C(1*b*)	−0.3078 (8)	0.0914 (7)	−0.0976 (7)	0.038 (3)
C(2*a*)	0.2843 (8)	0.2441 (7)	−0.0247 (6)	0.036 (3)
C(2*b*)	0.2698 (10)	0.3808 (8)	−0.0809 (8)	0.052 (4)
C(3*a*)	−0.3585 (8)	0.0082 (7)	0.2256 (6)	0.033 (3)
C(3*b*)	−0.3737 (9)	−0.0341 (8)	0.3594 (7)	0.046 (4)
C(4*a*)	−0.1535 (8)	0.3664 (6)	−0.0428 (6)	0.033 (3)
C(4*b*)	−0.3175 (10)	0.3758 (8)	−0.0447 (8)	0.053 (4)
C(5*a*)	0.0298 (8)	0.0229 (7)	0.3358 (6)	0.034 (3)
C(5*b*)	0.1901 (9)	0.0172 (8)	0.3497 (7)	0.046 (4)
C(6*a*)	0.4600 (15)	0.3257 (14)	−0.3575 (9)	0.100 (7)
C(6*b*)	0.5930 (15)	0.3845 (14)	−0.3691 (12)	0.095 (7)
C(7*a*)	0.0741 (10)	0.2969 (8)	0.3864 (8)	0.058 (4)
C(7*b*)	0.0191 (15)	0.3870 (12)	0.4341 (12)	0.115 (7)
C(8*a*)	−0.3580 (8)	0.2778 (7)	0.3456 (7)	0.041 (3)
C(8*b*)	−0.5115 (9)	0.3076 (9)	0.3212 (8)	0.057 (4)

Table 2. *Selected geometric parameters* (Å, °)

$[Ni_2Sb_4(C_2H_5O)_{16}]$		$[Mn_2Sb_4(C_2H_5O)_{16}]$	
Sb(1)—O(1)	2.313 (4)	Sb(1)—O(1)	2.311 (4)
Sb(1)—O(2)	1.996 (4)	Sb(1)—O(2)	1.994 (4)
Sb(1)—O(3′)	1.987 (4)	Sb(1)—O(3′)	1.998 (4)
Sb(1)—O(6)	1.995 (5)	Sb(1)—O(6)	2.006 (5)
Sb(2)—O(4)	2.182 (5)	Sb(2)—O(4)	2.206 (4)
Sb(2)—O(5)	2.034 (4)	Sb(2)—O(5)	2.029 (4)
Sb(2)—O(7)	2.033 (5)	Sb(2)—O(7)	2.041 (5)
Sb(2)—O(8)	1.950 (5)	Sb(2)—O(8)	1.940 (5)
Ni(1)—O(1)	2.097 (4)	Mn(1)—O(1)	2.233 (4)
Ni(1)—O(2)	2.082 (5)	Mn(1)—O(2)	2.229 (4)
Ni(1)—O(3)	2.066 (4)	Mn(1)—O(3)	2.174 (4)
Ni(1)—O(4)	2.010 (4)	Mn(1)—O(4)	2.074 (4)
Ni(1)—O(5)	2.117 (4)	Mn(1)—O(5)	2.211 (4)
O(1)—C(1*a*)	1.446 (8)	O(1)—C(1*a*)	1.442 (7)
O(2)—C(2*a*)	1.449 (8)	O(2)—C(2*a*)	1.436 (8)
O(3)—C(3*a*)	1.474 (8)	O(3)—C(3*a*)	1.457 (8)
O(4)—C(4*a*)	1.420 (8)	O(4)—C(4*a*)	1.427 (8)
O(5)—C(5*a*)	1.434 (8)	O(5)—C(5*a*)	1.445 (8)
O(6)—C(6*a*)	1.431 (10)	O(6)—C(6*a*)	1.379 (10)
O(7)—C(7*a*)	1.407 (10)	O(7)—C(7*a*)	1.399 (9)
O(8)—C(8*a*)	1.427 (9)	O(8)—C(8*a*)	1.425 (8)
O(1)—Sb(1)—O(2)	73.9 (2)	O(1)—Sb(1)—O(2)	75.1 (2)
O(1)—Sb(1)—O(3′)	73.7 (2)	O(1)—Sb(1)—O(3′)	74.0 (2)
O(1)—Sb(1)—O(6)	153.1 (2)	O(1)—Sb(1)—O(6)	154.8 (2)
O(2)—Sb(1)—O(3′)	96.3 (2)	O(2)—Sb(1)—O(3′)	96.2 (2)
O(2)—Sb(1)—O(6)	87.7 (2)	O(2)—Sb(1)—O(6)	87.2 (2)
O(3′)—Sb(1)—O(6)	89.4 (2)	O(3′)—Sb(1)—O(6)	90.4 (2)
O(4)—Sb(2)—O(5)	72.2 (2)	O(4)—Sb(2)—O(5)	72.8 (2)
O(4)—Sb(2)—O(7)	154.9 (2)	O(4)—Sb(2)—O(7)	156.6 (2)
O(4)—Sb(2)—O(8)	80.3 (2)	O(4)—Sb(2)—O(8)	80.7 (2)
O(5)—Sb(2)—O(7)	89.5 (2)	O(5)—Sb(2)—O(7)	89.9 (2)
O(5)—Sb(2)—O(8)	102.4 (2)	O(5)—Sb(2)—O(8)	100.5 (2)
O(7)—Sb(2)—O(8)	87.4 (2)	O(7)—Sb(2)—O(8)	87.3 (2)
O(1)—Ni—O(1′)	77.9 (2)	O(1)—Mn—O(1′)	80.4 (2)
O(1)—Ni—O(2)	77.0 (2)	O(1)—Mn—O(2)	72.4 (2)
O(1′)—Ni—O(2)	95.0 (2)	O(1′)—Mn—O(2)	96.4 (2)
O(1)—Ni—O(3)	98.0 (2)	O(1)—Mn—O(3)	100.6 (2)
O(1′)—Ni—O(3)	76.9 (2)	O(1′)—Mn—O(3)	72.5 (2)
O(1)—Ni—O(4)	103.5 (2)	O(1)—Mn—O(4)	103.9 (2)
O(1′)—Ni—O(4)	173.9 (2)	O(1′)—Mn—O(4)	172.2 (2)
O(1)—Ni—O(5)	173.5 (2)	O(1)—Mn—O(5)	169.5 (2)
O(1′)—Ni—O(5)	105.2 (2)	O(1′)—Mn—O(5)	105.0 (2)
O(2)—Ni—O(3)	171.3 (2)	O(2)—Mn—O(3)	168.0 (2)
O(2)—Ni—O(4)	91.1 (2)	O(2)—Mn—O(4)	91.1 (2)
O(2)—Ni—O(5)	97.0 (2)	O(2)—Mn—O(5)	97.7 (2)
O(3)—Ni—O(4)	97.0 (2)	O(3)—Mn—O(4)	100.2 (2)
O(3)—Ni—O(5)	88.3 (2)	O(3)—Mn—O(5)	89.7 (2)
O(4)—Ni—O(5)	74.0 (2)	O(4)—Mn—O(5)	71.9 (2)

The structure solution and the structural refinements were performed using *SHELXS*86 (Sheldrick, 1985) and *SHELX*76 (Sheldrick, 1976). Non-H atoms were refined with anisotropic displacement parameters, H atoms were refined isotropically with bond constraints of 1.00 Å between the C and H atoms. Geometric calculations of bond distances and bond angles were performed with *PLATON* (Spek, 1990). Molecular graphics were produced using *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances involving H atoms have been deposited with the IUCr (Reference: AB1151). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$[Mn_6O_2\{O_2C\text{-}3,5\text{-}(NO_2)_2\text{-}C_6H_3\}_{10}(C_5H_5N)_2\{(CH_3)_2CO\}_2].2(CH_3)_2CO.2(C_2H_5)_2O$ and $[Mn_6O_2(O_2CC_6H_5)_{10}(NCCH_3)_4]$

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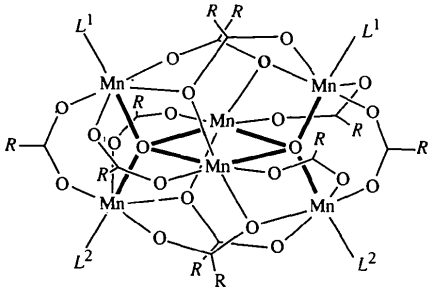
Abstract

The structures of di(acetone)tetrakis(μ^3-3,5-dinitrobenzoato-κ^2O:$\kappa O'$)hexakis(μ-3,5-dinitrobenzoato-κO:$\kappa O'$)-di-μ^4-oxo-di(pyridine)tetramanganese(II)dimanganese(III)–acetone–diethyl ether (1/2/2), (1), and tetrakis(acetonitrile)tetrakis(μ^3-benzoato-κ^2O:$\kappa O'$)hexakis(μ-benzoato-κO:$\kappa O'$)-di-μ^4-oxo-tetramanganese(II)dimanganese(III), (2), are reported. Both compounds contain six octahedrally coordinated Mn centres, arranged as two $Mn^{II}_2Mn^{III}_2(\mu^4\text{-O})$ tetrahedra sharing the Mn^{III}–Mn^{III} edge.

Comment

The title compounds were obtained during our continuing research into manganese carboxylate chemistry (Christou, 1989). Both complexes contain the $Mn_6O_2(O_2CR)_{10}(L)_x$ (x = 4) structural motif previously observed in manganese benzoate and pivalate chemistry (x = 4; Baikie, Howes, Hursthouse, Quick & Thornton, 1986; Gerbeleu, Batsanov, Timko, Struchkov, Indrichan & Popovich, 1987; Schake, Vincent, Li, Boyd, Folting, Huffman, Hendrickson & Christou, 1989; Köhler, Roesky, Noltemeyer, Schmidt, Freire-Erdbrügger & Sheldrick, 1993: x = 5; Blackman, Huffman, Lobkovsky & Christou, 1992); since the distances and angles within the $[Mn_6O_2]$ cores of (1) and (2) are identical to within 3σ, the structures will be considered together.



(1) R = 3,5-$(NO_2)_2$-C_6H_3; $L^1 = C_5H_5N$, $L^2 = OCMe_2$

(2) R = Ph; $L^1 = L^2$ = NCMe

The Mn aggregates in both structures possess crystallographic C_2 symmetry. The $Mn_4^{II}Mn_2^{III}$ oxidation state assignment for the clusters is confirmed by examination of the bond lengths to the Mn centres; Mn(1) exhibits shorter Mn—O distances with a pronounced Jahn–Teller elongation along the (equivalent) O(5)—Mn(1)—O(65) and O(5)—Mn(1)—O(32) directions in (1) and (2), respectively, and was therefore assigned as the Mn^{III} site. The disposition of the peripheral carboxylate and terminal ligands is in the more commonly observed arrangement for these complexes, with four μ^3-κ^2O:$\kappa O'$ and six μ^2-O,O' carboxylate ligands and one terminal ligand per Mn^{II} centre (Schake, Vincent, Li, Boyd, Folting, Huffman, Hendrickson & Christou, 1989). The Mn—O(carboxylate) and Mn—N distances are unexceptional and identical to within 3σ in (1) and (2), despite the differences in carboxylate and terminal ligation between the two compounds; the *cis*- and *trans*-O—Mn—X (X = O, N) angles vary from 79 to 103° and from 163 to 176°, respectively, the Mn^{II} and Mn^{III} centres showing similar degrees of distortion from ideal octahedral geometry. The acetone ligand in (1) is coordinated in the bent geometry typically observed for first-row metal complexes of this ligand [Mn(2)—O(86) 2.192 (5), O(86)—C(87) 1.244 (10) Å, Mn(2)—O(86)—C(87) 136.7 (6)°] (Gambarotta, Pasquali, Floriani, Villa & Guastini, 1981; di Vaira, Stoppioni & Mani, 1983; Smith, O'Reilly, Kennard, Mak & Yip, 1985; Zhang, Loebach, Wilson & Jacobsen, 1990). No close contacts are observed between the occluded solvent molecules in (1) and the Mn aggregate.

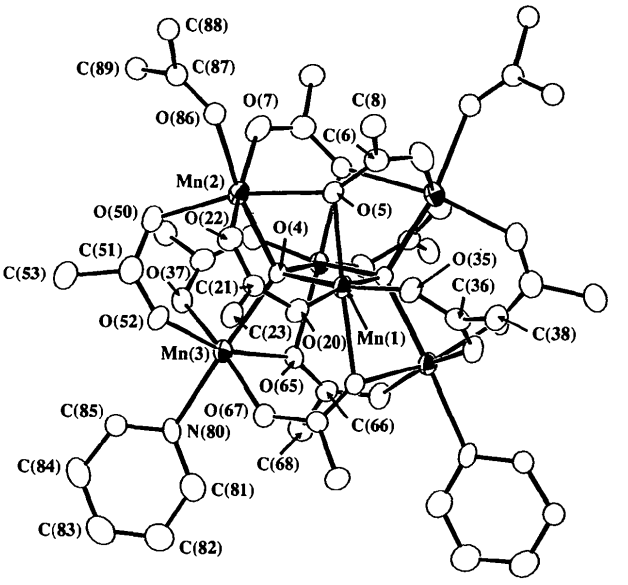


Fig. 1. An *ORTEP* (Johnson, 1965) representation of (1) showing 50% probability ellipsoids. For clarity, only the *ipso* C atoms of the 3,5-dinitrobenzoate phenyl groups are shown.

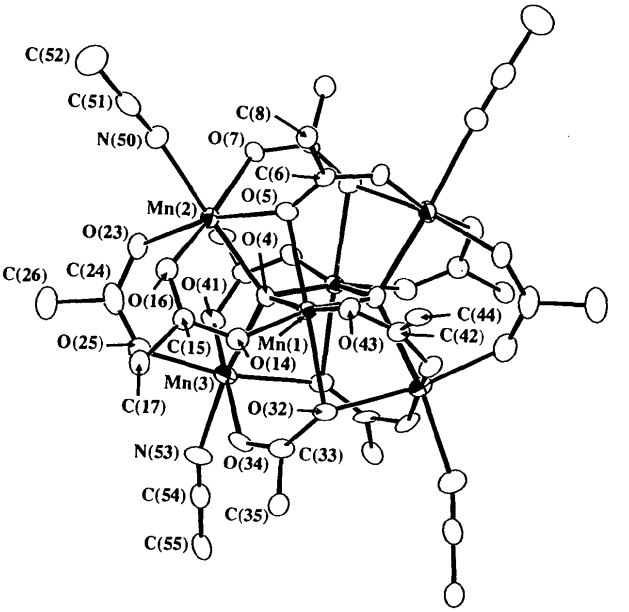


Fig. 2. An *ORTEP* (Johnson, 1965) representation of (2) showing 50% probability ellipsoids. For clarity, only the *ipso* C atoms of the benzoate phenyl groups are shown.

Experimental

Complex (1) was prepared by the reaction of $Mn(O_2CCH_3)_2.4H_2O$ with C_5H_5N, 3,5-$(NO_2)_2$-$C_6H_3CO_2H$ and $^nBu_4MnO_4$ in C_2H_5OH; crystals were grown from acetone/ether. Compound (2) was prepared by the reaction of $Ph_4P[Mn_4O_2(O_2CPh)_9(OH_2)]$ with $Na(2\text{-}Me_2N\text{-}C_6H_4CO_2)$ in MeCN at 263 K.

Compound (1)

Crystal data

$[Mn_6O_2(C_7H_3N_2O_6)_{10}(C_5H_5N)_2(C_3H_6O)_2].2C_3H_6O.2C_4H_{10}O$
$M_r = 3011.50$
Monoclinic
$C2/c$
$a = 23.512\,(4)$ Å
$b = 23.861\,(4)$ Å
$c = 22.417\,(4)$ Å
$\beta = 103.16\,(1)°$
$V = 12246\,(3)$ Å^3
$Z = 4$
$D_x = 1.633$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 58 reflections
$\theta = 9$–$14.5°$
$\mu = 0.687$ mm^{-1}
$T = 120$ K
Irregular, approximately equidimensional
0.24 × 0.24 × 0.24 mm
Dark orange

Data collection

Picker four-circle diffractometer
θ–2θ scans
Absorption correction: none
10 025 measured reflections
8032 independent reflections
6200 observed reflections $[F > 3\sigma(F)]$
$R_{int} = 0.035$
$\theta_{max} = 22.5°$
$h = 0 \rightarrow 25$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 23$
4 standard reflections monitored every 300 reflections
intensity decay: insignificant

Refinement

Refinement on F
$R = 0.0685$
$wR = 0.0666$
$S = 1.415$
6200 reflections
889 parameters
Only H-atom B's refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.048$
$\Delta\rho_{max} = 1.0$ e Å^{-3}
$\Delta\rho_{min} = -0.5$ e Å^{-3}
Extinction correction: secondary, isotropic
Extinction coefficient: 6.2×10^{-10}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

Atoms Mn(1) to C(89) correspond to the molecule of interest. Atoms O(90) to C(92) form a molecule of acetone lying across a crystallographic twofold axis, C(93) to C(97) a molecule of diethyl ether on a general position and C(98) to C(101) a disordered molecule of unknown solvent.

	x	y	z	B_{eq}
Mn(1)	1.03390 (4)	0.22125 (4)	0.30982 (4)	1.91 (3)
Mn(2)	1.09508 (5)	0.14326 (4)	0.22604 (5)	2.28 (3)
Mn(3)	1.07740 (4)	0.30021 (4)	0.19703 (4)	2.06 (3)
O(4)	1.0457 (2)	0.2212 (2)	0.2291 (2)	2.0 (1)
O(5)	1.0496 (2)	0.1302 (2)	0.3065 (2)	2.1 (2)
C(6)	1.0251 (3)	0.0958 (3)	0.3355 (3)	2.5 (3)
O(7)	1.0283 (2)	0.0949 (2)	0.1659 (2)	3.0 (2)
C(8)	1.0645 (3)	0.0548 (3)	0.3760 (3)	2.6 (3)
C(9)	1.0416 (3)	0.0152 (3)	0.4094 (3)	3.1 (3)
C(10)	1.0795 (4)	−0.0208 (3)	0.4480 (3)	3.3 (3)
C(11)	1.1388 (4)	−0.0190 (3)	0.4553 (3)	3.3 (3)
C(12)	1.1599 (3)	0.0210 (3)	0.4217 (3)	2.8 (3)
C(13)	1.1250 (3)	0.0576 (3)	0.3827 (3)	2.7 (3)
N(14)	1.0547 (3)	−0.0622 (3)	0.4844 (3)	4.4 (3)
O(15)	1.0025 (3)	−0.0597 (2)	0.4822 (3)	5.0 (3)
O(16)	1.0877 (3)	−0.0965 (3)	0.5138 (3)	6.0 (3)
N(17)	1.2238 (3)	0.0257 (3)	0.4287 (3)	3.7 (3)
O(18)	1.2548 (2)	−0.0002 (2)	0.4711 (3)	4.5 (2)
O(19)	1.2421 (2)	0.0563 (2)	0.3935 (3)	4.3 (2)
O(20)	1.1164 (2)	0.2343 (2)	0.3480 (2)	2.3 (2)
C(21)	1.1618 (3)	0.2098 (3)	0.3396 (3)	2.0 (2)
O(22)	1.1635 (2)	0.1712 (2)	0.3026 (2)	2.7 (2)
C(23)	1.2179 (3)	0.2292 (3)	0.3796 (3)	2.4 (3)
C(24)	1.2209 (3)	0.2801 (3)	0.4094 (3)	2.8 (3)
C(25)	1.2725 (3)	0.2952 (3)	0.4496 (3)	3.0 (3)
C(26)	1.3197 (3)	0.2614 (4)	0.4623 (4)	3.8 (3)
C(27)	1.3166 (3)	0.2107 (3)	0.4313 (3)	3.3 (3)
C(28)	1.2664 (3)	0.1944 (3)	0.3905 (3)	3.1 (3)
N(29)	1.2753 (3)	0.3494 (3)	0.4816 (3)	4.2 (3)
O(30)	1.2342 (3)	0.3807 (3)	0.4681 (3)	6.3 (3)
O(31)	1.3186 (3)	0.3583 (3)	0.5228 (3)	5.4 (3)
N(32)	1.3672 (3)	0.1737 (3)	0.4425 (3)	4.3 (3)
O(33)	1.4105 (3)	0.1880 (3)	0.4807 (4)	6.6 (3)
O(34)	1.3642 (3)	0.1301 (3)	0.4149 (3)	6.7 (3)
O(35)	1.0210 (2)	0.2106 (2)	0.3928 (2)	2.5 (1)
C(36)	0.9865 (3)	0.2355 (3)	0.4202 (3)	2.5 (2)
O(37)	1.0526 (2)	0.2692 (2)	0.1025 (2)	2.4 (1)
C(38)	0.9960 (3)	0.2221 (3)	0.4875 (3)	2.6 (2)
C(39)	0.9685 (3)	0.2539 (3)	0.5243 (3)	3.1 (2)
C(40)	0.9791 (4)	0.2416 (4)	0.5864 (3)	3.9 (3)
C(41)	1.0151 (4)	0.1980 (4)	0.6118 (4)	5.3 (3)
C(42)	1.0416 (4)	0.1679 (4)	0.5736 (4)	4.3 (3)
C(43)	1.0339 (3)	0.1803 (3)	0.5126 (3)	3.3 (3)
N(44)	0.9521 (4)	0.2756 (3)	0.6266 (3)	5.2 (3)
O(45)	0.9186 (3)	0.3134 (3)	0.6036 (3)	5.4 (2)
O(46)	0.9644 (4)	0.2649 (4)	0.6813 (3)	9.9 (4)
N(47)	1.0805 (4)	0.1212 (4)	0.5990 (4)	6.2 (3)
O(48)	1.0709 (4)	0.0963 (3)	0.6452 (3)	7.8 (3)
O(49)	1.1198 (3)	0.1078 (3)	0.5743 (3)	6.4 (3)
O(50)	1.1458 (2)	0.1762 (2)	0.1668 (2)	2.8 (2)
C(51)	1.1710 (3)	0.2234 (3)	0.1722 (3)	2.8 (2)
O(52)	1.1601 (2)	0.2646 (2)	0.2024 (2)	2.6 (2)
C(53)	1.2178 (3)	0.2327 (3)	0.1371 (3)	2.8 (2)
C(54)	1.2514 (3)	0.2811 (3)	0.1458 (4)	3.4 (3)
C(55)	1.2945 (3)	0.2882 (3)	0.1139 (4)	3.5 (3)
C(56)	1.3057 (3)	0.2502 (3)	0.0722 (4)	3.6 (3)
C(57)	1.2706 (3)	0.2027 (3)	0.0636 (3)	3.4 (3)
C(58)	1.2269 (3)	0.1924 (3)	0.0950 (3)	3.2 (3)
N(59)	1.3299 (3)	0.3407 (3)	0.1237 (4)	5.1 (3)
O(60)	1.3138 (3)	0.3781 (3)	0.1527 (3)	5.9 (3)
O(61)	1.3722 (3)	0.3432 (3)	0.0995 (3)	5.9 (3)
N(62)	1.2772 (3)	0.1642 (3)	0.0147 (3)	3.5 (2)
O(63)	1.3174 (2)	0.1736 (2)	−0.0107 (3)	4.3 (2)
O(64)	1.2422 (3)	0.1271 (2)	0.0002 (3)	4.3 (2)
O(65)	0.9797 (2)	0.3129 (2)	0.1799 (2)	2.1 (1)
C(66)	0.9387 (3)	0.3469 (3)	0.1800 (3)	2.0 (2)
O(67)	1.0935 (2)	0.3462 (2)	0.2827 (2)	2.6 (1)
C(68)	0.9278 (3)	0.3924 (3)	0.1318 (3)	2.3 (2)
C(69)	0.9584 (3)	0.3908 (3)	0.0856 (3)	2.4 (2)
C(70)	0.9476 (3)	0.4336 (3)	0.0424 (3)	2.9 (2)
C(71)	0.9106 (3)	0.4770 (3)	0.0438 (3)	3.2 (2)
C(72)	0.8815 (3)	0.4772 (3)	0.0907 (4)	3.2 (2)
C(73)	0.8889 (3)	0.4352 (3)	0.1343 (3)	2.9 (2)
N(74)	0.9797 (3)	0.4314 (3)	−0.0075 (3)	3.3 (2)
O(75)	1.0193 (2)	0.3971 (2)	−0.0032 (2)	4.3 (2)
O(76)	0.9649 (2)	0.4648 (2)	−0.0503 (2)	4.1 (2)
N(77)	0.8432 (3)	0.5244 (3)	0.0955 (3)	4.7 (3)
O(78)	0.8466 (3)	0.5665 (2)	0.0665 (3)	5.2 (2)
O(79)	0.8087 (3)	0.5186 (3)	0.1295 (3)	7.2 (3)
N(80)	1.1007 (2)	0.3817 (2)	0.1598 (2)	2.3 (2)
C(81)	1.0907 (3)	0.4316 (3)	0.1830 (3)	3.2 (2)
C(82)	1.1126 (4)	0.4808 (3)	0.1669 (4)	3.7 (2)

C(83)	1.1462 (4)	0.4801 (3)	0.1239 (4)	3.9 (3)
C(84)	1.1566 (3)	0.4294 (3)	0.0994 (4)	3.4 (2)
C(85)	1.1321 (3)	0.3822 (3)	0.1182 (3)	3.1 (2)
O(86)	1.1417 (2)	0.0631 (2)	0.2411 (2)	3.8 (2)
C(87)	1.1643 (4)	0.0302 (4)	0.2103 (4)	4.8 (3)
C(88)	1.1566 (5)	0.0363 (4)	0.1426 (5)	5.7 (3)
C(89)	1.2008 (5)	−0.0196 (4)	0.2390 (5)	6.5 (4)
O(90)	1	0.5021 (5)	1/4	6.0 (5)
C(91)	1	0.5513 (6)	1/4	3.2 (5)
C(92)	0.9859 (7)	0.5806 (7)	0.1927 (7)	6.8 (5)
C(93)	0.7052 (6)	0.1108 (6)	0.2502 (6)	5.0 (4)
C(94)	0.6615 (6)	0.1543 (6)	0.2506 (6)	5.2 (5)
O(95)	0.6775 (3)	0.2025 (4)	0.2254 (4)	4.8 (3)
C(96)	0.6422 (6)	0.2475 (7)	0.2262 (6)	6.1 (5)
C(97)	0.6653 (7)	0.2993 (7)	0.2027 (5)	6.4 (5)
C(98)	1	0.0436 (15)	−1/4	6.9 (7)
C(99)	1.0522 (10)	0.0653 (10)	−0.2215 (11)	6.8 (5)
C(100)	1.0260 (11)	0.1005 (13)	−0.2337 (13)	8.3 (7)
C(101)	1.0397 (11)	0.1431 (12)	−0.2341 (12)	8.1 (6)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

Mn(1)—Mn(1^i)	2.790 (2)	Mn(2)—O(4)	2.203 (4)
Mn(1)—Mn(2)	3.208 (1)	Mn(2)—O(5)	2.319 (4)
Mn(1)—Mn(3^i)	3.200 (2)	Mn(2)—O(7)	2.156 (5)
Mn(1)—Mn(2^i)	3.492 (2)	Mn(2)—O(22)	2.173 (5)
Mn(1)—Mn(3)	3.488 (1)	Mn(2)—O(50)	2.127 (5)
Mn(2)—Mn(3)	3.808 (1)	Mn(2)—O(86)	2.192 (5)
Mn(1)—O(4^i)	1.875 (4)	Mn(3)—O(4)	2.206 (4)
Mn(1)—O(4)	1.892 (4)	Mn(3)—O(37)	2.196 (4)
Mn(1)—O(5)	2.209 (4)	Mn(3)—O(52)	2.099 (4)
Mn(1)—O(20)	1.958 (4)	Mn(3)—O(65)	2.262 (4)
Mn(1)—O(35)	1.968 (4)	Mn(3)—O(67)	2.169 (4)
Mn(1)—O(65^i)	2.231 (4)	Mn(3)—N(80)	2.232 (5)
O(4)—Mn(1)—O(4^i)	84.43 (19)	O(4)—Mn(3)—N(80)	174.53 (19)
O(4^i)—Mn(1)—O(5)	98.10 (17)	O(37)—Mn(3)—O(52)	87.60 (17)
O(4)—Mn(1)—O(5)	84.62 (17)	O(37)—Mn(3)—O(65)	81.06 (16)
O(4^i)—Mn(1)—O(20)	170.75 (19)	O(37)—Mn(3)—O(67)	168.53 (18)
O(4)—Mn(1)—O(20)	94.12 (19)	O(37)—Mn(3)—N(80)	88.10 (18)
O(4^i)—Mn(1)—O(35)	95.04 (19)	O(52)—Mn(3)—O(65)	162.84 (17)
O(4)—Mn(1)—O(35)	172.54 (19)	O(52)—Mn(3)—O(67)	100.46 (18)
O(4^i)—Mn(1)—O(65^i)	84.11 (17)	O(52)—Mn(3)—N(80)	94.03 (19)
O(4)—Mn(1)—O(65^i)	98.90 (17)	O(65)—Mn(3)—O(67)	92.76 (17)
O(5)—Mn(1)—O(20)	90.84 (17)	O(65)—Mn(3)—N(80)	98.40 (18)
O(5)—Mn(1)—O(35)	88.10 (17)	O(67)—Mn(3)—N(80)	83.23 (18)
O(5)—Mn(1)—O(65^i)	176.04 (16)	Mn(1)—O(4)—Mn(1^i)	95.57 (19)
O(20)—Mn(1)—O(35)	87.58 (19)	Mn(1^i)—O(4)—Mn(2)	117.59 (21)
O(20)—Mn(1)—O(65^i)	87.11 (17)	Mn(1)—O(4)—Mn(2)	102.88 (19)
O(35)—Mn(1)—O(65^i)	88.43 (17)	Mn(1^i)—O(4)—Mn(3)	102.94 (19)
O(4)—Mn(2)—O(5)	75.51 (15)	Mn(1)—O(4)—Mn(3)	116.44 (20)
O(4)—Mn(2)—O(7)	99.08 (17)	Mn(2)—O(4)—Mn(3)	119.43 (19)
O(4)—Mn(2)—O(22)	90.97 (17)	Mn(1)—O(5)—Mn(2)	90.19 (16)
O(4)—Mn(2)—O(50)	94.68 (17)	Mn(1)—O(5)—C(6)	121.5 (4)
O(4)—Mn(2)—O(86)	168.78 (18)	Mn(2)—O(5)—C(6)	146.3 (4)
O(5)—Mn(2)—O(7)	90.91 (17)	Mn(2)—O(7)—C(6^i)	126.2 (4)
O(5)—Mn(2)—O(22)	79.41 (17)	Mn(1)—O(20)—C(21)	130.2 (4)
O(5)—Mn(2)—O(50)	163.54 (17)	Mn(2)—O(22)—C(21)	128.5 (4)
O(5)—Mn(2)—O(86)	93.74 (18)	Mn(1)—O(35)—C(36)	130.4 (4)
O(7)—Mn(2)—O(22)	163.91 (19)	Mn(3)—O(37)—C(36^i)	128.6 (4)
O(7)—Mn(2)—O(50)	103.84 (18)	Mn(2)—O(50)—C(51)	126.0 (4)
O(7)—Mn(2)—O(86)	84.06 (19)	Mn(3)—O(52)—C(51)	126.0 (5)
O(22)—Mn(2)—O(50)	87.71 (18)	Mn(1^i)—O(65)—Mn(3)	90.82 (16)
O(22)—Mn(2)—O(86)	83.79 (19)	Mn(1^i)—O(65)—C(66)	120.2 (4)
O(50)—Mn(2)—O(86)	95.02 (20)	Mn(3)—O(65)—C(66)	146.5 (4)
O(4)—Mn(3)—O(37)	89.50 (16)	Mn(3)—O(67)—C(66^i)	126.1 (4)
O(4)—Mn(3)—O(52)	90.78 (17)	Mn(2)—O(86)—C(87)	136.7 (6)
O(4)—Mn(3)—O(65)	76.37 (16)	Mn(3)—N(80)—C(81)	123.2 (4)
O(4)—Mn(3)—O(67)	98.48 (16)	Mn(3)—N(80)—C(85)	119.9 (5)

Symmetry code: (i) $2-x, y, \frac{1}{2}-z$.

Compound (2)

Crystal data

$[Mn_6O_2(C_7H_5O_2)_{10}(C_2H_3N)_4]$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
$M_r = 1736.99$
Orthorhombic
Pbna
$a = 18.441$ (3) Å
$b = 24.561$ (4) Å
$c = 17.497$ (3) Å
$V = 7924$ (2) Å^3
$Z = 4$
$D_x = 1.456$ Mg m^{-3}

Cell parameters from 84 reflections
$\theta = 8.5$–15°
$\mu = 0.962$ mm^{-1}
$T = 103$ K
Needle
0.34 × 0.20 × 0.16 mm
Orange–brown

Data collection

Picker four-circle diffractometer
θ–2θ scans
Absorption correction: none
7929 measured reflections
5162 independent reflections
3425 observed reflections $[F > 3\sigma(F)]$
$R_{int} = 0.069$

$\theta_{max} = 22.5°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 18$
4 standard reflections monitored every 300 reflections
intensity decay: insignificant

Refinement

Refinement on F
$R = 0.075$
$wR = 0.064$
$S = 1.072$
3425 reflections
491 parameters
Only H-atom B's refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 0.76$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2)

B_{iso} for C(42), $B_{eq} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	B_{iso}/B_{eq}
Mn(1)	0.3780 (1)	0.1933 (1)	0.0105 (1)	1.42 (4)
Mn(2)	0.4778 (1)	0.2426 (1)	0.1370 (1)	1.79 (4)
Mn(3)	0.2794 (1)	0.2826 (1)	0.1320 (1)	1.64 (4)
O(4)	0.3775 (3)	0.2571 (2)	0.0716 (3)	1.7 (2)
O(5)	0.4976 (3)	0.1885 (3)	0.0339 (3)	1.8 (2)
C(6)	0.5400 (5)	0.1758 (4)	−0.0203 (6)	2.0 (3)
O(7)	0.5396 (3)	0.3053 (3)	0.0858 (4)	2.0 (2)
C(8)	0.5953 (5)	0.1316 (4)	−0.0036 (6)	2.2 (3)
C(9)	0.6470 (6)	0.1192 (5)	−0.0588 (6)	3.5 (4)
C(10)	0.6967 (6)	0.0765 (5)	−0.0471 (7)	3.8 (4)
C(11)	0.6927 (6)	0.0473 (4)	0.0194 (7)	3.7 (4)
C(12)	0.6417 (6)	0.0599 (4)	0.0747 (7)	3.0 (3)
C(13)	0.5928 (5)	0.1026 (4)	0.0638 (6)	2.0 (3)
O(14)	0.3596 (3)	0.1422 (3)	0.0951 (4)	1.9 (2)
C(15)	0.3848 (5)	0.1408 (4)	0.1620 (5)	1.8 (3)
O(16)	0.4328 (3)	0.1701 (2)	0.1895 (3)	1.8 (2)
C(17)	0.3535 (5)	0.0975 (4)	0.2122 (6)	2.0 (3)
C(18)	0.3108 (5)	0.0563 (4)	0.1831 (6)	2.4 (3)
C(19)	0.2832 (6)	0.0148 (4)	0.2307 (7)	3.3 (4)
C(20)	0.2969 (6)	0.0180 (4)	0.3089 (6)	3.2 (3)
C(21)	0.3373 (5)	0.0594 (4)	0.3388 (6)	2.5 (3)
C(22)	0.3656 (5)	0.0996 (4)	0.2905 (6)	1.9 (3)
O(23)	0.4399 (4)	0.2869 (3)	0.2303 (4)	2.6 (2)
C(24)	0.3820 (6)	0.2797 (4)	0.2677 (5)	2.4 (3)
O(25)	0.3221 (4)	0.2636 (3)	0.2414 (3)	2.3 (2)
C(26)	0.3860 (6)	0.2944 (4)	0.3505 (6)	3.2 (3)
C(27)	0.4527 (7)	0.2993 (5)	0.3874 (7)	4.3 (4)
C(28)	0.4589 (8)	0.3130 (7)	0.4619 (8)	6.0 (5)
C(29)	0.3974 (10)	0.3206 (6)	0.5027 (7)	6.3 (6)

C(30)	0.3314 (9)	0.3192 (6)	0.4714 (7)	6.4 (6)
C(31)	0.3225 (8)	0.3031 (6)	0.3914 (7)	5.0 (4)
O(32)	0.2590 (3)	0.1861 (2)	−0.0103 (4)	1.7 (2)
C(33)	0.2155 (5)	0.1830 (4)	0.0450 (5)	1.6 (3)
O(34)	0.2180 (3)	0.2122 (2)	0.1050 (3)	1.8 (2)
C(35)	0.1559 (5)	0.1417 (4)	0.0432 (5)	1.8 (3)
C(36)	0.1556 (5)	0.1018 (4)	−0.0144 (6)	2.4 (3)
C(37)	0.1003 (6)	0.0634 (5)	−0.0152 (7)	4.0 (4)
C(38)	0.0474 (7)	0.0640 (5)	0.0412 (7)	4.1 (4)
C(39)	0.0482 (6)	0.1018 (4)	0.0964 (7)	2.9 (3)
C(40)	0.1024 (5)	0.1409 (4)	0.0980 (6)	2.2 (3)
O(41)	0.3202 (3)	0.3635 (2)	0.1505 (4)	2.1 (2)
C(42)	0.3735 (5)	0.1160 (4)	−0.1189 (5)	1.8 (2)
O(43)	0.3984 (3)	0.1298 (2)	−0.0533 (4)	1.7 (2)
C(44)	0.4140 (5)	0.0706 (3)	−0.1567 (5)	1.7 (3)
C(45)	0.3944 (5)	0.0544 (4)	−0.2287 (5)	2.0 (3)
C(46)	0.4303 (6)	0.0125 (5)	−0.2651 (6)	3.4 (3)
C(47)	0.4868 (6)	−0.0135 (5)	−0.2273 (7)	4.0 (4)
C(48)	0.5071 (6)	0.0031 (4)	−0.1560 (6)	2.8 (3)
C(49)	0.4714 (5)	0.0446 (4)	−0.1196 (6)	2.5 (3)
N(50)	0.5833 (4)	0.2167 (3)	0.1906 (5)	2.6 (3)
C(51)	0.6375 (6)	0.1964 (4)	0.1999 (6)	2.3 (3)
C(52)	0.7057 (6)	0.1700 (5)	0.2133 (6)	3.1 (3)
N(53)	0.1755 (4)	0.3174 (3)	0.1835 (5)	2.4 (3)
C(54)	0.1299 (6)	0.3429 (4)	0.2083 (6)	2.3 (3)
C(55)	0.0705 (6)	0.3757 (4)	0.2393 (7)	3.7 (4)

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

Mn(1)—Mn(1^{i})	2.807 (3)	Mn(2)—O(4)	2.203 (6)
Mn(1)—Mn(2)	3.122 (3)	Mn(2)—O(5)	2.271 (6)
Mn(1)—Mn(3^{i})	3.142 (3)	Mn(2)—O(7)	2.115 (6)
Mn(1)—Mn(2^{i})	3.538 (3)	Mn(2)—O(16)	2.169 (6)
Mn(1)—Mn(3)	3.554 (3)	Mn(2)—O(23)	2.082 (7)
Mn(2)—Mn(3)	3.789 (3)	Mn(2)—N(50)	2.252 (9)
Mn(1)—O(4^{i})	1.883 (6)	Mn(3)—O(4)	2.187 (6)
Mn(1)—O(4)	1.895 (6)	Mn(3)—O(25)	2.122 (6)
Mn(1)—O(5)	2.246 (6)	Mn(3)—O(32^{i})	2.294 (6)
Mn(1)—O(14)	1.970 (6)	Mn(3)—O(34)	2.120 (6)
Mn(1)—O(32)	2.232 (6)	Mn(3)—O(41)	2.148 (6)
Mn(1)—O(43)	1.955 (6)	Mn(3)—N(53)	2.283 (8)
O(4^{i})—Mn(1)—O(4)	84.04 (26)	O(4)—Mn(3)—N(53)	172.88 (27)
O(4^{i})—Mn(1)—O(5)	100.27 (25)	O(25)—Mn(3)—O(32^{i})	166.33 (23)
O(4)—Mn(1)—O(5)	86.92 (25)	O(25)—Mn(3)—O(34)	102.68 (24)
O(4^{i})—Mn(1)—O(14)	169.76 (27)	O(25)—Mn(3)—O(41)	86.46 (25)
O(4)—Mn(1)—O(14)	95.85 (26)	O(25)—Mn(3)—N(53)	92.13 (27)
O(4^{i})—Mn(1)—O(32)	85.53 (24)	O(32^{i})—Mn(3)—O(34)	88.79 (22)
O(4)—Mn(1)—O(32)	98.78 (25)	O(32^{i})—Mn(3)—O(41)	83.56 (23)
O(4^{i})—Mn(1)—O(43)	94.65 (26)	O(32^{i})—Mn(3)—N(53)	95.97 (25)
O(4)—Mn(1)—O(43)	169.16 (26)	O(34)—Mn(3)—O(41)	167.06 (25)
O(5)—Mn(1)—O(14)	89.94 (24)	O(34)—Mn(3)—N(53)	86.81 (26)
O(5)—Mn(1)—O(32)	172.31 (23)	O(41)—Mn(3)—N(53)	83.64 (27)
O(5)—Mn(1)—O(43)	82.72 (24)	Mn(1)—O(4)—Mn(1^{i})	95.96 (26)
O(14)—Mn(1)—O(32)	84.38 (24)	Mn(1^{i})—O(4)—Mn(2)	119.7 (3)
O(14)—Mn(1)—O(43)	87.35 (26)	Mn(1)—O(4)—Mn(2)	98.96 (26)
O(32)—Mn(1)—O(43)	91.83 (24)	Mn(1^{i})—O(4)—Mn(3)	100.78 (27)
O(4)—Mn(2)—O(5)	79.43 (22)	Mn(1)—O(4)—Mn(3)	120.9 (3)
O(4)—Mn(2)—O(7)	96.60 (23)	Mn(2)—O(4)—Mn(3)	119.30 (26)
O(4)—Mn(2)—O(16)	91.79 (22)	Mn(1)—O(5)—Mn(2)	87.45 (22)
O(4)—Mn(2)—O(23)	92.37 (25)	Mn(1)—O(5)—C(6)	118.9 (6)
O(4)—Mn(2)—N(50)	170.74 (28)	Mn(2)—O(5)—C(6)	146.8 (6)
O(5)—Mn(2)—O(7)	90.15 (24)	Mn(2)—O(7)—C(6^{i})	132.0 (6)
O(5)—Mn(2)—O(16)	85.24 (23)	Mn(1)—O(14)—C(15)	130.7 (6)
O(5)—Mn(2)—O(23)	169.30 (25)	Mn(2)—O(16)—C(15)	125.9 (6)
O(5)—Mn(2)—N(50)	91.51 (27)	Mn(2)—O(23)—C(24)	128.1 (6)
O(7)—Mn(2)—O(16)	169.54 (24)	Mn(3)—O(25)—C(24)	125.8 (6)
O(7)—Mn(2)—O(23)	97.66 (26)	Mn(1)—O(32)—Mn(3^{i})	87.91 (21)
O(7)—Mn(2)—N(50)	85.22 (26)	Mn(1)—O(32)—C(33)	120.4 (5)
O(16)—Mn(2)—O(23)	88.18 (25)	Mn(3^{i})—O(32)—C(33)	146.9 (6)
O(16)—Mn(2)—N(50)	85.52 (26)	Mn(3)—O(34)—C(33)	131.5 (6)
O(23)—Mn(2)—N(50)	96.4 (3)	Mn(3)—O(41)—C(42^{i})	126.1 (6)
O(4)—Mn(3)—O(25)	93.77 (24)	Mn(1)—O(43)—C(42)	130.9 (6)
O(4)—Mn(3)—O(32^{i})	77.48 (21)	Mn(2)—N(50)—C(51)	161.8 (8)
O(4)—Mn(3)—O(34)	95.75 (23)	Mn(3)—N(53)—C(54)	168.3 (8)
O(4)—Mn(3)—O(41)	92.77 (23)		

Symmetry code: (i) $x, \frac{1}{2} - y, -z$.

Procedures employed by the Molecular Structure Center for data collection and structure solution and refinement have been described elsewhere (Chisholm, Folting, Huffman & Kirkpatrick, 1984). The structures were solved by direct methods and refined using difference Fourier techniques. Anisotropic displacement parameters were refined for all non-disordered non-H atoms [except C(42) in structure (2), which was refined isotropically] while H atoms were included in calculated positions with freely refining B_{iso}. Figures were generated using *ORTEP* (Johnson, 1965).

In addition to the molecule of interest, structure (1) was found to contain a well ordered molecule of acetone lying on a crystallographic twofold axis, and a well ordered molecule of Et_2O at a general position. At a different twofold axis, a number of peaks were observed that could not be positively identified: these were refined as C atoms (site occupancy 0.5), and for the purposes of the density calculations this region of the structure was assumed to represent a disordered molecule of acetone. Structure (2) contained no occluded solvent molecules. High displacement parameters on some benzoate aromatic C atoms of structure (2), notably C(27)–C(31), may be indicative of orientational disorder in these groups, thus accounting for the slightly high R value associated with this structure. This was not modelled, however, because of the relatively low ratio of the number of refined parameters to observed reflections in this refinement.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1000). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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