07-Crystallography of Organometallic and Coordination Compounds

PS-07.01.13 CRYSTAL AND MOLECULAR STRUCTURES OF BENZIL-CROWN-5 RARE-EARTH METAL LE HYDRATED PLATOCRATES (La = Tb, Y). By Mao Zhihua, Zhou Zonghui and Hong Zhou, Department of Chemistry and Center of Analysis and Measurement, Sichuan University, Chengdu, Sichuan, China, Z. Zhou, Zh. Zhi, Z. Weng, Department of Chemistry, Zhejiang University, Zhejiang, China.

In the extraction of rare-earth metal nitrates with benzil-crown-5 (5:1), using slope method, it was found that a 5:2:5 complex was formed. The extraction requires the presence of water. However, the structures of the complex and mechanism of complexation are not clear. In combined solution of CH<sub>3</sub>OH and CH<sub>2</sub>Cl<sub>2</sub>, orange crystals of Yb[PC(6)][[(BIS5)5-2(5)] + 2(5)CH<sub>2</sub>Cl<sub>2</sub>] and (Y[PC(6)][[BIS5]5-2(5)CH<sub>2</sub>Cl<sub>2</sub>]] were obtained. Using PANalytical XRD diffractometer with MoKα radiation and in w/0mode, in the range of 2θ=0.2° to 2θ=25° for (1) and 2θ=25° for (11), a total of 7606 and 8646 unique reflections were collected, respectively. The reflections for F20(sin) were used in the determinations. All the intensity data were subjected to the corrections for L2 absorption and s/u error. On a countdown program package, the positions of all metal atom with frozen using heavy atom method. The coordinates of all other atoms were obtained by difference Fourier method. The crystallographic data are as follows: two crystals are triclinic, space group P1, crystal (1), a=21.753(1), b=1.3830(2), c=1.459(3), α=92.3, β=70.11(1), γ=70.17(1), Z=2, D=m.6466 cm<sup>-3</sup> the final R=0.031, Rw=0.035, max. Δρ=0.66 e/Å<sup>3</sup>, crystal (1), a=21.705(1), b=1.3830(3), c=1.957(2), α=95.05(3), β=70.92(3), γ=70.12(3), Z=2, D=m.6485 cm<sup>-3</sup>, the final R=0.065, Rw=0.076. Checking (1) against (11), we can find they are isomorphic. The following discussion is only for (1). Yb coordinates with three phenyl cyanate atoms and three water molecules. The distances from Yb to phenol oxygen atoms are the shortest (0.21951-1.21970nm), while the eight oxygen atoms form an abnormal tetragonal dipyramid with apex Yb and with bases OW(1), OW(3), OW(2), OW(1), OW(2), OW(3), OW(1), OW(3). Each of the 6-membered rings which Yb forms with picric acid molecules are planar and form dihedral angle of 53.6°, 32.7°, and 33.4°. The length of the two C-O bonds closest to the phenol oxygen (2.140(1) 1.446(1)) are longer than the others (2.123(5)-1.139(3)) in the picric rings. This suggests there are strong coordinate bonds between Yb and the picric bases. Because of an inductive effect in addition to static attraction. The n-electrons appear drawn away by Yb. The forces between phenol oxygen atoms and the Yb are strong, causing the C-O-C angle near the phenol oxygen (128.8°-114.3°) to be much smaller than 120°. Between OW(1) and OW(4) or OW(3) and between OW(2) and OW(1) or OW(4), there are hydrogen bonds which link the two crown ethers to the Yb ion. With the addition of these picric groups, Yb is surrounded tightly and forms a hydrophilic macromolecule. Therefore BIS5 easily extracts Yb hydrated picrates into the organic phase, consistent with the result of extraction experiments.

PS-07.01.14 MOLECULAR DISTORTION IN SOME SOLVATES OF URANYL SCHIFF'S BASE COMPLEXES. By A.J. Smith, Department of Chemistry, University of Sheffield, SHEFFIELD, S3 7HF, U.K.

The complex N<sub>N</sub>-bis(sulphocarboxylidene)-1,5-diamino-3-arylethenedioxouranium(VI) shows a butterfly-shaped molecule [1] with the two benzene rings symmetrically inclined at angles of about 30° to the coordination plane of the uranium. The compound forms a series of solvates with ethanol, acetonitrile, chloroform, benzene, etc. and the colours of the solvates differ according to the solvent molecule, ranging from yellow to deep red (M.N. Akhtar et al. Inorg. Chem. Letters, 1969, 5, 673-677). Crystal structure studies (e.g. J.J. Irons & A.J. Smith, Acta Cryst. (1991) C47, 2345-2346) show that the solvates are not bonded (not even hydrogen-bonded) to the complex, but they do produce some distortion of the shape of the parent molecule, in particular changes in the dihedral angles shown by the benzene rings [2]. These angles may be correlated with the colours of the solvates and related to the delocalised electrons in the π-bonding system. A number of related Schiff base complexes are known, in which the molecular skeleton is basically the same, but there may be different atoms bonded to the uranium or there may be other substituents present, but there is still a butterfly-shaped molecule with an extended π-bonding system. Several of these complexes produce similar solvates also.