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Structure of [2,2′-(Ethylene)dibiguanide]manganese(III) Nitrate Monohydrate

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Abstract. $[Mn(C_6H_{16}N_{10})](NO_3)_3.H_2O$, $M_r = 487{\cdot}23$, triclinic, $P\bar{1}$, $a = 9{\cdot}412\,(2)$, $b = 11{\cdot}452\,(3)$, $c = 8{\cdot}635\,(1)$ Å, $\alpha = 101{\cdot}10\,(2)$, $\beta = 102{\cdot}45\,(2)$, $\gamma = 102{\cdot}13\,(2)°$, $V = 860{\cdot}5\,(3)$ Å^3, $Z = 2$, $D_m = 1{\cdot}875$, $D_x = 1{\cdot}880$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}82$ mm^{-1}, $T = 298$ K, $F(000) = 500$, $R = 0{\cdot}024$ for 3369 observed reflections. The coordination around Mn^{III} is slightly distorted square pyramidal. Ethylenedibiguanide acts as a tetradentate ligand to one manganese(III) ion in a nearly square plane. An axial position is occupied by a water molecule.

Introduction. Biguanides and their substituted derivatives possess remarkable capacity for coordination with transitional metals giving rise to highly coloured chelate compounds of inner metallic type. Among the various substituted biguanides, ethylenedibiguanide coordinates very strongly and is one of the most interesting ligands. The silver ethylenedibiguanide serves as a unique instance of a cationic complex of the metal in the tripositive state (Ray & Ghosh, 1943). Tripositive manganese mostly forms complexes of the ionic type with ligands of high electronegativity containing oxygen as the donor atom. The cationic complexes of tripositive manganese are relatively scarce and hence the coordination of manganese with N atoms of the ligand molecules is a particularly interesting feature. The manganese(III) complex of the ethylendibiguanide was prepared by the method of Ray & Ray (1958) and was formulated with octahedral geometry (d^2sp^3 hybridization). The present crystallographic investigation was undertaken to confirm this proposal and provide knowledge of structures of Mn^{III} complexes containing nitrogen ligands which is still quite limited.

Experimental. Crystallized from 1 *M* nitric acid, dark chocolate-coloured needle-shaped crystals, density by flotation, space group $P\bar{1}$, crystal size 0·37 × 0·25 × 0·25 mm. Data collected on an AFC-4 Rigaku four-circle automatic diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) with 2θ–ω scanning mode. Three standard reflections measured every 100 reflections did not show appreciable variation in intensity. Unit-cell parameters determined by least-squares refinement from setting angles of 25 reflections with $22 < 2\theta < 33°$. 3839 unique reflections collected ($h = 0$ to 13, $k = -17$ to 17, $l = -12$ to 12; $0 \leq 2\theta \leq 55°$), data corrected for Lorentz and polarization effects, no absorption correction, 3369 observed reflections with $I > 3\sigma(I)$. Structure solved by the heavy-atom method, Mn position located from Patterson synthesis, location of other non-H atoms from Mn-phased Fourier synthesis. Full-matrix least-squares anisotropic refinement using *SHELX76* (Sheldrick, 1976) based on F with H's (located from ΔF synthesis) isotropic gave $R = 0{\cdot}024$, $wR = 0{\cdot}024$, $S = 1{\cdot}43$ with $w = 1/\sigma^2(|F_o|)$. In the final cycle shift/$\sigma < 0{\cdot}05$, final difference map had no peaks > 0·15 e Å^{-3}. Atomic scattering factors are those in *SHELX76*. The geometrical parameters of the molecule were computed with the program *PARST* (Nardelli, 1983).

Discussion. The molecular structure and atomic nomenclature are shown in Fig. 1. The final atomic positional parameters for non-H atoms are listed in

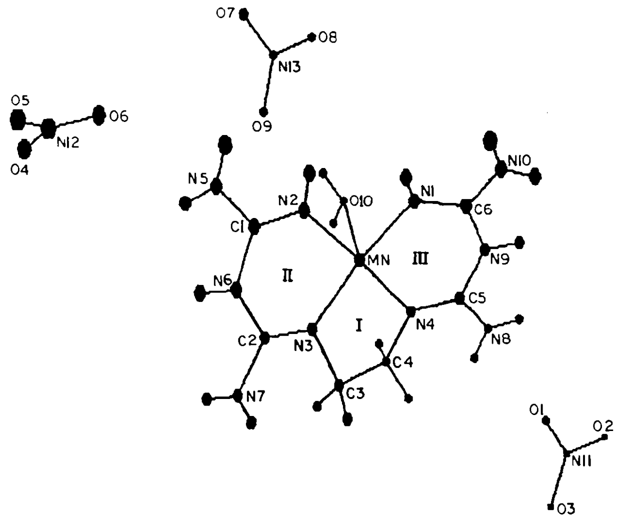

Fig. 1. Perspective view of the molecule (down **c**) showing the manganese coordination, ligand conformation and mode of ligand—Mn^{III} binding.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors for non-*H *atoms with e.s.d.'s in parentheses*

$$B_{\mathrm{eq}} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Mn	0·16821 (3)	0·25325 (2)	0·32617 (3)	1·69 (1)
N(1)	0·0876 (2)	0·1752 (1)	0·4782 (2)	1·89 (4)
N(2)	0·3757 (2)	0·2774 (1)	0·4457 (2)	2·02 (4)
N(3)	0·2350 (1)	0·3609 (1)	0·1903 (2)	1·69 (3)
N(4)	−0·0342 (1)	0·2409 (1)	0·1993 (2)	1·77 (3)
N(5)	0·6359 (2)	0·3346 (2)	0·4984 (2)	2·43 (4)
N(6)	0·4959 (2)	0·4134 (1)	0·3144 (2)	2·00 (4)
N(7)	0·4029 (2)	0·5168 (2)	0·1320 (2)	2·41 (4)
N(8)	−0·2943 (2)	0·1565 (2)	0·1075 (2)	2·77 (5)
N(9)	−0·1695 (2)	0·1385 (1)	0·3543 (2)	2·02 (4)
N(10)	−0·0923 (2)	0·1087 (2)	0·6092 (2)	2·35 (6)
N(11)	−0·6914 (2)	0·2039 (2)	−0·1197 (2)	2·42 (4)
N(12)	1·1296 (2)	0·4568 (1)	0·6610 (2)	2·20 (4)
N(13)	0·4765 (2)	−0·0641 (1)	0·3079 (2)	2·01 (4)
O(1)	−0·5770 (2)	0·2048 (2)	−0·0190 (2)	4·05 (5)
O(2)	−0·8137 (2)	0·1234 (1)	−0·1427 (2)	3·16 (4)
O(3)	−0·6901 (2)	0·2835 (1)	−0·2014 (2)	3·26 (4)
O(4)	1·1608 (2)	0·4466 (1)	0·5244 (2)	3·33 (4)
O(5)	1·2284 (2)	0·5281 (1)	0·7845 (2)	3·13 (4)
O(6)	1·0091 (2)	0·3989 (1)	0·6731 (2)	3·48 (4)
O(7)	0·5990 (1)	−0·0650 (1)	0·3971 (2)	2·71 (4)
O(8)	0·3627 (1)	−0·1529 (1)	0·2768 (2)	3·02 (4)
O(9)	0·4676 (2)	0·0262 (1)	0·2485 (2)	3·14 (4)
O(10)	0·1756 (2)	0·0739 (1)	0·1591 (2)	2·58 (4)
C(1)	0·4987 (2)	0·3384 (1)	0·4207 (2)	1·74 (4)
C(2)	0·3712 (2)	0·4280 (1)	0·2095 (2)	1·70 (4)
C(3)	0·1070 (2)	0·3896 (2)	0·0847 (2)	2·19 (5)
C(4)	−0·0334 (2)	0·2856 (2)	0·0501 (2)	2·15 (5)
C(5)	−0·1622 (2)	0·1808 (1)	0·2166 (2)	1·78 (4)
C(6)	−0·0525 (2)	0·1430 (1)	0·4825 (2)	1·68 (4)

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

Mn—N(1)	1·921 (2)	N(7)—C(2)	1·338 (3)
Mn—N(2)	1·936 (2)	N(8)—C(5)	1·326 (2)
Mn—N(3)	1·960 (2)	N(9)—C(5)	1·377 (2)
Mn—N(4)	1·943 (1)	N(9)—C(6)	1·367 (2)
Mn—O(10)	2·295 (1)	N(10)—C(6)	1·331 (3)
N(1)—C(6)	1·303 (3)	N(11)—O(1)	1·226 (2)
N(2)—C(1)	1·304 (2)	N(11)—O(2)	1·265 (2)
N(3)—C(2)	1·306 (2)	N(11)—O(3)	1·255 (3)
N(3)—C(3)	1·483 (2)	N(12)—O(4)	1·266 (3)
N(4)—C(4)	1·476 (3)	N(12)—O(5)	1·260 (2)
N(4)—C(5)	1·310 (2)	N(12)—O(6)	1·224 (2)
N(5)—C(1)	1·334 (3)	N(13)—O(7)	1·244 (2)
N(6)—C(1)	1·372 (2)	N(13)—O(8)	1·252 (2)
N(6)—C(2)	1·381 (2)	N(13)—O(9)	1·250 (2)
C(3)—C(4)	1·512 (3)		
N(1)—Mn—N(2)	93·7 (1)	O(3)—N(11)—O(1)	120·7 (2)
N(1)—Mn—N(3)	168·2 (1)	O(4)—N(12)—O(5)	117·2 (2)
N(1)—Mn—N(4)	90·6 (1)	O(5)—N(12)—O(6)	121·3 (2)
N(2)—Mn—N(3)	90·2 (1)	O(6)—N(12)—O(4)	121·5 (2)
N(2)—Mn—N(4)	175·2 (1)	O(7)—N(13)—O(8)	120·6 (2)
N(3)—Mn—N(4)	85·2 (1)	O(8)—N(13)—O(9)	119·9 (2)
N(1)—Mn—O(10)	95·4 (1)	O(9)—N(13)—O(7)	119·5 (2)
N(2)—Mn—O(10)	90·1 (1)	N(2)—C(1)—N(5)	122·7 (2)
N(3)—Mn—O(10)	95·7 (1)	N(2)—C(1)—N(6)	122·0 (2)
N(4)—Mn—O(10)	91·7 (1)	N(5)—C(1)—N(6)	115·2 (2)
Mn—N(1)—C(6)	128·3 (1)	N(6)—C(2)—N(3)	122·2 (1)
Mn—N(2)—C(1)	128·8 (1)	N(3)—C(2)—N(7)	123·8 (2)
Mn—N(3)—C(2)	127·6 (1)	N(6)—C(2)—N(7)	114·1 (1)
Mn—N(3)—C(3)	112·2 (1)	N(3)—C(3)—C(4)	109·1 (2)
C(2)—N(3)—C(3)	118·3 (1)	N(4)—C(4)—C(3)	108·9 (1)
Mn—N(4)—C(4)	112·0 (1)	N(4)—C(5)—N(9)	121·5 (2)
Mn—N(4)—C(5)	127·6 (1)	N(4)—C(5)—N(8)	124·2 (2)
C(4)—N(4)—C(5)	119·2 (1)	N(8)—C(5)—N(9)	114·2 (2)
C(1)—N(6)—C(2)	127·7 (2)	N(9)—C(6)—N(10)	115·2 (2)
C(5) N(9)—C(6)	127·8 (2)	N(9)—C(6)—N(1)	122·1 (2)
O(1)—N(11)—O(2)	120·8 (2)	N(1)—C(6)—N(10)	122·7 (2)
O(2)—N(11)—O(3)	118·5 (2)		

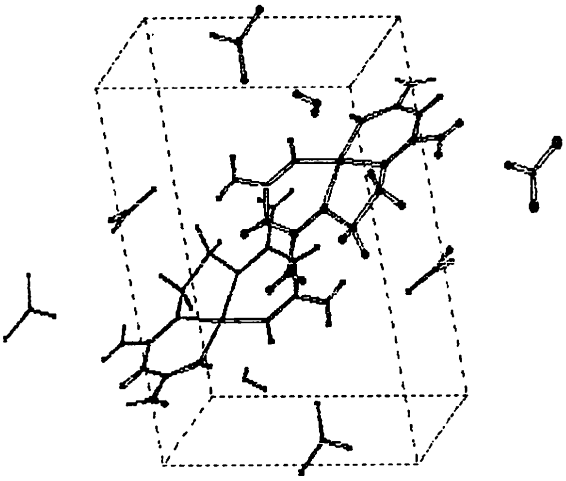

Fig. 2. Packing of the crystal structure of the complex as seen along [001].

Table 1.* The intramolecular bond lengths and angles are shown in Table 2.

The coordination geometry around the central $\mathrm{Mn^{III}}$ atom is slightly distorted square pyramidal (4 + 1), not as expected from the previous chemical work. A molecule of ethylenedibiguanide acts as a tetradenate ligand through its four N atoms with one manganese(III) ion in a square-planar configuration which results in the formation of one five-membered and two six-membered rings in the chelate compound. The atoms forming the basal plane are not strictly coplanar as they show the following deviations from the mean plane through them: N(1) − 0·149 (2), N(2) + 0·015 (2), N(3) − 0·130 (1), N(4) + 0·022 (1) Å; Mn is displaced from this plane by 0·047 (1) Å. The fifth coordinated atom, an O atom of the water molecule, at a distance of 2·295 (1) Å, lies at the apex of the pyramid. The coordination distances and angles around the $\mathrm{Mn^{III}}$ atom are given in Table 2.

The five-membered and the two six-membered rings are nearly planar. The dihedral angles between planes I and II is 2·76 (4)°, between I and III is 13·35 (4)° and between II and III is 14·30 (4)°. The non-planarity of the two biguanide residues can be explained as resulting from the strain in the five-membered ring containing the two methylene groups. None of these rings is planar in the Ag complex (Kunchur, 1968; Simms, Atwood & Zatko, 1973; Coghi & Pelizzi, 1975) while all three rings are planar

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, hydrogen-bond distances and angles and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52574 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in the Ni (Holian & Marsh, 1970; Coghi, Mangia, Nardelli & Pelizzi, 1969; Ward, Caughlan & Smith, 1971) and Cu (Mathew & Kunchur, 1970) complexes.

The bond distances N(sp^2)—C(sp^2) of the ligand molecule are not all equal; the larger ones [1·367 (2)–1·381 (2) Å] involve the N atoms of the NH groups, the medium ones [1·326 (2)–1·338 (3) Å] involve the N atoms of the NH_2 groups and the shorter ones [1·303 (3)–1·310 (2) Å] include the N atoms coordinating with Mn. All these values indicate that the π-electron cloud is delocalized and spread over the six-membered rings which are stabilized by resonance. All the independent nitrate ions are planar and have normal N—O distances ranging from 1·224 (2) to 1·266 (3) Å.

The packing of the molecule viewed down the *c* axis is shown in Fig. 2. The molecules are held together by normal van der Waals contacts and by a network of hydrogen bonds. The axial water molecules of the square pyramid are engaged in hydrogen bonding with the nitrate ions and all three nitrate ions are hydrogen bonded to the complex ion.

References

Coghi, L., Mangia, A., Nardelli, M. & Pellizzi, G. (1969). *Ric. Sci.* **39**, 438–441.

Coghi, L. & Pelizzi, G. (1975). *Acta Cryst.* **B31**, 131–134.

Holian, B. L. & Marsh, R. E. (1970). *Acta Cryst.* **B26**, 1049–1058.

Kunchur, N. R. (1968). *Nature (London)*, **217**, 539–541.

Mathew, M. & Kunchur, N. R. (1970). *Acta Cryst.* **B26**, 2054–2062.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Ray, M. M. & Ray, P. (1958). *J. Indian Chem. Soc.* **35**, 595–600.

Ray, P. & Ghosh, S. P. (1943). *J. Indian Chem. Soc.* **20**, 291–297.

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

Simms, M. L., Atwood, J. L. & Zatko, D. A. (1973). *J. Chem. Soc. Chem. Commun.* pp. 46–47.

Ward, D. L., Caughlan, C. N. & Smith, G. D. (1971). *Acta Cryst.* **B27**, 1541–1549.

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Structure of Two Polymorphic Forms of Phenothiazine Tetrachloroantimonate

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Abstract. The crystal structures of two polymorphic forms of phenothiazine tetrachloroantimonate, triclinic (I) and monoclinic (II), were determined. $C_{12}H_9NS.SbCl_4$, $M_r = 462{\cdot}8$. (I) Triclinic, $P\bar{1}$, $a = 12{\cdot}149$ (10), $b = 13{\cdot}023$ (9), $c = 11{\cdot}750$ (8) Å, $\alpha = 108{\cdot}57$ (5), $\beta = 107{\cdot}78$ (6), $\gamma = 104{\cdot}65$ (6)°, $V = 1547$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}99$, $D_m = 1{\cdot}99$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2{\cdot}61$ mm^{-1}, $F(000) = 892$, $T = 293$ K, $R = 0{\cdot}062$ for 4184 observed reflections. (II) Monoclinic, $P2_1/c$, $a = 12{\cdot}154$ (6), $b = 18{\cdot}116$ (3), $c = 7{\cdot}517$ (2) Å, $\beta = 108{\cdot}29$ (2)°, $V = 1571{\cdot}4$ (8) Å^3, $Z = 4$, $D_x = 1{\cdot}96$, $D_m = 2{\cdot}00$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2{\cdot}62$ mm^{-1}, $F(000) = 892$, $T = 293$ K, $R = 0{\cdot}061$ for 1502 observed reflections. All the phenothiazine (PT) molecules exist as cation radicals and are nearly planar. Each Sb atom is coordinated by six Cl atoms to form a distorted octahedral configuration. In form (I), both cation radicals and anions form separate tetramers, while in form (II) they each make up one-dimensional infinite columns.

Introduction. Phenothiazine (PT) is known to have multiple oxidation states : cation radical, cation, and dication (Billon, 1962; Shine & Mach, 1965; Iida, 1971). The neutral PT molecule is known to be folded along the S···N axis with a dihedral angle of 153·3 (monoclinic; Bell, Blount, Briscoe & Freeman, 1968) and 158·5° (orthorhombic; McDowell, 1976). In several structural works on the 'weak' charge-transfer complexes, the PT molecule has been found to have a similar structure to that of the neutral species except for the dihedral angles cited above. Crystals of several kinds of PT complexes were obtained from PT and the strong Lewis acids $SbCl_3$ or $SbCl_5$. In the PT–$SbCl_6$ crystals, PT was found to exist as a cation radical, and to be almost planar with a dihedral angle of 175·8° (Uchida, Ito & Kozawa, 1983). It was concluded that PT is easily changed to a relatively stable cation radical in the complex with strong electron acceptors, and that it adopts a conjugated planar system including the central thiazine ring. This paper concerns the refined

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