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Conversion of a Re(IV) Tetrahedral Cluster to a Re(III) Octahedral Cluster: Synthesis of $[(CH_3)C(NH_2)_2]_4[Re_6Se_8(CN)_6]$ by a Solvothermal Route

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The compound $[(CH_3)C(NH_2)_2]_4[Re_6Se_8(CN)_6]$ has been synthesized by the reaction at 200 °C for 3 days of $Re_4Te_4(TeCl_2)_4Cl_8$, KSeCN, and NH_4Cl in superheated acetonitrile. This compound crystallizes in the space group *C*2/*c* of the monoclinic system with four formula units in a cell of dimensions $a = 20.3113(14)$ Å, $b = 10.1332(7)$ Å, $c = 19.9981(14)$ Å, $\beta = 106.754(1)°$, $V = 3941.3(5)$ Å^3 ($T = 153$ K). The $[Re_6Se_8(CN)_6]^{4-}$ anion comprises an Re_6 octahedron face capped by μ_3-Se atoms, with each Re atom liganded by a CN group. The anions and cations are connected by an extensive network of hydrogen bonds. The conversion of a Re(IV) tetrahedral cluster to a Re(III) octahedral cluster appears to be unprecedented.

Superheated polar solvents, for example, water, methanol, and acetonitrile, at temperatures below about 200 °C provide reaction media that enhance solubility and crystallization but are mild enough to leave molecular building blocks intact to participate in the formation of larger entities.[1] Such solvothermal methods have been widely applied to the preparation of chalogenometalates containing rings and chains;[2] here, we demonstrate an application in which the Re(IV) tetrahedral cluster $Re_4Te_4(TeCl_2)_4Cl_8$ is converted to the octahedral Re(III) cluster $[Re_6Se_8(CN)_6]^{4-}$.

The compound $[(CH_3)C(NH_2)_2]_4[Re_6Se_8(CN)_6]$[3] has been synthesized reproducibly and in good yield by the reaction at 200 °C for 3 days of $Re_4Te_4(TeCl_2)_4Cl_8$, KSeCN, and NH_4Cl in superheated acetonitrile.[4] This is a remarkable reaction for two reasons. First, although the starting cluster has a $[Re_4Te_4]^{8+}$ cubane-like core containing Re(IV), the resulting compound has a $[Re_6Se_8]^{2+}$ octahedral core containing Re(III). Replacement of Te ligands by Se ligands is not unusual,[5] but the conversion of a Re_4 core to a Re_6 core appears to be unprecedented. Re_6 clusters are normally formed from reactions at temperatures of 600 °C or higher,[5] far higher than the present 200 °C. Second, although there is a standard two-step synthesis of acetamidinium chloride, $[(CH_3)C(NH_2)_2]Cl$, involving CH_3CN, C_2H_5OH, and HCl(g) to form the acetimido ethyl ester, which is then reacted with NH_3,[6] there is but one previous example[7] of a solvothermal synthesis of the acetamidinium cation, $(CH_3)C(NH_2)_2^+$.

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(3) Crystal data: $C_{14}H_{28}N_{14}Re_6Se_8$, fw 2141.38; space group *C*2/*c*; $a = 20.3113(14)$ Å, $b = 10.1332(7)$ Å, $c = 19.9981(14)$ Å, $\beta = 106.754(1)°$; $V = 3941.3(5)$ Å^3 at $T = 153$ K; $Z = 4$; $\rho_c = 3.609$ g/cm^3; μ(Mo Kα) = 257.7 cm^{-1}; $R_1(F) = 0.0385$; $R_w(F^2) = 0.0924$. Single-crystal diffraction data were collected at 153 K on a Bruker Smart-1000 CCD diffractometer with the program SMART.[15] Cell refinement and data reduction were carried out with the use of the program SAINT,[15] and a face-indexed absorption correction was performed numerically with the use of the program XPREP.[16] Then, the program SADABS[15] was employed to make incident beam and decay corrections. The structure was solved by means of the direct-methods program SHELXL of the SHELXTL suite of programs[16] and was refined by full-matrix least-squares techniques. In the asymmetric unit, the $[Re_6Se_8(CN)_6]^{4-}$ anion is on an inversion center, one $(CH_3)C(NH_2)_2^+$ cation lies on a 2-fold axis, another $(CH_3)C(NH_2)_2^+$ cation is in a general position, and a third $(CH_3)C(NH_2)_2^+$ cation half occupies a general position. This third cation, which is obviously disordered, did not refine well and gave a nonrepresentative C−C distance of 1.1 Å. Accordingly, the atoms of this third cation were removed from the refinement, and the program SQUEEZE[17] in the PLATON[18] suite of programs was used to assess the resultant voids in the unit cell. Electron density totaling 155 e$^-$ was found; this is in satisfactory agreement with the expected value of 132 e$^-$ for half occupancy of this third cation and thus with the charge of 4− on the anion.

(4) The compound $Re_4Te_4(TeCl_2)_4Cl_8$ was synthesized by a literature method.[14] A reaction mixture of $Re_4Te_4(TeCl_2)_4Cl_8$ (0.0233 g, 0.010 mmol), KSeCN (0.020 g, 0.14 mmol), and NH_4Cl (0.10 g, 1.9 mmol) was loaded into a fused-silica tube under an Ar atmosphere in a glovebox. Then, 0.4 mL of acetonitrile was added via syringe. The tube was frozen, evacuated to $\sim 10^{-3}$ Torr, flame-sealed, and thawed. It was then loaded into a high-pressure autoclave along with 1700 mL of H_2O to counter the pressure. The autoclave was heated at 200 °C for 3 days and then cooled to room temperature. Orange crystals of $[(CH_3)C(NH_2)_2]_4[Re_6Se_8(CN)_6]$ were recovered by suction filtration and washed with acetone. Yield of crystals was 0.007 g (50% based on Re). A second preparation afforded a yield of 40% based on Re. Examination of these crystals with an EDX-equipped Hitachi S-3500 SEM gave Re/Se = 3:4. The compound is stable in air.

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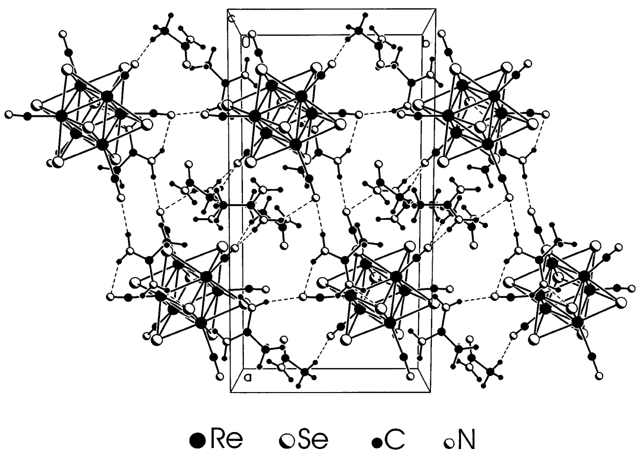

Figure 1. Part of the unit cell of $[(CH_3)C(NH_2)_2]_4[Re_6Se_8(CN)_6]$. The third independent $(CH_3)C(NH_2)_2^+$ cation, which half occupies a general position and which was modeled by the SQUEEZE option, is not shown.

In the crystal structure of $[(CH_3)C(NH_2)_2]_4[Re_6Se_8(CN)_6]$, cations and anions are interlinked through an extensive hydrogen-bonding network between the hydrogen atoms of the NH_2 groups of the cations and the CN ligands of the anions. Part of the unit cell is shown in Figure 1.

The structure of the cluster anion, $[Re_6Se_8(CN)_6]^{4-}$, may be discerned in Figure 1. The faces of the Re_6 octahedron are capped with μ_3-Se atoms. A CN group is attached to each Re atom. In the anion, Re−Re distances range from 2.6396(6) to 2.6453(6) Å, and the Re−(μ_3-Se) distances range from 2.5284(11) to 2.5832(10) Å; these may be compared with those of 2.622(2)−2.638(2) Å and 2.520(3)−2.550(3) Å, respectively, found earlier.[5]

Each of the two independent ordered acetamidinium cations has the expected structure, with the central C atom being trigonal and the two C atoms and two NH_2 groups being coplanar. The C−C distances of 1.40(2) and 1.45(2) Å and the C−N distances of 1.314(12), 1.317(12), and 1.320(13) Å are consistent with literature values.[8−10] The reaction of $SnSe_2 + Se$ in CH_3CN/H_2O at 145 °C affords $[(CH_3)C(NH_2)_2]_2[Sn_2Se_5]$.[7] In this instance, the formation of $(CH_3)C(NH_2)_2^+$ is ascribed to the reaction of the component solvents (CH_3CN and H_2O) with one another. Because the present reaction environment contains $SeCN^-$, in addition to CH_3CN and NH_4Cl, how $(CH_3)C(NH_2)_2^+$ forms is unknown: stoichiometrically, it is consistent with the 1:1 addition of NH_4^+ to superheated CH_3CN. Other salts containing the $(CH_3)C(NH_2)_2^+$ cation have resulted from the use of acetamidine[8−10] or oximes[11,12] as reactants.

This conversion of $Re_4Te_4(TeCl_2)_4Cl_8$ to $[Re_6Se_8(CN)_6]^{4-}$ involves at a minimum the formal reduction of Re^{4+} to Re^{3+} and the Se of $SeCN^-$ to Se^{2-}. The likely reductant is Te^{2-}, in which case the yield of $[(CH_3)C(NH_2)_2]_4[Re_6Se_8(CN)_6]$ is greater than that calculated from available Re. The reaction of the Re_3 cluster $[Re_3S_7Br_6]Br$, which contains Re(V), with KCN (aq) to afford the Re(IV) tetrahedral cluster $[Re_4S_4(CN)_{12}]^{4-}$ takes place under mild conditions and is believed to involve initially the $[Re_3S_7]^{7+}$ species.[13] Clearly, in the present reaction, the superheated acetonitrile provides a reaction medium mild enough to leave molecular building blocks intact to participate in the formation of the cluster anion. The nature of these molecular building blocks remains undetermined, but the solubilizing properties of the medium surely play a role in the facile break up of the $[Re_4Te_4]^{8+}$ core.

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Supporting Information Available: Crystallographic data in CIF format for $[(CH_3)C(NH_2)_2]_4[Re_6Se_8(CN)_6]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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