07-Crystallography of Organometallic and Coordination Compounds

A number of antimony(III) amidoglyoxylic acid acetates, in which the coordination polyhedron of Sb(III) is unexceptionally a distorted $\Phi$-pentagonal bipyramid, have been found to exhibit certain antitumor activity for a long time (Hu, S. Z. & Lin, W. F., J. Struct. Chem., 1989, 8, 249-256). In order to investigate the mechanism of antitumor activity, the interaction of Sb(III) complexes with some bases of nucleobases and nucleic acids have been considered in our laboratory. As a preliminary study, SbCl₅ was selected to react with adenine in the light of complex formation with N-donor ligands such as aniline, 2',3'-bipyridine and 4-phenylo-1,2-diazole (Lipka, A., Z. Naturforsch., 1983, 38, 341-346). We report here two crystal structures of the title compounds (C₂H₅N₃SbCl₅CH₄O) and (C₂H₅N₃SbCl₅H₂O). Complexes of stoichiometry SbCl₅ can feature either six-coordinate polymeric anions as in compound (I), or discrete five-coordinate anions ν in compound (II). The cations are linked through hydrogen bonding with the water molecule, consequently, there are no interactions between Sb(III) and adeninium moieties.

Crystal data: $\lambda$(MoKα) = 7.0173 Å, 296K

(I): FW = 454.18, F(000) = 872, monoclinic, P2₁/c, a = 11.043(1), b = 17.648(1), c = 17.544(1) Å, α = 103.98(1)°, γ = 1437.5 Å³, Z = 4, D = 2.02, De = 2.08 Mg/m³, μ = 28.6 cm⁻¹, R = 0.033 for 2084 observed reflections.

(II): FW = 589.30, F(000) = 556, triclinic, P-1, a = 8.696(1), b = 9.144(3), c = 12.763(2) Å, α = 79.50(2), β = 74.78(1), γ = 83.50(2)°, V = 960.6 Å³, Z = 2, D = 2.03, De = 2.03 Mg/m³, μ = 21.72 cm⁻¹, R = 0.037 for 3758 observed reflections.

07-07.05.15 CRYSTAL STRUCTURE OF (HYDROGEN ETHYLENE-DIAMINETRACETATO) BISMUTH(II) DIHYDRATE. By Hu Sheng-Zhi* and Xiao Zhao-Xiong, Chemistry Department, Xiamen University, Xiamen, Fujian, China, and R. L. Davidson, Institute of Chemistry, F. E. Branch, Russian Academy of Sciences, Vladivostok, Russia.

Two modifications of the dihydrate chelate of bismuth(II) with ethylenediamine-N,N',N'-tetraacetacetic acid (Hédta), Bi(Hédta)·2H₂O, have been crystallized and identified by the methods of IR spectroscopy and X-ray powder diffraction analysis (Davidovich, R. L. et al., Koord. Khim., 1988, 14, No. 11, 1511-1516). The α-modification is orthorhombic with cell dimensions a = 10.60, b = 18.25, c = 7.35 Å, which are similar to that of Sb(Hédta)·2H₂O (orthorhombic, α = 10.98, b = 18.496, c = 7.341 Å). The β-modification is monoclinic with cell dimensions a = 17.85(4), b = 6.848(2), c = 13.213(2) Å, β = 105.78(2)°, V = 1903.1 Å³, Z = 4, FW = 534.2, D = 2.361 Mg/m³, $\lambda$(MoKα) = 7.0173 Å, μ = 117.46 cm⁻¹, F(000) = 1016, 296K, R = 0.034 for 2003 unique reflections with I > 3σ(I). The structure reveals that the Hédta⁻ ligand performs a hexadentate chelating function (4-O + 2N) and a double bridging function (2O). Features of the coordination polyhedron of Bi(II) as well as the polymeric structure compared with that in Bi(Hédta) and NH₄[Bi(Hédta)]·H₂O (Shkol'nikova, L. M. et al., Koord. Khim., 1991, 17, No. 2, 253-261) will be presented.


In continuation of our studies of transition metal complexes (M) with stable nitrooxide radicals (NO) aimed to examination of peculiarities of exchange interaction in heterospin exchange clusters and obtaining a new class of magnetic materials (Zh. Strukt. Khim. 20, M5; 142-155 (1989); Zh. Strukt. Khim., 26, M3, 143-156 (1991)) we have performed crystallographic analysis of the structures of two different types of mixed-ligand NC with 3-imidazoline NR: 1 based on MnNO₂ bicobenolate (Mo60,11) and neutral molecules A. The complexes have $\lambda_1\lambda_2$ composition for A = H₂O or ROH (R = CH₃, C₆H₅, n-C₆H₅) and MnA composition when A = 1,4-butanediol. They have pseudo layered and framed structures, respectively. All the adducts except the H₂O one undergo ferrimagnetic phase transition at 5-8 K. This study is based on transition metal hexafluoroacetylacetates [M(fac)=C=O(NO)] and 3-imidazolino NR derivatives, M = Mn(fac)=[Cu(NOR)]=L²⁺ ratio equal to 1:2 (M:NR,N) have molecular structures in which Cu(fac)²⁺ are of molecular (L²⁺, R = CH₃, PhH or L²⁺, R = NH₂CH₃ or chain (L²⁺, R = CH₃, NH₂CH₂) type. Copper polyhedra are trinuclear or square bipyramidal. Trinuclear molecular complexes Cu(fac)=C=O(NR)=L²⁺ are formed when L²⁺, R = CH₃; Cu(H₂O), 1-C₆H₅ or L²⁺, R = Ph, the NR groups of NO being coordinated by copper atoms. The central and the terminal copper atoms have square and trigonal-bipyramidal geometry respectively. Cu(fac)=C=O(NR)=L²⁺ ratio 2:2:2 is realized when Cu(II) and Cu(I) ions are bridged by NR molecules (R = CH₃, 1-C₆H₅) to form chain structure, the Cu(I) ions having square-hexa- and Cu(II) ions - distorted tetrahedral environments. The geometry, the types of coordination polyhedra, packing modes, the arrangements of paramagnetic centers were analyzed for all compounds and compared to literature data.