

PHASE TRANSITION AND DECOMPOSITION OF A_2MX_4 [A = $(C_2H_5)_4N$; M = Co(II), Ni(II) AND Cu(II); X = Cl AND Br] IN THE SOLID STATE

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ABSTRACT

A_2MBr_4 undergoes endothermic reversible phase transitions at subambient and above ambient temperatures. The cooling curve of A_2MBr_4 (M = Cu and Ni) above 400 K is split compared to the corresponding heating curve and the nature of splitting appears to be dependent on time. The low temperature phase transitions are due to orientation of both T_d cations and anions and the high temperature phases are probably followed by the formation of several intermediate structures.

INTRODUCTION

Low temperature phase transitions of tetraethylammonium tetrachlorometallates of first row transition metals [1] and phase transitions due to the change in coordination geometry around copper(II) in $[(CH_3)_2CH-NH_3]_2CuCl_4$ and $[(C_2H_5)_2NH_2]_2CuCl_4$ are known [2], but the phase transitions of the corresponding tetrabromometallates and phase transitions of A_2MX_4 at temperatures above ambient have not yet been reported, except one report made recently by us [3]. We described the thermally induced solid state phase transition and decomposition of A_2MnX_4 [X = Cl and Br] where phase transitions were traced by DSC. In continuation of this work, this paper describes the phase transitions of A_2MX_4 starting from 233 K to their corresponding decomposition temperatures. It also includes their thermal decompositions.

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TABLE 1

Phase transition of A_2MX_4 [$A = (C_2H_5)_4N$]

Compound	Transition (heating)			Transition (cooling)			ΔH (kJ mol ⁻¹)
	Temp. range (K)	Peak temp. (K)	ΔH (kJ mol ⁻¹)	Cooling condition	Temp. range (K)	Peak temp. (K)	
A_2CoBr_4	281.0–288.0	284.5	5.2	Immediately after heating	281.0–275.0	278.5	5.4
	474.6–487.4	480.2sh, 482.1	6.0	Immediately after heating	442.0–433.5	440.2	8.1
A_2NiBr_4	267.3–273.7	271.3	4.3	Immediately after heating	267.5–262.0	265.5	4.3
	(i) 479.0–491.0	485.0	5.7	Immediately after heating	454.0–445.0	453.0	6.7
	(ii) 481.2–492.0	488.0	5.5	After keeping at 493 K for 10 min	454.0–445.0	454.5, 453sh, 452.5	7.1
	(iii) 481.2–492.0	488.0	5.5	After keeping at 493 K for 60 min	453.8–440.0	453.0, 451.3, 450.5, 450.0sh, 448.5sh, 445.8sh	7.9
	(iv) 480.0–488.8	484.0	5.4	After keeping at 493 K for 90 min	448.0–435.0	447.5, 445.5, 444.8, 444.2, 443.8, 443.0, 442.5sh, 441.5sh	7.5
	(v) 480.0–488.8	484.0	5.4	After keeping at 493 K for 180 min	443.0–428.0	442.0, 438.5, 438.0sh, 437.0sh, 436.0sh, 435.3, 434.2, 433.0sh	7.3
	(vi) 480.0–488.8	484.0	5.4	After keeping at 493 K for 240 min	443.0–428.0	436.0	7.3
A_2CuBr_4	256.0–302.0	266.0	6.1				
	(i) 442.0–450.5	445.3, 446.5sh	5.1	Immediately after heating	427.5–417.0	422.0, 420.9sh	6.3
	(ii) 442.8–449.0	447.0	5.0	After keeping at 451 K for 5 min	428.5–416.0	422.5, 421.0, 420.5	6.2
	(iii) 442.8–449.0	447.0	5.0	After keeping at 451 K for 10 min	429.0–415.2	423.2, 422.0sh, 420.6	6.2
	(iv) 442.8–449.0	447.0	5.0	After keeping at 451 K for 15 min	429.0–416.0	424.0, 421.8sh, 420.5	6.2
	(v) 442.8–449.0	447.0	5.0	After keeping at 451 K for 30 min	428.5–415.0	423.1sh, 421.0, 420.6	6.0
	(vi) 442.8–449.0	447.0	5.0	After keeping at 451 K for 60 min	423.0–414.5	420.0sh, 421.5sh, 421.0	5.7
(vii) 442.8–449.0	447.0	5.0	After keeping at 451 K for 120 min	426.0–415.5	422.1sh, 421.0	5.3	

^a For the high temperature phase transition of A_2NiBr_4 , six (i–vi) heating and cooling curves are taken.^b For the high temperature phase transition of A_2CuBr_4 , seven (i–vii) heating and cooling curves are taken.

EXPERIMENTAL

All the chemicals used were AR grade. A_2MX_4 compounds were prepared following the method reported earlier [4]. Elemental analyses of these complexes are in good conformity with their compositions. The apparatus employed for these investigations and other experimental conditions are the same as reported earlier [3]. Elemental analyses were carried out with a Perkin-Elmer 240C elemental analyzer. Thermal data of the complexes are presented in Tables 1 and 2.

RESULTS AND DISCUSSION

A_2CoCl_4 shows no phase transitions in the temperature range 233–565 K. The literature shows that this compound undergoes a phase transition at 225 K due to orientational disordering of T_d cations and anions. It starts to decompose at 565 K and transforms to $CoCl_2$ through two nonisolable intermediates, $ACoCl_3$ and ACo_2Cl_5 (Table 2). Below the ambient temperature, A_2CoBr_4 undergoes a structural endothermic phase transition in the temperature range 281–288 K and reverts to the original structure in the temperature range 281–275 K during cooling (Table 1, Fig. 1). Above ambient temperature, A_2CoBr_4 shows two overlapping endotherms in the

TABLE 2

Thermal decomposition of A_2MX_4 [$A = (C_2H_5)_4N$]

Decomposition reactions	Temp. range (K)	Peak temp. (K)	
		Endo	Exo
$A_2CoCl_4 \rightarrow ACoCl_3$	565–603	598	–
$ACoCl_3 \rightarrow ACo_2Cl_5$	603–630	–	629
$ACo_2Cl_5 \rightarrow CoCl_2$	630–661	–	659
$A_2CoBr_4 \rightarrow ACoBr_3$	549–595	583, 590	–
$ACoBr_3 \rightarrow ACo_2Br_5$	595–630	628	–
$ACo_2Br_5 \rightarrow CoBr_2$	630–666	638, 654	661
$A_2NiCl_4 \rightarrow NiCl_2$	551–650	591, 602	618
$A_2NiBr_4 \rightarrow A_3Ni_2Br_7$	555–585	581, 583	–
$A_3Ni_2Br_7 \rightarrow NiBr_2$	585–632	598, 610	630
$A_2CuCl_4 \rightarrow ACuCl_3$	503–532	526 ^a , 531	–
$ACuCl_3 \rightarrow CuCl_2$	532–693	–	653
$A_2CuBr_4 \rightarrow A_3Cu_2Br_7$	495–526	513 ^a , 525	–
$A_3Cu_2Br_7 \rightarrow CuBr_2$	526–608	–	~ 573

^a Peak due to melting.

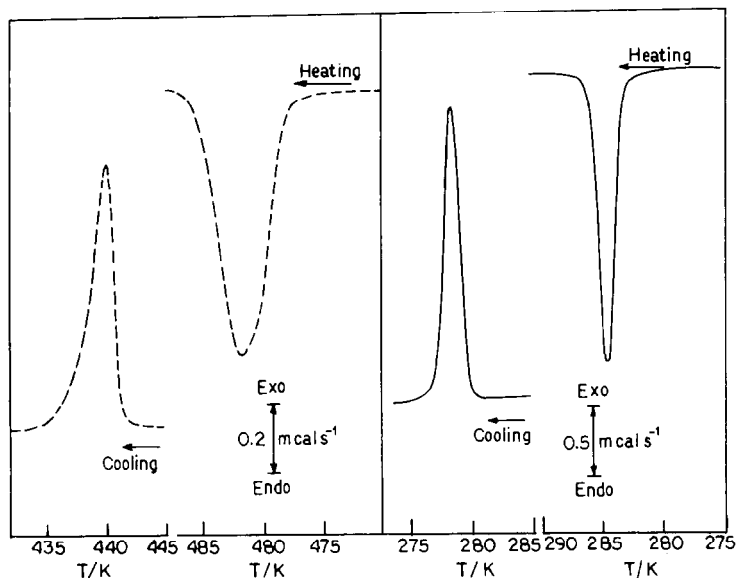


Fig. 1. DSC curves of $[\text{NEt}_4]_2\text{CoBr}_4$. Sample mass 11.43 mg (—) and 10.66 mg (---).

temperature range 474.6–487.4 K. Its cooling mode shows one endothermic peak in the temperature range 442.0–433.5 K on the DSC curve (Fig. 1, Table 1). This compound starts to decompose at 549 K and the nature of its decomposition is found to be similar to its corresponding tetrachloro salt (Table 2).

Like A_2CoCl_4 , A_2NiCl_4 shows no phase transitions in the temperature range 233–551 K. It decomposes at 551 K and affords NiCl_2 at 650 K. Although its TG curve indicates a single-step decomposition, the corresponding DTA curve shows two endothermic and one exothermic peaks (Table 2). Figure 2 shows the DSC curves of A_2NiBr_4 . The endothermic effect in the temperature range 267.3–273.7 K is due to a phase transition. The corresponding cooling curve (267.5–262.0 K) is observed due to its reversal. The phase transition of A_2NiBr_4 at a temperature above ambient is very interesting. It undergoes an endothermic phase transition (479–491 K) and reverts to its original structure during cooling, showing an exothermic peak in the temperature range 454–445 K. Recycling of this phase transition shows an interesting behavior. Its first, second and third heating curves (Fig. 2, Table 1), traced upon recycling appear to shift slightly towards higher temperatures, and the sharpness of the peak gradually increases whereas the corresponding cooling peaks become remarkably split. After the third consecutive heating (Fig. 2, Table 1) all the heating curves, i.e. fourth to seventh, become identical but more and more splitting and broadening is observed for their corresponding cooling exotherms and eventually a broad ex-

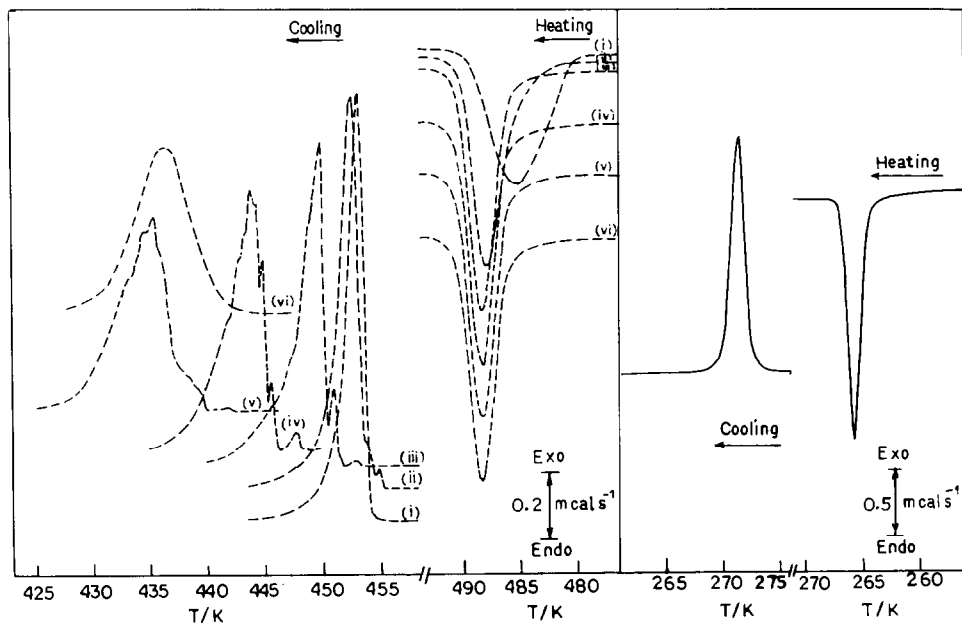


Fig. 2. DSC curves of [NEt₄]₂NiBr₄. Sample mass 10.00 mg (—) and 6.75 mg (---) (for the high temperature phase transition (---) six (i-vi) successive heating and cooling curves are taken).

othermic peak is observed (Fig 2, Table 1). A₂NiBr₄ starts decomposition at 555 K and transforms to NiBr₂ through the unstable intermediate A₃Ni₂Br₇ (Table 2).

A₂CuCl₄ undergoes no phase transition within the range 233–503 K like its corresponding Co and Ni analog. It starts to decompose at 503 K and transforms to its metal halide through the formation of a nonisolable intermediate, ACuCl₃. Below the ambient temperature, A₂CuBr₄ shows an endothermic phase transition in the heating curve (256–302 K) (Fig. 3, Table 1). Its reversible exothermic peak is not observed up to a temperature of 240 K in the cooling curve. If the after-phase species are kept at 233 K for ~ 1 h, an endothermic transition reappears. Above the ambient temperature this compound undergoes two overlapping endothermic transitions in the temperature range 442.0–450.5 K. Two overlapping exothermic peaks are observed in the corresponding cooling curve. Recycling of this phase transition also appears very interesting. During the second heating, only one sharp endotherm is observed but its corresponding cooling curve shows three exothermic peaks. If the heating-and-cooling cycle is continued, the former remains identical but the corresponding cooling behavior changes. It is also noticed that on long standing (~ 2 h) of its high temperature phase at 451 K, A₂CuBr₄ shows two exothermic peaks for the reversal of its high temperature structure to its room temperature structure. Details about the

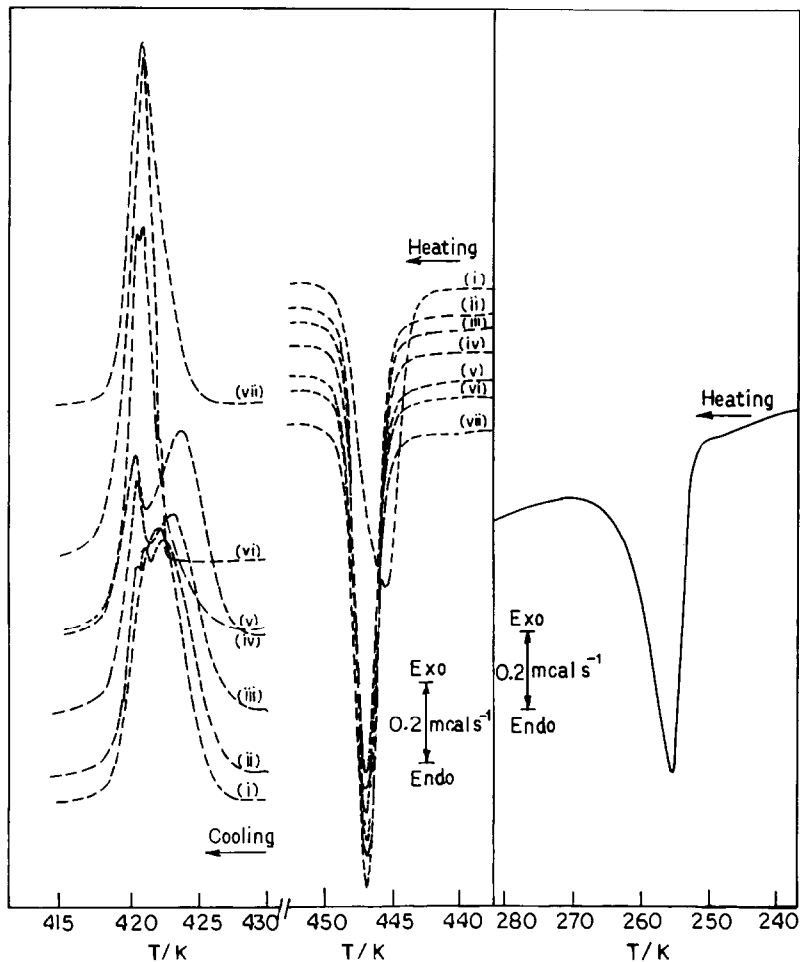


Fig. 3. DSC curves of $[\text{NEt}_4]_2\text{CuBr}_4$. Sample mass 13.67 mg (—) and 8.47 mg (---) (for the high temperature phase transition (---) seven (i-vii) heating and cooling curves are taken).

heating and cooling conditions are given in Table 1. This compound starts to decompose at 493 K and transforms to CuBr_2 at 608 K through the formation of an intermediate, $\text{A}_3\text{Cu}_2\text{Br}_7$. The sharp endothermic peak appearing at 513 K in the DTA curve is due to the melting of A_2CuBr_4 .

It is interesting to note that the tetrachloro salts do not show phase transitions at high temperatures. The corresponding tetrabromo salts undergo high temperature phase transitions. Due to limited facilities, we could not collect any data of the high temperature form of the A_2MBr_4 species. Some work relating to the phase transition of B_2MX_4 [$\text{B} = \text{Li}$ or CH_3NH_3] was reported [5]. These phase transitions are due to the transformation of tetragonal \rightarrow cubic or orthorhombic \rightarrow tetragonal structural transformations.

So the high temperature phase transitions appearing in A_2MBr_4 are probably due to this type of crystalline transformation. The exothermic effect caused by the transformation of the high temperature structure of A_2MBr_4 ($M = Ni$ and Cu) to its room temperature structure, in the cooling mode, is very interesting as recycling of this exothermic transition becomes split. The splitting of the peak is dependent upon the time of standing at its high temperature phase. After long standing at the high temperatures of 492 K for A_2NiBr_4 and 451 K for A_2CuBr_4 , one exothermic peak is observed in the cooling curve. This type of splitting of the cooling curves suggests the nucleation-controlling mechanism taking place in this type of transition. The formation of a room temperature phase nucleus from the high temperature phase follows the formation of several intermediate structures. It is an established fact that the low temperature phase transitions are due to orientations of both T_d cations and anions [6]. We proved this phenomenon in the case of A_2MnX_4 by EPR. We also recorded the EPR of A_2MX_4 complexes at room temperature and at liquid N_2 temperature, but a very short relaxation time broadened the EPR signal. As a result we were unable to form any ideas of these low temperature phase transitions with the help of EPR.

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