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## **Dithiocyanatobis[4,4,5,5-tetramethyl-2-(4-pyridyl- $\kappa$ N)-1H-imidazoline-1-oxyl]-zinc(II)**

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# Dithiocyanatobis[4,4,5,5-tetramethyl-2-(4-pyridyl- $\kappa$ N)-1H-imidazoline-1-oxyl]zinc(II)

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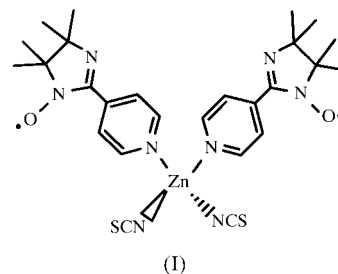
Data validation number: IUC0000273

In the title compound,  $[\text{Zn}(\text{NCS})_2(\text{C}_{12}\text{H}_{16}\text{N}_3\text{O})_2]$ , the  $\text{Zn}^{\text{II}}$  ion has a distorted tetrahedral coordination. It is bonded to two thiocyanate and two pyridyl N atoms. The metal ion and the two thiocyanate ligands lie on a mirror plane with the  $\text{Zn}-\text{N}_{\text{py}}$  and average  $\text{Zn}-\text{N}_{\text{NCS}}$  bond distances being 2.036 (2) and 1.931 (4) Å, respectively

## Comment

The field of molecular magnetic materials has been the subject of intensive investigation with the aim of designing new molecular magnets (Kahn, 1993; Enoki *et al.*, 1997; Ouahab, 1998). In this area, coordination chemistry stands as a powerful tool for the design of such materials. The objective is to build high dimensionality molecular assemblies involving spin carriers and favouring constructive magnetic interactions. Ligands bearing nitronyl nitroxide radicals appear as suitable building blocks for such materials owing to their high stability, as well as the possibility of chemical modification to introduce a bridging character (Ullman *et al.*, 1972). Actually, in most cases, the NO groups were found to be only weakly basic and do not coordinate even strongly electrophilic metal ions. We have already investigated the coordination chemistry of some pyridine-substituted nitronyl nitroxides and confirmed the weak basic character of the NO groups (Fettouhi *et al.*, 1999). In this context, the imino nitroxide radicals obtained by deoxygenation of the corresponding nitronyl nitroxides are better candidates for bridging through the pyridine and the imino groups. As far as the metal is concerned, zinc is considered at the borderline between soft and hard metals and, in the presence of the thiocyanate anion, it is known to bind either to the S (soft) or the N (hard) atom (Pearson, 1963; Ahrlund *et al.*, 1985; Bennett *et al.*, 1967). This feature may favour the formation of high dimensionality systems (Tian *et al.*, 1999). In order to study the coordination chemistry of an example of these interesting radical-bearing ligands in the presence of the ambidentate thiocyanate anion, we have

prepared a  $\text{Zn}^{\text{II}}$  complex, (I), with the ligand 2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl and the thiocyanate anion. We present herein its synthesis and X-ray crystal structure. The title compound crystallizes with imposed mirror symmetry. The  $\text{Zn}^{\text{II}}$  ion adopts a distorted tetrahedral coordination in which two positions are occupied by two pyridyl N atoms and the two others by two thiocyanate N atoms.



The metal and the NCS atoms lie on the special positions  $(x, \frac{1}{4}, z)$  and the  $\text{Zn}-\text{N}_{\text{py}}$  and average  $\text{Zn}-\text{N}_{\text{NCS}}$  bond distances are 2.036 (2) and 1.931 (4) Å, respectively. These values are in agreement with those observed in other zinc complexes involving a pyridine-type ligand and thiocyanate anions (Falvello *et al.*, 1995; Lu *et al.*, 1998).

## Experimental

2-(4-Pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl (PN) was prepared according to the literature procedure of Ullman *et al.* (1972). An aqueous solution of sodium thiocyanate (2 mmol) was added dropwise to a solution of zinc(II) nitrate hexahydrate (1 mmol) and PN (2 mmol) in water-ethanol (1/1). The precipitate was recrystallized from dimethylformamide to afford orange prismatic crystals.

### Crystal data

$[\text{Zn}(\text{NCS})_2(\text{C}_{12}\text{H}_{16}\text{N}_3\text{O})_2]$   
 $M_r = 618.09$   
 Monoclinic,  $P2_1/m$   
 $a = 6.1103$  (2) Å  
 $b = 20.6990$  (10) Å  
 $c = 11.7877$  (5) Å  
 $\beta = 95.302$  (3)°  
 $V = 1484.50$  (11) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.383$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 12252 reflections  
 $\theta = 1.018$ – $27.878^\circ$   
 $\mu = 1.006$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prism, orange  
 $0.12 \times 0.05 \times 0.04$  mm

### Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 13 554 measured reflections  
 3614 independent reflections  
 2469 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.0524$

$\theta_{\text{max}} = 27.88^\circ$   
 $h = -8 \rightarrow 8$   
 $k = -23 \rightarrow 27$   
 $l = -14 \rightarrow 15$   
 Intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.043$   
 $wR(F^2) = 0.117$   
 $S = 1.018$   
 3614 reflections  
 199 parameters  
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 0.2948P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.23$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.35$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.0098 (15)

**Table 1**

Selected geometric parameters (Å, °).

Zn—N2	1.919 (3)	N1—C1	1.163 (5)
Zn—N1	1.940 (4)	N2—C2	1.153 (5)
Zn—N3	2.036 (2)	C3—C4	1.367 (4)
S1—C1	1.605 (4)	C4—C5	1.389 (3)
S2—C2	1.603 (4)	C5—C6	1.380 (3)
O1—N4	1.230 (3)	C5—C8	1.475 (3)
O1'—N5	1.216 (12)	C6—C7	1.379 (3)
N2—Zn—N1	115.64 (15)	N3 <sup>i</sup> —Zn—N3	103.87 (11)
N2—Zn—N3	111.95 (8)	N1—C1—S1	179.5 (3)
N1—Zn—N3	106.27 (8)	N2—C2—S2	179.6 (4)

 Symmetry code: (i)  $x, \frac{1}{2} - y, z$ .

The O1 atom is disordered over two positions for which the occupancy factors were refined and found to be 0.85 and 0.15 for O1 and O1', respectively. H atoms were placed at calculated positions and refined with a riding model.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97*.

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