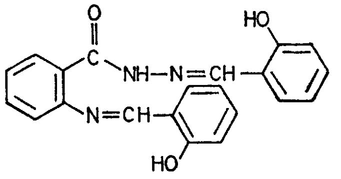
Spectroscopic and Magnetic Properties and Crystal Structure of Di-μ-methoxo-bis[salicylaldehyde anthraniloylhydrazonato(2−)]dimanganese-(III)–Bismethanol

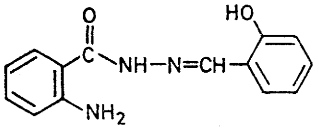
By **Alessandro Mangia, Mario Nardelli,* Corrado Pelizzi,** and **Giancarlo Pelizzi,** Istituto di Chimica Generale ed Inorganica, University of Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma, Italy

The title compound has been prepared and its spectroscopic and magnetic properties and *X*-ray structure have been studied. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by least-squares techniques to *R* 4·1% for 914 independent reflections. Crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions: $a = 12{\cdot}096(6)$, $b = 9{\cdot}084(5)$, $c = 15{\cdot}447(7)$ Å, $\beta = 106{\cdot}8(1)°$, $Z = 4$. The structure consists of dimers in which two atoms of manganese(III) are joined by two methoxo-groups (Mn–O 1·901, 2·227 Å). The co-ordination is tetragonally elongated (distorted) octahedral. The ligand salicylaldehyde anthraniloylhydrazone acts as a bridge between adjacent dimers and co-ordinates to one Mn through three atoms (Mn–O 1·895 and 1·912, Mn–N 1·967 Å) and to another through one atom (Mn–N 2·534 Å), so the whole structure is polymeric.

FROM the reaction of salicylaldehyde *N*-(salicylidene)-anthraniloylhydrazone (I) with alkaline methanolic manganese(II) chloride tetrahydrate in air, a dark brown crystalline product was isolated corresponding to the formula $[\mathrm{Mn(OMe)(C_{14}H_{11}N_3O_2)]MeOH}$, in which manganese exhibits the oxidation state (III) as indicated by its colour, electronic spectrum, magnetic properties, and crystal structure. The *X*-ray crystal analysis was carried out in order to determine the correct formulation of the complex, and showed the organic ligand to be present as salicylaldehyde anthraniloylhydrazone (II). From these data it must be inferred that oxidation of the metal and hydrolysis of the ligand have occurred during the formation of the complex.



(I)



(II)

We now report the synthesis, spectroscopic and magnetic properties, and the *X*-ray structural analysis of this $\mathrm{Mn^{III}}$ complex.

EXPERIMENTAL

Preparation.—Equimolar amounts of manganese(II) chloride tetrahydrate and (I) were mixed in methanol; after dropwise addition of concentrated ammonia, the resulting brown solution was heated under reflux (2 h) and then set aside for some days at room temperature. In this way small dark brown prismatic crystals were obtained (Found: C, 51·4; H, 4·6; Mn, 14·5; N, 11·5. $\mathrm{C_{16}H_{18}MnN_3O_4}$ requires C, 51·8; H, 4·9; Mn, 14·8; N, 11·3%).

Physical Measurements.—The i.r. spectrum was recorded (4000—250 $\mathrm{cm^{-1}}$) on a Perkin-Elmer 457 double-beam spectrophotometer by use of KBr discs. The electronic spectrum for methanol solution was measured on a Perkin-Elmer 402. Room-temperature magnetic susceptibility data were obtained, with a Gouy magnetic balance (Newport Instruments) for powdered samples; the effective magnetic moment for the metal was calculated from the formula $\mu_{\mathrm{eff}} = 2{\cdot}83\sqrt{\chi'_M T}$, where χ'_M is the molar susceptibility corrected for diamagnetic contributions calculated by use of Pascal's constants.[1]

X-Ray intensity data were collected on a Siemens single-crystal computer-controlled diffractometer.

Crystal Data.—$\mathrm{C_{16}H_{18}MnN_3O_4}$, $M = 371{\cdot}3$, Monoclinic, $a = 12{\cdot}096(6)$, $b = 9{\cdot}084(5)$, $c = 15{\cdot}447(7)$ Å, $\beta = 106{\cdot}8(1)°$, $U = 1625$ Å^3, $D_m = 1{\cdot}50$, $Z = 4$, $D_c = 1{\cdot}52$, $F(000) = 768$. Mo-K_α radiation, $\lambda = 0{\cdot}71068$ Å; μ(Mo-K_α) = 8·8 $\mathrm{cm^{-1}}$. Space group $P2_1/c$, from systematic absences.

Cell dimensions were determined from rotation and Weissenberg photographs (Co-K_α radiation, $\lambda = 1{\cdot}7902$ Å) and refined from diffractometer measurements (Mo-K_α radiation).

Data Collection.—A thin prismatic crystal with a mean cross-section radius of 0·03 mm was aligned with its [010] axis along the ϕ axis of the diffractometer, and all the reflections having $2\theta \leqslant 44°$ were collected; Mo-K_α radiation and the ω—2θ scan technique were used. In this way the

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[1] J. Lewis and R. G. Wilkins, 'Modern Co-ordination Chemistry,' Interscience, New York, 1964, p. 403.

intensities of 1986 independent reflections were measured, of which only 914 having $I > 2\sigma(I)$ were considered and used in the refinement; the reflections omitted from calculations also included three low-angle ($\theta < 2{\cdot}9°$) reflections (200, $\bar{2}10$, and 101). Lorentz and polarization corrections were applied, but no correction for absorption effects was made, because μr (0·03) was so small. The structure amplitudes were brought to an absolute scale by correlating the observed with calculated values.

Structure Analysis.—The structure was solved by the heavy-atom technique; the manganese atom was located from the Patterson map and the other non-hydrogen atoms were found by two subsequent Fourier syntheses. Refinement was carried out to R 5·8% by 9 × 9 block-diagonal least-squares with anisotropic thermal parameters. The quantity minimized was $\Sigma w(\Delta|F|)^2$; in the final stage of refinement the weighting scheme $1/w = A + B|F_o| + C|F_o|^2$ was used, where the coefficients $A = 13{\cdot}10 \times 10^{-2}$, $B = -6{\cdot}6 \times 10^{-4}$, and $C = -6 \times 10^{-6}$ were determined by plotting ΔF *vs.* F_o. Further improvement of the R index to 4·1% was achieved by adding to the structure factors the contributions of 14 hydrogen atoms directly located from a difference-Fourier map and refined isotropically. The hydrogen atoms of the solvated methanol had such high thermal effects or else disordered distribution as to cause any effort to locate them unsuccessful.

TABLE 1

Final atomic fractional co-ordinates ($\times 10^4$) and thermal parameters * ($\times 10^2$ Å^2), with estimated standard deviations for non-hydrogen atoms

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	−502(1)	8402(1)	−217(1)	325(3)	148(3)	263(3)	−23(4)	86(3)	37(4)
O(1)	928(3)	7377(4)	245(2)	425(19)	166(15)	330(17)	15(14)	159(16)	76(14)
O(2)	−2043(3)	9097(4)	−625(2)	373(19)	230(16)	340(18)	−51(14)	129(15)	43(15)
O(3)	80(3)	9866(4)	−849(2)	450(19)	163(15)	314(18)	−25(15)	148(15)	24(14)
O(4)	2269(5)	9990(6)	2497(3)	1334(43)	647(29)	429(26)	−171(30)	118(26)	−40(24)
N(1)	1002(4)	3267(5)	1590(3)	401(21)	181(18)	281(20)	−27(20)	34(17)	64(19)
N(2)	−69(4)	5936(4)	977(3)	396(24)	156(18)	343(23)	6(17)	136(19)	30(18)
N(3)	−976(3)	6868(4)	501(3)	359(21)	149(20)	249(19)	−27(17)	56(17)	−7(17)
C(1)	3009(5)	6190(5)	1241(4)	399(29)	161(25)	354(27)	−44(21)	106(23)	−20(21)
C(2)	4060(5)	5564(6)	1680(4)	382(31)	351(29)	424(31)	−110(26)	139(25)	−101(27)
C(3)	4086(5)	4213(6)	2102(4)	462(34)	344(28)	312(29)	60(26)	−4(25)	−46(26)
C(4)	3090(5)	3498(6)	2113(3)	492(29)	221(24)	289(25)	9(27)	7(22)	−68(26)
C(5)	2002(5)	4105(6)	1663(3)	474(32)	187(23)	178(23)	−41(23)	67(22)	−70(20)
C(6)	1980(4)	5487(5)	1240(3)	358(26)	152(22)	195(23)	20(22)	76(20)	−11(20)
C(7)	894(4)	6295(5)	805(3)	396(27)	158(24)	179(22)	−65(21)	49(20)	−87(19)
C(8)	−2000(4)	6600(6)	583(3)	369(25)	255(23)	279(23)	−132(26)	195(20)	−17(25)
C(9)	−3005(5)	7402(6)	112(4)	287(26)	238(25)	386(28)	12(22)	146(23)	−18(23)
C(10)	−4055(5)	6933(6)	219(4)	354(27)	369(33)	425(28)	56(24)	173(24)	102(26)
C(11)	−5078(5)	7589(7)	−239(4)	391(29)	433(32)	603(38)	−13(26)	267(29)	−28(29)
C(12)	−5052(5)	8761(6)	−791(4)	393(29)	377(33)	475(32)	27(25)	146(25)	−7(26)
C(13)	−4050(5)	9260(6)	−904(4)	306(28)	356(29)	393(30)	17(24)	101(24)	22(26)
C(14)	−2997(4)	8605(6)	−464(3)	374(26)	191(25)	304(24)	−48(23)	112(21)	−58(23)
C(15)	902(5)	9538(7)	−1321(4)	523(34)	372(31)	418(31)	−28(27)	308(28)	−41(26)
C(16)	2035(8)	8639(8)	2731(4)	1621(72)	350(38)	422(37)	−178(42)	346(42)	−15(31)

* The anisotropic temperature factor is expressed in the form: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

TABLE 2

Final atomic fractional co-ordinates ($\times 10^3$) and isotropic thermal parameters (Å^2) for hydrogen atoms

	x/a	y/b	z/c	B
H(1)	297(4)	732(6)	95(3)	5·2(1·4)
H(2)	478(4)	600(5)	170(3)	4·5(1·3)
H(3)	480(4)	371(5)	251(3)	4·0(1·2)
H(4)	311(5)	263(7)	228(4)	7·7(1·7)
H(5)	20(4)	369(6)	143(4)	6·6(1·5)
H(6)	113(4)	259(6)	209(4)	5·9(1·4)
H(7)	−213(4)	571(6)	97(3)	4·7(1·3)
H(8)	−409(4)	615(6)	61(3)	5·8(1·5)
H(9)	−572(4)	725(6)	−8(3)	4·6(1·4)
H(10)	−562(5)	936(6)	−117(4)	5·9(1·5)
H(11)	−411(4)	1011(6)	−137(3)	4·4(1·3)
H(12)	48(4)	909(6)	−197(3)	5·1(1·4)
H(13)	148(4)	878(6)	−107(3)	5·5(1·4)
H(14)	129(5)	1045(6)	−145(4)	6·4(1·5)

Tables 1 and 2 give the final atomic co-ordinates and thermal parameters. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20658 (9 pp., 1 microfiche).* Atomic scattering factors were taken from ref. 2 for non-hydrogen atoms and from ref. 3 for hydrogen atoms.

All calculations were performed on the CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, with programs by Immirzi.[4]

RESULTS AND DISCUSSION

I.r. Spectrum.—The i.r. spectrum of the complex (Table 3) is characterized by the methanol (O–H) and amino-group (N–H) vibrational bands in the 3500—3000 cm^{-1} region. The frequency values of the amide (I) (1615 cm^{-1}) and amide (II) (1510 cm^{-1}) bands suggest the –C(:O)–NH– system is co-ordinating through the oxygen atom. The 1510 cm^{-1} intense band can be also attributed to the –C=N– stretching mode. The strong bands at 1600, 1545, 1465, and 1440 cm^{-1} are assignable to the aromatic rings vibrational stretch, and the band at 1600 cm^{-1} can also contain the NH_2 deformation mode of the co-ordinated amino-group.

Electronic Spectrum.—Two broad bands (240 and 315

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* For details see Notice to Authors No. 7 in the Index issue of *J. Chem. Soc. (A)*, 1970.

[2] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[3] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[4] A. Immirzi, *Ricerca sci.*, 1967, **37**, 743.

nm), which can be assigned to π–π^* and n–π^* transitions in the organic ligand, are present in the u.v. region. The visible region shows a strong charge-transfer band around 415 nm and a broad multiple band around 520 nm (with shoulders at 555 and 595 nm); this latter band can be attributed to the *d-d* transition $^5T_{2g} \leftarrow {}^5E_g$ in an octahedral geometry.[5] The presence of shoulders near the 520 nm absorption can be justified by the distortion of the octahedral environment of the metal. There is also a low-energy band at 1150 nm, which is usually observed with Mn^{III} complexes.[6]

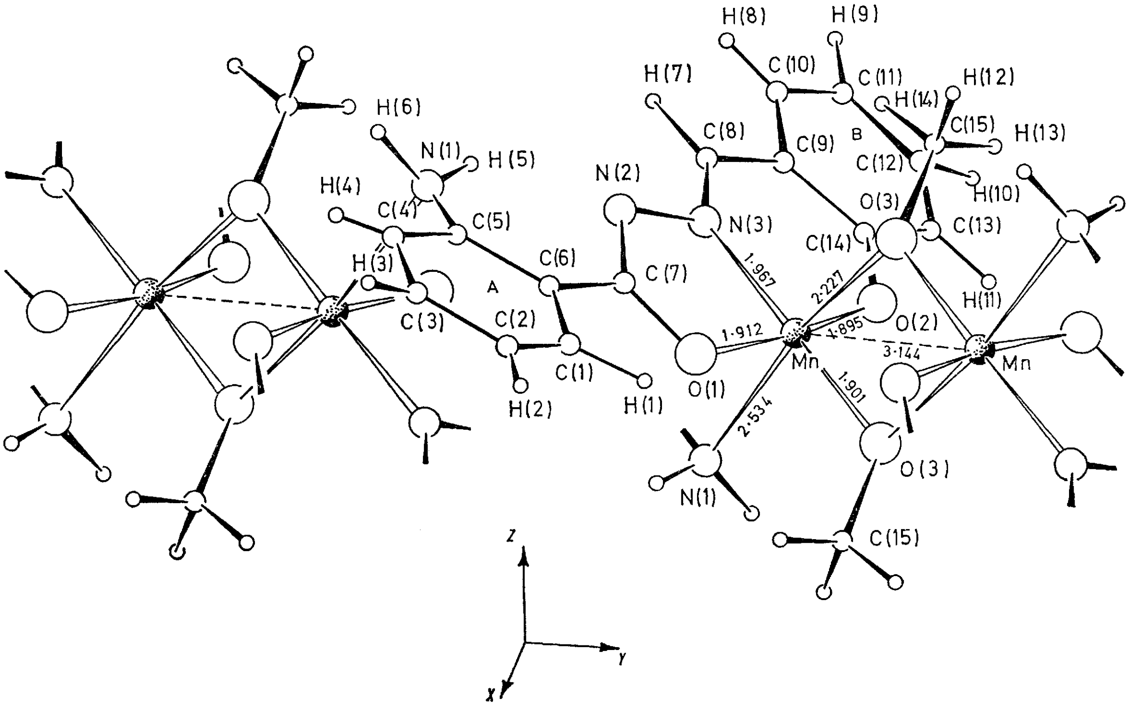

FIGURE 1 Clinographic projection of the structure

TABLE 3

Selected i.r. absorption bands (cm^{-1})

3440m,br	ν(O–H), ν(N–H)
3362m	
3320sh	
3215m	
1615vs	Amide (I)
1600vs,br	δ(N–H), Phenyl ring
1545s	Phenyl ring
1510s,br	Amide (II), ν(C=N)
1465m	Phenyl ring
1440s	Phenyl ring
1342s	Amide (III)
1282s	ν(C–O)
900m	ν(N–N)

br = Broad, m = medium, sh = shoulder, s = strong, vs = very strong.

Magnetic Data.—The magnetic moment of the complex (5·12 B.M.) lies at the upper limit of the range usually found (4·8—5·1 B.M.) for high-spin Mn^{III} compounds with four unpaired electrons.

X-*Ray Structure.*—The molecular structure of the complex is depicted in the clinographic projection of Figure 1. There are dimers in which two centrosymmetric manganese atoms are joined by two bridges formed by the oxygen atoms from the methoxo-groups; there is also an Mn $\cdots$ Mn contact of 3·144 Å. The dimers are then linked together by ligand (II), which is in a bridging situation, co-ordinating to one Mn through O(1), O(2), and N(3), and to another Mn through N(1); the whole crystal structure is therefore polymeric as indicated in Figure 2.

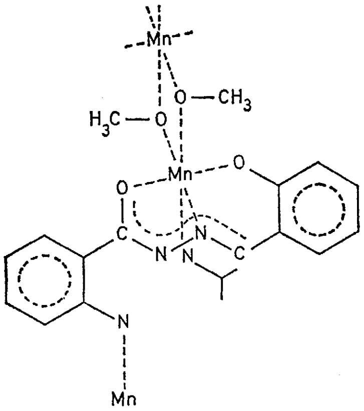

FIGURE 2 Molecular skeletal formula

Co-ordination around the metal is distorted octahedral; three atoms from ligand (II) and the oxygen

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[5] B. C. Sharma and C. C. Patel, *Indian J. Chem.*, 1970, **8**, 94.

[6] T. S. Davis, J. P. Fackler, and M. J. Weeks, *Inorg. Chem.*, 1968, **7**, 1994.

atom from a methoxo-group lie in the equatorial plane, while the apical positions are occupied by the oxygen atom from a methoxo-group centrosymmetrically related to the previous one and by the amino-nitrogen atom from ligand (II) belonging to an adjacent complex. There are small tetrahedral displacements for the atoms in the equatorial plane ranging from −0·04 to +0·05 Å with respect to the mean plane. A more severe distortion involves the apices of the octahedron, which is asymmetrically elongated with relevant inclination of the bonds $N(1^{I})$–Mn and $O(3^{II})$–Mn with respect to the co-ordination plane (88·5 and 81·5°). A distortion of this kind has already been observed in acetylacetonatobis-(*N*-phenylaminotroponiminato)manganese(III) [7] when it was suggested that the presence of non-equivalent ligands may remove the octahedral degeneracy of d_{z^2} and $d_{x^2-y^2}$ orbitals in the metal ion. In contrast, in tris(acetylacetonato)manganese(III) [8] the distortion of the octahedral configuration of the oxygen atoms co-ordinating to the metal involves only the angles, as all the Mn–O bond lengths are practically equal. In Table 4 the Mn–O and Mn–N bond distances found in the present complex are compared with those observed in the few Mn^{III} complexes examined by *X*-ray diffraction.[7-9] From these data it appears that, while correspondence is observed for the Mn–O distances, the apical Mn–N distance, responsible for the polymeric nature of the crystals, is significantly longer.

TABLE 4

Mn–N and Mn–O distances (Å) in octahedral Mn^{III} complexes *

	A	*B*	*C*	*D*
Mn–N(eq)	1·967(4)	1·959(5) 2·020(5)		
Mn–N(ap)	2·534(4)	2·153(5)		
Mn–O(eq)	1·895(7) 1·901(4) 1·912(6)	1·959(5)	1·940(17) 1·970(16)	1·860(8) 1·861(8) 1·868(8)
Mn–O(ap)	2·227(4)	2·134(5)	2·032(18) 2·273(19)	1·875(8) 1·880(8) 1·893(8)

* *A*, present work; *B*, acetylacetonatobis-(*N*-phenylaminotroponiminato)manganese(III); [7] *C*, $Na_4Mn_4Ti_5O_{18}$; [9] and *D*, tris(acetylacetonato)manganese(III).[8]

As can be seen from Figure 1, N(2) and O(2) are deprotonated. Table 5 lists bond distances and angles; the values in the benzene rings agree well with those usually found.

TABLE 5

Bond distances (Å) and angles (°), with standard deviations in parentheses

(*a*) In the co-ordination polyhedron

Mn–O(1)	1·912(6)	$Mn–N(1^{I})$	2·534(4)
Mn–O(2)	1·895(7)	Mn–N(3)	1·967(4)
Mn–O(3)	1·901(4)	$Mn–O(3^{II})$	2·227(4)
$O(3)–Mn–N(1^{I})$	91·3(1)	$N(1^{I})–Mn–N(3)$	90·6(2)
$O(3)–Mn–O(3^{II})$	81·1(1)	$O(3^{II})–Mn–O(1)$	94·5(1)
O(3)–Mn–O(1)	95·9(2)	$O(3^{II})–Mn–O(2)$	90·2(1)
O(3)–Mn–O(2)	94·1(2)	$O(3^{II})–Mn–N(3)$	97·2(1)
$N(1^{I})–Mn–O(1)$	89·6(1)	O(1)–Mn–N(3)	79·9(2)
$N(1^{I})–Mn–O(2)$	87·0(1)	O(2)–Mn–N(3)	90·3(2)

(*b*) In the ligand (II)

C(1)–C(2)	1·379(9)	N(2)–N(3)	1·412(6)
C(2)–C(3)	1·386(8)	N(3)–C(8)	1·304(8)
C(3)–C(4)	1·373(9)	C(8)–C(9)	1·424(8)
C(4)–C(5)	1·411(9)	C(9)–C(10)	1·394(9)
C(5)–N(1)	1·406(8)	C(10)–C(11)	1·371(9)
C(5)–C(6)	1·412(7)	C(11)–C(12)	1·370(9)
C(6)–C(1)	1·399(9)	C(12)–C(13)	1·352(9)
C(6)–C(7)	1·485(8)	C(13)–C(14)	1·392(8)
C(7)–O(1)	1·318(6)	C(14)–C(9)	1·411(7)
C(7)–N(2)	1·309(8)	C(14)–O(2)	1·326(8)
C(1)–C(2)–C(3)	119·3(5)	N(2)–N(3)–Mn	114·1(3)
C(2)–C(3)–C(4)	121·6(6)	N(2)–N(3)–C(8)	117·0(4)
C(3)–C(4)–C(5)	120·4(5)	C(8)–N(3)–Mn	128·8(4)
C(4)–C(5)–C(6)	117·7(5)	N(3)–C(8)–C(9)	123·3(5)
C(4)–C(5)–N(1)	119·1(5)	C(8)–C(9)–C(10)	117·1(5)
N(1)–C(5)–C(6)	122·9(5)	C(8)–C(9)–C(14)	123·9(5)
$C(5)–N(1)–Mn^{I}$	112·5(3)	C(10)–C(9)–C(14)	119·0(5)
C(5)–C(6)–C(1)	120·5(5)	C(9)–C(10)–C(11)	121·5(5)
C(6)–C(1)–C(2)	120·4(5)	C(10)–C(11)–C(12)	118·6(6)
C(5)–C(6)–C(7)	123·0(5)	C(11)–C(12)–C(13)	121·6(6)
C(1)–C(6)–C(7)	116·4(4)	C(12)–C(13)–C(14)	121·4(5)
C(6)–C(7)–O(1)	118·3(5)	C(13)–C(14)–C(9)	117·8(5)
C(6)–C(7)–N(2)	120·5(4)	C(13)–C(14)–O(2)	119·2(5)
N(2)–C(7)–O(1)	121·2(5)	C(9)–C(14)–O(2)	123·0(5)
C(7)–O(1)–Mn	114·3(3)	C(14)–O(2)–Mn	130·6(3)
C(7)–N(2)–N(3)	110·4(4)		

(*c*) In the methoxo-group

O(3)–C(15)	1·424(8)		
C(15)–O(3)–Mn	122·2(3)	$Mn–O(3)–Mn^{II}$	98·9(2)
$C(15)–O(3)–Mn^{II}$	118·8(3)		

(*d*) In the solvating methanol

O(4)–C(16) 1·333(9)

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

I $\bar{x}, \bar{y}+1, \bar{z}$ II $\bar{x}, \bar{y}+2, \bar{z}$

The arrangement of bonds around N(1) is flattened pyramidal, this atom being out of the C(5),H(5),H(6) plane by 0·24 Å; N(1) is also out of the benzene ring plane by 0·16 Å. This distortion, which is not unusual in substituted-benzene derivatives, is probably influenced by the co-ordination interactions. The value of the C(5)–N(1) distance (1·406 Å) lies at the upper limit of the range usually found[10-12] in aromatic amines (1·364—1·404 Å) in agreement with the character of single bond for this link. The two hydrogen atoms of the amino-group are involved in two different interactions, one intramolecular [N(1)–H(5) · · · N(2) 2·783 Å, N(1)–H(5)–N(2) 119°], the other intermolecular [N(1)–H(6) · · · $O(2^{I})$ 3·083 Å, N(1)–H(6)–$O(2^{I})$ 75°]. The phenolic oxygen atom, O(2), is slightly out (0·05 Å) of the mean plane of the benzene ring to which is attached, and the value of the bond it forms with the adjacent carbon atom [C(14)–O(2) 1·326 Å] agrees fairly well with

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[9] W. G. Mumme, *Acta Cryst.*, 1968, **B24**, 1114.

[10] J. C. Morrow and B. P. Huddle, *Acta Cryst.*, 1972, **B28**, 1748.

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values found in similar compounds.[13,14]. The two C–C bonds in the chain C(6),C(7),N(2),N(3),C(8),C(9) connecting the benzene rings are significantly different: C(6)–C(7) 1·485 Å corresponds to a single $C(sp^2)$–$C(sp^2)$ bond (calc. 1·482 Å[15]), while C(8)–C(9) 1·424 Å shows some double-bond character. The chain C(8),N(3),N(2),C(7) is planar; along it there is a complete double-bond delocalization as indicated by the distances [C(7)–N(2) 1·309, N(2)–N(3) 1·412, and N(3)–C(8) 1·304 Å], which are intermediate between single and double bonds. The π delocalization is extended also to O(1), as the O(1)–C(7) 1·318 Å distance is much longer than those observed when the double bond is localized.[16–18] The plane of the central part [O(1), C(7), N(2), N(3), C(8)] of the ligand makes an angle of 18·0° with benzene ring A and of 6·6° with benzene ring B. in agreement with the lack of π conjugation with the first ring and with the presence of some conjugation in the second ring. This situation is probably a consequence of the co-ordination interactions.

The methoxo-group is bridging two adjacent Mn atoms through its oxygen atom; the C–O (1·424 Å) distance corresponds closely to that for a single bond and agrees with the value (1·41 Å) observed in di-μ-methoxo-bis[chloro(2-methylpyridine)copper(II)].[19] The orientation of this group is defined by the internal rotation angle around the oxygen–metal bond [O(3)–Mn 50·9; O(3)–Mn^{II} 110·5°]. The oxygen atom of the methoxo-group is involved in several van der Waals contacts, all with oxygen atoms, in the range 2·80—2·90 Å, except O(3) · · · $O(3^{II})$ 2·696 Å, which is sensibly shorter than the sum of the van der Waals radii (2·80 Å).

The solvating methanol molecule shows a pronounced thermal vibration (or disorder) in agreement with its freedom in the structure as it is involved only in weak interactions with the phenolic and methoxo-oxygen atoms [O(4) · · · $O(2^{II})$ 2·944; O(4) · · · $O(3^{II})$ 3·223 Å]. This fact is responsible for failure in locating its hydrogen atoms and can perhaps justify the unusually short distance O(4)–C(14) 1·333 Å, as compared with the values found in methanol solvated crystals.[20,21]

All the hydrogen atoms, which have been located, show bond distances in the usual range and their distribution in the ligands is consistent with the oxidation state (III) for manganese, as suggested by the spectroscopic and magnetic evidence.

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