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Synthesis and Crystal Structure of Seven-Coordinate (*trans*-1,2-Cyclohexanediamine-*N*,*N*,*N′*,*N′*-tetraacetato)aquavanadate(III)

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Synopsis. Potassium, sodium, and ammonium salts of $[V(cydta)(H_2O)]^-$ complexes were prepared, where cydta denotes *trans*-1,2-cyclohexanediamine-*N*,*N*,*N′*,*N′*-tetraacetate. Crystal structure analysis of $Na[V(cydta)(H_2O)]\cdot 5H_2O$ revealed that the vanadium(III) atom adopts a capped trigonal-prism structure, a cydta acting as a sexidentate ligand and an aqua ligand occupying the capping position.

Usually vanadium(III) forms complexes with coordination number six.[1)] However, we have recently shown that vanadium(III) forms seven-coordinate complexes with edta and hedtra,[2)] the geometries of which are capped-trigonal prisms.[3—5)] Our current work investigates whether vanadium(III) adopts the same structure with other edta-type aminopolycarboxylates. Here we report the synthesis and crystal structure of a cydta complex of vanadium(III). In contrast to the well known pentagonal bipyramidal structures of iron(III)-EDTA complexes,[6—8)] the iron(III)–CyDTA complex adopts a capped trigonal prismatic structure.[9)] This suggests that vanadium(III)–CyDTA might also adopt a capped trigonal prismatic structure. This hypothesis is experimentally confirmed. The structures of capped trigonal-prism complexes with edta-like ligands are compared.

Experimental

General Procedure. The complexes were prepared under a nitrogen atmosphere. A column (10 mmϕ) of Dowex 50W-X8 (50—100 mesh) was used for exchanging cation in vanadium(III)–CyDTA complex.

Synthesis of $K[V(cydta)(H_2O)]\cdot 2H_2O$ (1a). To a suspension of 7.29 g (20 mmol) of H_4cydta in 50 cm³ of water was added 2.76 g (20 mmol) of potassium carbonate. The addition of VCl_3 (3.15 g, 20 mmol) to the solution results in a dark green gel. Upon addition of 4.00 g of potassium hydrogencarbonate (40 mmol), the gel dissolved and the color of the solution turned to brown. The solution volume was reduced to 20 cm³ by evaporation, and the pale brown precipitate was collected by filtration and washed with water and ethanol successively. Yield 6.67 g (69%). Found: C, 34.56; H, 4.86; N, 5.77%. Calcd for $C_{14}H_{24}KN_2O_{11}V$: C, 34.57; H, 4.97; N, 5.76%.

Syntheses of $Na[V(cydta)(H_2O)]\cdot 5H_2O$ (1b) and $NH_4[V(cydta)(H_2O)]\cdot 4H_2O$ (1c). An aqueous solution (5 cm³) of **1a** (1.0 g, 2.0 mmol) was passed through a column packed with 3.8 cm³ of Na-type cation exchange resin. Brown plate crystals suitable for X-ray diffraction work were obtained by standing the aqueous solution in a methanol vapor. Found: C, 32.74; H, 5.53; N, 4.90%. Calcd for $C_{14}H_{30}N_2NaO_{14}V$: C, 32.07; H, 5.77; N, 5.34%.[10)]

1c was obtained by almost the same procedure as the sodium salt. Found: C, 33.57; H, 6.11; N, 8.00%. Calcd for $C_{14}H_{32}N_3O_{13}V$: C, 33.54; H, 6.43; N, 8.38%.

X-Ray Crystal Structure Determination of 1b. General procedures for data collection and analysis are the same as those described in the previous paper.[5)] Crystal data are listed in Table 1. As one of the sites of water of crystallization was found to be partially occupied, the occupancy factor was also refined to give the value 0.25. Anisotropic temperature factors were applied for the non-hydrogen atoms except for the partially occupied oxygen atom. The coordinates of hydrogen atoms attached to carbon atoms were calculated and fixed.

Table 1. Crystal Data for $Na[V(cydta)(H_2O)]\cdot 5H_2O$

Formula	$C_{14}H_{30}N_2NaO_{14}V$
Fw	524.39
Crystal system	Orthorhombic
Space group	*Pbca*(No. 61)
a/Å	13.806(2)
b/Å	22.799(3)
c/Å	13.472(2)
U/Å³	4240(1)
Z	8
d_{calcd}/g cm^{-3}	1.60
d_{measd}/g cm^{-3}	1.59
μ(Mo $K\alpha$)/cm^{-1}	5.94
Cryst size/mm	0.4×0.3×0.4
Temp/°C	20
2θ range/deg	3—60
Scan mode	ω–2θ
ω-scan width/deg	$1.0+0.35\tan\theta$
No. of unique data	6856
No. of data used with $\lvert F_o\rvert>3\sigma(F_o)$	3057
R [a)]	0.078
R_w [b)]	0.090

a) $R=\sum\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$ b) $R_w=[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$; $w=[\sigma^2(\lvert F_o\rvert)+aF_o^2]^{-1}$, where a is 0.0015.

Results and Discussion

Bond lengths and angles around the vanadium atom were listed in Table 2.[11)] An ORTEP drawing of the $[V(cydta)(H_2O)]^-$ anion is shown in Fig. 1. Cydta acts as a sexidentate ligand and a water molecule occupies the seventh coordination site, thus the geometry is a monocapped twisted trigonal-prism which resembles $[V(hedtra)(H_2O)]$[3)] and $[V(edta)(H_2O)]^-$.[4,5)] The N(1)–O(1)–O(3) and N(2)–O(5)–O(7) planes are almost parallel, the dihedral angle between the planes being 4.1°. The complex has an approximate 2-fold axis through the vanadium–aqua bond, although it has some tendency to form a 4:3 piano stool structure[12)] like edta complexes: planarity of N(1)–N(2)–O(7)–O(1) (deviations from the least-squares plane are 0.15, −0.17, −0.11, and 0.17 Å) is much better than N(1)–N(2)–O(5)–O(3) (0.33, −0.26, −0.28, and 0.27 Å) and the former plane is parallel to O(3)–O(5)–O(W), the dihedral angle between the planes being 3.0°. The cyclohexane ring takes the chair form as expected.

Table 3 compares the torsion angles[13)] of edta and

Table 2. Interatomic Distances and Angles for $Na[V(cydta)(H_2O)]\cdot 5H_2O$ (**1b**)

Bond length	l/Å	Bond length	l/Å
V-N(1)	2.244 (5)	V-N(2)	2.240 (5)
V-O(1)	2.085 (4)	V-O(3)	2.045 (5)
V-O(5)	2.050 (4)	V-O(7)	2.043 (5)
V-O(W1)	2.083 (5)		
Bond angle	**ϕ/deg**	**Bond angle**	**ϕ/deg**
O(1)-V-O(W1)	73.5 (2)	O(3)-V-O(W1)	87.0 (2)
O(5)-V-O(W1)	78.3 (2)	O(7)-V-O(W1)	90.9 (2)
O(W1)-V-N(1)	134.1 (2)	O(W1)-V-N(2)	149.2 (2)
O(1)-V-O(3)	107.1 (2)	O(5)-V-O(7)	92.2 (2)
O(1)-V-O(7)	79.6 (2)	O(3)-V-O(5)	79.9 (2)
O(1)-V-N(1)	72.3 (2)	O(3)-V-N(1)	74.9 (2)
O(5)-V-N(2)	74.0 (2)	O(7)-V-N(2)	77.0 (2)
O(1)-V-O(5)	150.4 (2)	O(3)-V-O(7)	172.0 (2)
O(1)-V-N(2)	130.1 (2)	O(3)-V-N(2)	101.1 (2)
O(5)-V-N(1)	136.3 (2)	O(7)-V-N(1)	111.8 (2)
N(1)-V-N(2)	76.5 (2)		

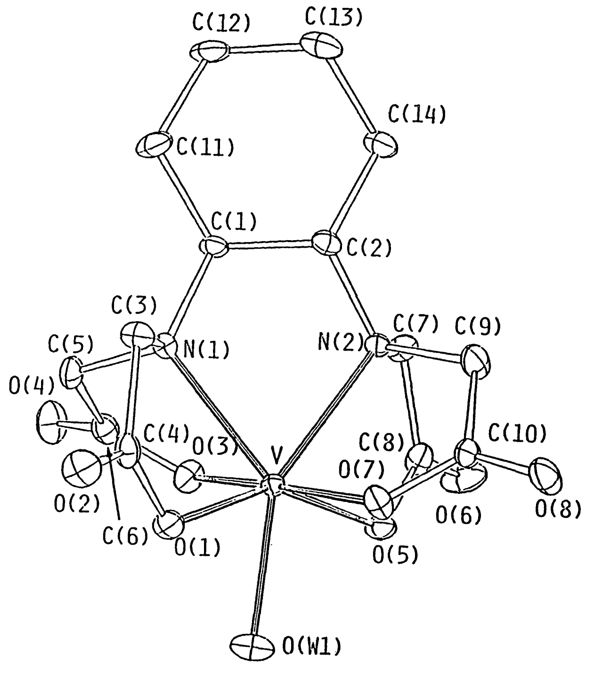

Fig. 1. ORTEP diagram of the $[V(cydta)(H_2O)]^-$ anion in $Na[V(cydta)(H_2O)]\cdot 5H_2O$. Hydrogen atoms are omitted for clarity.

Table 3. Comparison of Torsion Angles of Capped Trigonal-Prismatic Seven-Coordinate Complexes with edta and Related Ligands

Complex	θ_1/deg	θ_2/deg	θ_3/deg
$[V(hedtra)(H_2O)]$[a]	16.25 (6)	11.10 (7)	14.80 (7)
$Na[V(edta)(H_2O)]\cdot 3H_2O$[b]	14.79 (8)	3.49 (8)	21.09 (8)
$NH_4[V(edta)(H_2O)]\cdot 2.5H_2O$[b]	12.2 (1)	2.1 (1)	18.2 (1)
	9.7 (1)	4.2 (1)	18.2 (1)
$Na[V(cydta)(H_2O)]\cdot 5H_2O$[c]	20.0 (2)	13.0 (2)	22.3 (2)
$Ca[Fe(cydta)(H_2O)]\cdot 8H_2O$[d]	26.9 (2)	26.3 (2)	23.4 (2)

a) Ref. 3. b) Ref. 5. c) This work. d) Ref. 9.

edta-related complexes with capped trigonal prism structures. The range of angles is quite wide but all are less than 27°. In pentagonal bipyramidal structures such as $[Fe(edta)(H_2O)]^-$, the corresponding angles are more than 45°.[6–8] A capped trigonal-prism structure is also reported for $[Fe(cydta)(H_2O)]^-$,[9] but the torsion angles for $[Fe(cydta)(H_2O)]^-$ are much larger than those for $[V(cydta)(H_2O)]^-$. The average bond lengths between metal and donor atoms are 2.127 and 2.113 Å for the iron and vanadium complexes, respectively. This difference is slightly larger than that of Shannon's ionic radii ($r_{Fe^{3+}}=0.0645$ Å vs. $r_{V^{3+}}=0.0640$ Å).[14]

The sodium ion is six-coordinate with crystal water molecules and carboxylato oxygen atoms with Na-O bond lengths in the range 2.331 (6)—2.727 (5) Å. The sodium ions and water molecules form a hydrophilic sheet along the [020] plane, and the complex anions are layered between them. The partially occupied water molecule is not connected to any of the surrounding atoms via hydrogen bonding.

Thus, the cydta complex of vanadium(III) also forms a capped trigonal-prismatic seven-coordinate complex as do the edta and hedtra complexes. Although the geometry is more symmetrical than the edta complex, it shows some tendency towards a 4:3 piano stool structure similarly to the edta complex.

References

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2) Abbreviations used in this paper: cydta, *trans*-1,2-cyclohexanediamine-*N,N,N′,N′*,-tetraacetate; edta, ethylenediamine-*N,N,N′,N′*-tetraacetate; hedtra, *N′*-(2-hydroxyethyl)-ethylenediamine-*N,N,N′*-triacetate.

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10) As shown later, the fifth crystal water molecule is easy to effloresce and the analytical values are in better agreement with the calculated ones for $[V(cydta)(H_2O)]\cdot 4.25H_2O$ ($C_{14}H_{28.5}O_{13.25}N_2NaV$): C, 32.91; H, 5.62; N, 5.48%.

11) Final atomic parameters, some additional bond lengths and angles, crystal packing diagram, and F_o-F_c tables are deposited as Document No. 8950 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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

13) Torsion angles θ_1, θ_2, and θ_3 are defined as the dihedral angles N(1)-CE1-CE2-N(2), O(1)-CE1-CE2-O(7), and O(3)-CE1-CE2-O(5), where CE1 and CE2 are the centers of gravity of the triangles N(1)-O(1)-O(3) and N(2)-O(5)-O(7). See Ref. 5.

14) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969); R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).