Rasmussen, 1990). The calculations were made by the program *CFF* with the energy parameter set *NIKIPAR*6 (Niketić & Rasmussen, 1977) on an AMDAHL *VP*1100 computer. The lowest strain energy is found for the en(*lel*), tn(*p*-chair), tmd(*lel*) conformation. The observed conformation in the crystal is the second lowest on the energy scale with an energy difference of only $2 \cdot 2$ kJ mol^{-1}, which may be compensated by intermolecular interactions. The skew-boat form of the tn chelate ring has a strain energy which is larger than that of the chair form by *ca* 5 kJ mol^{-1}. However, the *lel*$_3$ conformation has the second lowest strain energy because of relatively small non-bonded H$\cdots$H repulsions between the chelate rings.

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Structure of *trans*-Bis[4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole-N^1,N']diaquamanganese(II) Dibromide

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Abstract. [Mn(C$_{12}$H$_{10}$N$_6$)$_2$(H$_2$O)$_2$]Br$_2$, $M_r = 727 \cdot 28$, orthorhombic, *Pbca*, $a = 10 \cdot 734$ (6), $b = 17 \cdot 084$ (0), $c = 15 \cdot 182$ (6) Å, $V = 2784$ Å^3, $Z = 4$, $D_x = 1 \cdot 734$ g cm^{-3}, λ(Mo $K\alpha$) = $0 \cdot 71073$ Å, $\mu = 33 \cdot 23$ cm^{-1}, $F(000) = 1450$, $T = 295$ K, final $R = 0 \cdot 032$ for 1493 reflections [$I > 2\sigma(I)$]. The title compound is the first reported mononuclear compound with the ligand 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole. The manganese ions, situated on an inversion centre, are coordinated by four nitrogen atoms with an N—Mn—N angle of $74 \cdot 1$ (1)° and Mn—N distances of $2 \cdot 188$ (4) and $2 \cdot 266$ (4) Å. Two axial water molecules [Mn—O = $2 \cdot 200$ (4) Å] complete the coordination sphere of the metal, which is pseudo-octahedral. The two bromide ions are not coordinated but are involved in an extended hydrogen-bridging network with the water ligands and the amino group of the triazole.

Introduction. In order to study magnetic exchange between first-row transition metals, the use of ligands derived from 1,2,4-triazole has proved to be of great value. Many studies have already been reported on polynuclear compounds (Engelfriet, Groeneveld & Nap, 1980, and references cited therein; Vos, Haasnoot, Verschoor, Reedijk & Schaminee, 1985, and references cited therein; Haasnoot & Groeneveld, 1979). In this respect, the ligand 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (hereafter abbreviated to abpt) which was first synthesized by Dallacker (1960), has been shown to act as a tetradentate nitrogen-donor ligand. Up to now, only nickel and

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cobalt compounds of abpt have been reported (Keij, de Graaff, Haasnoot & Reedijk, 1984). A closely related ligand such as 3,5-bis(pyridin-2-yl)-1,2,4-triazole, synthesized by Geldard & Lions (1965), has also been reported to yield dinuclear compounds with copper (Prins, Birker, Haasnoot, Verschoor & Reedijk, 1985). However, no further reports of this type of ligand with manganese have appeared. This paper describes the structure of a manganese compound $[Mn(C_{12}H_{10}N_6)_2(H_2O)_2]Br_2$, which is, surprisingly, the first mononuclear coordination compound containing the ligand abpt.

Experimental. The abpt ligand has been prepared by literature methods (Geldard & Lions, 1965). Crystals suitable for X-ray analysis were obtained as follows. 1 mmol of abpt was dissolved in 30 ml of warm methanol, to this solution was added an aqueous solution of 1 mmol of $MnBr_2.4H_2O$, yellow crystals were obtained on slow evaporation at room temperature. Experimental data are shown in Table 1. Enraf–Nonius CAD-4 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell constants were determined from setting angles of 24 reflections (θ between 10 and 12°). The intensities were corrected for Lorentz and polarization effects. Absorption correction was applied by the use of Monte-Carlo methods (de Graaff, 1973). Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Bromide ions were located from a Patterson map. The structure was solved by automatic Fourier techniques, using the computer program *AUTOFOUR* (Kinneging & de Graaff, 1984). Least-squares refinement, based on F, of non-hydrogen-atom positional and anisotropic thermal parameters. Positions of hydrogen atoms were calculated except those on the oxygen and the amino nitrogen. C—H = 1·00 Å for hydrogens belonging to the pyridyl group. Isotropic temperature factors for the hydrogen atoms were 4·0 Å². Leiden University Computer (IBM 3083); programs written or modified by Mrs E. W. Rutten-Keulemans and R. A. G. de Graaff.

Discussion. Positional parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table 2. Bond distances and angles are given in Table 3.* An *ORTEP* drawing (Johnson, 1965), with the atomic labelling used in Tables 2 and 3, is given in Fig. 1. A stereoview of the

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53192 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental data for* $[Mn(C_{12}H_{10}N_6)_2$-$(H_2O)_2]Br_2$

Quadrants	h, k, l
θ range (°)	2–30
Standard reflections (no variation)	$\bar{5}43, \bar{2}45, 642$
No. of reflections measured	4521
No. of independent reflections	4518
Significant reflections $[I > 2\sigma(I)]$	1493
h	0 to 24
k	0 to 15
l	0 to 21
Crystal size (mm)	0·42 × 0·30 × 0·14
Transmission factor range	0·40–0·71
Max. shift/e.s.d. in final cycle	0·10
$\Delta\rho_{max}(e\,Å^{-3})$	0·28
$\Delta\rho_{min}(e\,Å^{-3})$	−0·48
R	0·032
wR	0·038
Weighting scheme	$\sigma^2(F)$(counting stat.) + $0·014F^2$
S	1·043

Table 2. *Fractional atomic coordinates* [$\times 10^5$ *for* $Br(1)$ *and* $\times 10^4$ *for the other atoms*] *and equivalent isotropic thermal parameters* [$\times 10^3$ *for* $Br(1)$ *and* $\times 10^2$ *for the other atoms,* $B_{iso} = \frac{8}{3}\pi^2\,traceU$]

	x	y	z	$B_{iso}(Å^2)$
Mn(1)	5000	0	0	232 (2)
Br(1)	27151 (0)	10024 (6)	25463 (7)	3243 (11)
O(1)	4785 (3)	−343 (2)	−1389 (2)	425 (11)
N(11)	3052 (3)	−263 (2)	305 (2)	227 (9)
N(12)	2453 (3)	−884 (2)	679 (3)	251 (10)
C(13)	1375 (4)	−623 (2)	970 (3)	212 (11)
N(14)	1256 (3)	157 (2)	780 (2)	212 (9)
C(15)	2333 (4)	364 (2)	368 (3)	206 (10)
N(16)	322 (3)	697 (2)	1040 (3)	263 (10)
N(21)	3933 (4)	1123 (2)	−245 (2)	248 (10)
C(22)	4390 (5)	1776 (3)	−606 (3)	332 (14)
C(23)	3695 (5)	2446 (3)	−719 (3)	343 (14)
C(24)	2479 (5)	2452 (3)	−425 (3)	315 (13)
C(25)	1993 (5)	1782 (2)	−45 (3)	284 (12)
C(26)	2736 (4)	1130 (2)	35 (3)	219 (10)
N(31)	−598 (4)	−754 (2)	1685 (3)	295 (11)
C(32)	−1413 (5)	−1194 (3)	2130 (3)	369 (14)
C(33)	−1235 (5)	−1973 (3)	2329 (3)	381 (15)
C(34)	−170 (5)	−2332 (3)	2042 (3)	364 (14)
C(35)	707 (5)	−1893 (3)	1585 (3)	287 (13)
C(36)	462 (4)	−1116 (2)	1426 (3)	245 (12)

unit-cell contents is given in Fig. 2. The structure consists of $[Mn(C_{12}H_{10}N_6)_2(H_2O)_2]^{2+}$ cations and two Br^- anions, held together by various types of hydrogen bridges (Table 3). There is an inversion centre at the metal, which is in a pseudo-octahedral environment. The four equatorial coordinations are realized by two triazole N1 nitrogens and two pyridyl nitrogens. The octahedral coordination is completed by two axial water molecules. In contrast to the $[Ni_2(abpt)_2]^{4+}$ cation (Keij *et al.*, 1984) in which the ligand was nearly planar, we observe here a deviation in the planarity of the abpt ligand, especially beween the triazole ring and the coordinat-

ing pyridyl group: the dihedral angle between these rings is 8·6 (2)°. Between the triazole and the non-coordinating pyridyl ring, however, the dihedral angle is only 2·6 (2)°.

Bond distances and in-plane angles of the triazole and the coordinating pyridyl group are similar to those observed for the dinuclear nickel compound. Some differences are observed in the values of the angles around the exocyclic C—C bonds, which on one side connect the triazole ring to the non-coordinating pyridyl group and on the other side to the coordinating group whilst the angles at the triazole ring are similar [N(11)—C(15)—C(26) = 121·6 (4) and N(12)—C(13)—C(36) = 123·5 (4)°], the angle C(15)—C(26)—N(21) [112·4 (4)°] is much

smaller than the analogous C(13)—C(36)—C(35) [120·6 (4)°]. This difference is ascribed to the presence of the five-membered chelate ring formed by the ligand and the manganese atom. Moreover the effect is increased by the presence of nitrogen N(16) from the amino group which is hydrogen bonded to the non-coordinating pyridyl nitrogen N(31), pulling the non-coordinating pyridyl ring into a six-membered

Table 3. *Bond lengths* (Å) *and angles* (°) *within the* $[Mn(C_{12}H_{10}N_6)_2(H_2O)_2]^{2+}$ *ion* (*e.s.d.'s include allowance for cell-parameter e.s.d.'s*) *and interatomic distances* (Å) *and angles* (°) *for the hydrogen bridges* (*with e.s.d.'s in parentheses*)

Mn(1)—O(1)	2·200 (4)	C(33)—C(34)	1·367 (7)
Mn(1)—N(11)	2·188 (4)	C(34)—C(35)	1·388 (7)
Mn(1)—N(21)	2·266 (4)	C(35)—C(36)	1·374 (6)
N(11)—N(21)	2·684 (5)	C(15)—C(26)	1·468 (6)
N(12)—C(35)	2·894 (6)	C(26)—N(21)	1·353 (6)
N(11)—N(12)	1·364 (5)	N(21)—C(22)	1·336 (6)
N(12)—C(13)	1·317 (5)	C(22)—C(23)	1·377 (7)
C(13)—N(14)	1·369 (6)	C(23)—C(24)	1·379 (7)
N(14)—C(15)	1·361 (5)	C(24)—C(25)	1·384 (7)
C(15)—N(11)	1·324 (6)	C(25)—C(26)	1·376 (6)
N(14)—N(16)	1·420 (5)	O(1)—H(11)	0·83 (5)
C(13)—C(36)	1·467 (6)	O(1)—H(12)	0·75 (5)
C(36)—N(31)	1·353 (6)	N(16)—H(161)	0·99 (6)
N(31)—C(32)	1·336 (6)	N(16)—H(162)	1·00 (7)
C(32)—C(33)	1·378 (8)		

N(11)—Mn(1)—N(21)	74·1 (1)	C(24)—C(25)—C(26)	119·2 (5)
O(1)—Mn(1)—N(11)	92·7 (1)	C(25)—C(26)—N(21)	121·9 (4)
O(1)—Mn(1)—N(21)	90·8 (2)	N(12)—C(13)—C(36)	123·5 (4)
N(11)—N(12)—C(13)	106·9 (4)	N(14)—C(13)—C(36)	126·6 (4)
N(12)—C(13)—N(14)	109·9 (4)	C(13)—C(36)—N(31)	115·9 (4)
C13)—N(14)—C(15)	105·7 (4)	C(13)—C(36)—C(35)	120·6 (4)
N(14)—C(15)—N(11)	108·6 (4)	N(31)—C(32)—C(33)	124·2 (5)
C(15)—N(11)—N(12)	108·9 (4)	C(32)—C(33)—C(34)	118·6 (5)
C(13)—N(14)—N(16)	129·8 (4)	C(33)—C(34)—C(35)	119·0 (5)
C(15)—N(14)—N(16)	124·0 (4)	C(34)—C(35)—C(36)	118·6 (5)
N(11)—C(15)—C(26)	121·6 (4)	C(35)—C(36)—N(31)	123·5 (4)
N(14)—C(15)—C(26)	129·8 (4)	N(14)—N(16)—H(161)	106 (3)
C(15)—C(26)—N(21)	112·4 (4)	N(14)—N(16)—H(162)	107 (4)
C(15)—C(26)—C(25)	125·5 (4)	H(161)—N(16)—H(162)	108 (5)
N(21)—C(22)—C(23)	123·1 (5)	Mn(1)—O(1)—H(11)	119 (4)
C(22)—C(23)—C(24)	118·5 (5)	Mn(1)—O(1)—H(12)	129 (5)
		H(11)—O(1)—H(12)	109 (6)

Br(1)···O(1')	3·401 (4)	Br(1)···H(11')—O(1')	175 (6)
Br(1)···O(1")	3·330 (4)	Br(1)···H(12")—O(1")	177 (7)
Br(1)···N(16)	3·479 (5)	Br(1)···H(161)—N(16)	139 (4)
N(31)···N(16)	2·843 (6)	N(31)···H(162)—N(16)	134 (6)

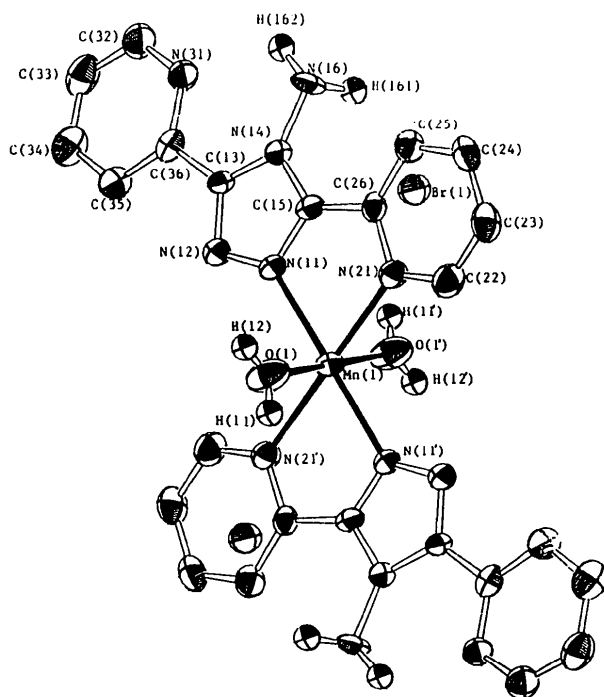Symmetry code: (i) $1 - x, -y, -z$; (ii) $\frac{1}{2} - x, -y, \frac{1}{2} + z$.

Fig. 1. Projection of $[Mn(C_{12}H_{10}N_6)_2(H_2O)_2]Br_2$ with the atomic labelling system. Hydrogen atoms that are bonded to carbon atoms are omitted for clarity. Primed atoms are generated by $1 - x, -y, -z$.
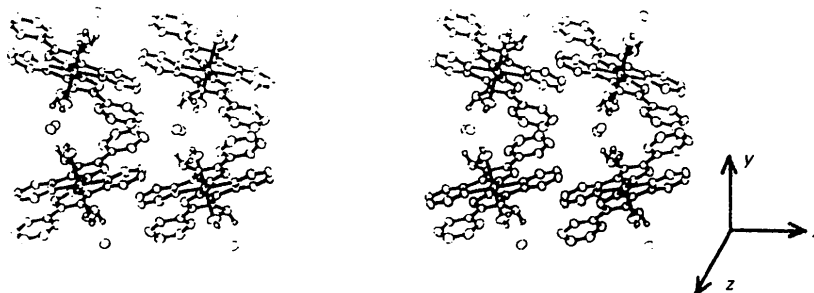

Fig. 2. Stereoview of the packing of $[Mn(C_{12}H_{10}N_6)_2(H_2O)_2]Br_2$.

chelate around one of the amino hydrogens (Table 3). Therefore a significant difference ($\sim 10°$) between the angles C(15)—C(26)—C(25) [125·5 (4)°] and C(13)—C(36)—N(31) [115·9 (4)°] is also observed.

Two other kinds of hydrogen bonds (Table 3) exist in the cell packing, firstly between the bromide ion and the amino nitrogen N(16), and secondly between the bromide ion and the oxygen of a water molecule. These different hydrogen bridges may be classified as intra- and intermolecular, respectively.

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Structure of a Copper(II) Complex of the Deprotonated Anion of 3,3,6,6,9,9-Hexamethyl-4,8-diazaundecane-2,10-dione Dioxime

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Abstract. Aqua(3,3,6,6,9,9-hexamethyl-4,8-diaza-undecane-2,10-dione dioximato)copper(II) perchlorate, [Cu(C$_{15}$H$_{31}$N$_4$O$_2$)(H$_2$O)](ClO$_4$), $M_r = 480·44$, monoclinic, $P2_1/c$, $a = 7·918$ (1), $b = 20·265$ (2), $c = 13·707$ (4) Å, $\beta = 104·34$ (2)°, $U = 2130·7$ (2) Å^3, $Z = 4$, $D_x = 1·498$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1·19$ mm^{-1}, $F(000) = 1011·79$, room temperature, final $R = 0·035$, $wR = 0·030$ for 2924 observed reflections. The coordination about Cu^{II} is distorted square pyramidal with the deprotonated diaza-dioxime equatorial and the O atom of the aqua group axial. The Cu atom is significantly (0·202 Å) out of the plane of the four nitrogens and towards the O atom of the aqua group. This O atom forms hydrogen bonds with the neighbouring oxime and perchlorate O atoms. The C-methyl groups in this complex impose significant constraint resulting in an increase of the N(amine)—M—N(amine) angle, decrease of the N(amine)—M—N(oxime) angles and elongation of the O···O distance. The important bond distances are Cu—O = 2·321 (3), average Cu—N(oxime) = 1·953 (3), average Cu—N(amine) = 1·993 (3) and O···O = 2·509 (5) Å for the intra-molecular hydrogen bond.

Introduction. The deprotonated diazadioxime metal complexes allow a comprehensive structural study of the variation in intramolecular hydrogen bonding with O···O distance for short hydrogen bonds (Gavel & Schlemper, 1979). Previously, structural studies have indicated that the O···O distance varies as a function of: (1) the size of the metal ion, (2) the constraint imposed by the methylene carbons bridging the amine N atoms, and (3) changing from an sp^3 amine nitrogen to an sp^2 imine nitrogen (Liss & Schlemper, 1975; Pal, Murmann, Schlemper, Fair & Hussain, 1986). The present study was undertaken to examine the steric effect of the copper(II) complex of deprotonated diazadioxime.

Experimental. The ligand, 3,3,6,6,9,9-hexamethyl-4,8-diazaundecane-2,10-dione dioxime (6,6-Me$_2$-PnAO), was prepared as described by Murmann (1957, 1958) and Vassian & Murmann (1967). Prepa-