

07-Crystallography of Organometallic and Coordination Compounds

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A number of antimony(III) aminopolycarboxylic acid chelates, in which the coordination polyhedron of Sb(III) is unexceptionally a distorted Ψ -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 nucleosides and nucleic acids have been considered in our laboratory. As a preliminary study, SbCl_3 was selected to react with adenine in the light of complex formation of N-donor ligands such as aniline, 2, 2'-bipyridine and 4-phenylpyridine (Lipka. A., *Z. Naturforsch.* 1983, **386**, 341-346). We report here two crystal structures of the title compounds $(\text{C}_5\text{H}_7\text{N}_3)\text{SbCl}_3\text{H}_2\text{O}$ (I) and $(\text{C}_5\text{H}_6\text{N}_3)_2\text{SbCl}_3\text{H}_2\text{O}$ (II). Complexes of stoichiometry SbCl_3^{2-} can feature either six-coordinate polymeric anions as in compound (I), or discrete five-coordinate anions as in compound (II). The counterions are linked through hydrogen bonding with the water molecule, consequently, there are no interactions between Sb(III) and adeninium moiety.

Crystal data: $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, 296K

(I): FW = 454.18, F(000) = 872, monoclinic, $P2_1/c$. $a = 11.043(1)$, $b = 7.646(1)$, $c = 17.544(1) \text{ \AA}$, $\beta = 103.98(1)^\circ$, $V = 1437.5 \text{ \AA}^3$, $Z = 4$, $D_x = 2.098$, $D_m = 2.08 \text{ Mg m}^{-3}$, $\mu = 28.61 \text{ cm}^{-1}$. $R = 0.033$ for 2084 observed reflections.

(II): FW = 589.30, F(000) = 576, triclinic, $P-1$. $a = 8.696(1)$, $b = 9.144(3)$, $c = 12.763(2) \text{ \AA}$, $\alpha = 79.50(2)$, $\beta = 74.78(1)$, $\gamma = 83.50(2)^\circ$, $V = 960.6 \text{ \AA}^3$, $Z = 2$, $D_x = 2.037$, $D_m = 2.03 \text{ Mg m}^{-3}$, $\mu = 21.72 \text{ cm}^{-1}$, $R = 0.032$ for 3758 observed reflections.

PS-07.05.15 CRYSTAL STRUCTURE OF (HYDROGEN ETHYLENE-DIAMINETETRAACETATO) BISMUTH(III) DIHYDRATE. By Hu Sheng-Zhi* and Xi Zhao-Xiong, Chemistry Department, Xiamen University, Xiamen, China, and R. L. Davidovich, Institute of Chemistry, F. E. Branch, Russian Academy of Sciences, Vladivostok, Russia.

Two modifications of the dihydrate chelate of bismuth(III) with ethylenediamine-N,N,N',N'-tetraacetic acid (H_4edta), $\text{Bi}(\text{Hedta}) \cdot 2\text{H}_2\text{O}$ have been synthesized and identified in the crystalline state 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 $a = 10.66$, $b = 18.25$, $c = 7.38 \text{ \AA}$, which are similar to that of $\text{Sb}(\text{Hedta}) \cdot 2\text{H}_2\text{O}$ (orthorhombic, $a = 10.98$, $b = 18.496$, $c = 7.341 \text{ \AA}$). It implies that, if both are isostructural, the coordination polyhedron of Bi(III) in α - $\text{Bi}(\text{Hedta})\text{H}_2\text{O}$ would be a distorted Ψ -pentagonal bipyramid as in the case of Sb(III) in $\text{Sb}(\text{Hedta}) \cdot 2\text{H}_2\text{O}$ (Shimoi, M. et al., *Bull. Chem. Soc. Jpn.*, 1980, **53**, No.11, 3189-3194). This aspect is being further investigated.

The crystal structure of the β -modification was determined using single crystal X-ray diffraction methods. The crystals are monoclinic Cc , $a = 17.185(4)$, $b = 6.848(2)$, $c = 13.273(2) \text{ \AA}$, $\beta = 105.78(2)^\circ$, $V = 1503.1 \text{ \AA}^3$, $Z = 4$, FW = 534.23, $D_x = 2.361 \text{ Mg m}^{-3}$, $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, $\mu = 117.46 \text{ cm}^{-1}$, F(000) = 1016, 296K, $R = 0.034$ for 2003 unique reflections with $I > 3\sigma(I)$. The structure reveals that the Hedta^{3-} ligand performs a hexadentate chelating function (4O + 2N) and a double bridging function (2O). Features of the octacoordinate polyhedron of Bi(III) as well as the polymeric structure compared with that in $\text{Bi}(\text{Hedta})$ and $\text{NH}_4[\text{Bi}(\text{edta})] \cdot \text{H}_2\text{O}$ (Shkolnikova, L. M. et al., *Koord. Khim.*, 1991, **17**, No.2, 253-261) will be presented.

PS-07.05.16 CRYSTAL CHEMISTRY OF MIXED-LIGAND COMPLEXES WITH 3-IMIDAZOLINE NITROXIDES. By N. V. Pervukhina*, G. V. Romanenko, N. V. Podberezskaya Inst. Inorg. Chem., Rus. Acad. Sci., Sib. Dep., Russia

In continuation of our studies of transition metal complexes (MC) with stable nitroxide radicals (NR) aimed to examination of peculiarities of exchange interaction in heterospin exchange clusters and obtaining a new class of magnetic materials (*Zh. Strukt. Khimii*, **30**, №5, 142-165 (1989); *Zh. Strukt. Khimii*, **34**, №3, 143-158 (1993)) we have performed crystallochemical analysis of the structures of two different types of mixed-ligand MC with 3-imidazoline NR: 1) based on ML_2^1 bischelates ($M = \text{Co}, \text{Ni}$) and neutral molecules A. The complexes have ML_2^1A_2 composition for $A = \text{H}_2\text{O}$ or ROH ($R = \text{CH}_3$, C_2H_5 , $n\text{-C}_4\text{H}_9$) and ML_2^1A composition when $A = 1,4$ -butane-diol. They have pseudo layered and framed structures respectively. All the adducts except the H_2O one undergo ferrimagnetic phase transition at 5-8 K. 2) based on transition metal hexafluoroacetylacetonates $\text{M}(\text{hfac})_2$ and 3-imidazoline NR derivatives. MC with $\text{M}(\text{hfac})_2 : \text{L}^2$ ratio equal to 1:2 ($M = \text{Co}, \text{Ni}$) have molecular structures with the octahedral environment of M. The structures of $\text{Cu}(\text{hfac})_2\text{L}$ are of molecular ($L = \text{L}^2$, $R = \text{NH}_2$, PhNH or $L = \text{L}^3$, $R = \text{NH}_2\text{CO}$) or chain ($L = \text{L}^2$, $R = \text{CH}_3$, NH_2CO) type. Copper polyhedra are trigonal or square bipyramidal. Trinuclear molecular complexes $\text{Cu}(\text{hfac})_2\text{L}_2$ are formed when $L = \text{L}^2$, $R = \text{C}_6\text{H}_5$, C_2H_5 , $i\text{-C}_3\text{H}_7$ or $L = \text{L}^3$, $R = \text{Ph}$, the N=O groups of NR being coordinated by copper atoms. The central and the terminal copper atoms have square and trigonal-bipyramidal geometry respectively. $\text{Cu}:\text{hfac}:\text{L}^2$ ratio 2:3:2 is realized when Cu(II) and Cu(I) ions are bridged by NR molecules ($R = \text{C}_2\text{H}_5$, $i\text{-C}_3\text{H}_7$) to form chain structure, the Cu(II) ions having square-bipyramidal while Cu(I) ions - distorted tetrahedral environment. The geometry, the types of coordination polyhedra, packing modes, the arrangements of paramagnetic centers were analyzed for all compounds and compared to literature data.

