Mononuclear to Tetranuclear Structural Transformation in Vanadyl Complexes of 3-Hydroxypyridine-2-carboxylic Acid (H_2hpic)

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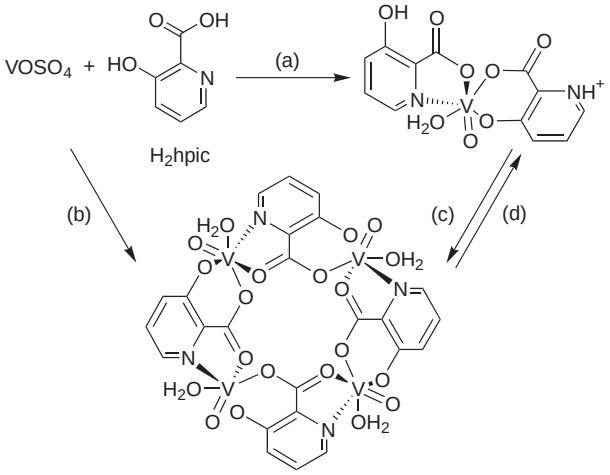
(Received June 13, 2002; CL-020501)

Reaction of vanadyl sulfate with 3-hydroxypyridine-2-carboxylic acid (H_2hpic) affords two chargeless complexes, [VO(Hhpic-*O*, *O*)(Hhpic-*O*, *N*)(H_2O)]·3H_2O (**1**) and unprecedented cyclic tetranuclear complex [$(VO)_4$(μ-(hpic-*O*, *O*′,*N*))(H_2O)$_4$]·8H_2O (**2**), which were characterized by X-ray crystallographic analysis. The unique structural transformation between complexes **1** and **2** was found.

The self-assembly of discrete cyclic nanostructures mediated by transition metals is a subject of relevance to the new field of molecular nanotechnology, so-called molecular architecture.[1] In this work, we have utilized 3-hydroxypyridine-2-carboxylic acid (H_2hpic) as a useful mediator of such transformations in vanadyl complexes. The complexes of vanadium ion with picolinic acid derivatives attract considerable attention as oxidation catalysts and insulin-enhancing agents; both vanadyl and vanadate can form oligomeric structures which may define the activity of these complexes.[2,3] For this aim, pyridine-2-carboxylate has been shown in the past to activate a vanadyl complex toward both oxidation catalysis and insulin enhancement. In this context, hence, it is important to optimize the conditions for oligomerization, as well as to find specific conditions for oligomerization from a discrete structure related to the oligomer. Recently, Kiss et al. suggested the M_4L_4 type aggregate of VO^{2+} with H_2hpic on the basis of the solution speciation, and speculate the square structure.[4] However, there are no evidence for their structure. We wish to report the synthesis and structural determination of new mononuclear and tetranuclear VO^{2+} complexes with the monoanion and dianion, respectively, of H_2hpic, and the unique structural transformation between these two complexes.

Two chargeless VO complexes, [VO(Hhpic-*O*, *O*)(Hhpic-*O*, *N*)(H_2O)]·3H_2O (**1**), wherein (Hhpic-*O*, *O*)$^-$ is 3-oxypyridinium-2-carboxylate, and (Hhpic-*O*, *N*)$^-$ is 3-hydroxypyridine-2-carboxylate, and [$(VO)_4$(μ-(hpic-*O*, *O*′,*N*))$_4$(H_2O)$_4$]·8H_2O (**2**), have been isolated from the methanolic solution of $VOSO_4$ and H_2hpic (Scheme 1).[5] **1** and **2** are soluble in methanol, ethanol and basic solvents such as DMF and DMSO. In both **1** and **2**, the absorption due to V=O stretching was observed at 960 cm^{-1}. Electronic spectra of both complexes show the two weak d-d bands (723.0 and 550.0 nm for **1**, 776.0 and 532.0 nm for **2**), which are characteristic for the monomeric octahedral V^{IV} species.[6] While the magnetic moment (μ_{eff} = 1.61) for **1** shows a typical vanadyl, $3d^1$ results, the value (μ_{eff} = 3.15) for **2** is slightly low.



Scheme 1. Conditions: (a) $VOSO_4$: H_2hpic = 1 : 2; (b) $VOSO_4$: H_2hpic = 1 : 1; (c) $VOSO_4$ MeONa; (d) H_2hpic, H_2SO_4.

In addition, the room temperature X-band EPR spectrum of **2** in DMSO shows line broadening while the eight line pattern anticipated for hyperfine-coupling ($g_{//}$ = 1.948, $A_{//} = 163.0 \times 10^{-4}$ cm^{-1}) was found in the EPR spectrum of **1**. These indicates the weak interaction between the unpaired electrons on V^{IV} center.

The solid state structures of **1** and **2** were established by single crystal X-ray crystallography (Figure 1).[7] In **1**, one of the Hhpic$^-$ contains deprotonated phenoxy and protonated pyridinium functionalities, and binds vanadyl via the phenolate and carboxylate oxygen atoms, and the other Hhpic$^-$ binds to the metal ion via the pyridine nitrogen and carboxylate oxygen atoms, in the usual way for picolinic acid chelates. Complex **2** comprises four distorted octahedral six coordinated V centers [VO_5N]. Each hpic^{2-} ligand is tetradentate, bidentate to each of two vanadyl moieties which it bridges, and the two remaining O atoms are the vanadyl oxo and a water molecule. The carboxylate group of hpic^{2-} bridges adjacent VO^{2+} ions to form an unusual cyclic arrangement of four octahedral [VO_5N]. The V=O distances of **1** and **2** (1.603(1) Å for **1**, 1.607(2) and 1.607(3) Å for **2**) agree well with the V=O bond lengths observed in other mononuclear

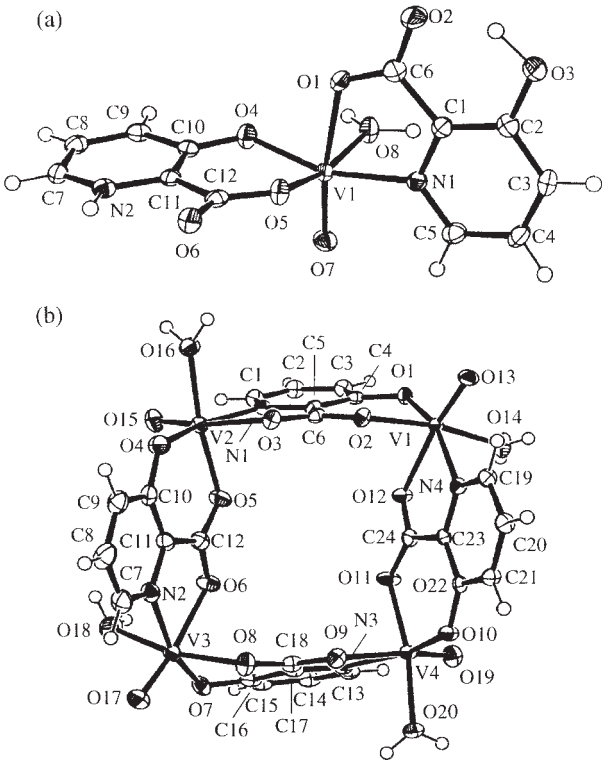


Figure 1. ORTEP drawings of complexes **1** (a) and **2** (b) showing 50% probability. Water molecules in the crystal of **1** and **2**, and one of the two independent molecules per asymmetric unit of **2** are omitted for clarity.

oxovanadium(IV) complexes.[8,9] Interestingly, vanadyl ions in both **1** and **2** have the same arrangement of coordinated atoms. The ESI mass spectrum of **2** in ethanol clearly shows that the cyclic tetramer found in the solid state is retained in solution.

The transformation between **1** and **2** was observed as shown in the Scheme 1.[10] It appears that each coordination environment ''remembers'' the other. In **1** and **2**, the vanadyl is coordinated by one $Hhpic^{-}$ or $hpic^{2-}$, respectively, via N,O-chelate with the carboxylate axial, and the other $Hhpic^{-}$ or $hpic^{2-}$, respectively, O,O-chelate on residual equatrial sites. This coordination pattern suggests stronger coordination for the O,O-chelate and weaker for O,N-coordination. These structures are mainly determined thermodynamically, and the transformation between **1** and **2** should be under thermodynamic control. Conclusively, the nature of the oligomerization of vanadyl moieties can be controlled with the appropriate ligand, H_2hpic.

This work suggests how to design a supramolecular architecture based on oligovanadyl complexes—we can strategically incorporate ligands to mimic biological aggregation patterns. In addition, the biological behavior (particularly of the tetramer **2**) should be interesting, especially since vanadate tetramer inhibits a large number of enzymes including dehydrogenases and isomerases, and also binds to a series of enzymes including superoxide dismutase, myosin and possibly adenylate kinase.[2]

This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan, and by a grant from the San-Ei Gen Foundation for Food Chemical Research.

References and Notes

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5 To the aqueous solution (10 mL) of $VOSO_4{\cdot}xH_2O$ ($x = 3$ to 5) (0.25 g) and H_2hpic (0.33 g) was added 10% $NaHCO_3$ (1.5 mL). After stirring for 3 hours at ambient temperature, the green precipitate was filtered and air-dried to give **1** (0.33 g, 81%). Anal. Calcd for $C_{12}H_{16}O_{11}N_2V$: C, 34.72; H, 3.74; N, 6.80. Found: C, 34.71; H, 3.88; N, 6.75. FAB-MS (m/z): 344 ($[M + H]^+$). μ_{eff} (BM) = 1.61. A similar procedure as that for **1** was applied to $VOSO_4{\cdot}xH_2O$ ($x = 3$ to 5) (0.75 g), H_2hpic (0.52 g), water (20 mL), 10% $NaHCO_3$ (3.3 mL) to afford a brown crystal **2** (0.54 g, 66%). Anal. Calcd for $C_{24}H_{36}O_{28}N_4V_4$: C, 27.92; H, 3.51; N, 5.43. Found: C, 27.58; H, 3.47; N, 5.36. ESI-MS (m/z): 816.8 ($[M + H]^+$). μ_{eff} (BM) = 3.15.
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7 X-ray Crystallography: A green crystal of **1** and a brown crystal of **2** were mounted in a loop and cooled in the cold stream of nitrogen gas. The reflections were collected on Rigaku/MSC Mercury CCD X-ray diffractometer, with graphite monochromated Mo Kα radiation, controlled by the Crystal Clear program (Rigaku). The structure was solved by direct methods (SIR97). For **1** ($C_{12}H_{15}N_2O_{10.50}V$, $M_r = 406.20$), $T = -160.0\,^{\circ}C$, monoclinic, space group $C2/c$, $a = 13.8448(2)$ Å, $b = 13.6256(3)$ Å, $c = 16.5871(2)$ Å, $\beta = 98.219(1)^{\circ}$, $V = 3096.91(9)$ Å^3, $Z = 8$, $R = 0.06$, $R_w = 0.06$, and GOF = 1.05. For **2** ($C_{24}H_{36.8}N_4O_{28.4}V_4$, $M_r = 1039.53$), $T = -150.0\,^{\circ}C$, triclinic, space group $P\bar{1}$, $a = 15.6911(4)$ Å, $b = 16.7726(7)$ Å, $c = 17.7166(4)$ Å, $\alpha = 63.755(1)^{\circ}$, $\beta = 98.219(1)^{\circ}$, $\gamma = 86.665(1)^{\circ}$, $V = 3096.91(9)$ Å^3, $Z = 4$, $R = 0.085$, $R_w = 0.157$, and GOF = 1.06. Details of crystallographic data (excluding structure factor) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-174193 for **1** and CCDC-174194 for **2**. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
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10 To convert **1** into **2**: **1** (0.910 g) and vanadyl sulfate (0.284 g) were dissolved in 40 mL of methanol-H_2O (1 : 1, v/v). To the solution was added CH_3ONa (0.128 g) with stirring at room temperature. After 1 h, the brown powder was filtered out and air-dried to yield **2** (0.359 g, 63%). To convert **2** into **1**: to a methanolic solution (30 mL) of **2** (0.201 g) was added H_2hpic (34 mg) with stirring at room temperature. After adjasting the pH of ca. 4 with 10% H_2SO_4, the solution stood at room temperature for a week. The green crystals formed were filtered out and air-dried to yield **1** (36 mg, 11%).