

Crystal structure of 4,4'-bipyridinium bis(pyridine-2,6-dicarboxylato)mercurate(II) — diaquabis(6-carboxypyridine-2-carboxylato)mercury(II) — water (2:1:12), $[C_{10}H_{10}N_2]_2[Hg(C_7H_3NO_4)_2]_2 \cdot Hg(H_2O)_2(C_7H_4NO_4)_2 \cdot 12H_2O$

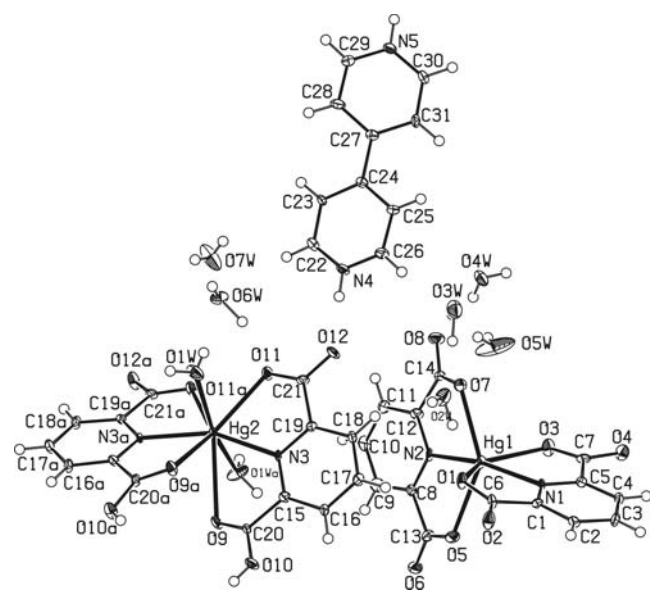
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Abstract

$C_{62}H_{68}Hg_3N_{10}O_{38}$, monoclinic, $C12/c1$ (no. 15), $a = 33.741(7)$ Å, $b = 9.394(2)$ Å, $c = 23.320(5)$ Å, $\beta = 104.26(3)^\circ$, $V = 7164.0$ Å³, $Z = 4$, $R_{gt}(F) = 0.041$, $wR_{ref}(F^2) = 0.111$, $T = 120$ K.

Source of material

The reaction of mercury(II) nitrate (81 mg, 0.25 mmol), 4,4'-bipyridine (4,4'-bipy, 78 mg, 0.50 mmol) and pyridine-2,6-dicarboxylic acid (pydcH₂, 85 mg, 0.50 mmol) in a 1 : 2 : 2 molar ratio in aqueous solution resulted in the formation of colorless block-shaped crystals of the title compound (yield 62 %, m.p. 493 K).

Experimental details

Hydrogen atoms attached to carbon atoms were positioned geometrically, with $d(C-H) = 0.93$ Å, and hydrogen atoms of the water molecules and NH groups were found in difference Fourier map and refined with $U_{iso}(H) = 0.065$ Å².

Discussion

In recent years in a strategy towards rational design of coordination compounds, based on proton transfer mechanism, we have used various dicarboxylic acids and amines derivatives [1]. Pyridine-2,6-dicarboxylic acid (pydcH₂) which incorporated in many biologically important systems, is subject of many studies in view of experimentally or/and theoretically [2–4]. It is a very interesting model, as a biologically important ligand incorporated into some enzymes and its molecule is an active agent in some drugs. It is the body's prime natural chelator of vital trace elements: chromium, zinc, manganese, copper, iron and molybdenum.

The structure features six-coordinated Hg²⁺ with a distorted octahedral geometry. Also there is another mercury(II) ion which presents the unusual coordination number of eight. Its coordination environment consists of two (pydcH)[−] ligands and two water molecules. Two (pydcH)[−] ligands coordinate the mercury center as tridentate ligands through nitrogen atom of pyridine and oxygen atoms of carboxylate functional groups. The Hg—N_{pyridine} distances [2.239(4) Å] in eight-coordinated mercury are longer than the Hg—N_{pyridine} distances [2.202(4) – 2.193(4) Å] in six-coordinated one. Extensive intermolecular O—H...O, N—H...O and C—H...O hydrogen bonding involving the pydc ligands, (4,4'-bipyH₂)²⁺ as a counter-ion and lattice water molecules forms a three-dimensional framework. Indeed, there are weak π – π stacking between pyridine–pyridine rings of pydc^{2−} and pyridine–pyridine rings of pydc^{2−} and bipyridinium counter-ion with a centroid-to-centroid distances of 3.710 Å and 3.682 Å, respectively. Also the crystal structure of the title compound contains (H₂O)_∞ cluster that may lead to the further stabilization of corresponding crystalline network [5].

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.38 × 0.45 × 0.5 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	65.21 cm ^{−1}
Diffractometer, scan mode:	STOE IPDS II, ω
$2\theta_{max}$:	58.36°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	24698, 9546
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 8523
$N(param)_{refined}$:	562
Programs:	SHELXS-97, SHELXL-97 [6], ORTEP-III [7], WinGX [8]

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

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(3)	8 <i>f</i>	0.2761	−0.0031	−0.0868	0.016
H(10)	8 <i>f</i>	−0.0108	0.3921	0.0533	0.026
H(4)	8 <i>f</i>	0.2437	0.2145	−0.1159	0.015
H(2)	8 <i>f</i>	0.2605	−0.1262	−0.0079	0.013
H(9)	8 <i>f</i>	−0.0068	0.1957	−0.0039	0.024
H(11)	8 <i>f</i>	0.0479	0.5175	0.0989	0.021
H(22)	8 <i>f</i>	0.0712	0.6697	0.3015	0.018
H(23)	8 <i>f</i>	0.0920	0.8965	0.3362	0.014
H(25)	8 <i>f</i>	0.1917	0.8474	0.2715	0.016
H(28)	8 <i>f</i>	0.1314	1.0451	0.3993	0.020
H(17)	8 <i>f</i>	0.1313	−0.0407	0.1302	0.019
H(16)	8 <i>f</i>	0.0811	−0.2084	0.1331	0.015
H(18)	8 <i>f</i>	0.1278	0.1833	0.1714	0.016
H(26)	8 <i>f</i>	0.1690	0.6199	0.2418	0.019
H(29)	8 <i>f</i>	0.1526	1.2722	0.4301	0.021
H(30)	8 <i>f</i>	0.2074	1.3167	0.3011	0.018
H(31)	8 <i>f</i>	0.1904	1.0860	0.2692	0.016

Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(4WA)	8 <i>f</i>	0.182(4)	0.66(1)	0.144(5)	0.065
H(4A)	8 <i>f</i>	0.112(3)	0.55(1)	0.255(5)	0.065
H(3WA)	8 <i>f</i>	0.226(3)	0.35(1)	0.205(5)	0.065
H(2WB)	8 <i>f</i>	0.216(3)	0.10(1)	0.156(5)	0.065
H(2WA)	8 <i>f</i>	0.236(3)	0.08(1)	0.214(5)	0.065
H(6WA)	8 <i>f</i>	0.041(3)	0.48(1)	0.359(5)	0.065
H(5A)	8 <i>f</i>	0.185(3)	1.40(1)	0.381(5)	0.065
H(4WB)	8 <i>f</i>	0.210(4)	0.74(1)	0.141(5)	0.065
H(5WA)	8 <i>f</i>	0.094(4)	0.82(1)	0.004(5)	0.065
H(5WB)	8 <i>f</i>	0.109(4)	0.73(1)	0.036(5)	0.065
H(3WB)	8 <i>f</i>	0.208(3)	0.48(1)	0.197(5)	0.065
H(7WA)	8 <i>f</i>	0.091(3)	0.41(1)	0.453(5)	0.065
H(7WB)	8 <i>f</i>	0.102(4)	0.50(1)	0.431(5)	0.065
H(6WB)	8 <i>f</i>	0.036(3)	0.44(1)	0.290(5)	0.065
H(1WB)	8 <i>f</i>	0.042(3)	0.11(1)	0.383(5)	0.065
H(1WA)	8 <i>f</i>	0.053(4)	0.21(1)	0.358(6)	0.065
H(10A)	8 <i>f</i>	0.006(3)	−0.38(1)	0.164(5)	0.065

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(2)	4 <i>e</i>	0	0.10242(2)	¼	0.0115(1)	0.0065(1)	0.0156(1)	0	0.00956(8)	0
Hg(1)	8 <i>f</i>	0.149379(5)	0.20671(2)	0.026917(8)	0.0111(1)	0.0117(1)	0.0183(1)	0.00390(5)	0.00893(6)	−0.00117(6)
O(7)	8 <i>f</i>	0.1593(1)	0.3946(4)	0.0999(2)	0.008(1)	0.020(2)	0.024(2)	−0.001(1)	0.007(1)	−0.007(1)
O(8)	8 <i>f</i>	0.1241(1)	0.5891(4)	0.1144(2)	0.020(2)	0.013(2)	0.026(2)	−0.000(1)	0.005(2)	−0.006(2)
O(3)	8 <i>f</i>	0.1576(1)	0.3837(4)	−0.0526(2)	0.017(2)	0.017(2)	0.032(2)	0.009(1)	0.015(2)	0.005(2)
O(1)	8 <i>f</i>	0.1850(1)	0.0122(4)	0.0848(2)	0.015(2)	0.017(2)	0.023(2)	0.006(1)	0.013(1)	0.006(1)
C(8)	8 <i>f</i>	0.0551(1)	0.2039(5)	0.0074(2)	0.011(2)	0.011(2)	0.020(2)	−0.001(2)	0.008(2)	−0.001(2)
C(14)	8 <i>f</i>	0.1269(1)	0.4648(5)	0.0967(2)	0.011(2)	0.012(2)	0.011(2)	−0.002(2)	0.003(2)	−0.003(2)
N(1)	8 <i>f</i>	0.1988(1)	0.1381(4)	−0.0134(2)	0.007(2)	0.010(2)	0.012(2)	0.001(1)	0.007(1)	0.001(1)
O(4)	8 <i>f</i>	0.1991(1)	0.4223(4)	−0.1126(2)	0.029(2)	0.013(2)	0.020(2)	0.005(2)	0.011(2)	0.006(1)
C(1)	8 <i>f</i>	0.2182(1)	0.0165(5)	0.0060(2)	0.012(2)	0.007(2)	0.013(2)	0.002(2)	0.004(2)	−0.002(2)
O(6)	8 <i>f</i>	0.0284(1)	0.0222(4)	−0.0603(2)	0.017(2)	0.024(2)	0.026(2)	−0.007(1)	0.008(1)	−0.010(2)
O(5)	8 <i>f</i>	0.0965(1)	0.0312(4)	−0.0241(2)	0.019(2)	0.013(2)	0.026(2)	0.002(1)	0.010(1)	−0.007(2)
C(3)	8 <i>f</i>	0.2570(1)	0.0330(5)	−0.0678(2)	0.015(2)	0.015(2)	0.014(2)	0.002(2)	0.010(2)	0.000(2)
C(7)	8 <i>f</i>	0.1859(2)	0.3512(5)	−0.0756(2)	0.018(2)	0.006(2)	0.013(2)	0.002(2)	0.002(2)	−0.001(2)
C(5)	8 <i>f</i>	0.2082(1)	0.2110(5)	−0.0582(2)	0.011(2)	0.011(2)	0.013(2)	−0.001(2)	0.004(2)	−0.002(2)
C(10)	8 <i>f</i>	0.0144(2)	0.3626(6)	0.0484(3)	0.009(2)	0.026(3)	0.036(3)	−0.002(2)	0.014(2)	−0.008(2)
O(2)	8 <i>f</i>	0.2264(1)	−0.1683(4)	0.0761(2)	0.027(2)	0.018(2)	0.027(2)	0.008(2)	0.017(2)	0.007(2)
C(4)	8 <i>f</i>	0.2372(1)	0.1620(5)	−0.0856(2)	0.014(2)	0.013(2)	0.012(2)	−0.002(2)	0.007(2)	0.001(2)
C(6)	8 <i>f</i>	0.2089(1)	−0.0529(5)	0.0600(2)	0.011(2)	0.018(2)	0.017(2)	−0.002(2)	0.009(2)	0.002(2)
C(13)	8 <i>f</i>	0.0600(2)	0.0748(5)	−0.0293(2)	0.019(2)	0.013(2)	0.015(2)	0.000(2)	0.008(2)	−0.003(2)
C(2)	8 <i>f</i>	0.2476(1)	−0.0406(5)	−0.0210(2)	0.012(2)	0.005(2)	0.018(2)	0.002(1)	0.006(2)	0.001(2)
C(9)	8 <i>f</i>	0.0166(2)	0.2460(6)	0.0143(3)	0.015(2)	0.018(2)	0.027(3)	0.001(2)	0.004(2)	−0.004(2)
C(12)	8 <i>f</i>	0.0866(1)	0.3903(5)	0.0681(2)	0.015(2)	0.007(2)	0.017(2)	0.002(2)	0.004(2)	0.000(2)
C(11)	8 <i>f</i>	0.0494(2)	0.4377(6)	0.0759(2)	0.015(2)	0.018(2)	0.024(2)	−0.001(2)	0.011(2)	−0.006(2)
O(11)	8 <i>f</i>	0.0425(1)	0.3114(4)	0.2467(2)	0.015(2)	0.012(2)	0.025(2)	0.000(1)	0.012(1)	−0.001(1)
O(12)	8 <i>f</i>	0.1032(1)	0.3685(4)	0.2303(2)	0.016(2)	0.011(2)	0.040(2)	−0.007(1)	0.017(2)	−0.009(2)
N(3)	8 <i>f</i>	0.0475(1)	0.0462(4)	0.2016(2)	0.006(1)	0.009(2)	0.012(2)	0.002(1)	0.006(1)	0.001(1)
C(15)	8 <i>f</i>	0.0494(1)	−0.0823(5)	0.1767(2)	0.011(2)	0.008(2)	0.016(2)	0.002(2)	0.004(2)	−0.001(2)
C(19)	8 <i>f</i>	0.0765(1)	0.1429(5)	0.1995(2)	0.013(2)	0.007(2)	0.013(2)	0.001(2)	0.005(2)	−0.001(2)
N(4)	8 <i>f</i>	0.1187(1)	0.6292(4)	0.2696(2)	0.014(2)	0.009(2)	0.021(2)	−0.003(1)	0.005(2)	−0.002(2)
C(22)	8 <i>f</i>	0.0957(2)	0.7066(5)	0.2965(2)	0.013(2)	0.013(2)	0.020(2)	−0.003(2)	0.005(2)	0.002(2)
C(23)	8 <i>f</i>	0.1080(1)	0.8423(5)	0.3172(2)	0.011(2)	0.009(2)	0.019(2)	−0.003(2)	0.009(2)	−0.003(2)
C(25)	8 <i>f</i>	0.1676(1)	0.8125(5)	0.2789(2)	0.015(2)	0.009(2)	0.015(2)	−0.002(2)	0.003(2)	−0.003(2)
C(28)	8 <i>f</i>	0.1469(2)	1.0980(5)	0.3791(2)	0.021(2)	0.011(2)	0.017(2)	−0.005(2)	0.003(2)	−0.004(2)
C(27)	8 <i>f</i>	0.1583(1)	1.0412(5)	0.3303(2)	0.016(2)	0.008(2)	0.010(2)	−0.001(2)	0.000(2)	0.002(2)
C(24)	8 <i>f</i>	0.1445(1)	0.8957(5)	0.3089(2)	0.012(2)	0.009(2)	0.011(2)	−0.001(2)	0.001(2)	0.002(2)
C(20)	8 <i>f</i>	0.0157(1)	−0.1864(5)	0.1789(2)	0.010(2)	0.009(2)	0.015(2)	−0.003(2)	0.008(2)	−0.002(2)
C(21)	8 <i>f</i>	0.0736(2)	0.2869(5)	0.2284(2)	0.016(2)	0.007(2)	0.013(2)	0.001(2)	0.004(2)	−0.001(2)
C(17)	8 <i>f</i>	0.1102(1)	−0.0188(5)	0.1479(2)	0.015(2)	0.012(2)	0.022(2)	0.002(2)	0.011(2)	−0.002(2)
C(16)	8 <i>f</i>	0.0804(1)	−0.1187(5)	0.1497(2)	0.012(2)	0.013(2)	0.016(2)	−0.002(2)	0.009(2)	−0.002(2)
C(18)	8 <i>f</i>	0.1083(1)	0.1144(5)	0.1727(2)	0.013(2)	0.012(2)	0.017(2)	−0.003(2)	0.010(2)	−0.001(2)
O(10)	8 <i>f</i>	0.0259(1)	−0.3176(4)	0.1682(2)	0.019(2)	0.010(2)	0.034(2)	−0.003(1)	0.013(2)	−0.006(2)
O(6W)	8 <i>f</i>	0.0274(1)	0.4972(4)	0.3301(2)	0.018(2)	0.017(2)	0.025(2)	0.006(1)	0.001(1)	−0.006(2)
O(9)	8 <i>f</i>	−0.0160(1)	−0.1496(4)	0.1889(2)	0.013(2)	0.010(2)	0.031(2)	−0.003(1)	0.013(1)	−0.003(1)

Table 3. Continued.

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O(4W)	8f	0.2030(1)	0.6861(5)	0.1648(2)	0.022(2)	0.021(2)	0.021(2)	−0.008(2)	0.004(2)	0.005(2)
O(2W)	8f	0.2245(1)	0.1475(5)	0.1916(2)	0.034(2)	0.030(2)	0.022(2)	0.004(2)	0.011(2)	0.001(2)
O(1W)	8f	0.0471(2)	0.1433(5)	0.3537(2)	0.035(2)	0.023(2)	0.020(2)	−0.015(2)	0.001(2)	0.005(2)
O(3W)	8f	0.2345(1)	0.4415(5)	0.2241(2)	0.024(2)	0.036(2)	0.022(2)	−0.007(2)	0.005(2)	0.003(2)
O(5W)	8f	0.1024(3)	0.7457(6)	0.0046(3)	0.180(9)	0.017(2)	0.024(3)	0.023(4)	−0.005(4)	0.000(2)
N(5)	8f	0.1806(1)	1.3126(5)	0.3673(2)	0.015(2)	0.011(2)	0.023(2)	−0.003(2)	0.007(2)	−0.005(2)
C(26)	8f	0.1537(2)	0.6776(5)	0.2606(2)	0.020(2)	0.010(2)	0.018(2)	−0.002(2)	0.005(2)	−0.002(2)
C(29)	8f	0.1593(2)	1.2342(6)	0.3969(2)	0.023(2)	0.013(2)	0.019(2)	−0.003(2)	0.009(2)	−0.005(2)
C(30)	8f	0.1922(1)	1.2603(6)	0.3206(2)	0.013(2)	0.016(2)	0.018(2)	−0.005(2)	0.007(2)	0.001(2)
C(31)	8f	0.1819(1)	1.1231(5)	0.3012(2)	0.012(2)	0.014(2)	0.018(2)	−0.001(2)	0.010(2)	−0.000(2)
N(2)	8f	0.0889(1)	0.2752(4)	0.0352(2)	0.008(2)	0.012(2)	0.014(2)	0.002(1)	0.008(1)	0.002(1)
O(7W)	8f	0.0864(2)	0.4611(7)	0.4251(3)	0.024(2)	0.055(3)	0.041(3)	−0.016(2)	−0.012(2)	0.029(3)

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