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ANISOTROPIC TEMPERATURE FACTORS AS MECHANISM INDICATORS OF THERMAL PROCESSES

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ABSTRACT

The crystal structures and TG curves of *trans*-tetrakis(pyrazole)bisisothiocyanatomanganese(II) [$(C_3H_4N_2)_4(NCS)_2Mn(II)$, $C2/c$, $Z = 4$], *trans*-tetrakis(pyrazole)bisaquamanganese(II)bispyrazolebisnitrate [$(((C_3H_4N_2)_4(H_2O)_2Mn(II))(C_3H_4N_2)_2(NO_3)_2)$, $P\bar{1}$, $Z = 1$], *trans*-hexakis(pyrazole)manganese(II)bisperchlorate [$((C_3H_4N_2)_6Mn(II))(ClO_4)_2$, $P\bar{3}$, $Z = 1$] and *trans*-tetrakis(pyrazole)bischloromanganese(II) [$(C_3H_4N_2)_4(Cl)_2Mn(II)$, $C2/c$, $Z = 4$] were determined recently. The TG curves point for the first complex to two, for the second to three, for the third to one and for the fourth to two kinds of pyrazole with different bonding strengths in the structures and in accord to the anisotropic temperature factors, coordination (symmetry) and hydrogen bonds.

It seems that the anisotropic temperature factor coefficients or their equivalent values, U_{eq} (Å^2), could be used as indicators of the thermal decomposition processes.

INTRODUCTION

Recently Gustafsson and Tellgren [1] showed, by neutron diffraction studies between 25 and 295 K for pentaerythritol ($C(CH_2OH)_4$), that the anisotropic temperature factors of the atoms increase linearly with increasing temperature and generally in the same order as at room temperature without crossing each other. Yamanaka et al. [2] have shown this for $MgAl_2O_4$ spinel at higher and wider temperature ranges. This behaviour of the anisotropic temperature factors of atoms seems thus to be general and independent of the atom kind, compound and crystal structure.

On the other hand, Zucker and Schulz [3] have shown for Li_3N that the mean-square displacements of the atoms from their equilibrium positions caused by their temperature vibrations increase linearly and approximately in the same way with increasing temperature. This is more exponentional as the temperature approaches the melting point of the compound and naturally even more so near the decomposition temperature, but the order for different atoms remains the same over the entire temperature range, like the

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anisotropic temperature factors [1,2]. The higher the temperature the more the harmonic temperature motion of atoms in crystals changes to become anharmonic when approaching the melting and decomposition temperatures of the compound. This is to be expected and self-evident.

The general structure factor equation assuming anharmonic thermal motion comprises the anisotropic thermal parameters and according to the above it makes no significant difference between the results if either Edgeworth's [4] or Gram-Charlier's [5] expansions, which are identical if an infinite number of terms are included, or some other [6] is used for the anisotropic temperature term when considered from the viewpoint of the present considerations. This because, as expressed before, the values of the anisotropic temperature factors, or U_{eq} (Å^2) values derived from these at room or lower temperatures are already adequate as indicators of the thermal processes without the need to determine them at higher temperatures.

The same conclusion may be drawn by comparison of the results of Yamanaka et al. [2] when refining the temperature factor ($T(Q)$) of each atom in the form of the anisotropic factors β_{ij} by assuming the ellipsoidal model of harmonic vibrations and the anharmonic refinement using cumulant expansion of the temperature factor ($T(Q)$). Their results show the second-order coefficients β_{ij} obtainable in the latter case to be practically equal to the former (in most cases within ESDs) at every temperature and the third- and fourth-order coefficients (in the latter case) indicating that the anharmonic thermal tensors are of minor importance compared with the β_{ij} values.

Therefore, the β_{ij} values obtainable at room or lower temperature from the ellipsoidal harmonic thermal vibrations of the atoms for their anisotropic temperature factors are as such sufficiently informative to be applied as indicators of thermal processes.

EXPERIMENTAL

The preparation, X-ray structure determination and thermal analysis of the compounds have been described recently [7–10].

RESULTS AND DISCUSSION

TG curves, ORTEP drawings and unit cells of the four complexes studied are shown in Figs. 1–3, respectively. The thermal processes elucidated from the TG curves and their correlation with the crystal structures are presented in Table 1. The equivalent values ($U_{eq} \times 10^4$ (Å^2)) of the anisotropic temperature factor coefficients of non-hydrogen atoms of the complexes studied are given in Table 2.

trans-*Tetrakis(pyrazole)bisisothiocyanatomanganese(II)*

At first the complex loses two pyrazole molecules between 363 and 437 K and the other two are then lost immediately between 437 and 570 K (Fig. 1 and Table 1). When compared with the crystal structure (Figs. 2 and 3, and Table 2) it can be suggested that the first two pyrazole molecules lost are those coordinated to the central Mn(II) ion through N(3) ring atoms and the last two those bonded via N(1) nitrogen atoms. Manganese(II)bisthiocyanate is stable between 570 and 580 K and then decomposes to 750 K giving up dicyan. The manganese(II)bissulfide formed decomposes further at higher temperatures (Fig. 1 and Table 1).

trans-*Tetrakis(pyrazole)bisaquamanganese(II)bispyrazolebisnitrate*

The parallelism between the escaping pyrazole molecule and U_{eq} values is not so one-strand in this case. In the first reaction this complex loses one

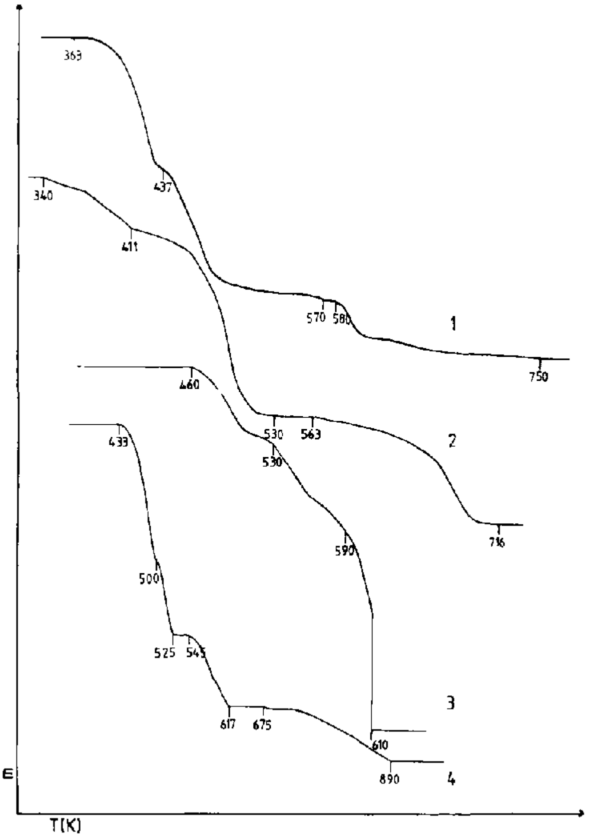

Fig. 1. TG curves of the Mn(II) complexes in dynamic N_2 or static air (∗) atmosphere. Heating rate 10 or 20 (+) deg min^{-1}. (1) $(C_3H_4N_2)_4(NCS)_2Mn(II)$; (2) $((C_3H_4N_2)_4(H_2O)_2Mn(II))(C_3H_4N_2)_2(NO_3)_2$; (3) $((C_3H_4N_2)_6Mn(II))(ClO_4)_2$ (∗); (4) $(C_3H_4N_2)_4(Cl)_2Mn(II)$ (∗ +).

pyrazole molecule and water between 340 and 411 K (Fig. 1 and Table 1). This is followed by the continued loss of four more pyrazole molecules and the final water to 530 K. The monopyrazole complex is stable between 530 and 563 K and then decomposes to Mn_2O_3, which stays above 716 K.

By comparing the thermal processes (Fig. 1 and Table 1) with the U_{eq} values (Table 2, Figs. 2 and 3) it may, however, be concluded that coordinated pyrazole molecules escape in the first step through N(5), in the second through N(5), N(3) and N(1), and in the last step through N(1).

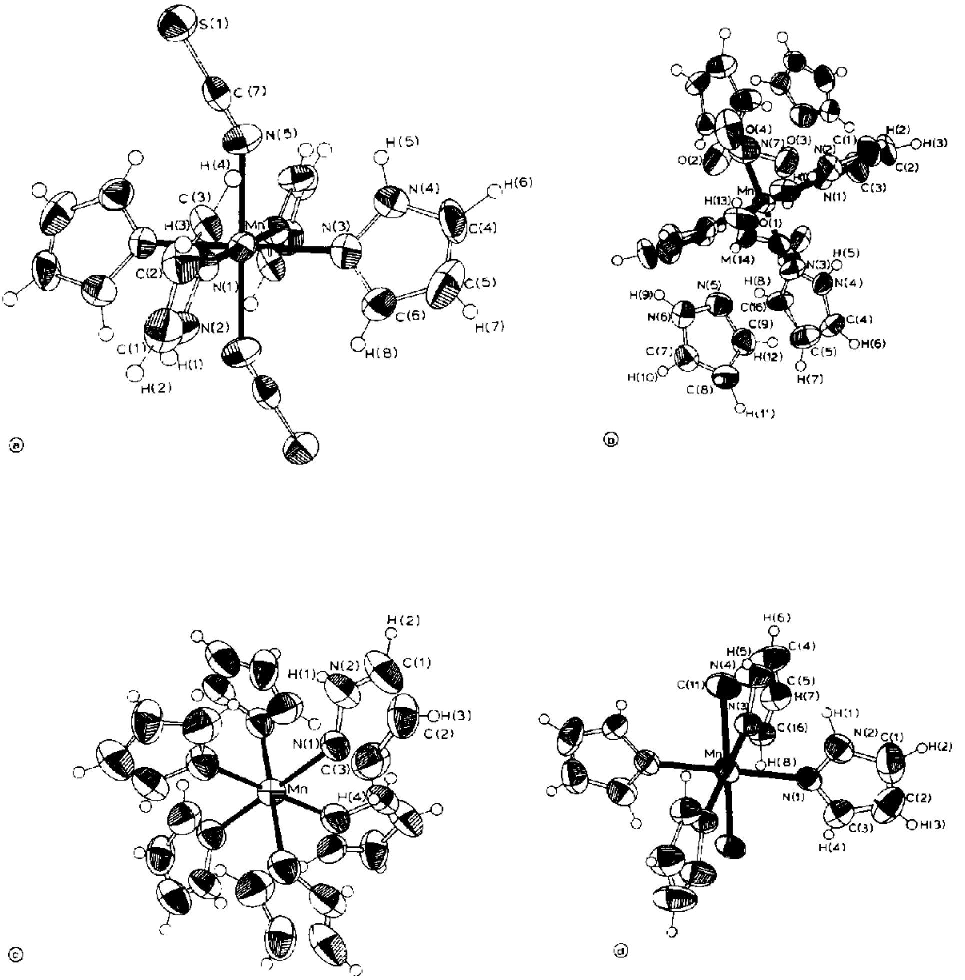

Fig. 2. ORTEP drawings of the Mn(II) complexes (with 295 K parameters) showing the molecular geometry and atom numbering scheme. Thermal ellipsoids are drawn at 50% probability level for the non-hydrogen atoms. (a) $(C_3H_4N_2)_4(NCS)_2Mn(II)$; (b) $((C_3H_4N_2)_4(H_2O)_2Mn(II))(C_3H_4N_2)_2(NO_3)_2$; (c) $((C_3H_4N_2)_6Mn(II))(ClO_4)_2$; (d) $(C_3H_4N_2)_4(Cl)_2Mn(II)$.

trans-*Hexakis(pyrazole)manganese(II)bisperchlorate*

According to crystal structure analysis (Table 2, Figs. 2 and 3) the complex contains only one kind of symmetrically and thermally equal pyrazole molecules. The TG curve (Fig. 1) mainly in harmony with this, shows an almost continuous curve. We may, however, conclude from the course of the TG curve that the complex gives up the first two pyrazole molecules at 460–530 K, the second two at 530–590 K and the last two at 590–610 K, where the perchlorate left explodes to form Mn_2O_3. No clear plateaus exist in the TG curve which may thefore also indicate a continuous release of pyrazole ligands.

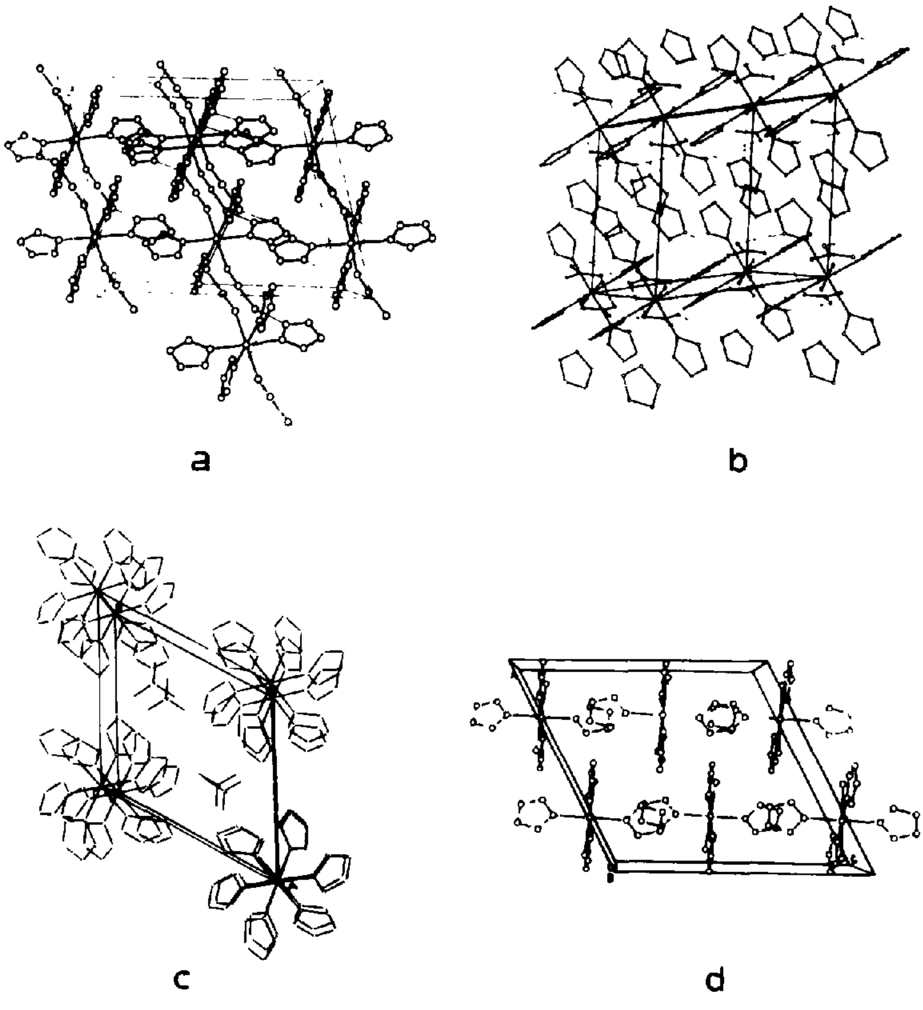

Fig. 3. Unit cells of the Mn(II) complexes viewed down *a*, *b* (•) or *c* (+) axes. (a) $(C_3H_4N_2)_4(NCS)_2Mn(II)$ (•); (b) $((C_3H_4N_2)_4(H_2O)_2Mn(II))(C_3H_4N_2)_2(NO_3)_2$; (c) $((C_3H_4N_2)_6Mn(II))(ClO_4)_2$ (+); (d) $(C_3H_4N_2)_4(Cl)_2Mn(II)$ (•).

TABLE 1

TG Data for Mn(II) complexes and correlation with pyrazole ligands in crystal structures [a]

Process	TG			Coordinating atom of the escaping organic ligand	$U_{eq}\times10^4$ (Å^2)
	Temp. range (K)	Residue (%)			
		Found	Calc.		
$(C_3H_4N_2)_4(NCS)_2Mn$	↓				
$-(2C_3H_4N_2)$	363–437			N(3)	427(37)
$(C_3H_4N_2)_2(NCS)_2Mn$	↓	69.7	69.3		
$-(2C_3H_4N_2)$	437–570			N(1)	370(33)
$Mn(SCN)_2$	↓	40.2	38.6		
$-(2CN)$	580–750				
MnS_2 ($\rightarrow\alpha$-$MnS+S$)	750 →	27.1	26.9		
$((C_3H_4N_2)_4(H_2O)_2Mn)$					
$-(C_3H_4N_2)_2(NO_3)_2$	↓				
$-(C_3H_4N_2+0.5H_2O)$	340–411			N(5)	544(19)
$((C_3H_4N_2)_4(H_2O)_{1.5}Mn)$		87.5	87.6		
$-(C_3H_4N_2)(NO_3)_2$	↓				
$-(4C_3H_4N_2+1.5H_2O)$	411–530			N(5), N(3), N(1)	544(19), 461(17), 443(17)
$(C_3H_4N_2)Mn(NO_3)_2$	↓	42.2	39.6		
$-(C_3H_4N_2+2NO_2+0.25O_2)$	563–716			N(1)	443(17)
Mn_2O_3 (unpure)	716 →	15.5	12.7		
$((C_3H_4N_2)_6Mn)(ClO_4)_2$	↓				
$-(2C_3H_4N_2)$	460–530			N(1)	605(27)
$((C_3H_4N_2)_4Mn)(ClO_4)_2$	↓	79.4	79.4		
$-(2C_3H_4N_2)$	530–590			N(1)	605(27)
$((C_3H_4N_2)_2Mn)(ClO_4)_2$	↓	59.0	58.9		
$-(2C_3H_4N_2)$	590–610			N(1)	605(27)
$Mn(ClO_4)_2$	↓	38.4	38.3		
$-(Cl_2+3.25O_2)$	610				
Mn_2O_3	610 →	8.5	11.9		
$(C_3H_4N_2)_4(Cl)_2Mn$	↓				
$-(2C_3H_4N_2)$	433–500			N(1)	447(12)
$(C_3H_4N_2)_2(Cl)_2Mn$	↓	67.3	65.8		
$-(C_3H_4N_2)$	500–525			N(3)	438(12)
$(C_3H_4N_2)(Cl)_2Mn$	↓	49.7	48.7		
$-(C_3H_4N_2)$	545–617			N(3)	438(12)
$MnCl_2$	↓	32.4	31.6		
$-(Cl_2-0.75O_2)$	675–890				
Mn_2O_3	890 →	19.3	19.8		

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[a] The idea under discussion was presented for the first time in 1982 [7a]. The conclusions are the same if we use $\Delta U_{eq}=U_{eq}$(ligand atom coordinated)$-U_{eq}$(metal atom) or $\Delta U_{ij}=\Sigma(U_{ij}$(ligand atom coordinated)$-U_{ij}$(metal atom)). The comparison base is naturally the central metal atom to which the ligand is coordinated [11].

TABLE 2

Equivalent values ($U_{eq} \times 10^4$ (Å^2)) of the anisotropic temperature factor coefficients [a] of non-hydrogen atoms with ESDs in parentheses for the Mn(II) complexes

$(C_3H_4N_2)_4(NCS)_2Mn(II)$								
Atom	N(1)	N(2)	C(1)	C(2)	C(3)	Mn		
U_{eq}	370(33)	500(45)	578(58)	516(51)	463(51)	337(8)		
Atom	N(3)	N(4)	C(4)	C(5)	C(6)	N(5)	C(7)	S(1)
U_{eq}	427(37)	556(47)	680(66)	770(79)	553(56)	513(38)	388(40)	567(13)
$((C_3H_4N_2)_4(H_2O)_2Mn(II))(C_3H_4N_2)_2(NO_3)_2$								
Atom	N(1)	N(2)	C(1)	C(2)	C(3)	Mn		
U_{eq}	443(17)	498(19)	677(31)	751(33)	613(26)	367(4)		
Atom	N(3)	N(4)	C(4)	C(5)	C(6)	O(1)		
U_{eq}	461(17)	481(18)	583(24)	678(27)	633(27)	619(18)		
Atom	N(5)	N(6)	C(7)	C(8)	C(9)	N(7)	O(2)	O(3)	O(4)
U_{eq}	544(19)	550(21)	606(28)	618(28)	597(26)	514(20)	779(21)	662(19)	788(21)
$((C_3H_4N_2)_6Mn(II))(ClO_4)_2$								
Atom	N(1)	N(2)	C(1)	C(2)	C(3)	Mn	Cl(1)	O(1)	O(2)
U_{eq}	605(27)	754(32)	906(49)	827(49)	772(44)	467(11)	712(17)	2109(70)	2286(78)
$(C_3H_4N_2)_4(Cl)_2Mn(II)$								
Atom	N(1)	N(2)	C(1)	C(2)	C(3)	Mn		
U_{eq}	447(12)	631(16)	737(23)	791(27)	460(15)	404(3)		
Atom	N(3)	N(4)	C(4)	C(5)	C(6)	Cl(1)		
U_{eq}	438(12)	598(15)	722(21)	636(19)	516(16)	534(4)		

[a] $U_{eq} = (1/3)\,\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \vec{a}_i \cdot \vec{a}_j \approx (1/3)(U_{11} + U_{22} + U_{33})$.

trans-*Tetrakis(pyrazole)bischloromanganese(II)*

The crystal structure analysis (Table 2, Figs. 2 and 3) shows the complex to contain two kinds of pyrazole molecules. In accordance with this the TG curve (Fig. 1 and Table 1) shows the complex to lose both the N(1) coordinated pyrazole molecules between 433 and 500 K, but the two N(3) coordinated pyrazoles are given up separately, the first one escaping between 500 and 525 K. The monopyrazole complex formed seems to be stable from 525 to 545 K. This then decomposes between 545 and 617 K to manganese(II)bischloride, which is stable between 617 and 675 K and finally decomposes to Mn_2O_3 from 675 to 890 K.

CONCLUSION

By considering the above described results of comparison of the TG curves and crystal structure analyses for the present series of manganese(II)pyrazole complexes it is obviously possible to draw the general conclusion that, at least under favourable conditions, the anisotropic temperature factors, or equivalent values, U_{eq}, derivable from them, can be used to indicate in which order uncharged similar organic ligands coordinated to the central metal ion escape in the thermal decomposition processes of the complex. Is this conclusion to be extended to comprehend the escaping order of different coordinated organic ligands? This needs further studies, but the answer seems to be affirmative.

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