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Synthesis and Structural Characterization of $[NEt_4]_4[Sn_2Te_6]$

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Introduction

During the past two decades the family of known homoleptic metal chalcogenide species ($M_nQ_m{}^{p-}$) (Q = S, Se, Te) has grown dramatically.[1-4] Most of this growth has been in metal sulfide species, but recent efforts in this and other laboratories have augmented significantly the number of known metal selenide and telluride species. Telluride anions include $[M(Te_4)_2]^{4-}$, M = Pd,[5] Hg,[6,7] Cd,[6,7] and Zn,[7] $[NbTe_{10}]^{3-}$,[8] and $[Cr_3Te_{24}]^{3-}$,[9] prepared by solution methods, and $[Au_4Te_4]^{4-}$,[10] $[Au_2Te_4]^{2-}$,[11] $[Hg_4Te_{12}]^{4-}$,[12] and $[Sn_2Te_6]^{4-}$,[13] prepared from the solubilization of solid-state materials. Encouraged by our recent syntheses of the $[Ni_4Te_{22}]^{4-}$ [14] and $[Pt_4Te_{22}]^{4-}$ [15] species, containing Ni^{IV} and Pt^{IV}, respectively, we have investigated the chemistry of other potential M^{IV} cations in the presence of polytelluride anions. Here we report an improved synthesis by solution methods of the $[Sn_2Te_6]^{4-}$ anion as well as the structure of $[NEt_4]_4[Sn_2Te_6]$.

Experimental Section

All reagents were purchased from Aldrich Chemical Co., Milwaukee, WI. Li_2Te was obtained by combining the stoichiometric amounts of freshly cut Li metal and Te powder in liquid ammonia under an Ar atmosphere. EDAX (energy dispersive analysis by X-rays) measurements were made with a Hitachi 570 scanning electron microscope. The microanalysis was performed by Oneida Research Services, Whiteboro, NY.

Synthesis of $[NEt_4]_4[Sn_2Te_6]$. Li_2Te (500 mg, 3.53 mmol), Te (1.0 g, 7.8 mmol), and $LiBH_4$ (100 mg, 4.6 mmol) were dissolved in DMF (30 mL). To this solution was added dropwise a solution of anhydrous $SnCl_2$ (189 mg, 1.00 mmol) in DMF (10 mL). The resulting solution was stirred at 90 °C for 45 min and filtered hot. Addition of NEt_4Cl (1 g in 10 mL of CH_3CN) onto the filtrate produced black, hexagonal plate-shaped crystals over a period of 2 days. Additional crystals were obtained by layering ether on the top of the filtrate. Total yield: 650 mg, 43% based on Sn. Quantitative analysis with EDAX on several crystals showed a Sn:Te ratio very close to 1:3. Anal. Calcd for $C_{32}H_{80}N_4Sn_2Te_6$: C, 25.22; H, 5.29; N, 3.67. Found: C, 24.86; H, 5.23; N, 3.65. The crystals are hygroscopic and are soluble in most polar solvents, including water.

Crystallography. Preliminary crystallographic information for $[NEt_4]_4[Sn_2Te_6]$ was obtained at -163 °C on an Enraf-Nonius CAD4 diffractometer. The crystal was then transferred to a Picker FACS-1 diffractometer for determination of the final cell constants and for data collection. Data collection and processing were carried out by methods standard in this laboratory.[16] The structure was solved and refined with the SHELXTL-PC[17] crystallographic package. Crystal data and some experimental details are given in Table I. Final positional parameters of all non-hydrogen atoms are given in Table II. Selected bond distances and bond angles for the $[Sn_2Te_6]^{4-}$ anion are given in Table III. Further crystallographic details, hydrogen atom parameters, and anisotropic thermal parameters are available as supplementary material.

Table I. Crystallographic Data for $[NEt_4]_4[Sn_2Te_6]$

empirical formula	$C_{32}H_{80}N_4Sn_2Te_6$	Z	4
		T, °C	-163
fw	1524	density (calcd), g/cm^3	2.045
space group	C_{2v}^{12}-$Cmc2_1$	μ, cm^{-1}	45
a, Å	17.485 (3)	transm coeff	0.588-0.861
b, Å	21.180 (4)	R on F_o ($F_o > 3\sigma(F_o)$)	0.046
c, Å	13.364 (3)	R_w on F_o ($F_o > 3\sigma(F_o)$)	0.043
V, Å^3	4949 (2)		

Table II. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for $[NEt_4]_4[Sn_2Te_6]$

	x	y	z	U_{eq}[a]
Sn(1)	0.5000	0.1535 (1)	0.3931 (1)	0.018 (1)
Sn(2)	0.5000	0.3287 (1)	0.3391 (1)	0.018 (1)
Te(1)	0.3666 (1)	0.0919 (1)	0.4130 (1)	0.023 (1)
Te(2)	0.5000	0.2226 (1)	0.2140 (1)	0.018 (1)
Te(3)	0.5000	0.2597 (1)	0.5193 (1)	0.020 (1)
Te(4)	0.3670 (1)	0.3897 (1)	0.3128	0.021 (1)
N(1)	0.2474 (7)	0.1794 (4)	0.1252 (9)	0.019 (3)
C(1)	0.3176 (6)	0.1401 (5)	0.1088 (1)	0.022 (4)
C(2)	0.3119 (8)	0.0975 (6)	0.0201 (13)	0.036 (5)
C(3)	0.1778 (6)	0.1380 (5)	0.1348 (10)	0.017 (3)
C(4)	0.1814 (8)	0.0886 (6)	0.2161 (13)	0.032 (4)
C(5)	0.2302 (7)	0.2239 (6)	0.0397 (10)	0.025 (4)
C(6)	0.2925 (8)	0.2733 (7)	0.0227 (12)	0.038 (5)
C(7)	0.2587 (7)	0.2168 (6)	0.2223 (10)	0.026 (4)
C(8)	0.1933 (8)	0.2580 (7)	0.2538 (11)	0.038 (5)
N(2)	0	0.0600 (6)	0.5098 (11)	0.011 (4)
C(9)	0	0.1275 (8)	0.5467 (14)	0.024 (5)
C(10)	0	0.1759 (9)	0.4650 (13)	0.032 (6)
C(11)	0.0692 (6)	0.0460 (6)	0.4439 (10)	0.028 (4)
C(12)	0.1464 (7)	0.0523 (7)	0.4971 (14)	0.039 (5)
C(13)	0	0.0174 (8)	0.6031 (14)	0.022 (5)
C(14)	0	-0.0514 (8)	0.5767 (14)	0.024 (6)
N(3)	0.5000	0.0659 (7)	0.7385 (12)	0.024 (5)
C(15)	0.5000	-0.0033 (9)	0.7165 (15)	0.029 (6)
C(16)	0.5000	-0.0213 (13)	0.6093 (17)	0.045 (8)
C(17)	0.5000	0.0744 (9)	0.8495 (14)	0.029 (6)
C(18)	0.5000	0.1429 (9)	0.8866 (16)	0.037 (7)
C(19)	0.4297 (8)	0.0977 (6)	0.6890 (10)	0.035 (4)
C(20)	0.3542 (7)	0.0714 (8)	0.7226 (14)	0.043 (5)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) in $[NEt_4]_4[Sn_2Te_6]$

Sn(1)···Sn(2)	3.781 (2)	Sn(1)-Te(3)	2.812 (2)
Sn(1)-Te(2)	2.804 (2)	Sn(2)-Te(2)	2.802 (2)
Sn(1)-Te(1)	2.686 (1)	Sn(2)-Te(4)	2.684 (1)
Sn(2)-Te(3)	2.818 (2)		
Te(1)-Sn(1)-Te(2)	109.8 (1)	Te(2)-Sn(1)-Te(3)	95.4 (1)
Te(1)-Sn(1)-Te(3)	109.2 (1)	Te(1)-Sn(1)-Te(1A)	120.5 (1)
Te(2)-Sn(2)-Te(3)	95.4 (1)	Te(3)-Sn(2)-Te(4)	111.2 (1)
Te(2)-Sn(2)-Te(4)	108.0 (1)	Te(4)-Sn(2)-Te(4A)	120.2 (1)
Sn(1)-Te(2)-Sn(2)	84.8 (1)	Sn(1)-Te(3)-Sn(2)	84.4 (1)

Results and Discussion

Reaction of $SnCl_2$ with a polysulfide solution affords the $[Sn(S_4)_2(S_6)]^{2-}$ [18] anion while reaction with a polyselenide solution

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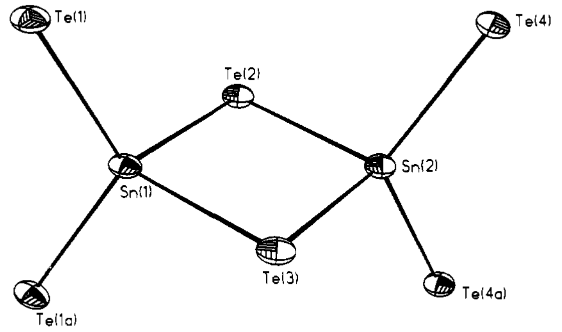

Figure 1. A view of the $[Sn_2Te_6]^{4-}$ anion. The 50% probability ellipsoids are shown.

affords the $[Sn(Se_4)_3]^{2-}$ anion.[19,20] Our attempts to prepare via a similar route the hypothetical $[Sn(Te_4)_3]^{2-}$ anion, or indeed any characterizable Sn/Te species, have not been successful. However, when we carry out the reaction of $SnCl_2$ with a polytelluride solution in the presence of $LiBH_4$, we obtain in good yield the binuclear anion $[Te_2Sn(\mu\text{-}Te)_2SnTe_2]^{4-}$ (herein abbreviated $[Sn_2Te_6]^{4-}$). The role of BH_4^- in the synthesis seems to be twofold. It not only provides dry reaction conditions, a must in Te chemistry, by reacting with traces of moisture present in DMF, but it also reacts with any Te formed from the decomposition of $[Sn_2Te_6]^{4-}$ or Te_n^{2-} species to regenerate soluble Te_n^{2-} species. The $[Sn_2Te_6]^{4-}$ anion has also been obtained from the solubilization of the solid-state material of stoichiometry K_4SnTe_4.[13] The synthesis described here is simpler and more convenient.

The sulfur and selenium analogues of the $[Sn_2Te_6]^{4-}$ anion are also known and were prepared by routes entirely different from the one described here.[21-25] The structures of all three anions $[Sn_2Q_6]^{4-}$ (Q = S, Se, Te) are the same, consisting of two edge-sharing SnQ_4 tetrahedra (Figure 1). In $[NEt_4]_4[Sn_2Te_6]$, the $[Sn_2Te_6]^{4-}$ ion possesses a crystallographically imposed mirror plane that passes through the Sn and bridging Te atoms; in $[NMe_4]_4[Sn_2Te_6]$,[13] the anion instead possesses a center of symmetry, but there are no significant differences in the structures of these two $[Sn_2Te_6]^{4-}$ anions. The Sn–Sn distances in $[NEt_4]_4[Sn_2Te_6]$ (3.781 (2) Å) and in $[NMe_4]_4[Sn_2Te_6]$ (3.782 (2) Å) are identical and are, as expected, much longer than those observed in $Cs_4[Sn_2Se_6]$ (3.504 (1) Å),[25] $Na_4[Sn_2Se_6]\cdot 13H_2O$ (3.554 (1) and 3.504 (1) Å),[23] and $Na_4[Sn_2S_6]\cdot 14H_2O$ (3.341 (1) Å).[26] The $Sn\text{–}Te_{bridging}$ distances in the $[Sn_2Te_6]^{4-}$ anion (NEt_4^+, 2.812 (2), 2.802 (2); NMe_4^+, 2.794 (1), 2.804 (1) Å) are significantly longer than the $Sn\text{–}Te_{terminal}$ distances (NEt_4^+, 2.686 (1), 2.689 (1); NMe_4^+, 2.689 (1), 2.700 (1) Å). These $Sn\text{–}Te_{terminal}$ distances are shorter than those in the solid-state compounds Na_4SnTe_4 (2.740–2.759 Å)[27] and $K_6Sn_2Te_6$ (2.725 (1)–2.729 (1) Å).[28]

$[NEt_4]_4[Sn_2Te_6]$ is soluble in DMF, CH_3CN, and H_2O. The resultant solution reacts instantly with Cu^+, Ni^{2+}, and Co^{2+}; characterization of the species thus formed is in progress.

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Supplementary Material Available: Tables of crystallographic details, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates (7 pages). Ordering information is given on any current masthead page.

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