Synthesis and Structure of a Trinuclear Manganese(II) Complex containing Low-spin Metal†

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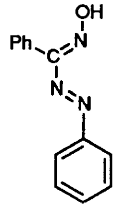
The reaction of α-phenylazobenzaldehyde oxime, HL, with manganese(II) salts has afforded the first known mixed-spin trinuclear complex $[Mn^{II}_3L_6]$. The structure of the benzene solvate $[Mn_3L_6]\cdot 2C_6H_6$ has been determined by *X*-ray crystallography. The Mn_3 fragment is exactly linear with the terminal low-spin ($S = \frac{1}{2}$) metal(II) atoms tris-chelated by azo- and oxime-nitrogen functions into facial pseudo-octahedral MnN_6 dispositions. Two such $[MnL_3]^-$ moieties sequester the central high-spin ($S = \frac{5}{2}$) manganese(II) atom into an O_6 environment using oximato oxygen donors. The average Mn ··· Mn, Mn–N, and Mn–O distances are 3.577(7), 1.956(18), and 2.146(15) Å respectively. It is proposed that oximato nitrogen co-ordination is primarily responsible for the low-spin configuration of the terminal manganese(II) atoms.

The high-spin ($S = \frac{5}{2}$) state is ubiquitous in manganese(II) chemistry but examples of low-spin ($S = \frac{1}{2}$) species are very rare.[1,2] In a recent communication we described the arylazo oxime complex $[Mn_3L_6]$ (HL = α-phenylazobenzaldehyde oxime), predicted to contain two terminal low-spin Mn^{II} atoms, and a central high-spin Mn^{II} atom, on the basis of molecular weight data, magnetic properties, and certain analogies.[3] In this work we report the synthetic details and the *X*-ray structure of a benzene solvate of this very unusual molecule which constitutes the only known system of trinuclear manganese(II) chelates[4–9] containing the metal in low-spin configuration.



HL

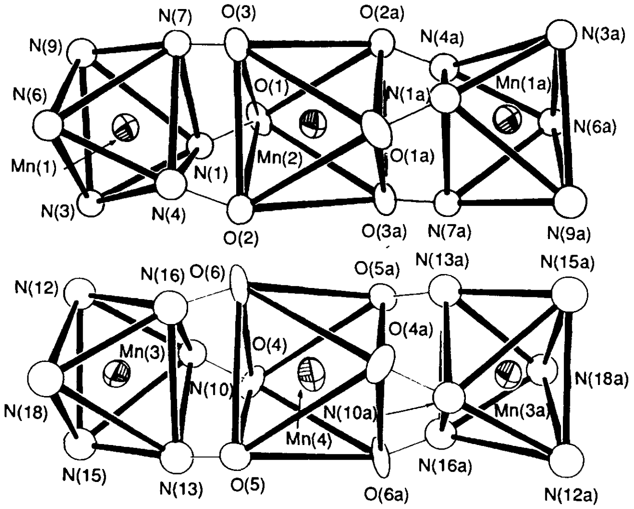


Figure 1. ORTEP plot of the co-ordination polyhedra about the manganese atoms

Results and Discussion

Synthesis.—In neutral methanolic solution HL does not react with manganese(II) salts. Upon deprotonation by base, however, a rapid reaction occurs affording a dark green solution from which the non-electrolyte $[Mn_3L_6]$ deposits as a dark solid. The complex $[Mn_3L_6]$ crystallises from benzene solutions as a disolvate which rapidly loses solvent and crystallinity in air without apparent loss of external shape. This misled us in our earlier unsuccessful attempts to obtain single crystals.[3]

Structure of $[Mn_3L_6]\cdot 2C_6H_6$.—Two inequivalent but similar trinuclear moieties are present in the unit cell. Views of relevant molecular fragments and the atom numbering scheme are depicted in Figures 1 and 2. Selected bond parameters are listed in Table 1. Owing to the relatively weakly diffracting nature of the crystals and consequently limited volume of the data set collected only moderate precision could be achieved for the derived bond parameters.

For both the independent molecules the Mn_3 fragment (Figure 1) is exactly linear with the central manganese atoms Mn(2) and Mn(4) occupying crystallographic inversion centres. In this regard $[Mn_3L_6]$ is similar to $[AsPh_4][Mn_3(CO)_{14}]$.[8c] Two of the four benzene molecules in the unit cell occupy general positions. The centroids of the other two lie at crystallographic inversion centres. A molecular packing diagram is displayed in Figure 3.

Each terminal manganese atom is tris-chelated by azo- and oxime-nitrogen atoms into a facial pseudo-octahedral disposition (Figure 2). The two $[MnL_3]^-$ moieties act as tridentate oximato-oxygen donors spanning three facial co-ordination sites of a centrally placed manganese(II) atom (Figure 1). The Mn(1) ··· Mn(2) and Mn(3) ··· Mn(4) distances are 3.589(7) and 3.565(5) Å respectively. The centrosymmetry of $[Mn_3L_6]$ indicates that it is a *meso* complex with the two $[MnL_3]^-$ fragments having opposite chirality, Δ and Λ.

The O_6 co-ordination spheres of Mn(2) and Mn(4) are approximately octahedral but with a discernible trigonal elongation along the Mn(1) ··· Mn(2) and Mn(3) ··· Mn(4) axes.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

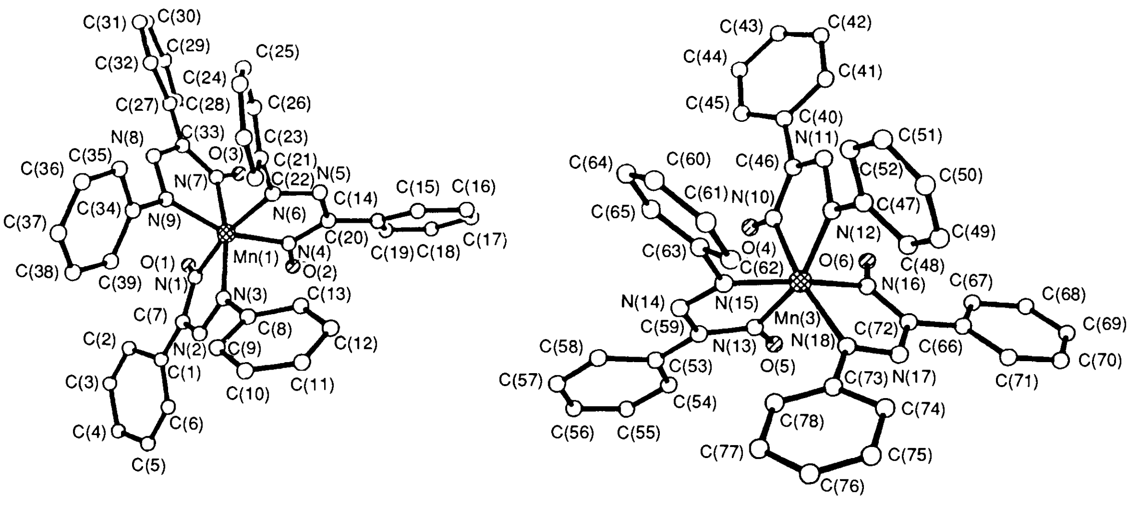

Figure 2. Structures of the two independent low-spin $[MnL_3]^-$ fragments

Table 1. Selected bond lengths (Å) and angles (°) for $[Mn_3L_6]\cdot 2C_6H_6$

Mn(1)-N(4)	1.926(17)	Mn(1)-N(6)	1.959(16)
Mn(1)-N(7)	1.987(17)	Mn(1)-N(3)	1.966(17)
Mn(1)-N(9)	1.971(14)	Mn(1)-N(1)	1.931(15)
Mn(2)-O(2)	2.153(13)	Mn(2)-O(1)	2.156(15)
Mn(2)-O(3)	2.146(9)	Mn(3)-N(12)	1.960(16)
Mn(3)-N(15)	1.935(15)	Mn(3)-N(10)	1.972(16)
Mn(3)-N(18)	1.976(18)	Mn(3)-N(16)	1.965(16)
Mn(3)-N(13)	1.923(18)	Mn(4)-O(4)	2.127(15)
Mn(4)-O(6)	2.123(13)	Mn(4)-O(5)	2.171(10)
N(4)-Mn(1)-N(6)	76.8(7)	N(4)-Mn(1)-N(7)	87.5(7)
N(6)-Mn(1)-N(7)	92.8(7)	N(4)-Mn(1)-N(3)	97.7(7)
N(6)-Mn(1)-N(3)	99.6(7)	N(7)-Mn(1)-N(3)	167.4(7)
N(4)-Mn(1)-N(9)	161.2(7)	N(6)-Mn(1)-N(9)	92.4(6)
N(7)-Mn(1)-N(9)	77.6(7)	N(3)-Mn(1)-N(9)	99.3(7)
N(4)-Mn(1)-N(1)	92.0(7)	N(6)-Mn(1)-N(1)	168.2(6)
N(7)-Mn(1)-N(1)	90.5(7)	N(3)-Mn(1)-N(1)	77.8(7)
N(9)-Mn(1)-N(1)	99.4(6)	O(2)-Mn(2)-O(1)	88.8(5)
O(2)-Mn(2)-O(3)	89.7(4)	O(1)-Mn(2)-O(3)	87.2(5)
N(12)-Mn(3)-N(15)	95.9(7)	N(12)-Mn(3)-N(10)	76.2(7)
N(15)-Mn(3)-N(10)	90.8(6)	N(12)-Mn(3)-N(18)	103.7(7)
N(15)-Mn(3)-N(18)	103.2(7)	N(10)-Mn(3)-N(18)	165.9(6)
N(12)-Mn(3)-N(16)	93.0(6)	N(15)-Mn(3)-N(16)	170.3(7)
N(10)-Mn(3)-N(16)	87.6(7)	N(18)-Mn(3)-N(16)	78.3(7)
N(12)-Mn(3)-N(13)	160.8(8)	N(15)-Mn(3)-N(13)	77.5(8)
N(10)-Mn(3)-N(13)	85.8(7)	N(18)-Mn(3)-N(13)	95.4(7)
N(16)-Mn(3)-N(13)	92.8(7)	O(4)-Mn(4)-O(6)	88.5(5)
O(4)-Mn(4)-O(5)	86.7(5)	O(6)-Mn(4)-O(5)	90.9(4)

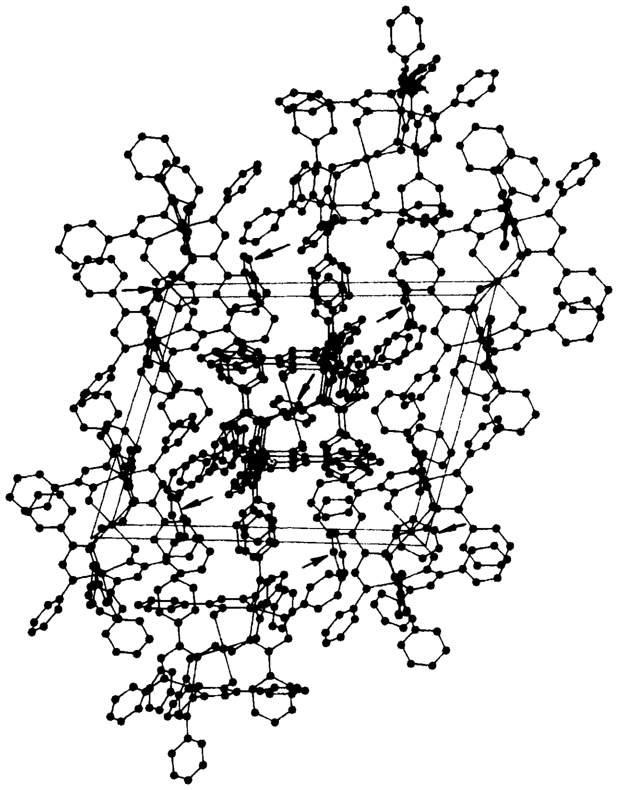

Figure 3. Packing diagram (down *a* axis) for $[Mn_3L_6]\cdot 2C_6H_6$. Solvent benzene molecules are indicated by arrows

Thus, for a given molecule *cis* O(*i*)-Mn(*j*)-O(*k*) angles are generally smaller or larger than 90° depending respectively on whether O(*i*) and O(*j*) belong to the same or different faces normal to the trigonal axis (Table 1). The MnN_6 co-ordination spheres in the $[MnL_3]^-$ fragments (Figure 2) display severe angular distortions from O_h symmetry as is evident in the average values of angles: chelate bite 77.3(8)°, *trans*-N^a-Mn-N^o 165.5(8)° (N^a and N^o are co-ordinated azo- and oxime-nitrogen atoms respectively). The average N^o-Mn-N^o and N^a-Mn-N^a angles are respectively 89.3(7) and 99.1(7)°. The triangular N^a_3 face is thus selectively subject to substantial trigonal compression but the corresponding N^o_3 face is hardly affected. Indeed the surface area of the N^a_3 face is $\approx 20\%$ larger than the N^o_3 face. The crowding of the pendant phenyl rings near the N^a_3 face is believed to be a reason for this. Each N^o_3 face abuts the corresponding O_3 face but the two are not eclipsed. The surface area of the O_3 face is approximately equal to that of the N^a_3 face. The fragments shown in Figure 1 can be envisaged approximately as cylinders with constrictions at the N^o_3 regions.

The average Mn-O distance in $[Mn_3L_6]$ is 2.146(15) Å. This compares well with Mn^{II}-O distances in aqua,[10a] phenolato,[10b] carboxylato,[10c] and acetylacetonato[10d] complexes wherein manganese(II) is uniformly high-spin ($S = \frac{5}{2}$). The average Mn-N^o and Mn-N^a distances in $[Mn_3L_6]$ are 1.951(18) and 1.961(18) Å respectively. These are significantly shorter than Mn^{II}-N bonds observed (2.1—2.4 Å) in numerous structurally characterised high-spin complexes. The effect of spin-state is thus clearly reflected in the metal-ligand bond distances. The five-membered chelate rings in all the $[MnL_3]^-$ fragments are

Table 2. Atomic co-ordinates (× 10^4) for $[Mn_3L_6]\cdot 2C_6H_6$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn(1)	1 541(2)	2 188(2)	85(2)	Mn(3)	−1 218(2)	3 214(2)	−4 374(2)
Mn(2)	0	0	0	Mn(4)	0	5 000	−5 000
O(2)	−453(9)	1 028(8)	−507(6)	O(4)	−1 255(9)	4 963(8)	−4 702(7)
O(1)	1 209(9)	225(7)	−392(6)	O(6)	611(8)	4 604(8)	−4 012(7)
O(3)	926(9)	1 063(8)	1 012(6)	O(5)	−728(9)	3 565(8)	−5 635(6)
N(4)	162(11)	1 879(11)	−122(8)	N(12)	−1 178(11)	3 547(10)	−3 329(8)
N(6)	1 392(11)	3 321(10)	624(8)	N(15)	−2 618(12)	2 720(10)	−4 830(8)
N(7)	1 642(12)	1 648(10)	953(8)	N(14)	−3 026(11)	2 728(10)	−5 522(9)
N(3)	1 536(10)	2 496(10)	−861(8)	N(10)	−1 303(10)	4 485(10)	−4 211(9)
N(9)	2 955(11)	2 590(10)	637(8)	N(17)	148(12)	2 237(10)	−4 205(8)
N(5)	527(11)	3 330(10)	597(8)	C(59)	−2 363(14)	2 989(12)	−5 874(10)
C(7)	1 485(13)	1 012(12)	−1 230(10)	N(18)	−787(12)	2 098(10)	−4 450(8)
N(2)	1 528(10)	1 840(10)	−1 384(8)	N(16)	194(11)	3 748(11)	−4 078(8)
N(8)	3 255(11)	2 414(9)	1 302(8)	N(13)	−1 447(13)	3 219(11)	−5 409(9)
C(20)	−182(14)	2 525(13)	182(10)	N(11)	−1 165(11)	4 385(10)	−3 005(8)
N(1)	1 406(10)	1 013(10)	−561(8)	C(72)	675(15)	3 133(14)	−4 008(10)
C(33)	2 520(14)	1 899(11)	1 458(10)	C(46)	−1 174(13)	4 917(13)	−3 517(11)
C(14)	−1 178(14)	2 433(12)	127(9)	C(40)	−1 097(14)	5 893(13)	−3 241(11)
C(15)	−1 443(15)	3 218(14)	233(10)	C(41)	−541(15)	6 349(14)	−2 508(12)
C(16)	−2 388(16)	3 190(15)	204(11)	C(42)	−407(16)	7 287(15)	−2 220(13)
C(17)	−3 052(16)	2 396(14)	75(11)	C(43)	−810(15)	7 764(15)	−2 670(12)
C(18)	−2 825(17)	1 558(16)	−64(11)	C(44)	−1 348(16)	7 342(15)	−3 403(13)
C(19)	−1 889(15)	1 591(14)	−37(10)	C(45)	−1 474(15)	6 403(14)	−3 687(12)
C(8)	1 444(13)	3 314(12)	−1 109(9)	C(47)	−1 245(13)	2 968(12)	−2 809(10)
C(9)	2 052(15)	3 636(13)	−1 494(11)	C(48)	−769(13)	2 322(11)	−2 768(10)
C(10)	1 892(17)	4 383(14)	−1 784(12)	C(49)	−873(14)	1 750(13)	−2 299(10)
C(11)	1 179(15)	4 733(13)	−1 700(11)	C(50)	−1 424(15)	1 852(14)	−1 868(11)
C(12)	603(14)	4 420(12)	−1 301(10)	C(51)	−1 837(14)	2 527(13)	−1 858(10)
C(13)	757(13)	3 686(11)	−998(9)	C(52)	−1 776(14)	3 091(12)	−2 344(10)
C(1)	1 409(12)	238(12)	−1 835(10)	C(53)	−2 737(14)	3 020(12)	−6 646(10)
C(2)	1 737(14)	−491(13)	−1 668(11)	C(54)	−2 142(15)	3 271(12)	−7 065(11)
C(3)	1 666(15)	−1 203(15)	−2 260(12)	C(55)	−2 589(16)	3 233(13)	−7 825(12)
C(4)	1 335(16)	−1 171(16)	−3 013(13)	C(56)	−3 567(16)	3 011(13)	−8 147(12)
C(5)	1 056(16)	−426(15)	−3 162(13)	C(57)	−4 157(18)	2 777(14)	−7 751(13)
C(6)	1 109(15)	271(15)	−2 572(12)	C(58)	−3 738(16)	2 797(13)	−7 000(12)
C(21)	2 150(13)	4 152(12)	1 122(10)	C(63)	−4 690(17)	2 071(14)	−3 829(11)
C(22)	2 515(15)	4 833(14)	815(13)	C(62)	−4 034(16)	1 611(15)	−3 770(12)
C(23)	3 240(16)	5 658(15)	1 343(12)	C(61)	−3 317(15)	1 827(13)	−4 117(11)
C(24)	3 512(14)	5 738(14)	2 081(11)	C(60)	−3 360(14)	2 539(13)	−4 471(10)
C(25)	3 157(15)	5 054(14)	2 368(12)	C(65)	−4 038(16)	2 956(15)	−4 535(12)
C(26)	2 448(15)	4 224(14)	1 865(12)	C(64)	−4 716(19)	2 751(16)	−4 205(13)
C(27)	2 816(14)	1 657(13)	2 162(10)	C(73)	−1 332(15)	1 131(13)	−4 696(10)
C(28)	2 340(16)	837(15)	2 264(12)	C(74)	−926(18)	553(16)	−4 316(13)
C(29)	2 636(16)	640(15)	2 967(13)	C(75)	−1 488(20)	−401(19)	−4 602(15)
C(30)	3 431(16)	1 245(15)	3 566(13)	C(76)	−2 380(18)	−709(16)	−5 113(12)
C(31)	3 907(17)	2 068(16)	3 460(13)	C(77)	−2 774(17)	−124(15)	−5 461(12)
C(32)	3 579(14)	2 235(13)	2 769(11)	C(78)	−2 224(16)	826(14)	−5 204(11)
C(34)	3 757(13)	3 164(12)	495(10)	C(66)	1 747(14)	3 378(13)	−3 710(10)
C(35)	4 439(13)	3 915(12)	1 071(11)	C(67)	2 370(17)	4 245(15)	−3 578(12)
C(36)	5 200(15)	4 389(13)	903(11)	C(68)	3 392(18)	4 418(17)	−3 215(12)
C(37)	5 320(15)	4 131(13)	235(12)	C(69)	3 728(22)	3 731(20)	−3 028(15)
C(38)	4 647(15)	3 376(14)	−317(12)	C(70)	3 165(22)	2 895(21)	−3 191(15)
C(39)	3 842(15)	2 858(13)	−206(11)	C(71)	2 146(18)	2 686(16)	−3 526(12)
C(79)	5 086(22)	−120(21)	7 432(15)	C(86)	4 655(19)	−389(18)	9 253(16)
C(80)	4 105(22)	−202(20)	7 274(15)	C(87)	5 277(20)	−737(19)	9 711(17)
C(81)	3 817(21)	525(19)	7 501(14)	C(85)	4 383(18)	301(18)	9 530(15)
C(82)	4 472(23)	1 377(22)	7 893(15)	C(89)	4 208(21)	4 504(17)	4 447(17)
C(83)	5 405(25)	1 440(23)	8 060(16)	C(90)	5 062(26)	4 716(20)	4 315(18)
C(84)	5 724(22)	731(19)	7 852(15)	C(88)	4 124(25)	4 750(21)	5 124(21)

virtually planar with no atoms deviating by 0.04 Å from the mean planes. The distances and angles within the chelate rings are generally comparable with those in other structurally characterised arylazo oximates.[11–17]

Other Observations and Comments.—Spin-pairing in manganese(II) requires deployment of very strong-field ligands, so that even complexes such as $[Mn(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) are high-spin.[18] The very strong-field ligand CN^- however does afford low-spin $[Mn(CN)_6]^{4-}$.[1] The position of the oximato-nitrogen atom in the spectrochemical series has not been defined precisely but there is good evidence to show that it can bring about large ligand field splitting in octahedral complexes.[19] We believe that oximato-nitrogen co-ordination is of crucial significance in making $[MnL_3]^-$ low-spin. Two other low-spin manganese(II) tris-chelates based on oximato ligands exist: nitrosoacetaldehyde oximates[2] and 1,2-quinone oximates.[20] In both these cases the co-ordination sphere is MnN_3O_3, unlike $[MnL_3]^-$ where the sphere is MnN_6. The common features of the three groups are oximato-nitrogen co-ordination and five-membered chelation. The non-oxime donor varies considerably: from azo-nitrogen in $[MnL_3]^-$ to nitroso-oxygen[2] to quinone-oxygen.[20]

We have previously demonstrated[11,12,21,22] that Fe^{II} and Os^{II} tris-chelates of type $[ML_3]^-$ can sequester a variety of metal (M′) ions affording trinuclear species of the type $[(ML_3)_2M']^z$ ($z = 0$ or $+1$), the binding mode being analogous to that in $[Mn_3L_6]$. A trinuclear family $[(FeL'_3)_2M']^z$ based on 1,2-quinone 2-oximates (L′) has also been described by us.[23] Attempts to prepare heteronuclear species of type $[(MnL_3)_2M']^z$ has however not yet been successful for the manganese system.

Experimental

α-Phenylazobenzaldehyde oxime was prepared by using the reported method.[24] Manganese(II) perchlorate hexahydrate was prepared by dissolving manganese carbonate in 70% aqueous perchloric acid followed by crystallisation. Microanalyses (*C*, *H*, N) were performed by using a Perkin-Elmer 240C elemental analyser.

Preparation of $[Mn_3L_6]$.—To a solution of HL (900 mg, 4.0 mmol) and $Mn(ClO_4)_2{\cdot}6H_2O$ (730 mg, 2 mmol) in methanol (35 cm^3) was added dropwise, with stirring, a solution of potassium hydroxide (110 mg, 2 mmol) in methanol (5 cm^3). Immediately a deep green colour developed and stirring was continued for 3 h. A dark solid precipitated which was collected by filtration and washed thoroughly with methanol and water. After drying *in vacuo* over P_4O_{10}, the compound was dissolved in benzene and filtered. The filtrate was evaporated *in vacuo* and the shining black solid so obtained was stored *in vacuo*. Yield 480 mg (48%) (Found: C, 62.10; H, 4.00; Mn, 10.95; N, 16.50. Calc. for $C_{78}H_{60}Mn_3N_{18}O_6$: C, 62.05; H, 4.00; Mn, 10.90; N, 16.70%).

For *X*-ray work dark parallelopiped crystals of composition $[Mn_3L_6]{\cdot}2C_6H_6$ were obtained by slow diffusion of a solution of $[Mn_3L_6]$ (80 mg, 0.05 mmol) in benzene (25 cm^3) into an overlying layer of hexane (25 cm^3). It was difficult to obtain single crystals and those obtained diffracted only weakly. The best available crystal was chosen and mounted in a thin-walled glass capillary (to avoid loss of solvent of crystallisation).

X-*Ray Structure Determination.*—*Crystal Data.* $C_{90}H_{72}Mn_3N_{18}O_6$, $M = 1\,666.5$, triclinic, space group $P\bar{1}$, $a = 15.101(8)$, $b = 15.473(7)$, $c = 19.261(5)$ Å, $\alpha = 100.81(3)$, $\beta = 107.11(3)$, $\gamma = 103.19(4)°$, $U = 4\,028(3)$ Å^3 (by least-squares refinement of 14 accurately measured reflections), $Z = 2$, $D_c = 1.374$ g cm^{-3}, dark parallelopiped (0.40 × 0.24 × 0.16 mm), $\mu(\text{Mo-}K_\alpha) = 5.08$ cm^{-1}, $\lambda = 0.710\,73$ Å, $F(000) = 1\,722$.

Data collection and processing. Nicolet R3m/V diffractometer, ω-scan method ($2 < 2\theta < 40°$), graphite monochromated Mo-K_α radiation; 7 924 independent measured reflections, 2 521 observed [$F > 6\sigma(F)$], corrected for Lorentz and polarisation factors; semiempirical absorption correction (transmission 0.8802—0.9195). Three standard reflections monitored showed no significant variations.

Solution and refinement. The structure was solved using the heavy-atom method, the positions of the manganese atoms being determined from a Patterson map. The remaining non-hydrogen atoms were determined from successive Fourier difference syntheses. Due to the limited number of observed data only the thermal parameters of the manganese and oxygen atoms were made anisotropic. Hydrogen atoms were included at calculated positions (C–H 0.96 Å, $U = 0.08$ Å^2). The final residuals R and R' were 0.0637 and 0.0691 respectively. The function minimised was $\Sigma w(|F|)^2$ with the weight, $w = 1/[\sigma^2(F) + 0.001(F^2)]$. The maximum and minimum residual electron densities in the final ΔF map were 0.28 and -0.24 e Å^{-3} respectively. Positional parameters for the non-hydrogen atoms are collected in Table 2. Computations were carried out on a Micro VAX II computer using the SHELXTL-PLUS program system.[25]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

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References

1 W. P. Griffith, *Coord. Chem. Rev.*, 1975, **17**, 177 and refs. therein.
2 P. Couzerh, Y. Jeannin, C. Rocchiccioli-Deltcheff, and F. Valentini, *J. Coord. Chem.*, 1979, **6**, 221.
3 P. Basu, S. Pal, and A. Chakravorty, *Inorg. Chem.*, 1988, **27**, 1848.
4 (*a*) S. Shibata, S. Onuma, and H. Inoue, *Inorg. Chem.*, 1985, **24**, 1723; (*b*) B. D. Murray, H. Hope, and P. Power, *J. Am. Chem. Soc.*, 1985, **107**, 169; (*c*) S. Gambarotta, C. Floriani, A. Chiesivilla, and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1983, 1128; (*d*) G. Vos, J. G. Haasnoot, G. C. Verchoor, J. Reedijk, and P. E. L. Schaminee, *Inorg. Chim. Acta*, 1985, **105**, 31; (*e*) A. Belforte, F. Calderazzalro, U. Englert, and J. Strahle, *J. Chem. Soc., Chem. Commun.*, 1989, 801.
5 J. L. Seela, K. Folting, R-J. Wang, J. Huffman, G. Chirstou, H-R. Chang, and D. N. Hendrickson, *Inorg. Chem.*, 1985, **24**, 4454; X. Li, D. P. Kessissoglou, M. L. Kirk, C. J. Bender, and V. L. Pecoraro, *ibid.*, 1988, **27**, 1; J. B. Vincent, H-R. Chang, K. Folting, J. C. Huffman, G. Christou, and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1987, **109**, 5703; A. R. E. Baikie, M. B. Hursthouse, D. B. New, and P. Thornton, *J. Chem. Soc., Chem. Commun.*, 1978, 62; D. P. Kessissoglou, M. L. Kirk, C. A. Bender, M. S. Lah, and V. L. Pecoraro, *J. Chem. Soc., Chem. Commun.*, 1989, 84.
6 R. Bhula, G. J. Gainsford, and D. C. Weatherburn, *J. Am. Chem. Soc.*, 1988, **110**, 7550.
7 M. C. Bohn, R. D. Ernst, R. Gleiter, and D. R. Wilson, *Inorg. Chem.*, 1983, **22**, 3815.
8 (*a*) S. W. Kirtley, J. P. Olsen, and P. Bau, *J. Am. Chem. Soc.*, 1973, **95**, 4532; (*b*) W. A. Herrmann, M. L. Ziegler, and K. Weidenhammer, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 368; (*c*) P. Bau, S. W. Kirtley, T. N. Sorrell, and S. Winkaro, *J. Am. Chem. Soc.*, 1974, **96**, 988.
9 K. Wieghardt, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1153.
10 (*a*) H. Tamura, K. Ogawa, T. Sakurai, and A. Nakahara, *Inorg. Chim. Acta*, 1984, **92**, 107; (*b*) B. Mabad, P. Cassoux, J-P. Tuchagues, and D. N. Hendrickson, *Inorg. Chem.*, 1986, **25**, 1420; D. P. Kessissoglou, W. M. Butler, and V. L. Pecoraro, *ibid.*, 1987, **26**, 495; (*c*) C. H. L. Kennard, G. Smith, E. J. O'Reilly, and K. E. Brown, *Inorg. Chim. Acta*, 1981, **52**, 55; (*d*) F. S. Stephens, *Acta Crystallogr., Sect. B*, 1977, **33**, 3492 and ref 4(*a*).
11 S. Pal, T. Melton, R. N. Mukherjee, A. R. Chakravarty, M. Tomas, L. R. Falvello, and A. Chakravorty, *Inorg. Chem.*, 1985, **24**, 1250.
12 S. Pal, R. N. Mukherjee, M. Tomas, L. R. Falvello, and A. Chakravorty, *Inorg. Chem.*, 1986, **25**, 200.
13 D. Bandopadhyay, P. Bandopadhyay, A. Chakravorty, F. A. Cotton, and L. R. Falvello, *Inorg. Chem.*, 1984, **23**, 1785.
14 D. Bandopadhyay, P. Bandopadhyay, A. Chakravorty, F. A. Cotton, and L. R. Falvello, *Inorg. Chem.*, 1983, **22**, 1315.
15 A. R. Chakravarty, A. Chakravorty, F. A. Cotton, L. R. Falvello, B. K. Ghosh, and M. Tomas, *Inorg. Chem.*, 1983, **22**, 1892.
16 P. Bandopadhyay, D. Bandopadhyay, A. Chakravorty, F. A. Cotton, L. R. Falvello, and S. Han, *J. Am. Chem. Soc.*, 1983, **105**, 6327.

17 M. H. Dickman and R. J. Doedens, *Inorg. Chem.*, 1980, **19**, 3112.
18 F. H. Burnstall and R. S. Nylholm, *J. Chem. Soc.*, 1952, 3570.
19 J. G. Mohanty, R. P. Singh, and A. Chakravorty, *Inorg. Chem.*, 1975, **14**, 2178.
20 P. Basu and A. Chakravorty, unpublished work.
21 S. Pal and A. Chakravorty, *Inorg. Chem.*, 1987, **26**, 4331.
22 B. K. Ghosh, R. N. Mukherjee, and A. Chakravorty, *Inorg. Chem.*, 1987, **26**, 1946.
23 P. Basu, S. Pal, and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1990, 9.
24 K. C. Kalia and A. Chakravorty, *J. Org. Chem.*, 1970, **35**, 2231.
25 G. M. Sheldrick, 'SHELXTL-PLUS 88, Structure Determination Software Programs,' Nicolet Instrument Corp., Madison, 1988.

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