

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 P2₁/b, $Z = 4$.

Crystals of I and II contain complexes $\text{Cu}(\text{C}_6\text{H}_6\text{NSO}_3)_2 \cdot \text{H}_2\text{O}$ 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).

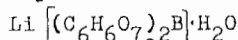
The copper atoms is five coordinate (2N+2O+H₂O). The surrounding of the copper atom in I is a slightly distorted trigonal bipyramid with axial arrangement of nitrogen atoms (N(1)-Cu-N(2) $173.3(2)^\circ$, ave. Cu-N 1.993 Å, ave. Cu-O 2.042 Å. In II-copper has a slightly distorted tetragonal pyramid coordinate 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 $\text{Li}[(\text{C}_6\text{H}_6\text{O}_7)_2\text{B}]\cdot\text{H}_2\text{O}$ AND SILVER DICITRATOBORATE PENTAHYDRATE $\text{Ag}[(\text{C}_6\text{H}_6\text{O}_7)_2\text{B}]\cdot 5\text{H}_2\text{O}$. 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 $\text{Li}[(\text{C}_6\text{H}_6\text{O}_7)_2\text{B}]\cdot\text{H}_2\text{O}$ (I) and $\text{Ag}[(\text{C}_6\text{H}_6\text{O}_7)_2\text{B}]\cdot 5\text{H}_2\text{O}$ (II) and have carried out their full X-ray-structural investigation (Syntex P1 diffractometer).

Crystal data for



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

$V = 3499.2(2.0)$ Å³

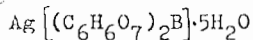
$Z = 8$

$d(\text{calc}) = 1.526$ g/cm³

$\mu = 1.31$ cm⁻¹

Space gr. P4₁2₁2

$R = 0.082$, $R_w = 0.095$



$a = 26.202(5)$ 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. P2₁/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

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structure in dependence on the metal's nature and on the location of substituents in the quinoline ring. The buildup of structures of bis(2-methyl-5-methylthio-8-oxyquinolinates) of palladium (I), platinum (II) and oxovanadium (III) is examined. The monocrystals of the compounds are studied on the automatic diffractometer. The parameters of triclinic cells are the following:

I- $a=6.945(2)$, $b=10.893(3)$, $c=13.840(4)$ Å, $\alpha=85.37(2)$, $\beta=81.07(2)$, $\gamma=79.10(2)^\circ$, space gr. $P\bar{1}$, $Z=2$; II- $a=6.932(2)$, $b=10.908(3)$, $c=13.859(4)$ Å, $\alpha=85.63(3)$, $\beta=80.50(3)$, $\gamma=79.29(3)^\circ$, space gr. $P\bar{1}$, $Z=2$; III- $a=4.88(2)$, $b=15.694(4)$, $c=13.408(3)$ Å, $\alpha=82.98(2)$, $\beta=82.97(2)$, $\gamma=93.51(2)^\circ$, space gr. $P\bar{1}$, $Z=4$. In all three compounds there are two crystallographically independent molecules.

The compounds I and II are isostructural, coordination polyhedron of the Pd and Pt atom in both independent molecules is a centrosymmetrical trans-square (2O+2N). The distances Pd-O are 1.978(5) and 1.992(6) Å, Pd-N are 2.03(1) and 2.045(9) Å. The intermolecular interactions Pd(1)...Pd(2) 3.472 Å, Pt(1)...Pt(2) 3.446 Å unite the molecules of complexes I and II in dimers.

The coordination polyhedron of the oxovanadium atom in both molecules is a distorted trigonal bipyramid (2N+2O+Ooxo) with axial location of nitrogen atoms (angle N(1)-V-N(2) 157.9(3) and 158.7(3)°, resp., V-N aver. 2.10 and 2.12 Å). The surrounding chelate atoms (2O+2N) of the oxovanadium atom have a form of swings (angle O(1)-V-O(2) 127.9(3) and 127.5(3)° correspond.), which to the trigonally-bipyramidal one is supplemented by Ooxo at the distance V-O(3) 1.576(6) and 1.592(6) Å. The distances V-O are 1.950 and 1.935 Å. The chelate angles are 80.3(2) and 79.9(3)° in V(1) and 80.4(3) in V(2). Metallo-cycles are non-planar. Twisting along the line O...N is 17.0 and 10.8° in V(1) and 10.8 and 12.8° in V(2).

The intermolecular distances: V(1)...O(3) 3.307, O(3)...O(1) 3.017, O(3)...O(2) 3.017, V(2)...O(3) 3.306, O(3)...O(1) 2.933, O(3)...O(2) 3.090 and S(1)A...S(2)B 3.620 Å. Complexes I and II as compared to the previously studied Pd and Pt complexes with 8-mercaptoquinolate and its derivatives.

As a result of comparative study of the complexes it has been established that the transition from 8-mercaptoquinolates to 8-oxyquinolates, judging by the existing structural data, causes substantial stereochemical changes.

PS-07.04.31 THE CRYSTAL AND MOLECULAR STRUCTURE OF [1,2-DIMETHYL-1,2-(DI-ISOBUTYL)ETHYL]BIS CYCLOPENTADIENYL ZIRCONIUM DICHLORIDE. By Shou-shan Chen, Xin-kan Yao and Hung-gen Wang, Institute of Elemento-organic Chemistry, Central Laboratory, Nankai University, Tianjin 300071, China.

The title compound, $C_{22}H_{32}Cl_2Zr$, is a new chiral bridged bis cyclopentadienylmetal complex. The sample was re-crystallized from a mixed solvent of dichloromethane and petroleum ether as colorless crystals. Intensities were collected on a CAD4 diffractometer, ω -2 θ scan mode, Mok_α in

the range of 2° 025°. 2043 independent reflections were measured, of which 1721 were observed with $I > 3\sigma(I)$. The intensities were corrected for Lp factors and absorption.

The crystal is monoclinic, space group $C 2/c$, with $a=13.330(3)$, $b=9.585(1)$, $c=16.492(3)$ Å, $\beta=94.76(2)^\circ$, $v=2099.8$ Å³, $M_r=458.63$, $Z=4$, $D_x=1.45$ g/cm³, $\mu=7.74$ cm⁻¹, $F(000)=952$.

The structure was solved by direct method (MALTAN-82) and difference Fourier syntheses. Full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms and isotropic for H atoms led to R of 0.037 and R_w of 0.044.

The view of the molecule is shown in Figure 1. Its molecular structure possesses C_2 symmetry which belongs to the type of equivalent homotopic faces of cyclopentadienyl ligands. The dihedral angle between the two cyclopentadienyl planes is 57.33°.

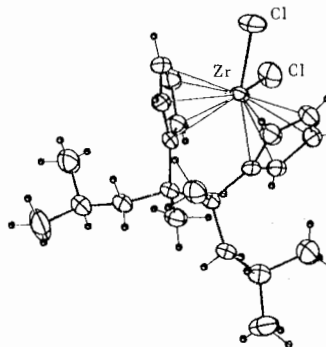


Fig. 1

PS-07.04.32 CRYSTAL STRUCTURE PECULIARITIES OF VOLATILE COMPLEXES USED AS PRECURSORS FOR CHEMICAL VAPOR DEPOSITION OF THIN-FILM SUPERCONDUCTORS. By T. M. Polyanskaya, Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch, Novosibirsk, Russia.

The crystal structures of the three types of volatile complexes used as molecular precursors for chemical vapor deposition of thin-film superconductors were discussed:

- I) Complexes of Cu(II), Ba, Ca, Sr and Y with β -diketons as ligands. The ligand substituents are as follows: CH_3 , CF_3 , $C(CH_3)_3$, $CF_2CF_2CF_3$.
- II) Alkaline-Earth-Metal β -diketonate complexes with the linear polyethers (di-, tri-, tetra-, hexaglyme).
- III) β -diketonate complexes with the macrocyclic polyethers, 18-crown-6 and 15-crown-5.

The only homoligand complexes of Cu and one of two forms of Y(dipivaloylmethanate)₃ are mononuclear ones among complexes of the type I, specified by donor-acceptor interaction of