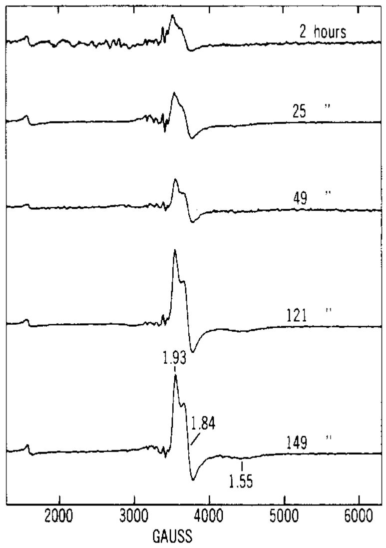

Figure 3. First-derivative EPR spectra of erythrocytes from *P. gouldii*. "Deoxygenated" (see text) coelomic fluid was filtered through cheesecloth. The erythrocytes were then spun down, resuspended in artificial seawater, and incubated aerobically for the indicated times at 4 °C. Zero time is that of removal of the fluid from the coelom. Spectral conditions: temperature, 4 K; frequency 9.57 GHz; power, 0.2 mW; receiver gain, 1.6×10^5. Other conditions are as given in the caption to Figure 2. Double integration against a $CuSO_4$ standard gave the following ratios of [semi-metHr]/[total Hr]: 25 h, 0.0038; 49 h, 0.0042; 121 h, 0.011; 149 h, 0.015.[23]

shows no reaction with 10 mM CN^- or gaseous CO.

The low isoelectric point listed in Table I means that near pH 7, *P. gouldii* cyt b_5 will have a net negative charge, while Hr, with an isoelectric point of ~8,[14] will have a net positive charge. Thus, a complex should form between hemerythrin and cytochrome b_5 at low [salt]. This putative complex provides an interesting contrast to that formed between human cytochrome b_5 and hemoglobin.[15] In the latter case a heme to heme one-electron transfer occurs, whereas in the case of Hr a heme to non-heme iron electron transfer would occur and two electrons are required to reach deoxyHr from metHr.

Like all other known cytochromes b_5, reduced *P. gouldii* cyt b_5 is rapidly oxidized by atmospheric oxygen and slowly autooxidizes under anaerobic conditions. Most importantly, reduced *P. gouldii* cyt b_5 rapidly reduces metHr. Under anaerobic conditions the rate constant for this reaction is 650 ± 50 $M^{-1}\ s^{-1}$ in 10 mM phosphate, pH 7.2, 0.5 mM EDTA at 20 °C.[16] This rate constant is much higher than that reported for reduction of *P. gouldii* metHr by deoxymyoglobin (0.25 $M^{-1}\ s^{-1}$ at pH 7.0 and 25 °C[17]), which could reflect the lower reorganizational energy required for electron transfer from low-spin heme.[18] On the basis of absorbance changes at 555 nm, a mixture of 0.019 mM reduced *P. gouldii* cytb_5 and 0.010 mM metHr in anaerobic buffer (pH 7.2) resulted in oxidation of 39% of the cyt b_5 within 2 min.[19] An EPR spectrum at 4 K of this mixture indicates that semi-metHr is the product of reduction, having *g* values at 1.95, 1.86, and 1.67. These *g* values are typical of $(\text{semi-met})_R$, the form produced by one-electron reduction of metHr.[22]

If reduction of metHr proceeds in this fashion within the erythrocyte, similar semi-met EPR signals should be observed. In fact, we observe no significant EPR intensity at 4 K from oxygenated erythrocytes even after 150 h incubation at 4 °C. However, if the worms are kept in seawater (20 °C) under a N_2 atmosphere for 12 h prior to isolation of the erythrocytes, which effectively deoxygenates the coelomic fluid, a characteristic semi-met EPR signal *is* observed to build up with time upon subsequent oxygenation as shown in Figure 3. At the longest incubation time the intensity of this signal accounts for less than 2% of the total Hr.[23] The *g* values reported in Figure 3 are similar to but not identical with those of $(\text{semi-met})_R$ (vide supra).[24] A possible explanation for these results is that prolonged oxygen deficiency followed by rapid reoxygenation induces increased levels of metHr and/or *P. gouldii* cyt b_5 within the erythrocytes. We have in fact noticed a significant (≥5-fold) increase in the yield of *P. gouldii* cyt b_5 from "deoxygenated" erythrocytes.

We have also isolated and partially purified a cytochrome b_5 reductase from the membrane fraction of *P. gouldii* erythrocytes. This reductase, when combined with *P. gouldii* cyt b_5, will catalyze the reduction of metHr to deoxyHr by NADH. The reactions between these various components and the role of the entire system in reduction of metHr in vivo are currently under study.

Acknowledgment. This research was supported by the National Institutes of Health (Grant GM 33157).

Registry No. Cytochrome b_5, 9035-39-6.

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(23) Total Hr concentrations were determined after EPR spectroscopy by diluting each thawed aliquot plus washings to 10 mL in buffer containing excess NaN_3. Quantitative conversion to $metHrN_3$ occurs upon overnight incubation at 4 °C. After the mixture was centrifuged to remove cell debris, the Hr concentration was determined from absorbance by using $\epsilon_{447} = 3700\ M^{-1}\ cm^{-1}$.[21]

(24) That the EPR signal of Figure 3 is due to intracellular Hr was verified by spinning down a portion of the erythrocytes after the longest incubation time and examining the supernatant by EPR at 4 K. No signal was observed.

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Synthesis and Characterization of the Polyoxothioanions $TaW_5O_{18}S^{3-}$ and $NbW_5O_{18}S^{3-}$

Sir:

Attempts to isolate early-transition-metal d^0 polyoxothioanions from polyoxoanions by oxygen-sulfur exchange are frequently frustrated by metal center reduction and/or metal-oxygen framework degradation.[1] In order to circumvent these difficulties, we have sought to introduce sulfur into polyoxoanions such as tantalo- and niobotungstates that contain labile metal-oxygen subunits embedded in relatively substitution-inert polyoxoanion

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(1) See Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1831 and references cited therein.

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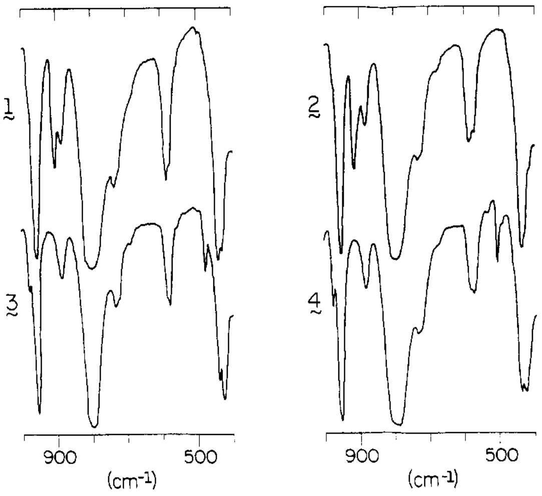


Figure 1. IR spectra of $TaW_5O_{19}[(n\text{-}C_4H_9)_4N]_3$ (**1**), $NbW_5O_{19}[(n\text{-}C_4H_9)_4$ (**2**), $TaW_5O_{18}S[(n\text{-}C_4H_9)_4N]_3$ (**3**), and $NbW_5O_{18}S[(n\text{-}C_4H_9)_4N]_3$ (**4**) measured from Nujol mulls. See ref 4 and 8 for numerical data.

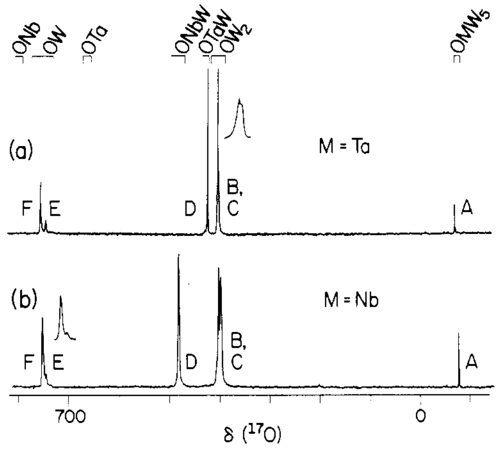
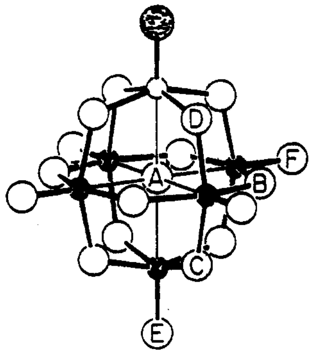


Figure 2. 33.9-MHz ^{17}O FTNMR spectra of (a) $TaW_5O_{18}S[(n\text{-}C_4H_9)_4N]_3$ (**3**) and (b) $NbW_5O_{18}S[(n\text{-}C_4H_9)_4N]_3$ (**4**). Chemical shift regions given are derived from data given in ref 13. Resonances are assigned according to the labeling scheme given in structure a, where one member of each set of symmetry-equivalent oxygens is labeled. See ref 8 for numerical data and experimental parameters.

frameworks[2] and are also appropriately weak oxidizing agents.[6] We report here an application of this approach to the synthesis of the first isolable early-transition-metal d^0 polyoxothioanions, $TaW_5O_{18}S^{3-}$ and $NbW_5O_{18}S^{3-}$.

Addition of 1.7 mL (8 mmol) of degassed $[(CH_3)_3Si]_2S$[7] to an air-filled, sealed 50-mL flask containing 3.0 g (1.4-1.5 mmol) of $MW_5O_{19}[(n\text{-}C_4H_9)_4N]_3$, M = Ta (**1**) or Nb (**2**),[4] in 15 mL of dry CH_3CN, followed sequentially by stirring at 22 °C until the solution changed color from dark green to red (ca. 1 h), 36 h of stirring at 42 °C, addition of 30 mL of $(C_2H_5)_2O$ over 1 min, and isolation of the resulting orange precipitate by suction filtration under dry N_2, yielded 2.1 g of crude reaction product. Cooling a CH_3CN solution of this material, saturated at ambient temperature, to 0 °C in a dry N_2 atmosphere resulted in the formation of orange crystalline $MW_5O_{18}S[(n\text{-}C_4H_9)_4N]_3$,[8] M = Ta (**3**) or Nb (**4**), which was isolated by suction filtration under N_2 in >50% yield based on **1** or **2** (1.6 g). Compounds **3** and **4** are stable in dry CH_3CN under N_2 for at least 6 h at 60 °C, as determined by ^{17}O NMR spectroscopy, but are completely hydrolyzed to **1** and **2**, respectively, by 5 equiv of water in acetonitrile after 2–3 days at 25 °C.

The IR spectra of **3** and **4** are extremely similar (see Figure 1) and closely resemble spectra of **1** and **2**, respectively, in the 400–1000-cm^{-1} region except for the absence of Ta=O (907 cm^{-1})[4] and Nb=O (913 cm^{-1})[4,9] stretching absorptions and the presence of Ta=S (481 cm^{-1})[10] and Nb=S (510 cm^{-1})[11] stretching absorptions. Infrared spectroscopy therefore implies C_{4v} structures for $TaW_5O_{18}S^{3-}$ and $NbW_5O_{18}S^{3-}$ derived from the $TaW_5O_{19}^{3-}$ and $NbW_5O_{19}^{3-}$[4,12] structures by replacement of terminally bonded OTa and ONb oxo ligands with thio ligands:



a

In structure a, tungsten atoms are represented by small filled circles, niobium or tantalum atoms by small open circles, oxygen atoms by large open circles, and the sulfur atom by a large shaded

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(2) According to ^{17}O-exchange studies, the oxo ligands in $Nb_2W_4O_{19}^{4-}$, $NbW_5O_{19}^{3-}$, and $TaW_5O_{19}^{3-}$ bonded solely to niobium centers exchange with water oxygens far more rapidly than those bonded to tungsten centers.[3-5]

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circle. Oxygen-17 NMR spectra of **3** and **4** shown in Figure 2 are fully consistent with this C_{4v} structure. The spectra of $MW_5O_{18}S^{3-}$, M = Ta and Nb, both show the following: no OM resonance; two OW resonances with intensity ratios of ca. 4:1; a single OMW resonance and two OW_2 resonances, all having approximately equal intensities; and a single OMW_5 resonance.[13]

Acknowledgment. We acknowledge the National Science Foundation for support of this research. NMR spectra were measured at the NSF Midwest Regional NMR Facility (Grant CHE 79-6100). We are indebted to Drs. Gregg Zank and Dean Giolando for invaluable advice and are grateful to Dr. Egbert Keller for a copy of his SCHAKAL program.

Registry No. **1**, 93529-95-4; **2**, 93529-90-9; **3**, 99268-93-6; **4**, 99268-95-8; $[(CH_3)_3Si]_2S$, 3385-94-2.

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(13) Oxygen-17 NMR chemical shifts for $TaW_5O_{19}^{3-}$ and $NbW_5O_{19}^{3-}$ have the following values:[4] δ 799 (ONb), 730–733 (OW), 666 (OTa), 456 (ONbW), 420 (OTaW), 392–394 (OW_2), −67 ($ONbW_5$), −73 ($OTaW_5$).

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Articles

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Electronic Coupling in Trigonal Mixed-Valence Dimers and the MCD and EPR Spectra of Tris(μ-halo)bis(triammineruthenium)(2+) Ions

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An electronic coupling model for trigonal mixed-valence dimers is presented. This model is used to interpret absorption, MCD, and EPR spectra of the trichloro- and tribromo-bridged title compounds. The absorption band positions and EPR *g* values are simply explained, but the MCD spectra show that the intense "intervalence" band in the visible region is substantially *XY* polarized rather than *Z* polarized as required by theory. Alternative assignments and their implication on the resonance Raman spectra are discussed.

Introduction

There is growing evidence[1-3] that the intensely colored species formed by the reaction of ruthenium ammines in concentrated halo acids has a cofacial bioctahedral geometry (Figure 1). Unfortunately no crystal structure data have been published. Absorption[2] and resonance Raman[3] (RR) studies have been interpreted within a (delocalized) molecular orbital model that accounts qualitatively for the absorption energies and RR spectra of the chloro-, bromo-, and iodo-bridged species. A semiclassical analysis of the temperature dependence of the absorption bandwidth gave an average frequency (200 cm^{-1} for the chloride) close to the bridging halogen mode frequencies, which were specifically enhanced by resonance with the main absorption band.[3] This analysis leads to an electronic origin lying some 8000 cm^{-1} lower in energy than the observed peak. Moreover, the MCD spectra have mixed signs and are not consistent with progressions of totally symmetric bands built upon a single electronic transition. The latter require identical profiles for absorption and MCD spectra.

Recently a series of MCD studies on strongly coupled mixed-valence dimers of ruthenium and osmium have been completed,[4-6] and a simple electronic model has been reasonably successful in explaining the spectroscopic data. Three types of transition dipoles contribute to the absorption and MCD spectra.[5] The largest dipole is the *Z*-polarized electron transfer. The static *XY* dipole is usually very small, and the corresponding absorption intensity in solution is dominated either by a vibronically induced electric dipole (Herzberg–Teller coupling) or by the static electron transfer, which may be induced by spin–orbit coupling. In odd-electron molecules the interference between the static *XY* and electron-transfer dipoles generates a small transverse MCD that is much larger that the axial MCD associated with the *XY* dipole.[7] The transverse MCD is equal and opposite in sign for the two states that are allowed in *Z* and *XY* polarizations and are coupled by a spin–orbit interaction. The MCD of the vibronically induced electric dipole is not as well characterized, but in specific cases, it may be of the same order as the static transverse MCD.

In this paper the theory is applied to delocalized mixed-valence dimers with trigonal symmetry. The electronic structure and spectra of the trihalo-bridged title compounds[1-3] are reexamined in more detail with the aid of EPR and MCD spectroscopies.

Experimental Section

The materials were prepared according to the procedures of Bottomley and Tong.[1] We were not able to prepare single crystals. MCD and absorption spectra were measured on solid solutions in the isotropic host poly(vinyl alcohol) (PVA). These were prepared by evaporation of aqueous solutions of the material and PVA under a stream of argon. It was not possible to measure the absorption spectra of the weak near-IR band of the bromide-bridged species, due to its lower solubility in PVA. The absorption spectra of thicker samples were obscured by bands of the PVA host medium. All MCD spectra were dominated by *C* terms. No deterioration of the dry foils was observed over a period of months. EPR spectra were measured of the neat material and frozen solutions of Me_2SO/glycerol (2:1) and DMF. The spectra in the two solvents were similar, and a broader resonance could be seen from the neat micro-

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† Visiting fellow.

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