The Molecular Structure of Some Transition-Metal Complexes with 1,2,3,4-Tetrazole-5-thiolate Anions☆

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The molecular structures of nine transition metal tetrazolethiolates have been determined by X-ray structure determinations. The ligand is invariably coordinated through its sulfur atom to the metal center [M = Pd^{II}, Cu^{I}, Ag^{I}, Au^{I}, Au^{III}, and Hg]. The M−S−C bond angles vary considerably, but this cannot be correlated with variations in the C−S bond lengths. Intermolecular association occurs for $Ph_3PAu(SCN_4Me)$ via Au−S contacts, leading to dimeric strands in the solid state. The copper compound $(Ph_3P)_3Cu_4(SCN_4Me)_4$ (**5**), possesses a rather asymmetric structure: one Cu atom is tricoordinated by 3 sulfur atoms, the other three are tetracoordinated by P and N as well as by S atoms.

Introduction

It is well known that mercaptotetrazoles exist as their tetrazinethione tautomers[1]. Deprotonation leads to the tetrazolethiolate anion, which can be considered as a 6π-electron ring system[2]. It binds to metal atoms via its sulfur atom as is evident from IR spectra[3]. However, as shown for organotin complexes of mercaptotetrazoles, one of the nitrogen atoms of the tetrazole ring can also be involved in coordination[4]. This is not necessarily indicated by IR data. Therefore, X-ray structure investigations were necessary to complement other methods of structure analysis that we have performed on neutral and anionic palladium, platinum, copper, silver, and mercury complexes of 2-methyl- and 2-phenyl-1,2,3,4-tetrazole-5-thiolates. These compounds were first reported in 1977[3].

Neutral Complexes

Two types of transition-metal complexes of the mercaptotetrazole ligand have hitherto been described: (i) neutral complexes of the type $L_nM(SCN_4R)_m$ and (ii) anionic complexes $[M(SCN_4R)_m]^{n-}$, while cationic complexes with these ligands are as yet unknown. Neutral mercury, gold, silver, and copper complexes **1**−**5** were available for X-ray structure analyses.

$(Ph_3P)_2Hg(SCN_4Ph)_2$ **1**

$(Ph_3P)AuSCN_4Me$ **2**

$(Ph_3P)AuSCN_4Ph$ **3**

$(Ph_3P)_2AgSCN_4Ph$ **4**

$(Ph_3P)_3Cu_4(SCN_4Me)_4$ **5**

The mercury complex **1** has a tetracoordinated metal center as shown in Figure 1. As has been suggested previously[3], only the sulfur atom of the tetrazolethiolate binds to the metal atom. In the case of compound **1**, the metal atom resides in a distorted tetrahedral environment. The mercury atom lies on a crystallographic twofold rotation axis and imposes C_2 point group symmetry on the molecule. There is a large variation in bond angles: the angle P1−Hg−P1a is rather wide [125.6(1)°] while the S1−Hg−S1a bond angle is compressed [95.7(1)°]. This reflects the larger steric requirement of the triphenylphosphane ligand. The two planes, P−Hg−P and S−Hg−S, are not perpendicular to one another; the twist angle is 78.9°. This is the result of an interaction between one phenyl group of the Ph_3P ligand and the tetrazole ring, which come into close contact and are oriented almost parallel to one another (interplanar angle: 18.4°). Moreover, the CN_4 plane is twisted with respect to the Hg1−S1−C1 plane by 17.8°, while the N-bonded phenyl group C2−C7 is in turn twisted by 125.6° with respect to the CN_4 plane.

Figure 1. ORTEP representation of the molecular structure of the mercury complex **1** in the solid state; hydrogen atoms are omitted for clarity

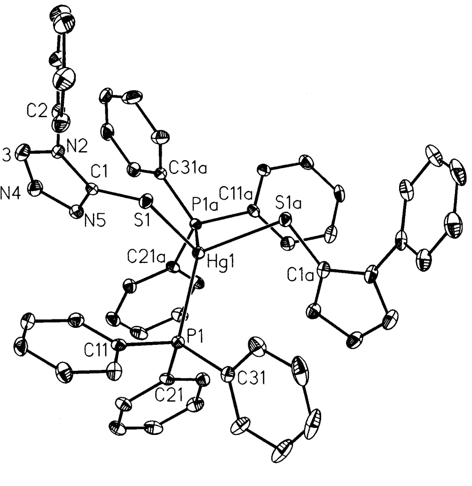

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Table 1. Selected bond lengths [Å] and bond angles [°] with estimated standard deviations (in parentheses) for compounds **1−9**

Lengths [Å]	$(Ph_3P)_2Hg$-$(SCN_4Ph)_2$ **1**[a]	$(Ph_3P)Au$-SCN_4Me **2**	$(Ph_3P)Au$-SCN_4Ph **3**	$(Ph_3P)_2Ag$-(SCN_4Ph) **4**	$(Ph_3P)_3Cu_4$-$(SCN_4Me)_3$ **5**[a]
M−P1	2.500(3)	2.261(1)	2.265(2)	2.478(1)	2.219(2)
M−P2	−	−	−	2.449(1)	−
M−S1	2.566(3)	2.325(1)	2.304(2)	2.530(1)	2.387(1)
M−S2	−	−	−	−	2.397(2) (S7)
S1−C1	1.716(5)	1.740(4)	1.733(7)	1.698(5)	1.717(7)
C1−N2	1.352(6)	1.342(5)	1.346(9)	1.363(6)	1.357(7)
N2−N3	1.364(6)	1.354(5)	1.378(8)	1.367(7)	1.354(8)
N3−N4	1.297(7)	1.289(5)	1.295(9)	1.291(7)	1.297(7)
N4−N5	1.361(6)	1.354(5)	1.366(8)	1.352(7)	1.376(7)
N5−C1	1.338(7)	1.331(5)	1.346(8)	1.345(7)	1.343(7)
Angles [°]					
P1−M−P2	125.6(1)	−	−	124.55(5)	−
P1−M−S1	100.37(6)	170.11(3)	172.68(5)	115.31(4)	117.26(6)
P2−M−S1	95.7(1)[b]	−	−	120.09(5)	−
M−S1−C1	103.2(2)	97.5(1)	105.3(2)	90.8(2)	106.9(2)
S1−C1−N2	123.5(4)	123.7(3)	123.9(4)	127.7(4)	124.0(5)
S1−C1−N5	128.9(4)	128.2(3)	127.1(5)	125.6(4)	130.1(4)
C1−N2−N3	108.9(4)	108.7(3)	107.8(5)	108.6(5)	110.4(5)
N2−N3−N4	105.9(4)	105.9(3)	106.3(6)	106.3(4)	106.2(5)
N3−N4−N5	111.6(4)	111.8(3)	111.9(5)	111.5(5)	110.4(5)
N4−N5−C1	106.1(4)	105.5(3)	105.0(6)	106.8(4)	107.2(5)
N5−C1−N2	107.6(4)	108.1(4)	109.0(5)	106.7(4)	105.9(6)

Table 1 *(Continued)*

Lengths [Å]	$Hg(SCN_4Me)_4^{2-}$ **6**[a]	$Pd(SCN_4Me)_4^{2-}$ **7**[a]	$Au(SCN_4Ph)_4^{-}$ **8**[a]	$Au(SCN_4Ph)_2^{-}$ **9**[a]
M−S1	2.535(3)	2.332(1)	2.356(1)	2.279(2)
M−S2	2.595(3)	2.339(1)	2.358(1)	2.288(2)
M−S3	2.507(2)	−	−	−
M−S4	2.534(3)	−	−	−
S1−C1	1.73(1)	1.727(4)	1.743(6)	1.748(7)
S2−C3	1.73(1)	1.735(4)	1.735(6)	1.725(7)
C1−N2	1.33(1)	1.342(5)	1.334(8)	1.360(8)
N2−N3	1.36(1)	1.363(5)	1.349(7)	1.351(8)
N3−N4	1.30(1)	1.284(5)	1.302(8)	1.299(8)
N4 -N5	1.33(1)	1.336(5)	1.353(7)	1.352(9)
N5−C1	1.33(1)	1.323(5)	1.325(8)	1.327(9)
Angles [°]				
S1−M−S2	106.22(9)	88.61(4)	89.41(5)	175.15(7)
S1−M−S	112.9(1) (S3)	91.39(4) (S2a)	90.59(5) (S2a)	−
M−S1−C1	100.5(4)	108.3(1)	106.8(2)	110.1(2)
M−S2−C2	98.1(3)	106.9(1)	107.2(2)	102.6(2)
S1−C1−N2	123.7(9)	126.0(3)	124.8(5)	128.9(5)
S1−C1−N5	126.4(8)	125.8(3)	126.9(5)	123.0(5)
C1−N2−N3	109.3(9)	108.2(4)	109.3(5)	108.2(5)
N2−N3−N4	104.3(9)	106.5(4)	105.2(5)	106.3(6)
N3−N4−N5	112.7(8)	110.9(4)	111.6(5)	111.4(6)
N4−N5−C1	105.7(9)	106.3(3)	105.5(5)	106.1(5)
N5−C1−N2	108(1)	108.1(4)	108.3(5)	107.9(6)

[a] Bond parameters for only one tetrazolethiolate unit is given. Those of the other tetrazolethiolate groups are similar within esd's. − [b] S1−M−S1a.

Surprisingly, the Hg−P bond is shorter than the Hg−S distance. The opposite might have been expected considering the atomic radii of P and S atoms. Trends in the bonding parameters of the tetrazole thiolate ligand will be discussed later.

Amongst the coinage metal tetrazolethiolates, those of Au^I are the simplest ones. Two closely related compounds, $Ph_3PAuSCN_4R$ [R = Me (**2**); Ph (**3**)], have been investigated, which differ considerably as far as intermolecular interactions are concerned. The methyl compound **2** shows a dicoordinated gold atom and an almost linear array of the core atoms P, Au and S and angle 170.1(3)°, see Figure 2]. There is clearly very little steric strain in the molecule because the C−P−C bond angles lie in the narrow range from 105.5 to 107.2(3)°; the largest deviation from the ideal tetrahedral angle is only 4°. It should also be noted that the Au1−S1−C1 bond angle is rather small for that of a thiolate.

Figure 2. ORTEP representation of the molecular structure of the gold 2-methyltetrazolethiolate **2** in the crystal; hydrogen atoms are omitted for clarity

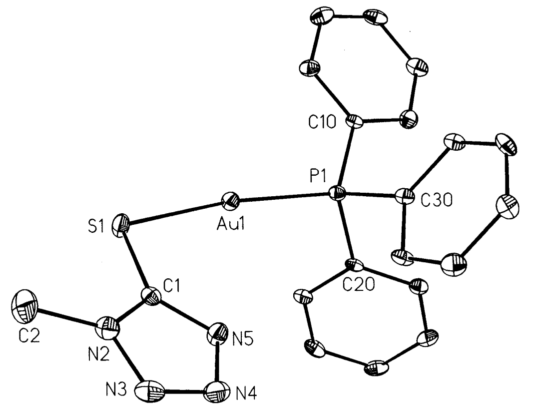
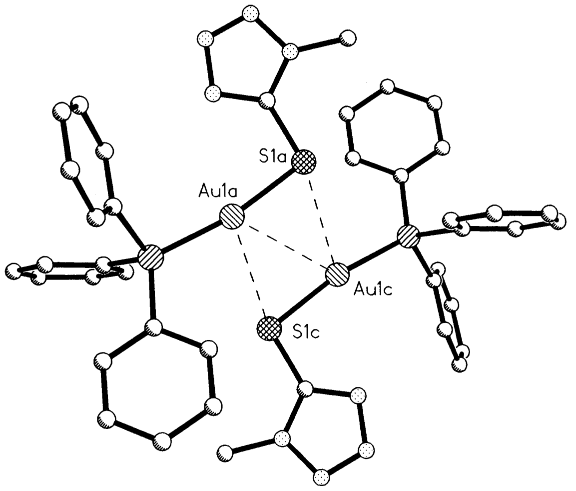


Figure 3. View of two associated molecules of **2** as present in the crystal



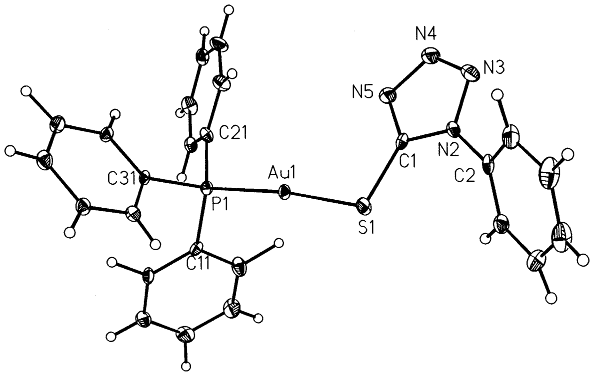
The tetrazole ring forms an angle of 13.2° with the P1−Au1−S1 plane. Interplanar angles between the phenyl groups range from 70.8 to 77.8°, and the C1−C6 plane is almost perpendicularly oriented to the P1−Au1−S1 plane. As in the case of compound **1**, we also observe a longer metal−S bond compared to the metal−P bond for the gold complex **2**, the difference between the bond lengths being

0.037 Å. This is, however, much smaller than that in **1** (0.066 Å).

In the lattice, the molecules of **2** are associated to dimers (see Figure 3) by weak intermolecular gold−sulfur contacts with a distance of 3.423 Å. However, the closest intermolecular Au−Au distance in **2** is 3.946 Å. Therefore, there is no bonding interaction between these atoms as is often found in gold(I) thiolates[5].

Although the overall molecular structure of the gold phenyltetrazolethiolate **3** (see Figure 4) resembles that of compound **2**, considerable differences become apparent upon close inspection. While the P1−Au1−S1 bond angles [172.68(5)°] and the C−P−C bond angles are very similar, the tetrazole ring is twisted out of the P1−Au1−S1 plane by 19.3°. More significant with regard to the packing of the molecules in the lattice is the effect of the phenyl group attached to the tetrazole ring. This group is twisted by 47.7° in relation to the nitrogen-containing ring. Compared with compound **2**, the Au−S bond is not significantly longer but at 105.3(2)° the Au1−S1−C1 bond angle is much wider. However, the most important difference between the two gold thiolates is the packing in the lattice: In compound **3** there are no intermolecular Au−S contacts. In fact, the shortest intermolecular distances between non-hydrogen atoms are between atom C16 of a PPh group and atoms C1, N2 and N3 (3.740, 4.014 and 4.165 Å, respectively).

Figure 4. ORTEP plot of the molecular structure of gold 2-phenyltetrazolethiolate **3**



In contrast to the gold complexes **2** and **3**, the silver 2-phenyltetrazolethiolate **4**, which crystallizes as $(Ph_3P)_2AgSCN_4Ph \cdot CH_2Cl_2$, coordinates to two triphenylphosphane ligands. This results in a planar P_2AgS structural unit (see Figure 6, sum of bond angles at Ag: 359.9°) with respect to which the CN_4 ring plane is twisted by 117.5°; the phenyl group bonded to the tetrazole ring forms an interplanar angle of 134.5° with the latter. The interplanar orientations of the phenyl rings of the phosphane ligands range from 88.0 to 97.0° for P1, and are 75.9, 94.4 and 114.0° for those at P2, the latter being much less evenly distributed than the former. Ag−P bond lengths are shorter by 0.08 and 0.05 Å for P2 and P1, respectively, compared to the Ag−S distance. Due to the rather acute Ag1−S1−C1 bond angle of 90.8(2)°, atom N5 comes relatively close to atom Ag1, the distance being 2.897 Å. This seems to be the reason why the two P−Ag1−S1 bond angles differ by 5.2°.

The copper methyltetrazolethiolate $Ph_3PCuSCN_4Me$ proved to be dimeric in solution suggesting a structure akin to type **A**[3]. However, crystals obtained from dichloromethane solution were shown by X-ray structure analysis to have a different composition: $Cu_4(SCN_4Me)_4(PPh_3)_3$ (compound **5**). Thus, one triphenylphosphane ligand is lost out of 4 monomeric units. The molecular structure of the tetranuclear complex **5**, which crystallizes with one molecule of CH_2Cl_2 per molecule of **5**, is depicted in Figure 7.

The assembly of the core atoms of **5** is rather asymmetric. Three copper atoms are tetracoordinated and one (Cu4) is only tricoordinated if Cu−Cu interactions are neglected [Cu4−Cu1: 2.745(1), Cu4−Cu3: 2.850(1) Å]. Atom Cu4 is the only one that has no triphenylphosphane as a coordination partner. It *only* coordinates to sulfur atoms. The S−Cu4−S bond angles range from 87.76(5) to 116.51(6)°. This corresponds to a strongly distorted trigonal-pyramidal array. A similar distortion is found for atom Cu1, where the tetrahedral angles span a range from 96.7(1) to 121.3(1)°. Deviations from tetrahedral symmetry are much smaller for atom Cu3 [103.5−121.5(2)°] and are smallest for atom Cu2 [101.6(1)−113.0(2)°]. Atoms Cu1 and Cu3 have one P, one N, and two S atoms as coordination partners, while atom Cu2 is surrounded by one P, one S, and two N atoms. The Cu−P bond lengths are different in terms of the 3σ criterion although the range (2.22−2.27 Å) does not suggest significant differences. This is not the case for the Cu−S bonds, which vary markedly (2.24−2.40 Å). Much less variation is observed for the Cu−N bond lengths [2.029−2.074(5) Å] and only the N atoms in the 5-position are found to be involved in bonding, as suggested previously (Formula **A**)[2].

Figure 8 gives a better perspective of the core structure of compound **5** than Figure 7. It represents a view almost down the Cu−S axis of the unique CuS_3 unit. One notes 5 six-membered rings and one eight-membered ring. The structure of this compound must be regarded as being rather unique.

Anionic Complexes

The anionic metal tetrazolethiolates **6**−**9** have in common a tetraphenylarsonium cation. Their AsC_4 core has a symmetry close to the point group T_d, which does not hold for the whole cation. In the tetraphenylarsonium salt of **6**, the As atom is located on a crystallographic twofold axis, but for all the other compounds the arsenic atom is found in a general position.

The mercury atom of the anion **6** (see Figure 9) resides in a general position, and out of the four Hg−S−C bond angles only two are equal [100.5(3)°] while the other two are 98.1(3)° and 103.0(4)°. This asymmetry becomes even more evident when one inspects the interplanar angles that the tetrazole rings form with the respective Hg−S−C planes: these range from 73.1° for S1 to 110.3° for S2 and 71.8° for S3, to finally 138.9° for S4. Two of the methyltetrazolethiolate units are mutually oriented in a "*syn*"

Figure 5. Stereoview of the unit cell of compound **3** showing the absence of intermolecular Au···S contacts

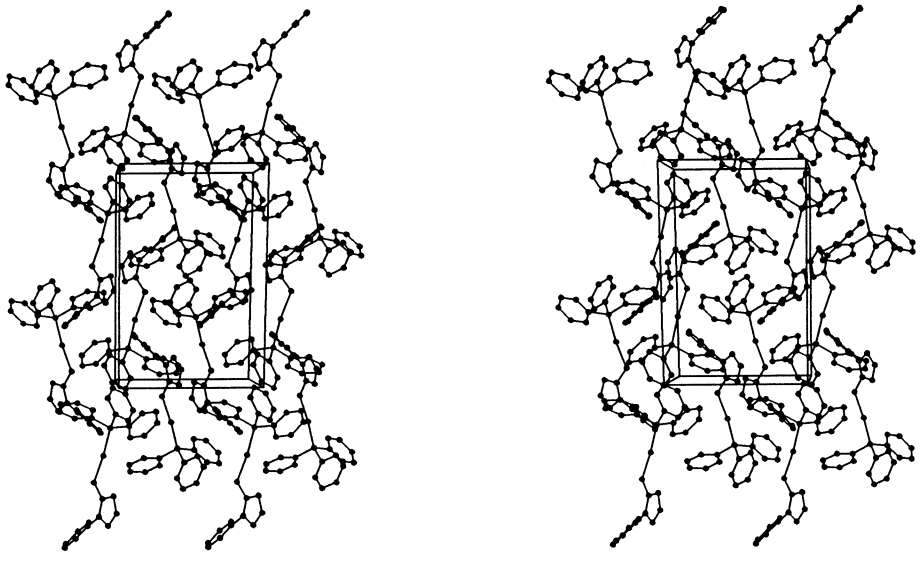


Figure 6. ORTEP representation of the molecular structure of the silver 2-methyltetrazolethiolate **4**; hydrogen atoms omitted for the sake of clarity

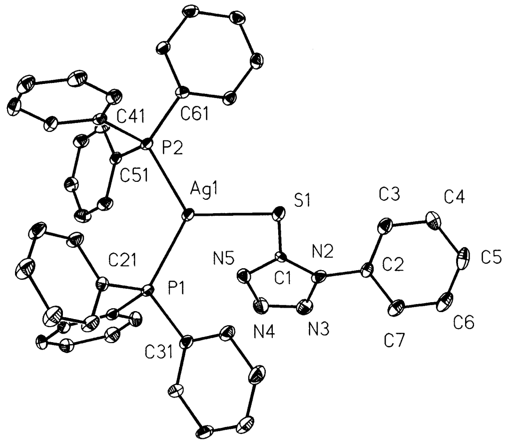
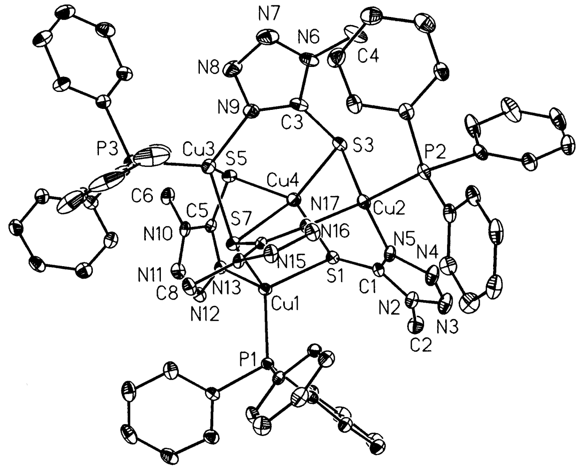


Figure 7. The molecular structure of the copper complex **5**; ORTEP representation of the molecule; hydrogen atoms omitted[a]



[a] Additional selected bond lengths [Å] and bond angles [°]: Cu2−N5 2.074(5), Cu2−P2 2.270(2), Cu2−N17 2.053(4), Cu2−S4 2.395(2), Cu3−P3 2.242(2), Cu3−S5 2.384(2), Cu3−S7 2.398(2), Cu4−S4 2.250(2), Cu4−S1 2.290(2), Cu4−S5 2.316(2), S4−C3 1.729(6), S5−C5 1.713(6), S4−C3 1.729(6); P1−Cu1−N13 121.3(1), S1−Cu1−N13 98.5(1), S1−Cu1−S7 113.47(5), S7−Cu1−N13 96.7(1), N17−Cu2−N5 112.8(2), N16−Cu2−P2 107.0(1), N5−Cu2−P2 111.4(1), N17−Cu2−S4 113.0(1), N5−Cu2−S4 101.6(2), S5−Cu3−S7 95.89(5), P3−Cu3−S7 104.42(6), P3−Cu3−S5 121.76(7), N9−Cu3−S5 103.5(2), S4−Cu4−S5 117.18(6), S1−Cu4−S7 103.66(5), S5−Cu4−S7 87.76(5), S4−Cu4−S7 112.92(6), S1−Cu4−S5 116.50(6).

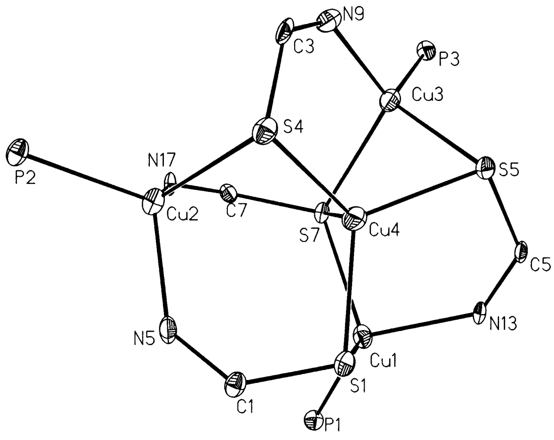
fashion (S2 and S4), while the other two (S1 and S3) adopt an "*anti*" orientation. It is, therefore, not surprising that the four Hg−S bond lengths are not equal [range 2.507(2)−2.595(3) Å]. There is no correlation between the Hg−S bond length and the Hg−S−C bond angle.

The Pd atom of the anion **7** (see Figure 10) lies on a center of inversion. Its tetrazole units are twisted with respect to the PdS_4 plane by 71.9 and 75.8° (S1 and S2), respectively. Hence, the point group symmetry for this anion approaches S_4. Bond angles at the sulfur atoms are 108.3(1) and 106.9(1)°, and the corresponding Pd−S bond lengths are 2.332(1) and 2.339(1) Å.

As in the case of the Pd^{II} complex anion **7**, we also find a planar geometry around the gold(III) atom in the complex anion **8** (see Figure 11). This anion also has a symmetry close to point group S_4 since its metal atom resides on an inversion center. In this case, the tetrazole units are oriented almost perfectly orthogonally to the AuS_4 plane, with interplanar angles of 89.4 and 89.7°. However, the Au−S−C planes are not coplanar and the plane Au1−S1−C1 forms an angle of 11.3° with the plane Au1−S2−C2. It is interesting to note that the bond angles Au−S−C are rather wide at 107.2(2) and 106.8(2)°, and that, like the angles, there is no significant difference between the Au−S bond lengths [2.356(1) and 2.358(1) Å].

A rather unusual geometry is observed for the Au^I anion **9** (see Figure 12). There is an almost linear arrangement of atoms S1−Au1−S2 [175.15(7)°]. The tetrazole units form grossly different interplanar angles with the S1−Au1−S2

Figure 8. The core structure of molecule **5**



$Hg(SCN_4Ph)_4^{2-}$ **6**

$Pd(SCN_4Me)_4^{2-}$ **7**

$Au(SCN_4Me)_4^{-}$ **8**

$Au(SCN_4Ph)_2^{-}$ **9**

Figure 9. ORTEP plot of the 2-methyltetrazolethiolato mercurate **6**; the cation is not depicted; hydrogen atoms are omitted for clarity

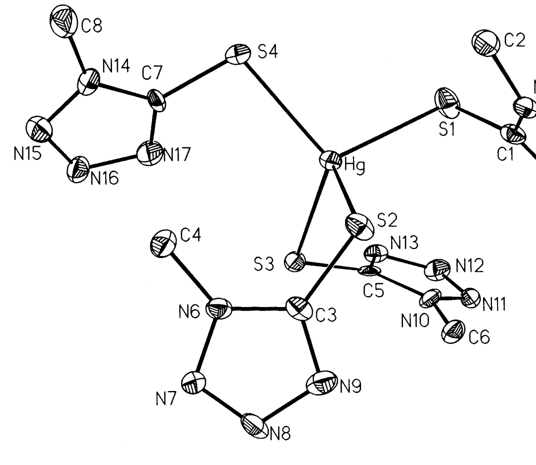


Figure 10. The molecular structure of the palladate anion **7**; hydrogen atoms omitted

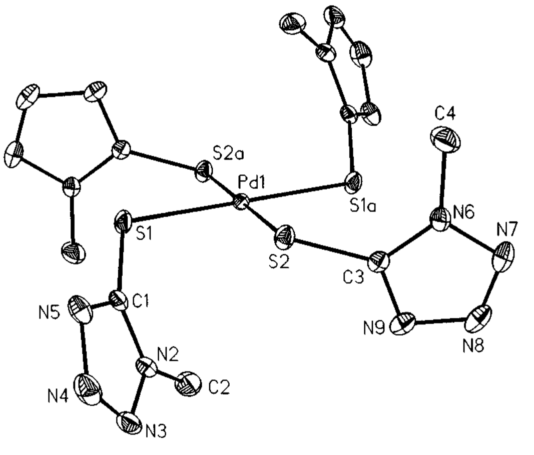
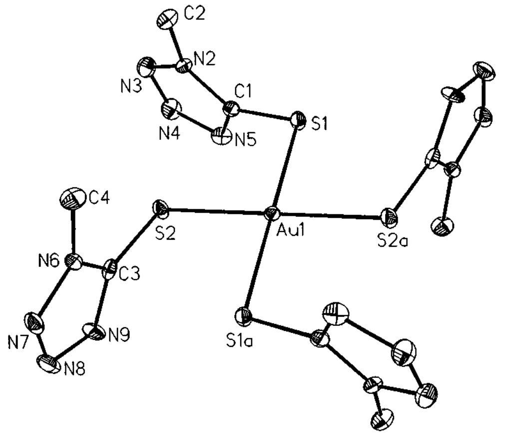
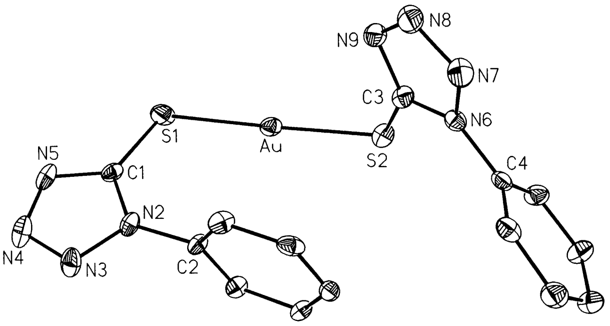


Figure 11. ORTEP representation of the molecular structure of the Au^{III} complex anion **8**; hydrogen atoms omitted for clarity



plane: 33° for tetrazole C1, and 114.8° for tetrazole C3. At least as different are the orientations of the planes of the phenyl groups in relation to the respective tetrazole rings. Interplanar angles are 92.2° and 130.8°, respectively. This leads to a molecular arrangement in which one of the two phenyl groups comes close to the gold center. In spite of this orientation, it is apparent that the Au−S1−C bond angle is wider [110.1(2)°] than the comparable angle at atom S2 [102.6(2)°]. If there were an η^6 interaction of a phenyl ring with the gold atom, one would expect that this phenyl group would be that with the more acute bond angle at the sulfur atom. This is obviously not the case.

Figure 12. The molecular structure of the bis(2-phenyltetrazolethiolato) aurate(I) (**9**), depicted in an orientation that shows the steric shielding of the gold atom by one phenyl group



Discussion

The present study on the molecular structures of 2-substituted metal tetrazolethiolates, as determined by X-ray structure analysis, confirm those suggested previously except in the case of the silver and copper compounds. All except the copper compound **5** show that the sulfur atom of the tetrazolethiolate coordinates to the metal center in accord with the hard/soft concept of acids and bases. Within the coinage group, compound **5** is also the only one in which nitrogen atoms are also involved in coordination, and this also fits with theory because the copper atom is the hardest in the coinage metal group. Moreover, the Cu−Cu atom distances calculated for **5** are too long to sug-

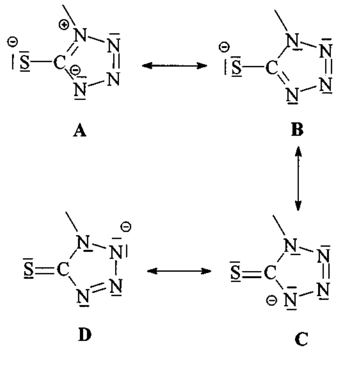
Table 2. Crystallographic data and data related to data acquisition and refinement for compounds **1−9**

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Chem. formula	$C_{50}H_{40}Hg$-$N_8P_2S_2$	$C_{20}H_{18}Au$-N_4PS	$C_{25}H_{20}Au$-N_4PS	$C_{44}H_{37}Ag$-$Cl_2N_4P_2S$	$C_{63}H_{59}Cl_2$-$Cu_4N_{16}P_3S_4$	$C_{56}H_{52}As_2$-$HgN_{16}S_4$	$C_{56}H_{52}As_2$-$N_{16}PdS_4$	$C_{32}H_{32}As$-$AuN_{16}S_4$	$C_{38}H_{30}As$-AuN_8S_2
Form. Wght.	1079.55	574.38	636.45	894.55	1586.47	1427.81	1333.62	1040.86	934.71
Cryst. size [mm]	0.2×0.3×0.42	0.12×0.21×0.35	0.1×0.1×0.5	0.2×0.2×0.3	0.1×0.1× 0.1	0.2×0.22×0.3	0.012×0.2×0.3	0.08×0.15×0.3	0.1×0.15×0.21
Cryst. system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2(1)/*n*	*P*2(1)/*n*	$P\bar{1}$	*P*2(1)/*n*	*P*2(1)	*P*2(1)/*n*	*C*2/*c*	*P*2(1)/*n*
a [Å]	19.561(3)	8.241(1)	13.0159(1)	10.126(2)	12.999(2)	10.4952(7)	7.498(4)	18.5892(7)	12.793(9)
b [Å]	9.996(1)	14.621(4)	10.8504(1)	13.314(3)	15.559(2)	22.762(1)	14.921(7)	6.4765(2)	13.677(1)
c [Å]	25.047(3)	16.895(4)	17.2007(1)	16.550(4)	34.030(1)	13.2473(7)	25.71(1)	33.105(1)	21.154(2)
α [°]	90.00	90.00	90.00	67.345(6)	90.00	90.00	90.00	90.00	90.00
β [°]	108.396(1)	103.848(1)	104.746(1)	84.590(9)	91.023(9)	112.741(1)	90.865(7)	103.103(1)	105.71(1)
γ [°]	90.00	90.00	90.00	80.29(1)	90.00	90.00	90.00	90.00	90.00
V [Å^3]	4647(1)	1976.6(7)	2349.21(3)	2028.3(8)	6881.3(15)	2918.6(3)	2876(2)	3881.9(2)	3563.2(5)
Z	4	4	4	2	4	2	2	4	4
ρ(calcd.) [Mg/m^3]	1.543	1.930	1.799	1.465	1.531	1.625	1.540	1.781	1.742
μ [mm^{-1}]	3.515	7.642	6.440	0.796	1.541	3.958	1.663	4.900	5.208
F(000)	2152	1104	1232	912	3232	1420	1352	2048	1832
Index range	$-25 \leq h \leq 25$	$-9 \leq h \leq 9$	$-16 \leq h \leq 16$	$-13 \leq h \leq 10$	$-11 \leq h \leq 11$	$-11 \leq h \leq 11$	$-9 \leq h \leq 9$	$-23 \leq h \leq 23$	$-14 \leq h \leq 13$
	$-11 \leq k \leq 11$	$-17 \leq k \leq 17$	$-13 \leq k \leq 13$	$-16 \leq k \leq 16$	$-19 \leq k \leq 19$	$-25 \leq k \leq 25$	$-19 \leq k \leq 19$	$-5 \leq k \leq 8$	$-17 \leq k \leq 17$
	$-32 \leq l \leq 31$	$-21 \leq l \leq 21$	$-22 \leq l \leq 11$	$-20 \leq l \leq 20$	$-43 \leq l \leq 43$	$-12 \leq l \leq 14$	$-27 \leq l \leq 27$	$-41 \leq l \leq 40$	$-26 \leq l \leq 26$
2θ [°]	55.02	55.06	57.60	57.82	55.38	46.70	55.16	58.02	55.00
Temp. [K]	293(2)	193	193	183	173	193	173	193	293(2)
Refl. collected	12181	10502	13008	11520	73528	13067	13961	10328	17994
Refl. unique	4496	2848	3760	6205	11158	7488	5345	3537	6645
Refl. obsd. (4σ)	3738	2526	3288	5591	8603	7095	4081	2467	4928
R (int.)	0.0733	0.0524	0.0495	0.0254	0.0584	0.0590	0.0495	0.0766	0.0708
No. variables	353	245	334	487	832	712	360	248	451
Weighting scheme[a] x/y	0.0344/ 20.4391	0.0234/ 3.2786	0.0478/ 7.3801	0.0643/ 8.1945	0.0000/ 33.1493	0.0403/ 14.4528	0.0077/ 4.1949	0.0188/ 34.7310	0.0285/ 17.7889
GOOF	1.083	1.069	1.143	1.063	1.256	1.151	1.197	1.316	1.127
Final *R* (4σ)	0.0380	0.0273	0.0348	0.0469	0.0589	0.0341	0.0421	0.0398	0.0395
Final *wR*2	0.0774	0.0482	0.0855	0.1259	0.1013	0.0965	0.0726	0.0834	0.0842
Larg. res. peak [e/Å^3]	1.488	1.374	2.451	0.907	1.127	0.726	0.460	1.157	1.012

[a] $w^{-1} = \sigma^2 F_o{}^2 + (xP)^2 + yP$; $P = (F_o{}^2 + 2\,F_c{}^2)/3$.

gest metal−metal bonding. Also, there are no close Au−Au contacts in **2**, although significant Au−Au interactions have been found in a related compound, Ph$_3$PAuSPh, which forms pairs in the crystal via Au−Au contacts [Au−Au 3.135(3), Au−S 2.30(1), and Au−P 2.26(1) Å][3].

The structural parameters obtained for complexes **1−9** show that there is *no* correlation between the magnitude of the M−S−C bond angle and the C−S bond length. It is, however, interesting to note that the M−S−C bond angle varies considerably. For the neutral complexes, the range covered is 97.5−106.9°, while for the anionic species it is 100.5−110.1°. There is also a range from 1.698(5)−1.740(4) Å for the C−S bond lengths found for the neutral complexes and a somewhat smaller range [1.72(1)−1.746(9) Å] for the anions. These bond lengths correspond to those found for thiourea [1.71(1)][6], thioacetamide [1.713(6)][7] and 3-hydrazino-5-mercapto-1,2,4-triazole [1.74(1)][7], but are definitely longer than the C=S double bond in CS$_2$ [1.555(1) Å]. Therefore, they are intermediate between the C−S single (1.82 Å) and C=S double bond lengths (see also the discussion in ref.[9]). Consequently, the bonding in this ligand is best described by the canonical formulae **B** to **D**.



Although the tetrazole ring can be considered as a 6π-electron heterocycle, the electron distribution is obviously not uniform because the N3−N4 bond is significantly shorter than the two other N−N bonds, let alone the C−N bonds[9]. Most notably, the N4−N5 bond is distinctly longer than the N3−N4 bond. This indicates that the canonical formulae **B** and **D** make the largest contributions to the ground state.

A comparison of the M−S bonds to the same metal center in neutral and anionic species reveals that these bonds are *longer* in the neutral complexes than in the anionic species, e.g. by 0.01 Å for M = Hg and by 0.05 and 0.03 Å, for M = Au^I. The longer Au−S bonds for the aurate anion **7** are clearly the consequence of the higher coordination number. However, the Au−S bond lengths for **2**, **3**, **8**, and **9** fall into the range observed for many other complexes with Au−S bonds (2.28−2.79 Å), while the Cu−S bond lengths of **5** are best compared with those in $(Me_4N)_2Cu_5(SPh)_7$ [2.159(3) Å][10].

The copper complex **5** demonstrates that the Cu−S bond lengths to the tetrazolethiolate units are elongated when the N5 atom is involved in coordination to the copper atoms. Thus, the canonical forms **B** and **C** become more significant in this situation. In contrast, the trimeric tetrazolethiolato complex $Me_3Sn(SCN_4Ph)$, where association occurs via the N3 atom, shows a shortening of the N4−N5 bond [1.35(2) Å] and a lengthening of the N3−N4 bond [1.35(2) Å]. This indicates that in this situation formula **D** makes a significant contribution to the ground state. It remains to investigate structures of tetrazolethiolates with truly hard acids in order to find out whether the hard cation will only bind to nitrogen and/or to sulfur as well. The only compound reported to date is the potassium crown compound (12-crown-4)$KSCN_4Me$[9], in which the S and one N atom coordinate to the potassium ion. In addition, there is a fairly short distance between the potassium ion and the ring carbon atom, but this cannot be considered as a potassium−carbon bond.

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Experimental Section

The compounds used for the X-ray structure determinations were the original samples[3]. Only the Cu complex **5** had to be crystallized from dichloromethane, and the structure determination showed the loss of a triphenylphosphane ligand.

All compounds were mounted on a glass fibre with a small amount of perfluoroether oil. After optical alignment at 193 K on a Siemens P4 diffractometer equipped with a Siemens CCD area detector, the unit cells were determined from the reflections of four sets of 15 frames each recorded at four different χ settings by changing ϕ by 0.3° between each frame. Data were recorded from a total of 1200 frames with 10-s exposures and changes in φ by 0.3° at two different χ settings. Data reduction was performed with the program SAINT, and an empirical absorption correction was applied using all data with esd's larger than 20. The structures were solved by the heavy-atom method; the model was complemented by difference Fourier synthesis and refined by using the programs SHELXL-93 and -97[10]. All non-hydrogen atoms were refined with anisotropic temperature parameters. Although many or all hydrogen positions could be located, the positions of hydrogen atoms were calculated and included as a riding model in the final cycles of the calculations. The crystallographic data are compiled in Table 2. Thermal ellipsoids in the figures represent a 25-% probability level. Further information on the crystal-structure determinations has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100802 and may be obtained from CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax (internat.): + 44 (0)1223/336033; e-mail: deposit@.cam.ac.uk].

☆ Dedicated to Prof. Dr. *G. Huttner* on the occasion of his 60th birthday.

Note Added in Proof **(December 3, 1997):** There has been a review on the coinage metals: M. D. Jansen, D. M. Grove, G. van Koten, *Prog. Inorg. Chem.* **1997**, *46*, 97−149.

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