Crystal structure of bis(biimidazole-κ^2N,N')-bis(isothiocyanato-κN)cobalt(II) — dimethylsulfoxide (1:2), $Co(C_6H_6N_4)_2(NCS)_2 \cdot 2C_2H_6SO$

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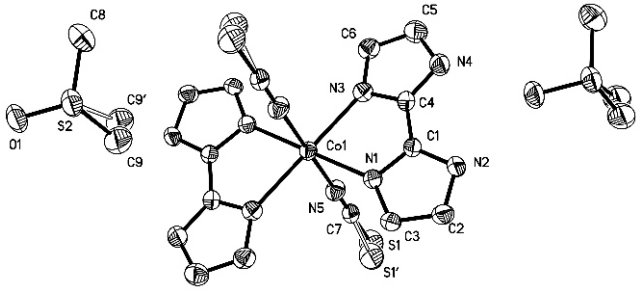

Abstract

$C_{18}H_{24}CoN_{10}O_2S_4$, monoclinic, $P2_1/n$ (no. 14), a = 8.021(1) Å, b = 16.120(2) Å, c = 10.480(2) Å, β = 90.903(1)°, V = 1354.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.063, $wR_{ref}(F^2)$ = 0.216, T = 298 K.

Source of material

An aqueous solution (5 mL) of cobalt sulphate (1 mmol, 0.250 g) was slowly poured dropwise into a hot aqueous solution (3 ml) of ammonium thiocyanate (1 mmol, 0.0761 g). The mixture was stirred for 10 mins. 2,2′-Biimidazole (H_2biim, 1 mmol, 0.134 g) and DMSO (4 ml) were added to this mixture. The resultant mixture was refluxed for 30 min and then allowed to cool to ambient temperature. The insoluble residues were removed by filtration, and the filtrate was evaporated slowly at room temperature for about one week to yield pink crystalline product. Block-shaped crystals suitable for single crystal X-ray diffraction were selected directly from the product.

Experimental details

The disorder of DMSO and isothiocyanate groups is the result of intense thermal vibration of the terminal group, which is also responsible for the huge R values. The occupation parameters were obtained by normalization refinement. There is no relationship between the parameters. S1 and C9 were refined with common ADPs, because a reasonable occupation could be obtained.

Discussion

Metal-organic supramolecular compounds have received much attention due to their structural diversities and potential applications as new materials [1-5]. The consideration and utilization of the coordination bonds, intermolecular hydrogen bonds and π–π packing interactions helps to control the molecular arrangement. H_2biim is an excellent candidate for building a supramolecular structure involving directed hydrogen bonding interactions. The uncoordinated N–H groups in H_2biim participate in various hydrogen bonds with counter anions or other acceptors [6-8]. We focus on the synthesis of metal-biimidazole supramolecular compounds [9-11].

The asymmetric unit of the title crystal structure consists of the neutral moiety $[Co(C_6H_6N_4)_2(NCS)_2]$ and two free DMSO molecules. The coordination environment around the Co(II) atom can be described as a distorted octahedron. Four nitrogen atoms of two chelate H_2biim ligands form the equatorial plane of the octahedron, whereas the apical positions are occupied by nitrogen atoms from two isothiocyanate anions. The difference of Co—N distances (d(Co—N1) = 2.146 Å, d(Co—N3) = 2.186 Å) shows an asymmetric coordination behavior. These bond distances and angles in the H_2biim ligand are comparable with those registered for Co-biimidazole complexes in the Crystal Structure Database (range for d(M—N) = 2.030-2.240 Å). Just like the isothiocyanate compounds which have in common the bridging coordination modes in their metal complexes such as $[Cu(H_2biim)(NCS)_2]_n$ [12], the two N atoms from two NCS^- anions are in a straight line with ∠N5–Co–N5 = 180° and d(Co—N5) = 2.126(5) Å. The coordination mode of isothiocyanate ion is different from those found in similar types of complexes such as $[Cd(H_2biim)_2(SCN)_2]$ [13]. Molecular packing is controlled to a great extent by the ability of coordinated H_2biim to form hydrogen bonds with solvent molecules. DMSO molecules and Co complexes are self-assembled via robust hydrogen bond of type $R_2^1(7)$ (d(N···O) = 2.741 Å, 2.792 Å, ∠N–H···O = 149.9(6)°, 151.5(5)°) formed by the DMSO molecule and H_2biim ligand. The intramolecular π–π interactions between biimidazole rings with an average distance of 3.6 Å along [001] help to stabilize the stacking arrangement.

Table 1. Data collection and handling.

Crystal:	pink block, size 0.20 × 0.30 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.77 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6652, 2386
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1796
$N(param)_{refined}$:	171
Programs:	SHELXS-97, SHELXL-97, SHELXTL [14]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(2)	4*e*		1.0514	0.5199	0.7015	0.060
H(4)	4*e*		0.9251	0.3718	0.7750	0.068
H(2A)	4*e*		1.0718	0.6514	0.5872	0.063
H(3)	4*e*		0.8085	0.6657	0.4676	0.057
H(5)	4*e*		0.7289	0.2598	0.7978	0.079
H(6)	4*e*		0.4818	0.3002	0.6712	0.067
H(8A)	4*e*		0.1421	0.3030	–0.0217	0.171
H(8B)	4*e*		0.3287	0.3008	0.0248	0.171
H(8C)	4*e*		0.2817	0.2752	–0.1155	0.171
H(9A)	4*e*	0.60	0.2674	0.5294	0.0174	0.146
H(9B)	4*e*	0.60	0.3586	0.4592	0.0951	0.146
H(9C)	4*e*	0.60	0.1637	0.4586	0.0813	0.146
H(9'1)	4*e*	0.40	0.2377	0.4994	0.0804	0.146
H(9'2)	4*e*	0.40	0.3006	0.4122	0.1266	0.146
H(9'3)	4*e*	0.40	0.1139	0.4242	0.0842	0.146

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	2*a*		½	½	½	0.0385(6)	0.0425(7)	0.0415(7)	0.0016(5)	–0.0016(4)	–0.0035(5)
N(1)	4*e*		0.7404(6)	0.5526(3)	0.5424(5)	0.039(3)	0.041(3)	0.048(3)	0.001(2)	–0.002(2)	–0.001(2)
N(2)	4*e*		0.9761(6)	0.5401(3)	0.6511(5)	0.044(3)	0.047(3)	0.057(3)	0.000(2)	–0.011(2)	0.006(3)
N(3)	4*e*		0.6075(6)	0.4064(3)	0.6279(5)	0.047(3)	0.047(3)	0.046(3)	–0.003(2)	0.004(2)	0.001(2)
N(4)	4*e*		0.8274(7)	0.3699(3)	0.7400(5)	0.057(3)	0.057(3)	0.056(3)	–0.004(3)	–0.007(3)	0.008(3)
N(5)	4*e*		0.4074(7)	0.5674(4)	0.6582(5)	0.054(3)	0.057(3)	0.049(3)	0.003(3)	0.002(2)	–0.011(3)
O(1)	4*e*		0.1270(7)	0.4319(4)	–0.1741(5)	0.083(4)	0.083(4)	0.075(4)	–0.008(3)	–0.034(3)	0.024(3)
S(1)	4*e*	0.78(2)	0.306(1)	0.6654(5)	0.8631(8)	0.116(4)	0.093(4)	0.063(3)	0.038(3)	–0.006(3)	–0.034(3)
S(1')	4*e*	0.22(2)	0.353(3)	0.688(2)	0.823(2)	0.116(4)	0.093(4)	0.063(3)	0.038(3)	–0.006(3)	–0.034(3)
S(2)	4*e*		0.2801(2)	0.4140(1)	–0.0953(2)	0.062(1)	0.080(1)	0.055(1)	0.013(1)	–0.0097(8)	0.0011(9)
C(1)	4*e*		0.8278(7)	0.5051(4)	0.6208(6)	0.043(3)	0.043(3)	0.042(3)	0.001(3)	–0.004(2)	–0.003(3)
C(2)	4*e*		0.9838(8)	0.6139(4)	0.5861(6)	0.051(4)	0.044(3)	0.064(4)	–0.004(3)	0.000(3)	0.002(3)
C(3)	4*e*		0.8380(8)	0.6213(4)	0.5199(6)	0.048(3)	0.038(3)	0.057(4)	0.002(3)	–0.004(3)	0.003(3)
C(4)	4*e*		0.7584(7)	0.4275(4)	0.6643(5)	0.046(3)	0.047(3)	0.040(3)	0.000(3)	–0.005(3)	–0.001(3)
C(5)	4*e*		0.716(1)	0.3085(5)	0.7511(7)	0.072(5)	0.061(4)	0.065(5)	–0.007(4)	0.002(4)	0.013(4)
C(6)	4*e*		0.5789(9)	0.3312(4)	0.6810(6)	0.062(4)	0.053(4)	0.053(4)	–0.011(3)	0.005(3)	0.005(3)
C(7)	4*e*		0.3712(8)	0.6094(4)	0.7386(7)	0.051(4)	0.052(4)	0.058(4)	0.007(3)	–0.014(3)	–0.006(3)
C(8)	4*e*		0.255(2)	0.3119(6)	–0.047(1)	0.16(1)	0.083(7)	0.103(8)	0.009(7)	–0.049(7)	0.023(6)
C(9)	4*e*	0.60(7)	0.266(6)	0.472(3)	0.039(4)	0.11(2)	0.08(2)	0.10(2)	0.02(2)	–0.02(2)	–0.03(2)
C(9')	4*e*	0.40(7)	0.227(9)	0.441(4)	0.068(7)	0.11(2)	0.08(2)	0.10(2)	0.02(2)	–0.02(2)	–0.03(2)

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