Discussion. The refined atomic coordinates and equivalent isotropic thermal parameters of the non-H atoms are given in Table 1.* Distances and bond angles are listed in Table 2. The crystals are isostructural to those of $[N(CH_3)_4]_2SnCl_6$ determined by Berg & Sotofte (1978). The Re, N and Cl atoms occupy special positions in the crystal. A stereoview of the crystal packing is shown in Fig. 1. The shortest Re···Re interatomic distances are 9.023 (2) Å (12 neighbours) and 12.760 (2) Å (6 neighbours). These fall between the comparable distances for $[N(C_2H_6)_4]_2ReCl_6$ and the alkali-metal salts K_2ReCl_6 and Cs_2ReCl_6 (Grundy & Brown, 1970; Bettinelli, Di Sipio, Valle, Aschieri & Ingletto, 1989). The Cl atoms occupy octahedral positions around the central Re atom, the Cl—Re—Cl angles being exactly 90°. In all other hexachlororhenates, although crystallographically significant, these angles only marginally deviate from 90°. The Re—Cl distance of 2.360 (2) Å also correlates well with other literature values.

The high temperature factors of the tetramethylammonium counterion indicate a thermal rigid-body motion around the central N atom similar to that reported for $[N(CH_3)_4]_2SnCl_6$ by Nielsen & Berg (1980). The reason for this rotational disorder compared with the other ammonium salts of hexachlororhenate may be due to a lack of hydrogen-bonding potential between the Cl atoms and the counterion.

This work was supported by the VLAB Biotechnology project of the VRWB. RL received financial support from the IWONL. DM is a research associate of the NFWO. The authors also acknowledge the receipt of NATO grant No. 900270.

References

Bagnall, K. W., Brown, D. & Coolton, R. (1964). *J. Chem. Soc.* **7**, 3017.

Berg, R. W. & Sotofte, I. (1978). *Acta Chem. Scand. Ser. A*, **32**, 241–244.

Bettinelli, M., Di Sipio, L., Valle, G., Aschieri, C. & Ingletto G. (1989). *Z. Kristallogr.* **188**, 155–160.

Bettinelli, M., Flint, C. D. & Ingletto, G. (1991). *J. Mater. Chem.* **1**, 437.

Drück, U. (1972). Diplomarbeit. Philipps-Univ. Marburg, Germany.

Grundy, H. D. & Brown, I. D. (1970). *Can. J. Chem.* **48**, 1151–1154.

Jones, T. A. (1985). *Methods Enzymol.* **115**, 157–171.

Nielsen, K. & Berg, R. W. (1980). *Acta Chem. Scand. Ser. A*, **34**, 153–154.

Roberts, P. & Sheldrick, G. M. (1979). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sperka, G. & Mautner, F. (1988). *Cryst. Res. Technol.* **23**, K109–K111.

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55444 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1000]

Acta Cryst. (1993). C**49**, 233–236

Structure of Hexa-μ-acetato-1κ^3O:2κ^3O';2κ^3O:3κ^3O'-bis(1,10-phenanthroline)-1κ^2N^1,N^{10};2κ^2N^1,N^{10}-trimanganese(II)

By Kazuhiko Tsuneyoshi

Taniguchi Ink Manufacturing Company Limited, 3950-3 *Uchimoriya-cho*, *Mitsukaido-shi*, *Ibaraki* 303, *Japan*

and Hidesaburo Kobayashi and Hiroshi Miyamae*

Department of Chemistry, *Faculty of Science*, *Josai University*, *Keyakidai*, *Sakado-shi*, *Saitama* 350-02, *Japan*

(*Received* 28 *October* 1991; *accepted* 15 *June* 1992)

Abstract. $[Mn_3(C_2H_3O_2)_6(C_{12}H_8N_2)_2]$, $M_r = 879.5$, monoclinic, $A2/a$, $a = 26.414$ (3), $b = 12.433$ (2), $c = 11.410$ (2) Å, $\beta = 98.63$ (2)°, $V = 3704.7$ (10) Å^3, $Z = 4$, $D_m = 1.576$, $D_x = 1.576$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.032$ mm^{-1}, $F(000) = 1796$, $T = 298$ K, $R = 0.073$ and $wR = 0.063$ for 2142 observed reflections. In the linear trinuclear compound, one of the Mn atoms is on the twofold axis and is coordinated by six O atoms of the acetate ions with an average Mn—O distance of 2.131 (8) Å. The other

---

* To whom correspondence should be addressed.

0108-2701/93/020233-04$06.00

two Mn atoms have N_2O_3 distorted tetragonal pyramidal coordination with one N atom at the axial position, having an average Mn—N distance of 2.269 (6) Å and Mn—O distances in the range 2.181 (5) to 2.353 (6) Å.

Introduction. Manganese(II) carboxylate chemistry was widely developed by Christou and his co-workers in the last decade (Christou, 1989, and references therein). They examined mainly the biological relevance of this chemistry at the water oxidation/oxygen evolution center in the photosynthetic process of green plants and cyanobacteria. They were interested in the $[Mn_3O]$ complex because of its potential as a mixed-valence complex. On the other hand, manganese(II) carboxylate with a long alkyl chain was used as a 'drier' catalyst for paint and ink (Myers, 1962), after treatment with 1,10-phenanthroline (phen). In order to study the catalytic behavior of manganese(II) carboxylate, we prepared a manganese(II) acetate–phen complex.

Experimental. 2 mmol of manganese acetate tetrahydrate was dissolved in 60 ml of ethanol. 2 mmol of 1,10-phenanthroline hydrate (powder) was added to the solution and stirred to make it homogeneous. After allowing the solution to stand for 24 h, yellow plate crystals were grown from the solution. The compound was dissolved in water where its color became brown. D_m by flotation in $CCl_4/CHCl_3$. Analytical data found: C 49.19, H 3.95, N 6.26%; calculated for $C_{36}H_{34}Mn_3N_4O_{12}$: C 49.16, H 3.90, N 6.37%.

A light-yellow crystal with dimensions *ca* 0.3 × 0.1 × 0.1 mm was used for data collection on a Rigaku AFC-5 four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation. θ–2θ scan mode, scan range $(1.0 + 1/2\tan\theta)°$. 6218 reflections ($2\theta \leq 60°$; h −37 to 37, k 0 to 17, l 0 to 16) were measured, of which 5621 were independent. 2142 observed reflections with $|F| \geq 6\sigma(|F|)$ were used for structure determination. Intensities were corrected for Lorentz and polarization effects but not for absorption and extinction. Unit-cell dimensions were obtained from least-squares fit of 25 2θ values ($25 < 2\theta < 29°$). 3 standard reflections measured every 150 measurements showed −5 to 1% fluctuation.

The structure was solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Location of two independent Mn atoms and a phen molecule obtained from E map. All other non-H atoms from successive Fourier maps. H atoms from geometrical calculations. Minimized quantity $\sum w(|F_o| - |F_c|)^2$, $w = 1/[\sigma^2(F_o) + 0.02F_o^2]$. Number of refined parameters 254. Final $R = 0.0725$ and $wR = 0.0632$, $S = 3.3385$, $(\Delta/\sigma)_{\max} < 0.06$ for non-H atoms, max. and min. $\Delta\rho = 0.49$ and -0.59 e Å^{-3}, respectively. Slightly high R value might be connected with the large thermal motion of one acetate ion. Complex neutral atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Structure refinement and characterization were carried out using the *UNICSIII* program system (Sakurai & Kobayashi, 1979) on a FACOM M-360 computer at Josai University. The final atomic coordinates with e.s.d.'s for non-H atoms are listed in Table 1* and the atomic numbering scheme is shown in Fig. 1.

Discussion. The structure of the compound is depicted in Fig. 1. Bond distances and angles around the Mn atoms are listed in Table 2. The central Mn atom is on a crystallographic twofold axis and is in a regular octahedral coordination (O_6) with an average Mn—O bond distance of 2.131 (8) Å, while the terminal Mn atoms are in a distorted tetragonal pyramid (N_2O_3) with one of the N atoms in the axial position. The bond distances of the two Mn—N bonds are similar, the average being 2.269 (6) Å. However, the Mn2—O2*A* bond distance, which is *cis* with respect to the Mn2—N2 bond, is longer than the other two [average 2.183 (6) Å] by about 0.17 Å. The Mn2—O1*A* distance of 2.508 (9) Å is too long to be included in the coordination sphere. Thus each pair of Mn atoms is bridged by three bidentate μ-acetato ligands. In this structure, heptacoordinated Mn2 has its sixth coordination site directed toward the central Mn1 atom. However, the Mn1···Mn2 distance is 3.394 (1) Å which indicates hardly any Mn···Mn interaction.

Christou and his co-workers produced a similar Mn^{II} trinuclear complex, $[Mn^{II}_3(O_2CC_6H_5)_6(bpy)_2]$ (Christou, 1989; bpy = 2,2′-bipyridine). A linear trinuclear complex, $[Mn^{II}_3(O_2CCH_3)_6(biphme)_2]$ [biphme = methoxybis(1-methylimidazol-2-yl)-phenylmethane], was recently reported by von Rardin, Bino, Poganiuch, Tolman, Liu & Lippard (1990). In this complex, one third of the carboxylato ions are monodentate μ-carboxylates, the others being bidentate. The resulting coordination geometry around the terminal Mn atoms is trigonal bipyramidal with the pseudo-C_3 axes defined by O(monodentate)—Mn—N in the biphme complex. In the title structure, although both O1*A* and O1*B* atoms show large thermal motion, the thermal motion of acetate-*A* is greater in a direction almost

---

* Lists of observed and calculated structure amplitudes, anisotropic thermal parameters for non-H atoms, parameters for H atoms and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55518 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0573]

Table 1. *Atomic coordinates* ($\times 10^5$ *for* Mn, $\times 10^4$ *for* C, O, N) *and equivalent isotropic temperature factors* (Å^2) *for the title compound*

B_{eq} = four thirds of the trace of the orthogonalized B_{ij} tensor.

	x	*y*	*z*	B_{eq}
Mn1	75000	24950 (15)	0	2.75 (4)
Mn2	62321 (3)	25232 (10)	2122 (9)	2.77 (3)
N1	5400 (2)	2452 (5)	469 (4)	2.80 (14)
N2	6031 (2)	4178 (5)	860 (5)	2.78 (16)
C1	5099 (3)	1601 (6)	286 (7)	3.36 (22)
C2	4605 (3)	1570 (6)	557 (7)	3.76 (23)
C3	4416 (2)	2450 (7)	1063 (6)	3.78 (20)
C4	4720 (3)	3375 (6)	1259 (6)	2.96 (20)
C5	4552 (3)	4354 (6)	1757 (7)	3.98 (24)
C6	4856 (3)	5226 (6)	1925 (6)	3.65 (23)
C7	5370 (3)	5211 (6)	1634 (6)	3.21 (21)
C8	5704 (3)	6088 (6)	1789 (6)	3.69 (23)
C9	6181 (3)	6004 (6)	1476 (6)	3.76 (24)
C10	6330 (3)	5038 (6)	1020 (6)	3.67 (23)
C11	5552 (2)	4261 (5)	1161 (5)	2.44 (18)
C12	5223 (2)	3342 (5)	951 (6)	2.51 (18)
O1*B*	6985 (3)	1279 (5)	−728 (7)	9.24 (28)
O2*B*	6231 (2)	834 (5)	−313 (5)	5.35 (19)
C1*B*	6645 (3)	607 (7)	−648 (7)	4.09 (24)
C2*B*	6752 (3)	−516 (7)	−981 (7)	4.44 (26)
O1*A*	7096 (4)	2536 (6)	1474 (7)	11.75 (36)
O2*A*	6475 (2)	1996 (5)	2198 (5)	5.96 (20)
C1*A*	6930 (3)	2112 (6)	2302 (7)	3.89 (24)
C2*A*	7263 (4)	1773 (8)	3361 (9)	7.97 (38)
O1*C*	6945 (2)	3646 (4)	−801 (5)	6.11 (20)
O2*C*	6169 (2)	3165 (4)	−1583 (4)	3.75 (16)
C1*C*	6595 (3)	3610 (6)	−1660 (6)	3.27 (21)
C2*C*	6655 (4)	4086 (7)	−2814 (8)	5.77 (32)

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

Mn1—O1*B*	2.118 (7)	Mn1—O1*A*	2.124 (9)	Mn1—O1*C*	2.152 (6)
Mn2—O2*B*	2.184 (6)	Mn2—O2*A*	2.353 (6)	Mn2—O2*C*	2.181 (5)
Mn2—N1	2.263 (5)	Mn2—N2	2.275 (6)	Mn2···O1*A*	2.508 (9)
Mn1···Mn2	3.394 (1)				

O1*B*—Mn1—O1*A*	87.6 (3)	O1*B*—Mn1—O1*C*	87.2 (2)
O1*B*—Mn—O1*B*^{i}	88.9 (3)	O1*B*—Mn1—O1*A*^{i}	94.4 (3)
O1*B*—Mn1—O1*C*^{i}	176.1 (2)	O1*A*—Mn1—O1*C*	86.0 (3)
O1*A*—Mn1—O1*A*^{i}	177.2 (3)	O1*A*—Mn1—O1*C*^{i}	92.3 (3)
O1*C*—Mn1—O1*C*^{i}	96.6 (2)	O2*B*—Mn2—O2*A*	89.1 (2)
O2*B*—Mn2—O2*C*	95.6 (2)	O2*B*—Mn2—N1	92.1 (2)
O2*B*—Mn2—N2	165.4 (2)	O2*A*—Mn2—O2*C*	167.8 (2)
O2*A*—Mn2—N1	89.7 (2)	O2*A*—Mn2—N2	89.0 (2)
O2*C*—Mn2—N1	101.4 (2)	O2*C*—Mn2—N2	89.2 (2)
N1—Mn2—N2	73.4 (2)		

Symmetry code: (i) $\frac{3}{2} - x, y, -z$.

parallel to Mn2···Mn1. This might indicate the possibility of bridging and dangling Mn—O distances as the carboxylate ligand moves from the bidentate bridging toward a monodentate bridging scheme which is the opposite of that proposed by von Rardin *et al.* (1990). The Mn2—O2*A* and Mn2—O1*A* distances are much longer than those of the other Mn—O bonds, while all Mn—O bond distances in [$Mn_3(O_2CCH_3)_6(biphme)_2$] are in the range 2.120 (6) to 2.242 (6) Å. The mobility of the carboxylate ligand, which could be controlled by crystal packing, might be the reason that this compound is used as an oxidative polymerization catalyst in the drying of paint and ink.

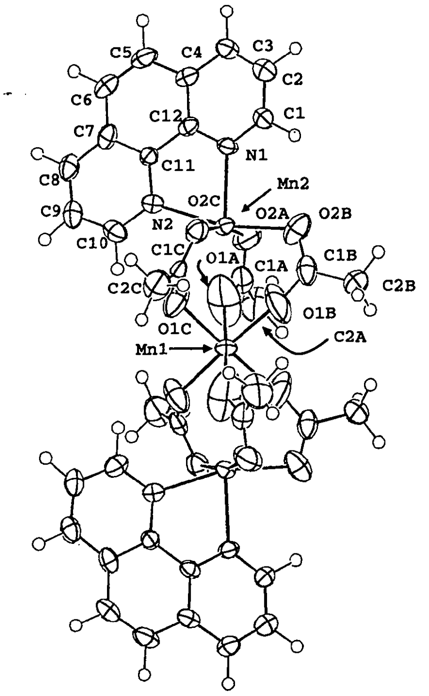

Fig. 1. Molecular structure of [(phen)Mn(μ-acetato)$_3$Mn(μ-acetato)$_3$Mn(phen)]. *ORTEP* (Johnson, 1976) drawing showing 50% probability thermal ellipsoids.

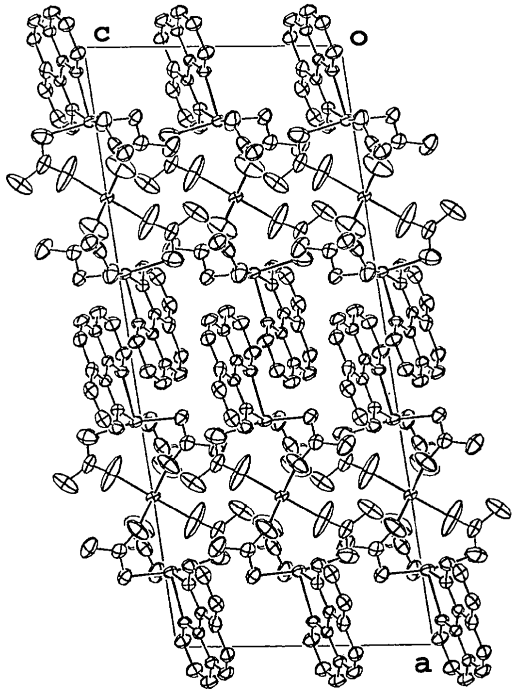

Fig. 2. Crystal packing diagram viewed along **b**.

The packing diagram is shown in Fig. 2. The molecules are packed so that the molecular planes of the phen ligand are almost parallel to the *ab* plane. It is interesting that only the acetate-*A* group, with its molecular plane almost in the *ac* plane and perpendicular to that of the phen molecule, has the greatest degree of mobility among the acetate groups in the crystal. From the thermal ellipsoids of O1*A* and C2*A*, it is apparent that the acetate-*A* group is dangling only within its molecular plane. The other chemically equivalent acetate, acetate-*C*, shows no such thermal motion. The ligand may be fixed in the crystal by the packing mode.

References

Christou, G. (1989). *Acc. Chem. Res.* **22**, 328–335.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Myers, R. R. (1962). *Off. Dig. Fed. Soc. Paint Technol.* **34**, 575.

Rardin, R. L., von, Bino, A., Poganiuch, P., Tolman, W. B., Liu, S. & Lippard, S. J. (1990). *Angew. Chem. Int. Ed. Engl.* **29**, 812–814.

Sakurai, T. & Kobayashi, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–72.

Acta Cryst. (1993). C**49**, 236–238

Structure of Chloro($\alpha,\beta,\gamma,\delta$-tetraphenylporphinato)manganese(III) Toluene Solvate

By Robert S. Armstrong, Garry J. Foran and Trevor W. Hambley*
Department of Inorganic Chemistry, University of Sydney, Sydney 2006, *Australia*

(*Received* 1 *November* 1991; *accepted* 30 *June* 1992)

Abstract. $[Mn(C_{44}H_{28}N_4)Cl].C_7H_8$, $M_r = 795.27$, monoclinic, $P2_1/m$, $a = 9.918$ (2), $b = 15.395$ (3), $c = 13.453$ (2) Å, $\beta = 103.68$ (1)°, $V = 1995.8$ (6) Å^3, $Z = 2$, $D_x = 1.323$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 3.91$ cm^{-1}, $F(000) = 824$, $T = 294$ K, final $R = 0.034$ for 3049 reflections. The manganese complex and the toluene molecule lie on a crystallographic mirror plane. The Mn atom is coordinated by a chloro ligand and a tetraphenylporphinato ligand in an approximate square-pyramidal arrangement with the latter ligand deformed to give a saddle conformation. The Mn—Cl and Mn—N(av.) bond lengths are 2.345 (1) and 2.015 Å, respectively. The toluene molecule lies perpendicular to the plane of the porphinato ligand and makes its closest contacts with pyrrole atoms.

Introduction. Manganese porphyrin complexes have been the subject of much study because of their biological and photochemical importance. During a study of the spectroelectrochemistry of derivatives of Mn^{III} porphyrin complexes, we isolated the title compound and determined its structure. The structure of the complex has been determined previously as the acetone solvate (Tulinsky & Chen, 1977) but the present study is more precise and reveals a number of small but significant differences in the geometry about the Mn atom.

Experimental. A crystal was mounted on a glass fibre with epoxy resin. Data were collected on an Enraf–Nonius CAD-4 automatic diffractometer using graphite-monochromated Mo $K\alpha$ radiation. 25 independent reflections with $2 < 2\theta < 30°$ were used for least-squares determination of cell constants. Intensities of three reflections were monitored, and indicated less than 1.0% decomposition. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least squares using *SHELX*76 (Sheldrick, 1976). Non-H atoms were refined with anisotropic thermal parameters. The positions of H atoms were calculated assuming planar or tetrahedral geometry with a constrained C—H distance of 0.97 Å and their thermal parameters were refined isotropically either individually or in groups. At convergence, all shifts were $<0.1\sigma$. Maximum excursions in a final difference map were 0.2 and -0.2 e Å^{-3}. Data reduction and application of corrections for absorption were carried out using the *Enraf–Nonius SDP-Plus Structure Determination Package* (Frenz, 1985). All other calculations were performed using the program *SHELX*76 (Sheldrick, 1976). A drawing of the title complex was produced using the program *ORTEP* (Johnson, 1965). Scattering factors and anomalous-dispersion terms for Mn (treated as neutral Mn) were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The values supplied in *SHELX*76 were used for all other atoms.

---

* Author to whom correspondence should be addressed.

0108-2701/93/020236-03$06.00