

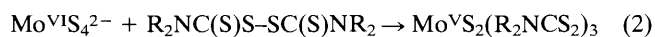
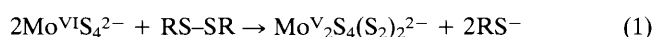
Analogous Reactivity of MoS_4^{2-} and WSe_4^{2-} : Preparation of $\text{WSe}_2(\text{Bu}^i_2\text{NCS}_2)_3$ by an Induced Internal Redox Reaction

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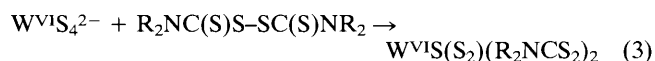
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Addition of tetraalkylthiuram disulfides $\text{R}_2\text{NC(S)S-SC(S)NR}_2$ ($\text{R} = \text{Et}$ and Bu^i) to WSe_4^{2-} yields the new complexes $\text{WSe}_2(\text{R}_2\text{NCS}_2)_3$, revealing that WSe_4^{2-} undergoes induced internal electron transfer similar to that of MoS_4^{2-} , but different from the reactivity of WS_4^{2-} , as predicted by comparison of the lowest energy charge transfer transitions of the reactants.

Induced internal redox processes have been established as a prominent feature of molybdenum/sulfur chemistry.¹ Addition of oxidants such as organic disulfides and thiuram disulfides to MoS_4^{2-} , which contains Mo^{VI} , leads to the formation of dinuclear² and mononuclear³ Mo^{V} species, respectively. The internal electron transfer from sulfide to Mo^{VI} is induced by external oxidants as shown in eqns. (1) and (2).



In contrast, thiuram disulfide does not induce internal electron transfer in tetrathiotungstate and produces instead a product that retains the W^{VI} oxidation state [eqn. (3)].³

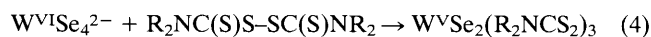


Recent studies have shown that the reactivity of metal selenides may differ significantly from that of metal sulfides.⁴ Therefore, lower valent tungsten selenide mononuclear compounds might be derived by using Se in place of S in the W coordination sphere. In this communication we report that tetraselenotungstate,⁵ WSe_4^{2-} , reacts with the oxidant, thiuram disulfide, by induced internal electron transfer from selenide (Se^{2-}) to tungsten(VI). A new neutral W^{V} chalcogenide complex is obtained.

Reaction of WSe_4^{2-} with tetraalkylthiuram disulfide in the mole ratio 1:2.76 in acetonitrile at room temperature yields a dark-brown solid in high yield (79%), which is purified by recrystallization from methylene chloride and hexane to give $\text{WSe}_2(\text{R}_2\text{NCS}_2)_3$ ($\text{R} = \text{Et}$ and Bu^i). Crystals were grown by slow evaporation of an acetonitrile solution and X-ray crystallography revealed the eight-coordinate metal complex shown in Fig. 1 for $\text{R} = \text{Bu}^i$.† The eight coordination positions are occupied by six sulfur atoms from three dithiocarbamate ligands and two selenium atoms of an Se_2^{2-} ligand. The Se–Se

distance is 2.291(3) Å, which is somewhat shorter than the Se–Se distances of 2.340 Å and 2.348 Å for Se_2^{2-} of $\text{W}_2\text{Se}_9^{2-}$ and $\text{W}_2\text{Se}_{10}^{2-}$, respectively. The W–Se distances in $\text{WSe}_2(\text{Bu}^i_2\text{NCS}_2)_3$ (2.552 and 2.596 Å) are longer than those in $\text{W}_2\text{Se}_9^{2-}$ (2.519 and 2.550 Å) and $\text{W}_2\text{Se}_{10}^{2-}$ (2.510 and 2.56 Å).⁶ An IR band at 320 cm^{-1} is assigned to the Se–Se stretch.‡ The UV–VIS spectrum of $\text{WSe}_2(\text{Bu}^i_2\text{NCS}_2)_3$ shows a peak at $25.8 \times 10^3 \text{ cm}^{-1}$ (388 nm, $\log \epsilon = 3.99$) and a shoulder at $20.83 \times 10^3 \text{ cm}^{-1}$ (480 nm) in acetonitrile. The electronic spectrum is similar to that of the Mo compound $\text{MoS}_2(\text{Bu}^i_2\text{NCS}_2)_3$, which shows a peak at $24.8 \times 10^3 \text{ cm}^{-1}$ (404 nm, $\log \epsilon = 3.86$). The ESR spectrum for $\text{WSe}_2(\text{Bu}^i_2\text{NCS}_2)_3$ shows $g = 1.898$ and $A_0(^{183}\text{W}) = 73$ Gauss.

The air-sensitive, pentavalent tungsten compound is structurally analogous to $\text{Mo}^{\text{V}}\text{S}_2(\text{R}_2\text{NCS}_2)_3$ and is formed by an entirely similar reaction [eqn. (4)]. W^{VI} is reduced to W^{V} and thiuram disulfide is reduced to the dithiocarbamate ligand, with bound Se^{2-} functioning as the reductant and being oxidized to Se_2^{2-} .



Instead of the ligand–ligand electron transfer process that occurs with WS_4^{2-} and thiuram disulfide, ligand to metal electron transfer occurs in the corresponding WSe_4^{2-} system, in complete analogy to the MoS_4^{2-} system. These results point to electronic properties of the group VIB metal chalcogenides as key determinants of redox properties in these synthetic reactions. Changing to the higher chalcogenide (Se) facilitates the reduction of the tungsten centre.

Specifically, we suggest that one may be guided by the energy of the ligand to metal charge transfer transition of the reactant in assessing the relative facility with which complexes

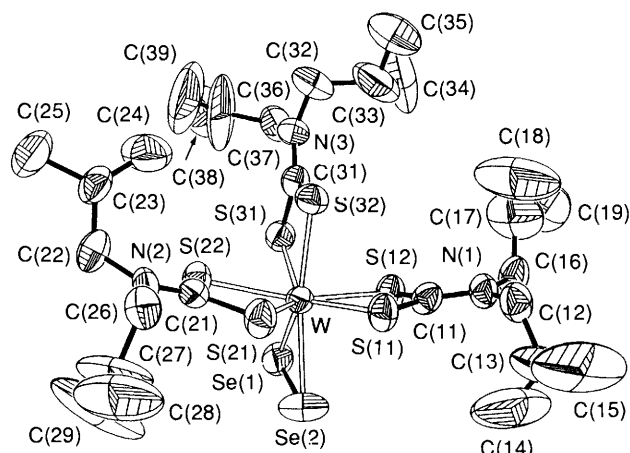


Fig. 1 Structure of $\text{WSe}_2(\text{Bu}^i_2\text{NCS}_2)_3$. Key distances are W–Se(1) 2.596(2), W–Se(2) 2.552(2), Se(1)–Se(2) 2.291(3), W–S(11) 2.549(4), W–S(12) 2.505(4), W–S(21) 2.530(4), W–S(22) 2.512(4), W–S(31) 2.495(3), W–S(32) 2.517(5) Å.

† Crystal data: $M_w = 954.86$, $T = 20 \pm 1^\circ\text{C}$, monoclinic, space group $\text{C}2\text{-C}2^3$ (No. 5) with $a = 25.437(6)$, $b = 16.512(4)$, $c = 10.906(3)$ Å, $\beta = 116.95(2)^\circ$, $V = 4083(2)$ Å³ and $Z = 4$, $d_c = 1.553 \text{ g cm}^{-3}$. A total of 4911 independent absorption-corrected reflections were collected; 3146 independent absorption-corrected reflections having $I > 3\sigma(I)$ were used in counter-weighted full matrix least-square technique and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms. The resulting structural parameters have been refined to convergence $R = 0.039$, $R_w = 0.046$, goodness of fit = 1.007.

The crystal structure was solved by Dr C. S. Day of Crystallitics, Lincoln, Nebraska. Data were obtained on a four-circle Nicolet (Siemens) Autodiffractometer using $\text{Mo-K}\alpha$ radiation. The intensity data were corrected empirically for absorption effects and were reduced by means of standard Lorentz and polarization corrections. The structure was solved using "heavy atom" techniques with the Siemens SHELXTL-PLUS software package as modified at Crystallitics Company. $R_w = \{\sum W(|F_o| - |F_c|)^2 / \sum W|F_o|^2\}^{1/2}$; G.O.F. (goodness of fit) = $\{\sum W(|F_o| - |F_c|)^2 / (N_o - N_v)\}^{1/2}$ where N_o is the number of observations and N_v is the number of variables. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ The IR band for Se–Se in Se_2^{2-} of $\text{W}_2\text{Se}_9^{2-}$ and $\text{W}_2\text{Se}_{10}^{2-}$ in ref. 6 is about 330 cm^{-1} (KBr pellet). Our spectrum is obtained in Nujol mull using a CsI window.

undergo chemical internal electron transfer reactions. The lowest energy charge transfer band⁸ occurs at $21.4 \times 10^3 \text{ cm}^{-1}$ (467 nm, $\log \epsilon = 4.11$) in MoS_4^{2-} , $25.5 \times 10^3 \text{ cm}^{-1}$ (392 nm, $\log \epsilon = 4.27$) in WS_4^{2-} , and $21.6 \times 10^3 \text{ cm}^{-1}$ (463 nm, $\log \epsilon = 4.20$) in WSe_4^{2-} . Clearly, the observed similarity between WSe_4^{2-} and MoS_4^{2-} of the first ligand to metal charge transfer transition energy parallels the observed similarity in reactivity. Extension of this correlation to VS_4^{3-} , $18.6 \times 10^3 \text{ cm}^{-1}$ ($\log \epsilon = 3.76$) and ReS_4^- , $19.8 \times 10^3 \text{ cm}^{-1}$ ($\log \epsilon = 3.98$) predicts facile internal electron transfer for these ions as well, as has been recently observed.^{9,10} Finally, the similarity of W-Se and Mo-S systems may be related to the presence of W and Se in the formate dehydrogenase from *Clostridium thermoaceticum*.¹¹ Most metallo formate dehydrogenases contain Mo and S.¹²

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