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Coinage-Metal Tellurides: Synthesis and Structural Characterization of the $[(Te_4)M(\mu\text{-}Te_4)M(Te_4)]^{4-}$ Anions (M = Cu, Ag)

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Reaction of Cu^+ and Ag^+ cations in DMF with a polytelluride solution in the presence of PEt_3, followed by addition of NEt_4Cl, affords the two new metal telluride salts $[NEt_4]_4[(Te_4)M(\mu\text{-}Te_4)M(Te_4)]$ (M = Cu, Ag), the first examples of soluble copper and silver tellurides. Single crystal X-ray diffraction results are as follows: Cu complex, space group $P2_1/c$, monoclinic, $a = 10.564(2)$ Å, $b = 10.697(2)$ Å, $c = 25.740(5)$ Å, $\beta = 94.55(3)°$, $Z = 2$, $R = 0.065$ for 1701 independent observed reflections; Ag complex, space group $P2_1/c$, monoclinic, $a = 10.584(2)$ Å, $b = 10.763(2)$ Å, $c = 25.895(5)$ Å, $\beta = 94.01(3)°$, $Z = 2$, $R = 0.058$ for 7232 independent observed reflections. The isostructural anions have crystallographically imposed centers of symmetry. In each anion, the metal atoms are bridged by a Te_4 chain and coordinated in a bidentate fashion by Te_4 rings. These anions have no known sulfur or selenium analogues.

Introduction

Our interest in the chemistry of soluble metal chalcogenides has led us to synthesize many new selenide and telluride anions, including $[W_2Se_9]^{2-}$,[1] $[V_2Se_{13}]^{2-}$,[2] $[PtSe_{12}]^{2-}$,[3] $[Ni(Se_2)(WSe_4)]^{2-}$,[4] $[Ni_4Se_4(Se_4)(Se_3)_5]^{4-}$,[5] $[Ni_4Te_4(Te_3)_4(Te_2)_2]^{4-}$,[6] and $[Pt_4Te_4(Te_3)_6]^{4-}$.[7] None of these anions has a sulfur analogue. To date it appears that Te_n^{2-} rings and chains are often shorter than the Se_n^{2-} units in the corresponding metal selenides. For example, $[Ni_4Se_4(Se_4)(Se_3)_5]^{4-}$ contains Se_4^{2-} and Se_3^{2-} rings whereas $[Ni_4Te_4(Te_3)_4(Te_2)_2]^{4-}$ possesses only Te_2^{2-} and Te_3^{2-} rings. Thus we expect the soluble metal tellurides often will differ from the selenides. This is true for the $[NbTe_{10}]^{3-}$ ion[8] but not for the $[Cr_3(Q_4)_6]^{3-}$ ions (Q = Se, Te).[9] While the coinage metals have a very rich sulfide and selenide chemistry,[10,11] the known tellurides are limited to the $[Au_4Te_4]^{4-}$, $[Au_9Te_7]^{5-}$, and $[Au_2Te_4]^{2-}$ anions obtained from solid-state materials by extraction with ethylenediamine.[12,13] Here we report the synthesis and characterization of the first soluble copper and silver telluride anions. These differ from the related sulfide and selenide complexes, with which we compare them.

Experimental Section

All manipulations were carried out under a dry dinitrogen atmosphere. Li_2Te was obtained by combining stoichiometric amounts of Li and Te in dry liquid ammonia. All solvents were dried and purged with dry N_2 before use. $[Ag(Me_3P)I]_4$ and CuCl were purchased from Strem Chemical Co., Newburyport, MA, and used as received. All other reagents were used as received from Aldrich Chemical Co., Milwaukee, WI. Microanalyses were performed by Oneida Research Services, Whitesboro, NY.

Synthesis of $[NEt_4]_4[(Te_4)Cu(\mu\text{-}Te_4)Cu(Te_4)]$. Li_2Te (424 mg, 3 mmol) and Te powder (1148 mg, 9 mmol) were dissolved in DMF (15 mL) in a 100-mL Schlenk flask. In another flask CuCl (198 mg, 2 mmol) and PEt_3 (0.5 mL) were added to THF (20 mL), and the mixture was warmed over a water bath until all of the CuCl was digested. This solution was slowly transferred to the polytelluride solution by means of a cannula, and the combined solution was stirred for 1 h. The resulting reddish-purple solution was filtered, and NEt_4Cl (1 g) in CH_3CN (15 mL) was layered over the filtrate. Within 24 h, numerous red-black crystals had grown in the flask, and more crystals were obtained by layering ether on top of the solution. Total yield: 525 mg, 24%. Semiquantitative elemental analysis by EDAX on several crystals indicated a Cu:Te ratio between 1:5.2 and 1:6. The exact composition $[NEt_4]_4[(Te_4)Cu(\mu\text{-}Te_4)Cu(Te_4)]$, herein written as $[NEt_4]_4[Cu_2Te_{12}]$, was established by chemical analysis and a crystal structure determination. Anal. Calcd for $C_{32}H_{80}Cu_2N_4Te_{12}$: C, 17.6; H, 3.7; N, 2.6. Found: C, 17.5; H, 3.7; N, 2.4. The IR spectrum shows only absorptions characteristic of NEt_4^+.

Synthesis of $[NEt_4]_4[(Te_4)Ag(\mu\text{-}Te_4)Ag(Te_4)]$. A polytelluride solution was generated as described above. A solution of $[Ag(Me_3P)I]_4$ (622 mg, 0.5 mmol) in DMF (10 mL) was prepared, and PEt_3 (0.5 mL) was added. This solution was slowly transferred by means of a cannula onto the stirred polytelluride solution. Initially some red precipitate formed, but it later redissolved. Stirring was continued for another 30 min, and then the solution was filtered through a medium glass frit. NEt_4Cl (1 g) in CH_3CN (10 mL) was added to the filtrate, and after 2 days, a few crystals had grown. More crystals of $[NEt_4]_4[(Te_4)Ag(\mu\text{-}Te_4)Ag(Te_4)]$, herein written as $[NEt_4]_4[Ag_2Te_{12}]$, were obtained by adding ether (about 100 mL) to the solution. Yield: 390 mg, 18%. Anal. Calcd for $C_{32}H_{80}Ag_2N_4Te_{12}$: C, 16.9; H, 3.6; N, 2.5. Found: C, 14.8; H, 3.1; N, 2.1.

Crystallographic Studies. Since the $[NEt_4]_4[Cu_2Te_{12}]$ crystals are hygroscopic, they were handled under Paratone oil (Exxon). Unit cells of suitable crystals of $[NEt_4]_4[Cu_2Te_{12}]$ and $[NEt_4]_4[Ag_2Te_{12}]$ were obtained at 113 K from setting angles of 40 reflections that had been centered on a Picker diffractometer.[14] For each data collection, the intensities of six standard reflections were monitored every 100 reflections. For the Cu compound, a uniform 5% drop in the intensities of these standards was observed over the course of the data collection, and an appropriate correction was applied before the final refinement. Some crystallographic details are listed in Table I; more are available as supplementary material (Table SI[15]).

Intensity data for both the compounds were processed by methods standard in this laboratory[16] and corrected for absorption.[17] The structures were solved by direct methods with the use of the SHELXTL PC[18]

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Table I. Crystal Data for $[NEt_4]_4[Cu_2Te_{12}]$ and $[NEt_4]_4[Ag_2Te_{12}]$

compound	$[NEt_4]_4[(Te_4)Cu(\mu\text{-}Te_4)Cu(Te_4)]$	$[NEt_4]_4[(Te_4)Ag(\mu\text{-}Te_4)Ag(Te_4)]$
chem formula	$C_{32}H_{80}N_4Cu_2Te_{12}$	$C_{32}H_{80}N_4Ag_2Te_{12}$
fw	2179.28	2267.94
color, habit	red plates	red blocks
crystal size, mm	0.2 × 0.1 × 0.04	0.5 × 0.3 × 0.2
crystal system	monoclinic	monoclinic
a, Å	10.564(2)	10.584(2)
b, Å	10.697(2)	10.763(2)
c, Å	25.740(5)	25.895(5)
β, deg	94.55(3)	94.01(3)
unit cell vol, Å^3	2900(1)	2943(1)
density (calc), g/cm^3	2.496	2.560
space group	$P2_1/c$	$P2_1/c$
Z	2	2
μ, cm^{-1}	66.75	65.20
transm coeff	0.82–0.88	0.32–0.50
t, °C^a	−163	−163
R on F_o ($F_o^2 > 2\sigma(F_o^2)$)	0.065	0.0585
R_w on F_o^2 (all data)	0.135	0.157

^{a} Reference 30.

Table II. Atomic Positions and Thermal Parameters for $[NEt_4]_4[(Te_4)Cu(\mu\text{-}Te_4)Cu(Te_4)]$

atom	x	y	z	$U_{eq}{}^a/U_{iso}$, Å^2
Cu	0.6793(3)	0.3364(3)	0.6169(1)	0.023(2)
Te(1)	0.7472(2)	0.2379(2)	0.5350(1)	0.022(1)
Te(2)	0.9605(2)	0.1128(2)	0.5781(1)	0.032(1)
Te(3)	0.8920(2)	0.0450(2)	0.6739(1)	0.030(1)
Te(4)	0.7668(2)	0.2529(2)	0.7037(1)	0.027(1)
Te(5)	0.5264(2)	0.5116(2)	0.6242(1)	0.030(1)
Te(6)	0.5166(2)	0.6102(2)	0.5259(1)	0.029(1)
N(1)	0.0329(21)	0.9196(23)	0.1221(9)	0.025(6)
N(2)	0.4194(19)	0.5072(22)	0.1372(8)	0.021(6)
C(1)	0.1471(26)	0.9145(29)	0.0917(11)	0.033(8)
C(2)	0.1577(26)	1.0213(28)	0.0546(11)	0.034(8)
C(3)	0.0396(31)	0.8135(34)	0.1613(13)	0.054(11)
C(4)	−0.0769(26)	0.8100(30)	0.1938(12)	0.037(9)
C(5)	−0.0916(29)	0.9105(32)	0.0881(13)	0.049(10)
C(6)	−0.0938(29)	0.7781(31)	0.0576(12)	0.047(10)
C(7)	0.0181(34)	1.0416(37)	0.1450(15)	0.069(12)
C(8)	0.1339(30)	1.0791(35)	0.1815(13)	0.059(11)
C(9)	0.3147(23)	0.5130(27)	0.0967(10)	0.021(7)
C(10)	0.3096(27)	0.4096(29)	0.0591(11)	0.035(9)
C(11)	0.4052(23)	0.3974(27)	0.1741(10)	0.020(7)
C(12)	0.2838(25)	0.4082(30)	0.2061(11)	0.035(9)
C(13)	0.5499(24)	0.4843(27)	0.1166(11)	0.024(8)
C(14)	0.5873(24)	0.5848(27)	0.0816(10)	0.023(8)
C(15)	0.4172(27)	0.6252(31)	0.1676(11)	0.036(9)
C(16)	0.5185(30)	0.6366(35)	0.2123(13)	0.060(11)

^{a} Only Cu and Te atoms were refined anisotropically, and for these atoms $U_{eq} = {}^1/_3\Sigma_i\Sigma_j(U_{ij}a^*_ia^*_j\mathbf{a}_i\cdot\mathbf{a}_j)$ is tabulated. For the lighter atoms U_{iso} is given. The temperature factor expression is $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{12}hka^*b^* + ...)]$.

Table III. Atomic Positions and Thermal Parameters for $[NEt_4]_4[(Te_4)Ag(\mu\text{-}Te_4)Ag(Te_4)]$

atom	x	y	z	U_{eq},^{a} Å^2
Ag	0.3273(1)	0.6596(1)	0.3808(1)	0.0179(2)
Te(1)	0.2501(1)	0.7663(1)	0.4680(1)	0.0191(2)
Te(2)	0.0387(1)	0.8865(1)	0.4225(1)	0.0245(2)
Te(3)	0.1086(1)	0.9595(1)	0.3276(1)	0.0226(2)
Te(4)	0.2291(1)	0.7575(1)	0.2903(1)	0.0219(2)
Te(5)	0.4907(1)	0.4704(1)	0.3763(1)	0.0228(2)
Te(6)	0.4884(1)	0.3872(1)	0.4758(1)	0.0207(2)
N(1)	0.0179(5)	0.9199(6)	0.1209(2)	0.017(2)
N(2)	0.4187(5)	0.4971(6)	0.1397(2)	0.017(2)
C(1)	0.1361(7)	0.9140(8)	0.0912(3)	0.025(3)
C(2)	0.1492(8)	1.0243(9)	0.0546(3)	0.030(4)
C(3)	−0.1007(7)	0.9061(8)	0.0844(3)	0.028(3)
C(4)	−0.1070(9)	0.7808(9)	0.0560(4)	0.034(4)
C(5)	0.0050(9)	1.0462(8)	0.1457(4)	0.032(5)
C(6)	0.1194(11)	1.0811(11)	0.1825(4)	0.042(6)
C(7)	0.0295(8)	0.8167(8)	0.1602(3)	0.026(4)
C(8)	−0.0846(9)	0.8108(9)	0.1950(3)	0.032(5)
C(9)	0.3129(7)	0.5090(7)	0.0972(3)	0.021(3)
C(10)	0.3092(9)	0.4088(10)	0.0570(4)	0.036(4)
C(11)	0.4171(8)	0.6148(7)	0.1716(3)	0.028(4)
C(12)	0.5178(10)	0.6216(11)	0.2160(4)	0.042(5)
C(13)	0.4016(7)	0.3825(8)	0.1722(3)	0.027(3)
C(14)	0.2862(8)	0.3862(9)	0.2054(4)	0.035(4)
C(15)	0.5462(7)	0.4814(7)	0.1168(3)	0.023(3)
C(16)	0.5830(7)	0.5837(8)	0.0816(3)	0.027(3)

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

crystallographic package and refined with the SHELXL-92[19] least-squares program. Upon anisotropic refinement, the thermal parameters of some of the carbon atoms in $[NEt_4]_2[Cu_2Te_{12}]$ became non-positive definite, so in the final structural model all carbon and nitrogen atoms were treated isotropically. Anisotropic refinement of all non-hydrogen atoms was possible for $[NEt_4]_4[Ag_2Te_{12}]$. In both refinements methylene hydrogen atoms were placed at calculated positions (0.96 Å) and refined with a riding model. The positions of the methyl hydrogen atoms were determined from residual electron density maps calculated in the H_3 plane determined from the tetrahedral geometry of the central carbon atom and a C–H distance of 0.95 Å. The maxima were well defined. H–C–C–H torsion angles that corresponded to the maxima were refined as additional least-squares parameters. No unusual features were observed in the final difference electron density map of either structure (Table SI[15]). Positional parameters for $[NEt_4]_4[Cu_2Te_{12}]$ and $[NEt_4]_4[Ag_2Te_{12}]$ are given in Tables II and III, respectively; thermal displacement parameters are provided in Tables SII and SIII, and hydrogen atom positions may be found in Tables SIV and SV.[15]

Results and Discussion

Synthesis. Reaction of CuCl and $[AgI(PMe_3)]_4$ in DMF in the presence of PEt_3 and NEt_4Cl affords the $[Cu_2Te_{12}]^{4-}$ and $[Ag_2Te_{12}]^{4-}$ anions, respectively:

$$2M^+ + 3Te_4^{\ 2-} \xrightarrow[\text{DMF}]{\text{NEt}_4^+,\ \text{PEt}_3} [NEt_4]_4[(Te_4)M(\mu\text{-}Te_4)M(Te_4)]$$

Under similar reaction conditions but without phosphine, only insoluble polymeric materials are obtained. The role of phosphine has not been explored, but it may be to provide basic conditions, as the same salts were obtained (in lower yield) with the use of excess NEt_3 in place of phosphine. The use of $[Ag(PMe_3)I]_4$ as starting material in the synthesis of the (phosphine free) $[Ag_2Te_{12}]^{4-}$ anion proves that alkylphosphines can be labile in the presence of polytellurides; perhaps this observation can be exploited in the synthesis of other late-transition-metal tellurides.

Structures. The $[Cu_2Te_{12}]^{4-}$ anion (Figure 1), which has a crystallographically imposed center of symmetry, features two five-membered $CuTe_4$ rings bridged by a Te_4^{2-} chain; the anion is thus $[(Te_4)Cu(\mu\text{-}Te_4)Cu(Te_4)]^{4-}$. This anion does not have an analogue in sulfur or selenium chemistry, although it resembles in broad outline the $[(S_6)Cu(\mu\text{-}S_8)Cu(S_6)_2]^{4-}$ and $[(Se_5)Cu(\mu\text{-}Se_5)Cu(Se_4)]^{4-}$ anions.[20,21] Again we observe that as the size of the chalcogen increases, the number of atoms in both the ring and the chain decreases. In the present anion, both Cu atoms possess trigonal planar geometry (Table IV). The $CuTe_4$ ring has the envelope conformation with a Te atom occupying the flap position. The three Cu–Te distances are equal in length (2.492(4)–2.514(4) Å) and may be compared to the Cu–Te distances in the known solid-state compounds KCuTe (2.58(2) Å) and $TlCu_3Te$ (2.593(2)–2.867(3) Å).[22,23] The ring exhibits an alternation of Te–Te distances—long (2.777(3) Å), short

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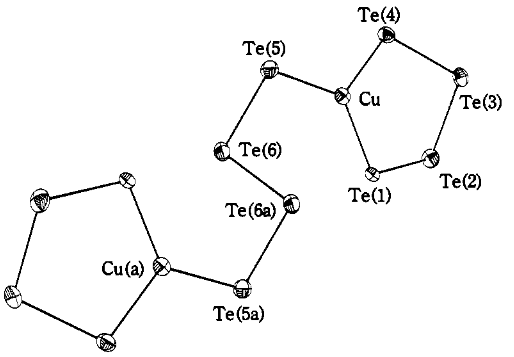

Figure 1. View of the $[Cu_2Te_{12}]^{4-}$ anion. In this figure and in Figure 2 the 50% probability thermal ellipsoids are shown.

Table IV. Bond Distances (Å) and Angles (deg)

$[NEt_4]_4[(Te_4)Cu(\mu\text{-}Te_4)Cu(Te_4)]$		$[NEt_4]_4[(Te_4)Ag(\mu\text{-}Te_4)Ag(Te_4)]$	
Cu–Te(1)	2.512(4)	Ag–Te(1)	2.710(1)
Cu–Te(4)	2.514(4)	Ag–Te(4)	2.709(1)
Cu–Te(5)	2.492(4)	Ag–Te(5)	2.680(1)
Te(1)–Te(2)	2.776(3)	Te(1)–Te(2)	2.774(1)
Te(2)–Te(3)	2.723(3)	Te(2)–Te(3)	2.730(1)
Te(3)–Te(4)	2.729(3)	Te(3)–Te(4)	2.732(1)
Te(5)–Te(6)	2.737(3)	Te(5)–Te(6)	2.731(1)
Te(6)–Te(6a)	2.717(4)	Te(6)–Te(6a)	2.735(1)
Te(1)–Cu–Te(4)	119.2(2)	Te(1)–Ag–Te(4)	115.86(3)
Te(1)–Cu–Te(5)	127.5(2)	Te(1)–Ag–Te(5)	126.25(3)
Te(4)–Cu–Te(5)	113.3(2)	Te(4)–Ag–Te(5)	117.89(3)
Cu–Te(1)–Te(2)	98.25(11)	Ag–Te(1)–Te(2)	97.19(3)
Te(1)–Te(2)–Te(3)	102.96(9)	Te(1)–Te(2)–Te(3)	104.76(3)
Te(2)–Te(3)–Te(4)	102.00(9)	Te(2)–Te(3)–Te(4)	104.60(3)
Cu–Te(4)–Te(3)	101.01(12)	Ag–Te(4)–Te(3)	99.41(3)
Cu–Te(5)–Te(6)	101.37(12)	Ag–Te(5)–Te(6)	99.22(3)
Te(5)–Te(6)–Te(6a)	96.48(11)	Te(5)–Te(6)–Te(6a)	97.72(3)

Table V. Comparison of Te–Te Distances (Å) in Free and Ligated Te_4 Units

compound		Te_{ext}–Te_{int}	Te_{int}–Te_{int}	ref
$[PPh_4]_2[Te_4]$		2.724(1)	2.762(1)	24
$[(2,2,2\text{-crypt})Na]_2$-$[Te_4]$		2.702(3), 2.702(3)	2.746(3)	31
$[NEt_4]_4[Cu_2Te_{12}]$	bridging	2.737(3)	2.717(4)	this paper
	ring	2.776(3), 2.729(3)	2.723(3)	
$[NEt_4]_4[Ag_2Te_{12}]$	bridging	2.731(1)	2.735(1)	this paper
	ring	2.774(1), 2.732(1)	2.730(1)	

(2.724(1) Å), and short (2.721(2) Å)—surprising when compared to the pattern found in the uncomplexed Te_4^{2-} anion[24]—short (2.724(1) Å), long (2.762(1) Å), and short (2.724(1) Å) (Table V). The bridging Te_4^{2-} group has the trans configuration and shows the expected Te–Te bond length alternation, which is the reverse of that seen in the uncomplexed Te_4^{2-} anion (Table V).

$[NEt_4]_4[Ag_2Te_{12}]$ is isostructural with $[NEt_4]_4[Cu_2Te_{12}]$. It has neither a sulfur nor a selenium analogue, but the related sulfur anion $[(S_6)Ag(\mu\text{-}S_8)Ag(S_6)]^{4-}$ exists.[25] The anion is shown in Figure 2, and important metrical data are provided in Table IV. The Ag atoms possess trigonal planar coordination, each coordinated doubly to the Te_4 ring and singly to one end of the bridging Te_4 ligand. Both the bridging and ring Te_4 units have features similar to those found in the $[Cu_2Te_{12}]^{4-}$ anion (Table V). The Ag–Te distances, which range from 2.680(1) to 2.701(1) Å, may be compared to those found in $Ag_4Te(NO_3)_2$ (2.89(1) Å)[26] and in the solid-state compound TlAgTe (2.782(8) and 2.843(4) Å).[27]

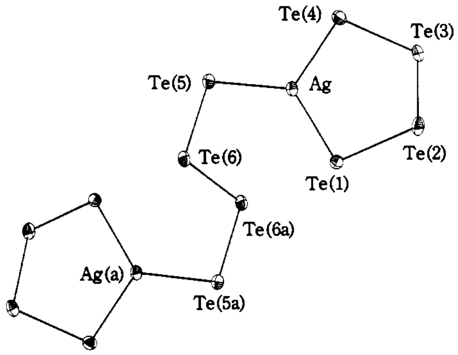

Figure 2. View of the $[Ag_2Te_{12}]^{4-}$ anion.

In each anion, the Te(1)–Te(2) bond is significantly longer than the other Te–Te bonds. This lengthening could conceivably arise from an incipient interaction between atoms Te(1) and Te(6a) (Figure 1), separated by only 3.488(4) Å in the Cu anion and 3.456(4) Å in the Ag anion, considerably shorter than the Te···Te van der Waals interaction of about 4 Å.[28] Indeed, by a different route[29] an $[AgTe_7]^{3-}$ ion has been obtained that has the structure that would result from the formation of a Te(1)–Te(6a) bond with concomitant cleavage of the Te(6a)–Te(5a) bond and loss of the $AgTe_5$ fragment.

In both of the present compounds, the metrical features of the cations are normal. Details are given in Table SVI.[15]

Similar reactions with Au(I) reagents have not produced the analogous $[Au_2Te_{12}]^{4-}$ anion, but rather the $[AuTe_7]^{3-}$ anion.[29]

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Supplementary Material Available: Tables of crystallographic details (Table SI), thermal displacement parameters (Tables SII and SIII), hydrogen atom coordinates (Tables SIV and SV), and distances and angles within the cations (Table SVI) (6 pages). Ordering information is given on any current masthead page.

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