SYNTHESIS, STRUCTURE, ANTIBACTERIAL ACTIVITY AND TOXICITY OF CO(II) COMPLEX WITH 5-SULFOSALICYLIC ACID.

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Abstract. *In this investigation, a synthesized octahedral aqua complex of 5-sulfosalicylic acid with Co(II) underwent thorough analysis of its composition and structure through elemental analysis, X-ray crystallography, infrared spectroscopy (FT-IR), and UV-visible spectroscopy. The compound, denoted as [Co(H2O)6][C7H5O3SO3]2·2H2O, features a Co(II) ion arranged octahedrally with six water molecules. The bond lengths between cobalt and oxygen atoms range from 2.062(3) to 2.112(1) Å. The equatorial plane of the octahedron, defined by oxygen atoms O7, O7', O9, and O9' from the water molecules, appears almost perfectly flat with merely a 0.074(1) Å deviation. Some distortion in the octahedral geometry, induced by the Jahn-Teller effect, leads to shorter Co-O8 bonds in contrast to the Co-O7 and Co-O9 bonds.*

Keywords: *5-Sulfosalicylic acid, Crystal Structure, Infrared spectroscopy, UV-visible spectroscopy, ligand-to-metal charge transfer*

Introduction. 5-Sulfosalicylic acid and its anions exhibit structural diversity and intriguing topology. Recently, there has been a growing interest in 5-sulfosalicylate ions and their metal complexes due to their antimicrobial, antifungal, and anti-inflammatory properties [1]. The 5-sulfosalicylic acid molecule contains three functional groups: SO3H, COOH, and OH. Five distinct forms of 5-sulfosalicylic acid have been identified: neutral, singly deprotonated at the sulfo group, singly deprotonated at the carboxy group, doubly deprotonated at the sulfo and carboxy groups, and triply (completely) deprotonated. The interactions of partially or fully deprotonated forms of 5-sulfosalicylic acid (H_2SSal^-, $HSSal^{2-}$, and $SSal^{3-}$) with metal ions can result in various coordination modes [2].

Cobalt, despite being present in the body in only about 1 mg, is crucial for life [3]. It is obtained from the diet, notably from green vegetables and cereals, and is frequently included in vitamin supplements [4]. A significant aspect of its biological significance

lies in its association with vitamin B12 [5], also known as cobalamin, with a few other cobalt-containing enzymes having been recognized so far [6].

Although cobalt is an essential metal, it poses systemic toxicity risks, encompassing neurological, cardiovascular, and endocrine disturbances, primarily linked to free ionic Co(II). Blood concentrations exceeding 300 mg/l are deemed worrisome [7]. Cobalt's toxicity is associated with its redox properties, triggering reactive oxygen species (ROS) production, and its capacity to replace iron in metalloenzymes to create substitutionally-inert complexes [8].

Crystal Structure. The Co(II) complex is crystallized in the P-1 triclinic system. The compound $[Co(H_2O)_6][C_7H_5O_3SO_3]_2 \cdot 2H_2O$ consists of hexaaquacobalt(II) cations, 3-carboxy-4-hydroxybenzenesulfonate anions, and water molecules (Fig.1.). The cobalt(II) ion is coordinated by six water molecules in an octahedral geometry. The Co-O bond lengths range from 2.062(3) to 2.112(1) Å. The oxygen atoms O7, O7', O9, and O9' of the water molecules form the equatorial plane of the octahedron, with a minimal deviation of 0.074(1) Å from perfect planarity. The calculated distortion indices for bond lengths and angles in the CoO6 octahedron are IDd(Co-O) = 0.95% and IDa(O-Co-O) = 3.41%, indicating a slightly distorted octahedral geometry. Due to the Jahn-Teller effect, the octahedron is slightly distorted, with shorter Co-O8 bonds compared to Co-O7 and Co-O9 bonds [9]. These bond lengths and angles are comparable to similar cobalt complexes. The crystal structure features alternating layers of hexaquacobalt(II) cations and organosulfonate anions.

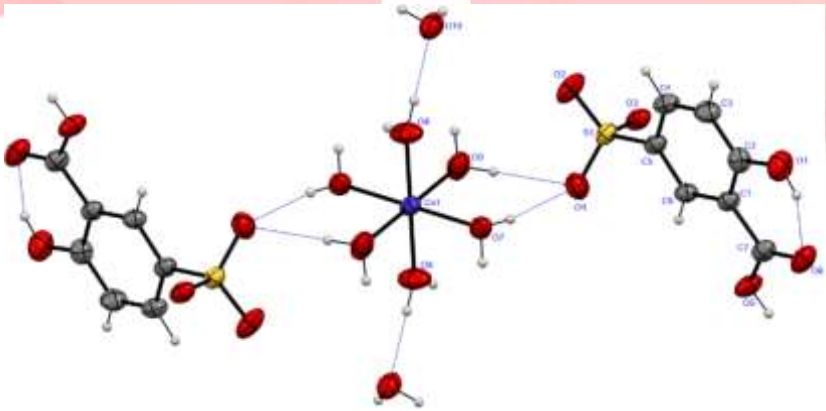

Figure 1. Molecular structure of $[Co(H_2O)_6][C_7H_5O_3SO_3]_2 \cdot 2H_2O$

The phenyl rings of the anions are nearly perpendicular to the b,c-plane. Within the sulfonate layer, adjacent organic molecules have sulfite groups pointing in opposite directions. Hydrogen bonding plays a crucial role in stabilizing the structure. Water molecules form short, linear O-H···O hydrogen bonds with sulfonate oxygen atoms. Additionally, phenyl-phenyl interactions between organic ligands contribute to the

formation of one-dimensional chains along the [100] direction. The shortest cobalt-cobalt distance is 7.66 Å.

Infrared spectroscopy. The infrared spectroscopic analysis of the cobalt coordination compound is shown in Table 1. The spectra indicate that the valence vibrations of the –OH group from water molecules in the compound were observed in the 3350 cm^{-1} region. Additionally, the asymmetric and symmetric valence vibrations of the carbonyl group were detected at 1699 cm^{-1} and 1663 cm^{-1}, respectively. The bonds between the metal and the ligand were noted in the 571 cm^{-1} region (Figure 2) [10].

Figure 2. Infrared spectrum of the compound.

Table 1. Infrared spectra of the compound with absorption peaks.

Compound	ν (-OH)	ν (C=O)	ν (xalqa)	ν (S=O)	δ (S=O)	δ_{as} (C-H)	δ_s (C-H)	ν (O-M)
$[Co(H_2O)_6](5\text{-}SSK)_2 \cdot 2H_2O$	3350	1699 1663	1610 1586	1474 1437	1320 1304	1151 1125	1078 1028	571

UV-visible spectroscopy. The electron transition phenomena in the compound were investigated using UV spectrophotometry over the range of 200-800 nm. Under UV light, the following electron transfer phenomena occurred in the compound: $t_{2g} \rightarrow e_2$, $n \rightarrow \pi^*$, ligand-to-metal charge transfer (LMCT), and $\pi \rightarrow \pi^*$ (Table 2 and Figure 3) [11].

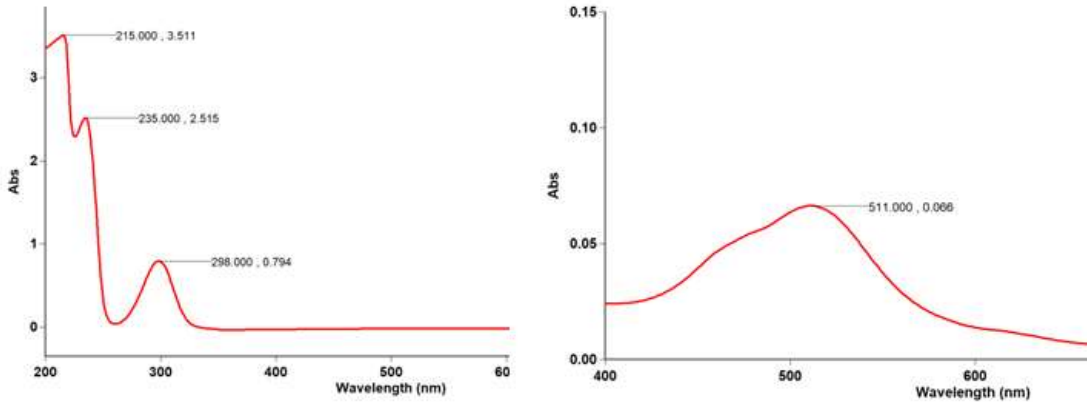

Figure 3. UV light absorption peaks in the compound.

Table 2. Electron transfer phenomenon of a coordination compound under UV light exposure.

Compound	$T_{2g} \rightarrow E_g$	$n \rightarrow \pi^*$	LMCT	$\pi \rightarrow \pi^*$
$[Co(H_2O)_6](5\text{-}SSK)_2 \cdot 2H_2O$	511	298	235	215

REFERENCES:

1. Fan, S. R., & Zhu, L. G. (2009). In situ 5-sulfosalicylate decarboxylation or dimethylformamide hydrolysis generating supramolecular assembly architectures. *Inorganica Chimica Acta*, *362*(9), 2962-2976.

2. Koksharova, T. V., Kurando, S. V., & Stoyanova, I. V. (2013). Coordination compounds of 3 d-metal 5-sulfosalicylates with thiosemicarbazide. *Russian Journal of General Chemistry*, *83*, 54-57.

3. Wedeen, R. P., Berlinger, B., Aaseth, J., Fowler, B. A., & Nordberg, M. (2015). Handbook on the Toxicology of Metals.

4. Hokin, B., Adams, M., Ashton, J., & Louie, H. (2004). Comparison of the dietary cobalt intake in three different Australian diets. *Asia Pacific Journal of Clinical Nutrition*, *13*(3).

5. Dolara, P. (2014). Occurrence, exposure, effects, recommended intake and possible dietary use of selected trace compounds (aluminium, bismuth, cobalt, gold, lithium, nickel, silver). *International Journal of Food Sciences and Nutrition*, *65*(8), 911-924.

6. Kobayashi, M., & Shimizu, S. (1999). Cobalt proteins. *European Journal of Biochemistry*, *261*(1), 1-9.

7. Leyssens, L., Vinck, B., Van Der Straeten, C., Wuyts, F., & Maes, L. (2017). Cobalt toxicity in humans—A review of the potential sources and systemic health effects. *Toxicology*, *387*, 43-56.

8. Chandel, N. S., Maltepe, E., Goldwasser, E., Mathieu, C. E., Simon, M. C., & Schumacker, P. (1998). Mitochondrial reactive oxygen species trigger hypoxia-induced transcription. *Proceedings of the National Academy of Sciences*, *95*(20), 11715-11720.

9. Canton, S. E., Biednov, M., Pápai, M., Lima, F. A., Choi, T. K., Otte, F., ... & Khakhulin, D. (2023). Ultrafast Jahn-Teller Photoswitching in Cobalt Single-Ion Magnets. *Advanced Science*, *10*(21), 2206880.

10. Arıcı, M., Yeşilel, O. Z., Yeşilöz, Y., & Şahin, O. (2014). One-and three-dimensional silver (I)-5-sulfosalicylate coordination polymers having ligand-supported and unsupported argentophilic interactions. *Journal of Solid State Chemistry*, *220*, 70-78.

11. Widowati, M. K., Rahardjo, S. B., Hastuti, S., & Ariyani, B. F. (2019, September). Synthesis and characterization complex Cobalt (II) with sulfadiazine. In *IOP Conference Series: Materials Science and Engineering* (Vol. 578, No. 1, p. 012007). IOP Publishing.