Crystal structure of 2,2′-bis(4,5-dimethylimidazole)(dithiocyanato)mercury(II), $Hg(C_{10}H_{14}N_4)(CNS)_2$

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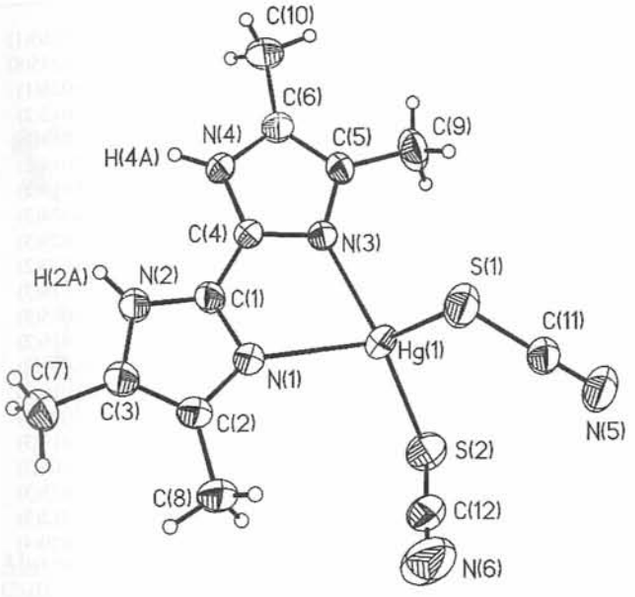

Abstract

$C_{12}H_{14}HgN_6S_2$, triclinic, $P\bar{1}$ (No. 2), a = 7.732(2) Å, b = 10.252(2) Å, c = 11.802(2) Å, α = 65.57(3)°, β = 72.19(3)°, γ = 88.13(3)°, V = 806.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.048, $wR_{ref}(F^2)$ = 0.123, T = 293 K.

Source of material

The complex was prepared by dissolving mercury(II) thiocyanate (0.316 g, 1 mmol) in distillation water and adding an alcoholic solution of 2,2′-bis(4,5-dimetyleimidazole) ligand (0.190 g, 2 mmol). The resulting solution was stirred for 5 h at room temperature, then it was allowed to stand for 2-3 days in a refrigerator (ca. 6 °C). Black crystals of the desired product precipitated, which were filtered off, washed with acetone and ether and air dried (0.354 g, yield 70%). Analysis: found – C, 28.61%; H, 2.68%; N, 16.43%; calculated for $C_{12}H_{14}HgN_6S_2$ – C, 28.40%; H, 2.76%; N 16.60%. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer.

Discussion

The ability of mercury(II) salts to form a wide variety of 1:1 and 1:2 complexes, with neutral ligands has been known for some time [1]. Most of these complexes contain halide ions and the thiocyanate ion have been rarely reported [2]. This ion is an ambidentate ligand and can coordinate via both N and S atoms. The coordination mode depends on the nature of the metal center. Hence N-donor atoms are found in Zn complexes, while in mercury(II) complexes, the S atom is undoubtedly the expected ligating site for Hg^{+2} [2]. The complex is built up of a monomeric $Hg(SCN)_2$ unit [d(Hg1—S1) = 2.539(2) Å and d(Hg1—S2) = 2.408(2) Å], with one 2,2′-bis(4,5-dimetylimidazole) ligand coordinating the Hg atom via the two N atoms. This gives rise to a five-member chelate ring Hg/N1/C1/C4/N3: d(Hg1—N1) = 2.250(5) Å and d(Hg1—N3) = 2.403(6) Å, and to a distorted tetrahedral environment for Hg atoms. The smallest and largest bond angles around the Hg atoms are ∠N3–Hg1–S2 = 140.5(2)° and ∠N1–Hg1–N3 = 74.2(2)°, respectively. There is π-π stacking interaction (charge-transfer arrays) [2] between the parallel aromatic rings belonging to adjacent chains. In the planar species the mean molecular planes are close to parallel and separated by a distance of ~ 3.5 Å, which is close to that of the planes in graphite. The complexes are linked by hydrogen bonds. The coordinating 2,2′-bis(4,5-dimetylimidazole) molecule is involved in hydrogen bonding acting as hydrogen-bond donor with N atoms of thiocyanate ions as potential hydrogen-bond acceptors. Each complex is bonded to two neighbors. Both amine H atoms are hydrogen bonded to N atoms.

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Table 1. Data collection and handling.

Crystal:	black prism, size 0.2 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	98.05 cm^{-1}
Diffractometer, scan mode:	Rebuild Syntex P2$_1$/Siemens P3, $\theta/2\theta$
$2\theta_{max}$:	56.12°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4204, 3922
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3367
$N(param)_{refined}$:	192
Programs:	SHELXTL-plus [4], SHELXTL-97 [5], SADABS [6]

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

Atom	Site	x	y	z	U_{iso}
H(11A)	2*i*	0.1859	–0.3725	0.5840	0.097
H(11B)	2*i*	0.2765	–0.4389	0.4846	0.097
H(11C)	2*i*	0.0654	–0.4287	0.5247	0.097
H(10A)	2*i*	0.2333	–0.1416	0.5722	0.084
H(10B)	2*i*	0.1583	0.0041	0.5033	0.084
H(10C)	2*i*	0.3693	–0.0067	0.4645	0.084
H(12A)	2*i*	0.3213	0.3226	–0.3151	0.079
H(12B)	2*i*	0.4504	0.3619	–0.2515	0.079

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(12C)	2*i*	0.2412	0.3784	–0.2064	0.079
H(13A)	2*i*	0.2622	0.1125	–0.3296	0.075
H(13B)	2*i*	0.1202	–0.0220	–0.2300	0.075
H(13C)	2*i*	0.3291	–0.0401	–0.2726	0.075
H(2A)	2*i*	0.2005	–0.2866	0.2494	0.040
H(4A)	2*i*	0.2091	–0.1528	0.0028	0.030

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg(1)	2*i*	0.32749(4)	0.24935(3)	0.11568(3)	0.0629(2)	0.0337(2)	0.0564(2)	0.0089(1)	–0.0306(1)	–0.0260(1)
S(1)	2*i*	0.0266(3)	0.3568(2)	0.1570(2)	0.0476(8)	0.0367(9)	0.070(1)	0.0044(7)	–0.0221(8)	–0.0245(8)
S(2)	2*i*	0.5583(3)	0.3612(2)	0.1551(2)	0.0517(9)	0.053(1)	0.064(1)	–0.0034(8)	–0.0237(9)	–0.026(1)
N(1)	2*i*	0.2617(8)	–0.0029(6)	0.2612(5)	0.056(3)	0.029(3)	0.035(3)	0.003(2)	–0.021(2)	–0.012(2)
N(2)	2*i*	0.2153(9)	–0.2185(6)	0.2721(5)	0.069(4)	0.030(3)	0.030(3)	0.004(2)	–0.018(3)	–0.013(2)
N(3)	2*i*	0.2997(8)	0.1375(6)	–0.0076(5)	0.052(3)	0.028(2)	0.029(2)	0.007(2)	–0.018(2)	–0.014(2)
N(4)	2*i*	0.2358(8)	–0.0621(6)	–0.0199(5)	0.056(3)	0.028(2)	0.036(3)	0.008(2)	–0.021(2)	–0.018(2)
N(5)	2*i*	0.166(1)	0.6196(8)	0.1293(8)	0.097(5)	0.035(3)	0.061(4)	0.006(3)	–0.028(4)	–0.024(3)
N(6)	2*i*	0.358(2)	0.328(1)	0.411(1)	0.19(1)	0.080(7)	0.055(5)	–0.023(8)	–0.031(6)	–0.029(5)
C(1)	2*i*	0.2450(9)	–0.0776(7)	0.1962(6)	0.052(3)	0.030(3)	0.027(3)	0.008(2)	–0.015(2)	–0.013(2)
C(2)	2*i*	0.241(1)	–0.1021(8)	0.3875(6)	0.055(4)	0.038(3)	0.031(3)	0.001(3)	–0.017(3)	–0.014(3)
C(3)	2*i*	0.213(1)	–0.2373(8)	0.3963(7)	0.064(4)	0.037(3)	0.032(3)	0.005(3)	–0.017(3)	–0.015(3)
C(4)	2*i*	0.2607(9)	–0.0054(7)	0.0584(6)	0.048(3)	0.028(3)	0.035(3)	0.008(2)	–0.020(3)	–0.016(2)
C(5)	2*i*	0.2956(9)	0.1724(7)	–0.1333(6)	0.047(3)	0.028(3)	0.030(3)	0.006(2)	–0.016(3)	–0.009(2)
C(6)	2*i*	0.2590(9)	0.0481(7)	–0.1417(6)	0.054(3)	0.034(3)	0.029(3)	0.005(3)	–0.017(3)	–0.016(2)
C(7)	2*i*	0.182(2)	–0.3822(9)	0.5072(8)	0.110(7)	0.039(4)	0.040(4)	0.002(4)	–0.030(4)	–0.008(3)
C(8)	2*i*	0.251(1)	–0.0576(9)	0.4911(7)	0.091(6)	0.048(4)	0.035(4)	0.000(4)	–0.026(4)	–0.019(3)
C(9)	2*i*	0.330(1)	0.3219(8)	–0.2355(8)	0.074(5)	0.033(3)	0.041(4)	0.010(3)	–0.019(3)	–0.005(3)
C(10)	2*i*	0.241(1)	0.0223(9)	–0.2535(7)	0.071(4)	0.052(4)	0.039(4)	0.008(4)	–0.027(3)	–0.025(3)
C(11)	2*i*	0.110(1)	0.5109(7)	0.1414(7)	0.056(4)	0.031(3)	0.035(3)	0.006(3)	–0.016(3)	–0.012(3)
C(12)	2*i*	0.434(1)	0.3393(9)	0.3075(9)	0.083(6)	0.043(4)	0.060(5)	–0.008(4)	–0.036(4)	–0.020(4)

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