of electrolyte necessary for precipitation to occur, as exemplified in Figure 2 for arabic gum as protective colloid and $PbCl_2$ as coagulating agent.

All these results suggest that the soluble Mn(IV) species is present in the medium in the form of colloidal particles of manganese dioxide with a negative electrostatic charge, which accounts for their stability in solution, due to the adsorption of anions (such as sulfate ions, for instance) on their surface. When an electrolyte is added, adsorption of the cation on the colloidal particles results in neutralization of their electrostatic charge; i.e., precipitation occurs. Divalent ions are more attracted by the negatively charged particles than monovalent ones, while for the same ionic charge adsorption will be easier for the less solvated bigger cations. Furthermore, when the colloidal particles are protected by arabic gum, the adsorption of cations on their surface is considerably more difficult.

Finally, the colloidal particles of this soluble form of manganese(IV) have been characterized by the use of a conventional nephelometric technique whose results are shown in Figure 3. From this study it follows that the colloidal particles are roughly spherical with a radius around 500 Å and a mass of 2×10^8 g mol^{-1}.

To the best of our knowledge this is the first time that the existence of a soluble form of colloidal manganese(IV) has been unquestionably proved. This might bear important consequences in relation to mechanistic and kinetic studies involving this species as a reactant[10] or as an autocatalytic product.[11]

Registry No. Mn, 7439-96-5; $KMnO_4$, 7722-64-7; $Na_2S_2O_3$, 7772-98-7.

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Solid-State Chalcogenide Anions of Ta and Nb: Synthesis and Structures of the $Ta_2S_{11}^{4-}$ and $Nb_4Se_{22}^{6-}$ Anions

An extensive set of soluble polynuclear metal sulfides of Mo[1-6] and W[7-11] has been obtained, most derived from the simple MS_4^{2-}[12] unit (M = Mo, W). The corresponding mononuclear selenides MSe_4^{2-}[13,14] are known, and there is a growing list of other mononuclear[15] and polynuclear[16] selenides. In contrast, the only known soluble discrete sulfur anions of Nb and Ta are $M'_6S_{17}^{4-}$ (M' = Nb, Ta)[17] and there are no examples of soluble selenium species. Although the VS_4^{3-} anion[18] exists in solution, it has not yet been shown to be a precursor to polynuclear species that contain only V and S. But for M' = Nb and Ta, discrete $M'Q_4^{3-}$ anions (Q = S, Se) have not been obtained in solution. Solid-state chemistry provides a valuable but often forgotten route to coordination compounds, especially where the transition metal is in a high oxidation state. One example is the production of Na_2CrO_4 by fusion of chromite ($FeCr_2O_4$) with Na_2CO_3 in air. Indeed, the existence of the NbQ_4^{3-} and TaQ_4^{3-} anions has been established in the solid state ($Cu_3M'S_4$,[19] $Tl_3M'S_4$,[20] $Ba_6[NbS_4][NbS_3O]_3$,[21] and $Cs_3M'Se_4$[22]). By solid-state means we have prepared in

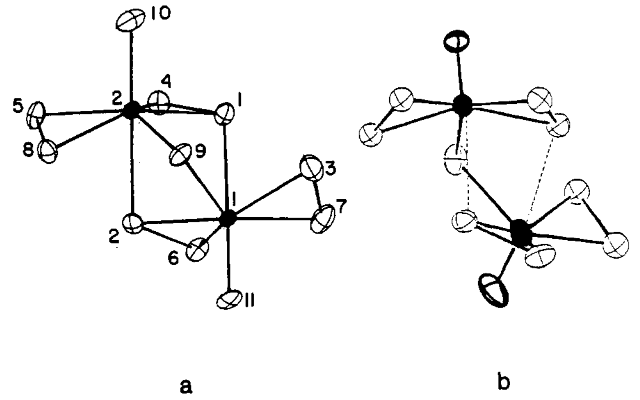

Figure 1. Structure of the $Ta_2S_{11}^{4-}$ ion (a) in comparison to that of the $Mo_2S_9O_2^{2-}$ ion (b).[25] In this figure and in Figure 2 85% probability ellipsoids are shown in part a, while 40% ellipsoids are shown in part b. The metal is represented as a black ellipsoid, and oxygen is represented as a darkened ellipsoid, while all remaining ellipsoids are sulfur or selenium.

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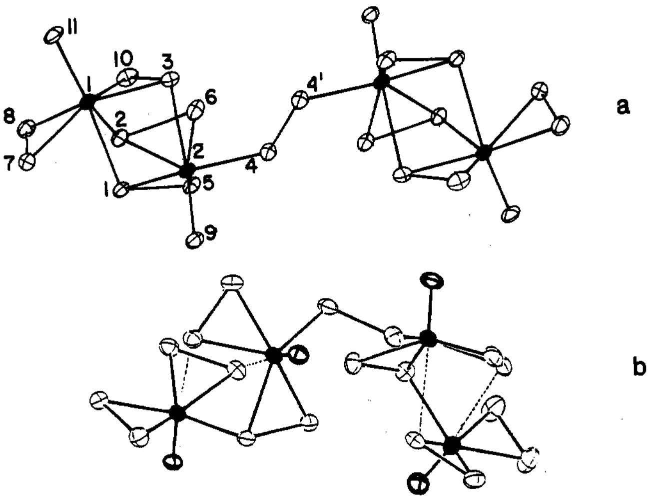

Figure 2. Structure of the $Nb_4Se_{22}^{6-}$ ion (a) in comparison to that of the $Mo_4S_{18}O_4^{2-}$ ion (b).[25]

reasonable yield two new chalcogenides of Ta and Nb: $K_4Ta_2S_{11}$ and $K_3Nb_2Se_{11}$. These contain the discrete anions $Ta_2S_{11}^{4-}$ and $Nb_4Se_{22}^{6-}$, which bear striking resemblances to closely related W and Mo species prepared by solution methods.

Transparent orange crystals and polycrystalline material of formula $K_4Ta_2S_{11}$ were prepared from the reaction among K_2S, Ta, and S (in 3:2:5 mole ratio) in a sealed evacuated quartz vessel that was kept at 800 °C for 48 h and then cooled at 100 °C/h. Electron microprobe analysis of the air- and moisture-sensitive crystals established their homogeneity and the presence of K, Ta, and S. The Guinier powder pattern suggested a novel structure type; i.e., lines for intercalated TaS_2 were not detected, nor was the K_3TaS_4-type structure. The presence of a TaS_4^{3-} unit was also ruled out by spectroscopic data since a characteristic IR band at 424 cm^{-1} was lacking. However, the spectroscopic data did suggest the presence of S_2^{2-} ligands, terminal Ta=S moieties, and Ta-bridging S^{2-} anions.[23] The structural details of the $Ta_2S_{11}^{2-}$ anion were determined by a single-crystal X-ray diffraction study on a thin translucent orange platelet of $K_4Ta_2S_{11}$.[24]

The crystal structure of $K_4Ta_2S_{11}$ consists of well-separated K^+ and $Ta_2S_{11}^{4-}$ ions (Figure 1a). The Ta···Ta distance of 3.442 (1) Å in the $Ta_2S_{11}^{4-}$ anion indicates no bonding between the Ta atoms. The Ta atoms are linked by one S^{2-} anion with an average Ta–S distance of 2.479 (5) Å and two S_2^{2-} ligands with average Ta–S and S–S distances of 2.579 (5) and 2.076 (7) Å, respectively. Each Ta atom is also bound to an additional S_2^{2-} ligand with average Ta–S and S–S distances of 2.465 (5) and 2.076 (9) Å, respectively. The coordination sphere of each Ta atom is completed by a short Ta=S interaction (average Ta–S distance = 2.235 (5) Å) to form a $Ta_2(\mu\text{-}S)(\mu\text{-}\eta^2,\eta^1\text{-}S_2)_2(\eta^2\text{-}S_2)_2(S)_2^{4-}$ anion with Ta in the 5+ oxidation state. This anion is closely related to the recently reported $[NEt_4]_2[Mo_2S_9O_2]$[25] complex prepared in solution; it contains the $Mo_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4(O)_2^{2-}$ discrete anion (Mo, 6+) (Figure 1b). In contrast to the Ta species, each Mo atom shows only a weak intramolecular (rather than a bonding) interaction to a neighboring S_2^{2-} ligand. The $[PPh_4]_2[W_2S_{11}]$[8] complex, prepared by solution chemistry, provides another example of a similar anion, $W_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4(S)_2^{2-}$.

$K_3Nb_2Se_{11}$ was prepared through the reaction of Nb metal with K_2Se and Se (in a 1:3:10 mole ratio) at 375 °C for 100 h with a 3 °C/h cooling rate to room temperature. Black chunky crystals were obtained upon dissolution of the excess melt with water. The structure was determined by single-crystal X-ray diffraction methods[26] after the homogeneity of the crystals and the presence of K, Nb, and Se were confirmed by electron microprobe analysis. The final formula, $K_3Nb_2Se_{11}$, was verified by quantitative analyses.

The crystal structure of $K_3Nb_2Se_{11}$ consists of well-separated K^+ and $Nb_4Se_{22}^{6-}$ ions. Within the $Nb_4Se_{22}^{6-}$ anion (Figure 2a) each nonbonding Nb pair (Nb···Nb distance = 3.679 (3) Å) is bridged by three Se_2^{2-} ligands with an average Nb–Se contact of 2.683 (3) Å and Se–Se interaction of 2.358 (3) Å. Each Nb atom is bound to a terminal Se anion to form a Nb–Se bond showing an average bond length of 2.361 (3) Å. The coordination sphere of the Nb atoms is completed by the addition of two Se_2^{2-} ligands (average Se–Se distance = 2.371 (4) Å) per Nb pair. One Se_2^{2-} ligand is bound to a Nb atom in a typical η^2-fashion while the second Se_2^{2-} links the other Nb atom to a neighboring dimer yielding a tetrameric anion best described as $[Nb_2(\mu\text{-}\eta^2,\eta^1\text{-}Se_2)_3(\eta^2\text{-}Se_2)(Se)_2]_2(\mu\text{-}\eta^1\text{-}Se_2)^{6-}$ with Nb in the 5+ oxidation state. This species is related to a soluble molybdenum oxysulfide, $[Et_4N]_2[Mo_4S_{18}O_4]$[25] (Mo, 6+) (Figure 2b). Again the major structural difference is related to the bridging $\eta^2,\eta^1\text{-}Q_2^{2-}$ ligands. In the Mo complex, the metal pairs are bridged by only one S_2^{2-} unit while the other two S_2^{2-} ligands show only weak intramolecular interaction yielding a $[Mo_2(\mu\text{-}\eta^2,\eta^1\text{-}S_2)(\eta^2\text{-}S_2)_3(O)_2]_2(\mu\text{-}\eta^1\text{-}S_2)^{2-}$ ion.

As evidenced by the structures of $K_4Ta_2S_{11}$ and $K_3Nb_2Se_{11}$, traditional solid-state synthesis provides a potentially useful route to new anionic chalcogenide species and possibly the only means to Nb and Ta analogues of Mo and W chalcogenide anions. The stability of these Nb and Ta anions in the solid-state can be exploited in an attempt to obtain isolated ions in solution for subsequent chemistry. The generation of quasi-isolated polyatomic Zintl,[27] polyarsenide,[28] and metal arsenide[29] anions has been achieved via the solubilization of their alkali-metal compounds. Presently, the solubilization of $K_4Ta_2S_{11}$ and $K_3Nb_2Se_{11}$ is being explored.

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Supplementary Material Available: A listing of positional parameters (1 page). Ordering information is given on any current masthead page.

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(23) IR (Nujol, CsI): Ta—S_2; ν(Ta—S), 331 (m), 319 (m), 301 (m) cm^{-1}; ν(S—S), 520 (m) cm^{-1}; ν(Ta=S), 505 (s) cm^{-1}; ν(Ta—S—Ta), 452 (s) cm^{-1}.

(24) Crystal data for $K_4Ta_2S_{11}$: orthorhombic, $C_{2v}^5\text{-}Pbc2_1$, $Z = 4$, $a = 7.409$ (3) Å, $b = 13.074$ (1) Å, $c = 17.881$ (3) Å, $V = 1732$ $Å^3$ at −166 °C; 1850 independent reflections measured out to $2\theta(\text{Cu K}\alpha_1) = 75°$; $R(F) = 0.049$ on 1790 reflections having $F_o^2 > 3\sigma(F_o^2)$.

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(26) Crystal data for $K_3Nb_2Se_{11}$: monoclinic, $C_{2h}^5\text{-}P2_1/a$, $Z = 4$, $a = 25.70$ (1) Å, $b = 8.943$ (5) Å, $c = 7.877$ (5) Å, $\beta = 97.92$ (2)°, $V = 1793$ Å at −160 °C; 6263 independent reflections measured out to $2\theta(\text{Mo K}\alpha_1) = 65°$; $R(F) = 0.090$ on 3421 reflections having $F_o^2 > 3\sigma(F_o^2)$.

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Bromide-Assisted Hydrogen Peroxide Disproportionation Catalyzed by Vanadium Bromoperoxidase: Absence of Direct Catalase Activity and Implications for the Catalytic Mechanism

Vanadium has been known for decades to be an essential element;[1] however, the first vanadium-containing enzymes, a bro-

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