

The Thermal Decomposition of Group IIB Metal(II) Halide Complexes. Part III*. Low Frequency Infrared Spectra and Thermal Behaviour of *N,N,N'*-Trimethylethylenediamine Complexes

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Abstract

The group IIB metal dihalide-*N,N,N'*-trimethylethylenediamine complexes are described. Low frequency infrared spectroscopic studies and conductance data have provided evidence for the formulation and structure of the complexes. The thermal behaviour of these complexes has been examined by thermogravimetry and differential scanning calorimetry. For cadmium and mercury complexes complete loss of ligand occurred followed eventually by sublimation of the metal halide, whereas the zinc complexes sublimed unchanged.

Introduction

In previous publications [1, 2] we have reported the thermal behaviour of some tertiary amine and phosphine coordinated group IIB metal dihalide complexes. The 1:1 complexes of the cadmium(II) halides with *p*-dimethylaminophenyldimethylphosphine (DAPDP) lost ligand at about 180 °C leaving the metal halide which then sublimed at higher temperatures. The 1:2 cadmium complexes of the same ligand did not produce a stable 1:1 complex under similar pyrolytic conditions, while the thermal decomposition of the mercury and zinc complexes of DAPDP afforded no recognizable intermediates. For these complexes, NMR spectroscopy showed unequivocally that the ligand moiety is bonded to the metal via the phosphorus [2].

With complexes formed by tertiary bidentate phosphine and nitrogen ligands [1], the thermal behaviour differed quite markedly. There was no evidence for the formation of stable or pseudo-stable intermediates with the complexes of 1,2-bis(diphenylphosphino)ethane, whereas with *N,N,N',N'*-tetramethylethylenediamine (TMED) the cadmium(II) halide complexes decompose by loss of

ligand, leaving the metal halide which then vaporizes at higher temperature.

The decomposition of the zinc complexes occurs by total weight loss at temperatures corresponding closely to their melting points, whereas the mercury complexes lose ligand on heating and this is then followed closely by vaporization of the metal halide.

There is a clear possibility that complexes of secondary amines with metal(II) halides may undergo aminolysis and eliminate hydrogen halide. We have therefore prepared the *N,N,N'*-trimethylethylenediamine complexes of MX_2 ($\text{M} = \text{Zn, Cd, Hg; X} = \text{Cl, Br, I}$) and formulated these complexes on the basis of their conductance behaviour and far infrared spectra as well as studying their thermal behaviour.

Experimental

A DuPont Model 900 thermal analyser with standard TG and DSC plug-in modules were used for the thermal measurements. Thermogravimetric analyses were conducted in a dynamic atmosphere, $150 \text{ cm}^3 \text{ min}^{-1}$, of oxygen-free nitrogen at atmospheric pressure, with linear heating rates of 5 and $15 \text{ }^\circ\text{C min}^{-1}$. Aluminium sample holders, loosely sealed with aluminium caps, were used for the differential scanning calorimetric measurements which were recorded under the same experimental conditions as the TG measurements. The instrument was calibrated using the latent heats of fusion of indium, tin, lead, resorcinol and diphenyl.

Low frequency infrared spectra were obtained as pressed discs in polyethene and were recorded using a Beckmann-RIIC FS720 interferometer and the data computed to a resolution of 5 cm^{-1} using an IBM 1130 computer.

Conductance measurements were carried out on nitromethane solutions ($10^{-3} \text{ mol dm}^{-3}$) of the complexes using a Wayne Kerr bridge at 25 °C.

Analyses for C, H and N were carried out by the Oxford Microanalytical Laboratory of Dr F. B. Strauss. The metal content was determined titrimetrically using EDTA.

*For Part II see ref. 1.

TABLE I. Analytical and Conductance Data for the Group IIB Metal(II) Halide-*N,N,N'*-Trimethylethylenediamine Complexes

Complex ^a	Metal (%)		C (%)		H (%)		N (%)		$\Lambda \times 10^3$ (S m ² mol ⁻¹)
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	
ZnCl ₂ ·L	26.90	27.40	25.40	25.20	6.10	5.90	11.80	11.75	1.98
ZnBr ₂ ·L	20.50	19.95	18.40	18.35	4.40	4.30	8.50	8.55	2.18
ZnI ₂ ·L	15.80	15.50	14.20	14.25	3.55	3.35	6.70	6.65	2.11
CdCl ₂ ·L	40.60	39.40	21.00	21.05	4.95	4.95	9.75	9.80	3.04
CdBr ₂ ·L	29.95	30.00	16.00	16.05	3.80	3.75	7.40	7.50	3.43
CdI ₂ ·L	24.60	24.00	12.90	12.80	3.15	3.00	6.10	5.95	3.37
HgCl ₂ ·L	53.10	53.70	16.45	16.05	3.75	3.80	7.85	7.50	5.41
HgBr ₂ ·L	42.75	43.35	13.15	13.00	3.40	3.05	6.30	6.05	4.62
HgI ₂ ·L	36.40	36.05	11.35	10.80	2.60	2.55	5.00	5.05	4.22

^aL = Me₂NC₂H₄NHMe.

TABLE II. Thermal Characteristics of the Group IIB Metal(II) Halide-*N,N,N'*-Trimethylethylenediamine Complexes

Complex	Onset of mass loss (°C)	Completion of mass loss (°C)	Mass loss (%)	Calculated mass loss (%)	Observed melting point (°C)	DSC observations ^f			ΔH (KJ mol ⁻¹)
						<i>T</i> _i	<i>T</i> _m	<i>T</i> _f	
ZnCl ₂ L ^a	150	360	97.4	100 ^b (15.3) ^e	94	85	100	108	18.1
ZnBr ₂ L	150	400	99.2	100 ^b (24.7)	91	85	98	118	16.4
ZnI ₂ L	150	330	99.4	100 ^b (30.3)	118	120	127	135	16.4
CdCl ₂ L	150	350	37.2	35.7 ^c	270–280 dec	192	272	350	22.7
	475	630	62.8	64.3 ^d (12.7)					
CdBr ₂ L	140	290	26.4	27.2 ^c	181	165	180	185	20.2
	375	580	73.6	72.8 ^d (21.6)					
CdI ₂ L	135	300	24.5	21.8 ^c	160	142	164	170	25.6
	325	470	75.5	78.2 ^d (27.3)					
HgCl ₂ L	120	170	29.4	27.3 ^c	132	125	135	137	28.1
	180	325	80.6	72.7 ^d (9.7)					
HgBr ₂ L	115	175	23.1	22.0 ^c	130	120	130	132	31.9
	185	330	76.7	70.8 ^d (17.4)					
HgI ₂ L	95	180	19.2	18.3 ^c	119	105	118	122	30.2
	170	310	80.5	81.7 ^d (23.0)					

^aL = Me₂NC₂H₄NHMe. ^bFor vaporization of complex. ^cFor loss of ligand. ^dFor sublimation of metal(II) halide. ^eFigures in parentheses calculated for elimination of hydrogen halide. ^f*T*_i = temperature at which trace first deviates from baseline, *T*_m = temperature at which enthalpy change is at a maximum, *T*_f = temperature at which trace returns to baseline.

Preparation of Complexes

The complexes were prepared by mixing a slight equimolar excess of the diamine and the anhydrous metal(II) halide in hot ethanol solutions. The solutions were filtered hot and solvent was then evaporated until crystallization was incipient. On cooling to room temperature, the colourless crystals which formed were filtered off, washed with ice-cold ethanol and dried *in vacuo*. Analytical data and melting points are listed in Tables I and II respectively.

Results and Discussion

The ligand *N,N,N'*-trimethylethylenediamine (TriMED) readily forms complexes with the group

IIB metal(II) halides. The complexes which have been prepared are listed in Table I, together with their analytical and conductance data. Melting points and thermal characteristics are listed in Table II. There is no evidence for the formation of complexes other than those having 1:1 stoichiometry. The complexes are essentially non-electrolytes and thus the halide ions are coordinated to the metal.

Since the ligand is potentially able to function as a bidentate chelating ligand and also as a bridging unit between two metal ions, a number of structural possibilities are available. Ethylenediamine (en) acts as both a bridging ligand as in MCl₂en (M = Zn, Cd, Hg) [3–6] or as a chelating ligand for example in some mercury(II) complexes [7, 8]. However, H₂NCH₂(CH₃)₂CCH₂NH₂ (dmpd) [9], *N,N'*-diethylethylenediamine [10] and *N,N,N',N'*-tetramethyl-

ethylenediamine (TMED) [11, 12] show only chelation of the bidentate ligands. The chelating or *cis* form of ethylenediamine can be readily distinguished from the *trans* bridging form by the far more symmetrical *trans* arrangement giving rise to few absorptions in the 1650–600 cm^{-1} infrared region while the less symmetrical *cis* form gives rise to many more absorptions [13]. All nine TriMED complexes prepared here show many bands in the 1650–600 cm^{-1} region supporting chelation of the ligand.

The complexes of ZnX_2 ($\text{X} = \text{Cl, Br, I}$) all show two well-resolved far infrared absorption bands attributable to metal–halogen stretching vibrations. The positions of the bands, which are sensitive to the mass of the halogen (Cl, 325vs, 307vs; Br, 259vs, 246vs; I, 191s, 175ms cm^{-1}) agree well with literature data for other pseudotetrahedral ZnX_2L_2 systems [14–29] and the ratios ZnBr/ZnCl , 0.80 and ZnI/ZnCl , 0.59–0.57 support an approximately tetrahedral distribution around zinc [22, 24]. Additionally X-ray structural studies have shown that the geometry about zinc in $\text{ZnX}_2(\text{TMED})$ ($\text{X} = \text{Cl}$ [11], I [12]) is approximately tetrahedral.

The cadmium complexes appear to be of two types and, as previously found in chelated cadmium halide complexes, the larger halogen favours tetrahedral coordination of the metal while the smaller halogens have octahedral halogen-bridged arrangements [9]. The cadmium iodide complex shows two strong peaks at 170 and 156 cm^{-1} corresponding to those found in $\text{CdI}_2(\text{dmpd})$ (165 and 150 cm^{-1}) [9] and other tetrahedral cadmium iodide complexes (140–168 cm^{-1}) [24, 30]. The crystal structure of $\text{CdBr}_2(\text{TMED})$ shows a single chain polymeric octahedral arrangement of 4 two-coordinate bromine and 2 nitrogen atoms from the chelate ligand around cadmium [32]. On the other hand $\text{CdBr}_2(\text{dmpd})$, although also containing octahedrally coordinated cadmium, exists as a double strand arrangement, with the metal being surrounded by 2 nitrogen, 1 mono-coordinate bromine atom and 3 three-coordinate bromine atoms shared among 3 metal atoms [9]. Our $\text{CdX}_2(\text{TriMED})$ complexes ($\text{X} = \text{Cl, Br}$) showed similar spectra to the TMED [32] rather than the dmpd complexes [9] and thus are believed to have a single chain polymeric octahedral structure. There are no bands in the far infrared region corresponding to those assigned to $\nu(\text{Cd}-\text{X}_{\text{term}})$ in $\text{CdX}_2(\text{dmpd})$ ($\text{X} = \text{Cl, Br}$) at 257 (Cl) and 186 (Br) cm^{-1} which lie in the region for terminal Cd–Cl (*ca.* 280 cm^{-1}) [33, 34] and terminal Cd–Br (180–200 cm^{-1}) vibrations [34–36] in octahedrally coordinated cadmium complexes. There are, however, bands at lower frequency suggestive of bridging vibrations. Up to four M–X stretching modes are expected in a halogen-bridged octahedral structure and these are assigned at 228vs, 202vs, 134vs, 104vs (chloride) cm^{-1} and 156s, 147s, 123s, 95s (bromide) cm^{-1} and correspond to those

assigned for $\text{CdX}_2(\text{TMED})$ ($\text{X} = \text{Cl}$, 224w, 190s, 160w, 155s; $\text{X} = \text{Br}$, 160s, 150w, 126ms, 112ms cm^{-1} [32]).

The complexes $\text{HgX}_2(\text{TriMED})$ ($\text{X} = \text{Cl, Br}$) have similar far infrared spectra to those of $\text{HgX}_2(\text{dmpd})$ which are believed to contain the double strand octahedral arrangement like that established for $\text{CdBr}_2(\text{dmpd})$ [9]. The bands at 286vs cm^{-1} in the chloride and 195vs cm^{-1} in the bromide compare very favourably with those found in the corresponding $\text{HgX}_2(\text{dmpd})$ complexes (288s and 199s cm^{-1} respectively). These have been assigned as $\nu(\text{Hg}-\text{X}_{\text{term}})$ and lie in the region found in other terminal mercury–halide systems [9, 21, 37]. Up to three other bands are expected for bridging vibrations and these lie at 190s, 170vs, 122vs cm^{-1} in the chloride and 173vs, 129m cm^{-1} in the bromide. Bridging vibrations have been assigned as strong broad bands at 168 and 121 cm^{-1} respectively in $\text{HgX}_2(\text{dmpd})$ ($\text{X} = \text{Cl, Br}$) [9]. X-ray work has suggested that $\text{HgCl}_2(\text{TMED})$ contains halogen in bridging environments [38]. Thus while the chloride and bromide appear to contain octahedrally coordinated mercury with halogen in terminal and bridging environments the iodide would seem to be pseudotetrahedral having two clear absorptions at 158s and 139ms in the region expected for tetrahedral coordination [24, 39] and these correspond to those found at 154s and 140s in the dmpd complex [9].

Reactions between bis organoderivatives of the group II metals, Be [40], Mg [41], Zn [42] and *N,N,N'*-trimethylethylenediamine result in the elimination of hydrocarbon at about room temperature or slightly above, with consequent formation of dimeric species as shown in Fig. 1. This type of structure has been confirmed for the methylmagnesium [43] and hydrido zinc [44] compounds by X-ray analysis. The considerably greater bond strength of the group IIB metal halides as compared to the metal alkyls would suggest that the reaction between the diamine and the metal halides to produce the corresponding halogeno derivatives would require more vigorous conditions than the reactions of the organometallics with the diamine. The thermal characteristics of the complexes are shown in Table II and show that aminolysis does not occur even at temperatures at which onset of weight loss commenced. The thermograms of the zinc

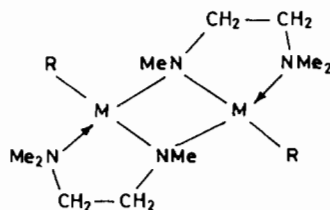
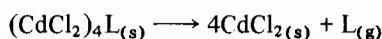
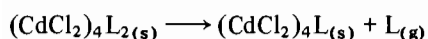
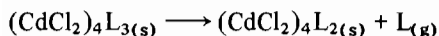
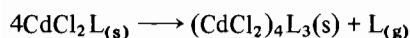


Fig. 1. Dimeric species.

complexes show only a single step, corresponding to total mass loss, at temperatures above their melting points. Since this vaporization occurs at lower temperatures than for the free metal halides it can be safely assumed that the complexes do not undergo dissociation and further, the infrared spectra of the sublimates are identical to those of the pure complexes.

The cadmium complexes thermally decompose by loss of ligand followed by vaporization of the metal halide. Only in one case, that of the cadmium iodide complex, did the intermediate mass loss closely correspond to that required for loss of hydrogen halide (observed mass loss, 24.5%; calculated for loss of diamine or hydrogen halide, 21.8 or 27.3% respectively). The infrared spectrum of the residue at this stage was however identical to that of cadmium iodide. This complex therefore decomposes via loss of ligand over the temperature range 135–300 °C and is closely followed by sublimation of the metal halide at higher temperatures. The chloride complex appears to lose ligand in four definite stages over the range 150–350 °C, though the intermediates are only stable over small temperature ranges. These mass losses approximate to loss of a quarter of a mole of ligand per mole of complex at each stage and correspond to the empirical processes:



At each stage of loss of ligand, further halogen bridges will be formed between metal atoms until ultimately the octahedral layer lattice of cadmium(II) chloride is produced. The intermediate $(\text{CdCl}_2)_4\text{L}_2$ which is stable over the largest temperature range in this system ($4\text{CdCl}_2\text{L} \longrightarrow (\text{CdCl}_2)_4\text{L}_2$ requires 17.9% mass loss; found 18.4%) is similar to that obtained in the analogous TMED system [1]. The thermal decomposition of the bromide complex showed only the presence of the intermediate of empirical formula $(\text{CdBr}_2)_2\text{L}$ whereas the iodide complex showed no evidence for the formation of intermediates.

The mercury compounds also decompose by loss of ligand leaving the metal(II) halide but due to the lower sublimation temperatures of the mercury(II) halides, complete loss of ligand did not occur before onset of sublimation of the metal halide. The situation became progressively worse along the series chloride → bromide → iodide. However, by derivative thermogravimetry, it was possible to verify that mass loss corresponded to that required for evolution of ligand.

Using the temperature of onset of decomposition as the criterion of thermal stability of the complexes, the stability decreases in the order $\text{Zn} > \text{Cd} > \text{Hg}$. This follows the order of increasing radii of the metals. Overlap of the more diffuse orbitals on mercury with lone pairs of electrons on the ligands results in a weaker bond than that produced by the overlap of the more compact orbitals of the other two elements with ligand orbitals. For the zinc complexes, the thermal stability differs little with variation of the halogen. For the complexes of the other two elements the stability decreases in the order $\text{Cl} > \text{Br} > \text{I}$. The greater electronegativity of chlorine as compared to bromine and iodine induces stronger bond formation between the metal and ligand. The steric requirement of the halogens also favours the same order of stability.

The DSC traces showed endotherms for all the complexes corresponding closely to their visual melting points but comparison with the TG traces shows that some decomposition is also occurring. Notably for the cadmium(II) chloride complex, considerable mass loss occurred before the melting point and two peaks were also present in the DSC trace at temperatures lower than the sharp endotherm which corresponds closely to the observed melting point. The zinc compounds did not show peaks which could be ascribed to enthalpy changes corresponding to loss of ligand and the cadmium complexes showed a series of multiple broad peaks which did not allow evaluation of the enthalpy changes of the decomposition reactions. The mercury complexes showed very strong exotherms directly after the melting points corresponding to reaction of the mercury complex with the aluminium sample holder.

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