

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

* 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.

$\text{C}_2\text{Cl}_3\text{HgCl(phen)}$	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} .
$\text{C}_2\text{Cl}_3\text{HgCl(dmp)}$	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} .
$\text{C}_2\text{Cl}_3\text{HgCl(tmp)}$	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} .
$\text{C}_2\text{Cl}_3\text{HgCl(bipy)}$	1587s, 1575m, 1480w, 1470m, 1438s, 1330m, 1260m, 1228w, 1183m, 1168m, 1127w, 1120w, 1065w, 1048w, 1020s, 1015s sh, 976w, 772vs, 737s, 653m, 630mw, cm^{-1} .
$\text{C}_2\text{Cl}_3\text{HgCl(tmed)}$	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} .
$\text{C}_2\text{Cl}_3\text{HgBr(phen)}$	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} .
$\text{C}_2\text{Cl}_3\text{HgBr(dmp)}$	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} .
$\text{C}_2\text{Cl}_3\text{HgBr(tmp)}$	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} .
$\text{C}_2\text{Cl}_3\text{HgBr(bipy)}$	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} .
$\text{C}_2\text{Cl}_3\text{HgBr(tmed)}$	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 $\nu(\text{CC})$ 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 $\text{C}_2\text{Cl}_3\text{HgX}\cdot\text{L}$ ($\text{X} = \text{Cl}, \text{Br}$, $\text{L} = \text{phen}$; $\text{X} = \text{Cl}$, $\text{L} = \text{bipy}$) 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 $\text{C}_2\text{Cl}_3\text{HgX(tmp)}$ ($\text{X} = \text{Cl}, \text{Br}$) shifts on complexation of the bands due to the ligands were very similar to those found for $(\text{C}_2\text{Cl}_3)_2\text{Hg(tmp)}$ 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 $(\text{C}_2\text{Cl}_3)_3\text{Hg}$ and indicate the greater acceptor character of $\text{C}_2\text{Cl}_3\text{HgX}$ as compared to $(\text{C}_2\text{Cl}_3)_2\text{Hg}$. This is confirmed by our thermal work (Table III) where onset of mass loss occurred at higher temperatures than for corresponding $(\text{C}_2\text{Cl}_3)_2\text{Hg}$ complexes [6]. The complexes of $\text{C}_2\text{Cl}_3\text{HgX}$ with phen and bipy and $\text{C}_2\text{Cl}_3\text{HgCl(tmed)}$ volatilised in a single step, in some cases leaving a slight residue doubtless from thermal degradation of the complexes. For $\text{C}_2\text{Cl}_3\text{HgBr(tmed)}$ 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, $\text{C}_2\text{Cl}_3\text{HgCl(dmp)}$ decomposes from 190–240 $^\circ\text{C}$ with loss of ligand (mass loss found 34.0%; calcd. 33.8%) and from 240–450 $^\circ\text{C}$ with loss of HgCl_2 (found 44.7%; calcd. 47.2%) leaving a residue of $(\text{C}_2\text{Cl}_2)_n$ which vaporises slowly up to 700 $^\circ\text{C}$.

Experimental

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

TABLE II. ^1H NMR Spectral Data for Ligands and their Complexes with $\text{C}_2\text{Cl}_3\text{HgX}$ ($\text{X} = \text{Cl}, \text{Br}$) in CDCl_3 Solutions^a ($\delta(\text{TMS}) = 0$ ppm).

	L	$\text{C}_2\text{Cl}_3\text{HgCl} \cdot \text{L}$	$\text{C}_2\text{Cl}_3\text{HgBr} \cdot \text{L}$
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

^aDeuteriodimethylsulphoxide for 2,2'-bipyridyl and its complex.TABLE III. Thermal Characteristics of $\text{C}_2\text{Cl}_3\text{HgX}$ and $\text{C}_2\text{Cl}_3\text{HgX} \cdot \text{L}$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{phen}, \text{dmp}, \text{tmp}, \text{bipy}, \text{tmed}$).

Compound	Temperature/ $^{\circ}\text{C}$	Thermal Behaviour*
$\text{C}_2\text{Cl}_3\text{HgCl}$	90–180	total mass loss in single step
$\text{C}_2\text{Cl}_3\text{HgBr}$	90–185	total mass loss in single step
$\text{C}_2\text{Cl}_3\text{HgCl}(\text{phen})$	160–355	mass loss in single step, leaving ~4% residue
$\text{C}_2\text{Cl}_3\text{HgBr}(\text{phen})$	210–350	major mass loss (residue 4.3%)
	350–500	steady decrease in mass to ~0.7% residue
$\text{C}_2\text{Cl}_3\text{HgCl}(\text{dmp})$	190–240	mass loss 34.0%, attributed to dmp (required 33.8%)
	(inflexion)	
	240–450	mass loss 44.7%, attributed to HgCl_2 (required 47.2%)
	450–>700	slow continuous loss of mass, attributed to loss of $(\text{C}_2\text{Cl}_2)_n$
$\text{C}_2\text{Cl}_3\text{HgBr}(\text{dmp})$	180–500	mass loss 68.1% with an indication of an inflexion at ~320 $^{\circ}\text{C}$
	500–>700	slow continuous mass loss
$\text{C}_2\text{Cl}_3\text{HgCl}(\text{tmp})$	190–230	mass loss 20.0%
	230–350	mass loss 60.0%
	350–500	steady mass loss leaving 10.0% residue
$\text{C}_2\text{Cl}_3\text{HgBr}(\text{tmp})$	205–230	mass loss 20.0%
	230–340	mass loss 58.7%
	340–600	slow mass loss leaving ~2% residue
$\text{C}_2\text{Cl}_3\text{HgCl}(\text{bipy})$	140–260	single step mass loss, leaving 2.3% residue
$\text{C}_2\text{Cl}_3\text{HgBr}(\text{bipy})$	155–255	single step mass loss, leaving 5.2% residue
$\text{C}_2\text{Cl}_3\text{HgCl}(\text{tmed})$	75–450	single step mass loss, zero residue
$\text{C}_2\text{Cl}_3\text{HgBr}(\text{tmed})$	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 $^{\circ}\text{C}$. Samples were injected via the direct insertion probe. ^1H 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 $^{\circ}\text{C min}^{-1}$ 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 ₂ Cl ₃ HgCl(phen)	colourless cubes	32.22	1.61	5.34	30.76	1.47	5.12	325–327	29
C ₂ Cl ₃ HgCl(dmp)	colourless cubes	33.16	2.73	4.68	33.44	2.10	4.87	213–216	35
C ₂ Cl ₃ HgCl(tmp)	colourless needles	36.19	2.82	4.76	35.86	2.68	4.64	>360	74
C ₂ Cl ₃ HgCl(bipy)	colourless needles	26.93	1.75	5.45	27.58	1.54	5.36	260–262	18
C ₂ Cl ₃ HgCl(tmed)	colourless plates	19.82	3.45	5.82	19.91	3.34	5.80	84–86	81
C ₂ Cl ₃ HgBr(phen)	colourless needles	28.22	1.58	4.82	28.45	1.36	4.74	362–364	35
C ₂ Cl ₃ HgBr(dmp)	colourless needles	30.68	2.39	4.60	31.04	1.95	4.52	300–302	20
C ₂ Cl ₃ HgBr(tmp)	colourless plates	33.81	2.71	4.12	33.40	2.49	4.32	>360	72
C ₂ Cl ₃ HgBr(bipy)	colourless needles	25.47	1.53	5.09	25.42	1.42	4.94	257–258	84
C ₂ Cl ₃ HgBr(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 Cl₂Cl₃HgBr(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.

C₃₈H₃₀Cl₄HgP₂ [C₂Cl₃HgCl(PPh₃)₂] calcd. C, 51.03; H, 3.38%; C₃₆H₃₀Cl₂HgP₂[HgCl₂(PPh₃)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. C₂₈H₂₄Cl₄HgP₂ [C₂Cl₃HgClPh₂PC₂H₄PPh₂] calcd. C, 43.97, H, 3.16%. C₂₆H₂₄Cl₂HgP₂[HgCl₂Ph₂PC₂H₄PPh₂] 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. C₃₈H₃₀BrCl₃HgP₂ [C₂Cl₃HgBr(PPh₃)₂] calcd. C, 48.61; H, 3.22%. C₃₆H₃₀Br₂HgP₂[HgBr₂(PPh₃)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. C₂₈H₂₄BrCl₃HgP₂ [C₂Cl₃HgBr(Ph₂PC₂H₄PPh₂)] calcd. C, 41.55; H, 2.99%. C₂₆H₂₄Br₂HgP₂(HgBr₂·Ph₂PC₂H₄PPh₂) lit. m.p. 298–299 °C [14], C, 41.15; H, 3.19%].

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