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# THE THERMAL DECOMPOSITION OF GROUP IIB METAL HALIDE COMPLEXES

## PART I. *p*-DIMETHYLAMINOPHENYLDIMETHYLPHOSPHINE COMPLEXES

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## ABSTRACT

Proton magnetic resonance studies show that in complexes of *p*-dimethylaminophenyldimethylphosphine–zinc(II), –cadmium(II) and –mercury(II) halides the ligand moiety is bonded to the metal via the phosphorus atom. Thermal studies in an atmosphere of nitrogen indicate that only the cadmium chloro and bromo complexes yield stable solid phases based on the divalent metal halide. The complexes containing two molecules of ligand per molecule of metal halide do not afford a recognisable 1:1 complex intermediate on pyrolysis. Differential scanning calorimetry has been used to determine selected latent heats of fusion.

## INTRODUCTION

Some complexes of *p*-dimethylaminophenyldimethylphosphine (DAPDP) with Group IIB metal halides were synthesised by Coates and coworkers in 1955[1]. Compounds of stoichiometry $MX_2DAPDP$ and $MX_2(DAPDP)_2$ (where M = Group IIB metal and X = Cl, Br or I) were reported. It was further inferred that the ligand molecules were in each case bonded to the metal atom via the phosphorus atom in spite of the known preference of zinc for class 'a' donors[2]. In this communication we present conclusive evidence that the ligand molecules are bonded in each case to the metal via the heavier Group VB element.

The thermal degradation of complexes of Group IIB metal halides with substituted amines and phosphines has attracted little attention. Sandhu and Dass[3] have recently reported on the complicated pyrolysis pattern in air of complexes of cadmium halides with diphosphines of the type $R_2P(CH_2)_n PR_2$ (where R = phenyl and $n = 2$ or 4). In view of the known stability of the halogen bridge in cadmium halide systems[4] it was of particular interest to study the thermal stability of $MX_2(DAPDP)_2$ and $MX_2DAPDP$ complexes. It was further hoped that differential scanning calorimetry might be used to determine metal–ligand bond strengths. Endotherms corresponding to metal–ligand cleavage were not observed.

## EXPERIMENTAL

### *Preparation of complexes*

*p*-Dimethylaminophenyldimethylphosphine was prepared from *p*-dimethylaminophenylphosphonous dichloride and methyl magnesium iodide as previously described[5]. The product was purified by fractional distillation. The fraction boiling between 86–88 °C at 0.2 mm was retained. The complexes were obtained by the method described by Coates *et al.*[1] except where described below.

*Cadmium iodide bis(dimethylaminophenyldimethylphosphine).* — Anhydrous cadmium iodide (1 mol) was mixed with the ligand (2.2 mol) in acetone and refluxed for 10 min. The complex separated on cooling as colourless crystals, m.p. 133–134 °C (Found: C, 32.37; H, 4.48; $C_{20}H_{32}CdI_2N_2P_2$ calc.: C, 32.96; H, 4.42%).

*Zinc iodide bis(dimethylaminophenyldimethylphosphine).* — A solution of zinc iodide was prepared by boiling an excess of zinc dust with iodine (1 mol) in ethanol until the colour due to free iodine was discharged. The ligand (2 mol) dissolved in a minimum of ethanol was added and the unreacted zinc removed by filtration. The filtrate was boiled until crystallisation of the product was incipient and then cooled. The complex separated as colourless crystals m.p. 204–205 °C (lit.: 159–160 °C) (Found: C, 34.97; H, 4.74; N, 4.21; $C_{20}H_{32}I_2N_2P_2Zn$ calc.: C, 35.24; H, 4.73; N, 4.11%).

*Mercuric iodide dimethylaminophenyldimethylphosphine.* — Equimolar quantities of the ligand and mercuric iodide were mixed in acetone. The pale yellow solution was refluxed for 15 min and then cooled slowly to 0 °C. The complex crystallised as pale yellow crystals, m.p. 163–164 °C (Found: C, 18.44; H, 2.34; $C_{10}H_{16}HgI_2NP$ calc.: C, 18.89; H, 2.54%).

### APPARATUS

Proton magnetic resonance spectra were obtained using a Jeol C-60HL high resolution spectrometer.

The instrument used for the thermal measurements was a DuPont Model 900 thermal analyser used in conjunction with their differential thermal analysis, differential scanning calorimetry and thermogravimetric attachments. Thermogravimetric analyses were conducted in a dynamic atmosphere of oxygen free nitrogen at atmospheric pressure ($250\ \mathrm{ml \cdot min^{-1}}$). Samples of 5–10 mg contained in platinum boats were heated at a rate of 10 or $15\,^{\circ}\mathrm{C \cdot min^{-1}}$. Aluminium sample holders, loosely sealed with aluminium caps, were used for differential scanning calorimetry. The heating rate in a static atmosphere of air at atmospheric pressure was 10 or $15\,^{\circ}\mathrm{C \cdot min^{-1}}$. The instrument was calibrated using the latent heats of fusion of metallic gallium, indium and tin.

### RESULTS AND CONCLUSIONS

The nitrogen methyl and phosphorus methyl signals of the proton magnetic resonance spectra of a selection of $MX_2DAPDP$ and $MX_2(DAPDP)_2$ complexes are listed in Table I. It can be seen that in each case studied there is little difference between the N-methyl proton signals in the free and the coordinated ligand, whereas the signal due to the P-methyl protons shows a significant downfield shift on coordination. The coordinating phosphorus atom is depleted of electrons with a subsequent deshielding of the methyl protons in spite of $d\pi$–$d\pi$ back donation from the

TABLE I

PROTON MAGNETIC RESONANCE SPECTRA OF ZINC(II), CADMIUM(II) AND MERCURY(II) COMPLEXES CHEMICAL SHIFTS (τ VALUES)

Measurements were made on 10% solutions in deuterodimethylsulphoxide or deuterated acetone at 294°K using tetramethylsilane as an internal standard. $\Delta$ and $\Delta'$ refer to the difference in chemical shift for the signals obtained in the free and coordinated ligand. $J$ values refer to the observed $^2J_{PCH}$ coupling constants.

| *Compound* | $NMe_2$ | $\Delta$ | $PMe_2$ | $\Delta'$ | $J$ *(c.p.s.)* |
|---|---|---|---|---|---|
| [a]DAPDP | 7.18 | | 8.82 | | 2.4 |
| [b]$ZnCl_2(DAPDP)_2$ | 7.04 | 0.14 | 8.52 | 0.30 | 4.2 |
| [b]$ZnBr_2(DAPDP)_2$ | 7.04 | 0.14 | 8.50 | 0.32 | 4.8 |
| [b]$ZnI_2(DAPDP)_2$ | 7.04 | 0.14 | 8.46[c] | 0.36 | 0 |
| [a]$CdCl_2DAPDP$ | 7.08 | 0.10 | 8.54 | 0.28 | 4.8 |
| [a]$CdBr_2DAPDP$ | 7.08 | 0.10 | 8.52 | 0.30 | 6.0 |
| [b]$CdI_2DAPDP$ | 7.04 | 0.14 | 8.40 | 0.42 | 7.2 |
| [a]$HgCl_2DAPDP$ | 7.03 | 0.15 | 8.07 | 0.75 | 11.4 |
| [a]$HgBr_2DAPDP$ | 7.04 | 0.14 | 8.07 | 0.75 | 9.6 |
| [a]$HgI_2(DAPDP)_2$ | 7.06 | 0.12 | 8.14 | 0.68 | 1.2 |

[a]Solvent deuterated dimethylsulphoxide. [b]Solvent deuterated acetone. [c]Singlet.

metal to the phosphorus atom. We regard this as conclusive evidence that the ligand molecules are bonded to the metal via the phosphorus atom. The τ values for the phosphorus methyl resonances fall in the order $X = Cl > Br > I$ for both the $ZnX_2(DAPDP)_2$ and $CdX_2DAPDP$ series of complexes. The trend has been previously noted[6,7] for $MX_2L_2$ square planar complexes of platinum(II) and palladium(II) (where M is a noble metal and L is a ligand based on a Group VB donor atom). It seems likely that this trend may be associated with the increased ability of the heavier halogen atoms to accept electrons from the metal *via* $d\pi$–$d\pi$ overlap. This effect must be sufficiently pronounced to overcome the expected opposing effect caused by the greater electronegativity of the smaller halogen atom.

The results of the thermogravimetric analysis (TGA) of the 1:1 DAPDP complexes of cadmium chloride and bromide in a dynamic atmosphere of nitrogen are shown in Fig. 1. Both systems produced stable intermediates at about 300°C. The weight losses observed (49.1 and 38.9%) correspond to the formation of the metal halide (weight loss required for formation of $CdCl_2$, 49.7 and $CdBr_2$, 39.9%). The adduct $CdI_2$ DAPDP decomposes similarly to afford cadmium iodide which undergoes simultaneous decomposition or volatilisation. The 1:2 complexes of the cadmium halides (Fig. 2) do not produce the 1:1 complexes as an intermediate under similar pyrolytic conditions. Loss of ligand was progressive affording eventually the simple metal chloride and bromide (weight loss observed 65.0; $CdCl_2(DAPDP)_2 \rightarrow CdCl_2$ requires 66.4%: weight loss observed 56.2; $CdBr_2(DAPDP)_2 \rightarrow CdBr_2$ requires 57.1%).

Of the zinc complexes only the 1:2 compounds were studied thermally; the results are shown in Fig. 3. The pyrolysis pattern was not as clear cut as with the

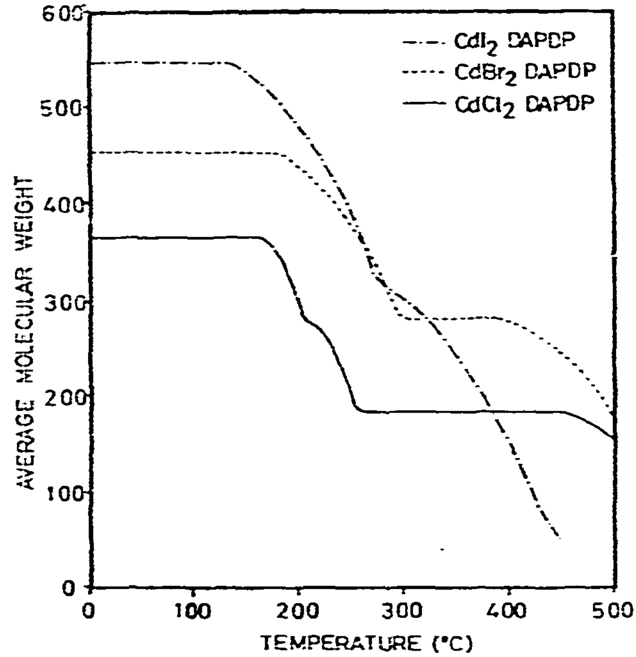

Fig. 1. TGA curves of $CdX_2DAPDP$ complexes in $N_2$ (250 ml·min$^{-1}$) at atmospheric pressure.

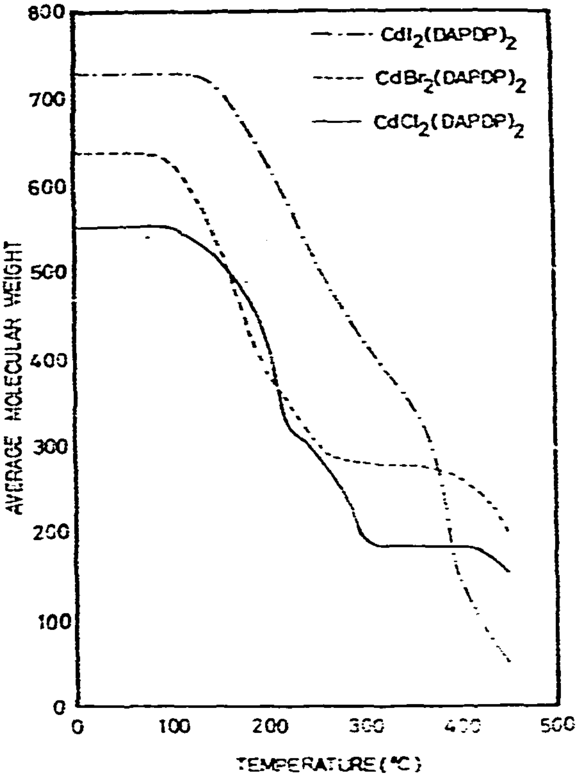

Fig. 2. TGA curves of $CdX_2(DAPDP)_2$ complexes in $N_2$ (250 ml·min$^{-1}$) at atmospheric pressure.

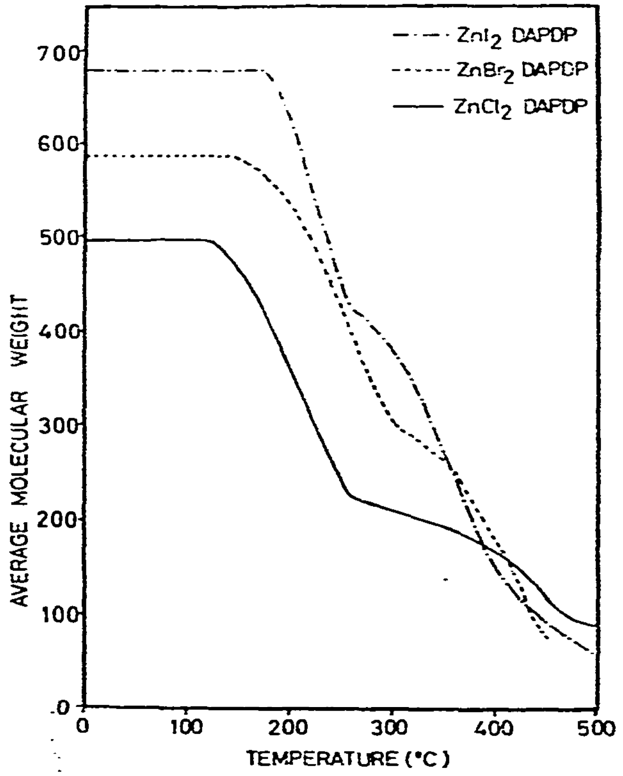

Fig. 3. TGA curves of $ZnX_2(DAPDP)$ complexes in $N_2$ (250 ml·min$^{-1}$) at atmospheric pressure.

cadmium analogues although an inflexion corresponding to a weight loss of 31% in the TGA curve for $ZnI_2(DAPDP)_2$ is thought to correspond approximately to the formation of $ZnI_2$DAPDP (weight loss required, 26.6%). In all cases the relatively low melting points of the zinc halides[9] meant that simultaneous volatilisation of the metal halide accompanies ligand loss.

The mercury complexes $HgCl_2$DAPDP and $HgI_2(DAPDP)_2$ all decomposed (Fig. 4) very rapidly in an atmosphere of nitrogen at temperatures in excess of 150°C. The mercuric iodide 1:2 complex did not afford a recognisable 1:1 compound as an intermediate.

Using the minimum TGA dissociation temperatures as the criteria for determining thermal stability, it is interesting to note that the order of stability of the complexes $MX_2(DAPDP)_2$ is I > Br > Cl whereas the order is Br > Cl > I for complexes of general formula $MX_2$DAPDP.

Differential scanning calorimetry (DSC) of the zinc and cadmium complexes allowed the determination of selected physical parameters. It was initially hoped to obtain some data on the strength of the metal–phosphorus bond in these compounds but we were only able however to determine latent heats of fusion. A single endotherm was noted for each complex studied whose maximum corresponded closely to the visual melting point of the compound. Barnes and Duncan[10] in a thermal study of the

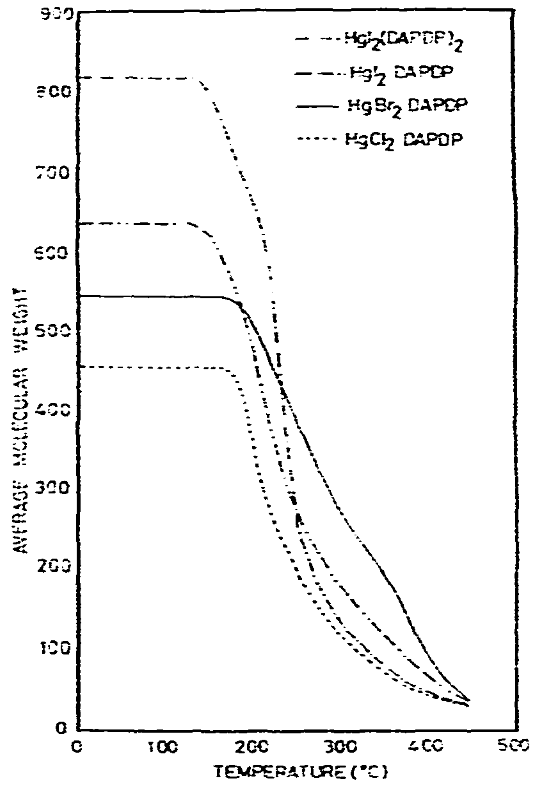

Fig. 4. TGA curves of $HgX_2DAPDP$ and $HgI_2(DAPDP)_2$ complexes in $N_2$ (250 ml·min$^{-1}$) at atmospheric pressure.

complexes of cadmium halides with oxygen heterocycles also reported a single endotherm but these workers suggested that the endotherm corresponded to fission of a metal ligand bond and subsequent loss of the ligand as a vapour. In our case the melts of the cadmium complexes may be formulated as the product of the processes summarised by Eqns. (1) or (3) below.

$$CdX_2DAPDP_{(crystal)} \rightarrow CdX_2DAPDP_{(liq.)} \quad (1)$$

$$CdX_2DAPDP_{(crystal)} \rightarrow CdX_{2(crystal)} + DAPDP_{(liq.)} \quad (2)$$

$$CdX_2DAPDP_{(crystal)} \rightarrow CdX_2 \text{ in } DAPDP_{(solution)} \quad (3)$$

Eqn. (1) represents a simple fusion process whereas the alternative (3) is a physical solution of the cadmium halide in dimethylaminophenyldimethylphosphine. The second possibility may be discounted since clear melts were produced in every case.

As was noted previously a change in the chemical shift of the P-methyl proton signal downfield compared with the free ligand is attributable to coordination through the phosphorus atom to an acceptor. The chemical shift of the N-methyl proton signal is not significantly altered. Accordingly the difference in chemical shifts of the P-methyl and N-methyl proton signals compared with the difference for the pure ligand at the same temperature will be diagnostic of the nature of the melt. The fusion product would give a typical coordinated ligand NMR spectrum whereas the solution of metal halide in dimethylaminophenyldimethylphosphine would afford a trace which corresponds closely to that of the free ligand. The difference in the case of the pure ligand was found to be 1.58 ppm at 155 °C. The corresponding values of the pure melts were found to be 1.42, 1.33 and 1.27 ppm for the $ZnCl_2(DAPDP)_2$, $ZnBr_2(DAPDP)_2$ and $CdI_2DAPDP$ melts respectively. The evidence clearly supports a simple fusion process. The NMR spectra of other cadmium and zinc complexes were not studied because of their high melting points and/or thermal instability.

It has been shown[11] that the area of a DSC trace may be quantitatively related to the enthalpy of a physical or chemical change. A selection of latent heats of fusion of a number of cadmium and zinc halide complexes with DAPDP are listed in Table II. The values are all of the order of 9 kcal·mole$^{-1}$ with the exception of $CdI_2(DAPDP)_2$ which is somewhat anomalous having a fusion value of 5.53 kcal·mole$^{-1}$. DSC studies of the mercury complexes were not possible because of the exothermic reaction of the pyrolysis products with the aluminium sample holders. Endotherms corresponding to metal ligand dissociations were not observed. This is rather surprising particularly for the zinc systems where the rate of ligand loss is relatively high.

TABLE II

THERMOCHEMICAL DATA FOR GROUP IIB METAL HALIDE DIMETHYLAMINOPHENYLDIMETHYLPHOSPHINE COMPLEXES

| *Complex* | *Melting point (°K)* | | *DSC endotherm (°K)*$^{a,f}$ | | | *ΔH(l) (kcal·mole$^{-1}$)* |
|---|---|---|---|---|---|---|
| | *Ref. 1* | *Visual* | $T_i$ | $T_m$ | $T_f$ | |
| $ZnCl_2(DAPDP)_2$ | 424.5–425 | 430–431 | 408 | 431 | 439 | 8.15 ± 0.15 |
| $ZnBr_2(DAPDP)_2$ | 419 | 418–419 | 393 | 418 | 427 | 8.20 ± 0.20 |
| $ZnI_2(DAPDP)_2$ | 432–433 | 478–479 | 400 | 480 | 488 | 10.40 ± 0.36 |
| $CdCl_2(DAPDP)_2$ | 411–412 | 411–412 | 393 | 412 | 420 | 9.10 ± 0.10 |
| $CdBr_2(DAPDP)_2$ | 427–428 | 425–426 | 393 | 427 | 435 | 9.03 ± 0.10 |
| $^{b}CdI_2(DAPDP)_2$ | | 406–407 | 373 | 408 | 415 | 5.53 ± 0.33 |
| $CdCl_2DAPDP$ | 488–490 | 498 | 481 | 497$^{d}$ | 503 | 8.56 ± 0.20 |
| $CdBr_2DAPDP$ | 494–495 | 505–506 | 490 | 503$^{d}$ | 508 | 8.26 ± 0.22 |
| $CdI_2DAPDP$ | 417–418 | 419–420 | 401 | 418$^{d}$ | 425 | 7.35 ± 0.25 |
| $HgI_2(DAPDP)_2$ | 443–444 | 442–444 | | $^{e}$435$^{c}$<br>422 | | |
| $HgCl_2DAPDP$ | 506–508 | 508–509 | | 509$^{c}$ | | |
| $HgBr_2DAPDP$ | 474–477 | 499–500 | | 498$^{c}$ | | |
| $^{b}HgI_2DAPDP$ | | 436–437 | | 438$^{c}$ | | |

[a] Heating rate 10 °C·min$^{-1}$. [b] Not previously reported. [c] DTA maxima at a heating rate of 10 °C·min$^{-1}$ in air at atmospheric pressure. [d] All compounds melted to give clear liquids. [e] Two endotherms recorded. [f] $T_i$ = temperature at which the trace first deviates from the baseline; $T_m$ = temperature at which the enthalpy change is at a maximum; $T_f$ = temperature at which the trace returns to the baseline.

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