Inorganic Chemistry Communication

Inorg. Chem. **2010**, *49*, 2029–2031 **2029**
DOI: 10.1021/ic902328m

Synthesis and Reactivity of Catecholate Complexes Containing Quadruply Bonded Metal Ions

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Received November 24, 2009

Quadruply bonded metal complexes of rhenium and molybdenum have been prepared with tetrachlorocatechol. Structural characterization on the $[Re_2(Cl_4Cat)_4]^{2-}$ anion has shown that it consists of distorted square-planar $Re(Cl_4Cat)_2$ units linked by a short (2.2067 Å) quadruple Re−Re bond. The addition of tetrachlorocatechol to molybdenum acetate was used to prepare the isoelectronic molybdenum analogue "$[Mo_2(Cl_4Cat)_4]^{4-}$". This complex was found to be far more reactive than the rhenium dimer. A dimer containing a Mo−Mo double bond, $[(Cl_4Cat)_2Mo(\mu\text{-}O)(\mu\text{-}OCH_3)Mo(Cl_4Cat)_2]^{3-}$, was obtained as the methanolysis product of the complex formed initially, and the oxomolybdenum(V) monomer $[MoO(Cl_4Cat)_2]^-$ was formed under more oxidative conditions. Both complexes are oxygen-sensitive, giving $[MoO_2(Cl_4Cat)_2]^{2-}$ as the final air-stable complex product.

Studies on transition-metal complexes containing multiple metal−metal bonds have defined a diverse area of coordination chemistry.[1] Quadruply bonded metal atoms are a unique feature of this research where the σ, π, and δ components of the bond are associated with the overlap of metal d orbitals. While the metal ions of quadruply bonded dimers of early-transition-metal ions are nucleophilic, complexes of these metals have been found to lack the versatile oxidative−addition chemistry of the triply bonded dimers of molybdenum- and tungsten-containing alkoxo and amidinato ligands developed by Chisholm and Hollandsworth.[2] As strong σ and π donors, these ligands further activate the metals by their interaction with orbitals that are also associated with the multiple bond between metals.

In a recent series of reports, Kitagawa and co-workers have described catecholate complexes of ruthenium that contain strong Ru−Ru bonds.[3] The treatment of $[Ru_2(OAc)_4Cl]$ with tetrachlorocatechol was observed to give the $[Ru_2(Cl_4Cat)_4]^{3-}$ dimer with a Ru−Ru bond order of 2.5. One-electron oxidation of this anion gave the triply bonded dianion $[Ru_2(Cl_4Cat)_4]^{2-}$. This research has been extended to other catecholate ligands to give a series of triply bonded dimers that contain remarkably short Ru−Ru bonds.[4] Here we describe the preliminary results of reactions that lead to the first examples of bimetallic catecholate complexes containing quadruply bonded metals.

The addition of tetrachlorocatechol to a tetrahydrofuran (THF) solution of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$, followed by the addition of triethylamine as a weak base, gave dark-red-brown prismatic crystals of $(Et_3NH)_2[Re_2(Cl_4Cat)_4]$. Crystallographic characterization revealed that the dimer has the cubic structural motif associated with quadruply bonded bimetallic complexes (Figure 1), with a Re−Re length of 2.2067(7) Å.[5] This length is well within the range of Re−Re lengths reported for quadruply bonded dimers,[6] leading to the conclusion that the strong Re−Re bond of the parent $[Re_2Cl_8]^{2-}$ ion is intact. Even with the short Re−Re separation, the planar Cl_4Cat ligands are eclipsed but bent away from the ReO_4 plane at each metal. Stacked quinone ligands generally have a graphitic interplanar separation of approximately 3.4 Å. Distortions of the planar structure at the Re atoms represent a balance of attractive and repulsive effects between ligands to accommodate the short Re−Re separation. Within the $[Re_2(Cl_4Cat)_4]^{2-}$ dianion, the Re−O lengths average to 1.996(8) Å and features of the catecholate ligands average to values found commonly for tetrachlorocatecholate ligands in other structures.[7]

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[1] Cotton, F. A. *Inorg. Chem.* **1998**, *37*, 5710.

[2] Chisholm, M. H.; Hollandsworth, C. B. In *Multiple Bonds Between Metal Atoms*, 3rd ed.; Cotton, F. A., Murillo, C. A., Walton, R. A., Eds.; Springer: New York, 2005; p 203

[3] (a) Kondo, M.; Hamatani, M.; Kitagawa, S.; Pierpont, C. G.; Unoura, K. *J. Am. Chem. Soc.* **1998**, *120*, 455. (b) Miyasaka, H.; Chang, H.-C.; Mochizuki, K.; Kitagawa, S. *Inorg. Chem.* **2001**, *40*, 3544.

[4] (a) Chang, H.-C.; Mochizuki, K.; Kitagawa, S. *Inorg. Chem.* **2005**, *44*, 3799. (b) Chang, H.-C.; Mochizuki, K.; Kitagawa, S. *Inorg. Chem.* **2005**, *44*, 3810. (c) Mochizuki, K.; Chang, H.-C.; Kawamura, T.; Kitagawa, S. *Chem. Lett.* **2005**, *34*, 1662. (d) Mochizuki, K.; Kawamura, T.; Chang, H.-C.; Kitagawa, S. *Inorg. Chem.* **2006**, *45*, 3990.

[5] See the Supporting Information for details on the synthesis and structure determination of $(Et_3NH)_2[Re_2(Cl_4Cat)_4]\cdot THF$.

[6] Walton, R. A. In *Multiple Bonds Between Metal Atoms*, 3rd ed.; Cotton, F. A., Murillo, C. A., Walton, R. A., Eds.; Springer: New York, 2005; p 271.

[7] See for example: deLearie, L. A.; Pierpont, C. G. *J. Am. Chem. Soc.* **1986**, *108*, 6393.

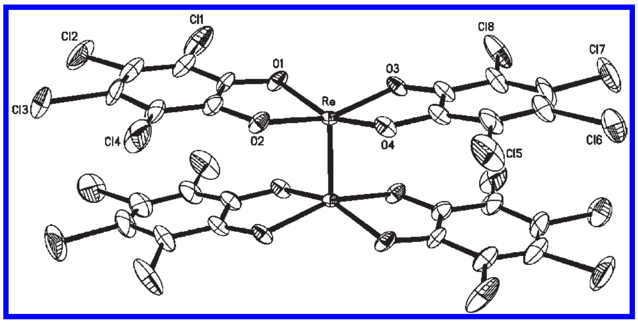

Figure 1. View of the $[Re_2(Cl_4Cat)_4]^{2-}$ anion. The Re−Re bond length is 2.2067(7) Å, the Re−O lengths average to 1.996(8) Å, and the catecholate C−O lengths average to 1.33(2) Å.

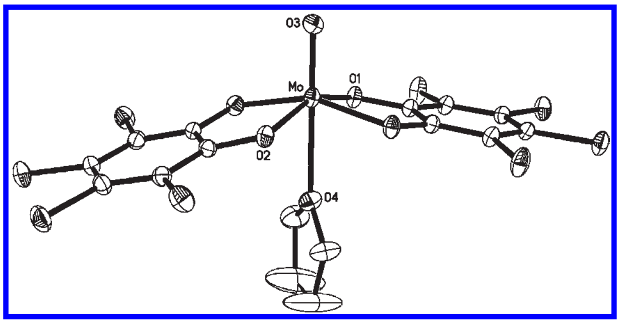

Figure 2. View of the $[Mo^VO(Cl_4Cat)_2(THF)]^-$ anion. The Mo−O3 length is 1.678(5) Å, the Mo−O lengths to the catecholate O atoms average to 2.001(3) Å, and the catecholate C−O lengths average to 1.342(5) Å.

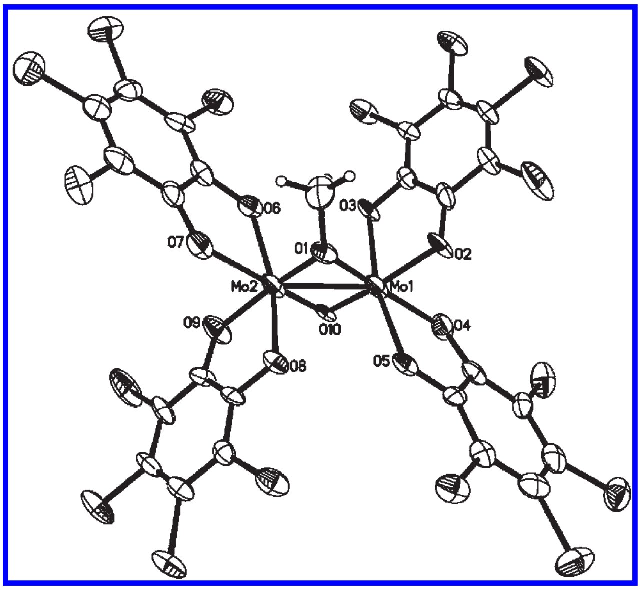

Figure 3. View of the $[(Cl_4Cat)_2Mo(\mu\text{-}O)(\mu\text{-}OCH_3)Mo(Cl_4Cat)_2]^{3-}$ anion. The Mo−Mo length is 2.436(1) Å, consistent with a double Mo−Mo bond.

In an attempt to extend this chemistry to a quadruply bonded dimolybdenum(II) dimer, reactions were carried out between molybdenum(II) acetate, $[Mo_2(OAc)_4]$, and tetrachlorocatechol. Details of these reactions are described in the Supporting Information, but it was clear from the outset that inert conditions would be required, in marked contrast to the aerobic stability of $[Re_2(Cl_4Cat)_4]^{2-}$. A reaction carried out under an argon atmosphere gave as the exclusive product dark-red crystals containing the $[Mo^VO(Cl_4Cat)_2(THF)]^-$ anion, isolated for crystallographic characterization as the NEt_4^+ salt.[8] A view of the anion is shown in Figure 2. Crystals of $(NEt_4)[Mo^VO(Cl_4Cat)_2(THF)]$ are extremely air-sensitive, reacting further with dioxygen to give the air-stable *cis*-$[Mo^{VI}O_2(Cl_4Cat)_2]^{2-}$ dianion or with argon containing roughly 3% dioxygen to give the type III Mo^V−Mo^{VI} mixed-valent bimetallic anion *cis*-$[(MoO(Cl_4Cat)_2)_2(\mu\text{-}O)]^{3-}$. The latter product is formed by the condensation of $[Mo^VO(Cl_4Cat)_2]^-$ with $[Mo^{VI}O_2(Cl_4Cat)_2]^{2-}$. Extreme oxygen sensitivity has been observed for reactions between $Mo(CO)_6$ and *o*-benzoquinones that lead to monooxomolybdenum(VI) products despite efforts at maintaining oxygen-free reaction conditions.[9] It appears reasonable from the chemistry leading to the formation of the $[Re_2(Cl_4Cat)_4]^{2-}$ dianion that the product formed initially in the reaction between $[Mo_2(OAc)_4]$ and H_2Cl_4Cat is the $[Mo_2(Cl_4Cat)_4]^{4-}$ anion containing a quadruple Mo−Mo bond. The difference in the overall negative charge, the shorter length of Mo−Mo quadruple bonds (2.09 Å),[10] and the increased nucleophilicity of Mo^{II} relative to Re^{III} accounts for the difference in reactivity between dimers of the two metals.

A second $[Mo_2(OAc)_4]/H_2Cl_4Cat$ reaction was carried out in a drybox in an oxygen-free dinitrogen atmosphere using THF as the solvent. An insoluble dark-red-brown product was observed to form. This product dissolved in a methanol solution containing NEt_4I, added to provide a countercation for crystallization. Dark-brown crystals were observed to form as the methanol solvent evaporated.[11] The bimetallic anion obtained as the product of this procedure, shown in Figure 3, is $(NEt_4)_3[(Cl_4Cat)_2Mo(\mu\text{-}O)(\mu\text{-}OCH_3)Mo(Cl_4Cat)_2]$. Each Mo center is chelated by two Cl_4Cat ligands. Bridging the Mo atoms are a methoxide ion and an oxo ligand. The Mo−Mo separation is 2.436(1) Å, a reasonable double bond length for strongly bound Mo^{IV} centers.[2,10] Bond lengths to both metals show an unusual axial compression that results in asymmetry in the lengths to the bridging O1 and O10 atoms in Figure 3. The Mo1−O10 length of 1.701(7) Å is significantly shorter than the Mo2−O10 length of 1.893(8) Å. Catecholate oxygen O2, located trans to O10, has a Mo1−O2 length of 1.872(6) Å, while other catecholate Mo1−O lengths are greater than 2.1 Å. Similarly, the Mo2−O1 length is 1.790(6) Å, while the Mo1−O1 length is 2.001(8) Å. The trans Mo2−O9 length is 1.839(7) Å, more than 0.3 Å shorter than other lengths to catecholate O atoms. Axially compressed octahedra have been observed for monomeric complexes of molybdenum(IV) containing strong π-donor ligands at trans coordination sites,[12] and this structural feature is frequently encountered for strong d^2 metal ions of the second and third transition series.[13]

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(8) See the Supporting Information for details on the synthesis and structure determination of $(NEt_4)[Mo^VO(Cl_4Cat)_2(THF)]\cdot THF$.

(9) (a) Buchanan, R. M.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 1616. (b) Cass, M. E.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 122. (c) Liu, C.-M.; Nordlander, E.; Schmeh, D.; Shoemaker, R.; Pierpont, C. G. *Inorg. Chem.* **2004**, *43*, 2114.

(10) Cotton, F. A. In *Multiple Bonds Between Metal Atoms*, 3rd ed.; Cotton, F. A., Murillo, C. A., Walton, R. A., Eds.; Springer: New York, 2005; p 69.

(11) See the Supporting Information for details on the synthesis and structure determination of $(NEt_4)_3[(Cl_4Cat)_2Mo(\mu\text{-}O)(\mu\text{-}OCH_3)Mo(Cl_4Cat)_2]$.

(12) See for example: Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *Inorg. Chem.* **1978**, *17*, 2944.

(13) (a) Lippard, S. J.; Nozaki, H.; Russ, B. J. *Chem. Commun.* **1967**, 118. (b) Lippard, S. J.; Russ, B. J. *Inorg. Chem.* **1967**, *11*, 1943. (c) Day, V. W.; Hoard, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 3374.

We speculate that the insoluble material formed initially in this procedure is the putative "$[Mo_2(Cl_4Cat)_4]^{4-}$" anion formed by the reaction between molybdenum(II) acetate and tetrachlorocatechol. Solvolysis in the methanol solution, with further oxidation by trace amounts of dioxygen, gives the oxomethoxide dimer with the Mo−Mo bond reduced in order, but intact. This is reasonable given the stability of the Mo_2^{4+} unit and the simple ligand replacement reaction observed for Re_2^{6+}.[14,15] Reactions carried out under an inert atmosphere outside the drybox, conditions where it is more difficult to control the presence of trace quantities of dioxygen, result in complete cleavage of the Mo−Mo bond with formation of the $[MoO(Cl_4Cat)_2]^-$ monomer and the other more oxidized products *cis*-$[(MoO(Cl_4Cat)_2)_2(\mu\text{-}O)]^{3-}$ and $[Mo^{VI}O_2(Cl_4Cat)_2]^{2-}$. The difference in reactivity between $[Re_2(Cl_4Cat)_4]^{2-}$ and $[Mo_2(Cl_4Cat)_4]^{4-}$ is indeed striking.

Acknowledgment. Research at Lund University was supported by the Swedish Research Council (to V.R.). Research at the University of Colorado was supported by the National Science Foundation (Grant CHE 0303487). C.P. thanks The Swedish Foundation for International Cooperation in Research (STINT) for a research fellowship.

Supporting Information Available: Experimental details and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. CIF files have also been deposited with the Cambridge Cryatallographic Data Centre as registry numbers CCDC 633012−633014. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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(14) See for example: Che, C.-M.; Chung, W.-C.; Lai, T.-F. *Inorg. Chem.* **1988**, *27*, 2801.

(15) Cotton, F. A.; Falvello, L. R.; Murillo, C. A. *Inorg. Chem.* **1983**, *22*, 382.