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Diaquabis(2,5-di-3-pyridyl-1,3,4-oxadiazole)dithiocyanatomanganese(II): a three-dimensional supramolecular network formed through O—H···N and C—H···S interactions

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.035
wR factor = 0.099
Data-to-parameter ratio = 13.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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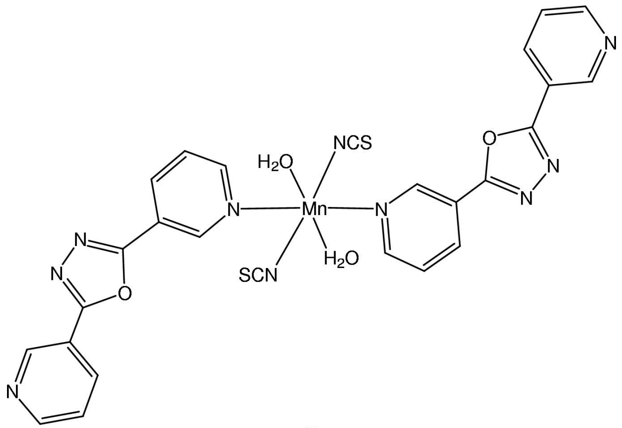
The molecular structure of the neutral mononuclear title complex, $[Mn(NCS)_2(C_{12}H_8N_4O)_2(H_2O)_2]$, is centrosymmetric; the Mn^{II} atom lies on an inversion center and is six-coordinate (MnN_4O_2), with an octahedral geometry comprising two *trans* monodentate 2,5-di-3-pyridyl-1,3,4-oxadiazole ligands, two thiocyanate ligands and two bound water molecules. Intermolecular O—H···N hydrogen bonds between these monomeric units result in two-dimensional supramolecular layers with a parallel arrangement, which are stabilized by intralayer aromatic stacking and further extended to a three-dimensional network *via* interlayer weak C—H···S interactions.

Comment

Considerable efforts have been devoted to constructing supramolecular architectures using covalent forces together with weaker hydrogen-bonding and/or other intermolecular cooperative interactions (Roesky & Andruh, 2003). Proper selection of the metal centers and organic building blocks is the key issue in the design of these polymeric networks. Recently, one of our research interests has been focused on assemblies based on bent dipyridyl ligands containing the oxadiazole spacer, mainly 2,5-di-4-pyridyl-1,3,4-oxadiazole (4-bpo) and its 3,3′-N-donor analog (3-bpo), which could produce both discrete (Du *et al.*, 2005) and infinite (Du *et al.*, 2004) coordination frameworks under appropriate conditions. Meanwhile, such *N*-heterocyclic organic compounds also have a promising ability to generate supramolecular arrays *via* hydrogen bonding and aromatic stacking interactions (Du & Zhao, 2003, 2004).



(I)

We have reported a series of M^{II}/4-bpo/NCS isostructural complexes [M^{II} = Co^{II}, Mn^{II}, Cd^{II} and Fe^{II}; Du & Zhao, 2004;

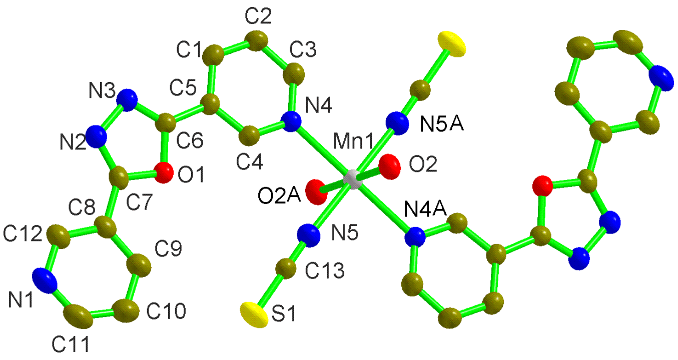


Figure 1
ORTEP-3 representation of (I), with the atomic labeling of the asymmetric unit and coordination sphere, shown with 30% probability displacement ellipsoids. H atoms have been omitted. [Symmetry code A: $1 - x, -y, 1 - z$.]

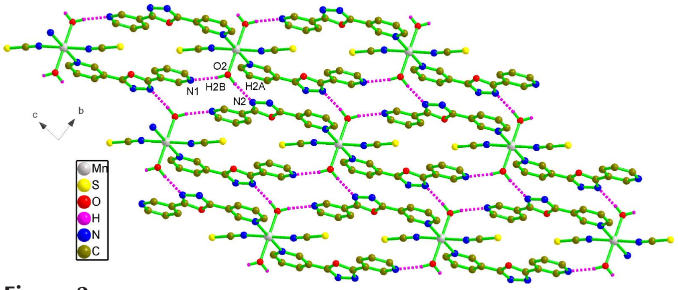


Figure 2
View of the two-dimensional supramolecular array of (I), formed *via* strong O—H···N hydrogen-bonding interactions (indicated by purple dashed lines).

Du, Liu & Bu, 2002; Fang *et al.*, 2002], which possess the general formula [M(4-bpo)$_2$(NCS)$_2$(H$_2$O)$_2$]. The mononuclear molecular species (both 4-bpo molecules and NSC$^-$ anions behave as monodentate terminal ligands) are extended to a three-dimensional supramolecular network *via* hydrogen-bonding and aromatic stacking interactions. Interestingly, by changing the metal/ligand ratio, in the Cd^{II} analog, a new three-dimensional covalent network with interesting porous properties is formed (Du, Chen & Bu, 2002). As a continuation of our investigation, we describe here the molecular/supramolecular structure of a new Mn^{II}/3-bpo/NCS complex, diaquabis(2,5-di-3-pyridyl-1,3,4-oxadiazole)dithiocyanatomanganese(II), (I).

The molecular structure of (I) reveals a neutral octahedral mononuclear centrosymmetric complex, depicted in Fig. 1. The Mn^{II} atom, on a crystallographic inversion center, is coordinated by two N-atom donors of two monodentate NSC$^-$ anions and two water molecules, forming the equatorial plane, and two pyridyl N atoms of a pair of monodentate 3-bpo ligands in *trans* arrangement at the axial sites. The axial Mn1—N4 distances [2.3449 (17) Å] are elongated in comparison with the Mn1—N5 and Mn1—O2 equatorial lengths [2.1431 (19) and 2.2107 (16) Å, respectively]. The 3-bpo ligand adopts an unusual *trans* configuration with regard to the two terminal pyridyl groups (Du & Zhao, 2003), in order to fulfill the formation of a hydrogen bond between the uncoordinated 3-pyridyl N-atom donor and the aqua ligand. The two terminal pyridyl groups make dihedral angles of 6.40 (14) and 8.80 (16)°, respectively, with the central oxadiazole ring, and the dihedral angle between the pyridyl rings is 4.23 (15)°. The NSC$^-$ ligands form C13—N5—Mn1 and N5—C13—S1 angles of 173.4 (2) and 179.8 (2)°, respectively.

Analysis of the crystal packing of the title complex suggests that the monomeric units are linked *via* hydrogen bonds to result in a three-dimensional supramolecular network. The relevant hydrogen-bonding geometries and the symmetry codes are listed in Table 2. As illustrated in Fig. 2, intermolecular O—H···N hydrogen bonds, involving the O atoms of aqua ligands and the N atoms of uncoordinated pyridyl and oxadiazole rings, extend these monomeric units to produce a two-dimensional supramolecular array. The center-to-center and center-to-plane distances between two neighboring almost antiparallel pyridyl rings are 3.87 and ~3.5 Å, revealing the existence of π–π stacking interactions, which further stabilize this structure. Furthermore, these two-dimensional hydrogen-bonding arrays are linked *via* weak interlayer C—H···S interactions between SCN$^-$ anions and 3-bpo ligands, generating a three-dimensional supramolecular network. Examination of this structure with *PLATON* (Spek, 2003) suggests that there are no solvent-accessible voids in the unit cell.

Experimental

A solution of MnCl$_2$·4H$_2$O (29 mg, 0.15 mmol) in water (5 ml) was added slowly to a solution of 3-bpo (35 mg, 0.16 mmol) in methanol/water (1:1 *v*/*v*, 10 ml) with constant stirring. An excess of NH$_4$SCN (27 mg, 0.35 mmol) was added to the above mixture under reflux for *ca* 30 min. The resulting solution was filtered and left to stand at room temperature. Colorless block crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent over a period of three weeks. Yield: 26 mg (50%). Analysis calculated for C$_{26}$H$_{20}$MnN$_{10}$O$_4$S$_2$: C 47.63, H 3.08, N 21.35%; found: C 47.76, H 2.88, N 20.90%. IR (KBr pellet, cm^{-1}): 3258 (*b*), 3068 (*m*,) 2070 (*vs*), 1603 (*s*), 1547 (*m*), 1484 (*s*), 1461 (*s*), 1435 (*s*), 1415 (*s*), 1336 (*m*), 1274 (*w*), 1197 (*m*), 1127 (*w*), 1088 (*s*), 1026 (*s*), 999 (*w*), 964 (*m*), 824 (*s*), 733 (*m*), 698 (*s*), 635 (*m*).

Crystal data

[Mn(NCS)$_2$(C$_{12}$H$_8$N$_4$O)$_2$(H$_2$O)$_2$]
$M_r = 655.58$
Triclinic, $P\overline{1}$
$a = 8.1951$ (19) Å
$b = 8.762$ (2) Å
$c = 10.619$ (3) Å
$\alpha = 82.472$ (3)°
$\beta = 77.181$ (3)°
$\gamma = 79.873$ (3)°
$V = 728.5$ (3) Å^3
$Z = 1$
$D_x = 1.494$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1513 reflections
$\theta = 2.6$–26.7°
$\mu = 0.65$ mm^{-1}
$T = 293$ (2) K
Block, colorless
0.40 × 0.24 × 0.11 mm

Data collection

Bruker APEX-II CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.772$, $T_{\max} = 0.931$
4203 measured reflections
2540 independent reflections
2005 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 25.0$°
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 9$
$l = -10 \rightarrow 12$

m486 Du *et al.* • [Mn(NCS)$_2$(C$_{12}$H$_8$N$_4$O)$_2$(H$_2$O)$_2$] *Acta Cryst.* (2005). E**61**, m485–m487

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.099$
$S = 1.04$
2540 reflections
196 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 0.1207P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—N5	2.1431 (19)	S1—C13	1.613 (2)
Mn1—O2	2.2107 (16)	N5—C13	1.157 (3)
Mn1—N4	2.3449 (17)		
N5—Mn1—O2^{i}	90.61 (7)	O2^{i}—Mn1—N4	86.54 (6)
N5—Mn1—O2	89.39 (7)	O2—Mn1—N4	93.46 (6)
N5—Mn1—N4	89.80 (7)	N5—C13—S1	179.8 (2)
N5^{i}—Mn1—N4	90.20 (7)		

Symmetry code: (i) $-x+1, -y, -z+1$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2A···N2^{i}	0.85	1.98	2.822 (3)	170
O2—H2B···N1^{ii}	0.85	1.96	2.796 (3)	165
C10—H10···S1^{iii}	0.93	2.84	3.582 (4)	138

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

Although all H atoms were visible in difference maps, they were placed in geometrically calculated positions, with C—H distances of 0.93 Å and O—H distances of 0.85 Å, and included in the final refinement in the riding-model approximation, with displacement parameters derived from their parent atoms [U_{iso}(H) = 1.2U_{eq}(C,O)].

Data collection: *APEX2* (Bruker, 2003); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXTL* (Bruker, 2001).

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Acta Cryst. (2005). E**61**, m485–m487 Du *et al.* • $[Mn(NCS)_2(C_{12}H_8N_4O)_2(H_2O)_2]$ **m487**