DUBLER, E., HÄNGGI, G. & SCHMALLE, H. (1987). Acta Cryst. C43, 1872–1875.

HÄNGGI, G., SCHMALLE, H. & DUBLER, E. (1988). Inorg. Chem. In the press.

HAWKES, T. R., GEORGE, G. N. & BRAY, R. C. (1984). Biochem. J. 218, 961–968.

HILLE, R. & MASSEY, V. (1985). In Nucleic Acid–Metal Interactions, edited by T. G. SPIRO (Metal Ions in Biology, Vol. 7), p. 443–518. New York: John Wiley.

HODGSON, D. J. (1977). Prog. Inorg. Chem. 23, 211–254.

JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

PRUSINER, P. & SUNDARALINGAM, M. (1972). Acta Cryst. B28, 2148–2152.

SCHOMAKER, V. & MARSH, R. E. (1983). Acta Cryst. A39, 819–820.

SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1985). SHELXS86. In Crystallographic Computing, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.

SHELDRICK, W. S. & BELL, P. (1987a). Z. Naturforsch. Teil B, 42, 195–202.

SHELDRICK, W. S. & BELL, P. (1987b). Inorg. Chim. Acta, 137, 181–188.

STIEFEL, E. J. (1977). Prog. Inorg. Chem. 22, 1–223.

TAYLOR, R. & KENNARD, O. (1982). J. Mol. Struct. 78, 1–28.

trans-Diaquatetrakis(pyrazole)manganese(II) Dinitrate–Pyrazole (1/2)

BY PAAVO LUMME,* EVA LINDELL AND ILPO MUTIKAINEN

Department of Inorganic Chemistry, University of Helsinki, Vuorik. 20, SF-00100 Helsinki, Finland

Abstract. $[Mn(C_3H_4N_2)_4(H_2O)_2](NO_3)_2.2C_3H_4N_2$, $M_r = 623.45$, triclinic, $P\bar{1}$, $a = 9.150$ (2), $b = 9.449$ (4), $c = 9.583$ (4) Å, $\alpha = 79.75$ (4), $\beta = 87.83$ (3), $\gamma = 65.33$ (3)°, $V = 740.2$ (5) Å^3, $Z = 1$, $D_m = 1.40$ (2), $D_x = 1.44$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 5.4$ cm^{-1}, $F(000) = 323$, $T = 296$ (2) K. Final $R = 0.045$ for 2538 observed unique reflections with $I > 3\sigma(I)$. The structure consists of centrosymmetric complex units in which the central Mn^{II} ion is in an octahedral arrangement. Two coordinated pyrazole molecules occupy the equatorial sites at distances of 2.245 (4) and 2.264 (3) Å, respectively, and the apical sites are occupied by coordinated water molecules at distances of 2.148 (3) Å. The asymmetric unit contains a further uncoordinated pyrazole molecule and a nitrate anion. The structure is formed from layers extending along the *ab* plane. The layer is held together primarily through hydrogen bonds involving the uncoordinated pyrazoles and nitrate ions approximately in the [100] and [1$\bar{1}$0] directions. In the **c** direction the layers are held together through weak van der Waals forces and loose stacking of parallel pyrazole rings, especially in the [0$\bar{1}$1] direction.

Introduction. Several manganese(II) complexes of pyrazole and its derivatives are reported to have been prepared and studied by different physical methods (Trofimenko, 1972), but the crystal structures of only three pyrazole complexes have been fully described (Reedijk, Stork-Blaisse & Verschoor, 1971; Gorter, van Ingen Schenau & Verschoor, 1974; Lumme,

Mutikainen & Lindell, 1983). Recently we prepared the crystals of the title compound and its crystal structure is described in this paper. The compound was also studied with respect to IR and reflectance spectra (Lumme, Lindell & Kivimäki, 1988) and thermal behaviour (Lumme, 1985).

Experimental. Colourless prism, approximately 0.20 × 0.35 × 0.63 mm, obtained by recrystallization from a hot aqueous solution was sealed into a capillary tube (Lindemann glass) in its mother liquor for data collection. Weissenberg photographs established the crystal system as triclinic. The space group $P\bar{1}$ was assigned on the basis of the composition and the complete structure analysis. The unit-cell parameters were determined by least-squares treatment of the adjusted angular settings of 21 reflections, $6.67 \leq \theta \leq 23.80°$, measured on a Nicolet P3F diffractometer. The intensity measurements were carried out at room temperature [296 (2) K] with graphite-monochromated Mo $K\alpha$ radiation and the ω–2θ scan technique. The scan rate varied from 1.5 to 29.3° min^{-1}, depending on the number of counts measured in a fast preliminary scan through the peak. A set of 3397 unique reflections was obtained from the 3612 reflections measured up to the maximum value of $2\theta = 55°$, the minimum being 3° (h: 0, 12; k: −13, 13; l: −13, 13). 2538 reflections with $I > 3\sigma(I)$ were considered as observed and used in the refinement which was based on F. Two strong reflections monitored periodically after each group of 48 reflections exhibited no significant variation of intensity. The intensities were corrected for Lorentz and polarization effects and empirically for absorption on

---

* Author to whom all correspondence should be addressed.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent values of the anisotropic temperature factor coefficients* ($\times 10^4$) *of non-*H *atoms with e.s.d.'s in parentheses*

	x	y	z	$U_{eq}*(Å^2)$
Mn	0	0	0	367 (4)
N(1)	1002 (3)	1471 (3)	888 (3)	443 (17)
N(2)	2557 (4)	1037 (4)	1243 (3)	498 (19)
N(3)	−98 (3)	1402 (3)	−2199 (3)	461 (17)
N(4)	796 (4)	2219 (4)	−2612 (3)	481 (18)
N(5)	3517 (4)	−2144 (4)	−3032 (3)	544 (19)
N(6)	4617 (4)	−3579 (4)	−3218 (4)	550 (21)
N(7)	5977 (4)	−3080 (4)	1737 (3)	514 (20)
C(1)	2767 (6)	2145 (6)	1795 (5)	677 (31)
C(2)	1306 (7)	3344 (6)	1830 (5)	751 (33)
C(3)	243 (5)	2889 (5)	1253 (5)	613 (26)
C(4)	509 (5)	2908 (5)	−3990 (4)	583 (24)
C(5)	−628 (5)	2549 (6)	−4509 (4)	678 (27)
C(6)	−967 (5)	1600 (6)	−3360 (4)	633 (27)
C(7)	5381 (5)	−3471 (6)	−4433 (5)	606 (28)
C(8)	4806 (6)	−1934 (5)	−5051 (4)	618 (28)
C(9)	3652 (5)	−1165 (5)	−4147 (4)	597 (26)
O(1)	2412 (3)	−1566 (4)	−396 (3)	619 (18)
O(2)	4881 (4)	−3481 (4)	1509 (3)	779 (21)
O(3)	5740 (4)	−1665 (3)	1422 (3)	662 (19)
O(4)	7255 (3)	−4085 (4)	2312 (4)	788 (21)

* $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ (Hamilton, 1959).

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

(a) Manganese coordination sphere

Mn—N(1)	2·245 (4)	Mn—N(1)—C(3)	129·8 (3)
Mn—N(3)	2·264 (3)	Mn—N(1)—N(2)	126·0 (2)
Mn—O(1)	2·148 (3)	Mn—N(3)—N(4)	125·2 (2)
		Mn—N(3)—C(6)	130·4 (3)
Mn⋯N(2)	3·224 (4)	N(1)—Mn—N(3)	89·7 (1)
Mn⋯N(4)	3·234 (4)	N(1)—Mn—N(3ⁱ)	90·3 (1)
Mn⋯C(3)	3·261 (6)	N(1)—Mn—O(1)	88·8 (1)
Mn⋯C(6)	3·287 (4)	N(1)—Mn—O(1ⁱ)	91·2 (1)
		N(3)—Mn—O(1)	87·6 (1)
		N(3)—Mn—O(1ⁱ)	92·4 (1)

(b) Pyrazole ligands

N(1)—N(2)	1·344 (5)	N(1)—N(2)—C(1)	111·9 (3)
N(2)—C(1)	1·337 (8)	N(2)—C(1)—C(2)	107·4 (5)
C(1)—C(2)	1·348 (6)	C(1)—C(2)—C(3)	105·2 (5)
C(2)—C(3)	1·382 (9)	C(2)—C(3)—N(1)	111·4 (4)
C(3)—N(1)	1·331 (5)	C(3)—N(1)—N(2)	104·2 (4)
N(3)—N(4)	1·347 (5)	N(3)—N(4)—C(4)	112·1 (4)
N(4)—C(4)	1·347 (5)	N(4)—C(4)—C(5)	107·3 (4)
C(4)—C(5)	1·356 (8)	C(4)—C(5)—C(6)	104·9 (4)
C(5)—C(6)	1·402 (7)	C(5)—C(6)—N(3)	111·3 (5)
C(6)—N(3)	1·332 (5)	C(6)—N(3)—N(4)	104·4 (3)
N(5)—N(6)	1·347 (4)	N(5)—N(6)—C(7)	111·0 (3)
N(6)—C(7)	1·346 (6)	N(6)—C(7)—C(8)	108·2 (4)
C(7)—C(8)	1·348 (6)	C(7)—C(8)—C(9)	104·0 (4)
C(8)—C(9)	1·382 (6)	C(8)—C(9)—N(5)	112·6 (4)
C(9)—N(5)	1·321 (6)	C(9)—N(5)—N(6)	104·1 (3)

(c) Nitrate ion

N(7)—O(2)	1·249 (6)	O(2)—N(7)—O(3)	119·6 (3)
N(7)—O(3)	1·243 (5)	O(2)—N(7)—O(4)	119·3 (4)
N(7)—O(4)	1·228 (4)	O(3)—N(7)—O(4)	121·0 (4)

Symmetry code: (i) $-x, -y, -z$.

the basis of φ-scan data with maximum transmission factor = 1·000 and minimum = 0·825, but corrections for extinction were considered unnecessary.

Table 3. *Distances* (Å) *and angles* (°) *in interactions of the type* D—H⋯A

D	H	A	D—H	D⋯A	H⋯A	D—H⋯A
N(2)	H(1)	O(3)	0·82 (4)	2·950 (4)	2·28 (3)	140 (4)
N(2)	H(1)	O(3ⁱⁱ)	0·82 (4)	3·039 (5)	2·79 (4)	100
N(4)	H(5)	O(4ⁱⁱ)	0·83 (4)	3·036 (6)	2·58 (5)	116
N(6)	H(9)	O(2ⁱⁱⁱ)	0·90 (4)	2·826 (5)	1·93 (4)	173 (3)
O(1)	H(13)	O(2)	0·65 (4)	2·726 (4)	2·08 (4)	174 (6)
O(1)	H(14)	N(5)	0·90 (4)	2·746 (4)	1·85 (4)	173 (3)

Symmetry code: (ii) $-x + 1, -y, -z$; (iii) $-x + 1, -y - 1, -z$.

In the space group $P\bar{1}$ with $Z = 1$ the Mn atoms must lie on centres of symmetry. The structure was solved from the heavy-atom positions and developed through successive Fourier syntheses. With anisotropic temperature factors for the non-H atoms, a difference map calculated after full-matrix refinement revealed the positions of all 14 H atoms. Full-matrix least-squares refinement with all non-H atoms as anisotropic and H atoms with fixed isotropic thermal parameters ($U = 0.05$ Å²) led after seven cycles to $R = 0.045$ and $wR = 0.055$, where $w = 1/\sigma(F_o^2)$. After the last cycle $(\Delta/\sigma)_{av}$ was 0·00256 and $(\Delta/\sigma)_{max}$ 0·0327. Maximum and minimum heights in final difference Fourier synthesis were $+0.25$ and -0.25 e Å⁻³, respectively. Scattering factors were from Cromer & Mann (1968) and an anomalous-dispersion correction was applied (*International Tables for X-ray Crystallography*, 1974). All calculations were performed on a UNIVAC 1100/61 E1 computer with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); for planes a program *MPLN* by Truter & Vickery (1973) was used. Densities of the crystals were determined by the flotation method in toluene—CCl_4 mixtures.

Discussion. The fractional atomic coordinates and the equivalent isotropic values of the anisotropic temperature factor coefficients for non-H atoms are listed in Table 1,* the bond lengths and angles in Table 2 and the hydrogen-bond data in Table 3. An *ORTEP* drawing (Johnson, 1965) of the complex showing the molecular geometry and the atomic numbering scheme is presented in Fig. 1 and the molecular packing and hydrogen-bond directions in the unit cell in Fig. 2.

Description of the structure

The coordination sphere of the Mnⁱⁱ ion in the present complex is nearly ideally octahedral following

---

* Lists of calculated fractional coordinates for H atoms, their bonds and angles, anisotropic temperature factors for non-H atoms, least-squares planes of the basal plane, pyrazole rings and nitrate ion and distances of the atoms from the planes, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51051 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

from its situation on the inversion centre (Figs. 1 and 2). In the equatorial plane there are two pairs of *trans*-coordinated pyrazole molecules around the Mn^{II} ion. The N(1) and N(1^i) pyrazole molecules form one coordinated pyrazole pair in the equatorial plane. The angle between the N(1) ring and equatorial planes is 99·1 (1)°. The other pair is formed by the N(3) and N(3^i) rings. The angle between the N(3) ring and the equatorial planes is 157·9 (3)°. The N(1) and N(3) pyrazole planes are tilted towards each other at an angle of 83·2 (2)°. The N(3) and N(3^i) pyrazoles form approximate columns. Between these there exist uncoordinated pyrazole molecules, N(5) and N(5^i) rings, in [110]-directed columns in the structure. The angle between the N(5) ring and the equatorial planes is 67·6 (1)°. The Mn—N(1) and Mn—N(3) bond distances are 2·245 (4) and 2·264 (3) Å, respectively (Table 2). The distance between the Mn and N(5) atoms is 4·786 (4) Å. The planarity of the pyrazole rings seems to be practically perfect (supplementary material) and
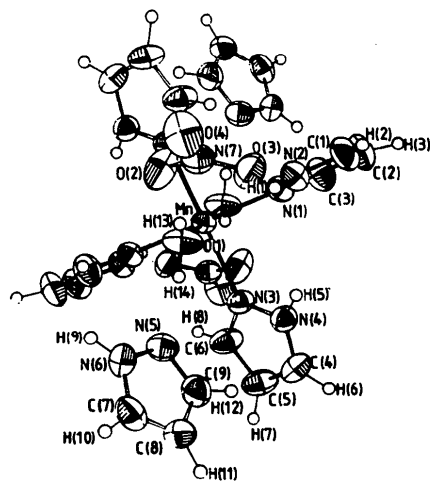

Fig. 1. An *ORTEP* drawing of $[Mn(C_3H_4N_2)_4(H_2O)_2](NO_3)_2.-2C_3H_4N_2$ showing the molecular geometry and atom-numbering scheme. Thermal ellipsoids are drawn at 50% probability level for the non-H atoms.
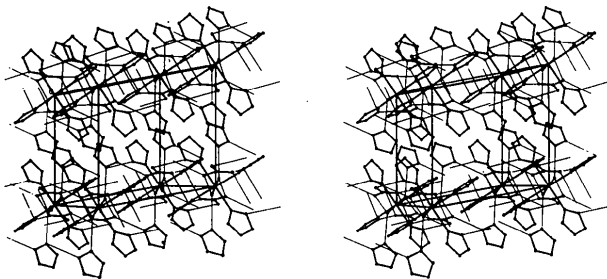

Fig. 2. Stereo arrangement of the molecules in a unit cell viewed down a.

independent of the degree of participation in hydrogen bonding (Fig. 2). The axial sites are occupied by two water molecules coordinated at O(1) and O(1^i), respectively, which complete the octahedral environment of the Mn atom. The Mn—O(1) bond distance is 2·148 (3) Å (Table 2).

Besides the half manganese ion, three pyrazoles and one water molecule the asymmetric unit also contains one nitrate ion. This is not coordinated to the Mn atom, but acts as a mediator in the hydrogen-bond network which leads to the formation of layers in the crystal structure. The nitrate ions are practically planar and the angle between the nitrate and basal planes is 110·9 (1)°.

Molecular arrangement and hydrogen bonds

Generally the chemical units are arranged in layers in the crystal structure along the *ab* plane (Fig. 2), linked *via* a hydrogen-bond network. No hydrogen bonds exist in the *c*-axis direction between the layers which must be held together only by weak van der Waals forces.

Every NO_3 ion participates in five hydrogen bonds. The N(7) nitrate ion is hydrogen bonded through O(4) to N(4^i) of the coordinated pyrazole molecule of the neighbouring unit. O(2) forms one hydrogen bond to O(1) of the water molecule of its own asymmetric unit and another to N(6^{ii}) of the uncoordinated pyrazole molecule of the adjoining unit. The third oxygen atom O(3) is hydrogen bonded to N(2) of the nearest coordinated pyrazole molecule of its asymmetric unit and to N(2^i) of a coordinated pyrazole molecule.

Each uncoordinated pyrazole molecule forms one hydrogen bond with the water molecule of its asymmetric unit [N(5)···H—O(1)] and another with one of the O atoms of the nitrate ion of the diagonally [in (110) plane] situated neighbouring asymmetric unit [N(6)—H···O(2^{ii})] (Table 3).

The hydrogen bonds formed by the uncoordinated pyrazole molecule are strongest and normal (Table 3), whereas two of the hydrogen bonds between the nitrate ion and the coordinated pyrazole molecules are weak and have rather small bond angles of 100 and 116° (Table 3).

The bonding strength of the pyrazole molecules in the structure is, however, naturally more dependent on their coordination. Accordingly the bond-strength order of the pyrazole molecules is: N(1)(two hydrogen bonds) > N(3)(one hydrogen bond) > N(5)(uncoordinated, two hydrogen bonds) (Table 2 and Fig. 2). This is in accordance with the Mn—N distances (Table 2) and the anisotropic thermal parameters or the thermal vibration tendency of the pyrazoles and thermal behaviour of the complex (Lumme *et al.*, 1988).

When the coordination geometries of the solved pyrazole complexes of the manganese(II) ion are compared it is seen that in the present nitrate complex the neutral water molecules occupying the apical sites

are able to penetrate closest to the central metal ion as compared with the negatively charged isothiocyanate (Lumme *et al.*, 1983), chloride (Lumme, Lindell & Kivimäki, 1984) and bromide (Lumme & Lindell, 1985) ions. This penetration tendency does not follow the size order of the ligands and must depend more on their electrical properties.

References

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
GORTER, S., VAN INGEN SCHENAU, A. D. & VERSCHOOR, G. C. (1974). *Acta Cryst.* B30, 1867–1871.
HAMILTON, W. C. (1959). *Acta Cryst.* 12, 609–610.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
LUMME, P. O. (1985). *Thermochim. Acta,* 86, 101–108.
LUMME, P. & LINDELL, E. (1985). Ninth European Crystallographic Meeting, Torino. Abstracts, Vol. I, pp. 201–203.
LUMME, P. O., LINDELL, E. & KIVIMÄKI, P.-R. (1984). XI Nordiske Strukturkjemikermøte, Tromsø. Program og Abstrakter, p. 33.
LUMME, P., LINDELL, E. & KIVIMÄKI, P.-R. (1988). *Thermochim. Acta,* 126, 187–198.
LUMME, P., MUTIKAINEN, I. & LINDELL, E. (1983). *Inorg. Chim. Acta,* 71, 217–226.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
REEDIJK, J., STORK-BLAISSE, B. A. & VERSCHOOR, G. C. (1971). *Inorg. Chem.* 10, 2594–2599.
STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY*76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
TROFIMENKO, S. (1972). *Chem. Rev.* 72, 497–509.
TRUTER, M. R. & VICKERY, B. L. (1973). *J. Appl. Cryst.* 6, 323; program accession No. 124.

Structure of Bis(isothiocyanato)[*N,N,N*-tris(1-pyrazolylmethyl)amine]zinc(II)

BY A. L. SPEK*

Vakgroep Algemene Chemie, afdeling Kristal- en Structuurchemie, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

AND W. L. DRIESSEN* AND W. G. R. WIESMEIJER

Department of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

(*Received* 24 *February* 1988; *accepted* 18 *May* 1988)

Abstract. [Zn($C_{12}H_{15}N_7$)(NCS)$_2$], $M_r = 438.83$, monoclinic, $P2_1/c$, $a = 10.202$ (3), $b = 14.730$ (3), $c = 13.415$ (2) Å, $\beta = 112.11$ (2)°, $V = 1867.7$ (8) Å^3, $Z = 4$, $D_x = 1.561$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 15.8$ cm^{-1}, $F(000) = 896$, $T = 295$ K, $R = 0.061$ for 1845 observed reflections with $I > 2.5\sigma(I)$. Zn is surrounded by two isothiocyanate N atoms at 1.928 (7) and 1.974 (9) Å and two azole N atoms at 2.004 (6) and 2.023 (6) Å in a distorted tetrahedral arrangement. The amine N atom is at 2.599 (7) Å which can be considered as semi-coordinated. This five-coordination is approximately trigonal bipyramidal. The coordination mode of the ligand is unusual in not utilizing one of its pyrazole groups.

Introduction. The tripodal ligand tris(3,5-dimethyl-1-pyrazolylmethyl)amine (amtd) coordinates to divalent transition-metal ions through its three pyrazole N atoms and its amine N atom (van Driel, Driessen & Reedijk, 1985; Kleywegt, Wiesmeijer, van Driel, Driessen, Reedijk & Noordik, 1985). The coordination mode of the ligand tris(1-pyrazolylmethyl)amine (amtp) is different from that of amtd, while amtp is only different from amtd by the lack of ring substituents. In several cases the ligand amtp loses one of its pyrazole groups upon coordination to transition-metal ions (Driessen, de Graaf & Wiesmeijer, 1987; Spek, Duisenberg, Driessen & Wiesmeijer, 1988), a behaviour which has not so far been encountered with amtd. Analytical data and infrared spectra of the Zn(amtp)(NCS)$_2$ compound show that the ligand amtp is intact, but its coordination mode seemed nevertheless different from that of amtd. To elucidate this enigma the crystal structure of this compound was determined and is presented in this paper.

Experimental. Crystals were grown from ethanol at room temperature. Data were collected (de Boer &

* To whom correspondence should be addressed.