Synthesis and electrochemical study of the first tetrazolate hexanuclear rhenium cluster complex

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The linkage isomers $[Re_6Se_8(PEt_3)_5(1,5\text{-}MeN_4C)]^+$ and $[Re_6Se_8(PEt_3)_5(2,5\text{-}MeN_4C)]^+$ were generated upon reaction of tetrabutylammonium azide with the corresponding acetonitrile complex, $[Re_6Se_8(PEt_3)_5(NCCH_3)]^{2+}$; these are the first (tetrazolato)rhenium complexes reported to date.

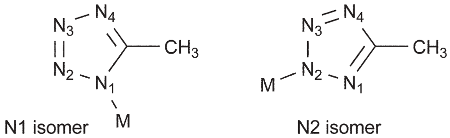
Hexanuclear transition metal cluster complexes are an important class of high nuclearity clusters. While the molybdenum halide clusters were the first of this type to be fully characterized, a variety of metal ions and bridging atoms have since been incorporated into this structural motif.[1] These clusters are of interest due to the fact that they are highly symmetric, robust, and have notable redox and photophysical properties.[2] The application of dimensional reduction to the synthesis of new cluster cores, as well as the seminal report involving the controlled substitution of the terminal halide ligands on the $[Re_6Se_8]^{2+}$ core, has greatly facilitated research in this area.[3,4] Numerous reports involving the preparation of novel molecular species as well as solid state materials containing hexanuclear clusters as building blocks have been reported.[5] However, the synthetic control over these systems is still limited compared to single metal complexes.

Our group has been interested in developing the fundamental chemistry of hexanuclear clusters even further by developing synthetic methodologies and investigating how the cluster core affects the reactivity of the coordinated ligands.[6] Towards this end, we tried to substitute the acetonitrile ligand on the site-differentiated cluster complex $[Re_6Se_8(PEt_3)_5(NCCH_3)]^{2+}$ with azide. Gray and Holm reported that these clusters are substitutionally inert ($k = 10^{-5}$–10^{-6} s^{-1} at 318 K);[7] therefore, we heated the original reaction mixture containing $[Re_6Se_8(PEt_3)_5(NCCH_3)]^{2+}$ and N_3^- at reflux to drive the reaction. Because nitriles are readily substituted by stronger ligands, complexes containing organonitrile ligands are often used as starting materials in the preparation of coordination complexes.[8] We had no reason to suspect that the chemistry of the nitrile coordinated to this cluster would differ since substitution of acetonitrile coordinated to hexanuclear rhenium chalcogenide cluster cores has been previously reported.[9] Other (acetonitrile)rhenium complexes have also been used as starting materials in the preparation of various complexes.[10] However, our attempts to substitute the acetonitrile ligand in this manner resulted in a product which did not contain coordinated azide or $NCCH_3$. Selby *et al.* recently reported the addition of methanol to $[Re_6Se_8(PEt_3)_5(NCCH_3)]^{2+}$, suggesting possible addition of the azide ligand.[11] Column chromatography of our product ultimately led to the isolation of the tetrazolate linkage isomers: $[Re_6Se_8(PEt_3)_5(1,5\text{-}MeN_4C)]^+$ and $[Re_6Se_8(PEt_3)_5(2,5\text{-}MeN_4C)]^+$, verifying that the cluster does activate the nitrile, which results in addition of the azide ion across the nitrile triple bond. These complexes represent the first octahedral hexanuclear cluster complex to contain this type of N-donor ligand.

Although 5-substituted tetrazolate ligands are potentially multitopic, they typically act as monodentate ligands coordinating through either the N1 or N2 atoms (Scheme 1). There has been a great deal of interest in these nitrogen containing heterocycles because they play a key role in a wide variety of applications.[12] One of the major synthetic routes to tetrazole formation is the [2 + 3] cycloaddition of an organonitrile and an azide salt. However, direct reaction of these two reagents usually requires forcing conditions. Transition metal ions have been shown to facilitate this reaction through coordination of the organonitrile or the azide ligand, allowing the reaction to be conducted under milder conditions. While a variety of metals have been successfully employed, those that are most common are Zn^{2+}, Pd^{2+} or Pt^{2+}.[13] In terms of the Group 7 metals, there are only a few examples where azido or nitrile manganese complexes have been shown to activate tetrazolate formation.[14] Therefore, our findings mark the first time rhenium has activated an organonitrile to a [2 + 3] cycloaddition with the azide ion.

A solution of $Bu_4N(N_3)$ (0.633 mmol) in 30 mL acetone was added dropwise to a solution of $[Re_6Se_8(PEt_3)_5(MeCN)](BF_4)_2$ (0.12 mmol) in 90 mL acetone. The solution was heated at reflux under an inert atmosphere for 24 h. The volume was reduced to afford a brown oil, which was purified *via* silica gel column chromatography. The first major band eluted with a 2 : 1 mixture of CH_2Cl_2 : CH_3CN, and was identified as the N2 isomer: $[Re_6Se_8(PEt_3)_5(2,5\text{-}CH_3N_4C)]^+$. After switching the eluent to methanol, a second major band was eluted which was identified as the N1 isomer: $[Re_6Se_8(PEt_3)_5(1,5\text{-}CH_3N_4C)]^+$. Both complexes were recrystallized and then characterized by IR, ^1H NMR and ^{31}P NMR spectroscopies, MS and elemental analysis.† Only $[Re_6Se_8(PEt_3)_5(1,5\text{-}CH_3N_4C)]^+$ afforded X-ray quality crystals.‡

Although our original synthesis involved heating the reaction mixture, we later discovered that the reaction between the coordinated nitrile and the azide ion is much faster than we



Scheme 1

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thought. Within 5 min at room temperature the N1 isomer can be prepared in 78% yield so the need for chromatography is avoided.† Allowing the reaction mixture to stir longer or heating the mixture, causes isomerization to occur, which is likely due to sterics. Similar linkage isomerism was observed for the 5-methyltetrazolato complex of pentaamminecobalt(III).[15] The equilibrium constant for the isomerization reaction is close to 1, which explains why our original syntheses generated a 50 : 50 mixture of products. In addition, free tetrazole can be displaced from the cluster but only after heating at reflux in the presence of acid; this corroborates the fact that these clusters are inert to substitution at room temperature.[16]

The N1 coordination of the tetrazolato ligand of $[Re_6Se_8(PEt_3)_5(1,5\text{-}CH_3N_4C)]^+$ is clearly shown in the ORTEP diagram (Fig. 1). The Re6–N1 bond length is 2.143(8) Å which is in the range of nitrogen donor ligands bonded to the $[Re_6Se_8]^{2+}$ cluster core.[4,9] The tetrazolate ring is planar and within the ring itself the bond lengths are: N1–N2 = 1.392(10), N2–N3 = 1.276(12), N3–N4 = 1.371(13), N4–C31 = 1.288(12) and N1–C31 = 1.357(12) Å. While all of these bond lengths are reasonable, what is unusual is that there is such a large difference (0.091 Å) between the two shorter bonds (average 1.282 Å) and the three longer bonds (average 1.373 Å). For similar tetrazolato complexes, *i.e.* N1 coordination and only one metal atom bonded to the tetrazolate ring, the average difference between analogous bonds is 0.024 Å.[17] This implies that the there is little delocalization in the heterocyclic ring in $[Re_6Se_8(PEt_3)_5(1,5\text{-}MeN_4C)]^+$.

The cyclic voltammogram of $[Re_6Se_8(PEt_3)_5(1,5\text{-}MeN_4C)]^+$ is shown in Fig. 2 along with the voltammograms of $[Re_6Se_8(PEt_3)_5(MeCN)]^{2+}$ and $[Re_6Se_8(PEt_3)_5I]^+$ under analogous conditions. Within the −0.20 to +1.0 V *vs.* $FeCp_2^+/FeCp_2$ range,[18] each complex contains one main oxidative couple; $[Re_6Se_8(PEt_3)_5(1,5\text{-}MeN_4C)]^+$ and $[Re_6Se_8(PEt_3)_5I]^+$ contain quasi-reversible waves at $E_{1/2}$ = 0.622 V and 0.540 V, respectively.[19] The analogous acetonitrile complex has one reversible wave at $E_{1/2}$ = 0.754 V. Oxidative coulometry of $[Re_6Se_8(PEt_3)_5(MeCN)]^{2+}$ was previously reported by Zheng *et al.* which indicates a one-electron process.[9] Based on this data, as well as on reported voltammetric data of analogous 24 e^- $[Re_6Q_8]^{2+}$ cluster complexes, we assign the oxidative waves of $[Re_6Se_8(PEt_3)_5(1,5\text{-}MeN_4C)]^+$ and $[Re_6Se_8(PEt_3)_5I]^+$ to the Re(III)$_5$Re(IV)/Re(III)$_6$ couple.[1]

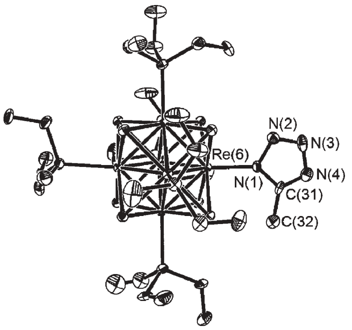

Fig. 1 ORTEP diagram of $[Re_6Se_8(PEt_3)_5(1,5\text{-}CH_3CN_4)]^+$ (ellipsoids at 50% probability). Hydrogen atoms omitted for clarity.

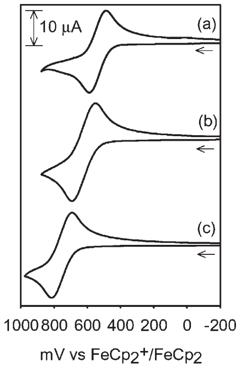

Fig. 2 Cyclic voltammograms of (a) $[Re_6Se_8(PEt_3)_5I](SbF_6)$, (b) $[Re_6Se_8(PEt_3)_5(1,5\text{-}CH_3CN_4)](BF_4)$ and (c) $[Re_6Se_8(PEt_3)_5(MeCN)](BF_4)_2$ in CH_2Cl_2 at 100 mV sec^{-1}.

In order to examine the electronic properties of the tetrazolate ligand, we determined its electrochemical parameter (E_L) value by using the model developed by Lever.[20] Plotting $E_{1/2}$ values for complexes containing the $[Re_6Se_8]^{2+}$ cluster core *versus* the sum of the electrochemical parameters for the six terminal ligands we obtained the linear correlation (R^2 = 0.9976).[21]

$$E_{1/2}\ [\mathrm{Re(III)_5Re(IV)/Re(III)_6}] = 0.378\ \Sigma E_L + 0.282$$

By using the redox potential for the $[Re_6Se_8(PEt_3)_5(1,5\text{-}MeN_4C)]^+$ complex, adjusted for the same reference and solvent, we determined the E_L value of the 1,5-methyltetrazolate ligand (E_L = −0.05 V). This value is consistent with the tetrazolate ligand being negatively charged and a strong Lewis donor.[20] In addition to being able to report the first E_L parameter for a tetrazolate ligand, our data also show that Lever's method can also be applied to higher nuclearity clusters.

When a more positive potential is accessed (+1.40 V *vs.* $FeCp_2^+/FeCp_2$) an irreversible oxidative peak ($E_{p,a}$ = 1.292 V) appears in the cyclic voltammogram of $[Re_6Se_8(PEt_3)_5(1,5\text{-}MeN_4C)]^+$. Conducting repeat scans (Fig. 3) shows a decrease in the peaks associated with the quasi-reversible couple at 0.622 V and reveals a new couple growing in with an $E_{1/2}$ of 0.740 V. We were not that surprised to see an irreversible oxidative peak in the tetrazolate complex. Electrochemical studies of iron(III) tetrazolato porphyrin complexes show an irreversible oxidation which was assigned to loss of the tetrazolate ligand and subsequent formation of a solvated porphyrin complex.[17] What is interesting about the data reported here is that the $E_{1/2}$ of the decomposition product (0.740 V) is so similar to the $E_{1/2}$ of the analogous acetonitrile complex (0.754 V). Since our electrochemical measurements were conducted in CH_2Cl_2, the only way the corresponding acetonitrile

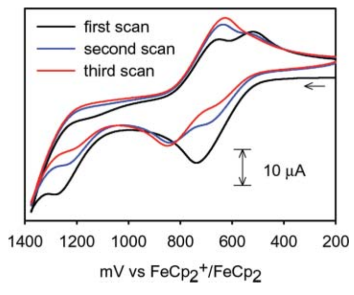

Fig. 3 Cyclic voltammogram of $[Re_6Se_8(PEt_3)_5(1,5\text{-}CH_3CN_4)](BF_4)$ in CH_2Cl_2 at 400 mV sec^{-1}.

complex could be formed from the tetrazolate complex is by loss of azide from the heterocyclic ring. This apparent oxidative decomposition of the tetrazolate ring is quite unusual and warrants further studies.

The $[Re_6Se_8]^{2+}$ core has been shown to activate the nitrile ligand to addition by the azide ion to form the first example of a rhenium tetrazolate complex. Studies involving the oxidative decomposition of the tetrazolate ring as well as formation of other hexanuclear rhenium tetrazolate complexes are currently underway.

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Notes and references

† *Synthesis and Characterization*: **Caution**: all reactions involving azides and tetrazoles should be treated as potentially explosive and handled in an appropriate manner!

$[Re_6Se_8(PEt_3)_5(1,5\text{-}CH_3CN_4)]Cl\cdot 2CH_2Cl_2$. Recrystallized by vapor diffusion of ether into CH_2Cl_2 (33% yield). (Found: C, 15.56; H, 3.10; N, 2.18%. Calc. for $Re_6Se_8P_5N_4C_{32}H_{78}Cl\cdot 2CH_2Cl_2$: C, 15.54; H, 3.14; N, 2.13%); ν_{max}/cm^{-1} 1256 (=N–N=N–). δ_H (400 MHz, $CDCl_3$, ppm) 2.35 (3H, s, CH_3CN_4), 2.14 (30H, m, $–CH_2CH_3$), 1.10 (45H, m, $–CH_2CH_3$). δ_C (100 MHz, $CDCl_3$, ppm) 162.9 (s, CH_3CN_4), 25.8 (d, PCH_2CH_3), 15.9 (s, CH_3CN_4), 8.8 (s, PCH_2CH_3). δ_P (162 MHz, $CDCl_3$, ppm) −28.55 (s), −29.47 (s). *m*/*z* (ESI^+) 2422.4 ($[Re_6Se_8(PEt_3)_5(CH_3CN_4)]^+$). **$[Re_6Se_8(PEt_3)_5(2,5\text{-}CH_3CN_4)](BF_4)$**. Recrystallized by slow diffusion of ether into acetone to afford red crystals (19% yield). This material always has a small amount of $[Re_6Se_8(PEt_3)_5(1,5\text{-}MeN_4C)]^+$ present. (Found: C, 15.35; H, 3.03; N, 2.21%. Calc. for $Re_6Se_8P_5N_4C_{32}H_{78}BF_4$: C, 15.31; H, 3.13; N, 2.23%); ν_{max}/cm^{-1} 1257 (=N–N=N–), 1055s (B–F); δ_H (400 MHz, $CDCl_3$, ppm) 2.42 (3H, s, CH_3CN_4), 2.17 (30H, m, $–CH_2CH_3$), 1.10 (45H, m, $–CH_2CH_3$). δ_P (162 MHz, $CDCl_3$, ppm) −28.27 (s), −30.17 (s). *m*/*z* (ESI^+): 1211.8 ($[Re_6Se_8(PEt_3)_5(CH_3CN_4)]^{2+}$). **Optimized synthesis of $[Re_6Se_8(PEt_3)_5(1,5\text{-}CH_3CN_4)]BF_4\cdot C_3H_6O$**. NaN_3 (0.15 mmol) was dissolved in a minimal amount of DI water then added to a solution of $[Re_6Se_8(PEt_3)_5MeCN](BF_4)_2$ (0.13 mmol) in ~100 mL acetone. The mixture was stirred at room temperature for 5 min then filtered through Celite to remove any $NaBF_4$. After the solvent was removed, the product was reprecipitated out of acetone–Et_2O and then recrystallized *via* vapor diffusion using acetone–Et_2O (247.7 mg, 78% yield). (Found: C, 16.64; H, 3.37; N, 2.04%. Calc. for $Re_6Se_8P_5C_{32}H_{78}N_4BF_4\cdot C_3H_6O$: C, 16.4; H, 3.30; N, 2.18%); $\lambda_{max}(CH_3CN)/nm$ 224 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 6.8×10^4), 256sh, 280sh, 360sh, 390sh, 460 (4.4×10^2). *m*/*z* (ESI^+) 2422.3 ($[Re_6Se_8(PEt_3)_5C_2H_3N_4]^+$).

‡ ***Crystal data* for $[Re_6Se_8(PEt_3)_5(1,5\text{-}CH_3CN_4)]Cl\cdot 2CH_2Cl_2$**. M 2628.02, monoclinic, space group $P2_1/c$ (No. 14), $a = 15.7625(11)$, $b = 16.9028(11)$, $c = 24.0359(16)$, $\beta = 100.974(1)°$, $V = 6286.8(7)$ Å^3, $Z = 4$, μ(Mo-Kα) = 16.507 mm^{-1}, $F(000) = 4784$, $T = 293(2)$ K, 38 283 total reflections, 12 796 unique, $R1 = 0.037$, $wR2 = 0.120$ (all data), GOF = 1.054 for 550 parameters. CCDC 659974. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b708390d

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19 Looking closely at the data, one observes that the electrochemistry of the iodo complex is not as clean as the other complexes; there is a very small oxidative peak at 0.741 V as well as a small reductive peak at 0.015 V, which only become apparent after the main oxidative couple has been accessed.

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