Crystal and Molecular Structure and Magnetic Properties of *catena*-μ-Acetato-[*NN*′-ethylenebis(salicylaldiminato)]manganese(III). A Linear-chain Complex Containing A Single *anti–anti* Acetate Bridge

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The crystal and molecular structure of the title compound have been determined by single-crystal *X*-ray analysis All non-hydrogen atoms conform to space group $P2/c$ with $a = 6{\cdot}536 \pm 0{\cdot}007$, $b = 7{\cdot}768 \pm 0{\cdot}008$, $c = 17{\cdot}194 \pm 0{\cdot}017$ Å, $\beta = 108{\cdot}8 \pm 0{\cdot}1°$, $Z = 2$. The structure has been determined from diffractometer data by Patterson and Fourier methods and refined to R 0·073 for 1211 observed reflections. The structure consists of linear polymeric chains of Mn(salen) moieties bridged by single acetate groups in an *anti-anti* configuration. The available magnetic data is shown to be consistent with this model.

THE complex Mn(salen)(AcO) [salen = *NN*′-ethylenebis(salicylaldiminato] has recently been used as an intermediate in the preparation of halogeno-species of the type M(salen)X (X = Cl, Br, or I),[1,2] and has also been obtained accidentally in the reaction of Mn^{II}(salen) with nitric oxide in acetic acid.[3] Earnshaw *et al.*[3] measured its magnetic susceptibility over the temperature range 300—85 K and suggested that antiferromagnetic interactions were present and that the structure was possibly polymeric. Similar conclusions

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[1] A. van den Bergen, K. S. Murray, M. J. O'Connor, and B. O. West, *Austral. J. Chem.*, 1969, **22**, 39.

[2] J. Lewis, F. E. Mabbs, and H. Weigold, *J. Chem. Soc.* (*A*), 1968, 1699.

[3] A. Earnshaw, E. A. King, and L. F. Larkworthy, *J. Chem. Soc.* (*A*), 1968, 1048.

have been reached for some other Schiff-base manganese(III) chelates.[1] The iron(III) analogue Fe(salen)(AcO) has also been studied, but is thought to be monomeric.[4]

Mn(salen)(AcO) is a member of a general class of compounds of the type M(chel)acetate (M = Mn or Fe; chel = quadridentate chelating ligand, such as a simple Schiff-base or the more biochemically significant phthalocyanines and porphyrins). We now report the crystal structure of Mn(salen)(AcO) which provides the first structural data for this class of compound. We further show that the magnetic measurements of Earnshaw *et al.*[3] are consistent with this structure.

EXPERIMENTAL

The compound was prepared as in ref. 1. Dark green single crystals were obtained by slow evaporation of an ethanolic solution.

Crystal Data.—$C_{18}H_{17}MnN_2O_4$, $M = 380{\cdot}3$, Monoclinic, $a = 6{\cdot}536 \pm 0{\cdot}007$, $b = 7{\cdot}768 \pm 0{\cdot}008$, $c = 17{\cdot}194 \pm 0{\cdot}017$ Å, $\beta = 108{\cdot}8 \pm 0{\cdot}1°$, $U = 826{\cdot}5$ Å^3, $D_m = 1{\cdot}53$ gm cm^{-3} (by flotation in carbon tetrachloride–chlorobenzene), $Z = 2$, $D_c = 1{\cdot}53$ gm cm^{-3}, $F(000) = 392$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å μ(Mo-K_α) = 8·68 cm^{-1}. Absent reflections: $h0l$ with $l = 2n + 1$; space group Pc (C_5^2) or $P2/c$ (C_{4h}^2). All non-hydrogen atoms conform to space group $P2/c$. No physical tests for the absence of centrosymmetry were carried out.

Unit-cell parameters were obtained by use of a Philips PW 1100 computer-controlled *X*-ray diffractometer, by least-squares refinement of the centred positions of eight reflections.

Intensity Measurements.—Intensity data were collected from a nearly spherical crystal of radius 0·08 mm by use of a Philips PW 1100 diffractometer, and graphite-monochromatized Mo-K_α radiation. A unique data set was collected out to 2θ 50°. The intensities of 1499 independent reflections were measured, of which 1211 had $F_o^2 > 3\sigma(F_o^2)$, and were used in subsequent calculations. Three standard reflections, monitored every 2 h throughout data collection, showed no significant variations in intensity.

Data were collected by the θ—2θ scan technique with a symmetric scan range of ±1·0° in 2θ from the calculated scattering angle, and a scan rate of 0·015° s^{-1}.

Intensity data were processed by use of a program[5] which enabled background-corrected intensities to be assigned standard deviations according to the formula: $\sigma(I) = [CT + (t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{\frac{1}{2}}$, where CT is the total integrated peak-count obtained in a scan time t_c, B_1 and B_2 are background counts each obtained in time $\frac{1}{2}t_b$, and $I = CT - (t_c/t_b)(B_1 + B_2)$; p was selected to be 0·04, to prevent unduly high weight being given to strong reflections. The values of I and $\sigma(I)$ were then corrected for Lorentz and polarization effects in the normal fashion.

No extinction or absorption corrections were applied, since μR was 0·07 and the estimated maximum effect on the intensities caused by neglect of absorption is <1%.

Structure Determination and Refinement.—In the least-squares calculations discussed here, the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized. Scattering factors were taken from ref. 6. The major programs used during the refinement were modified versions of the full-matrix least-squares of Busing, Martin, and Levy[7] and the Fourier summation program of White.[8] All calculations were performed on the Monash University CDC 3200 computer.

The structure determination was actually undertaken on the assumption that the material was Mn(salen)Cl which is prepared from Mn(salen)(AcO).[1] With two molecules of Mn(salen)Cl in the cell, a $P2/c$ structure would confine both manganese and chlorine atoms to lie on special two-fold positions. This is not compatible with the expected molecular configuration of Mn(salen)Cl because the special positions of $P2/c$, together with the unit-cell dimensions, preclude any possibility of a bonded manganese–chlorine distance. For this reason, space group Pc was initially adopted for the structure solution. An $N(z)$ test[9] for the presence or absence of centrosymmetry was performed on the intensity data but the result was inconclusive.

The large structure amplitudes of the $\bar{2}02$ and $\bar{4}04$ reflections together with the high density of vector peaks on the $\bar{2}02$ planes in the three-dimensional Patterson function indicated that the atoms of the salen ligand lie approximately in the ($\bar{2}02$) planes. This allowed simple interpretation of the Patterson function. A difference-Fourier phased on the manganese atom (with x and z co-ordinates arbitrarily assigned as 0) and atom O(2) (wrongly assigned as a chlorine atom) revealed the positions of all twenty atoms of the salen ligand. Attempts to refine the structure by use of a full-matrix least-squares procedure holding the x and z co-ordinates of the manganese atom fixed to define the origin, failed to reduce R below 0·163 and resulted in a high temperature-factor of 6·2 Å^2 for the ' chlorine ' atom. A subsequent-difference Fourier, phased on all atoms except the ' chlorine ' atom, revealed the positions of the four atoms of the acetate group. The resulting structure refined with isotropic temperature factors to give R 0·066 and R' 0·035 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$, but correlation coefficients $\delta_{ij} = b_{ij}/\sqrt{b_{ii}}\sqrt{b_{ij}}$, where b_{ij} is the ij^{th} element of the inverse matrix, varied from 0·2—0·8 for parameters related by the approximate diad axis through the manganese atom. In addition, the model contained many anomalous distances and angles. For instance, in the two benzene rings of the salen ligand, bond lengths varied between 1·66 and 1·17 Å while angles between any three adjacent carbon atoms varied between 111 and 131°. Although these individual distances and angles were unacceptably different from the expected values for salen,[10,11] the mean of any distances or angles related by the approximate diad axis was close to the expected value. This high correlation of parameters related by the approximate diad axis suggested that all

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[5] J. Hornstra and B. Stubbe, PW 1100 Data Processing Program, Philips Research Laboratories, Eindhoven, Holland.

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[11] M. Calligaris, G. Nardin, and L. Randaccio, *Co-ordination Chem. Rev.*, 1972, **7**, 385.

non-hydrogen atoms conform to space group *P*2/*c*. A least-squares refinement assuming *P*2/*c* with the manganese atom on the diad axis $(0,y,\frac{1}{4})$ and the two acetate carbon atoms on the related diad axis $(\frac{1}{2},y,\frac{1}{4})$ gave R 0·078 and R' 0·106. The resulting model did not contain any anomalous bond lengths or angles and all subsequent calculations were performed in space group *P*2/*c*.

We were unable to estimate the positions of the three acetate hydrogen atoms as these atoms cannot obey *P*2/*c* symmetry unless they are uniformly rotating about the C(9)–C(10) direction. A difference-Fourier synthesis calculated using the phases from the *Pc* refinement failed to indicate possible positions for these atoms.

A final difference-Fourier synthesis revealed no evidence for anisotropic thermal motion. A final structure factor calculation including the calculated positions of the salen hydrogen atoms gave R 0·073 and R' 0·094.

TABLE 1

Atomic positional and isotropic thermal parameters

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*/Å²
Mn	0·0000(0)	0·0986(2)	0·2500(0)	2·5(1)
O(1)	0·0615(7)	0·2640(6)	0·3349(3)	3·5(1)
O(2)	0·3399(7)	0·0615(6)	0·2579(3)	4·0(1)
N	0·0525(8)	−0·0950(7)	0·3297(3)	3·4(1)
C(1)	0·1574(10)	0·2372(8)	0·4157(4)	3·0(1)
C(2)	0·2188(13)	0·3834(11)	0·4648(5)	5·7(2)
C(3)	0·3242(14)	0·3662(12)	0·5514(6)	6·1(2)
C(4)	0·3643(12)	0·2024(11)	0·5873(4)	4·5(2)
C(5)	0·3009(11)	0·0609(9)	0·5395(5)	3·9(2)
C(6)	0·1969(10)	0·0733(8)	0·4526(4)	3·2(1)
C(7)	0·1348(11)	−0·0876(9)	0·4088(4)	3·8(1)
C(8)	−0·0238(13)	−0·2641(10)	0·2909(5)	4·9(2)
C(9)	0·5000(0)	0·3317(16)	0·2500(0)	5·9(3)
C(10)	0·5000(0)	0·1410(11)	0·2500(0)	3·0(2)

TABLE 2

Idealized positional co-ordinates for hydrogen atoms

	x/*a*	*y*/*b*	*z*/*c*
HC(2)	0·188	0·506	0·438
HC(3)	0·372	0·477	0·588
HC(4)	0·443	0·189	0·651
HC(5)	0·329	−0·061	0·567
HC(7)	0·157	−0·203	0·443
HC(8A)	0·060	−0·365	0·329
HC(8B)	−0·190	−0·278	0·280

Final values of the positional and vibrational parameters are listed in Table 1, together with their estimated standard deviations derived from the inverse least-squares matrix. Table 2 lists the predicted salen hydrogen positions. Observed and calculated structure factors are given in Supplementary Publication No. SUP 20756 (21 pp., 1 microfiche).*

DISCUSSION

The structure consists of linear polymeric chains of approximately planar Mn(salen) moieties bridged by single acetate groups in an *anti–anti* configuration. This is the first example of an acetate group bridging in this fashion. Tribenzyltin acetate[12] is a linear polymer with single acetate bridges but in the *anti–syn* configuration. Copper(II) formate[13] contains *anti–anti* formate bridges but in this case there are two such bridges between each copper atom. Figure 1 shows a view[14] of one such moiety and defines the labelling scheme for the atoms. Table 3 gives pertinent intramolecular distances and angles together with their estimated standard deviations. The procedure of

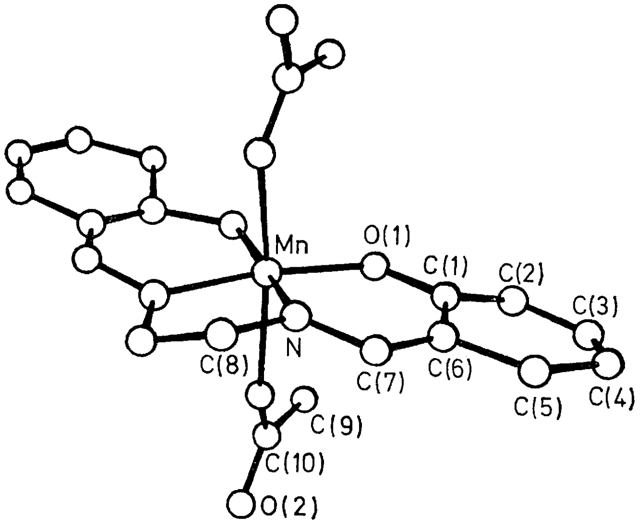

FIGURE 1 Molecular geometry of one Mn(salen) moiety showing the labelling scheme for the atoms

TABLE 3

Selected intramolecular distances and angles

(*a*) Distances (Å)

Mn–O(1)	1·888(4)	C(4)–C(5)	1·355(10)
Mn–O(2)	2·201(5)	C(5)–C(6)	1·432(9)
Mn–N	1·989(5)	C(6)–C(7)	1·448(9)
O(1) · · · O(1′)	2·768(7)	C(7)–N	1·293(8)
O(1) · · · N	2·790(7)	N–C(8)	1·485(9)
N · · · N′	2·602(7)	C(8)–C(8′)	1·535(12)
O–C(1)	1·344(7)	C(9)–C(10)	1·481(15)
C(1)–C(2)	1·395(10)	C(10)–O(2)	1·259(6)
C(1)–C(6)	1·409(8)	O(2)–O(2′)	2·195(7)
C(2)–C(3)	1·432(12)	O(2)–C(9)	2·369(12)
C(3)–C(4)	1·402(12)		

(*b*) Angles (°)

O(1)–Mn–O(1)	94·3(2)	C(1)–C(6)–C(5)	119·2(6)
O(1)–Mn–N	92·0(2)	C(1)–C(6)–C(7)	124·5(6)
N–Mn–N′	81·7(2)	C(2)–C(1)–C(6)	119·2(6)
O(1)–Mn–N′	173·7(2)	C(2)–C(3)–C(4)	120·1(8)
O(1)–Mn–O(2)	94·7(2)	C(3)–C(4)–C(5)	119·5(7)
N–Mn–O(2)	84·9(2)	C(4)–C(5)–C(6)	121·9(7)
Mn–O–C(1)	127·3(4)	C(5)–C(6)–C(7)	116·4(6)
Mn–N–C(7)	127·8(5)	C(6)–C(7)–N	122·5(6)
Mn–N–C(8)	113·6(4)	C(7)–N–C(8)	118·5(6)
Mn–O(2)–C(10)	141·9(3)	N–C(8)–C(8′)	105·9(6)
O–C(1)–C(2)	116·6(6)	C(9)–C(10)–O(2)	119·4(3)
O–C(1)–C(6)	124·2(6)	O(2)–C(10)–O(2′)	121·3(4)
C(1)–C(2)–C(3)	120·1(8)		

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[12] N. W. Alcock and R. E. Timms, *J. Chem. Soc.* (*A*), 1968, 1873.

[13] R. Kiriyama, H. Ibamoto, and K. Matsuo, *Acta Cryst.*, 1954, **7**, 482.

[14] C. K. Johnson, 1965, ORTEP, Fortran Ellipsoid Plot Program for crystal-structure illustrations, Report ORNL 3794, Oak Ridge National Laboratory, Tennessee.

Blow[15] was used to calculate least-squares planes for the two groups of atoms O, O′, N, N′, Mn † and O, C(1)—(7), N. The plane equations, together with the distances of the individual atoms from these planes, are given in Table 4.

There are no unusual intermolecular or intramolecular bond lengths. The manganese atom has a distorted octahedral configuration where the angles subtended at the manganese atom vary from 81 to 95°. Molar conductance measurements have indicated[3] that in solutions of ethanol and water, Mn(salen)(AcO) is considerably dissociated. This is consistent with the observed Mn–O(2) bond length of 2·201 Å which is considerably longer and therefore weaker than the Mn–O(1) bond length of 1·888. The dimensions of the acetate group are similar to those observed in basic beryllium acetate[16] and bond distances within the salen ligand are very similar to the mean values obtained from an analysis of seventeen structures containing salen.[11] The difference in the C–C bond lengths between the ' near ' and ' far ' sides (with respect to the metal atom) of the benzene ring has been explained on the basis of calculations using the simple Hückel MO method applied to the π-electron system of the salicylaldimate ion.[10]

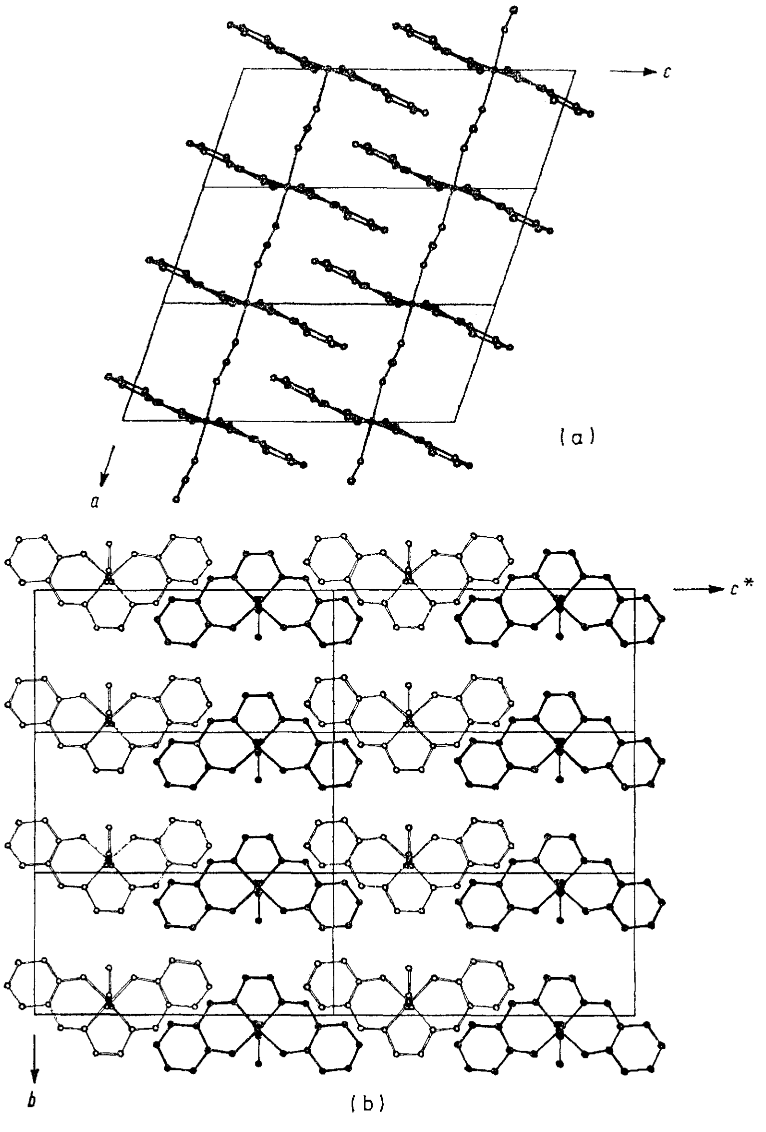

FIGURE 2 Projections of the structure on (a) the *ac* and (b) the *bc** planes. Unit-cell outlines are included

The salen ligand has a symmetric stepped conformation[11] and therefore a *gauche* conformation of the five-membered ring containing the ethylenediamine bridge.

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† Atoms in the same molecule as those given in Table 1, but related by the diad axis, are indicated by primed atom labels.

[15] D. M. Blow, *Acta Cryst.*, 1960, **13**, 168.

[16] A. Tulinsky, C. R. Worthington, and E. Pignataro, *Acta Cryst.*, 1959, **12**, 623.

This arrangement retains the trigonal nature of the imine nitrogen atoms as indicated by the sum of bond angles around these atoms (359·9°). The ethylene carbon atoms are symmetrically displaced ±0·34(1) Å from the co-ordination plane and the torsion angle around the CH_2–CH_2 bond is 46·2°. These values are typical of those observed for salen in both symmetric and asymmetric stepped conformations.[11]

TABLE 4

Equations of least-squares planes referred to orthogonal axes *a*, *b*, *c** and *X*, *Y*, and *Z* are co-ordinates in Å. Distances (Å) of atoms from the planes are given in square brackets

Plane (I): O(1), C(1)—(7), N

$$0{\cdot}9902X - 0{\cdot}0217Y - 0{\cdot}1383Z + 2{\cdot}2320 = 0$$

[O(1) − 0·003(4), C(1) − 0·003(6), C(2) − 0·009(9), C(3) 0·006(10), C(4) 0·016(8), C(5) − 0·001(8), C(6) − 0·005(8), C(7) − 0·041(7), N 0·039(6)]

Plane (II): Mn, O(1), O(1′), N, N′

$$-0{\cdot}09981X - 0{\cdot}0613Z - 1{\cdot}1312 = 0$$

[Mn 0·000(0), O(1) − 0·017(4), N′ − 0·018(6), O(1′) 0·017(4), N 0·018(6)]

Figure 2(a) and (b) shows projections of the structure on the *ac* and *bc** planes, illustrating the packing arrangement. The polymeric chains run parallel to the *a* axis and stack one on top of each other in the *b* direction. Chains separated by $\frac{1}{2}c$ are related by the *c* glide and therefore have different orientations relative to the crystal axes.

Magnetism.—Manganese(III) is a d^4 ion which gives a ^5E_g ground-term in octahedral ligand-fields. Since this is a Jahn–Teller configuration, the ^5E_g term undergoes a very large splitting to leave an orbital singlet ground-state. Monomeric high-spin complexes generally show $\mu_{\text{eff.}}$ values of *ca*. 4·9 BM and θ values close to 0 K, *i.e.* Curie behaviour. Any reduction from $\mu_{\text{eff.}}$ of 4·9 BM with an associated increase in the magnitude of θ can be indicative of the presence of magnetic interactions between neighbouring Mn^{III} centres. Mn(salen)(AcO) is such a case, with $\mu_{\text{eff.}}$ 4·68 BM at 300 K and θ 22 K.[3] This behaviour is compatible with the linear-chain polymeric structure reported here.

We have fitted the 300—80 K data of Earnshaw *et al.*[3] to the Heisenberg one-dimensional chain model. Fisher[17] has made calculations on this model and an exact solution has been obtained for infinite spin. Good experimental comparisons with the model have been obtained for the $S = 5/2$ (Mn^{2+}) (refs. 18 and 19) and $S = 3/2$ (Co^{2+}) (ref. 20) systems. We have therefore scaled the susceptibility calculations to $S = 2$ and the expression becomes: $\chi = 2N\beta^2g^2/kT\,.\,[(1 + u)/(1 - u)]$, where $u = \coth(12J/kT) - (kT/12J)$. This expression gives good agreement with the experimental data for Mn(salen)(AcO). The best fit parameters are *g* 1·96 ± 0·01 and J −1·4 ± 0·1 cm^{-1}. The small negative J value is indicative of very weakly antiferromagnetic intrachain coupling. The long Mn · · · Mn distance of 6·536 Å is compatible with this value of J. The mechanism of exchange coupling must involve a superexchange pathway which uses the π orbitals of the bridging acetate group.[21,22] Interchain interactions are expected to be negligible.

The experimental susceptibilities lie in a somewhat insensitive region of the temperature scale and single-crystal measurements down to helium temperatures are required for a more detailed analysis.

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