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Studies on Transition-Metal Oxo and Nitrido Complexes. 12.[1] Synthesis, Spectroscopic Properties, and Reactions of Stable Ruthenium(V) and Osmium(V) Oxo Complexes Containing α-Hydroxy Carboxylate and α-Amino Carboxylate Ligands

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Hypervalent oxoruthenium complexes are of current interest,[2] with ruthenium(VII),[3] ruthenium(VI),[1,4] and ruthenium(IV)[5] species widely used as organic oxidants. Few oxoruthenium(V) complexes have been isolated;[6-8] macrocyclic oxoruthenium(V) species in solution have been claimed.[9-11] We have recently reported the X-ray crystal structure of $({}^{n}Pr_4N)[RuO(O_2COCEt_2)_2]$ (I);[12] here we report new oxoruthenium(V) and oxoosmium(V) complexes with α-hydroxy carboxylate and α-amino carboxylate ligands. We also demonstrate that the low reactivity of these oxoruthenium(V) complexes, as exemplified by I, is comparable with that of analogous oxochromium(V) complexes.[13-15]

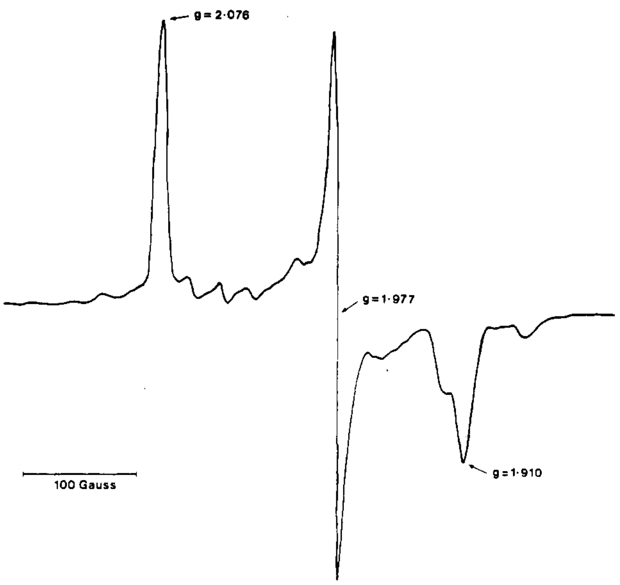

Figure 1. Low-temperature (flowing nitrogen gas cooled with liquid nitrogen) X-band ESR spectrum of I in CH_2Cl_2.

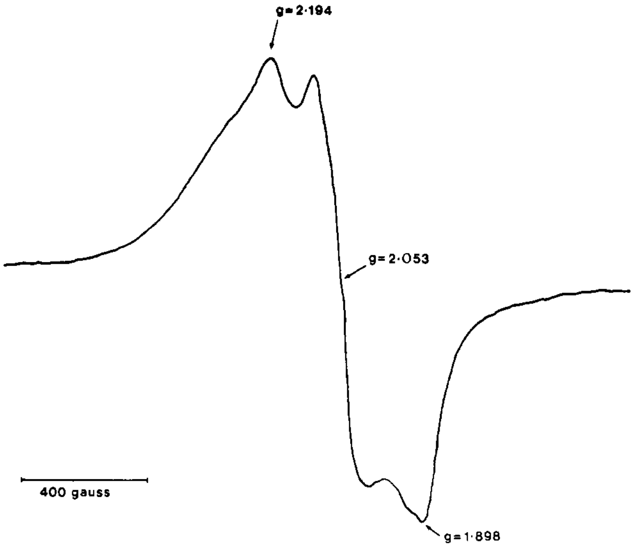

Figure 2. Low-temperature (flowing nitrogen gas cooled with liquid nitrogen) X-band ESR spectrum of CH_2Cl_2 solution containing $({}^{n}Pr_4N)[RuO_4]$ and norvaline (after 6-h reaction).

Results and Discussion

The red-brown complexes $({}^{n}Pr_4N)[RuO(O_2COCR^1R^2)_2]$ (R^1R^2 = Et_2, Me_2, EtMe, PhMe) are made by reaction of $({}^{n}Pr_4N)[RuO_4]$ with the appropriate acid in acetone. The reaction is slow, though much faster if $[(Ph_3P)_2N][RuO_4]$ is used. The osmium analogue, for which we could prepare only $(Ph_4P)[OsO(O_2COCEt_2)_2]$ in a pure state, was similarly made from $(Ph_4P)[OsO_4]$. With 2-aminobutyric acid, $({}^{n}Pr_4N)[RuO_4]$ in acetone gives $({}^{n}Pr_4N)[RuO(O_2C(NH)CHEt)_2]$; other secondary amino carboxylic acids and also ethylene glycol produced no isolable products, but ESR data indicated that similar ruthenium(V) oxo species were formed in solution.

It is likely that all the complexes have a structure similar to that of the anion of I, which is trigonal bipyramidal with the oxo ligand and the two deprotonated hydroxo groups from the 2-hydroxy-2-ethylbutyrate ligand occupying the equatorial positions.[12] In $Na[CrO(O_2COCEt_2)_2]\cdot{}^3/_2H_2O$ the anion has a very similar structure,[15f] while that in $K[CrO(O_2COCEtMe)_2]$ is closer to square-based pyramidal.[13]

The infrared spectra of solid $({}^{n}Pr_4N)[RuO(O_2COCR^1R^2)_2]$ (Table I) contain bands near 1670 cm^{-1} due to the carboxyl stretches of the coordinated hydroxy carboxylates, shifting to lower

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Table I. Analytical and Spectroscopic Data for Ruthenium(V) and Osmium(V) Oxo Complexes

	anal. data, %[a]			vibrational data, cm^{-1} [b]			ESR data		
complex	C	H	N	ν(M=O)	ν(C=O)[d]	μ_{eff}[c]	g_x	g_y	g_z
$(^nPr_4N)[RuO(O_2COCEt_2)_2]$	50.7 (51.0)	8.7 (8.6)	2.4 (2.5)	900 m (902)	1664 vs (1660)	1.70	2.076	1.977	1.910
$[(Ph_3P)_2N][RuO(O_2COCEt_2)_2]$	61.8 (62.9)	5.3 (5.5)	1.7 (1.5)	903 m	1661 vs		2.078	1.978	1.906
$(^nPr_4N)[RuO(O_2COCEtMe)_2]$	48.0 (49.3)	8.3 (8.3)	2.6 (2.6)	880 m	1668 vs	1.70	2.080	1.978	1.912
$(^nPr_4N)[RuO(O_2COCMe_2)_2]$	46.3 (45.9)	8.3 (7.7)	3.0 (2.7)	892 m	1664 vs	1.68	2.083	1.976	1.915
$(^nPr_4N)[RuO(O_2COCPhMe)_2]$	59.7 (60.0)	7.2 (7.4)	2.3 (2.3)	896 br	1645 vs	1.72	2.079	1.975	1.911
$(Ph_4P)[OsO(O_2COCEt_2)_2]$	52.7 (53.7)	4.5 (5.0)		958 sh	1664 vs				
$(^nPr_4N)[RuO(O_2C(NH)CHEt)_2]$	47.2 (47.7)	8.3 (8.0)	7.9 (8.3)	obsc	1608 vs		2.208 br	2.062 br	1.902 br
$K[RuO(O_2COCEt_2)_2]$[e]							2.072	1.978	1.913
TPAP + 2-phenylglycine[e]							2.217 br	2.04 br	1.928 br
TPAP + norvaline[e]							2.194 br	2.053 br	1.898 br

[a] Calculated values in parentheses. [b] Data for solids; acetone solution data in parentheses. [c] At 25 °C; μ_B. [d] C=O stretch of coordinated carboxylate ligand. [e] Complexes not isolated; ESR spectra of glasses at low temperature.

wavenumbers on coordination. The complexes display a band near 900 cm^{-1} assigned to the Ru=O stretch. In acetone solution the profiles of the infrared spectra are similar to those in the solid state, suggesting that the complexes retain their structures in solution. The spectrum of $(Ph_4P)[OsO(O_2COCEt_2)_2]$ shows bands due to the coordinated 2-hydroxy-2-ethylbutyrate ligand and a strong band at 958 cm^{-1} assigned to the Os=O stretch. Attempts to record the Raman spectra of these dark materials were unsuccessful. The negative FAB mass spectrum of I run in ONPOE (*o*-nitrophenyl *n*-octyl ether) yielded the molecular anion centered at m/z = 378. Isotopic simulation of the formula $C_{12}H_{20}RuO_7$ gave a very similar pattern. Similarly, $(^nPr_4N)[RuO(O_2COCR^1R^2)_2]$ (R^1R^2 = Me_2, EtMe, PhMe) yielded the molecular anions centered at m/z = 322, 350, and 446, respectively.

ESR spectroscopy has been widely used to study chromium(V) species,[13,15a,16-18] but there are no reports in the literature of such studies on ruthenium(V) species. We have recorded ESR spectra of our isolated oxoruthenium(V) complexes and used the technique to identify the presence of paramagnetic ruthenium(V) species in solution (Table I). The X-band ESR spectra of $(^nPr_4N)[RuO(O_2COCR^1R^2)_2]$ (R^1R^2 = Me_2, EtMe, PhMe) and $[(Ph_3P)_2N][RuO(O_2COCEt_2)_2]$ are similar to that for I (Figure 1). In dichloromethane at liquid-nitrogen temperatures the complexes show anisotropic spectra consistent with d^3 ($S = {}^1/_2$) electronic configurations in pentacoordinate oxoruthenium(V) species. The three main components of the spectra have g_x, g_y, and g_z values of ca. 2.08, 1.98, and 1.91, respectively; the small features probably represent hyperfine structure from the ^{99}Ru and ^{101}Ru magnetic nuclei ($I = {}^5/_2$). At room temperature solid I gives a sharp single-line ESR signal at g = 1.986. The ESR spectrum of the red-brown solution formed by a 1:2 mixture of $K[RuO_4]$ and 2-hydroxy-2-ethylbutyric acid at low temperature in water is almost identical with that of I (g_x = 2.072, g_y = 1.978, g_z = 1.913), indicating the presence of $[RuO(O_2COCEt_2)_2]^-$ in solution. The low-temperature spectrum of $(^nPr_4N)[RuO(O_2C(NH)CHEt)_2]$ in dichloromethane also has three components (g_x = 2.208, g_y = 2.062, g_z = 1.902), consistent with the presence of a pentacoordinate $S = {}^1/_2$ ruthenium(V) system. Although oxoruthenium(V) complexes with 2-phenylglycine (α-aminophenylacetic acid) and norvaline (2-aminopentanoic acid) were not isolated, the reaction of $(^nPr_4N)[RuO_4]$ in CH_2Cl_2 with these acids produced red-brown solutions, whose broad-lined low-temperature ESR spectra were similar to that of $(^nPr_4N)[RuO(O_2C(NH)CHEt)_2]$; it seems clear that $[RuO(O_2C(NH)CHR)_2]^-$ species are present in solution (Figure 2). The low-temperature ESR spectrum of $(Ph_4P)[OsO(O_2COCEt_2)_2]$ shows no well-resolved lines, perhaps due to the faster spin-lattice relaxation inherent in a third-row transition metal.

Reaction of $(^nPr_4N)[RuO_4]$ and ethylene glycol in 1:2 molar ratio in dichloromethane gives a brown solution, whose weak ESR spectrum has three main components (g_x = 2.030, g_y = 1.993, g_z = 1.933). This suggests that a ruthenium(V) bis(diolato) complex is present in solution [presumably similar to the species detected by ESR spectroscopy (g = 1.981) as an intermediate in the oxidation of ethylene glycol by $[Cr_2O_7]^{2-}$ and formulated as $[Cr^VO(OCH_2CH_2O)_2]^-$ [16f,g]].

As with the analogous oxochromium(V) species, these oxoruthenium(V) complexes are remarkably unreactive. The most labile analogue appears to be $(^nPr_4N)[RuO(O_2COCEt_2)_2]$ (I), on which our reactivity studies were concentrated. We have reported that I oxidizes primary alcohols to aldehydes, secondary alcohols to ketones, and triphenylphosphine to triphenylphosphine oxide.[12] Such reactions (catalytic in the presence of *N*-methylmorpholine *N*-oxide[12]) are slow in the absence of a cocatalyst and give low yields; in the case of *p*-methoxybenzyl alcohol for example, the yield of aldehyde is only 35% after 3 h. This is reminiscent of the oxochromium(V) complexes, which are less reactive toward alcohols than toward carboxylic acids.[15b] There is no competing C-C double-bond cleavage for unsaturated alcohols and no reaction of I with *cyclo*hexene in dichloromethane.

Although there are reports[15d] of reactions of $[CrO(O_2COCEt_2)_2]^-$ with hydrazine, hydroxylamine, and sulfite, no chromium-containing products were apparently isolated. The products of reactions of I with these and other inorganic reagents are also difficult to isolate. Reaction of I with aqueous sodium sulfite followed by precipitation with CsCl and acetone gives a green solid with an infrared spectrum similar to that of $K_3[Os(SO_3)_3(H_2O)_3]$.[19] Passage of nitric oxide into a solution of I in dichloromethane gives a brown solid, with strong infrared bands at 1900 and 1860 cm^{-1}, likely to be due to the N-O stretch of a nitrosyl ligand, as well as bands due to coordinated 2-

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hydroxy-2-ethylbutyrate; the Ru=O stretch at 900 cm^{-1} present in I is absent.

Although some of the oxochromium(V) complexes give well-defined oxidation and reduction waves,[15f,18] we were unable to obtain good, reproducible CV results for our oxoruthenium(V) complexes (using CH_2Cl_2, DMSO, and CH_3CN as solvents, with $(^nBu_4N)PF_6$ as supporting electrolyte). The reason for this is not clear, especially as oxoruthenium(V) complexes with a *trans*-dioxo unit exhibit good results.[4c,11]

Conclusions

These d^3 oxoruthenium(V) complexes show considerable similarities to the d^1 oxochromium(V) species. Both have a single unpaired electron, and they are similar structurally. The relative lack of reactivity of the oxoruthenium(V) species, especially toward organic substrates, is puzzling, though it is interesting to note that oxochromium(V) species are also quite unreactive. The ligands used in both systems, α-hydroxy carboxylic acids, lack an α-hydrogen atom, and it may be that, as proposed by Lay[15f] for oxochromium(V) hydroxy carboxylato complexes, steric protection by alkyl substituents in the α-positions is responsible for the stability of the species.

Experimental Section

Materials. Hydrated ruthenium trichloride, $RuCl_3{\cdot}nH_2O$, and OsO_4 were supplied by Johnson Matthey Ltd. $RuCl_3{\cdot}nH_2O$ was converted to $RuO_2{\cdot}nH_2O$ as reported previously.[3c]

Improved Preparation of $(^nPr_4N)[RuO_4]$ ("TPAP") and $[(Ph_3P)_2N][RuO_4]$. Ruthenium tetraoxide vapor was generated by stirring $RuO_2{\cdot}nH_2O$ (0.75 g) with sodium periodate (2.75 g) in water (15 cm^3) and swept into a second flask containing 1.0 M K_2CO_3 (20 cm^3) and 1.0 M $(^nPr_4N)OH$ (5 cm^3) at 0 °C. The olive green TPAP precipitated was collected after 3 h, washed with ice-cold water, and dried in vacuo. The orange mother liquor was returned to the reaction flask and passage of RuO_4 continued, with further precipitation of TPAP, until the ruthenium was consumed. Yield: 96% with respect to $(^nPr_4N)OH$ (ruthenium in excess). Anal. Found: C, 40.8; H, 7.9; N, 4.0. Calcd for $C_{12}H_{28}NO_4Ru$: C, 41.0; H, 8.0; N, 4.0. $[(Ph_3P)_2N][RuO_4]$ was similarly prepared by using $(Ph_3P)_2NCl$ in 1.0 M K_2CO_3. Anal. Found: C, 61.4; H, 4.2; N, 1.9. Calcd for $C_{36}H_{30}NO_4P_2Ru$: C, 61.4; H, 4.3; N, 2.0. IR: 828 cm^{-1} (strong) [$\nu^{as}(RuO_2)$]. Raman (KBr disk): 843 cm^{-1} (strong) [$\nu^{s}(RuO_2)$].

Preparation of $(^nPr_4N)[RuO(O_2COCR^1R^2)_2]$ [R^1R^2 = Et_2 (I), Me_2 (II), EtMe (III), PhMe (IV)]. The preparation of $(^nPr_4N)[RuO(O_2COCEt_2)_2]$ was typical. To a stirred solution of TPAP (0.50 g; 1.42 mmol) in acetone (25 cm^3) was added 2-hydroxy-2-ethylbutyric acid (0.375 g; 2.84 mmol). After the mixture was stirred for 24 h, a red-brown solid was isolated by addition of *n*-hexane and cooling to 5 °C for 24 h; it was washed with diethyl ether and dried in vacuo. The analogues were prepared from 2-methyl-2-hydroxypropionic, 2-methyl-2-hydroxybutyric, and 2-hydroxy-2-phenylpropionic acids, respectively. Mass spectra (negative FAB): (I) m/z = 378; (II) m/z = 322; (III) m/z = 350; (IV) m/z = 446 (due to $[RuO(O_2COCR^1R^2)_2]^-$ anions). Electronic spectra [nm (ϵ, dm^3 mol^{-1} cm^{-1})]: (I) 331 (3046), 365 (3261), 472 (5784); (II) 364 (3710), 460 (6771); (III) 324 (2968), 369 (3133), 466 (5928); (IV) 320 (4397), 357 (4763), 461 (6124).

Preparation of $(^nPr_4N)[RuO(O_2C(NH)CHEt)_2]$. A solution of TPAP (0.40 g; 1.14 mmol) and DL-2-aminobutyric acid (0.23 g; 2.28 mmol) in acetone (25 cm^3) was stirred for 24 h. The solution was reduced to ca. 5 cm^3 in volume, and the resulting red-brown oil was triturated with diethyl ether to give a hygroscopic microcrystalline solid. This was filtered, washed with diethyl ether, and dried in vacuo.

Preparation of $(Ph_4P)[OsO(O_2COCEt_2)_2]$. 2-Hydroxy-2-ethylbutyric acid (0.09 g; 0.67 mmol) and $(Ph_4P)[OsO_4]$ (0.20 g; 0.34 mmol; made by the literature method[3c]) were stirred in acetone (15 cm^3) for 48 h. Reduction in volume to ca. 5 cm^3 gave a red-purple oil, which was triturated with diethyl ether to give a hygroscopic microcrystalline solid. Electronic spectrum [nm (ϵ, dm^3 mol^{-1} cm^{-1})]: 318 (3852), 361 (4279), 460 (2941).

Instrumentation and General Experimental Details. Infrared spectra were run on a Perkin-Elmer 1720 (FTIR) instrument and Raman spectra on a Spex Ramalog 5 instrument with argon ion (5145 Å) laser excitation. ^1H NMR spectra were recorded on a Jeol 270 (FT) spectrometer and ^{13}C NMR spectra on a Bruker WM 250 (FT) spectrometer. ESR spectra were recorded on a Varian E12 X-band spectrometer (9.5 GHz), at low temperature with flowing liquid-nitrogen-cooled N_2 gas. Magnetic moments were determined by the Gouy method with a Johnson Matthey magnetic susceptibility balance. Mass spectra were recorded on a VG-Micromass 7070E-HS spectrometer.

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Synthesis and Characterization of Octakis(acetonitrile)dimolybdenum(II) Tetrafluoroborate

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Introduction

The preparation and properties of $[M_2]^{n+}$ cores surrounded only by weakly coordinated, often neutral, ligands has been of continuing interest for some years[1] although the whole body of results is not large. Reasons for this interest are first that loosely coordinated $[M_2]^{n+}$ species may serve as versatile starting materials in the synthesis of other complexes of the M_2 unit and second that they have potential catalytic activity for carbonylation and hydrogenation reactions.[1] Some examples of the previously reported compounds containing the $[Mo_2]^{4+}$ core surrounded partially or completely by weakly bound ligands are $[Mo_2(H_2O)_4(CF_3SO_3)_2](CF_3SO_3)_2$,[2] $[Mo_2(NCCH_3)_8](CF_3SO_3)_4$,[2] *cis*-$[Mo_2(O_2CCH_3)_2(NCCH_3)_6](X)_2$ (X = BF_4^-, $CF_3SO_3^-$),[3,4] $[Mo_2(EtO_2CCH_3)_4](CF_3SO_3)_4$,[5] $Mo_2(CF_3SO_3)_4$,[5] $[Mo_2(en)_4](Cl)_4$,[6,7] $Mo_2^{4+}(aq)$,[7] *trans*-$[Mo_2(O_2CCH_3)_2(dmpe)_2](BF_4)_2$,[8] and $[Mo_2(O_2CCH_3)_2(NCCH_3)_5](BF_3OH)_2$.[9] Unfortunately, many of these reported procedures lead to impure products or uncertain formulations, and only in the cases of $[Mo_2(O_2CCH_3)_2(NCCH_3)_6](X)_2$ (X = BF_4^-, $CF_3SO_3^-$)[3,4] were the actual structures determined crystallographically. For $[Rh_2]^{4+}$, the recently reported compounds $[Rh_2(NCCH_3)_{10}](BF_4)_4$[9] and $[Rh_2(H_2O)_2(NCCH_3)_8](PF_6)_4{\cdot}2H_2O$[10] are also of the type we are interested in here.

In this paper we report the synthesis and detailed characterization of the $[Mo_2]^{4+}$ compound $[Mo_2(NCCH_3)_8(ax\text{-}NCCH_3)_2](BF_4)_4{\cdot}2CH_3CN$ (**1**). We believe that this highly reactive compound will be of synthetic utility and perhaps also of value as a catalyst.

Experimental Section

Materials. Dimolybdenum(II) tetraacetate was prepared as reported.[11] Acetonitrile (2 L) was passed through a column (3 × 40 cm) of alumina gel (dried at 120 °C for 2 days) and then distilled from calcium hydride under an atmosphere of dry dinitrogen. Methylene chloride was distilled from phosphorus pentoxide under dinitrogen. Triethyloxonium tetrafluoroborate was used as purchased from Aldrich as a methylene chloride solution. All manipulations were performed by using standard vacuum-line and Schlenk techniques under a dry and oxygen-free atmosphere of argon.

Synthesis. Dimolybdenum(II) tetraacetate (1.00 g, 2.34 mmol) was partially dissolved in acetonitrile (30 mL) in a 100-mL three-neck flask that was equipped with a condenser and a glass rod to initiate crystallization of the product. The solution was not stirred. To this yellow solution was added triethyloxonium tetrafluoroborate (30.0 mL, 30.0 mmol, 1.0 M in CH_2Cl_2), which produced a red solution. This red color is due to the previously reported[3,4] *cis*-$[Mo_2(O_2CCH_3)_2(NCCH_3)_6](BF_4)_2$ species. The dimolybdenum(II) tetraacetate was dissolved completely upon warming the solution to reflux. The solution became brown after being refluxed for 1 day. It was then vigorously refluxed for 10 days. During this period, a large crop of bright blue microcrystals formed. The reaction mixture was cooled to room temperature and the supernatant liquid decanted.

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