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Chemical and Electrochemical Redox Transformations of Oxomolybdenum and Oxotungsten Tetrathiolate Complexes

Sir:

Molybdenum complexes with oxo and thiolate ligands have been the subject of extensive synthetic and electrochemical studies in an attempt to provide models for the active sites of molybdenum-containing enzymes.[1] Although dioxo Mo(VI) complexes with polydentate thiolate ligands and monooxo Mo(V) complexes with monodentate and polydentate thiolate ligands have been well characterized,[2–5] it has not been possible in either case to demonstrate a chemical redox or reversible electrochemical transformation to a $[Mo^{V}(O)_2]^+$ or a $[Mo^{VI}O]^{4+}$ thiolate complex. We report that $[(O)M^{V}(SR)_4]^-$ complexes of molybdenum and tungsten with sterically hindered thiolate ligands can be electrochemically and chemically oxidized to stable $[(O)M^{VI}(SR)_4]$ complexes.

Complexes of the anions, $[(O)M(SR)_4]^-$ (M = Mo and W; SR = 2,3,5,6-tetramethylbenzenethiolate (S-2,3,5,6-Me_4C_6H) and 2,4,6-triisopropylbenzenethiolate (S-2,4,6-*i*-$Pr_3C_6H_2$)), can be readily prepared by the reaction of $OMoCl_4$ and $OWCl_4$ with 5 equiv of the lithium thiolate in CH_3CN. The complexes can also be prepared by the reactions of the thiolates with $MCl_4(CH_3CN)_2$ in wet CH_3CN. The $[R_4N][(O)M(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]$ (Mo (**1**), W (**2**)) and $[Ph_4P][(O)M(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]$ (Mo (**3**), W (**4**)) complexes[6] display structural and spectroscopic properties that are similar to those of the well-characterized $[(O)Mo(SPh)_4]^-$ complexes.[5] Both $[Et_4N][(O)Mo(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]$ (**1**) and $[(n\text{-}Pr)_4N][(O)W(S\text{-}2,3,5,6\text{-}Me_4C_6H_4]$ (**2**) have been structurally characterized by X-ray crystallography.[7] The structures of the $[(O)M(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]^-$ anions show a square-pyramidal arrangement of the ligands about the metal center, analogous to that observed for $[(O)Mo(SPh)_4]^-$.[5c]

The electronic spectra of the $[(O)M(SR)_4]^-$ complexes are characterized by a single intense band in the visible region. For the $[(O)M(SPh)_4]^-$ compounds, Wedd has previously observed that electron-donating substituents on the phenyl ring (e.g. *p*-MeC_6H_4– vs. C_6H_5–) shift this sulfur 3p-to-metal charge-transfer band to lower energy.[5a] In contrast, the sterically hindered thiolates with their electron-donating substituents shift this band to higher energy, because the ortho substituents of these thiolate ligands prevent metal thiolate conformations in which the S 3p lone-pair orbital is conjugated with the aromatic ring. A similar trend has been observed in the low-energy transition in the electronic spectra of $[Fe_4S_4(SR)_4]^{2-}$ complexes with the same set of sterically hindered thiolate ligands.[8]

Electrochemical studies of compounds **1**–**4** show that they are central members of three-membered electron-transfer series:[9]

$$[(O)M^{VI}(SR)_4] \rightleftharpoons [(O)M^{V}(SR)_4]^- \rightleftharpoons [(O)M^{IV}(SR)_4]^{2-}$$

The compounds all display electrochemically reversible behavior for the M(V)/M(IV) redox couple in DMF. Compounds **1**–**4** show variations in the electrochemical behavior of their M(VI)/M(V) redox couples; the approach to electrochemical reversibility, which was evaluated by normal-pulse (NP) and reverse-pulse (RP) voltammetric techniques, is dependent on the metal (W > Mo), the ligands (S-2,4,6-i-$Pr_3C_6H_2$ > S-2,3,5,6-Me_4C_6H), and the solvent (CH_2Cl_2 > DMF). Controlled-potential oxidations of **3** and **4** show clean liberation of one electron to give a stable solution of the oxidized species, which can be reduced by one electron back to the starting $[(O)M(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]^-$ complexes. The electrochemical reversibility of the M(VI)/M(V) couple for the complexes with the sterically hindered ligands must be contrasted with the reported behavior of the $[(O)Mo(SPh)_4]^-$ complexes, which exhibited, at best, only a quasi-reversible oxidation for the tungsten complex at low temperature.[5b]

The oxidation of **3** and **4** can also be performed chemically. When acetonitrile solutions of $[Ph_4P][(O)M(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]$

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(6) (a) $(Et_4N)[(O)Mo(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]$: electronic spectrum ($CH_3CN$) 582 nm ($\epsilon = 3360\ M^{-1}\ cm^{-1}$); IR (Nujol) 939 cm^{-1}, ν(Mo–O); ESR (CH_3CN, room temperature) $g = 1.991$; magnetic moment (solid, room temperature) 1.85 μ_B. $(n\text{-}Pr_4N)[(O)W(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]$: 510 nm ($\epsilon = 3610$); 949 cm^{-1}, ν(W–O); $g = 1.935$; 1.58 μ_B. $(PPh_4)[(O)Mo(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]$: 573 nm ($\epsilon = 4620$); 941 cm^{-1}, ν(Mo–O); $g = 1.992$; 1.80 μ_B. $(PPh_4)[(O)W(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]$: 505 nm ($\epsilon = 4320$); 954 cm^{-1}, ν(W–O); $g = 1.933$; 1.59 μ_B. (b) Compound **3** has also been mentioned in: Dilworth, J. R. In *Sulfur, its Significance for Chemistry, for the Geo-, Bio-, and Cosmosphere and Technology*; Muller, A., Krebs, B. Eds.; Elsevier: Amsterdam, 1984.

(7) The details of these structures will be reported at a later date. Although the complexes crystallize in different space groups, they both show a similar crystallographic disorder in which the metal and the oxo group are disordered while the thiolate ligands are ordered. Structural diagrams and crystallographic details are given in the supplementary material.

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are reacted with 1 equiv of $[(C_5H_5)_2Fe]BF_4$, the oxidized products precipitate from the reaction mixture leaving the other products $[(C_5H_5)_2Fe$ and $(Ph_4P)BF_4]$ in solution. Pentane extraction of the precipitate gives $[(O)M(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H)_4]$ (Mo (**5**), W (**6**)) as microcrystals in 50–65% yields.[10] Electrochemical and electronic spectroscopic studies of the chemically oxidized compounds demonstrates that **5** and **6** are identical with the species produced by the electrochemical oxidations. The complexes dissolve in toluene and alkanes to give intense blue solutions. These solutions are stable for >24 h for **6** and for several hours for **5**. The crystalline solids show decomposition after several days at room temperature but they are stable at −20 °C for extended periods. The complexes react with donor solvents such as DMF as indicated by the substantial changes in the electronic spectra; again, **5** is more reactive than **6**. This reactivity trend provides a probable explanation for the electrochemical behavior in DMF solution.

The electronic spectra of **5** and **6** are characterized by intense absorptions at 803 and 644 nm, respectively. In both cases, this band is considerably shifted to lower energy in comparison to the low-energy band in the M(V) complexes; the shifts are consistent with their assignments as a S-to-metal charge-transfer transition. ^1H NMR spectroscopy demonstrates the diamagnetism of **5** and **6** and the equivalence of the four thiolate ligands; this is consistent with a square-pyramidal structure similar to that of the $[(O)M^V(SR)_4]^-$ complexes and to the structure of $[(O)Mo(OC_4F_9)_4]$.[11] This work serves as another example of the ability of sterically hindered thiolate ligands to stabilize metal–thiolate coordination for metals in high oxidation states.[8,12]

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Supplementary Material Available: Structural diagrams and tables of crystallographic information, fractional coordinates, bond distances and angles, and thermal parameters for **1** and **2** (8 pages). Ordering information is given on any current masthead page.

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(10) $[(O)Mo(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]$: electronic spectrum (pentane) 803 nm ($\epsilon = 8900$); IR (Nujol) 940 cm^{-1}, ν(Mo–O); ^1H NMR (C_6D_6) δ 1.203 (12 H, d), 1.208 (6 H, d), 2.782 (2 H, m), 3.549 (1 H, m), 7.058 (2 H, s). $[(O)W(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]$: 750 (sh) ($\epsilon = 5100$), 643 ($\epsilon = 9390$), 480 ($\epsilon = 1490$), 420 nm ($\epsilon = 1080$); 959 cm^{-1}, ν(W–O); δ 1.204 (12 H, d), 1.210 (6 H, d), 2.815 (2 H, m), 3.548 (1 H, m), 7.057 (2 H, s).

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Dichlorotetrakis(pyridine)cobalt(III): A Versatile and Facile Synthetic Precursor

Sir:

The *trans*-dichlorotetrakis(pyridine)cobalt(III) complex, $Co(py)_4Cl_2^+$, was first synthesized by Werner and Feenstra in 1906.[1] It was employed in the 1950s to aid in the elucidation of the S_N1cb mechanism.[2] Nevertheless, despite its long history, only a few research groups seem to be aware of the synthetic utility of the complex as a facile route to chelated complexes. In this paper, we note several applications of the complex to Co(III) synthesis, some advantages over other synthetic precursors, and some preliminary investigations into the mechanism(s) leading to complex formation.

Table I. Distribution of $Co(dien)_2^{3+}$ Geometric Isomers

isomer	proportion, %[a]	equilibrium proportion, %[b]
s-fac	1.3	7
u-fac	7.0	29
mer	91.7	64

[a] $Co(py)_4Cl_2^+$ precursor; this work. [b] Reference 16 (counterion = NO_3^-).

Chan and Hui used the title complex in the slurry synthesis of pentakis(alkylamine)chlorocobalt(III) complex.[3] However, Toftlund and Pedersen seem to be one of the first groups to employ the compound in a facile solution synthesis of chelated CoN_6^{3+} complexes.[4] Their syntheses, performed in 2-methoxyethanol solvent systems, utilized near-stoichiometric amounts of ligands (both *cis*- and *trans*-1,2-cyclopentanediamine) and produced yields as high as 82%.[4]

In the last 10 years,, a few other groups have utilized $Co(py)_4Cl_2^+$ to synthesize other tris(diamine), polyamine, and mixed multidentate amine–thioether complex.[5-11] Many of these syntheses involved the use of stoichiometric amounts of ligands and organic solvents such as methanol, ethanol, pyridine, and dimethyl sulfoxide. Most of these reports refer to an almost instantaneous reaction, which seems odd given the slow rate of aquation of this complex.[2,12] We, therefore, have examined in more detail the parameters affecting the complex formation reactions of this complex and the product distributions resulting from reactions of the title complex with multidentate ligands.

When an aqueous solution of *trans*-$[Co(py)_4Cl_2]NO_3$ is mixed with a solution containing an excess of tetrasodium ethylenediaminetetraacetate, Na_4EDTA, the pale green solution rapidly changes color to blue-green. The visible spectrum of the resulting solution identifies the product as $[Co(EDTA)Cl]^{2-}$ with peak maxima at 584 and 404 nm (lit.[13] 584 and 402 nm). The solution then slowly reverts to the violet $Co(EDTA)^-$ complex. The formation of the chloro complex implicates electron transfer rather than substitution as the pathway for rapid complex formation. Trace amounts of Co(II) will complex with the $EDTA^{4-}$, followed by facile oxidation by $Co(py)_4Cl_2^+$ via an inner-sphere electron-transfer reaction. Wilkins and Yelin have reported on the kinetics of this process with the preformed Co(II)–EDTA complex.[14]

The title complex also reacts rapidly with pentaethylenehexamine, linpen, in aqueous solution. Visual observation of the green to yellow color change indicates, again, a nearly instantaneous reaction. Due to the very intense peak at 295 nm for the $Co(py)_4Cl_2^+$ complex,[15] we were able to follow this reaction in very

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