

## METAL-ORGANIC COMPOUNDS

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### Tris(8-quinolinolato-*N,O*)manganese(III) Ethanol Solvate

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#### Abstract

Tris(8-quinolinolato-*N,O*)manganese(III) ethanol solvate,  $[\text{Mn}(\text{C}_9\text{H}_6\text{NO})_3] \cdot \text{C}_2\text{H}_5\text{OH}$ , has distorted *mer*-octahedral coordination about the central Mn atom composed of three N atoms and three O atoms from three 8-quinolinolato ligands. The ethanol solvate molecule is trapped in a cage-like cavity. The three Mn—O bond distances are in the range 1.897 (5)–1.916 (5) Å, while the three Mn—N bond distances range from 2.038 (6) to 2.243 (5) Å.

#### Comment

Extensive investigations have been carried out on the  $^1\text{H}$  NMR spectra, ligand-centered redox processes and EPR spectra of tris(8-quinolinolato)manganese(III) (Philippa, Dennis & Quero, 1987; Silvia, Paul & Donald, 1989; Dexheimer, Gohdes, Chan, Hagen, Armstrong & Klein, 1989), due in part to trivalent manganese being implicated in many redox-active metalloenzymes, including the photosynthetic oxygen-evolving complex superoxide dismutase, pseudocatalase and ribonucleotide reductase (Dexheimer *et al.*, 1989). Also, 8-quinolinol derivatives and complexes with transition metals have additional practical applications (Marguez, Zabala & Romas, 1992; Uma & Krishnamurthi,

1984). Although the synthesis and characterization of the title complex, (I), have been discussed previously (Burns, Cardwell & Catrall, 1971; Philippa *et al.*, 1987), its crystal structure, to our knowledge, has not been reported.

The central Mn atom in (I) is octahedrally coordinated by a meridional arrangement of three N and three O atoms. The octahedron is distorted as a result of the forced configuration of the five-membered chelate ring. The structure is very similar to that of tris(8-quinolinolato)chromium(III) ( $\text{CrQ}_3$ ) (Folting, Cox, Moore & Merritt, 1968) which has cell dimensions very similar to those of (I). Thus, (I) and  $\text{CrQ}_3$  appear to be isomorphous and isostructural. The ethanol molecules do not take part in the coordination, but are trapped in a cage-like cavity – an arrangement also found in the crystal of tris(8-quinolinolato)chromium(III) (Folting *et al.*, 1971). The Mn—O bond distances in (I) [1.912 (4), 1.916 (5) and 1.897 (5) Å] are slightly shorter than those in  $[\text{Mn}(\text{H-Quin})_3][\text{Mn}(\text{H}_2\text{O})_6]$  [2.131 (3)–2.173 (4) Å] ( $\text{H}_2\text{-Quin}$  = quinolinic acid) (Goher, Youssef, Zhou & Mak, 1993). Similarly, the Mn—N bond distances [2.038 (6), 2.209 (6) and 2.243 (5) Å] are somewhat shorter than those in  $[\text{Mn}(\text{H-Quin})_3][\text{Mn}(\text{H}_2\text{O})_6]$  [2.286 (3)–2.257 (4) Å]. It is worth noting that the Mn—N(1) bond distance [2.038 (6) Å] is by far the shortest of the three Mn—N distances, probably due to the differing *trans* influence of O and N donor atoms and perhaps also to the presence of solvent ethanol molecules. A similar trend is observed for the Cr—N distances in  $\text{CrQ}_3$ , but the differences are too small to be significant [2.053 (8)–2.075 (9) Å] (Folting *et al.*, 1971).

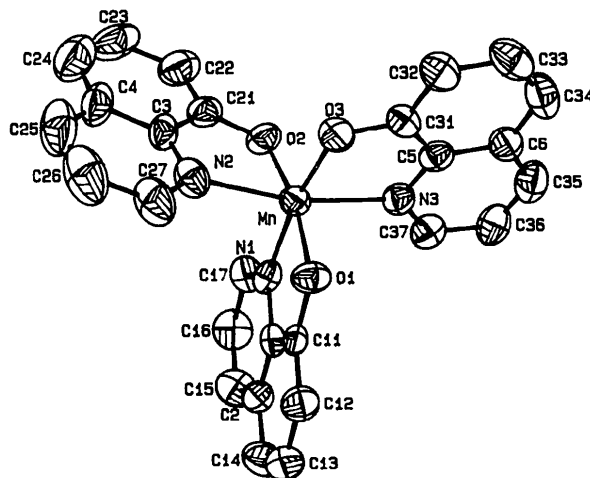
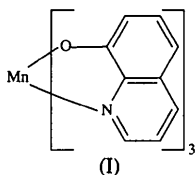


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

## Experimental

The title complex was prepared by heating  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , 8-quinolinol and 4-methylpyridine under reflux in  $\text{CHCl}_3/\text{EtOH}$  solution for 1 h. The resulting solution was evaporated at room temperature for a few weeks. Black plate-shaped crystals were obtained. The IR spectrum displayed a strong absorption band at  $3376 \text{ cm}^{-1}$  and X-ray photoelectron spectroscopy gave binding energies (eV) for  $\text{Mn}_{2p}$  (645),  $\text{N}_{1s}$  (402.3),  $\text{O}_{1s}$  (534.0) and  $\text{C}_{1s}$  (287.7).

### Crystal data

$[\text{Mn}(\text{C}_9\text{H}_6\text{NO})_3] \cdot \text{C}_2\text{H}_5\text{OH}$

$M_r = 533.47$

Monoclinic

$P2_1/n$

$a = 11.103(4) \text{ \AA}$

$b = 13.223(7) \text{ \AA}$

$c = 17.079(6) \text{ \AA}$

$\beta = 95.29(4)^\circ$

$V = 2497(3) \text{ \AA}^3$

$Z = 4$

$D_x = 1.42 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 14.09\text{--}16.75^\circ$

$\mu = 0.546 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Plate

$0.34 \times 0.34 \times 0.05 \text{ mm}$

Black

### Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$  scans

Absorption correction:

$\psi$  scans (Molecular

Structure Corporation,

1985)

$T_{\min} = 0.903$ ,  $T_{\max} =$

1.000

4749 measured reflections

4646 independent reflections

2304 observed reflections

$[I > 3\sigma(I)]$

$R_{\text{int}} = 0.009$

$\theta_{\max} = 25^\circ$

$h = -13 \rightarrow 13$

$k = 0 \rightarrow 15$

$l = 0 \rightarrow 20$

3 standard reflections

monitored every 300

reflections

intensity decay: 1%

### Refinement

Refinement on  $F$

$R = 0.064$

$wR = 0.069$

$S = 1.42$

2222 reflections

334 parameters

H-atom parameters not

refined

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.05$

$\Delta\rho_{\max} = 0.37 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from Cromer & Waber

(1974)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$B_{\text{eq}}$
Mn	0.0666 (1)	0.01230 (7)	0.25407 (6)	3.11 (5)
O(1)	-0.1037 (4)	0.0042 (3)	0.2623 (3)	3.8 (2)
O(2)	0.2300 (4)	0.0071 (4)	0.2267 (3)	4.0 (2)
O(3)	0.0776 (4)	0.1460 (3)	0.2944 (3)	3.9 (2)
N(1)	0.0455 (5)	-0.1372 (4)	0.2273 (3)	2.9 (3)
N(2)	0.0428 (6)	0.0699 (4)	0.1322 (4)	4.2 (3)
N(3)	0.1204 (5)	-0.0187 (4)	0.3817 (3)	3.5 (3)
C(1)	-0.0743 (6)	-0.1659 (5)	0.2289 (3)	2.8 (3)
C(2)	-0.1125 (7)	-0.2646 (5)	0.2131 (4)	3.8 (4)
C(3)	0.1507 (8)	0.0744 (5)	0.1033 (4)	4.0 (4)
C(4)	0.167 (1)	0.1121 (6)	0.0275 (5)	5.3 (5)
C(5)	0.1265 (6)	0.0715 (5)	0.4187 (4)	3.4 (4)

C(6)	0.1551 (6)	0.0820 (6)	0.5019 (5)	4.1 (4)
C(11)	-0.1511 (6)	-0.0870 (5)	0.2466 (3)	2.9 (3)
C(12)	-0.2730 (6)	-0.1089 (6)	0.2457 (4)	4.3 (4)
C(13)	-0.3137 (7)	-0.2076 (7)	0.2308 (5)	4.9 (4)
C(14)	-0.2378 (8)	-0.2844 (6)	0.2146 (5)	5.3 (5)
C(15)	-0.0265 (8)	-0.3351 (6)	0.1938 (5)	5.0 (4)
C(16)	0.0900 (8)	-0.3071 (6)	0.1936 (5)	5.0 (4)
C(17)	0.1242 (6)	-0.2063 (6)	0.2088 (4)	3.9 (4)
C(21)	0.2526 (7)	0.0403 (5)	0.1563 (5)	3.9 (4)
C(22)	0.3638 (8)	0.0419 (6)	0.1296 (6)	5.6 (5)
C(23)	0.377 (1)	0.0787 (8)	0.0526 (7)	7.2 (6)
C(24)	0.284 (1)	0.1118 (8)	0.0035 (6)	7.2 (7)
C(25)	0.062 (1)	0.1434 (8)	-0.0172 (6)	7.1 (6)
C(26)	-0.045 (1)	0.1393 (8)	0.0114 (6)	7.5 (6)
C(27)	-0.0544 (8)	0.1008 (6)	0.0867 (5)	5.7 (5)
C(31)	0.1046 (6)	0.1585 (5)	0.3718 (4)	3.3 (3)
C(32)	0.1114 (7)	0.2524 (5)	0.4050 (5)	4.2 (4)
C(33)	0.1409 (7)	0.2612 (6)	0.4869 (5)	5.1 (4)
C(34)	0.1614 (7)	0.1796 (7)	0.5333 (5)	5.1 (5)
C(35)	0.1713 (7)	-0.0102 (7)	0.5440 (4)	5.0 (4)
C(36)	0.1607 (7)	-0.0993 (6)	0.5069 (5)	4.9 (5)
C(37)	0.1365 (7)	-0.1004 (6)	0.4252 (5)	4.2 (4)
O(4)	0.4402 (6)	-0.0864 (5)	0.2898 (5)	9.2 (5)
C(7)	0.437 (1)	-0.146 (1)	0.358 (1)	11 (1)
C(8)	0.474 (1)	-0.087 (1)	0.431 (1)	14 (1)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Mn—O(1)	1.912 (4)	Mn—O(2)	1.916 (5)
Mn—O(3)	1.897 (5)	Mn—N(1)	2.038 (6)
Mn—N(2)	2.209 (6)	Mn—N(3)	2.243 (5)
O(1)—C(11)	1.333 (7)	O(2)—C(21)	1.327 (8)
O(3)—C(31)	1.340 (7)		
O(1)—Mn—N(1)	82.5 (2)	O(2)—Mn—N(2)	79.4 (2)
O(3)—Mn—N(3)	79.3 (2)	N(1)—Mn—N(2)	97.0 (2)
N(2)—Mn—N(3)	167.4 (2)	N(1)—Mn—N(3)	93.2 (2)
O(1)—Mn—O(2)	168.8 (2)	O(2)—Mn—O(3)	95.2 (2)
O(1)—Mn—O(3)	93.2 (2)	O(1)—Mn—N(2)	93.2 (2)
O(1)—Mn—N(3)	95.5 (2)	O(2)—Mn—N(1)	90.1 (2)
O(2)—Mn—N(3)	93.2 (2)	O(3)—Mn—N(1)	171.1 (2)
O(3)—Mn—N(2)	91.1 (2)		

Data collection was performed using *CONTROL* software (Molecular Structure Corporation, 1986). The structure was solved by direct methods using *MITHRIL* (Gilmore, 1983); the heavy atom Mn was located in an  $E$  map and the remaining non-H atoms were located using the *DIRDIF* (Beurskens, 1984) program. H atoms were placed in geometrically calculated positions with  $\text{C—H} = 0.95 \text{ \AA}$ , but were not included in the refinement. The structure was refined by full-matrix least-squares techniques with anisotropic displacement parameters for all atoms. Calculations were performed on a VAX3100 computer using the *TEXSAN* (Molecular Structure Corporation, 1985) program package.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1177). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Tetrameric Copper(II) Complex of 6-Hydroxy-3-methyl-1-phenyl-4-azahexa-3-en-1-one

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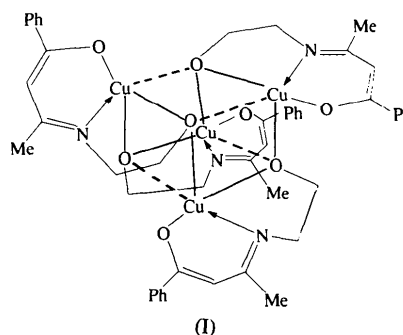
### Abstract

The title complex, tetrakis( $\mu_3$ -3-methyl-1-phenyl-4-azahexa-1,3-diene-1,6-diolato)tetracopper, [Cu<sub>4</sub>(C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub>)<sub>4</sub>] forms a cubane-like tetramer. Within the Cu<sub>4</sub>O<sub>4</sub> framework all four Cu atoms have square-pyramidal

CuNO<sub>4</sub> coordination and the alkoxide O atom of each ligand is triply bridging. The Cu—O bond distances within the Cu<sub>4</sub>O<sub>4</sub> framework are in the range 1.898 (9)–2.618 (7) Å, whereas the four Cu—N bond lengths range from 1.916 (9) to 1.929 (8) Å.

### Comment

Schiff base compounds have found applications in many fields, being particularly excellent candidates for building a novel type of conductive organic material (Hadjoudis, Vittorakis & Moustakali-Mavridis 1987). They have also attracted broad attention because of their ferromagnetic properties (Hines & Theriot, 1991). Although the title complex (I) has been prepared previously and some of its physical properties described, its crystal structure had not been reported (Hines & Theriot, 1991).



The structure of (I) consists of cubane-like tetramers with four square-pyramidally coordinated Cu atoms and four alkoxide O atoms at the corners of the cube (Fig. 1). It can also be described as containing a folded eight-membered ring in a boat-like conformation with short Cu—O distances [1.898 (9)–1.976 (7) Å] defining the ring, which forms the cubane-like molecule through two pairs of long mutually perpendicular Cu—O interactions [2.391 (7)–2.618 (7) Å]. Compared with  $\beta$ -CuEIA (EIA = 7-hydroxy-4-methyl-5-azahept-4-en-2-one) (Merghehenn, Merz, Haase & Allmann, 1976), which has a similar Cu<sub>4</sub>O<sub>4</sub> framework with Cu—O distances of 1.907–2.505 Å, the larger range of Cu—O distances observed in (I) shows that the cubic Cu<sub>4</sub>O<sub>4</sub> framework is more distorted. The Cu atoms have distorted square-pyramidal CuNO<sub>4</sub> coordination with one N and two O atoms of the same chelate ligand plus an O atom of another ligand of the tetramer forming the base of the pyramid; an O atom of another ligand occupies the axial position. The Cu—N bond lengths are in the range 1.916 (9)–1.929 (8) Å, and are in good agreement with values reported for comparable bonds in  $\beta$ -CuEIA and copper phthalocyanine (Brown, 1968). Bond lengths in the ligands are unexceptional. C9B has a highly anisotropic displacement tensor which may indicate positional disorder.