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Synthesis and Structure of a New Dinuclear Uranyl Complex

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Abstract: With a heptadentate compartmental Schiff-base ligand H3L (1, 3-di[o-(salicylimino) phenoxyl]-2-propanol), a new binuclear diuranyl complex $[(UO_2)_2L(OH)]\cdot 3DMF$, $C_{38}H_{45}N_5O_{13}U_2$, was synthesized and the crystal structure was determined by X-ray diffraction techniques. The coordination geometry are two pentagonal bipyramids. In each pentagon four kinds of U-O (phenoxido, hydroxo, alkoxo and ether oxo) bonds are discussed.

Keywords: Dinuclear, uranyl complex, synthesis, structure.

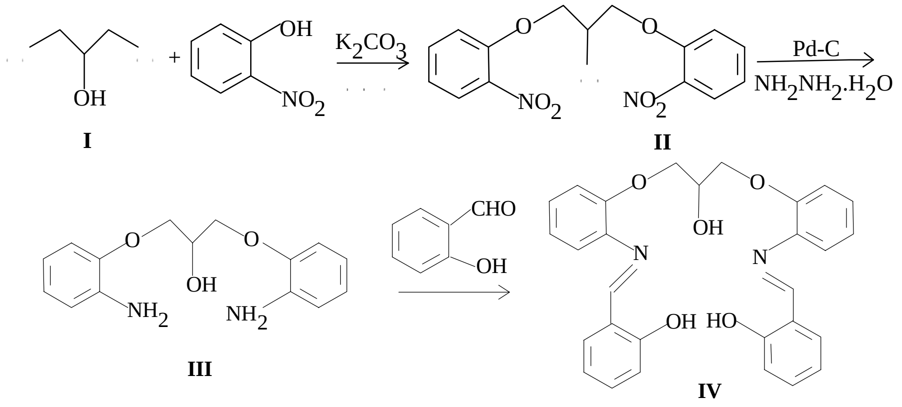
Dinuclear complexes have been widely investigated since 1970s when Robson proposed the conception of dinucleating ligand[1,2]. These compounds attracted much interests because of their applications as metal-enzemy model in bioinorganic chemistry or promising applications as functional materials. Most of these dinuclear complexes contain d transition metals as central ions. Few dinuclear U complexes have been reported.

It is known, in most complexes of axial ion, five donors from ligands should occupy the vertexes of an equatorial pentagonal coordination geometry. This complexing principle was successful used to direct the synthesizing homobinuclear uranyl complexes with compartmental Schiff-base ligands[3, 4], and the first crystal structure were determined, in which the formed two chambers were different[5]. Recently, we synthesized a new dinucleating ligand, and it may coordinate to metal ions with the equivalent chambers. But we found it is interesting that a homologous ligand takes another coordination method with Cu(II) and Ni(II)[6, 7]. In this paper, we will report the ligand coordinate to UO_2^{2+} with our considered structure.

The intermediate products (**I, II, III**) were synthesized according to our previous method[4]. To a solution of **III** (2.4 g, 10 mmol) in 30 mL hot ethanol, a solution of salicylaldehyde (2.4 g, 20 mmol) in 30 mL hot ethanol was added dropwise. After refluxing for 10 mins, a large amount of orange precipitate appeared. The product was filtered on cooling, recrystallized twice from ethanol for purification. Analytical data for the ligand: mp 153-154°C. Cacl. for $C_{29}H_{26}N_2O_5$: C, 72.2; H, 5.3; N, 5.8%. Found: C, 71.9; H, 5.1; N, 6.0. IR (KBr, cm^{-1}): 3400 (s, br, OH); 1619 (s, sh, C=N); 1246 (s, sh, Ar-O-R). ^1H NMR ($CDCl_3$, δppm): 9.90 (s, 1H, OH); 8.69 (s, 2H, ArOH); 7.20 (m, 8H, ArH); 7.04 (m, 8H, ArH); 4.37 (m, 1H, CH); 4.28 (s, 4H, CH_2).

The synthetic route of ligand H_3L is as follows (**Scheme 1**).

Scheme 1

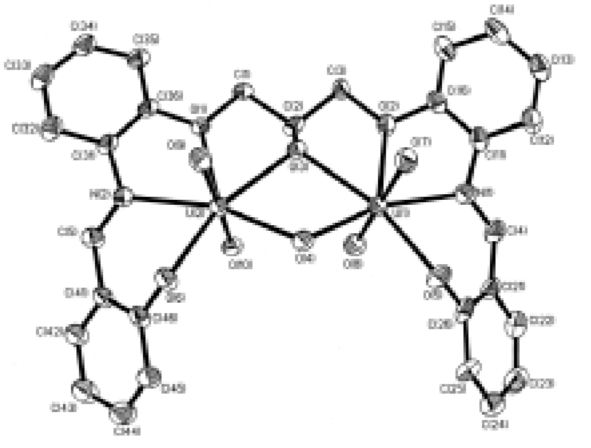


Equimolar $(UO_2)(NO_3)_2$•$6H_2O$ and H_3L (1, 3-di [o-(salicylimino)phenoxyl]-2-propanol in methanol solution were refluxed for 3 h. The product powder was separated, washed with methanol and dried *in vacuo*. The powder was dissolved in appropriate amount of DMF. After evaporating the solvent in atmosphere (about 5 days), the red color crystals appeared.

A single crystal of dimensions 0.5×0.4×0.2 mm was used to determine the crystal structure of the complex by X-ray structure analysis. Crystal data for $C_{38}H_{45}N_5O_{13}U_2$: M=1255.87, Monoclinic, a=13.808(3), b=11.747((2), c=26.561(5)Å, β=101.76(3), U=4218(3) Å^3, T=299±1 K, space group $P2_1/n$, Z=4, μ(Mo-K)=7.3366mm^{-1}, 7996 reflections measured, 6683 unique *(*R_{int} = 0.049) which were used in all calculations. The final $wR(F^2)$ was 0.046. The structure was solved by direct methods and refined by full-matrix least-squares on F^2.

The molecule and crystal structure are shown in **Figure 1** and **Figure 2**.

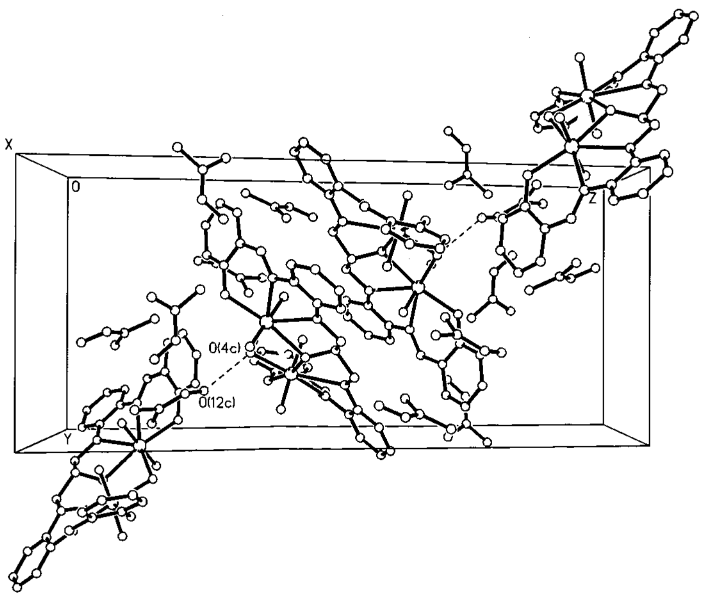
Figure 1 The molecule structure of $(UO_2)_2L^+$



Selected bond lengthens(Å) and angels(°): U(1)–N(1) 2.542(10), U(1)–O(2) 2.591(7), U(1)–O(3) 2.401(6), U(1)–O(4) 2.311(7), U(1)–O(5) 2.221(7), U(1)–O(7) 1.767(8), U(1)–O(8) 1.746(8), U(2)–N(2) 2.542(8), U(2)–O(1) 2.584(6), U(2)–O(3) 2.382(7), U(2)–O(4) 2.306(6), U(2)–O(6) 2.191(7), U(2)–O(9) 1.788(8), U(2)–O(10) 1.784(7); N(1)–U(1)–O(2) 61.6(2), O(2)–U(1)–O(3) 63.1(2), O(3)–U(1)–O(4) 69.7(2), O(4)–U(1)–O(5) 95.1(3), O(5)–U(1)–N(1) 70.6(3), O(7)–U(1)–O(8) 176.9(4), N(2)–U(2)–O(1) 61.6(2), O(1)–U(2)–O(3) 63.4(2), O(3)–U(2)–O(4) 70.1(2), O(4)–U(2)–O(6) 92.4(2), O(6)–U(2)–N(2) 72.4(2), O(9)–U(2)–O(10) 176.2(3), U(1)–O(3)–U(2) 104.2(2), U(1)–O(4)–U(2) 109.7(3)

In this complex (see **Figure 1**), the dicationic uranyl, O(7)-U(1)-O(8) and O(9)-U(2)-O(10) have usual bond lengths and angles. With aid of one hydroxo O(4) and one compartment O(3) as bridging groups, heptadentate L^{3-} binds equatiorially to two UO_2^{2+} within two equivalent pentagonal `NO_4' coordination chambers, respectively, whose two common vertexes are just occupied by O(3) and O(4). The distances from U(1) or U(2) to their own chamber plane is only 0.040 or 0.050 Å, and the dihedral angles between the planes is 26.9°. The distance between U(1) and U(2) is 3.774 Å. The tetrahedral U_2O_2 core of the binuclear molecule is leaded, and around the core two distortional pentagonal bipyramidal coordination sharing two vertexes is formed. The coordinated bond parameters, for example, mean lengths of U=O (acylic, 1.771 Å) and U-N (iminic, 2.542 Å), are comparable with these reported[3, 4]. But five bond angles concentrated on pentagon centre show more broad value range (61.6-94.2° or 95.4°), though each sums are approximate to 360°. It is interesting, that in any pentagonal chamber exist four kinds of U-O bonds of ether-oxo, alkoxo, hydroxo and phenoxido. Their average lengths are 2.588 Å, 2.392 Å, 2.308 Å and 2.206 Å, respectively, that successively decrease. It seems that their coordination abilities are increasing in the same order. Three DMF molecules presented in outer sphere, but only one is bonded to the hydroxo group by hydrogen bond O(4)······O(12) whose length is 2.738 Å (see **Figure 2**).

Figure 2 Arrangement of $[(UO_2)_2L(OH)]$•3DMF in unit cell



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8. Crystallographic parameters have been deposited in the editorial office of CCL.

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