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Structures and Properties of Vanadium(III) Complexes with 1,2-Diaminoethane-*N*,*N*′-diacetate-*N*,*N*′-dipropionate and *N*,*N*-Bis(carboxymethyl)-*β*-alanate

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The crystal structures of $K[V(eddda)]\cdot 2H_2O$ (**1**) and $[V(\beta\text{-alada})(H_2O)_2]\cdot H_2O$ (**2**) were determined by X-ray crystallography, where eddda and *β*-alada denote 1,2-diaminoethane-*N*,*N*′-diacetate-*N*,*N*′-dipropionate and *N*,*N*-bis(carboxymethyl)-*β*-alanate, respectively. The crystal of **1** is monoclinic, space group $P2_1/n$, $a=10.2753(8)$, $b=11.3007(8)$, $c=15.278(2)$ Å, $\beta=104.857(9)°$, $V=1714.7(3)$ Å^3, $Z=4$, and $R=0.052$. The crystal of **2** is orthorhombic, space group $P2_12_12_1$, $a=7.451(1)$, $b=11.852(2)$, $c=13.403(2)$ Å, $V=1183.6(3)$ Å^3, $Z=4$, and $R=0.053$. Complexes **1** and **2** adopt a hexacoordinate structure in contrast to the heptacoordinate one of the closely related ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate and nitrilotriacetate complexes. Complexes **1** and **2** yield oxo-bridged dinuclear complexes upon base hydrolysis. The reaction of **2** with $CO_3{}^{2-}$ results in the formation of the heptacoordinate species with the bidentate carbonato ligand.

The coordination chemistry of vanadium(III) has attracted considerable interest with regard to the role of vanadium(III) in biological systems.[1,2] From the standpoint of coordination stereochemistry, vanadium(III) is a structurally flexible ion, as demonstrated by its easy access to heptacoordination.[3] Namely, the structures of the vanadium(III) complex with multidentate ligands are significantly influenced by the structures of the ligands. Since the properties of transition metal complexes greatly depend on their structures, it is of importance to know the coordination structures of vanadium(III) complexes with varieties of aminopolycarboxylates, such as ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (edta), nitrilotriacetate (nta), and 1,3-diaminopropane-*N*,*N*,*N*′,*N*′-tetraacetate (trdta).

It has been shown that edta yields the heptacoordinate iron(III)[4] and vanadium(III)[3] complexes due to its insufficiently large bite angles to encircle well an iron(III) or a vanadium(III) ion in an octahedral fashion. It has also been found that the iron(III)[5] and vanadium(III)[6] complexes with trdta adopt a hexacoordinate structure as the result of an elongated diamine chain. However, a large extent of the distortion from the regular octahedron is still recognized in the structures of the iron(III)– and vanadium(III)–trdta complexes. As a consequence, the vanadium(III)–trdta complex is partly aquated in an aqueous solution.[6,7] On the other hand, the vanadium(III) complex with 1,2-diaminoethane-*N*,*N*′-diacetate-*N*,*N*′-dipropionate (eddda), which also has a hexacoordinate structure, is fairly stable in aqueous solution.[7] One concern in this manuscript is to demonstrate the difference in the structural characteristics between K[V(eddda)] and Na[V(trdta)].

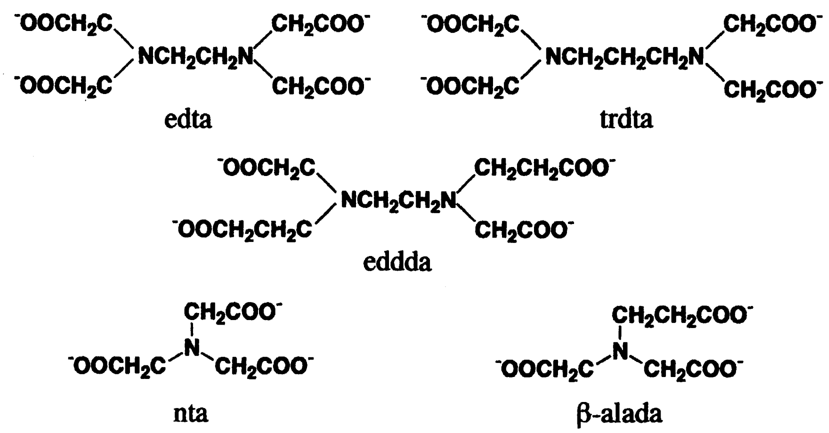
A tripodal quadridentate ligand, nta, also yields a heptacoordinate vanadium(III) as edta, though its coordination polyhedron is a capped octahedron,[8] which is different from that of the edta complex, being a capped trigonal prism.[3] It is, therefore, of interest to examine whether the substitution of an acetate group of nta with a propionate group can change the capped octahedral structure of the nta complex. We herein report on the structure and properties of the vanadium(III) complex with *N*,*N*-bis(carboxymethyl)-*β*-alanate (*β*-alada).

The aminopolycarboxylate ligands related to the present study are illustrated in Scheme 1 along with their abbreviations.

Experimental

Preparation of Ligands. Although Byers and Douglas first prepared eddda ligand,[9] the isolation of this ligand as a free acid has so far not been reported, as far as we know. We isolated H_4eddda by modifying the synthetic method for H_4edtp (1,2-diaminoethane-*N*,*N*,*N*′,*N*′-tetrapropionic acid).[10]

H_2eddp·2HCl (1,2-diaminoethane-*N*,*N*′-dipropionic acid)[10] was reacted with monochloroacetic acid according to a method described in the literature. The reaction solution was cooled to room temperature and acidified to pH 2 by adding concentrated HCl. After a small amount of meth-



Scheme 1.

anol was added to the solution, the solution was cooled in a refrigerator. The crude material which precipitated was filtered and washed with methanol. This crude product was recrystallized from hot water (20 cm^3 of water/1 g of the crude product). Yield 60%. Anal. Calcd for $C_{12}H_{26}N_2O_{11}$= H_4eddda·$3H_2O$: C, 38.50; H, 7.01; N, 7.49%. Found: C, 38.41; H, 6.72; N, 7.44%.

H_3β-alada was prepared according to the literature method.[11)]

Preparation of Complexes. All manipulations of air-sensitive vanadium(III) complexes were carried out under an Ar atmosphere using the Schlenk technique or in a N_2-filled glove box.

Crystallization of K[V(eddda)]·2H$_2$O (1). A reaction solution of K[V(eddda)] obtained by the method described in our previous paper[7)] was evaporated to dryness, and the residue was dissolved in 5 cm^3 of water. To this solution was added 3 cm^3 of ethanol. Blue crystals with a sufficiently good quality for X-ray crystal analysis were obtained by allowing the solution to stand at room temperature for several days.

[V(β-alada)(H$_2$O)$_2$]·H$_2$O (2). A suspension of H_3β-alada (4.1 g, 20 mmol) and $BaCO_3$ (5.9 g, 30 mmol) in 50 cm^3 of water was warmed until the evolution of CO_2 gas stopped. To the suspension was added a solution of $V_2(SO_4)_3$ (3.9 g, 10 mmol). After the mixture was kept standing at 40 °C, precipitated $BaSO_4$ was filtered off. The volume of the filtrate was reduced to 20 cm^3, and cooled in a refrigerator. Deposited green crystals were collected by filtration. Yield 44%. Anal. Calcd for $C_7H_{14}NO_7V$=[V(β-alada)(H_2O)$_2$]·H_2O: C, 27.37; H, 4.59; N, 4.56%. Found: C, 27.13; H, 4.60; N, 4.53%.

Crystals with an appropriate size and quality for X-ray analysis were obtained by slow evaporation of the solution of the complex using $CaCl_2$.

Preparation of K$_6$V$_2$(β-alada)$_2$(CO$_3$)$_3$·7H$_2$O (3). A suspension containing H_3β-alada (1.03 g, 5 mmol) and $BaCO_3$ (1.48 g, 7.5 mmol) was warmed until the evolution of CO_2 gas stopped. To this suspension was added a solution of $V_2(SO_4)_3$ (0.98 g, 2.5 mmol); the mixture was then left standing at 40 °C overnight. Deposited $BaSO_4$ was filtered off. A K_2CO_3 solution (0.25 mol dm^{-3}) was added to the filtrate until the pH of the solution reached 7. During this procedure the color of the solution changed from green to brownish orange. The volume of the solution was reduced to ca. 5 cm^3 by evaporation. Methanol was added to this solution until it became cloudy. The resulting solution was kept standing at 50 °C for several hours to yield yellow needles. Yield 24%. Calcd for $C_{17}H_{30}N_2O_{28}K_6V_2$: C, 19.86; H, 2.75; N, 2.73%. Found: C, 19.68; H, 3.05; N, 2.95%.

Measurements. UV-vis spectra were measured using a JASCO Ubest 50 spectrophotometer. Diffuse reflectance spectra were obtained for complexes diluted with MgO. Raman spectra were recorded on a JASCO R-800 laser Raman spectrophotometer with excitation by an Ar^+-ion laser line (514.5 nm). Infrared spectra were recorded on a JASCO FT/IR-8000S.

X-Ray Structure Determination. The crystallographic data are summarized in Table 1. A crystal of **1** or **2** was mounted on a glass fiber, coated with epoxy as a precaution against solvent loss, and centered on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The unit-cell parameters were determined by a least-squares refinement, using the diffraction angles of 25 reflections in the range of $24<2\theta<42°$ for **1** and in the range of $16<2\theta<20°$ for **2**. Data reduction and the application of Lorentz, polarization, linear decay correction (correction factor on I: 1.00 to 1.01 for **1** and 1.00 to 1.05 for **2**), and empirical absorption corrections based on a series of ψ scans (minimum and maximum transmission factors: 0.92 to 1.00 for **1** and 0.87 to 1.00 for **2**) were carried out.[12)]

The structures were solved by a direct method[12)] and conventional difference Fourier techniques. The structures were refined by full-matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically. All of the calculations were performed on a VAX computer using the crystallographic package MOLEN.[12)] The non-hydrogen atom coordinates for **1** and **2** are listed in Tables 2 and 4, respectively.[13)]

Results and Discussion

eddda Complex. Figure 1 shows a perspective view of [V(eddda)]$^-$, and Table 3 summarizes the selected bond distances and angles. The vanadium(III) ion adopts a hexacoordinate structure, as suggested earlier on the basis of the spectroscopic properties.[7)] It is well known that when edta coordinates to a metal center in an octahedral fashion two in-plane rings (G

Table 1. Crystallographic Data for K[V(eddda)]·H_2O and [V(β-alada)$(H_2O)_2$]·H_2O

	K[V(eddda)]·H_2O	[V(β-alada)$(H_2O)_2$]·H_2O
Formula	$C_{12}H_{20}N_2O_{10}KV$	$C_7H_{14}NO_9V$
Formula wt	442.34	307.13
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a/Å	10.2753(8)	7.451(1)
b/Å	11.3007(8)	11.852(2)
c/Å	15.278(2)	13.403(2)
β/°	104.857(9)	
V/Å^3	1714.7(3)	1183.6(3)
Z	4	4
D_{calcd}/g cm^{-3}	1.71	1.72
Crystal size	0.25×0.30×0.30	0.18×0.45×0.45
λ(Mo $K\alpha$)/Å	0.71073	0.71073
μ(Mo $K\alpha$)/cm^{-1}	8.6	8.5
Scan width/°	1.0+0.47tan θ	0.6+0.35tan θ
Temp/K	296	296
2θ range/°	0—60	0—60
Reflections		
Measured	5484	2007
$F_o > 3\sigma F_o$	4013	1887
F(000)	912	632
No. of variables	235	163
R/%	0.052	0.053 (0.060[a])
R_w/%	0.060	0.102 (0.104[a])

a) Value for the enantiomer.

Table 2. Final Atomic Coordinates and Equivalent Thermal Parameters (B_{eq}/Å^2) for Non-Hydrogen Atoms of K[V(eddda)]·$2H_2O$ ($B_{\text{eq}}=(8\pi^2/3)\Sigma\Sigma U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$)

Atom	x	y	z	B_{eq}
V	0.85242(5)	0.24442(5)	0.15574(4)	1.715(8)
K	0.78493(9)	0.50823(9)	0.49545(6)	3.39(2)
O1	0.6855(2)	0.1554(2)	0.1417(2)	2.47(5)
O2	0.4736(2)	0.1056(3)	0.1204(2)	3.13(6)
O3	0.9595(2)	0.1030(2)	0.1468(2)	2.91(5)
O4	1.1198(3)	−0.0018(3)	0.1126(3)	4.46(7)
O5	0.8358(3)	0.2701(3)	0.0255(2)	2.89(5)
O6	0.7666(4)	0.3838(3)	−0.0955(2)	4.27(7)
O7	0.8785(2)	0.2545(3)	0.2879(2)	2.85(5)
O8	1.0114(3)	0.3102(4)	0.4207(2)	4.37(8)
N1	0.7403(3)	0.4071(3)	0.1349(2)	1.96(5)
N2	1.0266(3)	0.3561(3)	0.1896(2)	1.97(5)
C1	0.5604(3)	0.1823(3)	0.1342(2)	2.05(6)
C2	0.5185(3)	0.3102(3)	0.1409(3)	3.00(8)
C3	0.6262(3)	0.4039(3)	0.1799(3)	2.57(6)
C4	0.8401(3)	0.4982(3)	0.1818(3)	2.52(7)
C5	0.9755(3)	0.4770(3)	0.1586(3)	2.63(7)
C6	1.1296(3)	0.3184(4)	0.1412(3)	2.85(7)
C7	1.1805(3)	0.1923(4)	0.1637(3)	3.31(8)
C8	1.0799(3)	0.0913(3)	0.1375(3)	2.59(7)
C9	0.7701(4)	0.3587(4)	−0.0175(3)	2.76(7)
C10	0.6932(4)	0.4325(4)	0.0363(3)	2.83(7)
C11	0.9865(4)	0.3040(4)	0.3388(3)	2.67(7)
C12	1.0833(3)	0.3551(4)	0.2899(2)	2.55(7)
O1w	0.4648(3)	0.2755(3)	0.3559(3)	4.71(8)
O2w	0.7655(4)	0.7708(4)	0.0513(3)	5.45(9)

rings) are more strained than two out-of plane rings (R rings).[14] As expected, the two six-membered chelate rings in [V(eddda)]$^-$ are situated in the in-plane positions to relax the strain within the ligand coordinated to

Table 3. Selected Bond Distances (Å) and Angles (degree) for K[V(eddda)]·$2H_2O$

	Bond distances		
V -O1	1.952(2)	V -O3	1.964(3)
V -O5	1.974(3)	V -O7	1.970(3)
V -N1	2.149(3)	V -N2	2.142(3)
	Bond angles		
O1 -V -O3	93.7(1)	O1 -V -O5	96.8(1)
O1 -V -O7	91.6(1)	O1 -V -N1	90.1(1)
O1 -V -N2	170.5(1)	O3 -V -O5	87.4(1)
O3 -V -O7	100.8(1)	O3 -V -N1	166.9(1)
O3 -V -N2	92.8(1)	O5 -V -O7	167.9(1)
O5 -V -N1	79.6(1)	O5 -V -N2	90.4(1)
O7 -V -N1	91.7(1)	O7 -V -N2	80.4(1)
N1 -V -N2	85.1(1)		

Table 4. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (B_{eq}/Å^2) for Non-Hydrogen Atoms of [V(β-alada)$(H_2O)_2$]·H_2O ($B_{eq} = (8\pi^2/3)\Sigma\Sigma U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$)

Atom	x	y	z	B_{eq}
V	0.9666(2)	0.0678(1)	0.3606(1)	1.52(2)
O1	1.0064(8)	−0.0649(5)	0.4489(5)	2.2(1)
O2	0.7788(9)	0.1425(6)	0.4445(5)	2.5(1)
O3	0.9087(9)	0.1627(6)	0.2485(6)	2.4(1)
O4	0.968(1)	−0.2482(6)	0.4692(5)	3.4(1)
O5	0.4916(8)	0.1582(6)	0.4728(6)	3.0(1)
O6	0.701(1)	0.2923(6)	0.2082(6)	3.4(2)
O7	1.1414(9)	0.1631(6)	0.4350(6)	2.9(1)
O8	1.1559(9)	−0.0048(6)	0.2688(5)	2.5(1)
N	0.7427(9)	−0.0392(5)	0.3231(5)	1.5(1)
C1	0.935(1)	−0.1608(7)	0.4266(7)	1.9(1)
C2	0.678(1)	−0.0197(8)	0.2182(7)	2.2(2)
C3	0.804(1)	−0.1571(7)	0.3383(6)	1.9(1)
C4	0.597(1)	−0.0145(7)	0.3973(7)	2.0(1)
C5	0.617(1)	0.1050(7)	0.4401(7)	2.0(1)
C6	0.613(2)	0.0984(8)	0.2022(8)	2.9(2)
C7	0.750(1)	0.1919(8)	0.2211(7)	2.1(2)
Ow1	0.802(1)	−0.4394(7)	0.4160(5)	2.9(1)

vanadium(III). The same arrangement has been found in the iron(III)–eddda complex.[5)]

In some cases, the packing mode in crystals affects the coordination structure of transition-metal complexes. For example, both hexa- and heptacoordinate structures were found in the lithium salt of iron(III)–edta complex.[4,15)] In the crystal of the present eddda complex, a potassium ion is surrounded by seven oxygen atoms, of which O1, O2, O4, and O2w are situated at a distance of 2.676—2.790 Å, and O3, O5, and O8 at a distance of 2.976—3.193 Å. Moderately strong hydrogen bonds are recognized between O1w and O2w, and O1w and O4 (average length, 2.76 Å). Weak hydrogen bonds are also found between O1w and O6, O2w and O8, and O2w and O7 (average length, 3.05 Å) A specific interatomic interaction that may influence the coordination structure of $[V(eddda)]^-$ was not discerned.

An examination of the bond distances and angles of $[V(eddda)]^-$ has revealed that the distortion from the regular octahedron is smaller in $[V(eddda)]^-$ than that in $[V(trdta)]^-$. This is well demonstrated by the sum of the deviations of the A–V–B angles from 90° ($\Sigma|\angle(\text{A–V–B})-90°|$, where A, B=N, or O) which amounts to 55.4° in the eddda complex and 74.6° in the trdta complex. This difference explains why although the eddda complex is fairly stable in aqueous solution,[7)] the trdta complex is partly aquated in solution.[6)] The V–O distances in the in-plane rings of the eddda complex (av 1.958 Å) are shorter than those in the trdta complex (av 1.984 Å), reflecting the less distorted in-plane rings of the eddda complex. The V–O distances in the out-of-plane rings of $[V(eddda)]^-$ (av 1.972 Å) are slightly longer than the corresponding ones of $[V(trdta)]^-$ (av 1.957 Å) and the V–N distances are virtually same in the two complexes.

It is of interest to compare the distortion from the regular octahedron between the iron(III) and vanadium(III) complexes with the same chelating ligand. The sum of

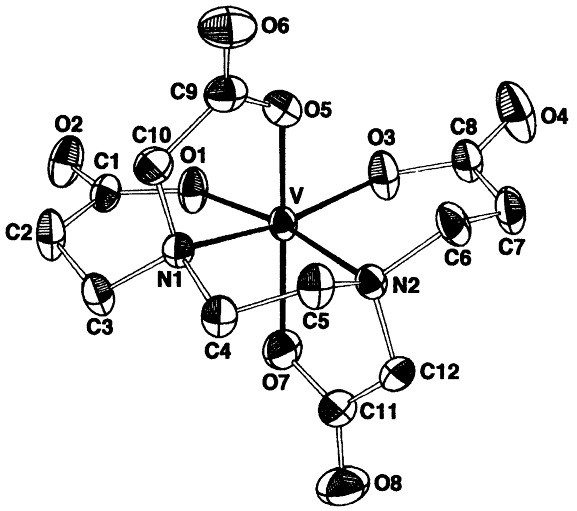


Fig. 1. Perspective view of $[V(eddda)]^-$.

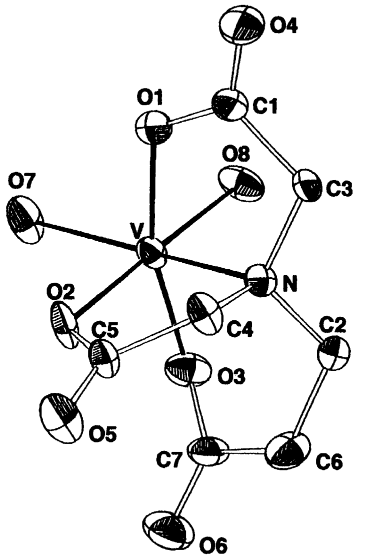


Fig. 2. Perspective view of $[V(\beta\text{-alada})(H_2O)_2]$.

the angle deviations is smaller in the vanadium(III) complexes than in the corresponding iron(III) complexes: 55.4° versus 77.0° for the eddda complexes and 74.6° versus 94.5° for the trdta complexes. This larger distortion of the iron(III) complexes would have resulted from the differences in the ionic radius and the electronic configuration between iron(III) and vanadium(III). Thus, iron(III) ion has a slightly larger ionic radius than does vanadium(III) ion (78.5 pm versus 78 pm), giving rise to a larger distortion in the iron(III) complexes. A deviation from the regular octahedron is unfavorable for the vanadium(III) ion with a d^2 configuration to obtain maximal ligand-field stabilization. On the other hand, the spherical property of a high-spin d^5 configuration of the iron(III) ion does not strictly require an octahedral environment for the ligand-field stabilization.

β-alada Complex. The vanadium(III) complex with nta adopts a heptacoordinate structure.[8] On the other hand, the hexacoordinate structure is suggested for the Fe(III)–nta complex due to the facts that the complex contains only two water molecules,[16] and the hydrolytic dimer adopts a hexacoordinate structure,[17] though the crystal structure has not been determined. This structural difference is curious considering that the vanadium(III) ion is expected to favor an octahedral arrangement to a larger extent than does the iron(III) ion (as discussed above). This question is left to be solved until the detailed structure of the Fe(III)–nta complex is revealed.

As expected from the transformation of the heptacoordinate structure of $[V(edta)(H_2O)]^-$ into the hexacoordinate one of $[V(eddda)]^-$, the substitution of an acetate group of nta by a 3-propionate group would change the coordination structure of the vanadium(III) complex containing a tripodal quadridentate ligand. X-Ray crystallography reveals the hexacoordinate structure of the vanadium(III)–β-alada complex, as shown in Fig. 2 and Table 4. The selected bond distances and angles are summarized in Table 5. The vanadium(III) center is in a rather distorted octahedral environment, as represented by an O1–V–N angle of 77.8°. The sum of the angle deviations from 90° amounts to 60.7°, being larger by ca. 5° than that in $[V(eddda)]^-$, but appreciably smaller than that in $[V(trdta)]^-$.[6]

Moderately strong hydrogen bonds are recognized in the crystal of the β-alada complex. They are Ow1–O1, Ow1–O4, Ow1–O8, O7–O5 (neighboring molecules), and O8–O6 (neighboring molecule), of which the average distance is 2.69 Å. These hydrogen bonds serve to connect adjacent molecules rather than to affect the coordination structure of each molecule.

It may be worth pointing out here that $[V(\beta\text{-alada})(H_2O)_2]$ is spontaneously resolved into its optical isomers, though this matter is irrelevant to the main subject of this study.

We have shown that the hexacoordinate vanadium(III) complexes with an aminopolycarboxylate yield an oxo-bridged dinuclear complex on base hydrolysis while the heptacoordinate ones do not.[7] Figure 3 depicts the pH dependence of the visible absorption spectrum of $[V(\beta\text{-alada})(H_2O)_2]$. The intense band at 442 nm that appears at higher pHs can be assigned to the charge-transfer transition of the V–O–V moiety,[7] indicating the formation of a dinuclear complex. The formation of an oxo-bridged dinuclear complex was also confirmed by the characteristic resonance Raman bands due to the V–O–V moiety: ν_s(V–O–V) appears at 435 cm^{-1}, ν_{as}(V–O–V) at 752 cm^{-1}, and $2\times\nu_{as}$(V–O–V) at 1492 cm^{-1}.

The tendency of the hydrolytic dimerization of $[V(\beta\text{-alada})(H_2O)_2]$ seems to be small compared with that of $[V(eddda)]^-$. The maximal absorbance of the CT band for the 9.5 $mmol\,dm^{-3}$ solution of $[V(\beta\text{-alada})(H_2O)_2]$ was 0.42 at pH 5.52, while that for the solution of $[V(eddda)]^-$ with a similar concentration passed over 1.

Table 5. Selected Bond Distances (Å) and Angles (degree) for $[V(\beta\text{-alada})(H_2O)_2]\cdot H_2O$

	Bond distances		
V -O1	1.991(6)	V -O2	2.002(7)
V -O3	1.926(7)	V -O7	1.992(7)
V -O8	2.061(7)	V -N	2.156(7)
	Bond angles		
O1 -V -O2	96.9(3)	O1 -V -O3	163.4(3)
O1 -V -O7	93.0(3)	O1 -V -O8	85.6(3)
O1 -V -N	77.8(3)	O2 -V -O3	91.4(3)
O2 -V -O7	85.7(3)	O2 -V -O8	177.4(3)
O2 -V -N	81.4(3)	O3 -V -O7	101.9(3)
O3 -V -O8	86.0(3)	O3 -V -N	89.3(3)
O7 -V -O8	95.0(3)	O7 -V -N	163.1(3)
O8 -V -N	95.0(3)		

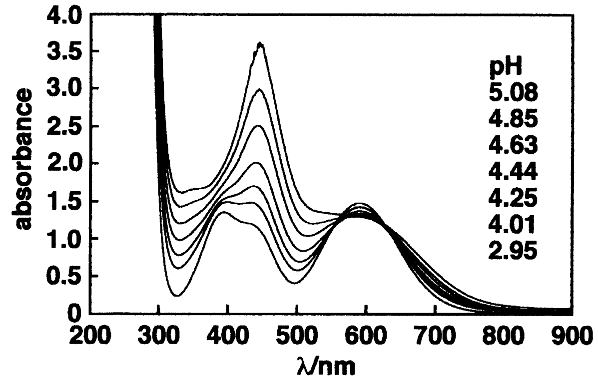


Fig. 3. pH dependence of the visible absorption spectrum of $[V(\beta\text{-alada})(H_2O)_2]$ (49.9 mmol dm^{-3}).

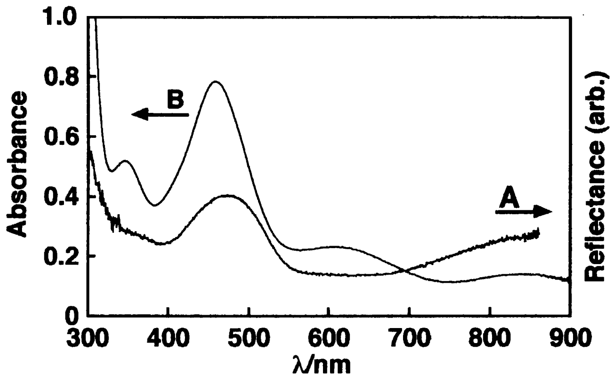


Fig. 4. Diffuse reflectance spectrum of the yellow complex in solid state (A) and the absorption spectrum of the solution containing $[V(\beta\text{-alada})(H_2O)_2]$ (30 mmol dm^{-3}) and $CO_3{}^{2-}$ (30 mmol dm^{-3}) (B).

The distorted structure of $[V(\beta\text{-alada})(H_2O)_2]$ leaves a large area around the coordinated water molecules, which can potentially accommodate a small bidentate ligand. Therefore, a heptacoordinate complex would be obtainable if the coordinated water molecule can be substituted with a small bidentate ligand. We examined the interaction of $[V(\beta\text{-alada})(H_2O)_2]$ with $CO_3{}^{2-}$, $SO_4{}^{2-}$, and $PO_4{}^{3-}$ on the basis of the visible spectra as a function of the concentration of the oxoacidates. Sulfate did not cause any significant change in the visible absorption spectrum of $[V(\beta\text{-alada})(H_2O)_2]$. The addition of phosphate changed the color of the complex solution from dark green to bright green. The isolation of the bright-green complex was unsuccessfully attempted, since a solution containing $[V(\beta\text{-alada})(H_2O)_2]$ and $PO_4{}^{3-}$ readily yielded an insoluble gel-like product. A reaction with carbonate turned the original dark green to brownish yellow, though the addition of an excess amount of carbonate produced small amounts of insoluble product probably due to a formation of vanadium(III) hydroxide. The absorption spectrum of the solution containing $[V(\beta\text{-alada})(H_2O)_2]$ and $CO_3{}^{2-}$ in a 1 : 1 ratio is shown in Fig. 4-B. The yellow complex was isolated from the reaction mixture of $[V(\beta\text{-alada})(H_2O)_2]$ and $CO_3{}^{2-}$, or was directly prepared from V^{3+}, β-alada, and $CO_3{}^{2-}$ (see Experimental section). An elemental analysis suggested the composition of the yellow complex to be $K_6V_2(\beta\text{-alada})_2(CO_3)_3\cdot 7H_2O$. The diffuse reflectance spectrum of the solid yellow complex is shown in Fig. 4-A. The band around 850 nm, observed for the solid sample, is characteristic of heptacoordinate vanadium(III) complexes,[6] indicating that the yellow complex adopts a heptacoordination. The solution spectrum also exhibits a band due to the heptacoordinate species at 840 nm. The band at 458 nm is considered to be the overlap of the band due to the heptacoordinate species, which appears at 471 nm in the solid sample, and the band due to the hexacoordinate one (see, Fig. 3). The band at 610 nm is assignable to the hexacoordinate complex including the oxo-bridged dimer, since there is no distinct band in this region of the spectrum of the solid sample. These spectral features indicate equilibrium between the heptacoordinate species and the hexacoordinate one.

The coordination mode of carbonate can be elucidated from the infrared spectrum. Namely, it has been demonstrated that the two CO stretching vibrations appears in the 1450 and 1370 cm^{-1} regions for [Co-

$(NH_3)_5CO_3]^+$, whereas they appear in the 1600 and 1270 cm^{-1} regions for $[Co(NH_3)_4CO_3]^+$.[18] A comparison of the infrared spectrum of the yellow complex with that of $[V(\beta\text{-alada})(H_2O)_2]$ revealed that the CO stretching vibration of the carbonate ion in the yellow complex is situated at 1544 cm^{-1}, suggesting that in the yellow complex the carbonate ion coordinates bidentately rather than unidentately. Another lower frequency band expected was obscured by the β-alada bands and could not be identified. Taking into account the result of the elemental analysis, the spectroscopic properties, and the structure of $[\{V(\text{bispicen})(SO_4)\}_2(\mu\text{-}SO_4)]$[19] (bispicen=*N*,*N′*-bis(2-methylpyridyl)-1,2-diaminoethane), the yellow complex is likely to be formulated as $K_6[\{V(\beta\text{-alada})(CO_3)\}_2(\mu\text{-}CO_3)]\cdot 7H_2O$, in which the vanadium(III) center adopts a heptacoordination comprised by a quadridentate β-alada, a bidentate $CO_3{}^{2-}$, and a bridging $CO_3{}^{2-}$. In aqueous solution, the bridging carbonate may be replaced by a water molecule to yield a monomeric species.

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