Crystal structure of bis{(hydroxy-methoxy-di(2-pyridyl)-methane-κ^3N,O,N')bis(μ_2-iodo)diiododimercury(II)}, $[Hg_2I_4(C_{12}H_{12}N_2O_2)]_2$

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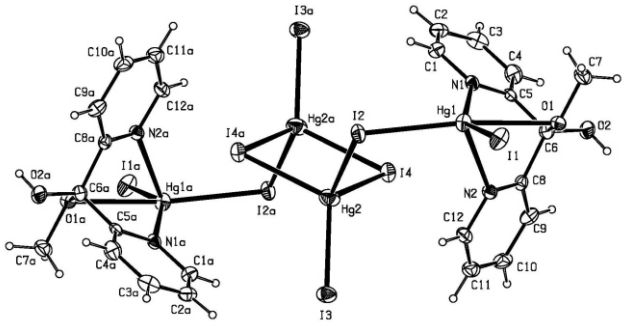

Abstract

$C_{24}H_{24}Hg_4I_8N_4O_4$, monoclinic, $P12_1/c1$ (no. 14), a = 16.249(3) Å, b = 9.963(2) Å, c = 15.045(3) Å, β = 117.48(3)°, V = 2160.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.067, $wR_{ref}(F^2)$ = 0.155, T = 298 K.

Source of material

For the preparation of the title compound, a solution of di(2-pyridyl)ketone (0.15 g, 0.80 mmol) in methanol (5 ml) was added to a solution of HgI_2 (0.36 g, 0.80 mmol) in methanol (15 ml) and the resulting colorless solution was stirred for 15 min at 40 °C. This solution was left to evaporate slowly at room temperature. After one week, yellow needle-shaped crystals of the title compound were isolated (yield 0.32 g, 71.1 %).

Experimental details

It is notable that the slightly high residual densities, 2.09 and –1.69 e/Å^3, are near to heavy I and Hg atoms (highest peak at 0.77 Å from I1, and deepest hole at 0.93 Å from Hg1). The structure was checked by PLATON [1] and no solvent accessible void has been found.

Discussion

The polydentate ligand di(2-pyridyl)ketone (dpk), its hydrolyzed derivatives $(py)_2C(OR)(OH)$ and $(py)_2C(OH)_2$ or its anions $(py)_2C(OR)(O)^-$, $(py)_2C(OH)(O)^-$ and $(py)_2C(O)(O)^{2-}$ are good chelating ligands that can exhibit different modes of coordination. The neutral ligands $(py)_2C(OR)(OH)$ and $(py)_2C(OH)_2$ coordinate metal centers as *N,O,N′* chelates [2-5]. Different interesting coordination modes have been seen when the ligands $(py)_2C(OR)(OH)$ and $(py)_2C(OH)_2$ are deprotonated to form mono- or dianions. The deprotonation of hydroxyl groups leads to a coordinative flexibility [6-8].

The asymmetric unit of the title crystal structure contains a half of $[(py)_2C(OMe)(OH)HgI]_2(\mu_2\text{-}I)_2[Hg_2I_2(\mu_2\text{-}I)_4]$ molecule. In the moiety $[(py)_2C(OMe)(OH)HgI]$, the Hg(II) atom is five-coordinated in a distorted trigonal-pyramidal configuration by two N atoms and one O atom from one hydroxy-methoxy-di(2-pyridyl)methane ligand, one terminal I atom and one bridging I atom. The distortion can be attributed to the *N,O,N′*-terdentate coordination of $(py)_2C(OMe)(OH)$ and the long distance d(Hg—O1). The bond lengths are d(Hg1—N1) = 2.31(1) Å, d(Hg1—N2) = 2.43(1) Å and d(Hg1—O1) = 2.75(1) Å. Also, in the Hg_2I_6 core, the Hg(II) atom is four-coordinated in a distorted tetrahedral configuration by one terminal I atom and one bridging I atom. The centrosymmetric structure contains a double halogen bridge between mercury atoms in the central Hg_2I_6 core with one of the two terminal iodines on each mercury linked via a single bridge to $[(py)_2C(OMe)(OH)HgI]$. This single bridge (2.8062(14) Å) is slightly longer than the terminal distances d(Hg1—I1) = 2.628(2) Å and d(Hg2—I3) = 2.667(2) Å. The Hg—Hg distances are d(Hg1···Hg2) = 4.61(2) Å and d(Hg2···Hg2^i) = 3.73(2) Å (symmetry code i: –x,1–y,–z). In the crystal structure, intermolecular O–H···I and C–H···O hydrogen bonds are effective in the stabilization of the whole crystal structure.

Table 1. Data collection and handling.

Crystal:	yellow needle, size 0.03 × 0.05 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	199.13 cm^{-1}
Diffractometer, scan mode:	STOE IPDS II, ω
$2\theta_{max}$:	58.48°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	16597, 5830
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3976
$N(param)_{refined}$:	201
Programs:	SHELXS-97, SHELXL-97 [9], ORTEP-3 [10], WinGX [11]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.0881	0.2971	0.2970	0.058
H(2A)	4*e*	–0.0053	0.4414	0.3256	0.061
H(3)	4*e*	0.0550	0.6306	0.4216	0.070
H(4)	4*e*	0.2126	0.6805	0.4770	0.071
H(7A)	4*e*	0.4400	0.4253	0.6306	0.093
H(7B)	4*e*	0.4217	0.2819	0.5823	0.093

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Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(7C)	4*e*	0.3380	0.3734	0.5682	0.093
H(9)	4*e*	0.3576	0.7887	0.3763	0.062
H(10)	4*e*	0.3575	0.8428	0.2241	0.073
H(11)	4*e*	0.3515	0.6729	0.1204	0.065
H(12)	4*e*	0.3454	0.4531	0.1629	0.063
H(2)	4*e*	0.4247	0.6636	0.5356	0.085

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*	0.113(1)	0.376(2)	0.333(1)	0.043(7)	0.053(8)	0.050(8)	–0.004(6)	0.023(6)	0.001(7)
C(2)	4*e*	0.058(1)	0.461(2)	0.351(1)	0.044(7)	0.060(9)	0.054(8)	0.008(6)	0.028(7)	0.017(7)
C(3)	4*e*	0.092(1)	0.574(2)	0.406(1)	0.08(1)	0.048(8)	0.07(1)	0.027(8)	0.046(9)	0.015(8)
C(4)	4*e*	0.187(1)	0.603(2)	0.440(1)	0.06(1)	0.056(9)	0.052(9)	0.006(8)	0.024(8)	–0.003(7)
C(5)	4*e*	0.2427(9)	0.517(1)	0.4182(8)	0.043(6)	0.034(6)	0.021(5)	–0.002(5)	0.016(5)	0.001(4)
C(6)	4*e*	0.342(1)	0.545(2)	0.450(1)	0.055(8)	0.044(7)	0.042(7)	–0.012(6)	0.027(6)	–0.015(6)
C(7)	4*e*	0.399(1)	0.373(2)	0.574(1)	0.049(8)	0.09(1)	0.042(8)	0.006(8)	0.018(7)	0.017(8)
C(8)	4*e*	0.3498(8)	0.587(1)	0.3545(9)	0.032(5)	0.035(6)	0.037(6)	–0.002(5)	0.015(5)	–0.009(5)
C(9)	4*e*	0.355(1)	0.722(2)	0.332(1)	0.048(7)	0.038(7)	0.07(1)	–0.005(6)	0.030(7)	–0.003(7)
C(10)	4*e*	0.355(1)	0.754(2)	0.242(1)	0.052(8)	0.054(9)	0.07(1)	–0.006(7)	0.022(8)	0.028(8)
C(11)	4*e*	0.351(1)	0.653(2)	0.181(1)	0.044(7)	0.07(1)	0.052(8)	0.004(7)	0.024(7)	0.012(8)
C(12)	4*e*	0.347(1)	0.522(2)	0.206(1)	0.066(9)	0.054(8)	0.035(7)	–0.010(7)	0.021(7)	0.004(6)
N(1)	4*e*	0.2064(8)	0.403(1)	0.3653(8)	0.046(5)	0.032(5)	0.031(5)	–0.002(4)	0.017(4)	–0.005(4)
N(2)	4*e*	0.3450(8)	0.491(1)	0.2929(8)	0.051(6)	0.033(5)	0.036(5)	–0.005(5)	0.022(5)	–0.004(4)
O(1)	4*e*	0.3967(6)	0.429(1)	0.4831(7)	0.042(5)	0.059(6)	0.038(5)	–0.004(4)	0.020(4)	0.005(4)
O(2)	4*e*	0.3707(8)	0.644(1)	0.5200(8)	0.067(7)	0.058(6)	0.051(6)	–0.025(5)	0.032(5)	–0.031(5)
I(1)	4*e*	0.44117(7)	0.1119(1)	0.3756(1)	0.0456(5)	0.0455(5)	0.0880(8)	0.0060(4)	0.0198(5)	–0.0025(5)
I(2)	4*e*	0.16024(7)	0.1937(1)	0.12136(7)	0.0577(5)	0.0503(5)	0.0361(4)	–0.0025(4)	0.0126(4)	–0.0059(4)
I(3)	4*e*	0.20033(9)	0.4922(1)	–0.09729(9)	0.0852(8)	0.0579(6)	0.0664(6)	–0.0140(5)	0.0528(6)	–0.0152(5)
I(4)	4*e*	0.08823(7)	0.6355(1)	0.12034(7)	0.0477(5)	0.0589(6)	0.0449(5)	0.0041(4)	0.0144(4)	–0.0073(4)
Hg(1)	4*e*	0.29626(4)	0.27022(6)	0.31898(4)	0.0470(3)	0.0384(3)	0.0500(3)	0.0034(2)	0.0179(2)	–0.0027(2)
Hg(2)	4*e*	0.10498(5)	0.42386(9)	0.00024(6)	0.0629(4)	0.0841(5)	0.0653(4)	0.0108(3)	0.0398(3)	0.0112(4)

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