

## Crystal Structure of Bis(*N*-ethyl-*N*-phenyldithiocarbamato- $\kappa^2S,S'$ )-(2-ethyl-2-oxazoline- $\kappa^1N$ )zinc(II)

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The title material was synthesised by the treatment of  $[Zn\{S_2CN(Et)(Ph)\}_2]_2$  with excess 2-ethyl-2-oxazoline. The crystal system is triclinic (space group  $P\bar{1}$  and  $Z = 2$ ). The unit-cell dimensions are  $a = 10.2310(4)\text{\AA}$ ,  $b = 11.4701(5)\text{\AA}$ ,  $c = 12.1981(5)\text{\AA}$  with  $\alpha = 85.952(1)^\circ$ ,  $\beta = 75.174(1)^\circ$ ,  $\gamma = 72.442(1)^\circ$  and  $V = 1319.30(9)\text{\AA}^3$ . The final  $R$  value is 0.0248 (4641 observed reflections:  $I > 2\sigma(I)$ ). The Zn atom coordinates with two chelating dithiocarbamato groups and one *N*-bound oxazoline.

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The zinc dithiocarbamates (ZDTC) represent an important class of compounds that have found applications as pesticide agents, additives to pavement asphalt, and precursors for chemical vapour deposition technology. In addition, ZDTC has found use as radical scavengers, lubricant additives, promoters of rubber vulcanization and Lewis acid frameworks in coordination chemistry. This latter facet often involves the use of *N*-donor ligands.<sup>1,2</sup> We recently disclosed the syntheses and structural characterization of the first ZDTC complexes containing the 2-oxazoline (*i.e.*, 4,5-dihydrooxazole) class of heterocycles.<sup>2</sup> These materials form readily upon reaction of the parent  $Zn^{2+}$  species and solutions of an oxazoline. In our previous investigation, only ZDTC precursors that contained a single type of organic functionality (*e.g.*, a benzyl group) were used.<sup>2</sup> In this report, we describe the crystallographic characterization of a complex containing 2-ethyl-2-oxazoline (ox) and a ZDTC containing two different organic functionalities, *viz.* the ethyl and phenyl groups.

The treatment of a  $CH_2Cl_2$  solution of the commercially available dimeric [bis- $\mu S,S'$ -(*N*-ethyl-*N*-phenyldithiocarbamato)-bis(*N*-ethyl-*N*-phenyldithiocarbamato- $\kappa^2S,S'$ )dizinc] with an excess of ox leads to the formation of a clear and colorless solution. Removal of volatile components (*vacuo*), followed by re-crystallization (boiling petroleum ether: 90 – 120°C bp range) of the resulting oily off-white solid leads to the isolation of

colorless crystals of the product (76%).

A single crystal of the complex of approximate dimensions  $0.12 \times 0.15 \times 0.28$  mm was used for a structure determination. A schematic representation of the resulting molecule appears in Fig. 1 and the molecular structure is shown in Fig. 2. Crystallographic data and the experimental details are given in Table 1. Selected atomic distance and angles are in Table 2.

The title complex contains a central Zn atom, which is coordinated by four *S*-atoms of two chelating dithiocarbamato fragments. Since the molecule contains no planes of symmetry, the four Zn-S bond lengths are all inequivalent. Three of these distances are all less than 2.50 Å, while the fourth is distinctly elongated relative to the others (~2.77 Å). The coordination sphere is completed by attachment of the oxazoline ligand *via* the *N*-atom (Zn-N: ~2.02 Å).<sup>3</sup> This material is an obvious relative of  $[Zn(S_2CNEt_2-\kappa^2S,S')(ox-\kappa^1N)]$  (I: CCDC No. 267555), which contains the identical oxazoline and a similar Zn-N (2.036(2)Å) bond length.<sup>2</sup> However, this latter complex has a coordination motif around the Zn atom that is distinctly more towards idealized trigonal bipyramidal ( $\tau = 0.61$ ).<sup>4</sup> The  $\tau$  value is equal to unity in truly tbp species and a  $\tau$  value of zero is assigned to pure sqp geometries.<sup>4</sup> In the case mentioned here, the coordination environment is less distorted towards tbp than

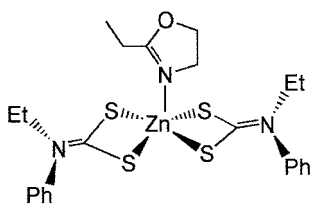


Fig. 1 Scheme of the title compound.

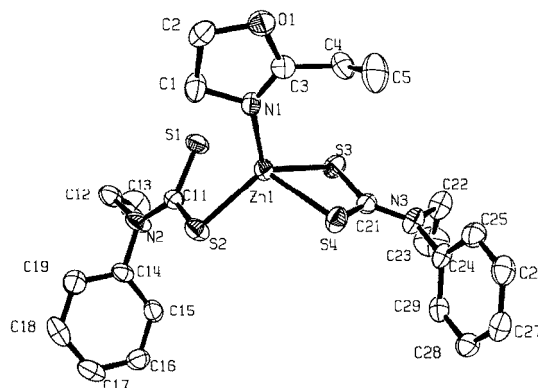


Fig. 2 Molecular structure of the title material with atom labeling.

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Table 1 Crystal data and structure refinement for the title complex

CCDC No. 682365
Empirical formula: C <sub>23</sub> H <sub>29</sub> N <sub>5</sub> OS <sub>4</sub> Zn
Formula weight = 557.10
T: 223 K
Crystal system: triclinic
Space group: $P\bar{1}$
$a = 10.2310(4)\text{\AA}$ , $\alpha = 85.952(1)^\circ$
$b = 11.4701(5)\text{\AA}$ , $\beta = 75.174(1)^\circ$
$c = 12.1981(5)\text{\AA}$ , $\gamma = 72.442(1)^\circ$
$V = 1319.30(9)\text{\AA}^3$ , $Z = 2$
$D_{\text{calc}} = 1.402\text{ g/cm}^3$
$\theta$ range for data collection: 1.73 to 25.00°
Reflections collected = 9841
Independent reflections = 4641
Final R indices [ $I > 2\sigma(I)$ ] $R_1 = 0.0248$ , $wR_2 = 0.0622$
$\lambda(\text{Mo } K\alpha) = 0.71073\text{\AA}$
$(\Delta\rho)_{\text{max}} = 0.599\text{ e.\AA}^{-3}$
$(\Delta\rho)_{\text{min}} = -0.236\text{ e.\AA}^{-3}$
Measurement: Bruker-AXS SMART APEX/CCD
Program system: SHELXTL
Structure determination: heavy atom methods
Refinement: full-matrix least-squares on $F^2$

that of **1**; in fact, the title complex is close to the midway point between **tbp** and **sqp** as  $\tau = 0.54$ .

If one defines an imaginary plane that bisects the complex through the N-atom and in between the two sulfur atoms of each dithiocarbamate chelate, then it can be seen that both ethyl groups are located on the same side of this plane (Figs. 1 and 2). As an obvious result, both phenyl groups are on the opposing side. The title material could therefore be viewed as the *syn*-isomer of a possible *syn-anti* isomeric pair. A similar *syn*-isomer has been identified by Tiekink *et al.* (CCDC No. 645548) in the structure of the diimine bridged dimer  $\{\text{Zn}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2\text{OH})\text{Et}]_2\}_2(4,4'\text{-bipyridine})$ .<sup>5</sup> The material reported here is the first oxazoline example of such isomeric behavior in ZDTC complexes.

## Acknowledgements

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## References

1. M. J. Cox and E. R. T. Tiekink, *Rev. Inorg. Chem.*, **1997**, 17, 1.
2. A. Decken, C. R. Eisnor, R. A. Gossage, and S. M. Jackson, *Inorg. Chim. Acta*, **2006**, 359, 1743.

Table 2 Bond lengths [Å] and angles [°] for crystal of the title complex

Zn(1)-N(1)	2.0227(15)	C(11)-S(1)-Zn(1)	77.96(7)
Zn(1)-S(2)	2.3281(5)	C(11)-S(2)-Zn(1)	91.39(6)
Zn(1)-S(3)	2.3897(6)	C(21)-S(3)-Zn(1)	85.16(7)
Zn(1)-S(4)	2.4884(5)	C(21)-S(4)-Zn(1)	82.50(7)
Zn(1)-S(1)	2.7657(6)	C(3)-O(1)-C(2)	107.02(15)
S(1)-C(11)	1.7007(19)	C(3)-N(1)-C(1)	107.50(16)
S(2)-C(11)	1.7219(19)	C(3)-N(1)-Zn(1)	131.26(13)
S(3)-C(21)	1.7279(19)	C(11)-N(1)-Zn(1)	121.16(12)
S(4)-C(21)	1.708(2)	C(11)-N(2)-C(14)	121.43(16)
O(1)-C(3)	1.336(2)	C(11)-N(2)-C(12)	122.05(19)
O(1)-C(2)	1.460(2)	C(14)-N(2)-C(12)	116.22(19)
N(1)-C(3)	1.280(2)	C(11)-N(2)-C(12)	118.5(3)
N(1)-C(1)	1.477(2)	C(14)-N(2)-C(12)	112.2(3)
N(2)-C(11)	1.341(2)	C(12)-N(2)-C(12)	34.4(3)
N(2)-C(14)	1.445(2)	C(21)-N(3)-C(24)	120.17(16)
N(2)-C(12)	1.480(5)	C(21)-N(3)-C(22)	123.12(17)
N(2)-C(12)	1.604(11)	C(24)-N(3)-C(22)	116.69(16)
N(3)-C(21)	1.337(2)	N(1)-C(1)-C(2)	104.34(16)
N(3)-C(24)	1.448(2)	O(1)-C(2)-C(1)	104.06(15)
N(3)-C(22)	1.511(3)	N(1)-C(3)-O(1)	116.95(18)
C(1)-C(2)	1.508(3)	N(1)-C(3)-C(4)	127.73(18)
C(3)-C(4)	1.481(3)	O(1)-C(3)-C(4)	115.31(17)
C(4)-C(5)	1.518(3)	C(3)-C(4)-C(5)	111.61(18)
C(12)-C(13)	1.500(8)	N(2)-C(11)-S(1)	122.23(14)
C(12)-C(13)	1.503(15)	N(2)-C(11)-S(2)	118.35(14)
C(14)-C(19)	1.374(3)	S(1)-C(11)-S(2)	119.40(11)
C(14)-C(15)	1.379(3)	N(2)-C(12)-C(13)	107.8(4)
C(15)-C(16)	1.379(3)	C(13)-C(12)-N(2)	102.8(9)
C(16)-C(17)	1.364(3)	C(19)-C(14)-C(15)	120.09(18)
C(17)-C(18)	1.378(3)	C(19)-C(14)-N(2)	120.11(18)
C(18)-C(19)	1.381(3)	C(15)-C(14)-N(2)	119.76(18)
C(22)-C(23)	1.481(3)	C(14)-C(15)-C(16)	119.80(19)
C(24)-C(25)	1.380(3)	C(17)-C(16)-C(15)	120.2(2)
C(24)-C(29)	1.381(3)	C(16)-C(17)-C(18)	120.22(19)
C(25)-C(26)	1.382(3)	C(17)-C(18)-C(19)	119.9(2)
C(26)-C(27)	1.382(3)	C(14)-C(19)-C(18)	119.8(2)
C(27)-C(28)	1.379(3)	N(3)-C(21)-S(4)	121.10(14)
C(28)-C(29)	1.388(3)	N(3)-C(21)-S(3)	120.89(14)
		S(4)-C(21)-S(3)	118.01(11)
N(1)-Zn(1)-S(2)	115.64(5)	C(23)-C(22)-N(3)	111.0(2)
N(1)-Zn(1)-S(3)	116.64(5)	C(25)-C(24)-C(29)	120.65(19)
S(2)-Zn(1)-S(3)	126.59(2)	C(25)-C(24)-N(3)	119.02(18)
N(1)-Zn(1)-S(4)	104.50(5)	C(29)-C(24)-N(3)	120.33(18)
S(2)-Zn(1)-S(4)	102.600(19)	C(24)-C(25)-C(26)	119.52(19)
S(3)-Zn(1)-S(4)	74.241(18)	C(25)-C(26)-C(27)	120.32(19)
N(1)-Zn(1)-S(1)	96.22(4)	C(28)-C(27)-C(26)	119.9(2)
S(2)-Zn(1)-S(1)	70.320(17)	C(27)-C(28)-C(29)	120.09(19)
S(3)-Zn(1)-S(1)	93.882(18)	C(24)-C(29)-C(28)	119.48(18)
S(4)-Zn(1)-S(1)	159.06(2)		

3. T. M. Barclay, I. del Rio, R. A. Gossage, and S. M. Jackson, *Can. J. Chem.*, **2003**, 81, 1482.
4. A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, and G. C. Vershuor, *J. Chem. Soc., Dalton Trans.*, **1984**, 1349.
5. R. E. Benson, C. A. Ellis, C. E. Lewis, and E. R. T. Tiekink, *CrystEngComm.*, **2007**, 9, 930.