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Conversion of Dinuclear, Diamagnetic $[Mo^{V}_2O_3(NCS)_8]^{4-}$ into Mononuclear, Paramagnetic $[Mo^{V}O(NCS)_5]^{2-}$ through Photolytic Ligand Redistribution

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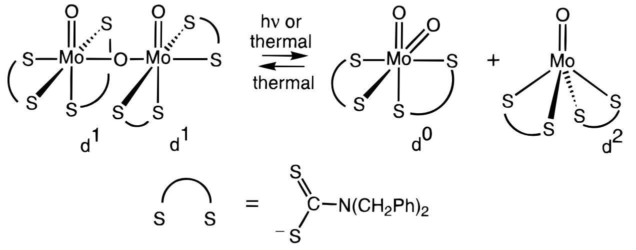
Dinuclear $[Mo^{V}_2O_3(NCS)_8]^{4-}$ ($\mathbf{1}^{4-}$) has been prepared as $[NMe_4]^+$ and $[NEt_4]^+$ salts in good yield by reduction of $[Mo^{VI}O_2(NCS)_4]^{2-}$ with 0.5 equiv of PMe_2Ph in tetrahydrofuran. A Beer's law plot of the band at 513 nm ($\epsilon = 22\,500$ mol^{-1} L cm^{-1}) from concentrations of 1×10^{-4}−1×10^{-3} mol L^{-1} established that $\mathbf{1}^{4-}$ does not participate in thermal disproportionation equilibria with mononuclear Mo(VI) and Mo(IV) species. A single crystal diffraction study has established that dark crystals containing $\mathbf{1}^{4-}$ and a noncoordinating $[NMe_4]^+$ counterion crystallize from acetone as the solvate $[NMe_4]_4[Mo^{V}_2O_3(NCS)_8]\cdot 2Me_2CO$ in the triclinic space group $P\bar{1}$ with $a = 9.455$ (2) Å, $b = 11.831$ (2) Å, $c = 12.772$ (3) Å, $\alpha = 110.52$ (3)°, $\beta = 105.17$ (3)°, $\gamma = 98.63$ (3)°, and $Z = 1$. The anion in these crystals has an anti orientation of the terminal oxo groups similar to that observed previously for a hydrate of the K^+ salt. Ion pairing in the K^+ salt has surprisingly modest effects on anion parameters for the anion, largely confined to increases in the bending at N of the isothiocyanate ligands. The tetraalkylammonium salts are photosensitive in CH_3CN, and purple solutions become orange within hours under ambient lighting. Disappearance of the absorbance at 513 nm and appearance of a new visible absorbance at 455 nm is accompanied by well-defined isosbestic points at 483, 394, 367, and 322 nm. The photolysis product is paramagnetic ($\mu_{\text{eff}} = 1.86$ BM in solution) and has been shown to be mononuclear $[Mo^{V}O(NCS)_5]^{2-}$ by comparison (UV/visible, IR, combustion analysis, EPR) with a reference sample. Reproducible synthetic photolysis of $[Mo^{V}_2O_3(NCS)_8]^{4-}$ requires an atmosphere of O_2, consistent with an initial photochemical redistribution of the isothiocyanate ligands to form $[Mo^{V}O(NCS)_5]^{2-}$ and a Mo(V) oxo complex which is then oxidized. The low disappearance quantum yield in the visible ($\Phi_{\lambda>460} = 1.3 \times 10^{-4}$) establishes that the reaction is not connected with the bridging oxo chromophore but probably involves initial NCS^- dissociation following UV excitation ($\Phi_{310} = 1.4 \times 10^{-3}$ under N_2).

Introduction

Dinuclear species containing $[Mo^{V}_2O_3]^{4+}$ cores with linear oxo bridges between the metal centers form an intriguing class of coordination complexes of Mo(V).[1] The bridges are flanked by terminal oxo groups, which are cis with respect to the bridging atoms[2] and which may be syn or anti with respect to each other,[3,4] and strong π-interactions through the linear oxo bridges spin pair the d^1 centers.[1,5] The coordination spheres of the metals are commonly completed by four anionic bis-chelate thiolato ligands (such as a dithiophosphate, $[S_2P(OR)_2]^-$, a dithiocarboxylate such as an xanthate, $[S_2COR]^-$, or a dithiocarbamate, $[S_2CNR_2]^-$) to give $[Mo^{V}_2O_3(S_2EX_n)_4]$ complexes.

Scheme 1



Dinuclear $[Mo^{V}_2O_3(S_2EX_n)_4]$ complexes are often in disproportion equilibria with mononuclear d^0 $[Mo^{VI}O_2(S_2EX_n)_2]$ and d^2 $[Mo^{IV}O(S_2EX_n)_2]$ complexes,[6,7] and in the case of the dithiocarbamate complex $[Mo^{V}_2O_3\{S_2CN(CH_2Ph)_2\}_4]$, we have recently reported that the disproportionation can be driven photochemically (Scheme 1).[8] Since disruption of the linear oxo bridge is thermally reversible and results in loss of the intense 519 nm absorbance responsible for the purple color of the species, this gives rise to marked type T photochromism.[9] Intense absorbances in this region are a common feature of

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(3) Recent evidence from our laboratory for facile intramolecular bridge and terminal oxo exchange in some of these systems, and the appearance of multiple examples of both syn and anti geometries in the growing data base of structurally characterized examples of such complexes, would suggest that there is no intrinsic preference for either the syn or anti geometry in these systems.[4]

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complexes in which linear oxo bridges spin pair d^1 centers,[10] and we have explored the generality of photodisproportionation in such systems; if this were a general reaction, it would allow access to a wide body of related photochromic materials which could facilitate the development of applications based on photochromic behaviors.

We have observed photodisproportionation reactions with the tungsten analog of $[Mo^{V}_2O_3\{S_2CN(CH_2Ph)_2\}_4]$[8] and with the dinuclear tungstenocene complex $[\{W(\eta^5\text{-}C_5H_5)_2(CH_3)\}_2(\mu\text{-}O)]^{2+}$,[11] and recently broadened our examination of the photochemical behavior of $[Mo^{V}_2O_3]^{4+}$ complexes to include the unusual tetraanionic thiocyanate complex $[Mo^{V}_2O_3(NCS)_8]^{4-}$ ($\mathbf{1}^{4-}$). We now report that $\mathbf{1}^{4-}$ is indeed photosensitive, but that photolysis leads to a ligand redistribution reaction which converts dinuclear, diamagnetic $\mathbf{1}^{4-}$ into mononuclear, paramagnetic $[Mo^{V}O(NCS)_5]^{2-}$.

Experimental Section

Solvents, Reagents, and General Data. Solvents were freshly distilled under nitrogen prior to use. Diethyl ether (ether) and tetrahydrofuran (THF) were predried over sodium ribbon and distilled from benzophenone/sodium. Pentane was treated with 5% HNO_3 in H_2SO_4, neutralized over K_2CO_3, and then distilled over CaH_2. Methylene chloride and acetonitrile were distilled over calcium hydride. Methanol, PMe_2Ph, and acetone were used as received from Aldrich (reagent grade). Deuterated acetonitrile (99.8 atom %) was used as received from Cambridge Isotopes. $[NMe_4]_2[Mo^{VI}O_2(NCS)_4]$ was prepared in a 76% yield on a 16 g scale by a literature procedure from ammonium paramolybdate by precipitation from a solution of molybdate which had been freshly acidified in the presence of a large excess of thiocyanate.[12] Elemental analyses were performed by Atlantic Microlab, Inc., of Norcross, GA.

Spectroscopy and Magnetic Measurements. Electronic spectra were recorded on a Perkin-Elmer Lambda 3B UV/visible spectrophotometer or an IBM 9430 UV/visible spectrophotometer and IR spectra (Nujol mulls or KBr pellets, polystyrene as an external standard) on a Perkin-Elmer Model 783 spectrophotometer. ^1H NMR spectra were recorded on a Bruker AF300 NMR spectrometer. EPR spectra were recorded on a Varian E-4 spectrometer in a quartz cell. Raman spectra were recorded as powders on a Nicolet Raman 950 ($Nd{:}YVO_4$ laser, $\lambda_{ex} = 1064$ nm, power 0.2−0.4 W) with a liquid nitrogen cooled germanium diode detector Model 203NR supplied by Applied Detector Corp. Solution magnetic susceptibilities were determined by the Evans NMR method.[13]

Synthesis of $[NMe_4]_4[Mo^{V}_2O_3(NCS)_8]$. Freshly prepared $[NMe_4]_2[Mo^{VI}O_2(NCS)_4]$ (3.56 g, 7.01 mmol) was dissolved in 100 mL of THF in a 250 mL three-neck round-bottom flask to give a yellow solution, which became dark orange upon addition of 0.50 mL (3.50 mmol) of PMe_2Ph. After 3 h at reflux, the purple precipitate was separated from the dark reddish purple solution by filtration on a frit and washed with THF (40 mL), cold CH_3OH (40 mL), ether (20 mL), CH_2Cl_2 (20 mL), and again with ether (20 mL). After initial air-drying, the solid was dried under vacuum overnight. Yield: 3.24 g, 3.24 mmol, 92%. The dinuclear complex was recrystallized in the dark from acetonitrile/toluene (72%). ^1H NMR (CD_3CN): δ 3.1 (s, CH_3). IR (KBr pellet): 3010 (mw), 2030 (vs, br, ν_{NCS}), 1580 (m), 948 (s, ν_{Mo-O}), 895 (sh), 843 (w), 770 (m), 725 (m), 480 (m, δ_{NCS}) 435 (ms) cm.$^{-1}$ Raman spectrum (powder): 2110 (w), 2030 (s, ν_{NCS}), 1530 (s), 955 (s, ν_{Mo-O}) cm^{-1}. Electronic spectrum (CH_3CN): $\lambda_{max} = 513$ nm ($\epsilon = 22\,500$ M^{-1} cm^{-1}). Anal. Calcd for $C_{24}H_{48}O_3N_{12}S_8Mo_2$: C, 28.80; H 4.83. Found: C, 28.20; H 4.70.

Synthesis of $[NEt_4]_4[Mo^{V}_2O_3(NCS)_8]$. This was prepared in 62% yield by a procedure similar to that described above for the tetramethylammonium salt. ^1H NMR (CD_3CN): δ 1.22 (t, 3 H, CH_3, $J = 7.5$ Hz), 3.2 (q, 2 H, CH_2, $J = 7.5$ Hz). IR (KBr pellet): 2985 (m), 2958 (w), 2040 (vs, br, ν_{NCS}), 1485 (s), 1455 (m), 1440 (m), 1392 (ms), 1368 (w), 1172 (ms), 1055 (w), 1001 (m), 953 (s) (ν_{Mo-O}), 895 (vw, sh), 782 (m) with 735 sh, 482 (m, δ_{NCS}), 435 (m) cm.$^{-1}$ Electronic spectrum (CH_3CN): $\lambda_{max} = 513$ ($\epsilon = 22\,500$ M^{-1} cm^{-1}), 308 ($\epsilon = 28\,200$ M^{-1} cm^{-1}), 235 nm ($\epsilon = 37\,300$ M^{-1} cm^{-1}). Anal. Calcd for $C_{40}H_{80}O_3N_{12}S_8Mo_2$: C, 39.20; H, 6.58; N 13.72. Found: C, 39.41; H 6.66; N 13.53.

Photolysis of $[NEt_4]_4[Mo^{V}_2O_3(NCS)_8]$. Recrystallized purple $[NEt_4]_4[Mo^{V}_2O_3(NCS)_8]$ (2.0 mg, 1.6×10^{-3} mmol) was placed in a 25 mL bulb fitted with a precision quartz UV/visible cell and evacuated on a Schlenk line. Acetonitrile (20.0 mL) was added in the dark to form a purple solution. An initial scan showed λ_{max} at 513 nm and no band at 455 nm. The sample was exposed to the wide spectrum light of a 200 W Hg−Xe arc lamp for 10 min and was then scanned again. An absorbance at 455 nm grew in intensity as the absorbance at 513 nm decreased. Exposures and scans were repeated until there was a λ_{max} at 455 nm and only a small inflection at 513 nm. The final solution was orange. Material from several experiments was collected and recrystallized from acetonitrile/toluene to give an analytical sample. Anal. Calcd for $C_{21}H_{40}MoN_7OS_5$: C, 38.05; H, 6.08. Found: C, 37.79; H, 6.02.

Photolytic Preparation of $[NMe_4]_2[Mo^{V}O(NCS)_5]$ from $[NMe_4]_4[Mo^{V}_2O_3(NCS)_8]$. In a typical synthetic experiment, 1.43 g (1.43 mmol) of recrystallized $[NMe_4]_4[Mo^{V}_2O_3(NCS)_8]$ was dissolved in acetonitrile (345 mL) in a quartz Schlenk flask. This was placed 28 cm from a 400 W Hg−Xe arc immersion lamp in a water-cooled jacket, and oxygen saturated with acetonitrile was bubbled through the flask throughout the reaction. Photolysis was monitored via electronic spectroscopy, and after 17.25 h, the λ_{max} was 455 nm and there was only a small inflection at 513 nm. The orange solution was filtered in air through a medium-porosity frit. Concentration of the acetonitrile solution precipitated a green-yellow solid (IR showed only MoO stretches). Toluene (200 mL) was added to the refiltered solution to precipitate $[NMe_4]_4[Mo^{V}O(NCS)_5]$ as a red solid, which was collected by filtration and washed with toluene. Anal. Calcd for $C_{13}H_{24}MoN_7OS_5$: C, 28.36; H, 4.39. Found: C, 28.35; H, 4.34. IR (KBr): 3010 (w), 2030 (s, br, ν_{NCS}), 1480 (m), 1410 (m), 950 (s, ν_{Mo-O}), 870 (w), 740 (w), 475 (m, δ_{NCS}) cm^{-1}. Raman spectrum (powder): 2025 (ν_{NCS}), 950 (ν_{Mo-O}) cm^{-1}. Effective magnetic moment (CD_3CN): 1.86 BM. EPR (acetone): $\langle g \rangle = 1.96$. Electronic spectrum (CH_3CN): $\lambda_{max} = 455$ ($\epsilon = 17\,600$ M^{-1} cm^{-1}), 328 ($\epsilon = 24\,500$ M^{-1} cm^{-1}), 260 nm ($\epsilon = 31\,700$ M^{-1} cm^{-1}).

Synthesis of $[NMe_4]_4[Mo^{V}_2O_4(NCS)_6]$. This was prepared from MoO_3 by the literature method[14] in a 60% yield on a 12 g scale. The red solid was recrystallized from ethanol and again from methylene chloride/pentane. IR (KBr): 2985 (m), 2080 (sh), 2030 (vs, br), 1485 (s), 1455 (sh), 1395 (s), 1365 (s), 1185 (sh), 1172 (s), 1001 (s), 945 (vs, $\nu_{Mo=O}$), 782 (s), 730 (vw), 480 (mw), 460 (sh), 435 (vw), 305 (vs) cm.$^{-1}$ UV/visible (ethanol): $\lambda_{max} = 445$ ($\epsilon = 8100$ M^{-1} cm^{-1}), 308 nm ($\epsilon = 21\,000$ M^{-1} cm^{-1}).

Synthesis of $[NMe_4]_2[Mo^{V}O(NCS)_5]$. This was prepared from ammonium paramolybdate by the literature method[15] in 76% yield on a 20 g scale. The red solid was recrystallized from THF/pentane. Anal. Calcd for $C_{13}H_{24}MoN_7OS_5$: C, 28.36; H, 4.39. Found: C, 28.39; H, 4.39. IR (KBr pellet): 3010 (w), 2030 (s, br, ν_{NCS}), 1480 (m), 1410 (m), 950 (s, ν_{Mo-O}), 870 (w), 475 (m, δ_{NCS}), cm^{-1}. Electronic spectrum (acetonitrile): $\lambda_{max} = 455$ ($\epsilon = 17\,600$ M^{-1} cm^{-1}), 328 ($\epsilon = 24\,500$ M^{-1} cm^{-1}), 260 nm ($\epsilon = 31\,700$ M^{-1} cm^{-1}). The effective magnetic moment in acetonitrile is 1.86 BM. EPR (in acetone): $\langle g \rangle = 1.96$.

X-ray Diffraction Study of $[NMe_4]_4[Mo^{V}_2O_3(NCS)_8]\cdot 2Me_2CO$. Crystals of a tetraalkylammonium salt of $[Mo^{V}_2O_3(NCS)_8]^{4-}$ suitable

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for crystallographic studies precipitated from an acetone solution of $[NMe_4]_2[Mo^VO(NCS)_5]$ under air at room temperature over a period of weeks. The crystals were dark with a green luster, and the selected crystal was cemented (epoxy) to a fine glass fiber. The crystal was triclinic and could be assigned on the basis of photographs and systematic absences to space group $P1$ or $P\bar{1}$. The choice of centrosymmetric $P\bar{1}$ was confirmed by the successful solution and refinement of the structure. Unit cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with $18° \leq 2\theta \leq 25°$. Diffraction data were collected as summarized in the deposited data. A semiempirical absorption correlation (XEMP) was applied to the diffraction data.

The structure was solved by means of the direct methods routine TREF, which located the Mo and S atoms. The remaining non-hydrogen atoms were located from subsequent Fourier syntheses and refined anisotropically. Hydrogen atoms were placed in idealized calculated positions ($d(C-H) = 0.96$ Å). The asymmetric unit consists of a half-molecule of $\mathbf{1}^{4-}$. The molecule resides on an inversion center with O(1) located at (0.5, 0.5, 0.5). The highest peak in the final difference Fourier synthesis corresponded to 0.529 e $Å^{-3}$ and was close to S(2). Inspection of F_o vs F_c values and trends based on sin θ, Miller indices, and parity groups failed to reveal any systematic errors in the X-ray data. All computer programs used in the collection, solution, and refinement of crystal data are contained in the Siemens' program package SHELXTL PLUS (UNIX version 5.1).

Quantum Yield Determinations. An air-cooled Oriel 200 W Hg−Xe arc lamp was used as the light source. The water-filtered beam (focused to a 1 cm^2 area) was monochromatized by the appropriate cutoff (Oriel 3-70, 460 nm) or interference filter (Oriel 53615, 310 nm, 30 nm bandwidth at half-height). Sample cells were thermostated in a brass cell holder cooled by a circulation bath (50% ethylene glycol in water). Temperature was monitored by a thermocouple attached to the cell holder. Absorbances were measured in an IBM 9430 UV/visible spectrophotometer after rapid transfer of the sample cells into a thermostated cell holder connected to the same cooling bath.

The lamp intensity was measured before each quantum yield determination by use of the chemical actinometer[16] Aberchrome 540. A small sample (11.3 mg) of the fulgide (*E*)-α-(2,5-dimethyl-3-furylethylidene)isopropylidene succinic anhydride was dissolved in 9.0 mL of toluene to give a 4.83×10^{-3} M solution. An aliquot (3.00 mL) of this solution was transferred to a 1.00 cm quartz cell and sealed under nitrogen. Aberchrome 540 undergoes a reversible ring-closure reaction to give 7,7a-dihydro-2,4,7,7a-pentamethylbenzo[*b*]furan-5,6-dicarboxylic anhydride.[17] The known quantum yields for the forward and reverse reactions[18] were used to measure lamp intensities in the 310−370 and 436−545 nm ranges, respectively, from plots of absorbance vs time and the relation $I = (V/\Phi_\alpha\epsilon_\alpha l)(\Delta A/t)$, where I is the intensity of the lamp (einstein/s), V is the solution volume (3.00×10^{-3} L), Φ_A is the forward or reverse quantum yield for Aberchrome 540 (0.20 and 0.06), ϵ_A is the extinction coefficient for Aberchrome 540 at 494 nm (8200 M^{-1} cm^{-1}), l is the cell length (1.00 cm), A is the absorbance, and t is time (s).

Sample solutions of known volume were allowed to equilibrate thermally in the dark for 10 min. Concentrations were such that the absorbance at the wavelength of irradiation was greater than 1.7 absorbance units (>98% incident intensity absorption), and the absorbance at the monitored wavelength was no more than 2.2. The samples were irradiated for time periods such that the absorbance at 513 nm decreased no more than 10−15%. Excess KNCS (>10 fold) was added to some samples, and samples run under O_2 atmosphere were purged with O_2 for 5 min. All samples were loaded in the dark. Quantum yields were determined from the slopes of plots of absorbance vs time at 513 nm; each quantum yield is an average of at least three trials.

Results and Discussion

Synthesis of Tetraalkylammonium Salts of $[Mo^V_2O_3(NCS)_8]^{4-}$ ($\mathbf{1}^{4-}$). Although it was not definitively characterized by a diffraction study for a further 55 years, the isothiocyanate Mo(V) dinuclear complex $[Mo^V_2O_3(NCS)_8]^{4-}$ ($\mathbf{1}^{4-}$) was correctly formulated by James and Wardlaw as early as 1928 as a product of the reaction of $[NMe_3H]^+$ and $[NMe_4]^+$ salts of $[Mo^VOCl_5]^{2-}$ with aqueous ammonium thiocyanate.[19] The compound has also been prepared as an hydrated potassium salt from $[Mo^{IV}_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ by elution of the trinuclear complex from a K^+ cation exchange column with aqueous KNCS to give an orange solution which was oxidized in an open beaker in air over several days.[20] We initially attempted to prepare the compound by this route, but this is a tedious and unreliable approach, and we developed an alternative synthesis using the approach to $[Mo^V_2O_3]^{4+}$ complexes established by McDonald and co-workers in which $[Mo^{VI}O_2]^{2+}$ precursors are reduced with phosphines.[21,22]

Dinuclear $[Mo^V_2O_3(NCS)_8]^{4-}$ can be prepared with a variety of counterions by reduction of $[Mo^{VI}O_2(NCS)_4]^{2-}$ with 0.5 equiv of PMe_2Ph in THF. The simple workup involves filtration, washing, and drying of the insoluble product, and the reaction provides reliable and convenient access to $\mathbf{1}^{4-}$ on a multigram scale in 92% crude yield (72% recrystallized) for the $[NMe_4]^+$ salt and 62% yield for the $[NEt_4]^+$ salt. The product was characterized by the presence of a strong absorbance at 513 nm and by comparison of IR spectra with those reported in the literature. Both salts gave satisfactory combustion analyses and are soluble only in highly polar solvents like acetonitrile and (to a limited extent) acetone. A strong, broad ν_{CN} band in IR spectra centered at 2030 cm^{-1}, and a δ_{NCS} mode at 480 cm^{-1} confirmed that the NCS^- ligands are coordinated through nitrogen.[23]

The distinctive purple of tetraalkylammonium salts of $[Mo^V_2O_3(NCS)_8]^{4-}$ in acetone and acetonitrile arises from a strong absorbance at 513 nm assignable to the $[Mo^V_2O_3]^{4+}$ chromophore.[1b,10] A Beer's law plot of this band in a solution of $[NEt_4]_4\mathbf{1}$ in CH_3CN at room temperature was linear ($R^2 = 0.999$) over concentrations from 1×10^{-4} to 1×10^{-3} M, establishing that $\mathbf{1}^{4-}$ does not participate in thermal disproportionation equilibria with mononuclear Mo(VI) and Mo(IV) complexes analogous to those observed with some other $[Mo^V_2O_3]^{4+}$ complexes,[6−8] and the extinction coefficient of the band was determined from the slope of this plot to be 22 500 M^{-1} cm^{-1}. The other major features of the electronic spectrum of $\mathbf{1}^{4-}$ are bands at 308 ($\epsilon = 28\,200$ M^{-1} cm^{-1}) and 235 nm ($\epsilon = 37\,300$ M^{-1} cm^{-1}). There were no significant differences between the spectra of the $[NMe_4]^+$ and $[NEt_4]^+$ salts of $\mathbf{1}^{4-}$.

Photolysis of Tetraalkylammonium Salts of $[Mo^V_2O_3(NCS)_8]^{4-}$ to give $[Mo^VO(NCS)_5]^{2-}$. Purple solutions of tetraalkylammonium salts of $\mathbf{1}^{4-}$ become orange within hours under ambient lighting. This previously unreported photosensitivity probably accounts for several aspects of the behavior of $\mathbf{1}^{4-}$ in earlier accounts (such as the statement that the color of solutions of $\mathbf{1}^{4-}$ changed from purple through orange to yellow upon dilution[19]) and for the 40% discrepancy between

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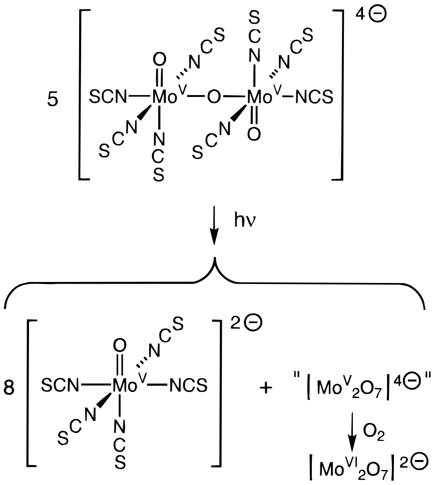
Scheme 2



our value for the extinction coefficient of the 513 nm band and the 16 000 M^{-1} cm^{-1} value reported previously.[1b]

The absorbance at 513 nm in electronic spectra of a sample of $\mathbf{1}^{4-}$ disappeared when the sample was irradiated with a 200 W Hg−Xe arc lamp, and a new absorbance appeared at 455 nm. The spectra exhibit isosbestic points at 483, 394, 367, and 322 nm, suggesting that only one new species with visible absorbances has been formed (see figure in synopsis and in Supporting Information). This might have been one of several oxothiocyanate Mo(V) complexes reported to have absorptions around 455 nm: a spectrophotometric study of molybdenum thiocyanate solutions, for example, suggested that a species with λ_{max} at 460 nm could be formulated as "$[MoO(NCS)_3]$".[24] This formulation could be eliminated on the basis of combustion analysis (see Experimental Section), and the di-μ-oxomolybdenum(V) complex $[Mo^V_2O_4(NCS)_6]^{4-}$, reported to have a band in the correct region, could also be eliminated by comparison with a reference sample of the $[NEt_4]^+$ salt of this anion;[14] IR spectra of the photolysis product and $[NEt_4]_4[Mo^V_2O_4(NCS)_6]$ were virtually identical, but the positions of some UV/visible bands differ slightly and the 8 100 M^{-1} cm^{-1} extinction coefficient of the absorption of $[NEt_4]_4[Mo^V_2O_4(NCS)_6]$ at 445 nm in acetonitrile (from the slope of a Beer's law plot) was too low to account for the strength of the main band of the photolysed product.

The photolysis product is paramagnetic, and this suggested formulation as the six-coordinate mononuclear species $[Mo^VO(NCS)_5]^{2-}$. This has been studied as a member of the series of d^1 complexes $[Mo^VOX_5]^{2-}$ (X = halide or pseudohalide),[1b,15,25] a subclass of the larger series of d^1 tetragonal $[MOX_4]$ and $[MOX_5]$ complexes.[26] A sample of $[NMe_4]_2[Mo^VO(NCS)_5]$ was prepared by the literature procedure[15] and shown to be identical to the photolysis product by IR and electronic spectroscopy. The paramagnetism of the compound was quantified in solution by the Evans NMR method and corresponded to an effective magnetic moment of 1.86 BM per Mo center. This is in reasonable agreement with the spin-only expectation for a six-coordinate d^1 complex in which the orbital contribution has been quenched by a reduction in symmetry. The purity of photochemically prepared samples of $[NMe_4]_2[Mo^VO(NCS)_5]$, and of reference samples, was confirmed analytically.

Reproducible synthetic-scale photolyses of $[Mo^V_2O_3(NCS)_8]^{4-}$ to $[Mo^VO(NCS)_5]^{2-}$ require added O_2. This is consistent with a reaction course such as that in Scheme 2, in which initial photolytic dissociation of thiocyanate ligands leads to ligand redistribution to form $[Mo^VO(NCS)_5]^{2-}$ together with a Mo(V) oxo complex which can be oxidized to $[Mo^V_2O_7]^{2-}$. The reaction is quite clean, and the spectroscopic yield of the anion is quantitative while the recrystallized yield of $[NMe_4]_2[Mo^VO(NCS)_5]$ is 58%.

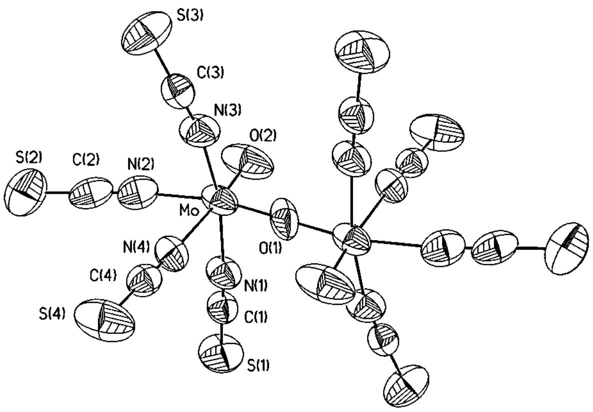


Figure 1. Molecular structure of $[Mo^V_2O_3(NCS)_8]^{4-}$ ($\mathbf{1}^{4-}$; 50% probability ellipsoids) in $[NMe_4]_4[Mo^V_2O_3(NCS)_8]\cdot 2Me_2CO$.

Table 1. Crystallographic Data for $[NMe_4]_4[Mo^V_2O_3(NCS)_8]\cdot 2Me_2CO$

formula	$C_{27}H_{54}Mo_2N_{12}O_4S_8$
fw	1059.18
space group	$P\bar{1}$ (triclinic)
a, Å	9.455 (2)
b, Å	11.831 (2)
c, Å	12.772 (3)
α, deg	110.52 (3)
β, deg	105.17 (3)
γ, deg	98.63 (3)
V, Å^3	1244.4 (4)
Z	1
T, °C	20 (2)
λ, Å	0.710 73
ρ (calcd), g cm^{-3}	1.413
μ, cm^{-1}	8.81
wR_F[a], % (based on 2549 data[b])	6.17
wR_F2[c], % (all data)	16.55

[a] $wR_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $F_o > 4_\sigma(F_o)$. [c] $wR_F2 = [\Sigma w(F_o^2 - F_c^2)/F_o^4]^{1/2}$; $w = [\sigma^2F_o^2 + (0.1F_o)^2]^{-1}$.

Disappearance quantum yields for photolysis of $\mathbf{1}^{4-}$ have been determined in the UV and visible regions, as tabulated in the Supporting Information. The UV quantum yields are modest under N_2 ($\Phi_{310} = 1.4 \times 10^{-3}$) and are insensitive to added KNCS. They are slightly higher under an O_2 atmosphere ($\Phi_{310} = 2.1 \times 10^{-3}$) and in the presence of KNCS under O_2 ($\Phi_{310} = 3.1 \times 10^{-3}$). The quantum yield in the visible region is essentially unaffected by whether the solution is under N_2 or O_2, or by the presence of KNCS, and is even lower than in the UV ($\Phi_{\lambda>460}$ under N_2, $= 1.3 \times 10^{-4}$), establishing that the reaction is not connected with the bridging oxo chromophore.

Solid State Structure of $[NMe_4]_4[Mo^V_2O_3(NCS)_8]\cdot 2Me_2CO$. The previous diffraction study of the $\mathbf{1}^{4-}$ anion involved a hydrate of the K^+ salt, and as might be expected, the K^+ counterions have close approaches to the anionic complex—the literature coordinates[20] were used to determine that one of the independent K^+ ions is associated with the terminal oxo ligand (K(1)−O(2) = 2.69 Å). This suggests significant ion pairing in the solid state, and since this is often an important perturbation on the structures of charged complexes, we took advantage of the availability of $\mathbf{1}^{4-}$ with a noncoordinating counterion to determine whether ion-pairing affects the structure of $K_4\mathbf{1}$.

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(24) Perrin, D. D. *J. Am. Chem. Soc.* **1958**, *80*, 3540.
(25) Mitchell, P. C. H. *Q. Rev.* **1966**, *20*, 103.
(26) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; Section 6.2.i.

Table 2. Selected Bond Lengths (Å) and Angles (deg) within $[Mo^{V}_2O_3(NCS)_8]^{4-}$ (**1**$^{4-}$) in $[NMe_4]_4[Mo^{V}_2O_3(NCS)_8]\cdot 2Me_2CO$

Mo−O(1)	1.842 (1)	Mo−O(2)	1.661 (5)
Mo−N(1)	2.081 (6)	Mo−N(2)	2.103 (8)
Mo−N(3)	2.080 (6)	Mo−N(4)	2.238 (6)
N(1)−C(1)	1.134 (8)	N(2)−C(2)	1.141 (10)
N(3)−C(3)	1.146 (8)	N(4)−C(4)	1.124 (8)
C(1)−S(1)	1.597 (7)	C(2)−S(2)	1.594 (11)
C(3)−S(3)	1.592 (8)	C(4)−S(4)	1.619 (8)

O(1)−Mo−O(2)	100.7 (3)	O(1)−Mo−N(1)	92.0 (2)
O(1)−Mo−N(2)	163.5 (2)	O(1)−Mo−N(3)	91.8 (2)
O(1)−Mo−N(4)	84.1 (2)	O(2)−Mo−N(1)	95.4 (3)
O(2)−Mo−N(2)	95.8 (3)	O(2)−Mo−N(3)	95.5 (3)
O(2)−Mo−N(4)	175.2 (3)	N(1)−Mo−N(2)	87.0 (3)
N(1)−Mo−N(3)	167.6 (2)	N(1)−Mo−N(4)	85.1 (2)
N(2)−Mo−N(3)	86.1 (3)	N(2)−Mo−N(4)	79.4 (2)
N(3)−Mo−N(4)	83.6 (2)		
Mo−N(1)−C(1)	172.4 (7)	Mo−N(2)−C(2)	164.4 (7)
Mo−N(3)−C(3)	167.3 (6)	Mo−N(4)−C(4)	176.7 (6)
N(1)−C(1)−S(1)	178.5 (7)	N(2)−C(2)−S(2)	178.5 (8)
N(3)−C(3)−S(3)	179.3 (6)	N(4)−C(4)−S(4)	177.1 (7)

We were unable to find conditions under which the $[NMe_4]^+$ or $[NEt_4]^+$ salts of **1**$^{4-}$ could be recrystallized to give crystals suitable for crystallographic studies, but appropriate crystals containing **1**$^{4-}$ could be obtained from the hydrolysis of $[NMe_4]_2[Mo^{V}O(NCS)_5]$ in acetone under air at room temperature over a period of weeks. The dark crystals with a green luster obtained under these conditions were used for the single-crystal diffraction study described in the Experimental Section, which established that they contained a bis-solvate of $[NMe_4]_4[Mo^{V}_2O_3(NCS)_8]$ ($[NMe_4]_4$**1**) in which the **1**$^{4-}$ anion has the structure shown in Figure 1. The bridging oxygen atom sits on a crystallographic inversion center and there is an anti orientation of the terminal oxo groups. Bond lengths and angles are listed in Table 2.

There are few statistically significant differences between the molecular parameters for this salt of **1**$^{4-}$ and the K^+ salt characterized by Bino (an overlay of the anion structures is available in the Supporting Information). The only chemically significant differences involve a small increase in bending at N of the isothiocyanate ligands in the K^+ structure (with Mo−N−C angles ranging from 156 to 170° and averaging 164°, as compared with a range of 164−177° and an average of 170° in the $[NMe_4]^+$ structure). This can be ascribed to bending of the ligands toward each other in the K^+ structure as a consequence of interactions with the S atoms of the isothiocyanate ligands (each K^+ has close approaches to six S atoms with ranges of 3.24−3.65 Å for K(1) and 3.36−3.78 Å for K(2)). None of the differences in bond lengths are of chemical significance, and in both structures, the Mo−isothiocyanate bonds trans to the terminal oxo ligand are longer than those trans to the bridging oxo ligand which are in turn longer than those which are mutually trans.

Conclusion

The $[NMe_4]^+$ and $[NEt_4]^+$ salts of the diamagnetic, dinuclear oxo-bridged molybdenum anion $[Mo^{V}_2O_3(NCS)_8]^{4-}$ can be conveniently prepared in good yield by PMe_2Ph reduction of $[Mo^{VI}O_2(NCS)_4]^{2-}$. The dinuclear complex does not participate in thermal disproportionation equilibria with mononuclear Mo(VI) and Mo(IV) but is photosensitive, decomposing in CH_3CN to paramagnetic, mononuclear $[Mo^{V}O(NCS)_5]^{2-}$. The reaction is not connected with the bridging oxo chromophore, and probably involves initial photolysis of isothiocyanate ligands. Comparison of the structure of a $[NMe_4]^+$ salt of the dinuclear complex with that of a K^+ salt establishes that ion pairing with the terminal oxo ligand in the K^+ salt has surprisingly little effect on the anion molecular parameters.

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Supporting Information Available: Figure showing the course of photolysis of a CH_3CN solution of $[NEt_4]_4[Mo^{V}_2O_3(NCS)_8]$ as monitored by electronic spectroscopy. Figure showing an overlay of the structures of the $[Mo^{V}_2O_3(NCS)_8]^{4-}$ anion in the $[NMe_4]^+$ salt and the K^+ salt. Table of the disappearance quantum yields for photolysis of $[Mo^{V}_2O_3(NCS)_8]^{4-}$ in CH_3CN at 20 °C (4 pages). One X-ray crystallographic file in CIF format is available. Access and/or ordering information is given on any current masthead page.

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