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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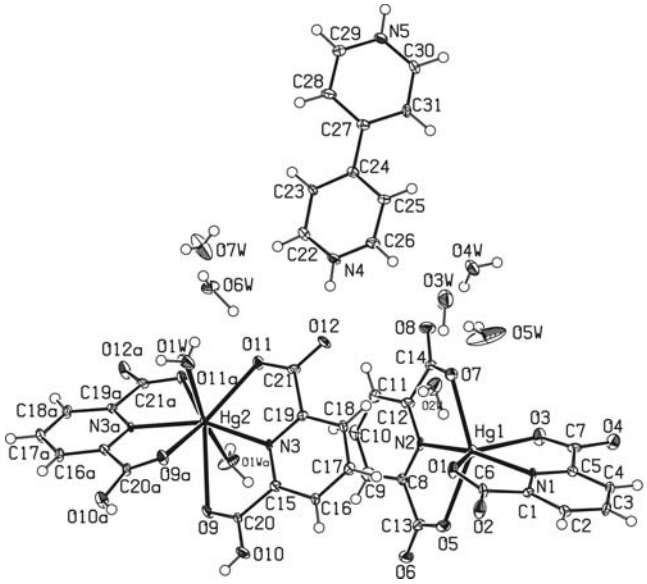

Abstract

$C_{62}H_{68}Hg_3N_{10}O_{38}$, monoclinic, *C*12/*c*1 (no. 15), *a* = 33.741(7) Å, *b* = 9.394(2) Å, *c* = 23.320(5) Å, *β* = 104.26(3)°, *V* = 7164.0 Å^3, *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 ($pydcH_2$, 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 Å^2.

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 ($pydcH_2$) 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 Hg^{2+} 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, $(4,4'\text{-bipy}H_2)^{2+}$ 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 $(H_2O)_\infty$ 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_α 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 Å^2).

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

Table 2. Continued.

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

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(2)	4*e*	0	0.10242(2)	¼	0.0115(1)	0.0065(1)	0.0156(1)	0	0.00956(8)	0
Hg(1)	8*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	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*f*	–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)	8*f*	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)	8*f*	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)	8*f*	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)	8*f*	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)	8*f*	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)	8*f*	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)	8*f*	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)	8*f*	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)	8*f*	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)	8*f*	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)	8*f*	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)	8*f*	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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References

1. Aghabozorg, H.; Manteghi, F.; Sheshmani, S.: A brief review on structural concepts of novel supramolecular proton transfer compounds and their metal complexes. J. Iran. Chem. Soc. **5** (2008) 184-227. and Refs. [31-140] therein.
2. Masui, H.: Metalloaromaticity. Coord. Chem. Rev. **219-221** (2001) 957-992 .
3. Beuerle, T.; Pichersky, E.: Purification and characterization of benzoate: Coenzyme A ligase from Clarkia breweri. Arch. Biochem. Biophys. **400** (2002) 258-264.
4. Song, R.; Kim, K. M.; Sohn, Y. S.: Synthesis and properties of (diamine)platinum(II) complexes of pyridinecarboxylate isomers and their antitumor activity. Inorg. Chim. Acta **292** (1999) 238-243.
5. Aghabozorg, H.; Eshtiagh-Hosseini, H.; Salimi, A. R.; Mirzaei, M.: A brief review on formation of $(H_2O)_n$ clusters in supramolecular proton transfer compounds and their complexes. J. Iran. Chem. Soc. **7** (2010) 289-300.
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
7. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.
8. Farrugia, L. J.: WinGX suite for small-molecule single-crystal crystallogrphy. J. Appl. Crystallogr. **32** (1999) 837-838.