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Note

PHASE TRANSITION AND DECOMPOSITION OF TETRAETHYLAMMONIUM TETRAHALOMANGANATE IN THE SOLID STATE

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The synthesis, magnetic and electronic spectral studies of tetrahedral tetrahalometallates have drawn much attention since 1958 [1]. A lot of studies have been made with tetraalkyltetrahalometallates due to their temperature-dependent spectral, magnetic, thermal, etc., properties [2]. Tetramethylammoniumtetrahalometallates undergo high-temperature normal phase transition to the incommensurate phase on cooling. The incommensurate phase undergoes a transition to the commensurate phase on further cooling [2]. Low-temperature phase transitions of tetraethylammoniumtetrachlorometallates of first-row transition metals are known [3], but the phase transitions of the corresponding tetrabromo compounds and above-ambient temperature phase transitions of $[NEt_4]_2MX_4$ are not yet reported. The present paper reports the phase transitions of $[NEt_4]_2MnX_4$ (X = Cl or Br) starting from 233 K to their corresponding decomposition temperatures. It also includes their thermal decompositions.

EXPERIMENTAL

All the chemicals used were AR grade purity. The compounds $[Et_4N]_2MnX_4$ (X = Cl or Br) were prepared following the method reported earlier [4]. Phase transitions were investigated with a Perkin-Elmer DSC-2 differential scanning calorimeter. Dry nitrogen gas was used as purge gas. The instrument was calibrated using the melting point of ice (273.15 K), the phase transition temperature of cyclohexane (279 K) and the melting point of indium (429.7 K). The enthalpy of melting of indium was used for the calculation of enthalpy changes associated with the phase transitions. The thermal decomposition was carried out in a Shimadzu DT-30 thermal analyzer in a nitrogen atmosphere. X-band EPR spectra of the samples were recorded in a Varian E-109C EPR spectrometer at room temperature and at liquid nitrogen temperature.

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RESULTS AND DISCUSSIONS

No noticeable phase transformation of $[Et_4N]_2MnCl_4$ is observed in the temperature range 233–300 K. The literature shows that the compound undergoes two phase transitions at 224 (normal → incommensurate) and 218 K (incommensurate → commensurate). The occurrence of the transitions is explained due to orientational disordering of both the tetrahedral cation and anion [3]. Above ambient temperature, $[NEt_4]_2MnCl_4$ shows two overlapping endotherms without any mass loss and reverts to the original species showing two distinctly separate exotherms in the cooling curve (Table 1, Fig. 1). It is interesting to note that recycling of the said transition shows only one endothermic peak at 499 K in the temperature range 491.5–503.6 K, but the cooling behavior remains unchanged. Above the ambient temperature, the compound $[NEt_4]_2MnCl_4$ possesses two crystalline modifications.

$[NEt_4]_2MnBr_4$ shows a structural phase transition in the temperature range 269.8–281 K and reverts to the original structure during cooling (Fig. 2, Table 1). Unlike $[NEt_4]_2MnCl_4$ this compound shows only one reversible phase transition (434.2–444.3 K) in the high-temperature region (Fig. 2, Table 1).

It is an established fact that the low-temperature phase transitions are due to orientations of both the T_d cations and anions [2,3]. We have recorded the EPR spectra of $[NEt_4]_2MnCl_4$ (1% by weight) doped in $[NEt_4]_2ZnCl_4$ at room temperature and at liquid nitrogen temperature (Fig. 3). In the room temperature phase, the spectrum shows six lines ($g \approx 2$) corresponding to ^{55}Mn hyperfine structure. However, splitting of each line is observed in its low-temperature (77 K) spectrum. This type of splitting may be due to the

TABLE 1

Phase transitions of $[NEt_4]_2MnX_4$ (X = Cl or Br) complexes

Compound	Transition (heating)			Transition (cooling)		
	Temp. range (K)	Peak temp. (K)	ΔH (kJ mol^{-1})	Temp. range (K)	Peak temp. (K)	ΔH (kJ mol^{-1})
$[NEt_4]_2MnCl_4$	–	218[a]	4.69	–	–	–
	–	224[a]	3.26	–	–	–
	487.5–505.5[b]	492.4 sh	2.55	491.2–472.0	484.9	0.46
		496.3		46.4–445.6	452.7	2.21
$[NEt_4]_2MnBr_4$	269.8–281.0	273.5	4.87	264.8–254.5	261.5	4.86
	434.2–444.3	439.8	12.10	400.0–381.8	392.0	12.20

[a] From ref. 3.

[b] Recycling of this transition shows only one endothermic peak in the heating curve (491.5–503.6 K) but its corresponding cooling curve remains the same (Fig. 1).

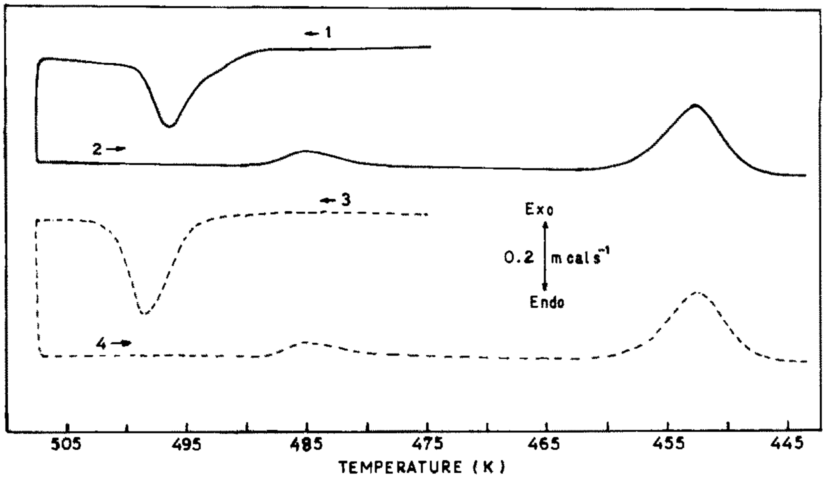

Fig. 1. DSC curves of $[NEt_4]_2MnCl_4$. Sample mass 5.18 mg. (1) First heating; (2) cooling; (3) second heating; (4) cooling.

effect of finite orientations of the $MnCl_4$ tetrahedra surrounding the alkyl groups in its commensurate phase [2]. Although the super-hyperfine structure of the low-temperature phase observed in the EPR spectra due to Cl

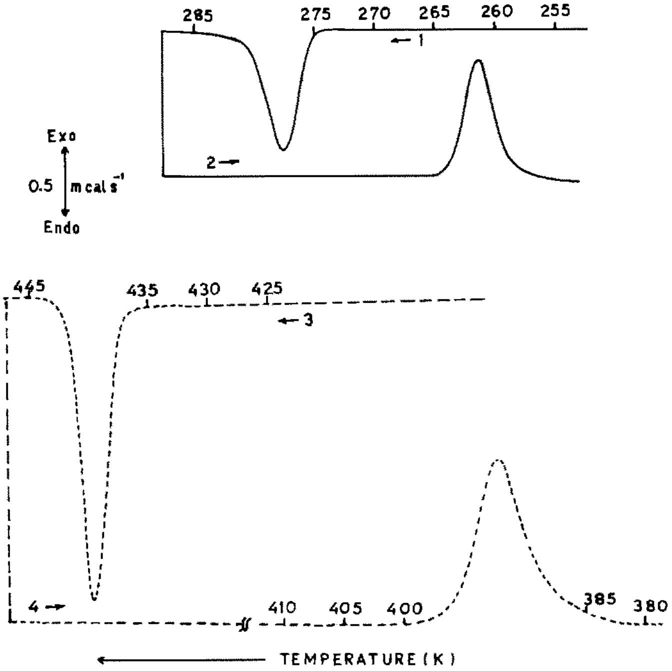

Fig. 2. DSC curves of $[NEt_4]_2MnBr_4$. Sample mass, 8.65 mg (———); and 7.13 mg (– – –). (1) Heating; (2) cooling; (3) heating; (4) cooling.

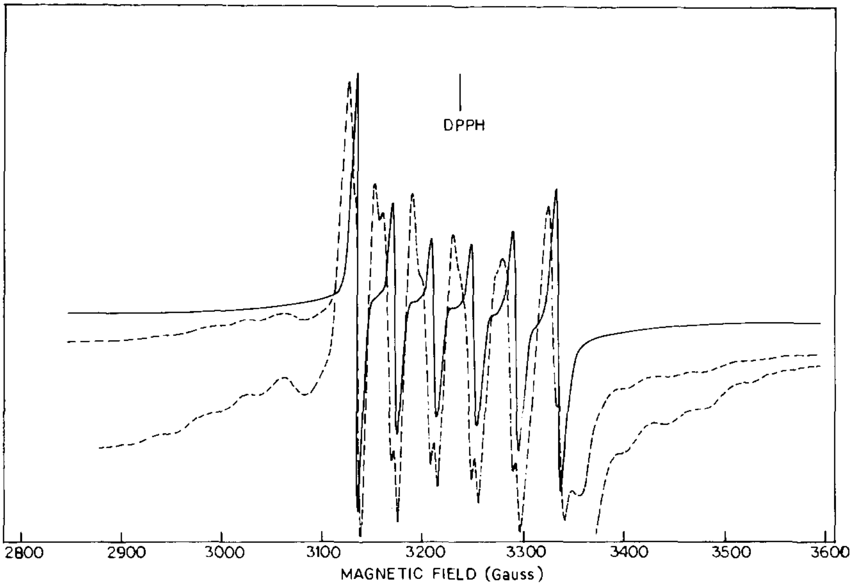

Fig. 3. EPR spectra of $[NEt_4]_2MnCl_4$ (1% by weight) doped in $[NEt_4]_2ZnCl_4$ at room temperature (———); and liquid nitrogen temperature (77 K) (– – –).

could not be ignored, the tetragonal distortion of MX_4 tetrahedra observed in its low-temperature crystal absorption spectra [5] suggests that the hyperfine structure (observed in low-temperature EPR spectra) is probably due to disorder of the $MnCl_4$ tetrahedra.

No data are reported on the high-temperature phase transitions of $[NEt_4]_2MX_4$ type compounds. Without any structural or spectral data of both the room temperature and high-temperature forms of $[NEt_4]_2MnX_4$, it is very difficult to come to any conclusions about this type of phase transition. Some work has been reported on the high-temperature phase transitions of $Li_2[MnBr_4]$ [6] and $[CH_3NH_3]_2MnCl_4$ [7]. These phase transi-

TABLE 2

Thermal decomposition of $[NEt_4]_2MnX_4$ (X = Cl or Br) complexes

Decomposition reactions	Temp. range (K)	Peak temp. (K)	
		Endo	Exo
$[NEt_4]_2MnCl_4 \rightarrow [NEt_4]MnCl_3$	541–603	588	–
$[NEt_4]MnCl_3 \rightarrow MnCl_2$	603–707	–	611, 635, 651 667 sh, 676
$[NEt_4]_2MnBr_4 \rightarrow [NEt_4]_2MnBr_4$	–	528[a]	–
$[NEt_4]_2MnBr_4 \rightarrow [NEt_4]MnBr_3$	533–598	578, 588	–
$[NEt_4]MnBr_3 \rightarrow MnBr_2$	598–688	–	628, 663

[a] Peak due to melting.

tions are due to the transformation of tetragonal (room temperature) → cubic (high temperature) (in the case of $Li_2[MnBr_4]$) and orthorhombic (room temperature) → tetragonal (high temperature) (in the case of $[CH_3NH_3]_2MnCl_4$) structures, respectively. The high-temperature phase transitions of $[NEt_4]_2MnX_4$ may be due to this type of structural transformation.

Thermal decomposition of tetraalkyltetraammoniumtetrahalometallates are scanty. Results about the thermal decomposition of both complexes are given in Table 2. It is observed that both compounds decompose through $[NEt_4]MnX_3$ to their corresponding metal halides. Although we could not isolate and characterize the trihalo compounds by the temperature arrest technique, their formation is not unlikely as these type of compounds are well known and can be prepared from solution [8]. It is noticed that the first step of decomposition is endothermic in character whereas the second step follows an exothermic decomposition.

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REFERENCES

1 B.F. Markov and R.V. Chernov, Ukr. Khim. Zh., 24 (1958) 139; P. Paoletti and A. Vacca, Trans. Faraday Soc., 60 (1964) 50; H.J. Scifert and F.W. Koknat, Z. Anorg. Allg. Chem., 341 (1965) 269.

2 K. Hasabe, H. Mashiyama and S. Tanisaki, J. Phys. Soc. Jpn., 52 (1982) 2049; M. Fukui, R. Abe and T. Tsuchida, J. Phys. Soc. Jpn., 52 (1983) 4369; R. Bline, M. Burgan, J. Slak, V. Rutaz and F. Milia, Phys. Status Solidi A, 56 (1979) K65; K. Gesi, J. Phys. Soc. Jpn., 51 (1982) 203; S. Ganguly, K.J. Rao and C.N.R. Rao, Spectrochim. Acta, Part A, 41 (1985) 307.

3 T.P. Melia and R. Messifield, J. Chem. Soc. A, (1971) 1258; (1970) 1166.

4 N.S. Gill and F.B. Taylor, Inorg. Synth., 9 (1967) 135.

5 J.C. Rivoal, B. Briat and M. Vala, Mol. Phys., 38 (1979) 1829.

6 H.D. Lutz, W. Schmidt and H. Haenseler, Naturwissenschaften, 68 (1981) 328.

7 T. Goto, B. Lüthi, R. Geick and K. Strobel, Phys. Rev. B, 22 (1980) 3452.

8 C. Lauer and H. Benner, Phys. Rev. B, 24 (1981) 329; B. Morosin and E.J. Graebner, Acta Crystallogr., 23 (1967) 766.