

09.4-41 THE STRUCTURAL FEATURES OF p-HYDROXYBENZOATES OF METALS. By A.N. Shnulin, G.N. Nadjafov and Kh.S. Mamedov, Institute of Theoretical Problems of Chemical Technology, Institute of Inorganic and Physical Chemistry, the Academy of Sciences of the Azerbaijan SSR, Narimanov prospect, 29, Baku, 370143, USSR.

The structure data for series of p-hydroxybenzoate complexes were obtained by single-crystal X-ray analysis: I- $M\text{L}_2 \cdot 8\text{H}_2\text{O}$, where M is Mg, Co, Zn, Fe, Ni, Mn, L = p-HOC₆H₄COO⁻ (Shnulin, Nadjafov, Amiraslanov, Usabaliyev, Mamedov, Koordinatsionnaya khimiya (1981), 7, 1409), II-CuI₂ · 8H₂O (Shnulin, Nadjafov, Mamedov, Ibid., (1981), 7, 1544), III-MnI₂ · 3H₂O; IV-BaI₂ · H₂O (Shnulin, Nadjafov, Mamedov, J. Struct. Chimii, in press); V-CdI₂ · 7H₂O (Nadjafov, Shnulin, Mamedov, Shil'nikov, Koordinatsionnaya khimiya (1982), 8, 1276). The aim of this work is the establishment of the ligand structure influence on the crystal structures of its complexes with different metals, that is the exposure of the structural functions of p-hydroxybenzoic acid. The realization of one or another crystal structure has been established to be the consequence of the energy ratio of the following competitive interactions: 1) coordination bonds between the metallic cation and the coordinating ligands (the water molecules and/or COO-groups of I); 2) H-bonds between the water molecules with each other and with polar groups of L and between OH-groups of the latter; 3) van der Waals forces between nonpolar benzoic nuclei of ligands. The nontriviality of such approach is favoured by the features of electronic structure, the geometry and para-position of phenolic OH-group which results in the clear exposure of complexes, their structures being determined by the ligand requirements. Such complexes include six isostructural compounds I, their realisation being connected with dominant role of the ligand structure which requires the highest possible amount of the water of crystallisation. As a result the main structural elements are the octahedral aquaions $M(\text{H}_2\text{O})_6^{2+}$, the organic anions L and the water molecules of crystallisation. Thus the absence of the structural influence of the metallic ion features in six isostructural octahydrates is explained. However, there exist two factors which affect the stability of such crystal structure: the entropy decrease with the increase of the hydrate water content and the dependence of the hydration energy on the ion nature. From six ions given above the lowest hydration energy is possessed by the ion Mn(2+) so that its complex is the least stable one. In the structure II at the same parameters of the unit cell and the same symmetry as for the complexes I the coordination sphere of Cu(2+) is changed, its composition including three water molecules and two O atoms of COO-groups of two ligands. The complex is unstable. Such reconstruction which is dictated by the known disclination of the Cu(2+) ion to hexaaquaion formation in crystals is observed also in crystals IV and V. In the latter two complexes the structure is mainly determined by the cations (the low values of the hydration energy).

09.4-42 THE STRUCTURAL FEATURES OF Cu(II) ACETATES AND FORMATES ADDUCTS WITH 2-, 3- AND 4-PYRIDINCARBOXYAMIDES. By G.V. Tsintsadze, R.A. Kiguradze, A.N. Shnulin, Kh.S. Mamedov, Georgian Polytechnical Institute, Tbilisi. Institute of Theoretical Problems of Chemical Technology Acad. of Sci. of the Azerbaijan SSR, Baku, USSR.

The work is devoted to the investigation of the influence of the carboxamide group position in a ligand pyridine ring on the structure of its complexes with transition metals. For this purpose there were determined the crystal structures of the following coordination compounds by X-ray analysis: I - Cu(CH₃COO)₂ · 2NA · 2H₂O, II - Cu(CH₃COO)₄ · 2INA · 2H₂O, III - Cu(HCOO)₂ · 2H₂O · 2INA, IV - Co(CH₃COO)₂ · 2PA · 6H₂O, where

NA is nicotinamide, INA - isonicotinamide and PA is picolinamide. Compound I is a binuclear compound of the cupric acetate monohydrate type (van Niekerk, Shoening, Acta Cryst. 1953, 6, 227) with the only difference that in this case the function of axial ligands is performed by two NA molecules. The molecules of crystallisation water, the amide groups and both of the coordinated oxygen atoms of the acetate groups form hydrogen bonds which join together the complexes in a crystal. Compounds II and III which differ only by the acid ligands have the same coordination environment about the copper atom. The coordination octahedron consists of 2N(Py), 2H₂O, 2CH₃COO⁻. The difference is in the arrangement of carboxylic ligands concerning the H₂O - Cu - OH₂ line. The systems of H-bonds in both structures are similar but in structure II the CH₃COO...HOH hydrogen bond is realised within the same coordination polyhedron, while in compound III the corresponding bond is intermolecular. In compound IV the five member bischelate cycle is realised, whereas N(Py) and carboxylic oxygen perform as donors. The coordination surrounding of Co is completed to octahedron by two water molecules. The acid anions and four water molecules are located outside the coordination sphere. In the case of NA there is observed a stronger dependence of dipole moment (5.11 ± 1.46 D) vs. rotation angle (0 - 180°) for the amide group relative to the heterocycle (Hofman, Kuthan, Collect. Czechosl. Chem. Commun. (1979) 44, 9, 2633) as compared with INA. This provides more considerable influence on the coordination sphere, its shape and geometry through the H-bonds, ion-dipole and dipole-dipole interaction. As a result more "unusual" coordination environments are formed in compounds I and Cu(HCOO)₂ · NA · H₂O (Antsyashkina, Porai-Koshits, a.o., Koordinatsionnaya khimiya. (1979) 5, 1716, Russ.) comparing with complexes II and III where the indicated structural fragments are similar. The replacement NH₂ → N(C₂H₅)₂ in the carboxamide group of NA prohibits its strong effect on the coordination sphere structure. The coordination sphere of Ni(CH₃COO)₂ · (DNA)₂ · 2H₂O is quantitatively maintained the same as in complexes II and III with INA ligand.