Oxo-single-bridged and Oxo-carboxylato-double-bridged Diruthenium(III) Complexes of Tris(2-pyridylmethyl)amine

Chikako Koshi, Keisuke Umakoshi, and Yoichi Sasaki*

Division of Chemistry, Graduate School of Science, Hokkaido University, Kita-ku, Sapporo 060

(Received August 7, 1997; CL-970623)

An oxo single-bridged and a series of oxo-carboxylato di-bridged diruthenium(III) complexes, $[Ru_2(\mu\text{-}O)Cl_2(tpa)_2]^{3+}$ and $[Ru_2(\mu\text{-}O)(\mu\text{-}RCOO)(tpa)_2]^{3+}$ (tpa = tris(2-pyridylmethyl)-amine; R = CH_3, C_2H_5, C_3H_7, and C_6H_5), show comparative structural, redox, magnetic and spectroscopic properties.

Tetradentate ligands, tris(2-pyridylmethyl)amine (tpa) and its derivatives, have been widely used for the preparation of structural model complexes of dinuclear metal centers of some metalloenzymes.[1] These ligands have been particularly useful for the preparation of edge-shared dinuclear complexes of di(μ-oxo)[2] and μ-oxo-μ-carboxylato type.[3] We have started the study of oxo-bridged heavy transition metal complexes using these ligands in order to obtain important systematic information on the direct and indirect metal-metal interactions and redox characteristics associated with oxo-bridged dinuclear units.[4,5] New dirhenium complexes, $[Re_2(\mu\text{-}O)_2(tpa)_2]^{3+,4+}$ (Re_2(III,IV) and Re_2(IV,IV)) have provided useful information on the structural and redox properties of di(μ-oxo) dimetal complexes.[5] We have now prepared a series of diruthenium(III) complexes with the μ-oxo-μ-carboxylato bridging groups, $[Ru_2(\mu\text{-}O)(\mu\text{-}RCOO)(tpa)_2](PF_6)_3$ (R = H (**1**), CH_3 (**2**), C_2H_5 (**3**), C_3H_7 (**4**) and C_6H_5 (**5**). These complexes are the first examples containing the μ-oxo-μ-carboxylato-diruthenium core. A mono-oxo bridged diruthenium complex, $[Ru_2(\mu\text{-}O)Cl_2(tpa)_2]^{2+}$ (**6**), has also been prepared. A monomeric tpa complex, $[RuCl_2(tpa)]^+$ has been reported recently by Kojima, which has useful catalytic activity toward alkane functionalization.[6]

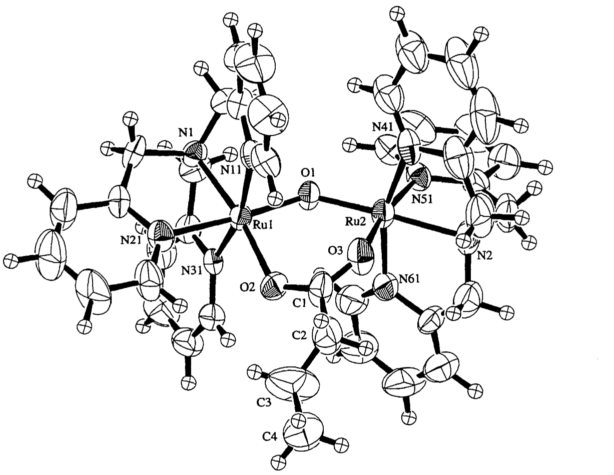

Figure 1. Molecular structure of the complex cation in **4**. Selected bond distances (Å) and angles (°): Ru1-Ru2, 3.399(1); Ru1-O1, 1.890(5); Ru1-O2, 2.076(6); Ru1-N1, 2.061(7); Ru1-N11, 2.086(8); Ru1-N21, 2.100(7); Ru1-N31, 2.052(8); Ru2-O1, 1.895(5); Ru2-O3, 2.094(7); Ru2-N2, 2.118(8); Ru2-N41, 2.063(9); Ru2-N51, 2.036(8); Ru2-N61, 2.050(9); Ru1-O1-Ru2, 127.9(3).

The new complexes **1** - **5** were prepared by keeping aqueous solution (20 mL; pH, ca. 8) containing $[RuCl_2(tpa)]PF_6$ (**7**)[6,7] (121 mg, 0.2 mmol) and sodium salt of the carboxylates (2 mmol) at 60 °C for 3 h. Addition of NH_4PF_6 (652 mg; 4 mmol) in a minimum amount of water gave the μ-oxo-μ-carboxylato complexes in 30 - 50% yield.[8,9] The μ-oxo complex **6** was prepared by heating an aqueous solution (20 mL) of **7** (243 mg; 0.4 mmol) at 80 °C for 3 h under argon atmosphere. Addition of NH_4PF_6 (652 mg; 4 mmol) in a minimum amount of water gave a crude salt of **6**, which was recrystallized from acetonitrile-ether. Yield, 105 mg (45.4%).[8,9]

X-Ray crystal structures of **4** and **6** were determined.[10,11] Figure 1 shows the structure of the complex cation in **4**. Two tpa ligands are not equivalent, one of them having tertiary nitrogen at the trans to the oxide bridge and the other at the cis to it. Such non-symmetrical structure is often observed for other oxo-carboxylato bridged dimetal complexes of tpa and analogous ligands.[3] The Ru-Ru distance of 3.399(1) Å is considerably longer than the corresponding distance (3.2 - 3.3 Å) of oxo-di(carboxylato)-bridged diruthenium(III) complexes.[12] ^1H NMR spectra of **1** - **5** showed ligand hydrogen signals in much wider range (+15 to 0 ppm) than expected for a diamagnetic complex, suggesting that the complexes are weakly paramagnetic. Magnetic measurement of the solid sample of **2** shows that μ_{eff} is 0.98 BM at 300 K. Temperature dependence (4.2 to 300 K) gives the antiferromagnetic coupling constant J = ca. $-480\ cm^{-1}$. The μ_{eff} value of a μ-oxo-di-μ-acetato complex with shorter Ru-Ru (3.251(2) Å) and smaller Ru-O-Ru (122.2(5) °), $[Ru_2(O)(CH_3COO)_2(pyridine)_6](PF_6)_2$,[12a,b] is ca. 0.16 BM at 300 K.[13]

Figure 2 shows the centrosymmetric structure of the complex

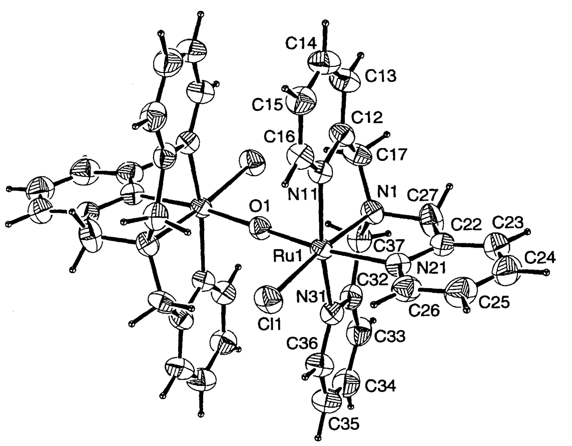

Figure 2. Molecular structure of the complex cation in **6**. Selected bond distances (Å) and angles (°): Ru1-Cl1, 2.411(1); Ru1-O1, 1.888(3); Ru1-N1, 2.067(2); Ru1-N11, 2.063(3); Ru1-N21, 2.102(2); Ru1-N31, 2.064(3); Ru1-O1-Ru1', 180.0; Cl1-Ru1-O1, 95.5(1); O1-Ru1-N21, 172.3(1).

cation in **6**. Both the positions trans to the oxide bridge are occupied by pyridyl nitrogens. The complex is paramagnetic with μ_{eff} of 2.50 BM at 300 K, which is consistent with the classical dπ-pπ molecular orbital description for a linear μ-oxo complex, in which the two antibonding orbitals are degenerated if the two axes (x and y) perpendicular to the M-O-M axis (z axis) are equivalent.[14] In the case of **6**, although two d^5 Ru(III) ions have slightly different ligand environments at x and y axis, two antibonding orbitals would still be closely spaced and are half-occupied giving a spin-triplet ground state. For the bent Ru-O-Ru complexes **2** and **7**, two anti-bonding orbitals are well separated, so that the ground state is a spin-singlet state. Small residual paramagnetism of **2** and **7** manifests appreciable contribution of the triplet state, the extent of which decreasing with decrease in the Ru-O-Ru angle. It appears that the dπ-pπ interaction is not as strong as previously considered.

The acetato-bridged tpa complex **2** in acetonitrile (0.1 M tetrabutylammonium hexafluorophosphate) shows two reversible one-electron waves at +0.95 V (III,III)/(III,IV) and -0.29 V ((III,II)/(III,III)) vs Ag/AgCl. An irreversible reduction wave at -1.14 V would probably correspond to the (II,II)/(II,III) process. The μ-oxo complex **6** shows two reversible waves corresponding to the (III,III)/(III,IV) and (III,IV)/(IV,IV) processes at +0.55 and +1.79 V, respectively. The comproportionation constant *K*c for the (III,IV) state is calculated to be 2.7 x 10^{21} which is significantly large. Such large *K*c values were observed for the Ru_2(III,IV) states of other linear Ru-O-Ru complexes,[14,15] and the Os_2(III,IV) state of $Os_2(\mu\text{-}O)Cl_5(CH_3COO)(pyridine)_4$.[16] It appears that the single-electron occupation of the two closely spaced dπ-pπ anti-bonding orbitals would be relevant to the observed large *K*c values. The values are much smaller for the d^3d^4 Re_2(III,IV) state of $[Re_2(\mu\text{-}O)Cl_2(2,2'\text{-bipyridine})_4]^{3+}$.[17]

We are grateful to Professor Hiroki Oshio of Tohoku University for the magnetic susceptibility measurement. This work was supported by Grant-in-Aids for Scientific Research No. 09554037 and 09237106 (Priority Area of "Electrochemistry of Ordered Interfaces") from the Ministry of Education, Science, Sports, and Culture, Japan.

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8 Elementary analyses (C, H, and N for **1** - **5**; C, H, N, and Cl for **6**) gave satisfactory results.

9 UV-vis absorption spectral data (nm(ε/(mol^{-1}dm^{3}cm^{-1})). **2** in acetonitrile: ca. 630sh, 572 (11900), 337 (14800), 246 (30800). **6** in acetonitrile: 606 (37900), 378 (10500), 251 (22900).

10 Crystal structure analyses: Intensity data of **4** and **6** were collected with a graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) on a Rigaku AFC5R and (λ = 0.71073 Å) a MacScience MXC18 diffractomer, respectively, at room temperature corrected for Lorentz polarization effect. Crystal data for **4** ($[Ru_2(O)(C_3H_7COO)(tpa)_2](PF_6)_3$): $C_{40}H_{43}N_8O_3P_3F_{18}Ru_2$, FW = 1320.86, monoclinic, space group $P2_1/n$ (no. 14); a = 18.488(4) Å, b = 18.571(4) Å, c = 14.581(4) Å, β = 90.03(2)°, V = 5006(2) Å^3, Z = 4, ρ_{calcd} = 1.752 g cm^{-3}. R = 0.050 (R_w = 0.059) against 4125 reflections ($I \geq 3\sigma(I)$). Crystal data for **6** ($[Ru_2(O)Cl_2(tpa)_2](PF_6)_2$: $C_{36}H_{36}N_8O_1Cl_2P_2F_{12}Ru_2$, FW = 1160.00, triclinic, space group $P\bar{1}$ (no. 2); a = 8.559(2) Å, b = 11.086(2) Å, c = 12.763(2) Å, α = 64.98(1), β = 71.12(1), γ = 88.69(2)°, V = 1029.2(3) Å^3, Z = 1, ρ_{calcd} = 1.871 g cm^{-3}. R = 0.032 (R_w = 0.036) against 4116 reflections ($I \geq 2\sigma(I)$). The structures were solved by a direct method (SIR92), and were refined with full-matrix least-square technique. Computational works for **4** and **6** were carried out by Crystallographic Software package in teXsan and Crystan, respectively.

11 A preliminary structural analysis of **5** disclosed similar structural characteristics to **4** with the Ru···Ru distance of 3.445(3) Å.

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