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Manganese Cupferronate

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Abstract

In the title compound, bis(N-nitroso-N-phenylhydroxyl-aminato)manganese, $[Mn(C_6H_5N_2O_2)_2]$, the Mn^{II} ion has distorted octahedral coordination defined by four O atoms from two cupferron ligands and two O atoms of the nitroso groups of two adjacent cupferron ligands [Mn—O 2.142 (2)–2.198 (2) Å]. Each nitroso O atom coordinates to two Mn^{II} ions resulting in an (—Mn—O—Mn—)$_n$ network. The plane of the nitroso-hydroxylaminato group is nearly coplanar with that of the phenyl ring.

Comment

As part of a series of studies aimed at clarifying the interaction modes of N-nitroso compounds with biologically important metal ions, the crystal structures of the Ni^{II} and Al^{III} complexes of cupferron, N-nitroso-N-phenylhydroxylamine, (I), have been determined (Okabe & Tamaki, 1995; Okabe, Tamaki, Suga & Kohyama, 1995). The structures of the related complexes iron cupferronate (van der Helm, Merritt & Degeilh, 1965), (N-nitroso-N-phenylhydroxylaminato-O,O')bis(triphenylphosphine)copper(I) (Charalambous, Haines, Harris, Henrick & Taylor, 1984) and bis-(cupferronato)copper(II) (Elerman, Atakol, Svoboda & Geselle, 1995) have been reported previously. In the present study, the crystal structure of the Mn^{II} complex of cupferron, (II), has been determined in order to clarify the binding scheme of the nitroso group to the Mn^{II} ion.

The molecular structure of the title complex is illustrated in Fig. 1. The four O atoms of two cupferron ligands (A and B) coordinate to the Mn^{II} ion and two O atoms of the nitroso groups of two adjacent cupferron ligands also coordinate to it from axial and equatorial directions. In each ligand, the plane of the nitrosohydroxylaminato group is nearly coplanar with that of the phenyl ring [O(1A)—N(1A)—N(2A)—O(2A) −0.7 (4), O(1A)—N(1A)—C(1A)—C(6A) −16.9 (5), O(1B)—N(1B)—N(2B)—O(2B) −0.7 (4) and O(1B)—N(1B)—C(1B)—C(6B) 1.2 (5)°] and the planes of the A and B ligands are nearly perpendicular to each other [O(1A)—
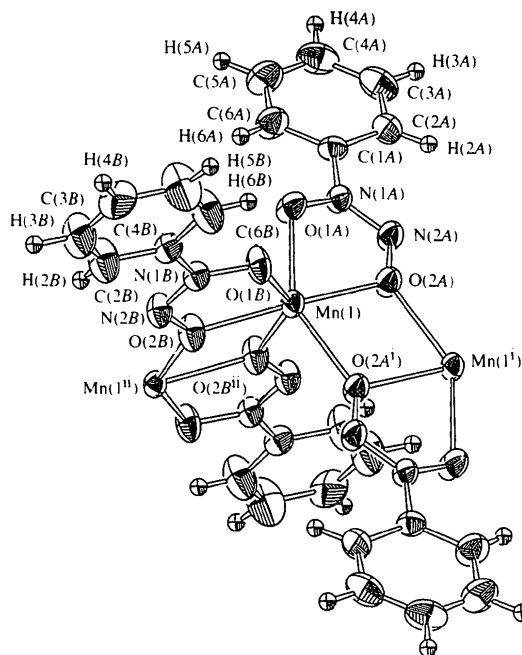

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability. Symmetry codes are as given in Table 2.
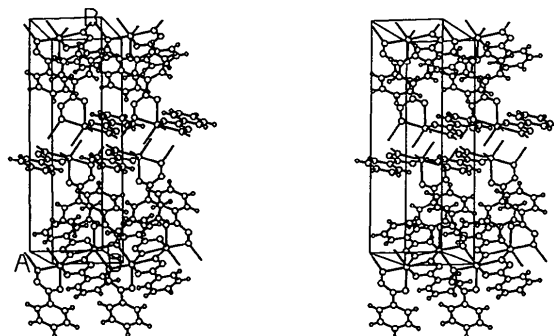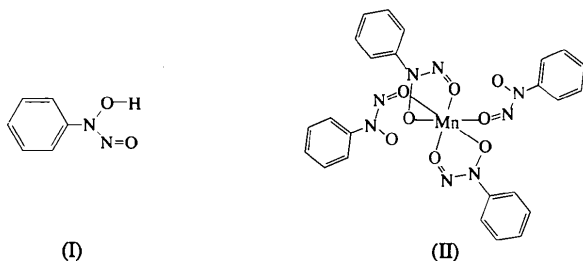

(I)   (II)

Fig. 2. Stereoview of the unit-cell packing of the title compound.

Mn(1)—O(1B) 94.12 (9)°]. As a result, the Mn^{II} ion has distorted octahedral coordination defined by six O atoms from four cupferron ligands. The O atom of the nitroso group is coordinated to two Mn^{II} ions resulting in an (— Mn—O—Mn—)$_n$ network, which stabilizes the crystal structure, as shown in Fig. 2.

Experimental

The brown prism crystal was obtained by slow evaporation of a 50% ethanol solution of a mixture of the N-nitroso-N-phenylhydroxylamine ammonium salt and $MnSO_4.5H_2O$ in a 3:1 molar ratio at room temperature.

Crystal data

[Mn(C$_6$H$_5$N$_2$O$_2$)$_2$]	Mo $K\alpha$ radiation
M_r = 329.18	λ = 0.71069 Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
a = 6.141 (1) Å	θ = 13.4–15.8°
b = 19.570 (2) Å	μ = 0.948 mm^{-1}
c = 11.366 (1) Å	T = 296 K
β = 91.64 (1)°	Prism
V = 1365.5 (3) Å^3	0.4 × 0.1 × 0.03 mm
Z = 4	Brown
D_x = 1.601 Mg m^{-3}	
D_m not determined	

Data collection

Rigaku AFC-5R diffractometer	R_{int} = 0.033
eter	θ_{max} = 27.5°
ω–2θ scans	h = 0 → 7
Absorption correction:	k = 0 → 25
ψ scans (North, Phillips & Mathews, 1968)	l = −14 → 14
	3 standard reflections
T_{min} = 0.92, T_{max} = 1.00	monitored every 150
3513 measured reflections	reflections
3226 independent reflections	intensity decay: none
2082 observed reflections	
[$I > 2\sigma(I)$]	

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.004
R = 0.040	$\Delta\rho_{max}$ = 0.30 e Å^{-3}
wR = 0.041	$\Delta\rho_{min}$ = −0.26 e Å^{-3}
S = 1.20	Extinction correction: none
2082 reflections	Atomic scattering factors
230 parameters	from International Tables
H atoms refined isotropically	for X-ray Crystallography
$w = 4F_o^2/\sigma^2(F_o^2)$	(1974, Vol. IV)

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Mn(1)	0.24529 (8)	0.03272 (3)	0.44850 (4)	2.19 (2)
O(1A)	0.2626 (4)	0.1364 (1)	0.5132 (2)	3.3 (1)
O(1B)	0.2867 (4)	0.0615 (1)	0.2687 (2)	3.2 (1)
O(2A)	−0.0405 (4)	0.0568 (1)	0.5517 (2)	2.9 (1)
O(2B)	0.5678 (4)	0.0059 (1)	0.3977 (2)	3.2 (1)
N(1A)	0.1336 (4)	0.1480 (1)	0.5996 (2)	2.4 (1)
N(1B)	0.4833 (4)	0.0513 (1)	0.2313 (2)	2.4 (1)
N(2A)	−0.0253 (4)	0.1089 (1)	0.6247 (2)	2.9 (1)
N(2B)	0.6343 (4)	0.0227 (2)	0.2926 (2)	2.8 (1)
C(1A)	0.1768 (5)	0.2066 (2)	0.6736 (3)	2.5 (1)
C(1B)	0.5314 (6)	0.0728 (2)	0.1129 (3)	2.7 (1)
C(2A)	0.0207 (6)	0.2296 (2)	0.7491 (3)	3.4 (2)
C(2B)	0.7320 (7)	0.0608 (3)	0.0679 (4)	4.5 (2)
C(3A)	0.0733 (8)	0.2825 (2)	0.8255 (4)	4.3 (2)
C(3B)	0.7688 (8)	0.0793 (3)	−0.0475 (4)	4.9 (2)
C(4A)	0.2756 (8)	0.3122 (2)	0.8252 (4)	4.4 (2)
C(4B)	0.6100 (8)	0.1088 (2)	−0.1142 (4)	4.6 (2)
C(5A)	0.4269 (7)	0.2898 (2)	0.7484 (4)	4.5 (2)
C(5B)	0.4131 (9)	0.1220 (3)	−0.0675 (4)	6.1 (3)
C(6A)	0.3782 (7)	0.2369 (2)	0.6710 (4)	3.7 (2)
C(6B)	0.3724 (7)	0.1036 (3)	0.0477 (4)	4.9 (2)

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

Mn(1)—O(1A)	2.159 (2)	N(1B)—C(1B)	1.448 (4)
Mn(1)—O(1B)	2.142 (2)	C(1A)—C(2A)	1.381 (5)
Mn(1)—O(2A)	2.190 (2)	C(1A)—C(6A)	1.373 (5)
Mn(1)—O(2A^i)	2.157 (2)	C(1B)—C(2B)	1.368 (5)
Mn(1)—O(2B)	2.144 (2)	C(1B)—C(6B)	1.351 (5)
Mn(1)—O(2B^{ii})	2.198 (2)	C(2A)—C(3A)	1.383 (5)
O(1A)—N(1A)	1.299 (3)	C(2B)—C(3B)	1.386 (5)
O(1B)—N(1B)	1.307 (3)	C(3A)—C(4A)	1.372 (6)
O(2A)—N(2A)	1.316 (3)	C(3B)—C(4B)	1.348 (6)
O(2B)—N(2B)	1.315 (3)	C(4A)—C(5A)	1.366 (6)
N(1A)—N(2A)	1.279 (4)	C(4B)—C(5B)	1.359 (6)
N(1A)—C(1A)	1.442 (4)	C(5A)—C(6A)	1.385 (6)
N(1B)—N(2B)	1.274 (4)	C(5B)—C(6B)	1.387 (6)
O(1A)—Mn(1)—O(1B)	94.12 (9)	O(1A)—N(1A)—C(1A)	118.3 (2)
O(1A)—Mn(1)—O(2A)	69.38 (8)	N(2A)—N(1A)—C(1A)	118.3 (3)
O(1A)—Mn(1)—O(2A^i)	141.86 (8)	O(1B)—N(1B)—N(2B)	123.6 (3)
O(1A)—Mn(1)—O(2B)	106.57 (9)	O(1B)—N(1B)—C(1B)	118.2 (3)
O(1A)—Mn(1)—O(2B^{ii})	91.8 (1)	N(2B)—N(1B)—C(1B)	118.2 (3)
O(1B)—Mn(1)—O(2A)	124.96 (9)	O(2A)—N(2A)—N(1A)	111.3 (2)
O(1B)—Mn(1)—O(2A^i)	107.3 (1)	O(2B)—N(2B)—N(1B)	111.5 (2)
O(1B)—Mn(1)—O(2B)	70.84 (8)	N(1A)—C(1A)—C(2A)	120.2 (3)
O(1B)—Mn(1)—O(2B^{ii})	140.89 (8)	N(1A)—C(1A)—C(6A)	118.8 (3)
O(2A)—Mn(1)—O(2A^i)	72.49 (9)	C(2A)—C(1A)—C(6A)	120.9 (3)
O(2A)—Mn(1)—O(2B)	163.26 (9)	N(1B)—C(1B)—C(2B)	120.5 (3)
O(2A)—Mn(1)—O(2B^{ii})	93.22 (9)	N(1B)—C(1B)—C(6B)	118.5 (3)
O(2B)—Mn(1)—O(2A^i)	110.10 (9)	C(2B)—C(1B)—C(6B)	121.0 (4)
O(2A^i)—Mn(1)—O(2B^{ii})	90.75 (9)	C(1A)—C(2A)—C(3A)	118.7 (4)
O(2B)—Mn(1)—O(2B^{ii})	70.41 (9)	C(1B)—C(2B)—C(3B)	118.8 (4)
Mn(1)—O(1A)—N(1A)	113.4 (2)	C(2A)—C(3A)—C(4A)	120.8 (4)
Mn(1)—O(1B)—N(1B)	114.0 (2)	C(2B)—C(3B)—C(4B)	120.6 (4)
Mn(1)—O(2A)—Mn(1)	107.51 (9)	C(3A)—C(4A)—C(5A)	119.9 (4)
Mn(1)—O(2A)—N(2A)	117.4 (2)	C(3B)—C(4B)—C(5B)	120.0 (4)
Mn(1)—O(2A^i)—N(2A^i)	131.4 (2)	C(4A)—C(5A)—C(6A)	120.5 (4)
Mn(1)—O(2B)—Mn(1)	109.59 (9)	C(4B)—C(5B)—C(6B)	120.4 (4)
Mn(1)—O(2B)—N(2B)	119.8 (2)	C(1A)—C(6A)—C(5A)	119.2 (4)
Mn(1)—O(2B^{ii})—N(2B^{ii})	129.8 (2)	C(1B)—C(6B)—C(5B)	119.1 (4)
O(1A)—N(1A)—N(2A)	123.3 (3)		

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $1 - x, -y, 1 - z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELX86* (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

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Bis(η^5-cyclopentadienyl)bis(formato-O)-titanium

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Abstract

The title compound, [Ti(C₅H₅)₂(CHO₂)₂], has a 'bent metallocene' structure type typically found for Cp₂MXY complexes. The Ti—O—C bond angles are larger than in related titanocene alkoxy complexes, suggesting enhanced π character in the Ti—O bonds of the title compound; however, the Ti—O bond lengths are longer than those in related alkoxy compounds.

Comment

In spite of their importance as probable intermediates in metal-catalyzed carbon dioxide hydrogenation reactions (Jessop, Ikariya & Noyori, 1995), relatively few η^1-formato complexes have been structurally characterized (see Fong, Fox & Cooper, 1987, and references therein; Hermann, Alt & Thewalt, 1990; Wöhrle & Thewalt, 1994). The title compound, (I), has been characterized in order to compare its properties with those of other formato complexes and with those of related bis(acyloxy) derivatives.

(I)
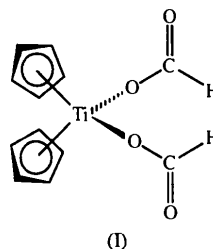
Considering the vectors from titanium to the centroids of the cyclopentadienyl rings, together with the bonds to the two O atoms of the formato ligands, the geometry about titanium can be described as distorted tetrahedral. The T—O bond lengths, 1.951 (2) and 1.952 (2) Å, indicate some π character in these bonds since both are less than 2 Å, but the electron-withdrawing nature of the formato groups reduces this character in comparison with that of an alkoxy complex. Thus, Cp₂Ti(OCH₂CH₃)Cl shows a Ti—O bond length of 1.855 (2) Å (Huffman, Moloy, Marsella & Caulton, 1980) and Cp₂Ti(OCH₃)Cl shows a Ti—O bond length of 1.839 (2) Å (Gibson, Ding, Mashuta & Richardson, 1996). The Ti—O—C bond angles have also been taken as further indicators of π character in the Ti—O bonds of alkoxy complexes; the shorter Ti—O bond lengths are attended by larger Ti—O—C angles [133.2 (2) and 141.4 (3)°, respectively]. With acyloxy derivatives, however, this relationship is not maintained. The Ti—O—C bond angles in (I) are 143.3 (2) and
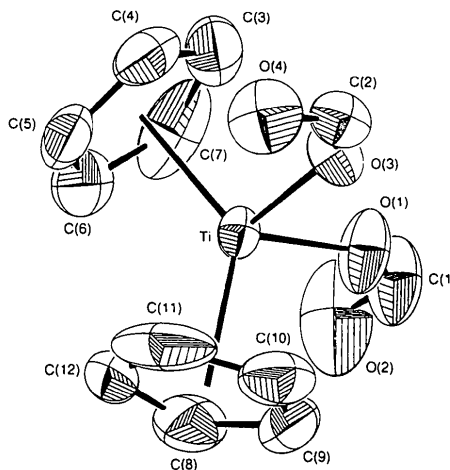

Fig. 1. *ORTEPII* (Johnson, 1976) plot of the title complex showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.