2909 reflections
180 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 0.8385P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| Cu1—N2 | 1.9880 (19) | Cu1—N3 | 2.0258 (17) |
| Cu1—N3$^i$ | 1.9951 (19) | Cu1—O1*W* | 2.442 (2) |
| Cu1—N1 | 2.0130 (17) | | |
| N2—Cu1—N3$^i$ | 163.07 (8) | N2—Cu1—N3 | 90.76 (8) |
| N2—Cu1—N1 | 95.52 (8) | N3$^i$—Cu1—N3 | 78.58 (8) |
| N3$^i$—Cu1—N1 | 95.72 (7) | N1—Cu1—N3 | 173.44 (7) |

Symmetry code: (i) $-x, 1-y, -z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1*W*—H1*W*···O4$^i$ | 0.90 (3) | 2.13 (3) | 2.980 (3) | 158 (3) |
| N2—H2*C*···O1*W*$^{ii}$ | 0.90 | 2.25 | 3.132 (3) | 164 |
| O1*W*—H2*W*···O2$^{iii}$ | 0.90 (3) | 2.05 (3) | 2.930 (3) | 167 (3) |

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $-x, -y, -z$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$.

After checking their presence in the difference map, the H atoms were fixed geometrically and allowed to ride on the atoms to which they were attached, except for the H atoms of the water molecules, which were located from a difference Fourier map and refined isotropically.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1311). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1999). C**55**, 1766–1769

# (1*R*,2*R*)-(−)-[Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine]chloromanganese(III), an (*R*,*R*)-Jacobsen catalyst

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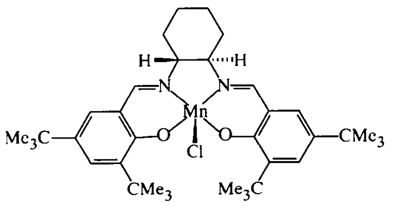
## Abstract

In the title compound, (−)-chloro{(1*R*,2*R*)-4,4′,6,6′-tetra-*tert*-butyl-2,2′-[cyclohexane-1,2-diylbis(nitrilomethylidyne)]diphenolato}manganese(III), $[MnCl(C_{36}H_{52}N_2O_2)]$, the Mn atom is pentacoordinated in a distorted square-pyramidal environment. Two independent molecules have similar bent structures, with dihedral angles between the two planar salicylideneimine moieties of 20.5 (1) and 27.7 (1)°.

## Comment

Optically pure amino alcohols are pharmaceutically important and can be produced efficiently from the corresponding chiral epoxides by acid- or base-catalysed epoxide ring-opening reactions. Cationic metal complexes of the salen ligand *N*,*N*′-ethylenebis(salicylideneaminate) are effective catalysts for the epoxidation of various olefins, and their catalytic activities can be modulated by substituents on the ligands (Srinivasan *et al.*, 1986). In particular, Jacobsen's catalyst, (I), a manganese(III) complex of a chiral salen ligand, catalyses highly enantioselective epoxidation of unfunctionalized olefins (Chang *et al.*, 1994). The crystal structures of several salen–metal complexes have been reported (Pahor *et al.*, 1976; Srinivasan *et al.*, 1986; Oki & Hodgson, 1990), but reports of chiral salen ligands and their metal complexes are rare. Pospisil *et al.* (1996) reported the crystal structures of (I) and its analogue containing triisopropylsiloxyl groups instead of *tert*-butyl groups at the *para* positions of both phenyl rings. However, the correct atomic coordinates of (I) have not been made available, although those of the analogue are available. We have determined the crystal structure of the free ligand of (I) (Yoon *et al.*, 1997) and report here a polymorphic structure of the complex (I).



(I)

The two molecules in the asymmetric unit have very similar structures, although there are small differences in detail. They are approximately related by a pseudo-centre of symmetry at [0.253 (14), 0.762 (3), 0.753 (5)], except for the cyclohexyl ring atoms. Crystal packing consists of van der Waals interactions only. The *tert*-butyl groups are subject to relatively large thermal motions. The overall structure seems to be similar to that reported by Pospisil *et al.* (1996) in space group *P*1, although a detailed comparison can not be made.

The Mn atom is pentacoordinated in a distorted square-pyramidal geometry, with four N and O atoms in the basal coordination plane and the Cl atom at the apex of the pyramid. The basal coordination plane is slightly distorted in a tetrahedral fashion. For molecule 1 (Fig. 1), the O1, N9, N16 and O24 atoms deviate by −0.062 (2), 0.063 (2), −0.063 (2) and 0.062 (2) Å, respectively, from the mean plane, and the Mn atom is displaced by 0.335 (2) Å toward the apex of the pyramid. For molecule 1′, the deviations of the O1′, N9′, N16′, O24′ and Mn′ atoms are 0.129 (2), −0.131 (2), 0.129 (2), −0.127 (2) and −0.381 (2) Å, respectively. The weighted average Mn—O distance of 1.867 (2) Å is shorter than the average Mn—N distance of 1.983 (2) Å. The O1—Mn—N9, O1—Mn—O24 and O24—Mn—N16 bite angles are all close to 90°, but the N9—Mn—N16 angles of 82.21 (15) and 82.02 (14)° are quite small owing to the constraints imposed by the five-membered chelate rings.

The molecular dimensions of the salicylideneimine moieties are comparable with those in compounds containing the same moieties (Srinivasan *et al.*, 1986; Oki & Hodgson, 1990; Pospisil *et al.*, 1996). The enol C—O bonds [average 1.317 (3) Å] are shorter by 0.046 Å, while the imine C=N bonds [average 1.296 (3) Å] are longer by 0.025 Å than the values of 1.363 and 1.271 Å in the free ligand (Yoon *et al.*, 1997). These variations are consistent with the notion that the ketamine form of the salen ligand contributes more to the resonance in the complex than in its free form (Pahor *et al.*, 1976). The four salicylideneimine moieties are planar, with maximum deviations of 0.060 (3), 0.062 (4), 0.038 (3) and 0.095 (3) Å for the O1, N16, N9′ and O24′ atoms, respectively.

The chiral ligands in the present complex molecules are distorted toward an umbrella shape, with dihedral angles between the two planar groups of 20.5 (1) and 27.7 (1)° for molecules 1 and 1′, respectively, while they are nearly perpendicular to each other with a dihedral angle of 76.32 (7)° in the free ligand. This bent conformation is significantly different from those of the salen complexes reported previously. The compound

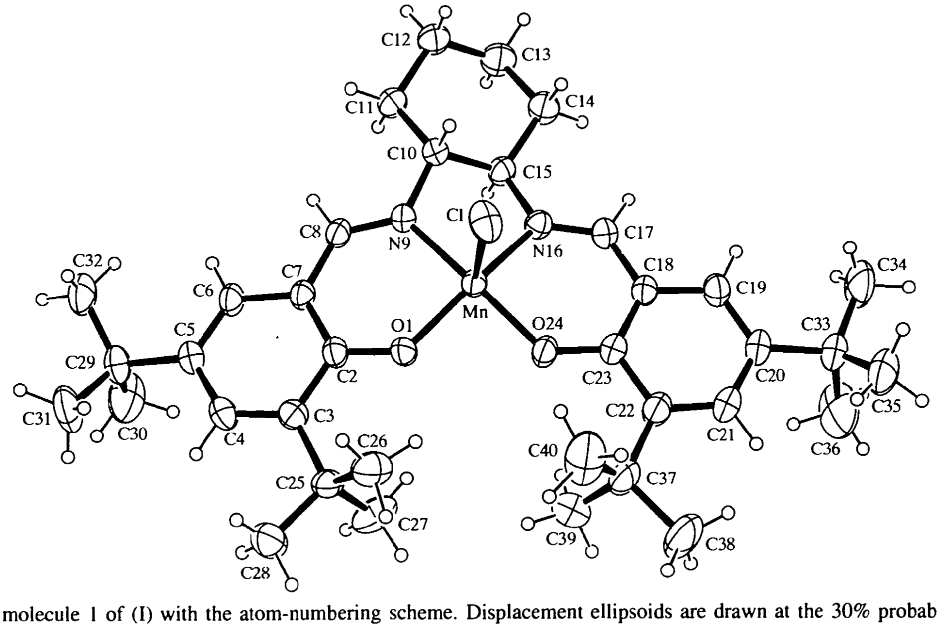


Fig. 1. View of molecule 1 of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

containing triisopropylsiloxyl groups instead of *tert*-butyl groups at C5 and C20, the most closely related compound (Pospisil *et al.*, 1996), assumes an essentially flat conformation. Other Co$^{II}$–salen and Mn$^{II}$–salen complexes also show relative planarity (Pahor *et al.*, 1976; Srinivasan *et al.*, 1986; Oki & Hodgson, 1990). Thus, the cyclohexyl ring joining the two salicylideneimine moieties seems to endow this chiral salen ligand with some, albeit small, conformational flexibility. The largest difference in the intracyclic torsion angles in the coordination sphere is in the C10—C15—N16—C17 angles of −154.4 (4) and −166.7 (4)° for molecules 1 and 1′, respectively. The intracyclic torsion angles of the cyclohexyl rings range from 54.7 (7) to 61.9 (5)°, with an average value of 57.4 (2)°.

## Experimental

The title compound was purchased from Strem Chemicals Inc. (CAS Registry Number: [138124–32–0]). Crystals were obtained from an aqueous acetone solution by slow evaporation at 277 K.

### *Crystal data*

[MnCl($C_{36}H_{52}N_2O_2$)]
$M_r$ = 635.19
Orthorhombic
$P2_12_12_1$
$a$ = 13.0824 (19) Å
$b$ = 18.808 (3) Å
$c$ = 29.608 (5) Å
$V$ = 7285.2 (19) Å$^3$
$Z$ = 8
$D_x$ = 1.158 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 49 reflections
$\theta$ = 2.21–17.62°
$\mu$ = 0.467 mm$^{-1}$
$T$ = 293 (2) K
Block
0.80 × 0.64 × 0.60 mm
Dark brown

### *Data collection*

Siemens *P*4 diffractometer
$\omega$ scans
Absorption correction: empirical $\psi$ scan (North *et al.*, 1968)
$T_{\min}$ = 0.708, $T_{\max}$ = 0.756
7745 measured reflections
7745 independent reflections

6237 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 26.01°
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 36$
3 standard reflections every 97 reflections intensity decay: none

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.138
$S$ = 1.029
7745 reflections
757 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0783P)^2 + 1.9535P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.398 e Å$^{-3}$
$\Delta\rho_{\min}$ = −0.216 e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.01 (2)

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

| | | | |
|---|---|---|---|
| Mn—O24 | 1.858 (3) | Mn′—O24′ | 1.862 (3) |
| Mn—O1 | 1.870 (3) | Mn′—O1′ | 1.878 (3) |
| Mn—N9 | 1.973 (4) | Mn′—N9′ | 1.969 (4) |
| Mn—N16 | 1.994 (4) | Mn′—N16′ | 1.994 (4) |
| Mn—Cl | 2.3850 (15) | Mn′—Cl′ | 2.3800 (16) |
| O1—C2 | 1.317 (5) | O1′—C2′ | 1.317 (5) |
| C7—C8 | 1.414 (6) | C7′—C8′ | 1.441 (6) |
| C8—N9 | 1.292 (6) | C8′—N9′ | 1.297 (5) |
| N9—C10 | 1.468 (5) | N9′—C10′ | 1.468 (5) |
| C15—N16 | 1.486 (6) | C15′—N16′ | 1.477 (6) |
| N16—C17 | 1.295 (5) | N16′—C17′ | 1.300 (5) |
| C17—C18 | 1.427 (6) | C17′—C18′ | 1.428 (6) |
| C23—O24 | 1.317 (5) | C23′—O24′ | 1.318 (5) |
| O24—Mn—O1 | 90.38 (14) | O24′—Mn′—O1′ | 89.63 (14) |
| O1—Mn—N9 | 90.68 (14) | O1′—Mn′—N9′ | 89.51 (14) |
| O24—Mn—N16 | 89.99 (14) | O24′—Mn′—N16′ | 90.82 (14) |
| N9—Mn—N16 | 82.21 (15) | N9′—Mn′—N16′ | 82.02 (14) |
| O24—Mn—Cl | 101.44 (12) | O24′—Mn′—Cl′ | 101.12 (12) |
| O1—Mn—Cl | 103.98 (12) | O1′—Mn′—Cl′ | 108.48 (13) |
| N9—Mn—Cl | 94.76 (12) | N9′—Mn′—Cl′ | 93.87 (11) |
| N16—Mn—Cl | 99.55 (12) | N16′—Mn′—Cl′ | 101.80 (12) |
| C2—O1—Mn | 132.6 (3) | C2′—O1′—Mn′ | 132.7 (3) |
| C8—N9—Mn | 125.6 (3) | C8′—N9′—Mn′ | 127.0 (3) |
| C17—N16—Mn | 124.6 (3) | C17′—N16′—Mn′ | 124.8 (3) |
| C23—O24—Mn | 131.9 (3) | C23′—O24′—Mn′ | 131.8 (3) |

H atoms were constrained geometrically with $U$(H) = 1.3$U_{\rm eq}$(C). The absolute structure was assumed to be that of the compound purchased and the Flack (1983) parameter of −0.01 (2) indicates that this is correct.

Data collection: *XSCANS* (Siemens, 1995). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Bruker, 1997). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1320). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1999). C**55**, 1769–1771

# Transition metal complexes with pyrazole-derived ligands. X. $[Zn(CH_3COO)_2L_2]\cdot 2MeOH$ ($L$ = 3-amino-5-phenylpyrazole)

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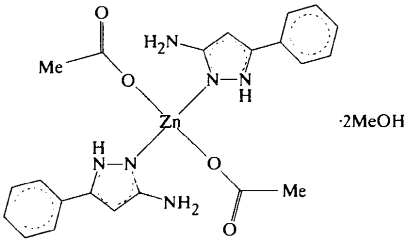
(*Received 18 February 1999; accepted 28 July 1999*)

## Abstract

Monocrystals of the title complex, bis(acetato-*O*)bis(3-amino-5-phenylpyrazole-$N^2$)zinc(II) dimethanol solvate, $[Zn(C_2H_3O_2)_2(C_9H_9N_3)_2]\cdot 2CH_4O$, were obtained by crystallization from a methanolic solution of $Zn(OAc)_2\cdot 2H_2O$ and 3-amino-5-phenylpyrazole ($L$) (1:2 molar ratio). The two pyridine-N atoms from the pyrazole derivative and two O atoms from the acetate groups are coordinated to the Zn atom in a distorted tetrahedral arrangement. The phenyl and aminopyrazole rings in both ligand molecules are planar within experimental accuracy. As a consequence of the arrangement of the molecules in the unit cell, the dihedral angles between the phenyl and aminopyrazole ring planes in the two ligand molecules are 5.6 (2) and 27.4 (2)°.

## Comment

Pyrazole derivatives and their metal complexes have recently attracted the attention of numerous researchers, which is evident from the publication of a large number of research papers and several reviews (Trofimenko, 1972, 1986, 1993; Cosgriff & Deacon, 1998). This class of ligand is characterized by a diversity of coordination modes whereby, in addition to the usual monodentate *N*-coordination, there are examples of *exo*- and less often *endo*-bidentate *N*,*N*-coordination of the pyrazole ring (Cosgriff & Deacon, 1998; Trofimenko, 1993). As a continuation of our research on the structures of metal complexes with this class of ligand (Herold-Brundić *et al.*, 1991; Kukushkin *et al.*, 1992; Jaćimović, Prelesnik *et al.*, 1998), the present work is concerned with the crystal and molecular structure of the newly synthesized complex of $Zn(OAc)_2$ with 3-amino-5-phenylpyrazole ($L$) of formula $[Zn(OAc)_2L_2]\cdot 2MeOH$, (I).



(I)

The zinc ion is coordinated with two O atoms from the carboxylate groups and two pyridine-N atoms from 3-amino-5-phenylpyrazole ligands in a distorted tetrahedral arrangement. Deviations from tetrahedral symmetry include widening of the N1*A*—Zn—N1*B* and O1*A*—Zn—N1*B* angles to 115.9 (1) and 114.5 (1)°, respectively, and narrowing of the O1*B*—Zn—N1*B* and O1*A*—Zn—O1*B* angles to 101.8 (1) and 102.9 (1)°, respectively. The bond distances between Zn and the pyrazole N atoms of 2.010 (3) and 1.995 (3) Å for Zn—N1*A* and Zn—N1*B*, respectively, are comparable with the values reported for $[Zn(NO_3)_2(L')_2]$ ($L'$ = 3-amino-4-acetyl-5-methylpyrazole; Herold-Brundić *et al.*, 1991), $[ZnCl_2(L'')_2]$ ($L''$ = 3,5-dimethylpyrazole; Bouwman *et al.*, 1984) and $[Zn_2(L''')_4(HL''')_2]$ ($L'''$ = 3,5-dimethylpyrazolate; Ehlert *et al.*, 1990), ranging from 1.991 (3) to 2.025 (3) Å. The Zn—O bond lengths are 1.960 (2) and 1.975 (2) Å for the *A* and *B* O atoms, respectively. These distances are within the range reported previously. In $Zn(CH_3COO)_2$ (Clegg *et al.*, 1986), where the acetate ligand acts as a bridge between Zn atoms, the average Zn—O distance is 1.957 (2) Å. In $[Zn_2(CH_3COO)_3(OCH_3)]$ (Chandler *et al.*, 1993), where the acetate group also acts as a bridge, this distance ranges from 1.948 (3) to 1.974 (7) Å. There are no significant differences between the bond lengths and angles involving the ring atoms of ligands *A* and *B*. All the values are comparable to those reported previously for pyrazole and phenyl rings (Herold-Brundić *et al.*, 1991; Kukushkin *et al.*, 1992; Jaćimović, Tomić *et al.*, 1998; Francisko *et al.*, 1980; Zukerman-Schpector *et al.*, 1990). The pyrazole and phenyl rings in the *A* and *B* ligands are planar within experimental accuracy. Maximum deviations from the least-squares planes are 0.003 (3) and 0.002 (4) Å for atoms C3*A* and C6*A*,

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