group. The largest peak in the final difference Fourier map (1.75 e Å^{-3}) is located 0.93 Å from the W1 atom.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1303). Services for accessing these data are described at the back of the journal.

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Zinc(II) complexes of bidentate Schiff base ligands containing methoxyphenyl and nitrophenyl groups

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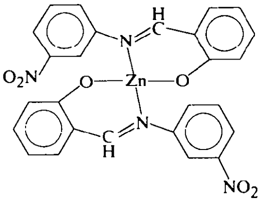
Abstract

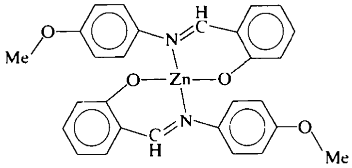
In the title compounds, bis[2-(3-nitrophenylnitrilomethylidyne)phenolato-*N*,*O*]zinc(II), [$Zn(C_{13}H_9N_2O_3)_2$], and bis[2-(3-methoxyphenylnitrilomethylidyne)phenolato-*N*,*O*]zinc(II), [$Zn(C_{14}H_{12}NO_2)_2$], the tricilinic unit cell contains two inversion-related molecules. In both compounds, the Zn atom is in a slightly distorted tetrahedral coordination involving O and N atoms of two bidentate ligands. The dihedral angle defined by the two chelate rings is 98.09 (4)° for the methoxyphenyl complex and 98.05 (7)° for the nitrophenyl complex. The molecules are crosslinked *via* intermolecular hydrogen bonds.

Comment

Metal complexes formed with *O*,*N*-type bidentate Schiff base ligands have a variety of coordination possibilities resulting in compounds with interesting properties. For instance, among the zinc compounds there are monomeric complexes in which the Zn atom is tetrahedrally coordinated (Frasson & Panattoni, 1961; Sogo *et al.*, 1988; Sakiyama *et al.*, 1990; Tatar *et al.*, 1999), as well as dimeric complexes with phenolate bridges and a trigonal-bipyramidal coordination around each Zn atom, as observed in (*N*-methylsalicylaldiminate)zinc(II) (Orioli *et al.*, 1965). We synthesized two new zinc complexes, namely, bis[2-(3-nitrophenylnitrilomethylidyne)phenolato-*N*,*O*]zinc(II), (1), and bis[2-(3-methoxyphenylnitrilomethylidyne)phenolato-*N*,*O*]zinc(II), (2), and report their structures here.



(1)



(2)

In both compounds, the structure consists of asymmetric monomers (Fig. 1), which are related by an inversion center of the triclinic unit cell and crosslinked by a set of intermolecular hydrogen bonds. The tetrahedral coordination around the Zn^{2+} ion, involving two phenolate O and two imine N atoms of two Schiff base ligands, is slightly distorted. The coordination bond angles are in the range 97.38 (6)–123.62 (7)° for the methoxyphenyl complex and in the range 95.5 (1)–126.1 (1)° for the nitrophenyl complex. The distortion from ideal tetrahedral geometry is a consequence of the limited opening of the bidentate ligands, which reduces the chelating O—Zn—N angle, and also steric repulsion of the groups bonded to N atoms, which in turn increases the N—Zn—N angle. The average Zn—O and Zn—N distances are 1.915 (2) and 2.007 (2) Å, respectively, for the methoxyphenyl complex, and 1.899 (2) and 2.027 (3) Å, respectively, for the nitrophenyl complex. These values are comparable with corresponding values reported in the above-cited literature.

An inspection of the possible C—H···O hydrogen bonds shows that adjacent molecules display several close contacts. In the methoxyphenyl complex, atoms C13 and C26 of the N-substituent groups are involved in intermolecular hydrogen bonding, so that molecules are crosslinked by hydrogen-bond interactions. Similar intermolecular hydrogen bonds are observed in the nitrophenyl complex. In all these interactions, donor–acceptor distances are shorter than the sum of the van der Waals radii. Details of the hydrogen-bonding geometry are given in Tables 2 and 4.

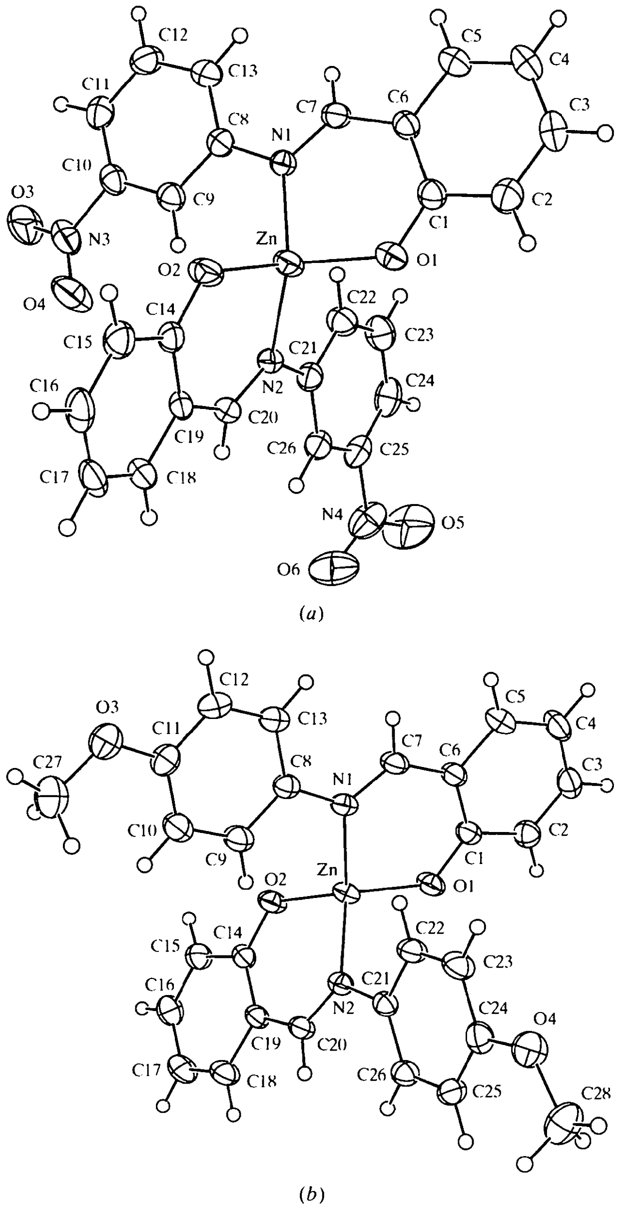


Fig. 1. *ORTEP*-3 (Farrugia, 1997) drawings of (*a*) [Zn(C$_{13}$H$_9$N$_2$O$_3$)$_2$] and (*b*) [Zn(C$_{14}$H$_{12}$NO$_2$)$_2$], with the atom-numbering schemes. The displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

Experimental

To obtain the title complexes, the appropriate ligand, *N*-(4-methoxyphenyl)salicylaldimine (0.227 g, 0.001 mol) or *N*-(4-nitrophenyl)salicylaldimine (0.242 g, 0.001 mol), was dissolved in hot methanol (50 ml). A solution of Zn(CH$_3$COO)$_2$·2H$_2$O (0.110 g, 0.0005 mol) in hot methanol (20 ml) was added, and the resulting solution mixed and set aside for 3 d. Crystals suitable for X-ray data collection were collected by filtration.

Compound (1)

Crystal data

[Zn(C$_{13}$H$_9$N$_2$O$_3$)$_2$]
$M_r = 547.827$
Triclinic
$P\overline{1}$
$a = 8.5966\ (7)$ Å
$b = 11.4966\ (14)$ Å
$c = 12.4867\ (11)$ Å
$\alpha = 70.432\ (8)°$
$\beta = 77.619\ (7)°$
$\gamma = 85.302\ (9)°$
$V = 1135.7\ (2)$ Å^3
$Z = 2$
$D_x = 1.6024$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.81–18.07°$
$\mu = 1.156$ mm^{-1}
$T = 295$ K
Prismatic
0.30 × 0.25 × 0.10 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan (Fair, 1990)
$T_{\min} = 0.781$, $T_{\max} = 0.848$
4704 measured reflections
4397 independent reflections

3695 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.010$
$\theta_{\max} = 25.9°$
$h = -10 \rightarrow 0$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 14$
3 standard reflections frequency: 120 min intensity decay: 0.023%

Refinement

Refinement on F
$R = 0.0412$
$wR = 0.0517$
$S = 1.01$
3695 reflections
334 parameters
H-atom parameters constrained
$w = 1/[\sigma F^2 + (0.02F)^2 + 1.25]$, except $w = 0$ if $F^2 <$ cutoff × σF^2 (cutoff = 3.0)

$(\Delta/\sigma)_{\max} = 0.0004$
$\Delta\rho_{\max} = 0.485$ e Å^{-3}
$\Delta\rho_{\min} = -0.137$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Zn—O1	1.898 (2)	O6—N4	1.209 (6)
Zn—O2	1.901 (2)	N1—C7	1.294 (4)
Zn—N1	2.027 (3)	N1—C8	1.431 (4)
Zn—N2	2.027 (2)	N2—C20	1.292 (4)
O1—C1	1.303 (4)	N2—C21	1.423 (4)
O2—C14	1.308 (4)	N3—C10	1.484 (4)
O3—N3	1.217 (5)	N4—C25	1.470 (4)
O4—N3	1.211 (5)	C6—C7	1.428 (4)
O5—N4	1.206 (5)	C19—C20	1.427 (4)
O1—Zn—O2	122.3 (1)	O2—Zn—N1	108.6 (1)
O1—Zn—N1	96.1 (1)	O2—Zn—N2	95.5 (1)
O1—Zn—N2	110.69 (9)	N1—Zn—N2	126.1 (1)

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13···O2^{i}	0.95	2.410	3.254 (4)	147.9 (2)
C17—H17···O1^{ii}	0.95	2.423	3.292 (5)	151.3 (2)

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

Compound (2)

Crystal data

$[Zn(C_{14}H_{12}NO_2)_2]$
$M_r = 517.885$
Triclinic
$P\overline{1}$
$a = 9.0778$ (11) Å
$b = 11.4052$ (13) Å
$c = 12.0973$ (12) Å
$\alpha = 84.898$ (2)°
$\beta = 87.619$ (3)°
$\gamma = 71.594$ (2)°
$V = 1183.6$ (2) Å^3
$Z = 2$
$D_x = 1.4531$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.90–20.85°$
$\mu = 1.097$ mm^{-1}
$T = 295$ K
Prismatic
0.35 × 0.25 × 0.15 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan (Fair, 1990)
$T_{\min} = 0.736$, $T_{\max} = 0.848$
4486 measured reflections
4252 independent reflections

3829 reflections with $I > 3\sigma(I)$
$R_{\text{int}} = 0.007$
$\theta_{\max} = 25.2°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 0.002%

Refinement

Refinement on *F*
$R = 0.0279$
$wR = 0.0371$
$S = 1.01$
3829 reflections
316 parameters
H-atom parameters constrained
$w = 1/[\sigma F^2 + (0.02F)^2 + 0.54]$ except $w = 0$ if $F^2 <$ cutoff × σF^2 (cutoff = 3.0)

$(\Delta/\sigma)_{\max} = 0.0005$
$\Delta\rho_{\max} = 0.342$ e Å^{-3}
$\Delta\rho_{\min} = -0.493$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Selected geometric parameters (Å, °) for (2)*

Zn—O1	1.909 (2)	O4—C28	1.417 (3)
Zn—O2	1.921 (1)	N1—C7	1.299 (3)
Zn—N1	2.006 (2)	N1—C8	1.430 (3)
Zn—N2	2.009 (2)	N2—C20	1.300 (2)
O1—C1	1.307 (3)	N2—C21	1.435 (2)
O2—C14	1.315 (2)	C6—C7	1.436 (3)
O3—C11	1.371 (3)	C19—C20	1.439 (2)
O3—C27	1.413 (4)	C21—C22	1.398 (3)
O4—C24	1.373 (2)	C21—C26	1.386 (3)
O1—Zn—O2	118.94 (7)	O2—Zn—N1	111.85 (6)
O1—Zn—N1	97.81 (7)	O2—Zn—N2	97.38 (6)
O1—Zn—N2	108.81 (7)	N1—Zn—N2	123.62 (7)

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13···O2^{i}	0.95	2.485	3.347 (3)	155.34
C26—H26···O1^{ii}	0.95	2.348	3.284 (2)	170.14

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

All non-H atoms were refined with anisotropic displacement parameters. Ring H atoms were placed geometrically at distances of 0.95 Å from their parent atoms, while the remaining H atoms were taken from a difference map; all H atoms were refined as riding with $U_{\text{eq}}(\text{H}) = 1.3U_{\text{eq}}(\text{C})$. The hydrogen-bond calculations were carried out with *PARST* (Nardelli, 1995).

For both compounds, data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *MolEN*; program(s) used to refine structures: *MolEN*; molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1243). Services for accessing these data are described at the back of the journal.

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