Inorg. Chem. **1993,** *32,* 3923-3927

Chalcogenide Substitution Reactions

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Received January 5, 1993

The feasibility of preparing tellurometalates from selenometalates has been demonstrated by the preparation of the compounds $[PPh_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ and $[PPh_4]_4[Pt_4Te_4(Te_3)_6]$ from the reactions in DMF of $TePEt_3$ with $[PPh_4]_2[Ni(Se_4)_2]$ and $[PPh_4]_2[Pt(Se_4)_3]$, respectively. The NEt_4^+ salt of the $[Pt_4Te_4(Te_3)_6]^{4-}$ ion could also be isolated from the reaction of $Pt(xan)_2$ with Li_2Te and Te in DMF. The anion $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ has a Ni_4Te_4 cubane core, with pairs of Te_2^{2-} chains bridging Ni^{IV} atoms on opposite faces of the core and four Te_3^{2-} chains bridging the Ni^{IV} atoms on the remaining cubane faces. The anion $[Pt_4Te_4(Te_3)_6]^{4-}$ possesses a Pt_4Te_4 cubane core and has six Te_3^{2-} chains bridging Pt^{IV} atoms on the cubane faces. In the cubane anions each metal atom is in a distorted octahedral environment, being coordinated by three Te atoms in the cubane framework and by three Te atoms in chains that bridge to the other three metal atoms. Unit cell data (−163 °C): $[PPh_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$, space group D_{2d}^{8}-$P\bar{4}n2$, $a = 18.925(3)$ Å, $c = 17.155(3)$ Å, $V = 6144(2)$ Å^3, $Z = 2$; $[PPh_4]_4[Pt_4Te_4(Te_3)_6]$, space group C_{3v}^{6}-$R3c$, $a = 27.024(3)$ Å, $\alpha = 59.91(2)°$, $V = 13954(3)$ Å^3, $Z = 4$; $[NEt_4]_4[Pt_4Te_4(Te_3)_6]\cdot 2DMF$, space group C_{2h}^{5}-$P2_1/c$, $a = 15.685(3)$ Å, $b = 40.103(8)$ Å, $c = 15.330(3)$ Å, $\beta = 119.10(3)°$, $V = 8426(3)$ Å^3, $Z = 4$.

Introduction

The chemistry of chalcogen-containing compounds has been the object of considerable interest over the last 25 years.[1–7] Several different sources of chalcogen have been used to make soluble chalcogen-containing compounds. The simplest sources are the elements, which are reduced by another reactant to Q^{2-} (Q = S, Se, Te).[8,9] The most common source is a solution of polychalcogenide, Q_n^{2-},[10–12] prepared by dissolving hydrogen chalcogenide or an alkali metal chalcogenide and elemental chalcogen in NH_3(l), DMF, THF, CH_3CN, or other solvents. Chalcogen delivery agents, such as phosphines, QPR_3,[13,14] and organotrisulfides, $(RS)_2S$,[15] have also been used. In addition, silyls, $(R_3Si)_2Q$,[16–18] have been employed, generally to replace O or Cl with S, Se, or Te. In an important variation on this approach[19] $SePPh_3$ was used to replace three S atoms from $[M_3S(S_2)_3X_6]^{2-}$ with Se atoms to form $[M_3S(SSe)_3X_6]^{2-}$ (M = Mo, W; X = Cl, Br):

$$[M_3S(S_2)_3X_6]^{2-} + 3SePPh_3 \rightarrow [M_3S(SSe)_3X_6]^{2-} + 3Ph_3PS \quad (1)$$

Is this a general reaction among soluble metal chalcogenides? Since $TePPh_3$ does not exist, we initiated reactivity studies of $TePEt_3$ with selenometalates, anticipating success in converting selenides to tellurides in the Ni triad because stable tellurides of that triad, i.e. $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$)[20] and $[Pd(Te_4)_2]^{2-}$,[21,22] have been prepared by other routes. We chose $[Ni(Se_4)_2]^{2-}$ [11] and $[Pt(Se_4)_3]^{2-}$ [23] as starting materials owing to their structural simplicity and ease of preparation. We expected to prepare $[Ni(Te_4)_2]^{2-}$ and $[Pt(Te_4)_3]^{2-}$. Not only was substitution of Se by Te successful but also structural rearrangement occurred to afford the $[PPh_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ and $[PPh_4]_4[Pt_4Te_4(Te_3)_6]$ cubanes. This paper reports this chemistry as well as the synthesis of $[NEt_4]_4[Pt_4Te_4(Te_3)_6]$ by a different route.

Experimental Section

All manipulations were carried out under N_2 with the use of standard Schlenk-line techniques. Solvents were distilled, dried, and degassed before use. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY, and G. D. Searle & Co., Skokie, IL. Li_2Te was prepared from the stoichiometric reaction of Li and Te in liquid NH_3. $[Ni(Se_4)_2]^{2-}$,[11] $[Pt(Se_4)_3]^{2-}$,[23] $Pt(xan)_2$,[24] and $TePEt_3$[25] were prepared by published methods.

Preparation of $[PPh_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ (1). $TePEt_3$ (197 mg, 0.8 mmol) dissolved in 5 mL of DMF was added to a solution of $[PPh_4]_2[Ni(Se_4)_2]$ (137 mg, 0.1 mmol) in 5 mL of DMF. The solution was stirred for 2 h and filtered. Next toluene (15 mL) was layered on top of the filtrate. Black crystals of **1** formed overnight (16 mg, 16% yield). Anal. Calc for $C_{96}H_{80}P_4Ni_4Te_{20}$: C, 27.82; H, 1.95; P, 2.99. Found: C, 27.45; H, 1.88; P, 2.79.

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Table I. Crystallographic Details

compd	$[PPh_4]_4[Ni_4Te_{20}]$ (**1**)	$[NEt_4]_4[Pt_4Te_{22}]\cdot 2DMF$ (**3**)
formula	$C_{96}H_{80}P_4Ni_4Te_{20}$	$C_{38}H_{94}N_6O_2Pt_4Te_{22}$
fw	4144	4255
a, Å	18.925(3)	15.685(3)
b, Å	18.925(3)	40.103(8)
c, Å	17.155(3)	15.330(3)
β, deg	90.00	119.10(3)
V, Å^3	6144(2)	8426(3)
Z	2	4
d(calcd), g/cm^3	2.240	3.354
space group	D^8_{2d}-$P\bar{4}n2$	C^5_{2h}-$P2_1/c$
t, °C	−163	−163
λ, Å	0.7093 (Mo Kα_1)	0.7093 (Mo Kα_1)
μ, cm^{-1}	53.6	142.1
transm coeff	0.557–0.645	0.051–0.464
$R(F_o)$ $(F_o^2 > 2\sigma(F_o^2))^a$	0.062	0.066
$R_w(F_o^2)$ (all data)	0.143	0.136

^{a} The threshold $F_o^2 > 2\sigma(F_o^2)$ was used only for computing *R* on F_o; all data were used in the refinement and in computing *R* on F_o^2.

Table II. Cubane Atomic Positions and Equivalent Isotropic Thermal Parameters for $[PPh_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ (**1**)

atom	*x*	*y*	*z*	U_{eq},^{a} Å^2
Ni	−0.961 6(2)	0.087 3(2)	−0.083 0(2)	0.045(2)
Te(1)	−0.917 35(9)	−0.038 25(10)	−0.066 38(11)	0.0487(13)
Te(11)	−1.002 59(10)	0.072 02(10)	−0.227 55(11)	0.0586(14)
Te(21)	−0.837 24(10)	0.136 71(10)	−0.111 15(12)	0.0552(13)
Te(22)	−0.777 86(10)	0.134 79(11)	0.033 75(12)	0.0599(13)
Te(23)	−0.782 24(9)	−0.006 96(10)	0.075 25(11)	0.0519(11)

^{a} $U_{eq} = {}^1/_3\Sigma_i\Sigma_j(U_{ij}a^*_ia^*_j\mathbf{a}_i\cdot\mathbf{a}_j)$.

Table III. Cubane Atomic Positions and Equivalent Isotropic Thermal Parameters for $[NEt_4]_4[Pt_4Te_4(Te_3)_6]\cdot 2DMF$ (**3**)

atom	*x*	*y*	*z*	U_{eq}, Å^2
Pt(1)	0.133 85(5)	0.331 58(3)	0.786 55(6)	0.0203(4)
Pt(2)	0.270 42(6)	0.377 38(3)	0.664 55(6)	0.0227(4)
Pt(3)	0.419 89(5)	0.329 73(2)	0.918 51(6)	0.0198(4)
Pt(4)	0.282 63(6)	0.411 95(3)	0.908 45(7)	0.0249(4)
Te(1)	0.271 22(9)	0.317 92(4)	0.738 43(10)	0.0206(6)
Te(2)	0.147 23(9)	0.392 41(4)	0.731 28(10)	0.0220(7)
Te(3)	0.284 40(9)	0.348 75(4)	0.959 46(10)	0.0214(6)
Te(4)	0.404 18(10)	0.391 11(4)	0.847 83(10)	0.0228(7)
Te(11)	−0.022 13(10)	0.316 18(5)	0.611 35(11)	0.0283(7)
Te(12)	0.061 35(11)	0.304 10(5)	0.493 21(11)	0.0332(8)
Te(13)	0.121 53(10)	0.366 44(5)	0.480 66(11)	0.0313(8)
Te(21)	0.116 33(10)	0.267 89(4)	0.828 24(11)	0.0267(7)
Te(22)	0.277 26(11)	0.252 71(5)	1.005 72(11)	0.0303(8)
Te(23)	0.422 73(10)	0.265 23(4)	0.960 88(12)	0.0278(7)
Te(31)	0.004 67(10)	0.343 97(5)	0.849 22(11)	0.0295(7)
Te(32)	−0.011 13(11)	0.412 26(5)	0.844 05(12)	0.0360(8)
Te(33)	0.171 25(12)	0.430 74(5)	0.987 21(12)	0.0355(9)
Te(41)	0.408 50(11)	0.364 73(5)	0.614 72(11)	0.0347(8)
Te(42)	0.466 86(10)	0.301 56(5)	0.681 63(12)	0.0333(7)
Te(43)	0.565 53(10)	0.310 97(5)	0.883 25(11)	0.0287(7)
Te(51)	0.265 57(12)	0.438 99(5)	0.589 28(13)	0.0420(10)
Te(52)	0.372 18(13)	0.477 22(5)	0.755 07(15)	0.0489(11)
Te(53)	0.257 83(14)	0.474 28(5)	0.843 25(15)	0.0459(11)
Te(61)	0.572 93(10)	0.346 73(5)	1.093 62(11)	0.0298(7)
Te(62)	0.501 50(11)	0.382 88(5)	1.192 79(11)	0.0364(8)
Te(63)	0.429 63(12)	0.437 93(5)	1.074 63(13)	0.0405(9)

Preparation of $[PPh_4]_4[Pt_4Te_4(Te_3)_6]$ (2). $TePEt_3$ (296 mg, 1.2 mmol) dissolved in 5 mL DMF was added to a solution of $[PPh_4]_2[Pt(Se_4)_3]\cdot DMF$ (189 mg, 0.1 mmol) dissolved in 5 mL of DMF. The solution was stirred for 2 h and filtered. Next toluene (15 mL) was layered on top of the filtrate. Black crystals of **2** formed overnight (31 mg, 26% yield). Anal. Calc for $C_{96}H_{80}P_4Pt_4Te_{22}$: C, 23.32; H, 1.63; P, 2.51. Found: C, 22.65; H, 1.41; P, 2.44.

Preparation of $[NEt_4]_4[Pt_4Te_4(Te_3)_6]\cdot 2DMF$ (3). A mixture of $Pt(xan)_2$ (218 mg 0.5 mmol), Li_2Te (212 mg, 1.5 mmol), Te(383 mg, 3 mmol), and NEt_4Cl (166 mg, 1 mmol) in DMF (30 mL) was stirred for 2 h and filtered. Next ether (60 mL) was layered on top of the filtrate. Black crystals of **3** formed overnight (159 mg, 30% yield). Anal. Calc for $C_{38}H_{94}N_6O_2Pt_4Te_{22}$: C, 10.73; H, 2.23; N, 1.98. Found: C, 10.34; H, 2.19; N, 1.75.

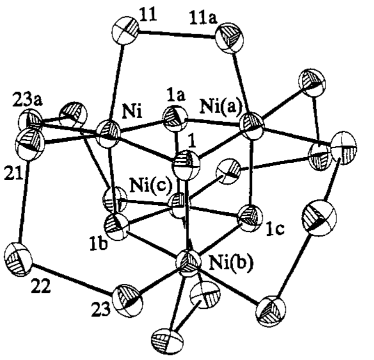

Figure 1. The $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ cubane in $[PPh_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ (**1**). The cubane lies on a $\bar{4}$ axis. In this and succeeding figures the 50% probability ellipsoids are shown.

Table IV. Cubane Bond Distances (Å) and Angles (deg) for $[PPh_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ (**1**)

Ni–Ni(a)	3.611(4)	Te(1)–Ni–Te(11)	95.79(13)
Ni–Ni(b)	3.826(4)	Te(1a)–Ni–Te(11)	78.12(11)
Te(1)–Te(1a)	3.447(4)	Te(1b)–Ni–Te(11)	160.7(2)
Te(1)–Te(1b)	3.336(4)	Te(1)–Ni–Te(21)	93.42(13)
Ni–Te(1)	2.536(4)	Te(1a)–Ni–Te(21)	175.8(2)
Ni–Te(1a)	2.489(4)	Te(1b)–Ni–Te(21)	101.58(13)
Ni–Te(1b)	2.565(4)	Te(1)–Ni–Te(23a)	168.9(2)
Ni–Te(11)	2.614(4)	Te(1a)–Ni–Te(23a)	98.08(13)
Ni–Te(21)	2.577(4)	Te(1b)–Ni–Te(23a)	88.90(12)
Ni–Te(23a)	2.543(4)	Te(11)–Ni–Te(21)	97.69(12)
Te(11)–Te(11a)	2.728(4)	Te(11)–Ni–Te(23a)	95.04(12)
Te(21)–Te(22)	2.728(3)	Te(21)–Ni–Te(23a)	82.63(11)
Te(22)–Te(23)	2.777(3)	Ni–Te(11)–Te(11a)	95.75(9)
		Ni–Te(21)–Te(22)	101.58(11)
Te(1)–Ni–Te(1a)	86.63(12)	Ni(b)–Te(23)–Te(22)	105.59(11)
Te(1)–Ni–Te(1b)	81.69(12)	Te(21)–Te(22)–Te(23)	103.54(9)
Te(1a)–Ni–Te(1b)	82.60(12)		
Ni–Te(1)–Ni(a)	91.89(12)		
Ni–Te(1)–Ni(b)	97.19(13)		
Ni(a)–Te(1)–Ni(b)	98.40(12)		

Crystallographic Studies. Intensity data for **1**–**3** were collected from single crystals with the use of an Enraf-Nonius CAD4 diffractometer. A crystal structure determination of **2** was deemed unlikely to be successful, not only because the crystals were of marginal quality as judged by the falloff of intensity with scattering angle but also because they belong to the trigonal system, generally a bad omen for complex materials. Nevertheless, we persisted with data collection since at that time crystals of **3** were unavailable. Data from the three compounds were processed by methods standard in this laboratory[26] and then corrected for absorption.[27] The positions of the heavy atoms of all three structures were located with the SHELXS86[28] direct-methods program; the structures were refined on F^2 with the SHELXL-92[29] least squares program, and the results were analyzed with the SHELXTL PC[30] graphics programs. In **1** the heavy atoms could be refined anisotropically but some of the light atoms could not. Consequently, in the final model all light atoms were refined isotropically. Our fears for the structure of **2** were confirmed: the PPh_4^+ cations could not be located; only the atoms of the anion were located and refined anisotropically, except for atoms Te(22) and Te(24), which are disordered and which were refined isotropically. As the data merged to $R_{int} = 0.06$ when anomalous dispersion effects were disregarded, the problem with the structure of **2** is not with the intensity data, but most likely with disorder and twinning (actually trilling), which is common in the trigonal system. In **3** all non-hydrogen atoms were refined aniso-

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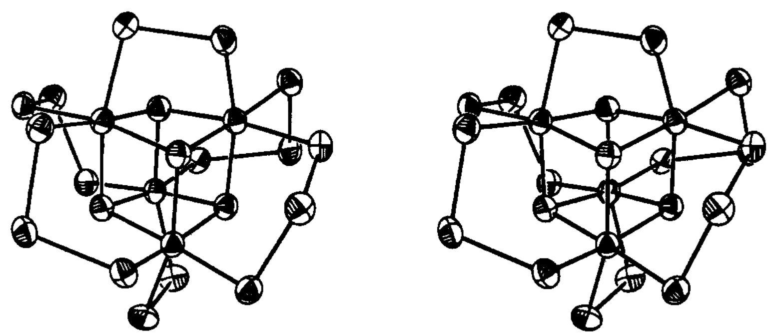

Figure 2. Stereoview of the $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ cubane in $[PPh_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ (**1**).

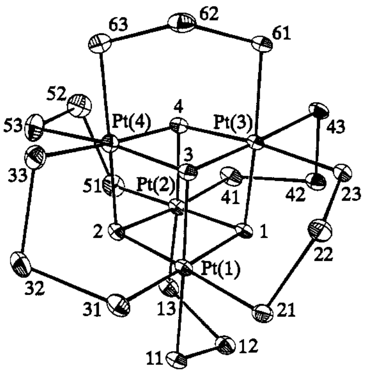

Figure 3. The $[Pt_4Te_4(Te_3)_6]^{4-}$ cubane in $[NEt_4]_4[Pt_4Te_4(Te_3)_6]$ (**3**).

tropically, except atom C(34), which could only be refined isotropically. Prior to the final refinements of **1** and **3**, hydrogen atoms were included at calculated positions. Some crystallographic details are listed in Table I. The final positional parameters and equivalent isotropic thermal parameters for the cubane portions of **1** and **3** are given in Tables II and III, respectively. Additional crystallographic details and results (including those for **2**) are given in Tables SI–SX.[31]

Results

Syntheses. Surprisingly, the reactions of $[Ni(Se_4)_2]^{2-}$ [11] and $[Pt(Se_4)_3]^{2-}$ [23] with $TePEt_3$[25] do not afford the corresponding $[M(Te_4)_n]^{2-}$ species, but rather provide convenient routes to the Ni^{IV} and Pt^{IV} tellurocubanes, $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ and $[Pt_4Te_4(Te_3)_6]^{4-}$:

$$4[PPh_4]_2[Ni(Se_4)_2] + 32TePEt_3 \rightarrow [PPh_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4] + 32SePEt_3 + 2\text{“}[PPh_4]_2Te_6\text{”} \tag{2}$$

$$4[PPh_4]_2[Pt(Se_4)_3] + 48TePEt_3 \rightarrow [PPh_4]_4[Pt_4Te_4(Te_3)_6] + 48SePEt_3 + 2\text{“}[PPh_4]_2Te_{13}\text{”} \tag{3}$$

We previously reported the synthesis of $[NEt_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$[20] by a different route. This result strongly suggests that the $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ anion, one of many possible anions of general formula $[Ni_4Te_4(Te_2)_n(Te_3)_{6-n}]^{4-}$, is the thermodynamic product in these reactions. The synthesis of **1** requires oxidation of Ni^{II} to Ni^{IV} with concomitant reduction of Se or Te. The crystals from these reactions were analyzed by EDAX (electron dispersive analysis by X-ray), and the Se content was judged to be less than 1%. If less than a stoichiometric amount of $TePEt_3$ was used, the resulting product was found to contain residual Se in addition to Te. As the amount of $TePEt_3$ was increased, the ratio of Te to Se in the final product also increased. We have no direct evidence for a mixture of materials rather than species containing both Se and Te, although species containing mixed $(Se/Te)_n^{2-}$ ligands seem more likely in view of the partial substitution of S for Se and the presence of a SSe^{2-} ligand in an earlier reaction.[19]

Previously, we reported the synthesis of the NEt_4^+ salts of $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ and $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$.[20,32] These salts are isolated from the reaction of $Ni(xan)_2$ with polyselenide or polytelluride in DMF. The synthesis of $[PPh_4]_4[Pt_4Te_4(Te_3)_6]$ (**2**), crystals of which were invariably of dismal crystallographic value, encouraged us to bypass this chalcogen substitution reaction and attempt the synthesis of $[NEt_4][Pt_4Te_4(Te_3)_6]$ by the polytelluride route in the hope that better crystals could be obtained with a different cation. Indeed, the reaction of $Pt(xan)_2$ with polytelluride in DMF yields **3**:

$$4Pt(xan)_2 + 6Li_2Te + 16Te + 4[NEt_4]Cl \rightarrow [NEt_4]_4[Pt_4Te_4(Te_3)_6] + 8Li(xan) + 4LiCl \tag{4}$$

Both **1** and **2** are insoluble in common organic solvents. They may exist in equilibrium with other Ni–Te and Pt–Te anions, such as $[Ni(Te_4)_2]^{2-}$ and $[Pt(Te_4)_3]^{2-}$, and crystallize out preferentially owing to their low solubility. Crystals of **3** dissolve in DMF, but attempts to obtain ^{195}Pt and ^{125}Te NMR spectra were unsuccessful. The anion appears to be unstable in solution. The brown color of **3** dissolved in DMF slowly turns to the red-purple of polytelluride, and Te is deposited on the sides of the NMR tube.

Structure of $[PPh_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ (1). The crystal structure of **1** consists of well-separated cations and anions. The one crystallographically independent PPh_4^+ cation shows the expected geometry around the P center with a mean P–C bond length of 1.83(2) Å and C–P–C angles ranging from 107.6(15) to 112.6(16)°. The mean C–C bond is 1.38(9) Å, and the C–C–C angles range from 105.9(55) to 124.2(47)°, with a median C–C–C angle of 119.8(39)° and a mean of 118.7(40)°. The P–C–C angles range from 115.7(33) to 122.0(30)°. More details are available in Table SVIII.[31]

The $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ anion, which has crystallographically imposed $\bar{4}$ symmetry, is shown in Figure 1 and 2. Bond distances and angles are summarized in Table IV. This $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ anion in the PPh_4^+ salt, though more symmetric owing to the imposed $\bar{4}$ symmetry, is almost identical to the same anion in the NEt_4^+ salt.[20] Magnetic susceptibility and ^{125}Te NMR measurements on the NEt_4^+ salt indicate that the salt is diamagnetic, and hence the Ni atoms have a d^6 electron configuration and are formally Ni^{IV}. In the present anion the Ni atom is in a distorted octahedral environment comprising three Te^{2-} ligands, which make up the other vertices of the cube, two Te_3^{2-} ligands, and one Te_2^{2-} chain, which bridges a face of the cube between the Ni atoms. Among Ni–Te distances the Ni–Te(11) distance of 2.614(4) Å is the longest, the others ranging from 2.489(4) to 2.577(4) Å. As anticipated for a species containing Ni^{IV} the Ni–Ni distances at 3.611(4) and 3.826(4) Å are too long for bonding interactions. The Te chains distort the cubane core, the Te_3^{2-} ligands causing the larger deviations from

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[31] Supplementary material.

[32] McConnachie, J. M.; Ansari, M. A.; Ibers, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 7078–7079.

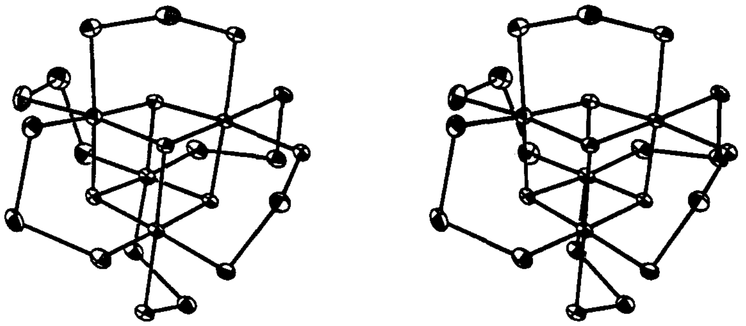

Figure 4. Stereoview of the $[Pt_4Te_4(Te_3)_6]^{4-}$ cubane in $[NEt_4]_4[Pt_4Te_4(Te_3)_6]$ (3).

Table V. Cubane Bond Distances (Å) and Angles (deg) for $[NEt_4]_4[Pt_4Te_4(Te_3)_6]\cdot2DMF$ (3)

Pt(1)–Pt(2)	3.919(2)	Pt(1)–Te(11)	2.681(2)	Pt(1)–Te(1)	2.652(2)	Te(11)–Te(12)	2.745(2)
Pt(1)–Pt(3)	3.924(2)	Pt(1)–Te(21)	2.679(2)	Pt(1)–Te(2)	2.624(2)	Te(12)–Te(13)	2.712(3)
Pt(1)–Pt(4)	3.884(2)	Pt(1)–Te(31)	2.677(2)	Pt(1)–Te(3)	2.643(2)	Te(21)–Te(22)	2.732(2)
Pt(2)–Pt(3)	3.928(2)	Pt(2)–Te(13)	2.681(2)	Pt(2)–Te(1)	2.637(2)	Te(22)–Te(23)	2.731(2)
Pt(2)–Pt(4)	3.904(2)	Pt(2)–Te(41)	2.672(2)	Pt(2)–Te(2)	2.658(2)	Te(31)–Te(32)	2.748(3)
Pt(3)–Pt(4)	3.900(2)	Pt(2)–Te(51)	2.712(2)	Pt(2)–Te(4)	2.620(2)	Te(32)–Te(33)	2.728(3)
Te(1)–Te(2)	3.537(2)	Pt(3)–Te(23)	2.662(2)	Pt(3)–Te(1)	2.650(2)	Te(41)–Te(42)	2.719(3)
Te(1)–Te(3)	3.517(2)	Pt(3)–Te(43)	2.698(2)	Pt(3)–Te(3)	2.606(2)	Te(42)–Te(43)	2.727(2)
Te(1)–Te(4)	3.518(2)	Pt(3)–Te(61)	2.677(2)	Pt(3)–Te(4)	2.652(2)	Te(51)–Te(52)	2.733(3)
Te(2)–Te(3)	3.551(2)	Pt(4)–Te(33)	2.670(2)	Pt(4)–Te(2)	2.625(2)	Te(52)–Te(53)	2.723(3)
Te(2)–Te(4)	3.526(2)	Pt(4)–Te(53)	2.650(2)	Pt(4)–Te(3)	2.649(2)	Te(61)–Te(62)	2.706(2)
Te(3)–Te(4)	3.531(2)	Pt(4)–Te(63)	2.679(2)	Pt(4)–Te(4)	2.631(2)	Te(62)–Te(63)	2.728(3)

Te(1)–Pt(1)–Te(2)	84.20(5)	Te(1)–Pt(1)–Te(11)	98.20(5)	Te(4)–Pt(3)–Te(23)	171.38(6)	Te(53)–Pt(4)–Te(63)	83.82(7)
Te(1)–Pt(1)–Te(3)	83.24(5)	Te(1)–Pt(1)–Te(21)	93.49(6)	Te(4)–Pt(3)–Te(43)	95.53(6)	Pt(1)–Te(11)–Te(12)	101.88(6)
Te(2)–Pt(1)–Te(3)	84.78(6)	Te(1)–Pt(1)–Te(31)	175.68(6)	Te(4)–Pt(3)–Te(61)	91.90(6)	Pt(2)–Te(13)–Te(12)	103.38(7)
Te(1)–Pt(2)–Te(2)	83.82(5)	Te(2)–Pt(1)–Te(11)	93.90(6)	Te(2)–Pt(4)–Te(33)	100.02(6)	Pt(1)–Te(21)–Te(22)	107.32(7)
Te(1)–Pt(2)–Te(4)	84.00(6)	Te(2)–Pt(1)–Te(21)	175.44(6)	Te(2)–Pt(4)–Te(53)	89.70(7)	Pt(3)–Te(23)–Te(22)	108.86(7)
Te(2)–Pt(2)–Te(4)	83.83(5)	Te(2)–Pt(1)–Te(31)	97.85(6)	Te(2)–Pt(4)–Te(63)	171.48(7)	Pt(1)–Te(31)–Te(32)	104.36(7)
Te(1)–Pt(3)–Te(3)	84.02(5)	Te(3)–Pt(1)–Te(11)	177.94(6)	Te(3)–Pt(4)–Te(33)	92.97(6)	Pt(4)–Te(33)–Te(32)	102.73(7)
Te(1)–Pt(3)–Te(4)	83.13(6)	Te(3)–Pt(1)–Te(21)	98.88(6)	Te(3)–Pt(4)–Te(53)	173.07(6)	Pt(2)–Te(41)–Te(42)	103.88(7)
Te(3)–Pt(3)–Te(4)	84.38(6)	Te(3)–Pt(1)–Te(31)	93.14(5)	Te(3)–Pt(4)–Te(63)	102.17(6)	Pt(3)–Te(43)–Te(42)	101.33(6)
Te(2)–Pt(4)–Te(3)	84.66(6)	Te(1)–Pt(2)–Te(13)	97.09(6)	Te(4)–Pt(4)–Te(33)	174.49(6)	Pt(2)–Te(51)–Te(52)	103.74(7)
Te(2)–Pt(4)–Te(4)	84.28(5)	Te(1)–Pt(2)–Te(41)	96.66(6)	Te(4)–Pt(4)–Te(53)	99.51(6)	Pt(4)–Te(53)–Te(52)	102.52(8)
Te(3)–Pt(4)–Te(4)	83.97(6)	Te(1)–Pt(2)–Te(51)	178.49(6)	Te(4)–Pt(4)–Te(63)	91.32(6)	Pt(3)–Te(61)–Te(62)	106.59(6)
Pt(1)–Te(1)–Pt(2)	95.62(6)	Te(2)–Pt(2)–Te(13)	90.99(5)	Te(11)–Pt(1)–Te(21)	82.52(6)	Pt(4)–Te(63)–Te(62)	101.73(8)
Pt(1)–Te(1)–Pt(3)	95.49(5)	Te(2)–Pt(2)–Te(41)	174.24(6)	Te(11)–Pt(1)–Te(31)	85.47(5)	Te(11)–Te(12)–Te(13)	100.27(8)
Pt(2)–Te(1)–Pt(3)	95.96(6)	Te(2)–Pt(2)–Te(51)	94.69(6)	Te(21)–Pt(1)–Te(31)	84.72(6)	Te(21)–Te(22)–Te(23)	100.88(7)
Pt(1)–Te(2)–Pt(2)	95.78(6)	Te(4)–Pt(2)–Te(13)	174.57(6)	Te(13)–Pt(2)–Te(41)	94.65(6)	Te(31)–Te(32)–Te(34)	101.71(8)
Pt(1)–Te(2)–Pt(4)	95.44(6)	Te(4)–Pt(2)–Te(41)	90.51(5)	Te(13)–Pt(2)–Te(51)	82.64(6)	Te(41)–Te(42)–Te(43)	101.54(8)
Pt(2)–Te(2)–Pt(4)	95.28(5)	Te(4)–Pt(2)–Te(51)	96.14(7)	Te(41)–Pt(2)–Te(51)	84.85(6)	Te(51)–Te(52)–Te(53)	100.63(8)
Pt(1)–Te(3)–Pt(3)	96.76(5)	Te(1)–Pt(3)–Te(23)	88.99(6)	Te(23)–Pt(3)–Te(43)	82.11(6)	Te(61)–Te(62)–Te(63)	102.17(7)
Pt(1)–Te(3)–Pt(4)	94.43(6)	Te(1)–Pt(3)–Te(43)	98.24(5)	Te(23)–Pt(3)–Te(61)	95.88(6)		
Pt(3)–Te(3)–Pt(4)	95.84(6)	Te(1)–Pt(3)–Te(61)	174.80(7)	Te(43)–Pt(3)–Te(61)	80.69(5)		
Pt(2)–Te(4)–Pt(3)	96.31(6)	Te(3)–Pt(3)–Te(23)	98.31(6)	Te(33)–Pt(4)–Te(53)	84.04(7)		
Pt(2)–Te(4)–Pt(4)	96.07(5)	Te(3)–Pt(3)–Te(43)	177.72(6)	Te(33)–Pt(4)–Te(63)	84.84(6)		
Pt(3)–Te(4)–Pt(4)	95.15(6)	Te(3)–Pt(3)–Te(61)	97.04(5)				

cubic symmetry. These and other geometric features of the $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ anion have been discussed previously.[20]

Structure of $[PPh_4]_4[Pt_4Te_4(Te_3)_6]$ (2). Information on this structure may be found in the supplementary material. The same anion is much better defined in 3.

Structure of $[NEt_4]_4[Pt_4Te_4(Te_3)_6]\cdot2DMF$ (3). The crystal structure of 3 consists of the packing of well-separated cations and anions and DMF solvent molecules. The four independent NEt_4^+ cations have their expected geometries as do the two independent DMF molecules. The mean N–C and C–C bond lengths in the NEt_4^+ ions are 1.50(2) and 1.56(6) Å, respectively, and the C–N–C and N–C–C angles range from 101.5(24) to 115.8(20)° and from 107.3(24) to 118.9(21)°, respectively. The DMF molecules have mean N–C and O–C distances of 1.39(5) and 1.21(1) Å, respectively, C–N–C angles ranging from 118.4(23) to 122.2(36)°, and N–C–O angles of 124.2(35) and 129.4(49)°. Further details are available in Table SX.[31]

The $[Pt_4Te_4(Te_3)_6]^{4-}$ anion with atom labels is shown in Figure 3, and a stereoview is shown in Figure 4. Metrical data for the anion are given in Table V. Each Pt atom has a slightly distorted octahedral coordination, being bound to three Te^{2-} ligands that make up the other vertices of the cube and three Te_3^{2-} chains that bridge the faces of the cube between the Pt atoms. The mean Pt–Pt distance is 3.910(17) Å and the mean Te–Te distance is 3.530(13) Å in the core. The Te–Pt–Te angles in the cube range from 83.13(6) to 84.78(6)° compared to the Te–Ni–Te angles of 81.69(12) and 82.60(12)° in the $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ anion; the Pt–Te–Pt angles in the cube range from 94.43(6) to 96.76(5)° compared with Ni–Te–Ni angles of 97.19(13) and 98.40(12)°. The Te_3^{2-} ligands are unremarkable and differ little from those in the Ni cubane; the pseudo Pt_2Te_3 five-membered rings have the envelope conformation.

The $[Pt_4Te_4(Te_3)_6]^{4-}$ cubane is an analogue of the $[Re_4S_4(S_3)_6]^{4-}$ cubane[33] and a variant of the $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ and $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ cubanes.[20,32] All these cubanes contain M^{IV} centers, unexceptional for Pt and Re and exceptional for Ni. Since the $[Pt_4Te_4(Te_3)_6]^{4-}$ anion has been prepared by two different routes and crystallized with two different cations, it again appears to be the thermodynamically stable species. Why

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then do we find $[Pt_4Te_4(Te_3)_6]^{4-}$ but $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$? The lengthening of the M–Te bond on going from Ni to Pt might help accommodate the Te_3^{2-} ligand that greatly distorts the Ni_4Te_4 core in **1**. Alternatively, the relative hardness of the ligand and metal center may dominate the ligand selection. A formal Ni^{IV} center is a hard acid; a Pt^{IV} center is softer. The Te_2^{2-} ligand has its negative charge spread over fewer atoms than does the Te_3^{2-} ligand and thus should be a harder base. Consequently, the Te_2^{2-} ligand might stabilize Ni^{IV}.

Discussion

We have demonstrated here the utility of chalcogenide substitution and rearrangement in the synthesis of new metal chalcogenide species. The driving force for chalcogenide substitution is presumably the relative strength of the Q–PR_3 bond, which is S–P > Se–P > Te–P. If the reaction is general, then $TePR_3$ should react with soluble metal sulfides and selenides, and $SePR_3$ should react with metal sulfides. Hence, all known sulfidometalates would be potential precursors for seleno- and tellurometalates, and all known selenometalates would be precursors for tellurometalates. In fact, depending on M–O and O–P versus M–Q and Q–P bond strengths, oxides might also succumb to phosphine chalcogenide substitution.

Three important factors for chalcogen substitution are the strength of M–Q bonds, the position of Q in a metal complex, and the phosphine basicity. (The phosphine chalcogenides are conveniently made by heating the phosphine and elemental chalcogen in toluene,[25] so obviously the formation of Q–P versus Q–Q bonds is not an important factor.) Various metals may form M–Q bonds that are too strong for chalcogen substitution to proceed fully. Chalcogen atoms may occupy different positions, e.g. terminal, bridging, and ring, within metal chalcogenide species and exhibit differing reactivities as a result of differing steric and electronic factors. And, of course, different phosphine chalcogenides will form Q–P bonds of different strengths, thus influencing the course of a chalcogen substitution reaction. When these factors are understood, phosphine chalcogenides should provide routes to seleno- and tellurometalates in systems where none currently exists, such as those with M = Re, Rh. While the differing thermodynamic and steric properties of the chalcogenide ligands may cause structural rearrangement during chalcogenide substitution, as in the reactions leading to **1** and **2** above, structural integrity may be retained and compounds common to all three chalcogens may be isolated. For example, we have found that structural integrity is maintained in the reaction of $TePEt_3$ with the $[M(Se_4)_2]^{2-}$ anions of the Zn triad.[34] In soluble metal chalcogenide systems with isostructural S, Se, and Te complexes, such as $[Hg(Q_4)_2]^{2-}$,[11,34,35] all possible combinations could ideally be isolated.

Chalcogenide substitution reactions may also lead to greater variability in the length of Se and Te chains. The most common Q_n^{2-} length is $n = 4$ in Se and Te complexes, but $n > 4$ is common for S.[35] If one were to start from sulfidometalates having $n > 4$, Se and Te chains of $n > 4$ might be obtained.

The growing interest[19,36,37] in mixed chalcogenide ligands will be well served by chalcogen substitution reactions. Even if a metal species does not substitute its chalcogens completely, the promise of novel mixed species is always present. If these new species follow the concept of topological charge stabilization,[38] as the recent work with heteropolychalcogenide anions suggests,[36,37,39,40] judicious use of a phosphine chalcogenide reagent could produce compounds with different chalcogens in specific positions.

Acknowledgment. This research was supported by the National Science Foundation (Grant Nos. CHE-8922754 and CHE-9224469).

Supplementary Material Available: Further details of data collection and refinement (Table SI), cation atomic positions for **1** (Table SII), atomic positions and equivalent isotropic thermal parameters for the anion of **2** (Table SIII), cation and solvent atomic positions for **3** (Table SIV), thermal displacement parameters (Tables SV–SVII), cation bond distances and angles for **1** (Table SVIII), anion bond distances and angles for **2** (Table SIX), and cation and solvent distances and angles for **3** (Table SX) (21 pages). Ordering information is given on any current masthead page.

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