

SYNTHESIS AND CRYSTAL STRUCTURE OF Hg(II) COORDINATION POLYMER WITH THE RIGID 4,4'-ABPY

Figen Arslan Biçer^{a*}, Semiha Yıldırım^b and Martina Bubrin^c

farslan@karabuk.edu.tr

^aDepartment of Chemistry, Karabük University, TR-78050 Karabük, Turkey

^bDepartment of Chemistry, Gebze Technical University, TR-41400 Gebze, Kocaeli, Turkey

^cInstitute of Inorganic Chemistry, Stuttgart University, Pfaffenwaldring 55, D-70550 Stuttgart, Germany

Abstract: The new coordination polymer with saccharinate (sac) and 4,4'-azobispyridine (azpy), namely $[\text{Hg}(\text{sac})_2(\mu\text{-azpy})_2]_n$ was synthesized and single crystal X-ray diffraction. Single crystal X-ray analysis reveals that sac ligand acts N-coordinated and 4,4'-abpy ligand exhibits as bridging ligand. In complex, the Hg(II) ion and all ligands are linked by coordination bonds and 4,4'-abpy ligands connect the Hg(II) centers forming a one-dimensional coordination polymer. In complex, the sac ligands N-coordinated to the Hg(II) ion and distorted tetrahedron geometry of Hg(II) ion is completed by bridging 4,4'-abpy ligands.

Keywords: 4,4'-Azobispyridine; Saccharinate complexes; Coordination polymers

Introduction

Saccharine is an important molecule in biological systems and forms a number of complexes with different metal ions rather easily. Moreover, it contains three functional groups, namely imino nitrogen, carbonyl and sulphonyl oxygen (Baran, 2005). All these properties make it a quite preferable ligand in coordination chemistry. The deprotonated form of this molecule, saccharinate anion, usually connected to the metal centers via negatively charged nitrogen atom (Bıyık, 2007). This mode is typically observed in the aquabis (saccharinato) complexes of transition metals (Baran, 2005). This type of metal saccharinates may be useful starting materials for the preparation of mixed-ligand saccharinate complexes. Our interest has been focused on metal-saccharin-azobispyridine system, in which azobispyridine plays an important role in the construction of supramolecular architectures organized by coordinated covalent or supramolecular contacts (such as hydrogen-bonding, π - π interaction etc.) (Li, 2001; Zhuang, 2006). Since, 4,4'-abpy possess a special structure with a larger π -bond conjugated system and two active nitrogen atoms, it is especially suitable to connect remote metal centers in the stepwise construction of polynuclear arrangements (Launay, 1991). 4,4'-abpy ligand has four possible sites of coordination, namely the two pyridine nitrogens and the two azo nitrogens. Pyridine nitrogens are much more accessible for coordination for sterical reasons.

Materials and Methods

All chemicals used were of analytical reagent quality. The 4,4'-abpy ligand was synthesized by oxidation of the 4-aminopyridine with NaOCl according to literature (Kirpal-Reiter method) (Baldwin, 1969). The X-ray diffraction data of complexes were collected with a Bruker Kappa Apex2duo diffractometer. The structures were solved and refined by full-matrix least-squares techniques on F^2 by using the SHELX-97 program (Sheldrick, 1997). The absorption corrections were done by the multiscan technique. All non-hydrogen atoms were refined anisotropically. All non-water hydrogen atoms were included in the refinement process by using a riding model.

Results and Discussion

Experimental

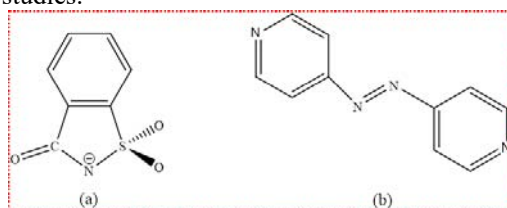
Synthesis of 4,4'-azobispyridine

4,4'-abpy was prepared by oxidative coupling of 4-aminopyridine by hypochlorite, using Kirpal-Reiter method (Baldwin, 1969). Sodium hypochlorite (50 ml) was cooled in the solid CO_2 -methyl alcohol bath. A solution of 4-aminopyridine (2 g) in water was added dropwise to stirred hypochlorite solution. 10 minutes later the resulting deep red solution was immediately extracted with diethyl ether. The solvent evaporated and the solid was recrystallized from petroleum ether.

Synthesis of $[\text{Hg}(\text{sac})_2(\mu\text{-azpy})_2]_n$

For the synthesis of mixed-ligand saccharinate complex with Hg(II), it is a common strategy to apply $[\text{Hg}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ as synthetic precursors. To prepare it, sodium saccharinate was dissolved in water and added to the hot water solution of Hg_2SO_4 . The mixture was stirred at 80 °C for 3 h and then cooled to room temperature. The precipitate formed was filtered out and washed with water and dried in a vacuum. The complex was prepared by the direct reaction of 4,4'-abpy with this starting aqua-saccharinate complex in solution. A solution of 4,4'-abpy

in ethanol was added dropwise to stirred aqueous solution of $[\text{Hg}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$. The mixture was heated under reflux for 2h and afterwards cooled to room temperature. After nearly a couple of weeks, well-formed crystals were selected for X-ray studies.



Scheme 1. (a) Schematic structure of saccharinate anion (sac); (b) Schematic structure of 4,4'-azobispyridine (azpy)

Description of Crystal Structures

A summary of crystallographic data, experimental details, and refinement results for the complex is given in Table 1. Selected bond lengths, angles and the hydrogen bonding geometry is given in Table 2.

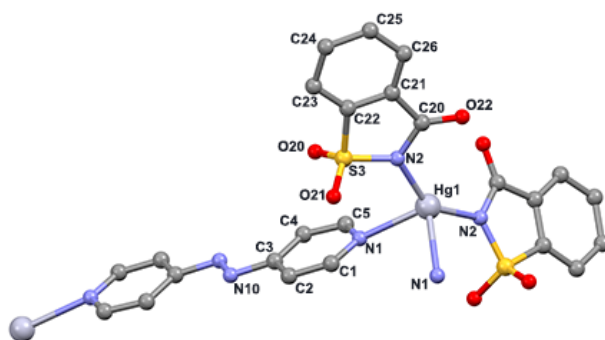


Fig. 1. The crystal structure of the complex showing the atom numbering scheme.

The asymmetric unit of the complex contains one Hg(II) ion, two sac and two 4,4'-abpy ligands (Fig. 1). In complex, the 4,4'-abpy ligands bridge the Hg(II) centers through the nitrogen atoms to form a one-dimensional polymeric structure (Fig. 2.). The sac anions connects to the metal center via the negatively charged nitrogen atom.

Table 1. Crystal data and structure refinement parameters for complex.

Crystal data	Complex
Empirical formula	$\text{C}_{24}\text{H}_{16}\text{N}_6\text{O}_6\text{S}_2\text{Hg}$
Formula weight	749.13
Crystal system	Orthorhombic
T (K)	100 (2)
λ (Å)	0.71073
Space group	P c c n
a (Å)	19.697(2)
b (Å)	8.4999(8)
c (Å)	15.3059(15)
V (Å ³)	2562.5(4)
Z	4
Dc (gcm ⁻³)	1.942
μ (mm ⁻¹)	6.222
Measured ref.	2471
q Range (°)	2.61–30.50
Crystal size (mm)	0.34 × 0.20 × 0.04
Rint	0.0815
R, Rw[I>2s(I)]	0.0699, 0.0807

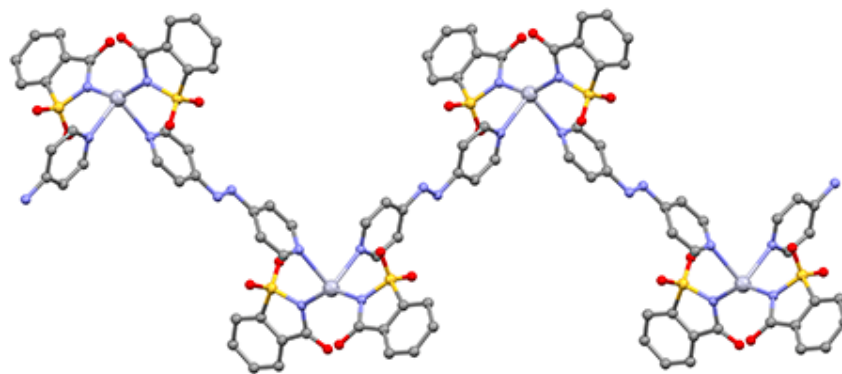


Fig. 2. View of the infinite 1D chain structure of the complex.

Table 2. Selected bond distances and angles for complex (Å, °)

Hg1-N2	2.111(4)	Hg1-N1	2.399(4)
N2-Hg1-N2	145.0(2)	N2-Hg1-N1	108.23(13)
N2-Hg1-N1	97.04(13)	N1-Hg1-N1	87.24(18)

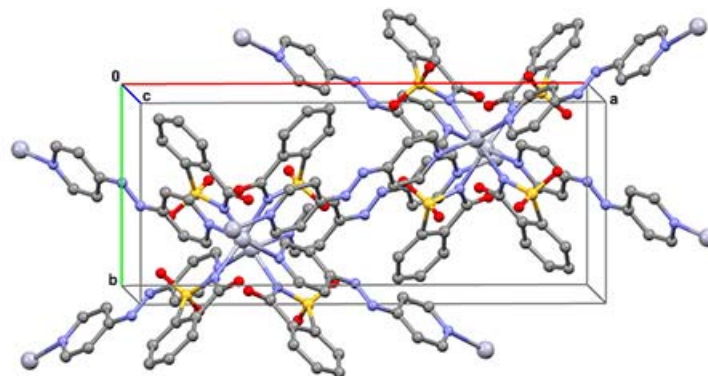


Fig. 3. View of the unit cell in the complex.

Conclusion

The new coordination polymer, $[\text{Hg}(\text{sac})_2(\mu\text{-azpy})_2]_n$, was synthesized and structurally characterized by single crystal X-ray diffraction. Azobispyridine plays an important role in the construction of supramolecular architectures organized by coordinated covalent or supramolecular contacts.

Acknowledgements

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