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catena-Poly[[bis[5-(4-pyridyl-κN)-2-(2-pyridylmethylsulfanyl)-1,3,4-oxadiazole]cadmium(II)]-di-μ-thiocyanato-κ^2N:S;κ^2S:N]

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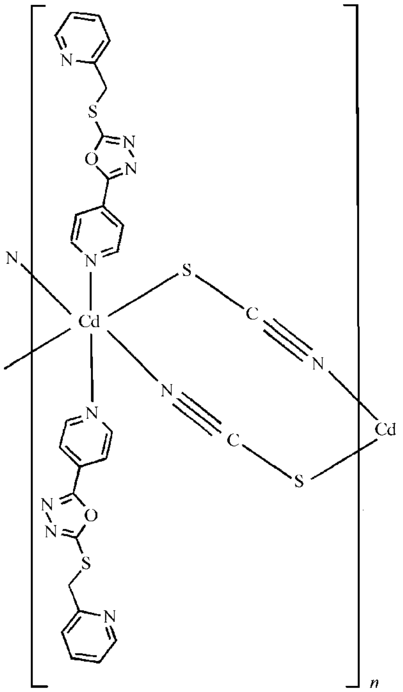
The title compound, $[Cd(NCS)_2(C_{13}H_{10}N_4OS)_2]_n$, contains SCN^- anions acting as end-to-end bridging ligands which utilize both S and N atoms to link cadmium(II) centers into one-dimensional double chains. The multidentate 5-(4-pyridyl)-2-(2-pyridylmethylsulfanyl)-1,3,4-oxadiazole ligands behave as monodentate terminal ligands, binding metal centers only through the N atoms of the 4-pyridyl groups. Two types of eight-membered rings are formed by two SCN^- anions bridging Cd^{II} centers, *viz.* planar and chair conformation, which are alternately disposed along the same chain. Finally, chains define a two-dimensional array through two different interchain π–π stacking interactions.

Comment

The formation of coordination polymers has attracted great attention in recent years because of their potential applications in separation and selective inclusion, and their ion exchange, catalysis, magnetism and nonlinear optical properties (Moulton & Zaworotko, 2001). 1,3,4-Oxadiazole exhibits the corresponding biological properties, such as antiphlogosis and antisepsis, which has given rise to an extensive variety of applications in both medicine and agriculture. Although many compounds containing symmetrical organic ligands bearing oxadiazole rings have been prepared (Du *et al.*, 2006), as far as is known coordination compounds containing asymmetric ligands with oxadiazole groups are uncommon. We purposely synthesized the pyridyl-containing asymmetric oxadiazole ligand 5-(4-pyridyl)-2-(2-pyridylmethylsulfanyl)-1,3,4-oxadiazole (pmpo). The asymmetric configuration, coordination variety and flexibility of pmpo are expected to meet metal coordination requirements (Du & Zhao, 2004). The heterocyclic groups in the ligand usually favor packing arrangements *via* π–π stacking interactions in the solid state (Atoub *et al.*, 2007). Furthermore, thiocyanate, well known for its versatile coordination modes, such as monodentate, end bridging and end-to-end bridging, was used in this research. We present here a new Cd^{II} thiocyanate complex of the asymmetrical pmpo ligand, *viz.* $[Cd(SCN)_2(pmpo)_2]_n$, (I).


(I)

The main structural feature of (I) is that the SCN^- anions act as end-to-end bridging spacers, linking Cd^{II} centers into a double chain structure, with the pmpo ligands bound edgeways; this structure is very similar to those of several reported cadmium(II) thiocyanate complexes with pyridyl-containing oxadiazole ligands (Marsh *et al.*, 2002). The Cd^{II} atom in (I) adopts an octahedral coordination geometry, with two S-bonded and two N-bonded thiocyanate ligands in the equatorial plane, and two N-bonded 4-pyridyl rings of different pmpo ligands at the axial sites (Fig. 1).

The average Cd—N and Cd—S bond lengths in the equatorial plane are 2.323 (11) and 2.77 (5) Å, respectively, and the average Cd—$N_{pyridyl}$ distance at the axial sites is 2.359 (4) Å, slightly longer than that of Cd—N_{NCS} in the equatorial plane. The average Cd—$N_{pyridyl}$ length is almost the same as that in $\{[Cd(SCN)_2(bpo)]\cdot CH_3CN\}_n$ [2.301 (4) Å; bpo is 2,5-di-4-pyridyl-1,3,4-oxodiazole; Du *et al.*, 2002] and slightly shorter than that in $[Cd(SCN)_2(bpo)_2]$ [2.463 (2) Å; Du *et al.*, 2006]. Furthermore, it is longer than that in $[Cd(NCS)(SCN)(imH)_2]_n$ [2.2749 (16) Å; imH is imidazole; Bose *et al.*, 2004]. The N—Cd—N bond angles around each Cd^{II} center are very close to 90° [mean 90.3 (15)°]; the N—Cd—S angles range from 82.45 (5) to 97.05 (5)°. The multidentate pmpo ligand behaves as a terminal ligand, with the 4-pyridyl group binding the metal center, and its two pyridyl rings subtending to each other a dihedral angle of 20.7°, deviating from the central oxadiazole plane by 14.3 and 6.7°.

Neighboring Cd$\cdots$Cd distances in a chain are 5.863 (1)–6.019 (1) Å, slightly shorter than the previously reported values [*e.g.* 6.067 (1) Å; Second *et al.*, 2000]. There are two

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types of eight-membered rings formed by the SCN^- anions bridging Cd^{II} centers in the same chain. As clearly portrayed in Fig. 1, the ring formed by the two SCN^- anions bridging atoms Cd1 and $Cd1^i$ is nearly planar, with a mean deviation from the least-square plane of 0.045 Å, while the other ring, constructed by the SCN^- anions binding atoms Cd1 and $Cd1^{ii}$, displays a chair conformation, with a corresponding mean deviation of 0.222 Å.

Adjacent one-dimensional polymeric chains are linked *via* two types of interchain π–π stacking interactions (Fig. 2). Type 1 takes place between the oxadiazole and 2-pyridyl rings, with homologous centroid-to-centroid separations of 3.603 (2) and 3.616 (2) Å, while type 2 occurs between two contiguous 4-pyridyl and 2-pyridyl rings, with a similar separation of 3.834 (2) Å. Through these interchain interactions, the one-dimensional polymeric chains stack to form a two-dimensional array.

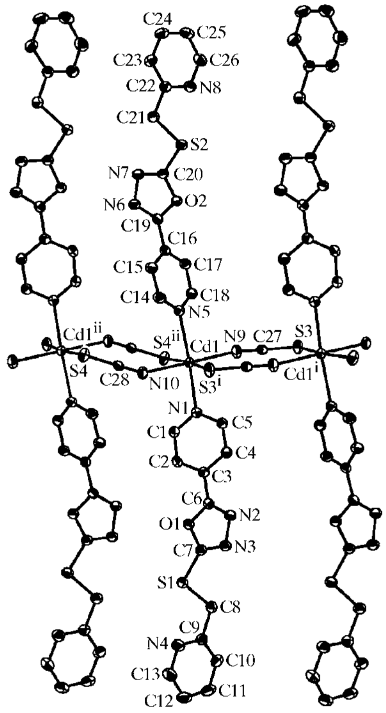

Figure 1
The structure of (I), with the atom-numbering scheme, showing the two types of eight-membered rings (30% probability displacement ellipsoids for all non-H atoms). The symmetry codes are as in Table 1.

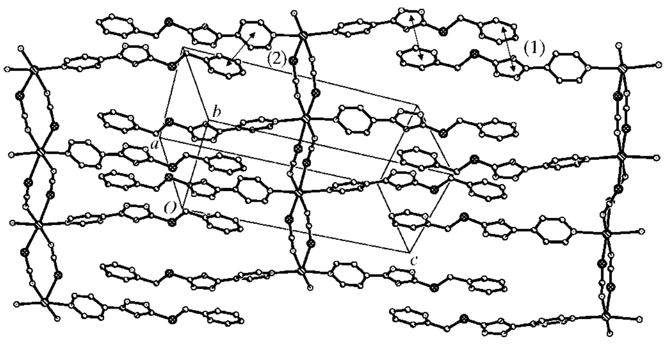

Figure 2
A view of the interchain array, showing the two types of π–π stacking interactions in (I).

Experimental

The pmpo ligand was synthesized following a procedure reported previously (Dodd & Nishi, 1997). At room temperature, to a solution of $Cd(NO_3)\cdot 4H_2O$ (0.0308 g, 0.1 mmol) in CH_3OH (5 ml) was added a solution of pmpo (0.0540 g, 0.2 mmol) in CH_3CN (5 ml) with vigorous stirring for 10 min, and then potassium thiocyanate (0.0194 g, 0.2 mmol) in aqueous solution (5 ml) was added slowly to the above mixed solution under reflux conditions. The reaction mixture was filtered and left to stand at room temperature. Well shaped colorless prismatic single crystals suitable for X-ray analysis were obtained after several days by slow evaporation of the solvent (yield 34%).

Crystal data

$[Cd(NCS)_2(C_{13}H_{10}N_4OS)_2]$
$M_r = 769.18$
Triclinic, $P\overline{1}$
$a = 7.8868\ (13)$ Å
$b = 11.1060\ (18)$ Å
$c = 19.050\ (4)$ Å
$\alpha = 104.686\ (4)°$
$\beta = 93.920\ (5)°$
$\gamma = 105.202\ (3)°$
$V = 1541.2\ (5)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.03$ mm^{-1}
$T = 291\ (2)$ K
0.50 × 0.21 × 0.12 mm

Data collection

Siemens SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.628$, $T_{max} = 0.887$
11469 measured reflections
5695 independent reflections
4955 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.054$
$S = 1.02$
5695 reflections
406 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Cd1—N9	2.3115 (19)	Cd1—N5	2.3630 (18)
Cd1—N10	2.3348 (19)	Cd1—$S3^i$	2.7172 (7)
Cd1—N1	2.3550 (17)	Cd1—$S4^{ii}$	2.8180 (8)

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

All H atoms were positioned geometrically, with C—H distances of 0.93 (CH) and 0.97 Å (CH_2), and constrained to ride on their parent atoms [$U_{iso}(H) = 1.2U_{eq}(C)$].

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3050). Services for accessing these data are described at the back of the journal.

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