

## An Investigation of Factors Governing Conformational Disorder of Hydrocarbon Chains in the Solid State

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Two families of transition-metal complexes, bis(di-*n*-alkylammonium)tetrachlorometallates and bis(*n*-alkylpyridine)dichlorometallates, were prepared and studied by differential scanning calorimetry. This study was undertaken in order to investigate the factors which govern conformational disorder of the *n*-alkyl chains in the solid state. Many of the compounds prepared displayed solid-solid phase transitions, but the thermodynamic quantities measured suggest that the bonding and structural features of these complexes control the reversibility and limit the extent of conformational disorder of the hydrocarbon chains in the solid state. © 1987 Academic Press, Inc.

### Introduction

There is considerable interest at present in the physical properties of molecular composites (1)—materials composed of organic constituents linked to inorganic matrices. Materials of this type can exhibit many unusual properties, especially with variation of temperature and pressure, and also with slight changes in composition. In cases in which the organic portion of the molecular composite includes long alkyl chains, one often sees smectic mesophases that can be used to model membrane bilayers (2).

For some years, we have been particularly interested in the thermodynamics of solid-solid phase transformations in a family of molecular composites of the general formula  $(RNH_3)_2MX_4$ , where  $R = n$ -alkyl,

$M = Cu, Mn, Cd$ , and  $X = Cl$  (3-7). The structure of these compounds consists of layers of corner-sharing  $MX_6^{2-}$  octahedra separated by alkylammonium groups (8-12). The ammonium headgroup points at the layer and is situated in a cavity of the layer (ca.  $7 \times 7 \text{ \AA}$ ) formed by eight chlorine atoms. If the alkyl chain length is sufficient, it is possible to have solid-solid phase transformations due to "melting" of the alkyl chains, while the integrity of the inorganic layer is retained. The origin of the unusual sandwich structure is thought to be the electrostatic interactions which cause the inorganic portions to separate into layers (13). These layers then remain stable to temperatures much above the threshold for thermal excitation of conformational disorder in the hydrocarbon chains.

In our studies of the "melting" of the alkyl chains in the environments of these molecular composites, we have found an interesting linear relationship between the

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transition entropy per carbon and the length of the alkyl chain—the  $S_nT$  equation (14). One of the aims of the present study was to extend the investigation of the “melting” of alkyl chains to those in other types of molecular composites in order to test the generality of the  $S_nT$  relationships.

A further motivation for the present work was the possibility of designing molecular composite materials for use in thermal energy storage. The latent heat due to alkyl chain “melting” in  $(RNH_3)_2MX_4$  compounds has been suggested (15) for this use, particularly since the materials have good heat-transfer properties due to the inorganic components and because the transformations occur in a useful temperature range (0 to 100°C). These materials have the particular advantage over latent-heat storage materials that involve melting in that the molecular composites remain as solids throughout the transformations. A major disadvantage to these materials is that their heat storage capability is somewhat less than that of most enthalpy-of-fusion materials, such as Glauber salts. However, the transition entropy (and hence enthalpy) will increase with increased alkyl chain density; paraffins have the maximum alkyl chain density, and although they have high-enthalpy transitions (16–18), the disorder of the alkyl chains causes true melting to a liquid phase. Paraffins have been suggested for energy storage (19), but they have the difficulties commonly associated with enthalpy-of-fusion materials, i.e., lack of reversibility, poor heat transfer properties, and containment problems. It was therefore our intention to delineate some of the essential structural and bonding features, and the effects of varying the hydrocarbon proportions, on the solid-state disorder of the alkyl chains.

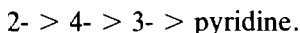
The preparation and properties of two families of transition-metal complexes containing alkyl chains will be described. The first includes compounds with increased al-

ky chain density: these compounds are of the general formula  $((C_nH_{2n+1})_2NH_2)_2MCl_4$ . While only a few short-chain members of this series had been synthesized previously, it is known that the structure of these compounds is different from the  $(RNH_3)_2MX_4$  materials.

A few investigations of branched-alkyl or dialkyl copper salts have been carried out previously (20–26). For  $CuCl_4^{2-}$  alkylammonium salts, if the cation is bulky enough it can prevent the formation of the two-dimensional layer structure. For  $R =$  isopropyl, the structure contains ribbons, rather than layers, of linked  $CuCl_6^{2-}$  octahedra and this material undergoes chromic phase transitions (20, 22, 24, 26). For  $R =$  diethyl, the structure contains discrete  $CuCl_4^{2-}$  ions, and a thermochromic phase transition from green to yellow is observed (22). As the temperature is increased, the  $N-H \cdots Cl$  hydrogen-bonding scheme changes as a result of thermal motion of the organic cation, and this forces the change of coordination around the copper ion from square-planar (green) to a much less constrained distorted-tetrahedral geometry (yellow). In the present investigation, complexes of dialkylammonium ions with transition-metal halides were prepared in order to observe the thermodynamic properties of longer-chain derivatives and to determine the effects of changing the transition metal.

The second family of compounds investigated is of the general formula  $ML_2Cl_2$ , where  $M = Mn, Cd$  and  $L = 4-n-C_nH_{2n+1}$  pyridine (abbreviated  $MC_npy$ ). This series was selected to meet the following requirements: a network structure, sufficient room for the packing of the alkyl chains, and strong bonding between the metal and the ligand. The pink  $Mnpy_2Cl_2$  has been shown to be polymeric with octahedral coordination around the Mn (27, 28), and some alkyl-substituted pyridine complexes have been prepared previously (29). It is generally accepted that the major factors govern-

ing coordinative bond strengths in  $ML_2Cl_2$  complexes are the electrostatic effect between  $M$  and  $L$ ,  $L \rightarrow M$  sigma-bonding,  $M \rightarrow L$  pi-bonding, and  $L \rightarrow M$  pi-bonding. The coordination strength, based on the position of electron-releasing substituents in the pyridine ring, decreases in the order (30)



Therefore, based on coordination considerations, the 2-substituted pyridines would be most favorable, but the steric effect is profound for 2-substituents. For these reasons, 4-alkyl-substituted pyridine complexes were investigated. Although this series has an alkyl chain density comparable to that of compounds of the type  $(RNH_3)_2MX_4$ , the investigation of 4-*n*-alkyl pyridine compounds was considered to be the first step before proceeding to similar compounds with higher alkyl chain proportions, such as 3,4-dialkyl pyridine compounds and 4-branched alkyl pyridine compounds.

## Experimental

### *Preparation of $((C_nH_{2n+1})_2NH_2)_2MCl_4$*

The synthesis was based on the method of Remy and Laves (32). The first step was the preparation of the dialkylammonium chlorides, carried out as follows. Dimethylammonium chloride (BDH) was recrystallized twice from ethanol, suction filtered, washed several times with anhydrous diethylether, dried under vacuum, and stored in a desiccator. Diethylammonium chloride was prepared by passing dry HCl gas through an ether solution of diethylamine (Aldrich); the precipitate was suction filtered, washed several times with diethylether, dried under vacuum, recrystallized from ethanol, suction filtered, dried under vacuum, and stored in a desiccator. Dipropylamine, dibutylamine, and dihexylamine (Pfaltz and Bauer) were downward dis-

tilled, and then prepared as for the diethylammonium chloride. Carbon, hydrogen, and nitrogen analyses confirmed empirical formulae.

The dialkylammonium metal chlorides were prepared by mixing stoichiometric amounts of hot saturated ethanol solutions of the metal halide and the appropriate dialkylammonium chloride. In most cases the products did not precipitate upon cooling to  $-20^\circ\text{C}$ , so the volume was reduced by evaporating at  $50^\circ\text{C}$ ; this was followed by the addition of *n*-propanol and/or diethylether before cooling to  $-20^\circ\text{C}$ . (To overcome solubility problems, some other solvent systems were used in some cases, as noted in Table I.) The precipitates were suction filtered, washed with anhydrous diethylether, and dried under vacuum. Compositions were confirmed by C, H, N analyses and although the analyses did not indicate the presence of water of hydration, it is possible that the compounds prepared were indeed hydrates as observed previously for bis(diethylammonium)tetrachlorozincate (33). The products prepared, solvents used, product description, and melting points determined are given in Table I.

### *Preparation of $M(4-n-C_nH_{2n+1}\text{pyridine})_2Cl_2$ Complexes*

The complexes were prepared by a method similar to that used to make the unsubstituted pyridine complexes (34), i.e., by the addition of the ligand to stoichiometric amounts of  $MnCl_2 \cdot 4H_2O$  or  $CdCl_2$  in hot methanol. In the case of ligands which were solids at room temperature, these were first dissolved in hot methanol. The ligands used were 4-methyl pyridine, 4-ethyl pyridine, 4-*n*-hexyl pyridine, 4-*n*-heptyl pyridine, 4-*n*-octyl pyridine, 4-*n*-decyl pyridine, 4-*n*-undecyl pyridine, and 4-*n*-dodecyl pyridine (Parish Chemicals). The desired products precipitated out on the addi-

TABLE I  
PHYSICAL PROPERTIES OF COMPOUNDS OF THE GENERAL FORMULA  
(C<sub>n</sub>H<sub>2n+1</sub>)<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>MCl<sub>4</sub>

<i>M</i>	<i>n</i>	Solvent	Physical appearance	Melting point (°C)
Zn	1	EtOH	White needles	172–173
Zn	2	EtOH	White needles	89–90
Zn	3	EtOH/ <i>n</i> -PrOH	White powder	83–84
Zn	4	EtOH/Et <sub>2</sub> O	White crystals	153–154
Zn	6	EtOH/ <i>i</i> -PrOH	White powder	91–92
Co	1	EtOH	Blue crystals	176–177
Co	2	EtOH	Blue crystals	87–88
Co	3	EtOH/Et <sub>2</sub> O	Blue crystals	81–83
Co	4	EtOH/Et <sub>2</sub> O	Blue crystals	152–153
Co	6	EtOH/ <i>i</i> -PrOH	Blue crystals	90–91
Cu	1	EtOH	Yellow powder	123–124
Cu	2	EtOH	Dark-green needles	83–84
Cu	3	EtOH/ <i>n</i> -PrOH	Lime-green needles	81–82
Cu	4	EtOH/ <i>n</i> -PrOH/Et <sub>2</sub> O	Orange crystals	92–93
Cu	5	<i>n</i> -PrOH/Et <sub>2</sub> O	Yellow needles	77–78
Cu	6	<i>i</i> -PrOH/ <i>n</i> -hexane	Yellow powder	87–89
Mn	1	EtOH/Et <sub>2</sub> O	Yellow-green needles	148–149
Mn	2	EtOH	Yellow-green needles	76–77
Mn	3	EtOH/ <i>n</i> -PrOH	Yellow-green crystals	60–61
Mn	4	EtOH/Et <sub>2</sub> O	Yellowish-green crystals	122–123
Mn	6	<i>i</i> -PrOH	Light yellow powder	74–75

tion of the ligand and were washed with ether and air dried.

The complexes were characterized by the changes in the infrared spectra of the substituted-pyridine ligands, which were consistent with expected frequency shifts on coordination (28). Empirical formulae were confirmed by C, H, N analyses. The physical appearance and melting points of the *M*(4-*n*-C<sub>n</sub>H<sub>2n+1</sub> pyridine)<sub>2</sub>Cl<sub>2</sub> complexes prepared are given in Table II.

#### Differential Scanning Calorimetry

All differential scanning calorimetry above room temperature (300 to 500 K) was carried out on a Perkin–Elmer DSC-1, modified to include a data acquisition system controlled by an IBM PC (35). The melting point of indium was used for enthalpy and temperature calibration. The subambient (120 to 300 K) results were ob-

TABLE II  
PHYSICAL PROPERTIES OF COMPOUNDS OF THE  
GENERAL FORMULA *M*(4-*n*-C<sub>n</sub>H<sub>2n+1</sub> PYRIDINE)<sub>2</sub>Cl<sub>2</sub>

<i>M</i>	<i>n</i>	Physical appearance	Melting Point (°C) <sup>a</sup>
Mn	1	Pale pink needles	>300
Mn	2	Pale pink powder	>300
Mn	6	Pale pink powder	121
Mn	7	Pale pink powder	93
Mn	8	Pale pink powder	140 d
Mn	10	Pale pink powder	d < m
Mn	11	Pale pink powder	153 d
Mn	12	Pale pink powder	150 d
Cd	1	White powder	>300
Cd	2	White powder	>300
Cd	6	White powder	187
Cd	7	White powder	180
Cd	8	White powder	164
Cd	10	White powder	149
Cd	11	White powder	160
Cd	12	White powder	148

<sup>a</sup> d = Decomposes; d < m = decomposes before melting.

tained on a Perkin–Elmer DSC-2C, calibrated with the solid–solid phase transition and melting point of cyclohexane. The accuracy in the transition temperatures (taken as onset temperatures) is  $\pm 2$  K, and enthalpies are  $\pm 10\%$ . Typical sample sizes for DSC were 10 mg, and all scans were performed at  $10 \text{ K min}^{-1}$ .

### Results and Discussion

The thermodynamic data from DSC experiments on compounds of the general formula  $((C_nH_{2n+1})_2NH_2)_2MCl_4$  (abbreviated  $DC_nM$ ) are given in Table III.

The phase transformations in the shorter-chain members of the  $((C_nH_{2n+1})_2NH_2)_2MCl_4$  series that are not associated with melting are most likely due to thermal motion of the organic cation, which causes changes in the hydrogen bonding between the ammonium headgroup and the chloride ions, as is observed in the shorter-chain compounds of the general formula  $(C_nH_{2n+1}NH_3)_2MCl_4$  (4, 5) and also in  $DC_2Cu$  (22).

In  $DC_2Cu$ , the thermochromic phase transition was quoted to occur at  $43^\circ\text{C}$  (22), whereas in this investigation it was seen at  $53^\circ\text{C}$ . It was observed that when  $DC_2Cu$  had been melted and then resolidified, it took several hours at  $-20^\circ\text{C}$  before the thermochromic transition reappeared, even though the melting transition could be reproduced, in general agreement with previous findings concerning hysteresis in this compound (36). This suggests that the thermal motion of the organic cation is very difficult to slow down and put into its minimum-energy position in the sterically crowded environment. This is also reflected in the observation that these compounds required very concentrated ethanolic solutions and extended periods at low temperatures before they could be crystallized from solution.

$DC_2M$  with  $M = Cu, Zn, Mn,$  and  $Co$  all

TABLE III  
THERMODYNAMIC PROPERTIES OF COMPOUNDS OF  
THE GENERAL FORMULA  $((C_nH_{2n+1})_2NH_2)_2MCl_4$

<i>M</i>	<i>n</i>	<i>T</i> <sub>onset</sub> (K)	$\Delta H$ (kJ mole <sup>-1</sup> )	$\Delta S$ (J K <sup>-1</sup> mole <sup>-1</sup> )	Notes <sup>a</sup>
Zn	1	437	23.9	54.8	
		445	13.5	30.3	m
Zn	2	330	2.42	7.3	
		362	16.7	46.1	m
Zn	3	356	31.7	89.0	m
Zn	4	222	3.06	13.8	
		427	29.5	69.0	m
Zn	6	365	50.9	139	pm/m
Co	1	438	24.1	55.0	
		448	12.8	28.6	m
Co	2	330	2.34	7.09	
		361	16.7	46.3	m
Co	3	354	31.0	87.5	m
Co	4	226	3.26	14.4	
		425	33.2	78.1	m
Co	6	364	47.8	131	m
Cu	2	327	14.7	44.9	
		359	21.6	60.1	m
Cu	3	330	4.26	12.9	<i>s</i> > 1
		353	38.2	108.2	m
Cu	4	368	27.5	74.7	pm/m
Cu	5	351	28.0	79.8	m
Cu	6	319	3.81	12.0	
		359	13.9	38.6	m
Mn	1	420	32.3	76.9	m
Mn	2	327	6.56	20.1	
		349	16.6	47.6	m
Mn	3	332	23.1	69.6	m
Mn	4	236	3.20	13.6	
		396	29.3	74.0	m
Mn	6	349	49.8	143	pm/m

<sup>a</sup> m = Melting; pm/m = premelting overlapped with melting; *s* > 1 = only appeared after first scan.

showed similar thermodynamic behavior. All of the compounds undergo solid–solid phase transitions at approximately 330 K but the entropies of the transitions differed. For  $M = Zn$  and  $Co$ , the solid–solid phase transitions had approximately the same entropy changes (0.9 R), whereas  $DC_2Cu$  had a very high entropy change (5.4 R). The differences may be due to varying degrees of hydration, as this transition has been shown to be sensitive to hydration in  $DC_2Zn$  (33).

$DC_4M$ , with  $M = Zn, Co,$  or  $Mn$ , showed subambient solid–solid phase transitions; these compounds are unique in this aspect with respect to all of the other dialkyl complexes prepared. The low entropy changes

(1.7 R) suggest that a simple motion occurs, quite possibly a rotator phase as is often seen in paraffins.

The thermodynamics of the Zn and Co derivatives were similar in both temperatures and entropies of transition and both metals favor a tetrahedrally coordinated metal center. Similar ionic radii and hydrogen-bond strengths could account for this behavior.

The most important difference between the monoalkyl and dialkyl compounds is that the former has a polymeric backbone. This results in high melting points (or decomposition temperatures) and the ability of the alkyl chains to undergo solid–solid phase transformations with large conformational disorder without breakdown of the lattice. In the dialkyl complexes, the structure is composed of discrete ions, and the thermal motion of the organic cation weakens the binding forces. Disordering of the organic cation occurs just below or at the melting point. The low melting points of the  $DC_nM$  complexes suggest that, like  $((C_2H_5)_2NH_2)_2CuCl_4$  (22) and  $((C_2H_5)_2NH_2)_2ZnCl_4$  (33), they are nonpolymeric. In the  $DC_nM$  complexes, crystal packing is important to the thermodynamic properties. If packing is very efficient, thermal motion of the organic cation will likely lead to melting of the complex, but if sufficient room is available for motion then a solid–solid phase transition could occur without collapse of the lattice. In cases where no solid–solid phase transitions were observed prior to melting, one can conclude that onset of thermal motion of the organic cation results in melting of the complex.

The thermodynamic data for DSC experiments on  $M(4-n-C_nH_{2n+1} \text{pyridine})_2Cl_2$  compounds are given in Table IV. With the exception of  $MnCl_0py$ , which decomposed before melting, compounds with alkyl chain lengths of fewer than 12 carbons gave solid–solid phase transformations that were stable on repeated thermal cycling to temperatures just below the melting point. The

general pattern of the phase transformations appears to be one or more transformations to new solid phases prior to melting. A number of these transformations involve substantial entropy changes, indicative of conformational disorder in the alkyl chains. In the same temperature range as these transformations, each sample became sticky (but not molten), which again is consistent with orientational disorder. As in the case of the compounds of the general formula  $(RNH_3)_2MX_4$ , the disorder of the alkyl chains appears to take place in a stepwise manner.

For the cases of  $MnCl_2py$  and  $CdCl_2py$ , the large-entropy solid–solid phase trans-

TABLE IV  
THERMODYNAMIC PROPERTIES OF COMPOUNDS  
OF THE GENERAL FORMULA  
 $M(4-n-C_nH_{2n+1} \text{PYRIDINE})_2Cl_2$

<i>M</i>	<i>n</i>	<i>T</i> <sub>onset</sub> <sup>a</sup> (K)	$\Delta H$ (kJ mole <sup>-1</sup> )	$\Delta S$ (J K <sup>-1</sup> mole <sup>-1</sup> )	Notes <sup>b</sup>
Mn	6	339	0.887	2.62	
		370	8.78	23.7	
		394	2.36	5.99	m
Mn	7	327	2.21	6.77	
		349	1.72	4.93	
		366	4.15	11.3	m
Mn	8	329	5.90	17.9	
		413	13.0	31.6	m
		329	12.2	36.9	
Mn	10	340	23.0	67.6	
		370	8.92	24.1	
Mn	11	376	3.40	9.05	
		426	30.0	70.4	m
		339b	53.1	157	s1
		339b	39.5	116	s2
		339b	26.5	78.3	s5
Cd	6	423	26.3	62.2	m
		460	9.19	20.0	m
Cd	7	453	35.5	78.4	m
		375	13.6	36.2	
Cd	8	407	5.06	12.4	
		437	15.8	36.1	m
		325	8.86	27.2	
Cd	10	349	3.30	9.46	
		422	18.9	44.8	m
		395	52.5	133	
Cd	11	433	15.2	35.1	m
		345b	27.8	80.6	s1
Cd	12	360	11.1	30.9	s2
		360	8.11	22.5	s5
		421	30.6	72.7	m

<sup>a</sup> b = Broad.

<sup>b</sup> m = Melting; s1 = first scan; s2 = second scan after first scan to 390 K; s5 = fifth scan after four scans to 390 K.

formations prior to melting were reduced considerably on subsequent scans. This appears to be an indication of breakdown of the lattice (possibly involving formation of nonstoichiometric compounds) concurrent with the disorder of the alkyl chains, and is not altogether surprising for the following reasons. In cases such as  $(RNH_3)_2MCl_4$ , where the hydrocarbon portion of the material is charged, it is known that there is a balance between the tendency for the inorganic portion to segregate into layers for electrostatic reasons and the tendency for the conformational disorder of the alkyl chains to break the layers (13). In the case of the alkyl-substituted pyridine complexes, where the ligand is not charged, the electrostatic component of this delicate balance is reduced, apparently to the detriment of the lattice at temperatures sufficient to thermally excite conformational disorder in the alkyl chains. It is interesting that we are able to see the switching point in this balance with the increase in alkyl chain length, from stable transformations in MC11py to instability in MC12py.

In summary, we have investigated the structural and bonding considerations that will allow conformational disorder in alkyl chain-containing materials, without complete disruption of the lattice. It appears that the polymeric backbone is necessary to achieve full conformational disorder in the chains in the solid state. This is allowed in monoalkylammonium transition-metal halide complexes, but in the dialkyl complexes chain disorder leads to melting. In addition, we have shown that it is important to have an ionic bond between the alkyl chain-containing moiety and the inorganic lattice; in the absence of an ionic bond the chain-melting process appears to degrade the lattice network.

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