Characterization of a High-valent Ruthenyl ($Ru^{IV}=O$) Cation stabilized by the Macrocyclic 1,4,8,11-Tetramethyl-1,4,8,11-tetra-azacyclotetradecane (tmc) Ligand: Crystal and Molecular Structure of *trans*-[Ru^{IV}(tmc)O(MeCN)][PF_6]$_2$

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trans-[Ru^{IV}(tmc)O(MeCN)][PF_6]$_2$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) has been obtained by the reaction of PPh_3 with *trans*-[Ru^{VI}(tmc)O_2][PF_6]$_2$ in MeCN; the Ru=O distance in this mono-oxo ruthenium(IV) (ruthenyl) species, as determined by *X*-ray crystallography, is 1.765(5) Å.

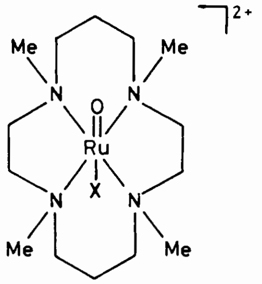
High-valent transition metal mono-oxo complexes have long been regarded as potentially useful oxidative catalysts.[1] However, relatively few reports on the isolation and characterization of this class of compounds have appeared and, to our knowledge, no *X*-ray structural work has been done on a d^4 ruthenium(IV) mono-oxo complex. We recently reported that H_2O_2 oxidation of *trans*-[Ru(tmc)Cl_2]Cl (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) in water produced a high-valent oxoruthenium(IV) (ruthenyl) complex formulated as *trans*-[Ru(tmc)O(OH_2)][ClO_4]$_2$.[2] However, subsequent work showed that the correct formulation of this compound is *trans*-[Ru^{VI}(tmc)O_2][ClO_4]$_2$ (**1**).† Here we describe the formation of a ruthenyl (Ru^{IV}=O) cation by the reaction of (**1**) with PPh_3 in MeCN and its characterization by single-crystal *X*-ray structure analysis.

Upon stirring (**1**) with PPh_3 in acetone–acetonitrile (1 : 1), a bright yellow crystalline solid, *trans*-[Ru^{IV}(tmc)O-(MeCN)][PF_6]$_2$ (**2**), slowly precipitated. Conductivity measurements showed that it was a 1 : 2 electrolyte (Λ_M = 246 ohm^{-1} mol^{-1} cm^2 in H_2O) in agreement with the chemical formulation. As expected for a Ru^{IV} mono-oxo complex with a triplet ground state $(d_{xy})^2(d_{xz})^1(d_{yz})^1$, (**2**) is paramagnetic. The measured μ_{eff}, 2.93 μ_B, is slightly higher than the spin-only value of 2.83 μ_B for two unpaired electrons. The i.r. spectrum of (**2**) displays a doublet in the nitrile region, with ν(CN) occurring at 2280 cm^{-1} and a combination band at 2395 cm^{-1} which derives its intensity from the proximity to ν(CN). This spectrum is closely analogous to that of [Ru(NH_3)$_5$-(MeCN)][ClO_4]$_3$.[3] Identification of the ν(Ru=O) band is uncertain since the co-ordinated tmc ligand absorbs strongly in the 700—820 cm^{-1} region.

Crystal Data: $C_{16}H_{35}F_{12}N_5OP_2Ru$ (**2**), yellow-green flat prisms from MeCN, *M* = 704.47. Monoclinic, space group $P2_1$, a = 9.726(1), b = 10.010(2), c = 14.592(4) Å, β = 109.42(2)°, U = 1339.8(7) Å^3, D_m (flotation in CCl_4–$BrCH_2CH_2Br$) = 1.753 g cm^{-3}, Z = 2, D_c = 1.746 g cm^{-3}, $F(000)$ = 712, μ(Mo-K_α) = 7.92 cm^{-1}. Crystal dimensions: 0.32 × 0.36 × 0.40 mm.

Intensities ($h,k,\pm l$; 3094 unique data) were measured at 22 °C on a Nicolet R3m diffractometer using the ω–2θ variable-scan (2.02—8.37° min^{-1}) technique in the bisecting mode up to $2\theta_{max}$ = 54°. Azimuthal scans of selected strong reflections over a range of 2θ values were used to define a pseudo ellipsoid for the application of absorption corrections (μr = 0.15, transmission factors 0.708—0.722).[4]

Atomic co-ordinates for the Ru atom were deduced from a sharpened Patterson function, and the other non-hydrogen atoms were located from subsequent difference Fourier maps. One of the two PF_6^- groups is disordered, with two distinct orientations of unequal population centered at the P(1) atom. A common site occupancy factor, *g*, was associated with the set of atoms F(1)—F(6) (representing the preferred orientation) and varied as a parameter, and that for the set F(1′)—F(6′) (less favoured orientation) was accordingly held at (1.0 – *g*). The tmc ligand also exhibits disorder in a subtle way: each pair of equatorial co-ordinating N atoms is spanned, on a statistical basis, by half-populated –[CH_2]$_2$– and –[CH_2]$_3$– bridges. Two sets of 'half-carbon' atoms, C(1)—C(10) and C(1′)—C(10′), thus correspond to two alternative orientations (I) and (II). To facilitate refinement of the disordered F and C atoms, the P–F, N–C(methylene), N–C(methyl), and C–C bond distances were treated as free variables (d_1, d_2, d_3, and d_4 respectively) by the method of observational equations[5] while holding the non-bonded F · · · F distances within each PF_6^- group at $\sqrt{2}d_1$. Blocked-cascade least-squares refinement proceeded with isotropic thermal parameters for all C atoms of the tmc ligand and anisotropic ones for the other atoms, H atoms being omitted in view of the disorder.



(**1**), X = =O
(**2**), X = MeCN

All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL programs,[6] and analytic expressions of neutral-atom scattering factors were employed.[7] Convergence for 2748 observed data ($|F_o| > 3\sigma|F_o|$) and 362 variables was reached at R = 0.061 and R_w = 0.083, with weighting scheme $w = [\sigma^2(|F_o|) + 0.0025|F_o|^2]^{-1}$. The final difference Fourier map showed residual extrema in the range +1.19 to –0.54 e Å^{-3}, with the four highest peaks lying in the neighbourhood of the disordered C atoms. The free variables d_1, d_2, d_3, d_4, and the occupancy factor *g* refined to 1.543(1), 1.532(2), 1.556(4), 1.529(2) Å and 0.671(7), respectively.‡

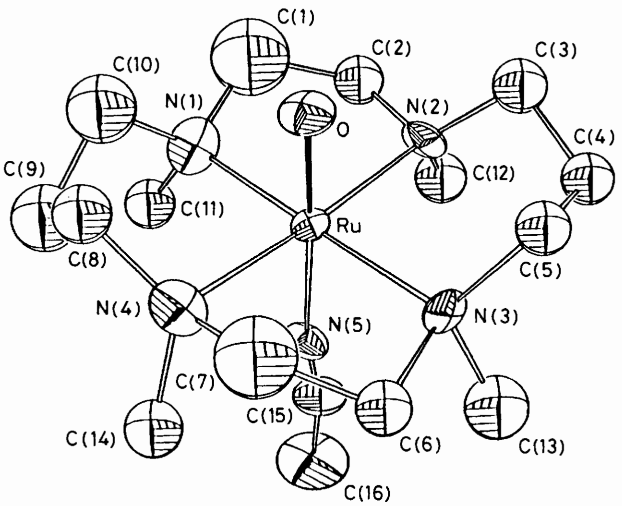


Figure 1. A perspective view of the [Ru^{IV}O(tmc)(MeCN)]$^{2+}$ cation (**2**); chelate rings shown correspond to orientation (I) of the tmc ligand generated from the set of disordered atoms C(1)—C(10). Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Ru–O, 1.765(5); Ru–N(1), 2.085(5); Ru–N(2), 2.141(5); Ru–N(3), 2.139(5); Ru–N(4), 2.125(7); Ru–N(5), 2.149(6); N(5)–C(15), 1.15(1); C(15)–C(16), 1.49(1); O–Ru–N(1), 88.1(4); O–Ru–N(2), 89.0(4); O–Ru–N(3), 89.9(4); O–Ru–N(4), 86.3(4); O–Ru–N(5), 177.6(7); N(1)–Ru–N(2), 89.5(2), N(1)–Ru–N(3), 178.0(2); N(1)–Ru–N(4), 89.0(2); N(1)–Ru–N(5), 90.1(4); N(2)–Ru–N(3), 90.2(2); N(2)–Ru–N(4), 175.1(2); N(2)–Ru–N(5), 92.6(4); N(3)–Ru–N(4), 91.1(2); N(3)–Ru–N(5), 91.9(4); N(4)–Ru–N(5), 92.1(4); Ru–N(5)–C(15), 170(2); N(5)–C(15)–C(16), 167(3).

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† Pure *trans*-[Ru^{VI}(tmc)O_2][Y]$_2$ (Y = ClO_4^- or PF_6^-) was obtained by H_2O_2 oxidation of *trans*-[Ru(tmc)(H_2O)$_2$]$^{3+}$ in H_2O. As expected, *trans*-[Ru^{VI}(tmc)O_2][Y]$_2$ is diamagnetic and its u.v.-visible absorption spectrum closely resembles that of *trans*-[Ru^{VI}(NH_3)$_4O_2$]Cl_2 prepared by W. P. Griffith and D. Pawson, *J. Chem. Soc., Dalton Trans.*, 1973, 1315. C. M. Che, K. Y. Wong, and C. K. Poon, unpublished work.

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

A perspective view of the *trans*-[Ru^{IV}(tmc)O(MeCN)]$^{2+}$ cation is given in Figure 1. The measured Ru=O bond length of 1.765(5) Å is consistent with the expected bond order of two, and also in accord with the value of 1.755 Å found in Ba[$Ru^{VI}O_3(OH)_2$].[8] The co-ordination geometry about the Ru atom is distorted octahedral, with the metal atom displaced by 0.06 Å from the mean plane of the four equatorial N atoms towards the axial N atom. In both orientations of the tmc ligand, the ordered methyl groups are *trans* to the Ru–O bond; a detailed comparison of the two sets of torsion angles around the 14-membered ring showed that orientation (II) may be approximated by a 90° clockwise rotation of orientation (I) about the Ru–O axis. The five- and six-membered chelate rings have *gauche* and chair conformations, respectively, and the overall symmetry of the cation is approximately C_s, with a pseudo mirror plane passing through C(4) and C(9) for orientation (I), or alternatively C(2′) and C(7′) for orientation (II) of the tmc ligand. The Ru–N distances [2.085—2.141(5) Å] are typical for ruthenium macrocyclic amine complexes.[9]

The reaction of PPh_3 with (**1**) yields O=PPh_3 as another product, indicating the operation of a two-electron oxygen atom transfer process.

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