07-Crystallography of Organometallic and Coordination Compounds


The 2-sulfoquinolamine (I) and 8-sulfoquinolamine (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 = 3.3604(7), b = 7.7004(1), c = 15.313(2)Å, α = 120.41(1), space group C2/c, Z = 8; II - a = 7.612(4), b = 9.064(1), c = 30.466(3)Å, v = 113.18(4), space group P2_1/c, Z = 4.

Crystals of I and II contain complexes Cu(C2H4N3O4), H2O and water 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-N=) (II) metalcycles. The metalcycles are non-planar. Two-angled angles between them are 67.5° (I) and 58.1° (II).

The copper atom 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 (N1-Cu-N2) 173.2(2), space group Cu-N·1.997(1), Cu-O-0.024(2). In II-copper has a slightly distorted trigonal bipyramidal geometric of Cu with a trans-quadric base (2N-2O). The linear axis of the compound is retained (N1-Cu-N2 177.46(1), Cu-N·2.005(1), Cu-O-0.939(1)). The water of crystallization in an axial position is bound with strongly (Cu-H·O 2.31(1)).

The average S-O (H2O) bond length is 1.800Å in I and 1.762Å in II, and the S-O average bond lengths are 1.460Å in I and 1.461Å in II. All water oxygen participate in hydrogen bonds linking the molecules in extended chains.


The anionic coordination of boron with trifluoromethane belongs to the azide type complexes. They are synthesized in crystalline state as a result of several reactions of difluoroborate (J. Schwartz, K. Khim. Khim., 1979, 5, 310-319). To fullfill the systematic investigation on the structure of difluoroborates we have synthesized two new compounds Li[(C6H5)2N]BF4·H2O (I) and Ag[(C6H5)2N]BF4·H2O (II) and have carried out their full X-ray-structural investigation (Synelix P1 diffractometer).

Crystal data for

Li[(C6H5)2N]BF4·H2O
a=9.993(2)Å, b=9.993(2)Å, c=35.041(6)Å,
V=3499.2(2.03)Å³,
ρd(calc)=1.526 g/cm³,
ρd(calc)=2.270 g/cm³,
μ=1.31 cm⁻¹,
Space gr. P4₂/2,
R=0.032, Rw=0.095

Ag[(C6H5)2N]BF4·H2O
a=26.202(5)Å,
b=16.393(4)Å,
c=30.97(2)Å,
V=6853.14(13)Å³,
ρd(calc)=2.70 g/cm³,
μ=12.66 cm⁻¹,
Space gr. P2₁/c,
R=0.075, Rw=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, 4, 4, 4.

The anion containing two five member carbon chains and four carboxylic groups. Tetrahedral BO₄ is symmetrically distorted. The B-O(hyd) bonds are 1.44Å and shorter than the B-O(carb) bonds 1.49Å. The boron hexacarbonyl is practically planar. The dihedral angle 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 structure.

The packing of dichromates is mostly determined by the spacing of the large anions, and cations, their nematic 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 author.


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 a mercury-catactic amine derivative. Crystals were grown by slow cooling of a saturated solution of the complex in ethanol/chloremene (1:3). The observed data: P1, a=8.932(2), b=2.725(2), c=12.217(1), α=66.58(1), β=84.34(1), γ=70.14(3), space group P1, Z=2, 2010 independent reflections recorded on a diffractometer, R=0.036.

The nonmonic complex crystallized with chlorform 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 2.37Å. One of the three distances observed here (2.396, 2.374, and 2.385Å) 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 are 2.02, 2.03 and 2.11Å. The arrangement of the mercaptoquinoline planes round the central axis is nearly orthogonol (93.0, 82.3 and 83.0°).


The aim of the present study is to discuss three inner complex compounds of 2-methyl-5-methylthio-3-oxyquinoline, to juxtapose their molecular and crystalline structures and to determine some regularities of their spatial