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*In celebration of the $60^{th}$ birthday of Dr. Andrew K. Galwey*

# SOLID, PRIMARY ALIPHATIC AMINE COMPLEXES OF TRANSITION METAL HALIDES*

# II. Thermal analysis studies of $RNH_2$ complexes of cadmium(II) chloride

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## Abstract

The thermal decomposition of some new primary aliphatic amine $RNH_2$ ($R$ =methyl-, ethyl-, *n*-propyl, *i*-propyl, *n*-butyl-, *i*-butyl-, *n*-amyl-, *i*-amyl-, cyclohexyl- and *i*-allyl-) complexes with cadmium(II) chloride, prepared by solid-gas phase chemisorption, have been investigated by simultaneous TG-DTG-DTA. The enthalpy changes during the degradation were followed by DSC. The course of the thermal decomposition is described in detail. The thermal properties observed were compared to the more recently reported nickel(II) analogues. The changes in thermal parameters in the series of cadmium(II) chloride aliphatic amine complexes are discussed on the basis of the inductive releasing effect of the aliphatic chain and the steric hindrance of the ligands.

**Keywords:** DSC, amine complexes, metal halides, TG-DTG-DTA

## Introduction

Since the early 1950's interest in the thermal properties of ammine and pyridine type complexes of transition metal halides has grown [1–3]. The thermal decomposition of these monodentate-ligand containing complexes starts with the fission of the metal-ligand coordinate bond and thus the thermal stability depends on the strength of this bond. While the thermal degradation of these

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complexes has been described in detail, little information is available in the literature concerning the primary aliphatic amine analogs [4–6]. The thermal properties of a series of primary aliphatic amine compounds are of interest, because of the expected changes in thermal properties from ammonia to pyridine type ligands, and to identify trends in thermal properties within the primary, secondary and tertiary amine complexes.

The relative scarcity of information available in the literature concerning the solid primary aliphatic amine complexes is probably due to the difficulties in preparation. Ephraim and Linn [4] reported on an apparatus developed for the preparation of primary aliphatic amine complexes. In addition to the compounds formed with zinc(II), cobalt(II), nickel(II), iron(II), copper(II) and manganese(II) halides, they described the dibromo- and diiodo-tris (methylamine)cadmium(II) derivatives.

We recently reported on the application of a solid-gas phase preparation method to obtain quaternary mixed pyridine type complexes [7–9], and primary aliphatic amine complexes of nickel(II) chloride [10]. This paper reports on the ternary mixed aliphatic amine derivatives formed with cadmium(II) chloride.

## Experimental

In the preparation, cadmium(II) chloride 2.5 hydrate (Reanal p.a.) and methyl-, ethyl- (Jansen Chimica, 40 and 70% aqueous solutions respectively), *n*-propyl-, *i*-propyl-, *n*-buthyl-, *i*-buthyl-, *n*-amyl, *i*-amyl-, cyclohexyl- and *i*-allylamine (Jansen Chimica 98–99%) were used.

The cadmium(II) chloride was dehydrated at 300°C in a drying oven and ground in a mortar carefully. The powdered chloride was then placed into the vapour of different primary aliphatic amines. The progress of the reaction could not be followed easily compared to the work with the nickel(II) analogues, because both the starting materials and the products are colourless. However, a large increase in volume was observed during the reaction.

The simultaneous TG-DTG-DTA curves were recorded on a Seiko TG/DTA 320 instrument (series SSC 5200) with a sample mass of 5 mg and aluminium crucibles in argon atmosphere (80 ml/min), with α-aluminium-oxide as the reference material. The ligand content was calculated from the thermogravimetric curves, because the cadmium(II) chloride is stable up to the temperature limit has been used.

The enthalpy changes were measured using a Perkin-Elmer DSC-7, with the same experimental conditions as in the simultaneous measurements. The instrument was calibrated by use of the enthalpy of fusion of indium.

The water content of the complexes was checked using a Perkin-Elmer TGA-7 thermogravimetric analyser interfaced with an INFICON IQ 2000 mass spectrometer [11].

## Results

Table 1 summarizes the results of the thermoanalytical investigations. In addition to the tittle compounds, results for the ammine analogue, prepared in the same way, are also presented.

The decomposition of the bis-ammine complex takes place in two separate steps:

$$[Cd(NH_3)_2Cl_2] \rightarrow [Cd(NH_3)Cl_2] + NH_3 \tag{1}$$

$$[Cd(NH_3)Cl_2] \rightarrow CdCl_2 + NH_3 \tag{2}$$

When the solid-gas phase preparation method was used, we obtained the bis-ammine complex, although the hexakis-derivative prepared from solution is better known in the literature [12]. After the release of the first four ligands, the thermal decomposition of the hexakis-derivative is similar to that described above [13].

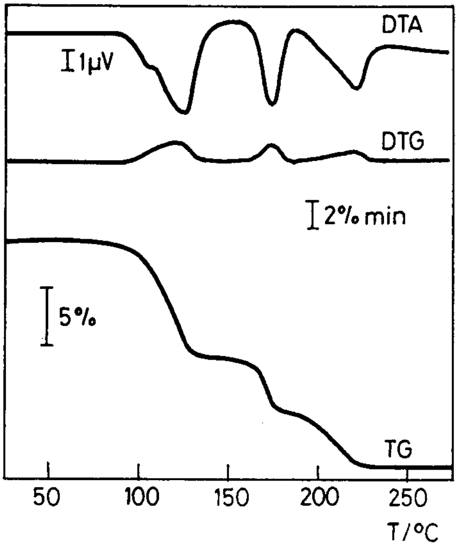

**Fig. 1** Thermal decomposition of dichloro-bis(methylamine)-cadmium(II)

**Table 1** Thermoanalytical data of ternary mixed cadmium(II) chloride aliphatic amine complexes

| Compound | Eq. No. | TG<br>$\Delta m_{calc.}$/ % | <br>$\Delta m_{found}$/ % | <br>$\Delta(\Delta m)$ / % | DTG<br>$T_{max.}$/ °C | DTA<br>$T_{max.}$/ °C | <br>$\Delta T$ / $\mu$Vs·mg$^{-1}$ | DSC<br>$T_{max.}$/ °C | <br>$\Delta H$ / J·g$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| $[Cd(NH_3)_2Cl_2]$ | (1) | 7.8 | 7.9 | 0.1 | 185 | 187 | 262 | 215 | 331.1 |
| $[Cd(NH_3)Cl_2]$ | (2) | 7.8 | 7.8 | 0.0 | 232 | 235 | 219 | 251 | 287.5 |
| $[Cd(MeNH_2)_2Cl_2]$ | (3) | 12.6 | 12.7 | 0.1 | 122 | 124 | 242 | 119 | 483.2 |
| $[Cd(MeNH_2)Cl_2]$ | (4) | 6.3 | 5.9 | −0.4 | 171 | 173 | 90 | 161 | 214.0 |
| $[Cd(MeNH_2)_{0.5}Cl_2]$ | (5) | 6.3 | 6.3 | 0.0 | 216 | 221 | 81 | 218 | 111.6 |
| $[Cd(EtNH_2)_2Cl_2]$ | (6) | 16.5 | 16.5 | 0.0 | 127 | 128 | 335 | 148 | 338.6 |
| $[Cd(EtNH_2)Cl_2]$ | (7) | 10.9 | 9.5 | −1.4 | 165 | 168 | 158 | 190 | 165.1 |
| $[Cd(EtNH_2)_{1/3}Cl_2]$ | (8) | 5.5 | 6.5 | 1.0 | 204 | 208 | 75 | 236 | 116.4 |
| $[Cd(n\text{–}PrNH_2)_2Cl_2]$ | – | – | – | – | – | 74 | 6 | 74 | 8.12 |
| $[Cd(n\text{–}PrNH_2)_2Cl_2]$ | (6) | 19.6 | 19.4 | −0.2 | 108 | 109 | 261 | 122, 135 | 241.1 |
| $[Cd(n\text{–}PrNH_2)Cl_2]$ | (7) | 13.1 | 12.5 | −0.6 | 179 | 180 | 106 | 212 | 124.4 |
| $[Cd(n\text{–}PrNH_2)_{1/3}Cl_2]$ | (8) | 6.5 | 6.7 | 0.2 | 205 | 208 | 52 | 242 | 88.7 |
| $[Cd(i\text{–}PrNH_2)_2Cl_2]$ | (6) | 19.6 | 16.7 | −2.9 | 70 | 72 | 141 | 90 | 129.4 |
| $[Cd(i\text{–}PrNH_2)Cl_2]$ | (12) | 6.5 | 7.4 | 0.9 | 169 | 170 | 67 | 190 | 59.5 |
| $[Cd(i\text{–}PrNH_2)_{2/3}C_2]$ | (13) | 13.1 | 11.8 | −1.3 | 203 | 208 | 71 | 237 | 73.9 |
| $[Cd(n\text{–}BuNH_2)_2Cl_2]$ | (6) | 22.2 | 22.0 | −0.2 | 122 | 124 | 318 | 140, 159 | 275.4 |
| $[Cd(n\text{–}BuNH_2)Cl_2]$ | (7) | 14.8 | 15.0 | 0.2 | 199 | 201 | 76 | 241 | 79.3 |
| $[Cd(n\text{–}BuNH_2)_{1/3}Cl_2]$ | (8) | 7.4 | 7.0 | -0.4 | 217 | 221 | 54 | 259 | 59.5 |

**Table 1** Continued

| Compound | * | TG |  |  | DTG | DTA |  | DSC |  |
|---|---|---|---|---|---|---|---|---|---|
|  | Eq. No. | $\Delta m_{\text{calc.}}$/ % | $\Delta m_{\text{found}}$/ % | $\Delta(\Delta m)$ / % | $T_{\text{max.}}$/ °C | $T_{\text{max.}}$/ °C | $\Delta T$ / $\mu$Vs·mg$^{-1}$ | $T_{\text{max.}}$/ °C | $\Delta H$ / J·g$^{-1}$ |
| [Cd($i$–BuNH$_2$)$_2$(H$_2$O)$_2$Cl$_2$] | (14) | 13.3 | 13.0 | –0.3 | 49 | 51 | – | 67 | – |
| [Cd($i$–BuNH$_2$)$_{4/3}$(H$_2$O)$_2$Cl$_2$] | (15) | 6.7 | 7.3 | 0.6 | 69 | 70 | 228 | 77 | 156.6 |
| [Cd($i$–BuNH$_2$)(H$_2$O)$_2$Cl$_2$] | (16) | 9.8 | 9.9 | 0.1 | 97 | 98 | – | 115 | 84.6 |
| [Cd($i$–BuNH$_2$)$_2$Cl$_2$] | (12)-(13) | 20.3 | 19.1 | –1.2 | 218 | 220 | 125 | 246, 255 | 154.9 |
| [Cd($n$–amylNH$_2$)$_2$Cl$_2$] | (9) | 12.2 | 11.8 | –0.4 | 117 | 117 | 230 | 134 | 231.8 |
| [Cd($n$–AmylNH$_2$)$_{1.5}$Cl$_2$] | (10) | 12.2 | 12.3 | 0.1 | 129 | 130 | – | 156 | – |
| [Cd($n$–AmylNH$_2$)Cl$_2$] | (7)-(8) | 24.4 | 24.0 | –0.4 | 213 | 219 | 106 | 236, 250 | 170.5 |
| [Cd($i$–AmylNH$_2$)$_2$Cl$_2$] | (9) | 12.2 | 11.5 | –0.7 | 68 | 70 | 100 | 89 | 65.2 |
| [Cd($i$–AmylNH$_2$)$_{1.5}$Cl$_2$] | (10) | 12.2 | 12.2 | 0.0 | 123 | 124 | 103 | 150 | 95.0 |
| [Cd($i$–AmylNH$_2$)Cl$_2$] | (12)-(13) | 24.4 | 23.9 | –0.5 | 217 | 221 | 161 | 252 | 174.4 |
| [Cd(CyclohexylNH$_2$)$_4$Cl$_2$] | (11) | 34.2 | 34.0 | –0.2 | 70 | 71 | 232 | 90 | 171.9 |
| [Cd(CyclohexylNH$_2$)$_2$Cl$_2$] | (6) | 17.1 | 17.0 | –0.1 | 123 | 124 | 160 | 146 | 131.1 |
| [Cd(CyclohexylNH$_2$)Cl$_2$] | (7) | 11.4 | 11.4 | 0.0 | 221 | 222 | 62 | 249 | 62.7 |
| [Cd(CyclohexylNH$_2$)$_{1/3}$Cl$_2$] | (8) | 5.7 | 5.5 | –0.2 | 250 | 255 | 21 | 276 | 38.0 |
| [Cd($i$–AllylNH$_2$)$_2$Cl$_2$] | – | – | – | – | – | 62 | 11 | 62 | 10.0 |
| [Cd($i$–AllylNH$_2$)$_2$Cl$_2$] | (17) | 12.8 | 13.0 | 0.2 | 124 | 125 | 121 | 145 | 90.4 |
| [Cd($i$–AllylNH$_2$)$_{4/3}$Cl$_2$] | (18) | 25.6 | 25.8 | 0.2 | 217 | 220 | 131 | 247 | 195.6 |

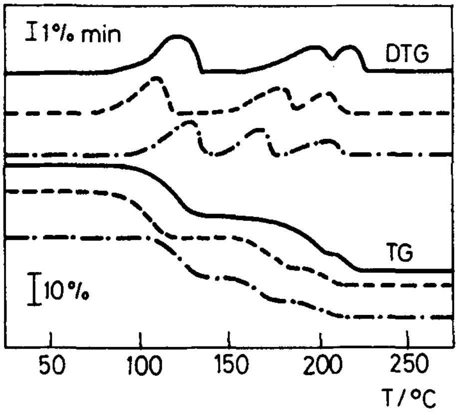

**Fig. 2** Thermal decomposition of dichloro-bis(ethylamine)-cadmium(II) — · — · —; dichloro-bis(*n*-propylamine)-cadmium(II) — — —; dichloro-bis(*n*-butylamine)-cadmium(II) ———

The thermal degradation of the bis-methylamine complex is somewhat different from that of the bis-ammine analogue. The first decomposition step of the bis-methylamine complex is the same as that observed for the ammine compound, but he last mole of the methylamine ligand decomposes in two separate steps, thus a half mole of methylamine containing intermediate is formed (Fig. 1):

$$[Cd(MeNH_2)_2Cl_2] \rightarrow [Cd(MeNH_2)Cl_2] + MeNH_2 \qquad (3)$$

$$[Cd(MeNH_2)Cl_2] \rightarrow [Cd(MeNH_2)_{0.5}Cl_2] + 0.5MeNH_3 \qquad (4)$$

$$[Cd(MeNH_2)_{0.5}Cl_2] \rightarrow CdCl_2 + 0.5MeNH_2 \qquad (5)$$

The existence of the complex containing half mole of the ligand is obvious in coordination chemistry [1]. This stoichiometry can be realized either by a binuclear or a polymeric structure.

The thermal decompositions of the bis-ethyl-, bis-*n*-propyl- and bis-*n*-butylamine complexes occur in similar steps (Fig. 2):

$$[Cd(L)_2Cl_2] \rightarrow [Cd(L)Cl_2] + L \qquad (6)$$

$$[Cd(L)Cl_2] \rightarrow [Cd(L)_{1/3}Cl_2] + 2/3L \qquad (7)$$

$$[Cd(L)_{1/3}Cl_2] \rightarrow CdCl_2 + 1/3L \qquad (8)$$

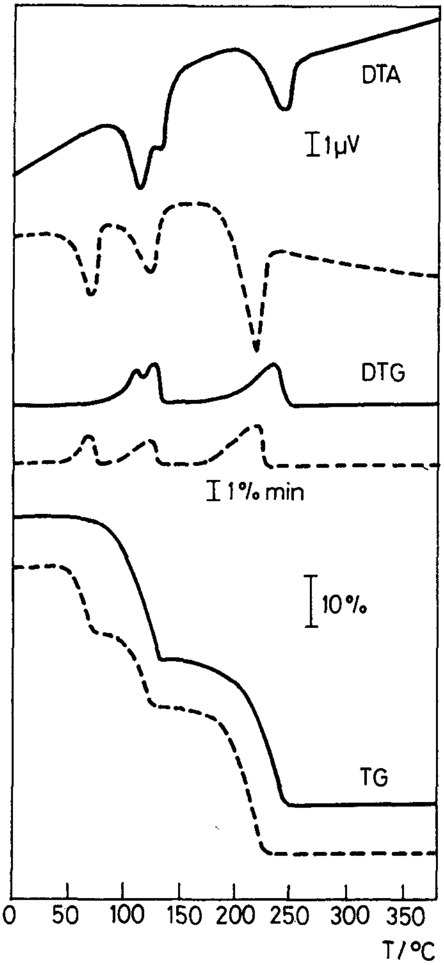

**Fig. 3** Thermal decomposition of dichloro-bis(*n*-amylamine)-cadmium(II) ———; dichloro-bis(*i*-amylamine)-cadmium(II) — — —

In the course of the thermal decomposition, intermediates containing one and one-third ligand were identified. Complexes having two-third or one-third mole of ligands are also well known in the thermoanalytical literature of transition metal complexes [1, 2]. For the *n*-propylamine derivative, an endothermic peak, assigned to a structural change, precedes the endothermic effects of the main decomposition as identified on the DTA and DSC curves. The endothermic peak related to the release of the first mole of the ligand splits into two peaks on the DSC curves of the *n*-propyl- and *n*-butylamine complexes. However, a single peak was observed for the ethylamine derivative.

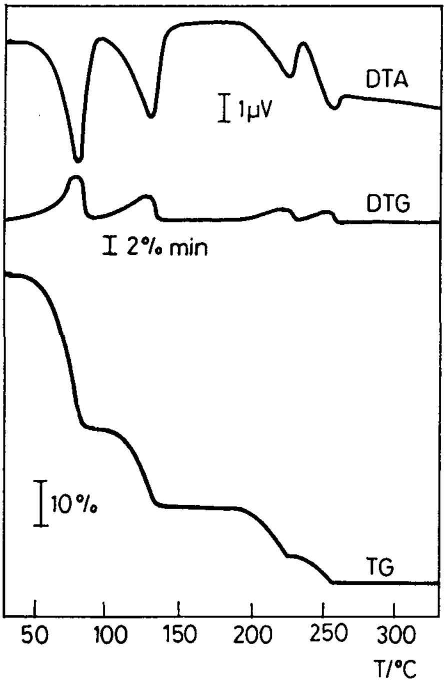

**Fig. 4** Thermal decomposition of dichloro-tetrakis(cyclohexylamine)-cadmium(II)

The DTG and DTA peaks for reactions (7) and (8) are less separated and shifted towards higher temperatures compared to those for the ethyl- to the *n*-butylamine compounds.

The release of the first mole of the ligand is separated into two distinct steps for the bis-*n*-amylamine complex (Fig. 3):

$$[Cd(n\text{-amylNH}_2)_2Cl_2] \rightarrow [Cd(n\text{-amylNH}_2)_{1.5}Cl_2] + 0.5n\text{-amylNH}_2 \quad (9)$$

$$[Cd(n\text{-amylNH}_2)_{1.5}Cl_2] \rightarrow [Cd(n\text{-amylNH}_2)Cl_2] + 0.5n\text{-amylNH}_2 \quad (10)$$

The decomposition of the mono-*n*-amylamine intermediate appears to be a single process on the DTG curve, however splitting was observed on the DSC curve. These facts indicate, that the merging tendency of the last two decomposition steps, represented by reactions (7) and (8), increases with the lengthening of the normal aliphatic chain. The decomposition of the bis-*i*-amylamine analogue is similar to that of the *n*-amylamine complex, however the separation of the release of the first ligand is more marked.

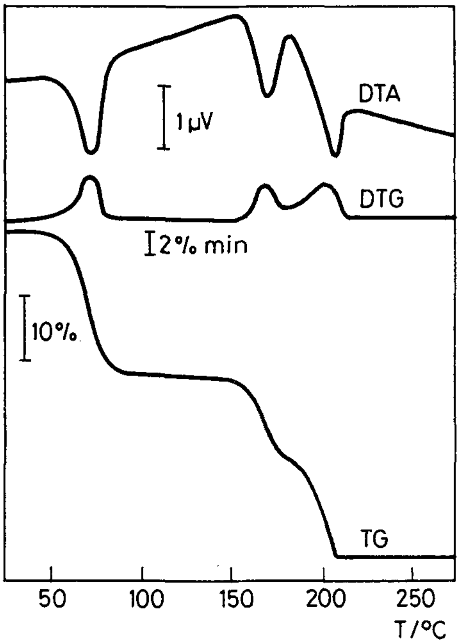

**Fig. 5** Thermal decomposition of dichloro-bis(*i*-propylamine)-cadmium(II)

The cyclohexylamine complex, prepared under the same experimental conditions as for the bis-aliphatic amine derivatives, contains four moles of the ligand. The thermal decomposition starts with the release of two ligands (Fig. 4):

$$[\mathrm{Cd(cyclohexylNH_2)_4Cl_2}] \rightarrow [\mathrm{Cd(cyclohexylNH_2)_2Cl_2}] + \\ + \mathrm{2cyclohexylNH_2} \qquad (11)$$

The decomposition thereafter is similar to that of the normal aliphatic amine complexes (reactions (6)–(8)). The DTG peak temperatures of the first two decomposition steps of the bis-cyclohexylamine complex are similar to those for the ethyl- and *n*-butylamine analogues, but the thermal events for the monocomplex and for compounds containing the one-third mole of ligand are at significantly higher temperatures, compared to the intermediates formed with normal aliphatic amine ligands.

The decomposition pathway for the iso-aliphatic amine complexes is different from that observed for the compounds containing ligands with normal aliphatic chains. For the *i*-propylamine derivative, after the formation of the mono-compound, the release of the last mole of the ligand splits into two steps, similarly to the normal aliphatic amine complexes, but with inverse mass ratio (Fig. 5):

$$[Cd(i\text{-}PrNH_2)Cl_2] \rightarrow [Cd(i\text{-}PrNH_2)_{2/3}Cl_2] + 1/3i\text{-}PrNH_2 \quad (12)$$

$$[Cd(i\text{-}PrNH_2)_{2/3}Cl_2] \rightarrow CdCl_2 + 2/3i\text{-}PrNH_2 \quad (13)$$

The *i*-butylamine compound contains two moles of the ligand and two moles of water. The amount of water is due to the inadequate dehydration or was taken from the moisture of the air. The presence of water was corroborated by TG-MS measurements. The following decomposition scheme is proposed (Fig. 6):

$$[Cd(i\text{-}BuNH_2)_2(H_2O)_2Cl_2] \rightarrow [Cd(i\text{-}BuNH_2)_{4/3}(H_2O)_2Cl_2]+2/3i\text{-}BuNH_2 \quad (14)$$

$$[Cd(i\text{-}BuNH_2)_{4/3}(H_2O)_2Cl_2] \rightarrow [Cd(i\text{-}BuNH_2)(H_2O)_2Cl_2]+1/3i\text{-}BuNH_2 \quad (15)$$

$$[Cd(i\text{-}BuNH_2)(H_2O)_2Cl_2] \rightarrow [Cd(i\text{-}BuNH_2)Cl_2] + 2H_2O \quad (16)$$

The degradation of the mono-complex is a single step on the TG-DTG-DTA curves, but splitting was observed on the DSC curve.

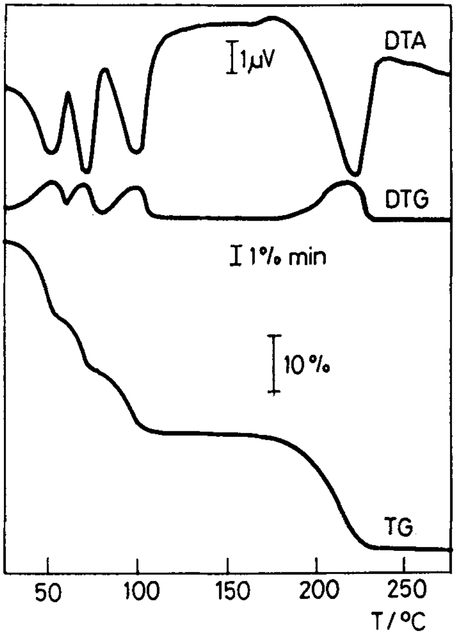

Fig. 6 Thermal decomposition of dichloro-diaqua-bis(*i*-butylamine)-cadmium(II)

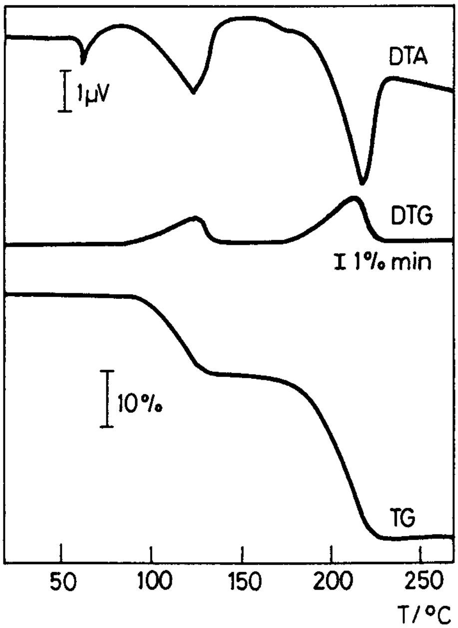

**Fig. 7** Thermal decomposition of dichloro-bis(*i*-allylamine)-cadmium(II)

The thermal decomposition of the bis-*i*-allylamine complex is a two-step process (Fig. 7):

$$[Cd(i\text{-allylNH}_2)_2Cl_2] \rightarrow [Cd(i\text{-allylNH}_2)_{4/3}Cl_2] + 2/3i\text{-allylNH}_2 \quad (17)$$

$$[Cd(i\text{-allylNH}_2)_{4/3}Cl_2] \rightarrow CdCl_2 + 4/3i\text{-allylNH}_2 \quad (18)$$

The endothermic effects of the degradation immediately follow the endothermic process, due to some structural change on the DTA and DSC curves.

## Discussion

Cadmium(II) chloride forms bis-aliphatic amine complexes when prepared by the solid-gas phase method. The only exceptions are the tetrakis-cyclohexyl amine complex and the compound formed with *i*-butylamine, which contains two moles of water. One of the possible reasons why cyclohexylamine forms a tetrakis-complex with cadmium(II) chloride is the close-packing of the ligand, which leads to decreased steric hindrance, compared to the analogues, having ligands with straight aliphatic chains. For the cadmium(II) ion, which has a $d^{10}$ closed electron shell, the polarising effect of the chloride ion is less marked compared to that in the nickel(II) analogues [10]. This leads to a high electronic charge on the central cadmium ion, which reduces the affinity for the amine ligands. Thus only two moles of the aliphatic amines are chemisorbed from the vapour phase, while tetrakis-compounds were obtained with nickel(II) chloride. These results are in good agreement with the observations of Ephraim and Linn [4]. They obtained parent, hexakis-aliphatic amine complexes with nickel(II) halides, but tris-methylamine compounds were described with cadmium(II) bromide and iodide.

On the DTA and DSC curves of *n*-propyl and *i*-allylamine complexes an endothermic effect was found, which precedes the decomposition steps. These processes are assigned to a structural change, because melting was not observed in hot-stage microscopy studies.

The thermal decomposition of the bis-methylamine complex is similar to that of the bis-ammine analogue, but the release of the last mole of the ligand split into two steps. The following general decomposition scheme was found for these derivatives:

$$[Cd(L)_2Cl_2] \rightarrow [Cd(L)Cl_2] \rightarrow [Cd(MeNH_2)_{0.5}Cl_2] \rightarrow CdCl_2$$

The thermal degradation process changes when the number of carbon atoms in the aliphatic chain is equal or higher than two. The cyclohexylamine complex decomposes in a similar way after the release of the first two moles of ligands. The general decomposition pattern was observed for normal aliphatic amine complexes as follows:

$$[Cd(L)_2Cl_2] \rightarrow [Cd(L)_{1.5}Cl_2] \rightarrow [Cd(L)Cl_2] \rightarrow [Cd(L)_{1/3}Cl_2] + CdCl_2$$

The thermal stability sequence of the bis-compounds, deduced from the temperatures of the DTG peaks, is:

$$NH_3 > MeNH_2 > EtNH_2 \geq n\text{-}BuNH_2 \geq CyclohexylNH_2 > n\text{-}PrNH_2$$

The bis-*n*-amylamine compound is not included in this series, because of the slightly different decomposition pathway, although the thermal stability seems to be close to that observed for the *n*-butylamine and cyclohexylamine analogues. The thermal stability decreases with increasing length of the aliphatic chain, with the exception of the *n*-propylamine derivative, which has a very low thermal stability. The basicity can be represented by the $pK_a$ values of the ligands, and the steric hindrance increases with the lengthening of the carbon chain in the normal aliphatic amines [14]. These factors lead to the decreasing thermal stability of the cadmium(II)-nitrogen coordinate bond in the bis-complexes from ammonia to cyclohexylamine.

The first stage of decomposition of the bis-normal aliphatic amine complexes splits into two steps, thus formation of intermediates containing one and a half mole of ligand are expected. This effect becomes more marked with the increasing length of the aliphatic chain. While for *n*-propyl- and *n*-butylamine complexes, split peaks were observed only on the DSC curves, for the *n*-amylamine compound the splitting can also be seen on the TG and DTG curves. The thermal stability for the monocomplexes and the intermediates containing one-third mole of ligand is reversed compared to that of the bis-compounds:

$$\text{CyclohexylNH}_2 > n\text{-BuNH}_2 > n\text{-PrNH}_2 > \text{EtNH}_2$$

The same effect was observed for the nickel(II) chloride analogues. In the course of their thermal decomposition a polymeric structure is formed with halide bridges [10]. We suppose that, in this structure, the steric effects become less marked.

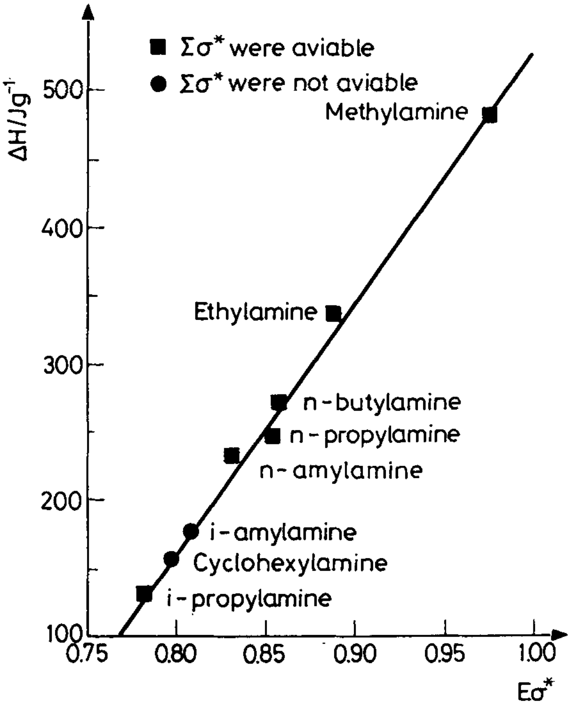

**Fig. 8** The enthalpy reaction for $Cd(L)_2Cl_2 \rightarrow Cd(L)Cl_2 + L$ *vs.* $\Sigma\sigma^*$

The thermal decompositions of the complexes with branched aliphatic chains are different from those of the normal analogues, described above. Although we can not make comparisons between the thermal degradation of the compounds containing normal- and iso-aliphatic amine, it seems that the tendency of intermediate formation increases as the ligands become more bulky.

In Fig. 8 we plot the enthalpy of the decomposition step from bis-amine to mono-amine as a function of $\Sigma\sigma^*$, which is the measure of the inductive releasing effect for aliphatic amines [15, 16]. This type of plotting was previously used with success in the discussion of properties observed in the liquid state for primary, secondary and tertiary amine complexes [17, 18]. The points fall on a straight line indicating that the inductive effect is the main factor which determines the strength of the metal-ligand bond for bis-complexes.

The thermal stability of the complexes is determined by both the inductive releasing and steric effects of the ligands. In Fig. 9 lg(1/*T*) *vs.* $\Sigma\sigma^*$ is plotted,

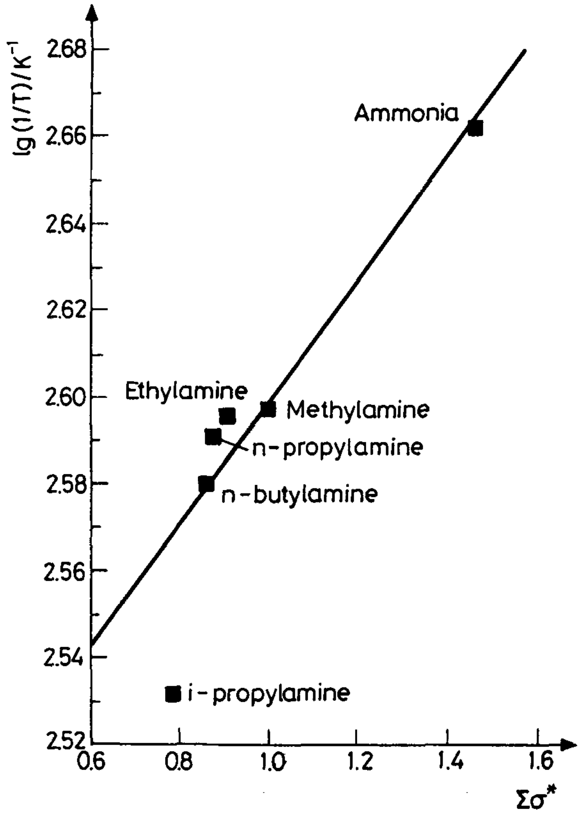

**Fig. 9** –lg(1/*T*) *vs.* $\Sigma\sigma^*$ for the $Cd(L)_2Cl_2 \rightarrow Cd(L)Cl_2$ decomposition

where $T$ is the DTG peak temperature. The values for the normal primary amine complexes fall on a straight line. The $\lg(1/T)$ for the *i*-propylamine compound falls somewhat below the line, which indicates possible steric hindrance of the branched aliphatic chain in the bulky *i*-propylamine complex.

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**Zusammenfassung** — Mittels simultaner TG-DTG-DTA wurde die thermische Zersetzung von einigen neuen primären aliphatischen (Methyl-, Ethyl-, *n*-Propyl-, *i*-Propyl-, *n*-Butyl-, *i*-Butyl-, *n*-Amyl-, *i*-Amyl-, Cyclohexyl- und *i*-Allyl-) Aminkomplexen mit Cadmium(II)-chlorid untersucht, die durch eine Feststoff-Gasphasen Chemisorption hergestellt wurden. Die Enthalpieänderungen während der Zersetzung wurden mittels DSC verfolgt. Der Verlaufsweg der thermischen Zersetzung wird detailliert beschrieben. Die beobachteten thermischen Eigenschaften wurden mit denen der zuvor beschriebenen Nickel(II)-Analoge verglichen. Die Änderungen bei den thermischen Parametern in der Serie der Komplexe von Cadmium(II)-chlorid mit aliphatischen Aminen wurden auf der Grundlage des induktiven Freisetzungseffektes der aliphatischen Kette und der sterischen Behinderung der Liganden erörtert.