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Electrocatalytic Reduction of Sulfuric Acid to Hydrogen Sulfide by a Trinuclear Niobium Cluster

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It is thought that metal cluster compounds hold great potential as catalysts for the multiple-electron reduction of small molecules, since they contain several metal atoms in close proximity, available for multiside bonding.[1,2] However, very few examples of catalysis by metal clusters have been documented so far.[3,4] In the course of the electrochemical investigation of Nb(5+) in H_2SO_4 and the mechanism for the formation of the trinuclear cluster anion $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$, we found that the niobium cluster electrocatalyzes the reduction of 12 M H_2SO_4 to H_2S on a Hg electrode at room temperature at –1.2 V vs Hg/Hg_2SO_4 (–0.6 V vs NHE). The reduction of sulfate to sulfide is an important step in the sulfur biological cycle.[5,6] In plants and some bacteria, the reduction is achieved through several intermediate steps, each requiring a different enzyme. Concentrated H_2SO_4 can be reduced by a variety of metals at elevated temperatures (>230 °C) to H_2 and SO_2.[7] With Zn and Cd, some H_2S was also formed. It was also previously reported that solid KI crystals in the presence of I_2 can reduce 9 M H_2SO_4 at 36 °C to SO_2, H_2S, and elemental S depending upon the I^-/I_2 concentrations.[8,9] This latter reaction, however, required solid KI and was not established to be catalytic.

The cluster anion $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ has been assigned[10,11] to the M_3X_{17} structural type (see Figure 1). It is composed of a discrete triangular Nb_3 unit with oxygen atoms above and below the triangular plane. The SO_4^{2-} ligands bridge each side of the triangle and three H_2O ligands occupy the equatorial positions. The formal oxidation state of Nb is 3.67+; thus 4 electrons occupy the metal-bonding molecular orbitals, giving a Nb–Nb bond order of $^2/_3$.

A cyclic voltammogram of $K_4H_5O_2[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot 5H_2O$ in 9 M H_2SO_4 at 0 °C using a hanging mercury drop electrode (HMDE) is shown in Figure 2A.[12] It displays a reversible reduction peak at $E_{pc} = -1.3$ V vs Hg_2SO_4/Hg and a large irreversible oxidation peak at $E_{pa} = -0.45$ V. On the basis of the criteria of cyclic voltammetry (CV) ($\Delta E_p = 60$ mV, $i_{pc}/i_{pa} = 1$) and coulometry ($n_{app} = 1$), the reduction peak corresponds to a 1-electron electrochemically reversible process: $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-} + e \rightarrow [Nb_3O_2(SO_4)_6(H_2O)_3]^{6-}$. Constant-potential reduction of the red anion $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ at E = –1.4 V yields a green solution which contains the Nb(3.33+) cluster $[Nb_3O_2(SO_4)_6(H_2O)_3]^{6-}$. A cyclic voltammogram of the green reduced solution is similar to that obtained before electrolysis, except that the peak at $E_p = -1.3$ V becomes anodic (Figure 2A, dotted line). The reversibility of this electrochemical reduction is indicative of the similar geometry of the $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ and $[Nb_3O_2(SO_4)_6(H_2O)_3]^{6-}$ anions. The large oxidation peak at $E_{pa} = -0.45$ V in Figure 2A corresponds to a 4-electron oxidation of $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ to a Nb(5+) species, as confirmed by coulometry and CV of the solution obtained after electrolysis.

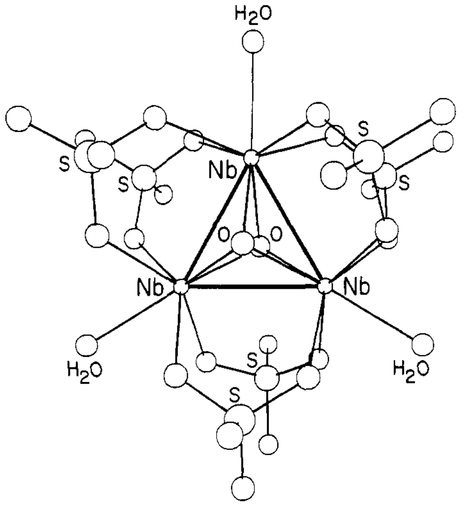

Figure 1. Structure[10] of the cluster anion $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$.

The Nb(5+) species[13] in 12 M H_2SO_4 gives two reduction peaks at $E_{pc} = -1.15$ and –1.30 V vs the Hg/Hg_2SO_4 electrode (peaks 1 and 2 in Figure 2B). On a reverse scan, in addition to the two coupled anodic peaks (peaks 3 and 4) of the two reduction peaks, three new anodic peaks at $E_{pa} = -0.90$, –0.82, and –0.45 V were observed (peaks 5–7). On the basis of the data obtained from CV ($\Delta E_p = 150$ mV, $i_{pc}/i_{pa} > 1$), coulometry ($n_{app} = 1.35$), and DC polarography ($\log[(I_L - I)/I]$ vs E gave a slope of 47 mV), it was concluded that the first reduction peak involves a quasi-reversible 2-electron-transfer process, followed by chemical step(s). Constant-potential electrolysis at 0 °C, at a potential slightly more negative than that of the first reduction peak (–1.22 V), consumed 1.35 mol of electrons/mol of Nb and produced a red solution of $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$, whose identity was confirmed by spectroscopy and cyclic voltammetry. The following reaction sequence for the conversion of Nb(5+) to $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ is proposed:

$$\mathrm{Nb(5+)} + 2e \rightarrow \mathrm{Nb(3+)} \rightarrow {}^1/_2\text{“}Nb_2^{6+}\text{”}$$

$$Nb_2^{6+} + \mathrm{Nb(5+)} \rightarrow [Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$$

$$[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-} + e \rightleftarrows Nb_3O_2(SO_4)_6(H_2O)_3]^{6-}$$

After the initial 2-electron reduction of Nb(5+), the product,

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(12) Electrochemical measurements were performed in an H-type cell with a hanging mercury drop working electrode (HMDE), a platinum-gauze auxiliary electrode, and a Hg_2SO_4/Hg (saturated K_2SO_4) reference electrode. The constant-potential electrolyses were done using a Hg-pool electrode. A spectroscopic quartz cuvette (attached on the side of the H-type cell) was used for the spectroelectrochemical measurements during the coulometry experiments.

(13) The Nb(5+) solution in 12 M H_2SO_4 was prepared by dissolving freshly precipitated niobium(V) hydroxide in 12 M H_2SO_4 with heating. The nature of the Nb(5+) species in 12 M H_2SO_4 is not known with certainty. Previous electrochemical studies of the dc polarographic wave of Nb(5+) in 12 M H_2SO_4 at $E_{1/2} = -1.1$ V indicate that Nb(5+) in 12 M H_2SO_4 is present as a monomer.[16]

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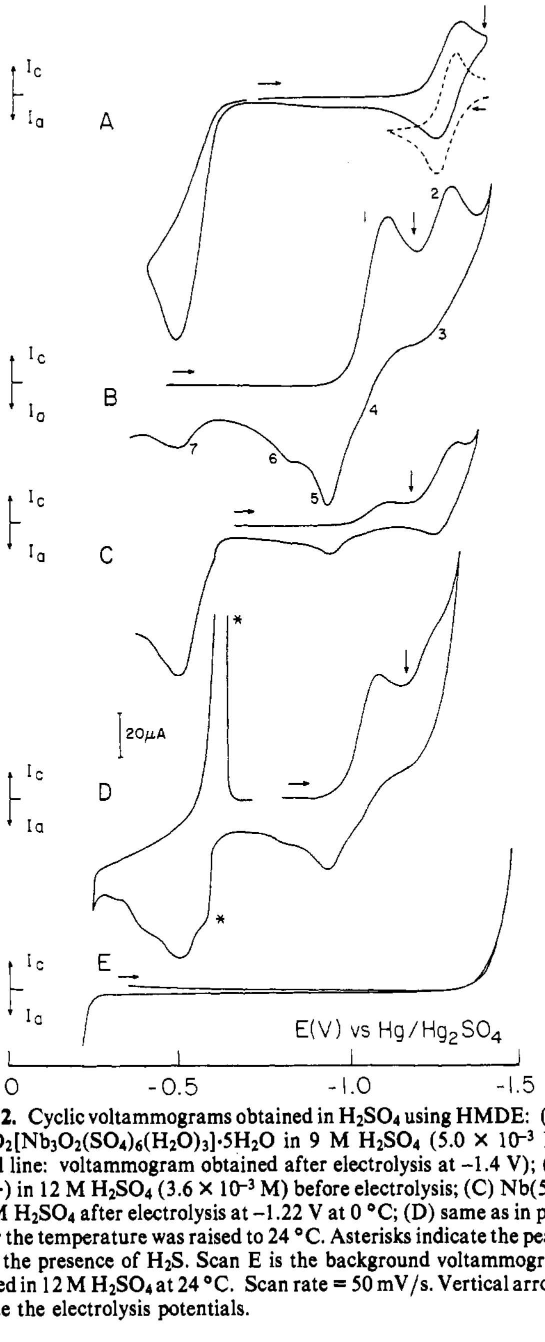

Figure 2. Cyclic voltammograms obtained in H_2SO_4 using HMDE: (A) $K_4H_5O_2[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot5H_2O$ in 9 M H_2SO_4 (5.0×10^{-3} M) (dotted line: voltammogram obtained after electrolysis at -1.4 V); (B) Nb(5+) in 12 M H_2SO_4 (3.6×10^{-3} M) before electrolysis; (C) Nb(5+) in 12 M H_2SO_4 after electrolysis at -1.22 V at 0 °C; (D) same as in part C after the temperature was raised to 24 °C. Asterisks indicate the peaks due to the presence of H_2S. Scan E is the background voltammogram obtained in 12 M H_2SO_4 at 24 °C. Scan rate = 50 mV/s. Vertical arrows indicate the electrolysis potentials.

Nb(3+), is not chemically stable and produces an intermediate species, probably a soluble Nb_2^{6+} dimer, which reacts with the starting material Nb(5+) and produces a $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ cluster anion. Further reduction at $E = -1.40$ V yields a Nb(3.33+) cluster, $[Nb_3O_2(SO_4)_6(H_2O)_3]^{6-}$, which is stable in solution at 0 °C.

We have observed that if the cluster anion $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ is generated by the reduction of Nb(5+) at -1.22 V at 0 °C and then the temperature of the solution is increased to 24 °C, the generation of H_2S commences.[14] It is important to notice that no reduction of 12 M H_2SO_4 takes place at this potential in the absence of $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ (see background current in Figure 2E). The electrochemical reduction of Nb(5+) to $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ at 0 °C is quantitative (yield >98%), and the reduction current decays to its background value. After the temperature increased to 24 °C, the reduction current increases from the background value to two-thirds of the initial value and remains constant, with the continuous generation of H_2S. The current increases even more if the potential is increased to -1.26 V, where the formation of $[Nb_3O_2(SO_4)_6(H_2O)_3]^{6-}$ begins.[15] The turnover number based on the mol of H_2S/mol of Nb_3 is 31.

Cyclic voltammograms of Nb(5+) in 12 M H_2SO_4 obtained before electrolysis at 0 °C, after electrolysis at -1.22 V at 0 °C, and after raising the temperature of the electrolyzed solution to 24 °C are shown respectively in Figure 2B–D. After electrolysis at -1.22 V at 0 °C, the first peak almost completely disappears, while at the same time the large anodic peak at -0.45 V increases dramatically. Electronic spectra collected in situ during electrolysis also confirm the formation of the $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ anion. After the temperature is increased to 24 °C, the cyclic voltammogram, in addition to the peaks characteristic of the presence of H_2S (designated by asterisks in Figure 2D), contains the peak at $E = -1.15$ V characteristic of the Nb(5+) species. These results indicate that the reduction of H_2SO_4 first involves the oxidation of the cluster $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ to Nb(5+). Continued electrolysis at $E = -1.22$ V then regenerates $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ and makes the whole process electrocatalytic.

The question arises, as in the previous examples of catalysis by metal clusters,[3] concerning whether it is the cluster species itself that is doing the catalysis or rather a cluster fragment or monomeric intermediate. For that reason, we performed an experiment in which Nb(5+) was reduced at -1.22 V at 24 °C, without first generating $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ at 0 °C. H_2S was not detected at the beginning of the electrolysis, but as the electrolysis proceeded and the amount of $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ increased, the generation of H_2S commenced. This indicates that it is not Nb(3+) or some other intermediate involved in the catalytic reduction, since their concentrations are highest at the surface of the electrode at the beginning of the electrolysis (when the concentration of Nb(5+) is also highest). In a separate experiment, we found that 12 M H_2SO_4 could also be catalytically reduced to H_2S by the *chemically* synthesized $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ cluster anion. Soluble Nb(5+) was reduced by Zn metal in 12 M H_2SO_4 to a red solution containing the $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ anion, and H_2S was generated. Further reduction with zinc produced a green solution of the $[Nb_3O_2(SO_4)_6(H_2O)_3]^{6-}$ anion, with the continued evolution of H_2S. No H_2S gas was detected in a control experiment in which Zn metal was reacted with 12 M H_2SO_4.

We do not presently know much about the mechanism of this catalytic reduction of H_2SO_4 to H_2S. The overall reduction process requires 8 electrons and therefore involves a rather complicated reaction mechanism. Since the $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ cluster has only 4 electrons available for reduction, the overall reduction process probably involves the formation of partially reduced sulfate, which is further reduced to H_2S.

It is interesting to note that $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ is the only example of a metal cluster with sulfate groups bridging two metal atoms. It is possible that this geometry facilitates the transfer of electrons from the metal orbitals in Nb_3 units to SO_4^{2-}. We are not aware of any previous example in which an "electron-poor" type cluster was involved in catalytic activity.[3,4]

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(14) During the formation of H_2S, the electrolyzed solution was purged with N_2, and H_2S was absorbed in a $Cu(ClO_4)_2$ solution. The amount of H_2S was determined gravimetrically by weighing CuS.

(15) In a typical experiment, 43 mL of a 3.6×10^{-3} M solution of Nb(5+) (0.155 mmol of Nb) electrolyzed on a Hg-pool cathode (area ~15 cm^2) at -1.22 V at 0 °C consumed 19.2 C, during which the current decreased from 8 to 0.1 mA. After the temperature was increased to 24 °C, the current increased to 5 mA and remained at that value for several days, during which time 1.6 mmol of H_2S was recovered.

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