by one SO_4^{2-} group, four H_2O molecules and one triazole group, coordinating by its N(4) atom only (Gorter, 1979).

The table shows that there are no large differences between coordinated and uncoordinated trz, with the exception of the Ni complex. This compound is a different case altogether, since here the trz ring is 1,2 coordinating and therefore can be considered as existing in another tautomeric form. For the trz rings in the other four compounds, the best agreement is found with trz at low temperature, probably because the parameters at 118 K were determined more accurately than those at room temperature. The bond lengths in the coordinated triazole are systematically smaller than those in the free molecule. At least in part this may be attributed to the fact that no correction for librational motion was applied (mean correction in free triazole is 0·005 Å). Slight changes may also be caused by coordination.

Further, it should be noted that the trz rings in the Cu and Zn compounds differ somewhat. The N(1) atom of the trz ring in the Cu compound is shifted towards the C(5) atom with respect to that in the Zn compound. We have been unable to find an explanation for this.

Finally, as can be seen from Table 5, the trz rings are planar within experimental error. The metal atoms are at fairly short distances from the trz planes, except for the Cu attached to the N(2) atom.

The authors are indebted to Drs W. L. Groeneveld and J. G. Haasnoot for their stimulating interest in this study.

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1,2,4-Triazole Complexes.

VI.* The Crystal Structure of Tris-μ-(4-methyl-1,2,4-triazole-N^1,N^2)-bis[(4-methyl-1,2,4-triazole-N^1)bis(thiocyanato-N)manganese(II)], Mn$_2$(C$_3$H$_5$N$_3$)$_5$(NCS)$_4$

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Abstract

The crystal structure of Mn$_2$(C$_3$H$_5$N$_3$)$_5$(NCS)$_4$, C$_{19}$H$_{25}$Mn$_2$N$_{19}$S$_4$, has been determined by single-crystal X-ray diffraction techniques. The compound is orthorhombic, space group $P2_12_12$ with $a = 12·424$ (1), $b = 14·144$ (2), $c = 9·336$ (1) Å, and $Z = 2$, $D_m = 1·532$ (2), $D_c = 1·534$ Mg m^{-3}. Data were collected with a four-circle diffractometer. The structure was solved by direct and Fourier methods and was refined by block-diagonal least squares to a final $R = 0·0251$ ($R_w = 0·0345$) for 1910 independent reflexions. The compound consists of dimeric units in which two Mn^{II} ions are bridged by three methyltriazole groups. Two N-donating NCS$^-$ groups and a methyltriazole group coordinating by only one N atom complete the MnN$_6$ octahedra.

Introduction

In the structures of complexes containing 1,2,4-triazole (trz) reported previously, this ligand acts as a bridging ligand, as is to be expected from its structural formula.
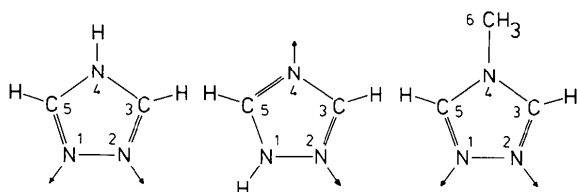
Fig. 1. Structural formulae of 1,2,4-triazole in its 1,2- and 2,4-bridging forms and of 4-methyl-1,2,4-triazole.

The possibility of its existence in two tautomeric forms gives rise to complexes with 1,2- and 2,4-bridging trz units (see Fig. 1). 1,2-Bridging trz occurs in $CuCl_2.trz$ (Jarvis, 1962) and in $Ni_3(trz)_6(H_2O)_6(NO_3)_6.2H_2O$ (Reimann & Zocchi, 1971). 2,4-Bridging trz groups are found in the layered structures of β-$Ni(trz)_2(NCS)_2$ and related compounds with Mn, Fe, Co, Cu and Zn (Engelfriet, Haasnoot & Groeneveld, 1977; Engelfriet & Groeneveld, 1978). trz units coordinating by only one N atom [N(4)] were found in the monomeric $Mn(trz)(H_2O)_4SO_4$ (Gorter, 1979). It is to be expected, therefore, that 4-methyl-1,2,4-triazole (Metrz) complexes may be formed containing 1,2-bridging Metrz, or Metrz coordinating by only one N atom.

Magnetic-susceptibility measurements on a powdered sample of composition $Mn(Metrz)_{2.5}(NCS)_2$ revealed a broad maximum at about 2·5 K. The value of the magnetic moment showed the presence of Mn in its divalent state (Engelfriet & Groeneveld, 1979). This result strongly suggests that either linear chains of bridged Mn^{II} atoms are present or that the compound is built up of linear clusters containing an even number of Mn^{II} atoms. On stoichiometric grounds a dimeric structure was thought to be the most acceptable possibility. In order to verify this assumption a crystal structure determination of this complex was undertaken.

Experimental

An aqueous solution containing equimolar quantities of Metrz and NH_4NCS was added to an acidified solution of $Mn(NO_3)_2(H_2O)_4$. The metal to ligand ratio was 1:2 and the concentration of Mn^{II} in the solution of the complex was approximately 1 mmol ml^{-1}. Very pale green crystals were formed on slow evaporation at 343 K. A single crystal which appeared to be of good quality after Weissenberg photographs were taken was mounted on an Enraf–Nonius CAD-4 four-circle diffractometer. Mo $K\alpha$ radiation, monochromated by graphite, was used for determination of the unit-cell parameters, the space group and for measuring the reflexion intensities. The data were corrected for Lorentz and polarization effects and for absorption (de Graaff, 1973). Equivalent reflexions were averaged. Reflexions with intensities less than twice the standard

deviation (calculated from counting statistics, inaccuracies of attenuation filters and absorption correction) were considered insignificant. After reduction to F_o values, a Wilson plot was calculated, yielding starting values for the scale parameter and the overall isotropic thermal parameter B.

Solution and refinement of the structure

All calculations were carried out on the Leiden University IBM 370-158 computer, using a set of programs written or modified by Mrs E. Rutten-Keulemans and Dr R. A. G. de Graaff. The programs NORMAL and MULTAN were taken from the MULTAN 78 program package (Main, 1976). Relevant crystal and diffraction data are given in Table 1. Scattering factors and anomalous-dispersion corrections were taken from International Tables for X-ray Crystallography (1974). The function minimized during the least-squares refinement was $\sum w(\Delta F)^2$, with $\Delta F = |F_o| - |F_c|$ and the weighting scheme $w = (\sigma_F)^{-2}$. Discrepancy indices referred to are defined as $R = \sum |\Delta F|/\sum |F_o|$ and $R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$.

A three-dimensional Patterson synthesis revealed the position of the Mn^{II} ion. A further analysis was hampered by the presence of a pseudo mirror plane at $x = 0$. The program NORMAL was used to calculate the 188 strongest E values, making use of the position of the Mn. The program MULTAN produced eight solutions. The one with the highest combined FOM led to a structure wherein two manganese ions are bridged by three Metrz groups, one of which is positioned on a twofold axis. However, at each Mn^{II} three NCS groups were found, resulting from the already mentioned pseudosymmetry. After five cycles of isotropic refinement ($R = 0.21$), one of the NCS^- groups could be rejected because of its abnormally high temperature factor. By means of a difference Fourier synthesis the position of non-bridging Metrz was found instead, together with the H(3) and H(5) atoms of all Metrz groups. Six cycles of isotropic refinement yielded $R = 0.096$ ($R_w = 0.15$) and after anisotropic refinement of the non-hydrogen atoms R dropped to 0.038 ($R_w = 0.056$). Further cycles were computed by block-diagonal refinement. The parameters of the Mn^{II} atom, the NCS^- groups and the Metrz groups were allocated to separate blocks. With the methyl H atoms found from a difference Fourier synthesis the R index

Table 1. Diffraction data for $Mn_2(C_3H_5N_3)_5(NCS)_4$

Crystal dimensions	$0.53 \times 0.32 \times 0.20$ mm
θ range	2–27·5°
Measured reflexions	4147
Independent reflexions	2156
Significant reflexions	1910

decreased to 0·030 (R_w = 0·044) after five cycles of refinement. Since the temperature parameters of some H atoms tended to attain unusually high values, their positions were calculated. The H atoms attached to the Metrz rings were placed 0·95 Å from the C atoms. The positions of the H atoms of the methyl groups were calculated by combining results from difference and slant Fourier syntheses and assuming a regular tetrahedral arrangement. Slack constraints (Waser, 1963) were imposed upon the methyl groups and the thermal

parameters of each group of three H atoms were coupled. Refining the H parameters only, four cycles yielded R = 0·027 (R_w = 0·039) and after another five cycles with all parameters R = 0·0251 (R_w = 0·0345) was obtained. No improvement resulted from an extinction correction. In the last cycle the calculated shifts were <0·1 e.s.d. for the non-hydrogen atoms and <0·5 e.s.d. for the H atoms. The refinement was then terminated.

A final difference Fourier synthesis only showed some small peaks of 0·3 e Å^{-3} in the vicinity of S(2) (statistical height = 0·13 e Å^{-3}).

Lastly, in order to make sure the structure thus obtained did not represent the enantiomorph, one cycle was calculated introducing the enantiomorphous structure. Because of the slightly higher value of R = 0·0256 (R_w = 0·0380) resulting from this procedure, this possibility was rejected.

Positional parameters are listed in Tables 2 and 3.*

Table 2. *Fractional coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å^2) *of the non-hydrogen atoms*

	x	y	z	B_{Iso}
Mn	3336·7 (3)	78·3 (3)	2143·5 (4)	2·45 (1)
N(1)	2502 (2)	46 (3)	121 (3)	4·26 (6)
C(1)	2163 (2)	−165 (2)	−975 (3)	3·00 (5)
S(1)	1686·9 (8)	−495·2 (7)	2519 (1)	4·78 (2)
N(2)	2352 (2)	−1029 (2)	3167 (4)	4·24 (6)
C(2)	2035 (2)	−1785 (2)	3029 (4)	3·47 (6)
S(2)	1620 (1)	−2863 (7)	2811 (2)	6·63 (3)
N(1,1)	4490 (2)	1228 (2)	1374 (3)	2·77 (5)
N(1,2)	5582 (2)	1095 (2)	1178 (3)	2·90 (5)
C(1,3)	5940 (3)	1866 (2)	585 (4)	3·30 (6)
N(1,4)	5150 (2)	2496 (2)	389 (3)	3·05 (5)
C(1,5)	4271 (3)	2070 (2)	894 (4)	3·26 (6)
C(1,6)	5244 (3)	3453 (2)	−229 (5)	4·56 (9)
N(2,2)	4444 (2)	28 (2)	4109 (2)	2·65 (4)
C(2,3)	4145 (2)	39 (3)	5451 (3)	2·82 (5)
N(2,4)	5000	0	6325 (3)	2·63 (6)
C(2,6)	5000	0	7887 (4)	4·06 (9)
N(3,1)	2238 (2)	1138 (2)	3170 (3)	3·26 (5)
N(3,2)	2247 (3)	2083 (2)	2826 (4)	5·00 (7)
C(3,3)	1591 (4)	2486 (3)	3702 (5)	5·34 (8)
N(3,4)	1136 (2)	1866 (2)	4601 (3)	3·75 (6)
C(3,5)	1566 (3)	1041 (3)	4221 (4)	3·85 (6)
C(3,6)	376 (4)	2069 (4)	5766 (5)	5·97 (11)

Table 3. *Fractional coordinates* ($\times 10^3$) *and isotropic temperature factors* (Å^2) *of the hydrogen atoms*

The numbers in parentheses after the atom symbol are those of the atoms to which the H atoms are attached.

	x	y	z	B_{Iso}
H(1,3)	660 (3)	193 (2)	36 (4)	3·2 (6)
H(1,5)	365 (3)	239 (3)	100 (5)	4·8 (8)
H1(1,6)*	486 (4)	355 (3)	−107 (4)	
H2(1,6)*	491 (4)	387 (3)	38 (5)	7·5 (6)
H3(1,6)*	590 (3)	359 (3)	580 (4)	
H(2,3)	347 (3)	3 (3)	579 (4)	4·3 (6)
H1(2,6)*	526 (6)	61 (3)	810 (5)	
H2(2,6)*	541 (5)	−44 (4)	824 (5)	2·0 (6)
H3(2,6)*	435 (3)	0 (6)	831 (5)	
H(3,3)	152 (3)	308 (3)	385 (5)	5·8 (9)
H(3,5)	150 (3)	51 (2)	475 (5)	4·9 (8)
H1(3,6)*	−31 (3)	185 (4)	539 (4)	
H2(3,6)*	50 (4)	177 (4)	177 (4)	10·3 (9)
H3(3,6)*	26 (3)	265 (3)	265 (3)	

* Refined with constraints.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34706 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
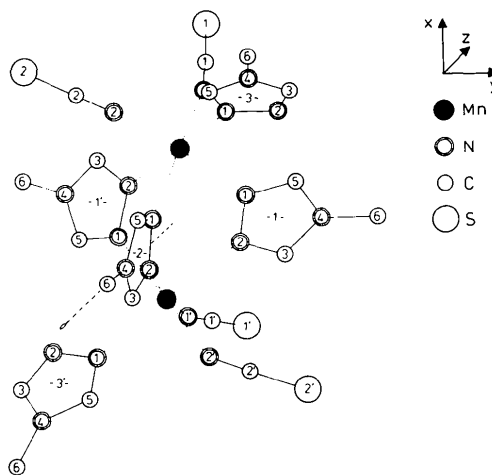
Description of the structure

The structure is built up by dimeric units, wherein two Mn^{II} ions are bridged by three 1,2-coordinating Metrz groups, one of which is positioned on a twofold axis.

Fig. 2. Perspective view of the binuclear unit of Mn$_2$(Metrz)$_5$-(NCS)$_4$. The H atoms have been omitted. The twofold axis running through the unit has been indicated. The atom numbering corresponds to that in Table 2. The Metrz rings have been numbered. Rings 1' and 3' are related to rings 1 and 3 by a rotation about the twofold axis. The same applies to the primed numbers of the atoms of the NCS$^-$ groups. This drawing was produced using the program *FIGATOM* (Langlet, 1972).
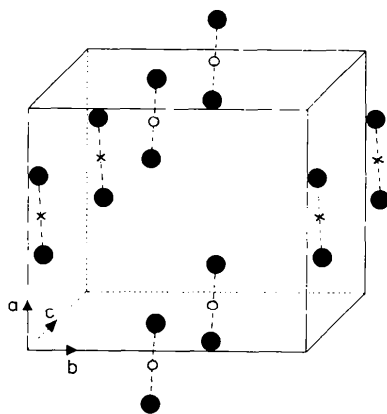
Fig. 3. Positions of the pairs of Mn^{II} ions in the dimeric units in Mn(Metrz)$_5$(NCS)$_4$. The points halfway between the Mn ions have been indicated. Points marked by × are at ($\frac{1}{2}$, 0, 0·21435). The dimeric units as given in Fig. 2 correspond to the pairs marked by ○, which are at (0, $\frac{1}{2}$, −0·21435).

Each Mn is further coordinated to two N-donating NCS$^-$ groups and a non-bridging Metrz, coordinating by only one N atom.

One complete unit is depicted in Fig. 2, which also gives the atom numbering. The positions of the binuclear units in the unit cell are shown in Fig. 3. Relevant distances and angles are given in Tables 4 and 5.

As can be seen from Table 4, the MnN$_6$ octahedra are fairly distorted. The geometries of the Metrz rings 1 and 2 agree within experimental accuracy, except for

the N(4)–C(6) distances. There is reasonable agreement between the geometries of the trz rings in Ni$_3$(trz)$_6$(H$_2$O)$_6$(NO$_3$)$_6$.2H$_2$O and those of Metrz rings 1 and 2. It is not clear why the distances in the trz rings in CuCl$_2$.trz are so different. As can be seen from Table 6, the Metrz rings are quite planar.

Intermolecular distances up to 3·5 Å are given in Table 7. Since all H atoms mentioned in this table are

Table 4. *Intramolecular distances* (Å) *and angles* (°) *in* Mn$_2$(Metrz)$_5$(NCS)$_4$, *except* Metrz *groups*

E.s.d.'s include errors in the cell parameters.

Mn–Mn	4·139 (1)	N(1)–C(1)	1·146 (4)
Mn–N(1)	2·155 (3)	N(2)–C(2)	1·147 (4)
Mn–N(2)	2·206 (3)	C(1)–S(1)	1·626 (3)
Mn–N(1,1)	2·284 (3)	C(2)–S(2)	1·622 (3)
Mn–N(1,2)	2·318 (3)		
Mn–N(2,1)	2·295 (2)		
Mn–N(3,1)	2·242 (3)		

N(1)–Mn–N(2)	95·6 (1)	Mn–N(1)–C(1)	164·7 (3)
–Mn–N(1,1)	92·4 (1)	Mn–N(2)–C(2)	143·5 (3)
–Mn–N(1,2)	85·6 (1)	N(1)–C(1)–S(1)	178·4 (3)
–Mn–N(2,1)	171·4 (1)	N(2)–C(2)–S(2)	178·3 (3)
–Mn–N(3,1)	95·5 (1)		
N(2)–Mn–N(1,1)	172·0 (1)	N(1,2)–N(1,1)–Mn	124·1 (2)
–Mn–N(1,2)	89·0 (1)	C(1,5)–N(1,1)–Mn	128·9 (2)
–Mn–N(2,1)	88·0 (1)	N(1,1)–N(1,2)–Mn	128·0 (2)
–Mn–N(3,1)	87·2 (1)	C(1,3)–N(1,2)–Mn	125·5 (2)
N(1,1)–Mn–N(1,2)	91·4 (1)	N(2,2)–N(2,1)–Mn	126·9 (5)
–Mn–N(2,1)	84·1 (1)	C(2,5)–N(2,1)–Mn	126·6 (2)
–Mn–N(3,1)	92·3 (1)	N(3,2)–N(3,1)–Mn	123·0 (2)
N(1,2)–Mn–N(2,1)	86·7 (1)	C(3,5)–N(3,1)–Mn	130·2 (2)
–Mn–N(3,1)	176·1 (1)		
N(2,1)–Mn–N(3,1)	92·5 (1)		

Table 5. *Bond lengths* (Å) *and angles* (°) *in the* Metrz *rings in* Mn$_2$(Metrz)$_5$(NCS)$_4$ *and in the* trz *rings in two complexes containing* 1,2-*bridging* trz

	Ring 1	Ring 2	Ring 3	Ni$_3$(trz)$_6$(NO$_3$)$_6$(H$_2$O)$_8$*	CuCl$_2$.trz†
N(1)–N(2)	1·382 (3)	1·383 (3)	1·375 (4)	1·379 (5)	1·390
N(2)–C(3)	1·301 (4)	1·306 (3)	1·287 (6)	1·312 (6)	1·293
C(3)–N(4)	1·338 (4)	1·341 (3)	1·339 (5)	1·346 (6)	1·312
N(4)–C(5)	1·334 (4)	1·341 (3)	1·331 (5)	1·351 (6)	1·312
C(5)–N(1)	1·300 (4)	1·306 (3)	1·296 (5)	1·314 (6)	1·293
N(4)–C(6)	1·476 (4)	1·458 (5)	1·469 (6)		
H(3)–C(3)	0·85 (4)	0·90 (4)	0·86 (4)		
H(5)–C(5)	0·90 (4)	0·90 (4)	0·91 (4)		
H1(6)‡–C(6)	0·93 (4)	0·94 (5)	0·95 (5)		
H2(6)‡–C(6)	0·92 (4)	0·88 (6)	0·85 (5)		
H3(6)‡–C(6)	0·87 (4)	0·90 (4)	0·84 (4)		
N(1)–N(2)–C(3)	106·2 (3)	106·5 (2)	105·1 (3)	107·3 (3)	105·6
N(2)–C(3)–N(4)	111·4 (3)	111·0 (2)	112·1 (3)	109·8 (3)	111·7
C(3)–N(4)–C(5)	104·6 (3)	105·0 (3)	103·7 (3)	106·1 (3)	105·3
N(4)–C(5)–N(1)	111·3 (3)	111·0 (2)	111·6 (3)	109·8 (3)	111·7
C(5)–N(1)–N(2)	106·6 (3)	106·5 (2)	106·5 (3)	107·0 (4)	105·6
C(3)–N(4)–C(6)	127·3 (3)	127·5 (2)	127·4 (4)		
C(5)–N(4)–C(6)	128·1 (3)	127·5 (2)	128·8 (4)		

* Reimann & Zocchi (1971).
† Jarvis (1962).
‡ Refined with constraints.

Table 6. *Distances (Å) from the ring atoms and the coordinated metal atoms to the least-squares planes (of non-hydrogen* trz *atoms) of the* Metrz *groups in* $Mn_2(Metrz)_5(NCS)_4$

The equations of the planes in direct space are:

Ring 1: $-0.1782X + 0.3844Y - 0.9058Z + 8.2625 = 0$
Ring 2: $-0.0535X - 0.9986Y \qquad + 14.4558 = 0$
Ring 3: $-0.7462X - 0.1447Y + 0.6498Z + 6.2731 = 0.$

	Ring 1	Ring 2	Ring 3
N(1)	0.001 (1)	0.003 (1)	-0.003 (1)
N(2)	-0.001 (1)	-0.003 (1)	0.004 (2)
C(3)	0.001 (2)	0.002 (2)	-0.004 (2)
N(4)	-0.000 (1)	0.0000 (5)	0.001 (2)
C(5)	-0.000 (2)	-0.002 (2)	0.002 (2)
C(6)	-0.018 (2)	0.0000 (6)	-0.043 (2)
H(3)	-0.00 (2)	0.06 (2)	-0.14 (2)
H(5)	-0.01 (2)	-0.06 (2)	-0.15 (2)
Mn	0.232 (1)	0.000 (1)	-0.183 (1)
Mn'*	0.426 (1)	0.000 (1)	

* Related to the unprimed Mn by a rotation about the twofold axis.

attached to C atoms, it is unlikely that they are involved in hydrogen bonding; therefore intermolecular bonding will probably be of the van der Waals type.

The authors are indebted to Dr N. C. Klijn for preparing the compound.

Table 7. *Intermolecular distances (Å) (≤ 3.5 Å) between neighbouring dimeric units in* $Mn_2(Metrz)_5(NCS)_4$

S(1)—H(2,3)	2.81 (4)	S(2)—H2(2,6)	2.98 (6)
—H(3,5)	2.93 (4)	—H1(1,6)	3.16 (5)
—H1(2,6)	2.95 (5)	—H(2,3)	3.26 (4)
—H(3,3)	3.23 (4)	—H1(2,6)	3.32 (5)
—H(1,5)	3.33 (4)	—H2(3,6)	3.41 (5)
—H2(3,6)	3.47 (5)		

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The Structure of Tetraphenylphosphonium Dioxo[4-(2-pyridylazo)-resorcinolato]vanadate(V), $C_{24}H_{20}P^+.C_{11}H_7N_3O_4V^-$

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Abstract

$[P(C_6H_5)_4][V(C_{11}H_7N_3O_2)O_2]$, $[Ph_4P][VO_2par]$, is monoclinic, space group $P2_1/c$, with $a = 9.264$ (5), $b = 18.28$ (1), $c = 17.50$ (1) Å, $\beta = 95.10$ (3)°; $Z = 4$, $D_m = 1.430$, $D_c = 1.430$ Mg m^{-3}. The structure has been refined to $R = 0.036$ for 4555 counter reflections with $I > 2\sigma(I)$. The V atom has a pentagonal environment of two oxo O atoms, the phenolic O atom, the azo N atom adjacent to the resorcinol ring, and the pyridine N atom. Thus, two five-membered chelate rings are formed with par acting as a terdentate ligand. The VO$_2$