ELSEVIER

Coordination Chemistry Reviews 237 (2003) 197–203

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Reactions of di-2-pyridylketone oxime in the presence of vanadium(III): crystal structures of the coordination products

Hitoshi Kumagai [a], Masanori Endo [b], Mitsuru Kondo [c], Satoshi Kawata [d,1], Susumu Kitagawa [c,*]

[a] *Institute for Molecular Science, Nishigounaka 38, Myoudaiji, Okazaki 444-8585, Japan*
[b] *Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Minami Ohsawa, Hachiouji, Tokyo 192-0312, Japan*
[c] *Department of Synthetic Chemistry and Biological Chemistry, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan*
[d] *Department of Chemistry, Faculty of Science, Shizuoka University, Shizuoka 422-8529, Japan*

Received 25 January 2002; accepted 23 August 2002

Contents

Abstract

The reaction of di-2-pyridylketone oxime (dpko) in the presence of $VCl_3(THF)_3$ results in di-2-pyridylimine (dpi) with THF, amino-di-2-pyridyl-methyl ethyl ether (adpe) with ethanol and amino-di-2-pyridyl-methyl methyl ether (adpm) with methanol. The coordination complexes of these resulting ligands with vanadium, [$VOCl_2$(dpi)(THF)] (**1**) ($Pna2_1$, $a = 20.516(3)$, $b = 6.479(3)$, $c = 13.065(3)$ Å, $V = 1736(1)$ Å^3, $Z = 4$), [$VOCl_2$(adpe)] (**2**) ($P2_1/n$, $a = 8.496(2)$, $b = 12.640(3)$, $c = 15.036(2)$ Å, $\beta = 95.84(2)°$, $V = 1606.4(5)$ Å^3, $Z = 4$), [$VOCl_2$(adpm–NH_2)] (**3a**) ($P2_1/n$, $a = 9.47(2)$, $b = 12.67(1)$, $c = 12.48(1)$ Å, $\beta = 95.0(1)°$, $V = 1490(3)$ Å^3, $Z = 4$) and [$VOCl_2$(adpm–OMe)]·MeOH (**3b**) ($P2_1/n$, $a = 8.529(3)$, $b = 15.293(2)$, $c = 13.619(2)$ Å, $\beta = 100.17(2)°$, $V = 1748.3(6)$ Å^3, $Z = 4$), have been characterized by X-ray crystal structure determination and EPR spectroscopy. All the compounds are monomers with a $VOCl_2$ common unit. In contrast to the N–O bond cleavage and C–O bond formation to afford new tripodal ligands for **2** and **3**, only the N–O bond cleavage reaction was observed for **1**. The two isomers of **3** differ in the choice of coordination atom of the ligand, the amine nitrogen atom in **3a** and the ether oxygen atom in **3b**.

Keywords: Vanadium; Polypyridyl ligand; Structures; ESR; Oxidation

1. Introduction

The chemistry of low-valent vanadium has attracted much interest due to several specific features [1–28] such as the relatively stable oxo-vanadium(IV), or vanadyl moiety, the usual oxophilicity and air-sensitivity [29]. A

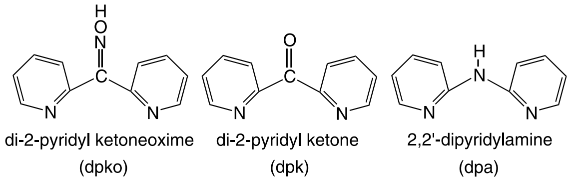
---

[*] Corresponding author. Tel.: +81-75-753-5652; fax: +81-75-753-7979

E-mail address: kitagawa@sbchem.kyoto-u.ac.jp (S. Kitagawa).

[1] Present address: Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan.

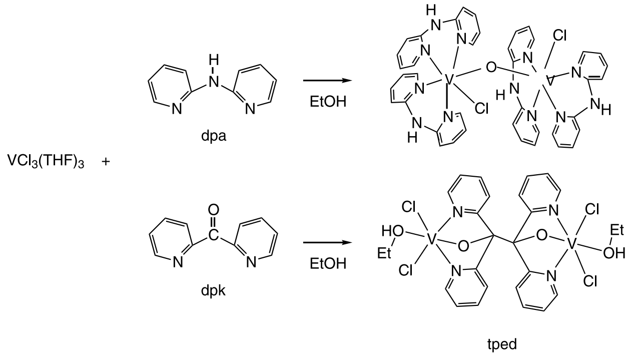
0010-8545/02/$ - see front matter
PII: S0010-8545(02)00246-1



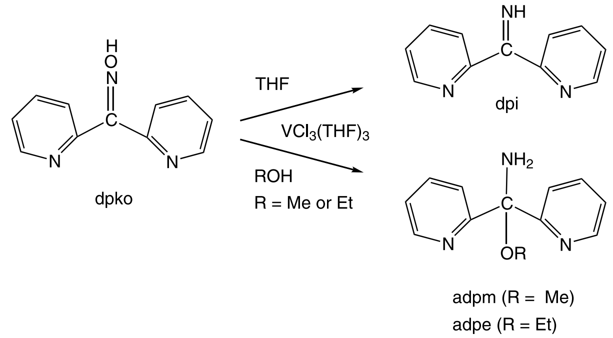
Scheme 1.

further key feature is that many organic molecules undergo transformation upon reaction with vanadium complexes and in some cases, the products coordinate to the vanadium [30,31].

Metal compounds containing polypyridyl-like ligands of the type $(C_5H_4N)_2X$ (Scheme 1) are of current interest for their rich physico-chemical properties, diverse reactivity patterns, and potential applications in many important chemical processes [32–34]. Our interest in the chemistry of polypyridyl-like compounds was aroused because of their ability to undergo a variety of interesting reactions upon binding to transition metal ions and we were intrigued to explore how variations in the bridging group X of the ligands affect the structure of their vanadium complexes. Several studies have characterized a range of coordination complexes with pyridine and diimine ligands, such as bpy (bpy = 2,2′-bipyridine) and phen (phen = 1,10-phenanthroline) [17,18,35–39]. We reported structures and properties of μ-oxo dinuclear vanadium(III) complexes of di-2-pyridylamine (dpa) formed in ethanol [39] (Scheme 2). In alcoholic media, $VCl_3(THF)_3$ was found to react with di-2-pyridylketone (dpk) to afford the dinuclear vanadium(III) complex, in which the reductive coupling of two dpk molecules forms the bis-tridentate bridging ligand [30] (Scheme 2). The product is quite different from those with other transition-metal ions [33,40–45]. Our present interest is to extend the chemistry beyond the reaction between a trivalent vanadium ion and dpko in relation to carbonyl system to the reactivity of oximes and amide oximes towards oxo-vanadium compounds [28,30,46,47]. This work is concerned with some unique reaction products of dpko with vanadium(III) in different solvents and determination of their X-ray crystallographic structures together with their spectroscopic properties (Scheme 3).



Scheme 2.



Scheme 3.

2. Experimental

All manipulations were carried out by using standard schlenck technique. Solvents were purified by standard methods before use. VCl_3 and di-2-pyridylketone oxime (dpko) were purchased from Aldrich Chemical Co. and used without further purification. $VCl_3(THF)_3$ was prepared according to the literature method [48]. The IR spectra of the KBr disks were measured on a Hitachi I-5040-FT-IR spectrometer. The EPR spectra were recorded at X-band with modulation frequency of 100 kHz and modulation amplitude of 1 mT with a JEOL RE-3X spectrometer. The resonance frequency was measured on an Anritsu MF76A microwave frequency counter. Magnetic fields were calibrated by an ECHO Electronics EFM-2000AX NMR field meter. NMR spectra were measured with a JEOL GSX-270 FT-NMR spectrometer or an EX-400 FT-NMR spectrometer.

2.1. *Preparation of [$VOCl_2$(dpi)(THF)] (**1**) (dpi = di-2-pyridylimine)*

To a solution of $VCl_3(THF)_3$ (0.3 g, 0.8 mmol) in THF was added a solution of dpko (0.16 g, 0.8 mmol) at room temperature (r.t.). The brown precipitate formed was filtrated off, and then C_6H_{14} was layered gently on the resultant brown solution to form brown crystals. The complex easily changes color from brown to blue and satisfactory elemental analysis was not obtained. The yield could not be calculated.

2.2. *Preparation of [$VOCl_2$(adpe)] (**2**) (adpe = amino-di-2-pyridyl-methyl ethyl ether)*

$VCl_3(THF)_3$ (0.3 g, 0.8 mmol) was dissolved in 4 ml of EtOH. To this solution, an ethanolic solution of dpko (0.16 g, 0.8 mmol) was added. The mixed solution was stirred for 2 h at r.t. and a blue precipitate was filtred off. To the resultant green solution, C_6H_{14} was allowed to diffuse slowly. Blue crystals of **2** were obtained. (Yield: 40%) Anal. Calc. for $C_{13}H_{13}Cl_2N_3O_2V$: C, 42.77; H, 3.59; N, 11.51. Found: C, 42.80; H, 3.45; N, 11.65%.

2.3. Preparation of [$VOCl_2$(adpm–NH_2)] (**3a**) and [$VOCl_2$(adpm–OMe)]·MeOH (**3b**) (adpm = amino-di-2-pyridyl-methyl methyl ether)

$VCl_3(THF)_3$ (0.3 g, 0.8 mmol) was dissolved in 4 ml of MeOH. To this solution, the methanolic solution of dpko (0.16 g, 0.8 mmol) was added, and the mixed solution was stirred for 2 h at r.t. The blue precipitate was filtrated off and dried in vacuo. Crystals of **3a** and **3b** were obtained in every attempt and consequently the separation is difficult due to the crystals having the same color and form. The yield could not be calculated. Anal. Calc. for $C_{12}H_{11}Cl_2N_3O_2V$: C, 40.94; H, 3.44; N, 11.93. Found: C, 40.53; H, 3.77; N, 11.61%.

2.4. X-ray crystallography and structure solution

Crystals were glued on top of glass fibers. Intensity data for the complexes were collected on a Rigaku AFC7R at r.t. The diffractometer employs graphite monochromated Mo–K_α radiation. An empirical absorption correction was applied in each case. The data were corrected for Lp effects. The structure was solved by Patterson methods for complex **1** and direct methods for complex **2**–**3b**, respectively, and expanded using Fourier techniques [49,50]. Hydrogen atoms are located at ideal positions. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on no. of observed reflections ($I > 3.00\sigma(I)$) and n variable parameters and converged (large parameter shift was σ times its e.s.d.) with unweighted agreement factors of $R = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$, $Rw = [\Sigma\,w(|F_o| - |F_c|)^2/\Sigma\,w|F_o|^2]^{1/2}$. . No extinction corrections have been applied. For the complex **1**, over the course of data collection, the intensity of the standard peaks decreased by 26%. A linear correction factor was applied to the data to account for this phenomenon. Crystallographic data are given in Table 1.

3. Results and discussion

3.1. Structure of **1**

The structure of **1** is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. The X-ray crystal structure of the complex **1** reveals two important effects: (a) the oxidation of the initial vanadium(III) ion to oxo-vanadium(IV) ion; and (b) the reaction of the ketone oxime group to an imino group. The vanadium ion exhibits distorted octahedral $VO_2N_2Cl_2$ geometry, formed in the equatorial plane by the O(2), Cl(1), N(1), Cl(2) atoms and an axial oxo group and the imino nitrogen atom of the ligand. The vanadium atom is 0.33Å away from the least-squares plane defined by the equatorial atoms and toward the vanadyl oxygen. Previous studies on known vanadium(IV) complexes with the terminal oxo ligand have shown that six-coordinated complexes have mean V=O distances of 1.615 Å, while five-coordinated compounds have normally shorter distances, 1.518 Å [51]. The corresponding distance (1.588(4) Å) in **1** is closer to the values for the six-coordinate species than those of five-coordinate ones. Two chlorine atoms Cl(1) and Cl(2) are in the *trans* position. The V–Cl distances are similar to those found in structurally characterized complexes [35,37,51–54].

One of the interesting features in this structure is the coordination mode of the dpi ligand. There are three coordination sites in dpi ligand, two pyridyl groups and one imine nitrogen. Because of the sp^2 character of the C(6) atom, dpi has no flexibility to form a tripodal ligand such as pyrazolyl borate. Consequently, the dpi ligand chelates to vanadium ion through one of the two pyridyl nitrogen and an imine nitrogen atom, exhibiting diimine type coordination mode with the N–V–N bite angle of 72.7(2)°. The bond angle is similar to rigid bpy chelate ring which has been known to enforce a N–V–N angle less than 80° for the mono- and di-nuclear vanadium complexes [35,37,52–55].

3.2. Structures of **2**, **3a** and **3b**

The molecular structure of complex **2** and **3a**, with the atomic numbering scheme is given in Figs. 2 and 3, respectively. Selected bond lengths and angles for complex **2** and **3a** are given in Tables 3 and 4, respectively. The adpm and adpe ligands can coordinate to a vanadium(IV) ion either via three nitrogen atoms (*N*,*N*,*N*-coordination) or two nitrogen atoms and one oxygen atom (*N*,*N*,*O*-coordination). X-ray single-crystal structure determinations of complexes **2** and **3a** revealed that they have similar coordination environments (*N*,*N*,*N*-coordination). The complexes exhibit distorted octahedral geometry with two pyridyl nitrogen atoms, two chloride ions, amino nitrogen and a terminal oxo group (VON_3Cl_2 coordination environment). The chloride ions and pyridyl nitrogen atoms constitute a plane from which the vanadium atom is shifted towards the terminal oxygen atom by 0.33 Å for the both complexes, **2** and **3a**. While two chloride ions occupied *trans* positions in **1**, those in **2** and **3a** are in the *cis* positions. The V–Cl distances are close to each other and similar to those found in structurally characterized complexes [35,37,52–55]. The V(1)–N(2) distances (2.290(4) and 2.283(8) Å) of complex **2** and **3a** are

Table 1
Summary of crystal data and experimental parameters for the X-ray crystallographic studies of [$VOCl_2$(dpi)(THF)] (**1**), [$VOCl_2$(adpe)] (**2**), [$VOCl_2$(adpm–NH_2)] (**3a**) and [$VOCl_2$(adpm–OMe)]·MeOH (**3b**)

Complex	**1**	**2**	**3a**	**3b**
Empirica formula	$C_{15}H_{16}Cl_2N_3O_2V$	$C_{13}H_{15}Cl_2N_3O_2V$	$C_{12}H_{13}Cl_2N_3O_2V$	$C_{13}H_{17}Cl_2N_3O_3V$
Formula weight	392.16	367.13	353.10	385.14
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$Pna2_1$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	20.516(3)	8.496(2)	9.47(2)	8.529(3)
b (Å)	6.479(3)	12.640(3)	12.67(1)	15.293(2)
c (Å)	13.065(3)	15.036(2)	12.48(1)	13.619(2)
β (°)		95.84(2)	95.0(1)	100.17(2)
V (Å^3)	1736(1)	1606.4(5)	1490(3)	1748.3(6)
Z	4	4	4	4
D_{calc} (g cm^{-3})	1.500	1.501	1.573	1.463
μ(Mo–K_α) (cm^{-1})	8.89	8.25	8.90	8.85
Crystal size (mm^3)	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.1	0.2 × 0.3 × 0.5	0.3 × 0.15 × 0.1
Transmission factors	0.94–1.00	0.73–1.08	0.91–1.00	0.93–1.00
Observations [$I > 3.00\sigma(I)$]	1622	2107	1053	1772
Variables	207	190	181	199
R	0.038 (0.054)	0.060 (0.047)	0.059 (0.035)	0.067 (0.088)
Residual (e Å^{-3})	0.48/−0.41	0.72/−0.58	0.42/−0.50	0.81/−0.66

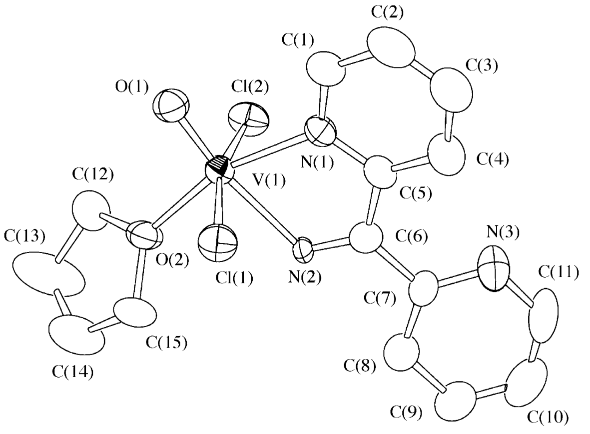


Fig. 1. ORTEP drawing of [$VOCl_2$(dpi)(THF)] (**1**) showing the atom-labeling scheme with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) of **1**

Bond distances			
V(1)–Cl(1)	2.357(2)	V(1)–Cl(2)	2.360(2)
V(1)–O(1)	1.587(3)	V(1)–O(2)	2.038(4)
V(1)–N(1)	2.119(4)	V(1)–N(2)	2.227(3)
Bond angles			
Cl(1)–V(1)–Cl(2)	163.87(5)	Cl(1)–V(1)–O(1)	97.7(1)
Cl(1)–V(1)–O(2)	90.9(1)	Cl(1)–V(1)–N(1)	86.3(1)
Cl(1)–V(1)–N(2)	81.8(1)	Cl(2)–V(1)–O(1)	97.9(1)
Cl(2)–V(1)–O(2)	89.7(1)	Cl(2)–V(1)–N(1)	87.7(1)
Cl(2)–V(1)–N(2)	82.16(9)	O(1)–V(1)–O(2)	102.2(2)
O(1)–V(1)–N(1)	97.5(2)	O(1)–V(1)–N(2)	170.2(2)
O(2)–V(1)–N(1)	160.3(2)	O(2)–V(1)–N(2)	87.6(1)
N(1)–V(1)–N(2)	72.7(2)	V(1)–O(2)–C(15)	126.6(4)
V(1)–N(1)–C(1)	121.5(3)	V(1)–N(1)–C(5)	118.7(3)
V(1)–N(2)–C(6)	117.8(3)		

slightly shorter than that observed in [VO(L^2)](ClO_4)$_2$ (L^2 = 6,13-dimethyl-1,4,8,11-tetra-azacyclotetradene-6,13-diamine) (2.337(2) Å), in which amine group coordinates trans to the vanadyl oxygen [56]. The V=O distance of complex **3a** (1.600(7) Å) lies within the range (1.55–1.68 Å) of well-characterized oxo-vanadium complexes [57,58]. On the other hand, the V=O distance of complex **2** (1.721(4) Å) is significantly longer compared to the others. However, such long V=O distances have been found in V_2O_4 (1.76 Å) [59] and VOCl(pbha)$_2$ (1.801(4) Å) (pbha = *N*-phenylbenzylhydroxamato) [60].

The carbon atom of the ketone oxime moiety forms a new C–O bond to afford sp^3 hybridization of the C(6) atom. While one pyridyl nitrogen atom exhibits no interaction with vanadium ion in **1** due to the sp^2 character of C(6) atom, the coordination of the pyridyl nitrogen atom has been observed for complex **2** and **3a** as a result of flexibility of C(6) atom due to sp^3 hybridization. The six-membered chelate moieties in **2** and **3a**, V(1)N(1)C(5)C(6)C(7)N(3), are in boat conformations. A similar boat conformation is found in [V_2Cl_4(tped)(EtOH)$_2$] (tped = tetrapyridyl-1,2-ethanediol) in which the ligand was formed by reductive coupling reaction of dpk molecules [30] in ethanol.

A molecular diagram of complex **3b** is shown in Fig. 4 and selected bond lengths and angles are given in Table 5. The crystal of **3b** consists of a mononuclear [$VOCl_2$(adpm–OMe)] complex with a methanol molecule of crystallization. The methanol molecule is hydrogen bonded to the N(2) atom. The chloride ions also occupy the *cis* positions and the V–Cl distances are similar to those found in **2** and **3a**. In contrast to

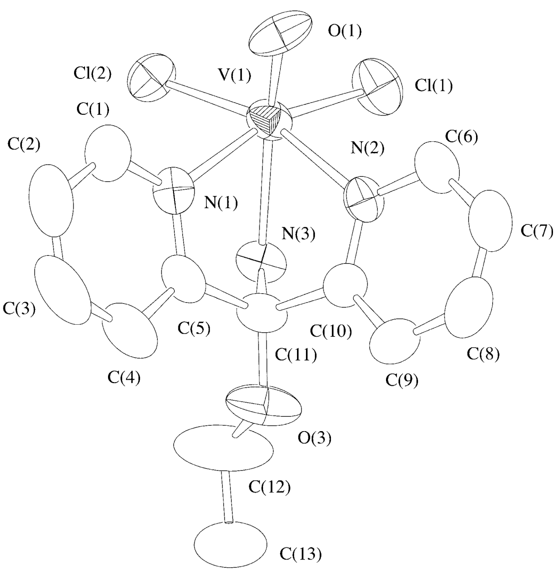


Fig. 2. ORTEP drawing of [$VOCl_2$(adpe)] (**2**) showing the atom-labeling scheme with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

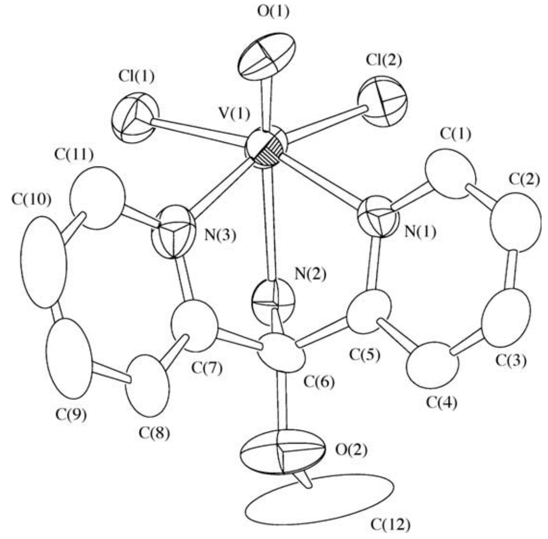


Fig. 3. ORTEP drawing of [$VOCl_2$(adpm–NH_2)] (**3a**) showing the atom-labeling scheme with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 3
Bond distances (Å) and angles (°) of **2**

Bond distances			
V(1)–Cl(1)	2.287(2)	V(1)–Cl(2)	2.340(2)
V(1)–O(1)	1.721(4)	V(1)–N(1)	2.166(4)
V(1)–N(2)	2.290(4)	V(1)–N(3)	2.145(4)
Bond angles			
Cl(1)–V(1)–Cl(2)	95.40(6)	Cl(1)–V(1)–O(1)	101.1(1)
Cl(1)–V(1)–N(1)	162.6(1)	Cl(1)–V(1)–N(2)	91.1(1)
Cl(1)–V(1)–N(3)	88.7(1)	Cl(2)–V(1)–O(1)	103.8(1)
Cl(2)–V(1)–N(1)	86.9(1)	Cl(2)–V(1)–N(2)	91.1(1)
Cl(2)–V(1)–N(3)	161.8(1)	O(1)–V(1)–N(1)	95.0(2)
O(1)–V(1)–N(2)	159.5(2)	O(1)–V(1)–N(3)	92.7(2)
N(1)–V(1)–N(2)	71.6(2)	N(1)–V(1)–N(3)	84.1(2)
N(2)–V(1)–N(3)	71.0(2)	V(1)–N(2)–C(6)	102.2(3)
V(1)–N(1)–C(1)	124.9(4)	V(1)–N(1)–C(5)	116.6(3)
V(1)–N(3)–C(7)	117.2(3)	V(1)–N(3)–C(11)	124.4(3)

Table 4
Bond distances (Å) and angles (°) of **3a**

Bond distances			
V(1)–Cl(1)	2.342(3)	V(1)–Cl(2)	2.340(4)
V(1)–O(1)	1.600(7)	V(1)–N(1)	2.144(8)
V(1)–N(2)	2.283(9)	V(1)–N(3)	2.13(1)
Bond angles			
Cl(1)–V(1)–Cl(2)	94.4(1)	Cl(1)–V(1)–O(1)	103.5(3)
Cl(1)–V(1)–N(1)	162.6(3)	Cl(1)–V(1)–N(2)	90.2(2)
Cl(1)–V(1)–N(3)	88.8(3)	Cl(2)–V(1)–O(1)	101.3(3)
Cl(2)–V(1)–N(1)	88.3(2)	Cl(2)–V(1)–N(2)	90.5(3)
Cl(2)–V(1)–N(3)	161.9(3)	O(1)–V(1)–N(1)	92.8(4)
O(1)–V(1)–N(2)	161.1(3)	O(1)–V(1)–N(3)	95.2(4)
N(1)–V(1)–N(2)	72.6(3)	N(1)–V(1)–N(3)	83.6(3)
N(2)–V(1)–N(3)	71.7(3)	V(1)–N(2)–C(1)	125.5(7)
V(1)–N(1)–C(1)	115.5(6)	V(1)–N(1)–C(6)	100.1(6)
V(1)–N(3)–C(7)	118.6(7)	V(1)–N(3)–C(11)	124.6(8)

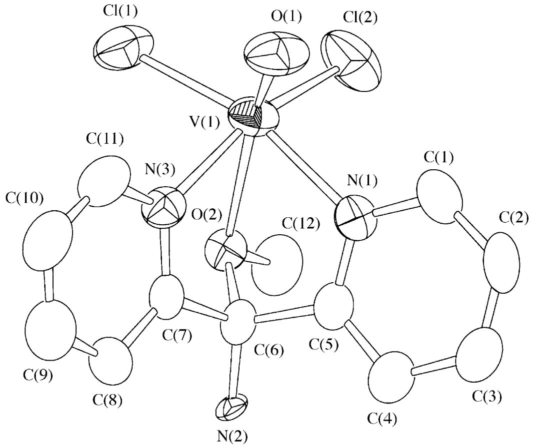


Fig. 4. ORTEP drawing of [$VOCl_2$(adpm–OMe)] (**3b**) showing the atom-labeling scheme with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

N,*N*,*N*-coordination found in complex **3a**, the ligand exhibits *N*,*N*,*O*-coordination to afford a distorted octahedral geometry around the vanadium ion in complex **3b** ($VO_2N_2Cl_2$ coordination environment). While bond distances and angles of the basal plane (formed by two chloride ions and pyridyl nitrogen atoms) are normal, the V=O distance (1.584(8) Å) is slightly shorter than that of complex **3a** as the result of a weak interaction to the O(2) atom as indicated by longer V(1)–O(2) distance of 2.377(7) Å. The *N*,*N*,*O*-coordination in **3b** is similar to that found in tped ligand [30]. However, the V(1)–O(2) distance is longer due to weak coordination ability of ether oxygen. The vanadium ion is displaced toward the apical oxygen by 0.37 Å from the basal plane.

Table 5
Selected bond distances (Å) and angles (°) of **3b**

Bond distances			
V(1)–Cl(1)	2.333(4)	V(1)–O(2)	2.377(7)
V(1)–Cl(2)	2.331(4)	V(1)–N(1)	2.147(9)
V(1)–O(1)	1.584(8)	V(1)–N(3)	2.137(9)
Bond angles			
Cl(1)–V(1)–Cl(2)	93.4(2)	Cl(2)–V(1)–N(3)	159.9(3)
Cl(1)–V(1)–O(1)	103.6(3)	O(1)–V(1)–O(2)	160.4(4)
Cl(1)–V(1)–O(2)	89.9(2)	O(1)–V(1)–N(1)	94.8(4)
Cl(1)–V(1)–N(1)	160.6(3)	O(1)–V(1)–N(3)	95.7(4)
Cl(1)–V(1)–N(3)	88.3(3)	O(2)–V(1)–N(1)	70.7(3)
Cl(2)–V(1)–O(1)	103.3(4)	O(2)–V(1)–N(3)	70.3(3)
Cl(2)–V(1)–O(2)	89.7(2)	N(1)–V(1)–N(3)	83.8(3)
Cl(2)–V(1)–N(1)	88.1(3)		

These structural features indicate that the adpm and adpe can be regarded as the new tripodal ligands and the adpm ligand can exhibit flexible coordination mode.

X-ray crystallographic analysis of these complexes revealed oxidation of the vanadium(III) ions and de-oxygenation of dpko was observed. The oxygen atom of alcohol forms a new C–O bond to a carbon atom of ketone oxime group with concomitant N–O bond cleavage. The dpko was stirred in ethanol under the same experimental conditions but without $VCl_3(THF)_3$ and the solvent was evaporated and the ^{1}H-NMR spectrum was measured in CD_3CN. The spectrum showed no change from that of dpko. Although the IR spectrum of the vanadium complexes exhibit a band attributed to $\nu(NH_2)$ around 3240 cm^{-1}, the IR spectrum of the product obtained without the vanadium does not show a band attributed to $\nu(NH_2)$ and is identical with that of free dpko. These results indicate that dpko is not converted into adpe in the absence of vanadium(III) ion. When the reaction of $VCl_3(THF)_3$ with dpko was carried out in THF complex **1** was obtained. The X-ray structural analysis reveals that this vanadium complex has also shown the oxidation of the vanadium(III) to oxo-vanadium(IV) and N–OH bond cleavage to afford a diimine type ligand. The IR spectrum of the complex **1** showed a band at 1535 cm^{-1} assigned to $\nu(C{=}N)$. Thus, we may conclude that the vanadyl oxygen atom comes from the dpko. De-oxygenation reaction of amide oximes into amidines has been reported for oxo-vanadium complexes [46,47]. Because of the oxophilicity of vanadium(III) ion, ligand dpi has been obtained from de-oxygenation of dpko.

On dissolving complex **1** in methanol under anaerobic condition blue crystals of complex **3b** was obtained. The reaction at the imine carbon was identified by the disappearance of the characteristic band $\nu(C{=}N)$ from the IR spectrum of the reaction product and by X-ray crystallography. From these results, it was assumed that the reaction for methanol system proceeded through the de-oxygenation step to afford complex **1**.

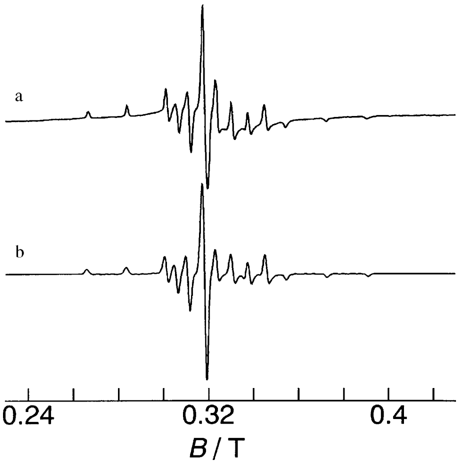


Fig. 5. (a) Frozen methanol solution EPR spectrum of complex **2** at 77 K ($\nu = 8.9998$ GHz); (b) EPR spectrum simulated with the following parameter values: $g_{\parallel} = 1.956$, $g_{\perp} = 1.981$, $A_{\parallel} = 163 \times 10^{-4}$, $A_{\perp} = 58 \times 10^{-4}$ cm^{-1}.

The tetravalent vanadium complexes ($s = 1/2$) are EPR-active displaying axial spectra with well-resolved ^{51}V ($I = 7/2$) hyperfine lines. The parameters for complex **2** are given in the figure caption (Fig. 5) and the observed and simulated EPR spectra are shown in Fig. 5. The $g_{\parallel} < g_{\perp}$ and $A_{\parallel} > A_{\perp}$ relationships are characteristic of an axially compressed d_{xy^1} configuration [61,62]. While the complex **2** exhibits a long V=O distance, the parameters are within the range found in previously characterized complexes [35,51,56,61,63–66]. In this case the variation in the structure around the vanadium atom would not reflect the EPR parameters possibly because of perpendicular components of d_{xy^1} configuration.

Acknowledgements

This research was supported by a Grant-in-Aid for scientific research on Priority Area 'Metal-assembled complexes' (No. 12023216) and by a Grant-in-Aid for scientific research (No. 12640537) from the Ministry of Education, Science and Culture, Japan.

References

[1] J.J.H. Edema, W. Stauthamer, F. van Bolhuis, S. Gambarotta, W.J.J. Smeets, A.L. Spek, Inorg. Chem. 29 (1990) 1302.
[2] G.A. Solan, P.G. Cozzi, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Organometallics 13 (1994) 2572.
[3] J.J.H. Edema, A. Meetsma, S. Gambarotta, J. Am. Chem. Soc. 1989 (1989) 6878.
[4] J. Jubb, S. Gambarotta, J. Am. Chem. Soc. 115 (1993) 10410.
[5] J. Jubb, S. Gambarotta, Inorg. Chem. 33 (1994) 2503.
[6] J. Jubb, L. Scoles, H. Jenkins, S. Gambarotta, Chem. Eur. J. 2 (1996) 767.

[7] P. Berno, S. Hao, R. Minhas, S. Gambarotta, J. Am. Chem. Soc. 116 (1994) 7417.
[8] J.-I. Song, P. Berno, S. Gambarotta, J. Am. Chem. Soc. 116 (1994) 6927.
[9] F.A. Cotton, M. Millar, J. Am. Chem. Soc. 99 (1977) 7886.
[10] F.A. Cotton, R.A. Walton, Multiple Bonds Between Metal Atoms, 2nd ed., Oxford University Press, New York, 1993.
[11] F.A. Cotton, L.M. Daniels, C.A. Murillo, Inorg. Chem. 32 (1993) 2881.
[12] F.A. Cotton, L.M. Daniels, C.A. Murillo, Angew. Chem. Int. Ed. Engl. 31 (1992) 737.
[13] F.A. Cotton, M.P. Diebold, I. Shim, Inorg. Chem. 24 (1985) 1510.
[14] F.A. Cotton, G.E. Lewis, G.N. Mott, Inorg. Chem. 22 (1983) 560.
[15] J.J.H. Edema, A. Meetsma, F. van Bolhuis, S. Gambarotta, Inorg. Chem. 30 (1991) 2056.
[16] S. Gambarotta, M. Mazzanti, C. Floriani, M. Zehnder, J. Chem. Soc. Chem. Commun. (1984) 1116.
[17] N.S. Dean, S.L. Bartley, W.E. Streib, E.B. Lobkovsky, G. Christou, Inorg. Chem 34 (1995) 1608.
[18] N.S. Dean, F.K.E. Lobkovsky, G. Christou, Angew. Chem. Int. Ed. Engl. 32 (1993) 594.
[19] T.A. Cooper, J. Am. Chem. Soc. 95 (1973) 4158.
[20] D.E. Ryan, K.B. Grant, K. Nakanishi, Biochemistry 35 (1996) 8640.
[21] D.E. Ryan, K.B. Grant, K. Nakanishi, P. Frank, K.O. Hodgson, Biochemistry 35 (1996) 8651.
[22] E.M. Oltz, S. Pollack, T. Delohery, M.J. Smith, M. Ojika, S. Lee, K. Kustin, K. Nakanishi, Experientia 45 (1989) 186.
[23] R.C. Bruening, E.M. Oltz, J. Furukawa, K. Nakanishi, J. Am. Chem. Soc. 107 (1985) 5298.
[24] M. Smith, D. Kim, B. Horenstein, K. Nakanishi, K. Kustin, Acc. Chem. Res. 24 (1991) 117.
[25] D. Rehder, Angew. Chem. Int. Ed. Engl. 30 (1991) 148.
[26] K. Kanamori, K. Ino, H. Maeda, K. Miyazaki, M. Fukagawa, J. Kumada, T. Eguchi, K. Okamoto, Inorg. Chem. 33 (1994) 5547.
[27] K. Kanamori, Y. Ookubo, K. Ino, K. Kawai, H. Michibata, Inorg. Chem. 30 (1991) 3832.
[28] Y. Kataoka, I. Makihira, M. Utunomiya, K. Tani, J. Org. Chem. 62 (1997) 8540.
[29] J.R. Rambo, S.L. Bartley, W.E. Streib, G. Christou, J. Chem. Soc. Dalton Trans. (1994) 1813.
[30] H. Kumagai, S. Kawata, M. Kondo, M. Katada, S. Kitagawa, Inorg. Chim. Acta 224 (1994) 199.
[31] J.H. Freudenberger, A.W. Konradi, S.F. Pedersen, J. Am. Chem. Soc. 111 (1989) 8014.
[32] M. Bakir, A.M. McKenzie, J. Chem. Soc. Dalton Trans. (1997) 3571.
[33] S.R. Breeze, S. Wang, J.E. Greedan, N.P. Raju, Inorg. Chem. 35 (1996) 6944.
[34] G. Psomas, A.J. Stemmler, C. Dendrinou-Samara, J.J. Bodwin, M. Schneider, M. Alexiou, J.W. Kampf, D.P. Kessissoglou, V.L. Pecoraro, Inorg. Chem. 40 (2001) 1562.
[35] S.G. Brand, N. Edelstein, C.J. Hawkins, G. Shalimoff, M.R. Snow, R.T. Tiekink, Inorg. Chem. 29 (1990) 434.
[36] Y. Zhang, R.H. Holm, Inorg. Chem. 29 (1990) 911.
[37] T. Otieno, M.R. Bond, L.M. Mokry, R.B. Walter, C.J. Carrano, Chem. Commun. (1996) 37.
[38] S.L. Castro, Z. Sun, J.C. Bollinger, D.N. Hendrickson, G. Christou, J. Chem. Soc. Chem. Commun. (1995) 2517.
[39] H. Kumagai, S. Kitagawa, M. Maekawa, S. Kawata, H. Kiso, M. Munakata, J. Chem. Soc. Dalton Trans. (2002) 2390.
[40] J.L. Ortego, D.L. Perry, J. Inorg. Nucl. Chem. 35 (1973) 3031.
[41] I.J. Bakker, M.C. Feller, R. Robson, J. Inorg. Nucl. Chem. 33 (1971) 747.
[42] R.R. Osborne, W.R. McWhinnie, J. Chem. Soc. (A) (1967) 2075.
[43] S. Bhaduri, N.Y. Sapre, P.G. Jones, J. Chem. Soc. Dalton Trans. (1991) 2539.
[44] G. Annibale, L. Canovese, L. Cattalini, G. Natile, M. Biagini-Cingi, A.-M. Manotti-Lanfredi, A. Tiripicchio, J. Chem. Soc. Dalton Trans. (1981) 2280.
[45] J.D. Ortego, S. Upalawanna, S. Amanollahi, J. Inorg. Nucl. Chem. 41 (1979) 593.
[46] V. Zerbib, F. Robert, P. Gouzerh, J. Chem. Soc. Chem. Commun. (1994) 2179.
[47] J. Grigg, D. Collison, C.D. Garner, M. Helliwell, P.A. Tasker, J.M. Thorpe, J. Chem. Soc. Chem. Commun. (1993) 1807.
[48] E. Kurras, Naturwissenschaften 46 (1959) 171.
[49] G.M. Sheldrick, Crystallographic Computing 3, Oxford University Press, New York, 1985.
[50] F. Hai-Fu, SAPI 91: Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, 1991.
[51] I. Cavaco, C.J. Pessoa, D. Costa, M.T. Duarte, R.D. Gillard, P. Matias, J. Chem. Soc. Dalton Trans. (1994) 149.
[52] F.A. Cotton, J. Lu, Inorg. Chem. 34 (1995) 2639.
[53] N. Azuma, T. Ozawa, K. Ishizu, Polyhedron 13 (1994) 1715.
[54] M. Pasquali, F. Marchetti, C. Floriani, Inorg. Chem. 18 (1979) 2401.
[55] J. Coetzer, Acta Crystallogr. Sect. B 26 (1970) 872.
[56] P.V. Bernhardt, G.A. Lawrance, P. Comba, L.L. Martin, T.W. Hambley, J. Chem. Soc. Dalton Trans. (1990) 2859.
[57] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th ed., Wiley-Interscience, New York, 1988.
[58] N.N. Greenwood, A. Earnshaw, Chemistry of the Element, Pergamon, New York, 1984.
[59] J. Selbin, Chem. Rev. (1965) 153.
[60] C. Weidemann, W. Priebsch, D. Rehder, Chem. Ber. 122 (1989) 235.
[61] J. Chakravarty, S. Dutta, A. Dey, A. Chakravorty, J. Chem. Soc. Dalton Trans. (1994) 557.
[62] C.R. Cornman, J. Kampf, M.S. Lah, V.L. Pecoraro, Inorg. Chem. 31 (1992) 2035.
[63] D. Collison, D.R. Eardley, F.E. Mabbs, A.K. Powell, S.S. Turner, Inorg. Chem. 32 (1993) 664.
[64] J. Chakravarty, S. Dutta, S.K. Chandra, P. Basu, A. Chakravorty, Inorg. Chem. 32 (1993) 4249.
[65] A. Neves, A.S. Ceccatto, C. Eransmus-Buhr, S. Gehring, W. Haase, H. Paulus, O.R. Nascimento, A.A. Batista, J. Chem. Soc. Chem. Commun. (1993) 1782.
[66] D.C. Crans, A.D. Keramidas, S.S. Amin, O.P. Anderson, S.M. Miller, J. Chem. Soc. Dalton Trans. (1997) 2799.