

TMS) and EI MS data ($m/e=132$; M^+) with those of an authentic sample.

Isolation of 9. After evacuation of the loaded polyethylene was completed, the polyethylene was extracted with diethyl ether and the extract was concentrated at room temperature and reduced pressure. From the remaining solid residue (160 mg), one could isolate 51 mg (3%) of **9** by flash chromatography (15 g of silica gel; *n*-pentane/diethyl ether=10:1). Compound **9** was identified on the basis of its ^1H NMR ($\delta=1.46$, s; CDCl_3 , TMS) and ^{13}C NMR data ($\delta=21.30$, 107.47; CDCl_3 , TMS) with those reported.¹⁰

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The Crystal Structure of Diammonium (Nitrilotriacetato)dioxovanadate (V)

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With the recent discoveries of the first two naturally occurring vanadium-containing enzymes, the bromoperoxidase and nitrogenase, the coordination chemistry and reactivity of vanadium is receiving renewed attention.¹ Of various ligands, many carboxylates are known to form anhydrides with vanadate in solution, when they have additional hydroxyl or amine groups available for chelation. Oxalate²⁻⁴ gives the simple mono- and bis-oxalato octahedral complexes, presumably with *cis*-VO₂ species. Also aminopolycarboxylate such as ethylenediaminetetraacetate (EDTA) forms similar octahedral complex having *cis*-VO₂ species.⁵⁻⁸ However, α -hydroxycarboxylates such as lactate, glycerate etc. form a variety of derivatives, including simple esters, chelates having trigonal bipyramidal coordination, and two binuclear complexes with mixed coordination.^{3,9,10}

But X-ray diffraction studies of vanadium (V) complexes are not much known yet. Only crystal structures of vanadium (V) complexes with oxalate^{11,12} and EDTA ligands^{13,14} have been determined. These complexes are confirmed to have a *cis*-VO₂ core, in which the anion has irregular octahedral geometry with two double-bonded oxygen atoms. In vanadium (V) complexes of oxalate^{11,12} it is known that the V-O (oxalate) bonds *trans* to V=O are longer than those *cis* to V=O.

In this paper, we report the synthesis of a new vanadium (V) complex, diammonium (nitrilotriacetato)dioxovanadate (V) ((NH₄)₂[VO₂NTA]), as well as its crystal structure determined by X-ray crystallography.

Experimental

Materials. All reagent grade chemicals were used without further purification. Ammonium metavanadate (NH₄VO₃), nitrilotriacetic acid (H₃NTA) and 25% ammonia water were purchased from Aldrich Chemical Company.

Preparation of vanadium(V) complex. The reaction of NH₄VO₃ (0.02 mole, 2.34 g) with H₃NTA (0.02 mole 3.82 g) and 25% ammonia water (0.02 mole, 1.3 mL) in 100 mL water produced yellow solution which was concentrated by passing a stream of dry air at room temperature for 2 days. The pale yellow crystals were formed and then filtered. The complexes were recrystallized from water. The yield was 1.95 g (63.1%). The single crystals were obtained by evaporating the aqueous solution of the complex. The chemical formula, VN₃O₈C₆H₁₄, of the complex was obtained from the elemental analysis. Analytical data (%) are in the range of good agreement (calculated; C 23.46, H 4.59, N 13.68, found; C 23.34 H 4.68 N 13.83).

X-ray measurements. Preliminary experiment and data collection for X-ray crystal structure determination were performed on a Enraf-Nonius CAD4/Turbo diffractometer using Mo K α radiation ($\lambda=0.71069$ Å). A small single crystal, 0.5×0.5×0.5 mm, was cut from a larger one and glued to a glass fiber with an epoxy resin. 25 reflections in 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)¹⁵ 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 were performed. Crystal structure was solved and refined with full-matrix least-squares by using MolEN, the Enraf-Nouius structure determination package, resulting in final R_1 and R_w indices of 0.049 and 0.076, respectively. Other details of crystallographic data are summarized in Table 1. The final structural parameters are presented in Table 2. The selected bond distances and angles are tabulated in Table 3. The structure model was drawn using ORTEP, Oak Ridge Thermal Ellipsoid Plot Program.¹⁶

Result and Discussion

It is reported from the kinetic study that vanadium (V) formed 1:1 complex with NTA ($K_{VO_2-NTA}=10^{13.8}$ at 25°C).¹⁷ Nitrilotriacetate, containing a nitrogen and three oxygen atoms, is considered to react with VO_2^+ ion as a tetradentate ligand. The synthesized vanadium complex is stable at room temperature and its synthesis is readily accomplished in good yield. Large single crystals were easily grown by slow evaporation of the aqueous solution and showed no evidence of twinning and other defects.

The solid-state structure of the complex is remarkable simple, as shown in Figure 1. There is no particular interactions between adjacent molecules in the unit cell and the geometry around the vanadium (V) ion may be regarded as distorted octahedral.

The anion $[VO_2NTA]^{2-}$ has a slightly irregular octahedral geometry in which two oxo ligands are *cis* to each other as

Table 1. X-ray Crystallographic Parameter

Formula	$VN_3O_8C_6H_{14}$
Formula wt.	307.1
a , Å	6.923 (1)
b , Å	8.814 (2)
c , Å	19.218 (11)
β , deg.	91.60 (3)
V , Å ³	1172.1 (7)
Z	4
d_{calc} , g cm ⁻³	1.714
Space group	$P2_1/n$
Temperature	ambient
Radiation, Å	Mo K_α (0.71073)
Lin. abs. coeff., cm ⁻¹	8.5
Scan mode	θ - 2θ
$2\theta_{max}$, deg.	50
No. of obsd. refl.	1874
No. of variables	164
R_1^a	0.049
R_w^b	0.076
Goodness of fit ^c	2.60

^a $R_1 = \sum |F_o - |F_c|| / \sum F_o$. ^b $R_w = [\sum w(F_o - |F_c|)^2 / \sum w F_o^2]^{1/2}$.

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

shown in oxalate^{11,12} and EDTA^{13,14} complexes. These two oxygens have short V-O bonds (1.653 and 1.613 Å) which indicate strong multiple bond character. The O-V-O angle ($107.1(2)^\circ$) in VO_2 moiety is larger than 90° that is the standard octahedral value. The small difference (0.040 Å) of V=O bonds observed in the unconstrained complex might be due to interactions with the asymmetric environments. The average V=O bond length (1.633 Å) in the complex is shorter than that (1.648 Å) found in EDTA complex.¹⁴ This would be consistent with the slight increase in O-V-O angle

Table 2. Final Atomic and Thermal Parameters^a

Atom	x	y	z	B^b (Å ²)
V	8736(1)	1864(1)	8501(1)	1.82(1)
O(1)	10050(4)	364(4)	8720(2)	2.93(6)
O(2)	9266(5)	2305(4)	7716(2)	2.77(6)
O(3)	10309(4)	3459(3)	8969(2)	2.51(6)
O(4)	7539(4)	1658(3)	9559(1)	2.11(5)
O(5)	6183(4)	969(3)	8227(1)	2.16(5)
O(6)	10685(5)	5913(4)	9188(2)	3.85(7)
O(7)	5279(4)	2407(4)	10278(1)	2.57(6)
O(8)	3641(5)	1349(3)	7525(2)	2.90(6)
N(1)	6622(5)	3784(4)	8579(2)	1.72(6)
N(2)	6413(6)	3365(4)	5226(2)	2.77(7)
N(3)	1796(5)	3459(4)	6590(2)	2.32(7)
C(1)	7879(6)	5133(5)	8531(2)	2.38(8)
C(2)	9741(6)	4857(5)	8932(2)	2.46(8)
C(3)	5541(7)	3761(5)	9241(2)	2.78(9)
C(4)	6175(6)	2493(5)	9730(2)	1.73(7)
C(5)	5320(7)	3550(5)	7974(2)	2.31(8)
C(6)	4963(6)	1840(4)	7895(2)	2.02(7)

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

Table 3. Selected Bond Distances and Angles^a

(a) Selected Bond Distances (Å)			
Bond	Distance	Bond	Distance
V-O(1)	1.653(3)	V-O(2)	1.613(3)
V-O(3)	1.980(3)	V-O(4)	2.225(3)
V-O(5)	1.995(3)	V-N(1)	2.246(3)
(b) Selected Bond Angles (deg)			
Bond	Angle	Bond	Angle
O(1)-V-O(2)	107.1(2)	O(1)-V-O(3)	99.2(2)
O(1)-V-O(4)	85.3(1)	O(1)-V-O(5)	103.2(1)
O(1)-V-N(1)	160.2(1)	O(2)-V-O(3)	96.8(2)
O(2)-V-O(4)	167.6(1)	O(2)-V-O(5)	94.1(2)
O(2)-V-N(1)	92.6(1)	O(3)-V-O(4)	81.8(1)
O(3)-V-O(5)	150.9(1)	O(3)-V-N(1)	77.6(1)
O(4)-V-O(5)	81.9(1)	O(4)-V-N(1)	75.0(1)
O(5)-V-N(1)	75.0(1)		

^a Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameters.

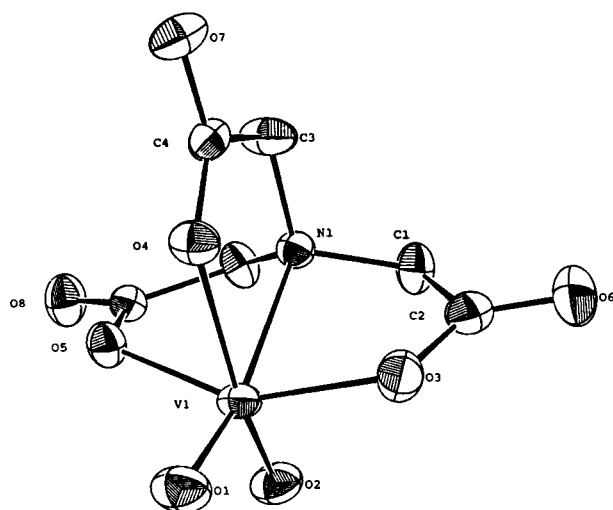


Figure 1. ORTEP of $[\text{VO}_2\text{NTA}]^{2-}$ anion.

from 106.96° in EDTA complex to 107.1° in NTA complex.

The remaining four coordination sites of vanadium atom are occupied by a nitrogen atom and three oxygen atoms of the NTA ligand, giving three five-membered glycinate rings in the complex. Three carboxylate oxygen atoms of the NTA ligand in the complex fall into two groups depending on whether or not they are *trans* to a $\text{V}=\text{O}$ bond. The *trans* $\text{V}-\text{O}$ bond ($2.225 \text{ \AA}$) is significantly longer than the other bonds (1.980 and $1.995 \text{ \AA}$), showing a good illustration of the structural *trans* effect. This lengthening (by $0.237 \text{ \AA}$, averaged) and weakening of $\text{V}-\text{O}$ bond which is *trans* to the oxo ligands can also be found in the crystal structure of vanadium (V)-oxalate complex (by $0.23 \text{ \AA}$).¹¹ This weakening of σ bond strength is reflected throughout the rest of the anion, as the stronger inner $\text{C}-\text{O}$ bonds are adjacent to the weaker $\text{V}-\text{O}$ bonds. It is assumed that the hydrogen bonding to the vanadyl oxygen atoms occurs in the complex, also giving unsymmetric $\text{V}=\text{O}$ bond lengths. The longer bond among the non-equivalent $\text{V}=\text{O}$ bonds is the one which has the stronger hydrogen-bond to it.

The bond length of $\text{V}-\text{N}$ is shorter in NTA complex ($2.246 \text{ \AA}$) than those in EDTA complex (2.359 and $2.366 \text{ \AA}$),¹⁴ indicating stronger bond in NTA complex. Short $\text{V}-\text{N}$ bond would give some reduction of strain within the glycinate rings in the complex. Since a difference of $\sim 0.04 \text{ \AA}$ in $\text{V}-\text{O}$ and $\text{V}-\text{N}$ distance is predicted from consideration of the covalent radii of oxygen and nitrogen,¹⁸ the $\text{V}-\text{N}$ bond seems to be much stronger than the $\text{V}-\text{O}$ bond in the complex. It appeared that the difference ($0.021 \text{ \AA}$) between the

$\text{V}-\text{N}$ distances and $\text{V}-\text{O}$ (carboxylate oxygen), which are *trans* to $\text{V}=\text{O}$ in the NTA complex, is indicative of the lower affinity of VO_2^+ ion for carboxylate oxygen than that for the amino nitrogen. Minor variation in lengths of $\text{C}=\text{O}$ bonds can be attributed to hydrogen bondings with ammonium ions. The oxygens of $\text{C}=\text{O}$ groups are the atoms that are mostly influenced by the environment of the anion.

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