

## 07-Crystallography of Organometallic and Coordination Compounds

Metal alkoxides might represent an alternative, especially as they are generally more attractive for the design of mixed metal species. Barium alkoxides involving fluorinated groups, namely perfluoroisopropoxide  $\text{OCH}(\text{CF}_3)_2$  (ORf) have been obtained either by direct reaction between the metal and the alcohol or by alcoholysis reactions. Crystal structure and chemical formula of one of them, crystallized from hexane/tetrahydrofuran (THF), have been determined by single crystal X-ray diffraction at 220 K.

Crystal data are as follows: monoclinic symmetry; space group  $P2_1/C$ ; cell parameters at 220 K:  $a = 24.667(7)$  Å,  $b = 13.925(3)$  Å,  $c = 25.856(9)$  Å,  $\beta = 113.15(3)^\circ$ ; asymmetric unit: one  $\text{Ba}_5(\text{OH})(\text{OCH}(\text{CF}_3)_2)_9$  (THF) $_4$   $\text{H}_2\text{O}$  molecule + one not bonded THF molecule;  $Z = 4$ . The molecular structure consists of a classical pentanuclear cluster of barium atoms, arranged in a square based pyramid. A  $\mu_5$ -oxo ligand lies at the center of the pyramid squared basis; 5  $\mu_3$ -ORf ligands, 4  $\mu_2$ -ORf ligands, 4 THF and 1  $\text{H}_2\text{O}$  ligands are surrounding the cluster. Thus, each barium atom has 7 to 11 oxygen or fluor atoms as neighbours. Such a high coordination number for barium atoms explains the relative stability of this alkoxide

PS-07.05.12 THE MODULATED CRYSTAL STRUCTURE OF A METALLOPORPHYRIN  $\pi$ -CATION RADICAL.

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The hexachloroantimonate salt of chloroiron tetramesityl porphyrin radical monocation crystallizes as a modulated structure with a tetragonal  $I4/m$  parent space group;  $a = 18.008$ ,  $c = 9.028$  Å,  $Z = 2$ . A commensurate modulation exists corresponding to  $h+k+l = 2n+1$  data being weakly present. The absence condition  $h+k = 2n+1$  is maintained for the  $l = 0$  data. There are also weak satellite reflections corresponding to a modulation wave vector  $0.46 c^*$ .

A hierarchical approach to structure elucidation was used, starting with a disordered average structure in  $I4/m$  and progressing to structure refinement attempts in  $P4_2/n$ , and  $P4/n$  to try to identify the nature of the modulation. The cation was located on a  $4/m$  site in  $I4/m$  with the mesityl groups on four separate cations defining a channel about the  $4_2$  axis which contains the  $\text{SbCl}_6^-$  counterions. These ions appear streaked along  $c$  and individual atoms are not resolved. Reduction of symmetry to  $P4_2/n$  or  $P4/n$  allows the cation to adopt either a  $\bar{4}$  or  $4$  symmetry respectively. Packing requires the  $\text{SbCl}_6^-$  to have a 2 axis between adjacent Cl coincident with a 2 fold crystal axis parallel to  $c$ . In either spacegroup symmetry creates a second anion  $90^\circ$  rotated translated along the same axis. Both of these cannot fit in the axial repeat and one is not required by chemistry. Ordering to lower the spacegroup to  $P\bar{4}$  causes the  $n$  glide absence condition to be violated. The anions appear to contribute very little to the  $h+k+l = 2n+1$  data. The  $h+k+l = 2n+1$  data has intensity distributed in  $h$  and  $k$  rather than  $l$ . This appears to correspond to a correlated rotation of the mesityl groups which provides a mechanism for creating the necessary correlation between columns to see the incommensurate reflections. The  $c$  repeat distance would appear to be determined by contacts between the mesityl groups of different molecules but there appears to be a three atom contact between adjacent cations along  $c$ . This is consistent with having an asymmetric  $\text{Cl}_3^-$  ion linking Fe atoms rather than a  $\text{Cl}^-$

Dimensions are compatible. This would further enhance the necessary communication for the incommensurate modulation to be observed. Resolution of the structure options requires an ability to model the anions. The anions were initially included in the model, as a series of spherically averaged  $\text{SbCl}_6^-$  spaced at  $1/8c$  with large  $U_{33}$  thermal parameters. Subsequent to this fractional oriented anions streaked along  $c$  have been used. The progress of refinement has been monitored by assessing data of different index condition. Refinement was kept in control using RAELS89 to refine rigid body thermal parameters and impose localised symmetry constraints. The anions appear to have restricted orientation and be clustered around the same  $z$  heights as the cations,  $1/2c$  apart in the average structure. Refinement is continuing. The observed incommensurate modulation appears to be the result of the  $c$  axial length being longer than required to have anions touching. This allows extra species, presumably solvent, to be fitted into the channels.

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## PS-07.05.13 STRUCTURAL CHEMISTRY STUDIES ON RARE EARTH AMINOACID COMPLEXES By Y.H.Lin\*, Y. Xin, A.Z.Ma, L.M.Li and S.Q.Xi, Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, China

This report gives a brief account of some of structural chemistry studies on rare earth aminoacid (REA). During the past years, our research group has succeeded in synthesizing a series of REA. These complexes respectively belong to  $([\text{Er}(\text{pro})_2(\text{H}_2\text{O})_2\text{Cl}_2])_n$  (Ma, Li, Lin and Xi, Acta Cryst. (1993), C49)  $\text{Sm}(\text{ClO}_4)_2(\text{Val})_n \cdot 4\text{H}_2\text{O}$ ,  $\text{Sm}(\text{ClO}_4)_2(\text{ASP})_n \cdot n\text{H}_2\text{O}$ ,  $\text{Sm}(\text{ClO}_4)_2(\text{Gly}) \cdot 4\text{H}_2\text{O}$ ,  $\text{YbCl}_2(\text{Ala}) \cdot 4\text{H}_2\text{O}$ ,  $\text{YbCl}_2(\text{pro}) \cdot 6\text{H}_2\text{O}$ ,  $\text{Er}(\text{ClO}_4)_2(\text{pro}) \cdot n\text{H}_2\text{O}$ ,  $\text{La}(\text{ClO}_4)_2(\text{Ala}) \cdot 4\text{H}_2\text{O}$ ,  $\text{La}(\text{ClO}_4)_2(\text{Gly}) \cdot 4\text{H}_2\text{O}$ ,  $\text{Sm}(\text{ClO}_4)_2(\text{Ala}) \cdot 3\text{H}_2\text{O}$  and  $\text{Er}(\text{ClO}_4)_2(\text{His}) \cdot 5\text{H}_2\text{O}$ . The chemical structures of these complexes have been identified by elemental analyses, IR and mass spectra. Among them, the molecular configuration and the bond parameters of eleven typical complexes have been determined by careful X-ray structural analyses.

The characteristics of the molecular structure of REA have been summarized. First, the amino groups in REA are protonated and not coordinated. Secondly, rare earth atoms are separated from each other by a distance about  $4\text{Å}$ , so that there are no metal-metal bonds between them. Thirdly, the coordination number of rare earth metals are 8-10, their coordinate configuration forming square antiprism, tricapped trigonalprism and bicapped square antiprism respectively. Finally, these structure can be divided into infinite three-dimensional network, one-dimensional chain and binuclear bridge three classes.

PS-07.05.14 CRYSTAL STRUCTURES OF  $(\text{AdeH}_2)\text{SbCl}_5\text{H}_2\text{O}$  AND  $(\text{AdeH})_2\text{SbCl}_5\text{H}_2\text{O}$  (Ade = ADENINE). By Tu Lian-Dong\* and Hu Sheng-Zhi, Chemistry Department, Xiamen University, Xiamen, China.

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A number of antimony(III) aminopolycarboxylic acid chelates, in which the coordination polyhedron of Sb(III) is unexceptionally a distorted  $\Psi$ -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,  $\text{SbCl}_3$  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  $(\text{C}_5\text{H}_7\text{N}_3)_2\text{SbCl}_3\cdot\text{H}_2\text{O}$ (I) and  $(\text{C}_5\text{H}_6\text{N}_3)_2\text{SbCl}_3\cdot\text{H}_2\text{O}$ (II). Complexes of stoichiometry  $\text{SbCl}_3^{2-}$  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 ( $\text{H}_4\text{edta}$ ),  $\text{Bi}(\text{Hedta}) \cdot 2\text{H}_2\text{O}$  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  $\alpha$ -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  $\alpha$ - $\text{Bi}(\text{Hedta})\text{H}_2\text{O}$  would be a distorted  $\Psi$ -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  $\beta$ -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  $\text{Hedta}^{3-}$  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  $\text{ML}_2^1$  bischelates ( $M = \text{Co}, \text{Ni}$ ) and neutral molecules A. The complexes have  $\text{ML}_2^1\text{A}_2$  composition for  $A = \text{H}_2\text{O}$  or ROH ( $R = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $n\text{-C}_4\text{H}_9$ ) and  $\text{ML}_2^1\text{A}$  composition when  $A = 1,4$ -butane-diol. They have pseudo layered and framed structures respectively. All the adducts except the  $\text{H}_2\text{O}$  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 ( $L = \text{L}^2$ ,  $R = \text{NH}_2$ ,  $\text{PhNH}$  or  $L = \text{L}^3$ ,  $R = \text{NH}_2\text{CO}$ ) or chain ( $L = \text{L}^2$ ,  $R = \text{CH}_3$ ,  $\text{NH}_2\text{CO}$ ) type. Copper polyhedra are trigonal or square bipyramidal. Trinuclear molecular complexes  $\text{Cu}(\text{hfac})_2\text{L}_2$  are formed when  $L = \text{L}^2$ ,  $R = \text{C}_6\text{H}_5$ ,  $\text{C}_2\text{H}_5$ ,  $i\text{-C}_3\text{H}_7$  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  $\text{Cu}(\text{II})$  and  $\text{Cu}(\text{I})$  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  $\text{Cu}(\text{II})$  ions having square-bipyramidal while  $\text{Cu}(\text{I})$  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.

