Synthesis and Crystal Structure of a Cationic Oxo-Bridged Nitridoruthenium(VI) Complex with a Chelating Diamine Ligand Having No α-CH Group

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Received April 26, 1995

Introduction

Due to the oxidizing nature of the ruthenium ion in high oxidation states, high-valent Ru≡N complexes are expected to be electrophilic and reactive and to have potential applications in nitrogen atom transfer reactions.[1,2] The cationic Ru≡N complexes should be of particular interest, and in fact these species have been proposed to be important reactive intermediates in the ruthenium-catalyzed interconversion between bound ammonia and nitrite.[3] While neutral and anionic Ru^{VI}≡N species are known, to our knowledge, there has been no well-characterized cationic Ru^{VI}≡N species.[1−5] Our previous studies on oxoruthenium complexes showed that a chelating saturated amine is a good ligand system for the generation of high-valent ruthenium complexes at relatively low $E°$ values.[1,2] Herein are described the preparation and X-ray crystal structure of a cationic Ru^{VI}≡N complex with the chelating primary diamine ligand L (L = 2,5-dimethyl-2,5-hexanediamine). This ligand was chosen for the study because it contains no α-CH group, rendering oxidative dehydrogenation of the amine to imine difficult.

Experimental Section

Materials. $[(n\text{-Bu})_4N][RuNCl_4]$ was synthesized according to the published method.[5a] 2,5-Dimethyl-2,5-hexanediamine (94% Aldrich) was used as received.

Instrumentation. UV−vis spectra were obtained on a Shimadzu UV-240 spectrophotometer, NMR spectra were run on a JEOL 270 MHz FT-NMR spectrometer, and infrared spectra were obtained as Nujol mulls on a Nicolet 20 SXC FT-IR spectrophotometer. Elemental analyses were performed by Butterworth Co. Ltd.

Preparation of $[(Ru^{VI}(L)_2N)_2(\mu\text{-}O)]Cl_4$ (1). To a solution of $[(n\text{-Bu})_4N][RuNCl_4]$ (0.1 g in 10 mL of acetone) was added a solution of L (0.1 g in 5 mL of acetone). The solution was stirred at room temperature for 12 h. The resulting yellow solid was filtered off, washed with diethyl ether, and air-dried (yield 60%). Anal. Calcd for $[Ru_2C_{32}H_{80}N_{10}O]Cl_4 \cdot H_2O$: C, 39.06; H, 8.34; N, 14.24. Found: C, 39.20; H, 8.40; N, 14.40. UV−vis in $CHCl_3$ [λ_{max}/nm (ϵ_{max}/mol^{-1} dm^3 cm^{-1})]: 452 (5900), 374 (8350), 275 (5560)]. ^{1}H NMR (δ in $CDCl_3$): 1.47 (s, Me, 24H), 1.62 (s, Me, 24H), 1.70 (d, J = 3 Hz, CH_2, 8H), 1.76 (d, J = 5 Hz, CH_2, 8H), 2.34 (m, NH_2, 4H), 3.15 (m, NH_2, 4H), 8.20 (m, NH_2, 4H), 8.29 (m, NH_2, 4H)].

X-ray Crystal Structure Determination of Complex 1·H_2. Empirical formula: $Ru_2O_2N_{10}C_{32}H_{82}Cl_4$. Fw = 983.03. A crystal of dimensions 0.15 × 0.2 × 0.3 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized MoKα radiation (λ = 0.710 73 Å). A total of 1306 independent reflections were obtained; 949 reflections with $F_o \geq 6\sigma(F_o)$ were considered observed and used in the structural analysis. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares using the Enraf-Nonius SDP-1985 programs on a MicroVAX II computer. The Ru, Cl, N, and C atoms and the bridging O atom were refined anisotropically. The O atom of the water molecule, O(2), has a high temperature factor and was refined isotropically, and the two H atoms were not located. The H atoms at calculated positions with isotropic thermal parameters equal to 1.3 times that of the attached C atom were not refined. The H atoms on N(2) and N(3) were not located and were not included in the calculation. The Ru, O(1), N(1), and O(2) atoms are at special positions. Convergence for 113 variables by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.080F_o^2)^2]$ for reflections with $I > 3\sigma(I)$, was reached at R = 0.047, R_w = 0.073, GoF = 1.78, and $(\Delta/\sigma)_{max}$ = 0.01. A final difference Fourier map was featureless, with maximum positive and negative peaks of 1.13 and −1.00 e Å^{-3}, respectively.

Table 1. Crystallographic Data for $[(Ru^{VI}(L)_2N)_2(\mu\text{-}O)]Cl_4 \cdot H_2O$

$Ru_2O_2N_{10}C_{32}H_{82}Cl_4$	fw = 983.03
a = 14.730(3) Å	$I\bar{4}$, tetragonal (No. 82)
c = 11.437(3) Å	T = 24 °C
V = 2481.5(1.0) Å^3	μ(Mo Kα) = 16.99 cm^{-1}
Z = 4	D_{calcd} = 2.63 g cm^{-3}
R^a = 0.047	$F(000)$ = 2064
$R_w{}^a$ = 0.073	

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w^2(|F_o| - |F_c|)^2/\Sigma w^2|F_o|^2]^{1/2}$.

Table 2. Atomic Coordinates and Temperature Factors (Å^2), with Standard Deviations in Parentheses, for Non-Hydrogen Atoms of $[(Ru^{VI}(L)_2N)_2(\mu\text{-}O)]Cl_4 \cdot H_2O$

atom	x	y	z	B_{eq}/B_{iso} (Å^2)
Ru	0.000	0.000	0.17397(7)	2.14(2)
Cl	0.1256(2)	0.2289(2)	0.0411(2)	3.78(5)
O(1)	0.000	0.000	0.000	2.1(1)
O(2)	0.000	0.500	0.250	14.1(9)[a]
N(1)	0.000	0.000	0.3188(9)	3.7(2)
N(2)	0.1420(5)	0.0329(5)	0.1569(6)	2.2(1)
N(3)	0.0518(6)	−0.1360(5)	0.1554(7)	3.1(2)
C(1)	0.2074(8)	0.0311(8)	0.260(1)	4.1(2)
C(2)	0.1932(9)	−0.0556(9)	0.333(1)	5.1(3)
C(3)	0.1859(8)	−0.1479(9)	0.276(1)	5.1(3)
C(4)	0.1004(7)	−0.1911(7)	0.242(1)	3.4(2)
C(5)	0.3010(8)	0.040(1)	0.205(1)	6.0(3)
C(6)	0.1920(9)	0.1107(9)	0.334(1)	5.0(3)
C(7)	0.043(1)	−0.2101(9)	0.348(1)	5.0(3)
C(8)	0.122(1)	−0.2781(8)	0.179(1)	5.5(3)

[a] O(2) was refined isotropically.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) of $[(Ru^{VI}(L)_2N)_2(\mu\text{-}O)]^{4+}$

Ru−O(1)	1.9896(8)	C(1)−C(5)	1.53(2)
Ru−N(1)	1.66(1)	C(1)−C(6)	1.47(2)
Ru−N(2)	2.156(7)	C(2)−C(3)	1.51(2)
Ru−N(3)	2.155(8)	C(3)−C(4)	1.46(2)
N(2)−C(1)	1.53(1)	C(4)−C(7)	1.50(2)
N(3)−C(4)	1.47(1)	C(4)−C(8)	1.50(2)
C(1)−C(2)	1.54(2)		
O(1)−Ru−N(1)	180.0(2)	Ru−N(2)−C(1)	122.7(7)
O(1)−Ru−N(2)	84.8(2)	Ru−N(3)−C(4)	128.4(6)
O(1)−Ru−N(3)	84.3(2)	N(2)−C(1)−C(2)	110.5(9)
N(1)−Ru−N(2)	95.2(2)	N(2)−C(1)−C(5)	105(1)
N(1)−Ru−N(3)	95.7(2)	N(2)−C(1)−C(6)	109.6(9)
N(2)−Ru−N(3)	81.7(3)		

Crystallographic data are summarized in Table 1. Table 2 lists the atomic coordinates of non-hydrogen atoms and selected bond distances and angles are listed in Table 3.

Molecular Orbital Calculations. Extended Hückel molecular orbital (EHMO) calculations were carried out on the complex $[(Ru^{VI}(L)_2N)_2(\mu\text{-}O)]^{4+}$ by using the ICON program. The geometric factors were obtained from the X-ray diffraction data. After transformation of the Cartesian coordinates, the μ-O atom was designated at the origin of Cartesian coordinates. A total of 125 atoms and 270 valence orbitals were employed. The parameters of Ru were taken from Hoffmann *et al.*,[6] and those of the other atoms were acquired as standard values.

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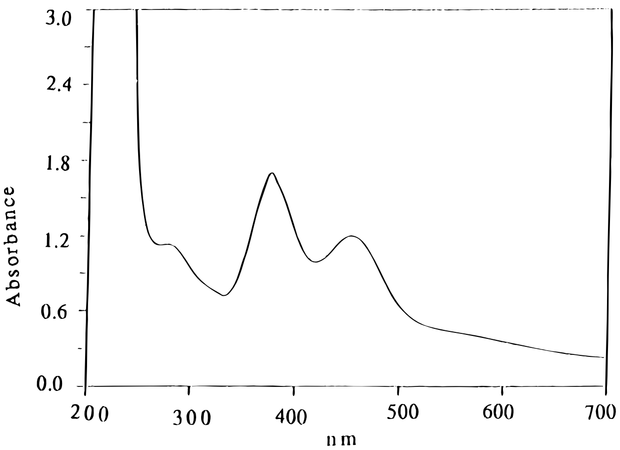

Figure 1. UV−vis absorption spectrum of $[(\mathrm{Ru^{VI}(L)_2N})_2(\mu\text{-O})]\mathrm{Cl_4}$ (0.204 mM) in $\mathrm{CHCl_3}$.

Resuts and Discussion

There have been very few reports on the coordination chemistry of chelating primary diamines containing no α-CH groups. Recent studies established the rich coordination chemistry of 2,3-diamino-2,3-dimethylbutane (tmen), which forms a number of interesting high-valent Ru[7] and Os[8] complexes. However the reaction of tmen with $[\mathrm{RuNCl_4}]^-$ in acetone did not give any $\mathrm{Ru^{VI}}{\equiv}\mathrm{N}$ species; instead a Ru(IV)−bis(amide) complex has been isolated.[9]

The ligand L was previously used by Gray and co-workers for the synthesis of 2,5-dimethyl-2,5-diisocyanohexane, a bridging diisocyanide ligand for binuclear rhodium(I) complexes.[10] However, its coordination chemistry has scarcely been explored. Presumably, it is not a good chelating ligand since a seven-memberd chelated ring would be formed. In this work, it reacts with $[(n\text{-Bu})_4\mathrm{N}][\mathrm{RuNCl_4}]$ in acetone to give $[(\mathrm{Ru^{VI}(L)_2N})_2(\mu\text{-O})]\mathrm{Cl_4}$ **(1)**.

Complex **1** is stable in chloroform for a few days. It is diamagnetic with well-resolved ^{1}H NMR signals. Its IR spectrum shows the $\nu(\mathrm{Ru{\equiv}N})$ band at 999 $\mathrm{cm^{-1}}$, which is at a lower frequency than those of 1095 $\mathrm{cm^{-1}}$ for $[(n\text{-Bu})_4\mathrm{N}][\mathrm{RuNCl_4}]$[5a] and 1094 $\mathrm{cm^{-1}}$ for $[\mathrm{Ru(N)(NHCOCH_2CH_2S)_2}]^-$.[5c] The UV−vis absorption spectrum of **1** in $\mathrm{CHCl_3}$ is shown in Figure 1. It is quite similar to that of the reported systems with linear Ru−O−Ru groups such as $[\mathrm{Ru_2OCl_{10}}]$.[4−11] The two absorption bands at 374 and 452 nm are likely to be metal-localized transitions within the Ru−O−Ru π system.[11]

Figure 2 shows a perspective view of the complex cation. The structure is the first example of a cationic $\mathrm{Ru^{VI}}{\equiv}\mathrm{N}$ complex. Its interesting structural features are the seven-membered chelating ring formed by L and Ru and the linear N≡Ru−O−Ru≡N unit. The Ru≡N distance of 1.66(1) Å is longer than those of 1.570 Å in $[\mathrm{RuNCl_4}]^-$ [12] and 1.595(8) Å in $[\mathrm{Ru(N)(NHCOCH_2CH_2S)_2}]^-$.[5c] This could be attributed to the competitive π-bonding of the ruthenium ion with the $\mathrm{N^{3-}}$ and μ-oxo ligands. This Ru≡N distance, however, is shorter than most Ru=O distances[2] and that of Ru−N(imide) [1.785(6) Å in *trans*-$\mathrm{Ru(2,6\text{-}Pr^i{}_2C_6H_3N)_2(PMe_3)_2}$].[13] The Ru−O distance of 1.9896(8) Å is similar to that of 1.93(1) Å in $[\mathrm{Ru_2O_6(py)_4}]$[14] (py = pyridine) but is longer than that of 1.80 Å in $\mathrm{K_4[Ru_2OCl_{10}]}$.[15] The geometry of the two coordinated ligands around the metal is distorted with the four nitrogen atoms bent away from the nitrido group. This kind of distortion has been found in other nitridoruthenium(VI) and nitridoosmium(VI) complexes and is ascribed to the repulsion between metal−nitride π-bonding electrons, localized on the metal, and σ-bonding electrons of the ligands.[5c,16]

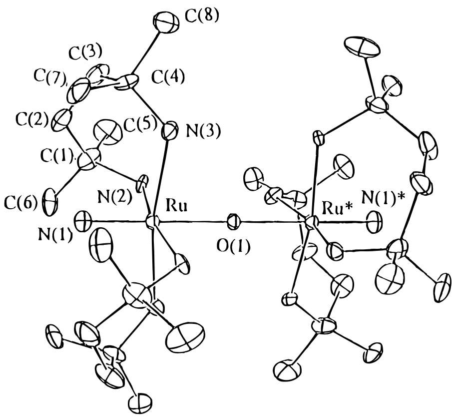

Figure 2. Perspective view of the $[(\mathrm{Ru^{VI}(L)_2N})_2(\mu\text{-O})]^{4+}$ cation.

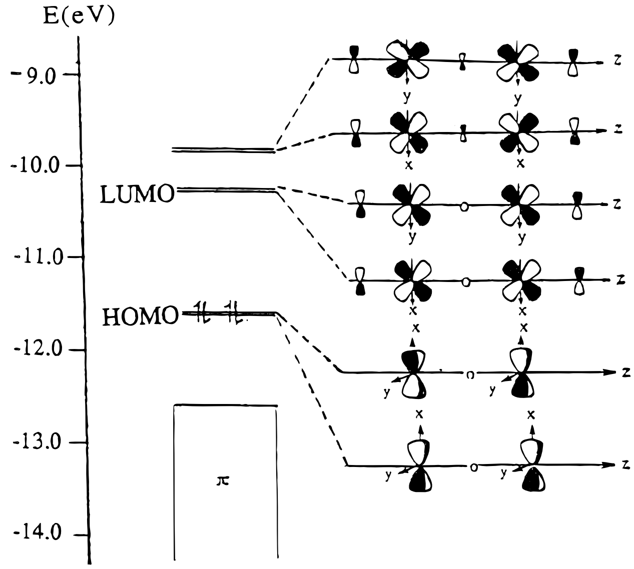

Figure 3. Molecular orbital diagram of $[(\mathrm{Ru^{VI}(L)_2N})_2(\mu\text{-O})]^{4+}$.

The diagram of some of the near frontier orbitals from EHMO analysis is depicted in Figure 3. The result indicates that the highest occupied molecular orbital (HOMO) and the next highest occupied molecular orbital (NHOMO) are composed of the d_{xy} orbitals of two Ru atoms. The lowest unoccupied molecular orbital (LUMO) and the next lowest unoccupied molecular orbital (NLUMO) are mainly composed of the Ru d_{xz} and d_{yz} orbitals. The four valence electrons of the two Ru(VI) ions occupy the HOMO and NHOMO. The ground state configuration of the complex is $^1[(d_{xy})^2(d_{xy})^2]$, and this is in accordance with the diamagnetism of complex **1**.

Acknowledgment. We acknowledge support from The University of Hong Kong and The Hong Kong Research Grants Council.

Supporting Information Available: Tables of anisotropic thermal parameters, calculated positional parameters for hydrogen atoms, and complete bond distances and angles (4 pages). Ordering information is given on any current masthead page.

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