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An Unprecedented Tetranuclear Niobium Aqua Ion with a Capping μ_4-Sulfido Ligand

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The aqueous solution chemistry of niobium is rather unexplored, and well characterized aqua complexes are scarce. In this work, a new niobium aqua ion is obtained upon treatment of Zn-reduced ethanolic solutions of $NbCl_5$ with HCl in the presence of a sulfide source. The red aqua ion, obtained upon cation-exchange chromatography, forms readily the thiocyanate complex which has been crystallized as $Cs_{4.26}Na_{1.74}[Nb_4SO_5(NCS)_{10}]\cdot 0.33H_2O$. X-ray crystallography revealed an unprecedented metal–metal bonded tetranuclear $Nb_4(\mu_4\text{-}S)(\mu_2\text{-}O)_5^{4+}$ core with a capping μ_4-S ligand.

Although the aqueous solution chemistry of group 6 molybdenum is very well investigated, that of group 5 niobium remains largely unexplored. The first aqua ion of niobium, purportedly the triangular $Nb(III)(IV)_2$ cluster, $[Nb_3O_4(H_2O)_9]^{3+}$, was reported in 1986.[1] Upon reaction of the green aqua ion with thiocyanate, crystals of $(NH_4)_3(Me_4N)_3[Nb_3SO_3(NCS)_9]\cdot MeOH$ were obtained, and the structure determined by X-ray crystallography revealed the presence of a μ_3-S. The μ_3-S is believed to originate from the thiocyanate. However, EXAFS studies suggested the formula $[Nb_3(\mu_3\text{-}Cl)O_3(H_2O)_9]^{4+}$ rather than $[Nb_3O_4(H_2O)_9]^{3+}$ for the aqua ion.[2] Although there is still a lack of direct structural proof for this niobium aqua ion, it has provided indications that niobium can form species similar to molybdenum in acidic aqueous solutions, where the triangular $[Mo_3O_{4-x}Q_x(H_2O)_9]^{4+}$ ($Q = S$, Se) aqua ions are very well characterized.[3] These aqua ions are characteristic of molybdenum in the $+4$ oxidation state, and they contain metal−metal bonds. Studies on their ligand substitution and redox properties have provided important information on the reactivity of metal−metal bonded cluster compounds. The only other aqua ion of niobium that has so far been reported is the $[Nb_2(\mu_2\text{-}S_2)_2(H_2O)_8]^{4+}$ ion, which has been crystallized as $[Nb_2(\mu_2\text{-}S_2)_2(H_2O)_8](pts)_4\cdot 4H_2O$ and characterized by X-ray crystallography.[4] This dimeric Nb(IV) ion has two $\eta^2{:}\eta^2$ disulfido ligands between the adjacent Nb atoms and was synthesized from the polymeric NbS_2Cl_2 lead-in compound.

In our recent studies to develop the relatively unexplored aqueous chemistry of niobium, we have devised convenient and versatile synthetic routes which resulted in new aqua complexes of niobium. We report here a discovery that bears significance on the aqueous solution chemistry of niobium, namely the synthesis, characterization, and properties of a new Nb(IV) aqua ion, $[Nb_4(\mu_4\text{-}S)(\mu_2\text{-}O)_5(H_2O)_{10}]^{4+}$.

All manipulations were carried out under an argon atmosphere in a fumecupboard. Niobium pentachloride (2 g) was dissolved in 30 mL of absolute ethanol and reduction carried out using zinc powder (1 g). The solution turned from yellow to green and finally brown in a few hours. After filtration to remove excess zinc, the reduced mixture was added to 4 M HCl (120 mL) in the presence of sodium sulfide nonahydrate (14 g). When the vigorous effervescence ceased, the resulting dark brown solution was filtered and then purged with a vigorous stream of argon. After 3-fold dilution with water, the solution was adsorbed on a Dowex 50W-X2 cation-exchanger. An uncharged brown species was removed by washing with 0.8 M HCl. Upon washing with 1 and 1.5 M HCl, a red and a green species separate from each other. The red species eluted first in 2 M HCl, followed by the green. Sometimes a small amount of yellow species, identified by UV−vis spectroscopy to be the dimeric $[Nb_2(\mu_2\text{-}S_2)_2(H_2O)_8]^{4+}$, preceded closely these two species. Upon washing with 3 M HCl, a highly charged yellow species eluted. A dark brown band remained on the column and eluted very slowly with 4−5 M HCl. The red species eluted in 2 M HCl was purified on two further Dowex 50W-X2 columns. The yield was ca. 12% based on niobium. Solutions in Hpts (p-tolouenesulfonic acid) can be obtained by exchanging HCl with Hpts on a cation-exchanger.

The charge of the ion was estimated to be at least $4+$ based on the elution behavior on the cation-exchanger,

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10.1021/ic048659j CCC: $30.25

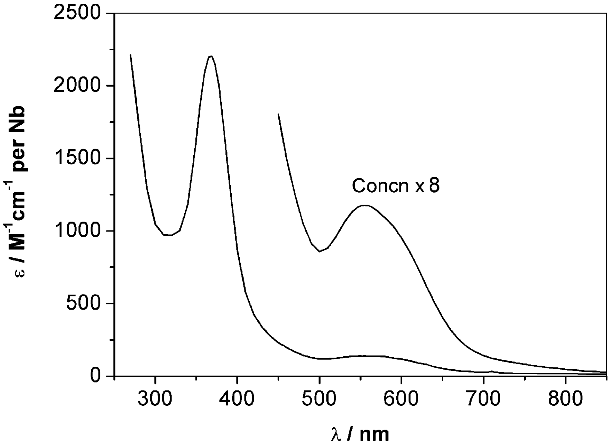

Figure 1. Electronic spectra of $[Nb_4(\mu_4\text{-}S)(\mu_2\text{-}O)_5(H_2O)_{10}]^{4+}$ in 2 M HCl.

whereby it was eluted just after the $[Mo_3S_4(H_2O)_9]^{4+}$ and the $[Nb_2(\mu_2\text{-}S_2)_2(H_2O)_8]^{4+}$ ions, the structures and charges of which have been confirmed by X-crystallography of the paratoluenesulfonate salts, $[Mo_3S_4(H_2O)_9](pts)_4{\cdot}9H_2O$[5] and $[Nb_2(\mu_2\text{-}S_2)_2(H_2O)_8](pts)_4{\cdot}4H_2O$,[4] respectively.

The electronic spectrum of the red aqua ion in 2 M HCl, shown in Figure 1, has λ_{max} /nm (ϵ/M^{-1} cm^{-1} per Nb) at 369 (2200), 555 (145), and a possible shoulder at ca. 600[6] (see Figure 1). The aqua ion is unstable with respect to air oxidation, and the smell of H_2S is often detected upon storage. Solutions of the aqua ion (ca. 1−2 mM) showed ca. 80% decay in absorbance at 369 nm after less than 1 h exposure to air.

X-ray structure analysis[7] of the thiocyanate derivative, $Cs_{4.26}Na_{1.74}[Nb_4SO_5(NCS)_{10}]{\cdot}0.33H_2O$, prepared from the reaction of the red aqua ion with sodium thiocyanate,[8] revealed an unprecedented tetranuclear core structure, $Nb_4(\mu_4\text{-}S)(\mu_2\text{-}O)_5^{4+}$, in the $[Nb_4(\mu_4\text{-}S)(\mu_2\text{-}O)_5(NCS)_{10}]^{6-}$ anion (Figure 2).

In the structure, the atoms Nb1, Nb3, O2, S7, N1, C1, S1, N5, and S5 are positioned on a mirror-plane. A schematic representation of the Nb_5SO_5 core is shown in Figure 3. Four oxygen atoms O1, O1A, O3A, and O3 are in the same plane, and the fifth oxygen atom O2 sits above this plane. Two of the Nb atoms, Nb2 and Nb2A, are slightly below the plane O1−O1A−O3A−O3, while Nb1 and Nb3 are displaced toward the μ_4-S atom. This gives rise to a totally new cluster form, which can be likened to an open basket. Upon closer inspection, the triangular Nb_3SO_3 unit (of the type seen in the $[Nb_3SO_3(NCS)_9]^{6-}$ anion[1]) can be recognized. Two triangular Nb_3SO_3 units are fused together at the Nb2−S7−Nb2A−O2 face (perpendicular to mirror plane) to give the tetranuclear core.

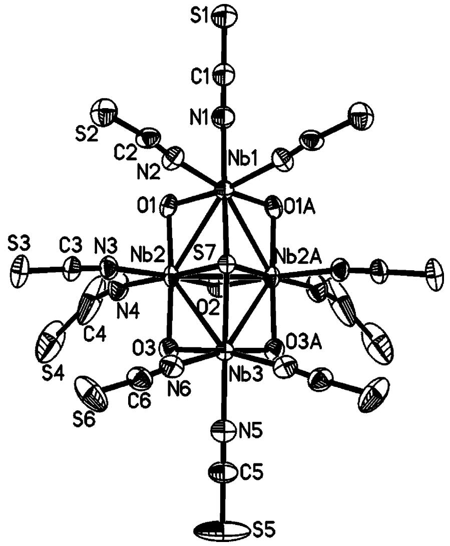

Figure 2. Perspective view of $[Nb_4(\mu_4\text{-}S)(\mu_2\text{-}O)_5(NCS)_{10}]^{6-}$ anion. The thermal ellipsoids are drawn at 50% probability level.

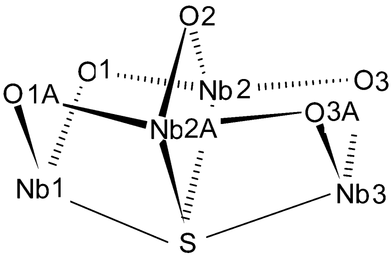

Figure 3. Schematic representation of the $Nb_4(\mu_4\text{-}S)(\mu_2\text{-}O)_5^{4+}$ core. All Nb−Nb bonds are neglected for clarity.

The determined charge of the complex indicates a d^4 electronic configuration for the Nb(IV)$_4$ core, hence giving an average Nb−Nb bond order of 2/5. The Nb2 and Nb2A atoms bind to four bridging ligands and Nb1 and Nb3 to three in the $Nb_4SO_5^{4+}$ core with the corresponding differences in thiocyanate nonbridging ligands. The Nb2−Nb2A bond distance of 2.8024(14) Å is significantly shorter than the other Nb−Nb distances of 2.8564(12) and 2.8763(12) Å. All Nb−Nb distances are however longer than those of the d^4 Nb_3 core in $[Nb_3SO_3(NCS)_9]^{6-}$, where the Nb−Nb (2.763 Å) bond order is 2/3. The Nb−S 2.395(3)−2.507(2) Å, Nb−O 1.959(6)−2.055(6) Å, and Nb−N 2.143(8)−2.196(8) Å ranges are not significantly different from those of the $[Nb_3SO_3(NCS)_9]^{6-}$ anion. Some important angles are Nb−O−Nb 86.0(3)−92.4(3)°, Nb−S−Nb 71.25(7)−71.85(8)°, Nb2−S−Nb2 67.97(8)°, and Nb1−S7−Nb3 135.13(12)°.

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(6) Beer's law is obeyed in the concentration range 0.4−8 mM (per Nb).

(7) $Cs_{4.26}Na_{1.74}[Nb_4SO_5(NCS)_{10}]{\cdot}0.33H_2O$, MW = 1676.70, T = 120(2) K, hexagonal space group $P6_3/m$, a = 20.8033(6) Å, b = 20.8033(6) Å, c = 18.1398(8) Å, γ = 120°, V = 6798.7(4) Å^3, Z = 6, R_1 = 0.0696 [$I > 2\sigma(I)$], GOF = 1.071. The cations and the water molecules are arranged in a highly disordered manner in the structure, thereby giving rise to different models. In the model chosen here, the number of cations per anion is six. The modifications of the positions and the population factors of the cations do not change the structure of the anion.

(8) Crystals of $Cs_{4.26}Na_{1.74}[Nb_4S_5(NCS)_{10}]{\cdot}0.33H_2O$ were prepared under an argon atmosphere by addition of excess NaNCS (0.1 g) to the aqua ion (2 mL, 5 mM per Nb in 2 M HCl). The color of the solution turned immediately from red to brown-green. After reaction for an hour at room temperature, the brown-green solution was layered on a 3 M CsCl solution. Dark brown needle-shaped crystals were deposited upon standing at 4 °C. Due to the great solubility of the crystals (in, e.g., methanol, ethanol, acetone, etc.), problems were encountered in washing them free of excess CsCl and NaNCS. This, coupled with their air sensitivity, rendered elemental analysis unsatisfactory. X-ray powder diffraction on a sample which was not washed after removal of the mother liquor showed the presence of the complex (ca. 40%) and CsCl up to as high as 58%. However, elemental analysis of the pyridinium salt (obtained by using a solution of pyridine in 2 M HCl instead of 3 M CsCl) agrees well with the proposed formula, $(C_5H_6N)_6[Nb_4(\mu_4\text{-}S)(\mu_2\text{-}O)_5(NCS)_{10}]$. $Nb_4O_5S_{11}C_{40}H_{36}N_{16}$ Calcd: C 31.1%, H 2.3%, N 14.5%, S 22.8%. Found: C 31.9%, H 2.6%, N 14.1%, S 23.5%.

The more acute Nb2−O2−Nb2A angle of 86.0(3)° and the Nb2−O2 of 2.055(6) Å along with the significantly shorter Nb2−Nb2A bond distance of 2.8024(14) Å could suggest that O2 is an OH. The X-ray data could not unambiguously rule out this possibility. For balancing the charges on the complex, a hydroxide instead of an oxide would require that the Nb centers be $Nb(IV)_3Nb(III)$, hence giving a paramagnetic d^5 species. However, magnetic susceptibility measurements on the complex gave a diamagnetic compound, and no EPR signals were observed for a ca. 20 mM solution of the red aqua ion in 2 M HCl, in the temperature range 100 K to room temperature. Thus, the formulation of O2 as an oxide is the preferred.

Although there is precedence for bicapped $(\mu_4\text{-S})M_4$ groups, which among others are the square, sulfur-bicapped tetraniobium clusters of Christou et al.[9] and Cotton et al.,[10] the occurrence of a monocapping $(\mu_4\text{-S})$ group, especially in aqua complexes is unique to the best of our knowledge. Numerous cluster aqua ions of molybdenum have been reported, but none of these bear a capping $(\mu_4\text{-S})$ group. However, axially flattened tetrahedral $(\mu_4\text{-S})$ bridging groups have been reported in a range of double-cubes, $[(H_2O)_9Mo_3S_4MMS_4Mo_3(H_2O)_9]^{8+}$ M = Co, Cu, Pd), and in the face-sharing double cuboidal complex, $[Yb_6S_6(SPh)_6(py)_8]$.[11]

The solution properties along with the X-ray structure analysis supports the existence of a $Nb_4(\mu_4\text{-S})(\mu_2\text{-O})_5^{4+}$ core, most likely $[Nb_4(\mu_4\text{-S})(\mu_2\text{-O})_5(H_2O)_{10}]^{4+}$ aqua ion in solution, where all niobium atoms are in the +4 oxidation state. Although ICP-AES analyses[12] on the red aqua did not yield very reliable S/Nb ratio (values from 0.6−1.2S/4Nb), one can conclude that sulfur is present, and the values are most consistent with the presence of a single sulfur in the tetrameric Nb_4 core as revealed in the thiocyanate derivative.

A preliminary kinetic study on the equilibration of thiocyanate with $[Nb_4(\mu_4\text{-S})(\mu_2\text{-O})_5(H_2O)_{10}]^{4+}$ in 2 M Hpts has been carried out. Only a single thiocyanate-dependent reaction was observed. Rate constants with thiocyanate in excess correspond to those obtained with $[Nb_4(\mu_4\text{-S})(\mu_2\text{-O})_5(H_2O)_{10}]^{4+}$ in excess only if a statistical factor of 4 is applied. The statistical factor of 4, previously reported for $[Mo_4S_4(H_2O)_{12}]^{4+}$, has been attributed to the four equivalent metal sites in the cluster.[13] However, in $[Nb_4(\mu_4\text{-S})(\mu_2\text{-O})_5(H_2O)_{10}]^{4+}$, there are two structurally different types of Nb. The results therefore suggest that the waters on the two different types of Nb do not have substantially different substitution rates, and as such an averaged rate constant of 10 $M^{-1}\ s^{-1}$ is observed. Further studies on ligand substitution properties of $[Nb_4(\mu_4\text{-S})(\mu_2\text{-O})_5(H_2O)_{10}]^{4+}$ are underway.

In conclusion, we describe here the successful synthesis and characterization of an unprecedented tetranuclear niobium-sulfido aqua ion in solution. This should make possible further development of the aqueous chemistry of niobium.

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Supporting Information Available: X-ray crystallographic details (PDF) and data (CIF) and X-ray powder diffraction pattern (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Analysis of sulfur is often more difficult and gives erratic results, whereas analysis of niobium is very reproducible. In the case of the red aqua ion, the sulfur analyses more often than not gave lower than the expected values. This is probably due to decomposition of the aqua ion, whereupon some sulfur is converted to hydrogen sulfide.

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