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The mononuclear cobalt(II) complex $Co^{II}(DMBDIZ)_2(NCS)_2$, where DMBDIZ is 2,6-dimethylbenzo-[1,2-*d*:4,5-*d*′]diimidazole

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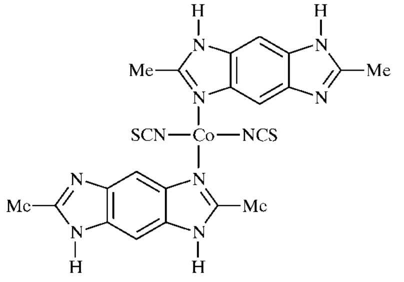
In the title mononuclear cobalt complex, bis(2,6-dimethyl-1*H*,7*H*-benzo[1,2-*d*:4,5-*d*′]diimidazole-κN^3)bis(thiocyanato-κN)-cobalt(II), $[Co^{II}(NCS)_2(DMBDIZ)_2]$ or $[Co(NCS)_2(C_{10}H_{10}N_4)_2]$, the cobalt(II) ion is coordinated to four N atoms, from two thiocyanate anions and two DMBDIZ ligands, in a distorted tetrahedral geometry. In the DMBDIZ ligand, the two imine N atoms are positioned *cis* with respect to one another. The crystal packing of the complex is dominated by both hydrogen bonding, involving two N—H···N and two N—H···S interactions, and aromatic π–π stacking.

Comment

The supramolecular architecture created by non-covalent forces has become increasingly important in crystal engineering. Current interests focus on designing multidentate aromatic nitrogen heterocycles (Stang & Olenyuk, 1997; Steel, 1990) and polycarboxylic acid ligands (Eddaoudi *et al.*, 2002; Abrahams *et al.*, 1999). In order to construct novel frameworks through both coordination and hydrogen bonding, we have recently become interested in the synthesis of metal complexes of DMBDIZ (2,6-dimethylbenzo[1,2-*d*:4,5-*d*′]-diimidazole). This ligand is not only capable of adopting various coordination modes, but can also form multiple hydrogen bonds, which may provide a tool in crystal-engineering design for assembling building blocks into multi-dimensional structures (Aakeröy *et al.*, 2001; Holman *et al.*, 2001). We present here the crystal structure of a mononuclear cobalt complex, (I), which forms a three-dimensional network through hydrogen bonding and aromatic π–π stacking.

As shown in Fig. 1, the cobalt ion has a distorted tetrahedral geometry with four nitrogen binding sites, one from the each of the two DMBDIZ ligands and two from the *N*-bonded thiocyanate anions. The N9—Co1 and N10—Co1 bond distances are slightly different, and the C21—N10—Co1 and C22—N9—Co1 angles are notably different (Table 1), indicating that the environments of the two thiocyanate anions are not the same, which is also consistent with the IR spectrum, which shows two peaks due to the *N*-bonded thiocyanate anions. Both DMBDIZ ligands are planar; the dihedral angle between the two ligand planes is 63.39 (7)° and the bond lengths are all within the expected range for a delocalized imidazole system (Tomlin *et al.*, 2000).



(I)

The geometry of the imidazole rings is asymmetrical about the line passing through the apical C atoms (C1/C10 and C11/C20 in the two ligands); this is seen in the N1—C2/N2—C2 and N7—C12/N8—C12 bond lengths being different, thereby indicating that atoms N2 and N8 are amine as opposed to imine. Thus, the imine N atoms are located *cis* with respect to one another in the two DMDBIZ ligands.

The hydrogen-bond network of this *cis* isomer leads to an efficient crystal packing. Since only one N atom in each ligand takes part in the metal coordination, the second imine N atom acts as an H-atom acceptor, forming a hydrogen bond with the NH moiety of an adjacent ligand. In total, each complex is connected to the adjacent complex molecules *via* eight hydrogen bonds (see Table 2).

As shown in Fig. 2, the complexes are linked into a one-dimensional chain along the *c* axis though hydrogen bonds between the DMDBIZ ligands and the thiocyanate anions (N8—H8*A*···S1^{i} and N2—H2*A*···S2^{iv}; see Table 2 for symmetry codes). Furthermore, these chains are linked into a three-dimensional network through intermolecular hydrogen bonds between the DMDBIZ ligands (N3—H3*A*···N1^{iii} and N6—H6*A*···N7^{ii}; see Table 2 for symmetry codes) along the *a* and *b* axes. The two pairs of DMDBIZ ligands formed through S···H—N hydrogen bonds are each arranged in an anti-parallel fashion, with mean distances between the DMDBIZ planes of 3.419 (5) and 3.556 (3) Å, indicative of aromatic π–π-stacking interactions (Ho *et al.*, 1999).

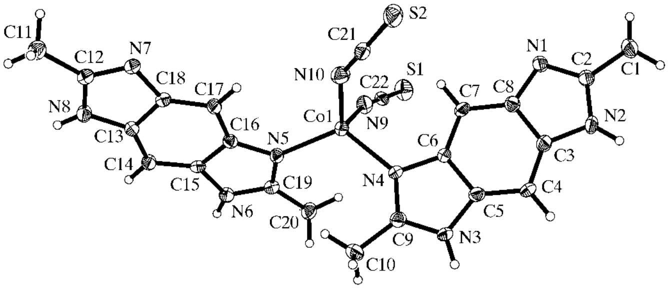


Figure 1
The structure of (I), showing 30% probability displacement ellipsoids and the atomic numbering scheme.

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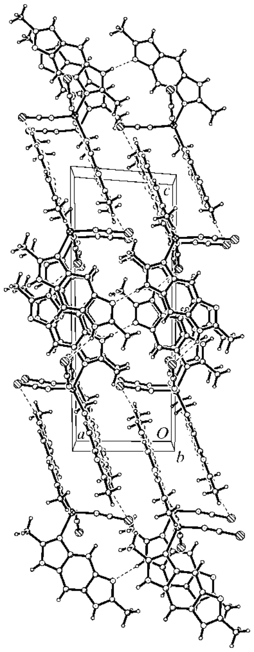

Figure 2
The crystal packing of (I), showing the hydrogen bonding viewed along the *b* axis.

Experimental

DMDBIZ was synthesized from 1,2,4,5-benzenetetramine according to Arient *et al.* (1960). 1,2,4,5-Benzenetetramine was synthesized from 2-dichlorobenzene by a three-step reaction (Cai, 2002). The free ligand DMBDIZ (0.25 mmol) and $Co(ClO_4)_2 \cdot 6H_2O$ (0.125 mmol) were each dissolved in ethanol (10 ml); the Co^{II} salt solution was added slowly to the ligand solution followed by a slight excess of NH_4SCN in ethanol. The resulting blue solution was allowed to stand at room temperature. Large dark-blue crystals formed slowly over a period of several days (yield: 80%). Elemental analysis: C 48.8, H 3.3, N 25.0%; calculated: C 48.2, H 3.6, N 25.5%. IR spectrum (KBr, cm^{-1}): 2082 ν(CN), 2052 ν(CN).

Crystal data

$[Co(NCS)_2(C_{10}H_{10}N_4)_2]$
$M_r = 547.53$
Triclinic, $P\overline{1}$
$a = 7.9459$ (13) Å
$b = 7.9698$ (12) Å
$c = 20.111$ (3) Å
$\alpha = 80.527$ (3)°
$\beta = 84.183$ (3)°
$\gamma = 67.291$ (3)°
$V = 1157.8$ (3) Å^3

$Z = 2$
$D_x = 1.571$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1139 reflections
$\theta = 2.8$–21.6°
$\mu = 0.96$ mm^{-1}
$T = 293$ (2) K
Block, dark blue
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.762$, $T_{max} = 0.832$
5908 measured reflections

3999 independent reflections
2919 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 25.0°$
$h = -9 \rightarrow 9$
$k = -5 \rightarrow 9$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.127$
$S = 1.01$
3999 reflections
320 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2)]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N4	2.011 (3)	N3—C9	1.323 (5)
Co1—N5	2.014 (3)	N4—C9	1.327 (5)
Co1—N9	1.958 (4)	N5—C19	1.327 (5)
Co1—N10	1.943 (4)	N6—C19	1.342 (5)
S1—C22	1.606 (5)	N7—C12	1.299 (5)
S2—C21	1.614 (5)	N8—C12	1.351 (5)
N1—C2	1.314 (5)	N9—C22	1.163 (5)
N2—C2	1.347 (5)	N10—C21	1.162 (5)
N4—Co1—N5	120.65 (13)	N10—Co1—N5	114.40 (15)
N9—Co1—N4	105.60 (14)	C21—N10—Co1	147.6 (4)
N9—Co1—N5	103.63 (14)	C22—N9—Co1	167.4 (4)
N10—Co1—N9	110.31 (16)	N9—C22—S1	178.7 (4)
N10—Co1—N4	101.89 (14)	N10—C21—S2	178.5 (4)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2A⋯S2^{iv}	0.86	2.70	3.458 (4)	148
N3—H3A⋯N1^{iii}	0.86	2.14	3.001 (4)	177
N6—H6A⋯N7^{ii}	0.86	2.05	2.899 (4)	170
N8—H8A⋯S1^{i}	0.86	2.59	3.439 (4)	172

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

All H atoms were located, placed in idealized positions and refined using a riding model (C—H = 0.93 and 0.96 Å).

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1029). Services for accessing these data are described at the back of the journal.

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