High-valent Dioxo-ruthenium(VI) Complexes of Macrocyclic Tetradentate Tertiary Amines: *X*-Ray Crystal Structures of *trans*-[Ru^{VI}(15-tmc)O_2](ClO_4)$_2$ (15-tmc = 1,4,8,12-tetramethyl-1,4,8,12-tetra-azacyclopentadecane) and *trans*-[Ru^{VI}(16-tmc)O_2](ClO_4)$_2$ (16-tmc = 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane)

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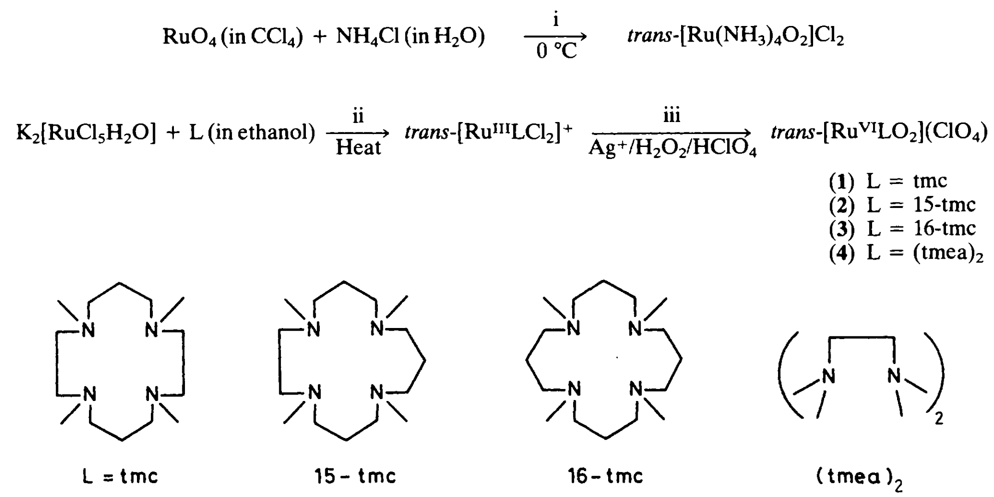
The *X*-ray crystal structures of *trans*-[Ru^{VI}(15-tmc)O_2](ClO_4)$_2$ (15-tmc = 1,4,8,12-tetramethyl-1,4,8,12-tetra-azacyclopentadecane) and *trans*-[Ru^{VI}(16-tmc)O_2](ClO_4)$_2$ (16-tmc = 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane) have been determined; the Ru=O bond distances in these two complexes, 1.718(5) and 1.705(7) Å respectively, appear to be insensitive to the ring size of the macrocycle.

High-valent oxo complexes of ruthenium are of current interest in view of their potential usefulness as oxidative catalysts.[1] Despite the fact that the existence of *trans*-[$Ru^{VI}O_2$]$^{2+}$ complexes of tetra-ammine,[2] 2,2′-bipyridine,[3] 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (tmc),[4] and porphyrin[5] are either known or well documented, no structural work on this class of compounds has ever been reported. Recent work showed that H_2O_2 oxidation of *trans*-[Ru(tmc)(H_2O)$_2$]$^{3+}$ yielded *trans*-[Ru^{VI}(tmc)O_2](ClO_4)$_2$ (**1**). Although (**1**) had been obtained in crystalline form, the crystals gradually decomposed either in solution or in the dry state to give a straw-coloured amorphous solid, and specimens sealed in glass capillaries lasted only 2—3 h upon exposure to *X*-rays. We tentatively surmised that if the tmc ligand of (**1**) assumes the same 'four *N*-methyl groups up' conformation (*R,S,R,S* isomer) as found in *trans*-[Ru^{IV}(tmc)O(MeCN)](PF_6)$_2$,[6] a large steric repulsive effect between the *N*-methyl groups and the proximal oxo ligand



$$RuO_4\,(\text{in }CCl_4) + NH_4Cl\,(\text{in }H_2O) \xrightarrow[0\,^{\circ}C]{i} trans\text{-}[Ru(NH_3)_4O_2]Cl_2$$

$$K_2[RuCl_5H_2O] + L\,(\text{in ethanol}) \xrightarrow[Heat]{ii} trans\text{-}[Ru^{III}LCl_2]^+ \xrightarrow[Ag^+/H_2O_2/HClO_4]{iii} trans\text{-}[Ru^{VI}LO_2](ClO_4)$$

(**1**) L = tmc
(**2**) L = 15-tmc
(**3**) L = 16-tmc
(**4**) L = (tmea)$_2$

Scheme 1. Synthesis of *trans*-ruthenium(VI) dioxo complexes of saturated amines. i, W. P. Griffith and D. Pawson, *J. Chem. Soc., Dalton Trans.*, 1973, 1315; ii, L = tmc, C. M. Che, S. S. Kwong, and C. K. Poon, *Inorg. Chem.*, in the press; L = 15-tmc, 16-tmc, and (tmea)$_2$, C. M. Che, K. Y. Wong, and C. K. Poon, unpublished results; iii, L = tmc, C. M. Che, K. Y. Wong, and C. K. Poon, *Inorg. Chem.*, in the press; L = 15-tmc, 16-tmc, and (tmea)$_2$, this work.

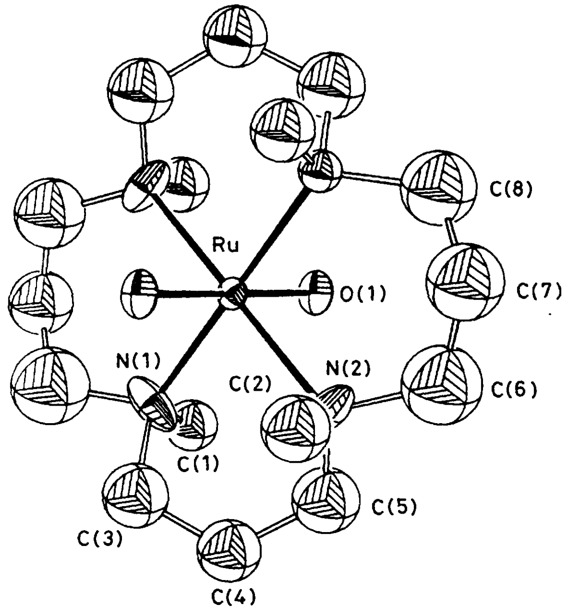


Figure 1. A perspective view of the centrosymmetric [Ru^{VI}(16-tmc)O$_2$]$^{2+}$ cation in (**3**) with atom labelling. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å), bond angles (°), and torsion angles (°); Ru–O(1), 1.705(7); Ru–N(1), 2.21(1); Ru–N(2), 2.24(1); O(1)–Ru–N(1) 88.9(4); O(1)–Ru–N(2) 91.0(4); N(1)–Ru–N(2) 90.6(5); N(1)–C(3)–C(4)–C(5) 38(3); C(3)–C(4)–C(5)–N(2) 40(3); C(4)–C(5)–N(2)–C(6) 165(2); C(5)–N(2)–C(6)–C(7) 172(2); N(2)–C(6)–C(7)–C(8) −69(4); C(6)–C(7)–C(8)–N(1′) 73(3); C(7′)–C(8′)–N(1)–C(3) 177(2); C(8′)–N(1)–C(3)–C(4) 168(2); C(1)–N(1)–C(3)–C(4) 61(2); C(2)–N(2)–C(5)–C(4) 61(3).

Table 1. I.r. and electrochemical data for some *trans*-ruthenium(VI) dioxo complexes.

Compound	$\nu_{asym.}$(Ru=O)/ cm^{-1}	E°_{f}[Ru^{VI}O$_2$/ Ru^{IV}O(H$_2$O)] V *vs.* S.C.E.^{a}	Ref.
[Ru(tmea)$_2$O$_2$]$^{2+}$	860	0.67	^{b}
[Ru(14-tmc)O$_2$]$^{2+}$	850	0.66	^{c}
[Ru(15-tmc)O$_2$]$^{2+}$	855	0.65	^{a}
[Ru(16-tmc)O$_2$]$^{2+}$	860	0.66	^{a}
[Ru(NH$_3$)$_4$O$_2$]$^{2+}$	845	*ca.* 0.40 (irreversible)	^{a}

^{a} S.C.E. = saturated calomel electrode. ^{b} This work. ^{c} Ref. 4.

would result. In this regard, enlargement of the macrocyclic ring by replacing tmc with 1,4,8,12-tetramethyl-1,4,8,12-tetra-azacyclopentadecane (15-tmc) or 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane (16-tmc)[7] might possibly relieve the steric constraint and hence increase the stability of the dioxo-Ru^{VI} species. The synthesis of *trans*-[Ru^{VI}(15-tmc)O$_2$](ClO$_4$)$_2$ (**2**), *trans*-[Ru^{VI}(16-tmc)O$_2$](ClO$_4$)$_2$ (**3**), and *trans*-[Ru^{VI}(tmea)$_2$O$_2$](ClO$_4$)$_2$ (**4**) (tmea = tetramethylethylenediamine) were accordingly undertaken and the results are shown in Scheme 1. As expected, complexes (**2**) and (**3**) are much more stable than (**1**) towards exposure to u.v. light, and their structures have now been determined by *X*-ray crystallography.†

Crystal Data: C$_{14}$H$_{32}$N$_4$O$_{10}$Cl$_2$Ru (**1**), yellow prisms, M = 588.40, triclinic, space group $P1$ or $P\bar{1}$, a = 6.499(9), b = 9.980(7), c = 10.063(9) Å, α = 59.78(5), β = 85.30(9), γ = 87.50(9)°, U = 562(1) Å^3, Z = 1, D_c = 1.739 g cm^{-3}. C$_{15}$H$_{34}$N$_4$O$_{10}$Cl$_2$Ru (**2**), brownish-yellow prisms, M = 602.43, monoclinic, space group $C2$, a = 17.594(4), b = 10.237(2), c = 6.503(1) Å, β = 99.73(2)°, U = 1155.6(4) Å^3, Z = 2, D_c = 1.731 g cm^{-3}, F(000) = 619.91, μ(Mo-K_α) = 9.54 cm^{-1}, crystal size 0.24 × 0.20 × 0.06 mm, mean μr = 0.05, transmission factors 0.843 to 0.934. C$_{16}$H$_{36}$N$_4$O$_{10}$Cl$_2$Ru (**3**), light brown prisms, M = 616.45, monoclinic, space group $P2_1/c$, a = 6.492(1), b = 17.958(6), c = 10.379(3) Å, β = 99.74(2)°, U = 1192.6(6) Å^3, D_m (flotation in CCl$_4$–BrCH$_2$CH$_2$Br) = 1.72 g cm^{-3}, Z = 2, D_c = 1.717 g cm^{-3}, F(000) = 635.91, μ(Mo-K_α) = 9.26 cm^{-1}, crystal size 0.20 × 0.14 × 0.08 mm, mean μr = 0.04, transmission factors 0.838 to 0.908.

Compounds (**1**) and (**2**) were handled in the same manner. A single crystal was sealed inside a 0.5 mm Lindemann glass capillary, and intensities [h, k, $\pm l$; $2\theta_{max.}$ = 52°; 1203 unique and 1181 observed data for (**1**); 2226 unique and 1708

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

observed data for (**2**)] were recorded on a Nicolet R3m four-circle diffractrometer using graphite-monochromatized Mo-K_α radiation (λ = 0.71069 Å). Azimuthal scans of selected strong reflections over a range of Bragg angles were used to define a pseudo ellipsoid for the application of absorption corrections.[8]

The complex cation in compounds (**2**) and (**3**) occupies sites of symmetry 2 and $\bar{1}$, respectively. With the Ru atom fixed at the origin, the other non-hydrogen atoms were located from subsequent difference Fourier syntheses. In compound (**2**), the 15-tmc ligand was found to be badly disordered; on a statistical basis, its two independent N atoms occupy three sites of occupancy factors 0.8, 0.8, and 0.4, and the C atoms were approximated by fifteen 'half-atoms'. With omission of all H atoms, refinement proceeded with isotropic thermal parameters for the fractional ligand atoms and anisotropic ones for the remaining atoms. For compound (**3**), which has an ordered structure, the C atoms were varied isotropically, the heavier atoms anisotropically, and all H atoms generated geometrically (C–H = 0.96 Å) with assigned isotropic thermal parameters. The methyl groups were treated as rigid groups, and the methylene H atoms were allowed to ride on their respective parent C atoms. The N–C(methyl), N–C(methylene), and C–C bond lengths were treated as free variables (d_1, d_2, and d_3, respectively) by the method of observational equations.[9]

All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL program package.[10] Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[11] The weighting scheme employed for the blocked-cascade[12] least-squares refinement and analysis of variance was $w = [\sigma^2(|F_o| + 0.0015|F_o|^2)]^{-1}$. Convergence was reached at R_F = 0.051 and R_w = 0.064 (132 variables) for (**2**), and R_F = 0.097 and R_w = 0.125 [121 variables; d_1 = 1.513(15), d_2 = 1.479(18), d_3 = 1.480(15) Å] for (**3**).

As illustrated in Figure 1, both independent six-membered chelate rings in (**3**) are in the chair conformation, and the overall symmetry of the centrosymmetric cation (exactly planar RuN_4 co-ordination) is approximately C_{2h} [molecular axis passing through C(4), Ru, and C(4′)]. The *N*-methyl groups of the 16-tmc ligand thus assume the 'two up, two down' configuration, presumably the most stable conformation of L in a *trans*-$[Ru^{VI}LO_2]^{2+}$ species. The Ru–N distances in (**2**) [2.17(1)—2.22(3) Å] and (**3**) [2.21(1)—2.24(1) Å] are typical of those found in other ruthenium macrocyclic amine complexes.[6,13]

The Ru=O bond lengths in (**2**) [1.718(5) Å, accuracy not affected by the disorder of the 15-tmc ligand] and (**3**) [1.705(7) Å] are in close agreement, but substantially shorter than that [1.765(5) Å] in *trans*-$[Ru^{IV}(tmc)O(MeCN)](PF_6)_2$,[6] in accord with the lower oxidation state of the metal in the latter species. Interestingly, the ν(Ru=O) and $E_f°$\{*trans*-$[Ru^{VI}O_2]^{2+}$/*trans*-$[Ru^{IV}O(H_2O)]^{2+}$\} couples of complexes (**1**)—(**4**) are similar (Table 1), indicating that the nature of the equatorial ligand(s) and the macrocyclic ring size both play a minor role in affecting the $[Ru^{VI}O_2]^{2+}$ chromophore.

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