

07-Crystallography of Organometallic and Coordination Compounds

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PS-07.04.27 SYNTHESIS AND STRUCTURE OF DIHYDRATES OF 2-SULFOQUINOLINATE AND 8-SULFOQUINOLINATE OF COPPER. By Yu. A. Bankovsky, J. E. Lejejs, E. J. Silina*, V. K. Belsky, V. E. Zavodnik, L. J. Pech, Institute of Inorganic Chemistry, Latvian Academy of Sciences, Latvia.

The 2-sulfoquinolate (I) and 8-sulfoquinolate (II) of copper have been synthesized for the first time and studied by X-ray structural analysis. I and II were synthesized by mixing solutions of copper sulfate and the corresponding sulfonic acids.

Crystal data: I- $a = 33.650(7)$, $b = 7.700(1)$, $c = 15.315(2)$ Å, $\beta = 101.41(2)^\circ$, space group $C2/c$, $Z = 8$; II- $a = 7.642(1)$, $b = 9.048(1)$, $c = 30.466(3)$ Å, $\gamma = 113.18(1)^\circ$, space group $P2_1/b$, $Z = 4$.

Crystals of I and II contain complexes $Cu(C_9H_6NSO_3)_2 \cdot H_2O$ and waters of crystallization of two sulfonic acids of quinoline. The oxygen and nitrogen atoms act as bidentate ligands, forming five membered (-Cu-O-S-C-N-) (I) and six-membered (-Cu-O-S-C-C-N-) (II) metalocycles. The metalocycles, are non-planar. Two-edge angles between them are 67.5° (I) and 58.7° (II).

The copper atoms is five coordinate ($2N+2O+H_2O$). The surrounding of the copper atom in I is a slightly distorted trigonal bipyramid with axial arrangement of nitrogen atoms (N(1)-Cu-N(2) $173.3(2)^\circ$, ave. Cu-N 1.993 Å, ave. Cu-O 2.042 Å. In II-copper has a slightly distorted tetragonal pyramid coordinate with a trans-quadratic base ($2N+2O$). The linear axis of the compound is retained (N(1)-Cu-N(2) $177.6(1)^\circ$, ave. Cu-N 2.058 Å, ave. Cu-O 1.956 Å. The water of crystallization in an axial position is bound less strongly (Cu-H₂O $2.231(4)$ Å).

The average S-C(B) bond length is 1.800 Å in I and 1.762 Å in II, and the S-O average bond lengths are 1.4661 Å in I and 1.481 Å in II. All water oxygens participate in hydrogen bonds linking the molecules in extended chains.

PS-07.04.28 CRYSTAL STRUCTURE AND SYNTHESIS OF LITHIUM DICITRATOBORATE MONOHYDRATE $Li[(C_6H_6O_7)_2B] \cdot H_2O$ AND SILVER DICITRATOBORATE PENTAHYDRATE $Ag[(C_6H_6O_7)_2B] \cdot 5H_2O$. By I. Zviedre V. Belsky, J. Schwartz, Institute of Inorganic Chemistry, Academy of Sciences of Latvia, Latvia

The anionic coordination compounds of boron with citric acid belong to the spyran type complexes. They are synthesized in crystalline state as salts of several cations dicitratoborates (G. Sergejeva, J. Schwartz, Koord. Khim. (Russ.), 1979, 5, 1782-1787). To fulfill the systematic investigation on the structure of dicitratoborates we have synthesized two new compounds $Li[(C_6H_6O_7)_2B] \cdot H_2O$ (I) and $Ag[(C_6H_6O_7)_2B] \cdot 5H_2O$ (II) and have carried out their full X-ray-structural investigation (Syntex P1 diffractometer).

Crystal data for

$Li[(C_6H_6O_7)_2B] \cdot H_2O$

$a = 9.993(2)$ Å
 $b = 9.993(2)$ Å
 $c = 35.041(6)$ Å

$V = 3499.2(2.0)$ Å³

$Z = 8$

$d(\text{calc}) = 1.526$ g/cm³

$\mu = 1.31$ cm⁻¹

Space gr. $P4_12_12$

$R = 0.082$, $R_w = 0.095$

$Ag[(C_6H_6O_7)_2B] \cdot 5H_2O$

$a = 26.202(5)$ Å
 $b = 18.393(4)$ Å
 $c = 14.305(3)$ Å

$\beta = 90.97(2)^\circ$
 $V = 6893.1(4.3)$ Å³

$Z = 16$

$d(\text{calc}) = 2.270$ g/cm³

$\mu = 12.66$ cm⁻¹

Space gr. $P2_1/c$

$R = 0.079$, $R_w = 0.094$

The crystal structure is composed of cations, large complex anions and water molecules. In the structure of (I) there are two series of cations; half the Li⁺ ions are located in the center of a distorted tetrahedron, the other half are statically distributed. In the structure of (II) there are four types of Ag⁺ cations with coordination numbers 4,3,4,4. The anion contains two five member carbon chains and four carboxylic groups. Tetrahedral BO₄ is symmetrically distorted. The B-O(hydr) bonds aver. 1.44 Å and shorter than the B-O(carb) bonds (1.498 Å). The boron heterocycles are practically planar. The dihedral angles of carboxylic groups range from 13° to 57° . Anions from bonds with metal ions, molecules of H₂O and other anions due to the flexibility of the carboxylic groups. Hydrogen bonding of water is critical to the overall structures.

The packing of dicitratoborates is mostly determined by the spacing of the large anions, and cations, their numeric ratio and the water molecules. In structures (I) and (II) all non-aliphatic hydrogen atoms participate in the hydrogen-bonding scheme.

The data about crystalline structures (I) and (II) are compared to 11 crystalline structures previously investigated by the authors.

PS-07.04.29 SYNTHESIS AND STRUCTURE OF 8-MERCAPTOQUINOLINATE OF RHODIUM (III). By I. R. Berzina*, Yu. A. Bankovsky, V. K. Belsky, G. E. Jansons, Institute of Inorganic Chemistry, Academy of Sciences of Latvia, Latvia.

The title compound is of interest as a member of a family of chelate compounds having metal sulfur bonds. This is the first reported complex of a trivalent transition metal with 8-mercaptoquinoline or its derivatives. Crystals were grown by slow cooling of a saturated solution of the complex in ethanol/chloroform (1:3). Experiment data: $P1$, $a = 8.932(2)$, $b = 12.725(5)$, $c = 14.212(7)$, $\alpha = 66.03(3)$, $\beta = 84.44(3)$, $\gamma = 70.14(3)^\circ$, space group $P1$, $Z = 2$, 2010 independent reflections recorded on a diffractometer, $R = 0.56$. The monomeric complex cocrystallized with chloroform molecules that do not contact the metal ion. The rhodium ion has distorted octahedral coordination to three sulfur atoms, and three nitrogen atoms. The sum of the covalent radii of rhodium and sulfur is 2.37 Å. One of the three distances observed here (2.296 , 2.374 , and 2.385 Å) is significantly shorter than that. The atoms are situated in *cis* as well as *trans* positions relative to one another. The observed rhodium-nitrogen distances of 2.02 , 2.03 and 2.11 Å. The arrangement of the mercaptoquinoline planes round the central atom is nearly orthogonal (93.0 , 92.3 and 83.0°).

PS-07.04.30 X-RAY STRUCTURAL STUDY OF BIS(2-METHYL-5-METHYLTHIO-8-OXYQUINOLINATES) OF PAL-LADIUM, PLATINUM AND OXOVANADIJUM. By L. Pech,* Yu. Bankovsky, A. Sobolyev, J. Asaks, Institute of Inorganic Chemistry, Latvian Academy of Sciences, Latvia.

The aim of the present study is to discuss three inner complex compounds of 2-methyl-5-methylthio-8-oxyquinoline, to juxtapose their molecular and crystalline structures and to determine some regularities of their spatial