Ni^{IV} cubanes: synthesis and characterization of the $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ and $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ anions

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Abstract

The compounds $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)]\cdot xNEt_4Cl$ ($x=0$, 1) and $[NEt_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ have been prepared from the reaction in DMF of $Ni(S_2COEt)_2$ with Li_2Se and Se or Li_2Te and Te, respectively. These compounds result from spontaneous assembly reactions in which Ni^{II} centers are oxidized to Ni^{IV} with concomitant reduction of Se- or Te-containing species. The anion $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ possesses a Ni_4Se_4 cubane core and has five Se_3^{2-} chains and one Se_4^{2-} chain bridging the Ni atoms on the cubane faces. The anion $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ has a Ni_4Te_4 cubane core and has two Te_2^{2-} chains bridging Ni atoms on opposite faces of the cubane core and four Te_3^{2-} chains bridging the Ni^{IV} atoms on the remaining cubane faces. The presence of Ni^{IV} is necessitated by charge balance. As expected for such d^6 systems the compounds are diamagnetic. The $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ anion exhibits a sharp, albeit complex, ^{77}Se NMR spectrum with fifteen resonances at δ 103, 134, 289, 361, 387, 401, 411, 470, 660, 680, 726, 749, 773, 789 and 804 ppm. The $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ anion exhibits a simpler ^{125}Te NMR spectrum with five resonances at δ -632, -324, 65, 325 and 766 ppm. In the cubane anions each Ni atom is in a distorted octahedral environment, being coordinated by three Se or Te atoms in the cubane framework and by three Se or Te atoms in chains that bridge to the other three Ni atoms. While the bridging Se_3^{2-} chains appear to produce little strain on the 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. In contrast, the bridging Te_3^{2-} chains distort the Ni_4Te_4 cubane core as evidenced from the Ni–Ni distances, the Te_{cub}–Te_{cub} distances and the cubane bond angles; the Te_2^{2-} chains produce less strain. $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)]\cdot NEt_4Cl$ crystallizes in the monoclinic space group C_{2h}^5–$P2_1/n$ with $a=21.817(4)$, $b=14.319(1)$, $c=26.421(5)$ Å, $\beta=112.69(2)°$, $V=7615$ Å^3 and $Z=4$ (-120 °C). $[NEt_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ crystallizes in the triclinic space group C_i^1–$P\bar{1}$ with $a=14.399(2)$, $b=15.153(2)$, $c=18.069(3)$ Å, $\alpha=70.97(1)$, $\beta=79.05(1)$, $\gamma=74.20(1)°$, $V=3564$ Å^3 and $Z=2$ (-167 °C).

Introduction

While the development of the chemistry of the heteropolymetallates is at least a century old and continues to be an active field [1], the synthesis and characterization of soluble transition-metal sulfides has been an active area of research for only the last twenty years or so, although some species, such as $Pt(S_5)_3^{2-}$ [2] have been known for many years. A number of exciting and unusual soluble transition-metal sulfides such as $Mo_3S_{13}^{2-}$ [3], AuS_9^- [4] and $Na_2Fe_{18}S_{30}^{8-}$ [5] are now known. But despite the expectation that the different redox properties and ionic radii of Se and Te compared to S would yield new and different species possessing no sulfur analogues, as late as 1987 the only isolated systems contained the ions $MoSe_4^{2-}$ [6], WSe_4^{2-} [7] and $Fe_2Se_{12}^{2-}$ [8], all of which have sulfur analogues. Since our work began on oligomers in the W/Se system [9] and that of Flomer and Kolis began on telluride species [10], a rapidly growing literature has developed of new and diverse soluble transition-metal selenide and telluride anions [11]. Many of these, for example $V_2Se_{13}^{2-}$ [12], $(AgSe_4)_n^{n-}$ [13], $Hg_2Se_{12}^{2-}$ [14] and $NbTe_{10}^{3-}$ [10], have no known sulfur analogues.

We were attracted to the Ni triad because interesting sulfides in this triad, such as PdS_{11}^{2-} [15], $Pd_2S_{28}^{4-}$ [16] and $Pt(S_5)_3^{2-}$ [2], were known. We have subsequently synthesized the species $M(Se_4)_2^{2-}$ (M = Ni, Pd, Pt) [17] and $Pt(Se_4)_3^{2-}$ [18]. Recently we presented a brief report of the synthesis of the remarkable Ni^{IV} cubane complex $[NEt_4]_4[Ni_4Se_4(Se_3)_5Se_4]\cdot NEt_4Cl$ [19]. In this paper we present further details concerning the synthesis and characterization of that compound and we also report the synthesis and characterization of $[NEt_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$. While a homoleptic sulfide cubane $Re_4S_4(S_3)_6^{4-}$ is known [20], the ions $[Ni_4Se_4(Se_3)_5Se_4]^{4-}$ and $Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ (herein abbreviated $[Ni_4Se_{23}]^{4-}$ and $[Ni_4Te_{20}]^{4-}$, respectively) are the first homoleptic seleno- and tellurocubanes.

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Experimental

Syntheses

All the manipulations were carried out under N_2 with the use of standard Schlenk-line techniques. Solvents were used as received. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, USA and Analytical Laboratories, Elbach, FRG. ^{77}Se NMR spectra were obtained on a Varian XLA-400 spectrometer with a 10 mm tunable probe and deuterium lock. All chemical shifts are referenced to Ph_2Se_2, a secondary standard, at $\delta = 460$ ppm. The detailed experimental procedures are outlined elsewhere [9]. ^{125}Te NMR spectra were obtained similarly, but the spectra were referenced to K_2TeO_3, a secondary standard, at $\delta = 1732$ ppm. Ni(xan)$_2$ was prepared by published methods [21]. Li_2Se and Li_2Te were prepared by the reaction of stoichiometric amounts of Li and Se or Te, respectively, in liquid ammonia.

Preparation of $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)]\cdot NEt_4Cl$ (1)

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 filtered; next ether (60 ml) was layered on top of the filtrate. A mixture of $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)]\cdot NEt_4Cl$ (481 mg, 35% yield), $[NEt_4]_2[Ni(Se_4)_2]$ (175 mg) and $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)]$ (2) (159 mg) formed over a period of a week. These products can be separated manually. *Anal.* Calc. 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%. ^{77}Se NMR (DMF, δ): 103, 134, 289, 361, 387, 401, 411, 470, 660, 680, 726, 749, 773, 789, 804 ppm.

Preparation of $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)]$ (2)

A solution of Li_2Se (279 mg, 3 mmol), Se (672 mg, 8.5 mmol) and NEt_4Cl (330 mg, 2 mmol) in DMF (25 ml) was added dropwise over 10 min with stirring to a solution of Ni(xan)$_2$ (600 mg, 2 mmol) dissolved in DMF (25 ml). The solution was stirred for 1 h and filtered; next ether (50 ml) was layered on top of the filtrate. Black fibrous crystals of **2** were produced in 4 days (475 mg, 35% yield). *Anal.* Calc. for $C_{32}H_{80}N_4Ni_4Se_{23}$: C, 14.94; H, 3.14; N, 2.17. Found: C, 13.74; H, 3.23; N, 2.12%. ^{77}Se NMR (DMF, δ): 103, 134, 289, 361, 387, 401, 411, 470, 660, 680, 726, 745, 773, 785, 804 ppm.

Preparation of $[NEt_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ (3)

A solution of Li_2Te (212 mg, 1.5 mmol), Te (447 mg, 3.5 mmol) and NEt_4Cl (165 mg, 1 mmol) in DMF (10 ml) was added dropwise over 10 min with stirring to a solution of Ni(xan)$_2$ (300 mg, 1 mmol) dissolved in DMF (10 ml). The solution was stirred for 1 h and then filtered; next ether (30 ml) was layered on top of the filtrate. Black crystals of **3** formed over 4 days (10 mg, ~1%). Insufficient sample did not allow complete chemical analysis; however EDAX measurements on a scanning electron microscope gave a consistent Ni/Te ratio of 1:5 on numerous crystals. ^{125}Te NMR (DMF, δ): −632, −324, 65, 325, 766 ppm.

TABLE 1. Crystallographic details

Compound	$[NEt_4]_4[Ni_4Se_{23}]\cdot NEt_4Cl$	$[NEt_4]_4[Ni_4Te_{20}]$
Formula	$C_{40}H_{100}ClN_5Ni_4Se_{23}$	$C_{32}H_{80}N_4Ni_4Te_{20}$
Formula weight	2572	3308
a (Å)	21.817(4)	14.399(2)
b (Å)	14.319(1)	15.153(2)
c (Å)	26.421(5)	18.069(3)
α (°)	90	70.97(1)
β (°)	112.69(2)	79.05(1)
γ (°)	90	74.20(1)
Volume (Å^3)	7615	3564
Z	4	2
D_{calc} (g/cm^3)	2.243	3.081
Space group	C_{2h}^5–$P2_1/n$	C_i^1–$P\bar{1}$
T (°C)	−120	−165
λ (Å)	1.540562 (Cu(Kα_1))	0.7093 (Mo(Kα_1))
μ (cm^{-1})	143	91.2
Trans. coefficient	0.077–0.498	0.608–0.743
R on F_o^2		0.109
R_w on F_o^2		0.131
R on $F_o(F_o^2 > 3\sigma(F_o^2))$	0.089	0.052
R_w on $F_o(F_o^2 > 3\sigma(F_o^2))$	0.093	0.056

Crystallographic studies

A suitable crystal of $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)] \cdot NEt_4Cl$ was mounted in the cold stream (−120 °C) of an Enraf-Nonius CAD4 diffractometer and the unit cell was determined from 25 automatically centered reflections. Owing to crystal decomposition, data collection was rapid and redundant data were not collected. The intensities of six standard reflections monitored every 3 h throughout data collection decreased 20%. Some crystallographic details are given in Table 1.

A crystal of $[NEt_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ was treated similarly, except that the temperature of data collection was −165 °C. The intensities of the six standard reflections decreased 7%. Some crystallographic details are given in Table 1.

Procedures standard in this laboratory were employed in the solution and refinement of the structures [22]. The atoms of the cubane core were located by direct methods and the remaining non-hydrogen atoms were found from successive difference electron density maps. A linear correction for crystal decomposition was included with the analytical absorption correction. Prior to the final refinement, methylene H atoms were included at calculated positions (C–H = 0.95 Å). Methyl H atoms could not be located on difference electron density maps and were not included. Each hydrogen atom was given an isotropic thermal parameter 1 Å^2 greater than the isotropic thermal parameter of the carbon atom to which it is attached.

The final refinement on F_o for $(NEt_4)_4[Ni_4Se_4(Se_3)_5(Se_4)] \cdot NEt_4Cl$ included anisotropic thermal parameters for the anion and chloride ion and isotropic thermal parameters for the cation and converged to $R(F) = 0.089$ for 433 variables and those 4708 reflections having $F_o^2 > 3\sigma(F_o^2)$. The refinement on F_o^2 for $[NEt_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ included anisotropic thermal parameters for the anion and isotropic thermal parameters for the cations. It converged to $R(F_o^2) = 0.109$ for 361 variables and 19 664 reflections (including those with $F_o^2 \leqslant 0$). For both compounds the final positional and equivalent isotropic thermal parameters of all non-hydrogen atoms are given in Table 2. See also 'Supplementary material'.

Results and discussion

Synthesis

The $[Ni_4Se_{23}]^{4-}$ and $[Ni_4Te_{20}]^{4-}$ anions represent the first homoleptic selenium and tellurium cubanes. The homoleptic sulfur cubane $[Re_4S_4(S_3)_6]^{4-}$ was synthesized previously [20]. Both nickel species can be made by the general reaction

$$Ni(S_2COEt)_2 + Q_x^{2-} + NEt_4Cl \xrightarrow[DMF]{} Ni_4Q_x^{4-} + \ldots$$

TABLE 2. Positional parameters and B_{eq} for $[NEt_4]_4[Ni_4Se_{23}] \cdot NEt_4Cl$ and $[NEt_4]_4[Ni_4Te_{20}]$

Atom	x	y	z	B (Å^2)
Ni(1)	0.20222(29)	0.60910(39)	−0.00651(24)	2.3(2)
Ni(2)	0.31656(30)	0.77494(40)	0.07422(25)	2.8(2)
Ni(3)	0.17027(29)	0.84458(39)	−0.03183(24)	2.3(2)
Ni(4)	0.30163(31)	0.72988(40)	−0.06015(28)	3.1(2)
Se(1)	0.20283(19)	0.74431(25)	0.04478(16)	2.0(1)
Se(2)	0.31547(20)	0.64279(28)	0.01839(18)	2.9(1)
Se(3)	0.18625(19)	0.71512(27)	−0.07946(16)	2.2(1)
Se(4)	0.28580(19)	0.85806(27)	−0.01022(18)	2.6(1)
Se(11)	0.23396(24)	0.49746(28)	0.06622(18)	3.5(2)
Se(12)	0.25837(26)	0.58920(31)	0.14480(18)	4.2(2)
Se(13)	0.35143(25)	0.67291(33)	0.15209(18)	4.5(2)
Se(21)	0.08750(21)	0.57344(27)	−0.02510(18)	2.9(1)
Se(22)	0.03102(19)	0.68020(29)	−0.09428(17)	3.0(1)
Se(23)	0.05619(18)	0.82143(27)	−0.04728(16)	2.5(1)
Se(31)	0.19282(21)	0.47637(26)	−0.06346(16)	2.6(1)
Se(32)	0.29583(22)	0.46789(29)	−0.07158(19)	3.5(2)
Se(33)	0.29905(22)	0.60300(31)	−0.12016(19)	3.4(2)
Se(41)	0.31763(21)	0.91527(29)	0.12458(18)	3.3(1)
Se(42)	0.20565(22)	0.94531(29)	0.10691(18)	3.3(1)
Se(43)	0.16051(22)	0.98609(26)	0.01401(18)	3.3(1)
Se(51)	0.43469(23)	0.80467(36)	0.10831(24)	5.6(2)
Se(52)	0.45398(28)	0.85057(42)	0.03511(26)	6.6(2)
Se(53)	0.42289(26)	0.72615(38)	−0.02431(26)	5.9(2)
Se(61)	0.11822(21)	0.93053(29)	−0.11552(17)	3.3(1)
Se(62)	0.19482(27)	0.99322(35)	−0.14694(20)	5.1(2)
Se(63)	0.21992(30)	0.87029(40)	−0.19241(23)	6.3(2)
Se(64)	0.31983(27)	0.82122(37)	−0.12771(23)	5.4(2)
Cl	0.44211(57)	0.22197(70)	0.21301(51)	4.5(5)
N(1)	−0.4879(13)	0.2552(18)	0.4106(11)	1.9(6)
N(2)	−0.2779(14)	0.2470(19)	−0.2952(12)	2.4(6)
N(3)	0.0298(16)	0.0161(21)	−0.3424(13)	3.2(7)
N(4)	0.4109(16)	0.0478(21)	−0.2497(13)	3.6(7)
N(5)	0.3603(16)	0.1621(22)	0.0145(13)	2.9(7)
C(1)	−0.5547(17)	0.2163(22)	0.4092(13)	2.2(7)
C(2)	−0.5674(18)	0.1111(23)	0.3932(14)	2.5(8)
C(3)	−0.4277(16)	0.1959(21)	0.4471(13)	1.9(7)
C(4)	−0.4239(24)	0.1850(31)	0.5055(20)	5(1)
C(5)	−0.4809(18)	0.3543(24)	0.4316(15)	3.0(8)
C(6)	−0.5310(21)	0.4253(28)	0.3990(17)	4(1)
C(7)	−0.4858(22)	0.2559(29)	0.3520(18)	5(1)
C(8)	−0.4275(20)	0.2927(26)	0.3461(16)	4(1)
C(9)	−0.2390(20)	0.1958(26)	−0.2391(16)	4(1)
C(10)	−0.1781(19)	0.1356(25)	−0.2433(16)	3.2(8)
C(11)	−0.3033(20)	0.1766(28)	−0.3421(17)	4(1)
C(12)	−0.3483(21)	0.1027(27)	−0.3301(17)	4(1)
C(13)	−0.3361(21)	0.2970(27)	−0.2874(17)	4(1)
C(14)	−0.3827(23)	0.3534(29)	−0.3328(19)	5(1)
C(15)	−0.2343(19)	0.3173(26)	−0.3094(16)	3.8(9)
C(16)	−0.2013(22)	0.3958(30)	−0.2692(19)	5(1)
C(17)	0.0216(21)	−0.0824(30)	−0.3543(18)	5(1)
C(18)	0.0766(21)	−0.1222(27)	−0.3728(18)	4(1)
C(19)	−0.0276(23)	0.0394(29)	−0.3214(19)	5(1)
C(20)	−0.0213(26)	0.0061(33)	−0.2673(22)	6(1)
C(21)	0.0852(26)	0.0496(34)	−0.3023(22)	7(1)
C(22)	0.1045(21)	0.1505(28)	−0.2858(17)	4(1)
C(23)	0.0137(23)	0.0683(31)	−0.3961(19)	6(1)
C(24)	−0.0438(23)	0.0389(29)	−0.4482(19)	5(1)
C(25)	0.3970(19)	0.0666(25)	−0.1994(16)	3.3(9)
C(26)	0.3283(22)	0.1094(28)	−0.2128(18)	5(1)

(*continued*)

TABLE 2. (*continued*)

Atom	x	y	z	B (Å^2)
C(27)	0.4827(20)	0.0126(26)	−0.2335(16)	3.4(9)
C(28)	0.5096(22)	0.0016(29)	−0.2784(19)	5(1)
C(29)	0.3636(17)	−0.0259(23)	−0.2853(14)	2.8(7)
C(30)	0.3661(20)	−0.1204(26)	−0.2563(17)	4(1)
C(31)	0.4012(19)	0.1361(25)	−0.2842(15)	3.5(8)
C(32)	0.4454(19)	0.2201(26)	−0.2599(16)	3.3(9)
C(33)	0.2982(33)	0.1344(41)	0.0067(27)	11(2)
C(34)	0.2395(31)	0.2034(41)	−0.0579(27)	11(2)
C(35)	0.4070(37)	0.1025(47)	0.0583(31)	16(2)
C(36)	0.4677(22)	0.1183(27)	0.0915(17)	4(1)
C(37)	0.3659(36)	0.1982(49)	−0.0354(32)	16(2)
C(38)	0.3818(34)	0.0639(46)	−0.0531(28)	9(2)
C(39)	0.3538(37)	0.2487(51)	0.0429(32)	16(2)
C(40)	0.3163(32)	0.2652(41)	0.0786(28)	10(2)
Ni(1)	0.29369(12)	0.24213(12)	0.76669(10)	1.02(5)
Ni(2)	0.04303(12)	0.22476(12)	0.842216(94)	0.90(4)
Ni(3)	0.18162(12)	0.08947(12)	0.695232(96)	0.87(4)
Ni(4)	0.10054(12)	0.34840(12)	0.620310(96)	0.91(4)
Te(1)	0.201189(58)	0.110270(59)	0.825940(48)	0.87(2)
Te(2)	0.129607(59)	0.354835(60)	0.755336(50)	0.97(2)
Te(3)	0.263785(59)	0.226957(60)	0.636201(49)	0.90(2)
Te(4)	0.025324(57)	0.212969(58)	0.706946(48)	0.83(2)
Te(11)	0.266597(72)	0.295146(77)	0.894758(57)	1.86(3)
Te(12)	0.114871(67)	0.208486(71)	0.971287(53)	1.50(3)
Te(21)	0.459099(65)	0.124528(73)	0.793201(57)	1.64(3)
Te(22)	0.490758(65)	0.031354(72)	0.681447(59)	1.68(3)
Te(23)	0.328920(63)	−0.049342(64)	0.716458(56)	1.38(3)
Te(31)	0.395947(62)	0.359831(66)	0.683051(54)	1.36(3)
Te(32)	0.263161(67)	0.529072(65)	0.629124(55)	1.41(3)
Te(33)	0.162993(61)	0.498618(62)	0.525138(52)	1.13(2)
Te(41)	−0.058679(60)	0.099746(62)	0.900310(50)	1.05(2)
Te(42)	0.066690(63)	−0.075790(63)	0.902916(52)	1.24(2)
Te(43)	0.099477(63)	−0.054058(62)	0.742484(52)	1.17(2)
Te(51)	−0.119495(66)	0.337147(67)	0.871650(56)	1.50(3)
Te(52)	−0.193843(64)	0.394979(68)	0.729806(58)	1.64(3)
Te(53)	−0.048845(62)	0.482128(62)	0.630031(53)	1.21(2)
Te(61)	0.183331(64)	0.113786(63)	0.545961(51)	1.20(2)
Te(62)	0.050123(63)	0.286970(63)	0.514393(51)	1.19(2)
N(1)	0.21684(81)	−0.13186(81)	0.39946(66)	1.7(2)
N(2)	0.44118(79)	0.31597(79)	0.37653(65)	1.4(2)
N(3)	0.01165(99)	0.33558(97)	0.18743(80)	2.6(2)
N(4)	−0.4127(10)	0.1874(10)	0.00657(84)	2.7(3)
C(1)	0.10698(99)	−0.09056(98)	0.41511(81)	1.5(2)
C(2)	0.0781(11)	0.0179(11)	0.40396(90)	2.1(3)
C(3)	0.2571(11)	−0.0818(10)	0.31880(87)	2.0(2)
C(4)	0.2095(12)	−0.0844(12)	0.2498(10)	2.9(3)
C(5)	0.2707(10)	−0.1144(10)	0.45721(84)	1.7(2)
C(6)	0.2438(10)	−0.1619(10)	0.54391(86)	1.9(2)
C(7)	0.2290(10)	−0.2394(10)	0.41041(81)	1.6(2)
C(8)	0.3314(12)	−0.2945(12)	0.39604(97)	2.5(3)
C(9)	0.4606(12)	0.3839(12)	0.29694(96)	2.6(3)
C(10)	0.5707(13)	0.3845(12)	0.2706(10)	2.8(3)
C(11)	0.33053(96)	0.32695(96)	0.39668(79)	1.4(2)
C(12)	0.2828(11)	0.2990(11)	0.34238(87)	1.8(2)
C(13)	0.4770(12)	0.3399(12)	0.4402(10)	2.5(3)
C(14)	0.4457(13)	0.4430(12)	0.4432(10)	2.7(3)
C(15)	0.4898(11)	0.2136(11)	0.37647(91)	2.0(3)
C(16)	0.4699(12)	0.1375(11)	0.45140(94)	2.4(3)
C(17)	0.0537(16)	0.4254(16)	0.1393(13)	4.3(4)
C(18)	0.1019(19)	0.4253(19)	0.0570(16)	6.0(6)
C(19)	0.0845(12)	0.2456(12)	0.18724(98)	2.3(3)
C(20)	0.1791(16)	0.2264(15)	0.2250(13)	4.5(4)
C(21)	−0.0183(13)	0.3467(13)	0.2699(11)	2.9(3)
C(22)	−0.0664(12)	0.2670(12)	0.3259(10)	2.4(3)
C(23)	−0.0740(13)	0.3341(13)	0.1501(10)	3.1(3)
C(24)	−0.1603(18)	0.4204(17)	0.1501(14)	5.0(5)
C(25)	−0.3741(26)	0.2372(25)	−0.0812(21)	10(1)
C(26)	−0.4259(20)	0.2903(19)	−0.1406(16)	6.4(6)
C(27)	−0.5051(35)	0.2379(34)	0.0392(29)	25(1)
C(28)	−0.5550(23)	0.2000(22)	0.1175(19)	8.7(8)
C(29)	−0.4107(34)	0.0840(33)	−0.0039(27)	21(1)
C(30)	−0.3342(19)	0.0298(18)	−0.0285(15)	5.8(5)
C(31)	−0.3352(31)	0.1563(30)	0.0570(25)	16(1)
C(32)	−0.3226(19)	0.2520(19)	0.0819(15)	6.1(6)

(*continued*)

The Ni^{II} centers in nickel xanthate undergo a two-electron oxidation to Ni^{IV} with concomitant reduction of the chalcogenide species. The NEt_4^+ ion appears to be a necessary part of the reaction mixture as the reaction between $Ni(xan)_2$ and Li_2Se_x in the presence of $PEtPh_3^+$ affords $[PEtPh_3]_2[Ni(Se_4)_2]$ [17]. Product dependency on countercation size has been observed extensively in the chemistry of soluble transition-metal chalcogenides (see, for example ref. 13). The product is not dependent on the presence of xanthate because the $[Ni_4Se_{23}]^{4-}$ anion is also formed when either $Ni(acac)_2$ or $Ni(OAc)_2$ is used as a starting material. The very low yield of the telluride product may be the result of the extreme instability of polytelluride in solution. In the synthesis of both cubanes large quantities of insoluble black precipitate remain at the bottom of the flask after the reaction solution has been filtered.

Structures

Stereoviews of the $[Ni_4Se_{23}]^{4-}$ and $[Ni_4Te_{20}]^{4-}$ anions are shown in Figs. 1 and 2, respectively, while the labeling schemes are shown in Figs. 3 and 4. Selected bond distances and bond angles in these anions are given in Tables 3 and 4, respectively; some bond distances and angles in the NEt_4^+ cations are non-representative. In both structures each Ni atom lies in a distorted octahedral environment, being coordinated by three Q (Q = Se or Te) atoms in the cubane framework and three Q atoms belonging to chains that crisscross the cubane faces and connect the Ni atoms. The $[Ni_4Se_{23}]^{4-}$ anion possesses five Se_3^{2-} chains and one Se_4^{2-} chain while the $[Ni_4Te_{20}]^{4-}$ anion possesses two Te_2^{2-} chains and four Te_3^{2-} chains. The two Te_2^{2-} chains are on opposite faces of the cube. In the $[Ni_4Se_{23}]^{4-}$ anion the Ni–Se bonds range from 2.338(8) to 2.442(8) Å (Table 3). For comparison, the Ni–Se bond lengths in the square-planar $[Ni(Se_4)_2]^{2-}$ anion average 2.307(6) Å [17]. The different coordination

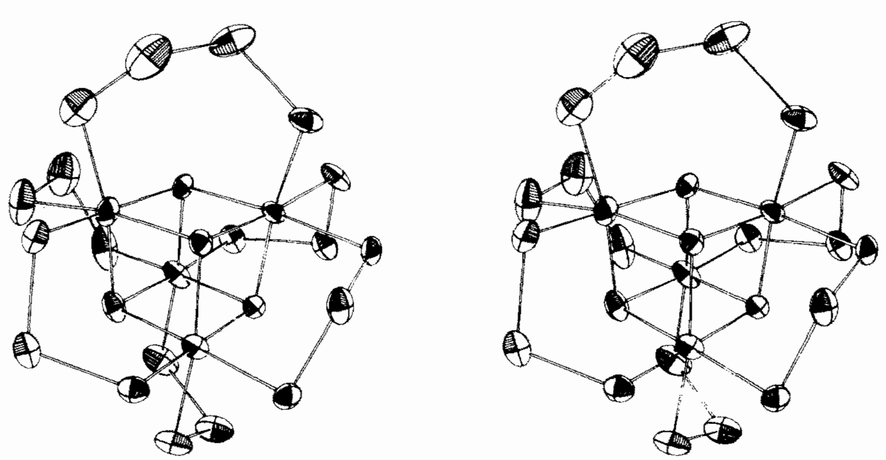

Fig. 1. A stereoview of the $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ anion. Here and in subsequent figures the 50% probability ellipsoids are shown.

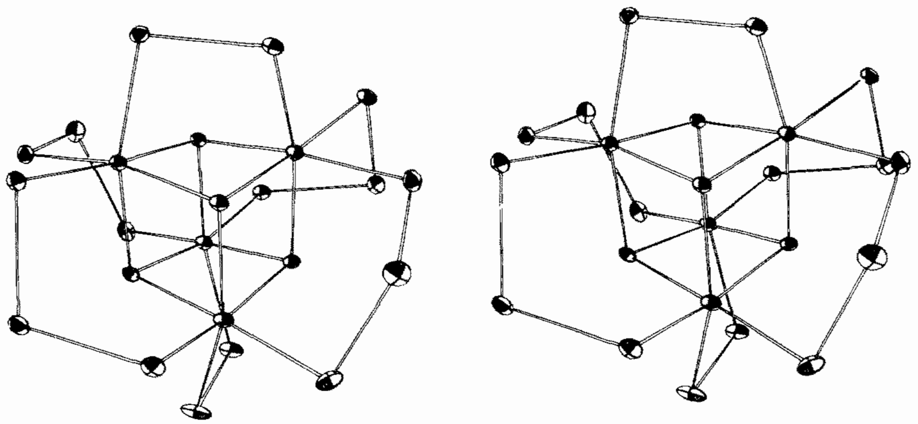

Fig. 2. A stereoview of the $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ anion.

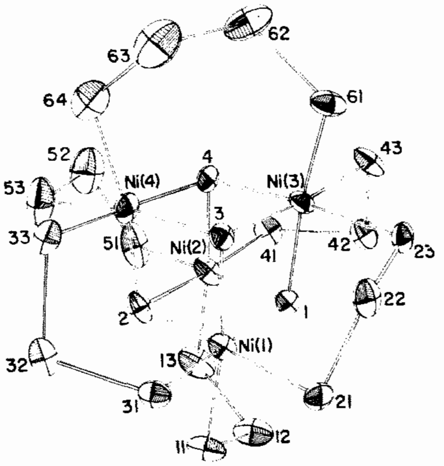

Fig. 3. A drawing of the $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ anion with the labeling scheme.

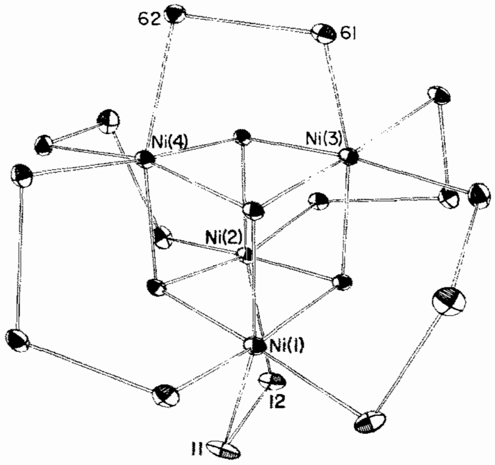

Fig. 4. A drawing of the $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ anion. Only the labels on the rings that differ from those of Fig. 3 are shown.

geometry may account for the lack of bond shortening expected on going from Ni^{II} to Ni^{IV}. The Ni–Te distances in the $[Ni_4Te_{20}]^{4-}$ anion range from 2.492(2) to 2.667(2) Å (Table 3). A Ni–Te average bond length of 2.981(2) Å for octahedrally coordinated Ni^0 is found in $Ni_9Te_6(PEt_3)_8$ [23]. In this instance the bond shortening on going from Ni^0 to Ni^{IV} is apparent.

Each of the two nickel cubanes may be considered electronically in two ways: as a 72 valence electron cluster or as a species possessing four 18-electron Ni

TABLE 3. Interatomic distances (Å) in the $[Ni_4Se_{23}]^{4-}$ and $[Ni_4Te_{20}]^{4-}$ ions

	Q = Se	Q = Te
Ni(1)–Ni(2)	3.508(8)	3.657(2)
Ni(1)–Ni(3)	3.456(8)	3.794(2)
Ni(1)–Ni(4)	3.475(9)	3.860(2)
Ni(2)–Ni(3)	3.483(8)	3.814(2)
Ni(2)–Ni(4)	3.498(9)	3.868(2)
Ni(3)–Ni(4)	3.623(9)	3.638(2)
Q(1)–Q(2)	3.156(6)	3.429(1)
Q(1)–Q(3)	3.188(6)	3.382(1)
Q(1)–Q(4)	3.173(6)	3.346(1)
Q(2)–Q(3)	3.175(6)	3.350(1)
Q(2)–Q(4)	3.180(5)	3.335(1)
Q(3)–Q(4)	3.031(5)	3.467(1)
Ni(1)–Q(1)	2.360(7)	2.535(2)
Ni(1)–Q(2)	2.349(8)	2.510(2)
Ni(1)–Q(3)	2.371(7)	2.567(2)
Ni(2)–Q(1)	2.338(7)	2.492(2)
Ni(2)–Q(2)	2.394(7)	2.546(2)
Ni(2)–Q(4)	2.385(8)	2.572(2)
Ni(3)–Q(1)	2.357(7)	2.558(2)
Ni(3)–Q(3)	2.341(7)	2.508(2)
Ni(3)–Q(4)	2.368(7)	2.529(2)
Ni(4)–Q(2)	2.338(8)	2.589(2)
Ni(4)–Q(3)	2.377(7)	2.559(2)
Ni(4)–Q(4)	2.362(7)	2.511(2)
Ni(1)–Q(21)	2.412(7)	2.577(2)
Ni(1)–Q(31)	2.383(7)	2.542(2)
Ni(2)–Q(41)	2.405(7)	2.543(2)
Ni(2)–Q(51)	2.417(8)	2.570(2)
Ni(3)–Q(23)	2.385(7)	2.534(2)
Ni(3)–Q(43)	2.412(7)	2.582(2)
Ni(4)–Q(33)	2.398(8)	2.631(2)
Ni(4)–Q(53)	2.442(8)	2.545(2)
Ni(1)–Q(11)	2.388(7)	2.617(2)
Ni(2)–Q(12)		2.640(2)
Ni(2)–Q(13)	2.396(8)	
Ni(3)–Q(61)	2.399(7)	2.597(2)
Ni(4)–Q(62)		2.667(2)
Ni(4)–Q(64)	2.367(8)	
Q(21)–Q(22)	2.336(6)	2.727(1)
Q(22)–Q(23)	2.325(6)	2.795(1)
Q(31)–Q(32)	2.342(6)	2.755(1)
Q(32)–Q(33)	2.338(6)	2.789(1)
Q(41)–Q(42)	2.343(6)	2.770(1)
Q(42)–Q(43)	2.339(6)	2.771(1)
Q(51)–Q(52)	2.231(9)	2.748(1)
Q(52)–Q(53)	2.297(8)	2.806(1)
Q(11)–Q(12)	2.338(6)	2.764(1)
Q(12)–Q(13)	2.301(7)	
Q(61)–Q(62)	2.315(7)	2.755(1)
Q(62)–Q(63)	2.313(8)	
Q(63)–Q(64)	2.300(8)	

atoms. Both considerations preclude interaction between the Ni atoms across the cubane faces. The average Ni–Ni distances of 3.504(60) Å in $[Ni_4Se_{23}]^{4-}$ and 3.772(100) Å in $[Ni_4Te_{20}]^{4-}$ indicate that no Ni–Ni

TABLE 4. Bond angles (°) in the $[Ni_4Se_{23}]^{4-}$ and $[Ni_4Te_{20}]^{4-}$ ions

	Q = Se	Q = Te
Q(1)–Ni(1)–Q(2)	84.2(2)	85.7(1)
Q(1)–Ni(1)–Q(3)	84.7(3)	83.0(1)
Q(2)–Ni(1)–Q(3)	84.6(3)	82.6(1)
Q(1)–Ni(2)–O(2)	83.7(2)	85.8(1)
Q(1)–Ni(2)–Q(4)	84.4(2)	82.7(1)
Q(2)–Ni(2)–Q(4)	83.4(3)	81.3(1)
Q(1)–Ni(3)–Q(3)	85.5(2)	83.7(1)
Q(1)–Ni(3)–Q(4)	84.4(2)	82.2(1)
Q(3)–Ni(3)–Q(4)	80.1(2)	86.7(1)
Q(2)–Ni(4)–Q(3)	84.6(3)	81.2(1)
Q(3)–Ni(4)–Q(4)	85.1(3)	81.7(1)
Q(3)–Ni(4)–Q(4)	79.5(2)	86.3(1)
Ni(1)–Q(1)–Ni(2)	96.6(3)	93.3(1)
Ni(1)–Q(1)–Ni(3)	94.2(2)	96.3(1)
Ni(2)–Q(1)–Ni(3)	95.8(3)	98.1(1)
Ni(1)–Q(2)–Ni(2)	95.4(3)	92.7(1)
Ni(1)–Q(2)–Ni(4)	95.7(3)	98.4(1)
Ni(2)–Q(2)–Ni(4)	95.3(3)	97.7(1)
Ni(1)–Q(3)–Ni(3)	94.3(2)	96.7(1)
Ni(1)–Q(3)–Ni(4)	94.1(3)	97.7(1)
Ni(3)–Q(3)–Ni(4)	100.3(3)	91.7(1)
Ni(2)–Q(4)–Ni(3)	94.2(3)	96.8(1)
Ni(2)–Q(4)–Ni(4)	94.9(3)	99.1(1)
Ni(3)–Q(4)–Ni(4)	100.0(3)	92.4(1)
Q(1)–Ni(1)–Q(31)	175.3(3)	168.0(1)
Q(2)–Ni(1)–Q(21)	175.8(3)	174.3(1)
Q(3)–Ni(1)–Q(11)	171.4(3)	160.9(1)
Q(1)–Ni(2)–Q(51)	177.7(4)	175.2(1)
Q(2)–Ni(2)–Q(41)	175.6(4)	167.0(1)
Q(4)–Ni(2)–Q(12)		162.7(1)
Q(4)–Ni(2)–Q(13)	171.6(3)	
Q(1)–Ni(3)–Q(61)	169.3(3)	162.7(1)
Q(3)–Ni(3)–Q(43)	174.6(3)	174.4(1)
Q(4)–Ni(3)–Q(23)	175.0(3)	167.1(1)
Q(2)–Ni(4)–Q(62)		159.8(1)
Q(2)–Ni(4)–Q(64)	164.2(3)	
Q(3)–Ni(4)–Q(53)	168.6(4)	165.8(1)
Q(4)–Ni(4)–Q(33)	170.7(3)	174.6(1)
Q(1)–Ni(1)–Q(11)	98.7(3)	95.0(1)
Q(1)–Ni(1)–Q(21)	93.8(3)	92.8(1)
Q(2)–Ni(1)–Q(11)	88.0(2)	78.3(1)
Q(2)–Ni(1)–Q(31)	99.5(3)	98.3(1)
Q(3)–Ni(1)–Q(21)	98.9(2)	102.7(1)
Q(3)–Ni(1)–Q(31)	92.7(3)	86.3(1)
Q(1)–Ni(2)–Q(12)		80.3(1)
Q(1)–Ni(2)–Q(13)	96.7(3)	
Q(1)–Ni(2)–Q(41)	97.1(3)	96.5(1)
Q(2)–Ni(2)–Q(12)		94.4(1)
Q(2)–Ni(2)–Q(13)	88.4(2)	
Q(2)–Ni(2)–Q(51)	97.1(3)	96.8(1)
Q(4)–Ni(2)–Q(41)	92.7(3)	86.3(1)
Q(4)–Ni(2)–Q(51)	98.9(3)	101.7(1)
Q(1)–Ni(3)–Q(23)	90.6(3)	87.8(1)
Q(1)–Ni(3)–Q(43)	97.8(3)	101.7(1)
Q(3)–Ni(3)–Q(23)	99.2(3)	100.0(1)
Q(3)–Ni(3)–Q(61)	91.5(3)	79.1(1)
Q(4)–Ni(3)–Q(43)	95.9(3)	94.7(1)
Q(4)–Ni(3)–Q(61)	105.2(3)	95.4(1)

(*continued*)

TABLE 4. (*continued*)

	Q=Se	Q=Te
Q(2)–Ni(4)–Q(33)	98.3(3)	100.8(1)
Q(2)–Ni(4)–Q(53)	83.9(3)	85.3(1)
Q(3)–Ni(4)–Q(33)	92.2(3)	98.8(1)
Q(3)–Ni(4)–Q(62)		95.1(1)
Q(3)–Ni(4)–Q(64)	111.0(3)	
Q(4)–Ni(4)–Q(53)	99.8(3)	96.4(1)
Q(4)–Ni(4)–Q(62)		78.3(1)
Q(4)–Ni(4)–Q(64)	95.5(3)	
Q(11)–Ni(1)–Q(21)	88.7(3)	96.4(1)
Q(11)–Ni(1)–Q(31)	84.4(2)	96.9(1)
Q(21)–Ni(1)–Q(31)	82.7(2)	84.3(1)
Q(12)–Ni(2)–Q(41)		98.6(1)
Q(13)–Ni(2)–Q(41)	95.9(3)	
Q(12)–Ni(2)–Q(51)		95.4(1)
Q(13)–Ni(2)–Q(51)	81.2(3)	
Q(41)–Ni(2)–Q(51)	82.3(2)	81.8(1)
Q(23)–Ni(3)–Q(43)	85.1(2)	79.3(1)
Q(23)–Ni(3)–Q(61)	79.7(2)	96.5(1)
Q(43)–Ni(3)–Q(61)	86.0(2)	95.5(1)
Q(33)–Ni(4)–Q(53)	89.2(3)	79.1(1)
Q(33)–Ni(4)–Q(62)		99.4(1)
Q(33)–Ni(4)–Q(64)	83.6(3)	
Q(53)–Ni(4)–Q(62)		99.1(1)
Q(53)–Ni(4)–Q(64)	80.4(3)	
Ni(1)–Q(21)–Q(22)	102.3(2)	103.0(1)
Ni(1)–Q(31)–Q(32)	104.3(2)	104.7(1)
Ni(2)–Q(41)–Q(42)	104.8(2)	106.3(1)
Ni(2)–Q(51)–Q(52)	105.0(3)	100.9(1)
Ni(3)–Q(23)–Q(22)	103.2(2)	106.4(1)
Ni(3)–Q(43)–Q(42)	103.5(2)	100.1(1)
Ni(4)–Q(33)–Q(32)	105.2(3)	98.7(1)
Ni(4)–Q(53)–Q(52)	103.8(3)	106.8(1)
Ni(1)–Q(11)–Q(12)	103.6(2)	97.7(1)
Ni(2)–Q(12)–Q(11)		95.8(1)
Ni(2)–Q(13)–Q(12)	105.6(3)	
Ni(3)–O(61)–Q(62)	112.3(3)	97.1(1)
Ni(4)–Q(62)–Q(61)		95.3(1)
Ni(4)–Q(64)–Q(63)	110.0(3)	
Q(21)–Q(22)–Q(23)	101.9(2)	102.1(1)
Q(31)–Q(32)–Q(33)	103.9(2)	106.3(1)
Q(41)–Q(42)–Q(43)	103.9(3)	98.9(1)
Q(51)–Q(52)–Q(53)	105.0(3)	100.4(1)
Q(11)–Q(12)–Q(13)	105.0(3)	
Q(61)–Q(62)–Q(63)	103.9(3)	
Q(64)–Q(63)–Q(62)	101.1(3)	

interactions exist. The lack of interactions implies that most of the distortions within the cubane frameworks arise from the steric demands on the chains that cross the faces of the cubane.

The [Ni_4Se_{23}]$^{4-}$ anion

While the bridging Se_3^{2-} chains appear to produce little strain on the Ni_4Se_4 cubane core, the Se_4^{2-} chain does distort it, as evidenced from the Ni–Ni distances, the Se_{cub}–Se_{cub} distances, and the bond angles within the cubane core. The Se_4^{2-} chain bridges atoms Ni(3) and Ni(4) and pushes these Ni atoms away from one another. The Ni(3)–Ni(4) distance is 3.623(9) Å, much longer than the 3.456(8)–3.508(8) Å range in the five other Ni–Ni distances. Conversely the Se(3)–Se(4) 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(3)–Se(3,4)–Ni(4) angles at 100.3(3) and 100.0(3)°, respectively, are much greater than the other Ni–Se_{cub}–Ni cubane bond angles (94.1(3)–96.6(3)°). The Se(3)–Ni(3,4)–Se(4) 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 Ni_2Se_3 five-membered rings are in the envelope conformation. In each case the Se on the interior of the Se_3 chain is in the flap position. The five-membered ring containing Ni(2)–Ni(4) has a conformation between that of an envelope and a half chair. This difference is probably the results of crystal packing as the conformational energy differences are small. The bond lengths and angles within the two types of five-membered rings may differ. The Ni(2)–Se(51) distance of 2.417(8) Å and the Ni(4)–Se(53) distance of 2.442(8) Å) may be compared with the other Ni–Se_{ring} bonds (2.383(7)–2.412(7) Å) and the Se(51)–Se(52) distance at 2.231(9) Å and the Se(53)–Se(52) distances of 2.297(8) Å may be compared with the Se–Se distances found in rings with the envelope conformation (2.301(7)–2.343(6) Å). At 87.0(3) and 94.5(3)° the Ni–Ni–Se angles in the distorted ring fall above and below the range (90.9(2)–93.9(2)°) of the Ni–Ni–Se angles in the four rings with the envelope conformation. The Se–Se–Se angle within the five-membered rings averages 103.6(13)°.

The six-membered Ni_2Se_4 ring has a chair conformation. As mentioned previously, the Ni(3)–Ni(4) distance is longer than the Ni–Ni distances in the five-membered rings. Other significant departures from the five-membered rings are the Ni–Ni–Se and Ni–Se–Se bond angles. While the chair conformation relieves some strain from a planar six-membered ring with 120° angles, the Ni atoms are locked in an octahedral environment with idealized 90° angles. The conformational effects are stronger than the octahedral preference, as evidenced by the average Ni–Ni–Se angle of 103.2(45)° (compared to 109° for a puckered six-membered ring or the 90° in the octahedron). The Ni–Se–Se angles average 111.2(16)°. Surprisingly, at 102.5(2)° the average Se–Se–Se angle in the six-membered ring does not differ from the average Se–Se–Se angle of 103.6(13)° in the five-membered rings.

The [Ni_4Te_{20}]$^{4-}$ anion

The Te_2^{2-} chains in the [Ni_4Te_{20}]$^{4-}$ anion fit nicely across the face of the cube and thus minimally perturb the core. The Te_3^{2-} chains, however, do not fit as well as their Se counterparts and cause some distortion of the cubane faces. The Te_3^{2-} chains, like the Se_4^{2-} chain, push those Ni atoms they bridge apart, making the Te–Ni–Te angles on the cubane faces more acute. The Te–Ni–Te angles on the Te_3^{2-} faces average 82.3(9)° compared to 86.2(6)° for the Te–Ni–Te angles on the Te_2^{2-} chain faces. Accordingly the average Ni–Ni distance on the Te_3^{2-} faces is longer at 3.834(36) Å than is that of 3.648(13) Å on the Te_2^{2-} faces. Conversely, the Ni–Te–Ni angles (97.6(10)°) and Te–Te distances (3.353(20) Å) are more obtuse and shorter on the Te_3^{2-} faces than on the Te_2^{2-} faces (92.5(7)° and 3.448(27) Å).

While the Te_2^{2-} chains may not overtly affect the cubane core, their positions over the cube faces may account for why this particular combination of Te_2/Te_3 ligands and this particular configuration is stable. The Te atoms of these Te_2^{2-} chains may interact with (and are twisted towards) the Te atoms on the cubane vertices. The interactions in question are between Te(1)···Te(12), Te(2)···Te(11), Te(3)···Te(61) and Te(4)···Te(62), and the distances range from 3.238(1) to 3.310(1) Å, within the commonly accepted range for Te–Te interactions in the solid state [24]. While short 1,3 interactions are the norm, there is some indication from the ^{125}Te NMR results that these interactions persist on the NMR time scale. The particular 1,3-interactions noted in general are shorter than other 1,3 interactions in the anion.

The Te_2^{2-} and Te_3^{2-} chains are otherwise nondescript. The four Ni_2Te_3 five-membered rings are in the envelope conformation. The two Ni_2Te_2 four-membered rings are in a butterfly conformation. The Te–Te distances in the Te_3^{2-} and Te_2^{2-} chains are similar, averaging 2.770(26) and 2.760(6) Å, respectively. The Te–Te–Te angles within the Te_3^{2-} chains average 101.9(32)°.

Spectroscopy

The existence of sharp ^{77}Se and ^{125}Te NMR spectra for $[Ni_4Se_{23}]^{4-}$ and $[Ni_4Te_{20}]^{4-}$, respectively, indicates that the anions are diamagnetic. While an octahedral Ni^{II} d^8 system would not exhibit tetragonal distortions owing to the presence of a non-distorted triplet state, the system would be paramagnetic with two unpaired electrons. On the other hand, a low spin d^6 octahedral Ni^{IV} system would be diamagnetic. The formulation of Ni^{IV} in these anions is consistent with charge balance. The Re atoms in the sulfide cubane $[Re_4Se_{22}]^{4-}$ have also been assigned as Re^{IV} [20].

The $[Ni_4Se_{23}]^{4-}$ anion exhibits a complex ^{77}Se NMR spectrum with fifteen resonances at δ 103, 134, 289, 361, 387, 401, 411, 470, 660, 680, 726, 749, 773, 789 and 804 ppm. From previous results [9, 17] we would expect the selenium rings to be fluxional. Thus a nine line spectrum would be expected, one line from each of the following groups of Se atoms: 1, 2; 3, 4; 11, 13; 12; $n3$ ($n=2$–5); $n2$ ($n=2$–5); $n1$ ($n=2$–5); 61, 64; 62, 63. The presence of fifteen lines could imply some Se exchange among the rings, but this has not been seen in similar systems [9, 17]. Rather the presence of more than one species in solution seems likely. The only other Ni triad d^6 system $[Pt(Se_4)_3]^{2-}$ has resonances at δ 680 and 790 ppm [18], but in $[Pt(Se_4)_3]^{2-}$ the rings are bound to a single metal center. Our ^{77}Se NMR data for the $[M(Se_4)_2]^{2-}$ system (M = Ni, Pd, Pt) indicate that the ring Se that is bound to the metal resonates downfield relative to the inner Se of the ring. This result of metal bound Se resonating downfield to inner ring Se is also found in the oligomeric W/Se systems [9]. The W/Se system also has bridging Se atoms, as well as Se_3^{2-} and Se_4^{2-} ligands; however, these ligands do not bridge metal centers, as in the cubanes, but are attached to a single metal, as in the $[M(Se_4)_2]^{2-}$ and $[Pt(Se_4)_3]^{2-}$ systems. If shielding is similar then the relative scale of chemical shifts for the W/Se system, namely bridging Se > metal bound $Se_{4\text{ring}}$ > metal bound $Se_{3\text{ring}}$ > $Se_{4\text{ring}}$ > $Se_{3\text{ring}}$, may apply to the $[Ni_4Se_{23}]^{4-}$ anion.

The ^{125}Te NMR spectrum of the $[Ni_4Te_{20}]^{4-}$ anion is far simpler than the ^{77}Se NMR spectrum of the $[Ni_4Se_{23}]^{4-}$ anion, exhibiting five resonances at δ −632, −324, 65, 325 and 766 ppm. If the Te_n^{2-} rings were fluxional on the NMR time scale then a four line spectrum would be expected, namely one line from each of the following groups of Te atoms: 1–4; $n1$ and $n2$ ($n=1$ and 6); $n1$ and $n3$ ($n=2$–5); and $n2$ ($n=2$–5). If an interaction of the Te_2^{2-} rings with the Te atoms of the core persists on the NMR time scale, then the Ni-bound Te atoms would be inequivalent and a five line spectra could result.

Ni^{IV} complexes

Ni^{IV} compounds are relatively rare, and those that exist fall into two categories: (i) systems with hard ligands, such as F^- and O^{2-}; (ii) systems with softer ligands but possessing π electrons, such as the chalcogenide containing dithio- and diselenocarbamates and diphos(diars)/halide compounds, capable of donating extra electron density into the Ni^{IV} center [25]. The $[Ni_4Se_{23}]^{4-}$ and $[Ni_4Te_{20}]^{4-}$ anions fall into neither of these categories. Polyselenide and especially polytelluride species are not hard ligands, and no π systems capable of donating extra electron density into the Ni^{IV} centers exist among what are normally considered σ bonding ligands. These remarkable structures are probably stabilized in part from a beneficial orbital overlap in the cubane core. Note that the Ni cubanes are low-spin d^6-octahedral systems while the homoleptic sulfur cubane $[Re_4S_{22}]^{4-}$ is a d^3-octahedral system. In the first instance the t_{2g} orbitals are completely filled while in the second the t_{2g} orbitals are also electronically symmetrical, with one electron in each orbital. Thus none of the structures should suffer instability from a Jahn–Teller effect. This favorable symmetry may provide the necessary stability for the cubanes to form. Note that despite the intense interest in soluble molybdenum sulfides, no homoleptic sulfide cubanes of Mo^{IV} (a d^2 system subject to Jahn–Teller distortions) have been reported.

Supplementary material

Hydrogen-atom positions, anisotropic thermal parameters, and structure amplitudes are available; see NAPS document No. 04935 of 85 pages. Order from ASIS/NAPS. Microfiche publication, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $5.00 for microfiche copy or $27.25 for photocopy. All orders must be prepaid. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material, $1.75 for postage of any microfiche orders.

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