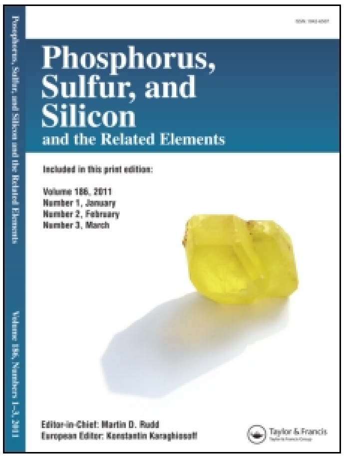

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Gold Inorganic Rings Based on Polychalcogenide Chains

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GOLD INORGANIC RINGS BASED ON POLYCHALCOGENIDE CHAINS

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ABSTRACT The reaction of AuCN with Se_x^{2-} and Te_x^{2-} in dimethylformamide in the presence of organic cations forms complexes with ring structures such as $(Ph_4P)_2[Au_2Se_5]$ (I), $(Ph_4P)_2[Au_2Se_6]$ (II), $(Ph_3PNPPh_3)_2K_2[Au_4Te_4]\cdot 2DMF$ (III). The reaction of $AuCl_3$ with Te^{2-} yielded $(Ph_4P)_2[Au_2(Te_2)_2]$ (IV). (I) crystallizes in the triclinic space group P-1 with a=10.381(4) Å, b=11.002(5) Å, c=21.181(9) Å, α=75.50(4)°, β=74.74(3)°, γ=81.40(4)°, V=2250 Å^3 (-93 °C). (II) crystallizes in the monoclinic space group C2/c with a=28.409(7) Å, b=10.97(1) Å, c=19.762(5) Å, β=130.49(1)°, V=4680 Å^3 (23 °C). (III) crystallizes in the orthorhombic space group Pbcn with a=29.90(2)Å, b=17.39(2)Å, c=17.707(8)Å, V=9206Å^3 (23 °C). (IV) crystallizes in the triclinic space group P-1 with a=10.526(3)Å, b=11.237(2)Å, c=10.453(4)Å, α=103.03(2)°, β=106.95(3)°, γ=81.66(2)°, V=1148 Å^3 (-95 °C). Single-crystal X-ray diffraction studies of (I) and (II) show that both compounds possess the same structural feature. Two linearly-coordinated Au(I) atoms interact with each other at 3.004 Å in (I) and 3.132Å in (II) with a bridging Se_2^{2-} unit on one side and a bridging triselenide Se_3^{2-} ligand (for I) and tetraselenide Se_4^{2-} ligand (for II) on the other, forming respectively seven and eight membered rings each containing two gold atoms. The structure of (III) consists of a distorted square where the Te atoms occupy the corners and the Au atoms lie in the center of the square's edges. Ionic interactions between the Au and K atoms result in a one-dimensional structure. The structure of (IV) is similar to those of (I) and (II) except two Te_2^{2-} ligands are involved.

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INTRODUCTION

Molecular metal-chalcogenide complexes represent one of the most structurally diverse class of compounds in which ring structures abound[1,2]. Recently, we reported on the chemistry of silver-polyselenide complexes, a system characterized by great structural diversity[3]. Furthermore, our preliminary exploration on the Au/Se_x^{2-} system revealed an intriguing and unanticipated redox chemistry[4]. The reaction of $AuCl_3$ with Na_2Se_5 resulted in the isolation of $[Se_{11}]^{2-}$, an oxidation product of Na_2Se_5 while replacement of AuCN for $AuCl_3$ in the presence of $[(Ph_3P)_2N]Cl$ gave

$[Au_2Se_2(Se_4)_2]^{2-}$, a Au(III) compound. In order to influence the aforementioned redox chemistry, we examined the reactivity of AuCN towards, the more difficult to reduce, shorter polyselenide Se_x^{2-} ligands (i.e. x=1-4) in the presence of different counterions such as Ph_4P^+, Pr_4N^+, Et_4N^+, etc. We also present results from our investigation of the Au/Te system. Here we present various related gold complexes with ring structures of variable size. These are $(Ph_4P)_2[Au_2(Se_2)(Se_3)]$ (I), $(Ph_4P)_2[Au_2(Se_2)(Se_4)]$ (II), $(Ph_3PNPPh_3)_2$-$K_2[Au_4Te_4]\cdot 2DMF$ (III) and $(Ph_4P)_2[Au_2(Te_2)_2]$ (IV). (Abbrev. Ph_3PNPPh_3 =PPN)

SYNTHESIS

The complexes presented here were synthesized either by simple metathetical reactions of AuCN and Q_x^{2-} ligands (Q=Se, Te) or by a redox reaction between Au^{3+} and Te^{2-}, in the presence of a counterion, according to equations 1-4. Equation 4 is a redox reaction. The solvent typically used was dimethylformamide. In a typical reaction AuCN or $AuCl_3$ is added slowly to a solution of the Q_x^{2-} and organic counterion.

$$2AuCN + 2Na_2Se_x + 2Ph_4P^+ \longrightarrow [Au_2(Se_2)(Se_3)]^{2-} + 2NaCN \quad \text{Eq. 1}$$
$$2AuCN + 2Na_2Se_x + 2Ph_4P^+ \longrightarrow [Au_2(Se_2)(Se_4)]^{2-} + 2NaCN \quad \text{Eq. 2}$$
$$4AuCN + 4K_2Te + 2[Ph_3PNPPh_3]^+ \longrightarrow [Au_4Te_4]^{4-} + 2KCN \quad \text{Eq. 3}$$
$$2AuCl_3 + 2K_2Te + 2Ph_4P^+ \longrightarrow [Au_2(Te_2)_2]^{2-} + 3KCl \quad \text{Eq. 4}$$

The precise structures of the complexes were established by single crystal X-ray crystallographic techniques. Crystal data and information concerning the structure solution and refinement are given in Table 1.

GOLD-CONTAINING POLYSELENIDE RINGS

The $[Au_2(Se_2)(Se_3)]^{2-}$ anion forms an envelop-shaped seven-membered ring containing two gold and five selenium atoms. The structure is shown in Figure 1. It has a C_s symmetry with two linearly-coordinated Au(I) centers bridged by Se_2^{2-} and Se_3^{2-} ligands. Two Au^+ ions and their associated Se atoms (e.g. Au(1)/Se(1)/Se(2)/-Au(2)/Se(3)/Se(5)) form a nearly perfect plane with the Se(4) atom being 1.172 Å above it. The Au-Se bonds average 2.397(5) Å. The Au····Au distance is 3.004(2) Å, similar to other reported Au····Au distances in Au^+/polychalcogenide compounds[6]. The Se(1)-Se(2) distance in the diselenide unit is long at 2.402(5) Å. The Se-Se bonds in the Se_3^{2-} unit, Se(3)-Se(4) and Se(4)-Se(5) are 2.283(5) Å and 2.280(9) Å respectively.

The $[Au_2(Se_2)(Se_4)]^{2-}$ anion in (II) is shown in Figure 2 and it is structurally similar to $[Au_2(Se_2)(Se_3)]^{2-}$. It has a C_2 symmetry with the two-fold axis running perpendicular to the Au····Au and Se(1)-Se(1) axes. The Au-Au separation between the two linearly-coordinated Au atoms is 3.132(3) Å. The Au-Se bond lengths separate into two sets. The Au-Se bonds to Se_2^{2-} are long at 2.433(5) Å, while the Au-Se bonds to Se_4^{2-} are short at 2.355(5) Å. Although the Se-Se bond distances in Se_4^{2-} are all normal, the Se-Se distance of 2.46(1) Å in Se_2^{2-} is even longer than that in (I). The eight-membered ring is puckered.

TABLE 1. Data for crystal structure analyses of $(Ph_4P)_2[Au_2(Se_2)(Se_3)]$ (I), $(Ph_4P)_2[Au_2(Se_2)(Se_4)]$ (II), $(PPN)_2K_2[Au_4Te_4]\cdot2DMF$ (III) and $(Ph_4P)_2[Au_2Te_4]$ (IV).

Formula	(I)	(II)	(III)	(IV)
FW	1467.5	1546.5	2585.57	1583.12
Crystal color, habit	dark red needle	dark red needle	orange needl	brown platelet
Temperature(°C)	-93	23	23	-95
a(Å)	10.381(4)	28.409(7)	29.90(2)	10.526(3)
b(Å)	11.002(5)	10.97(1)	17.39(2)	11.237(2)
c(Å)	21.181(9)	19.762(5)	17.707(8)	10.453(4)
α(°)	75.50(4)	90.00	90.0	103.03(2)
β(°)	74.74(3)	130.49(1)	90.0	106.95(3)
γ(°)	81.40(4)	90.00	90.0	81.66(2)
Z, V(Å^3)	2; 2250	4; 4680	16, 9206	2, 1148
Space group	P-1	C2/c	Pbcn	P-1
$D_{calc.}$(g cm^{-3})	2.17	2.19	3.73	2.29
μ(MoKα)^5	106	110	153.5	89.63
Crystal size(μm)	50x80x210	100x130x310	70x90x240	30x90x240
$2\theta_{max}$(°)	45	45	40	50
No. of data collected	5927	3358	4320	4303
No. of data unique	5491	3280	4315	4063
Data used($I>3.00\sigma(I)$)	3230	1475	1404	2609
No. of variables	274	142	204	153
No. of atoms/asym. unit	97	49	89	48
Final R/R_w(%)	5.5/6.8	7.6/7.9	10.6/13.5	5.2/5.9

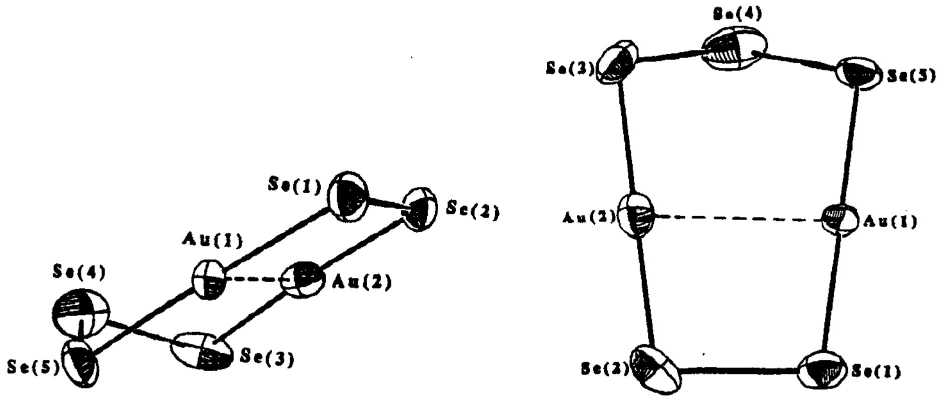


Figure 1. Two perspectives of the $[Au_2(Se_2)(Se_3)]^{2-}$ anion with labeling.

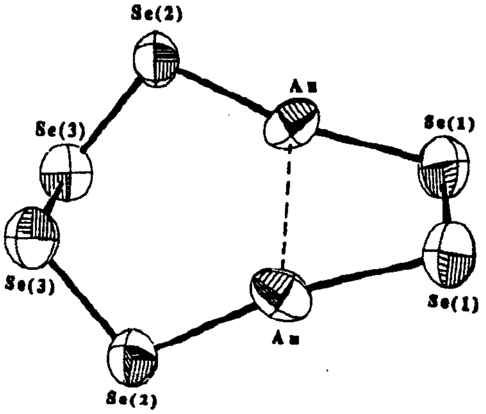
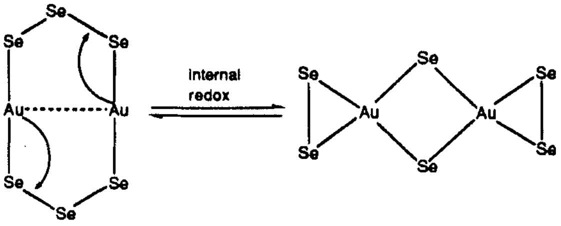


Figure 2. The structure of $[Au_2(Se_2)(Se_4)]^{2-}$ anion with labeling.

The long Se(1)-Se(2) distance of the Se_2^{2-} unit in (I) and (II) suggests considerable strain and originates from the need of this unit to span the Au····Au distance. Instead of forming a molecule with Se_2^{2-} ligands on both sides, (I) adopts a Se_3^{2-} ligand on one side and a Se_2^{2-} on the other. The Se-Se bonds in Se_2^{2-} can not be stretched to such a distance as to accommodate two Au atoms (2.9-3.0 Å apart) to form a planar molecule of $[Au_2(Se_2)_2]^{2-}$ because it would cause severe deviations in the linear coordination of Au. This structure is only found possible in the Au^+/Te_2^{2-} system (i.e. $[Au_2(Te_2)_2]^{2-}$)[7] (vide infra), where the Te-Te distance is 2.781 Å, closer to the Au-Au distance of 2.908 Å. Why the more symmetric compound $(Ph_4P)_2[Au_2(Se_x)_2]$ (x=3 or 4) does not form in reactions 1 and 2 appears unexplainable especially when a sulfur analogue, $[Au_2(S_4)_2]^{2-}$, is known[6a]. The preferential formation of (I) and (II) may be due to the stability of the $Au_2(Se_2)$ unit. Furthermore, it might be speculated that if the $[Au^I_2(Se_x)_2]^{2-}$ (x=3 or 4) formed in solution, it could be susceptible to internal redox chemistry between Au(I) and the Se-Se bonds according to scheme (A)[4].

It is more difficult to reduce the shorter Se_2^{2-} than it is to reduce Se_3^{2-} or Se_4^{2-}; this would make the Au^{3+} species unfavorable.



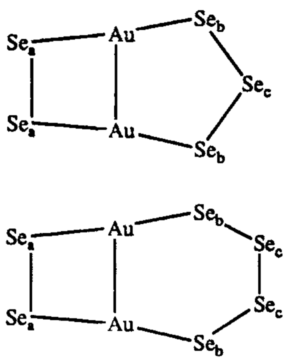
Scheme (A)

The isolation of two Au^+ and one Au^{3+}, [4] polyselenide compounds, as a function of Se_x^{2-} length and counterion size attests to the vacillating nature of redox chemistry between Au(I)/Au(III) and polyselenide ligands. Thus far, analogous redox chemistry with S_x^{2-} and Te_x^{2-} ligands is not known.

TABLE 2. Distances (Å) and Angles (°) for $[Au_2(Se_2)(Se_3)]^{2-}$ and $[Au_2(Se_2)(Se_4)]^{2-}$ Anions.

	(I)	(II)
Au--Se_a	2.394(4)	2.433(5)
Au--Se_b	2.401(3)	2.355(5)
Se_a--Se_a	2.402(5)	2.46(1)
Se_b--Se_c	2.281(5)	2.280(6)
Se_c--Se_c	——	2.301(7)
Au--Au	3.004(2)	3.132(3)
Se_a-Au-Se_b	177.4(1)	169.6(1)
Au-Se_a-Se_a	97.3(2)	95.4(1)
Au-Se_b-Se_c	101.1(2)	105.3(2)

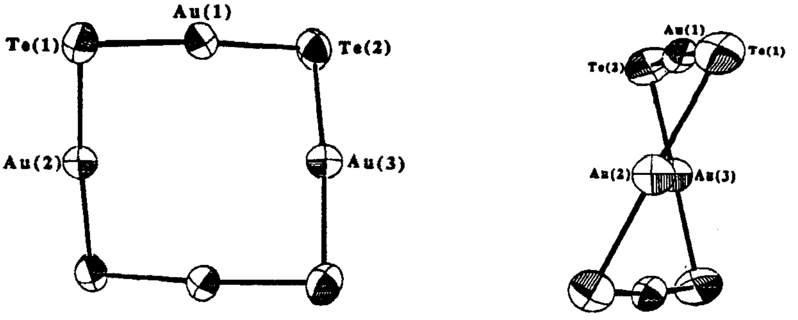
Labeling for Table 2.



GOLD-CONTAINING POLYTELLURIDE RINGS

The corresponding Au/Te chemistry is different from that of Se. In this system we have isolated two complexes, one with monotelluride and one with ditelluride ligands. The first complex, (III), is a remarkable ring structure shown in figure 3. The $[Au_4Te_4]$ ring approximates a square in which the Te atoms occupy the corners while the linearly coordinated Au atoms occupy the centers of the edges. This ring has been found in the related compounds $(Ph_4P)_2K_2[Au_4Te_4]\cdot 2DMF(CH_3OH)_2$ (V) and $(Ph_4P)_2$-$K_2[Au_4Te_4]\cdot 2en$ (VI) (en=ethylene diamine)[8]. The conformation of the $[Au_4Te_4]$ rings in (V) and (VI) are similar and show a planar geometry and a rhombohedral distortion, with two Au-Te-Au angles near 100° and two near 80°. On the contrary, the conformation of the $[Au_4Te_4]$ ring in (III) is non-planar and the Au-Te-Au angles are very close to 90°, see figure 3. The Te-Au-Te angles average 175.3°. Selected bond distances and angles are given in Table 3. The rhombohedral distortion found in (V) and (VI) is driven by the pairwise formation of d^{10}-d^{10} bonding interactions between Au atoms. Interestingly the Au atoms in (III) do not interact in thia fashion (min. Au-Au distance 3.60Å). The $[Au_4Te_4]$ ring in (III) sits on a crystallographic two-fold axis. The gold atoms lie approximately on a plane while the tellurium atoms are alternating ±0.8Å above and below this plane, see figure 3. The compounds (III) and (V) are closely related with differences in counterion and the solvate methanol molecules present in (V). The dramatic differences in the conformation between the $[Au_4Te_4]$ rings in (III) and those in (V) and (VI) must arise predominantly from packing effects.

As observed in (V) and (VI), (III) also shows significant bonding interactions of all Au atoms in the molecule with the K^+ ions in the lattice where each $[Au_4Te_4]^{4-}$ ring binds two alkali metal ions. Each K^+ atom also binds to two DMF molecules to complete its coordination sphere. The DMF molecules bridge, in a μ-oxo fashion, two K^+ atoms to form a $[K_2(DMF)_2]^{2+}$ dimer. This results in a stacked arrangement forming one-dimensional chains of alternating $[Au_4Te_4]^{4-}$ rings and $[K_2(DMF)_2]^{2+}$ dimers along the c-axis. This is shown in figure 4. The organic $[PPN]^+$ counterions are well separated and do not interact with the $\{[Au_4Te_4]K_2(DMF)_2\}_n{}^{2n-}$ fragment. A similar fragment exists in (V)[8]. The Au-K interactions observed in (III) find precedence in (V), (VI) and $[K(Au_9Te_7)]^{4-}$,[8] and reveal a considerable, albeit unexpected, nucleophilic character for the gold atoms.



(A) (B)

Figure 3. Two views of the $[Au_4Te_4]^{4-}$ ring with labeling scheme. The puckering of this structure is evident in (B).

TABLE 2. Selected Bond Distances (Å) and Angles (°) for $(Ph_3PNPPh_3)_2K_2[Au_4Te_4]\cdot 2DMF$

Au(1)-Te(1)	2.58(1)	Au(1)-Au(2)	3.60(1)
Au(1)-Te(2)	2.60(1)	Au(1)-Au(3)	3.61(1)
Au(2)-Te(1)	2.54(1)	Au(1)-K	3.50(2)
Au(3)-Te(2)	2.57(1)	Au(2)-K	3.52(2)
Au-Te (mean)	2.57(3)	Au(3)-K	3.54(2)
		Au-K (mean)	3.52(5)
Te(1)-Au(1)-Te(2)	175.5(3)		
Te(1)-Au(2)-Te(1)	174.4(4)	Au(1)-Te(1)-Au(2)	89.3(3)
Te(2)-Au(3)-Te(3)	175.1(4)	Au(1)-Te(2)-Au(3)	88.5(3)

TABLE 3. Selected Bond Distances (Å) and Angles (°) for $(Ph_4P)_2[Au_2(Te_2)_2]$ and Comparison with $(Ph_3PNPPh_3)_2[Au_2(Te_2)_2]$[7]

	$[Ph_4P]^+$ salt	$[Ph_3PNPPh_3]^+$ salt
Au-Au	2.905(2)	2.908
Au-Te(1), Au-Te(2)	2.573(2), 2.572(2)	2.543, 2.552
Te(1)-Te(2)	2.816(2)	2.781
Te(1)-Au-Te(2)	177.72(6)	176.64
Au-Te(1)-Te(2)	91.69(6)	88.79
Au-Te(2)-Te(1)	90.30(6)	94.05

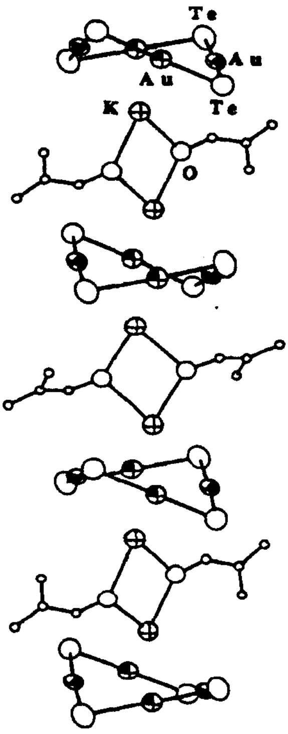


Figure 4. The one-dimensional stacking of the $[Au_4Te_4]^{4-}$ complex and the $[K_2(DMF)_2]^{2+}$ dimer interacting through ionic Au-K bonds.

The $(Ph_4P)_2[Au_2(Te_2)_2]$ complex was formed by the oxidation of Te^{2-} by Au^{3+}. It is composed of non interacting Ph_4P^+ cations and $[Au_2(Te_2)_2]^{2-}$ anions which are sitting on an inversion center. The latter are almost identical to those found in $(Ph_3PNPPh_3)_2$-$[Au_2(Te_2)_2]^7$. The structure of the anion in (IV) is shown in figure 5. It is a planar molecule. The structural motif is analogous to the $[Au_2(Se_2)(Se_x)]^{2-}$ (x=3,4) described above. The similar lengths of the Au-Au and Te-Te vectors in $[Au_2(Te_2)_2]^{2-}$ are probably responsible for the stability of this symmetric molecule. An analogous selenium or sulfur complex with S-S and Se-Se distances respectively of ~2.1Å and ~2.4 Å would be severely strained and therefore destabilized (vide supra). Compared to the $Au_2(Se_2)$ unit in (I) and (II) the strain in the corresponding $Au_2(Te_2)$ unit in (IV) should be considerably smaller. Selected bond lengths and angles are given in Table 3.

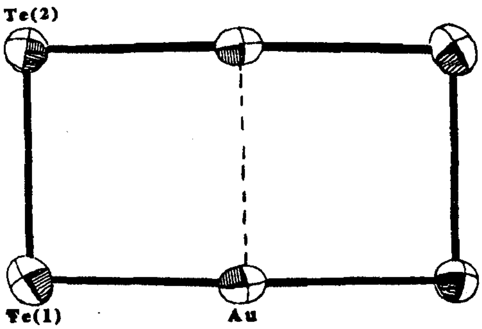


Figure 5. The structure and labeling scheme of the $[Au_2(Te_2)_2]^{2-}$ anion.

CONCLUSION

The unique ability of gold(I) to form linear two-coordinate bonds and the catenating ability of selenium and tellurium, combine to form a variety of new structural types including interesting ring structures. The spectroscopic properties and reactivity of these molecules is not explored yet. The strain associated with the $Au_2(Se_2)$ fragment may exhibit enhanced reactivity at the dichalcogenide unit. The ability of Au^+ to interact with alkali metal ions may be common in the A/Au/Q (A=alkali metal) system and suggests that interesting new compounds could be stabilized because of such interactions.[9]

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