The structure of the $UO_2(CH_3COO)_3^-$ anion is the same as was found in sodium uranyl acetate (Zachariasen & Plettinger, 1959).

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catena-μ-Acetato-N,N'-ethylenebis[(2-hydroxy-1-naphthyl)methaniminato]manganese(III)

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Abstract. $C_{26}H_{21}MnN_2O_4$, orthorhombic, $a = 20.30$ (1), $b = 6.609$ (7), $c = 15.24$ (1) Å, $U = 2045$ (1) Å³, $D_m = 1.54$, $D_c = 1.56$ Mg m⁻³, $F(000) = 1800$, $Z = 4$, Mo K radiation, $\lambda = 0.7107$ Å, $\mu = 0.462$ mm⁻¹; space group $Pccn$ from the systematic absences $hk0$, $h + k = 2n + 1$, $h0l$, $l = 2n + 1$, $0kl$, $l = 2n + 1$; 886 independent reflections; $R = 0.079$. The structure is made up of N,N'-ethylenebis[(2-hydroxy-1-naphthyl)-methaniminato]manganese moieties with imposed C_2 symmetry [Mn—N, Mn—O 2.006 (9), 1.885 (7) Å] bridged by single acetate groups [Mn—O 2.220 (7) Å] in an *anti–anti* configuration to form a one-dimensional polymer.

Introduction. The crystal structure of the 1:1 molecular complex of nickel and N,N'-ethylenebis-[(2-hydroxy-1-naphthyl)methanimine] ($=L$) and its characteristics compared to those of the corresponding salicylideneimine complex have been reported previously (Akhtar, 1981). We now report the structure of the complex [MnL(acetate)] (I). These structures can be compared to those containing the analogous trimethylene ligand L^1 {*viz* N,N'-propylenebis[(2-hydroxy-1-naphthyl)methanimine]}, namely [NiL^1] and [CuL^1(dmso)$_{0.5}$] (dmso = dimethyl sulphoxide) (Akhtar & Drew, 1982).

The compound MnL was prepared by refluxing an equimolar mixture of manganese acetate dihydrate and the ligand N,N'-ethylenebis[(2-hydroxy-1-naphthyl)-methanimine] (Hussain, 1978). Dark purple-brown elongated prisms were obtained on slow recrystallization from methanol. A crystal of approximate size $0.4 \times 0.3 \times 0.1$ mm was mounted along c in a Lindemann tube and intensities were measured on a

Stoe STADI2 diffractometer equipped with a graphite monochromator. 1950 reflections with a 2θ maximum of 50° were measured by ω scans with a scan speed of $0.0333°$ s⁻¹ and a background count of 20 s. Of these, 886 independent reflections with $I > 2\sigma(I)$ were used in subsequent calculations. Neither absorption nor extinction corrections were applied. The positions of the Mn atoms in (I) were obtained from the Patterson function and the positions of the remaining non-hydrogen atoms were obtained from Fourier maps. Atoms were refined anisotropically. H atoms were fixed in trigonal and

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å² $\times 10^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq}
Mn	2500	2500	4022 (1)	34 (2)
O(1)	1805 (3)	2377 (14)	3203 (4)	43 (9)
N(1)	1844 (5)	2653 (16)	5004 (5)	37 (10)
C(1)	841 (5)	2355 (21)	4160 (6)	40 (12)
C(2)	1170 (6)	2091 (14)	3348 (7)	38 (12)
C(3)	793 (6)	1462 (20)	2609 (8)	46 (14)
C(4)	119 (6)	1287 (21)	2655 (8)	45 (15)
C(5)	−236 (6)	1686 (18)	3469 (8)	50 (12)
C(6)	−928 (6)	1557 (21)	3489 (10)	66 (16)
C(7)	−1247 (6)	1931 (19)	4245 (11)	68 (16)
C(8)	−895 (6)	2467 (22)	4998 (8)	63 (17)
C(9)	−224 (5)	2590 (22)	4981 (7)	54 (14)
C(10)	140 (6)	2195 (19)	4207 (7)	46 (12)
C(11)	1215 (5)	2650 (20)	4941 (7)	45 (13)
C(12)	2176 (6)	3067 (19)	5863 (7)	49 (13)
O(2)	2505 (5)	−834 (11)	4202 (5)	53 (10)
C(21)	2500	7500	3803 (10)	42 (12)
C(22)	2500	7500	2807 (11)	64 (18)

Table 2. *Interatomic distances* (Å) *and angles* (°)

Mn–O(1)	1·885 (7)	C(2)–C(3)	1·424 (15)
Mn–N(1)	2·006 (9)	C(3)–C(4)	1·374 (16)
Mn–O(2)	2·220 (7)	C(4)–C(5)	1·459 (17)
O(1)–C(2)	1·321 (13)	C(5)–C(6)	1·409 (17)
N(1)–C(11)	1·279 (13)	C(5)–C(10)	1·400 (16)
N(1)–C(12)	1·497 (13)	C(6)–C(7)	1·345 (19)
C(11)–C(1)	1·426 (14)	C(7)–C(8)	1·397 (18)
C(12)–C(12*)	1·515 (23)	C(8)–C(9)	1·365 (15)
O(2)–C(21)	1·258 (10)	C(9)–C(10)	1·416 (15)
C(21)–C(22)	1·518 (22)	C(10)–C(1)	1·429 (15)
C(1)–C(2)	1·416 (15)		

O(1)–Mn–O(1*)	97·1 (3)	O(1)–C(2)–C(1)	126·0 (10)
O(1)–Mn–N(1)	89·9 (3)	O(1)–C(2)–C(3)	115·8 (10)
N(1)–Mn–N(1*)	83·5 (4)	C(1)–C(2)–C(3)	118·2 (10)
O(1)–Mn–N(1*)	171·3 (4)	C(2)–C(3)–C(4)	121·4 (11)
O(1)–Mn–O(2)	92·4 (3)	C(3)–C(4)–C(5)	121·3 (11)
N(1)–Mn–O(2)	87·7 (3)	C(4)–C(5)–C(6)	120·0 (12)
O(1)–Mn–O(2*)	97·0 (4)	C(4)–C(5)–C(10)	117·2 (10)
N(1)–Mn–O(2*)	81·7 (4)	C(6)–C(5)–C(10)	122·8 (12)
O(2)–Mn–O(2*)	165·8 (3)	C(5)–C(6)–C(7)	119·2 (14)
Mn–O(1)–C(2)	128·7 (6)	C(6)–C(7)–C(8)	120·3 (12)
Mn–N(1)–C(11)	127·3 (7)	C(7)–C(8)–C(9)	120·7 (11)
Mn–N(1)–C(12)	111·2 (7)	C(8)–C(9)–C(10)	121·7 (11)
C(11)–N(1)–C(12)	121·0 (9)	C(1)–C(10)–C(5)	121·3 (9)
N(1)–C(11)–C(1)	126·5 (10)	C(1)–C(10)–C(9)	123·3 (10)
N(1)–C(12)–C(12*)	107·5 (9)	C(5)–C(10)–C(9)	115·4 (11)
C(11)–C(1)–C(2)	119·7 (9)	Mn–O(2)–C(21)	144·0 (7)
C(11)–C(1)–C(10)	119·9 (9)	O(2)–C(21)–C(22)	118·9 (6)
C(2)–C(1)–C(10)	120·3 (9)	O(2)–C(21)–O(2*)	122·2 (13)

* Atoms related by the symmetry element $0·5 - x$, $1·5 - y$, z relative to the x,y,z set listed in Table 1.

tetrahedral positions at 1·08 Å from the C atoms and an overall thermal parameter was refined. However, the H atoms on C(22) could not be located even when we took into account the fact that the group had to be disordered. The final R value was 0·079. Calculations were carried out using the *SHELX* 76 system (Sheldrick, 1976) at the University of Manchester Computer Centre. Scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The weighting scheme was chosen to give similar values of $w\Delta^2$ over ranges of $\sin\theta/\lambda$ and F_o: $w = 1/[\sigma^2(F) + 0·002F^2]$ where $\sigma(F)$ was taken from counting statistics. The difference Fourier maps showed no significant peaks. Zero-weighted reflections showed no serious discrepancies. Atomic coordinates for (I) are given in Table 1 and molecular dimensions in Table 2.*

Discussion. The molecular structure is shown in Fig. 1, together with the atomic numbering scheme. The molecule has crystallographically imposed C_2 symmetry with the Mn atoms on a twofold axis. These MnL moieties, which have *cis* configurations, are

bridged by single acetate groups in an *anti–anti* configuration forming a linear polymeric (–Mn–acetate–Mn–acetate–) chain along **b**. The two C atoms in the acetate group are also on a twofold axis but at $\frac{1}{2}$ in y from the metal atom. The Mn atom is in a distorted octahedral environment with angles subtended at the metal atom ranging from 81·7 to 97·1°. The Mn–O(1), Mn–N(1) and Mn–O(2) bond lengths are 1·885 (7), 2·006 (9), and 2·220 (7) Å respectively. The compound is considerably dissociated in water-alcohol mixture, which is consistent with the supposition that the longer Mn-to-acetate bond is weaker than the Mn–O(1) bond. The structure is thus analogous to that of μ-acetato-[N,N'-ethylenebis-(salicylideneiminato)]manganese(III) (Davis, Gatehouse & Murray, 1973) which also has a polymeric structure with Mn–O(1), Mn–N(1), Mn–O(2) bond lengths of 1·884 (4), 1·989 (5), and 2·201 (5) Å respectively. These are remarkably similar to our dimensions and the structure also has an equivalent repeat distance ($a = 6·54$ Å) and the same atoms on the twofold axes, but the space group is different, $P2/c$. A noticeable feature of both structures is that the Mn–O–C angles are 144·0 (7) and 141·9 (3)° respectively. These unusual angles are an indication of the strain in the polymeric chain and of its stabilizing influence on the MnL moiety. In *catena-μ*-acetato-diamminebromocopper(II) (Ferrari, Cappacchi, Fava & Nardelli, 1972), the only other similar polymeric structure we could find in the Cambridge Crystallographic Database (February 1981 version), the Cu$\cdots$Cu distance is 4·88 Å. The Cu–O–C angles are 117·9 and 124·7°, which shows less strain in the polymeric chain and appears to be due to the Cu atoms being related by glide planes and not having to lie on twofold rotation axes as in the former two cases. The dimensions of the acetate group in the present structure are similar to those in [Mn(salen)(AcO)] and in basic beryllium acetate (Tulinsky & Worthington, 1959). The dimensions of the ligand in the six membered metallocycle are C–O 1·321 (13), C–N 1·279 (13), C–C
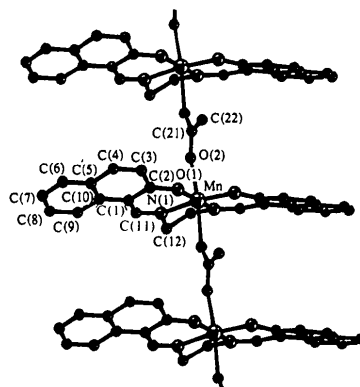

Fig. 1. The molecular structure and the atomic numbering.

Table 3. *Least-squares planes and deviations* (Å) *of atoms from the planes*

E.s.d.'s are *ca* 0·01 Å and 0·2°.

Plane (1): O(1) 0·09, N(1) −0·09, O(1*) −0·09, N(1*) 0·09
Plane (2): Mn −0·03, O(1) 0·08, N(1) −0·02, C(1) 0·00, C(2) −0·07, C(11) 0·04
Plane (3): Mn, N(1), N(1*) 0·00, C(12)† 0·32

The plane containing atoms C(*n*), *n* = 1 to 10 inclusive is planar within experimental error: it makes an angle of 20·3° with plane (2). The two symmetry-related metallocycles intersect at 11·8°.

† Atom not contributing to the plane.

1·416 (15) and 1·426 (15) Å, and the angle between the planes of the metallocycle is 11·8 (1)° (Table 3), compared to 4·8° in the four-coordinate structure of [NiL] (Akhtar, 1981), 6·0° in [CuL^1(dmso)$_{0.5}$] and 37·1° in [NiL^1] (Akhtar & Drew, 1982). The [NiL] and [CuL^1(dmso)$_{0.5}$] structures contain centrosymmetric dimers with Ni···Ni 3·324 and Cu···Cu 3·613 Å whereas the [NiL^1] complex exists as monomers (closest Ni–Ni distance is 4·07 Å). Thus the angle between the metallocycle rings is decreased by metal···metal interaction and the resulting steric repulsion between adjacent ligands. The effect of the polymer formation is not so restrictive but keeps the angle well below the value found in [NiL^1], which we take to be an unstrained value. The average distance in the naphthyl ring is 1·403 Å which is close to expected values. The sum of the bond angles around the N atom is 359·5° indicating the trigonal nature of the bonding. The angle at the C atoms of the ethylenediamine groups is 107·5 (9)° showing tetrahedral configuration. The ethylene C atoms are displaced by 0·32 Å from the coordination plane (Table 3) indicating a symmetrical

gauche form and the torsion angle around the −CH$_2$−CH$_2$− bond is 47·2 (1)°; these values are similar to those observed for some ethylenediamine complexes (Davies, Gatehouse & Murray, 1973; Shkol'nikova, Yumal, Shugam & Voblikova, 1970; Llewellyn & Waters, 1960; Scouloudi, 1953).

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Bis(di-*n*-propyldithiophosphinato)zinc(II)

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Abstract. [Zn{(*n*-C$_3$H$_7$)$_2$PS$_2$}$_2$], C$_{12}$H$_{28}$P$_2$S$_4$Zn, triclinic, P1̄, *a* = 8·409 (5), *b* = 9·771 (6), *c* = 13·451 (7) Å, *α* = 90·99 (5), *β* = 99·28 (4), *γ* = 105·27 (5)°, *Z* = 2, *D$_x$* = 1·35 Mg m^{-3}, *M$_r$* = 427·9, *μ*(Mo *Kα*) = 1·72 mm^{-1}; final *R* = 0·057 for 3111 X-ray data. The complex forms dimers with point symmetry 1̄. The endocyclic dithiophosphinato groups link the Zn atoms into an eight-membered ring while the exocyclic groups function as chelating ligands. Their geometry is affected by a disorder which can be described by split-atom positions of one S atom and of the *n*-propyl groups.

Introduction. A review on the preparation of dithiophosphinato complexes has been given by Kuchen &