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A butterfly-shaped Schiff base complex: bis[2-(cyclopropyliminiomethyl)naphthalato]-dithiocyanatozinc(II)

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Key indicators

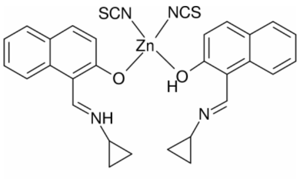
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
R factor = 0.073
wR factor = 0.172
Data-to-parameter ratio = 13.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Zn(NCS)_2(C_{14}H_{13}NO)_2]$, is a butterfly-shaped mononuclear compound. The Zn^{II} atom is coordinated by two N atoms from two thiocyanate anions and two O atoms from two Schiff base ligands in a slightly distorted tetrahedral geometry.

Comment

Transition metal compounds containing Schiff base ligands have been of great interest for many years (Yamada, 1999; Chang *et al.*, 1998; Chaturvedl, 1977; Archer & Wang, 1990). These compounds play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures (Costamagna *et al.*, 1992; Bhatia *et al.*, 1981). Zinc, the second most abundant transition metal in biology, functions as the active site of hydrolytic enzymes, such as carboxypeptidase and carbonic anhydrase where it is in a hard-donor coordination environment of nitrogen and oxygen (Lipscomb & Sträter, 1996; Bertini *et al.*, 1994). Zinc has long been recognized as an important cofactor in biological molecules, either as a structural template in protein folding or as a Lewis acid catalyst that can readily adopt four-, five- or six-coordination (Vallee & Auld, 1993). Recent reports have suggested that zinc is able to play a catalytic role in the activation of thiols as nucleophiles at physiological pH (Matthews & Goulding, 1997; Wilker & Lippard, 1997; Myers *et al.*, 1993). The crystal structure of a mononuclear zinc(II) compound, (I), is reported here.



(I)

The title compound, (I), is an electronically neutral butterfly-shaped mononuclear zinc(II) compound (Fig. 1). The central Zn1 atom in the compound is in a tetrahedral geometry and is four-coordinated by two N atoms from two thiocyanate anions and two O atoms from two Schiff base ligands. This ZnO_2N_2 coordination forms a slightly distorted tetrahedral geometry, as observed in the structure of the Zn^{II} complex we reported recently (You *et al.*, 2003), with angles subtended at the Zn1 atom in the range 101.5 (2)–114.5 (2)° (Table 1). The average Zn—O bond length of 1.942 (4) Å is a little longer than the value of 1.898 (8) Å observed in the same Schiff base zinc complex cited above. The mean Zn—N bond length of 1.946 (6) Å is a little shorter than the value of

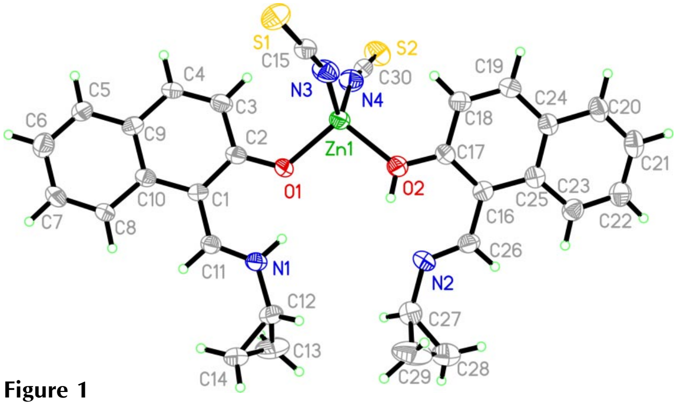


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

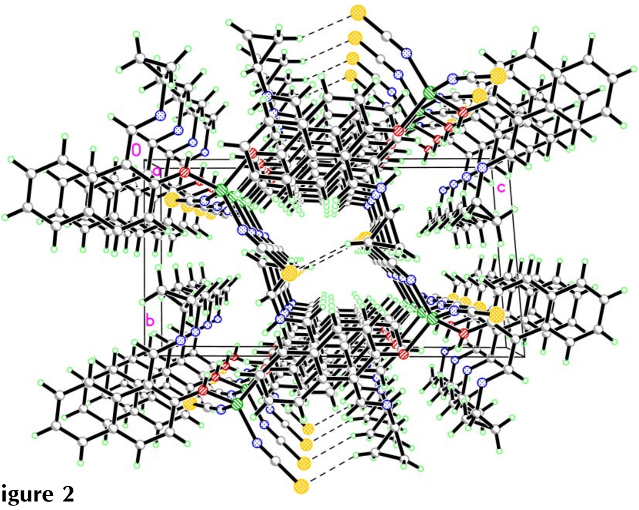


Figure 2
The crystal packing of (I), viewed along the *a* axis. Dashed lines indicate hydrogen bonds.

1.984 (7) Å observed in another zinc(II) complex coordinated by thiocyanate anions (Lu *et al.*, 1998). The dihedral angle between the two naphthalene ring system is 14.4 (6)°. The torsion angles Zn1—N3—C15—S1 and Zn1—N4—C30—S2 are 81.5 (2) and 82.1 (2)°, respectively. The dihedral angle between the two cyclopropane rings is 69.0 (9)°.

All the O atoms and the imine N atoms contribute to the formation of intramolecular N—H···O hydrogen bonds.

Experimental

Cyclopropylamine (2.0 mmol, 114 mg) and 2-hydroxy-1-naphthaldehyde (2.0 mmol, 344 mg) were dissolved in methanol (20 ml). The mixture was stirred for 1 h to give a clear yellow solution of *L* (2.0 mmol), where *L* is 1-[(E)-cyclopropyliminomethyl]naphthalen-2-ol. To the solution of *L* was added a methanol solution (8 ml) of $Zn(ClO_4)_2 \cdot 6H_2O$ (1.0 mmol, 372 mg) and a methanol solution (5 ml) of ammonium thiocyanate (2.0 mmol, 152 mg), with stirring. After keeping the resulting solution at room temperature in air for 18 d, yellow crystals were formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol and dried in a vacuum desiccator using P_4O_{10} (yield 72.8%). Analysis found: C 59.68, H 4.38, N 9.32%; calculated for $C_{30}H_{26}N_4O_2S_2Zn$: C 59.65, H 4.34, N 9.27%.

Crystal data

$[Zn(NCS)_2(C_{14}H_{13}NO)_2]$
$M_r = 604.04$
Triclinic, $P\overline{1}$
$a = 8.849$ (2) Å
$b = 9.803$ (2) Å
$c = 17.019$ (3) Å
$\alpha = 86.25$ (3)°
$\beta = 86.22$ (3)°
$\gamma = 67.20$ (3)°
$V = 1356.8$ (5) Å^3
$Z = 2$
$D_x = 1.479$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1459 reflections
$\theta = 2.5$–21.3°
$\mu = 1.10$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.27 × 0.25 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.756$, $T_{max} = 0.827$
6752 measured reflections
4577 independent reflections
2544 reflections with $I > 2\sigma(I)$
$R_{int} = 0.079$
$\theta_{max} = 25.0$°
$h = -10 \rightarrow 10$
$k = -8 \rightarrow 11$
$l = -19 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.073$
$wR(F^2) = 0.172$
$S = 0.93$
4577 reflections
352 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0777P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	1.940 (4)	Zn1—N3	1.944 (6)
Zn1—O2	1.943 (4)	Zn1—N4	1.949 (6)
O1—Zn1—O2	101.46 (18)	O1—Zn1—N4	112.0 (2)
O1—Zn1—N3	111.0 (2)	O2—Zn1—N4	109.5 (2)
O2—Zn1—N3	114.5 (2)	N3—Zn1—N4	108.3 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···N2	0.85	1.94	2.581 (7)	132
N1—H1*A*···O1	0.90	1.86	2.565 (6)	133

The H atoms on N1 and O2 were located in a difference Fourier map and were refined as riding on their respective parent atoms. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.96 Å and N—H = 0.90 Å, and with U_{iso}(H) values fixed at 0.08 Å^2.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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References

Archer, R. D. & Wang, B. (1990). *Inorg. Chem.* **29**, 39–43.

Bhatia, S. C., Bindlish, J. M., Saini, A. R. & Jain, P. C. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1773–1779.

Bertini, I., Gray, H. B., Lippard, S. J. & Valentine, J. S. (1994). In *Bioinorganic Chemistry*. Mills Valley, CA: University Science Books.

Chang, S., Jones, L., Wang, C. M., Henling, L. M. & Gruubbs, R. H. (1998). *Organometallics*, **17**, 3460–3465.

Chaturvedl, K. K. (1977). *J. Inorg. Nucl. Chem.* **39**, 901–903.

Costamagna, J., Vargas, J., Latorre, R., Alvarado, A. & Mena, G. (1992). *Coord. Chem. Rev.* **119**, 67–88.

Lipscomb, W. N. & Sträter, N. (1996). *Chem. Rev.* **96**, 2375–2434.

Lu, T.-H., Lo, J.-M., Chen, B.-H., Yeh, M.-Y., Tung, S.-F., Huang, W.-T. & Yao, H.-H. (1998). *Acta Cryst.* C**54**, 1067–1068.

Matthews, R. G. & Goulding, C. W. (1997). *Curr.* Opin. *Chem. Biol.* **1**, 332–339.

Myers, L. C., Terranova, M. P., Frentz, A. E., Wagner, G. & Verdine, G. L. (1993). *Science*, **261**, 1164–1167.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*a*). *SHELXTS*97 and *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Vallee, B. L. & Auld, D. S. (1993). *Acc. Chem. Res.* **26**, 543–551.

Wilker, J. J. & Lippard, S. J. (1997). *Inorg. Chem.* **36**, 969–978.

Yamada, S. (1999). *Coord. Chem. Rev.* **190–192**, 537–555.

You, Z.-L., Lin, Y.-S., Liu, W.-S., Tan, M.-Y. & Zhu, H.-L. (2003). *Acta Cryst.* E**59**, m1025–m1027.