A Stable Ruthenium(v) Oxo Complex. *X*-Ray Crystal Structure and Oxidising Properties of Tetra-n-propylammonium Bis-2-hydroxy-2-ethylbutyrato(oxo)-ruthenate(v)

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The title complex, made from $[\mathrm{Pr^n{}_4N}][\mathrm{RuO_4}]$ and 2-hydroxy-2-ethylbutyric acid, contains a distorted trigonal bipyramidal anion with a short Ru=O equatorial bond (1.687 Å) and functions as a mild oxidant towards alcohols giving carbonyl compounds; such oxidations are catalytic with *N*-methylmorpholine *N*-oxide.

Oxo complexes of ruthenium are of current interest since a number of them function as mild and selective oxidants for organic substrates.[1—3] Most of the known examples are of ruthenium(VI)[1,2] though one of the most effective, $[\mathrm{Pr^n{}_4N}][\mathrm{RuO_4}]$, is of ruthenium(VII).[3] In order to obtain very mild oxidants we have been trying to isolate oxo complexes of ruthenium(v); although Schiff's base complexes of the form $[\mathrm{RuOLX}]^{n+}$ [L = *N*,*N*'-bis(salicylidene)-*o*-phenylenediaminato; X = $\mathrm{Cl^-}$, imidazole, or 2-methylimidazole] have been isolated,[4] no *X*-ray studies of ruthenium(v) oxo complexes have been reported.

We find that reaction of $[\mathrm{Pr^n{}_4N}][\mathrm{RuO_4}]$ in acetone with

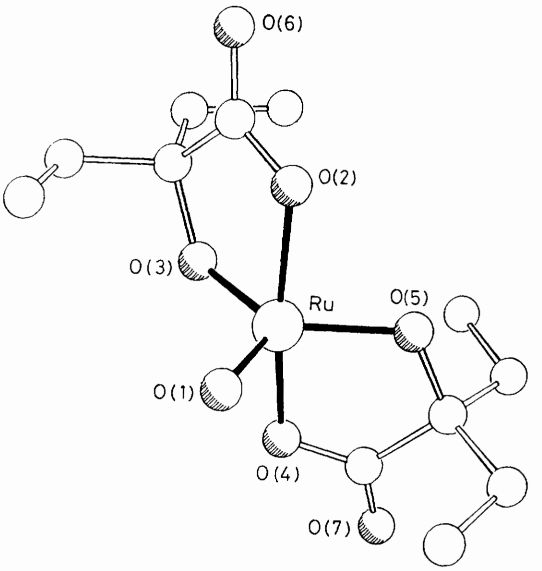

Figure 1. Perspective view of the structure of the $[RuO(O_2COCEt_2)_2]^-$ anion. Selected bond lengths (Å) and bond angles (°): Ru–O(1) 1.697(5), 1.676(6); Ru–O(2) 1.999(6), 2.013(5); Ru–O(3) 1.860(5), 1.869(4); Ru–O(4) 2.006(6), 2.010(5); Ru–O(5) 1.859(5), 1.858(5); O(1)–Ru–O(2) 97.2(3), 95.3(3); O(1)–Ru–O(3) 116.3(3), 116.6(2); O(2)–Ru–O(3) 83.5(2), 84.9(2); O(1)–Ru–O(4) 96.3(3), 97.0(3); O(2)–Ru–O(4) 166.4(2), 167.7(2); O(3)–Ru–O(4) 91.3(2), 90.0(2); O(1)–Ru–O(5) 117.1(3), 118.5(3); O(2)–Ru–O(5) 89.3(2), 90.7(2); O(3)–Ru–O(5) 126.6(2), 124.9(2); O(4)–Ru–O(5) 83.8(2), 83.0(2). The second figure in each case relates to the other crystallographically independent molecule.

2-hydroxy-2-ethylbutyric acid in a 1 : 2 mole ratio over 48 h at 25 °C gives a red–brown solution from which brown crystals of $[Pr^n{}_4N][RuO(O_2COCEt_2)_2]$ **(1)** can be precipitated by addition of n-hexane (satisfactory elemental analysis was obtained for $C_{24}H_{48}NO_7Ru$).

The *X*-ray crystal structure of the anion of **(1)**† (Figure 1) shows one of the pair of crystallographically independent anions (the only major difference between the two anions lies in the relative orientations of the ethyl substituents). The geometry about the Ru centres can best be described as trigonal bipyramidal with the Ru–O(2) and Ru–O(4) bonds forming the apices. These two bonds are not exactly colinear, subtending an angle of 166° at the metal atom. The bonds to the three equatorial oxygen atoms [O(1), O(3), and O(5)] each subtend angles within 7° of 120° at the ruthenium atom, with which these three oxygen atoms are coplanar within 0.08 Å. Both five-membered O,O′donor rings are planar to within 0.06 Å, and the dihedral angle between them is 48°.‡

In both molecules the equatorial Ru=O(1) distances of 1.697(5) and 1.676(6) Å are slightly shorter than those observed in *trans* O=Ru=O units in ruthenium(VI) 'ruthenyl' complexes (1.71—1.76 Å),[1,5] and also shorter than the Ru=O distance in the mono-oxo ruthenium(IV) complex *trans*-$[Ru(O)Cl(py)_4](ClO_4)$[6] (py = pyridine) [1.862(8) Å]; indeed, these distances compare with those of the shortest Ru=O bonds observed in any ruthenium oxo complex [*e.g.* 1.703(5) Å in RuO_4].[7] Again in both molecules the bonds between the ruthenium atom and the hydroxy-derived oxygen atoms O(3) and O(5) are significantly shorter by *ca.* 0.15 Å than those from the carboxy-derived oxygen atoms O(2) and O(4).

A powdered sample of the complex is found to be paramagnetic (μ_{eff} 1.70 μ_B at 25 °C by the Gouy method) and gives a sharp single-line ESR signal ($g = 1.986$) at the same temperature. In a CH_2Cl_2–MeOH glass at *ca.* 100 K it gave an anisotropic ESR spectrum typical of a $S = 1/2$ system with $g_x = 2.076$, $g_y = 1.977$ and $g_z = 1.910$. These observations indicate that the complex has a single unpaired electron in a ground state which is well removed from excited states, consistent with the presence of penta-co-ordinate Ru(V), and suggest that the structure of the anion is retained in solution. The IR spectrum shows, in addition to bands due to the co-ordinated ligand, a strong band at 900 cm^{-1} assigned to the Ru=O stretch [in ruthenyl complexes $\nu_{as}(RuO_2)$ and $\nu_s(RuO_2)$ fall near 830 and 850 cm^{-1}, respectively].[1] The profiles of the IR spectra of the solid and of the acetone solution are similar, again suggesting retention of the solid state structure in solution.

We find that **(1)** functions as a mild oxidant in acetonitrile, slowly converting primary alcohols to aldehydes, secondary alcohols to ketones, and triphenylphosphine to triphenylphosphine oxide. With excess of *N*-methylmorpholine *N*-oxide (NMO) as co-oxidant in acetonitrile the reactions are catalytic with turnovers (mol product/mol catalyst) of the order of 25 for primary and secondary alcohols [thus, *e.g.*, *p*-methoxybenzyl alcohol (20.0 mmol) is converted to *p*-methoxybenzaldehyde (96%) by **(1)** (0.77 mmol) in the presence of excess of NMO in acetonitrile at room temperature].

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† *Crystal data* for $C_{24}H_{48}NO_7Ru$, $M = 563.7$, triclinic, $a = 11.743(2)$, $b = 14.939(4)$, $c = 17.717(4)$ Å, $\alpha = 100.83(2)$, $\beta = 104.97(2)$, $\gamma = 99.58(2)°$, $U = 2872$ Å^3, space group $P\bar{1}$, $Z = 4$ (2 crystallographically independent molecules), $D_c = 1.30$ g cm^{-3}, $\mu(Cu\text{-}K_\alpha) = 48$ cm^{-1}. Data were measured on a Nicolet R3m diffractometer using Cu-K_α radiation (graphite-monochromated) and ω-scans. The structure was solved by the heavy atom method and refined anisotropically using absorption-corrected data to give $R = 0.066$, $R_w = 0.070$ for 6102 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leq 116°$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ In the second crystallographically independent molecule, the departures from trigonal bipyramidal geometry are even smaller, with a maximum deviation of 5° from trigonal geometry of the equatorial substituents and an angle of 168° subtended between the two apical bonds.

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