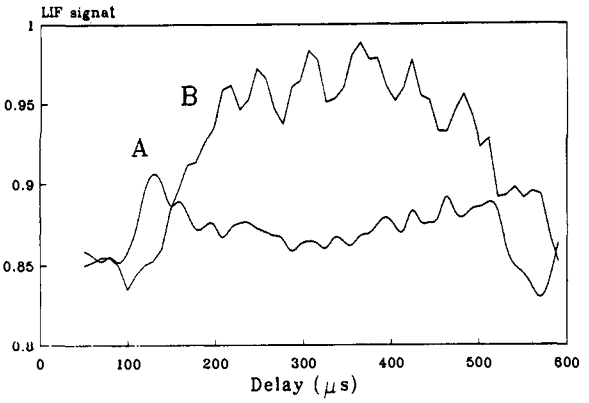

Figure 1. The LIF signal from the OH product at two expansion conditions: 100 Torr of cyclohexane seeded with 2.4 atm of He (A) and 100 Torr neat cyclohexane (B).

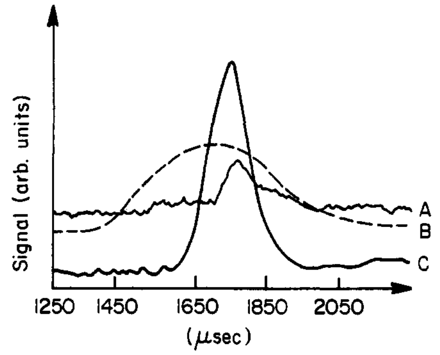

Figure 2. The time of arrival signal at the mass spectrometer when it is set to probe the cyclohexanol (A), the cyclohexane monomers (B), and the dimers (C). Curves A and C were taken with a sensitivity one-hundred times larger than that used for curve B.

molecular beam. Figure 2A shows the signal for mass 82, the strongest peak in the $C_6H_{11}OH$ mass spectrum. It was obtained by averaging over 200 nozzle pulses, with and without the oxygen beam, and taking the difference. For comparison we present the signal of the cyclohexane monomers (curve B) and dimers (curve C). Neither $(C_6H_{12})_2$ nor $C_6H_{11}OH$ was observed in the neat cyclohexane beam. The data indicate that the alcohol is produced from dimers and larger clusters but not from the monomers. The following considerations suggest that this reaction does not occur on the triplet potential energy surface, but proceeds via the singlet surface due to intersystem crossing in the entrance channel.

The reaction of $O(^3P)$ with the monomer has a barrier of 4.5 kcal/mol,[2] while the mean collision energy in our experiment did not exceed 2 kcal/mol. Therefore, the reaction was fed only by the upper edge of the collision energy distribution. When a saturated hydrocarbon looses a hydrogen to become a radical, its three remaining orbitals tend to be coplanar. This is accomplished by a conformational change of the molecule and a corresponding increase, ΔE, in the conformational energy. ΔE is larger in dimers than in monomers because the equilibrium of the intermolecular van der Waals interaction is disturbed. We calculated ΔE, using the empirical force field method with the MM2 program,[6] and obtained 0.7 and 3.2 kcal/mol for monomers and dimers, respectively. This implies a 2.5 kcal/mol increase of the barrier from 4.5 to about 7 kcal/mol, sufficient to block the reaction in the dimers. Due to the high density of states in the dimer and since the direct reaction channel is closed, the collision complex oxygen–cyclohexane dimer can have a long lifetime.

In gas-phase reactions of $O(^1D)$ with hydrocarbons, an efficient intersystem crossing between the singlet and the low-lying triplet potential energy surfaces was suggested.[7] The crossing region lies farther out in the entrance channel than in the case of O + H_2.[8] For low-energy collisions and when a long-lived collision complex is formed, intersystem crossing can take place with probability close to unity.[9,10] The mechanism of low-energy collision-complex formation followed by intersystem crossing is well suited for explaining the reaction of the cyclohexane clusters with $O(^3P)$. Crossing from the triplet to the singlet surface, an insertion instead of abstraction reaction takes place and cyclohexanol is formed. This mechanism is also consistent with the results of liquid cyclohexane studies.

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Registry No. H_2, 1333-74-0; O, 17778-80-2; OH, 3352-57-6; cyclohexane, 110-82-7; cyclohexanol, 108-93-0; cyclohexyl radical, 3170-58-9.

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Synthesis and Characterization of the $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ Anion, a Ni^{IV} Cubane Species

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The chemistry of soluble metal chalcogenides has afforded some diverse and unusual species, such as $Mo_3S_{13}^{2-}$,[1] $Na_2Fe_{18}S_{30}^{8-}$,[2] $V_2Se_{13}^{2-}$,[3] $In_2(Se_4)_4(Se)_5^{4-}$,[4] and $NbTe_{10}^{3-}$.[5] The chemistry of the selenides and tellurides frequently differs markedly from that of the sulfides,[6] but the anions $M(Q_4)_2^{2-}$ are now known for all three chalcogens (M = Pd and Hg; Q = S, Se, and Te).[7-9] We recently reported the synthesis, characterization, and some reaction chemistry of the soluble transition-metal selenide ions $M(Se_4)_2^{2-}$, M = Ni, Pd, Pt, Zn, Cd, Hg, and Mn.[8a] Further investigation into the chemistry of the soluble chalcogenides of the nickel triad has uncovered a remarkable Ni^{IV} cubane complex: $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)]\cdot NEt_4Cl$. The anion (Figure 1) possesses a Ni_4Se_4 cubane core and has five Se_3^{2-} chains and one Se_4^{2-} chain bridging the cubane faces between the Ni^{IV} atoms.

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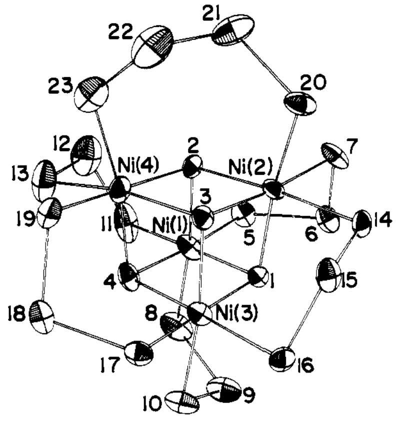

Figure 1. A drawing of the $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ anion. The 50% probability ellipsoids are shown.

The $[Ni_4Se_{23}]^{4-}$ ion results from a spontaneous assembly reaction in which the Ni^{II} centers are oxidized to Ni^{IV}, with concomitant reduction of Se species. (The average formal oxidation state of Se in the initial polyselenide solution is −0.52 while it is −0.87 in the resultant $[Ni_4Se_{23}]^{4-}$ product.) A solution of Li_2Se (279 mg, 3 mmol), Se (672 mg, 8.5 mmol), and NEt_4Cl (455 mg, 2.75 mmol) in DMF (20 mL) was added dropwise over 10 min with stirring to a solution of $Ni(xan)_2$ (xan = S_2COEt) (600 mg, 2 mmol) dissolved in DMF (20 mL). The solution was stirred for 1 h and then filtered; next, ether was layered on top of the filtrate. A mixture[10] of $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)]\cdot NEt_4Cl$ (481 mg, 35% yield),[11a] $[NEt_4]_2[Ni(Se_4)_2]$ (175 mg),[11b] and a fibrous crystalline material (159 mg)[11c] formed over a period of a week. These products can be separated by hand. As we have noted before,[12] once diverse polyselenide species are formed, as presumably is the case here, the metal selects out the species it desires. It is reasonable to expect that other species of the type $[Ni_4Se_4(Se_3)_n(Se_4)_{6-n}]^{4-}$, n = 0–6, might well be present and that the cubane product that crystallized is the least soluble. Indeed a related sulfide ion, $[Re_4S_4(S_3)_6]^{4-}$, has been structurally characterized,[13,14] and the existence of the $[Re_4S_4(S_3)_n(S_4)_{6-n}]^{4-}$ ions has been mentioned.[15] The $[Re_4S_{22}]^{4-}$ ion was prepared in an entirely different manner from that described here for the $[Ni_4Se_{23}]^{4-}$ ion, but it also cocrystallized with NH_4Cl. Of course, Re^{IV} species are far more common than Ni^{IV} species.

The presence of Ni^{IV} is necessitated by charge balance. Supporting this, the compound is diamagnetic,[16] as expected for a d^6 system; as a result it exhibits a clean, albeit complex, ^{77}Se NMR spectrum. Fifteen resonances at δ 103, 134, 289, 361, 387, 401, 411, 470, 660, 680, 726, 749, 773, 789, and 804 ppm are found. The peaks from δ 660 to 804 ppm fall in the range associated with metal-bound and ring Se centers in the $[Pt(Se_4)_3]^{2-}$ ion,[12] another d^6 system, but in contrast to the chains that bridge the Ni atoms, the Se rings on the $[Pt(Se_4)_3]^{2-}$ ion are attached to a single Pt center. Ni^{IV} complexes are very rare, although those that have been reported often involve nickel–chalcogenide bonding. Dithio(seleno)carbamates (dtc and dsc) are capable of stabilizing Ni^{IV}, and crystal structures of $Ni(Bu_2dtc)_3Br$ and $Ni(Bu_2dsc)_3Br$ are known.[17-19] The isomaleonitrilediselenolate (imns = $Se_2C{=}C(CN)2$) ligand forms the Ni^{IV} complex $Ni(imns)_3{}^{2-}$.[20] In contrast to the dtc, dsc, and imns ligands, whose unsaturated character is thought to help stabilize the Ni^{IV} state, the Se^{2-}, $Se_3{}^{2-}$, and $Se_4{}^{2-}$ ligands are normally considered saturated and thus $[Ni_4Se_{23}]^{4-}$ represents a new type of Ni^{IV} complex.

In the structure[21] of the $[Ni_4Se_{23}]^{4-}$ anion shown in Figure 1, each Ni atom is in a distorted octahedral environment, being coordinated by three Se atoms in the cubane framework and by three Se atoms in rings that bridge to the other three Ni atoms. The two types of Ni^{IV}–Se distances differ slightly, with $Ni{-}Se_{cub}$ bonds averaging 2.362 (2) Å and $Ni{-}Se_{ring}$ bonds averaging 2.402 (2) Å. For comparison, the Ni^{II} center in $[Ni(Se_4)_2]^{2-}$ is square-planar and the Ni–Se bond lengths average 2.307 (6) Å.[8a] In the only other known Ni_4Se_4–cubane cluster, $Ni_4Se_4(PPh_3)_4$,[22] Ni^{II} is in a distorted tetrahedral environment; however, the Ni–Se distances were not reported. While the bridging $Se_3{}^{2-}$ chains appear to produce little strain on the present Ni_4Se_4 cubane core, the $Se_4{}^{2-}$ chain distorts it, as evidenced from the Ni–Ni distances, the $Se_{cub}{-}Se_{cub}$ distances, and the cubane bond angles. The $Se_4{}^{2-}$ chain bridges atoms Ni(2) and Ni(4) and pushes these Ni atoms away from each other. The Ni(2)–Ni(4) distance is 3.623 (9) Å, much longer than the 3.456 (8)–3.508 (8) Å range seen in the five other Ni–Ni distances. Conversely, the Se(2)–Se(3) distance at 3.031 (5) Å is significantly shorter than the five other $Se_{cub}{-}Se_{cub}$ distances (3.156 (6)–3.189 (6) Å). The Ni(2)–Se(2,3)–Ni(4) angles at 100.3 (3) and 100.0 (3)°, respectively, may be compared with the other $Ni{-}Se_{cub}{-}Ni$ cubane bond angles (94.1 (3)–96.6 (3)°). The Se(2)–Ni(2,4)–Se(3) angles (80.1 (2) and 79.5 (2)°, respectively) are more acute than the other $Se_{cub}{-}Ni{-}Se_{cub}$ angles (83.4 (2)–85.5 (2)°). Four of the five-membered Ni_2Se_3 rings are in the envelope conformation while that containing atoms Ni(3) and Ni(4) is between the envelope and half-chair conformations. The six-membered Ni_2Se_4 ring is in the chair conformation.

The driving force for the formation of $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)]\cdot NEt_4Cl$ is certainly not clear. While the cubane core is a familiar facet of coordination chemistry, the Ni^{IV} species is not. The formation of this compound illustrates the remarkable chemistry to be found in the soluble anions of the chalcogenides. The cyclic voltammetry of the present compound is being investigated, and a search is underway for similar reactions in other starting species.

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Supplementary Material Available: Positional parameters and isotropic thermal parameters for $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)]\cdot NEt_4Cl$ (2 pages). Ordering information is given on any current masthead page.

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(10) All attempts to make $[Ni_4Se_{23}]^{4-}$ exclusively by varying solvents and starting materials have yielded a mixture of products.

(11) (a) Anal. Calcd for $C_{40}H_{100}ClN_5Ni_4Se_{23}$: C, 17.55; H, 3.68; Cl, 1.29; N, 2.56; Ni, 8.58; Se, 66.34. Found: C, 17.27; H, 3.51; Cl, 1.21; N, 2.44; Ni, 8.33; Se, 66.50. (b) $[NEt_4]_2[Ni(Se_4)_2]$ was characterized with the use of ^{77}Se NMR spectroscopy and EDAX measurements on a scanning electron microscope. (c) The ^{77}Se NMR spectrum of the fibrous crystalline material is identical with that of $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)]\cdot NEt_4Cl$, but EDAX measurements do not show the presence of Cl. This product may be $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)]$. Attempts to grow crystals suitable for X-ray crystallography have been unsuccessful.

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(21) Crystal data for $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)]\cdot NEt_4Cl$: $C_{40}H_{100}ClN_5Ni_4Se_{23}$, monoclinic, $C_{2h}{}^5$-$P2_1/n$, $Z = 4$, a = 21.817 (4) Å, b = 14.319 (1) Å, c = 26.421 (5) Å, β = 112.69 (2)°, V = 7615 Å^3 at −120 °C. The material does not diffract well, and data collection was terminated at $\theta(Cu\ K\alpha_1)$ = 64.5°. Owing to crystal decomposition, data collection was rapid and redundant data were not collected. A linear correction for the approximately 20% decomposition that occurred was included with an analytical absorption correction. The final model, involving anisotropic thermal parameters for the anion and the chloride ion and isotropic thermal parameters for the cation, converged to $R(F) = 0.09$ for 433 variables and 4708 reflections having $F_o{}^2 > 3\sigma(F_o{}^2)$. The disordered $NEt_4{}^+$ ion of crystallization is responsible, in part, for the high R index.

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