

## Synthesis and Structure of Vanadium-barium Complex of 2, 4, 6-Tripicolinato with 20-Member Macrocyclic Cavities

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**Abstract:** A new heteronuclear complex, dimer  $[(\mu_2\text{-OH}_2)_2\text{Ba}_2(\text{H}_2\text{O})_4][\text{VO}_2(\text{tpa})]_2 \cdot 4\text{H}_2\text{O}$  (tpa: 2,4,6-tripicolinate trianion), was synthesized and structurally determined by X-ray diffraction technique where all hydrogen atoms have been located directly. The coordination geometry of V(V) ion is a distorted trigonal bipyrimid and that of Ba(II) ion is a capped square antiprism. One  $\mu_2\text{-O}$  bridging bond and two hydrogen bonds act between the coordination geometries. A 1-D extended porous construction containing 20-member cavities is observed in the crystal.

**Keywords:** Heteronuclear, vanadium-barium complex, synthesis, cavity, structure.

Recently, the thermal decomposition of heteronuclear complexes has become a promising method for the preparation of di- or tri-metallic oxides because the complex as precursor has the special microstructure, the controlled stoichiometry of the metals and lower decomposition temperature<sup>1</sup>. In order to investigate Ba-V-O system, which has the special magnetic behavior<sup>2</sup>, we synthesized the title complex as the precursor of this material. On the other hand, microporous constructions existing in the present complex make it more significant because of the potential applications, such as size-selective separation, gas absorptions and catalysis for organic reactions<sup>3</sup>. In addition, considering the ligand tpaH<sub>3</sub>, few structures of complexes with it have been reported, as far as we know.

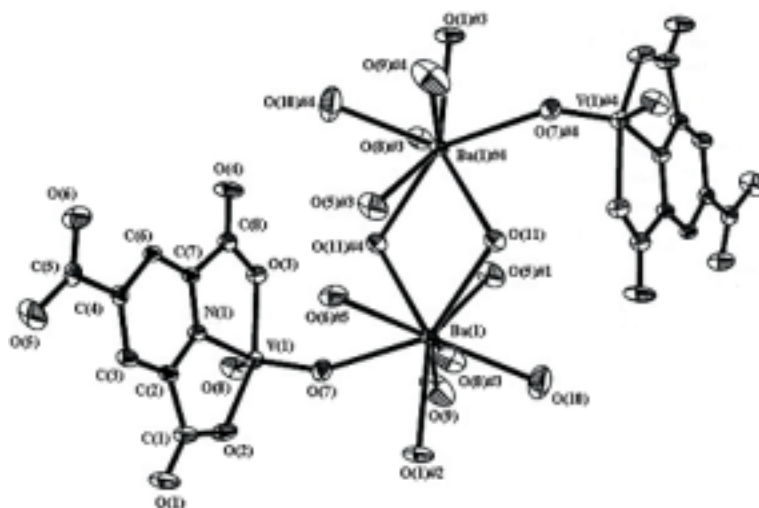
### Experimental

The ligand, tpaH<sub>3</sub>, was synthesized as previously reported<sup>4</sup>. V<sub>2</sub>O<sub>5</sub> (0.182 g, 1 mmol) was portion-wisely added to the aqueous solution (20 mL) containing tpaH<sub>3</sub> (0.211 g, 1 mmol) and Ba(OH)<sub>2</sub>·8H<sub>2</sub>O (0.325g, 1.1 mmol). The mixture was stirred for 1h and then filtered. The filtrate was stored at 25°C. The yellow crystals were obtained from the system by natural evaporation for two weeks. Analytical data for the ligand: mp 228-229°C. IR: the same as that in lit.<sup>5</sup>. <sup>1</sup>H NMR (ppm.): 8.77(s, 3H, COOH), 5.19(s, 2H, py). <sup>13</sup>C NMR (ppm.): 165.29 (3C, COOH), 149.76 (2C, py-2,6), 143.20(1C, py-4), 127.95(2C, py-3,5). Those NMR data are firstly given here.

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The structure has been deposited with its number CCDC190925. A single crystal of dimensions 0.25×0.20×0.20 mm was used to determine the crystal structure of the complex by X-ray diffraction technique. Crystal data for C<sub>8</sub>H<sub>12</sub>BaNO<sub>13</sub>V (monomer): M=518.47, triclinic,  $a=7.219(4)$ ,  $b=10.795(5)$ ,  $c=11.662(6)$  Å,  $\alpha=113.686(7)$ ,  $\beta=102.814(7)$ ,  $\gamma=95.069(8)$ ,  $V=759.4(7)$  Å<sup>3</sup>, T=273(2) K, space group *P*-1, Z=2,  $\mu(\text{Mo-K}\alpha)=0.71073$  Å. 3296 reflections were measured and 2786 unique ( $R_{\text{int}}=0.0150$ ) were used in all calculations. The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$ . The final  $R$  [ $I>2\sigma(I)$ ] is 0.0222,  $\rho_{\text{max}}$  and  $\rho_{\text{min}}$  are 0.574 and  $-0.611$  e·Å<sup>-3</sup> respectively.

**Figure 1** The molecule structure of  $[(\mu_2\text{-OH}_2)_2\text{Ba}_2(\text{H}_2\text{O})_4][\text{VO}_2(\text{tpa})]_2$



Symmetry code: #1:  $x, y, z+1$ ; #2:  $-x+1, -y+1, -z$ ; #3:  $x-1, y, z$ ; #4:  $-x+1, -y+2, -z+1$ ; #5:  $-x+1, -y+2, -z$

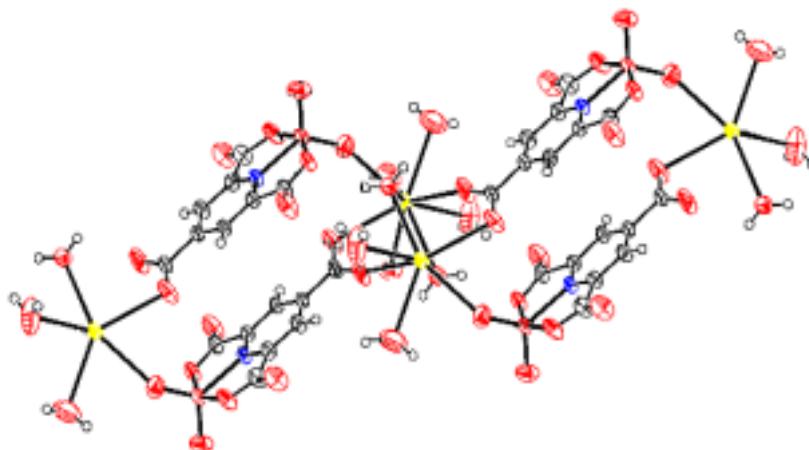
In this dimer complex molecule (**Figure 1**), the coordination geometry of V(1) atom,  $[\text{VO}_2(\text{tpa})]$  dianion, has a distorted trigonal bipyramidal geometry, in which its trigonal sites are occupied by two *cis* vanadyl oxygen atoms and pyridine nitrogen atom with V(1)-O(7) 1.614(3) Å, V(1)-O(8) 1.609(3) Å and V(1)-N(1) 2.097(3) Å, while two oxygen atoms from deprotonated 2- and 6- carboxy group locate at two opposite apices of the bipyramid with V(1)-O(2) 1.976(3) Å and V(1)-O(3) 2.029 Å. As the sum of three bond angles around V(1) atom on the plane is 359.87°: V(1) falls on it; but the distortion of the polyhedron is clearly displayed in that the bond angle along the axis, O(1)-V(1)-O(3) (148.97°) deviates from regular 180°. Although vanadyl oxygen atoms as  $\mu_2$ -bridges are bonded to the different barium atoms, both V(1)-O(7) and V(1)#3-O(8)#3 bond lengths (1.614 Å and 1.609 Å) fall in the normal range of vanadyl double bond, the corresponding compared values are 1.604 Å and 1.610 Å<sup>5</sup>, 1.610 Å and 1.615 Å<sup>6</sup>, respectively.

The nine-coordination geometry of Ba(1) atom is best described as a capped square antiprism, where O(1)#2 occupies the vertex and four bottom atoms ( $O_b$ ) are O(5)#1,

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O(6)#5, O(11) and O(11)#4 with O(1)#2-Ba(1)-O<sub>b</sub> bond angles of 133.25°, 99.16°, 136.52° and 112.70°, respectively. All ligands are involved in the three kinds: four water molecules of  $\mu_2$ -O(11) and O(11)#4, O(9) and O(10); two vanadyl O(7) and O(8)#3 from the different V units; the remaining O atoms, O(1)#2, O(5)#1 and O(6)#5, from carboxyls of the adjacent three tpa, respectively. The resultant nine Ba-O coordinated bond lengths range in 2.701-2.928 Å with the average value 2.81 Å which is less than the sum (2.87Å) of effective ionic radius of barium and van der Waals radius of oxygen atom. Thus it can be seen that all of the Ba-O bonds are formed by electrostatic interactions. Ba(1)-O(5)#1 of them is specially short, since O(5)#1 is acted as the unique ionic donor from the deprotonated 4-carboxyl group.

**Figure 2** The view of 20-member macrocyclic cavities in the title complex



The bridging action of the Ba(1)···Ba(1)#4 (distance 4.443 Å) dimer is of interest. Using the dimer, not only are the coordination geometries of V(1) and V(1)#4 linked up into this complex molecule, but also two 20-member macrocyclic cavities are arranged on its opposite sides (**Figure 2**). Further, those cavities are 1-D extended and built the porous construction of this crystal.

Besides the above bridging bonding action of V(1)-O(7)-Ba(1), another weaker linking form exists between the coordination geometries of V(1) and Ba(1). The two sets of intramolecular hydrogen bonds, O(10)#4-H(10)#4···O(4) and O(11)#4-H(11)#4···O(3), are observed with D(donors)-H 0.918Å and 0.920Å, H···A(acceptors) 2.250 Å and 2.239 Å, D-H···A 3.123Å and 2.955 Å, and  $\angle$  DHA 158.59° and 134.27°, respectively. In addition, there are two sets of lattice water molecules (H<sub>2</sub>O(12) and H<sub>2</sub>O(13)) which participate in formation of hydrogen bonds.

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**References and Note**

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