THERMAL BEHAVIOUR OF COMPLEXES OF GENERAL FORMULA $(n\text{-}C_nH_{2n+1}NH_2)_2CuCl_2$

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ABSTRACT

The thermal behaviour and some relationships between the physical properties and structure of complexes of general formula $(n\text{-}C_nH_{2n+1}NH_2)_2CuCl_2$, with $n = 10, 12, \cdots 18$, have been investigated by DSC and X-ray powder diffraction techniques. The high enthalpy solid—solid phase transitions observed for the complexes in the temperature range 350—390 K could be associated with the disordering of the hydrocarbon regions of the structure, as already observed for other similar layer compounds.

INTRODUCTION

Several papers have recently been published on the relationship between the structure and properties of complexes of transition metals with long chain amines. In a previous work, in particular ref. 1, such a relationship was investigated for compounds of general formula $(n\text{-}C_nH_{2n+1}NH_2)_2ZnCl_2$, with $n = 6, 8, \cdots 16$. As reported in that paper, these compounds were found to be characterized by a "sandwich structure" constituted by the regular alternation of inorganic and hydrocarbon layers, and the complexes with $n > 10$ show — in analogy with systems of the kind $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$, where M is a divalent metal atom and $9 \leqslant n \leqslant 17$ [2—8] — high enthalpy reversible solid—solid phase transitions, associated with the disordering of the alkyl chains in the hydrocarbon regions from a conformationally ordered state to a "liquid-like" one, in which the conformational freedom of the hydrocarbon chains is comparable with that they would have in the melt.

In the present work the preparation and some physico-chemical data of complexes of the type $(n\text{-}C_nH_{2n+1}NH_2)_2CuCl_2$, with $n = 10, 12, \cdots 18$, are discussed.

EXPERIMENTAL

A general method of preparing the compounds under examination could be the reaction between stoichiometric amounts of a long chain alkylamine and cupric chloride, both dissolved in absolute ethanol. On the other hand, it

is well known from the literature that the high molecular weight amines are unable to displace water from metal salt hydrates; consequently, if water is present, the usual product of the reaction between an amine and a metal salt is a basic salt of the metal [9]. Therefore, to obtain the desired complexes, it would be necessary to use anhydrous reactants and solvents.

An alternative synthesis [9] starts from a long chain alkylammonium tetrachlorocuprate(II) which is allowed to react, in hot ethanolic solution, with the appropriate long chain alkylamine in the molar ratio 1 : 2, precipitating the complex and leaving alkylammonium halide in solution. In this case, it is not necessary to remove water from the reaction vessel; in fact the presence of the alkylammonium tetrachlorocuprate hinders the formation of a hydrate, and the amine is able to react. This method of preparation was used for the compounds under discussion.

In a typical preparation, 0.02 mole of the alkylamine, dissolved in 50 cm^3 of absolute EtOH, was treated with 0.02 mole of concentrated HCl (aq.), followed by 0.01 mole of CuCl$_2$ hydrate. The hot yellow-green solution was added dropwise, with continuous stirring, to a hot solution of 0.02 mole of the same alkylamine dissolved in 50 cm^3 of absolute EtOH. The resulting solution was then allowed to cool to room temperature, the blue microcrystalline precipitate filtered off, recrystallized twice from chloroform and dried in vacuo.

The thermograms of all the compounds were registered between 320 and 420 K on a Perkin—Elmer DSC-1 differential scanning calorimeter, in a flowing N$_2$ atmosphere, at a scan rate of 8 K min^{-1}.

The X-ray powder spectra were taken by reflection on a Philips PW-1100 diffractometer (CuKα radiation, Ni filter). For more details on the experimental techniques, see ref. 1.

TABLE 1

Transition temperatures, enthalpies and entropies obtained by DSC[b] for various complexes of general formula (n-C$_n$H$_{2n+1}$NH$_2$)$_2$CuCl$_2$

n	T (K)	ΔH (kJ mole^{-1})	ΔS (J K^{-1} mole^{-1})
10	352	21	60
	406 [a]	43	106
12	352	18	51
	405 [a]	50	123
14	377	29	78
	404 [a]	58	145
16	376	41	110
	402 [a]	65	162
18	382	53	138
	400 [a]	70	175

[a] Melting.
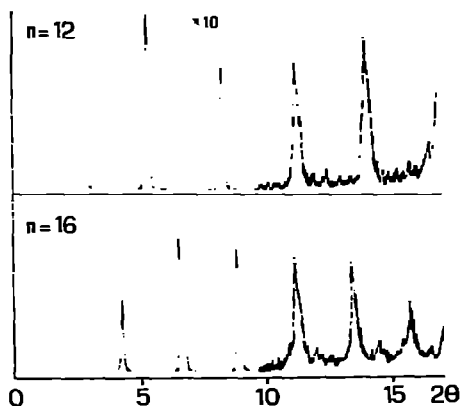[b] Data deduced from DSC heating scans; scanning rate 8 K min^{-1}.

Fig. 1. Low angle portion of the room-temperature X-ray powder spectra of the complexes with $n = 12$ and 16. (Diffraction patterns taken by reflection, using Cu$K\alpha$ radiation, Ni filter.)

RESULTS

All the compounds examined in this work show high enthalpy solid—solid phase transitions in the temperature range 350—390 K, and melt with decomposition between 395 and 410 K. The reproducibility of the transitions, which are reversible up to the melting temperature, is obtained only after annealing (30 min at 385 K in an atmosphere of N_2 for each compound).

Table 1 gives the transition temperatures, enthalpies and entropies which refer to heating DSC scans after the annealing process. The solid—solid phase transitions observed by DSC appear as sharp endotherms; the transition temperatures of Table 1 refer to the maxima of the peaks.

Figure 1 shows the low angle portion of the X-ray powder spectra taken by reflection at room temperature for two representative complexes of the series. The interplanar spacings, c, were deduced from the diffraction patterns and are given in Table 2.

TABLE 2

Interlayer spacings, c as obtained from the room-temperature X-ray powder spectra for several compounds of general formula $(n\text{-}C_nH_{2n+1}NH_2)_2CuCl_2$

n	c (Å)
10	27.6
12	31.7
14	35.7
16	40.5
18	44.3

DISCUSSION

The room-temperature X-ray powder spectra of all the compounds under examination are characterized by the presence of a series of reflection maxima which correspond to a unique interlayer spacing for each compound. These diffraction patterns are very similar to those for layer structures of general formula $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ and $(n\text{-}C_nH_{2n+1}NH_2)_2ZnCl_2$ described in detail elsewhere[1—8]; therefore, a layer structure characterized by the regular alternation of inorganic and hydrocarbon regions may be assumed for the compounds under examination.

As for the packing of the hydrocarbon chains in the room-temperature stable forms of the compounds, a mean increment of the interlayer spacing between contiguous inorganic layers, $\overline{\Delta c}$, for $\Delta n = 1$, of the order of 2.1 Å was deduced from the data of Table 2. The value of this parameter, together with the high values of the interlayer distances, c, could be interpreted on the basis of a double-layer chain packing, without intercalation of chains from adjacent layers (Fig. 2). If the chains are in a planar zig-zag conformation, and are inclined at an angle α with respect to the perpendicular to the inorganic layers

$$\overline{\Delta c} = 2\,l \sin \varphi/2 \cos \alpha$$

where $l = 1.54$ Å is the carbon—carbon bond length, $\varphi = 112°$ is the C—C—C valence angle and α is as in Fig. 2. Substituting the symbols by their known values, we find $\alpha \cong 35°$; this means that the alkyl chains in the compounds are less inclined than those in the ordered polymorphs of systems with this
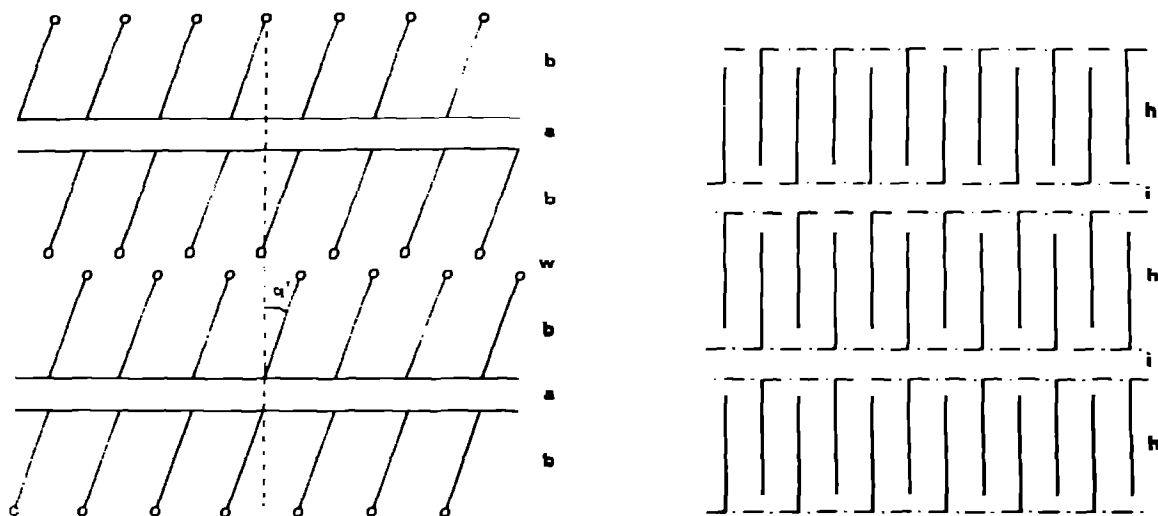

Fig. 2. Double layer chain packing without intercalation of chains from adjacent layers. a = Inorganic layers, b = hydrocarbon layers, w = Van der Waals area, o = chains' methyl ends.

Fig. 3. Double layer chain packing with intercalation of chains from adjacent layers. i and h = Inorganic and hydrocarbon regions, respectively.

kind of chain packing, as, for example, $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ with M = Mn ($\alpha = 45°$, cf. refs. 2 and 3) and Hg ($\alpha = 54°$, cf. ref. 8). On the other hand, we can exclude a priori a structure of the kind schematically shown in Fig. 3, with intercalation of chains from adjacent layers, which has a limiting value for $\overline{\Delta c}$ given by

$$\overline{\Delta c} = l \sin \varphi/2 = 1.28 \text{ Å } [8]$$

As the data of Table 1 show, the thermal behaviour of the compounds is quite similar to that of the homologous complexes with M = Zn [1], as well as the thermal behaviour of systems of formula $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ [2—8]. In particular, all the complexes show high enthalpy reversible solid—solid phase transitions, whose order—disorder nature has been extensively discussed in the literature cited.

On the other hand, in contrast to the compounds described in refs. 1—8, in which the alkyl chains in the high temperature stable polymorphs show a conformational freedom comparable with that they would have in the melt, in the case of the complexes under examination the total transition entropies per mole of hydrocarbon chains are quite low, especially when compared with the total molar melting entropies of the corresponding n-paraffins. On the contrary, the melting entropies of the compounds under consideration are unusually high (if compared, for example, with those of the homologous complexes with M = Zn [1]), and considerably higher than the total solid—solid transition entropies.

These data could be interpreted by making the hypothesis that in the low temperature stable polymorphs of compounds of the kind $(n\text{-}C_nH_{2n+1}NH_2)_2\text{-}CuCl_2$, with $n = 10, 12, \cdots 18$, the alkyl chains are totally ordered from a conformational point of view, with their carbon—carbon bonds in *trans* states, while in the high temperature stable polymorphs the hydrocarbon chains are partially disordered, but do not reach the "liquid-like" state characteristic of the disordered polymorphs of other similar layer systems [1—8].

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