Crystal structure of 2,2'-bis(4,5-dimethylimidazole)(dithiocyanato)mercury(II), $\text{Hg}(\text{C}_{10}\text{H}_{14}\text{N}_4)(\text{CNS})_2$

A. R. Mahjoub^{*,I}, A. Ramazani^{II} and A. Morsali^I^I Tarbiat Modarres University, School of Science, Department of Chemistry, P. O. Box 14155-4838, Tehran, I. R. Iran^{II} University of Zanjan, Department of Chemistry, P. O. Box 45195-313, Zanjan, I. R. Iran

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Abstract

$\text{C}_{12}\text{H}_{14}\text{HgN}_6\text{S}_2$, triclinic, $P\bar{1}$ (No. 2), $a = 7.732(2)$ Å, $b = 10.252(2)$ Å, $c = 11.802(2)$ Å, $\alpha = 65.57(3)^\circ$, $\beta = 72.19(3)^\circ$, $\gamma = 88.13(3)^\circ$, $V = 806.2$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.048$, $wR_{\text{ref}}(F^2) = 0.123$, $T = 293$ 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-dimethylimidazole) 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 $\text{C}_{12}\text{H}_{14}\text{HgN}_6\text{S}_2$ – 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 $\text{Hg}(\text{SCN})_2$ unit [$d(\text{Hg1}—\text{S1}) = 2.539(2)$ Å and $d(\text{Hg1}—\text{S2}) = 2.408(2)$ Å], with one 2,2'-bis(4,5-dimethylimidazole) ligand coordinating the Hg atom via the two N atoms. This gives rise to a five-member chelate ring $\text{Hg}/\text{N1}/\text{C1}/\text{C4}/\text{N3}$: $d(\text{Hg1}—\text{N1}) = 2.250(5)$ Å and $d(\text{Hg1}—\text{N3}) = 2.403(6)$ Å, and to a distorted tetrahedral environment for Hg atoms. The smallest and largest bond angles around the Hg atoms are $\angle\text{N3}—\text{Hg1}—\text{S2} = 140.5(2)^\circ$ and $\angle\text{N1}—\text{Hg1}—\text{N3} = 74.2(2)^\circ$, 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-dimethylimidazole) 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.

Table 1. Data collection and handling.

Crystal:	black prism, size $0.2 \times 0.3 \times 0.4$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	98.05 cm ⁻¹
Diffractometer, scan mode:	Rebuild Syntex P21/Siemens P3, $\theta/2\theta$
$2\theta_{\text{max}}$:	56.12°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4204, 3922
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3367
$N(\text{param})_{\text{refined}}$:	192
Programs:	SHELXTL-plus [4], SHELXTL-97 [5], SADABS [6]

Table 2. Atomic coordinates and displacement parameters (in Å²).

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

* Correspondence author (e-mail: mahjoub@net1cs.modares.ac.ir)

Table 2. Continued.

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

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Hg(1)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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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