

## Synthesis and Crystal Structure of Triammonium (Propylenediaminetetraacetato)dioxovanadate(V) Monohydrate Complex

Man-Ho Lee,<sup>\*</sup> Nam Ho Heo, and Young Kee Oh<sup>†</sup>

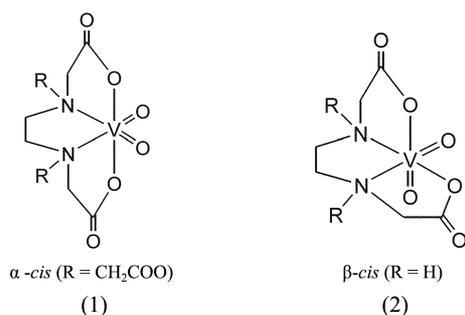
*Department of Industrial Chemistry, Kyungpook National University, Daegu 702-701, Korea*

*<sup>†</sup>Household and Personal Care Products R&D Institute, LG Chemical Ltd., Daejeon 305-343, Korea*

*Received July 27, 2002*

**Key Words :** Vanadium(V) complex, Propylenediaminetetraacetate, Dioxovanadate(V) complex, X-Ray crystallography

Vanadium has been recognized to play important roles in biological systems.<sup>1</sup> Recently it is reported that bis(malto)oxovanadium(IV) complex is a potent insulin mimic agent.<sup>2,3</sup> The structure, stability and lability of vanadium(V) compounds are important to the mechanisms by which these compounds act in biological systems and in part have contributed to the mechanisms by which vanadate mimics insulin action.<sup>4</sup> But the chemistry of vanadium has not much known yet. Of the representative vanadium(V) complexes, the crystal structures of vanadium(V) complexes with oxalate (Ox),<sup>5,6</sup> ethylenediaminetetraacetate (EDTA),<sup>7,8</sup> nitrilotriacetate (NTA),<sup>9</sup> and N-(2-hydroxyethylimino)diacetate<sup>10</sup> ligands have been studied by X-ray crystallography. Vanadium(V)-EDTA complexes are confirmed to have a  $\alpha$ -*cis* structure (1), in which the anion has an irregular octahedral geometry with VO<sub>2</sub> core. But ethylenediaminediacetate (EDDA) is known to form a  $\beta$ -*cis* structure (2) with vanadium(V).<sup>11</sup> According to the solution studies,<sup>11,12</sup> EDDA forms  $\alpha$ -*cis* and  $\beta$ -*cis* isomers with vanadium(V) while EDTA forms only the  $\alpha$ -*cis* isomer with vanadium(V). The steric hindrance makes stable the  $\alpha$ -*cis* form of the isomers because the substitution of an acetate group on nitrogen increases steric bulk.



In this paper we report the synthesis of a new vanadium (V) complex, triammonium (propylenediaminetetraacetato)dioxovanadate(V) monohydrate, as well as its crystal structure determined by X-ray crystallography. Propylenediaminetetraacetate (PDTA) is similar to EDTA in structure. PDTA has an asymmetric carbon on ethylenic backbone according to the substitution of a methyl group, while EDTA has a symmetric structure.

### Experimental Section

**Materials.** All reagent grade chemicals were used without further purification. Ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>) and propylenediaminetetraacetic acid (H<sub>4</sub>PDTA) were purchased from Aldrich Chemical Company.

**Preparation of vanadium(V) complex.** The reaction of NH<sub>4</sub>VO<sub>3</sub> (0.02 mole, 2.34 g), H<sub>4</sub>PDTA (0.02 mole, 6.13 g) and 25% ammonia water (0.03 mole, 2.0 mL) in 100 mL water produced a yellow solution which was concentrated by passing a stream of dry air at room temperature. Ethanol was added and the resulting solution was kept in a refrigerator. The pale yellow crystals were formed and then filtered. The yield was 30%. The single crystals were obtained by dissolving the powders in water and keeping the solution in a refrigerator for several days. The chemical formula, VN<sub>3</sub>O<sub>11</sub>·C<sub>11</sub>H<sub>28</sub>, of the complex was obtained from the elemental analysis. Analytical data (%) are in the range of good agreement (calculated: C, 28.89; H, 6.17; N, 15.32. found: C, 28.83; H, 6.10; N, 15.26).

**X-Ray measurements.** Preliminary experiments and data collection for X-ray crystal structure determination were performed on a Enraf-Nonius CAD4/Turbo diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). A small single crystal, 0.5 × 0.5 × 0.5 mm, was glued to a glass fiber with an epoxy resin. 25 reflections in the diverse reciprocal space were centered by an automatic search program and used to obtain cell parameters. After the preliminary cell was confirmed, high-angle data ( $2\theta > 20^\circ$ ) were collected and 25 of these reflections were centered and used to obtain more accurate cell parameters. Unit cell parameters and the systematic absences indicated the monoclinic space group  $P2_1/n$  (No. 14)<sup>13</sup> with  $Z = 4$ . Data were collected on this improved unit cell at ambient temperature up to  $2\theta = 50^\circ$ . Data reduction including the corrections for Lorentz polarization, decay, and absorption correction were performed. The crystal structure was solved and refined with full-matrix least-squares by using MolEN, the Enraf-Nonius structure determination package, resulting in final  $R_1$  and  $R_w$  indices of 0.067 and 0.080, respectively. Other details of crystallographic data are summarized in Table 1. The final structural parameters are presented in Table 2. Selected bond distances and angles are tabulated in Table 3. The structure

**Table 1.** X-ray Crystallographic Parameters

Formula	VN <sub>5</sub> O <sub>11</sub> C <sub>11</sub> H <sub>23</sub>
Formula wt.	457.32
<i>a</i> , Å	12.274 (2)
<i>b</i> , Å	11.769 (3)
<i>c</i> , Å	13.360 (3)
β, deg.	97.41 (2)
<i>V</i> , Å <sup>3</sup>	1913.9 (7)
<i>Z</i>	4
<i>d</i> <sub>calc.</sub> , g cm <sup>-3</sup>	1.524
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)
Temperature	ambient
Radiation, Å	Mo Kα (0.71073)
Scan mode	θ-2θ
2θ <sub>max.</sub> , deg.	50
No. of obsd. refl.	4234
No. of variables	302
<i>R</i> <sub>1</sub> <sup>a</sup>	0.067
<i>R</i> <sub>w</sub> <sup>b</sup>	0.080
Goodness of fit <sup>c</sup>	1.29

<sup>a</sup> $R_1 = \sum |F_o - F_c| / \sum F_o$ , <sup>b</sup> $R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$ , <sup>c</sup>Goodness of fit =  $[\sum w(F_o - F_c)^2 / \sum w(m - s)]^{1/2}$ , where *m* = number of observed data and *s* = number of variables.

**Table 2.** Final Atomic and Thermal Parameters<sup>a</sup>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B <sup>b</sup> (Å <sup>2</sup> )
V(1)	0.13891(5)	0.13943(5)	0.35688(4)	1.604(8)
O(1)	0.0957(2)	0.2229(3)	0.2620(2)	2.53(5)
O(2)	0.0621(2)	0.1690(3)	0.4437(2)	2.40(5)
O(3)	0.2638(2)	0.2298(2)	0.4235(2)	2.22(5)
O(4)	0.4241(2)	0.3116(3)	0.4185(3)	3.56(6)
O(5)	0.0663(2)	0.0024(2)	0.2993(2)	2.30(5)
O(6)	-0.0123(2)	-0.1619(3)	0.3288(2)	2.75(5)
O(7)	0.4350(3)	0.0202(4)	0.1303(3)	4.45(8)
O(8)	0.3083(3)	0.0687(4)	0.0061(2)	4.26(8)
O(9)	0.2524(3)	-0.1602(3)	0.6443(2)	3.07(6)
O(10)	0.2917(3)	-0.0072(3)	0.7384(2)	4.57(8)
O(11)	0.9007(3)	0.1542(5)	0.1256(3)	5.9(1)
N(1)	0.2883(2)	0.0804(3)	0.2760(2)	1.89(5)
N(2)	0.2218(2)	-0.0138(3)	0.4613(2)	1.62(5)
N(3)	0.1351(4)	0.3496(3)	0.5991(3)	3.60(8)
N(4)	0.1219(3)	0.0933(5)	0.8662(3)	4.9(1)
N(5)	-0.0963(3)	0.3331(3)	0.3412(3)	3.37(8)
C(1)	0.3659(3)	0.1738(4)	0.2909(3)	3.03(8)
C(2)	0.3524(3)	0.2437(4)	0.3836(3)	3.26(6)
C(3)	0.1376(3)	-0.1021(3)	0.4474(3)	2.50(7)
C(4)	0.0566(3)	-0.0879(3)	0.3520(3)	1.93(6)
C(5)	0.3260(4)	-0.0301(4)	0.3184(4)	4.34(9)
C(6)	0.3298(4)	-0.0375(5)	0.4272(4)	4.17(9)
C(7)	0.3897(4)	-0.1465(4)	0.4680(3)	3.33(8)
C(8)	0.2510(3)	0.0647(4)	0.1667(3)	3.05(8)
C(9)	0.3409(3)	0.0493(4)	0.0974(3)	2.32(7)
C(10)	0.2384(4)	0.0270(4)	0.5671(3)	2.77(7)
C(11)	0.2647(3)	-0.0571(4)	0.6550(3)	2.41(7)

<sup>a</sup>Positional parameters × 10<sup>4</sup> are given. Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameters. <sup>b</sup>All atoms were refined anisotropically and are given in the form of the isotropic equivalent displacement parameter defined as  $(4/3) [a^2 B_{11} + b^2 B_{22} + c^2 B_{33} + ab^2 (\cos \gamma) B_{12} + ac^2 (\cos \beta) B_{13} + bc^2 (\cos \alpha) B_{23}]$

**Table 3.** Selected Bond Distances and Angles<sup>a</sup>

(a) Selected Bond Distances (Å)			
Bond	Distance (Å)	Bond	Distance (Å)
V-O(1)	1.637(3)	V-O(2)	1.624(3)
V-O(3)	1.981(3)	V-O(5)	1.952(3)
V-N(1)	2.350(3)	V-N(2)	2.423(3)
(b) Selected Bond Angles (deg)			
Bond	Angle	Bond	Angle
O(1)-V-O(2)	105.4(2)	O(1)-V-O(3)	100.4(1)
O(1)-V-O(5)	96.0(1)	O(1)-V-N(1)	90.9(1)
O(1)-V-N(2)	164.3(1)	O(2)-V-N(3)	92.9(1)
O(2)-V-O(5)	100.4(1)	O(2)-V-N(1)	162.0(1)
O(2)-V-N(2)	89.3(1)	O(3)-V-O(5)	155.3(1)
O(3)-V-N(1)	76.1(1)	O(3)-V-N(2)	84.1(1)
O(5)-V-N(1)	85.3(1)	O(5)-V-N(2)	75.4(1)
N(1)-V-N(2)	75.5(1)		

<sup>a</sup>Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameters.

model was drawn using ORTEP. Oak Ridge Thermal Ellipsoidal Plot Program.<sup>14</sup>

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-193564). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perf-catreq-catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

## Results and Discussion

PDTA is expected as a tetradentate ligand to coordinate to VO<sub>2</sub><sup>+</sup>. In PDTA ligand, the methyl substituent on the ethylenic backbone causes two iminodiacetate (IDA) groups to become chemically different.

The (NH<sub>4</sub>)<sub>3</sub>[VO<sub>2</sub>PDTA]·H<sub>2</sub>O complex has a *α-cis* structure as shown in Figure 1. There is no particular interaction between neighboring molecules in the unit cell. The anion [VO<sub>2</sub>PDTA]<sup>3-</sup> has a distorted octahedral geometry in which the VO<sub>2</sub> group is in the *cis* configuration as shown in oxalate, EDTA and NTA complexes.<sup>5-9</sup> The two oxo oxygens have short V=O bonds (1.637 and 1.624 Å) which indicate a strong multiple bond character. The average V=O bond length (1.631 Å) in the complex is shorter than that (1.648 Å) found in EDTA complex.<sup>7</sup> The O=V=O angle (105.4°) in VO<sub>2</sub> moiety is larger than 90° that is the standard octahedral value. The methyl group (C7) of the ethylenic backbone is located at the parallel position to the plane formed by O<sub>1</sub>O<sub>2</sub>N<sub>2</sub>N<sub>1</sub> atoms in the complex.

The remaining four coordination sites of vanadium atom are occupied by two amine nitrogen and two carboxylate oxygen atoms of the PDTA ligand, giving two five-membered glycinato rings in the complex. The bond lengths of V-O (carboxylate) are 1.981 and 1.952 Å (average 1.967 Å), indicating a single bond character. The bond lengths of

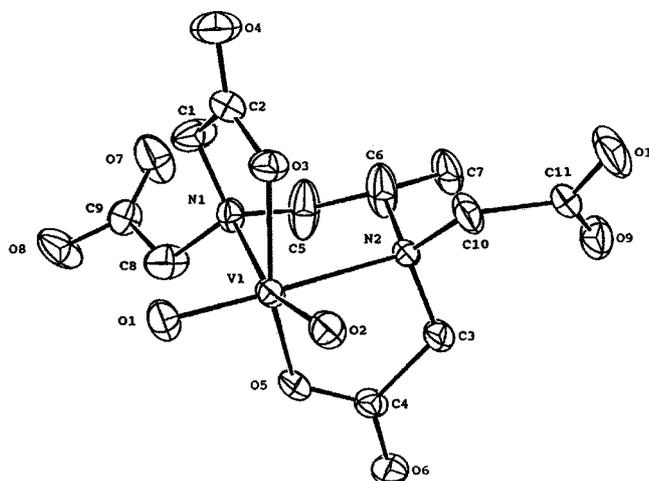


Figure 1. ORTEP of  $[\text{VO}_2\text{PDTA}]^{3-}$  anion.

V-N are 2.350 and 2.423 Å (average 2.387 Å), which are larger than those (average 2.363 Å) in EDTA complex.<sup>8</sup> This means that V-N bonds in PDTA complexes are weaker than those in EDTA complexes. It is consistent that shorter V=O (oxo) bonds cause longer V-N bonds, showing the stronger structural *trans* effect in *cis*-VO<sub>2</sub> complexes. The insertion of methyl group into ethylenic backbone might cause the increase of strain in the ring, giving long V-N bonds; longer V-N bonds would give some reduction of strain within the chelate ring. Two glycinate arms of the PDTA ligand in the complex remain uncoordinated.

The difference between the average of the V-O bond lengths and the V-N bond lengths in the PDTA complex is 0.42 Å. Since a difference of about 0.04 Å in M-N and M-O distances is predicted from the consideration of the covalent radii of oxygen and nitrogen,<sup>15</sup> the V-O bond can be taken as much stronger than the V-N bond. About 0.24 Å of the 0.42 Å difference between the bond distances might come from the *trans* effect as in NTA complexes.<sup>9</sup> The substantial remainder of 0.14 Å is indicative of a low affinity of the VO<sub>2</sub> for the amino nitrogen relative to that for the carboxylate oxygen. Perhaps the most interesting feature here is the long V1-N2 bond (2.423 Å), which is among the longest bond lengths observed in vanadium-aminopolycarboxylate complexes. Also, two V-O (carboxylate) bond lengths (1.952 and 1.981 Å) are nonequivalent and smaller compared to those of V-EDTA complexes.

From the infrared spectroscopic studies, the PDTA complex shows two absorption bands, *i.e.*, one symmetric and one asymmetric, at 895 and 918 cm<sup>-1</sup> which arise from

the V=O bonds in the VO<sub>2</sub><sup>-</sup> group in (NH<sub>4</sub>)<sub>3</sub>[VO<sub>2</sub>PDTA]·H<sub>2</sub>O. The frequencies for V=O bonds in other *cis*-VO<sub>2</sub> complexes were noted for comparison: 866 and 923 cm<sup>-1</sup> for (NH<sub>4</sub>)<sub>3</sub>[VO<sub>2</sub>Ox]·2H<sub>2</sub>O, 895 and 935 cm<sup>-1</sup> for K<sub>3</sub>[VO<sub>2</sub>EDTA]·4H<sub>2</sub>O, and 857 and 905 cm<sup>-1</sup> for NH<sub>4</sub>[VO<sub>2</sub>EDDA].<sup>11</sup> The stretching frequencies for the (NH<sub>4</sub>)<sub>3</sub>[VO<sub>2</sub>PDTA]·H<sub>2</sub>O are very similar to those for K<sub>3</sub>[VO<sub>2</sub>EDTA]·4H<sub>2</sub>O, indicating that two complexes have a similar structure.

In conclusion, the substitution of methyl group in the ethylenic backbone in PDTA complex favors a *α-cis* structure and has some significant effect on the octahedral structure of the complex, especially the stronger *trans* effect on the V-N bond lengths. The isomerization between *α-cis* and *β-cis* isomers occurs in aqueous solution and is now under investigation by NMR spectroscopy.

**Acknowledgment.** This work is supported by International Research Fund 1998, Korea Research Foundation.

## References

1. *Vanadium in Biological System*, Chasteen, N. D., Ed.; Kluwer Academic Press: Dordrecht, Netherlands, 1990.
2. McNeill, J. H.; Yuen, V. G.; Hoveyda, H. R.; Orvig, C. *J. Med. Chem.* **1992**, *35*, 1489.
3. Caravan, P.; Gelmini, L.; Glover, N.; Herring, F. G.; Li, H.; McNeill, J. H.; Rettig, S. J.; Setyawati, I. A.; Shuter, E.; Sun, Y.; Tracey, A. S.; Yuen, V. G.; Orvig, C. *J. Am. Chem. Soc.* **1995**, *117*, 12759.
4. Crans, D. C.; Mahroof-Tahir, M.; Shin, P. K.; Keramidas, A. D. *Mol. Cell. Biochem.* **1995**, *153*, 17.
5. Scheidt, W. R.; Tsai, C.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3867.
6. Drew, R. E.; Einstein, F. W. B.; Gransden, S. E. *Can. J. Chem.* **1974**, *52*, 2184.
7. Scheidt, W. R.; Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3873.
8. Scheidt, W. R.; Countryman, R.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3878.
9. Lee, M.-H.; Heo, N. H.; Hayashi, S. *Polyhedron* **1998**, *17*, 55.
10. Mahroof-Tahir, M.; Keramidas, A. D.; Goldfarb, R. B.; Anderson, O. P.; Miller, M. M.; Crans, D. C. *Inorg. Chem.* **1997**, *36*, 1657.
11. Crans, D. C.; Keramidas, A. D.; Mahroof-Tahir, M.; Anderson, O. P.; Miller, M. M. *Inorg. Chem.* **1996**, *35*, 3599.
12. Amos, L. W.; Sawyer, D. T. *Inorg. Chem.* **1972**, *11*, 2692.
13. *International Tables for X-Ray Crystallography*; Henry, N. F. M.; Lonsdale, K., Eds.; Kynoch Press: Birmingham, England, 1952; Vol. 1.
14. Johnson, C. K. *ORTEP-III*; Oak Ridge National Laboratory, Oak Ridge, Tenn, 1976.
15. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed.; Cornell University Press: Ithaca, N.Y. 1960.