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(Piperazin-1-ium- κ N⁴)tris(thiocyanato- κ N)zinc(II)

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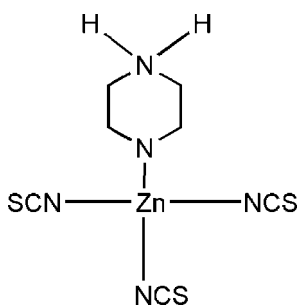
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.064; wR factor = 0.154; data-to-parameter ratio = 15.1.

Hydrothermal reaction of NaSCN, piperazine, Zn^{II} and 2,6-naphthalenedicarboxylic acid in aqueous solutions gave rise to the title complex, $[\text{Zn}(\text{NCS})_3(\text{C}_4\text{H}_{11}\text{N}_2)]$. The Zn^{II} atom is four-coordinate with distorted tetrahedral geometry and lies in a mirror plane. $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds assemble the molecules to form a three-dimensional framework.

Related literature

For related literature, see: Bie *et al.* (2005); Dai *et al.* (2002); Gu *et al.* (2007); Liu *et al.* (2007); Ouyang *et al.* (2003); Tao *et al.* (2003).



Experimental

Crystal data

$[\text{Zn}(\text{NCS})_3(\text{C}_4\text{H}_{11}\text{N}_2)]$
 $M_r = 326.72$
Orthorhombic, $Pnma$
 $a = 16.8975$ (8) Å
 $b = 11.0467$ (4) Å
 $c = 7.3097$ (3) Å

$V = 1364.44$ (10) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 2.24$ mm⁻¹
 $T = 293$ (2) K
 $0.40 \times 0.20 \times 0.15$ mm

Data collection

Bruker SMART APEXII CCD
area-detector diffractometer
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.830$, $T_{\text{max}} = 1.000$
(expected range = 0.593–0.715)

3079 measured reflections
1237 independent reflections
901 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.154$
 $S = 1.03$
1237 reflections

82 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.62$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.48$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N4}-\text{H4C}\cdots\text{S1}^{\text{i}}$	0.90	2.72	3.470 (6)	141
$\text{N4}-\text{H4D}\cdots\text{S2}^{\text{ii}}$	0.90	2.38	3.281 (7)	175

Symmetry codes: (i) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, y, -z + \frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2286).

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supporting information

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(Piperazin-1-ium- κ N⁴)tris(thiocyanato- κ N)zinc(II)**Xiang He, Hong-Jiang Liu and Ming-Xing Li****S1. Comment**

d¹⁰ metal complexes have been found to exhibit intriguing structural and photoluminescent properties (Liu *et al.*, 2007; Dai *et al.*, 2002; Ouyang *et al.*, 2003; Gu *et al.*, 2007; Tao *et al.*, 2003). When trying to prepare the zinc complex containing 2,6-naphthalenedicarboxylic acid, piperazine and thiocyanate ligands by hydrothermal reaction, we did not obtain the expected compound but instead of the tri-isothiocyanato-(piperazinium-N⁺)-zinc(II) compound (I). The new complex has been characterized by elemental analysis and single-crystal diffraction analysis.

The Zn atom adopts a distorted tetrahedral coordination geometry and is coordinated by three N atoms from the thiocyanate anions and one piperazine N atom (Fig. 1). The Zn atom, one thiocyanate ligands and N atoms of piperazine ligands are located on a mirror plane. The Zn—N3 (piperazine) bond length is 2.054 (6) Å and the Zn-NCS bond lengths are almost equal at 1.935 (5) Å for N1 and 1.933 (8) Å for N2, respectively. The N—Zn—N angles are in the range 107.7 (3) ° ~ 112.3 (3) °. All bond distances and angles are as observed for other zinc(II) complexes with piperazine and thiocyanate ligands (Bie *et al.*, 2005). There are intermolecular N—H...S hydrogen bonds in the compound, which assemble the molecules to form a three dimensionnal framework.(Table 1 and Fig. 2)

S2. Experimental

A mixture of ZnCl₂·6H₂O (0.49 g, 2 mmol), 2,6-naphthalenedicarboxylic acid (1 mmol, 0.26 g), piperazine (2 mmol, 0.17), NH₄SCN (10 mmol, 0.15) and H₂O (10 ml) was stirred for 0.5 h at room temperature. The reaction was carried out in a Teflon-lined steel autoclave, which was heated at 160°C for 2 d followed by slow cooling to room temperature. The resulting colorless prism-shaped crystals suitable for X-ray analysis were filtered off and washed with water. Analysis, calculated for C₇H₁₁N₅S₃Zn: C 25.96, H 3.13, N 21.79%; found: C 25.73, H 3.39, N 21.43%.

S3. Refinement

H atoms were placed in idealized positions, with C—H distances of 0.97 Å, N—H distances of 0.90 Å, and allowed to ride on their respective parent C atoms with the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

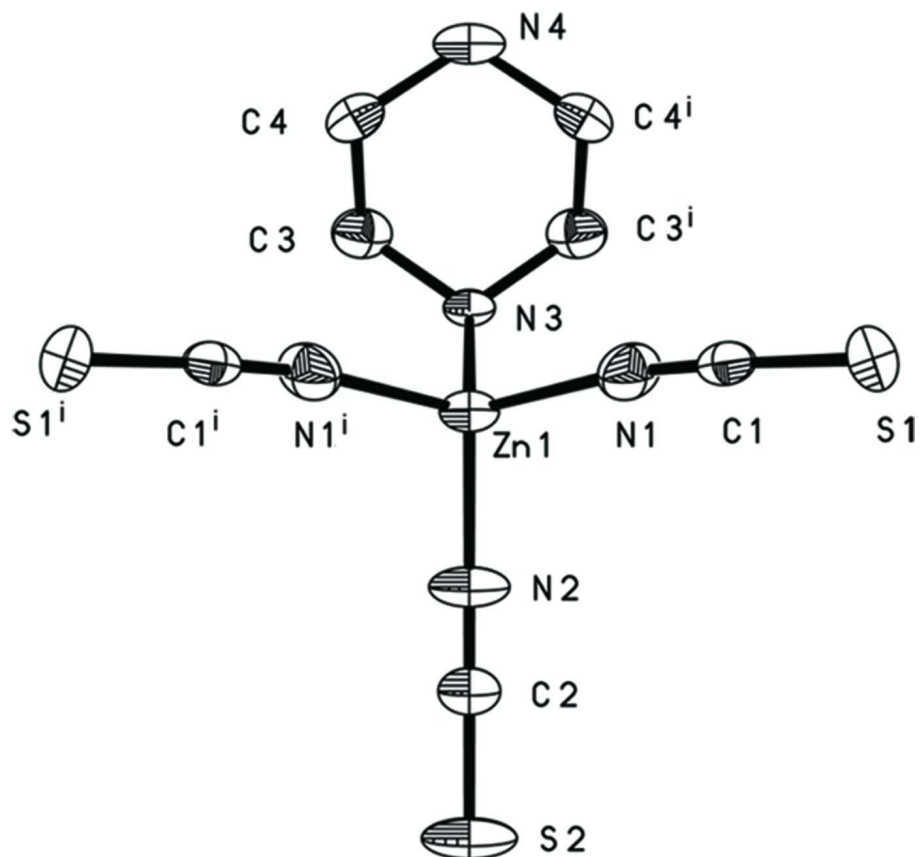


Figure 1

View of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. [symmetry codes: (i) $x, -y + 1/2, z$].

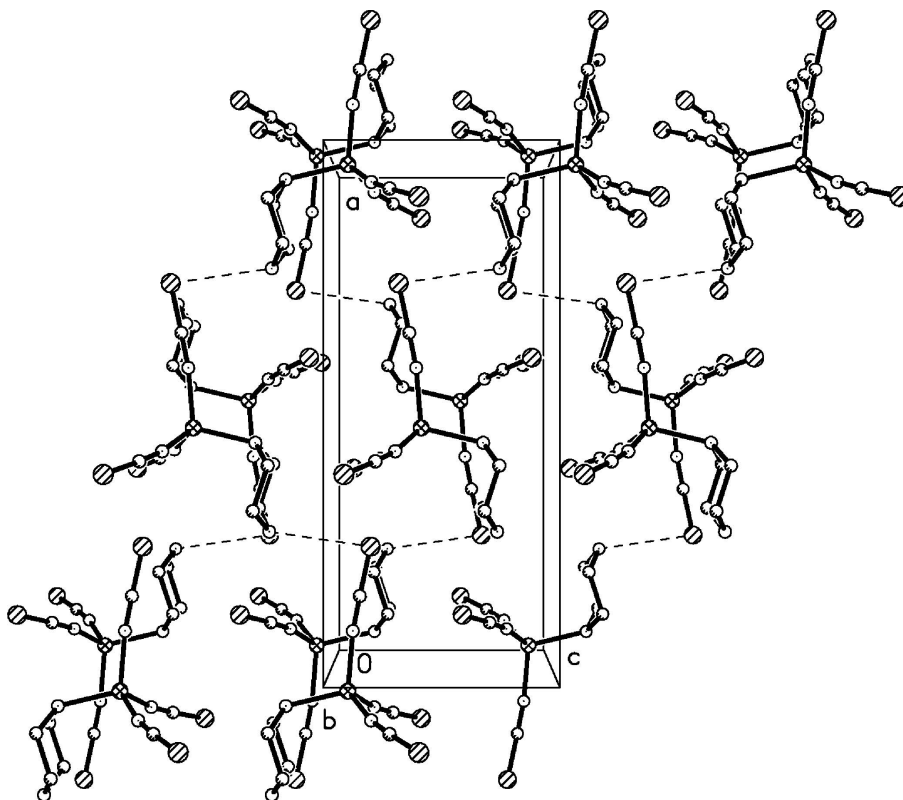


Figure 2

Crystal packing diagram of compound (I), Hydrogen bonding is indicated by dashed lines.

(Piperazin-1-ium- κN^4)tris(thiocyanato- κN)zinc(II)

Crystal data

$[\text{Zn}(\text{NCS})_3(\text{C}_4\text{H}_{11}\text{N}_2)]$

$M_r = 326.72$

Orthorhombic, $Pnma$

Hall symbol: $-P\ 2ac\ 2n$

$a = 16.8975\ (8)\ \text{\AA}$

$b = 11.0467\ (4)\ \text{\AA}$

$c = 7.3097\ (3)\ \text{\AA}$

$V = 1364.44\ (10)\ \text{\AA}^3$

$Z = 4$

$F(000) = 664$

$D_x = 1.590\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 75 reflections

$\theta = 3.0\text{--}25.0^\circ$

$\mu = 2.24\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Prism, colorless

$0.40 \times 0.20 \times 0.15\ \text{mm}$

Data collection

Bruker SMART APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: empirical (using
intensity measurements)

(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.830$, $T_{\max} = 1.000$

3079 measured reflections

1237 independent reflections

901 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -19 \rightarrow 13$

$k = -13 \rightarrow 8$

$l = -8 \rightarrow 7$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.154$
 $S = 1.03$
 1237 reflections
 82 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0605P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.62 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.48 \text{ e } \text{Å}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.02672 (5)	0.2500	-0.08930 (13)	0.0469 (4)
S1	0.10918 (11)	0.59639 (14)	-0.4058 (3)	0.0696 (6)
S2	-0.24789 (14)	0.2500	-0.1884 (4)	0.0884 (10)
N1	0.0695 (3)	0.3956 (5)	-0.1985 (8)	0.0658 (16)
N2	-0.0875 (4)	0.2500	-0.1112 (11)	0.073 (2)
N3	0.0549 (3)	0.2500	0.1831 (8)	0.0402 (15)
H3C	0.0077	0.2500	0.2430	0.048*
N4	0.2239 (4)	0.2500	0.2443 (9)	0.060 (2)
H4C	0.2729	0.2500	0.1964	0.072*
H4D	0.2285	0.2500	0.3670	0.072*
C1	0.0871 (3)	0.4790 (5)	-0.2800 (8)	0.0456 (14)
C2	-0.1538 (5)	0.2500	-0.1416 (11)	0.050 (2)
C3	0.0968 (3)	0.1421 (6)	0.2496 (9)	0.0622 (17)
H3A	0.0697	0.0702	0.2063	0.075*
H3B	0.0956	0.1412	0.3822	0.075*
C4	0.1817 (3)	0.1387 (5)	0.1857 (9)	0.0579 (17)
H4A	0.2079	0.0682	0.2366	0.069*
H4B	0.1833	0.1323	0.0534	0.069*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0334 (6)	0.0679 (7)	0.0394 (7)	0.000	-0.0036 (5)	0.000
S1	0.0691 (12)	0.0427 (9)	0.0970 (15)	-0.0117 (8)	-0.0099 (11)	0.0037 (8)
S2	0.0325 (14)	0.185 (3)	0.0474 (17)	0.000	-0.0027 (12)	0.000

N1	0.057 (4)	0.072 (4)	0.068 (4)	0.000 (3)	-0.001 (3)	0.028 (3)
N2	0.033 (4)	0.129 (7)	0.056 (5)	0.000	-0.007 (4)	0.000
N3	0.027 (3)	0.057 (4)	0.037 (4)	0.000	0.000 (3)	0.000
N4	0.033 (4)	0.104 (6)	0.044 (5)	0.000	-0.003 (4)	0.000
C1	0.036 (3)	0.055 (4)	0.046 (4)	0.009 (3)	-0.009 (3)	-0.014 (3)
C2	0.044 (6)	0.078 (6)	0.028 (5)	0.000	0.004 (4)	0.000
C3	0.054 (4)	0.076 (4)	0.056 (4)	-0.005 (3)	-0.004 (4)	0.015 (3)
C4	0.050 (4)	0.066 (4)	0.057 (4)	0.014 (3)	-0.007 (3)	0.006 (3)

Geometric parameters (Å, °)

Zn1—N2	1.937 (8)	N3—H3C	0.9100
Zn1—N1 ⁱ	1.936 (5)	N4—C4	1.484 (7)
Zn1—N1	1.936 (5)	N4—C4 ⁱ	1.484 (7)
Zn1—N3	2.048 (6)	N4—H4C	0.9000
S1—C1	1.633 (7)	N4—H4D	0.9000
S2—C2	1.626 (9)	C3—C4	1.509 (7)
N1—C1	1.136 (7)	C3—H3A	0.9700
N2—C2	1.143 (10)	C3—H3B	0.9700
N3—C3 ⁱ	1.469 (6)	C4—H4A	0.9700
N3—C3	1.469 (6)	C4—H4B	0.9700
N2—Zn1—N1 ⁱ	109.77 (18)	C4—N4—H4D	109.2
N2—Zn1—N1	109.77 (18)	C4 ⁱ —N4—H4D	109.2
N1 ⁱ —Zn1—N1	112.4 (3)	H4C—N4—H4D	107.9
N2—Zn1—N3	108.2 (3)	N1—C1—S1	176.9 (6)
N1 ⁱ —Zn1—N3	108.30 (19)	N2—C2—S2	179.0 (8)
N1—Zn1—N3	108.30 (19)	N3—C3—C4	112.1 (5)
C1—N1—Zn1	170.9 (5)	N3—C3—H3A	109.2
C2—N2—Zn1	173.5 (8)	C4—C3—H3A	109.2
C3 ⁱ —N3—C3	108.5 (6)	N3—C3—H3B	109.2
C3 ⁱ —N3—Zn1	115.7 (4)	C4—C3—H3B	109.2
C3—N3—Zn1	115.7 (4)	H3A—C3—H3B	107.9
C3 ⁱ —N3—H3C	105.3	N4—C4—C3	110.3 (5)
C3—N3—H3C	105.3	N4—C4—H4A	109.6
Zn1—N3—H3C	105.3	C3—C4—H4A	109.6
C4—N4—C4 ⁱ	111.9 (6)	N4—C4—H4B	109.6
C4—N4—H4C	109.2	C3—C4—H4B	109.6
C4 ⁱ —N4—H4C	109.2	H4A—C4—H4B	108.1

Symmetry code: (i) $x, -y+1/2, z$.*Hydrogen-bond geometry (Å, °)*

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4—H4C ⁱⁱ —S1 ⁱⁱ	0.90	2.72	3.470 (6)	141
N4—H4D ⁱⁱⁱ —S2 ⁱⁱⁱ	0.90	2.38	3.281 (7)	175

Symmetry codes: (ii) $-x+1/2, -y+1, z+1/2$; (iii) $x+1/2, y, -z+1/2$.