

Thermal Behaviour of Some Crystal Solvates of Manganese(III) Complexes

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Abstract. The thermal behaviour of some crystal solvates of square pyramidal Mn(III) complexes has been studied. The nature of interaction of the water of crystallization has been clarified, and a correlation was found between the hardness of the axial anions and the desolvation temperatures. The decomposition pathways of the investigated complexes have also been discussed.

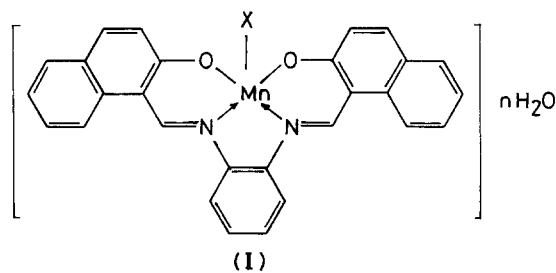
Keywords. Manganese complexes; Desolvation; Crystal solvates.

Thermisches Verhalten einiger Kristallsolvate von Mangan(III)-Komplexen

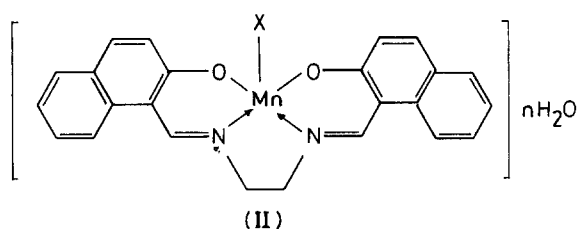
Zusammenfassung. Es wurde das thermische Verhalten einiger Kristallsolvate von quadratisch-pyramidalen Mangan(III)-Komplexen untersucht. Die Natur der Wechselwirkung des Kristallwassers wurde geklärt und eine Korrelation zwischen der Härte der axialen Anionen und der Solvatationstemperatur gefunden. Der Verlauf der thermischen Zersetzung der Komplexe wird ebenfalls diskutiert.

Introduction

A number of manganese(III)-Schiff base (derived from *o*-phenylenediamine and ethylenediamine) complexes (**I**, **II**) have recently been prepared and characterized [1, 2]. According to our program on studying the thermal behaviour of manganese



- 1: $X = \text{OAc}$, $n = 3$; 2: $X = \text{SCN}$, $n = 0$;
3: $X = \text{Cl}$, $n = 0$; 4: $X = \text{Br}$, $n = 0$;
5: $X = \text{I}$, $n = 0$



- 1: $X = \text{Cl}$, $n = 2.5$; 2: $X = \text{Br}$, $n = 2.5$;
 3: $X = \text{I}$, $n = 4$; 4: $x = \text{SCN}$, $n = 2$

containing complexes [2, 3], the effect of axial anions on the thermal stabilities and the decomposition pathways of the complexes of *o*-phenylenediamine derivative (I) has been studied [2]. The present study is directed to investigate the effect of substitution of *o*-phenylenediamine (*o*-phen) by ethylenediamine (*en*) on both the thermal behaviour and decomposition pathways of the square pyramidal manganese(III) complexes (1–4-II). On the other hand, light has been thrown on the nature of interaction of the water of crystallization.

Experimental Part

The complexes 1–4 were prepared by the earlier reported method. The ligand (0.01 mol) suspended in hot ethanol was mixed with solid NaOH (0.02 mol). When the base had dissolved, a solution (0.02 mol) of $\text{MnX}_2 \cdot 4\text{H}_2\text{O}$ ($X = \text{Cl}, \text{Br}, \text{I}$ or SCN) in ethanol was added dropwise to the ligand solution. The reaction mixture was stirred for 3 days with no attempt to exclude air or light. The resulting solid was filtered off, washed with ethanol and dried in vacuo. The analytical and spectral measurements are consistent with the structures (II).

Thermal analyses (d.t.a.) were carried out in air using a Shimadzu XD-30 thermal analyzer with a heating rate of $10^\circ\text{C}/\text{min}$. Thermogravimetric analyses (t.g.) were carried out using a Shimadzu DT-30 thermal analyzer with a heating rate of $10^\circ\text{C}/\text{min}$. X-ray powder diffraction were recorded using a Shimadzu XD-3 diffractometer with Cu K_α radiation. IR spectra were measured as KBr discs using a Perkin-Elmer 598 spectrophotometer.

Results and Discussion

The complexes show exothermic d.t.a. peaks in the $280\text{--}330^\circ\text{C}$ temperature range (Fig. 1). These peaks are assigned to phase change and/or material decomposition as a result of desolvation. This assignment was obtained from the t.g. weight loss (Table 1) and the IR spectra of the complexes before and after heating in that temperature range, which indicate that the decomposition of all complexes start at 315°C . The higher temperature of desolvation together with the decomposition during the desolvation emphasize the higher interaction of water of crystallization (water make a great contribution to the forces in the lattice). The exothermic phase change of complex 4 was confirmed by the exothermic d.t.a. peak at $253\text{--}310^\circ\text{C}$ (Fig. 1), the t.g. weight loss (1.8%), which corresponds to $0.5\text{H}_2\text{O}$ (1.8%) and the X-ray diffraction patterns of the complex before and after heating up to 310°C (Fig. 2), which indicate a change from the crystalline phase to an amorphous one. The IR spectra of the two phases are mainly the same, indicating that no

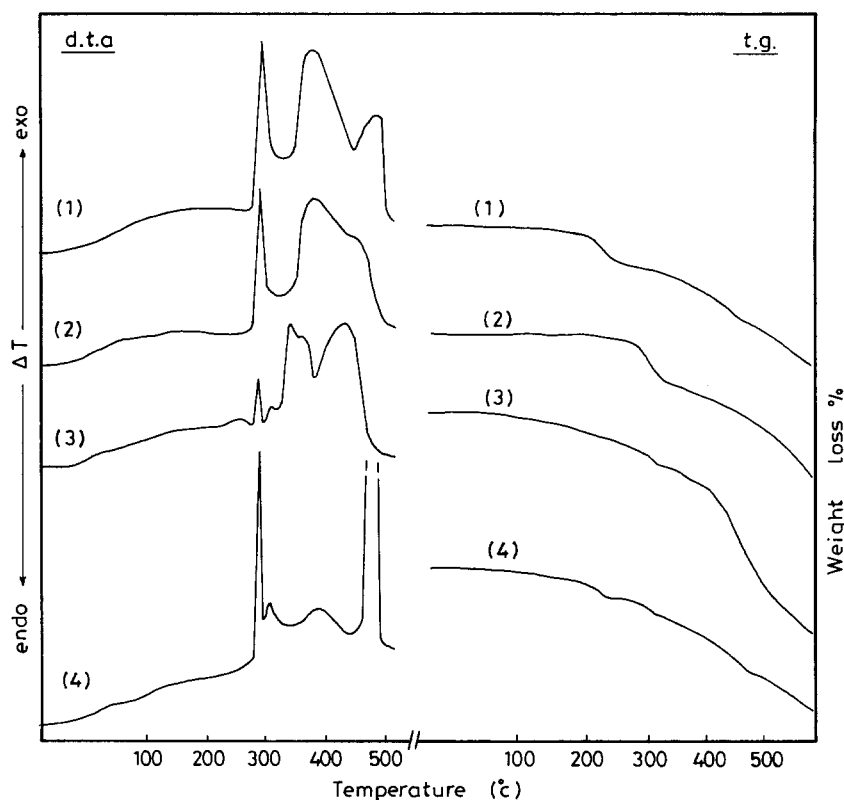


Fig. 1. D.t.a. and t.g. curves of the complexes

decomposition takes place during the change. But the observed broadening, together with the lower intensity of the peaks of the amorphous form are attributed to the phase change [4–7]. This structure collapse (phase change) is taken as a good evidence for the effective role of water of crystallization in the lattice forces [7, 8].

As shown in Table 1, the complexes 3, 4 show also a weight loss corresponding to $1.5\text{H}_2\text{O}$ in the $45\text{--}266^\circ\text{C}$ temperature range. The lower temperature of desolvation together with the IR spectra of the complexes before and after heating at that temperature range (which are quite similar) indicate that this part of water of crystallization makes no contribution in the lattice forces and is trapped in the crystal voids [2, 6, 7]. This can also be confirmed by the very broad/weak endothermic d.t.a. peaks in that temperature range [3] (Fig. 1). Therefore, these complexes have two types (according to the nature of interaction) of water of crystallization.

If the initial temperatures of desolvation of the lattice water (highly interacted) are taken as a measure of the strength of interaction in the lattice, the complexes follow the order $\text{I} > \text{SCN} > \text{Br} > \text{Cl}$ (Table 1). This result leads to the conclusion that the axial anions play an important role in the lattice forces through a hydrogen bonding. This effective role is confirmed by the correlation obtained between the hardness of the axial anions [9] and the inversion of absolute temperatures of

Table I. T. g. data of the complexes and absolute hardness of the axial anions

Complex	t.g.	Temperature range (°C)	Weight loss %		Number of water molecules lost	t.g. Initial temperatures desolvation (°C)	$1/T \times 10^5$ K ⁻¹	Absolute hardness of the axial anions
			calcd. (found)					
[MnLCl]2.5H ₂ O	225-240	5.4 (5.3)	1.5	225	200	(4.70)Cl		
	240-330	3.8 (4.0)	1					
[MnLBr]2.5H ₂ O	237-280	1.65 (1.68)	0.5	237	196	(4.24)Br		
	280-330	6.7 (6.8)	2					
[MnL]4H ₂ O	96-266	4.4 (4.3)	1.5	266	186	(3.70)I		
	266-416	7.6 (7.4)	2.5					
[MnLSCN]2H ₂ O	46-226	5.3 (5.4)	1.5	253	190	(4.12)*SCN		
	253-310	1.8 (1.8)	0.5					

* Absolute hardness of sulphur (S)

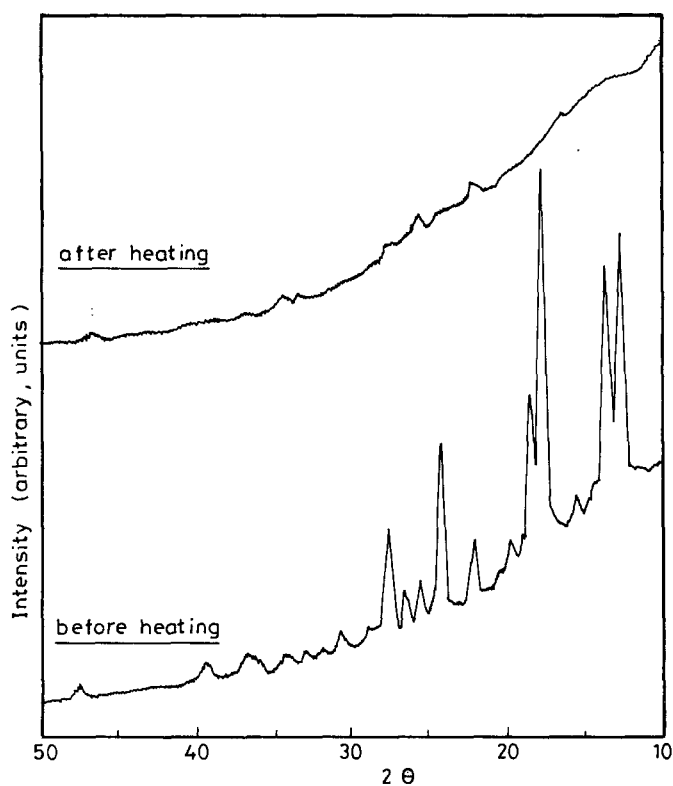


Fig. 2. X-ray diffraction patterns of the isothiocyanato complex 4

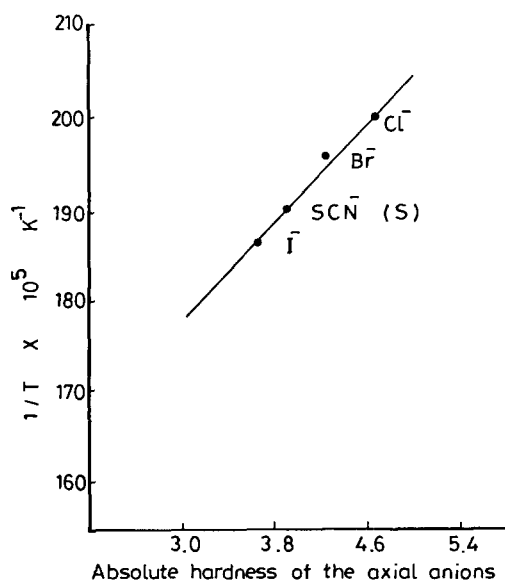


Fig. 3. Correlation between desolvation temperatures and hardness of the axial anions

desolvation (Fig. 3). It is seen that as the hardness decreases the desolvation temperature increases. This can be explained in terms of the concept of chemical hardness and softness [9–11]. As the hardness decreases the polarizability increases and the electronegativity decreases. So, for the axial anions (which are considered

Lewis bases), as the hardness decreases the polarizability increases giving a stronger interaction with the partially charged hydrogen of water, which results in higher temperature of desolvation (Table 1). It is noteworthy that the isothiocyanate anion participates in the hydrogen bonding through the sulphur (S) end as shown from the correlation (Fig. 3).

Again, the decomposition of all complexes start around 315 °C as demonstrated from d.t.a. and IR spectra (*vide infra*). Moreover, the correlation between the axial bond strength and the thermal stabilities has not been found as reported earlier [2]. This phenomenon may be explained by the fact that thermal decomposition in the complexes does not begin by a scission of the axial bond, but by the cleavage of another bond in the chelate ring. A comparison of the structures (I, II) shows that the five membered chelate ring of *en* complexes (II) is the weakest ring, because it has no double bonds (higher bond energy) like the other chelate rings. On the other hand, an increase in strength of the coordinative bond (metal–nitrogen) results in a weakening in the other bonds of the chelate ring [12]. This, together with the higher interaction of the axial anions in the lattice, indicates that the rupture of the five membered chelate ring is the initial step of the decomposition reaction. Therefore, the complexes begin their decompositions nearly at the same temperature (315 °C).

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