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1,2,4-Triazole Complexes.

XV. The Structure of Tetraaquasulphato(1,2,4-triazole)manganese(II)

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Abstract

$[Mn(C_2H_3N_3)(H_2O)_4SO_4]$ is monoclinic, space group $P2_1/c$ with $a = 6{\cdot}5022\ (4)$, $b = 12{\cdot}134\ (4)$, $c = 12{\cdot}849\ (2)$ Å, $\beta = 90{\cdot}57\ (6)°$, $Z = 4$. Final $R = 0{\cdot}029$ for 1529 independent reflexions. The coordination polyhedron around Mn consists of four O atoms of water molecules, one O atom of the sulphate group and N(4) of the triazole ring *cis* with respect to the sulphate ligand. There is extensive hydrogen bonding.

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Introduction

Coordination complexes with 1,2,4-triazole as a ligand (hereafter trz) have interesting features because of the many modes of coordination. In an attempt to prepare an Mn analogue of the trimeric $Ni(trz)_2(NO_3)_2 . (H_2O)_{8/3}$ (Engelfriet, Haasnoot & Groeneveld, 1977; Reimann & Zocchi, 1971) the title compound was found. Since the infrared data (Haasnoot, Vos & Groeneveld, 1977) pointed to an unknown mode of coordination the crystal structure of $[Mn(trz)(H_2O)_4SO_4]$ was determined.

Unit cell and space group

Crystals were prepared by precipitation at room temperature from concentrated aqueous solutions of $MnSO_4$ and 1,2,4-triazole in a ratio of 1:2. The crystals are stable in air. The Laue diffraction symmetry ($2/m$) and systematic extinctions for $h0l$, l odd, and $0k0$, k odd, indicate the space group $P2_1/c$. Cell parameters were determined on a single-crystal diffractometer at room temperature with Mo $K\alpha$ radiation (λ = 0·71069 Å) from θ, φ and χ measurements of ten $h00$, $0k0$, $00l$ reflexions. The density of 1·90 (3) Mg m^{-3} (flotation) agrees with 1·91 Mg m^{-3} calculated for Z = 4 and a molecular weight of 292·14; $F(000) = 598$.

Collection and reduction of X-ray diffraction data

A crystal 0·30 × 0·28 × 0·10 mm was mounted in a glass capillary on a Nonius three-circle diffractometer. Intensities were recorded at room temperature by the θ–2θ scan method for all reflexions with θ between 3·5 and 25°. Mo $K\alpha$ radiation monochromatized by graphite was used. The total scan width varied according to $\Delta\theta$ (°) = 0·90 + 0·86 tan θ. 2538 reflexions were measured. After symmetry-related reflexions were averaged, 1783 independent reflexions were obtained, including 21 not observed as well as 233 with $I < 2\sigma(I)$. The intensities were corrected for Lorentz and polarization effects. At a later stage absorption corrections were also applied (de Graaff, 1973). Calculated transmission factors vary between 0·70 and 0·91 [μ(Mo $K\alpha$) = 1·59 mm^{-1}]. After reduction of the intensities to F values, a Wilson plot was calculated from which approximate values of the scale and thermal factors were obtained.

Table 1. *Fractional coordinates* (Mn *and* S ×10^5, C, N *and* O ×10^4) *and isotropic temperature parameters* (Å^2 ×10^2) *of the heavy atoms*

In this and the following tables e.s.d.'s in the least significant digits are given in parentheses. The isotropic temperature factors in the table are calculated from the anisotropic temperature factors according to: $B_{eq} = \frac{8}{3}\pi^2$ trace $\tilde{U}$.

	x	y	z	B_{eq}
Mn	65519 (6)	91518 (3)	28868 (3)	185 (1)
C(3)	7183 (4)	9189 (2)	326 (2)	238 (7)
C(5)	7720 (4)	10732 (2)	998 (2)	272 (8)
N(1)	7807 (4)	10826 (2)	−18 (2)	260 (7)
N(2)	7472 (4)	9835 (2)	−478 (2)	255 (6)
N(4)	7320 (3)	9700 (2)	1262 (2)	214 (6)
O(1)	3533 (4)	9911 (3)	2629 (3)	479 (9)
O(2)	5650 (5)	8748 (3)	4449 (2)	457 (9)
O(3)	5332 (5)	7624 (2)	2226 (2)	398 (8)
O(4)	9253 (4)	8162 (2)	3172 (2)	343 (6)
S	91619 (9)	114272 (5)	40189 (5)	176 (3)
O(S1)	8088 (4)	10604 (2)	3405 (2)	521 (8)
O(S2)	8656 (3)	12514 (1)	3557 (2)	288 (6)
O(S3)	8453 (3)	11427 (2)	5091 (2)	353 (6)
O(S4)	11388 (3)	11266 (2)	3976 (2)	329 (6)

Table 2. *Fractional coordinates* (×10^3) *and isotropic temperature parameters* (Å^2 ×10) *of the* H *atoms*

	x	y	z	B_{iso}
H(C3)	689 (5)	846 (3)	27 (3)	36 (7)
H(C5)	793 (4)	1129 (2)	146 (3)	29 (7)
H(N1)	796 (5)	1138 (3)	−39 (3)	29 (7)
H(101)	292 (7)	1013 (3)	300 (4)	49 (12)
H(201)	310 (6)	1003 (3)	215 (4)	48 (12)
H(102)	654 (7)	889 (3)	494 (4)	61 (12)
H(202)	466 (7)	878 (3)	463 (3)	48 (12)
H(103)	424 (7)	758 (3)	203 (3)	54 (12)
H(203)	604 (9)	711 (3)	213 (3)	93 (18)
H(104)	995 (6)	838 (3)	358 (3)	45 (11)
H(204)	1005 (7)	799 (4)	257 (4)	70 (12)

Solution and refinement

The Patterson synthesis gave positions for all atoms except H. Full-matrix least-squares refinement of positional parameters and individual thermal parameters for the 15 non-hydrogen atoms converged to R = 0·100 for the significant reflexions. Anisotropic thermal parameters led to R = 0·053.

A difference synthesis revealed all the H atoms. Further refinement included the positional parameters of all atoms, anisotropic thermal parameters of all non-hydrogen atoms and individual isotropic thermal parameters for all H atoms. At this stage (R = 0·0351) an extinction correction (Zachariasen, 1967) was applied to the 1529 significant reflexions. Final refinement led to R = 0·0293 (R_w = 0·0315). In the last cycle the calculated shifts were <1/150th of the e.s.d.'s. The positional parameters of the non-hydrogen and H atoms are in Tables 1 and 2 respectively. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Corrections for f' and f'' were applied and the function minimized was

$\sum w(|F_o| - |F_c|)^2$ with the weighting scheme $w = \sigma(F)^{-2}$. Agreement factors refer to $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.*

The molecular structure

Bond distances and angles are shown in Tables 3 and 4. The stereochemistry of the ligands and the atomic labelling are depicted in Fig. 1 and the intermolecular arrangement is shown in Fig. 2. The triazole is monodentate. Each Mn atom is surrounded by four water molecules, one O atom of the sulphate group and one N of the triazole ring *cis* with respect to the sulphate in an octahedral arrangement. The molecule has a heavily distorted C_s symmetry, which may be due to hydrogen bonding, the angle between the triazole ring and the least-squares plane through Mn, N(4), O(2), O(3) and O(S1) being 162·3 (1)° and the angle between this plane and the line O(S2)–O(S4) being 76·4 (1)°. The coordinating atom from the triazole ring is N(4) instead of the expected N(1) or N(2) (Haasnoot *et al.*, 1977), due to hydrogen bonding of H(N1) to O(S2) with the symmetry relation x, $2·5 - y$, $0·5 + z$. If either N(1) or N(2) were bonded to the Mn atom there would have been a C atom at the position of N(1) and so no hydrogen bond to O(S2) would have been possible. There is also a hydrogen bond from N(2) to O(1) with the symmetry relation $1 - x$, $2 - y$, $-z$. A striking feature of this structure is the large number of hydrogen bonds. In Fig. 2, in which the orientation of the plot is the same as in Fig. 1, the Mn atom is placed in the centre of the drawing and hydrogen bonds to surrounding molecules are depicted as line bonds. The bond lengths and angles are given in Table 5. Table 5 and Fig. 2 show that O(S3) and O(S4) are involved

Table 3. *Intramolecular distances* (Å)

Mn–N(4)	2·253 (2)	S–O(S3)	1·457 (2)
Mn–O(S1)	2·130 (2)	S–O(S4)	1·462 (2)
Mn–O(1)	2·191 (3)	C(3)–H(C3)	0·91 (3)
Mn–O(2)	2·154 (3)	C(5)–H(C5)	0·91 (3)
Mn–O(3)	2·186 (2)	N(1)–H(N1)	0·83 (3)
Mn–O(4)	2·156 (2)	O(1)–H(101)	0·68 (5)
N(4)–C(3)	1·355 (4)	O(1)–H(201)	0·68 (5)
C(3)–N(2)	1·312 (4)	O(2)–H(102)	0·86 (5)
N(2)–N(1)	1·357 (3)	O(2)–H(202)	0·69 (5)
N(1)–C(5)	1·311 (4)	O(3)–H(103)	0·76 (4)
C(5)–N(4)	1·324 (4)	O(3)–H(203)	0·79 (6)
S–O(S1)	1·448 (2)	O(4)–H(104)	0·74 (4)
S–O(S2)	1·482 (2)	O(4)–H(204)	0·96 (6)

Table 4. *Bond angles* (°)

N(4)–Mn–O(1)	86·8 (1)	Mn–N(4)–C(3)	132·4 (2)
N(4)–Mn–O(2)	175·2 (1)	Mn–N(4)–C(5)	124·3 (2)
N(4)–Mn–O(3)	88·5 (1)	Mn–O(1)–H(101)	126 (4)
N(4)–Mn–O(4)	97·6 (1)	Mn–O(1)–H(201)	126 (4)
N(4)–Mn–O(S1)	86·4 (1)	Mn–O(2)–H(102)	116 (3)
O(1)–Mn–O(2)	89·1 (1)	Mn–O(2)–H(202)	124 (4)
O(1)–Mn–O(3)	88·6 (1)	Mn–O(3)–H(103)	122 (3)
O(1)–Mn–O(4)	170·8 (1)	Mn–O(3)–H(203)	122 (4)
O(1)–Mn–O(S1)	96·8 (1)	Mn–O(4)–H(104)	114 (3)
O(2)–Mn–O(3)	93·9 (1)	Mn–O(4)–H(204)	115 (3)
O(2)–Mn–O(4)	86·9 (1)	Mn–O(S1)–S	164·5 (2)
O(2)–Mn–O(S1)	91·7 (1)	C(5)–N(4)–C(3)	102·5 (3)
O(3)–Mn–O(4)	83·5 (1)	N(4)–C(3)–N(2)	114·6 (3)
O(3)–Mn–O(S1)	172·4 (1)	C(3)–N(2)–N(1)	102·2 (3)
O(4)–Mn–O(S1)	91·6 (1)	N(2)–N(1)–C(5)	110·4 (3)
O(S1)–S–O(S2)	107·0 (1)	N(1)–C(5)–N(4)	110·4 (3)
O(S1)–S–O(S3)	111·0 (2)	N(4)–C(3)–H(C3)	122 (2)
O(S1)–S–O(S4)	111·1 (2)	N(2)–C(3)–H(C3)	124 (2)
O(S2)–S–O(S3)	107·9 (1)	N(2)–N(1)–H(N1)	120 (2)
O(S2)–S–O(S4)	108·7 (1)	C(5)–N(1)–H(N1)	130 (2)
O(S3)–S–O(S4)	111·0 (1)	N(1)–C(5)–H(C5)	125 (2)
		N(4)–C(5)–H(C5)	125 (2)

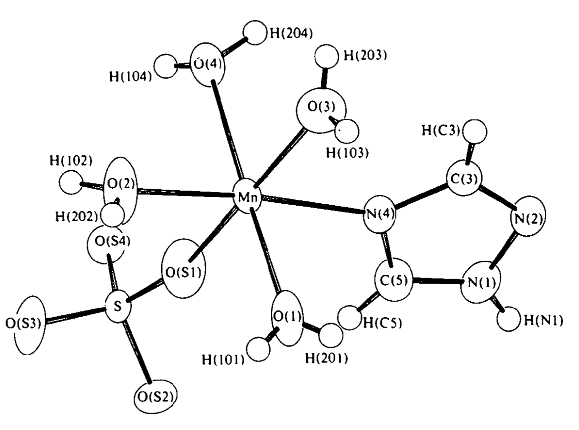

Fig. 1. The stereochemistry and atom labelling of [Mn(trz)$(H_2O)_4SO_4$].

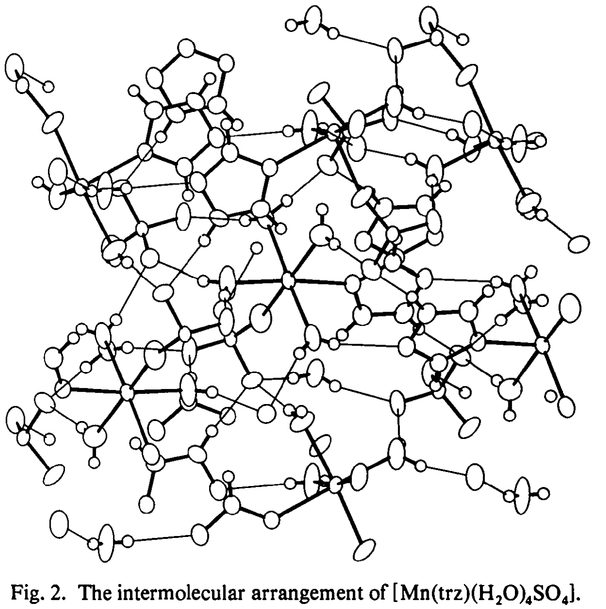

Fig. 2. The intermolecular arrangement of [Mn(trz)$(H_2O)_4SO_4$].

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36000 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in two hydrogen bonds and O(S2) in three. O(1), O(2) and O(4) are involved in two hydrogen bonds, O(3), N(1) and N(2) are only involved in one. O(S2) is surrounded by one S atom and three H atoms in a tetrahedral arrangement with angles between 90 and 120°.

In Table 6 the results for the triazole ring are collected. The ring is flat with very small deviations from its least-squares plane. After an investigation of the Cambridge Crystallographic Data Base for sulphate groups coordinated to metal ions and for the number of hydrogen bonds to the non-metal coordinated O atoms of the sulphate group, 22 entries with published atom coordinates were found. In 11 of these the sulphate formed a bridge between two metal ions (Tedenac, Phung, Avinens & Mauren, 1976; Healy, Kennard, Smith & White, 1978; Cavalca, Domiano, Gasparri & Boldrini, 1967; Allen, Lerbscher & Trotter, 1971; Volodina, Pethukov, Ablov & Gerbeleu, 1974; Morimoto & Lingafelter, 1970; Baggio, de Benyacar, Perazzo & de Perazzo, 1977; Girerd, Jeannin, Jeannin & Kahn, 1978; Korvenranta, 1973; Fransson & Lundberg, 1972; Kuskov, Kurkutova, Treushnikov, Ionov, Ilyukhin & Belov, 1977).

Table 5. *Bond lengths and angles of the intermolecular hydrogen bonds*

	Distance (Å)	Angle (°)
$O(1)–H(101)\cdots O(S4^{i})$	2·775 (4)	162 (5)
$N(1)–H(N1)\cdots O(S2^{ii})$	2·782 (3)	168 (3)
$O(3)–H(103)\cdots O(S2^{iii})$	2·782 (4)	177 (4)
$O(1)–H(201)\cdots N(2^{iv})$	2·851 (4)	163 (5)
$O(2)–H(202)\cdots O(S3^{v})$	2·754 (4)	167 (5)
$O(4)–H(204)\cdots O(S2^{vi})$	2·733 (3)	173 (5)
$O(2)–H(102)\cdots O(S4^{vii})$	2·783 (4)	163 (4)
$O(4)–H(104)\cdots O(S3^{vii})$	2·722 (3)	163 (4)

All these hydrogen bonds occur twice in the structure.

Symmetry relations:

None	x,	y,	z	(iv)	$1-x$,	$2-y$,	$-z$
(i)	$-1+x$,	y,	z	(v)	$1-x$,	$2-y$,	$1-z$
(ii)	x,	$2\cdot5-y$,	$-0\cdot5+z$	(vi)	$2-x$,	$-0\cdot5+y$,	$0\cdot5-z$
(iii)	$1-x$,	$0\cdot5+y$,	$0\cdot5-z$	(vii)	$2-x$,	$2-y$,	$1-z$.

Table 6. *Geometry of the bonds to the triazole ring and least-squares plane through the ring*

Coefficients of the plane function $AX + BY + CZ + D = 0$

$A = -0\cdot9801\ (3)$ $C = -0\cdot038\ (1)$

$B = 0\cdot195\ (2)$ $D = 2\cdot42\ (2)$

Transformation matrix for X, Y and Z

$$\begin{pmatrix} 1 & 0 & \cos\beta \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta \end{pmatrix}\begin{pmatrix} a \\ b \\ c \end{pmatrix}=\begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

Distances (Å) of the ring atoms to the plane

C(3)	0·0001 (2)	N(1)	0·002 (2)
C(5)	−0·002 (2)	N(2)	−0·002 (2)
N(4)	0·000 (2)		

Angles of the different bonds outside the ring to the plane of the ring (°)

Mn–N(4)	7·7 (1)	N(1)–H(N1)	3 (2)
C(3)–H(C3)	0·8 (7)	N(2)–H(201)″	12 (1)
C(5)–H(C5)	1 (2)		

Double prime denotes symmetry operation (iv) from Table 5.

Table 7. S–O *lengths and* $S–O(\cdots M)$ *bond length and angle compared with the values for the current compound*

Number of hydrogen bonds	Mean value in literature	Mean value of current compound
0	1·451 (9) Å	—
1	1·463 (6)	—
2	1·471 (4)	1·461 (2) Å
3	1·478 (3)	1·482 (2)
Metal-bonded	1·471 (5)	1·448 (2)
Angle	137 (2)°	164·5 (2)°

These entries were only used for intramolecular calculations. From the remaining 11 entries the intermolecular distances were calculated to obtain the number of possible hydrogen bonds. In seven entries (six compounds) of this group (Caira, Nassimbeni & Orpen, 1976; Corao & Baggio, 1969; Cavalca, Chiesi Villa, Mangia & Palmieri, 1970; Ponomarenko, Kurkutova, Porai-Koshits, Aslanov & Sulaimankulov, 1976; Andreetti, Cavalca & Musatti, 1968; Fransson & Lundberg, 1974; Chiesi Villa, Manfredotti & Guastini, 1972) the existence of three possible hydrogen bonds to the same non-metal bonded O atom of the sulphate group was found. The remaining four entries (Balvich, Fivizzani, Pavkovic & Brown, 1976; Kivekas, 1978; Hoskins & Whillans, 1975; Vimala & Swaminathan, 1969) were also only used for intramolecular calculations. These calculations concerned S–O lengths as well as the angle $S–O\cdots M$. Comparison of the values for these bond lengths according to the number of atom–atom contacts suitable for hydrogen bonding gave mean values as shown in Table 7. Although the dependence of the S–O lengths on the number of hydrogen bonds is not statistically significant, there is a tendency towards greater distances with a larger number of hydrogen bonds. Our results confirm this tendency. Although the e.s.d.'s of the mean values of the angle $S–O\cdots M$ and of the S–O length seem to have low values, there is a great difference in the extremes (109·3 and 166·3° for the angle, 1·428 and 1·508 Å for the length). Nevertheless the value of the angle in the current compound seems to be rather high [164·5 (2)°] and of the length rather short [1·448 (2) Å].

All calculations were carried out on an IBM 370/158, and later on an Amdahl V7B computer at Leiden University.

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Structures du Biphényléno[2,3-*c*]phénanthrène, $C_{24}H_{14}$, du Benzo[*g*]biphényléno-[2,3-*c*]phénanthrène, $C_{28}H_{16}$, et du Biphényléno[2,3-*a*]pentahélicène, $C_{32}H_{18}$

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Abstract

The structures of the title compounds have been solved by direct methods (*MULTAN*) from diffractometer data. $C_{24}H_{14}$ is monoclinic, $P2_1/n$, with $a = 23{\cdot}539\ (5)$, $b = 6{\cdot}290\ (2)$, $c = 22{\cdot}505\ (5)$ Å, $\beta = 113{\cdot}39\ (2)°$ and $Z = 8$ for $D_x = 1{\cdot}31$ Mg m^{-3}, $V = 3058\ (1)$ Å^3. $C_{28}H_{16}$ is monoclinic, $P2_1$, with $a = 13{\cdot}656\ (4)$, $b = 5{\cdot}463\ (2)$, $c = 12{\cdot}450\ (4)$ Å, $\beta = 107{\cdot}92\ (2)°$ and $Z = 2$ for $D_x = 1{\cdot}32$ Mg m^{-3}, $V = 884\ (1)$ Å^3. $C_{32}H_{18}$ is monoclinic, $P2_1/n$, with $a = 17{\cdot}580\ (5)$, $b = 7{\cdot}972\ (3)$, $c = 14{\cdot}719\ (4)$ Å, $\beta = 92{\cdot}21\ (2)°$ and $Z = 4$ for $D_x = 1{\cdot}30$ Mg m^{-3}, $V = 2061\ (1)$ Å^3. The structures were refined to $R = 0{\cdot}045$, $0{\cdot}053$, $0{\cdot}061$ for 2061, 787, 1387 observed reflections for $C_{24}H_{14}$, $C_{28}H_{16}$, $C_{32}H_{18}$ respectively. The molecular dimensions of the *ortho*-fused aromatic rings are very similar to the corresponding

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