CHEMISTRY LETTERS, pp. 1675-1678, 1989.

Syntheses of M[V(edta)(H_2O)]•nH_2O (M = Na, K, NH_4) and X-Ray Crystal Structure of Na[V(edta)(H_2O)]•$3H_2O$

Mamoru SHIMOI, Yoko SAITO, and Hiroshi OGINO*
Department of Chemistry, Faculty of Science,
Tohoku University, Aoba-ku, Sendai 980

K[V(edta)(H_2O)]•$2H_2O$ was prepared by the reaction of VCl_3 with K_4edta. The salt was converted to sodium and ammonium salts by use of a cation exchange resin. Crystal structure analysis of the sodium salt exhibits that edta acts as a sexidentate ligand and a water molecule completes seven-coordinatin. The geometry is described as a cappe trigonal-prism or alternatively as a 4:3 piano stool.

Coordination chemistry of vanadium(III) is attracting the attention in connection with its biological importance such as tunichromes$^{1)}$ and vanadium-containing nitrogenase.$^{2)}$ Vanadium(III) usually forms complexes with coordination number six,$^{3)}$ but its chemistry has not been fully investigated.

The kinetics of the electron transfer reactions between [V^{III}(hedtra)(H_2O)] (hedtra = *N*'-(2-hydroxyethyl)ethylenediamine-*N*,*N*,*N*'-triacetate) and halogenopentaamminecobalt(III) complexes were found to obey the novel zeroth-order rate law when $[V(III)]_0 >> [Co(III)]_0$.$^{4)}$ To elucidate the mechanism of this reaction, we have recently analyzed the crystal structure of [V(hedtra)(H_2O)]•$2H_2O$ and the final product K[VO(hedrta)]•H_2O. To our surprise, V(III) takes seven-coordinate structure: The coordinated ligand hedtra acts as a sexidentate ligand and the complex contains one water molecule in the first coordination sphere.$^{5)}$ This prompted us to study the structure of edta complex of vanadium (III), where edta denotes ethylenediamine-*N*,*N*,*N*',*N*'-tetraacetate.

K[V(edta)(H_2O)]•$2H_2O$ was prepared by the reaction of VCl_3 with K_4edta in an aqueous solution under a nitrogen atmosphere. Evaporation of the solvent under reduced pressure followed by the addition of ethanol afforded pale brown flocculent crystals. The sodium and ammonium salts, Na[V(edta)(H_2O)]•$3H_2O$ and NH_4[V(edta)(H_2O)]•$2.5H_2O$, were obtained by use of the cation exchange resin Dowex 50W-X8.$^{6)}$ This preparation method is more convenient than the reported one.$^{7)}$ Crystals of the sodium salt suitable for X-ray crystal structure analysis were obtained by leaving a saturated aqueous solution standing in a desiccator containing phosphorus pentoxide filled with argon. The crystal of the sodium salt exhibits dichroism and looks purple or grayish green depending on the direction.

Diffraction data were collected by using a Rigaku AFC-6A automated four-circle diffractometer using graphite monochromated Mo Kα radiation. Crystal data are as follows: formula $C_{10}H_{20}N_2NaO_{12}V$, *F.W.* 434.20, monoclinic with the space

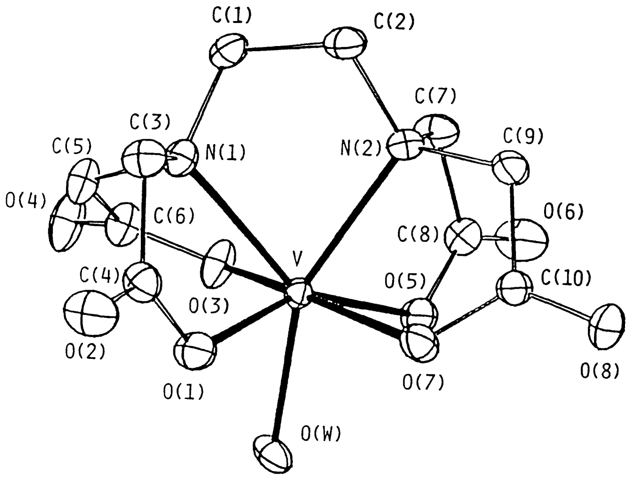

Fig. 1. ORTEP drawing for $[V(edta)(H_2O)]^-$ anion. Hydrogen atoms are omitted for clarity.

Table 1. Bond lengths(l/Å) and angles(ϕ/°) for $Na[V(edta)(H_2O)]\cdot 3H_2O$

Bond lengths (l/Å)

V-N(1)	2.225(2)	V-N(2)	2.217(3)
V-O(1)	2.070(2)	V-O(3)	2.069(4)
V-O(5)	2.057(2)	V-O(7)	2.013(3)
V-O(W)	2.066(2)		

Bond angles (ϕ/°)

O(1)-V-O(W)	75.60(8)
O(3)-V-O(W)	84.66(13)
O(5)-V-O(W)	80.03(9)
O(7)-V-O(W)	88.37(12)
O(1)-V-O(3)	112.04(12)
O(5)-V-O(7)	84.41(11)
O(1)-V-O(7)	80.68(1)
O(3)-V-O(5)	79.4(12)
O(1)-V-N(1)	72.20(8)
O(3)-V-N(1)	74.18(12)
O(5)-V-N(2)	74.86(8)
O(7)-V-N(2)	78.82(12)
N(1)-V-N(2)	76.21(9)

group $P2_1/a$ (variant of No.14), a = 17.831(3), b = 8.408(1), c = 11.595(2) Å, β = 109.39(1)°, U = 1639.8(5) $Å^3$, Z = 4, d_{measd} = 1.74, d_{calcd} = 1.76 g cm^{-3}, and R = 0.045 for 4216 reflections with $|F_o| > 3\sigma(F_o)$.

The ORTEP drawing of $[V(edta)(H_2O)]^-$ is shown in Fig. 1. Bond lengths and angles around the vanadium atom are listed in Table 1.

In the complex, edta acts as a sexidentate ligand forming a twist trigonal-prism and a water molecule is also coordinated to the vanadium atom from a capping position.[8)] The geometry around the vanadium atom is a capped trigonal-prism. In this respect the structure is quite similar to that of $[V(hedtra)(H_2O)]$.[5)] The averaged V-O(carboxylato) bond length is 2.052(23) Å which is almost equal to that for $[V(hedtra)(H_2O)]$ (2.048(13) Å). However, the bond lengths range more widely than those for the latter. This difference is reflected in the difference of configurations of the both complexes. Figure 2 shows the projections of coordination spheres for $[V(edta)(H_2O)]^-$ and $[V(hedtra)(H_2O)]$ along the axis passing through the centers of gravity, CE1 and CE2, of the N(1)-O(1)-O(3) and N(2)-O(5)-O(7) triangle faces. In the both complexes these triangles are almost parallel (dihedral angles between the planes are 4.90° for $[V(edta)(H_2O)]^-$ and 2.20° for $[V(hedtra)(H_2O)]$), but they are twisted. Twist angles defined by N(1)-CE1-CE2-N(2), O(1)-CE1-CE2-O(7), and O(3)-CE1-CE2-O(5) are also shown in Fig. 2. Although $[V(hedtra)(H_2O)]$ has an approximate C_2 axis along V-H_2O, $[V(edta)(H_2O)]^-$ has no such symmetry. However, O(1), O(7), N(1), and N(2) atoms for $[V(edta)(H_2O)]^-$ are almost coplanar; they deviate from the least-squares plane by

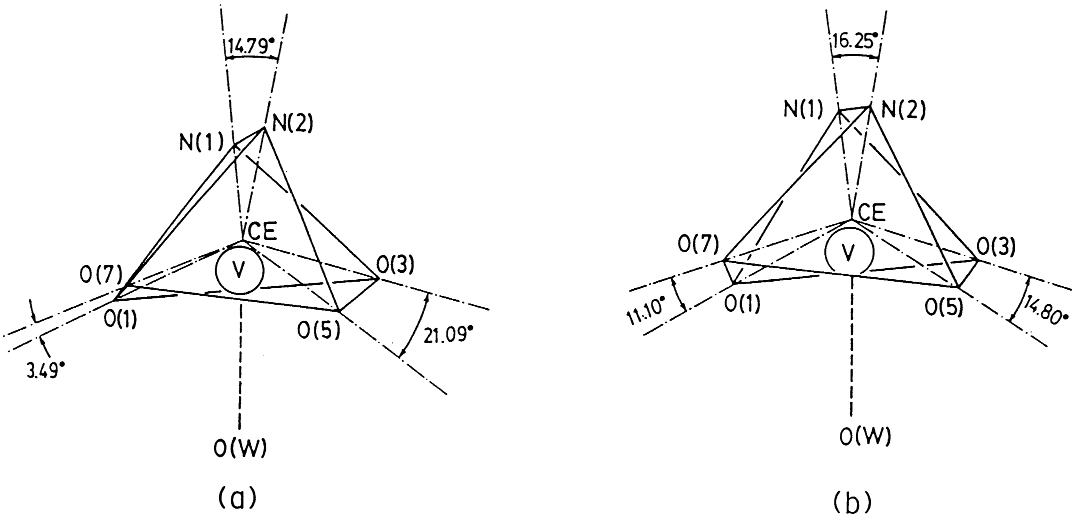

Fig. 2. Projections of the coordination spheres for $[V(edta)(H_2O)]^-$ (a) and $[V(hedtra)(H_2O)]$ (b) along the axis passing through the centers of gravity of the triangle faces.

only -0.028, 0.026, 0.029, and -0.027 Å. This plane is almost parallel to the O(3)-O(5)-O(W) plane. The dihedral angle between the planes is 4.96°. Thus the geometry of $[V(edta)(H_2O)]^-$ is also described as a 4:3 piano stool[9] or tetragonal base-trigonal base.[10] It is of interest to note that the more symmetrical edta ligand takes less symmetrical coordination structure than the less symmetrical hedtra ligand.

Some typical elements as well as transition metals are known to have seven-coordinate structure with edta and aqua ligands. $[Mg(edta)(H_2O)]^{2-}$ in $Mg[Mg(edta)(H_2O)]\cdot 8H_2O$,[11] $[Cd(edta)(H_2O)]^{2-}$,[12] $[Ti(edta)(H_2O)]$,[13] and $[Fe(edta)(H_2O)]^-$ [14] have pentagonal bipyramidal configuration; $[Mg(edta)(H_2O)]^{2-}$ in $Na_2[Mg(edta)(H_2O)]\cdot 5H_2O$,[15] $[Mn(edta)(H_2O)]^{2-}$,[16] and $[Os(edta)(H_2O)]$[17] take capped trigonal-prism configuration. All these complexes have an approximate or exact two-fold axis along the M-H_2O bond. Only $[V(edta)(H_2O)]^-$ is exceptionally deformed among these complexes. It is uncertain at present whether this is due to the crystal packing forces or intrinsic to the $[V(edta)(H_2O)]^-$ anion. To solve the problem we are undertaking the structure analysis of other salts.

By the combination of the crystal structure analysis of $[V(hedtra)(H_2O)]\cdot 2H_2O$ and $Na[VO(hedtra)]\cdot 5H_2O$ and kinetic study for electron transfer reactions between $[V(hedtra)(H_2O)]$ and halogenopentaamminecobalt(III) complexes, we showed that the reactive intermediate is six-coordinate V(III) complex, hydroxyethyl group being detached from the vanadium center. This argument suggests that $[V(edta)(H_2O)]^-$ should be less reactive than $[V(hedtra)(H_2O)]$, because edta has no weakly binding site anymore. In fact, a preliminary experiment showed that the reaction of $[V(edta)(H_2O)]^-$ with $[Co(N_3)(NH_3)_5]^{2+}$ also followed the pseudo-zeroth order rate law under the condition $[V(III)]_0 > [Co(III)]_0$, and the reaction rate was much slower than that of the hedtra complex.

References

1) E. M. Oltz, R. C. Bruening, M. J. Smith, K. Kustin, and K. Nakanishi, J. Am. Chem. Soc., 110, 6162 (1988).

2) B. J. Hales, E. E. Case, J. E. Morningster, M. F. Dzeda, and L. A. Mauterer, Biochemistry, 25, 7251 (1986); J. M. Arber, B. R. Dobson, R. R. Eady, P. Stevens, S. S. Hasnain, C. D. Garner, and B. E. Smith, Nature, 325, 372 (1987).

3) L. V. Boas and J. C. Pessoa, "Comprehensive Coordination Chemistry," ed by G. Wilkinson, Pergamon, Oxford (1987), Vol. 3, pp.453-583.

4) H. Ogino, M. Shimura, N. Yamamoto, and N. Okubo, Inorg. Chem., 27, 172 (1988).

5) H. Ogino, M. Shimoi, and Y. Saito, Inorg. Chem., in press.

6) Elementary analyses for the complexes are as follows. Found for $K[V(edta)(H_2O)]\cdot 2H_2O$: C, 27.55; H, 4.36; N, 6.61%. Calcd for $C_{10}H_{18}KN_2O_{11}V$: C, 27.78; H, 4.20; N, 6.48%. Found for $Na[V(edta)(H_2O)]\cdot 3H_2O$: C, 28.43; H, 4.44; N, 6.18%. Calcd for $C_{10}H_{20}N_2NaO_{12}V$: C, 27.66: H, 4.64; N, 6.45%. Found for $NH_4[V(edta)(H_2O)]\cdot 2.5H_2O$: C, 28.45; H, 5.78; N, 9.94%. Calcd for $C_{10}H_{23}N_3O_{11.5}V$: C, 28.58; H, 5.52; N, 10.00%.

7) G. Schwarzenbach and J. Sandera, Helv. Chim. Acta, 36, 1089 (1953).

8) Coordination of a water molecule was suggested by the measurement of an infrared spectrum and the analysis of pH titration. F. J. Kristine and R. E. Shepherd, J. Am. Chem. Soc., 99, 6562 (1977).

9) E. B. Dreyer, C. T. Lam, and S. J. Lippard, Inorg. Chem., 18, 1904 (1979).

10) E. L. Muetterties and C. M. Wright, Quart. Rev., 21, 109 (1967).

11) E. Passer, J. G. White, and K. L. Cheng, Inorg. Chim. Acta, 24, 13 (1977).

12) X. Solans, S. Gali, M. Font-Altaba, J. Oliva, and J. Herrera, Acta Crystallogr., Sect. C, 39, 438 (1983); X. Solans, M. Font-Altaba, J. Oliva, and J. Herrera, ibid., 41, 1020 (1985).

13) J. P. Fackler, Jr., F. J. Kristine, A. M. Mazany, T. J. Moyer, and R. E. Shepherd, Inorg. Chem., 24, 1857 (1985).

14) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, Inorg. Chem., 3, 34, (1964); X. Solans, M. F. Altaba, and J. Garcia-Oricain, Acta Crystallogr., Sect. C, 40, 635 (1984); X. Solans, M. Font-Altaba, and J. Garcia-Oricain, ibid., 41, 525 (1985).

15) J. J. Stezowski, R. Countryman, and J. L. Hoard, Inorg. Chem., 12, 1749 (1973).

16) S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, Inorg. Chem., 3, 27 (1964).

17) M. Saito, T. Uehiro, F. Ebina, T. Iwamoto, A. Ouchi, and Y. Yoshino, Chem. Lett., 1979, 997.

(Received June 28, 1989)