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THE THERMAL DECOMPOSITION OF GROUP IIB METAL HALIDE COMPLEXES

PART II. *N,N,N',N'*-TETRAMETHYLETHYLENEDIAMINE AND 1,2-DIPHENYLPHOSPHINOETHANE COMPLEXES

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ABSTRACT

The preparation and pyrolysis procedures for 1/1 complexes $MX_2 \cdot L$ (where M=Group IIB metal, X=Cl, Br or I and L=*N,N,N',N'*-tetramethylethylenediamine (TMED) or 1,2-diphenylphosphinoethane (DPE)) is reported. The decomposition of the cadmium chloride and bromide TMED complexes afford intermediates of varying stability. From far infrared spectrophotometry we conclude that the chloride intermediate is a four coordinate polymeric complex. Differential scanning calorimetry has been used to determine selected latent heats of fusion.

INTRODUCTION

In a recent communication[1] we reported on the thermal decomposition of a number of Group IIB metal halide complexes of *p*-dimethylaminophenyldimethylphosphine. The cadmium halide complexes and the chloro species in particular were found to form the anhydrous metal salt at temperatures of about 250 °C in an atmosphere of nitrogen. Further it has been noted that the anhydrous cadmium halides are stable to temperatures above 500 °C[2]. It seemed probable that pyrolysis of suitable Group IIB metal halide complexes of bidentate ligands might afford complexes with unusual coordination numbers at the metal atom. In this communication we report on the thermal decomposition of complexes MX_2L (where M = Zn, Cd or Hg and L = *N,N,N',N'*-tetramethylethylenediamine, TMED, or 1,2-diphenylphosphinoethane, DPE).

Some evidence is presented which suggests that a stable polymeric four coordinate complex is transiently formed on pyrolysis of the cadmium chloride amine complex.

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EXPERIMENTAL

Preparation of complexes

N,N,N′,N′-Tetramethylethylenediamine complexes. — The chloride and bromide complexes were prepared by the previously described methods[3,14]. Satisfactory analyses were obtained for these compounds. The iodide complexes were obtained by crystallisation from an ethanolic solution of the anhydrous metal halide to which a slight excess of the diamine had been added. The complexes were filtered off and dried *in vacuo* as white crystalline solids. Analytical data for these complexes are given in Table 1.

TABLE 1

ANALYTICAL DATA FOR TMED COMPLEXES

	Found (%)		*Required* (%)	
	C	*H*	*C*	*H*
ZnI_2·TMED	16.48	3.55	16.55	3.70
CdI_2·TMED	15.29	3.10	14.93	3.34
HgI_2·TMED	13.15	2.73	12.63	2.83

1,2-Diphenylphosphinoethane complexes. — The zinc[3,4], cadmium[3,5] and mercury[3,6] complexes with this bidentate phosphine ligand have been reported by Coates and Ridley and Sandhu *et al.* The described synthetic procedures proved to be satisfactory for the isolation of the phosphine complexes of the Group IIB metal halides. Analytical data obtained were close to calculated values.

APPARATUS

A DuPont Model 900 thermal analyser with standard TG and DSC plug-in modules was used for the thermal measurements. Thermogravimetric analyses were conducted in a dynamic atmosphere of oxygen-free nitrogen at atmospheric pressure (200 ml min^{-1}). Samples of 4–8 mg contained in platinum boats were heated at a linear rate of 15 °C min^{-1}. Aluminium sample holders, loosely sealed with aluminium caps, were used for differential scanning calorimetry. The heating rate in a static atmosphere of oxygen-free nitrogen at atmospheric pressure was 15 °C min^{-1}. The instrument was calibrated using the latent heats of fusion of metallic gallium, indium and tin.

Far infrared spectra in the range 350–100 cm^{-1} were obtained by use of 5% solid solutions of the complexes in polyethylene in a Beckman RIIC model FS 720 interferometer. Sufficient data were recorded to give a resolution of ±2.5 cm^{-1}.

RESULTS AND CONCLUSIONS

The tetramethylethylenediamine complexes of cadmium chloride and bromide exhibit inflexions in their TG curves at 398 and 378 K respectively (Fig. 1). The inflexion in the former was a short but well defined plateau corresponding to the formation of $CdCl_2 \cdot 0.5TMED$ (weight loss observed 19.7%; $CdCl_2 \cdot TMED \rightarrow CdCl_2 \cdot 0.5TMED$ requires 19.4%). The intermediate was isolated and on analysis was found to correspond to $CdCl_2 \cdot 0.5TMED$. (Found: C, 15.06; H, 3.59; required C, 14.92; H, 3.34%).

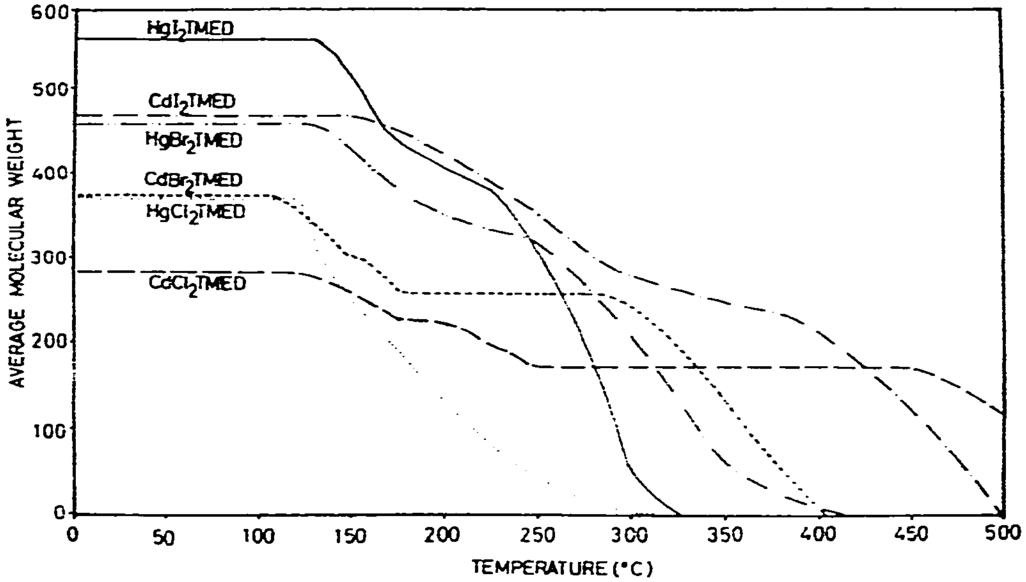
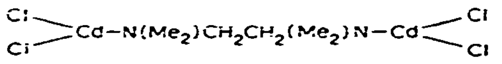


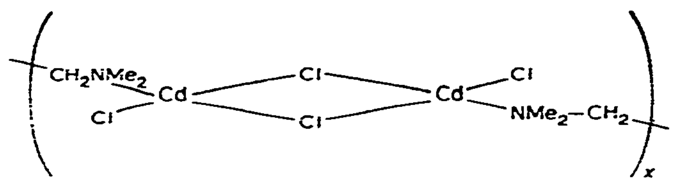
Fig. 1. Thermogravimetric curves of $CdX_2 \cdot TMED$ and $HgX_2 \cdot TMED$ complexes in N_2 (200 ml min^{-1}) at atmospheric pressure.

The structure of this hemi-diamine complex poses an interesting problem, there being two viable alternatives. A three coordinate structure (1) may be proposed presumably involving a planar arrangement of the bonds around each cadmium atom. A more probable structure (2) involves both bridging chlorine atoms and ligand molecules to afford a polymeric complex with four coordinate cadmium atoms.



$Cl_2Cd{-}N(Me_2)CH_2CH_2(Me_2)N{-}CdCl_2$

(1)

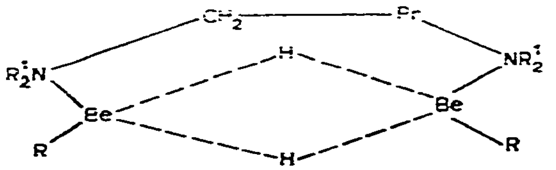


(2)

X-ray diffraction studies[7] have shown that TMED acts as a chain-propagating ligand in its 1/1 aluminium hydride complex (3).

$$-\left(CH_2-Me_2N-AlH_3-NMe_2-CH_2\right)_x- \qquad (3)$$

A similar situation probably exists in the solid state for $(CH_3BeH)_2TMED$ in which both hydrogen and the diamine will act as bridging groups. Other organoberyllium hydride complexes of the type $(RBeH)_2TMED$ are monomeric in solution[9] and have been assigned structure (4).



(4)

A similar structure is unlikely for the cadmium complex, $CdCl_2 \cdot 0.5TMED$, for steric reasons. The much larger sizes of cadmium and chlorine compared to beryllium and hydrogen would preclude the formation of such a structure.

In structure (1) only terminal halogen atoms are present in contrast to (2). It should therefore be possible to distinguish the two isomers by far infrared spectrophotometry since Cd–Cl frequencies have been observed in the 100–350 cm^{-1} region[3,14]. The principle absorptions shown by $CdCl_2 \cdot TMED$ and $CdCl_2 \cdot 0.5TMED$ in the region 100–350 cm^{-1} are listed in Table 2. The absorption at about 105 is common to both compounds and also to the 1/1 bromide complex. This absorption we consider to be associated with the ligand moiety of the complex. It has been well established that the terminal Cd–Cl bonds as in the tetrahalogenocadmate(II)ion[3] give rise to absorptions at about 260 cm^{-1} and neutral complexes in which the *terminal* chlorines are in a tetrahedral environment give rise to absorptions in the range 250–200 cm^{-1}. The frequency of *bridging* metal–halogen vibrations is usually 70 cm^{-1} lower than the corresponding *terminal* halogen mode[10]. Octahedral coordination would give rise to absorptions below 200 cm^{-1}.

TABLE 2

PRINCIPLE ABSORPTIONS OF $CdCl_2 \cdot TMED$ AND $CdCl_2 \cdot 0.5TMED$ IN REGION 100–350 cm^{-1}

$CdCl_2 \cdot TMED$	224s	190vs	152s		105m
$CdCl_2 \cdot 0.5TMED$	217s, sh	200vs	156s	123m	109w, sh

w = weak; m = moderate; s = strong; vs = very strong; sh = shoulder.

We believe our interpretation of the far infrared spectrum of $CdCl_2 \cdot 0.5TMED$ confirms the polymeric structure (2) as the most likely structure, the strong absorption bands at 217 and 156 cm^{-1} being *terminal* and *bridging* metal–halogen vibrations respectively in a tetrahedral environment. The Cd–N frequencies[11] are well characterised at 190 and 200 cm^{-1} for the parent complex and pyrolysis product respectively although the latter is hidden to a large extent by the broad Cd–Cl absorption at 217 cm^{-1}.

Although four and six coordinated species are known to be favoured by cadmium the TMED links of the intermediate are a clear weakness in the structure and it is not surprising that decomposition to the metal salt takes place at temperatures only slightly greater than 450 K.

The decomposition of the 1/1 zinc halide TMED complexes occur at temperatures which correspond closely to their melting points. Unlike the cadmium complexes there was no indication of the formation of intermediates of significant stability. Differential scanning calorimetry of each zinc and cadmium complex afforded a single endotherm associated with fusion. The endotherms were sufficiently well characterised to allow calculation of latent heats of fusion as described previously[1].

Exceptions were the zinc chloride and cadmium bromide compounds which exhibited additional endotherms at 373 and 417 K respectively. It is probable that these correspond to rearrangements from polymeric six coordinate species with bridging halogens and TMED groups to complexes based on a simple tetrahedral unit. Far infrared studies are presently being undertaken to clarify these transformations. The mercury TMED complexes decomposed at temperatures of around 400 K. Each TG trace showed an inflexion corresponding approximately to total loss of ligand. DSC studies of these compounds were not possible because of the exothermic reaction between the mercury halides produced and the aluminium sample holders. The *N,N,N'*-trimethylethylenediamine complexes of the Group IIB metal halides behave thermally very similar to the corresponding TMED complexes[12].

In view of the preference of cadmium and mercury to accept electrons from ligands based on atoms with π-bonding capacity[13] it was expected that the 1/1 complexes of 1,2-diphenylphosphinoethane would have superior thermal stability with respect to decomposition to metal halide and free ligand than their TMED analogues. This has been confirmed (Table 3).

Indian workers have subjected some Group IIB metal halide diphosphine adducts to thermogravimetric investigation but were not able to study the nature of intermediate or decomposition products. They report an increase in weight in the initial stages of decomposition of the cadmium complexes which may be ascribed to their partial oxidation to the more stable diphosphine oxide complexes[5]. They also report that the mode of decomposition of the corresponding mercury complexes is complicated[6]. In order to prevent any complicating oxidation reactions occurring we studied the decomposition of our complexes in the complete absence of oxygen and moisture. There was no evidence of pyrolysis proceeding via stable or pseudo stable complex intermediates. Both the $CdCl_2$ and $CdBr_2$ complexes yielded almost quantitatively the uncomplexed salt at 673 and 648 K respectively. $CdCl_2DPE$ did exhibit an inflexion at 618 K; from weight loss data this corresponds approximately to

TABLE 3

THERMOCHEMICAL DATA FOR GROUP IIB METAL HALIDE TMED AND DPE COMPLEXES

Complex	*Melting point* (*K*)		*DSC endotherm* (*K*)[a]			ΔH (*l*) *kcal* $mole^{-1}$	*TG Temperature of onset of decomposition* (*K*)
	Lit.	*Visual*	T_i	T_m	T_f		
$ZnCl_2$·TMED	450[3]	447	360	373	389		428
			434	451	458		
$ZnBr_2$·TMED	451[3]	449	443	453	460	4.32±0.10	438
ZnI_2·TMED	477[14]	463	427[b]	469	477	4.28±0.10	468
$CdCl_2$·TMED	513[3]d	523 d	472	517	528[c]	13.80±0.22	398
$CdBr_2$·TMED	518–520[14]	506	407	417	427		373
			488	514	525		
CdI_2·TMED	483–484[14]	472–473	471	483	496	6.25±0.16	438
$HgCl_2$·TMED	437[3]	433					383
$HgBr_2$·TMED	438[3]	432					413
HgI_2·TMED	435[14]	431					400
$ZnCl_2$·DPE	563–564[3,4]	593–594					473
$ZnBr_2$·DPE	560[3]	562–563	543	552			548
	557–558[4]			567	579[d]		
ZnI_2·DPE	>563[4]	607–608	590	617	631	10.90±0.80	578
$CdCl_2$·DPE	538–539[3,5]	530	530	535	546	14.25±0.75	513
$CdBr_2$·DPE	558–559[3,5]	543	547	552	565	15.25±0.35	543
CdI_2·DPE	553–558[5]	543	537	550	559		528
			559	570	580		
$HgCl_2$·DPE	577–580[6]	565–566[e]					483
$HgBr_2$·DPE	592–593[6]	571–572					518
HgI_2·DPE	558–563[6]	538–544[f]					413

[a] 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 the baseline. [b] Endothermic shoulder at 456 K. [c] Endothermic shoulder at 524 K. [d] Two endotherms separated by small exotherm T_{min} 556 K. [e] Melts at 292–293 °C to give red-brown liquid completely clear by 300 °C. [f] Shrinks and starts to melt at 265 °C to give cloudy yellow liquid. Clear yellow liquid by 285 °C.

one fifth of the mole of ligand per mole of salt. In a number of instances, notably the $ZnCl_2$–, $HgCl_2$– and HgI_2–DPE complexes, loss of ligand occurred before the onset of melting (Table 3). Ideal DSC single fusion endotherms for the $CdCl_2$–, $CdBr_2$– and ZnI_2–DPE complexes were obtained. Latent heats of fusion are tabulated in Table 3.

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