Novel Ligand-Unsupported Diruthenium Compounds, $[Ru_2(Cl_4Cat)_4]^{n-}$ (Cl_4Cat = Tetrachlorocatecholate; *n* = 2 and 3)

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Diruthenium compounds have received considerable attention in studies on the electronic and molecular structure of multiply bonded dimetallic complexes[1,2] and, most recently, on the synthesis of polymeric materials consisting of strongly bonded dimetallic subunits.[3] Much of the research on diruthenium chemistry has been based on the Ru_2^{n+} ($n = 4$ and 5) core. Compounds of Ru_2^{6+}, which may formally contain a Ru−Ru triple bond ($\sigma^2\pi^4\delta^2\delta^{*2}$), have been more elusive.[4,5] Although many Ru_2^{n+} ($n = 5$ and 6) compounds have been reported, still lacking are pairs of well-characterized Ru_2^{n+} ($n = 5$ and 6) compounds with the same ligand system.[1,3,4,6−8] Among these Ru_2 compounds, ligand-unsupported Ru_2^{n+} ($n = 5$ and 6) compounds are very rare,[9] which would add an important dimension to multiple Ru−Ru bonding chemistry. We have succeeded in the syntheses of two novel ligand-unsupported Ru_2^{n+} ($n = 5$ and 6) compounds with tetrachlorocatecholate (Cl_4Cat) ligands, $Na_3[Ru_2(Cl_4Cat)_4(thf)]\cdot 3THF\cdot 3H_2O$ (**1**) and $Na_2[Ru_2(Cl_4Cat)_4(thf)_2]\cdot 2H_2O$ (**2**).

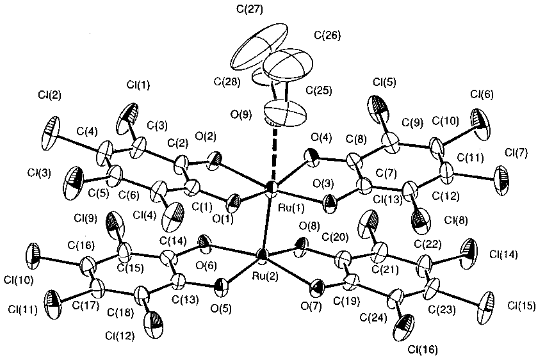

Figure 1. A view of the $[Ru_2(Cl_4Cat)_4]^{3-}$ anion including a weakly associated THF solvate molecule. Selected bond distances (Å): Ru(1)−Ru(2) 2.273(1), Ru(1)−O(1) 2.017(6), Ru(1)−O(2) 2.026(6), Ru(1)−O(3) 2.038(5), Ru(1)−O(4) 2.012(6), Ru(1)−O(9) 2.434(7), Ru(2)−O(5) 1.997(5), Ru(2)−O(6) 2.021(5), Ru(2)−O(7) 2.030(6), Ru(2)−O(8) 2.011(6), O(1)−C(1) 1.33(1), O(2)−C(2) 1.35(1), O(3)−C(7) 1.33(1), O(4)−C(8) 1.32(1), O(5)−C(13) 1.33(1), O(6)−C(14) 1.34(1), O(7)−C(19) 1.30(1), O(8)−C(20) 1.34(1).

The reaction between $[Ru_2(OAc)_4Cl]$ and tetrachlorocatechol (H_2Cl_4Cat) has been found to produce the $[Ru_2(Cl_4Cat)_4]^{3-}$ anion, isolated in the synthetic procedure as the sodium salt of the mixed H_2O/THF solvate, **1**.[10] Crystallographic characterization has shown that the dimer consists of two cofacial $Ru(Cl_4Cat)_2$ moieties linked by an unsupported Ru−Ru bond of 2.273(1) Å.[11] A view of the dimer and a weakly associated THF solvate molecule is shown in Figure 1.

One-electron oxidation of **1** with $AgClO_4$ gave the $[Ru_2(Cl_4Cat)_4]^{2-}$ anion obtained as the sodium salt, **2**.[10] In the solid state, the Ru_2^{6+} core of **2**·2THF is located about a crystallographic inversion center, resulting in a perfectly eclipsed arrangement for the Cl_4Cat ligands.[11] A view of the anion including axially associated thf ligands is shown in Figure 2. The Ru−Ru bond length in **2**·2THF is exceptionally short with a value of 2.2233(6) Å. In both structures the metal atoms are displaced out of the O_4 plane defined by the oxygen donor atoms and toward the adjacent metal atom by 0.31 Å for **1**·4THF and 0.33 Å for **2**·2THF. The Ru−Ru separations are more than 1 Å shorter than the usual distance between planes of stacked aromatic molecules. Repulsive interactions between eclipsed ligands that would normally prefer a separation of 3.5 Å[12] result in dihedral angles between the ring C_6 and donor atom O_4 planes that range from 4.1° to 10.5° for **1**·4THF and **2**·2THF.

Oxidation of the Ru_2^{5+} core of **1**·4THF leads to a contraction in the Ru−Ru length of 0.050(1) Å, and the site of oxidation is

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[9] It was reported that $[Ru_2(tmtaa)_2]^{2+}$ (tmtaa = dibenzotetraazaannulene dianion) as a dimer that may potentially contain an unsupported Ru−Ru triple bond, but no structural characterization was provided for the compound.[1,6]

[10] Compound **1**. Anal. Calcd for $C_{40}H_{38}Cl_{16}Na_3O_{15}Ru_2$: C, 30.08; H, 2.40. Found: C, 30.40; H, 2.29. IR data [ν/cm^{-1}] on KBr disks: 1612 (br), 1414 (s), 1379 (s), 1254 (s), 1047 (m), 966 (s), 812 (s), 801 (s), 577 (s) 490 (m). UV−vis (THF) λ_{max} 310 nm ($\epsilon = 2.38 \times 10^4$), 538 nm ($\epsilon = 9.30 \times 10^3$), 796 nm (sh). Compound **2**. Anal. Calcd for $C_{32}H_{20}Cl_{16}Na_2O_{12}Ru_2$: C, 27.22; H, 1.43. Found: C, 27.92; H, 1.87. IR data [ν/cm^{-1}] on KBr disks: 1655 (br), 1375 (s), 1254 (s), 1235 (w), 1046 (m), 926 (s), 766 (m), 749 (s), 600 (s). UV−vis (THF) λ_{max} 306 nm ($\epsilon = 2.15 \times 10^4$), 576 nm ($\epsilon = 6.87 \times 10^3$), 798 nm (sh).

[11] Crystal data for **1**·4THF: triclinic, $P\bar{1}$, $a = 20.428(7)$ Å, $b = 21.657(6)$ Å, $c = 9.443\ (1)$ Å, $\alpha = 93.50(2)°$, $\beta = 101.26(2)°$, $\gamma = 108.38(2)°$, $V = 3854(1)$ Å,^{3} $T = 298$ K, $Z = 2$, $R = 0.054$, $R_w = 0.067$. For **2**·2THF: triclinic, $P1$, $a = 12.176(3)$ Å, $b = 12.958(3)$ Å, $c = 9.3523(6)$ Å, $\alpha = 93.19(1)°$ $\beta = 102.49(1)°$, $\gamma = 103.48(2)°$, $V = 1392.2(5)$ Å,^{3} $T = 298$ K, $Z = 1$, $R = 0.038$, $R_w = 0.046$.

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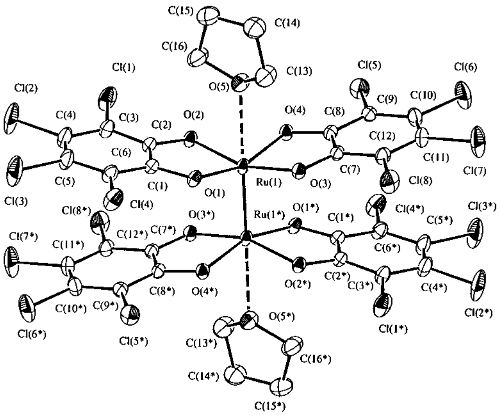

Figure 2. A view of the $[Ru_2(Cl_4Cat)_4]^{2-}$ anion. Selected bond distances (Å): Ru(1)−Ru(1*) 2.2233(6), Ru(1)−O(1) 1.998(2), Ru(1)−O(2) 1.965(2), Ru(1)−O(3) 1.990(2), Ru(1)−O(4) 1.973(2), Ru(1)−O(5) 2.647(3), O(1)−C(1) 1.354(4), O(2)−C(2) 1.352(4), O(3)−C(7) 1.354(4), O(4)−C(8) 1.350(4).

the metal−metal bond rather than the catecholate ligands.[13] The electrochemical properties of **1** have been investigated using thin-layer cyclic voltammetry in THF.[14] Two quasireversible waves were observed at −0.19 and −1.05 V (vs SCE) which are assigned as the Ru_2^{6+}/Ru_2^{5+} and Ru_2^{5+}/Ru_2^{4+} couples, respectively, on the basis of bulk solution rest potential measurements. Constant potential coulometry has revealed that the waves are one-electron transfer processes, indicating that the dimeric structures are retained in solution. Values for these redox couples are shifted negatively by approximately 1.0 V of potentials reported for carboxylate-bridged dimers.[5,15] Magnetic measurements on **1** and **2** show that **2** is diamagnetic and **1** contains a single unpaired electron. The ESR spectrum of **1** in THF glass at 77 K consists of three components at *g*-values of 2.21, 1.82, and 1.61.

Monomeric complexes of general formula $RuL_2(Cat)_2$ have been prepared with tetrachlorocatechol and 3,5-di-*tert*-butylcatechol and with pyridine and phosphine ancillary ligands.[16] The dependence of electrochemical potentials on catecholate substituents indicated that the quinone ligands are the sites of redox activity for these complexes. While the electronic levels associated with the Ru−Ru bonds of **1**·4THF and **2**·2THF are clearly the centers of electrochemical activity, the oxidation wave of catecholate ligands may also undergo oxidations at more positive potentials. The diamagnetism of **2**·2THF, together with the short Ru−Ru separation points to a $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration for the unsupported metal−metal bond. The separation between metals of $[Ru_2(Cl_4Cat)_4(thf)_2]^{2-}$ is the shortest Ru−Ru bond yet reported, supporting the triple-bond formulation.[1,4]

This study represents novel-type ligand-unsupported diruthenium compounds in the two oxidation states with the same equatorial ligand that differs from any previously encountered for diruthenium analogues.

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Supporting Information Available: X-ray crystallographic details (28 pages). An X-ray crystallographic file, in CIF format, is available through the Internet only. See any current masthead page for ordering and Internet access instructions.

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[13] The decrease could result from the removal of either an antibonding δ^* or π^* electron. Oxidation of $Ru_2(ap)_4Cl$ (ap = anilinopyridinate; Ru_2^{5+}, $\sigma^2\pi^4\delta^2\pi^{*2}\delta^*$) to $[Ru_2(ap)_4Cl]^+$ (Ru_2^{6+}, $\sigma^2\pi^4\delta^2\pi^{*2}$) was accompanied by an increase in the Ru−Ru length from 2.275 to 2.301 Å.[4,2b]

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