07-Crystallography of Organometallic and Coordination Compounds

PS-07.01.13 CRYSTAL AND MOLECULAR STRUCTURES OF BENZO-15-CROWN-5 RARE-EARTH METAL IOD HYDRATED PHRACATES (Ln = Tb, Y). By Mao Zhina, Zhou Zongha and Hong Zhou. Department of Chemistry and Center of Analysis and Measurement, Sichuan University, Chengdu, Sichuan, China; Zhou Zhikai, Zheng Wenhao, Department of Chemistry, Zhengzhou University, Zhengzhou, Henan, China.

In the extraction of rare-earth metal picrates with benzo-15-crown-5-bis-(5), using slope method, it was found that a bis[(5) bis(bis)] formed. Extrusion requires the presence of water. However, the structure of the complex and mechanism of extraction are not clear. In combined solution of CH2CN and CH3CN, orange crystals of Tb[(5) bis(bis)] 2H2O, CN and Y((5) bis(bis)) 2H2O, CN were obtained. By using a X-ray diffractometer with MoKa radiation and in W2 mode, in the range of 2°-60° for [1] and 2°-50° for [11], a total of 7660 and 8644 unique reflections were collected, respectively. The reflections for [1] were used in the determinations. All the intensity data were subjected to the corrections for L2 absorption and Lorentz polarization. By using the program package, the structure of metal atom was found using heavy atom method. The coordinates of all other atoms were obtained by difference Fourier methods. The crystallographic data are as follows: two crystals are tetragonal, space group P41, crystal (1), No. 227, a=293.15(1), b=3830(2), c=1.0509(3), etc. 0.7(2), b=70.58(1), y=70.73(1)°, Z=2, D=1.469 g/cm3, the final R = 0.031, Rw= 0.035, max.d=0.668 cm, crystal (2), a=2779.1, b=0.1389(3), c=1.957(4), D=0.812(2), b=70.98(3), y=70.95(3)°, Z=2, D=1.448 g/cm3, the final R = 0.066, Rw= 0.078. Checking (1) against (11), we can find they are homomorphic. The following discussion is only for (1). Tb coordinates with three phenyl carbonyl atoms and three water oxygen atoms and two water molecules. The distances from Tb to phenol oxygen atoms are the shortest (0.2191-1.2197(3)), and the eight oxygen atoms form an abnormal tetragonal pyramidal with apex Tb and with bases Ow1, Ow2, Ow3, Ow4. Each of the 6-membered rings which Tb forms with picric acid molecules are planar and form dihedral angles of 53.6°, 38.2°, and 174°. The lengths of the two C-C bonds closest to the phenol oxygen (0.140-0.144(8)) are longer than the others (0.135-0.139(3)) in the picric rings. This suggests there are strong coordinate bonds between Tb and the picric bases, because of an inductive effect in addition to static attraction. The n-electrons appear drawn away by Tb. The forces between phenol oxygen atoms and the Tb are strong, causing the C-C angles near the phenol oxygen (128°-114°-93°) to be much smaller than 120°. Between Ow1 and Ow2 and between Ow2 and Ow3 and Ow4, there are hydrogen bonds which link the two crowns together. With the addition of three picric groups, Tb is surrounded tightly and forms hydrophilic macrocyclic. Therefore, BIS(5) easily extracts Tb 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,N'-bis(2-methylbenzylidene)-1,5-diamino-3-azepane(dioxiduranum)VI shows a butterfly-shaped molecule [1] with the 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. A. A. H. Elmag. Chem. Letters, 1969, 5, 631-637). Crystal structure studies (e.g. N. J. Irms. & A. J. Smith, Acta Cryst. (1991) C47, 2345-2346) show that the solvent molecules 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 a-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 atomic bonding to the uranium or there may be other substituents present, but there is still a butterfly-shaped molecule with an extended a-bonding system. Several of these complexes produce similar solvates also.

Fig. 1. The perspective view of (1).

Fig. 2. The perspective view of (2).

Fig. 3. The perspective view of (3).