Microcalorimetric Studies of the Thermal Decomposition of Ammonia–Halide and Amine–Halide Complexes of Platinum(II), $[Pt(NH_2R)_2X_2]$

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Microcalorimetric measurements at elevated temperatures of the enthalpies of thermal decomposition of selected *cis*-$[PtL_2X_2]$ complexes (L = NH_3, amines, or pyridine; X = Cl, Br, or I) have been used to derive the standard enthalpies of formation, ΔH_f°(c)/kJ mol^{-1}, of the following crystalline compounds: $[Pt(NH_3)_2Cl_2] = -(467 \pm 3)$; $[Pt(NH_3)_2Br_2] = -(404 \pm 7)$; $[Pt(NH_3)_2I_2] = -(295 \pm 6)$; $[Pt(NH_2Me)_2Cl_2] = -(424 \pm 8)$; $[Pt(NH_2Pr^i)_2Cl_2] = -(599 \pm 6)$; $[Pt(NH_2Bu)_2Cl_2] = -(646 \pm 12)$; $[Pt(en)Cl_2] = -(437 \pm 7)$ (en = ethylenediamine); $[Pt(NC_5H_5)_2Cl_2] = -(21 \pm 7)$; $[Pt(NH_2Pr^i)_2Br_2] = -(551 \pm 13)$; $[Pt(NH_2Me)_2I_2] = -(233 \pm 8)$; $[Pt(NH_2Et)_2I_2] = -(334 \pm 6)$; $[Pt(NH_2Pr)_2I_2] = -(424 \pm 9)$; $[Pt(NH_2Pr^i)_2I_2] = -(465 \pm 7)$; $[Pt(NH_2Bu^i)_2I_2] = -(562 \pm 8)$. Attempts to measure the enthalpies of sublimation directly were not successful. An estimated $\Delta H_{sub} \approx 170$ kJ mol^{-1} for the pyridine complex, $[Pt(NC_5H_5)_2Cl_2]$, leads to *ca.* 122 kJ mol^{-1} for the *average* pyridine–platinum bond-dissociation enthalpy [$= \frac{1}{2}\Delta H_D$(g)] in the gaseous molecule. Accepting that the differences in ligand-bonding power of amines reported previously apply to amine–$PtCl_2$ complexes, average bond-dissociation enthalpies are slightly less than with pyridine, falling to $\frac{1}{2}\Delta H_D$(g) = *ca.* 97 kJ mol^{-1} in the case of NH_3. These values imply sublimation heats of the order of 270—300 kJ mol^{-1} in $[Pt(NH_2R)_2Cl_2]$ complexes.

Enthalpies of formation have been reported for the square-planar ammonia–halide complexes of Pt^{II}, obtained mainly from solution-calorimetry studies by Chernyaev and Palkin and co-workers.[1-5] Thermochemical information on amine–halide platinum(II) complexes is totally lacking; differential scanning calorimetric (d.s.c.) studies on the thermal decomposition of the *cis* and *trans* isomers of dichlorobis(pyridine)platinum(II) were briefly reported by Ashcroft and Mortimer,[6] but otherwise few such studies on compounds of this type have been made. The present studies on the thermal decomposition of amine–halide platinum(II) complexes made use of the Calvet high-temperature microcalorimeter, and the 'drop' technique,[7] to measure the enthalpy change for a process (1),

$$[PtL_2X_2](c, 298) \longrightarrow \text{Products } (T) \qquad (1)$$

where T is the temperature of the hot zone in the calorimeter.

The primary decomposition (2) is inadequate to account for

$$[PtL_2X_2](c) \longrightarrow 2L(g,T) + PtX_2(c,T) \qquad (2)$$

the reaction at temperatures >250 °C; in the case of complexes of $PtCl_2$, there is abstraction of chlorine from $PtCl_2$ by the ligand, with formation of HCl and (on cooling) the separation of amine hydrochloride, [HL]Cl. There is some abstraction of bromine from $PtBr_2$ in complexes $[PtL_2Br_2]$, with formation of HBr, and separation of the amine hydrobromide salt; and with complexes $[PtL_2I_2]$, the primary decomposition is accompanied by dissociation of PtI_2 to Pt + I_2 and the appearance of iodine vapour in the hot reaction vessel.

Attempts to sublime these compounds in the microcalorimeter by the vacuum-sublimation technique[8] were not successful. The rate of sublimation was too small at temperatures below 250 °C, and on increasing the temperature, decomposition occurred.

Experimental

Calorimeter.—The Calvet twin-cell high-temperature microcalorimeter (ambient to 1 000 °C; Setaram, Lyon) was adapted to the 'drop-microcalorimetric' technique;[7] the net thermopile output was amplified (NV 724 A nanovoltmeter) and the thermograms recorded (Rikadenki DBE 2). Thermogram areas were simultaneously evaluated by an ITC integrator and printer. The calorimeter was calibrated from sublimation measurements on naphthalene, iodine, and benzoic acid, by use of the microcalorimetric 'vacuum-sublimation' technique.[8]

Compounds.—Samples of *cis*-diamminedichloroplatinum(II) and of dichloro(ethylenediamine)platinum(II) were obtained from Johnson Matthey Ltd. The remaining platinum complexes were synthesized by established methods,[9-13] and characterized by elemental analysis, i.r., ^1H n.m.r., and/or electronic spectra.

Auxiliary Data.—The following auxiliary standard enthalpy of formation data (kJ mol^{-1}) were used in evaluation of the present results: $PtCl_2(c) = -(140.6 \pm 4)$;[14,15] $PtBr_2(c) = -(100 \pm 8)$;[16] $PtI_2(c) = -(60 \pm 8)$;[17] $HCl(g) = -(92.3 \pm 0.1)$;[18] $HBr(g) = -(36.4 \pm 0.2)$;[18] $HI(g) = (26.4 \pm 0.8)$;[18] $I_2(g) = (62.4 \pm 0.1)$;[18] $Br_2(g) = (30.9 \pm 0.1)$;[18] $NH_3(g) = -(45.9 \pm 0.4)$;[18] $NH_2Me(g) = -(23.0 \pm 0.4)$;[19] $NH_2Et(g) = -(47.5 \pm 0.7)$;[19] $NH_2Pr(g) = -(70.2 \pm 0.4)$;[19] $NH_2Pr^i(g) = -(83.8 \pm 0.5)$;[19] $NH_2Bu^n(g) = -(92.0 \pm 2.7)$;[19] $NH_2Bu^i(g) = -(98.9 \pm 0.4)$;[19] $C_2H_4(NH_2)_2(g) = -(17.8 \pm 2.1)$;[19] $NC_5H_5(g) = (140.2 \pm 1.2)$;[20] $NHMe_2(g) = -(18.5 \pm 0.4)$;[19] $NHEt_2(g) = -(72.6 \pm 1.9)$;[19] $NHPr_2(g) = -(116.0 \pm 1.4)$;[19] $NHPr^i_2(g) = -(144.0 \pm 0.4)$;[19] $NHBu_2(g) = -(156.6 \pm 1.5)$;[19] $NHBu^i_2(g) = -(179.2 \pm 0.6)$;[19] $(H_2NCH_2CH_2)_2NH(g) = -(13.2 \pm 5)$ (estimated); $NC_5H_4Cl(g) = (108.8 \pm 5)$ (estimated).

Measured reaction heats, ΔH^T, at elevated temperatures, T,

Table 1. Thermal decomposition of *cis*-$[Pt(NH_3)_2Cl_2]$

Sample mass (mg)	T/K	$\Delta H_3{}^T$/kJ mol^{-1}	$\Delta H_3{}^{298}$/kJ mol^{-1}
1.951	590	260.8	217.4
1.486	590	268.0	224.5
1.511	590	262.1	218.6
1.242	590	263.7	220.2
1.300	615	269.0	220.5
1.914	615	274.2	226.7
			Mean 221.3 ± 3

Table 2. Thermal decomposition of *cis*-$[Pt(NH_3)_2Br_2]$

Sample mass (mg)	T/K	$\Delta H_4{}^T$/kJ mol^{-1}	$\Delta H_4{}^{298}$/kJ mol^{-1}
1.689	653	296.4	241.3
1.631	653	286.3	231.2
1.414	653	294.7	239.6
1.634	676	298.1	239.2
2.210	676	297.9	239.0
			Mean 238.1 ± 4

$\Delta H_f^\ominus[Pt(NH_3)_2Br_2$, *cis*, c$] = -(403.9 \pm 7)$ kJ mol^{-1}

were converted into room-temperature values, ΔH^{298}, using $(H_T - H_{298})$ data tabulated by Stull *et al.*[21] and by Barin and Knacke.[22]

Results

Diamminedichloroplatinum(II), *cis*-$[Pt(NH_3)_2Cl_2]$.—Thermal decomposition in argon, and *in vacuo*, was studied in the microcalorimeter at 590 and 615 K. A bright platinum mirror formed in the capillary-tube sample container and nearby walls of the reaction vessel, and a white powder film (ammonium chloride) settled in the cooler parts of the exit-tube from the hot zone. From analysis of the chlorine content of the soluble white powder, the overall decomposition in the hot zone is approximated by equation (3). The results (Table 1)

$$[Pt(NH_3)_2Cl_2](cis,c,\ 298) \longrightarrow [Pt(c) + 2HCl(g) + \tfrac{4}{3}NH_3(g) + \tfrac{1}{3}N_2(g)](T) \quad (3)$$

are interpreted on this basis, and the derived standard enthalpy of formation $\Delta H_f^\ominus[Pt(NH_3)_2Cl_2$, *cis*, c$] = -(467.2 \pm 3)$ kJ mol^{-1} compares satisfactorily with that $[-(471.7 \pm 6)$ kJ mol$^{-1}]$ obtained by Chernyaev *et al.*[2]

Diamminedibromoplatinum(II) *cis*-$[Pt(NH_3)_2Br_2]$.—Thermal-decomposition studies were made over the range 590—676 K; decomposition was incomplete below 600 K, and even at temperatures >650 K the solid residue was a black powder, contrasting with the shiny metallic mirror formed on decomposition of the dichloro-complex. A white powder (NH_4Br) settled in the cooler exit-tube; Br^- analysis indicated this contained *ca.* 45% of the total bromine in the added complex, the hot-zone decomposition being approximated by equation (4). Results interpreted on the basis of equation (4) are summarized in Table 2. The derived $\Delta H_f^\ominus$ compares reasonably with $-(406.7 \pm 8)$ kJ mol^{-1} reported by Palkin and Kuzina[23] from solution calorimetric studies.

$$[Pt(NH_3)_2Br_2](cis,\ c,\ 298) \longrightarrow 0.45\ Pt(c,T) + 0.55\ PtBr_2(c,T) + (0.9\ HBr + 1.7\ NH_3 + 0.15\ N_2)(g,T) \quad (4)$$

Table 3. Thermal decomposition of $[Pt(NH_3)_2I_2]$

Sample mass (mg)	T/K	$\Delta H_5{}^T$/kJ mol^{-1}	$\Delta H_5{}^{298}$/kJ mol^{-1}
1.732	615	276.9	229.2
1.794	615	287.7	240.0
2.995	615	290.8	243.1
3.137	607	285.7	239.4
3.404	638	290.0	238.6
			Mean 239.2 ± 5

$\Delta H_f^\ominus[Pt(NH_3)_2I_2$, *cis*, c$] = -(295.2 \pm 6)$ kJ mol^{-1}

Table 4. Thermal decomposition of $[Pt(NH_2Me)_2Cl_2]$

Sample mass (mg)	T/K	$\Delta H_6{}^T$/kJ mol^{-1}	$\Delta H_6{}^{298}$/kJ mol^{-1}
2.221	590	268.4	209.7
2.055	590	288.5	229.2
2.503	615	288.9	222.9
1.558	615	290.4	224.4
			Mean 221.6 ± 8

$\Delta H_f^\ominus[Pt(NH_2Me)_2Cl_2$, *cis*, c$] = -(423.6 \pm 8)$ kJ mol^{-1}

Diamminedi-iodoplatinum(II), *cis*-$[Pt(NH_3)_2I_2]$.—Thermal-decomposition studies at 590 K indicated that the initial decomposition to give ammonia and PtI_2 is accompanied by some decomposition of PtI_2, liberating iodine vapour which was visible in the hot reaction vessel on removing it from the microcalorimeter. Decomposition studies at 607—638 K gave a black residue in the capillary-tube container, free iodine vapour, and traces of a white powder admixed with solid iodine which condensed in the exit-tube. The black residue evolved iodine on further heating. Analysis of free iodine, and of iodine retained by the black residue, indicated that the cell reaction at 615—638 K can be approximated by equation (5).

$$[Pt(NH_3)_2I_2](cis,\ c,\ 298) \longrightarrow 0.75\ Pt(c,T) + 0.25\ PtI_2(c,T) + (0.55\ I_2 + 0.4\ HI + 1.87\ NH_3 + 0.065\ N_2)(g,T) \quad (5)$$

Values of $\Delta H_5{}^T$ are given in Table 3, and were evaluated on the basis of equation (5) to derive $\Delta H_f^\ominus$ for the *cis* complex. The solution calorimetric studies of Palkin *et al.*[5] gave $\Delta H_f^\ominus = -(295.4 \pm 7)$ kJ mol^{-1}.

cis-*Dichlorobis*(*methylamine*)*platinum*(II), $[Pt(NH_2Me)_2Cl_2]$.—Thermal-decomposition studies were made over the range 555—615 K. The residue in the reaction zone was shiny black, and the white powder which settled in the exit-tube contained *ca.* 60% of the total chlorine in the added sample. Results (summarized in Table 4) are interpreted for the presumed hot-zone decomposition in equation (6).

$$[Pt(NH_2Me)_2Cl_2](cis,\ c,\ 298) \longrightarrow 0.6\ Pt(c,T) + 0.4\ PtCl_2\ (c,T) + (1.2\ HCl + 1.2\ NH_2Me + 0.4\ NHMe_2 + 0.2\ N_2)(g,T) \quad (6)$$

cis-*Dichlorobis*(*isopropylamine*)*platinum*(II), $[Pt(NH_2Pr^i)_2Cl_2]$.—Thermal-decomposition studies were made at 615 and at 676 K, with results as summarized in Table 5. The solid black residue was admixed with patches of platinum mirror, and the soluble white product in the exit-tube contained 55—

Table 5. Thermal decomposition of $[Pt(NH_2Pr^i)_2Cl_2]$

Sample mass (mg)	T/K	$\Delta H_7{}^T$/kJ mol^{-1}	$\Delta H_7{}^{298}$/kJ mol^{-1}
1.532	615	380.1	274.4
2.115	615	384.4	278.7
1.980	615	384.7	279.0
1.596	615	383.6	277.9
2.345	676	395.2	264.5
1.683	676	397.5	266.8
2.007	676	408.3	277.6
			Mean 274.1 ± 5

$\Delta H_f^\ominus[Pt(NH_2Pr^i)_2Cl_2$, *cis*, c$] = -(599.3 \pm 6)$ kJ mol^{-1}

Table 6. Thermal decomposition of $[Pt(NH_2Bu)_2Cl_2]$

Sample mass (mg)	T/K	$\Delta H_8{}^T$/kJ mol^{-1}	$\Delta H_8{}^{298}$/kJ mol^{-1}
1.974	615	419.9	294.1
1.392	615	448.9	323.1
1.993	615	442.6	316.8
1.906	615	439.7	313.9
2.646	676	448.1	292.4
2.124	676	453.4	297.7
			Mean 306.3 ± 11

$\Delta H_f^\ominus[Pt(NH_2Bu)_2Cl_2$, *cis*, c$] = -(646.5 \pm 12)$ kJ mol^{-1}

Table 7. Thermal decomposition of $[Pt(NC_5H_5)_2Cl_2]$

Sample mass (mg)	T/K	$\Delta H_9{}^T$/kJ mol^{-1}	$\Delta H_9{}^{298}$/kJ mol^{-1}
1.409	551	248.8	173.4
1.690	551	243.2	167.8
1.615	551	240.4	165.0
2.065	551	247.4	172.0
2.264	586	271.5	183.8
2.015	586	249.1	161.4
3.600	615	286.9	188.4
1.395	615	274.6	176.1
3.159	615	259.9	161.4
			Mean 172.1 ± 6

$\Delta H_f^\ominus[Pt(NC_5H_5)_2Cl_2$, *cis*, c$] = -(20.6 \pm 7)$ kJ mol^{-1}

Table 8. Thermal decomposition of $[Pt(en)Cl_2]$

Sample mass (mg)	T/K	$\Delta H_{10}{}^T$/kJ mol^{-1}	$\Delta H_{10}{}^{298}$/kJ mol^{-1}
1.756	615	324.6	261.7
1.270	615	316.0	253.1
1.457	615	330.5	267.6
1.603	615	324.8	261.9
			Mean 261.1 ± 6

$\Delta H_f^\ominus[Pt(en)Cl_2$, c$] = -(436.9 \pm 7)$ kJ mol^{-1}

Table 9. Thermal decomposition of $[Pt(NH_2Pr^i)_2Br_2]$

Sample mass (mg)	T/K	$\Delta H_{11}{}^T$/kJ mol^{-1}	$\Delta H_{11}{}^{298}$/kJ mol^{-1}
1.832	615	400.3	293.7
1.868	615	408.6	302.0
2.465	615	398.9	292.3
1.653	615	428.1	321.5
1.278	615	416.2	309.6
3.904	635	435.0	320.1
			Mean 306.5 ± 12

$\Delta H_f^\ominus[Pt(NH_2Pr^i)_2Br_2$, *cis*, c$] = -(551.2 \pm 13)$ kJ mol^{-1}

60% of total chlorine in the added sample. The hot-zone reaction was presumed to follow the pattern for the methylamine complex, equation (7).

$$[Pt(NH_2Pr^i)_2Cl_2](cis,\ c,\ 298) \longrightarrow 0.6\ Pt\ (c,T) + 0.4\ PtCl_2(c,T) + (1.2\ HCl + 1.2\ NH_2Pr^i + 0.4\ NHPr^i{}_2 + 0.2\ N_2)(g,T) \quad (7)$$

cis-*Bis(butylamine)dichloroplatinum*(II), $[Pt(NH_2Bu)_2Cl_2]$.—Thermal-decomposition studies were made at 615 and 676 K, giving a black residue, small patches of platinum mirror, and a white powder which contained *ca.* 60% of the total chlorine in the added sample. Results are listed in Table 6, interpreted on the basis of the presumed decomposition (8).

$$[Pt(NH_2Bu)_2Cl_2]\ (cis,\ c,\ 298) \longrightarrow 0.6\ Pt\ (c,T) + 0.4\ PtCl_2(c,\ T) + (1.2\ HCl + 1.2\ NH_2Bu + 0.4\ NHBu_2 + 0.2\ N_2)(g,T) \quad (8)$$

cis-*Dichlorobis(pyridine)platinum*(II), *cis*-$[Pt(NC_5H_5)_2Cl_2]$.—Thermal-decomposition studies were made over the range 530—615 K. The residue in the capillary tube container was a black deposit, and the white film which settled in the exit-tube was soluble in water. Analysis for Cl^- indicated this to contain *ca.* 35% of the total chlorine present in the added sample. The measured $\Delta H_9{}^T$ (Table 7) are interpreted on the basis of the presumed hot-zone reaction (9).

$$[Pt(NC_5H_5)_2Cl_2]\ (cis,\ c,\ 298) \longrightarrow 0.3\ PtCl_2(c,T) + 0.7\ Pt(c,T) + (1.3\ NC_5H_5 + 0.7\ NC_5H_4Cl + 0.7\ HCl)(g,T) \quad (9)$$

Dichloro(ethylenediamine)platinum(II), $[Pt(en)Cl_2]$.—Thermal-decomposition measurements at 615 K gave a shiny black residue, and a white powder which settled in the exit-tube. The soluble white powder, analysed for Cl^-, contained *ca.* 60% of the total chlorine in the added sample. Results (Table 8) are interpreted on the basis of the presumed hot-zone reaction (10).

$$[Pt(en)Cl_2](c,\ 298) \longrightarrow 0.6\ Pt(c,T) + 0.4\ PtCl_2(c,T) + [0.2\ en + 0.4\ (H_2NCH_2CH_2)_2NH + 1.2\ HCl + 0.2\ N_2](g,T) \quad (10)$$

cis-*Dibromobis(isopropylamine)platinum*(II), $[Pt(NH_2Pr^i)_2Br_2]$.—Thermal-decomposition studies were made at 615 and 635 K. The black shiny deposit in the capillary tube container was admixed with patches of platinum mirror, and the white powder which settled in the exit-tube contained *ca.* 55% of the total bromine present in the added sample. The measured $\Delta H_{11}{}^T$ (Table 9) are interpreted for the presumed cell reaction (11).

$$[Pt(NH_2Pr^i)_2Br_2](cis,\ c,\ 298) \longrightarrow 0.55\ Pt(c,T) + 0.45\ PtBr_2(c,T) + (1.10\ HBr + 1.27\ NH_2Pr^i + 0.37\ NHPr^i{}_2 + 0.18\ N_2)(g,T) \quad (11)$$

cis-*Di-iodobis(methylamine)platinum*(II), $[Pt(NH_2Me)_2I_2]$.—Thermal-decomposition studies were made at 619 and 655 K, giving a black shiny residue, free iodine, and traces of a white product. Analysis of free iodine, and of bound iodine in the

Table 10. Thermal decomposition of $[Pt(NH_2Me)_2I_2]$

Sample mass (mg)	T/K	ΔH_{12}^{T}/kJ mol^{-1}	ΔH_{12}^{298}/kJ mol^{-1}
1.960	619	277.9	212.7
2.151	619	282.7	217.5
2.093	619	296.2	231.0
2.334	619	280.9	215.7
1.312	655	298.8	225.0
			Mean 220.4 ± 7

$\Delta H_f^{\circ}[Pt(NH_2Me)_2I_2, cis, c] = -(233.3 \pm 8)$ kJ mol^{-1}

Table 11. Thermal decomposition of $[Pt(NH_2Et)_2I_2]$

Sample mass (mg)	T/K	ΔH_{13}^{T}/kJ mol^{-1}	ΔH_{13}^{298}/kJ mol^{-1}
3.199	619	357.4	270.9
2.193	619	350.8	264.3
2.333	619	355.6	269.1
2.896	619	364.0	277.5
2.611	655	376.7	278.5
			Mean 272.1 ± 5

$\Delta H_f^{\circ}[Pt(NH_2Et)_2I_2, cis, c] = -(334.5 \pm 6)$ kJ mol^{-1}

black residue, indicated the cell reaction to be approximated by equation (12). The measured ΔH_{12}^{T} are listed in Table 10, and interpreted according to equation (12).

$$[Pt(NH_2Me)_2I_2](cis, c, 298) \longrightarrow 0.75\,Pt(c,T) + 0.25\,PtI_2(c,T) + (1.8\,NH_2Me + 0.6\,I_2 + 0.3\,HI + 0.1\,NHMe_2 + 0.05\,N_2)(g,T) \quad (12)$$

cis-*Bis(ethylamine)di-iodoplatinum*(II), $[Pt(NH_2Et)_2I_2]$.—Thermal-decomposition studies were made at 619 and 655 K; the free iodine liberated amounted to 60—65% of the total iodine content. Results in Table 11 are based on the presumed hot-zone reaction (13).

$$[Pt(NH_2Et)_2I_2](cis, c, 298) \longrightarrow 0.75\,Pt(c,T) + 0.25\,PtI_2(c,T) + (1.8\,NH_2Et + 0.1\,NHEt_2 + 0.6\,I_2 + 0.3\,HI + 0.05\,N_2)(g,T) \quad (13)$$

cis-*Di-iodobis(propylamine)platinum*(II) $[Pt(NH_2Pr)_2I_2]$.—Thermal-decomposition measurements were made at 640 K; analysis of products indicated that 70—75% of the iodine content was liberated as iodine vapour. The results, interpreted in terms of the presumed cell reaction (14), are summarized in Table 12.

$$[Pt(NH_2Pr)_2I_2]\ (cis, c, 298) \longrightarrow 0.8\,Pt(c,T) + 0.2\,PtI_2(c,T) + (0.7\,I_2 + 0.2\,HI + 1.87\,NH_2Pr + 0.07\,NHPr_2 + 0.03\,N_2)(g,T) \quad (14)$$

cis-*Di-iodobis(isopropylamine)platinum*(II), $[Pt(NH_2Pr^i)_2I_2]$.—Thermal-decomposition studies were made from 619 to 663 K, with results as summarized in Table 13. These are interpreted for the presumed cell reaction (15) indicated from analysis of free iodine in the reaction products.

$$[Pt(NH_2Pr^i)_2I_2](cis, c, 298) \longrightarrow 0.75\,Pt(c,T) + 0.25\,PtI_2(c,T) + (1.8\,NH_2Pr^i + 0.1\,NHPr^i_2 + 0.6\,I_2 + 0.3\,HI + 0.05\,N_2)(g,T) \quad (15)$$

Table 12. Thermal decomposition of $[Pt(NH_2Pr)_2I_2]$

Sample mass (mg)	T/K	ΔH_{14}^{T}/kJ mol^{-1}	ΔH_{14}^{298}/kJ mol^{-1}
2.275	640	426.7	311.8
2.541	640	443.8	328.9
2.145	640	441.3	326.4
2.155	640	433.6	318.7
			Mean 321.5 ± 9

$\Delta H_f^{\circ}[Pt(NH_2Pr)_2I_2, cis, c] = -(423.9 \pm 9$ kJ) mol^{-1}

Table 13. Thermal decomposition of $[Pt(NH_2Pr^i)_2I_2]$

Sample mass (mg)	T/K	ΔH_{15}^{T}/kJ mol^{-1}	ΔH_{15}^{298}/kJ mol^{-1}
2.722	619	424.8	318.3
2.021	619	436.2	329.7
2.469	619	432.1	325.6
2.389	619	437.7	331.2
2.571	655	455.1	333.9
2.333	655	466.9	345.7
2.416	663	448.0	323.6
			Mean 329.7 ± 6

$\Delta H_f^{\circ}[Pt(NH_2Pr^i)_2I_2, cis, c] = -(464.6 \pm 7)$ kJ mol^{-1}

Table 14. Thermal decomposition of $[Pt(NH_2Bu^i)_2I_2]$

Sample mass (mg)	T/K	ΔH_{16}^{T}/kJ mol^{-1}	ΔH_{16}^{298}/kJ mol^{-1}
2.451	629	521.8	389.8
1.804	629	535.8	403.8
2.991	629	531.7	399.7
2.386	655	531.7	387.0
2.708	655	548.7	404.0
			Mean 396.9 ± 7

$\Delta H_f^{\circ}[Pt(NH_2Bu^i)_2I_2, cis, c] = -(562.3 \pm 8)$ kJ mol^{-1}

cis-*Di-iodobis(isobutylamine)platinum*(II), $[Pt(NH_2Bu^i)_2I_2]$.—Thermal-decomposition studies were made at 629 and 655 K. The free iodine formed amounted to *ca.* 60% of the total iodine in the added sample, and the results (Table 14) are evaluated for the presumed hot-zone reaction (16).

$$[Pt(NH_2Bu^i)_2I_2](cis, c, 298) \longrightarrow 0.75\,Pt(c,T) + 0.25\,PtI_2(c,T) + (1.8\,NH_2Bu^i + 0.1\,NHBu^i_2 + 0.6\,I_2 + 0.3\,HI + 0.05\,N_2)(g,T) \quad (16)$$

Discussion

The derived enthalpies of formation, $\Delta H_f^{\circ}(c)$, of the crystalline complexes are listed in Table 15. The quoted error limits include uncertainties in auxiliary data, but do not allow for deviations of the actual thermal-decomposition process from the presumed reaction. (Complete analysis of decomposition products was not attempted.) Table 15 includes the derived enthalpies of dissociation, $\Delta H_D(c)$, for ligand removal at 298 K [equations (17a) and (17b)]. The variations in $\Delta H_D(c)$ for these amine ligands are shown diagrammatically in the Figure.

$$[PtL_2X_2](c) \longrightarrow 2L(g) + PtX_2(c) \quad (17a)$$

$$[Pt(en)X_2](c) \longrightarrow en(g) + PtX_2(c) \quad (17b)$$

Table 15. Values (kJ mol^{-1}) of $\Delta H_f^\ominus$(c) and ΔH_D(c) for $[PtL_2X_2]$

Compound	$\Delta H_f^\ominus$(c)	ΔH_D(c)
cis-$[Pt(NH_3)_2Cl_2]$	$-(467 \pm 3)$	235 ± 3
cis-$[Pt(NH_2Me)_2Cl_2]$	$-(424 \pm 8)$	237 ± 8
cis-$[Pt(NH_2Pr^i)_2Cl_2]$	$-(599 \pm 6)$	291 ± 6
cis-$[Pt(NH_2Bu)_2Cl_2]$	$-(646 \pm 12)$	321 ± 12
$[Pt(en)Cl_2]$	$-(437 \pm 7)$	279 ± 7
cis-$[Pt(NC_5H_5)_2Cl_2]$	$-(21 \pm 7)$	161 ± 7
cis-$[Pt(NH_3)_2Br_2]$	$-(404 \pm 7)$	212 ± 7
cis-$[Pt(NH_2Pr^i)_2Br_2]$	$-(551 \pm 13)$	283 ± 13
cis-$[Pt(NH_3)_2I_2]$	$-(295 \pm 6)$	143 ± 6
cis-$[Pt(NH_2Me)_2I_2]$	$-(233 \pm 8)$	130 ± 8
cis-$[Pt(NH_2Et)_2I_2]$	$-(334 \pm 6)$	181 ± 6
cis-$[Pt(NH_2Pr)_2I_2]$	$-(424 \pm 9)$	224 ± 9
cis-$[Pt(NH_2Pr^i)_2I_2]$	$-(465 \pm 7)$	237 ± 7
cis-$[Pt(NH_2Bu^i)_2I_2]$	$-(562 \pm 8)$	304 ± 8

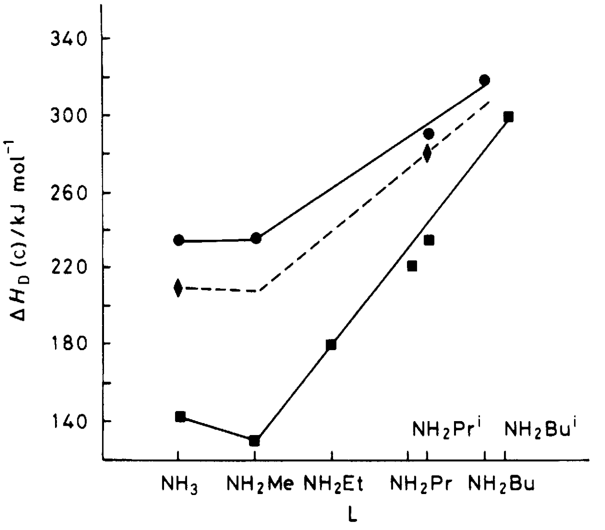

Figure. ΔH_D(c) values for amine ligands in $[PtL_2X_2]$: X = Cl (●), Br (♦), and I (■)

Evaluation of the ligand-bonding power of the amine donors requires values of the enthalpies, ΔH_D(g), of the *gaseous-phase* disruptions (18) which are related to the measured ΔH_D(c) through equation (19). The enthalpies of

$$[PtL_2X_2](g) \longrightarrow 2L(g) + PtX_2(g) \qquad (18)$$

$$\Delta H_D(g) = \Delta H_D(c) + \Delta H_{sub}(PtX_2) - \Delta H_{sub}(PtL_2X_2) \qquad (19)$$

sublimation are, however, not available, except for ΔH_{sub}-($PtCl_2$). The crystal structure of $[Pt(NH_3)_2Cl_2]$, reported by Milburn and Truter,[24] implies hydrogen bonding, N-H · · · Cl, each N forming two hydrogen bonds to a neighbouring chlorine. The sublimation energies of $[Pt(NH_2R)_2X_2]$ complexes are presumably enhanced in all cases by this effect. In the pyridine complex, $[Pt(NC_5H_5)_2Cl_2]$, this cannot apply, and the low ΔH_D(c) value may reflect a relatively low sublimation energy in this case. The vacuum-sublimation microcalorimetric technique has been satisfactorily applied to trialkylphosphine complexes of $PtCl_2$, including *cis*- and *trans*-$[Pt(PEt_3)_2Cl_2]$;[25] the crystal structure of the latter, determined by Messmer and Amma,[26] indicated van der Waals interactions only between molecules in the crystal. This suggests that the ΔH_{sub} value for $[Pt(NC_5H_5)_2Cl_2]$ may be within the range of known ΔH_{sub} for trialkylphosphine–$PtCl_2$ complexes of comparable molecular weight. On this basis, we estimate that $\Delta H_{sub}[Pt(NC_5H_5)_2Cl_2] \approx (170 \pm 10)$ kJ mol^{-1}; the value $\Delta H_{sub}(PtCl_2) \approx 252 \pm 9$ kJ mol^{-1} follows from the high-temperature studies by Schaefer,[27] giving $\Delta H_f^\ominus(PtCl_2, g) = 111 \pm 8$ kJ mol^{-1}. Substituting these values into equation (19) leads to ΔH_D(g) for $[Pt(NC_5H_5)_2Cl_2]$ of *ca.* 243 ± 16 kJ mol^{-1}, as a measure of the heat required to remove the two pyridine ligands from the gaseous complex molecule.

Recent ion-cyclotron resonance spectral studies by Kappes and Staley[28] on gaseous complex ions, $[NiL_2]^+$ and $[FeL_2Br]^+$ (L = NH_3, amines, or pyridine), have established the relative order of ligand-bonding power of these nitrogen donors to Ni^+ as $NC_5H_5 > NH_2Pr^i > NH_2Et > NH_2Me > NH_3$. The difference between ΔH_D(g) for $[Ni(NC_5H_5)_2]^+$ and $[Ni(NH_3)_2]^+$ amounts to *ca.* 50 kJ mol^{-1}. Accepting that the differences in ligand-bonding power reported by Kappes and Staley apply to amine–$PtCl_2$ complexes, we obtain the ΔH_D(g) and ΔH_{sub} values shown below. The high sublimation heats for amine ligands are consistent with appreciable intermolecular bonding (*e.g.* hydrogen bonding) in the crystal state. The relatively high ΔH_D(c) value for $[Pt(en)Cl_2]$ points to a ligand-bonding power for ethylenediamine comparable with NH_2Pr rather than with NH_2Me. The lack of ΔH_{sub} values for $PtBr_2$ and PtI_2 prevents a similar evaluation of ΔH_D(g) values for the $[PtL_2Br_2]$ and $[PtL_2I_2]$ complexes.

Compound	ΔH_D(g)/kJ mol^{-1}	ΔH_{sub}/kJ mol^{-1}
cis-$[Pt(NH_3)_2Cl_2]$	193 ± 16	294 ± 16
cis-$[Pt(NH_2Me)_2Cl_2]$	216 ± 16	273 ± 18
cis-$[Pt(NH_2Pr^i)_2Cl_2]$	235 ± 16	308 ± 17
cis-$[Pt(NC_5H_5)_2Cl_2]$	243 ± 16	170 ± 10

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