Cocrystallized Mixtures and Multiple Geometries: Syntheses, Structures, and NMR Spectroscopy of the Re_6 Clusters $[NMe_4]_4[Re_6(Te_{8-n}Se_n)(CN)_6]$ ($n = 0-8$)

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Abstract: The mixed tellurium/selenium Re_6 clusters $[NMe_4]_4[Re_6(Te_{8-n}Se_n)(CN)_6]$ ($n = 0-8$) have been prepared from the reactions of Re_6Te_{15} with the appropriate stoichiometry of NaCN and Se at 600 °C, followed by cation exchange with NMe_4Br. A typical anion comprises an Re_6 octahedron with its eight faces capped by μ_3-chalcogen atoms to form a pseudocube, and each Re atom has a terminal cyanide ligand. These anions have essentially idealized cubic symmetry. In the $[Re_6Te_8(CN)_6]^{4-}$ anion, Re−Re bond distances range from 2.673(1) to 2.690(1) Å and Re−(μ_3-Te) distances range from 2.683(1) to 2.705(1) Å. In the $[Re_6Se_8(CN)_6]^{4-}$ anion the Re−Re and Re−(μ_3-Se) distances range from 2.622(2) to 2.638(2) Å and 2.520(3) to 2.550(3) Å, respectively. The "$[Re_6Te_{4.34}Se_{3.66}(CN)_6]^{4-}$" anion, with disordered Se/Te positions, displays intermediate bond distances with Re−Re distances ranging from 2.653(1) to 2.665(1) Å and Re−(μ_3-Q) (Q = Se, Te) distances ranging from 2.581(1) to 2.673(1) Å. Whereas single-crystal X-ray diffraction results provide the barest indication of the complicated nature of the mixed Te/Se crystalline products, NMR spectroscopy indicates that they comprise cations and mixtures of geometric isomers of $[Re_6(Te_{8-n}Se_n)(CN)_6]^{4-}$ anions (^{125}Te NMR (δ, ppm): $[NMe_4]_4[Re_6Te_8(CN)_6]$, −1112; $[NMe_4]_4[Re_6Te_7Se(CN)_6]$, ≥10 peaks, −643 to −1231; $[NMe_4]_4[Re_6Te_4Se_4(CN)_6]$, ≥18 peaks, −705 to −1234; $[NMe_4]_4[Re_6TeSe_7(CN)_6]$, ≥12 peaks, −648 to −1114. ^{77}Se NMR (δ, ppm): $[NMe_4]_4[Re_6TeSe_7(CN)_6]$, ≥8 peaks, 928 to 966; $[NMe_4]_4[Re_6Se_8(CN)_6]\cdot 3^1/_3H_2O$, 933).

Introduction

The Re_6 octahedron is a molecular building block that is seen throughout much of the chemistry of rhenium clusters. This chemistry has been studied extensively in recent years, with emphasis on compounds containing chalcogens or halides.[1−9] Typically, the eight faces of the Re_6 octahedron are capped by μ_3-ligands to form a pseudocube and each Re atom has a terminal ligand. A recent example illustrating these modes of ligation is $[Re_6Te_8(TeBr_2)_6]Br_2$;[10] no disorder occurs in the structure of the cationic Re^{III} cluster where there are eight μ_3-Te ligands and six $TeBr_2$ terminal ligands. The terminal ligands in some Re_6 clusters can also bridge clusters together to afford polymeric or three-dimensional structures. This is illustrated by the solid state compounds Re_6Te_{15}[11,12] and $Re_6Te_{16}Cl_{18}$.[13] Both of these structures are three-dimensional. In the former, the Re_6Te_8 pseudocubes are interconnected by terminal Te_7 ligands; in the latter each pseudocube is coordinated by a $Te_8Cl_{18}{}^{2-}$ ligand and in turn each $Te_8Cl_{18}{}^{2-}$ ligand chelates six $Re_6Te_8{}^{2+}$ clusters.

The structural chemistry of Re_6 clusters is often plagued with problems of disorder. As one example, the molecular cluster $Re_6Q_4X_{10}$ (Q = S, Se; X = Cl, Br)[2,14,15] consists of a Re_6 metal−metal bonded octahedron circumscribed by a Q_4X_4 cube with a terminal X atom bonded to each Re atom. Insofar as can be determined from single-crystal X-ray diffraction studies, each corner of the Q_4X_4 cube is 50% Q and 50% X. It is important to point out that such diffraction studies do not distinguish *geometrical* from *orientational* disorder.[16]

Some mixed chalcogen systems have been synthesized. For example, $Re_6Se_8Te_7$ has an ordered structure similar to that of Re_6Te_{15} ($Re_6Te_8(Te_7)$); Se atoms occupy all of the μ_3-capping positions, and the resultant Re_6Se_8 clusters are interconnected by Te_7 ligands.[5] But in mixed chalcogen systems there is the possibility of cocrystallized mixtures. Consider the Cs^+/K^+ salts of S/Te Re_6 octahedral clusters that were synthesized recently

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(1) Perrin, A.; Sergent, M. *New J. Chem.* **1988**, *12*, 337−356.

(2) Gabriel, J.-C.; Boubekeur, K.; Batail, P. *Inorg. Chem.* **1993**, *32*, 2894−2900.

(3) Yaghi, O. M.; Scott, M. J.; Holm, R. H. *Inorg. Chem.* **1992**, *31*, 4778−4784.

(4) Long, J. R.; Williamson, A. S.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 226−229.

(5) Harbrecht, B.; Selmer, A. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1861−1866.

(6) Huan, G.; Greaney, M.; Greenblatt, M. *Mater. Res. Bull.* **1988**, *23*, 905−912.

(7) Bronger, W.; Schuster, T. *Z. Anorg. Allg. Chem.* **1990**, *587*, 74−79.

(8) Lutz, H. D.; Müller, B.; Bronger, W.; Loevenich, M. *J. Alloys Compd.* **1993**, *190*, 181−184.

(9) Long, J. R.; McCarty, L. S.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4603−4616.

(10) Mironov, Y. V.; Pell, M. A.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 2709−2710.

(11) Klaiber, F.; Petter, W.; Hulliger, F. *J. Solid State Chem.* **1983**, *46*, 112−120.

(12) Fedorov, V. E.; Podberezskaya, N. V.; Mischenko, A. V.; Khudorozko, G. F.; Asanov, I. P. *Mater. Res. Bull.* **1986**, *21*, 1335−1342.

(13) Mironov, Y. V.; Pell, M. A.; Ibers, J. A., *Angew. Chem.* In press.

(14) Leduc, L.; Perrin, A.; Sergent, M.; Le Traon, F.; Pilet, J. C.; Le Traon, A. *Mater. Lett.* **1985**, *3*, 209−215.

(15) Fedorov, V. E.; Mischenko, A. V.; Kolesov, B. A.; Gubin, S. P.; Slovokhotov, Y. L.; Struchkov, Y. T. *Sov. J. Coord. Chem. (Engl. Transl.)* **1985**, *11*, 980−984.

(16) We use the term geometrical disorder to describe the disorder that results from the packing in the solid state of different geometric isomers, in this instance of individual cubes with different dispositions of the four Q and four X corners. We use the term orientational disorder to describe the disorder that results from the packing of a single geometric isomer in a variety of different orientations.

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Table 1. Crystal Data and Structure Refinement Details

compound	$[NMe_4]_4[Re_6Te_8(CN)_6]$ (**1**)	$[NMe_4]_4[Re_6Te_{4.34}Se_{3.66}(CN)_6]$ (**3**)	$[NMe_4]_4[Re_6Se_8(CN)_6]\cdot3^1/_3H_20$ (**5**)
formula	$C_{22}H_{48}N_{10}Re_6Te_8$	$C_{22}H_{48}N_{10}Re_6Se_{3.66}Te_{4.34}$	$C_{22}H_{54.666}N_{10}O_{3.333}Re_6Se_8$
fw	2590.70	2414.14	2261.65
a, Å	10.959(7)	10.947(5)	11.324(3)
b, Å	11.020(4)	10.945(5)	31.793(9)
c, Å	19.038(7)	18.814(8)	20.049(5)
β, deg	93.08(2)	93.24(3)	101.70(2)
V, Å^3	2296(2)	2250(2)	7068(3)
T, K	113(2)	113(2)	113(2)
Z	2	2	6
d(calcd), g/cm^3	3.748	3.563	3.188
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
λ, Å	0.7093 (Mo Kα_1)	0.7093 (Mo Kα_1)	1.54056 (Cu Kα_1)
μ, cm^{-1}	208	218	367
transm coeff	0.081−0.230	0.075−0.154	0.046−0.244
$R(F_o)$ $(F_o^2 > 2\sigma(F_o^2))$	0.0284	0.0384	0.0503
$R_w(F_o^2)$	0.0696	0.0833	0.1069

through the use of KSCN.[17] In the resultant products, CN^- ligands occupy all terminal positions and S^{2-} anions displace some or all of the Te^{2-} anions at the face caps. The diffraction data were interpreted in terms of the cocrystallization of the two chemically distinct anions, $[Re_6S_8(CN)_6]^{4-}$ and *trans*-$[Re_6S_6Te_2(CN)_6]^{4-}$, with the latter anion displaying two different orientations. This interpretation of the diffraction data may be deficient in view of the present work.

In the present paper, we describe the mixed Se/Te compounds $[NMe_4]_4[Re_6(Te_{8-n}Se_n)(CN)_6]$, where $n = 0$ (**1**), $n = 1$ (**2**), $n = 4$ (**3**), $n = 7$ (**4**), and $n = 8$ (**5**). These were synthesized through standard solid state techniques and were recrystallized after cation exchange. Compounds **1**, **3**, and **5** have been characterized by single-crystal X-ray diffraction techniques. The results on compound **3** led us to examine this series of compounds through the use of ^{77}Se and ^{125}Te NMR spectroscopies. The complications of cocrystallized mixtures, geometrical disorder, and orientational disorder are found.

Experimental Section

All starting materials were used as received. Re_6Te_{15} was prepared as described previously.[18] Elemental (CHN) microanalyses were performed by Oneida Research Services. Samples for ICP analyses for Re, Se, and Te were prepared by dissolving the compounds in a 2:1 mixture of concentrated NH_4OH and 30% H_2O_2; the resultant solutions were boiled for 20 min. Analyses were performed on a Thermo Jarrell Ash Atomscan 25 with the use of standards purchased from GFS Chemicals, Inc. NMR spectra were recorded at 0 or 20 °C with the use of a Varian 400 MHz Unity Plus spectrometer equipped with a 10 mm tunable broad-band probe and a deuterium lock. A sample was prepared by dissolving 0.100−0.130 g of the given compound in 3 mL of distilled H_2O or acetonitrile and filtering the solution just prior to data acquisition. ^{77}Se chemical shifts are referenced to an external Ph_2Se_2 standard at δ 460 ppm; ^{125}Te chemical shifts are referenced to an external Et_2Te standard at δ 380 ppm. ^{125}Te windows of ±3000 ppm and ^{77}Se windows of 0−2500 ppm were scanned.

$[NMe_4]_4[Re_6Te_8(CN)_6]$ (1). Re_6Te_{15} (0.600 g, 0.2 mmol) and NaCN (0.080 g, 1.6 mmol) were combined in a fused-silica tube that was evacuated to 10^{-4} Torr and sealed. The tube was held at 600 °C for 24 h and then cooled at a rate of 20 °C/h. The product, $Na_4[Re_6Te_8(CN)_6]$, was extracted from the reaction mixture with methanol (10 mL) and then precipitated by the addition of ether (20 mL). The precipitate was filtered and washed with ether. This precipitate (0.350 g of $Na_4[Re_6Te_8(CN)_6]$) and 0.150 g of NMe_4Br were dissolved in 15 mL of water. The solution was heated, reduced in volume to 5 mL, and cooled to 25 °C. After 24 h, dark red crystals of $[NMe_4]_4[Re_6Te_8(CN)_6]$ were separated by filtration and dried under vacuum. Yield: 0.320 g, 62%. ^{125}Te NMR (δ, ppm): −1112. IR (KBr, ν, cm^{-1}): 2086. Anal. Calcd for $C_{22}H_{48}N_{10}Re_6Te_8$: C, 10.20; H, 1.87; N, 5.41; Re, 43.12; Te, 39.40. Found: C, 10.17; H, 1.59; N, 5.28; Re, 45.90; Te, 40.1.

$[NMe_4]_4[Re_6Te_7Se(CN)_6]$ (2). Re_6Te_{15} (0.15 g, 0.050 mmol), Se (0.0049 g, 0.0506 mmol), and NaCN (0.019 g, 0.39 mmol) were combined and reacted as described above. Cation exchange followed the above procedure. Yield: 0.046 g, 37%. ^{125}Te NMR (δ, ppm): ≥10 peaks −643 to −1231. Anal. Calcd for $C_{22}H_{48}N_{10}Re_6SeTe_7$: Se, 3.10; Te, 24.56. Found: Se, 3.00; Te, 23.74.

$[NMe_4]_4[Re_6Te_4Se_4(CN)_6]$ (3). Re_6Te_{15} (0.2 g, 0.066 mmol), elemental Se (0.021 g, 0.27 mmol; Aldrich, 99.5%), and NaCN (0.027 g, 0.55 mmol) were employed. Yield: 0.060 g, 38%. ^{125}Te NMR (δ, ppm): ≥18 peaks −705 to −1234. IR (KBr, ν, cm^{-1}): 2095. Anal. Calcd for $C_{22}H_{48}N_{10}Re_6Se_4Te_4$: C, 11.03; H, 2.02; N, 5.85; Se, 13.18; Te, 21.30. Found: C, 10.96; H, 1.74; N, 5.64; Se, 10.60; Te, 22.70.

$[NMe_4]_4[Re_6TeSe_7(CN)_6]$ (4). Re_6Te_{15} (0.2 g, 0.066 mmol), elemental Se (0.042 g, 0.54 mmol), and NaCN (0.027 g, 0.55 mmol) were employed. Yield: 0.070 g, 46%. ^{77}Se NMR (δ, ppm): ≥8 peaks, 928 to 966; ^{125}Te NMR (δ, ppm): ≥12 peaks, −648 to −1114. IR (KBr, ν, cm^{-1}): 2107. Anal. Calcd for $C_{22}H_{48}N_{10}Re_6Se_7Te$: C, 11.74; H, 2.15; N, 6.23; Re, 49.65; Se, 24.56; Te, 5.67. Found: C, 11.49; H, 2.10; N, 6.09; Re, 50.40; Se, 25.86; Te, 5.50.

$[NMe_4]_4[Re_6Se_8(CN)_6]\cdot3^1/_3H_2O$ (5). Re_6Te_{15} (0.2 g, 0.066 mmol), Se (0.042 g, 0.54 mmol), and NaCN (0.019 g, 0.39 mmol) were employed to prepare $Na_4[Re_6Te_8(CN)_6]$). The conversion to the NMe_4^+ salt was carried out as described above. Overall yield: 0.062 g, 43%. ^{77}Se NMR (δ, ppm): 933. IR (KBr, ν, cm^{-1}): 2108. Anal. Calcd for $C_{22}H_{54.666}N_{10}O_{3.333}Re_6Se_8$: C, 11.68; H, 2.44; N, 6.19; Re, 49.40; Se, 27.93. Found: C, 11.79; H, 1.95; N, 5.96; Re, 52.14; Se, 29.40.

Crystallographic Studies. Preliminary crystallographic information for **1**, **3**, and **5** were obtained from Weissenberg photographs taken at 25 °C. Final unit cells were obtained at 113 K[19] from the setting angles of 33, 34, and 25 reflections, respectively, that had been centered on a Picker (**1** and **3**) or CAD4 (**5**) diffractometer. For each data collection, the intensities of six standard reflections, which were monitored every 100 reflections, exhibited no significant variations. Intensity data were processed and corrected for absorption.[20] Some crystallographic details are given in Table 1; more are available as Supporting Information. The structures were solved and refined with the use of the SHELXTL PC[21] crystallographic package. In these refinements, methyl hydrogen atoms were placed at calculated positions and the rotation angles were refined. The final refinements included displacement parameters for all non-hydrogen atoms and a secondary extinction parameter. For

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(17) Mironov, Y. V.; Virovets, A. V.; Fedorov, V. E.; Podberezskaya, N. V.; Shishkin, O. V.; Struchkov, Y. T. *Polyhedron* **1995**, *14*, 3171−3173.

(18) Opalovskii, A. A.; Fedorov, V. E.; Erenburg, B. G.; Lobkov, E. U.; Vasil'ev, Y. V.; Senchencko, L. N.; Tsikanovskii, B. I. *Russ. J. Phys. Chem. (Engl. Transl.)* **1971**, *45*, 1197.

(19) Huffman, J. C. Ph.D. Dissertation, Indiana University, 1974.

(20) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014−1018.

(21) Sheldrick, G. M. SHELXTL PC Version 5.0 An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1994.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for the Anion of $[NMe_4]_4[Re_6Te_8(CN)_6]$ (**1**)

atom	*x*	*y*	*z*	U_{eq} (Å^2)[a]
Re(1)	0.09893(3)	0.92865(3)	0.573338(13)	0.01031(7)
Re(2)	0.11706(3)	1.12528(3)	0.491674(13)	0.01045(7)
Re(3)	0.08146(3)	0.90552(3)	0.433377(13)	0.01023(7)
Te(1)	0.06207(5)	0.70717(4)	0.51471(2)	0.01399(10)
Te(2)	0.13639(4)	1.14837(4)	0.63214(2)	0.01375(10)
Te(3)	−0.09948(5)	0.89851(4)	0.64918(2)	0.01413(10)
Te(4)	0.29907(4)	0.96038(5)	0.49908(2)	0.01411(11)
C(1)	0.2099(7)	0.8487(7)	0.6537(3)	0.0143(14)
N(1)	0.2710(6)	0.8020(7)	0.6978(3)	0.022(2)
C(2)	0.2456(7)	1.2660(7)	0.4824(4)	0.016(2)
N(2)	0.3143(7)	1.3442(7)	0.4770(4)	0.029(2)
C(3)	0.1764(7)	0.8042(7)	0.3602(4)	0.018(2)
N(3)	0.2288(7)	0.7497(6)	0.3189(3)	0.0214(14)

[a] U_{eq} is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for the Anion of $[NMe_4]_4[Re_6Te_{4.34}Se_{3.66}(CN)_6]$ (**3**)

atom	*x*	*y*	*z*	U_{eq} (Å^2)	occupancy
Re(1)	0.09851(4)	0.92965(4)	0.57378(2)	0.01134(11)	1
Re(2)	0.11528(4)	1.12595(4)	0.49173(2)	0.01195(11)	1
Re(3)	0.08133(4)	0.90647(4)	0.43313(2)	0.01140(11)	1
Te(1)	0.06324(8)	0.70955(8)	0.51456(5)	0.0189(3)	0.666(9)
Se(1)	0.06324(8)	0.70955(8)	0.51456(5)	0.0189(3)	0.334(9)
Te(2)	0.13267(8)	1.14677(8)	0.63006(5)	0.0184(3)	0.503(9)
Se(2)	0.13267(8)	1.14677(8)	0.63006(5)	0.0184(3)	0.497(9)
Te(3)	−0.09533(9)	0.90079(9)	0.64499(6)	0.0185(3)	0.298(9)
Se(3)	−0.09533(9)	0.90079(9)	0.64499(6)	0.0185(3)	0.702(9)
Te(4)	0.29579(8)	0.96285(8)	0.49930(5)	0.0192(3)	0.705(9)
Se(4)	0.29579(8)	0.96285(8)	0.49930(5)	0.0192(3)	0.295(9)
C(1)	0.2094(10)	0.8491(11)	0.6555(6)	0.016(2)	1
N(1)	0.2728(9)	0.8041(9)	0.7000(5)	0.026(2)	1
C(2)	0.2447(10)	1.2671(11)	0.4823(6)	0.022(3)	1
N(2)	0.3125(9)	1.3470(10)	0.4772(6)	0.029(3)	1
C(3)	0.1777(10)	0.8046(10)	0.3587(6)	0.017(2)	1
N(3)	0.2312(8)	0.7505(9)	0.3184(5)	0.019(2)	1

compound **3**, the Te/Se occupancy was refined at each of the four μ_3-Te/-Se capping positions. The resultant composition is $[NMe_4]_4[Re_6Te_{4.34(2)}Se_{3.66(2)}(CN)_6]$. No unusual features were observed in the final difference electron density maps. Positional parameters for anions of **1**, **3**, and **5** are given in Tables 2, 3, and 4, respectively; additional crystallographic tabulations are in the Supporting Information.

X-ray Powder Diffraction Measurements. X-ray powder diffraction patterns of $[NMe_4]_4[Re_6(Te_{8-n}Se_n)(CN)_6]$, where $n = 0$ (**1**), $n = 1$ (**2**), $n = 4$ (**3**), $n = 7$ (**4**), and $n = 8$ (**5**), were obtained with the use of Cu radiation and a Rigaku diffractometer from samples derived solely from crystalline products after cation exchange. Theoretical powder diffraction patterns for **1**, **3**, and **5** were calculated with the use of the program XPOW of the SHELXTL-PC program package.[21] The unit cell change (Table 1) from that of $[NMe_4]_4[Re_6Te_8(CN)_6]$ (**1**) to that of $[NMe_4]_4[Re_6Se_8(CN)_6]\cdot 3^1/_3H_2O$ (**5**) occurs at approximately $n = 5$. The samples are homogenous and are not mixtures of the two cell types.

Results

Syntheses. Re_6Te_{15} reacts with NaCN to form the salt $Na_4[Re_6Te_8(CN)_6]$:

$$Re_6Te_{15} + 6NaCN \rightarrow Na_4[Re_6Te_8(CN)_6] + Na_2Te_y + (7 - y)Te \quad (1)$$

Re_6Te_{15} reacts with a mixture of Se and NaCN to give the salts $Na_4[Re_6Te_{8-n}Se_n(CN)_6]$:

$$Re_6Te_{15} + n\mathrm{Se} + 6\ NaCN \rightarrow Na_4[Re_6Te_{8-n}Se_n(CN)_6] + Na_2Te_y + (7 - y + n)Te \quad (2)$$

Table 4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for the Anion of $[NMe_4]_4[Re_6Se_8(CN)_6]\cdot 3^1/_3H_2O$ (**5**)

atom	*x*	*y*	*z*	U_{eq} (Å^2)
Re(1)	0.89674(9)	−0.01436(3)	1.05794(5)	0.0147(3)
Re(2)	1.06877(9)	−0.05328(3)	1.01168(5)	0.0147(3)
Re(3)	0.88699(9)	−0.01950(3)	0.92575(5)	0.0148(3)
Re(4)	0.34098(10)	−0.30318(3)	1.03515(5)	0.0191(3)
Re(5)	0.37971(10)	−0.36956(3)	0.96364(5)	0.0169(3)
Re(6)	0.55398(9)	−0.32914(3)	0.92160(5)	0.0171(3)
Re(7)	0.51469(10)	−0.26270(3)	0.99277(5)	0.0184(3)
Re(8)	0.33665(9)	−0.29571(3)	0.90409(5)	0.0168(3)
Re(9)	0.55858(9)	−0.33620(3)	1.05277(5)	0.0184(3)
Se(1)	1.0758(2)	−0.04638(7)	1.13825(11)	0.0173(6)
Se(2)	0.8577(2)	−0.08351(7)	0.99472(11)	0.0167(6)
Se(3)	1.0565(2)	−0.05643(7)	0.88402(11)	0.0165(6)
Se(4)	1.2749(2)	−0.01896(7)	1.02728(11)	0.0167(6)
Se(5)	0.7222(2)	−0.29610(7)	1.00876(12)	0.0204(6)
Se(6)	0.1729(2)	−0.33547(7)	0.94681(12)	0.0195(6)
Se(7)	0.3870(2)	−0.37399(7)	1.09083(12)	0.0211(6)
Se(8)	0.5906(2)	−0.39912(7)	0.98184(12)	0.0193(6)
Se(9)	0.5077(2)	−0.25772(7)	0.86569(12)	0.0197(6)
Se(10)	0.3030(2)	−0.23304(7)	0.97552(12)	0.0193(6)
Se(11)	0.3771(2)	−0.35989(7)	0.83808(12)	0.0205(6)
Se(12)	0.5164(2)	−0.27191(7)	1.11817(12)	0.0223(6)
N(1)	0.729(2)	−0.0406(6)	1.1653(10)	0.031(5)
N(2)	1.185(2)	−0.1465(6)	1.0428(9)	0.026(5)
N(3)	0.693(2)	−0.0549(6)	0.7952(10)	0.035(5)
N(4)	0.153(2)	−0.2831(7)	1.1371(11)	0.044(6)
N(5)	0.267(2)	−0.4636(6)	0.9284(9)	0.028(5)
N(6)	0.747(2)	−0.3559(6)	0.8291(10)	0.032(5)
N(7)	0.635(2)	−0.1695(6)	1.0159(9)	0.031(5)
N(8)	0.137(2)	−0.2603(7)	0.7789(11)	0.043(6)
N(9)	0.762(2)	−0.3738(7)	1.1776(11)	0.044(6)
N(10)	−0.050(2)	−0.3642(6)	0.7004(9)	0.029(5)
N(11)	0.936(2)	−0.4022(6)	1.3859(9)	0.030(5)
N(12)	−0.021(2)	−0.0061(6)	0.6637(9)	0.025(5)
N(13)	1.429(2)	−0.3099(6)	0.6460(9)	0.029(5)
N(14)	−0.487(2)	0.0795(5)	0.4303(9)	0.022(4)
N(15)	−0.876(2)	0.1922(7)	1.1612(11)	0.043(6)
C(1)	0.786(2)	−0.0328(7)	1.1261(11)	0.022(6)
C(2)	1.145(2)	−0.1123(7)	1.0282(11)	0.027(6)
C(3)	0.757(2)	−0.0417(6)	0.8406(10)	0.007(5)
C(4)	0.221(2)	−0.2892(7)	1.0991(12)	0.032(6)
C(5)	0.304(2)	−0.4307(7)	0.9440(12)	0.028(6)
C(6)	0.676(2)	−0.3436(7)	0.8602(12)	0.031(6)
C(7)	0.590(2)	−0.2034(6)	1.0077(10)	0.015(5)
C(8)	0.209(2)	−0.2727(7)	0.8239(11)	0.020(5)
C(9)	0.686(2)	−0.3606(7)	1.1337(12)	0.033(6)

These salts are very soluble in water and methanol; they are easily separated from the reaction mixtures by extraction with methanol. The substitution of Se for Te in the $[Re_6Te_{8-n}Se_n(CN)_6]^{4-}$ anions is dependent upon both Se/Te and Se/NaCN stoichiometry. This has been previously observed in $[Re_6Te_{8-n}S_n(CN)_6]^{4-}$ cluster chemistry.[17,22] The preparation of $Na_4[Re_6Se_8(CN)_6]$ ($n = 8$) requires the use of an excess of 2 equiv of Se compared to NaCN. If an equimolar ratio of Se and NaCN is used, the composition $Na_4[Re_6TeSe_7(CN)_6]$ is obtained. NMe_4^+ salts were obtained by cation exchange with NMe_4Br in water. The resultant compounds form as dark-red, air-stable crystals.

Structures. The structures of compounds **1**, **3**, and **5** are not identical. Whereas **3** shows the cell contraction from **1** expected for substitution of Se for Te, **5** crystallizes in a different cell. The crystal structures of **1** and **3** consist of the packing of two cations and two anions in the unit cell. Each anion has a crystallographically imposed center of symmetry. The ions are well packed. For example, the minimum cation−anion contact in **1** is 2.43 Å between atoms N(1) and H(54C). The

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(22) Slougui, A.; Mironov, Y. V.; Perrin, A.; Fedorov, V. E. *Croat. Chem. Acta* **1995**, *68*, 885−890.

Table 5. Summary of Bond Distances and Angles for the $[Re_6Te_{8-n}Se_n(CN)_6]^{4-}$ and Related Anions

anion	Re−Re (Å) (mean)	Re−Q (Å) (mean)	Re−C (Å) (mean)	Re−Q−Re (deg) (mean)
$[Re_6Te_8(CN)_6]^{4-}$ (**1**)	2.673(1)−2.690(1) (2.681(3))	2.683(9)−2.705(1) (2.694(2))	2.097(7)−2.109(8) (2.103(4))	59.36(3)−60.02(2) (59.71(6))
$[Re_6Te_{4.34}Se_{3.66}(CN)_6]^{4-}$ (**3**)	2.653(1)−2.665(1) (2.658(2))	2.581(1)−2.673(1) (2.625(6))	2.098(1)−2.118(1) (2.109(6))	59.72(4)−61.99(3) (60.66(18))
$[Re_6Se_8(CN)_6]^{4-}$ (**5**)	2.622(2)−2.638(2) (2.633(1))	2.520(3)−2.550(3) (2.533(1))	2.06(2)−2.14(2) (2.09(1))	62.22(7)−63.02(7) (62.64(3))
$[Re_6S_6(Te_{0.66}S_{0.34})_2(CN)_6]^{4-}$ [a]	2.615(2)−2.630(2) (2.623(8))	2.423(9)−2.675(6) (2.490(5))	2.10(4)	
$[Re_6S_8(CN)_6]^{4-}$ [b]	2.601(1)−2.611(1) (2.606(5))	2.402(4)−2.593(3) (2.460(5))	2.125(2)	

[a] Reference 17. [b] Reference 22.

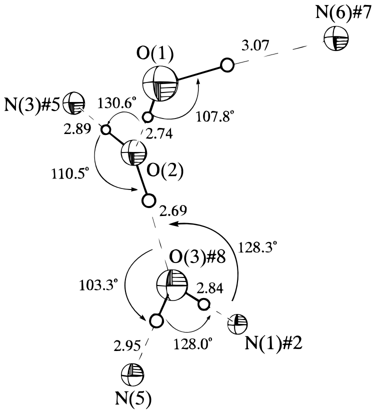

Figure 1. Part of the hydrogen-bonding network in **5** showing O−H···O and O−H···N interactions.

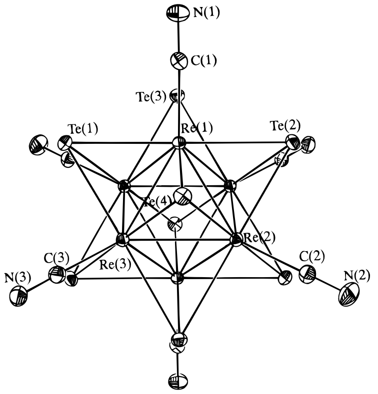

Figure 2. A $[Re_6Te_8(CN)_6]^{4-}$ anion. This anion has a crystallographically imposed center of symmetry. Displacement ellipsoids are drawn at the 50% level.

asymmetric unit of the crystal structure of **5** comprises six cations, one anion with a crystallographically imposed center of symmetry, one anion with no imposed symmetry, and five water molecules. The unit cell thus contains four units of formula $[NMe_4]_6[Re_6Se_8(CN)_6]_{1.5}\cdot 5H_2O$. For ease of discussion, we describe this compound **5** as $[NMe_4]_4[Re_6Se_8(CN)_6]\cdot 3^1/_3H_2O$. In **5** the anions are interlinked through extensive hydrogen-bonding networks. One such network, which involves three water molecules, is shown in Figure 1.

Although there are some variations, idealized cubic symmetry is essentially found for these anions. The structure of the $[Re_6Te_8(CN)_6]^{4-}$ anion, typical for this series, is shown in Figure 2. In this anion, Re−Re bond distances range from 2.673(1) to 2.690(1) Å and Re−(μ_3-Te) distances range from 2.683(1) to 2.705(1) Å. In the $[Re_6Se_8(CN)_6]^{4-}$ anion, the Re−Re and Re−(μ_3-Se) distances range from 2.622(2) to 2.638(2) Å and 2.520(3) to 2.550(3) Å, respectively. The $[Re_6Te_{4.34}Se_{3.66}(CN)_6]^{4-}$ anion, as expected, displays intermediate bond distances with Re−Re distances ranging from 2.653(1) to 2.665(1) Å and Re−(μ_3-Q) (Q = Se, Te) distances ranging from 2.581(1) to 2.673(1) Å. Other trends may be discerned from Table 5, where metrical data on related anions are also presented.

NMR Spectroscopy. ^{125}Te resonances of the various Re_6 clusters are localized between −643 and −1269 ppm; peaks were not found in any other spectral windows. ^{77}Se resonances are found at approximately 900 ppm, the region expected for Se atoms bound to a low d-count metal, in this instance d^4 Re^{III}.[23] Consistent with its idealized cubic symmetry the $[Re_6Te_8(CN)_6]^{4-}$ anion of **1** gives rise to a single ^{125}Te resonance at −1112 ppm. This singlet is observed at the same shift for both the Na^+ and NMe_4^+ cations, suggesting that there is no significant ion pairing in solution. Similarly, the $[Re_6Se_8(CN)_6]^{4-}$ anion of **5** gives rise to a single ^{77}Se resonance at 933 ppm. Figure 3 shows the geometrical isomers of the anions $[Re_6Te_{8-n}Se_n]^{4-}$, $n = 0$ to 4, with the number of ^{125}Te (T) and ^{77}Se (S) resonances expected if idealized symmetry is maintained. NMR spectra for products that correspond by reaction stoichiometry to $[Re_6Te_8(CN)_6]^{4-}$, $[Re_6Te_7Se(CN)_6]^{4-}$, $[Re_6Te_4Se_4(CN)_6]^{4-}$, $[Re_6TeSe_7(CN)_6]^{4-}$, and $[Re_6Se_8(CN)_6]^{4-}$ are summarized in Table 6.

Clearly, many more resonances are observed than were expected. Samples of $[NMe_4]_4[Re_6Te_8(CN)_6]$ and $[NMe_4]_4[Re_6Se_8(CN)_6]$ were dissolved together in water or in acetonitrile and allowed to stir for several days. These solutions exhibited only the single ^{125}Te and ^{77}Se resonances expected for the pure substances. Thus, intermolecular chalcogen exchange does *not* occur in these systems and is not the explanation for the abundance of resonances. Rather, we are dealing with cocrystallized mixtures and multiple geometric isomers. Thus, consider the observation of at least 18 ^{125}Te resonances for the NMe_4^+ salt of the "Te_4Se_4" anion. If the compound were pure but a mixture of all possible geometrical isomers, then from Figure 3 we would anticipate at most 10 resonances. Clearly, the $[NMe_4]_4[Re_6Te_4Se_4(CN)_6]$ product is a mixture of compounds. In order to obtain greater solubility in nonaqueous media of the $[Re_6Te_4Se_4(CN)_6]^{4-}$ anion and a higher resolution ^{125}Te spectrum, we exchanged the Na^+ cations with $[N(n\text{-}Bu)_4]^+$ cations. Figure 4 shows a ^{125}Te spectrum of $[N(n\text{-}Bu)_4]_4[Re_6Te_4Se_4(CN)_6]$ in acetonitrile at 20 °C. This spectrum provides the clear resolution of 33 resonances. This indicates that the mixture is not limited to the Te_4Se_4, Te_5Se_3, and Te_3Se_5 compounds but must extend to include at least seven of the nine possible compounds as most if not all of their geometric isomers. The maximum number of resonances for all nine Te-containing compounds in all possible geometries is 40.

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(23) Several attempts were made to obtain the ^{77}Se NMR from highly concentrated solutions containing $[Re_6Te_7Se(CN)_6]^{4-}$ and $[Re_6Te_4Se_4(CN)_6]^{4-}$. However, we were unsuccessful owing to the smaller number of Se atoms and the lower NMR sensitivity of the ^{77}Se nucleus relative to ^{125}Te.

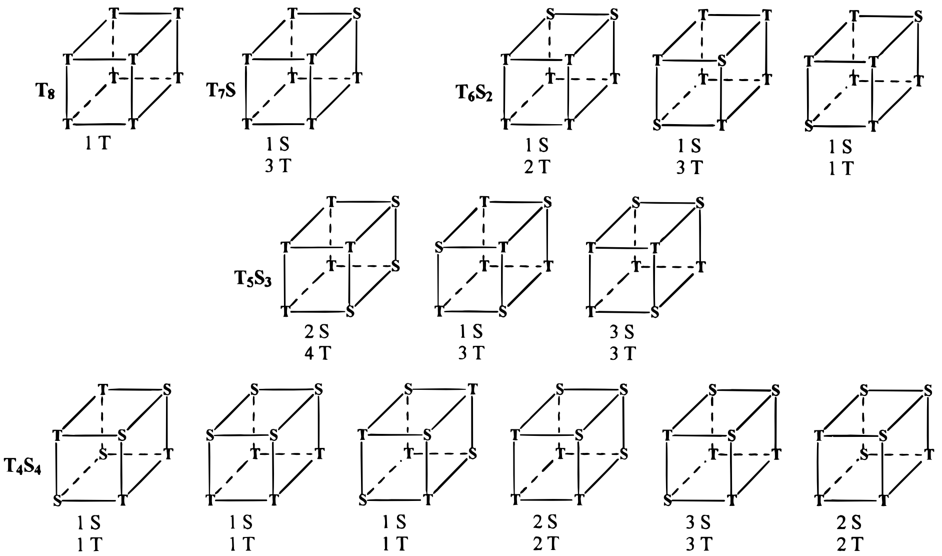

Figure 3. Geometric isomers of $[Re_6Te_{8-n}Se_n(CN)_6]^{4-}$ ($n = 0-4$). For each isomer the numbers of possible Te (T) and Se (S) resonances are shown.

Table 6. Comparison of ^{125}Te and ^{77}Se NMR Resonances for $[NMe_4]_4[Re_6Te_{8-n}Se_n(CN)_6]$ (n = 0, 1, 4, 7, 8)

	^{125}Te			^{77}Se		
anion	no. of peaks	range	primary resonances	no. of peaks	range	primary resonances
$[Re_6Te_8(CN)_6]^{4-}$ **(1)**	1	−1112	−1112			
$[Re_6Te_7Se(CN)_6]^{4-}$ **(2)**	10	−643 to −1231	−1112 −1173 −996			
$[Re_6Te_4Se_4(CN)_6]^{4-}$ **(3)**	18[a]	−705 to −1234	−1112 −1054 −993 −943			
$[Re_6TeSe_7(CN)_6]^{4-}$ **(4)**	12	−648 to −1114	−1055 −946 −898	8	928 to 966	930
$[Re_6Se_8(CN)_6]^{4-}$ **(5)**				1	933	933
$[N(n\text{-}Bu)_4]_4[Re_6Te_4Se_4(CN)_6]$	33	−898 to −1269	−1155 −1104 −1044 −999			

[a] As the N(n-Bu)$_4$ salt, this anion shows 33 resonances; see Figure 4.

Discussion

While the determination of composition through the use of single-crystal X-ray data and the refinement of site occupancies has become more common, it is fraught with dangers.[24] In the ideal instance of error-free data, independent knowledge of the elements present in the chosen crystal, and a simple structure in which the question to be answered is the amount of a given element at a specific site, such a determination can provide reliable information on stoichiometry that would be difficult to obtain otherwise. To extrapolate from the composition of the chosen crystal to the composition of the bulk remains very risky. In the nonideal instance of X-ray data improperly corrected for absorption, extinction, and other systematic errors, no independent knowledge of the elements present, and a complex structure for which more ambitious questions are posed, such a determination of stoichiometry can be deceiving at best. We illustrated this point earlier in the somewhat simpler example of the $[M(Te_nSe_{8-n})]^{2-}$ ($n = 0-4$) (M = Zn, Cd, Hg) system.[25] However, consider the more complicated present determination of a crystal of nominal composition $[NMe_4]_4[Re_6(Te_{8-n}Se_n)(CN)_6]$, n = 4 (**3**). From the X-ray data the refinement of site occupancies leads to n = 3.66(2). Note the reasonable agreement between nominal and "actual" composition, especially if one ignores the deceptively low standard deviation on n and the dubious assumptions made in the determination, for example

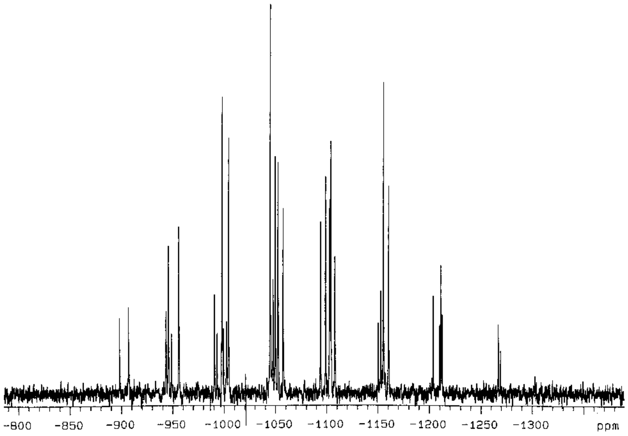

Figure 4. ^{125}Te spectrum of $[N(n\text{-}Bu)_4]_4[Re_6Te_4Se_4(CN)_6]$ (acetonitrile, 20 °C).

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(24) Mitchell, J. F.; Burdett, J. K.; Keane, P. M.; Ibers, J. A.; DeGroot, D. C.; Hogan, T. P.; Schindler, J. L.; Kannewurf, C. R. *J. Solid State Chem.* **1992**, *99*, 103−109.

(25) Bollinger, J. C.; Ibers, J. A. *Inorg. Chem.* **1995**, *34*, 1859−1867.

that the Se and Te atoms at a given site have the same positional and thermal parameters. There are three ways in which this Te/Se disorder at the cube corners can come about: cocrystallization of different compounds, geometrical disorder, and orientational disorder. There is the possibility of the cocrystallization of $[NMe_4]_4[Re_6(Te_{8-n}Se_n)(CN)_6]$, where $n = 0$, 1, 2,...8. While the crystal unit cell changes at around $n = 5$ as the result of inclusion of water molecules in the cell, this may not occur when small amounts of $n > 5$ are imbedded, so to speak, in a milieu of $n = 4$. Thus, there are nine possible chemical species. There are 21 different geometric isomers among these nine species (Figure 3). And finally, any given Re_6Q_8 cube is capable of up to eight different orientations if one assumes that substitution of Se for Te in this inner core of the $[Re_6Q_8(CN)_6]^{4-}$ anion has no effect on orientation. As was illustrated above, NMR spectroscopy on solutions of these materials provides information on geometrical and compositional variations but, of course, not on orientational disorder (which will disappear in solution). Indeed, the spectra, although too complex to defy quantitative interpretation, are consistent with the presence of multiple species and geometric isomers. The refinement of the X-ray data has provided the barest indication of such complexities, since the site occupancies at the four μ_3-Te/-Se capping positions are unequal (Table 3). The refinement is not capable of distinguishing among these three ways that lead to the disorder and hence has told us nothing of chemical or structural significance!

Although Re_6Te_{15}, with its $[Re_6(\mu_3\text{-}Te)_8]^{2+}$ core, was employed as a starting material in the syntheses described above, many syntheses of Re_6 clusters begin with other sources of Re, including $ReCl_5$[10] or even Re metal.[26] Consequently, Re_6 clusters are readily formed and are stable. In the present instance of a Re_6Te_{15}/NaCN reaction mixture, we speculate that the Re_6Te_{15} three-dimensional structure, containing as it does $[Re_6Te_8]$ clusters bridged by Te_7 units, breaks apart, the CN^- ions replacing the bridges to afford isolated $[Re_6Te_8(CN_6]^{4-}$ anions; the Te_7 ligands form a polytelluride flux. If Se is added to this reaction mixture in sufficient excess compared with Te and NaCN, then the μ_3-Te face-capping ligands are replaced by μ_3-Se ligands to form $[Re_6Se_8(CN)_6]^{4-}$ anions. Under other conditions, as we demonstrated above, a mixture of $[Re_6Te_{8-n}Se_n(CN)_6]^{4-}$ anions forms. That a mixture results implies that there is no clear preference for Se over Te in the face-capping positions. This lack of preference would also lead to different geometric isomers for a given $[Re_6(Te_{8-n}Se_n)(CN)_6]^{4-}$ molecular unit. Even when the μ_3-capping atoms are very different, as in the $[Re_6Q_4X_4]^{6+}$ core,[2,14,15] the Q/X positions are found to be statistically distributed. Whether this results from geometrical disorder or orientational disorder or both is not known. It appears that distinctly different terminal ligands on the Re atoms, as in $Re_6(\mu_3\text{-}Te)_6(\mu_3\text{-}Cl)_2Cl_4(TeCl_2)_2$,[10] are necessary to bring about an ordered arrangement of μ_3-capping atoms.

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Supporting Information Available: Tables of crystallographic details, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates (30 pages). See any current masthead page for ordering and Internet access instructions.

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(26) Bronger, W.; Loevenich, M.; Schmitz, D.; Schuster, T. *Z. Anorg. Allg. Chem.* **1990**, *587*, 91−102.