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Synthesis and Structures of Vanadium–Cerium Trinuclear Complexes with Schiff-Base Ligands

Masanobu Tsuchimoto,*[1] **Toshio Ishii,**[2] **Takane Imaoka,**[3] **Kimihisa Yamamoto,**[3]
Naoki Yoshioka,[4] **and Yukinari Sunatsuki**[5]

[1]Department of Life and Environmental Sciences, Chiba Institute of Technology,
2-1-1 Shibazono, Narashino 275-0023

[2]Department of Chemistry, Faculty of Engineering, Chiba Institute of Technology,
2-1-1 Shibazono, Narashino 275-0023

[3]Department of Chemistry, Faculty of Science and Technology, Keio University,
3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522

[4]Department of Applied Chemistry, Faculty of Science and Technology, Keio University,
3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522

[5]Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530

Received February 27, 2006; E-mail: tmoto@sea.it-chiba.ac.jp

A vanadium(V)–cerium(IV) trinuclear complex, $[\{V^{V}O_2(L_1)\}_2Ce^{IV}]$ (**1**) (H_3L_1: *N*,*N′*-bis-3-ethoxysalicylidene-2-hydroxy-1,3-propanediamine), was prepared by the reaction of $[V^{IV}O(acac)_2]$ and $[Ce^{III}(acac)_3]\cdot 3H_2O$ with H_3L_1 in CH_3CN, followed by oxidation of the product in air. The structure of complex **1** was determined by X-ray crystal structure analysis. The complex has a V^{V}–Ce^{IV}–V^{V} trinuclear structure with two dioxovanadium(V) moieties on each side of the cerium(IV) moiety. Complex **1** has two L_1 ligands to form a trinuclear structure. The basal oxo atoms of the dioxovanadium(V) moieties are coordinated to the cerium atom with Ce–O distances of 2.322(3) and 2.343(3) Å. The apical two non-coordinating oxo atoms are oriented to the same direction to form an *endo* structure. IR data of complex **1** show V=O stretching bands at 975 cm^{-1} for the apical non-coordinated oxo atoms and 802 cm^{-1} for the basal coordinated oxo atoms. The cyclic voltammogram of complex **1** in CH_3CN shows a quasi-reversible two-electron redox couple with $E_{1/2} = -0.60$ V vs Fc/Fc^{+}.

Recently, heteronuclear metal complexes with transition metal and lanthanide ions have been extensively studied because of their magnetic[1–3] and fluorescence[4] properties. For 3d–4f mixed-metal complexes with the Schiff-base ligands, like 3-MeOsalen ($H_2$3-MeOsalen: *N*,*N′*-bis-3-methoxysalicylidene-1,2-ethanediamine), preparation and magnetic properties of dinuclear V^{IV}–Gd^{III},[5] Cu^{II}–Ln^{III} $\{Ln^{III} = Gd^{III}$, Ce^{III}, and $Yb^{III}\}$,[6–8] Ni^{II}–Ln^{III} $\{Ln^{III} = Gd^{III}$ and $Dy^{III}\}$[8,9] complexes have been reported. In these complexes, two phenolate oxygen and two methoxy oxygen atoms of the [M(L)] (M = VO, Cu, and Ni; L: Schiff-base ligand) moiety are coordinated to a Ln^{3+} ion to form a $[M(L)Ln]^{3+}$ dinuclear structure. However, different structures and properties are expected for 3d–4f mixed-metal complexes with the Schiff-base ligands that have another alcohol group (Fig. 1). This study reports the preparation and structures of new vanadium(V)–cerium(IV) heteronuclear complexes, $[\{V^{V}O_2(L_1)\}_2Ce^{IV}]$ (**1**) (H_3L_1: *N*,*N′*-bis-3-ethoxysalicylidene-2-hydroxy-1,3-propanediamine) and $[\{V^{V}O_2(L_2)\}_2Ce^{IV}]$ (**2**) (H_3L_2: *N*,*N′*-bis-3,5-*tert*-butylsalicylidene-2-hydroxy-1,3-propanediamine). As vanadium and cerium complexes often have more than one oxidation state, several oxidation states are also expected for the heteronuclear complexes. Electrochemical properties for the complexes are also discussed.

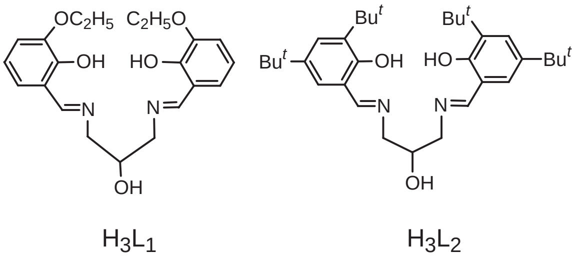

Fig. 1. H_3L_1 and H_3L_2.

Results and Discussion

Synthesis and Structures. Brown vanadium(V)–cerium(IV) heteronuclear complexes, $[\{V^{V}O_2(L_1)\}_2Ce^{IV}]$ (**1**) and $[\{V^{V}O_2(L_2)\}_2Ce^{IV}]$ (**2**) were prepared by the reaction of $[V^{IV}O(acac)_2]$ and $[Ce^{III}(acac)_3]\cdot 3H_2O$ with the Schiff-base ligand in CH_3CN, followed by oxidation of the product in air. Complex **1** was also obtained by the reaction of $[V^{IV}O(HL_1)]$ with $[Ce^{III}(acac)_3]\cdot 3H_2O$ in CH_3CN, followed by oxidation of the product in air.[10,11]

The structure of complex **1** was determined by X-ray crystal structure analysis (Fig. 2). The complex has a V^{V}–Ce^{IV}–V^{V} trinuclear structure with two dioxovanadium(V) moieties

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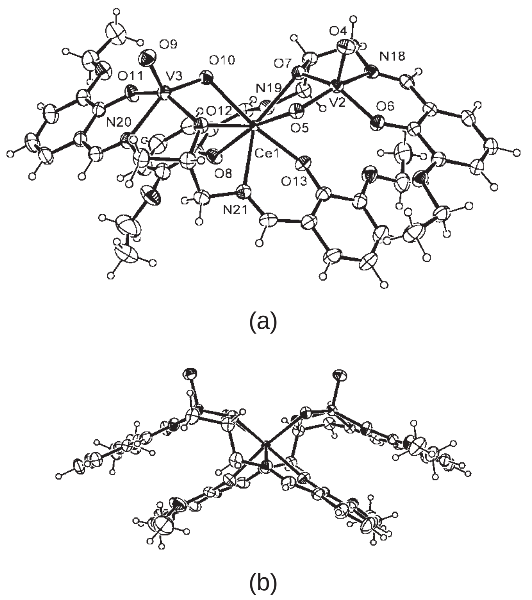
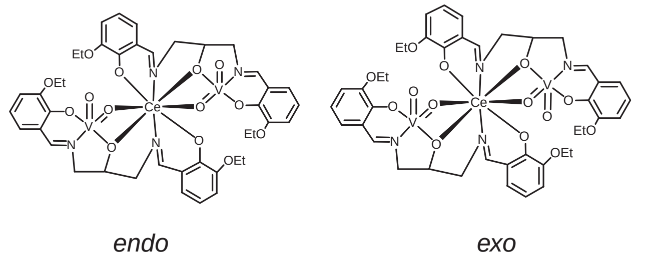


(a)

(b)

Fig. 2. (a) ORTEP drawing and (b) side view of complex **1** with 30% probability ellipsoids. Water and DMSO molecules are eliminated. Selected bond lengths (Å): Ce1–O5 2.322(3), Ce1–O7 2.399(2), Ce1–O8 2.178(3), Ce1–O10 2.343(3), Ce1–O12 2.400(3), Ce1–O13 2.176(3), Ce1–N19 2.548(3), Ce1–N21 2.525(3), V2–O4 1.599(3), V2–O5 1.709(3), V2–O6 1.851(3), V2–O7 1.949(2), V2–N18 2.135(3), V3–O9 1.587(3), V3–O10 1.712(3), V3–O11 1.859(3), V3–O12 1.944(3), V3–N20 2.115(3).



endo *exo*

Fig. 3. Two possible isomers for **1**.

on each side of the cerium(IV) moiety. Two L_1 ligands are coordinated to the cerium atom with phenolate oxygen (O8 and O13), imine nitrogen (N19 and N21), and alcoholate oxygen (O7 and O12) atoms. Coordination of two Schiff-base ligands to a central cerium(IV) ion is also observed for [Ce(5-Clsalen)$_2$] ($H_2$5-Clsalen: *N*,*N'*-bis-5-chlorosalicylidene-1,2-ethanediamine) and other cerium(IV) complexes with tetradentate Schiff-base ligands.[12] The central cerium(IV) moiety has an eight-coordinate square-antiprismatic structure, and both of the dioxovanadium(V) moieties have a five-coordinate square-pyramidal structure. Basal oxo atoms of the dioxovanadium(V) moieties (O5 and O10) are coordinated to the cerium atom with Ce1–O5 and Ce1–O10 distances of 2.322(3) and 2.343(3) Å, respectively. The vanadium–basal oxo atom distances of complex **1** (V2–O5: 1.709(3) Å, V3–O10: 1.712(3) Å) are longer than those of monomeric dioxovanadium(V) complexes with a tridentate Schiff-base ligand (1.659(1)–1.675(3) Å), and the vanadium–apical oxo atom distances of complex **1** (V2–O4 1.599(3) Å, V3–O9 1.587(3) Å) are shorter than those of monomeric dioxovanadium(V) complexes (1.607(1)–1.621(5) Å).[13] Two apical non-coordinated oxo atoms (O4 and O9) are oriented to the same direction to form an *endo* structure (Fig. 3). The Ce1···V2 and Ce1···V3 distances are 3.274(1) and 3.292(1) Å, respectively, and the V2···V3 distance is 5.800(1) Å.

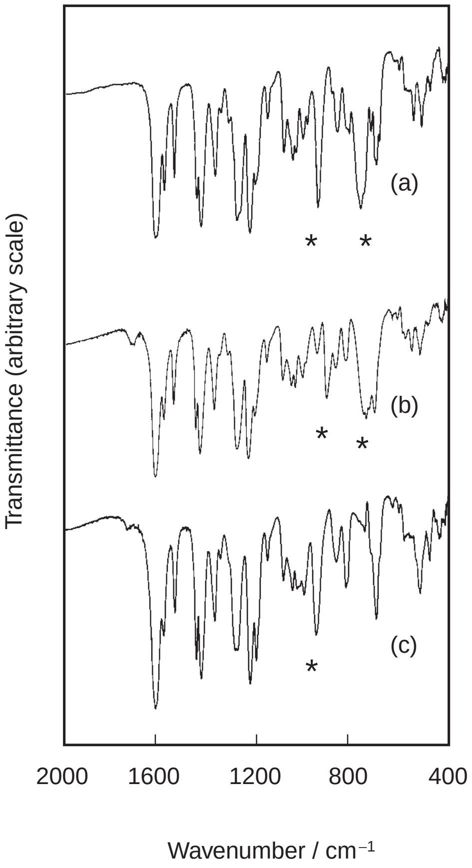


Fig. 4. IR spectra of (a) complex **1**, (b) ^{18}O-labelled complex **1**, (c) complex $\mathbf{1_{Red}}$. The V=O stretching bands are shown in the figures with asterisks.

To assign the V=O stretching bands, ^{18}O-labelled complex **1** was prepared by the reaction of the complex with $H_2{}^{18}O$ in dry acetonitrile.[14–16] The oxygen atom exchange reaction between the oxo ligands of complex **1** and $H_2{}^{18}O$ proceeded very slowly. The ^{18}O-labelled complex **1** was obtained after stirring the reaction mixture for 10 days at 30 °C.[17] Figure 4 shows the IR spectra of complex **1** and ^{18}O-labelled complex **1**. The spectrum of the ^{18}O-labelled complex **1** in Fig. 4b shows two new strong broad bands at 934 and 771 cm^{-1} with a large decrease in intensity of the strong bands at 975 and 802 cm^{-1} in the spectrum of complex **1** in Fig. 4a. Thus, the strong bands at 975 and 802 cm^{-1} in the spectrum of complex **1** are assigned to the V=O (apical) and V=O (basal) stretching bands, respectively. The frequency of the V=O (apical) stretching band of complex **1** is higher than those of monomeric dioxovanadium(V) complexes with a tridentate Schiff-base ligand (920–960 cm^{-1}), and the frequency of V=O (basal) stretching band of complex **1** is lower than those of monomeric dioxovanadium(V) complexes (850–880 cm^{-1}).[13] The oxygen atom exchange reaction did not proceed for complex **2**, which has bulky hydrophobic *tert*-butyl groups.

The V^{V}–Ce^{IV}–V^{V} trinuclear complexes with a d^0–f^0–d^0 electron configuration are diamagnetic. The ^{13}C NMR spectrum of complex **1** in DMSO-d_6 shows 21 signals at δ 166.2, 164.7, 156.9, 153.9, 147.3, 144.9, 124.3, 123.5, 122.4, 121.2, 118.5, 118.2, 117.0, 113.9 (Ar and N=$\underline{C}$H–C), 80.4 (–O$\underline{C}$H-(CH_2–)$_2$), 64.3, 64.1 (O–$\underline{C}H_2$–C), 63.9, 62.4 (N–$\underline{C}H_2$–C), 14.8, 14.6 ($\underline{C}H_3$). The structure of complex **1** in the solution is considered to be an *endo* structure (C_2 symmetry), similar to the structure in crystals. However, the ^{13}C NMR spectrum of complex **2** in $CDCl_3$ is complicated. More than 60 carbon signals were observed in the ^{13}C NMR spectrum of complex **2**. All the signals could not be assigned because of weak intensities and overlapping signals.[18] However, two strong and four weak N–$\underline{C}H_2$–C carbon signals (δ 64.9, 65.2, 65.4, 65.8, 66.2, 67.4) with a relative intensity ca. 2:1, and one strong and two weak –O$\underline{C}$H(CH_2–)$_2$ carbon signals (δ 80.6, 80.9, 84.3) with a relative intensity ca. 2:1 in the spectrum of complex **2** suggest two possible structures for **2**: (1) a mixture of the *endo* (C_2 symmetry) and *exo* (C_1 symmetry) isomers (Fig. 3) in the ratio of ca. 1:1; (2) another heteronuclear structure different from the trinuclear structure of complex **1**. Unfortunately, structure of complex **2** could not be determined by X-ray structure analysis because single crystals were not obtained. Steric repulsions between the *tert*-butyl groups in the ligand L_2 may cause the structural difference between complexes **1** and **2**.

Electrochemistry. Cyclic voltammograms of complex **1** and [$V^{V}O(L_1)$] with 1 mM concentrations in acetonitrile are shown in Fig. 5. The voltammogram of complex **1** shows a quasi-reversible redox couple with $E_{1/2} = -0.60$ V vs Fc/Fc^+. Peak separation of the redox couple is 226 mV. The redox potential of complex **1** is shifted positive by 230 mV compared to that of [$V^{V}O(L_1)$], which shows a quasi-reversible V^{V}/V^{IV} redox couple with $E_{1/2} = -0.83$ V.[10] The current peak values for the redox couple of complex **1** is about two times larger than those for the redox couple of [$V^{V}O(L_1)$]. This result would indicate a two-electron redox reaction for the redox process of complex **1**. The cyclic voltammogram of complex **2** shows an irreversible redox couple with a reduction wave at -0.99 V and an oxidation wave at -0.41 V.[18] Chemically reduced products of complexes **1** and **2** (abbreviated as $\mathbf{1_{Red}}$ and $\mathbf{2_{Red}}$) were prepared by the reaction of complexes **1** and **2** with equimolar amounts of ascorbic acid in methanol, respectively. The brown reduced complexes $\mathbf{1_{Red}}$ and $\mathbf{2_{Red}}$ were rather unstable. When complexes **1** and **2** were reacted with excess ascorbic acid in methanol, respectively, the trinuclear complexes decomposed to yield yellow monomeric oxovanadium(IV) complexes. Moreover, complexes $\mathbf{1_{Red}}$ and $\mathbf{2_{Red}}$ were air-unstable, and gradually oxidized in air to give complexes **1** and **2**, respectively, even in the solid state. IR spectrum of complex $\mathbf{1_{Red}}$ is shown in Fig. 4c. In the spectrum of complex $\mathbf{1_{Red}}$, there is no V=O (basal) stretching band, and only the V=O (apical) stretching band at 982 cm^{-1} is observed. Similar tendency is also observed in the IR spectrum of complex $\mathbf{2_{Red}}$.[18] Disappearance of the V=O (basal) stretching band for the two-electron reduced complex $\mathbf{1_{Red}}$ may suggest that complex $\mathbf{1_{Red}}$ is a hydroxo-bridged (V–OH–Ce) trinuclear complex (Fig. 6). The reduced complex may have a V^{IV}–Ce^{IV}–V^{IV} trinuclear structure with a d^1–f^0–d^1 electron configuration. Further investigations will be necessary to elucidate the electronic structure of the reduced complexes.[19]

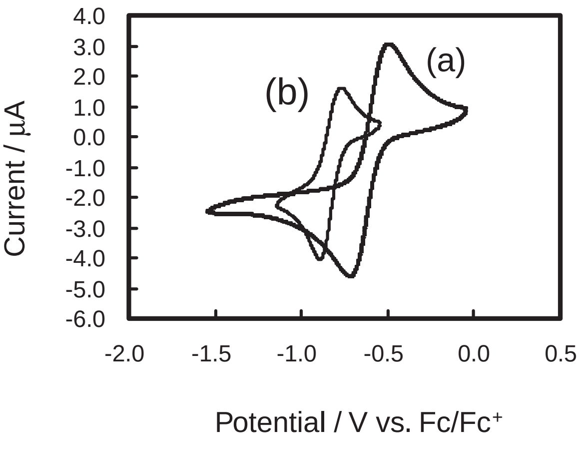


Fig. 5. Cyclic voltammograms of (a) complex **1** and (b) [$V^{V}O(L_1)$] in CH_3CN with a scan rate of 100 mV s^{-1}.

Experimental

Preparation of the Ligands. The ligand H_3L_1 was prepared by the literature method.[10] The ligand H_3L_2 was prepared by the reaction of 2-hydroxy-1,3-propanediamine with 2 equiv amounts of 3,5-*tert*-butyl-2-hydroxybenzaldehyde in ethanol. The reaction mixture was evaporated to dryness to yield a yellow oily product. The oily product was poured into water, and the mixture was stirred for 1 day. The resulting yellow powder was collected by filtration and used for further reactions without purification. ^{13}C NMR ($CDCl_3$) δ 168.4, 158.0, 140.2, 136.7, 127.2, 126.2, 117.8 (Ar and N=$\underline{C}$H–C), 70.6 (–O$\underline{C}$H(CH_2–)$_2$), 63.3 (N–$\underline{C}H_2$–C), 35.0, 34.1 (C–$\underline{C}$–(CH_3)$_3$), 31.5, 29.4 ($\underline{C}H_3$).

[{$V^{V}O_2(L_1)$}$_2$$Ce^{IV}$]·0.5$H_2O$ (1). **Method 1:** The ligand H_3L_1 (1.93 g, 5 mmol), [$V^{IV}O(acac)_2$] (1.33 g, 5 mmol), and [$Ce^{III}(acac)_3$]·H_2O (1.23 g, 2.5 mmol) were added to 1 dm^3 of CH_3CN, and the reaction mixture was vigorously stirred in air for 3 h at 70 °C. The brown reaction mixture was filtered, and the filtrate was evaporated to dryness. The resulting brown residue was dissolved in 600 cm^3 of dichloromethane–ethanol solution (1:1 v/v), and the solution was left for two days in air. The result-

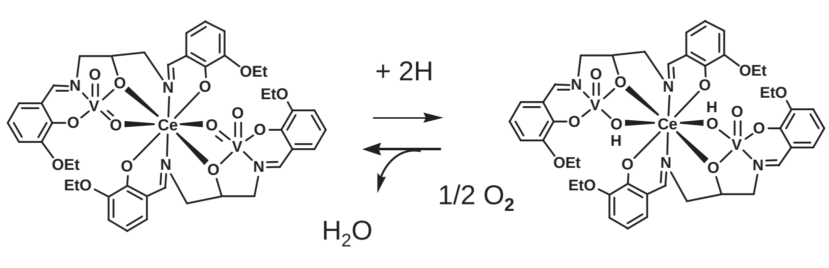


Fig. 6. Proposed mechanism for the redox reaction of complex **1**.

ing brown crystals were collected by filtration. Yield: 3.77 g (70%). Found: C, 46.32; H, 4.39; N, 5.11%. Calcd for $C_{42}H_{47}Ce_1N_4O_{14.5}V_2$: C, 46.62; H, 4.37; N, 5.14%. IR (KBr, cm^{-1}): 802, 975 [ν(V=O)].

Method 2: [$Ce^{III}(acac)_3$]•H_2O (0.49 g, 1 mmol) was added to an acetonitrile solution (300 cm^3) of [$V^{IV}O(HL)$]•H_2O (0.938 g, 2 mmol),[10] and the reaction mixture was vigorously stirred in air for 3 h at 70 °C. The reaction product was treated by the method similar to that for Method 1. Yield: 1.32 g (81%).

[$\{V^VO_2(L_2)\}_2Ce^{IV}$]•4CH_3CN (2). The complex was prepared by the method similar to that for [$\{V^VO_2(L_1)\}_2Ce^{IV}$]•0.5H_2O (Method 1). For complex **2**, the product was recrystallized from acetonitrile in air. Yield: 3.51 g (93%). Found: C, 58.69; H, 7.00; N, 7.48%. Calcd for $C_{74}H_{106}Ce_1N_8O_{10}V_2$: C, 58.86, H, 7.07; N, 7.42%. IR (KBr, cm^{-1}): 812, 974 [ν(V=O)].

Oxygen Atom Exchange Reaction for 1. To a dry acetonitrile solution (10 cm^3) of complex **1** (0.005 mmol) was added 0.04 cm^3 (ca. 2 mmol) of $H_2{}^{18}O$ (97 > atom%). The solution was stirred at 30 °C under an argon atmosphere for 10 days and then evaporated to dryness.

Reduction of the Vanadium(V)–Cerium(IV) Trinuclear Complexes. The reaction was carried out under a nitrogen atmosphere. Ascorbic acid (0.035 g, 0.2 mmol) was added to a methanol solution of complexes **1** or **2** (400 cm^3 for 0.2 mmol of complex **1**, 100 cm^3 for 0.2 mmol of complex **2**), and the mixture was stirred for 30 min at 10 °C. The mixture was evaporated to dryness below 20 °C, and washed with water. Yield: 80–90%. The brown reduced products were rather unstable and gradually oxidized in air even in the solid state. IR data (KBr, cm^{-1}): 982 [ν(V=O)] for $\mathbf{1_{Red}}$; 980, 998 [ν(V=O)] for $\mathbf{2_{Red}}$.

Crystal Structure Determination of [$\{V^VO_2(L_1)\}_2Ce^{IV}$]•2H_2O•2DMSO. Crystals suitable for X-ray crystal structure analysis were obtained by recrystallization of complex **1** from DMSO. Crystal data of [$\{VO_2(L_1)\}_2Ce$]•2H_2O•2DMSO: $Ce_1V_2S_2O_{18}N_4C_{46}H_{62}$, M = 1265.13, crystal size: 0.43 × 0.40 × 0.30 mm^3, orthorhombic, space group *Pbca* (No. 61), $a = 18.286(3)$, $b = 32.985(8)$, $c = 17.887(3)$ Å, $V = 10789(3)$ Å^3, $Z = 8$, $\mu(\text{Mo K}\alpha) = 1.319$ mm^{-1}, 13411 reflections measured, 12356 independent reflections. The intensity data were collected at 298 K on a Rigaku AFC-7R diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) up to $2\theta = 55°$ by ω scans. Three standard reflections were measured at every 150 reflections. Absorption corrections were made by the Ψ scans method.[20] The structures were solved by direct methods on a Silicon Graphics O^2 workstation with the program system teXsan,[21] and refined with SHELXL-97.[22] The sulfur (S65) and oxygen (O67) atoms of the DMSO molecule were disordered, and two positions were assigned for these atoms. Site occupancy factors for the S65A, O67A atoms and the S65B, O67B atoms were 60 and 40%, respectively. Non-hydrogen atoms were treated anisotropically. All H-atom positions attached to the carbon atoms of the complex and C70 and C71 atoms of the DMSO molecule were caluculated geometrically. H-atoms attached to C72 and C73 atoms of the disordered DMSO molecule were not introduced. H-atom positions attatched to the O68 atom of the water molecule were found by difference synthesis. The positions for the H-atoms attached to the O69 atom of another water molecule could not be found by difference synthesis. The refinement was based on F^2 with $R_w = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w^{-1} = \sigma^2(F_o{}^2) + (0.0603P)^2 + 8.3885P$, where $P = (F_o{}^2 + 2F_c{}^2)/3$ against all of the 12356 reflections. The R_w value was 0.118. The R value $(\Sigma|F_o{}^2 - F_c{}^2|/\Sigma F_o{}^2)$ was 0.038 for the 8477 reflections with $I > 2\sigma(I)$. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-606023 for compound [$\{VO_2(L_1)\}_2Ce$]•2H_2O•2DMSO. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Electrochemical Measurements. Cyclic voltammetric measurements were carried out using a ALS 600 electrochemical analyzer at 25 °C (1 mM complex, 0.1 M $N(C_4H_9)_4BF_4$). A platinum electrode, an Ag/Ag$^+$ electrode (Ag/0.01 M $AgNO_3$), and a platinum wire were employed as the working, reference, and auxiliary electrodes.

Magnetic Measurements. Magnetic susceptibility measurements were carried out using a Quantum Design MPMS XL5 magnetometer in the temperature range of 1.9–300 K using a magnetic field of 0.1 T. The susceptibilities of complex $\mathbf{2_{Red}}$ have been corrected for the diamagnetic contribution of $\chi_{dia} = -766.6 \times 10^{-6}$ cm^3 mol^{-1}, calculated by Pascal's method.

Other Measurements. IR spectra were recorded on a JASCO A-202 spectrophotometer. The ESR spectrum in benzene at room temperature was recorded on a JEOL JES-RE3X spectrometer with a 100 kHz field modulation. The ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer with a TMS reference.

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Supporting Information

The ^{13}C NMR spectrum of complex **2** (Fig. S1), IR spectra of complexes **2** and $\mathbf{2_{Red}}$ (Fig. S2), cyclic voltammogram of complex **2** (Fig. S3), χ_mT–T plots of complex $\mathbf{2_{Red}}$ (Fig. S4), and ESR spectrum of complex $\mathbf{2_{Red}}$ (Fig. S5) in PDF files. This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

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11 Complex **1** was also prepared by the reaction of a mono-oxovanadium(V) complex $[\mathrm{V^VO(L)}]$ with $[\mathrm{Ce^{III}(acac)_3}]\cdot 3\mathrm{H_2O}$ in $\mathrm{CH_3CN}$ followed by oxidation of the product in air. Yield: 74%.

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17 Clear difference between the reactivity of the basal and apical oxo atoms of complex **1** with $\mathrm{H_2{}^{18}O}$ was not observed.

18 The ^{13}C NMR spectrum of complex **2**, IR spectrum of complexes **2** and $\mathbf{2_{Red}}$, and cyclic voltammogram of complex **2** are part of the supporting material.

19 As complex $\mathbf{1_{Red}}$ was too unstable to obtain magnetic data, complex $\mathbf{2_{Red}}$ was used for the magnetic and ESR measurements. Elemental anlysis for complex $\mathbf{2_{Red}}$; Found: C, 58.05; H, 7.26; N, 3.97%. Calcd for $[\{\mathrm{VO(OH)(L_2)}\}_2\mathrm{Ce}]\cdot\mathrm{H_2O}$ ($\mathbf{2_{Red}}$) $\mathrm{C_{66}H_{98}N_4O_{11}Ce_1V_2}$: C, 58.04; H, 7.23; N, 4.10%. Magnetic moment of complex $\mathbf{2_{Red}}$ at 300 K is 2.36 μ_B, which is a little smaller than the calculated spin-only magnetic moment value for two $S = 1/2$ centers with no interaction, $\{(1(1+2)+1(1+2))\}^{1/2}\mu_B = 2.45\ \mu_B$. However, the $\chi_m T$–T plots of complex $\mathbf{2_{Red}}$ show a complicated behavior. Complex $\mathbf{2_{Red}}$ was ESR-silent in a benzene solution at 298 K, but showed an ESR signal at $g_{iso} = 1.957$ in the solid state at 298 K. The $\chi_m T$–T plots and ESR spectrum of complex $\mathbf{2_{Red}}$ are deposited.

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