass loss, zero residue |
| $C_2Cl_3HgBr$(tmed) | 70–200 | mass loss 36.2% |
| | 200–350 | mass loss 56.3% |
| | 350–500 | slow mass loss, leaving ~5% residue |

*Mass loss and residue are expressed as % of the mass of the original compound.

Mass spectra were recorded using an AEI MS30 mass spectrometer at a bombarding voltage of 20 eV and a source temperature of 200 °C. Samples were injected via the direct insertion probe. $^1$H NMR spectra were recorded as solutions in deuteriochloroform or deuteriodimethylsulphoxide using a Hitachi Perkin Elmer R600 high resolution spectrometer. Thermal measurements were recorded using a DuPont Model 900 thermal analyser. Samples were heated at a rate of 5 °C min$^{-1}$ under a flow of nitrogen of 50 cm$^3$

TABLE IV.

| Complex | Appearance | Found (%) | | | Calcd. (%) | | | M.P. (°C) | Yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | C | H | N | | |
| $C_2Cl_3HgCl$(phen) | colourless cubes | 32.22 | 1.61 | 5.34 | 30.76 | 1.47 | 5.12 | 325–327 | 29 |
| $C_2Cl_3HgCl$(dmp) | colourless cubes | 33.16 | 2.73 | 4.68 | 33.44 | 2.10 | 4.87 | 213–216 | 35 |
| $C_2Cl_3HgCl$(tmp) | colourless needles | 36.19 | 2.82 | 4.76 | 35.86 | 2.68 | 4.64 | >360 | 74 |
| $C_2Cl_3HgCl$(bipy) | colourless needles | 26.93 | 1.75 | 5.45 | 27.58 | 1.54 | 5.36 | 260–262 | 18 |
| $C_2Cl_3HgCl$(tmed) | colourless plates | 19.82 | 3.45 | 5.82 | 19.91 | 3.34 | 5.80 | 84–86 | 81 |
| $C_2Cl_3HgBr$(phen) | colourless needles | 28.22 | 1.58 | 4.82 | 28.45 | 1.36 | 4.74 | 362–364 | 35 |
| $C_2Cl_3HgBr$(dmp) | colourless needles | 30.68 | 2.39 | 4.60 | 31.04 | 1.95 | 4.52 | 300–302 | 20 |
| $C_2Cl_3HgBr$(tmp) | colourless plates | 33.81 | 2.71 | 4.12 | 33.40 | 2.49 | 4.32 | >360 | 72 |
| $C_2Cl_3HgBr$(bipy) | colourless needles | 25.47 | 1.53 | 5.09 | 25.42 | 1.42 | 4.94 | 257–258 | 84 |
| $C_2Cl_3HgBr$(tmed) | colourless needles | 18.50 | 3.11 | 5.45 | 18.23 | 3.06 | 5.31 | 132–135 | 22 |

$min^{-1}$. Infrared spectra (4000–400 $cm^{-1}$) were recorded as KBr discs using a Unicam SP1200 spectrometer. Low frequency infrared spectra were recorded as pressed polythene discs using a Beckmann-RIIC FS720 interferometer.

### *Reagents*

Trichlorovinylmercury chloride (m.p. 105–107 °C, lit. [12] 109 °C) and trichlorovinylmercury bromide (m.p. 98–100 °C, lit. [12] 99–100 °C) were prepared in good yields from bis(trichlorovinylmercury) and the appropriate mercury(II) halide by previously described methods [12]. The ligands were commercially available and were used without further purification.

### *Preparation of Complexes*

The complexes were prepared by adding a solution containing the trichlorovinylmercury halide in ethanol to the ligand also in ethanol. The solutions were warmed to dissolve the materials if necessary. After mixing the two solutions, solvent was evaporated to crystallisation and the deposit recrystallised from ethanol (in the case of $Cl_2Cl_3HgBr$(tmp), acetone was used as recrystallisation solvent). Analytical data, melting points, appearance and yield are reported in Table IV and infrared data in Table I.

### *Reactions with Phosphanes*

#### *Trichlorovinylmercury chloride and triphenylphosphane*

Trichlorovinylmercury chloride (0.50 g, 1.36 mmol) in ethanol was added to the ligand (0.72 g, 2.72 mmol) also in ethanol. The solution was evaporated to crystallisation and then the white deposit was recrystallised from ethanol yielding colourless cubes. M.p. 282–285 °C. [Found: C, 54.58; H, 3.87. $C_{38}H_{30}Cl_4HgP_2$ [$C_2Cl_3HgCl(PPh_3)_2$] calcd. C, 51.03; H, 3.38%; $C_{36}H_{30}Cl_2HgP_2$[$HgCl_2(PPh_3)_2$] lit. m.p. 273 °C [13]; calcd. C, 54.09, H. 3.78%].

#### *Trichlorovinylmercury chloride and diphos*

Trichlorovinylmercury chloride (0.50 g, 1.36 mmol) in ethanol was added to diphos (0.54, 1.36 mmol) in boiling ethanol. The solution was evaporated to crystallisation and the deposit recrystallised from ethanol, yielding colourless cubes. M.p. 293–295 °C. [Found: C, 47.16; H, 4.21. $C_{28}H_{24}Cl_4HgP_2$ [$C_2Cl_3HgClPh_2PC_2H_4PPh_2$] calcd. C, 43.97, H, 3.16%. $C_{26}H_{24}Cl_2HgP_2$[$HgCl_2Ph_2PC_2H_4PPh_2$] lit. m.p. 292–293 °C [14], C 46.61; H 3.61%].

#### *Trichlorovinylmercury bromide and triphenylphosphane*

Trichlorovinylmercury bromide (0.50 g, 1.22 mmol) in ethanol was added to the ligand (0.64 g, 2.44 mmol) also in ethanol. Solvent was evaporated to crystallisation and the deposit recrystallised from ethanol yielding colourless cubes. M.p. 275–280 °C. [Found: C, 48.91; H, 3.85. $C_{38}H_{30}BrCl_3HgP_2$ [$C_2Cl_3HgBr(PPh_3)_2$] calcd. C, 48.61; H, 3.22%. $C_{36}H_{30}Br_2HgP_2$[$HgBr_2(PPh_3)_2$] lit. m.p. 258–259 °C [15], C, 49.68; H 3.48%].

#### *Trichlorovinylmercury bromide and diphos*

Trichlorovinylmercury bromide (0.50 g, 1.22 mmol) in ethanol was added to the ligand (0.49 g, 1.22 mmol) in ethanol. Solvent was evaporated to crystallisation and the white deposit recrystallised from ethanol as colourless plates. M.p. 301–302 °C. [Found: C, 42.81; H, 3.54. $C_{28}H_{24}BrCl_3HgP_2$ [$C_2Cl_3HgBr(Ph_2PC_2H_4PPh_2)$] calcd. C, 41.55; H, 2.99%. $C_{26}H_{24}Br_2HgP_2(HgBr_2\cdot Ph_2PC_2H_4PPh_2)$ lit. m.p. 298–299 °C [14], C, 41.15; H, 3.19%].

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