

**TRANSITION METAL COMPLEXES WITH LONG-CHAIN AMINES  
THERMAL BEHAVIOUR AND CRYSTAL STRUCTURE OF  
(n-C<sub>n</sub>H<sub>2n+1</sub>NH<sub>2</sub>)<sub>2</sub>ZnCl<sub>2</sub>**

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**ABSTRACT**

The thermal behaviour of (n-C<sub>n</sub>H<sub>2n+1</sub>NH<sub>2</sub>)<sub>2</sub>ZnCl<sub>2</sub> complexes with  $n = 6, 8, \dots, 16$  has been investigated by DSC and by temperature variable IR and X-ray powder diffraction techniques. Complexes with  $n = 12, 14, 16$  show solid-solid phase transitions which are "melting" transitions of the hydrocarbon regions of the structure. The crystal structure of both the low and the high temperature polymorphs is characterized by the piling of sandwiches, each formed by an "inorganic" layer sandwiched between two alkylammonium layers.

**INTRODUCTION**

In previous papers we showed that compounds of the type (n-C<sub>n</sub>H<sub>2n+1</sub>NH<sub>2</sub>)<sub>2</sub>MCl<sub>4</sub> with M = Mn, Cu, Co ( $n = 9, 10 \dots 17$ )<sup>1-4</sup> and M = Fe, Hg, Zn ( $n = 12$  and  $n = 16$ )<sup>5</sup> can exist, at temperatures near room temperature, in crystalline forms which are characterized by the presence of "inorganic" layers sandwiched between hydrocarbon layers in a "liquid-like" state. The conformational freedom of the alkyl chains in the latter has been found to be comparable to that present in the liquid n-alkanes. The thermal behaviour of the salts with M = Mn, Cu, Fe, Hg is different from the behaviour of the salts with M = Co, Zn<sup>5</sup>. This is related to a different kind of structural organization in the hydrocarbon regions, due to the presence in the inorganic layers of the former of two-dimensional macroanions with octahedral coordination at the metal atom, while unassociated MCl<sub>4</sub><sup>2-</sup> tetrahedra are present in the latter<sup>6</sup>. Thus, both ionic interactions and a two-dimensional network of covalent bonds hold together the structural units in the first case, while only ionic interactions are present in the second. Since we are interested in a more detailed understanding of these unusual disordered solids, we have extended this investigation to a series of Zn(II) complexes of composition (n-C<sub>n</sub>H<sub>2n+1</sub>NH<sub>2</sub>)<sub>2</sub>ZnCl<sub>2</sub>, in which both types of forces seem to be absent.

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TABLE I

CALCULATED AND FOUND COMPOSITION OF  $(n-C_nH_{2n-1}NH_2)_2ZnCl_2$  COMPLEXES WITH VARIOUS  $n$ 'S

$n$	C		H	
	Calc. (%)	Found (%)	Calc. (%)	Found (%)
6	42.60	42.53	8.88	8.92
8	48.73	48.80	9.64	9.61
10	53.33	53.26	10.22	10.28
12	56.92	57.01	10.67	10.70
14	59.79	59.82	11.03	10.98
16	62.14	62.07	11.33	11.37

## EXPERIMENTAL

Compounds were prepared by mixing hot ethanolic solutions of zinc chloride and alkylamine in the molar ratio 1:2. After boiling for 5 min, the resulting solutions were allowed to cool to room temperature, the white precipitates filtered and recrystallized twice from absolute ethanol. The analyses of the compounds examined in this work are given in Table I. The thermograms of all the compounds have been registered between 190 and 470 K on a Perkin-Elmer DSC-1 apparatus at the scanning rate of 8 K min<sup>-1</sup> in N<sub>2</sub> atmosphere. Pure reference compounds were used to calibrate the temperature scale. Transition enthalpies have been obtained using as a reference standard a weighed sample of indium ( $\Delta h = 28.5$  J g<sup>-1</sup>). The reported transition enthalpies and entropies represent mean values of several measurements on independent samples. For each set of measurements the standard deviation is in the order of 5%.

X-ray diffraction patterns of compacted samples of the powders were taken by reflection with a Philips diffractometer using Cu K $\alpha$  radiation. The diffractometer was equipped with an oil-heated apparatus, which allows to obtain diffraction patterns at various temperatures with temperature controls as good as  $\pm 1$  K. Details of this apparatus have been previously described<sup>6</sup>. Infrared spectra were taken with a Perkin-Elmer 457 IR. Spectrophotometer equipped with a heatable sample cell. Samples were prepared by gently pressing the finely powdered compounds between KBr windows. Sample thicknesses were in the order of 0.05 mm.

## RESULTS

Figure 1 shows typical heating thermograms of the compounds examined in this work. With the exception of the hexylamine complex, all the compounds show solid-solid phase transitions at temperatures lower than 370 K and melt between 404 and 422 K, giving a liquid-crystalline material which is stable in a short range of temperatures. In the case of the hexylamine complex, a solid-solid phase transition is observed also at 440 K, very close to the melting temperature. Table 2 shows transition and melting temperatures, enthalpies and entropies as obtained from

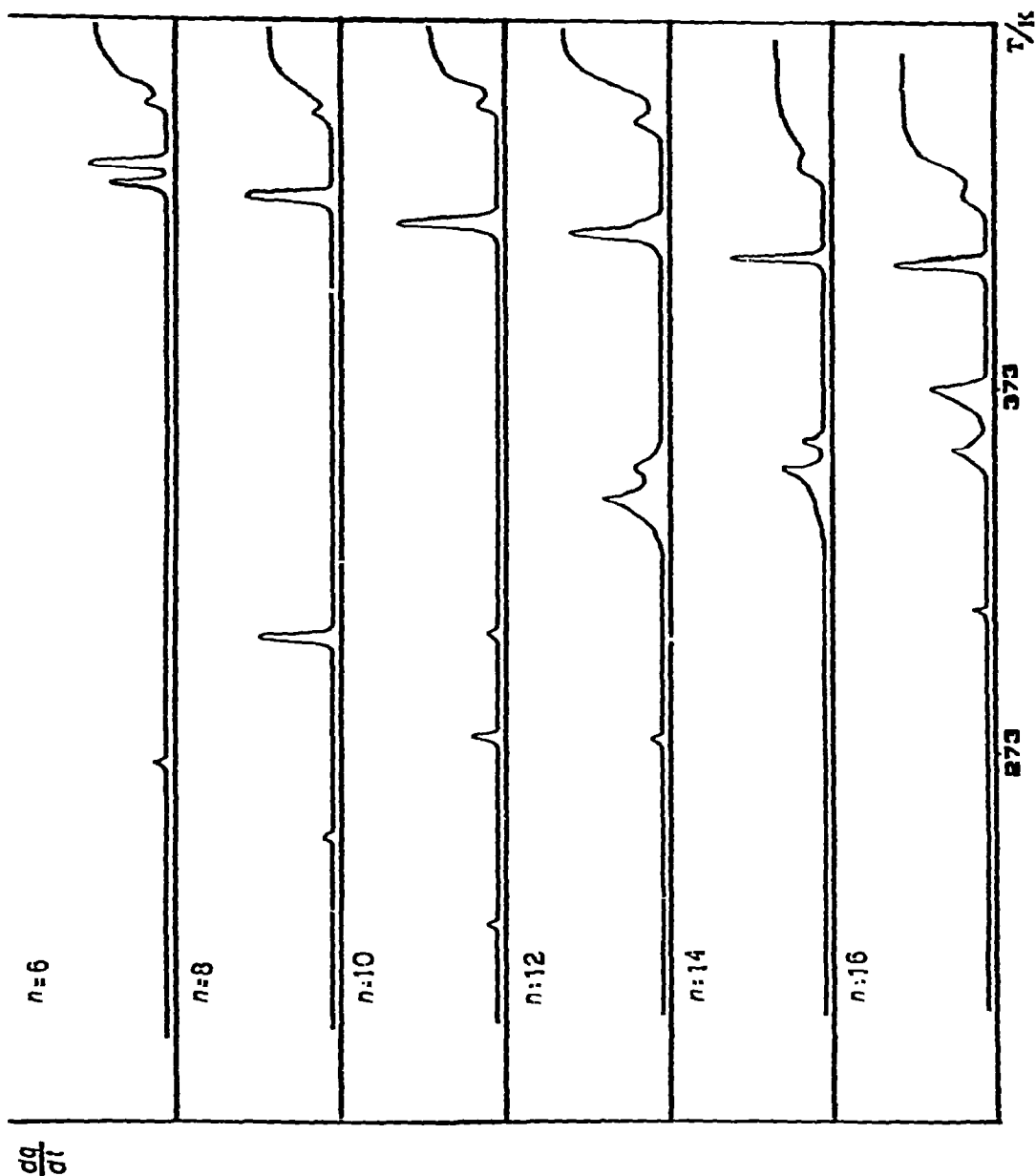


Fig. 1. Typical heating thermograms of  $(n\text{-C}_n\text{H}_{2n+1}\text{NH}_2)_2\text{ZnCl}_2$  complexes with various  $n$ 's.

heating thermograms. Where two or more transition maxima are unresolved, the molar enthalpies have been obtained from the total areas under the curves.

X-ray diffraction patterns taken by reflection have been obtained, for all the complexes investigated in this work, at room temperature and at 380 K. Figure 2 shows the low angle portion of the patterns obtained when  $n = 6, 8, 16$  at low and high temperatures. The diffraction patterns of all the complexes are characterized by the presence of a series of maxima which correspond to a unique interlayer spacing.

TABLE 2

TRANSITION AND MELTING TEMPERATURES, ENTHALPIES AND ENTROPIES FOR  $(n\text{-C}_n\text{H}_{2n+1}\text{NH}_2)_2\text{ZnCl}_2$  COMPLEXES (DSC, HEATING SCANS)

$n$	$T(K)$	$\Delta H(kJ\ mol^{-1})$	$\Delta S(J\ K^{-1}\ mol^{-1})$
6	269	1.3	4.8
	427	8.5	20
	440 <sup>a</sup>	14	31
8	250	1.2	4.8
	301	19	63
	422 <sup>a</sup>	20	48
10	235	1.8	7.7
	276	5.4	20
	304	1.9	6.3
	417 <sup>a</sup>	22	52
12	277	1.3	4.7
	335-343	28	83
	413 <sup>a</sup>	24	57
14	342-351	36	104
	407 <sup>a</sup>	26	64
16	310	1.1	3.5
	351-368	43	120
	404 <sup>a</sup>	29	72

<sup>a</sup> Melting.

TABLE 3

DISTANCES BETWEEN SUCCESSIVE "INORGANIC" LAYERS IN  $(n\text{-C}_n\text{H}_{2n+1}\text{NH}_2)_2\text{ZnCl}_2$  COMPLEXES AT 295 AND 380K

$n$	$c(\text{Å})$	
	$T = 295K$	$T = 380K$
6	18.7	19.0
8	23.6	23.8
10	27.4	28.3
12	28.6	32.5
14	31.5	37.4
16	34.8	41.5

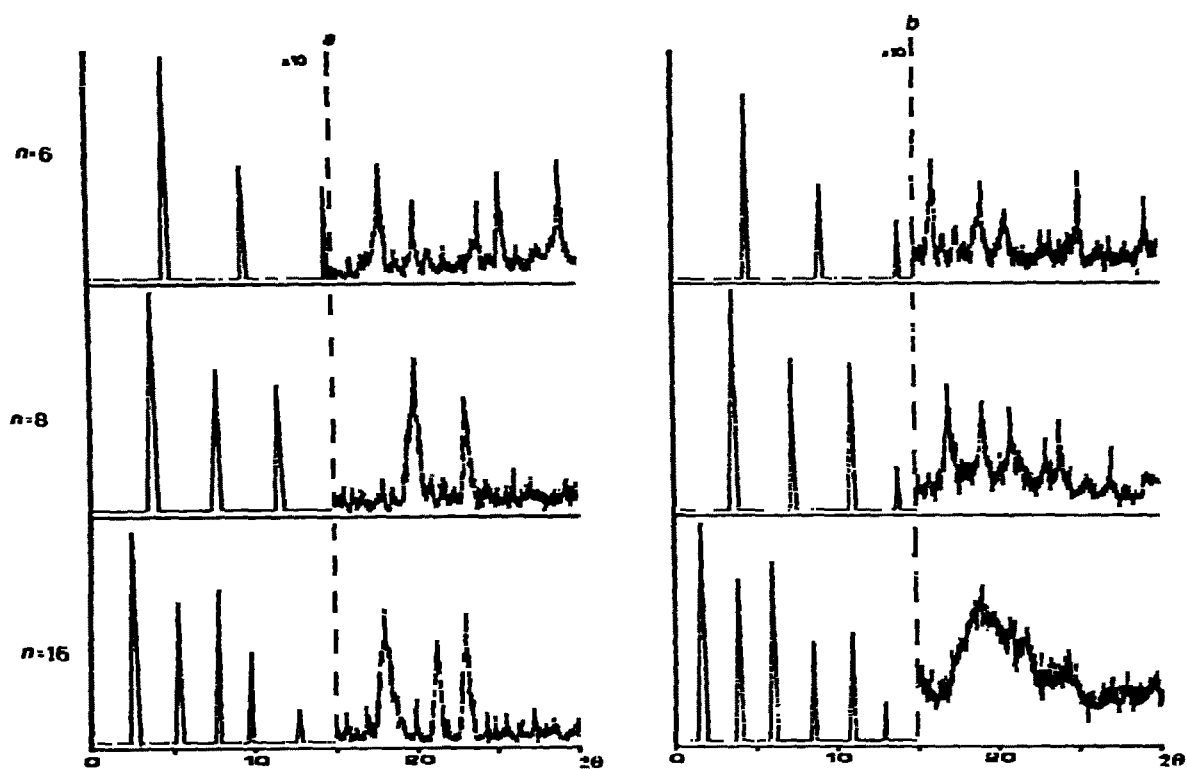


Fig. 2. Low angle portion of the X-ray diffraction patterns of the title complexes with  $n = 6$ ,  $n = 8$  and  $n = 16$  taken by reflection at room temperature (a) and at 380K (b). Cu  $K\alpha$  radiation, Ni filter.

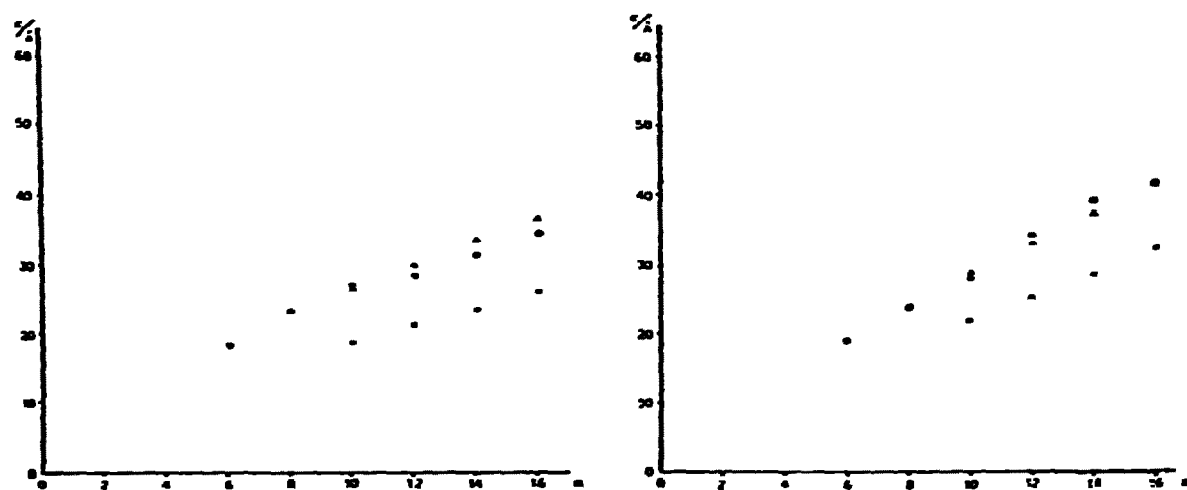


Fig. 3. Comparison of the interlayer distances deduced from the X-ray diffraction patterns of the title complexes (★) and of  $(n-C_nH_{2n+1}NH_2)_2MCl_4$  salts with  $M = Mn$  (▲) and  $M = Co$  (■), taken by reflection at room temperature (left-hand side) and around 380K (right-hand side).

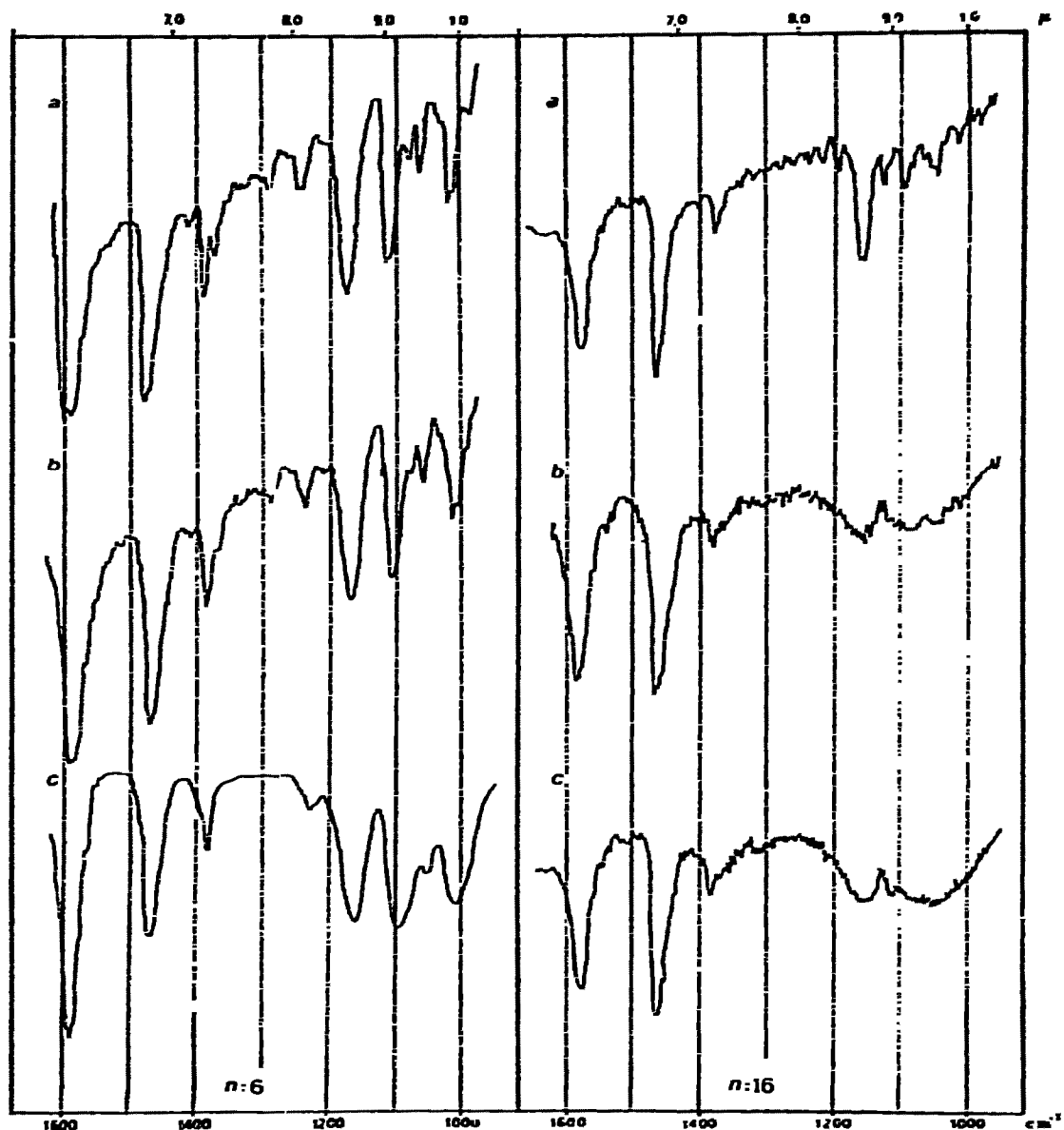


Fig. 4. The  $1600\text{-}1000\text{ cm}^{-1}$  region of the infrared spectra of the title complexes with  $n = 6$  and  $n = 16$  taken at room temperature (a), at  $380\text{K}$  (b) and at a few degrees above the respective melting points.

Table 3 shows the interlayer spacing deduced from the patterns at both temperatures, and Fig. 3 compares these values with the corresponding data found in the case of the tetrachloromanganates and tetrachlorocobaltates. Figure 4 shows the  $1600\text{-}1000\text{ cm}^{-1}$  region of the infrared spectra of the complexes with  $n = 6$  and  $n = 16$  taken at various increasing temperatures.

## DISCUSSION

The thermal behaviour of compounds containing long-chain alkyl groups is often characterized in the solid state by a number of phase transitions, which may be associated to very large entropic effects due to the liberation of rotation movements about the C–C skeletal bonds. A limiting case in this respect, recently investigated by us, are the alkylammonium tetrachlorocobaltates, in which the melting entropy is very small if compared with the entropy increase at the solid–solid transition point<sup>4</sup>. This is mainly due to the high conformational freedom of the alkyl chains in the disordered polymorphs. Table 2 shows, however, that this is not the case for the complexes examined in this work. The melting entropy is in fact greater than the total transition entropy when  $n = 6, 8, 10$  and of the same order in the remaining cases. The X-ray powder diffraction patterns and the infrared spectra of Figs. 2 and 4 show, on the other hand, that the observed phase transitions are mainly of the order–order kind when  $n = 6, 8, 10$  and of the order–disorder kind in the other cases. This is decidedly shown by the presence of a typical amorphous halo<sup>7</sup>, centered around 4.93 Å, in the high-temperature patterns of the longer-chain complexes, while sharp peaks are observed in the same region when  $n = 6, 8, 10$ . The same conclusion can be derived from the infrared spectra of Fig. 4. While in fact no significant differences are observed between low- and high-temperature spectra for the compound with  $n = 6$  in the solid state, the high-temperature spectrum of the hexadecylamine complex is very different from the low-temperature one, and practically identical to the spectrum obtained from the molten compound. A more detailed discussion on this kind of spectra can be found in ref. 9. The solid–solid transitions observed for the higher members of the series are thus order–disorder phase transitions, and the alkyl chains are conformationally disordered in the high-temperature polymorphs.

Further information on the structure of the low- and the high-temperature polymorphs can be obtained from the X-ray diffraction patterns. These are very similar to the patterns observed in the case of the alkylammonium tetrachlorometalates<sup>1–3, 6, 9</sup>, and can be considered as indicative of a layer structure in which

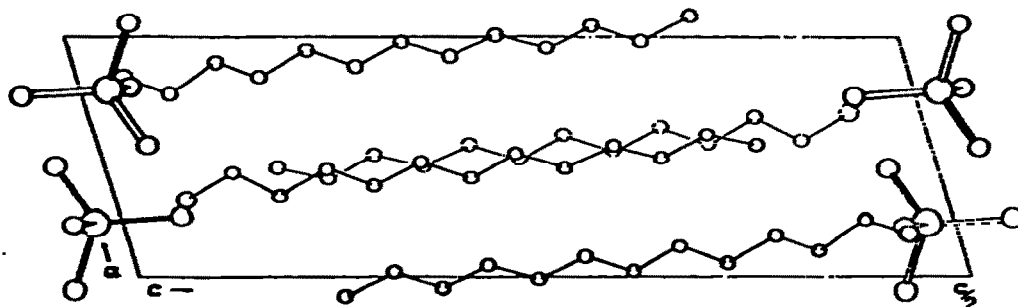


Fig. 5. View of the layer structure of  $(n\text{-C}_{2n+1}\text{NH}_3)_2\text{MCl}_4$  salts with  $M = \text{Co}$  and  $M = \text{Zn}$ , showing intercalation among chains from successive inorganic layers (room temperature form).

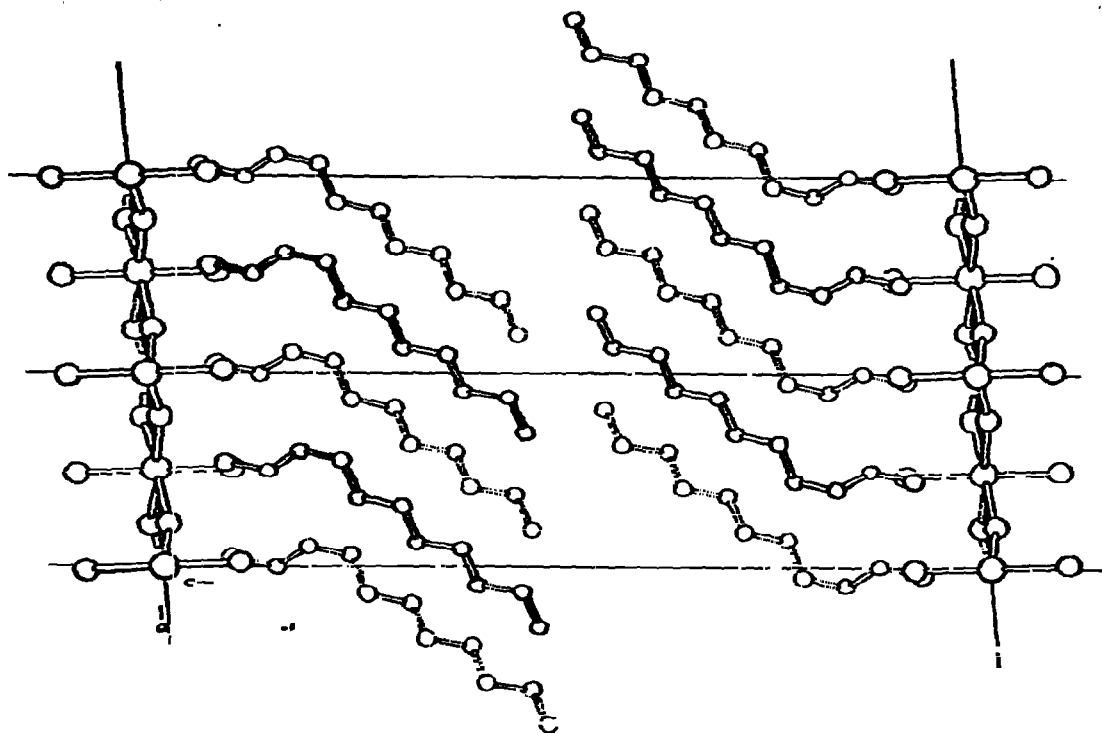


Fig. 6. View of the layer structure of  $(n\text{-C}_{12}\text{H}_{25-1}\text{NH}_3)_2\text{MnCl}_4$  salts with  $M = \text{Mn}$  (room temperature form).

hydrocarbon and inorganic layers are alternate. The main structural difference between  $\text{Mn(II)}$  and  $\text{Co(II)}$  or  $\text{Zn(II)}$  alkylammonium salts lies in the mode of packing of the alkyl chains in the low-temperature polymorphs. In the case of the  $\text{Mn(II)}$  salts, the macroanions are sandwiched each between two alkylammonium layers with the  $-\text{NH}_3^+$  groups in contact with the macroanions. Successive sandwiches face each other with the methyl ends of the chains. In the case of the  $\text{Co(II)}$  and  $\text{Zn(II)}$  salts, however, adjacent layers of alkylammonium ions are intercalated. The alkyl chains are perpendicular to the inorganic layers in the latter (Fig. 5), while they are bent at an angle of the order of  $45^\circ$  in the  $\text{Mn(II)}$  salts (Fig. 6)<sup>6, 8</sup>. The presence of intercalation of the alkyl chains causes the  $\text{Co(II)}$  and  $\text{Zn(II)}$  salts to show smaller values of the distance between successive inorganic layers. The structure of the high-temperature polymorphs seems to be in both cases characterized by facing disordered hydrocarbon layers without intercalation.

The plots of Fig. 3 show that the main structural features of the  $\text{Zn(II)}$  complexes examined in this work are probably similar to those of the tetrachloromanganates, both in the low- and high-temperature disordered forms of the higher members of the series. If it is so, an interesting point can be the reason why structures like that in Fig. 6 are preferred with respect to structures with intercalation like that shown in Fig. 5. We intend to perform a single crystal structure determination of the complex with  $n = 16$  in order to obtain more direct information on this point.



## ACKNOWLEDGEMENT

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