

## Tetrakis(pyridinium-2-thiolato)zinc(II) dinitrate

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Received 25 March 2004

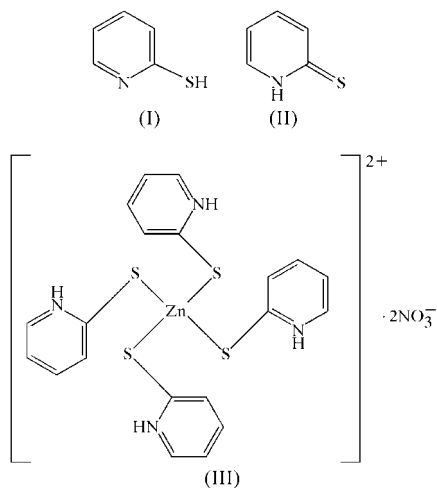
Accepted 2 April 2004

Online 11 May 2004

The crystal structure of the title compound,  $[\text{Zn}(\text{C}_5\text{H}_5\text{NS})_4](\text{NO}_3)_2$ , consists of a  $[\text{Zn}(\text{C}_5\text{H}_5\text{NS})_4]^{2+}$  ( $\text{C}_5\text{H}_5\text{NS}$  is pyridinium-2-thiolate) cation and two nitrate anions. The central  $\text{Zn}^{\text{II}}$  atom lies at a site with imposed  $\bar{4}$  symmetry and is surrounded by four S atoms [ $\text{Zn}-\text{S} = 2.3371(5) \text{ \AA}$ ] from four symmetrical pyridinium-2-thiolate ligands in a distorted tetrahedral geometry. There are  $\text{N}-\text{H}\cdots\text{O}$  hydrogen-bonding interactions between the pyridinium-2-thiolate ligands and nitrate O atoms. In addition,  $\pi-\pi$  interactions *via* aromatic N-containing ligands are discussed.

### Comment

The pyridine-2-thiol [PySH, (I)] ligand gives rise to an extensive chemistry with structural diversity, since it can coordinate both in the 'thiolate' and the tautomeric 'thione', (II), forms. Some structural reports on transition metal complexes containing the PySH ligand have appeared in the



literature, in which it binds in monodentate (Lobana *et al.*, 1998), bidentate chelating (Block *et al.*, 1991), bidentate bridging (Lobana *et al.*, 1999) or doubly bridging modes (Hong

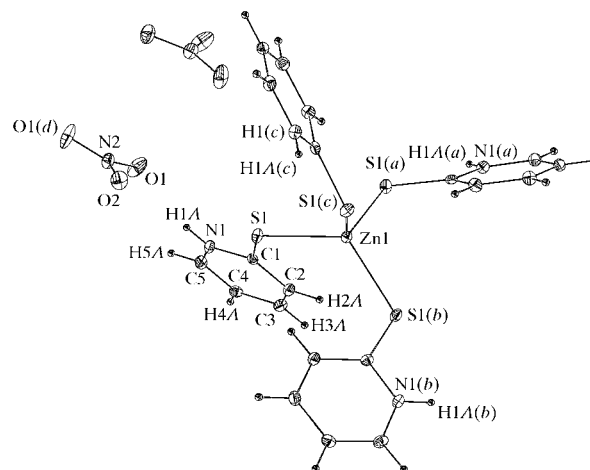


Figure 1

A view of the structure of (III), showing 30% probability displacement ellipsoids [symmetry codes: (a)  $\frac{1}{4} - y, x - \frac{1}{4}, \frac{1}{4} - z$ ; (b)  $2 - x, \frac{3}{2} - y, z$ ; (c)  $\frac{1}{4} + y, \frac{7}{4} - x, \frac{1}{4} - z$ ; (d)  $x, 2 - y, \frac{1}{2} - z$ ].

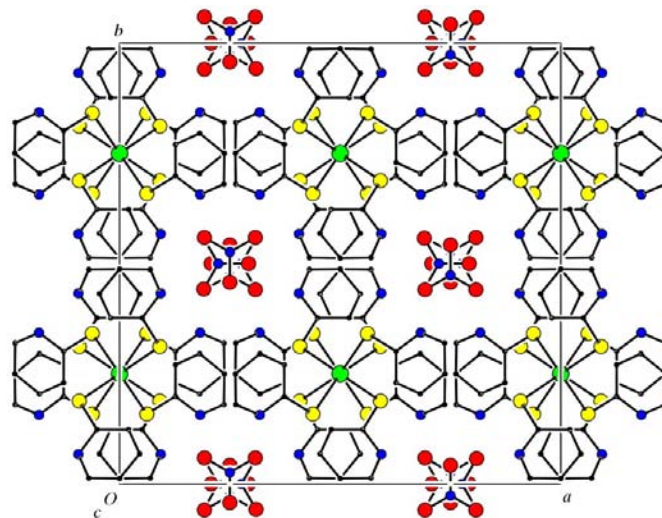


Figure 2

A perspective view, along the *c* axis, of the crystal packing in (III), showing the carpet-like structure. H atoms have been omitted for clarity. Zn atoms are shown as the largest sphere type and the nitrate anions can be seen occupying the interstices of the lattice.

*et al.*, 1999). We report here the synthesis and structural characterization of the title compound, (III), a mononuclear zinc compound.

The present X-ray single-crystal diffraction study reveals that the crystal structure of (III) contains a discrete  $[\text{Zn}(\text{C}_5\text{H}_5\text{NS})_4]^{2+}$  cation with the Zn atom on a site with imposed  $\bar{4}$  symmetry; the unique nitrate anion has twofold imposed symmetry. As illustrated in Fig. 1, the Zn atom displays a distorted tetrahedral geometry, and each Zn atom is coordinated by four S atoms [ $\text{Zn}-\text{S} = 2.3371(5) \text{ \AA}$ ; Table 1] from four pyridinium-2-thiolate ligands. The cations and anions are further linked by hydrogen bonding between pyridinium-2-thiolate ligands and nitrate O atoms (Table 2).

Although the PySH ligand has two coordination sites, only the S atom bonds to the metal ion in (III). This  $\text{Zn}[\text{S}_4]$  coord-

dination is also of interest because it clearly demonstrates the preference for S-coordination over N-coordination, an observation that is in accord with the prevalence of tetrahedral  $Zn[S_4]$  coordination in zinc enzymes (Vallee & Auld, 1993; Holm *et al.*, 1996; Lipscomb & Sträter, 1996).

A most interesting structural feature of (III) is that it presents a regular motif along the *c* axis. As shown in Fig. 2, open 'cavities' are constructed by the cations, and the nitrate anions proportionately occupy these cavities, forming a carpet-like framework structure.

In addition, it is worth noting that there are relatively short distances [centroid separation = 3.484 (2) Å, interplanar spacing = 3.359 (1) Å and centroid shift = 0.92 (9) Å] between the pyridine-ring plane and the symmetry-related plane at  $(\frac{3}{2} - x, \frac{3}{2} - y, \frac{1}{2} - z)$  in an adjacent cation, implying strong  $\pi$ - $\pi$  interactions in (III). According to Janiak (2000), these  $\pi$ - $\pi$  interactions should be assigned to an offset stacking;  $\pi$ - $\pi$  stacking, is an important motif in forming extended structures, from low to multidimensional. In (III),  $\pi$ - $\pi$  interactions and hydrogen-bonding interactions lead to the formation of a three-dimensional network structure.

## Experimental

A mixture of pyridine-2-carboxylic acid (0.062 g, 0.5 mmol) and  $Zn(NO_3)_2 \cdot 6H_2O$  (0.149 g, 0.5 mmol) was dissolved in a mixed solution of MeOH-H<sub>2</sub>O (3:2 v/v, 25 ml) and stirred at 333 K for 30 min. PySH (0.056 g, 0.5 mmol) was then added and the resulting mixture was stirred continuously for 1 h. Green prism-shaped crystals of (III) were obtained by slow evaporation of the solution at room temperature.

### Crystal data

$[Zn(C_5H_5NS)_4](NO_3)_2$   
 $M_r = 634.03$   
 Tetragonal,  $I4_1/acd$   
 $a = 18.534$  (3) Å  
 $c = 14.693$  (4) Å  
 $V = 5047.2$  (18) Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 1.669$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 6926 reflections  
 $\theta = 2.2$ - $25.0^\circ$   
 $\mu = 1.35$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prism, green  
 $0.38 \times 0.38 \times 0.30$  mm

### Data collection

Bruker P4 diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (SADABS; Sheldrick, 1996)  
 $T_{min} = 0.629$ ,  $T_{max} = 0.666$   
 14 775 measured reflections  
 1112 independent reflections

1109 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.015$   
 $\theta_{max} = 25.0^\circ$   
 $h = -22 \rightarrow 19$   
 $k = -15 \rightarrow 22$   
 $l = -17 \rightarrow 17$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.020$   
 $wR(F^2) = 0.055$   
 $S = 1.03$   
 1112 reflections  
 85 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 6.9441P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.003$   
 $\Delta\rho_{max} = 0.22$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.18$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Zn1—S1	2.3371 (5)		
S1 <sup>i</sup> —Zn1—S1	103.666 (10)	C1—S1—Zn1	108.05 (5)
S1 <sup>ii</sup> —Zn1—S1	121.84 (2)		
Symmetry codes: (i) $\frac{1}{4} + y, \frac{7}{4} - x, \frac{1}{4} - z$ ; (ii) $2 - x, \frac{3}{2} - y, z$ .			

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...O2	0.86	2.18	3.0223 (13)	168

All H atoms were located theoretically, with C—H distances of 0.93 Å and an N—H distance of 0.86 Å, and treated as riding, with  $U_{iso}(H) = 1.2U_{eq}(C, N)$ .

Data collection: SMART (Siemens, 1996); cell refinement: SMART and SAINT (Siemens, 1994); data reduction: XPREP in SHELXTL (Siemens, 1994); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

This work was supported financially by the State Key Basic Research and Development Plan of China (grant No. 001CB108906), the National Natural Science Foundation of China (grant Nos. 29733090 and 20173063), the Key Project in KIP of CAS (grant No. KJCX2-H3) and the Natural Science Foundation of Fujian Province (grant No. E0020001).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1653). Services for accessing these data are described at the back of the journal.

## References

- Block, E., Ofori-Okai, G., Kang, H., Wu, J. & Zubieta, J. (1991). *Inorg. Chem.* **30**, 4784–4788.
- Holm, R. H., Kennepohl, P. & Solomon, E. I. (1996). *Chem. Rev.* **96**, 2239–2314.
- Hong, M., Su, W., Cao, R., Zhang, W. & Lu, J. (1999). *Inorg. Chem.* **38**, 600–602.
- Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
- Lipscomb, W. N. & Sträter, N. (1996). *Chem. Rev.* **96**, 2375–2433.
- Lobana, T. S., Paul, S. & Castineiras, A. (1999). *J. Chem. Soc. Dalton Trans.* pp. 1819–1824.
- Lobana, T. S., Verma, R. & Castineiras, A. (1998). *Polyhedron*, **17**, 3753–3758.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Siemens (1994). *SAINTE* and *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Vallee, B. L. & Auld, D. S. (1993). *Acc. Chem. Res.* **26**, 543–551.