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# Electrochemistry Studies of $[Nb_3(\eta^6\text{-HMB})_3Cl_6]^+$ (HMB = Hexamethylbenzene), a Trinuclear Metal Cluster Complex That Reversibly Attains Four Oxidation States

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Our continuing interest in the photochemistry of transition-metal–arene complexes[1] led us to consider photochemical investigations of the trinuclear $[M_3(HMB)_3Cl_6]^{n+}$ (HMB = $\eta^6$-hexamethylbenzene; M = Nb, Ta, Zr, Ti; $n$ = 1, 2) cations first prepared by Fischer and Rohrscheid in 1966.[2] These compounds contain a planar, triangular arrangement of the metal centers, two bridging chloride ions along each edge, and an $\eta^6$-HMB ligand coordinated to each metal atom.[3-5]

During the initiation of preliminary photochemical studies on the $[Nb_3(HMB)_3Cl_6]^+$ system, we became aware of several inconsistencies present in its previously reported oxidation chemistry.[6,7] Chemical oxidation of this niobium compound led to the isolation of salts of empirical formula $[Nb_3(HMB)_3Cl_6]X_2$ ($X^-$ = $SCN^-$, $I_3^-$, $PF_6^-$). The cation in these salts was believed to exist as a dimer of the trimetallic oxidized niobium cluster, with a structure similar to those of known hexametallic niobium and tantalum halide complexes.[8] The proposed dimeric structure was based on the diamagnetic behavior observed for the odd electron, oxidized product. More recently,[9] a crystal structure, ESR spectrum and ESR spin-counting of the oxidized cation as the 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) salt demonstrated that the cation is a simple one electron oxidation product of $[Nb_3(HMB)_3Cl_6]^+$ in the solid state.

We sought to further demonstrate the paramagnetism in solution and the solid state of the simple $PF_6^-$ salt of $[Nb_3(HMB)_3Cl_6]^{2+}$ and investigate[10] the redox chemistry of $[Nb_3(HMB)_3Cl_6]^+$ by means of cyclic voltammetry, square-wave voltammetry and controlled-potential electrolysis at inert, solid electrodes. Our experiments demonstrate the paramagnetism of $[Nb_3(HMB)_3Cl_6](PF_6)_2$ and describe the redox behavior of this interesting niobium cluster system.

## Experimental Section

$[Nb_3(HMB)_3Cl_6]Cl$, $[Nb_3(HMB)_3Cl_6]PF_6$, and $[Nb_3(HMB)_3Cl_6](PF_6)_2$ were prepared by the procedures of Fischer[2] and King.[7] In our hands, the preparation of the latter compound was best accomplished via the air oxidation procedure.

Electrochemical experiments were performed with a Bioanalytical Systems Model 100 electrochemical analyzer. A three-electrode configuration consisting of working, platinum spiral auxiliary, and aqueous AgCl/Ag reference electrodes containing 1.0 M KCl was utilized in all electrochemical experiments. Voltammetric experiments were performed at 20 ± 2 and −40 °C ($CH_3CN$ slush) at a highly polished glassy-carbon electrode of area 0.07 cm$^2$ (Bioanalytical Systems). Electrolyses were performed either at 20 ± 2 or −40 °C at a platinum-gauze working electrode. The working compartment of the electrochemical cell was separated from the auxiliary compartment by a fritted-glass salt bridge and from the reference compartment by a modified Luggin capillary. All three compartments contained a 0.1 M solution of supporting electrolyte. Acetonitrile (Burdick and Jackson Laboratories, Inc.) and tetra-*n*-butylammonium hexafluorophosphate (TBAH) (Southwestern Analytical Chemicals, Inc.) were used without further purification. Working solutions were deoxygenated with purified, solvent-saturated argon. Solutions of complex were prepared from solvent/supporting electrolyte stored over 80–200 mesh activated alumina (Fisher Scientific, Inc.). Potentials are reported vs. aqueous AgCl/Ag and are not corrected for the junction potential. In the low-temperature experiments, the AgCl/Ag reference electrode was held at 20 °C. The $E°'$ at 20 °C of the ferrocenium/ferrocene couple was observed at +0.41 V at the glassy-carbon working electrode.[11] No *iR* compensation was used in any of the electrochemical studies.[12]

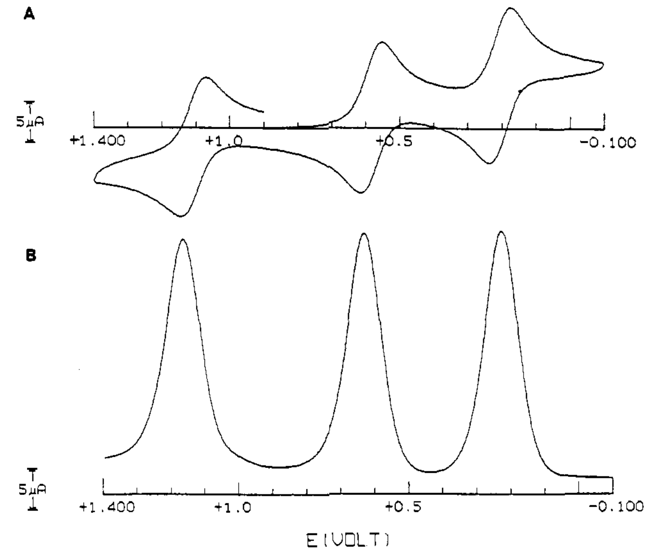

**Figure 1.** (A) Cyclic voltammogram at −40 °C of $[Nb_3(HMB)_3Cl_6]^{3+}$ generated from a 0.81 mM $[Nb_3(HMB)_3Cl_6]^+$ solution after bulk electrolyses at +0.4 and +0.9 V. The 100 mV/s scan is initiated in the negative direction. (B) Square-wave voltammogram at 20 °C of 0.81 mM $[Nb_3(HMB)_3Cl_6]^+$. The scan is initiated in the positive direction; square-wave amplitude = 25 mV; frequency = 15 Hz; $E_{step}$ = 4 mV. Anodic currents are plotted in the positive direction.

Magnetic data for solid samples were collected on a Faraday system using $HgCo(SCN)_4$ as a calibrant.[13] Weight changes were measured at two field strengths and the results averaged. The diamagnetic correction for $[Nb_3(HMB)_3Cl_6](PF_6)_2$ was estimated to be $-685 \times 10^{-6}$ cgsu/mol from Pascal's constants.[14,15] The Evans method[16] was employed to measure the magnetic moment of the cluster in solution.

## Results and Discussion

The cyclic and square-wave voltammograms of the $[Nb_3(HMB)_3Cl_6]^+$ system in $CH_3CN$/TBAH are shown in Figure 1. Three quasi-reversible oxidations are observed at $E°'$ = +0.223, +0.627, and +1.160 V at 20 °C, and $E°'$ = +0.204, +0.583, and +1.106 V at −40 °C. The separation between the anodic and cathodic peaks ($E_{p,a} - E_{p,c}$) is about 65 mV while the peak current ratios ($i_c/i_a$) are 1.00 ± 0.05 at a scan rate of 100 mV/s. These processes are sequential, one-electron metal-centered oxidations (Scheme I). The number of electrons passed in each oxidative process was confirmed by means of controlled-potential electrolyses. *Each* of the four oxidation states indicated in Scheme I

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may be accessed electrochemically to produce solutions that are stable for many hours if kept under a blanket of dry argon. If one starts with a millimolar acetonitrile solution of $[Nb_3(HMB)_3Cl_6]^+$, millimolar solutions of all four oxidation states may be generated *reversibly* over the course of one experiment. Previously, only the $[Nb_3(HMB)_3Cl_6]^{2+}$ dication has been prepared chemically. The 3+ and 4+ cations are extremely moisture-sensitive and have not yet been isolated in pure form. We are presently refining our synthetic techniques in order to obtain these highly oxidized materials.

**Scheme I**

$$e^- + [Nb_3(HMB)_3Cl_6]^{2+} \rightleftarrows [Nb_3(HMB)_3Cl_6]^+ \qquad E^{\circ\prime}_{2+/1+} = +0.223\ \text{V}$$

$$e^- + [Nb_3(HMB)_3Cl_6]^{3+} \rightleftarrows [Nb_3(HMB)_3Cl_6]^{2+} \qquad E^{\circ\prime}_{3+/2+} = +0.627\ \text{V}$$

$$e^- + [Nb_3(HMB)_3Cl_6]^{4+} \rightleftarrows [Nb_3(HMB)_3Cl_6]^{3+} \qquad E^{\circ\prime}_{4+/3+} = +1.160\ \text{V}$$

With respect to the confusion in the literature concerning the magnetic behavior of $[Nb_3(HMB)_3Cl_6]^{2+}$, the high degree of chemical reversibility and the one-electron nature of the 3+/2+ couple imply that this odd-electron dication is *tri*nuclear in solution as well as in the solid state. No $^1H$ NMR spectrum is observed from $CD_2Cl_2$ solutions of $[Nb_3(HMB)_3Cl_6]^{2+}$ that are carefully protected from atmospheric moisture. A $CH_3CN$ solution magnetic moment, determined by the Evans method gave $\mu = 1.81$ $\mu_B$. Additionally, in contrast to the report of King et al., the solid material was also found to be paramagnetic by Faraday balance measurements. A magnetic moment of 1.74 $\mu_B$ was measured for the dication ($\chi_g = +0.474 \times 10^{-6}$ cgsu/g) indicating the presence of one unpaired electron. This moment is consistent with the ESR spin-counting data reported by Eisenberg et al. for the dicationic TCNQ salt.

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**Registry No.** $[Nb_3(HMB)_3Cl_6]^+$, 55521-51-2; $[Nb_3(HMB)_3Cl_6]^{2+}$, 51509-93-4; $[Nb_3(HMB)_3Cl_6]^{3+}$, 99594-60-2; $[Nb_3(HMB)_3Cl_6]^{4+}$, 99594-61-3; $[Nb_3(HMB)_3Cl_6](PF_6)_2$, 37328-53-3.

# Additions and Corrections

## 1985, Volume 24

**Sumio Kaizaki,* Mieko Ito, Noriko Nishimura, and Yukie Matsushita**: Circular Dichroism of Chromium(III) Complexes. 10. Circular Dichroism Spectra in the Spin-Forbidden Transitions of $Cr^{III}(N)_6$ Type Complexes with Chiral Diamines.

Page 2083. In the caption to Figure 2, the key is incorrect. It should read as follows. Key: $x = 0$ (*lel*$_3$) (—); $x = 1$ (*lel*$_2$*ob*) (···); $x = 2$ (*lelob*$_2$) (·--); $x = 3$ (*ob*$_3$) (–·–).—Sumio Kaizaki

**Leonard E. Bogan, Jr., Thomas B. Rauchfuss,* and Arnold L. Rheingold***: $(RC_5H_4)MoFe(Te_2X)(CO)_5$: Carbonyl Clusters Containing Hypervalent Main-Group Centers.

Page 3721. In the structure displayed in column 1 the labels on the Te atoms should be reversed: the four-coordinate tellurium is Te(1). Also in column 1, last line of the first complete paragraph, the 2.81 Å value quoted for the Te···Te distance in elemental tellurium should be 2.83 Å.—Thomas B. Rauchfuss