

NEW DISORDERED POLYMORPHS IN LONG CHAIN ALKYLAMMONIUM TETRACHLOROCOBALTATES(II)

ERNESTO LANDI AND MICHELE VACATELLO

Istituto Chimico, University of Naples, Via Mezzocannone 4, Naples (Italy)

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ABSTRACT

The thermal behavior of compounds of the type $(n\text{-C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CoCl}_4$ with $n = 9, 10 \dots 17$ is investigated by means of differential scanning calorimetry in the temperature range 280–470 K.

All compounds show solid–solid phase transitions at temperatures lower than 380 K and melt around 440 K.

Total molar transition and melting entropies are discussed in terms of conformational disorder of the alkyl chains in the high temperature stable modifications.

INTRODUCTION

Compounds having a crystal structure characterized by ordered regions separated by large disordered hydrocarbon regions, seem to possess very interesting physical and chemical properties in the solid state. Structures of the above-mentioned type may be found in compounds in which long hydrocarbon chains are bound to a fixed matrix at one end.

In previous works we have reported that compounds of the type $(n\text{-C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MCl}_4$, with $\text{M} = \text{Mn}^{1,2}$ and $\text{M} = \text{Cu}^{3,4}$ and n between 9 and 17, show solid–solid phase transitions associated with very large entropy changes in the temperature range 273–373 K. The crystal structure of the low-temperature polymorphs has been found to be characterized by MCl_4^{2-} layers, sandwiched between two hydrocarbon layers with their ammonium groups in contact with the anionic layer. The overall crystal structure results from the packing of successive sandwiches one on the top of the other, the only binding forces among adjacent sandwiches being of the Van der Waals type. The reported solid–solid phase transitions are of the kind order–disorder, with hydrocarbon chains in liquid-like motion in the high-temperature polymorphs, while the ionic regions of the structures remain practically unchanged.

The environments of the manganese and copper atoms are octahedral and distorted octahedral, respectively. Thus, in both cases, the binding forces between adjacent MCl_4^{2-} units in the ionic layers are high, giving rise to bidimensionally extended macroanions. These, in turn, determine the mode of packing of the hydro-

carbon chains in the low-temperature polymorphs and their degree of conformational disorder in the high-temperature ones⁵.

Therefore, it was interesting to study the behavior of a system with weaker binding forces between MCl_2^{2-} units. Here we report the results obtained through a differential scanning calorimetric investigation on the series of compounds $(n-C_nH_{2n+1}NH_3)_2CoCl_4$, with n between 9 and 17. No compounds of this series have been reported previously in the literature. However, some physical properties of the ethyl- and propylammonium salts have been discussed⁶ in terms of tetrahedral coordination at the cobalt atoms, without evidences pointing to some kind of association of tetrahedra.

EXPERIMENTAL

Compounds were prepared according to the following general method. In a typical preparation 0.02 mol of the alkylamine were dissolved in 50 cm³ of absolute ethanol and allowed to react with 0.02 mol of concentrated HCl(aq). 0.01 mol of cobaltous chloride hydrate dissolved in 50 cm³ of the same solvent were added, and the resulting blue solution was boiled for 10 min. After cooling to room temperature, the blue crystalline precipitate was filtered off and recrystallised twice from absolute ethanol. The yields varied with n , the members of the series with shorter alkyl chains being more soluble. The analyses of the compounds examined in this work are given in Table 1. The thermograms have been registered between 280 and 470 K on a Perkin-Elmer DSC-1 apparatus at a scanning rate of 8 K min⁻¹ in N₂ atmosphere.

TABLE 1

CALCULATED AND FOUND COMPOSITION OF $(n-C_nH_{2n+1}NH_3)_2CoCl_4$ SALTS ($9 \leq n \leq 17$)

n	C		H	
	Calc. (%)	Found (%)	Calc. (%)	Found (%)
9	44.19	44.06	9.06	8.90
10	46.44	46.68	9.35	9.28
11	48.45	48.61	9.61	9.78
12	50.26	50.23	9.84	10.06
13	51.91	51.97	10.06	10.13
14	53.42	53.18	10.25	10.33
15	54.79	54.92	10.42	10.34
16	56.05	56.18	10.59	10.38
17	57.21	57.14	10.73	10.84

The transition enthalpies have been obtained using as a reference standard a sample of indium ($\Delta h = 28.5 \text{ J g}^{-1}$). The reported values are the mean values of several measurements on independent samples. For each set of measurements the standard deviation is of the order of 4%.

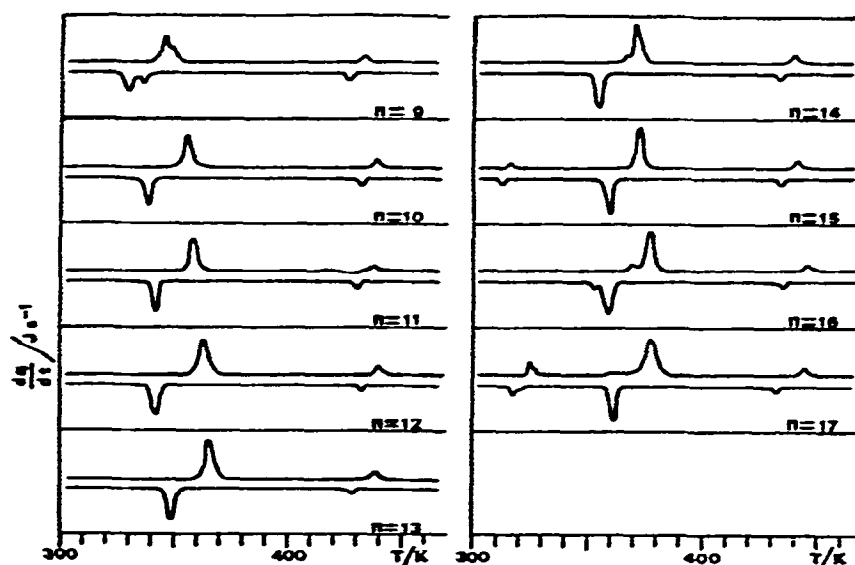


Fig. 1. Results obtained in differential scanning calorimeter during heating and cooling scans (upper and lower curves, respectively).

TABLE 2

TRANSITION TEMPERATURES, ENTHALPIES AND ENTROPIES FOR
 $(n\text{-C}_{2n}\text{H}_{2n+1}\text{NH}_3)_2\text{CoCl}_4$ SALTS ($9 \leq n \leq 17$) AS OBSERVED AT DSC IN HEATING AND
 COOLING SCANS

n	Heating			Cooling		
	T (K)	ΔH_m (kJ mol^{-1})	ΔS_m (R)	T (K)	ΔH_m (kJ mol^{-1})	ΔS_m (R)
9	345	25	8.7	328	27	9.9
	433 ^a	5.8	1.6	428	5.2	1.5
10	355	37	13	338	41	15
	438 ^a	7.1	1.9	432	7.6	2.1
11	358	36	12	341	36	13
	437 ^a	7.5	2.1	430	7.5	2.1
12	363	45	15	342	48	17
	439 ^a	7.9	2.2	432	8.2	2.3
13	366	48	16	348	47	16
	437 ^a	6.6	1.8	427	6.3	1.8
14	370	59	19	354	61	21
	440 ^a	6.5	1.8	434	6.9	1.9
15	317	2.2	0.8	313	2.3	0.9
	373	52	17	357	56	19
16	441 ^a	6.7	1.8	434	7.9	2.2
	378	78	25	358	77	26
17	444 ^a	8.0	2.2	435	7.7	2.1
	325	11	4.1	317	11	4.2
	378	72	23	360	67	22
	443 ^a	6.1	1.7	432	5.8	1.6

^a Melting.

RESULTS

All the compounds examined crystallize as blue thin platelets, the colour intensity decreasing with increasing number of carbon atoms in the alkyl chains. The melting transition is observed at a temperature around 440 K, nearly constant in the series. In all cases the melting transition is preceded by solid–solid phase transitions. Typical heating and cooling thermograms (upper and lower curves, respectively) are shown in Fig. 1. The thermograms are always reproducible, both in transition temperature and enthalpy, after heating and cooling cycles. In Table 2 are reported the corresponding transition temperatures, enthalpies and entropies (values per mole of $(n\text{-C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CoCl}_4$).

In all the cases a solid–solid phase transition with large entropy change is observed in the temperature range 345–380 K, the transition temperature roughly increasing with n . When $n = 15$ and $n = 17$ a new transition is found at lower temperatures (317 and 325 K, respectively). In some thermograms (see Fig. 1) two or more transition maxima are seen in short temperature ranges; the reported transition temperatures correspond in this case to the highest one, while reported enthalpies cover the overall transition.

DISCUSSION

The crystal structure of compounds of the type $(n\text{-C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CoCl}_4$ is unknown. However, Cs_2CoCl_4 has been shown to contain CoCl_4^{2-} tetrahedra with a small angular distortion⁷. The intense light absorption in the 650–750 nm region and the magnetic moments in the 4.55–4.75 B.M. range in the ethyl- and propylammonium salts have been taken as indicative of tetrahedral coordination at the cobalt atom⁶. In all the known literature examples, the blue colour in M_2CoCl_4 compounds has always been related to the presence of tetrahedral CoCl_4^{2-} ions⁶. Hence, the blue colour of the compounds examined in this work may be taken as indicative of this type of coordination at the cobalt atom. A further indirect support in favour of this hypothesis may be found in the thermal behavior of the title compounds, as compared with the behavior of the analogous Mn(II) and Cu(II) salts. In these cases, the octahedral coordination at the metal atom gives rise to the formation of bidimensionally extended macroanions in which neighbouring MCl_4^{2-} units are firmly held together. Hence, only order–disorder transitions of the organic layers are observed before the decomposition temperature, the macroanions remaining practically unchanged in the transitions. The compounds examined in this work melt at relatively low temperatures (around 440 K) without appreciable decomposition in N_2 atmosphere, so that the presence in the solid-state polymorphs of CoCl_4^{2-} macroanions of the previous kind can be excluded. Thus, the binding forces between CoCl_4^{2-} units must be weaker.

The molar melting entropies of compounds containing long chain alkyl groups like those examined in this work, can be considered as a summation of positional, orientational and conformational contributions, the last term increasing with increasing number of conformationally flexible bonds in the alkyl chains.

However, the true melting transition is often preceded, in compounds of this type, by solid–solid phase transitions in which the alkyl groups become more and more conformationally disordered. In this case the molar melting entropy decreases, the extent of such a decrease depending on the degree of conformational disorder possessed by the alkyl chains in the high-temperature stable polymorphs.

Table 2 shows that for all the title compounds the melting transition is preceded by solid–solid phase transitions. The melting temperature is nearly constant in the series, as well as the molar melting entropy, which is of the order of $1.9 R$. This value appears very small if compared with the molar melting entropies of other long chain compounds, and is of the same order of the molar melting entropy of ionic A_2B type compounds lacking conformationally flexible bonds⁸. Thus, the molar melting entropy can account only for positional and orientational disorder.

The symbol $\Delta S_{m,tr}$ (total molar transition entropy) denotes in the following the overall molar solid–solid transition entropy; the symbol $\Delta S_{m,t}$ (total molar melting entropy) denotes the sum of $\Delta S_{m,tr}$ and of the molar melting entropy. Table 2 shows that $\Delta S_{m,t}$ and $\Delta S_{m,tr}$ increase with increasing n , showing the characteristic alternation between odd and even members of the series, already observed for other long chain compounds like hydrocarbons, alcohols etc.⁹. However, the actual trend is opposite to that observed for the analogous Mn(II) and Cu(II) compounds³, the $\Delta S_{m,t}$ and $\Delta S_{m,tr}$ values for the even members being similar or sometimes higher than those for the following odd members. Nevertheless the $\Delta S_{m,tr}$ values are of the same order of those found in the order–disorder transitions of the Mn(II) and Cu(II) salts with equal number of carbon atoms in the alkyl chains.

In a homologous series of long chain compounds the conformational part of $\Delta S_{m,t}$ may be expressed, in the limit of large p , as in ref. 8,

$$\Delta S_{m,conf} = (\Delta S_{m,conf})_0 + p\Delta S'_{m,conf}$$

p being the number of conformationally flexible bonds in the chains. Since $\Delta S_{m,t} = \Delta S_{m,pos} + \Delta S_{m,or} + \Delta S_{m,conf}$ and the first two terms (positional and orientational contributions, respectively) may be assumed to be independent of p , it follows

$$\Delta S_{m,t} = (\Delta S_{m,t})_0 + p\Delta S'_{m,conf}$$

Here $\Delta S'_{m,conf}$ is the mean conformational contribution of conformationally flexible chain bonds to $\Delta S_{m,t}$ and may be assumed as a good estimate of the degree of conformational disorder in the melt. In Fig. 2 we compare the total melting entropy per mole of alkyl chains of the title compounds (i.e. $\frac{1}{2}\Delta S_{m,t}$) with that of the linear hydrocarbons having the same number p of conformationally flexible bonds. The mean increase of $\frac{1}{2}\Delta S_{m,t}$ (and of $\frac{1}{2}\Delta S_{m,tr}$) when $\Delta p = 1$, i.e. $\Delta S_{m,conf}$ is of the order of R in the case of Co(II) compounds while the corresponding value of the linear hydrocarbons is of the order of 1.2 – $1.3 R$ and for polyethylene it is $1.18 R$ (ref. 9). Hence, both in the melt and in the high temperature solid polymorphs of the Co(II) compounds the conformational disorder is similar, and is comparable to the conformational disorder in the liquid hydrocarbons. The high temperature polymorphs,

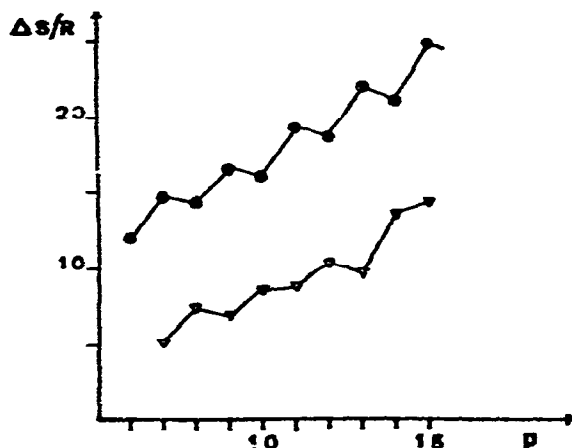


Fig. 2. Comparison between the total melting entropy of $(n\text{-C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CoCl}_4$ salts per mole of alkyl chains (i.e. $\frac{1}{2}\Delta S_{m,t}$) and $\Delta S_{m,t}$ of the linear hydrocarbons having the same number p of conformationally flexible bonds in the chains⁹.

which are stable in a temperature range of 70–80 K, are then formed of ionic regions separated by “liquid” hydrocarbon regions.

In the case of the analogous Mn(II) and Cu(II) salts, $\Delta S'_{m,\text{conf}}$ is of the order of R and $0.9 R$, respectively. This value, lower than that reported for the linear hydrocarbons, has been interpreted in terms of persistence of some degree of conformational ordering in the high temperature polymorphs⁵. Thus in the case of the Co(II) compounds, the conformational freedom of the alkyl chains is reduced, even in the melt, by some type of structural organization.

We are currently investigating these compounds, both in the low and in the high temperature stable modifications, by means of X-ray diffraction, with the aim to obtain information on the structural changes connected to the order–disorder phase transitions discussed in this work.

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