

Structural Identification of the Reactive Vanadium(III) Intermediate Formed in the Electron-Transfer Reactions of [N'-(2-Hydroxyethyl)ethylenediamine-N,N,N'-triacetato]aquavanadium(III) Complex ([V(hedtra)(H₂O)]) with Halogenopentaamminecobalt(III) Complexes: X-ray Crystal Structures of [V(hedtra)(H₂O)]·2H₂O and K[VO(hedtra)]·H₂O

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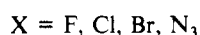
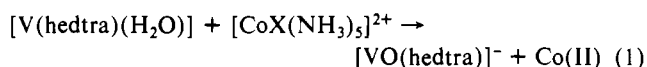
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The structures of the title compounds were determined by single-crystal X-ray structure analyses. [V(hedtra)(H₂O)]·2H₂O was found to be seven-coordinate; hedtra³⁻ (=N'-(2-hydroxyethyl)ethylenediamine-N,N,N'-triacetate) acts as a sixidentate ligand, and the complex contains one water molecule in the first coordination sphere. The complex can be described as a trigonal prism capped with the water ligand. The bond between the vanadium and hydroxyethyl group is the longest among all five V-O bonds. K[VO(hedtra)]·H₂O has a considerably distorted octahedral geometry; hedtra³⁻ acts as a quinquedentate ligand, and the oxo ligand occupies the position trans to the nitrogen atom of the aminodiacetate segment. This nitrogen atom coordinates to vanadium atom only weakly. The reactions of [V(hedtra)(H₂O)] with [CoX(NH₃)₅]²⁺ (X = F, Cl, Br, N₃) were found previously to proceed through the formation of a reactive vanadium(III) intermediate. From the results of the X-ray crystal structure analyses, the structure of the reactive intermediate was estimated to be octahedral; the complex contains quinquedentate hedtra³⁻ and one water molecule in the first coordination sphere. Crystallographic data are as follows: C₁₀H₂₁N₂O₁₀V ([V(hedtra)(H₂O)]·2H₂O), *a* = 14.335 (2) Å, *b* = 9.529 (2) Å, *c* = 11.568 (3) Å, β = 111.83 (1)°, *Z* = 4, monoclinic, space group *Aa*, *R* = 0.035; C₁₀H₁₇KN₂O₉V (K[VO(hedtra)]·H₂O), *a* = 13.023 (3) Å, *b* = 29.529 (8) Å, *c* = 8.168 (2) Å, β = 105.91 (2)°, *Z* = 8, monoclinic, space group *P2₁/c*, *R* = 0.043.

Introduction

Vanadium(III) complexes are attracting much attention particularly because of their biological significance,¹ though vanadium(III) chemistry has been poorly investigated.

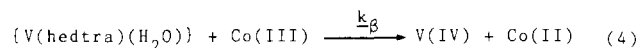
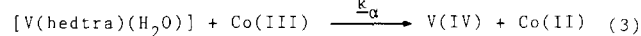
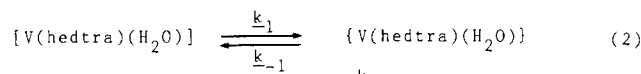
In our efforts to collect some fundamental properties of vanadium(III) complexes, we found that the vanadium(III)-hedtra complex [V(hedtra)(H₂O)]² reduces halogenopentaamminecobalt(III) complexes in acidic hedtra buffer solution (eq 1),³ whereas the reduction of cobalt(III) complexes with [V(H₂O)₆]³⁺ is immeasurably slow.⁴



Reaction 1 obeyed the zeroth-order rate law in the presence of excess vanadium(III) complex. From the kinetic study, we proposed that the rate of the reaction is controlled by the conversion of [V(hedtra)(H₂O)] to a species {V(hedtra)(H₂O)} that is either the deaquated species or an isomer of the parent [V(hedtra)(H₂O)] and that only {V(hedtra)(H₂O)} is reactive toward the electron transfer to [CoX(NH₃)₅]²⁺ complexes (X = F, Cl, Br, N₃). For the reaction of [CoF(NH₃)₅]²⁺, the direct reduction by [V(hedtra)(H₂O)] was also found to contribute to the electron-transfer reaction. Therefore, the general mechanism for the reactions of [V(hedtra)(H₂O)] with [CoX(NH₃)₅]²⁺ can be expressed as in Scheme I.

This paper describes the crystal structure determination for the starting material [V(hedtra)(H₂O)]·2H₂O and the final product K[VO(hedtra)]·H₂O of the reaction. Inferring the structure of a reactive intermediate formed during a chemical reaction is often very dangerous. However, the appropriate combination of the structure determination and the kinetic results may allow one to

Scheme I



identify a convincing structure of the reactive vanadium(III) intermediate {V(hedtra)(H₂O)} formed in reaction 1.

Experimental Section

Materials. The compounds were prepared by the method reported in the previous paper.³ [V(hedtra)(H₂O)]·2H₂O was recrystallized from water to give brown spindle-shaped crystals. K[VO(hedtra)]·H₂O was recrystallized by keeping an aqueous solution of the complex under an acetone atmosphere at room temperature. Two forms of crystals were obtained. At first the solution gave blue needle crystals, and then blue plate crystals grew slowly. Comparison of the unit cell volumes of both crystals showed that the former crystals contain more than one crystalline water molecules per formula,⁵ but they effloresced quite readily. The latter crystals K[VO(hedtra)]·H₂O, which were used for the structure determination, do not effloresce. The efflorescence property of the former crystals might explain the smaller hydration number of the complex prepared in the previous paper (0.25 H₂O) compared to that of the complex used in this work.

X-ray Crystal Structure Determination of [V(hedtra)(H₂O)]·2H₂O and K[VO(hedtra)]·H₂O. Diffraction data were collected on a Rigaku AFC-6A four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Crystallographic and experimental data for both complexes are listed in Table I. The reflection data were corrected for Lorentz and polarization factors. No correction was applied for absorption and extinction. The structure of [V(hedtra)(H₂O)]·2H₂O was solved by the conventional heavy-atom method. The structure of K[VO(hedtra)]·H₂O was solved by using direct methods together with the heavy-atom method. Among solutions of the direct method, the structure that was consistent with the Patterson function was chosen as an initial solution. The parameters were refined by the block-diagonal least-squares method. Anisotropic temperature factors were applied for the

- Oltz, E. M.; Bruening, R. C.; Smith, M. J.; Kustin, K.; Nakanishi, K. *J. Am. Chem. Soc.* **1988**, *110*, 6162-6172 and references cited therein.
- Abbreviations: hedtra³⁻, N'-(2-hydroxyethyl)ethylenediamine-N,N,N'-triacetate; edta⁴⁻, ethylenediamine-N,N,N',N'-tetraacetate; en, ethylenediamine.
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- Parker, O. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 1313-1318.

- Unit cell constants of the former crystal are as follows: *a* = 8.552 (3), *b* = 15.681 (4), *c* = 6.615 (3) Å; α = 96.08 (3), β = 112.87 (4), γ = 74.14 (2)°; *V* = 786.2 Å³. The volume per formula is larger than the latter crystal by 26.4 Å³.

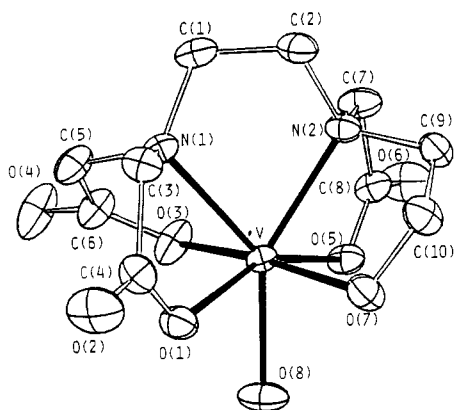


Figure 1. ORTEP drawing of the [V(hedtra)(H₂O)] molecule. Hydrogen atoms are omitted for clarity.

Table I. Crystallographic Data for [V(hedtra)(H₂O)]·2H₂O and K[VO(hedtra)]·H₂O

	[V(hedtra)(H ₂ O)]·2H ₂ O	K[VO(hedtra)]·H ₂ O
formula	C ₁₀ H ₂₁ N ₂ O ₁₀ V	C ₁₀ H ₁₇ KN ₂ O ₉ V
fw	380.23	399.29
space group	Aa (variant of No. 9)	P2 ₁ /c (No. 14)
a/Å	14.335 (2)	13.023 (3)
b/Å	9.529 (2)	29.529 (8)
c/Å	11.568 (3)	8.168 (2)
β/deg	111.83 (1)	105.91 (2)
V/Å ³	1466.9 (2)	3020.7 (13)
Z	4	8
ρ _{obsd} /g cm ⁻³	1.71	1.79
ρ _{calcd} /g cm ⁻³	1.72	1.76
λ/Å	0.71073	0.71073
μ(Mo Kα)/cm ⁻¹	7.80	10.2
T/°C	20	20
R(F _o)	0.035	0.043
R _w (F _o)	0.061	0.082

non-hydrogen atoms. Positions of hydrogen atoms except for those of water molecules were deduced from difference Fourier syntheses and refined with isotropic temperature factors; some of them were fixed at the calculated positions. For [V(hedtra)(H₂O)]·2H₂O, the structure with the inverse chirality was also refined but gave a larger *R* value (3.9%). Atomic scattering factors for non-hydrogen atoms and hydrogen atom were taken from ref 6 and 7, respectively. The calculations were performed on a Nippon Electric Co. ACOS-2000 computer at the Computer Center of Tohoku University using the Universal Computation Program System UNICS III.⁸

Other Measurements. Electronic spectra were recorded on a Hitachi 330 spectrophotometer for aqueous solutions and on a Shimadzu UV-260 spectrophotometer for KBr disks. Infrared spectra were recorded as Nujol mulls on a JASCO IR-810 infrared spectrophotometer.

Results and Discussion

Structure of [V(hedtra)(H₂O)]·2H₂O. Figure 1 shows an ORTEP drawing of the complex molecule. Table II summarizes the positional parameters with equivalent isotropic temperature factors. Relevant bond lengths and angles are listed in Table III and IV.

To our surprise, [V(hedtra)(H₂O)] was found to be a seven-coordinate complex that contains one water molecule in the first coordination sphere. The hedtra³⁻ acts as a sexidentate ligand; even the hydroxyethyl group is coordinated to the vanadium(III) center. As shown in Figure 1, the geometry of the coordination is described as a monocapped trigonal prism with pseudo-C_{2v} symmetry; the aqua ligand occupies the capping position. The plane [O(1)–O(3)–N(1)] and the plane [O(5)–O(7)–N(2)] form the basal planes of the trigonal prism, and they are almost parallel

Table II. Atomic^a and Thermal^b Parameters for [V(hedtra)(H₂O)]·2H₂O and K[VO(hedtra)]·H₂O

atom	x	y	z	B _{eq} /Å ²
[V(hedtra)(H ₂ O)]·2H ₂ O				
V ^c	5000	6993.2 (2)	5000	1.4
O(1)	3987 (1)	7441 (1)	5825 (1)	2.2
O(2)	2753 (2)	6670 (2)	6405 (2)	3.5
O(3)	6315 (1)	6988 (2)	6495 (2)	2.6
O(4)	7123 (1)	6476 (2)	8492 (2)	3.7
O(5)	5970 (1)	7504 (1)	4131 (1)	2.1
O(6)	7173 (2)	6749 (2)	3500 (3)	3.7
O(7)	3712 (1)	7264 (2)	3409 (1)	2.4
O(8)	5069 (2)	9155 (1)	5158 (2)	2.9
O(W1)	6619 (2)	876 (3)	5605 (2)	4.8
O(W2)	3439 (2)	880 (3)	4491 (3)	5.0
N(1)	4900 (1)	5099 (1)	6115 (1)	1.7
N(2)	5026 (1)	5154 (1)	3810 (1)	1.8
C(1)	5208 (1)	3807 (2)	5650 (2)	2.1
C(2)	4756 (2)	3808 (2)	4251 (2)	2.3
C(3)	3848 (1)	5010 (2)	6035 (2)	2.0
C(4)	3482 (1)	6481 (2)	6106 (2)	2.1
C(5)	5560 (1)	5368 (2)	7422 (2)	2.4
C(6)	6404 (1)	6336 (2)	7482 (2)	2.3
C(7)	6055 (1)	5075 (2)	3796 (2)	2.4
C(8)	6438 (1)	6550 (2)	3793 (2)	2.1
C(9)	4321 (1)	5454 (2)	2515 (2)	2.2
C(10)	3375 (1)	6123 (2)	2558 (2)	2.4
K[VO(hedtra)]·H ₂ O				
V(1)	8850.1 (3)	8856.3 (1)	4907 (1)	2.1
K(1)	8044.3 (5)	9822.8 (2)	7866 (1)	2.9
O(11)	10009 (1)	9318 (1)	5308 (2)	2.5
O(12)	11215 (1)	9717 (1)	4473 (3)	3.1
O(13)	7914 (1)	9217 (1)	2998 (2)	2.8
O(14)	7291 (2)	9343 (1)	231 (3)	5.0
O(15)	8040 (1)	8298 (1)	4004 (3)	2.9
O(16)	7972 (2)	7557 (1)	4258 (4)	5.7
O(17)	11063 (2)	7850 (1)	9498 (3)	4.7
O(18)	8409 (2)	8984 (1)	6492 (3)	3.5
O(W1)	10350 (2)	9764 (1)	8479 (3)	5.1
N(11)	9573 (1)	8758 (1)	2644 (3)	2.2
N(12)	10039 (2)	8356 (1)	5996 (3)	2.6
C(11)	10127 (2)	8318 (1)	2960 (4)	3.0
C(12)	10741 (2)	8296 (1)	4851 (4)	3.1
C(13)	10306 (2)	9136 (1)	2637 (3)	2.5
C(14)	10544 (2)	9416 (1)	4245 (3)	2.2
C(15)	8639 (2)	8778 (1)	1140 (3)	2.9
C(16)	7888 (2)	9139 (1)	1433 (4)	3.0
C(17)	9432 (2)	7937 (1)	6094 (4)	3.4
C(18)	8405 (2)	7919 (1)	4660 (4)	3.4
C(19)	10657 (3)	8510 (1)	7739 (4)	3.7
C(110)	11506 (2)	8210 (1)	8762 (5)	4.0
V(2)	3649.9 (3)	8864.4 (1)	4380.9 (5)	1.6
K(2)	2899.9 (5)	9846.5 (2)	7085 (1)	3.1
O(21)	4838 (1)	9298 (1)	5422 (2)	2.2
O(22)	6232 (1)	9711 (1)	5276 (3)	3.0
O(23)	2902 (1)	9286 (1)	2499 (2)	2.3
O(24)	2451 (2)	9436 (1)	-251 (3)	3.8
O(25)	2861 (1)	8371 (1)	2931 (2)	2.3
O(26)	2785 (2)	7639 (1)	2340 (3)	3.5
O(27)	5931 (2)	7620 (1)	7635 (3)	4.1
O(28)	3037 (1)	8934 (1)	5822 (2)	2.7
O(W2)	5120 (2)	9667 (1)	8590 (3)	4.2
N(21)	4672 (1)	8873 (1)	2479 (2)	1.8
N(22)	4722 (1)	8313 (1)	5366 (2)	1.9
C(21)	5272 (2)	8442 (1)	2725 (3)	2.2
C(22)	5650 (2)	8346 (1)	4630 (3)	2.1
C(23)	5375 (2)	9271 (1)	2865 (3)	2.2
C(24)	5513 (2)	9444 (1)	4657 (3)	2.1
C(25)	3904 (2)	8927 (1)	807 (3)	2.3
C(26)	3018 (2)	9240 (1)	1004 (3)	2.3
C(27)	4111 (2)	7886 (1)	4795 (3)	2.5
C(28)	3193 (2)	7960 (1)	3238 (3)	2.3
C(29)	5086 (2)	8346 (1)	7269 (3)	2.7
C(210)	6071 (2)	8077 (1)	8130 (4)	3.2

(6) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp 72–98, and Table 2.3.1, pp 149–150.

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^a Atomic coordinates are multiplied by 10⁴. ^b Given by the equivalent isotropic temperature factors: $B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \bar{a}_i \bar{a}_j$. ^c The vanadium atom is placed at 0.5 in *x* and *z* to define the origin.

(2.20°). These triangles are almost equilateral with a longer base (O···O) and are twisted a little from eclipsed conformation. The

Table III. Interatomic Distances (Å) for [V(hedtra)(H₂O)]·2H₂O

V—O(1)	2.057 (2)	V—O(3)	2.030 (1)
V—O(5)	2.054 (2)	V—O(7)	2.082 (1)
V—O(8)	2.067 (1)	V—N(1)	2.254 (2)
V—N(2)	2.238 (2)		
N(1)···O(1)	2.545 (2)	N(1)···O(3)	2.624 (2)
N(2)···O(5)	2.571 (2)	N(2)···O(7)	2.675 (2)
O(1)···O(3)	3.162 (2)	O(5)···O(7)	3.036 (2)
O(1)···O(7)	2.679 (2)	O(3)···O(5)	2.638 (3)
N(1)···N(2)	2.739 (2)		
O(8)···O(1)	2.561 (3)	O(8)···O(3)	2.791 (2)
O(8)···O(5)	2.588 (3)	O(8)···O(7)	2.863 (2)

Table IV. Bond Angles (deg) for [V(hedtra)(H₂O)]·2H₂O

O(1)—V—O(8)	76.78 (8)	O(3)—V—O(8)	85.89 (7)
O(5)—V—O(8)	77.78 (8)	O(7)—V—O(8)	87.24 (7)
O(1)—V—O(3)	101.38 (7)	O(5)—V—O(7)	94.42 (6)
O(1)—V—O(7)	80.65 (6)	O(3)—V—O(5)	80.46 (7)
O(1)—V—N(1)	72.21 (6)	O(3)—V—N(1)	75.36 (6)
O(5)—V—N(2)	73.43 (6)	O(7)—V—N(2)	76.45 (6)
N(1)—V—N(2)	75.18 (6)		
O(8)—V—N(1)	139.36 (8)	O(8)—V—N(2)	145.43 (9)
O(1)—V—O(5)	154.27 (5)	O(3)—V—O(7)	172.17 (7)
O(1)—V—N(2)	128.64 (5)	O(3)—V—N(2)	107.44 (6)
O(5)—V—N(1)	131.94 (5)	O(7)—V—N(1)	112.39 (6)

deviation of the vanadium atom from the least-squares plane [O(1)—O(3)—O(5)—O(7)] is only 0.29 Å, which is much smaller than those from the other planes of the prism. Thus, the vanadium atom is pulled from the center of the prism toward the capping ligand. The vector V—O(8) is almost perpendicular to the plane [O(1)—O(3)—O(5)—O(7)] (89.3°).

The V—O bond lengths range from 2.030 (1) to 2.082 (1) Å, and the longest V—O(7) bond length indicates that the bond between the vanadium and hydroxyethyl group is weaker than those between the vanadium and the carboxylate and aqua ligands.

Vanadium(III) usually forms six-coordinate complexes, and only K₄[V(CN)₆]·2H₂O⁹ and [enH₂][V(hedtra—H)]₂·H₂O¹⁰ have been so far known to be seven-coordinate complexes. These complexes take distorted pentagonal-bipyramidal structures. The latter dimeric complex contains a deprotonated hedtra⁴⁻ ligand, N'-(2-oxidoethyl)ethylenediamine-*N,N,N'*-triacetato ligand. The bridging atoms are the alkoxy oxygens. The bond lengths of V—O (1.997–2.098 Å) and V—N (2.206–2.278 Å) for [V(hedtra—H)]₂²⁻ are comparable with those for [V(hedtra)(H₂O)]. Quite recently, Na[V(edta)(H₂O)]·3H₂O was also found to have a seven-coordinate configuration.¹¹ Its structure is more distorted from a capped trigonal prism than that of [V(hedtra)(H₂O)], or it may be described as a 4:3 piano stool structure.

[Mn^{II}(edta)(H₂O)] in Mn₃(Hedta)₂·10H₂O was observed to have a structure similar to that of [V(hedtra)(H₂O)]: a capped twist-trigonal prism.¹² [Fe^{III}(edta)(H₂O)]⁻ is also known to have a seven-coordinate structure, but it has a pentagonal-bipyramidal structure.¹³

Judging from the fact that vanadium(III)-, manganese(II)-, and iron(III)-edta complexes as well as the vanadium(III)-hedtra complex take seven-coordinate structures, first-row transition-metal ions have a tendency to form seven-coordinate structure with edta-like ligands. In other words, edta and hedtra are insufficient to saturate the coordination ability of these metal ions. This suggests that edta and hedtra are too small to wrap up these metal ions. Chromium(III)-edta and -hedtra complexes undergo abnormally fast ligand substitution with various anions (X⁻) to form [CrX(edta)]²⁻ and [CrX(hedtra)]⁻.¹⁴ On the assumption that

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Table V. Interatomic Distances (Å) for K[VO(hedtra)]·H₂O

V(1)—O(11)	1.994 (2)	V(2)—O(21)	2.010 (2)
V(1)—O(13)	2.003 (2)	V(2)—O(23)	2.010 (2)
V(1)—O(15)	1.987 (2)	V(2)—O(25)	1.979 (2)
V(1)—O(18)	1.598 (3)	V(2)—O(28)	1.606 (2)
V(1)—N(11)	2.311 (2)	V(2)—N(21)	2.306 (2)
V(1)—N(12)	2.149 (2)	V(2)—N(22)	2.153 (2)

the chromium(III)-edta or -hedtra complex contains one water molecule in the first coordination sphere and that the coordinated edta⁴⁻ or hedtra³⁻ in the chromium(III) complex acts as a quinque-dentate ligand, we proposed that the reactions proceed through seven-coordinate intermediates in which the pendant CH₂COO⁻ or CH₂CH₂OH group coordinates to the chromium(III) center.^{14–16} The fact that some first-row transition-metal ions form seven-coordinate structures easily with edta or hedtra provides an indirect support for the proposal that the transient coordination of the pendant group labilizes the sixth coordination position of chromium(III) ion.

Structure of K[VO(hedtra)]·H₂O. The positional parameters are listed in Table II. The crystal consists of two crystallographically independent [VO(hedtra)]⁻ ions. As shown in Figure 2 and Tables V and VI, the structures of the two complex anions are almost the same, with small difference in the direction of the hydroxyethyl group. The hedtra³⁻ acts as a quinque-dentate ligand with a pendant hydroxyethyl group. The structure of [VO(hedtra)]⁻ is that of a considerably deformed octahedron, and a strong trans influence is observed in the complex: The V—N bond trans to V=O is much longer (by 0.153 and 0.162 Å) than the V—N bond cis to V=O, and the nitrogen atom trans to V=O coordinates to the vanadium atom only weakly. Hence, the coordination geometry might be rather described as a square pyramid. The vanadium atom deviates from the least-squares basal plane by about 0.40 Å in the direction of the oxo ligand. This is the general feature for octahedral or square-pyramidal vanadium(IV)-oxo complexes.²² This structure remarkably resembles that of Ba[VO(edta)]·6H₂O²³ in not only the bond lengths but also the configuration around the vanadium center.

For octahedral [Co(edta)]⁻ complex glycinato rings were found to be strained, and this strain is manifested more in the G rings (in equatorial plane) than in the R rings (in axial position).²⁴ [VO(hedtra)]⁻ as well as [VO(edta)]²⁻ has two R rings and one G ring, oxo ligand occupying the position in the equatorial plane instead of a more strained G ring. This configuration is apparently more stable than that with two G rings and one R ring.

The average bond length of V—O(carboxylato) in [VO(hedtra)]⁻ is 1.997 (12) Å and is shorter than that of [V(hedtra)(H₂O)] (2.047 (12) Å). The difference (0.05 Å) corresponds to that of Shannon's effective ionic radii (*r*_{V³⁺} = 0.78, *r*_{V⁴⁺} = 0.72 Å).²⁵

Infrared Spectra. K[VO(hedtra)]·H₂O showed a band at 3390 cm⁻¹ in the region of ν(OH). On the other hand, [V(hedtra)(H₂O)]·2H₂O showed a very broad band ranging 3600–3000 cm⁻¹ with peaks at 3500, 3390, and 3190 cm⁻¹. The peak of the

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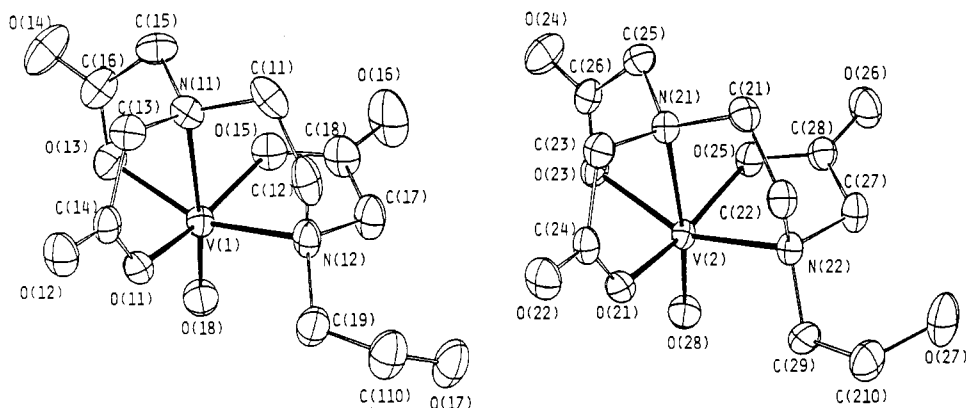


Figure 2. ORTEP drawings of the [VO(hedtra)]⁻ ions. Hydrogen atoms are omitted for clarity.

Table VI. Bond Angles (deg) for K[VO(hedtra)]·H₂O

O(11)-V(1)-O(13)	92.03 (7)	O(21)-V(2)-O(23)	94.81 (7)
O(13)-V(1)-O(15)	90.23 (8)	O(23)-V(2)-O(25)	86.30 (7)
O(15)-V(1)-N(12)	80.35 (7)	O(25)-V(2)-N(22)	81.00 (7)
O(11)-V(1)-N(12)	88.60 (7)	O(21)-V(2)-N(22)	88.80 (7)
O(11)-V(1)-N(11)	76.17 (8)	O(21)-V(2)-N(21)	76.01 (7)
O(13)-V(1)-N(11)	74.81 (8)	O(23)-V(2)-N(21)	74.09 (7)
O(15)-V(1)-N(11)	83.71 (8)	O(25)-V(2)-N(21)	84.61 (7)
N(11)-V(1)-N(12)	80.77 (8)	N(21)-V(2)-N(22)	79.92 (7)
O(11)-V(1)-O(18)	97.45 (10)	O(21)-V(2)-O(28)	95.08 (8)
O(13)-V(1)-O(18)	103.20 (10)	O(23)-V(2)-O(28)	104.35 (8)
O(15)-V(1)-O(18)	102.95 (10)	O(25)-V(2)-O(28)	104.57 (8)
O(18)-V(1)-N(12)	101.83 (10)	O(28)-V(2)-N(22)	102.96 (9)
O(11)-V(1)-O(15)	158.39 (9)	O(21)-V(2)-O(25)	159.43 (8)
O(13)-V(1)-N(12)	154.66 (9)	O(23)-V(2)-N(22)	152.00 (8)
O(18)-V(1)-N(11)	173.13 (9)	O(28)-V(2)-N(21)	170.66 (8)

lowest frequency may be assigned to $\nu(\text{OH})$ of the coordinated hydroxyethyl group, because $\nu(\text{OH})$ of alcohol was reported to shifted to lower frequency on coordination.²⁶ But $\nu(\text{OH})$ of coordinated alcohol was also reported to be influenced by the counterions;²⁷ more investigation is required to employ $\nu(\text{OH})$ as a criterion for coordination of hydroxyethyl group.

Structure of the Reactive Intermediate in the Electron-Transfer Reactions between [V(hedtra)(H₂O)] and [CoX(NH₃)₅]²⁺. The electronic spectrum of [V(hedtra)(H₂O)] in an aqueous solution showed maximum absorptions at 454 ($\epsilon = 19.4$), 530 (10.3) and 755 nm ($9.2 \text{ M}^{-1} \text{ cm}^{-1}$),²⁸ and the solid-state spectrum (KBr disk) also showed the corresponding peaks. This indicates that the major component in the solution has the same structure as that in the crystal: seven-coordinate monocoordinated trigonal prism.

In the previous paper,³ we reported that reaction 1 showed a kinetic anomaly as described above. It was assumed previously that the {V(hedtra)(H₂O)} intermediate reactive toward [CoX(NH₃)₅]²⁺ is either the deaquated species or an isomer of the parent [V(hedtra)(H₂O)]. However, it is quite unlikely that {V(hedtra)(H₂O)} is the deaquated species, because the immediate product of the k_{β} path is an energetically very unfavorable [V^{IV}(hedtra)] in which hedtra³⁻ acts as a sexidentate ligand. The [V^{IV}(hedtra)] species must abstract an oxide ion from water to give the final product [VO(hedtra)]⁻. If we take into consideration the weakness of the V-O(hydroxyethyl) bond, it is most likely that {V(hedtra)(H₂O)} is the six-coordinate species, where the hydroxyethyl group is detached from the vanadium center and one water molecule occupies the coordination position trans to the nitrogen atom in the aminodiacetate segment. The structure of {V(hedtra)(H₂O)} is more productlike than the reactant [V(hedtra)(H₂O)]: The reactant contains a sexidentate hedtra³⁻, while {V(hedtra)(H₂O)} and the product [VO(hedtra)] contain quinquedentate hedtra³⁻. Both the coordinated water ligand in

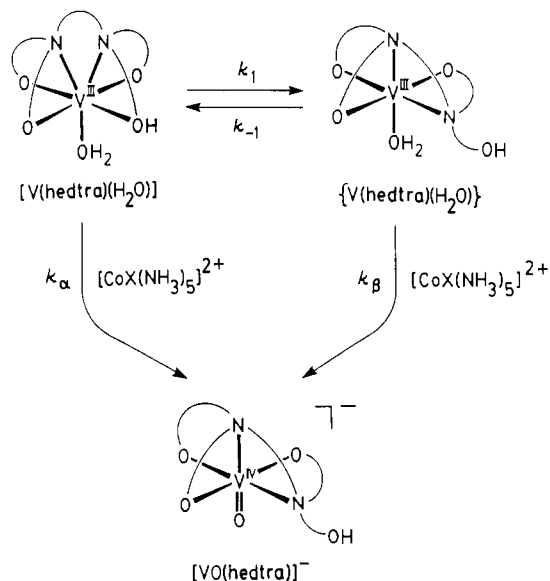


Figure 3. Structural presentation of the scheme for the electron-transfer reaction of [V(hedtra)(H₂O)] with [CoX(NH₃)₅]²⁺.

the former complex and the oxo ligand in the latter complex occupy the coordination position trans to the nitrogen atoms in the aminodiacetate segment. The reaction scheme may be drawn as given in Figure 3. The seven-coordinate [V(hedtra)(H₂O)] is in equilibrium with the thermodynamically less stable six-coordinate {V(hedtra)(H₂O)}. The k_1 path is the rearrangement process to form the six-coordinate complex. In the k_{β} path, {V(hedtra)(H₂O)} thus formed is converted to the product [VO(hedtra)]⁻ by transfer of an electron to a cobalt(III) complex accompanied with the liberation of two protons from the aqua ligand. This process does not need substantial inner-sphere rearrangement. On the other hand, the k_{α} path needs more energy because this reaction requires electron transfer, liberation of two protons from the aqua ligand, and very large inner-sphere rearrangement. Thus, the k_{β} path is more favorable than the k_{α} path. On the whole, the k_1 - k_{β} route is more favorable than the k_{α} path even at the expense of the k_1 path. For the reaction of [CoF(NH₃)₅]²⁺, however, it should be noted that the direct bimolecular electron transfer between [V(hedtra)(H₂O)] and [CoF(NH₃)₅]²⁺ was detected as a minor pathway.³

Thus, the reactive intermediate whose existence was suggested by the kinetic analysis is reasonably estimated to be a six-coordinate V(III)-hedtra complex containing a water ligand from the structural study of the starting complex [V(hedtra)(H₂O)] and the final product [VO(hedtra)]⁻.

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Supplementary Material Available: Tables SI-SIX, containing a full tabular presentation of crystallographic and experimental data, additional atomic parameters, and complete lists of interatomic distances and bond

angles (15 pages); Tables SX and SXI, containing F_o-F_c values for $[V(\text{hedtra})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ and $\text{K}[\text{VO}(\text{hedtra})] \cdot \text{H}_2\text{O}$ (27 pages). Ordering information is given on any current masthead page.

Notes

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Monomer-Dimer Equilibrium of Copper(II) Decanoate in Benzene Containing Decanoic Acid

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Polymerization and adduct formation are quite common to metal carboxylates² and play a very important role in understanding their stability and reactivity in solutions. Copper(II) carboxylates are particularly interesting because they are present almost exclusively as a dimer and give adduct compounds not only in the solid state but also in organic solvents.³ Thus Kochi and Subramanian have determined the dimerization constant as $\log K'_{\text{dim}} = 3.24$ at 57 °C from kinetic data for copper(II) acetate in glacial acetic acid.⁴ Extrapolation of their data to 25 °C results in $\log K'_{\text{dim}} = 4.1$, which seems too low, judging from spectral changes of the complex in the UV region.⁵ Another evidence for the dissociation of copper(II) acetate in this solvent has been given by the two groups⁶⁻⁹ as a function of water or alcohol concentration. Dissociation of copper(II) decanoate in solvating solvents has recently been studied by means of the solvent extraction method¹⁰⁻¹² and potentiometry.¹³ The results from these studies show that solvent molecules with strong coordination power replace the solvating carboxylic acids to give rise to breakdown of the dinuclear structure. On the other hand, a previous extraction study has clearly revealed partial dissociation of the copper(II) decanoate dimer in benzene, which is a typical nonsolvating solvent, with $\log K'_{\text{dim}}$ of about 6.¹⁴ At that time, however, only a semiquantitative conclusion could be drawn concerning the chemical formula of the monomeric species and the corresponding equilibrium constant, since the equilibrium lies so far to the dimer that it is inevitable to work at extremely low levels of copper(II) concentrations. Modern development of equipment has enabled us to determine a very low concentration of copper(II) with accuracy, and in this paper, we report some results on the dissociation of the dimeric copper(II) decanoate in benzene containing decanoic acid from a solvent extraction study.

Experimental Section

Reagents. *n*-Decanoic acid (chemically pure) was double distilled, and the middle fraction distilling at 269–271 °C was collected. Its purity turned out to be 99.5 ± 0.5% from alkalimetry. Copper(II) perchlorate was prepared by dissolving copper metal (99.99%) in hot aqueous perchloric acid. The copper(II) perchlorate hydrate crystallized from water was dissolved in a 0.1 mol dm⁻³ sodium perchlorate aqueous solution. The dilute copper(II) solution was freshly prepared and its concentration was determined colorimetrically by the use of 1-(2-pyridylazo)-2-naphthol as a chromogenic reagent. Sodium perchlorate (analytical grade) was recrystallized from water after precipitation of heavy metal impurities as hydroxides. All other chemicals were of analytical grade and used without further purification.

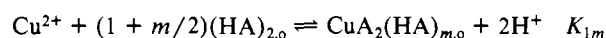
Measurements. All measurements were performed in a room thermostated at 25 ± 0.5 °C. Partition of copper(II) was carried out at 1 × 10⁻⁴ mol dm⁻³ initial concentration of copper(II) in the aqueous phase and 0.25–2 mol dm⁻³ decanoic acid in the organic phase. The ionic strength in the aqueous phase was kept constant at 0.1 mol dm⁻³ in (Na,H)ClO₄. A portion (15 cm³) of the aqueous phase was equilibrated with an organic phase of equal volume in a 50 cm³ stoppered centrifuge tube by vigorous shaking for 1 h in a water bath at 25.0 ± 0.2 °C. Hydrogen ion concentration was measured with an Orion M-901 microprocessor ionalyzer. The pH reading of the equipment was converted to hydrogen ion concentration by using a calibration curve prepared in advance. The copper(II) content in an aliquot of organic phase was back-extracted quantitatively with 10 cm³ of 0.1 mol dm⁻³ hydrochloric acid by shaking for 10 min, followed by the determination of the copper(II) concentration by anodic stripping voltammetry.¹⁵ A Yanaco P-1100 polarographic analyzer was employed for preelectrolysis and for monitoring current-voltage curves. A glassy-carbon electrode, GC-30 (5 mm o.d. × 50 mm), was used as a working electrode for stripping analysis. The relative error was about 3% at the 5 × 10⁻⁸ mol dm⁻³ level of copper(II) concentration after blank correction.

Results and Discussion

The dominant copper(II) decanoate species is dimeric in most nonpolar solvents according to the literature so far published,^{2,3} though the previous study has unambiguously shown the dissociation into monomers to a certain extent.¹⁴ When monomeric and dimeric copper(II) decanoates are denoted as $\text{CuA}_2(\text{HA})_m$ and $\text{Cu}_2\text{A}_4(\text{HA})_n$, respectively, the total copper(II) concentration in the organic solution, $C_{\text{M},o}$, is written as

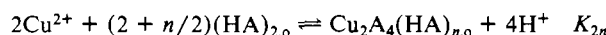
$$C_{\text{M},o} = \sum_m [\text{CuA}_2(\text{HA})_m]_o + 2 \sum_n [\text{Cu}_2\text{A}_4(\text{HA})_n]_o \quad (1)$$

where the subscript o refers to the organic phase. Extraction of the respective species may be formulated as follows:



$$K_{1m} = [\text{CuA}_2(\text{HA})_{m,o}][\text{H}^+]^2 / [\text{Cu}^{2+}][(\text{HA})_{2,o}]^{(1+m/2)} \quad (2)$$

and



$$K_{2n} = [\text{Cu}_2\text{A}_4(\text{HA})_{n,o}][\text{H}^+]^4 / [\text{Cu}^{2+}]^2[(\text{HA})_{2,o}]^{(2+n/2)} \quad (3)$$

Substitution of eq 2 and 3 into eq 1 gives

$$C_{\text{M},o}[\text{H}^+]^2 / [\text{Cu}^{2+}] = \sum_m K_{1m}[(\text{HA})_{2,o}]^{(1+m/2)} + 2 \sum_n K_{2n}[(\text{HA})_{2,o}]^{(2+n/2)}[\text{Cu}^{2+}] / [\text{H}^+]^2 \quad (4)$$

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