

PS07.00.42 BORON COORDINATION COMPOUNDS WITH HYDROXYCARBOXYLIC ACIDS. J. Schwartz, I. Zviedre, Institute of Inorganic Chemistry, Latvian Academy of Sciences, Latvia

The dependence of some properties of coordination compounds of boron, for example, the solubility in water (25°C), IR-spectra, on structural type of boron oxygen polyhedron, size of heterocycle, the nature of cation and hydrogen bonds, is shown on the examples of 8 crystal and molecular structures of the salts of DLmalato- (I); citrato- (II); salicylato- (III); p-aminosalicylatoI (IV); tartrato- (V,VI); xylotrihydroxyglutarato- (VII,VIII) borates.

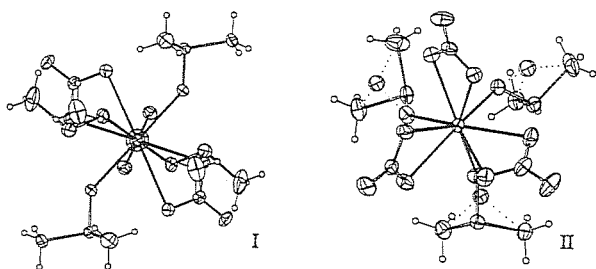
- I - $K[(HOOCCH_2CHCOCOO)_2B] \cdot H_2O$,
 II - $K[(HOOCCH_2)_2HCOCOO)_2B] \cdot 2H_2O$,
 III - $[Zn(H_2O)_4][(C_6H_4OCOO)_2B] \cdot 4H_2O$,
 IV - $K[(p-NH_2C_6H_3OCOO)_2B] \cdot H_2O$,
 V - $NH_4Sr[(OOCHCOHCOCOO)B(OH)_2] \cdot 4H_2O$,
 VI - $Na_3[(OOCHCOHCOCOO)_2B] \cdot 5H_2O$,
 VII - $NH_4Sr_2[(OOCHCOHHCOCOO)_2B] \cdot 4H_2O$,
 VIII - $(NH_4)_2[Zn_2(H_2O)_2(OOCHCOHCOHHCOCOO)(HO)B-O-B(OH)(OOCHCOHCOHHCOCOO)] \cdot 4H_2O$.

The authors synthesized I - VIII and determined the structures of I - V, VII - VIII by X-ray analysis. The solubility depends on the nature of the cation, on the size of boron heterocycle, on the existence of some lyophilic OH-groups in the ligand, on the hydrogen bonds system. For example, the great solubility of VII, which firstly was regarded as Zn-salt, could be explained only after the determination of the crystal structure, which showed, that VII is the ammonium salt, but Zn enters in the inner coordination sphere. Most potassium salts of the ligands with six-membered Bheterocycle are insoluble or little soluble in water, but - with five membered one - very well soluble.

The correlation of IR-absorption spectra and crystal structure is made.

PS07.00.43 CRYSTALLOGRAPHIC STUDIES OF DIMETHYL SULFOXIDE COMPLEXES OF RARE EARTH (III) NITRATES. Lioubov I. Semenova, Brian W. Skelton and Allan H. White Department of Chemistry, University of Western Australia, Nedlands, W.A. 6907

Adducts $[(dmsO)_nLn(O_2NO)_3]$ have been the subject of a series of room temperature single crystal X-ray studies, defining more clearly the manner in which stoichiometry and structure systematically vary with change in metal ion radius. All complexes studied are mononuclear, the metal ion being complexed by three bidentate nitrate ligands and a number of dmsO ligands: $n = 4$ for the light rare earths and $n = 3$ for the heavier. The array La - Sm is monoclinic $C2/c$, $a \sim 14.9$, $b \sim 15.5$, $c \sim 15.5$ Å, $\beta \sim 108.4^\circ$, $Z = 4$ f.u.; the metal atom is disposed on a crystallographic 2 axis, which also passes through one of the nitrate groups (I). The series Eu - Tm (inclusive also of Y) is monoclinic, $P2_1/n$, $a \sim 11.5$, $b \sim 12.7$, $c \sim 13.6$ Å, $\beta \sim 100^\circ$, $Z = 4$ f.u., while Yb, Lu are also monoclinic, $P2_1/c$, $a \sim 10.0$, $b \sim 12.6$, $c \sim 16$ Å, $\beta \sim 100.6^\circ$, $z = 4$ f.u.(II).



PS07.00.44 STRUCTURE OF COBALT 8-OXYQUINOLINATE, 8-MERCAPTO- AND 2-METHYL-8-MERCAPTOQUINOLINATE. E. Silina, Yu Bankovsky, V. Belsky, A. Stash, J. Ashaks, L. Pech, Institute of Inorganic Chemistry, Latvian Academy of Sciences, Latvia

In the discussed complexes $Co(C_9H_6NO)_3 \cdot CH_3OH$ (I), $Co(C_9H_6NS)_3 \cdot CHCl_3$ (II) and $Co[C_9H_5(CH_3)NS]_2$ (III) the 8-oxyquinolinate and 8-mercaptoquinolinate acts as bidentate ligand forming five membered metallocycles with the help of oxygen, sulphur and nitrogen atoms. The monomeric complex I is cocrystallized with methanol molecule. The molecule of methanol forms hydrogen bond with the weaker bonded oxygen atom. The complex II - with chloroform molecule which does not contact the metal atom. The coordination polyhedron of Co(III) ion is a slightly distorted octahedron, but Co(II) - tetrahedron. The dihedral angles between the coordination planes O-Co-N, S-Co-N (1/2, 1/3, 2/3) in the complexes I-III are 87.6° , 88.2° , 91.8° (I); 89.3° , 95.0° , 88.0° (II) and 90.7° (III). The angles O-Co-O and S-Co-S of chelate metallocycles I-III are 177.2° , 91.7° and 90.3° in I; 90.8° , 173.0° and 86.0° in II and 123.2° in III.

Planarity of the metal containing ring is not identical. Therefore formed the breach in five membered metallocycles through the lines O...N, S...N by dihedral angles: 0.3° , 2.8° and 2.9° (I); 1.9° , 4.9° and 0.7° (II) and 1.2° and 17.4° (III).

Crystal data: I - $a=11.392(3)$, $b=12.774(3)$, $c=16.672(5)$ Å, $\beta=92.56(2)^\circ$, $Z=4$, sp.gr. $P2_1/n$; II - $a=8.762(3)$, $b=20.237(4)$, $c=16.073(4)$ Å, $\beta=101.05(2)^\circ$, $Z=4$, sp.gr. $P2_1/c$; III - $a=7.494(2)$, $b=9.985(2)$, $c=12.516(4)$ Å, $\alpha=80.48(2)$, $\beta=86.82(2)$, $\gamma=69.27(2)^\circ$, $Z=2$, sp.gr. $P\bar{1}$.

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PS07.00.45 DIMETHYLSULFOXIDE SOLVATES OF BISMUTH(III) IODIDE. Brian W. Skelton, Peter C. Junk and Allan H. White, Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6907, Australia

At room temperature, bismuth(III) iodide crystallises from solutions of dimethylsulfoxide (dmsO) in at least two substantial, well-defined crystalline solvates, $BiI_3 \cdot 2dmsO$ (orange) and $BiI_3 \cdot 8/3dmsO$ (red). $BiI_3 \cdot 2dmsO$ is triclinic $P\bar{1}$, a 12.558(2), b 8.962(2), c 8.342(1) Å, α 61.85(1), β 78.27(1), γ 76.89(2)° $Z=2$, conventional R on $|F|$ being 0.048 for N_O 1953 independent 'observed' reflections. The complex is a centrosymmetric binuclear array, one dimer in the unit cell: $[(O-dmsO)_2I_2Bi(\mu-I)_2BiI_2(O-dmsO)_2]$, bismuth atoms being six-coordinate with the dmsO oxygen atoms *trans*. Bi-O are 2.37(2), 2.41(2), Bi-I (terminal) 2.941(7), 2.922(9) and Bi-I (bridging) 3.211(7), 3.25(1) Å. Bi-O-S are 123.9(7), 125.8(7) and Bi-I-Bi 96.03(7)°. The badly-twinned crystals of $BiI_3 \cdot 8/3dmsO$ are also triclinic $P\bar{1}$, a 16.435(6), b 14.926(2), c 12.396(3) Å, α 74.89(2), β 73.24(2), γ 79.18(2)°, $Z=6$, R 0.059 for N_O 5858. The complex is $[Bi(O-dmsO)_8]^{3+}[I_3Bi(\mu-I)_3BiI_3]^{3-}$ (i.e. $[Bi_2I_9]^{3-}$) the bismuth environment of the novel cation being, unusually, dodecahedral rather than square anti-prismatic, the 'inner' sites of the trapezoidal planes having perhaps slightly longer Bi-O (2.41(2)-2.49(2) Å) than the peripheral (2.36(2)-2.44(2) Å). In the anion, Bi-I (bridging) are 3.152(2)-3.337(3) and Bi-I (terminal) 2.903(3)-3.012(2) Å. In the cation, half of the ligand sulfur atoms are disordered in the usual way; for the more precisely determined ordered species, Bi-O-S are 118.8(9)-131(1)°.