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Synthesis, Crystal and Molecular Structure of 2-Pyridylethanolbis(saccharinato)mercury(II)

2-Pyridylethanolbis(saccharinato)mercury(II), [Hg(sac)$_2$(pyet)], where sac and pyet are the saccharinate anion and the 2-pyridylethanol molecule, respectively, crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with a = 10.4518(6), b = 11.3796(6) (5), c = 19.9945(12) Å, α = 102.758(3)° β = 98.146(3)°, γ = 104.751(3)°, Z = 4, V = 2193.0(2) Å^3. The unit cell contains two crystallographically independent [Hg(sac)$_2$(pyet)] units in which the mercury(II) ion is tetrahedrally coordinated by two nitrogen atoms of two sac ligands, and one nitrogen and one oxygen atoms of one neutral pyet ligands. The pyet acts as a bidentate N- and O-donor ligand forming a six-membered chelate ring, while sac behaves as a monodentate N-donor ligand. The average bite angle of the pyet ligand is 75.8(5)°. The Hg-N_{sac} bond distances are in the range 2.0874(18) and 2.1931(18) Å, whereas the Hg-N_{pyet} and Hg-O_{pyet} bond distances are 2.2452(19)-2.3202(19) and 2.6036(17)-2.5902(16) Å, respectively. The crystal exhibits two strong hydrogen bonds between the hydroxyl O atom of pyet and sulfonyl O atoms of sac and the C-H…O type weak hydrogen bonds between H atoms of the aromatic rings of the pyet and the sulfonyl O atoms of the sac ligands. Furthermore, packing of the molecules in the solid-state results in aromatic π-π interactions associated with the aromatic rings of sac-sac and py-py.

Keywords: saccharinato complexes, 2-Pyridylethanol complexes, mercury(II) complexes

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Introduction

Saccharin (sacH) (also named 1,2-benzisothiazoline-3-(*2H*)one 1,1-dioxide or *o*-sulphobenzimide) in the form of its water soluble sodium salt is widely used as a non-caloric artificial sweetener and food additive (AGER et al.). Sacharinate anion (sac) readily forms complexes with a large number of metal ions. A great number of metal complexes of sac were characterized in the last years and the structural data were reviewed by NAUMOV and JOVANOVSKI.

Although transition metal complexes with sac have received much attention, the mixed-ligand mercury(II) complexes of sac are very rare. Recently, we studied the structural characterization of [Hg(ea)$_2$(sac)$_2$], where ea is monoethanolamine, (TOPCU et al.) and in this paper, we report the synthesis and crystal structure of 2-pyridylethanolbis (saccharinato) mercury(II).

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Experimental

$[Hg(sac)_2]$ (0.56 g, 1.0 mmol), prepared by the method of KAMENAR et al., was dissolved in 30 mL of butanol with stirring at room temperature. Then, 2-pyridylethanol (pyet) (0.25 g, 2.0 mmol) was added to the solution drop wise. The resulting colourless solution was stirred for 30 min at room temperature and left at room temperature. Transparent crystals suitable for X-ray diffraction analysis were obtained after a month.

Table 1: Summary of crystal data and refinement parameters for $[Hg(sac)_2(py)]$

Formula	$C_{21}H_{17}N_3O_7S_2Hg$
Molecular weight	688.09
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	a = 10.4518(6) Å, b = 11.3796(6) Å
	c = 19.9945(12) Å, α = 102.758(3)°
	β = 98.146(3)°, γ = 104.751(3)°
Volume	2193.0(2) Å^3
Z	4
Calculated density	2.084 Mg/m^3
μ	7.260 mm^{-1}
F(000)	1328
Crystal size	0.25 x 0.25 x 0.15 mm
θ range	1.07 to 30.03 °
Index ranges	-14<=h<=14; -16<=k<=15; -28<=l<=28
Reflections collected	45800
Independent reflections	12766 [R(int) = 0.0235]
Reflections observed (>2σ)	11311
Absorption correction	Multi-scans
Max. and min. transmission	0.8622 and 0.5736
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12766 / 2 / 621
Goodness-of-fit on F^2	1.047
Final R indices [I>2σ(I)]	$R1$ = 0.0199, $wR2$ = 0.0496
R indices (all data)	$R1$ = 0.0239, $wR2$ = 0.0506
Largest diff. peak and hole	1.976 and -1.049e. Å^{-3}

All measurements were made on a BRUKER SMART 1000 CCD area detector diffractometer with graphite monochromated Mo-K_α radiation at 298(2) K. An absorption correction of SADABS program (BRUKER) was applied. The structure was solved by direct-methods using SHELXS-97 (SHELDRICK, 1990) and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97 (SHELDRICK, 1997). All non-hydrogen atoms were refined with

anisotropic parameters. Hydrogen atoms bonded to carbon were included using a riding model, starting from calculated positions. The hydroxyl hydrogen atoms were found in the difference Fourier synthesis and refined with fixed *U*-values. The details of the crystal data, parameters for data collection, structure solution and refinement are given in Table 1.

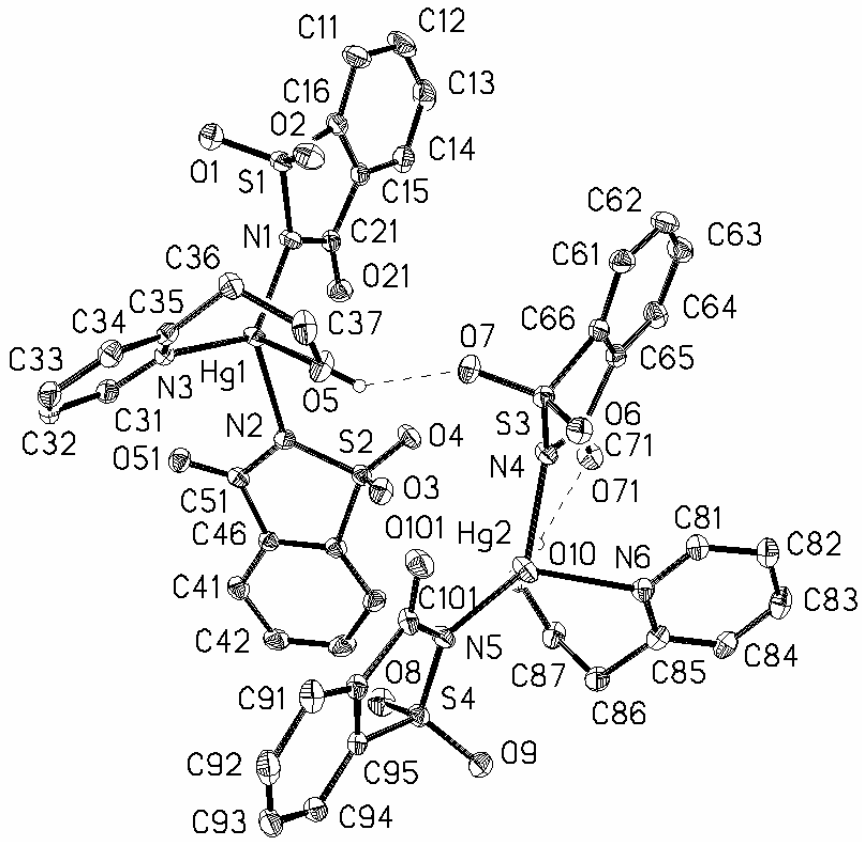

Fig. 1: A view of $[Hg(sac)_2(pyet)]$ showing the labelling of non-hydrogen atoms in two crystallographically independent molecules. Displacement ellipsoids are plotted at the 50% probability level for the non-hydrogen atoms. H atoms are removed for clarity.

Results and Discussion

Molecular structure of 2-pyridylethanolbis(saccharinato)mercury(II) is illustrated in Fig. 1, while Table 2 lists selected bond lengths and angles together with hydrogen bonding geometry. The structure of the complex consists of isolated $[Hg(sac)_2(pyet)]$ molecules and the unit cell contains two crystallographically independent $[Hg(sac)_2(pyet)]$ units. The mercury(II) ion is tetrahedrally coordinated by two nitrogen atoms of two sac ligands, and one nitrogen and one oxygen atoms of one neutral pyet ligands. The pyet ligand is neutral and acts as a bidentate N- and O-donor ligand forming a six-membered chelate ring, while the sac ligand is N-coordinated.

Table 2: Selected bond distances (Å), angles (°) and hydrogen bonding geometry for $[Hg(sac)_2(py)]$[a]

Hg1-N1	2.117(2)	Hg2-N4	2.193(2)
Hg1-N2	2.182(2)	Hg2-N5	2.087(2)
Hg1-N3	2.245(2)	Hg2-N6	2.320(2)
Hg1-O5	2.604(2)	Hg2-O10	2.590(2)
N1-Hg1-N2	130.86(7)	N5-Hg2-N4	136.77(7)
N1-Hg1-N3	125.19(7)	N5-Hg2-N6	133.71(7)
N2-Hg1-N3	103.92(7)	N4-Hg2-N6	88.26(7)
N1-Hg1-O5	106.38(7)	N5-Hg2-O10	107.60(7)
N2-Hg1-O5	85.04(6)	N4-Hg2-O10	90.68(6)
N3-Hg1-O5	76.36(6)	N6-Hg2-O10	75.28(6)

Hydrogen bonding

D-H…A	D-H (Å)	H…A (Å)	D…A (Å)	<DHA(°)
O5-H5…O7	0.80(2)	2.26(3)	2.938(2)	143(4)
O10-H10…O71	0.80(2)	1.99(2)	2.778(2)	167(3)
C33-H33...O1[i]	0.95	2.52	3.252(3)	134
C61-H61…O1[ii]	0.95	2.53	3.291(3)	138
C33-H33…O6[iii]	0.95	2.65	3.239(3)	120
C34-H34…O7[iii]	0.95	2.50	3.277(3)	139
C41-H41…O9[iv]	0.95	2.54	3.463(3)	163

[a]Symmetry codes: (i) 1-x,2-y,1-z; (ii) x-1,y,z; (iii) -x,2-y,1-z; (iv) 1+x,y,z

The average bite angle of the pyet ligand is 75.8(5)°, which indicates an extreme distortion of the coordination tetrahedron around the mercury(II) ion. The average Hg-O bond distance is 2.60(1) Å, while the mean Hg-N_{pyet} distance is 2.28(4) Å. The Hg-N_{sac} distances in the title compound range from 2.087(2) to 2.193(2) Å, which are significantly longer than the values observed in $[Hg(sac)_2]$ [2.040 Å] (KAMENAR et al.), [Hg(Cl)(sac)] [2.019 Å] (JOVANOVSKI et al.) and $[Hg_2(\mu\text{-}Cl)_2(sac)_2(py)]$ [2.106 Å] (GRUPCE et al.), while they are much shorter than that reported for $[Hg(ea)_2(sac)_2]$ [2.739(3) Å] (TOPCU et al.) and comparable with that found in $[Hg(sac)_2(bipy)]$ [2.130 Å] (HERGOLD-BRUNDIC et al.).

The interatomic distances within the sac ligand are similar to the corresponding values found in $[Hg(ea)_2(sac)_2]$ (TOPCU et al.). All sac ligands are essentially planar. The RMS deviations of the sac planes are *ca.* 0.025(1) and 0.014(7) Å in the independent molecules with Hg1 and Hg2, respectively. Both pyet ligands are also planar and the RMS deviation of the best planes of the py rings with the carbon atom is 0.012(4) Å. The OH group of the pyet ligand deviates by *ca.* 1.79(4)Å from the plane of the py ring. The dihedral angles between the least square planes of the sac and pyet ligands differ in a wide range. These are as follows: in the Hg1 unit: sac1 (C11-C16)-pyet, 133.2°; sac2 (C41-C46)-pyet, 114.0°; sac1-sac2, 114.7° and in the Hg2 unit: sac3 (C61-C66), 134.4°; sac4 (C91-C96), 137.7°; sac3-sac4, 174.3°. The different sac1-sac2 and sac3-sac4 angles suggest a remarkable conformational variation between the two independent molecules.

The structure exhibits a number of hydrogen bonds as shown in Fig. 2 and Table 2. The hydroxyl hydrogen atom of pyet forms an intramolecular hydrogen bond with the carbonyl oxygen atom and intermolecular hydrogen bond with sulfonyl oxygen atom of the other

$[Hg(ea)_2(sac)_2]$ unit. The some phenyl hydrogens of both pyet and sac ligands are involved in intermolecular hydrogen bonding with the sulfonyl oxygen atoms of the sac in the adjacent molecules. One hydrogen atom (C33-H33) of the phenyl group of the pyet ligand forms a bifurcated hydrogen bond. The sac and pyet ligands of the neighbouring molecules adopt a parallel alignment with interplanar angles ranging from 0.03 to 10.37°. This type of packing of the molecules in the crystal results in aromatic π-π interactions between the phenyl rings. The three sac ligands show a parallel alignment in the order sac1-sac4-sac3 and the angle of the line passing through the centres of their phenyl rings is 159°. The Cg-Cg distances between the phenyl rings of the three sac ligands are sac1-sac4, 3.54 Å and sac4-sac3, 3.78 Å (symmetry code: x, y-1, z). The Cg-Cg distance between pyet (C31-N3)-pyet (C31-N3) (symmetry code: 1-x, 2-y, 1-z) is 3.37 Å. As well as the π-π interactions, the hydrogen bonds help to stabilize the crystal structure by forming a three-dimensional network.

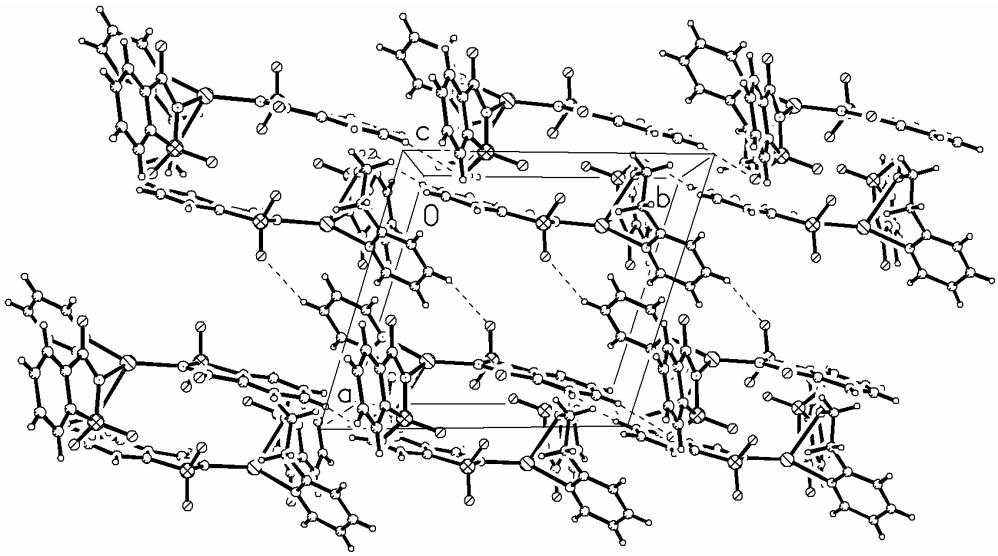

Fig. 2: Crystal packing and hydrogen bonding scheme of $[Hg(sac)_2(pyet)]$

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