Disproportionation of a Ruthenium(III) Nitro Complex of a Macrocyclic Tertiary Amine in an Aqueous Medium†

Kwok-Yin Wong,[a] Chi-Ming Che,*[,a] Wai-Hing Yip,[b] Ru-Ji Wang[b] and Thomas C. W. Mak*[,b]
[a] *Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong*
[b] *Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong*

The reaction of *trans*-$[RuLCl_2]^+$ (L = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) with NO_2^- in water at 60 °C leads to the formation of *trans*-$[RuL(O)Cl]^+$ and *trans*-$[RuL(OH)(NO)]^{2+}$. The formation of the products can be rationalized by the disproportionation of *trans*-$[RuL(Cl)(NO_2)]^+$. The structures of the products have been determined by X-ray crystallography: *trans*-$[RuL(O)Cl]ClO_4$, space group *Pna*2_1 (no. 33), *a* = 12.616(1), *b* = 15.421(3), *c* = 11.292(3) Å; Ru=O and Ru–Cl 1.75(1) and 2.435(6) Å; *trans*-$[RuL(OH)(NO)][ClO_4]_2$, space group *Pbca* (no. 61), *a* = 20.459(3), *b* = 29.16(1), *c* = 25.13(1) Å; average Ru–OH and Ru–NO 1.906(9) and 1.74(1) Å.

The study of metal nitro complexes is of considerable interest because of the multiple-electron interconversion between M–NO_2 and M–NH_3.[1] Although a variety of transition-metal nitro complexes have been studied, the chemistry of ruthenium(III) nitro complexes remains relatively unexplored.[2,3a] It has been suggested that this class of compounds are unstable and would undergo rapid disproportionation.[2,3] Recently, Mukaida and co-workers[3] reported the synthesis of a monooxoruthenium(IV) complex by oxidation of nitrosylruthenium(II) with NaOCl. Their results suggested that the Ru^{III}–NO_2 species undergoes disproportionation to give Ru^{IV}=O and Ru^{II}–NO^+. In order further to investigate the chemistry of Ru^{III}–NO_2 complexes with macrocyclic tertiary amine ligands we have attempted to prepare Ru^{III}–NO_2 by substitution of the Cl^- ligand in *trans*-$[RuLCl_2]^+$ (L = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) with NO_2^-. The products of the reaction were identified by X-ray crystallography as *trans*-$[RuL(O)Cl]^+$ and *trans*-$[RuL(OH)(NO)]^{2+}$.

Experimental

Physical Measurements.—The UV/VIS absorption spectra were recorded on a Milton Roy (Spectronic 3000 Array) diode-array spectrophotometer, infrared spectra as Nujol mulls on a Nicolet 20FXC FT-IR spectrophotometer, and ^1H NMR spectra on a JEOL 270 MHz FT-NMR spectrometer. Elemental analyses were performed at National Taiwan University.

Preparation of trans-$[RuL(O)Cl]ClO_4$ *and trans-*$[RuL(OH)(NO)][ClO_4]_2$.—The complex *trans*-$[RuLCl_2]Cl$ was prepared as described previously.[4] Other chemicals were obtained as reagent grade and used without further purification.

A mixture of *trans*-$[RuLCl_2]Cl$ (0.5 g) and $NaNO_2$ (0.1 g) in deionized water was warmed at 60 °C for 20 min. The colour of the solution changed from yellow to greenish blue. Upon cooling to 30 °C, $NaClO_4$ (*ca.* 1 g) was added to cause immediate precipitation of blue crystalline *trans*-$[RuL(O)Cl]ClO_4$ (yield *ca.* 0.13 g) which was filtered off. The filtrate was left to stand in air. Yellow crystals of *trans*-$[RuL(OH)(NO)][ClO_4]_2$ (yield *ca.* 0.19 g) were obtained after about 1 d. Both complexes could be recrystallized from hot water, although the quality of the crystals of the oxo complex was poor. *trans*-$[RuL(O)Cl]ClO_4$: IR, ν(Ru=O) 840 cm^{-1}; UV/VIS (CH_3CN), λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 570 (160), *ca.* 360 (250) and 295 (1600) (Found: C, 35.6; H, 6.8; N, 10.3. Calc.: C, 35.8; H, 6.7; N, 10.4%). *trans*-$[RuL(OH)(NO)][ClO_4]_2$: IR, ν(NO) 1825 cm^{-1}; UV/VIS (water), λ/nm (ε/dm^3 mol^{-1} cm^{-1}): *ca.* 375 (340), 320 (1000) and 244 (26 300); ^1H NMR (CD_3CN), δ 2.12–2.4 (m, CH_2), 2.76, 2.8 (s, NCH_3) and 3.1–3.6 (m, NCH_2) (Found: C, 30.2; H, 6.0; N, 10.9. Calc.: C, 30.4; H, 5.85; N, 11.1%).

X-Ray Structure Determination.—Details of crystal parameters, data collection and structure refinement are given in Table 1. Raw intensities collected were processed with the profile-fitting procedures of Diamond[5] and corrected for absorption using ψ-scan data.[6] For *trans*-$[RuL(O)Cl]ClO_4$, the L ligand exhibits slight configurational disorder and distance constraints of 1.48(2), 1.52(2) and 1.54(2) Å were applied to the N–C(methylene), N–C(methyl) and C–C bonds, respectively. In addition, two major orientations of the ClO_4^- group were identified with half site occupancy assigned to the oxygen atoms, and distance constraints of 1.44(2) and 2.35(2) Å applied to the Cl–O bonds and O···O separations, respectively. Refinement proceeded with isotropic thermal parameters for the C atoms and anisotropic ones for the remaining non-hydrogen atoms in the asymmetric unit. The H atoms were generated geometrically (C–H 0.96 Å) and included in structure-factor calculations with fixed isotropic thermal parameters. Reversal of the polarity of the structure produced no significant improvement. Table 2 lists the atomic coordinates for the non-hydrogen atoms of *trans*-$[RuL(O)Cl]ClO_4$, Table 3 selected bond distances and angles.

The asymmetric unit in *trans*-$[RuL(OH)(NO)][ClO_4]_2$ contains three independent RuN_5O co-ordination polyhedra. One of the three L ligands exhibits two-fold disorder, which was modelled by two sets of atoms: N(12)–N(15) plus C(33)–C(48) and N(12′)–N(15′) plus C(33′)–C(48′), each of half site occupancy. Distance constraints of 1.48(2), 1.52(2) and 1.54(2) Å were applied to the N–C(methylene), N–C(methyl) and C–C bonds in order to overcome correlation problems caused by overlapping atoms. The non-hydrogen atoms except those of the disordered L ligand were subjected to anisotropic blocked-matrix refinement. The H atoms belonging to the hydroxide and disordered L ligand were not included in structure-factor calculations, whereas the others were generated geometrically

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Data collection and processing parameters for* *trans*-[RuL(O)Cl]ClO$_4$ and *trans*-[RuL(OH)(NO)][ClO$_4$]$_2$

	trans-[RuL(O)Cl]ClO$_4$	*trans*-[RuL(OH)(NO)][ClO$_4$]$_2$
Molecular formula	$C_{16}H_{36}Cl_2N_4O_5Ru$	$C_{16}H_{37}Cl_2N_5O_{10}$
M	536.53	632.48
Colour and habit	Blue plate	Yellow polyhedron
Space group	$Pna2_1$ (No. 33)	$Pbca$ (No. 61)
a/Å	12.616(1)	20.459(3)
b/Å	15.421(3)	29.16(1)
c/Å	11.292(3)	25.13(1)
U/Å^3	2196.9(7)	14 992(10)
Z	4	24
F(000)	1112	7848
D_c/g cm^{-3}	1.622	1.681
Standard reflections	(112), (120)	(008), (641)
Intensity variation (%)	±6	±2
R_{int} (from merging of equiv. reflections)	0.034	0.080
μ/cm^{-1}	9.78	8.87
Crystal size/mm	0.04 × 0.34 × 0.42	0.28 × 0.32 × 0.34
Mean μr	0.13	0.121
Transmission factors	0.154–0.563	0.686–0.709
Scan type and rate	ω–2θ, 2.49–15.63° min^{-1}	ω, 3.01–15.63° min^{-1}
Scan range	0.60° below Kα_1 to 0.70° above Kα_2	0.65° below Kα_1 to 0.65° above Kα_2
Collection range	h,k,l; $2\theta_{max} = 50°$	h,k,l; $2\theta_{max} = 45°$
Unique data measured	2051	13 169
Obs. data with $\lvert F_o\rvert \geqslant 6\sigma(\lvert F_o\rvert)$, n	1309	6079
No. of variables, p	208	683
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.097	0.072
Weighting scheme, w	$[1 - \exp(-6 \sin^2 \theta/\lambda^2)]/[\sigma^2(F_o) + 0.0010\lvert F_o\rvert^2]$	$[1 - \exp(-8 \sin^2 \theta/\lambda^2)]/[\sigma^2(F_o) + 0.0008\lvert F_o\rvert^2]$
$R' = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$	0.107	0.086
$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n - p)]^{\frac{1}{2}}$	1.752	1.338
Residual extrema in final difference map/e Å^{-3}	+3.42 to −2.01	+1.42 to −0.62

* Details in common: crystal system orthorhombic, graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å); stationary counts for one-fifth of scan time at each end of scan range.

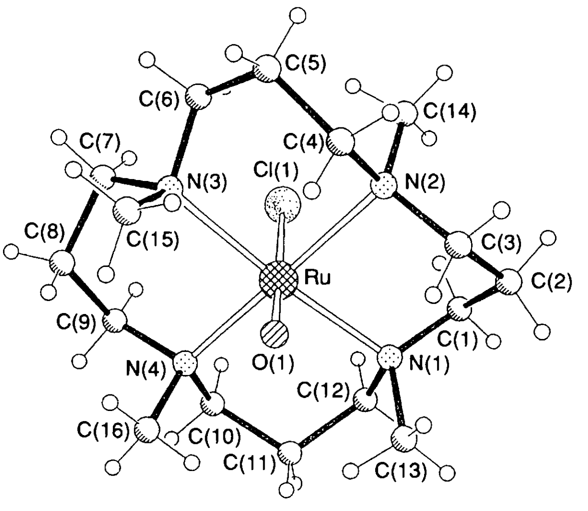

Fig. 1 A perspective view and atom numbering of the *trans*-[RuL(O)Cl]$^+$ cation

and assigned the same isotropic thermal parameter U = 0.12 Å^2. All computations were performed using the SHELXTL-PLUS program package[7] on a DEC microVAX-II computer. Analytical expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[8] Tables 4 and 5 list the atomic coordinates of the non-hydrogen atoms and selected bond distances respectively of *trans*-[RuL(OH)(NO)][ClO$_4$]$_2$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The formation of Ru^{IV}=O and Ru^{II}–NO$^+$ complexes from Ru^{III}–NO$_2$ has previously been suggested.[3b] In this work the reaction of *trans*-[RuLCl$_2$]$^+$ with NaNO$_2$ gave similar products instead of the desired *trans*-[RuL(NO$_2$)$_2$]$^+$. The UV/VIS spectrum of *trans*-[RuL(O)Cl]$^+$ is similar to those of the Ru^{IV}=O complexes of tmc (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane),[9] which have been reported previously. Since *trans*-[RuL(O)Cl]$^+$ is paramagnetic its ^{1}H NMR spectrum has not been recorded. According to Schreiner *et al.*,[10] ruthenium nitrosyl complexes such as *trans*-[Ru(NH$_3$)$_4$(OH)(NO)]Cl$_2$ and [Ru(NH$_3$)$_5$(NO)]Cl$_3$ should be formulated as [Ru^{II}–NO$^+$] species. A direct comparison between *trans*-[RuL(OH)(NO)]$^{2+}$ and *trans*-[Ru(NH$_3$)$_4$(OH)(NO)]$^{2+}$ revealed that their UV/VIS spectra and ν(NO) stretching frequencies {ν(NO) 1834 cm^{-1} for *trans*-[Ru(NH$_3$)$_4$(OH)(NO)]$^{2+}$ ref. 10} are similar, thereby suggesting they may have similar electronic configurations. Assignment of a co-ordinated OH$^-$ group in *trans*-[RuL(OH)(NO)]$^{2+}$ based on the short average Ru–O(OH) distance of 1.906(9) Å is discussed in a later section. The ^{1}H NMR spectrum of *trans*-[RuL(OH)(NO)]$^{2+}$ in CD$_3$CN exhibits two peaks at δ 2.8 and 2.76 with unequal intensities, and two sets of multiplets at δ 3.1–3.6 and 2.12–2.4. The two peaks at δ 2.8 and 2.76 are assigned to NCH$_3$ protons. The multiplets at δ 3.1–3.6 are due to NCH$_2$ protons.

The reaction of *trans*-[RuLCl$_2$]$^+$ with NaNO$_2$ can be followed by measuring the UV/VIS spectrum periodically. A peak at λ_{max} 570 nm characteristic of *trans*-[RuL(O)Cl]$^+$ appeared in the early stages of the reaction. The formation of *trans*-[RuL(O)Cl]$^+$ could not be due to aerial oxidation of *trans*-[RuL(OH)(OH$_2$)]$^{2+}$ as the related *trans*- [RuL′(OH)(OH$_2$)]$^{2+}$ (L′ = macrocyclic tertiary amine ligands) complexes were found to be stable under similar reaction conditions.

Table 2 Atomic coordinates (× 10^4) for *trans*-$[RuL(O)Cl]ClO_4$

Atom*	*x*	*y*	*z*
Ru	8 393(1)	8 617(1)	7 500
Cl(1)	10 230(4)	9 099(4)	7 566(14)
O(1)	7 075(11)	8 264(10)	7 570(20)
Cl(2)	502(5)	6 381(4)	2 552(11)
O(2)	− 109(20)	6 511(20)	1 511(17)
O(2′)	466(20)	6 042(16)	1 369(14)
O(3)	1 421(15)	5 839(15)	2 266(22)
O(3′)	755(20)	5 707(13)	3 380(19)
O(4)	− 104(17)	5 922(16)	3 439(17)
O(4′)	− 538(13)	6 726(17)	2 833(21)
O(5)	869(19)	7 177(12)	3 046(22)
O(5′)	1 269(18)	7 062(14)	2 628(24)
N(1)	8 741(13)	7 667(11)	6 057(15)
N(2)	8 820(18)	7 481(20)	8 754(21)
N(3)	8 058(13)	9 475(13)	9 088(16)
N(4)	8 011(14)	9 705(13)	6 310(16)
C(1)	9 665(17)	7 097(17)	6 273(24)
C(2)	9 151(21)	6 421(17)	7 106(20)
C(3)	8 421(20)	6 698(18)	8 136(21)
C(4)	8 126(22)	7 630(19)	9 786(21)
C(5)	8 397(21)	8 334(14)	10 686(21)
C(6)	8 685(19)	9 215(16)	10 140(20)
C(7)	8 445(18)	10 374(13)	9 018(19)
C(8)	7 913(18)	10 821(16)	7 968(15)
C(9)	8 337(19)	10 584(14)	6 732(19)
C(10)	8 574(19)	9 735(15)	5 171(18)
C(11)	8 480(21)	8 892(15)	4 450(22)
C(12)	9 128(23)	8 145(20)	4 993(23)
C(13)	7 731(18)	7 328(20)	5 496(24)
C(14)	9 955(20)	7 486(23)	9 219(26)
C(15)	6 910(14)	9 466(16)	9 448(22)
C(16)	6 826(15)	9 768(19)	6 075(24)

* Disordered oxygen atoms of perchlorate anion were treated as O(2)–O(5) and O(2′)–O(5′), each of half site occupancy.

Table 3 Selected bond lengths (Å) and angles (°) for *trans*-$[RuL(O)Cl]ClO_4$

Ru–Cl(1)	2.435(6)	Ru–O(1)	1.75(1)
Ru–N(1)	2.23(2)	Ru–N(2)	2.32(3)
Ru–N(3)	2.27(2)	Ru–N(4)	2.20(2)
Cl(1)–Ru–O(1)	175.7(8)	Cl(1)–Ru–N(1)	92.0(5)
O(1)–Ru–N(1)	90.9(8)	Cl(1)–Ru–N(2)	89.5(6)
O(1)–Ru–N(2)	87.6(8)	N(1)–Ru–N(2)	84.5(8)
Cl(1)–Ru–N(3)	88.6(3)	O(1)–Ru–N(3)	88.2(8)
N(1)–Ru–N(3)	174.6(6)	N(2)–Ru–N(3)	90.1(8)
Cl(1)–Ru–N(4)	89.7(5)	O(1)–Ru–N(4)	93.2(7)
N(1)–Ru–N(4)	95.6(6)	N(2)–Ru–N(4)	179.1(7)
N(3)–Ru–N(4)	89.8(7)		

Meyer[11] and Mukaida[3c] and their co-workers proposed the transfer of an oxygen atom from one Ru^{III}–NO_2 group to another to give the intermediate $[ClRu–N(O)O–N(O)–O–RuCl]^{2+}$ which easily decomposes into $[Cl–Ru^{II}–NO^+]^{2+}$ and $[O{=}Ru^{IV}–Cl]^+$. It is likely that a similar mechanism operates here.

Structure of trans-$[RuL(O)Cl]ClO_4$.—Fig. 1 shows a perspective drawing of the *trans*-$[RuL(O)Cl]^+$ cation. The Ru atom has distorted octahedral co-ordination comprising four nitrogen atoms of L and the chloro and oxo ligands which are *trans* to each other. The Ru atom lies on the equatorial plane composed of the four N atoms such that the mean deviation of the four N atoms from the plane is 0.01(2) Å and the Ru atom is displaced 0.003 Å from it towards O(1). The respective Ru=O and Ru–Cl bond lengths of 1.75(1) and 2.435(6) Å are matched closely by values of 1.765(7) and 2.505(3) Å in its analogue *trans*-$[Ru(tmc)O(Cl)]^+$.[12] The configuration of the L ligand in the present complex is 'three up, one down', the same as in *trans*-$[Ru(tmc)O(Cl)]^+$, but different from the 'two up, two down' configuration in *trans*-$[RuLO_2]^{2+}$.[13] The crystal structure consists of a packing of discrete cations and anions with normal van der Waals separations.

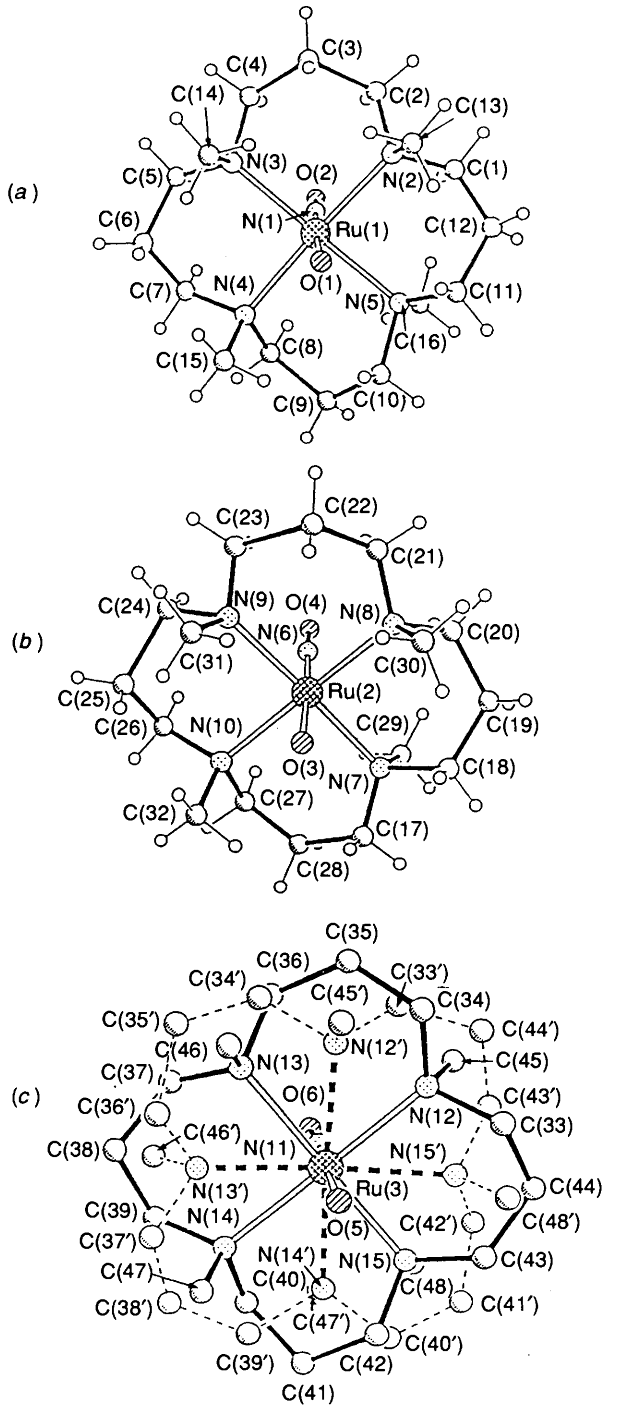

Fig. 2 Perspective view and atom numbering of (*a*) cation **I**, (*b*) cation **II** and (*c*) the two-fold disordered cation **III** of *trans*-$[RuL(OH)(NO)]^{2+}$. In (*c*), atoms representing one possible orientation of the L ligand are linked by solid lines and those representing the other orientation by broken lines

Structure of trans-$[RuL(OH)(NO)][ClO_4]_2$.—There are three independent *trans*-$[RuL(OH)(NO)]^{2+}$ cations (labelled **I**–**III**) and six perchlorate anions in a crystallographic asymmetric unit of this complex. The co-ordination environment about each Ru atom can be described as a compressed

Table 4 Atomic coordinates (× 10^4) for *trans*-$[RuL(OH)(NO)][ClO_4]_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cation **I**							
Ru(1)	426(1)	1 474(1)	9 119(1)	C(5)	−748(11)	831(8)	8 841(9)
O(1)	39(4)	1 997(3)	9 450(4)	C(6)	−907(10)	755(7)	9 437(9)
O(2)	1 085(5)	709(4)	8 609(5)	C(7)	−243(13)	674(9)	9 714(11)
N(1)	829(5)	1 008(3)	8 814(4)	C(8)	758(12)	859(9)	10 053(9)
N(2)	670(6)	1 940(4)	8 438(4)	C(9)	1 180(11)	1 253(7)	10 371(7)
N(3)	−514(5)	1 282(4)	8 724(5)	C(10)	1 259(10)	1 718(7)	10 113(7)
N(4)	177(6)	1 068(4)	9 832(4)	C(11)	1 480(9)	2 198(6)	9 412(9)
N(5)	1 354(5)	1 705(4)	9 513(5)	C(12)	1 719(10)	2 259(7)	8 834(8)
C(1)	1 405(10)	2 015(8)	8 397(8)	C(13)	379(11)	2 409(7)	8 471(8)
C(2)	542(13)	1 749(8)	7 911(8)	C(14)	−1 047(9)	1 609(8)	8 824(9)
C(3)	−272(12)	1 701(9)	7 855(8)	C(15)	−170(13)	1 315(8)	10 264(8)
C(4)	−452(10)	1 252(8)	8 137(7)	C(16)	1 930(8)	1 441(7)	9 407(9)
Cation **II**							
Ru(2)	4 662(1)	9 006(1)	973(1)	C(21)	6 033(11)	8 826(9)	474(10)
O(3)	4 696(5)	8 639(3)	1 602(3)	C(22)	6 364(10)	9 084(8)	955(9)
O(4)	4 593(6)	9 584(3)	45(4)	C(23)	5 996(15)	9 571(9)	1 009(14)
N(6)	4 640(6)	9 357(3)	419(4)	C(24)	5 260(14)	9 943(11)	1 405(13)
N(7)	3 881(6)	8 560(5)	642(5)	C(25)	4 667(11)	10 007(8)	1 792(9)
N(8)	5 442(6)	8 577(4)	616(5)	C(26)	4 059(12)	9 903(8)	1 464(10)
N(9)	5 442(6)	9 437(4)	1 335(5)	C(27)	3 250(11)	9 390(9)	1 119(11)
N(10)	3 902(7)	9 410(5)	1 407(5)	C(28)	2 952(9)	8 957(8)	1 034(9)
C(17)	3 367(13)	8 459(10)	993(12)	C(29)	3 641(11)	8 674(9)	126(8)
C(18)	4 124(14)	8 073(8)	583(11)	C(30)	5 647(10)	8 173(7)	962(9)
C(19)	4 677(12)	8 018(7)	152(9)	C(31)	5 558(14)	9 357(10)	1 893(7)
C(20)	5 225(13)	8 384(9)	115(10)	C(32)	3 733(11)	9 237(9)	1 934(8)
Disordered cation **III**							
Ru(3)	7 152(1)	6 266(1)	2 367(1)	C(47)	6 948(16)	5 307(11)	1 822(15)
O(5)	6 445(5)	5 885(4)	2 575(4)	C(48)	8 389(11)	6 087(11)	3 051(12)
O(6)	8 220(8)	6 831(6)	2 061(7)	N(12′)	6 463(13)	6 840(9)	2 280(11)
N(11)	7 824(6)	6 606(4)	2 203(5)	N(13′)	7 021(13)	6 055(10)	1 532(11)
N(12)*	6 829(11)	6 815(8)	2 908(9)	N(14′)	7 849(13)	5 675(10)	2 511(10)
N(13)	6 619(12)	6 620(8)	1 698(10)	N(15′)	7 251(11)	6 420(8)	3 225(10)
N(14)	7 431(10)	5 705(8)	1 822(8)	C(33′)	6 694(17)	7 254(10)	2 589(12)
N(15)	7 684(8)	5 930(6)	3 017(7)	C(34′)	6 356(26)	6 988(17)	1 722(13)
C(33)	6 712(18)	6 634(17)	3 457(12)	C(35′)	6 210(22)	6 664(13)	1 256(18)
C(34)	6 217(18)	7 067(18)	2 796(17)	C(36′)	6 372(16)	6 151(13)	1 291(17)
C(35)	6 258(19)	7 298(14)	2 243(13)	C(37′)	6 977(19)	5 566(11)	1 381(19)
C(36)	6 632(16)	7 130(9)	1 743(12)	C(38′)	7 634(20)	5 331(18)	1 519(14)
C(37)	6 941(19)	6 540(12)	1 181(13)	C(39′)	7 629(18)	5 246(13)	2 122(13)
C(38)	6 975(16)	6 048(11)	957(14)	C(40′)	7 787(19)	5 441(12)	3 031(11)
C(39)	7 553(14)	5 822(11)	1 252(9)	C(41′)	7 982(23)	5 806(12)	3 448(18)
C(40)	8 082(12)	5 527(11)	1 994(11)	C(42′)	7 932(14)	6 327(12)	3 407(15)
C(41)	8 052(15)	5 219(10)	2 493(10)	C(43′)	7 267(14)	6 916(8)	3 338(12)
C(42)	7 653(16)	5 419(8)	2 959(12)	C(44′)	6 619(17)	7 164(16)	3 184(13)
C(43)	7 342(13)	5 967(9)	3 536(9)	C(45′)	5 753(15)	6 707(15)	2 372(17)
C(44)	7 325(17)	6 463(10)	3 751(15)	C(46′)	7 521(20)	6 196(18)	1 119(16)
C(45)	7 316(21)	7 194(15)	3 022(21)	C(47′)	8 554(15)	5 807(14)	2 425(17)
C(46)	5 891(14)	6 491(16)	1 707(18)	C(48′)	6 762(19)	6 204(16)	3 600(16)
Perchlorate anions							
Cl(1)	3 174(2)	2 379(2)	5 125(2)	Cl(2)	2 733(2)	1 338(2)	7 623(2)
O(7)	3 061(9)	2 678(8)	4 747(11)	O(11)	3 034(8)	989(6)	7 314(7)
O(8)	3 795(8)	2 267(8)	5 037(10)	O(12)	2 326(10)	1 087(7)	7 981(7)
O(9)	2 823(15)	2 412(12)	5 535(11)	O(13)	3 149(12)	1 598(6)	7 901(9)
O(10)	2 854(14)	2 015(10)	5 046(12)	O(14)	2 346(9)	1 613(6)	7 306(7)
Cl(3)	683(2)	2 751(2)	6 726(2)	Cl(4)	7 504(2)	114(2)	5 009(2)
O(15)	1 284(10)	2 575(10)	6 720(14)	O(19)	7 206(10)	267(6)	5 468(7)
O(16)	616(11)	3 074(7)	7 116(8)	O(20)	7 960(12)	−173(8)	5 130(8)
O(17)	269(9)	2 385(5)	6 806(6)	O(21)	7 169(10)	−3(10)	4 600(11)
O(18)	584(15)	2 923(7)	6 254(8)	O(22)	7 850(13)	462(10)	4 805(8)
Cl(5)	5 061(3)	323(2)	3 401(2)	Cl(6)	307(3)	1 231(2)	3 696(2)
O(23)	5 645(13)	209(8)	3 541(13)	O(27)	305(12)	1 097(7)	3 164(6)
O(24)	4 706(11)	259(8)	3 849(7)	O(28)	−63(12)	1 626(7)	3 785(9)
O(25)	4 771(16)	2(11)	3 133(9)	O(29)	31(17)	941(7)	4 007(8)
O(26)	5 054(11)	746(7)	3 222(11)	O(30)	878(14)	1 500(13)	3 865(12)

* The two-fold disordered ligand in cation **III** was treated as N(12)–C(48) and N(12′)–C(48′), each of half site occupancy.

Table 5 Selected bond lengths (Å) and angles (°) for *trans*-[RuL(OH)(NO)][ClO_4]$_2$

Ru(1)–O(1)	1.909(9)	Ru(1)–N(1)	1.76(1)
Ru(1)–N(2)	2.24(1)	Ru(1)–N(3)	2.23(1)
Ru(1)–N(4)	2.21(1)	Ru(1)–N(5)	2.25(1)
O(2)–N(1)	1.14(2)		
Ru(2)–O(3)	1.910(9)	Ru(2)–N(6)	1.73(1)
Ru(2)–N(7)	2.22(1)	Ru(2)–N(8)	2.22(1)
Ru(2)–N(9)	2.23(1)	Ru(2)–N(10)	2.24(1)
O(4)–N(6)	1.15(2)		
Ru(3)–O(5)	1.90(1)	Ru(3)–N(11)	1.74(1)
Ru(3)–N(12)	2.20(2)	Ru(3)–N(13)	2.25(2)
Ru(3)–N(14)	2.21(2)	Ru(3)–N(15)	2.19(2)
Ru(3)–N(12′)	2.20(3)	Ru(3)–N(13′)	2.20(3)
Ru(3)–N(14′)	2.27(3)	Ru(3)–N(15′)	2.21(2)
O(6)–N(11)	1.10(2)		
O(1)–Ru(1)–N(1)	176.6(4)	N(2)–Ru(1)–N(5)	88.1(4)
N(1)–Ru(1)–N(2)	91.8(4)	N(4)–Ru(1)–N(5)	89.9(4)
N(1)–Ru(1)–N(3)	90.9(4)		
O(1)–Ru(1)–N(4)	88.8(4)	Ru(1)–N(1)–O(2)	179(1)
N(2)–Ru(1)–N(4)	175.1(4)	O(1)–Ru(1)–N(2)	86.6(4)
O(1)–Ru(1)–N(5)	85.4(4)	O(1)–Ru(1)–N(3)	92.1(4)

octahedron with the hydroxide and nitrosyl ligands aligned in the short axial direction. The Ru atom in each cation is displaced by 0.01(1)–0.07(1) Å from the mean plane of the four equatorial N atoms towards the nitrosyl ligand. The Ru–N (macrocycle) bonds varying over a narrow range of 2.19–2.27 Å [average 2.22(2) Å] are typical of those found in other ruthenium macrocyclic amine complexes.[13,14] The Ru–O distances in the three cations are 1.909(9), 1.910(9) and 1.90(1) Å respectively, and the average length of 1.906(9) Å is comparable to that [1.910(3) Å] of the Ru–OH bond in *trans*-[Ru(py)$_4$(OH)(NO)]$^{2+}$ (py = pyridine)[3d] but shorter than those in *trans*-[Ru(NH_3)$_4$(OH)(NO)]$^{2+}$ (1.961 Å),[10] Na_2[Ru(NO_2)$_4$(OH)(NO)] (1.950 Å)[15] and [Ru(NO_2)$_2$(NH_3)$_2$(OH)(NO)] (1.945 Å).[16] As in the case of *trans*-[Ru(NH_3)$_4$(OH)(NO)]$^{2+}$ and *trans*-[Ru(py)$_4$(OH)(NO)]$^{2+}$ the Ru–NO unit is essentially linear. The average Ru–N(NO) distance is 1.74 Å, which is comparable to those found in other ruthenium nitrosyl complexes. The L ligands in the three cations exhibit different configurations. As illustrated in Fig. 2, three *N*-methyl groups are *cis* to the Ru–O bond in cations **I** and **II** so that the L ligand assumes the 'three up, one down' configuration. On the other hand, the two-fold disordered L ligand in cation **III** adopts the 'two up, two down' configuration [Fig. 2(*c*)]. The observed disorder of cation **III** may be described in terms of two equally populated orientations related by an approximately 90° rotation about their common O–Ru–NO axis.

The crystal structure consists of a packing of discrete cations and anions with normal van der Waals separations except for two short O···O distances [O(1)···O(8) 2.96(2) and O(3)···O(17) 3.03(2) Å] which are indicative of hydrogen bonding between the hydroxyl ligand [O(1) and O(3)] and the oxygen atoms of the perchlorate groups [O(8) and O(17)].

Acknowledgements

We acknowledge support from the University of Hong Kong, the Chinese University of Hong Kong and the Hong Kong Research Grants Council. C.-M. C. thanks the Microanalytical Service Unit at the Chemistry Department of National Taiwan University.

References

1 W. R. Murphy, jun., K. Takeuchi, M. H. Barley and T. J. Meyer, *Inorg. Chem.*, 1986, **25**, 1041; J. N. Armor and M. Z. Hoffman, *Inorg. Chem.*, 1975, **14**, 444.

2 R. A. Leising and K. J. Takeuchi, *J. Am. Chem. Soc.*, 1988, **110**, 4079; L. F. Szczepura and K. J. Takeuchi, *Inorg. Chem.*, 1990, **29**, 1772.

3 (*a*) H. Nagao, M. Mukaida, K. Shimizu, F. S. Howell and H. Kakihana, *Inorg. Chem.*, 1986, **25**, 4312; (*b*) H. Nagao, F. S. Howell, M. Mukaida and H. Kakihana, *J. Chem. Soc., Chem. Commun.*, 1987, 1618; (*c*) H. Nagao, H. Nishimura, Y. Kitanaka, F. S. Howell, M. Mukaida and H. Kakihana, *Inorg. Chem.*, 1990, **29**, 1693; (*d*) H. Nishimura, H. Matsuzawa, T. Togano, M. Mukaida, H. Kakihana and F. Bottomley, *J. Chem. Soc., Dalton Trans.*, 1990, 137.

4 C. M. Che, K. Y. Wong and C. K. Poon, *Inorg. Chem.*, 1986, **25**, 1809.

5 R. Diamond, *Acta Crystallogr., Sect. A*, 1969, **25**, 43.

6 G. Kopfmann and R. Huber, *Acta Crystallogr., Sect. A*, 1968, **24**, 348.

7 G. M. Sheldrick, in *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, New York, 1985, pp. 175–189.

8 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 55, 99, 149.

9 C. M. Che, T. F. Lai and K. Y. Wong, *Inorg. Chem.*, 1987, **26**, 2289.

10 A. F. Schreiner, S. W. Lin, P. J. Hauser, E. A. Hopcus, D. J. Hamm and J. D. Gunter, *Inorg. Chem.*, 1972, **11**, 880.

11 F. R. Keene, D. J. Salmon, J. L. Walsh, H. D. Abruna and T. J. Meyer, *Inorg. Chem.*, 1980, **19**, 1896.

12 C. M. Che, K. Y. Wong and T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, 1985, 988.

13 T. C. W. Mak, C. M. Che and K. Y. Wong, *J. Chem. Soc., Chem. Commun.*, 1985, 986.

14 D. D. Walker and H. Taube, *Inorg. Chem.*, 1981, **20**, 2828.

15 S. H. Simonsen and M. H. Mueller, *J. Inorg. Nucl. Chem.*, 1965, **27**, 309.

16 T. S. Khodashova, V. S. Vergienko and M. A. Porai-Koshits, *J. Struct. Chem.*, 1971, **12**, 439.

Received 30*th September* 1991; *Paper* 1/05019B