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## Structure Reports

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# Monoclinic form of (cyanato- $\kappa N$ ){2,2'-[ethane-1,2-diylbis(nitrilomethylidene)]-diphenolato- $\kappa^4 O, N, N', O'$ }manganese(III)

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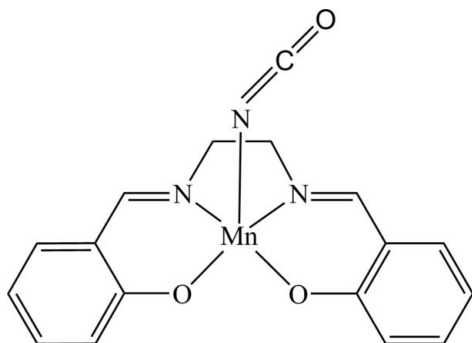
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(C-C) = 0.006$  Å;  $R$  factor = 0.048;  $wR$  factor = 0.131; data-to-parameter ratio = 12.4.

The title compound,  $[Mn(C_{16}H_{14}N_2O_2)(NCO)]$ , is a monoclinic polymorph of the previously published orthorhombic form [Lu *et al.* (2006). *Inorg. Chem.* **45**, 3538–3548]. The  $Mn^{III}$  ion is chelated by a tetradentate Schiff base ligand and coordinated by the N atom of a cyanate ligand in a distorted square-pyramidal arrangement. In the crystal, there are short intermolecular  $Mn \cdots O_{phenolate}$  distances of 2.752 (3) Å between pairs of inversion-related molecules.

## Related literature

For the orthorhombic polymorph of the title compound, see: Lu *et al.* (2006). For related structures, see: Mikuriya *et al.* (1992); Li *et al.* (1997); Wang *et al.* (2008).



## Experimental

### Crystal data

$[Mn(C_{16}H_{14}N_2O_2)(NCO)]$	$V = 1584.0 (5) \text{ \AA}^3$
$M_r = 363.25$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.6399 (16) \text{ \AA}$	$\mu = 0.85 \text{ mm}^{-1}$
$b = 10.9133 (18) \text{ \AA}$	$T = 293 \text{ K}$
$c = 15.198 (3) \text{ \AA}$	$0.37 \times 0.35 \times 0.23 \text{ mm}$
$\beta = 97.826 (3)^\circ$	

### Data collection

Bruker APEXII CCD area-detector diffractometer	7377 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2698 independent reflections
$T_{min} = 0.743$ , $T_{max} = 0.828$	1769 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.047$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	217 parameters
$wR(F^2) = 0.131$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{max} = 0.53 \text{ e \AA}^{-3}$
2698 reflections	$\Delta\rho_{min} = -0.33 \text{ e \AA}^{-3}$

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5164).

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## supporting information

*Acta Cryst.* (2010). E66, m1656 [https://doi.org/10.1107/S1600536810048270]

## Monoclinic form of (cyanato- $\kappa$ N){2,2'-[ethane-1,2-diylbis(nitrilomethylidene)]diphenolato- $\kappa^4$ O,N,N',O'}manganese(III)

Daopeng Zhang

### S1. Comment

Because of their excellent chelating ability for metal atoms, the tetradentate schiff-base ligands containing N<sub>2</sub>O<sub>2</sub> coordination unit have been widely studied in coordination chemistry field. Here, we report a Mn(III) complex based on tetradentate ligand *N,N'*-bis(salicylidene)-1,2-diphenyl-1,2-ethanediamine.

The molecular structure of the title complex is shown in Figure 1. The Mn<sup>III</sup> ion is involved in a distorted square-pyramidal arrangement by a N<sub>3</sub>O<sub>2</sub> unit, in which the four basal sites are occupied by two N atoms and two O atoms from the Schiff base ligand, and the apical position is occupied by the N atom of a cyanato ligand. The bond distances can be compared to this those found in the related structures (Lu, *et al.*, 2006; Mikuriya, *et al.*, 1992; Li, *et al.*, 1997; Wang, *et al.*, 2008). The Mn<sup>III</sup> ion lies above the basal plane formed by N<sub>2</sub>O<sub>2</sub> unit by 0.228 Å. The short intermolecular distance of Mn...O<sub>phenolate</sub> 2.752 (3) Å indicates that there exists weak interaction between the two complexes related by inversion centers in the crystal.

### S2. Experimental

The synthesis of the title complex was carried out by mixing Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1mmol), NaNCO (0.1mmol) and the schiff-base ligand (0.1mmol) in methanol (20ml). The mixture was stirred for about half an hour at room temperature and then filtered and the filtrate allowed to partially evaporate in air for several days to produce crystals suitable for X-ray diffraction with a yield about 64%.

### S3. Refinement

All the H atoms bonded to the C atoms were placed using the HFIX commands in *SHELXL-97* (Sheldrick, 2008) with C—H distances of 0.93 and 0.97 Å, respectively, and were allowed for as riding atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

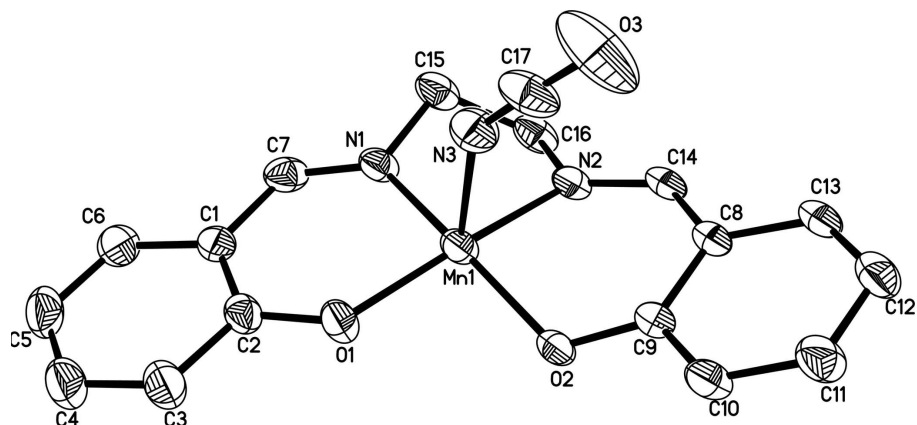


Figure 1

The molecular structure of the title complex with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are not shown.

(cyanato- $\kappa$ N){2,2'-[ethane-1,2-diylbis(nitrilomethylidene)]diphenolato- $\kappa^4$ O,N,N',O'}manganese(III)

#### Crystal data

[Mn(C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>)(NCO)]

$M_r = 363.25$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$a = 9.6399$  (16) Å

$b = 10.9133$  (18) Å

$c = 15.198$  (3) Å

$\beta = 97.826$  (3)°

$V = 1584.0$  (5) Å<sup>3</sup>

$Z = 4$

$F(000) = 744$

$D_x = 1.523$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1289 reflections

$\theta = 2.6$ – $26.6$ °

$\mu = 0.85$  mm<sup>-1</sup>

$T = 293$  K

Block, dark-brown

$0.37 \times 0.35 \times 0.23$  mm

#### Data collection

Bruker APEXII CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

$T_{\min} = 0.743$ ,  $T_{\max} = 0.828$

7377 measured reflections

2698 independent reflections

1769 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$

$\theta_{\max} = 24.7$ °,  $\theta_{\min} = 2.3$ °

$h = -11 \rightarrow 11$

$k = -8 \rightarrow 12$

$l = -17 \rightarrow 17$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.131$

$S = 1.01$

2698 reflections

217 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0695P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.53$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.33$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.10463 (6)	0.63253 (5)	0.52050 (4)	0.0420 (2)
O1	-0.0313 (3)	0.7121 (2)	0.57698 (17)	0.0489 (7)
O2	0.1015 (3)	0.4886 (2)	0.58923 (17)	0.0472 (7)
O3	0.5003 (4)	0.6657 (5)	0.6799 (3)	0.1254 (17)
N1	0.0793 (3)	0.7500 (3)	0.4211 (2)	0.0453 (8)
N2	0.2150 (3)	0.5430 (3)	0.4394 (2)	0.0425 (8)
N3	0.2893 (4)	0.7093 (3)	0.5904 (2)	0.0566 (10)
C1	-0.1070 (4)	0.8699 (4)	0.4711 (3)	0.0476 (10)
C2	-0.1116 (4)	0.8071 (4)	0.5515 (3)	0.0463 (10)
C3	-0.2089 (5)	0.8453 (4)	0.6060 (3)	0.0621 (13)
H3	-0.2123	0.8054	0.6598	0.075*
C4	-0.2991 (5)	0.9395 (4)	0.5824 (4)	0.0715 (14)
H4	-0.3638	0.9619	0.6196	0.086*
C5	-0.2956 (5)	1.0021 (4)	0.5037 (4)	0.0724 (15)
H5	-0.3568	1.0667	0.4879	0.087*
C6	-0.2003 (4)	0.9674 (4)	0.4492 (3)	0.0605 (12)
H6	-0.1974	1.0096	0.3963	0.073*
C7	-0.0106 (4)	0.8380 (4)	0.4105 (3)	0.0530 (11)
H7	-0.0132	0.8849	0.3593	0.064*
C8	0.3143 (4)	0.3997 (3)	0.5504 (3)	0.0415 (9)
C9	0.2170 (4)	0.4207 (4)	0.6109 (3)	0.0423 (9)
C10	0.2394 (4)	0.3634 (4)	0.6929 (3)	0.0503 (10)
H10	0.1770	0.3776	0.7334	0.060*
C11	0.3501 (4)	0.2868 (4)	0.7163 (3)	0.0626 (13)
H11	0.3630	0.2503	0.7721	0.075*
C12	0.4445 (4)	0.2632 (4)	0.6557 (3)	0.0638 (13)
H12	0.5195	0.2103	0.6709	0.077*
C13	0.4252 (4)	0.3189 (4)	0.5740 (3)	0.0524 (11)
H13	0.4872	0.3025	0.5337	0.063*
C14	0.2980 (4)	0.4541 (4)	0.4634 (3)	0.0451 (10)
H14	0.3511	0.4225	0.4220	0.054*
C15	0.1771 (4)	0.7294 (4)	0.3564 (3)	0.0569 (12)
H15A	0.2662	0.7686	0.3763	0.068*
H15B	0.1395	0.7634	0.2992	0.068*
C16	0.1964 (4)	0.5929 (4)	0.3489 (3)	0.0533 (11)

H16A	0.1150	0.5565	0.3141	0.064*
H16B	0.2780	0.5752	0.3201	0.064*
C17	0.3891 (6)	0.6904 (5)	0.6329 (3)	0.0659 (14)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Mn1	0.0320 (4)	0.0509 (4)	0.0445 (4)	0.0037 (3)	0.0098 (3)	0.0052 (3)
O1	0.0417 (16)	0.0560 (18)	0.0502 (17)	0.0124 (14)	0.0108 (13)	0.0024 (13)
O2	0.0324 (16)	0.0555 (17)	0.0570 (19)	0.0080 (13)	0.0174 (13)	0.0130 (13)
O3	0.051 (2)	0.238 (5)	0.081 (3)	0.023 (3)	-0.012 (2)	-0.046 (3)
N1	0.0299 (18)	0.057 (2)	0.049 (2)	0.0001 (16)	0.0062 (15)	0.0068 (16)
N2	0.0301 (18)	0.057 (2)	0.042 (2)	0.0001 (16)	0.0086 (14)	0.0047 (16)
N3	0.043 (2)	0.065 (3)	0.059 (3)	-0.0037 (19)	0.0009 (19)	-0.0029 (19)
C1	0.034 (2)	0.045 (2)	0.063 (3)	-0.003 (2)	0.0041 (19)	0.001 (2)
C2	0.035 (2)	0.046 (2)	0.057 (3)	-0.001 (2)	0.004 (2)	-0.010 (2)
C3	0.056 (3)	0.063 (3)	0.069 (3)	0.008 (2)	0.015 (2)	-0.007 (2)
C4	0.053 (3)	0.068 (3)	0.095 (4)	0.014 (3)	0.014 (3)	-0.007 (3)
C5	0.052 (3)	0.054 (3)	0.109 (5)	0.015 (2)	0.003 (3)	-0.006 (3)
C6	0.044 (3)	0.056 (3)	0.080 (3)	0.002 (2)	0.001 (2)	0.011 (2)
C7	0.038 (2)	0.060 (3)	0.059 (3)	-0.007 (2)	-0.001 (2)	0.016 (2)
C8	0.028 (2)	0.050 (2)	0.048 (2)	-0.0009 (17)	0.0096 (17)	-0.0012 (19)
C9	0.030 (2)	0.048 (2)	0.049 (3)	-0.0021 (18)	0.0077 (18)	0.0004 (19)
C10	0.034 (2)	0.068 (3)	0.049 (3)	0.000 (2)	0.0102 (18)	0.005 (2)
C11	0.040 (3)	0.087 (4)	0.059 (3)	0.008 (2)	0.004 (2)	0.023 (3)
C12	0.034 (3)	0.080 (3)	0.078 (3)	0.011 (2)	0.008 (2)	0.016 (3)
C13	0.028 (2)	0.065 (3)	0.066 (3)	0.000 (2)	0.013 (2)	0.003 (2)
C14	0.026 (2)	0.059 (3)	0.052 (3)	-0.0040 (19)	0.0122 (18)	-0.006 (2)
C15	0.040 (3)	0.081 (3)	0.051 (3)	0.008 (2)	0.013 (2)	0.022 (2)
C16	0.039 (2)	0.085 (3)	0.037 (2)	0.003 (2)	0.0105 (18)	0.005 (2)
C17	0.048 (3)	0.100 (4)	0.054 (3)	-0.013 (3)	0.021 (3)	-0.029 (3)

*Geometric parameters (Å, °)*

Mn1—O1	1.874 (2)	C5—C6	1.371 (6)
Mn1—O2	1.889 (3)	C5—H5	0.9300
Mn1—N1	1.971 (3)	C6—H6	0.9300
Mn1—N2	1.991 (3)	C7—H7	0.9300
Mn1—N3	2.118 (4)	C8—C13	1.394 (5)
O1—C2	1.320 (4)	C8—C9	1.418 (5)
O2—C9	1.340 (4)	C8—C14	1.438 (5)
O3—C17	1.235 (6)	C9—C10	1.386 (5)
N1—C7	1.288 (5)	C10—C11	1.364 (5)
N1—C15	1.469 (5)	C10—H10	0.9300
N2—C14	1.280 (5)	C11—C12	1.403 (6)
N2—C16	1.466 (5)	C11—H11	0.9300
N3—C17	1.102 (6)	C12—C13	1.372 (5)
C1—C6	1.403 (5)	C12—H12	0.9300

C1—C2	1.408 (5)	C13—H13	0.9300
C1—C7	1.437 (6)	C14—H14	0.9300
C2—C3	1.397 (5)	C15—C16	1.508 (6)
C3—C4	1.363 (6)	C15—H15A	0.9700
C3—H3	0.9300	C15—H15B	0.9700
C4—C5	1.382 (7)	C16—H16A	0.9700
C4—H4	0.9300	C16—H16B	0.9700
O1—Mn1—O2	93.85 (11)	N1—C7—C1	125.7 (4)
O1—Mn1—N1	91.64 (12)	N1—C7—H7	117.1
O2—Mn1—N1	162.75 (13)	C1—C7—H7	117.1
O1—Mn1—N2	167.59 (13)	C13—C8—C9	119.1 (4)
O2—Mn1—N2	89.12 (12)	C13—C8—C14	118.8 (3)
N1—Mn1—N2	82.24 (13)	C9—C8—C14	122.0 (3)
O1—Mn1—N3	100.33 (13)	O2—C9—C10	119.5 (3)
O2—Mn1—N3	97.30 (13)	O2—C9—C8	122.1 (3)
N1—Mn1—N3	97.78 (14)	C10—C9—C8	118.3 (4)
N2—Mn1—N3	91.22 (14)	C11—C10—C9	122.1 (4)
C2—O1—Mn1	130.4 (2)	C11—C10—H10	119.0
C9—O2—Mn1	121.3 (2)	C9—C10—H10	119.0
C7—N1—C15	120.9 (3)	C10—C11—C12	119.8 (4)
C7—N1—Mn1	126.2 (3)	C10—C11—H11	120.1
C15—N1—Mn1	112.9 (2)	C12—C11—H11	120.1
C14—N2—C16	122.7 (3)	C13—C12—C11	119.5 (4)
C14—N2—Mn1	124.2 (3)	C13—C12—H12	120.3
C16—N2—Mn1	113.0 (2)	C11—C12—H12	120.3
C17—N3—Mn1	145.7 (4)	C12—C13—C8	121.2 (4)
C6—C1—C2	118.7 (4)	C12—C13—H13	119.4
C6—C1—C7	118.8 (4)	C8—C13—H13	119.4
C2—C1—C7	122.5 (4)	N2—C14—C8	124.2 (3)
O1—C2—C3	118.3 (4)	N2—C14—H14	117.9
O1—C2—C1	123.4 (3)	C8—C14—H14	117.9
C3—C2—C1	118.2 (4)	N1—C15—C16	107.4 (3)
C4—C3—C2	121.6 (5)	N1—C15—H15A	110.2
C4—C3—H3	119.2	C16—C15—H15A	110.2
C2—C3—H3	119.2	N1—C15—H15B	110.2
C3—C4—C5	120.8 (5)	C16—C15—H15B	110.2
C3—C4—H4	119.6	H15A—C15—H15B	108.5
C5—C4—H4	119.6	N2—C16—C15	107.2 (3)
C6—C5—C4	118.9 (4)	N2—C16—H16A	110.3
C6—C5—H5	120.5	C15—C16—H16A	110.3
C4—C5—H5	120.5	N2—C16—H16B	110.3
C5—C6—C1	121.8 (5)	C15—C16—H16B	110.3
C5—C6—H6	119.1	H16A—C16—H16B	108.5
C1—C6—H6	119.1	N3—C17—O3	178.2 (6)