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METAL-DEPENDENT THERMAL BEHAVIOUR IN $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$

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ABSTRACT

Compounds of the type $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ with $n = 12$ or $n = 16$ and with M = Mn, Cu, Co, Fe, Hg, Zn show order–disorder solid–solid phase transitions in the temperature range 300–380 K. Three general types of thermal behaviour can be observed for compounds with different metals, but with the same n. The different thermal behaviour appears to be related to different coordination geometries at the metal atoms.

INTRODUCTION

We have recently investigated the thermal behaviour of the compounds of general formula $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ with $n = 9, 10 \ldots 17$ and M = Mn, Cu, Co[1–4]. All the compounds examined show solid–solid phase transitions in the temperature range 280–380 K. The high values of the total molar transition entropies and their roughly linear increase with increasing n have been interpreted in terms of conformational melting of the alkyl chains at the transition temperatures, the ionic regions of the structures remaining practically unchanged in the high-temperature stable polymorphs.

The thermal behaviour of Mn(II) and Cu(II) compounds with the same number n of carbon atoms in the chains is similar, but different from the behaviour of the corresponding Co(II) compounds. An attempt to explain these differences has been made considering the coordination geometry around the metal atoms[4].

In this work we show the results of a comparative study of the thermal behaviour of compounds of the title type with $n = 12$ or $n = 16$ and M = Mn, Cu, Co, Fe, Hg, Zn.

EXPERIMENTAL

The new compounds have been prepared as previously described for the corresponding Mn, Cu and Co alkylammonium tetrachlorometallates[2–4]. All the

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compounds were recrystallized twice from absolute ethanol. The synthesis of the Fe(II) compounds was performed in absence of oxygen, and the resulting tetrachloroferrates were handled in N_2 atmosphere. The crystals of the Fe(II) salts are pale yellow platelets, while those of the Hg(II) and Zn(II) salts are white platelets. The analyses of these newly prepared compounds are reported in Table 1.

TABLE 1

	C (%)		*H* (%)	
	Calc.	*Found*	*Calc.*	*Found*
$(C_{12}H_{25}NH_3)_2FeCl_4$	50.54	50.60	9.90	9.98
$(C_{12}H_{25}NH_3)_2ZnCl_4$	49.71	49.86	9.73	9.61
$(C_{12}H_{25}NH_3)_2HgCl_4$	40.31	40.40	7.89	7.87
$(C_{16}H_{33}NH_3)_2FeCl_4$	56.31	56.29	10.63	10.57
$(C_{16}H_{33}NH_3)_2ZnCl_4$	55.53	55.57	10.49	10.48
$(C_{16}H_{33}NH_3)_2HgCl_4$	46.46	46.49	8.77	8.72

The thermal behaviour has been examined by means of a Perkin Elmer DSC-1 differential scanning calorimeter. Thermograms between 280 and 500 K have been obtained in N_2 atmosphere at the scanning rate of 8 K min^{-1}. The temperature scale was calibrated by using pure reference compounds. The transition enthalpies have been obtained by comparing the areas under the transition peaks with those of a reference made of pure indium ($\Delta h = 28.5$ J g^{-1}).

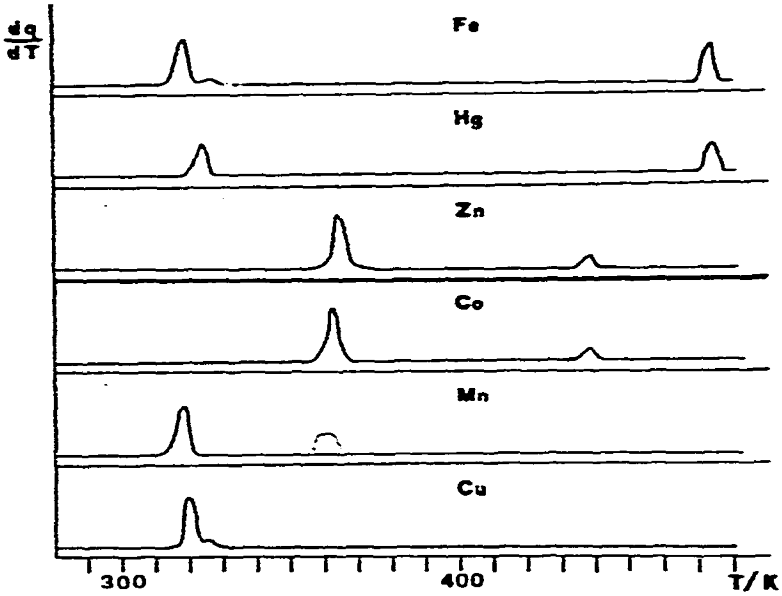

Fig. 1. Results obtained in differential scanning calorimeter during heating scans for $(n\text{-}C_{12}H_{25}NH_3)_2MCl_4$ with various M's.

The molar transition enthalpies and entropies represent mean values for various independent samples. For each set of measurements the standard deviation is of the order of 5%.

The thermal behaviour has been examined also by optical microscopy using a Kofler hot stage of the Leitz Co.

RESULTS

Figures 1 and 2 show typical heating thermograms for the compounds with $n = 12$ and $n = 16$, respectively. Thermograms of the corresponding Mn, Cu, and Co compounds are also shown. All the compounds show phase transitions in the temperature range 300–380 K, but the Co and Zn salts show a new phase transition around 440 K, and the Fe and Hg salts around 470 K. All the observed transitions are reproducible both in temperature and enthalpy after heating and cooling cycles throughout the transition temperatures, with the exception of the Fe(II) salts, whose behaviour is somewhat different.

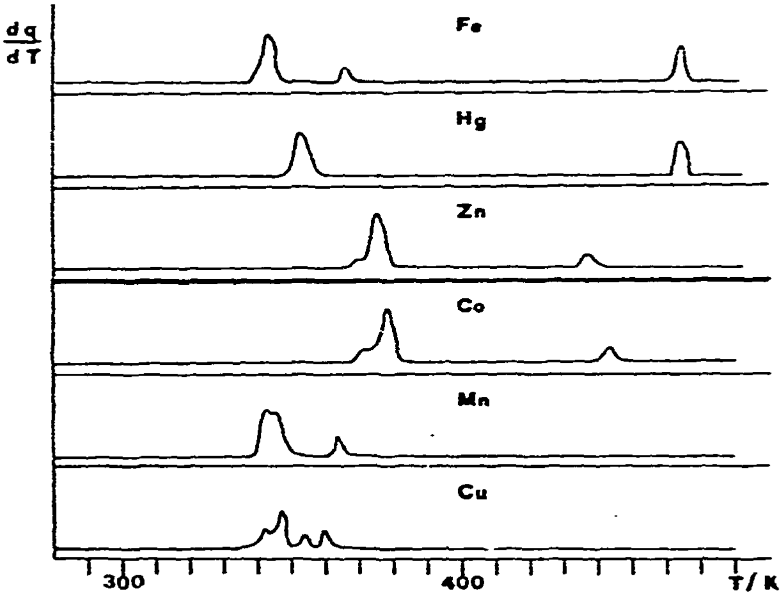

Fig. 2. Results obtained in differential scanning calorimeter during heating scans for $(n\text{-}C_{16}H_{33}NH_3)_2MCl_4$ with various M's.

In fact in this case the transition around 470 K is always reproducible, but if a sample is heated above this temperature and then cooled, the transition peaks at lower temperatures become broad and difficult to analyse. Total reproducibility is observed, on the contrary, in samples not heated above 470 K. All the transitions in the temperature range 300–380 K are solid–solid phase transitions, as revealed by microscopic observations, while the transitions around 440 K for the Co and Zn compounds and the transitions around 470 K for the Fe and Hg compounds correspond to the melting, giving in all the cases liquid-crystalline materials which become isotropic around 530 K. Slow decomposition is, however, observed in all the cases in the range of stability of the liquid-crystalline phases, the decomposition rate increasing rapidly with increasing temperature, so that no reliable enthalpic data about the liquid crystal–isotropic transitions could be obtained.

TABLE 2

M	*Heating*			*Cooling*		
	T (*K*)	*H* (*kJ mol*$^{-1}$)	*S* (*JK*$^{-1}$ *mol*$^{-1}$)	*T* (*K*)	*H* (*kJ mol*$^{-1}$)	*S* (*JK*$^{-1}$ *mol*$^{-1}$)
Mn	318	39	124	312	39	124
Cu	320	42	131	314	42	134
Co	363	45	124	342	48	140
	439[a]	7.9	18	432	8.2	19
Zn	363	46	127	345	51	148
	439[a]	7.2	16	430	8.7	20
Hg	325	27	83	316	27	85
	475[a]	26	55	469	26	55
Fe	319	44	138	306	43	141
	475[a]	40	84	465	40	86

[a] Melting.

In Tables 2 and 3, transition temperatures, enthalpies and entropies per mole of $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ obtained from heating and cooling scans for compounds with $n = 12$ and $n = 16$, respectively, are shown. Data for the corresponding

TABLE 3

M	*Heating*			*Cooling*		
	T (*K*)	*H* (*kJ mol*$^{-1}$)	*S* (*JK*$^{-1}$ *mol*$^{-1}$)	*T* (*K*)	*H* (*kJ mol*$^{-1}$)	*S* (*JK*$^{-1}$ *mol*$^{-1}$)
Mn	345	60	174	338	56	167
	364	11	31	361	12	32
Cu	345	36	104	339	39	115
	354	7.5	21	346	9.7	28
	360	14	39	356	14	39
Co	378	78	206	358	77	215
	444[a]	8.0	18	435	7.7	18
Zn	376	74	197	361	78	216
	436[a]	7.7	18	431	8.1	19
Hg	354	48	136	344	48	140
	469[a]	26	55	463	26	56
Fe	344	54	157	329	54	164
	367	12	33	353	12	34
	465[a]	39	84	459	40	87

[a] Melting.

compounds with M = Mn, Cu, Co are also reported. The cooling data refer, in the case of the low-temperature transitions of tetrachloroferrates, to samples not heated above the melting temperature. In some thermograms (see Figs. 1 and 2) two or more transition maxima are unresolved. In such cases the transition temperature reported in the tables refer to the highest maximum, while the molar enthalpies and entropies have been obtained from the total areas under the curves.

DISCUSSION

Tables 2 and 3 show that all the observed solid–solid phase transitions are associated with large entropy effects. In compounds containing long-chain alkyl groups, phase transitions of this kind are characterized by the thermal liberation of rotations about C–C skeletal bonds. Hence, the total molar transition entropy increases with increasing chain-length, its mean increase for the addition of one C–C skeletal bond being a good estimate of the conformational freedom of the alkyl chains in the disordered phases. As may be seen in Tables 2 and 3, the observed increase of the total molar transition entropies from compounds with $n = 12$ to the corresponding compounds with $n = 16$ is of the order of 70, 50 and 60 J K^{-1} mol^{-1} for Zn, Hg and Fe compounds, respectively. These values are of the same order of the corresponding values found for the order–disorder phase transition in the Mn, Cu and Co compounds and in other long-chain compounds like hydrocarbons, alcohols etc.[5]. All the observed phase transitions are thus of the order–disorder type, with the alkyl chains in a "liquid like" state in the high-temperature stable polymorphs.

Figures 1 and 2 show that the general aspect of the thermograms of the compounds examined in this work depend on both n and M. However, from a thermal behaviour point of view compounds with the same n may be divided into three groups.

The first group (group A) includes compounds with M = Mn, Cu, while compounds with M = Fe, Hg belong to the second group (group B) and compounds with M = Co, Zn belong to the third group (group C).

In the case of the dodecylammonium salts, group A compounds show only a single solid–solid phase transition at a temperature around 320 K. Group C compounds also show a single solid–solid phase transition, but at the temperature of 363 K, and melt at 439 K. The behaviour of group B compounds appears to be intermediate. In fact, the single solid–solid phase transition is found in this case at a temperature around 320 K, like for group A compounds, but the Fe and Hg salts melt at 475 K. A similar behaviour is found in the case of the hexadecylammonium salts, in which group A and group B compounds show a number of solid–solid phase transitions in the range 340–370 K, the highest maximum of thermograms being centered around 350 K, while group C compounds show a single solid–solid transition around 377 K and melt around 440 K. Melting is observed, in the case of group B compounds, at a temperature around 467 K.

The observed thermal behaviour may be rationalized in terms of two fundamental types of structural organization in the ionic regions of the crystal lattice, both in the low and in the high-temperature solid phases. The crystal structure of the new compounds prepared in this work is unknown. However, $(CH_3NH_3)_2FeCl_4$ has been described to be isomorphous with the corresponding Mn(II) salt[6]. The crystal structure of $(n\text{-}C_nH_{2n+1}NH_3)_2$ MCl_4 salts with M = Mn and M = Cu is characterized by the presence of two-dimensional macroanions of composition MCl_4^{2-} sandwiched between two alkylammonium layers (Fig. 3). The coordination of the metal atoms is octahedral in the case of the Mn(II) compounds and distorted octahedral in the case of the Cu(II) compounds. Such main features of the crystal structure have been found[1,2,7,8] to be independent of *n*. If we assume that also in the case of tetrachloroferrates an increase of chain-length does neither substantially affect the ionic regions of the structure, the solid–solid thermal behaviour of these compounds, very similar to the behaviour of group A compounds, is not surprising.

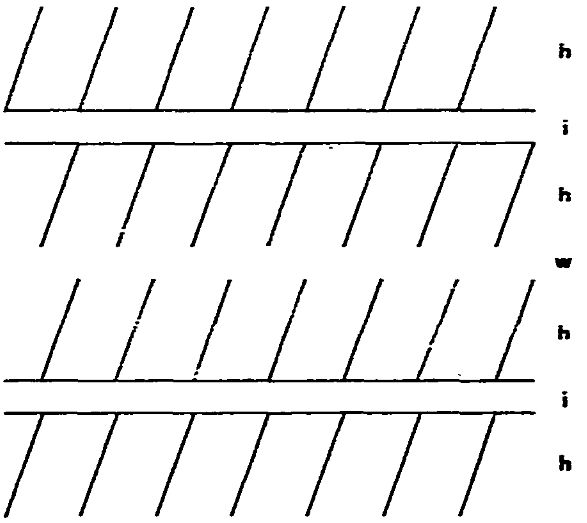

Fig. 3. Schematic view of the layer structure of compounds of the type $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ with M = Mn or M = Cu. h = hydrocarbon layers, i = ionic layers, w = Van der Waals zone.

The case of tetrachloromercurates may be different. The crystal lattice of $K_2HgCl_4 \cdot H_2O$ and $(NH_4)_2HgCl_4 \cdot H_2O$ has been shown to contain one-dimensional macroanions built up of octahedral $HgCl_6$ units sharing edges[9–11]. However, we cannot exclude that the presence in the structure of long alkyl chains may lead to the formation of two-dimensional macroanions of the previous type. This is the case with tetrachloromanganates, in which the coordination of the metal atoms is dependent of the counterions geometry. In fact, among the mono-, di-, tri- and tetramethylammonium salts, the presence of macroanions with hexacoordinated metal atoms has been found only in the first case, while in the remaining compounds tetrahedral $MnCl_4^{2-}$ units are present[12].

In any way, the thermal behaviour of group A and group B compounds may be considered as peculiar of structures containing macroanions built up of octahedral or distorted octahedral units.

The thermal behaviour of group C compounds is probably characteristic of structures containing unassociated MCl_4^{2-} units. In fact, Cs_2ZnCl_4 and $(NH_4)_2ZnBr_4$ have been shown to be isostructural with Cs_2CoCl_4 and Cs_2ZnBr_4, respectively, both containing unassociated CoX_4^{2-} tetrahedra[13–16]. Furthermore, $(C_2H_5NH_3)_2CoCl_4$ and $(n\text{-}C_3H_7NH_3)_2CoCl_4$ are supposed to contain $CoCl_4^{2-}$ tetrahedra[17]. On the other hand, the finding that group C compounds melt at lower temperature and with lower value of the molar melting enthalpy shows that the binding forces among MCl_4^{2-} units are in this case weaker than those present in the group B compounds.

The different thermal behaviour among compounds with different coordination at the metal atoms is probably due to the influence of the latter on the packing of the alkyl chains in the crystal lattice. A structural investigation of these compounds, both in the low- and in the high-temperature stable polymorphs, is in progress in our laboratory in order to achieve a more detailed understanding of this problem.

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