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Polymorphism in the Bis(phenalkylammonium)tetrachlorometallates

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Compounds of the general formula, $(C_6H_5C_nH_{2n}NH_3)_2MCl_4$, where $n = 1$ to 10; M = Cd, Cu, Zn, and Co; were prepared and characterized by differential scanning calorimetry. All of the compounds prepared with $n > 1$ were observed to undergo solid–solid phase transitions and the high entropies of the solid–solid phase transitions indicate that there is a considerable amount of disorder in the high-temperature phase. Similarity of the thermodynamic results divides the compounds into two groups: the Cd and Cu derivatives, and the Co and Zn derivatives. Trends within each group and between groups can be attributed to the influence that phenyl group packing has on the thermodynamic behavior.

Introduction

One area of high current interest is the synthesis and characterization of low-dimensional solids (*1–4*). Early studies in low-dimensional solids concentrated on properties that arise when the interactions between atoms and molecules are confined to one or two dimensions, especially magnetic interactions. Another interaction which is of interest in low-dimensional systems is order–disorder phase transitions. By fixing one end of a molecule to a surface, phenomena such as two-dimensional order–disorder transitions have been observed. Such phenomena are seen in biological systems, such as lipid bilayers, as well as molecules adsorbed on surfaces.

Compounds of the general formula $C_nH_{2n+1}NH_3)_2MCl_4$, (abbreviated C*nM*), where *M* is a divalent transition metal ion, have been the subject of many recent investigations because they show a variety of two-dimensional structures and undergo both structural and magnetic phase transitions. The structures and the thermodynamics of the phase transitions are a function of both the metal and the chain length.

When *M* = Cr, Mn, Cu, Cd, Pd, or Fe, these compounds form layered perovskite structures, consisting of infinite layers of corner-sharing MX_6 octahedra separated by alkylammonium groups (*5–11*). The ammonium head group points at the layer and is situated in a cavity of the layer formed by eight chlorine atoms. All of the chlorine atoms in the box are potential hydrogen bond acceptors; either box distortion (i.e., octahedral tilting) controls the hydrogen-bonding scheme or the hydrogen-bonding scheme controls the box distortion; both effects seem to operate (*12, 13*).

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The alkyl chains of adjacent layers do not interdigitate in these compounds and this kind of structure, with hydrophobic organic chains and hydrophilic tails, has an obvious similarity to that of the lipid bilayers. It is not surprising, therefore, that the complicated sequences of structural phase transitions that exist in the layered pervoskites make a very close analogue to those of the lipid bilayers.

The alkyl chains themselves can undergo phase transitions due to "chain melting." When the alkyl chain is sufficiently long, most of these systems exhibit two or more phase transitions due to the step-wise disorder of the alkyl chains. The entropy change at the minor transition for C10Cd is approximately 0.9 R per mole of chain and can be attributed to an order–disorder transition of rigid chains between two equivalent sites (*7*). The entropy change of the major transition is approximately 6.3 R per mole of chain and has been attributed to chain melting, and the trend to increased temperature and enthalpy of the transition with increasing chain length is similar to that observed for the melting of *n*-alkanes (*14–16*) and the melting transition observed in the lipid bilayers (*17*).

The layers stack upon each other and are held together by weak van der Waals forces; the interlayer distance is linearly dependent on the length of the alkyl chain. The distance between adjacent alkyl chains within a layer is dictated by the spacing between the cavities in the layer, and is therefore metal dependent. The direction of the packing arrangement is also metal dependent. In C10Cd, the low-temperature structure has the alkyl chains oriented in opposite directions on opposite sides of the inorganic layer (+40° or −40°) (*7*), forming a "herringbone" structure and there are two inequivalent types of chains. In the Cu and Mn derivatives all of the alkyl chains are oriented parallel to one another forming a "striped" structure (*18*) in which all the alkyl chains are of the same type. The thermodynamics indicate that the transitions are metal dependent (*19*), as is the minor–major transition sequence (*5*). In most cases, the temperature of the minor transition increases more rapidly with chain length than the major transition, and this is as one might expect if one considers the nature of the two transitions: the minor transition involves the disorder of the chain as a whole, whereas the major transition involves the formation of local disorder (kink formation) (*5*).

Compounds with M = Co or Zn are structurally different from the other members of the family. Instead of the formation of a two-dimensional layer, these compounds form unassociated MCl_4^{2-} tetrahedra (*20*). A crystallographic study of C12Zn has shown that there is sufficient room for the chains to interdigitate (*20*). The thermodynamic properties of these compounds (*21, 22*) are quite different from those of the layered perovskites; in particular, these compounds actually melt (the layered perovskites decompose) due to their nonpolymeric structures. The solid–solid phase transition involving chain melting for a given length of alkyl chain is at a higher temperature and involves a smaller entropy change than that for the corresponding layered perovskite. In addition, these compounds show odd–even effects (i.e., different trends for even and odd alkyl chain lengths), unlike the layered perovskites (*23*).

A detailed investigation of C14Zn revealed that the transition at T = 362.5 K was characterized by the onset of rotation of the alkyl chains (*24, 25*). The transition at T = 367 K involved chain melting and no intercalation of the alkyl chains.

The present investigation deals with compounds formed by the replacement of the terminal methyl group of the alkylammonium layered perovskites with a phenyl group to give $(C_6H_5C_nH_{2n}NH_3)_2MCl_4$, n = 1 to 10, M = Co, Cd, Zn, Cu. The phase transitions of these compounds have been investigated by differential scanning calorimetry.

A little is known about compounds of this type. The magnetic properties have been studied for a number of the phenalkylammonium transition metal halides of the general formula $(C_6H_5C_nH_{2n}NH_3)_2MCl_4$. Magnetic susceptibility measurements have been performed on the 4-substituted anilinium complexes of the general formula $(4\text{-}XC_6H_4NH_3)_2MnCl_4$ where X = F, Cl, Br, and *n*-butyl (*26*), which are structurally similar to the layered perovskites and display the same two-dimensional magnetism. The bis(4-chloroanilinium)tetrachloromanganate(II), tetrachlorocuprate(II), and tetrabromocuprate(II) were investigated by ^{35}Cl NQR (*27*). All of these compounds were observed to have both magnetic and structural phase transitions. Structural phase transitions were observed to occur at T = 343 K in the manganese complex, at T = 275 and 277 K in the tetrachlorocuprate complex, and at T = 198 K in the tetrabromocuprate complex. The experimental results from the NQR experiments suggest that the phase transition was either due to reorientational motion of the ammonium group or small-angle twisting of the phenyl group (*27*).

The magnetic susceptibility (*28*) and lattice constants for M = Cu and n = 1–4 have been determined and they appear to be the same as for the layered perovskites (*29*). Nuclear magnetic resonance experiments from T = 1.4 to 4.2 K were used to determine the temperature and field dependence of the magnetization (*30*) and magnetic susceptibility measurements of $(C_6H_5CH_2NH_3)_2CuCl_4$ indicated that this compound undergoes two consecutive magnetic phase transitions at T = 6 and 6.9 K (*31*).

Experimental

Benzylamine, 2-phenylethylamine, 3-phenylpropylamine, and 4-phenylbutylamine were purchased from Aldrich and used as received. The amines, 5-phenylpentylamine through to 10-phenyldecylamine, were not available commercially and therefore were synthesized. The phenalkylamines were prepared by the reduction of their corresponding amides using lithium aluminum hydride. The amides were prepared from the carboxylic acids by first preparing the acid chlorides followed by reaction with aqueous ammonia in benzene (*32*).

The chloride salts of the amine were prepared by either passing dry HCl gas through an ether solution of the amine or adding aqueous HCl to an ethanol solution of the amine until slightly acidic to litmus. The amine hydrochloride precipitated on cooling and was suction filtered, recrystallized from ethanol/ether or isopropanol/*n*-hexane. The amine hydrochlorides were dried under vacuum over P_2O_5.

Complexes of the general formula $(C_6H_5C_nH_{2n}NH_3)_2MCl_4$, where n = 1–10; M = Cu, Cd, Zn, and Co, were prepared by mixing stoichiometric amounts of hot ethanol solutions of the appropriate amine hydrochloride and transition metal halide (*33*). If precipitation did not occur upon cooling to room temperature or −20°C then the solution was concentrated at 50°C and then the product was precipitated at either room temperature or −20°C. In some cases the solution had to be cooled for several hours in a freezer (−20°C) to obtain a precipitate. If a product was still not obtained then the ethanol was removed and a different solvent or solvent combination was used. When the product was obtained, it was suction filtered and washed with anhydrous diethyl ether. The absence of occluded solvent was confirmed by infrared spectroscopy.

The metal and the corresponding alcohol used, as well as the compound appearance and melting point, where appropriate, are listed in Table I.

All differential scanning calorimetry experiments above room temperature (300–

TABLE I

PROPERTIES OF COMPOUNDS OF THE GENERAL FORMULA $(C_6H_5C_nH_{2n}NH_3)_2MCl_4$

n	M	Solvent[a]	Appearance	M.Pt.[b] (°C)
1	Cd	MeOH/EtOH	White platelets	$d > 268$
1	Cu	MeOH/EtOH	Yellow platelets	$d > 240$
1	Co	EtOH/Et_2O	Blue needles	165–167
1	Zn	EtOH/Et_2O	White needles	160–162
2	Cd	MeOH/EtOH	White platelets	$d > 259$
2	Cu	EtOH	Yellow platelets	$d > 250$
2	Co	EtOH/Et_2O	Blue needles	205–206
2	Zn	EtOH/Et_2O	White needles	203–204
3	Cd	MeOH/EtOH	White platelets	$d > 245$
3	Cu	EtOH	Yellow platelets	$d > 231$
3	Co	EtOH/Et_2O	Blue needles	187–188
3	Zn	EtOH/Et_2O	White needles	183–184
4	Cd	MeOH/EtOH	White platelets	$d > 193$
4	Cu	EtOH	Yellow platelets	$d > 236$
4	Co	EtOH/Et_2O	Blue needles	176–178
4	Zn	EtOH/Et_2O	White needles	$d > 177$
5	Cd	EtOH/Et_2O	White platelets	$d > 179$
5	Cu	EtOH	Yellow platelets	$d > 221$
5	Co	EtOH/Et_2O	Light blue platelets	$d > 177$
5	Zn	EtOH/Et_2O	White platelets	$d > 169$
6	Cd	EtOH/Et_2O	White platelets	$d > 158$
6	Cu	EtOH	Yellow platelets	$d > 226$
6	Co	EtOH/Et_2O	Light blue platelets	$d > 153$
6	Zn	i-PrOH/Et_2O	White platelets	$d > 147$
7	Cd	EtOH/Et_2O	White platelets	$d > 172$
7	Cu	EtOH	Yellow platelets	$d > 220$
7	Co	EtOH/Et_2O	Light blue platelets	$d > 139$
7	Zn	i-PrOH/hex	White platelets	$d > 128$
8	Cd	EtOH/Et_2O	White platelets	$d > 178$
8	Cu	EtOH	Yellow platelets	$d > 226$
8	Co	i-PrOH/hex	Light blue platelets	$d > 131$
8	Zn	i-PrOH/hex	White platelets	$d > 141$
9	Cd	EtOH/Et_2O	White platelets	$d > 170$
9	Cu	EtOH	Yellow platelets	$d > 215$
9	Co	i-PrOH/hex	Light blue platelets	$d > 131$
9	Zn	i-PrOH/hex	White platelets	$d > 138$
10	Cd	EtOH/Et_2O	White platelets	$d > 169$
10	Cu	EtOH	Yellow platelets	$d > 227$
10	Co	i-PrOH/hex	Light blue platelets	$d > 134$
10	Zn	i-PrOH/hex	White powder	$d > 136$

[a] EtOH = absolute ethanol, Et_2O = diethyl ether, i-PrOH = isopropyl alcohol, hex = n-hexane.

[b] M.Pt. = melting point, $d>$ = decomposes above.

475 K) were carried out on a Perkin-Elmer DSC-1, modified to a data acquisition system controlled by an IBM-PC (*34*). The melting point of indium was used for enthalpy and temperature calibration. The subambient (120–300 K) results were obtained on a Perkin-Elmer DSC-2C, calibrated with both the solid–solid phase transition and the melting point of cyclohexane. The accuracy in the transition temperatures (taken as onset temperatures) is ±2 K and the enthalpies are ±10%. Typical sample sizes for DSC runs were 3–10 mg and all scans were performed at heating rates of 10 K min^{-1}.

Results and Discussion

Summaries of the thermodynamic data of the solid–solid phase transitions observed from differential scanning calorimetry experiments on the bis(phenalkylammonium) tetrachlorometallates, of the general formula $(C_6H_5C_nH_{2n}NH_3)_2MCl_4$, where M = Cd, Cu, Zn and Co, n = 1 to 10 (abbreviated PhCnM) are given in Table II.

Like the bis(n-alkylammonium)tetrachlorometallates, the bis(phenalkylammonium)tetrachlorometallates can be separated into two groups according to the transition metal; the Cu and Cd complexes form one group and the Zn and Co complexes form the other. The members of these groups have similar phase behaviors, probably due to their similar crystal structures.

The lattice constants of the PhCnCu complexes are known for n = 1 to 4; they appear to form the layered perovskite structure (*29*) also found in CnCu and CnCd. The physical appearances of the phenalkylammonium complexes are similar to their alkyl chain counterparts; they form highly reflective, thin plates. It seems likely that the PhCnCd complexes form structures similar to CnCd and PhCnCu.

For $n < 4$, the PhCnCo and PhCnZn complexes form needles, and for longer al-

TABLE II

SUMMARY OF THERMODYNAMIC DATA FOR BIS(PHENALKYLAMMONIUM)TETRACHLOROMETALLATES (II), $(C_6H_5C_nH_{2n}NH_3)_2MCl_4$

n	M	T_{tr}(K)	ΔH_{tr} (kJ mole^{-1})	ΔS_{tr}(R)
1	Zn	406*	2.2	0.66
2	Cd	382	12.	3.8
2	Cu	338	0.78	0.28
		410	2.0	0.59
2	Co	296	1.2	0.49
		440	21.	5.8
2	Zn	296	1.2	0.49
		440	22.	5.9
3	Cd	231	2.8	1.5
		456	11.	2.8
3	Cu	202	0.69	0.41
		261	0.16	0.01
		474	12.	2.9
3	Co	417	11.	3.1
		424	3.2	0.89
3	Zn	377*	2.7	0.86
		414	7.7	2.2
		429	4.5	1.3
4	Cd	255	0.90	0.42
		339	6.5	2.3
4	Cu	340	14.	4.8
4	Co	341	20.	7.1
		388	1.2	0.36
4	Zn	339	20.	7.2
		389	1.1	0.35
5	Cd	188	0.46	0.30
5	Cu	197	0.27	0.17
		321*	12.	4.3
		321^{+}	9.4	3.5
5	Co	353*	16.	5.6
		385*	22.	6.8
		343^{+}	16.	5.6
		385^{+}	18.	5.6
5	Zn	349*	17.	5.8
		384*	21.	6.5
		368^{+}	12.	3.9
6	Cd	193	4.5	2.8
		345*	26.	9.0
		344^{+}	25.	8.9
6	Cu	172	5.2	3.6
		343	3.8	1.3
		355	23.	7.7
6	Co	348	19.	6.6
		418	8.1	2.3
6	Zn	348	19.	6.6
		418	8.1	2.3
7	Cd	322	18.	6.8
7	Cu	317*	22.	8.2
		317^{+}	13.	4.8
7	Co	360	47.	16.
7	Zn	361	52.	17.
8	Cd	355*	40.	14.
		355^{+}	39.	13.
8	Cu	358*	45.	15.
		358^{+}	44.	15.
8	Co	244	0.24	0.12
		355*	31.	10.
		355^{+}	29.	9.9
8	Zn	251	0.29	0.14
		356	33.	11.
9	Cd	162	2.8	2.0
		325*	39.	14.
		323^{+}	39.	14.
9	Cu	143	4.2	2.3
		315	12.	4.6
		324	30.	11.
9	Co	355	60.	20.
9	Zn	355/360*	60.	20.
		355/360^{+}	59.	20.
10	Cd	361*	61.	20.
		360^{+}	60.	20.
10	Cu	152	2.7	2.1
		366*	64.	21.
		364^{+}	61.	20.
10	Co	360*	36.	12.
		356^{+}	36.	12.
10	Zn	358*	37.	12.
		356^{+}	37.	13.

* = only seen on the initial scan of a virgin sample.
\+ = observed on successive scans.

kyl chains they have an appearance similar to the layered perovskites: highly reflective thin plates. Crystallographic data are not available for these complexes and it is not known, therefore, if they have an interdigitated bilayer structure like C12Zn. The size of the phenyl group may prevent this. It is known that *n*-decylammonium chloride forms an interdigitated bilayer-type structure (*35*) like C12Zn (*20*) but phenethylammonium chloride and bromide form a chain-type structure where the phenalkyl groups do not interdigitate (*36, 37*). It seems more likely that the structure of the phenalkylammonium complexes of Co and Zn are similar to phenethylammonium chloride and bromide.

No solid–solid phase transitions were observed for the benzylammonium complexes of Cu and Cd (PhC1Cu, PhC1Cd) in the temperature range examined. The inorganic layer and the neighboring phenalkyl groups may restrict the motion of the phenyl group preventing it from flipping or undergoing any motion. Adding one methylene group to the chain results in phase transitions in all of the compounds examined. Moving the phenyl group further away from the layer apparently permits it to undergo order–disorder phase transitions which may in turn facilitate hydrogen-bonding changes.

PhC1Zn displayed one solid–solid phase transition but this transition disappeared after the first scan. PhC1Co did not display any solid–solid phase transitions.

The DSC results for all of the phenethylammonium (PhC2) complexes indicate solid–solid phase transitions. The cadmium derivative (PhC2Cd) displayed only one phase transition and the associated entropy change is more than four times greater than the sum of the two solid–solid phase transitions in PhC2Cu. The small transition entropy observed in PhC2Cu indicates that the changes that occur are minor. It is not known whether the packing difference of the alkyl chains (herringbone vs striped) in the alkyl chain layered perovskites is also present in the phenalkyl layered perovskites. If so, this may be one of the causes for the difference. Although the entropy change associated with the solid–solid phase transition in PhC2Cd is quite large, no changes were seen when a single crystal was heated on a hot stage microscope.

PhC2Co and PhC2Zn each undergo two phase transitions prior to fusion, at approximately the same temperatures and with similar entropy changes. Small transition entropies are seen at T = 296 K and large transition entropies are seen at T = 440 K. A small-entropy transition is seen in anilinium bromide (PhBr) at T = 296.9 K; this has been assigned to disorder of the $-NH_3^+$ group (*38, 39*). Comparable transition temperatures and associated entropy changes for PhBr, PhC2Co, and PhC2Zn suggest that the transition at T = 296 K probably is due to hydrogen-bonding changes associated with disordering of the ammonium group.

The entropy change of the solid–solid phase transition in PhC2Co and PhC2Zn at T = 440 K is greater than the sum of the two solid–solid phase transitions seen in PhC2-Cl (*32*). The larger anion in the metallates may provide more room for disorder of the phenethyl group to occur.

The transitions at T = 440 K in PhC2Zn and PhC2Co have entropy changes which are twice the entropy change seen in PhC2-Cu and PhC2Cd. If the Zn and Co complexes form a nonpolymeric structure like their alkylammonium counterparts, then this may allow greater conformational freedom; an additional factor may be that the interchain distance in the Zn and Co salts likely is greater than that of the Cu and Cd salts also allowing for more conformational changes to take place.

All the phenpropyl ammonium complexes (PhC3*M*) examined displayed at least two solid–solid phase transitions. In PhC3Cu, the low-temperature transitions have small entropy changes. The phase transition at T = 231 K in PhC3Cd is quite close in temperature to that observed in C2-Cd (T_{tr} = 223 K) which suggests that it is due to dynamic hydrogen-bonding changes. The high-temperature phase transitions in

PhC3Cu and PhC3Cd have approximately the same entropy changes suggesting that a similar process is occurring in both of these salts; the high temperature and large entropy change suggests that it is due to disordering of the phenpropylammonium ion. Crystal modifications were seen when PhC3Co and PhC3Zn were examined on a hot stage microscope. At approximately T = 414 K, a crystal of PhC3Zn was observed to crack and lose its transparent appearance. The phase transition in PhC3Co was more dramatic; a large single crystal was observed to split into small flat platelets.

PhC4Co and PhC4Zn each undergo two solid–solid phase transitions with similar large entropy changes for the lower-temperature transitions. On a hot stage microscope, needles of PhC4Zn were observed to split into smaller needles in the direction of the longest axis when heated through this phase transition. The same behavior was seen when PhC4Co was heated through the phase transition; in addition, internal lines could be seen at an angle of ±60° with respect to the crystal edge, making a cross-hatched arrangement across the crystal.

Figure 1 is a plot of the transition temperature vs the number of carbons in the chain for the PhCnCu and PhCnCd complexes. From the plot one can see a dramatic drop in the temperature of the highest-entropy solid–solid phase transition when the chain length is increased from three to four carbons in the PhCnCu and PhCnCd complexes. This appears to be the point where the alkyl chain is of sufficient length and/or flexibility to allow the phenalkyl group to disorder. In the case of n-alkyl chains, it takes four methylene groups to form a kink and this is probably allowed with the phenbutylammonium ion. This may also be the chain length where the electrostatic attractions between the layers are weakened to the point where disorder of the phenalkylammonium ion is easily allowed.

The highest-temperature transitions for the Cu and Cd complexes form two general trends, one for the even-numbered chain lengths and one for the odd-numbered

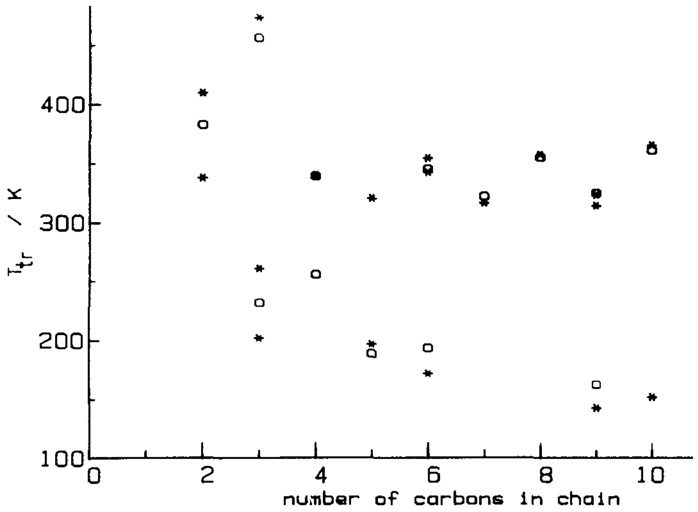

FIG. 1. Transition temperature, T_{tr}, as a function of the number of carbons in the chain, $-C_nH_{2n}-$, for compounds of the general formula $(C_6H_5C_nH_{2n}NH_3)_2MCl_4$. The open symbols represent M = Cd; the asterisks represent M = Cu.

chain lengths. The trend to increasing transition temperature with increasing chain length is observed for the even-numbered chain lengths, whereas the temperature of the transition of the odd-numbered chain lengths appears to decrease slightly. The transition temperature for the even-numbered chain lengths is much greater than the odd-numbered chain lengths. The large odd–even effect that is observed in the phenalkylammonium complexes may be attributed to the difficulty in packing the phenyl group. The packing of the methyl end groups affects the thermodynamics and crystal structures of the *n*-alkanes; the packing of a larger end group such as the phenyl should have a greater effect on the thermodynamics of these phenalkylammonium complexes. The phenyl groups will pack as efficiently as possible and the alkyl chains will be forced to take up a suitable conformation. This may make the alkyl chains more flexible due to a decrease in interalkyl chain cohesive forces, possibly forcing kinks to form in the chains. If the chains are in high energy conformations and there is a decrease in the cohesive forces then one would expect a decrease in the thermal energy required to cause disorder. This may be the reason for the slight decrease in transition temperature for the odd-numbered PhCnCu complexes.

Figure 2 is a plot of the total entropy change of the solid–solid phase transitions vs the number of carbons in the chain for the PhC*n*Cu and PhC*n*Cd complexes. For the longer chain lengths, there is a general increase in the total entropy change of the phase transitions as the chain length is increased. The entropy changes of the phase transitions for the PhC*n*Cd and PhC*n*Cu complexes are greater than those observed in the C*n*M layered perovskite complexes of the same alkyl chain length, which suggests that the entire phenalkylammonium ion is disordered in the high-temperature phase.

Figure 3 is a plot of the transition temperature vs the number of carbons in the chain for the PhC*n*Co and PhC*n*Zn complexes. The first point to note is that in most cases the transition temperatures of these two

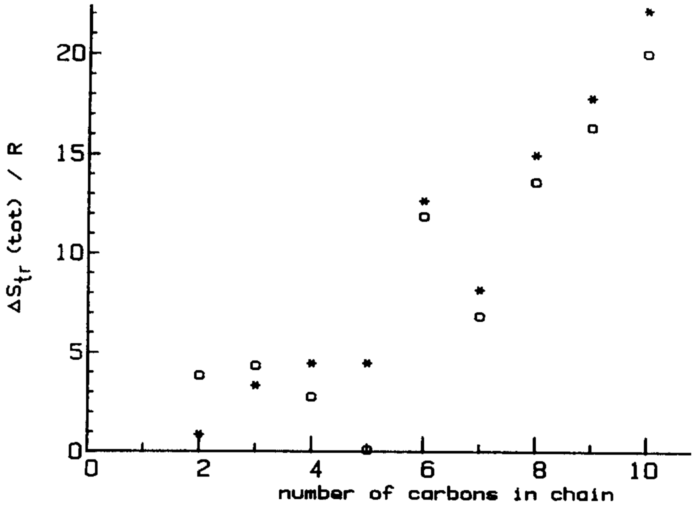

FIG. 2. The sum of the entropy changes of the solid–solid phase transitions, ΔS_{tr} (tot), as a function of the number of carbons in the chain, $-C_nH_{2n}-$, for compounds of the general formula $(C_6H_5C_nH_{2n}NH_3)_2MCl_4$. The open symbols represent M = Cd; the asterisks represent M = Cu.

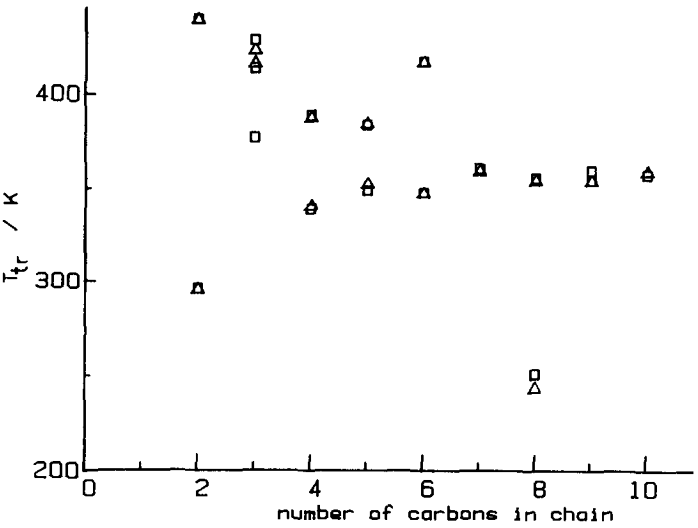

FIG. 3. Transition temperature, T_{tr}, as a function of the number of carbons in the chain, $-C_nH_{2n}-$, for compounds of the general formula $(C_6H_5C_nH_{2n}NH_3)_2MCl_4$. The triangles represent M = Co; the squares represent M = Zn.

complexes are approximately the same for a given chain length. The Co and Zn complexes are more similar to one another than are the Cu and Cd complexes. The Co and Zn complexes are probably isostructural, whereas the Cu and Cd may be slightly different in terms of chain packing, as are the *n*-alkyl layered perovskites (herringbone vs striped chain packing). Like the Cu and Cd complexes, the Co and Zn complexes show a dramatic drop in transition temperature when the alkyl chain is increased from $n = 3$ to $n = 4$.

There does not seem to be as large an odd–even or end-group effect with respect to the temperature of the solid–solid phase transitions in the PhC*n*Co and PhC*n*Zn complexes, in comparison with the PhC*n*Cd and PhC*n*Cu complexes. The plateau in the temperature of the solid–solid phase transition at approximately 355 to 360 K as the chain is lengthened in the PhC*n*Co and PhC*n*Zn complexes that it requires about the same amount of thermal energy to cause disordering of the phenalkyl chain, almost independent of chain length. Since the general trend of an increase in transition temperature or melting point as the chain length is increased is a common behavior of *n*-alkanes and other *n*-alkyl chain derivatives, the behavior observed in the PhC*n*Co and PhC*n*Zn complexes must be because the thermodynamics is controlled by the packing of the phenyl group.

Figure 4 is a plot of the total entropy change of the solid–solid phase transitions in the PhC*n*Co and PhC*n*Zn complexes vs the number of carbons in the chain. Two general trends are seen in these complexes, one for the even-numbered chain lengths and one for the odd-numbered chain lengths. In both cases, the total transition entropy appears to be linearly dependent on the chain length. The most remarkable trend is the large odd–even effect observed in the transition entropy in these complexes; the total transition entropy for the odd-numbered chain lengths is much greater than for the even-numbered chain lengths. The odd-numbered chain lengths may form a different crystal structure than even-numbered chain lengths allowing for

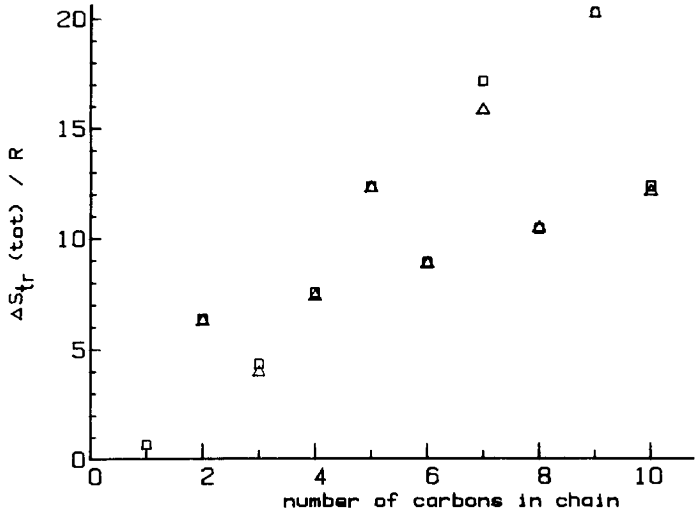

FIG. 4. The sum of the entropy changes of the solid–solid phase transitions, ΔS_{tr} (tot), as a function of the number of carbons in the chain, $-C_nH_{2n}-$, for compounds of the general formula $(C_6H_5C_nH_{2n}\text{-}NH_3)_2MCl_4$. The triangles represent M = Co; the squares represent M = Zn.

greater conformational disorder of the phenalkylammonium ion.

Concluding Remarks

In summary, the thermodynamics of the phase transitions of the bis(phenalkylammonium)tetrachlorometallates have been investigated by differential scanning calorimetry. These complexes can be separated into two groups according to the transition metal; the Cd and Cu complexes form one group and the Zn and Co complexes form another. Different trends in thermodynamic behavior between the groups may be attributed to different crystal structures. The phenalkylammonium layered perovskites form a semirigid backbone of corner-sharing MCl_6 octahedra, whereas the Co and Zn phenalkylammonium complexes most likely form a layer consisting of unassociated MCl_4 tetrahedra. In the former, the phenyl groups are forced to pack according to the polymeric anionic layer, whereas the flexible backbone of the latter can allow for more efficient packing of the phenyl groups. Differences in the thermodynamic trends within each group can be attributed to phenalkyl group packing; differences in trends between the PhC*n*Cu complexes and the PhC*n*Cd complexes may be due to formation of herringbone or striped chain packing similar to the *n*-alkyl layered perovskites, whereas the behavior of the PhC*n*Co and PhC*n*Zn complexes closely parallel each other probably because they are isostructural. Odd–even affects are observed in these complexes and can be attributed to the influence that the packing of the phenyl group has on the cohesive forces between neighboring alkyl chains and phenyl groups.

The high entropies of the solid–solid phase transitions observed in these complexes suggest that there is considerable conformational disorder in the high-temperature phases of these complexes, probably involving the entire phenalkylammonium ion.

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References

1. N. G. Parsonage and L. A. K. Staveley, "Disorder in Crystals," Claredon Press, Oxford (1978).
2. J. S. Miller and A. J. Epstein (Eds.), "Synthesis and Properties of Low Dimensional Materials," Vol. 313, Ann. N.Y. Acad. Sci. (1978).
3. L. Alacer (Ed.), "The Physics and Chemistry of Low Dimensional Solids," Reidel, Dordrecht (1980).
4. P. Day, *Philos. Trans. R. Soc. London A* **314,** 145 (1985).
5. G. F. Needham, R. D. Willett, and H. F. Franzen, *J. Phys. Chem.* **88,** 674 (1984).
6. M. J. M. Van Oort and M. A. White, *J. Chem. Soc. Faraday Trans. 1* **81,** 3059 (1985).
7. R. Kind, S. Plesko, H. Arend, R. Blinc, B. Zeks, J. Seliger, B. Lozar, J. Slak, A. Levstik, C. Filipic, V. Zagar, G. Lahajnar, F. Milia, and G. Chapius, *J. Chem. Phys.* **71,** 2118 (1979).
8. R. Blinc, M. Kozelj, V. Rutar, I. Zupanicic, B. Zecs, H. Arend, R. Kind, and G. Chapuis, *Faraday Discuss. Chem. Soc.* **69,** 58 (1980).
10. M. A. White, *J. Chem. Phys.* **81,** 6100 (1984).
11. R. Kind, *Ferroelectrics* **24,** 81 (1981).
12. W. Depmeier, *Ferroelectrics* **66,** 109 (1986).
13. W. Depmeier, *J. Solid State Chem.* **29,** 15 (1979).
14. F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimental, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, PA (1963).
15. H. L. Fink, M. E. Gross, G. Waddington, and H. M. Huffmann, *J. Amer. Chem. Soc.* **76,** 333 (1954).
16. A. A. Schaerer, C. J. Busso, A. E. Smith, and L. B. Skinner, *J. Amer. Chem. Soc.* **77,** 2017 (1955).
17. M. K. Jain and R. C. Wagner, "Introduction to Biological Membranes," Wiley, New York (1980).
18. M. R. Ciajola, P. Corradini, and V. Pavone, *Gazz. Chim. Ital.* **106,** 807 (1976).
19. M. A. White, N. J. Davies, and L. A. K. Staveley, *J. Chem. Soc. Faraday Trans. 2* **79,** 1653 (1983).
20. M. R. Ciajolo, P. Corradina, and V. Pavone, *Acta Crystallogr. B* **33,** 553 (1973).
21. V. Busico, C. Carfagna, V. Salerno, and M. Vacatello, *Solar Energy* **24,** 575 (1980).
22. C. Socias, M. A. Arriandiago, M. J. Tello, and J. Fernandez, *Phys. Stat. Sol. A* **57,** 405 (1980).
23. J. Fernandez, C. Socias, M. A. Arriandiaga, M. J. Tello, and A. Lopez Echarri, *J. Phys. C* **15,** 1151 (1982).
24. M. A. Arriandiaga, M. J. Tello, J. Fernandez, H. Arend, and J. Roos, *Phys. Stat. Sol. A* **48,** 53 (1978).
25. C. Almirante, G. Minoni, and G. Zerbi, *J. Phys. Chem.* **90,** 852 (1986).
26. A. Blake and W. E. Hatfield, *J. Chem. Soc. Dalton Trans.*, 1725 (1979).
27. J. Ishikawa, T. Asaji, and D. Nakamura, *J. Magn. Res.* **51,** 95 (1983).
28. W. E. Estes, D. B. Losee, and W. E. Hatfield, *J. Chem. Phys.* **72,** 630 (1980).
29. A. Daoud, A. Thrierr-Sorel, R. Perret, B. Charillot, and J. E. Guerchais, *Bull. Soc. Chim. France* **3–4,** 535 (1975).
30. A. Dupas, K. Le Dang, J. P. Renard, P. Veillet, A. Daoud, and R. Perret, *J. Chem. Phys.* **65,** 4099 (1976).
31. Y. Kimishima and H. Nagano, *Solid State Commun.* **52,** 275 (1984).
32. M. J. M. Van Oort and M. A. White, to be published.
33. H. Arend, W. Huber, F. H. Mischgofsky, and G. K. Richter-van Leeuwen, *J. Crystal Growth* **43,** 213 (1978).
34. B. Miller, M. Van Oort, and M. A. White, *J. Chem. Ed.* **62,** 64 (1985).
35. K. Schenk and G. Chapuis, *Acta Crystallogr. C* **42,** 1076 (1986).
36. G. Tsoucaris, *Acta Crystallogr.* **14,** 909 (1961).
37. T. S. Cameron, O. Knop, and S. Roe, unpublished work.
38. G. Fecher, A. Weiss, W. Joswig, and H. Fuess, *Z. Naturforsch* **36a,** 956 (1981).
39. H. Suga, *Bull. Chem. Soc. Japan* **34,** 426 (1961).