

07-Crystallography of Organometallic and Coordination Compounds

PS-07.01.13 CRYSTAL AND MOLECULAR STRUCTURES OF BENZO-15-CROWN-5 RARE-EARTH METAL Ln HYDRATED PICRATES (Ln = Yb, Y). By Mao Zhihua, Zhou Zhonghua* and Hong Zhou, Department of Chemistry and Center of Analysis and Measurement, Sichuan University, Chengdu, Sichuan, China; Zhou Zhixian, Zheng Wengcao, Department of Chemistry, Zhengzhou University, Zhengzhou, Henan, China.

In the extraction of rare-earth metal picrates with benzo-15-crown-5 (B15C5), using slope method, it was found that a B15C5: Ln=2:1 formed. Extraction requires the presence of water. However, the structure of the complex and mechanism of complexation are not clear. In combined solution of CH_3CN and $\text{CH}_3\text{CH}_2\text{OH}$, orange crystals of $\text{Yb}(\text{PIC})_3 \cdot (\text{B15C5})_2 \cdot 2\text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$ (I) and $(\text{Y}(\text{PIC})_3 \cdot (\text{B15C5})_2 \cdot 2\text{H}_2\text{O} \cdot \text{CH}_3\text{CN})$ (II) were obtained. On NONIUS CAD4 diffractometer with MoK α radiation and in $\omega/2\theta$ mode, in the range of $2^\circ \leq \theta \leq 22^\circ$ for (I) and $2^\circ \leq \theta \leq 23^\circ$ for (II), a total of 7807 and 8846 unique reflections were collected, respectively. The reflections for I230(I) were used in the determinations. All the intensity data were subjected to the corrections for LP factors and absorption. On a PDP11/44 computer with SDP program package, the position of metal atom was found using heavy atom methods. The coordinates of all other atoms were obtained by Difference Fourier methods. The crystallographic data are as follows: Two crystals are triclinic, space group P1, crystal (I), $a=1.2753(1)$, $b=1.3810(2)$, $c=1.9609(2)\text{nm}$, $\alpha=81.37(2)$, $\beta=71.58(3)$, $\gamma=70.71(2)^\circ$, $Z=2$, $D_c=1.466\text{g}\cdot\text{cm}^{-3}$ the final $R=0.031$, $R_w=0.039$, $\text{max}\cdot\Delta\rho=966\text{e}/\text{nm}^3$; crystal (II), $a=1.2785(1)$, $b=1.3850(3)$, $c=1.9571(2)\text{nm}$, $\alpha=81.05(3)$, $\beta=70.92(2)$, $\gamma=70.62(3)^\circ$, $Z=2$, $D_c=1.485\text{g}\cdot\text{cm}^{-3}$, the final $R=0.065$, $R_w=0.078$. Checking (I) against (II), we can find they are homomorphic. The following discussion is only for (I). Yb coordinates with three phenol oxygen atoms and three nitro oxygen atoms and two water molecules. The distances from Yb to phenol oxygen atoms are the shortest (0.2191-0.2197nm). Yb and the eight oxygen atoms form an abnormal tetragonal dipyrmaid with apex Yb and with bases O_w(1), O(1), O(2), O(3) and O_w(2), O(3), O(11), O(22). Each of the 6-membered rings which Yb forms with picric acid molecules are planar and form dihedral angles of 53.8° , 38.2° , and 117.4° .

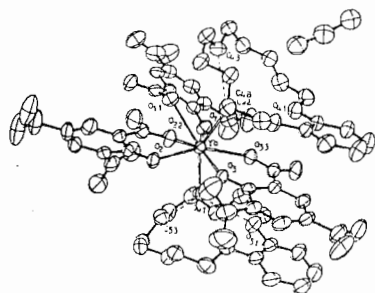
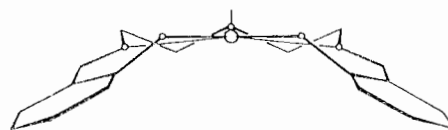


Fig. 1. The perspective view of (I)

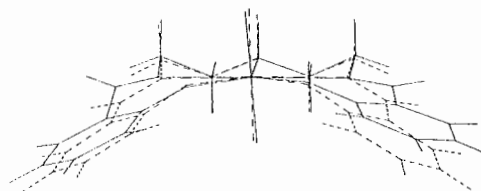
The lengths of the two C-C bonds closest to the phenol oxygens (0.140-0.144nm) are longer than the others (0.135-0.139nm) in the picric rings. This suggests there are strong coordinate bonds between Yb and the picric bases, because of an inductive effect in addition to static attraction. The π -electrons appear drawn away by Yb. The forces between phenol oxygen atoms and the Yb are strong, causing the C-C-C angles near the phenol oxygen (112.8° - 114.3°) to be much smaller than 120° . Between O_w(1) and O(41) or O(43) and between O_w(2) and O(51) or O(53), there are hydrogen bonds which link the two crowns ethers to the Yb ion. With the addition of three picric groups, Yb is surrounded tightly and forms a hydrophobic molecule macromolecule. Therefore B15C5 easily extracts Yb hydrated picrate 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.



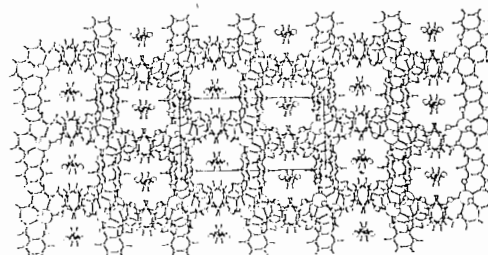
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The compound N,N'-bissalicylidene-1,5-diamino-3-azapentanedioxouranium(VI) shows a butterfly-shaped molecule (I) with the two benzene rings symmetrically inclined at angles of about 30° to the coordination plane of the uranium. The compound forms a 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. Nucl. Chem. Letters, 1969, 5, 673-677.) Crystal structure studies (e.g. N.J. Irons & A.J. Smith, Acta Cryst. (1991) C47, 2345-2348) 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 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 p-bonding system. Several of these complexes produce similar solvates also.



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The complex molecules in the solvates do not always pack in the same way as the unsolvated compound does. The changes of crystal packing give rise to quite interesting structures in some of which the solvent molecules are accommodated in channels which run through the lattice [3]. This structural feature leads to some understanding of the easy exchange of solvents in these systems, which was noted from the first.



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