Crystal structure of [hydroxy-methoxy-di(2-pyridyl)methane-κ^2N,N'](μ_2-thiocyanato-*N*:*S*)(thiocyanato-κS)mercury(II), $Hg(C_{12}H_{12}N_2O_2)(SCN)_2$

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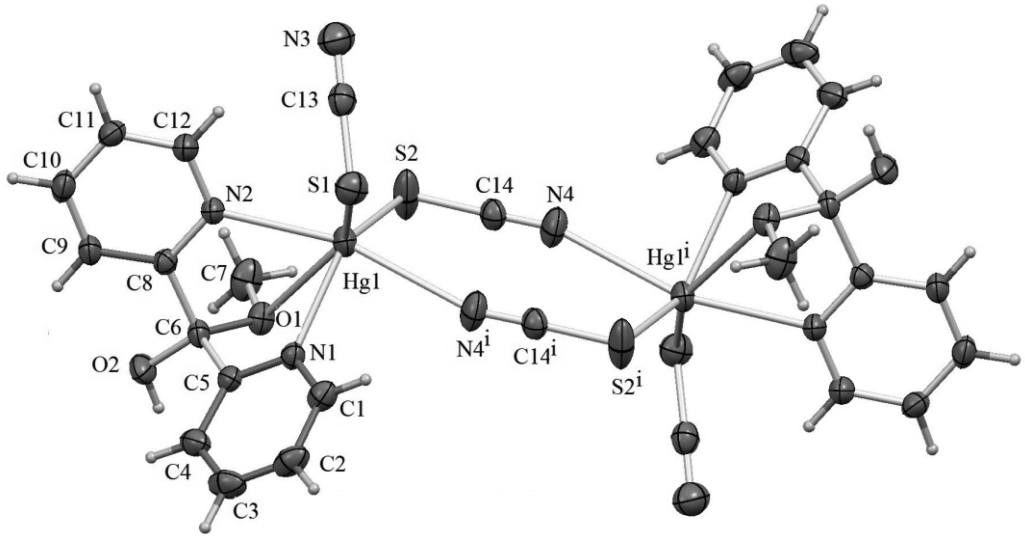

Abstract

$C_{14}H_{12}HgN_4O_2S_2$, monoclinic, $P2_1/n$ (no. 14), a = 9.099(1) Å, b = 14.167(1) Å, c = 13.192(2) Å, β = 101.035(9)°, V = 1669.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.038, $wR_{ref}(F^2)$ = 0.081, T = 298 K.

Source of material

A solution of di(2-pyridyl)ketone (0.20 g, 1.10 mmol) in methanol (20 ml) was added to a solution of $Hg(SCN)_2$ (0.35 g, 1.10 mmol) in methanol (20 ml) and the resulting colorless solution was stirred for 20 min at 40 °C. This solution was left to evaporate slowly at room temperature. After one week, colorless block-shaped crystals of the title compound were isolated (yield 0.42 g, 71.6 %).

Discussion

Di(2-pyridyl)ketone (dpk) is a molecule that can exhibit different modes of coordination. As a bidentate ligand, it may present an *N*,*O*-coordination giving a five-membered chelate ring or an *N*,*N*′-coordination forming a three or six-membered ring [1-3]. Frequently, the coordinated dpk undergoes nucleophilic addition of water or an alcohol at the carbonylic carbon atom to form the diol or the corresponding hemiacetal, $(py)_2C(OR)(OH)$, which, deprotonated, acts as mononegative, tridentate *N*,*O*,*N*′-donor ligand. The three donor atoms may be coordinated to one metal atom [4-6] or two metal atoms in a bridging mode [7-9].

The asymmetric unit of the title crystal structure consists of one mercury(II) cation, one hydroxy-methoxy-di(2-pyridyl)methane molecule, one bridging SCN anion and one terminal SCN anion. In the centrosymmetric dinuclear unit, two SCN anions bridge two Hg(II) atoms, and each Hg(II) atom is also bonded to a terminal SCN anion and a hydroxy-methoxy-di(2-pyridyl)-methane (dpk·CH_3OH) ligand. The latter functions in an *N*,*O*,*N*′-tridentate mode, resulting in a distorted octahedral coordination of Hg1. This distortion can be attributed to the *N*,*O*,*N*′-terdentate coordination of dpk·CH_3OH and the long distance d(Hg—N4). The bond lengths are d(Hg—N1) = 2.336(4) Å, d(Hg—N2) = 2.477(4) Å, d(Hg—N3) = 2.817(7) Å, d(Hg—S1) = 2.541(2) Å and d(Hg—S2) = 2.430(2) Å. The distance d(Hg···Hg) is 6.261 Å. The $\pi\cdots\pi$ interaction between the pyridine rings [d(Cg2···Cg2^i) = 3.712(3) Å, symmetry code i: 1–x,–y,1–z, where Cg3 is centroid of the ring (N1/C1-C5)] and intermolecular C–H···N, O–H···N and C–H···O hydrogen bonds are effective in the stabilization of the crystal structure.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.28 × 0.30 × 0.31 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	94.85 cm^{-1}
Diffractometer, scan mode:	APEX II CCD, φ/ω
$2\theta_{max}$:	58.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18450, 4507
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3845
$N(param)_{refined}$:	209
Programs:	SHELXTL [10], WinGX [11]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.4204	–0.0594	0.6970	0.062
H(2)	4*e*	0.4138	–0.1653	0.5637	0.077
H(3)	4*e*	0.6059	–0.1669	0.4733	0.081
H(4)	4*e*	0.8091	–0.0648	0.5222	0.069
H(7A)	4*e*	1.0077	0.1617	0.8293	0.085
H(7B)	4*e*	1.1083	0.0737	0.8192	0.085
H(7C)	4*e*	1.0300	0.0833	0.9147	0.085
H(9)	4*e*	0.9402	0.1797	0.5361	0.059
H(10)	4*e*	0.8607	0.3321	0.4941	0.066
H(11)	4*e*	0.7042	0.4056	0.5894	0.059
H(12)	4*e*	0.6245	0.3228	0.7172	0.059
H(2A)	4*e*	1.0131	–0.0158	0.6474	0.089

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}
C(1)	4*e*	0.5001(6)	–0.0615(4)	0.6622(4)	0.056(3)	0.050(3)	0.045(2)	–0.011(3)	0.000(2)	0.005(2)
C(2)	4*e*	0.4946(8)	–0.1244(4)	0.5815(4)	0.081(4)	0.048(3)	0.054(3)	–0.018(3)	–0.010(3)	0.000(2)
C(3)	4*e*	0.6086(9)	–0.1258(5)	0.5286(4)	0.097(5)	0.054(4)	0.045(3)	0.003(3)	–0.005(3)	–0.012(2)
C(4)	4*e*	0.7303(7)	–0.0650(4)	0.5580(4)	0.083(4)	0.045(3)	0.046(2)	0.008(3)	0.015(3)	–0.003(2)
C(5)	4*e*	0.7317(6)	–0.0053(4)	0.6408(3)	0.055(3)	0.035(2)	0.038(2)	0.001(2)	0.014(2)	0.004(2)
C(6)	4*e*	0.8646(5)	0.0589(4)	0.6785(3)	0.043(2)	0.048(3)	0.037(2)	–0.002(2)	0.018(2)	0.003(2)
C(7)	4*e*	1.0201(7)	0.0952(6)	0.8421(5)	0.048(3)	0.091(6)	0.070(4)	–0.018(3)	0.001(3)	0.014(3)
C(8)	4*e*	0.8225(5)	0.1618(3)	0.6502(3)	0.036(2)	0.039(2)	0.038(2)	–0.006(2)	0.010(2)	–0.002(2)
C(9)	4*e*	0.8745(6)	0.2094(4)	0.5719(4)	0.058(3)	0.052(3)	0.043(2)	–0.008(2)	0.024(2)	0.001(2)
C(10)	4*e*	0.8287(7)	0.3002(4)	0.5476(4)	0.071(3)	0.056(3)	0.043(2)	–0.017(3)	0.019(2)	0.006(2)
C(11)	4*e*	0.7350(6)	0.3435(4)	0.6033(4)	0.065(3)	0.036(3)	0.048(2)	–0.006(2)	0.011(2)	0.002(2)
C(12)	4*e*	0.6879(6)	0.2933(4)	0.6796(4)	0.059(3)	0.042(3)	0.052(3)	–0.003(2)	0.025(2)	0.000(2)
C(13)	4*e*	0.3710(6)	0.2878(5)	0.7885(4)	0.048(3)	0.063(4)	0.057(3)	–0.001(3)	0.018(2)	0.005(3)
C(14)	4*e*	0.6472(6)	0.0699(4)	1.0632(3)	0.054(3)	0.057(3)	0.036(2)	–0.002(3)	0.008(2)	0.002(2)
N(1)	4*e*	0.6159(4)	–0.0036(3)	0.6918(3)	0.049(2)	0.041(2)	0.033(2)	–0.009(2)	0.009(1)	0.001(2)
N(2)	4*e*	0.7283(5)	0.2036(3)	0.7031(3)	0.051(2)	0.039(2)	0.047(2)	–0.002(2)	0.024(2)	0.001(2)
N(3)	4*e*	0.3862(7)	0.3626(5)	0.8186(5)	0.077(4)	0.064(4)	0.102(4)	–0.001(3)	0.030(3)	–0.003(3)
N(4)	4*e*	0.5843(7)	0.0282(5)	1.1156(4)	0.082(3)	0.081(4)	0.051(2)	–0.019(3)	0.016(2)	0.019(3)
O(1)	4*e*	0.8933(4)	0.0463(3)	0.7874(2)	0.041(2)	0.057(2)	0.043(2)	–0.003(2)	0.006(1)	0.008(2)
O(2)	4*e*	0.9859(5)	0.0386(3)	0.6336(3)	0.062(2)	0.055(2)	0.073(2)	0.010(2)	0.039(2)	0.007(2)
Hg(1)	4*e*	0.60079(2)	0.10917(2)	0.81860(1)	0.0565(1)	0.0514(1)	0.03732(9)	–0.0017(1)	0.01786(7)	0.00422(8)
S(1)	4*e*	0.3453(2)	0.1785(1)	0.7444(1)	0.0507(7)	0.065(1)	0.0730(9)	–0.0081(7)	0.0122(6)	–0.0045(8)
S(2)	4*e*	0.7434(2)	0.1315(2)	0.9925(1)	0.097(1)	0.140(2)	0.0404(6)	–0.071(1)	0.0146(7)	–0.0017(8)

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