In $Mo_3S_9^{2-}$ several molecular orbitals correspond directly to orbitals of the MoS_4^{2-} fragments. However, because of its larger size and lower symmetry, the mixing and delocalization of orbitals is much greater.

The highest occupied molecular orbitals in $Mo_3S_9^{2-}$ are π^*-antibonding S(end) orbitals (analogous to the t_1 orbitals in MoS_4^{2-}) and the central Mo $d(x^2 - y^2)$ orbital. The latter is not easily accessible due to the surrounding ligands, making the S(end)–S(end) π^*-antibonding orbital the most probable frontier donor orbital. Since the central Mo $d(x^2 - y^2)$ orbital is occupied by two electrons, the formal oxidation states of molybdenum are Mo(VI) for the end molybdenum atoms and Mo(IV) for the central one. These results are in agreement with earlier assignments.[4] The calculated HOMO–LUMO gap in this system is 1.9 eV. The low-lying acceptor orbitals in $Mo_3S_9^{2-}$ are the Mo(center)–S(top), Mo(end)–S(bridging), and Mo(end)–S(end) π^*-antibonding orbitals. Description of the binding in terms of the two MoS_4^{2-} fragments and the MoS^{2+} central core confirms the idea that MoS_4^{2-} can act as an acceptor as well as a donor ligand.

Acknowledgment. We thank Drs. W.-H. Pan, T. R. Halbert, and S. Harris for useful discussions.

Registry No. MoS_4^{2-}, 16330-92-0; $Mo_3S_9^{2-}$, 95344-47-1.

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Crystal Structure of Iodo(tetrahydrothiophene)gold(I) at 200 K: A Compound with an Infinite Array of Gold–Gold Bonds

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The crystal structure of $[\mathrm{Au}[\overline{\mathrm{S}(\mathrm{CH_2})_3\mathrm{CH_2}}]\mathrm{I}]_\infty$ has been determined from X-ray intensity data collected at 200 K with a CAD4 diffractometer. The space group is orthorhombic, $Pc2_1n$ with $Z = 8$, $a = 8.149$ (2) Å, $b = 11.460$ (4) Å, and $c = 15.956$ (3) Å. The refinement converged to $R = 0.062$. There are two different Au atoms in the asymmetric unit. One coordinates two iodides in an almost linear fashion. Both Au–I distances are 2.565 (2) Å, and the I–Au–I angle is 177.57 (7)°. The other Au atom coordinates two S atoms, also in an almost linear fashion. The Au–S distances are 2.306 (7) and 2.335 (6) Å, respectively, and the S–Au–S angle is 172.4 (2)°. The two Au units are repeated alternately with another throughout the structure, forming zigzag-shaped chains running along *b*, with Au–Au–Au angles 155.46 (4) and 161.25 (4)°. There are only van der Waals bonds between the chains. The Au–Au distances within a chain are very short, 2.967 (2) and 2.980 (2) Å. Since there are no ligand bridges between the gold atoms, these short distances certainly indicate a fairly strong metal–metal bonding. The gold atoms are thus four-coordinated, with the coordination figures most aptly described as very compressed tetrahedra.

Introduction

The monovalent oxidation states of the coinage metals copper, silver, and gold are typically soft acceptors, strongly preferring soft ligands. Consequently, they are preferentially solvated by solvents coordinating via soft donor atoms such as nitrogen and, even more markedly, sulfur. The present investigation is part of an extensive study of the interplay between solvation and complex formation for these acceptors, involving various soft solvents and ligands.[1-4] So far, these investigations have concerned copper(I) and silver(I). Presently, they are extended to gold(I).

Soft solvents, as soft ligands generally do, strongly stabilize the monovalent state of these metals, i.e. the d^{10}-electron configuration, both relative to the metal and to the higher oxidation states. In the case of copper(I), this has been established both for acetonitrile (AN) and for pyridine (py),[1-6] and in the case of gold(I) for AN.[6-8] Also, silver(I) is much less oxidizing in these solvents than in a hard solvent such as water.[1,9] In solvents coordinating via sulfur, softer than nitrogen, the d^{10} configurations should be still more strongly stabilized.

Aliphatic sulfides are good electron donors and should thus be strongly solvating solvents of the soft category. Among these, the cyclic thioether tetrahydrothiophene (THT) has been selected for the present investigation, on account of its favorable liquid range (−96 to +119 °C), ready availability, and ease of purification and handling.

Table I. Crystal Data for Au(THT)I

orthorhombic	space group $Pc2_1n$
$a = 8.149$ (2) Å	mol wt 412.04
$b = 11.460$ (4) Å	$T = 200$ K
$c = 15.956$ (3) Å	$\mu(\mathrm{Mo\ K\alpha}) = 239.5\ \mathrm{cm^{-1}}$
$V = 1490.0\ \text{Å}^3$	$\rho(\mathrm{calcd}) = 3.673\ \mathrm{g\ cm^{-3}}$
$Z = 8$	

The solvates and complexes studied previously have been investigated by thermodynamic, structural, and spectroscopic methods.[1-4] The latter methods have been applied both to species in solution and to solids crystallized from the solutions. The present study concerns the structure of a THT solvate of gold(I) iodide, containing the components in the molar ratio Au:I:THT = 1:1:1. The structure turns out to possess several remarkable features; it is moreover completely different from that of the corresponding silver(I) compound of the same stochiometric composition.[10]

Experimental Section

Materials. $[\mathrm{Au}[\overline{\mathrm{S}(\mathrm{CH_2})_3\mathrm{CH_2}}]\mathrm{I}]_\infty$ was prepared by treating a gold foil (0.57 g) with a solution of I_2 (0.37 g) in THT (5 mL), at 60–70 °C. After the mixture was cooled to room tempeature, single crystals of the title compound were formed. These were prismatic and light yellow. One of these crystals was used for the collection of the X-ray intensity data. Later on, we observed that the gold foil reacts with the iodine solution even at room temperature, with the formation of beautiful crystals on the metal surface. The same compound was formed irrespective of the mode

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Table II. Final Positional and Thermal Parameters for the Non-Hydrogen Atoms[a]

atom	x/a	y/b	z/c	$B/\text{Å}^2$	atom	x/a	y/b	z/c	$B/\text{Å}^2$
Au(1)	0.4626 (1)	0.0000 (0)	0.5236 (1)	1.52 (2)[b]	C(12)	0.7995 (36)	0.2295 (28)	0.2800 (18)	2.2 (5)
Au(2)	0.5524 (1)	0.2519 (1)	0.5292 (1)	1.40 (2)[b]	C(13)	0.8456 (36)	0.3457 (26)	0.3201 (18)	2.0 (4)
I(1)	0.6648 (2)	−0.0522 (2)	0.6410 (1)	2.19 (4)[b]	C(14)	0.8923 (37)	0.3164 (27)	0.4075 (18)	2.1 (5)
I(2)	0.2505 (3)	0.0516 (2)	0.4107 (1)	2.16 (4)[b]	C(21)	0.2892 (35)	0.1843 (28)	0.6901 (18)	2.1 (5)
S(1)	0.7608 (9)	0.1912 (6)	0.4417 (4)	1.67 (13)[b]	C(22)	0.1127 (41)	0.1629 (30)	0.6502 (19)	2.5 (5)
S(2)	0.3673 (8)	0.3128 (6)	0.6320 (4)	1.54 (14)[b]	C(23)	0.0432 (40)	0.2797 (32)	0.6318 (21)	2.7 (6)
C(11)	0.6711 (40)	0.1723 (29)	0.3347 (19)	2.4 (5)	C(24)	0.1772 (36)	0.3444 (27)	0.5773 (17)	2.0 (4)

[a] Estimated standard deviations in the last significant digit(s) are given in parentheses. See Figure 1 for the atom-labeling scheme. The positions of the hydrogen atoms are not included. They were calculated by assuming tetrahedral geometry around carbon, with the distance C–H = 1.00 Å. [b] Anisotropic thermal parameters transformed to B_{eq} by $B_{\text{eq}} = {}^4/_3\Sigma_i\Sigma_j\beta_{ij}a_ia_j$.

Table III. Summary of Important Interatomic Distances (Å) and Angles (deg)[a]

A. Coordination Geometry around the Two Gold Atoms

bond	value	angle	value	angle	value
Au(1)-Au(2)	2.980 (2)	Au(2)′-Au(1)-I(1)	90.57 (6)	Au(1)-Au(2)-S(1)	82.54 (19)
Au(1)-Au(2)′	2.967 (2)	Au(2)′-Au(1)-I(2)	89.67 (6)	Au(1)-Au(2)-S(2)	98.74 (18)
Au(1)-I(1)	2.565 (2)	Au(2)-Au(1)-I(1)	92.65 (6)	Au(1)′-Au(2)-S(1)	98.52 (18)
Au(1)-I(2)	2.565 (2)	Au(2)-Au(1)-I(2)	87.89 (6)	Au(1)′-Au(2)-S(2)	83.47 (18)
Au(2)-S(1)	2.306 (7)	Au(2)′-Au(1)-Au(2)	161.25 (4)	Au(1)′-Au(2)-Au(1)	155.46 (4)
Au(2)-S(2)	2.335 (6)	I(1)-Au(1)-I(2)	177.57 (7)	S(1)-Au(2)-S(2)	172.35 (23)

B. Bond Angles around the Sulfur Atoms

angle	value	angle	value	angle	value
Au(2)-S(1)-C(11)	107 (1)	C(11)-S(1)-C(14)	93 (1)	Au(2)-S(2)-C(24)	106 (1)
Au(2)-S(1)-C(14)	111 (1)	Au(2)-S(2)-C(21)	110 (1)	C(21)-S(2)-C(24)	96 (1)

C. Geometry of the Tetrahydrothiophene Groups

bond	value	angle	value	bond	value	angle	value
S(1)-C(11)	1.87 (3)	S(1)-C(11)-C(12)	102 (2)	S(2)-C(21)	1.85 (3)	S(2)-C(21)-C(22)	103 (2)
C(11)-C(12)	1.51 (4)	C(11)-C(12)-C(13)	108 (2)	C(21)-C(22)	1.59 (4)	C(21)-C(22)-C(23)	107 (3)
C(12)-C(13)	1.52 (4)	C(12)-C(13)-C(14)	105 (2)	C(22)-C(23)	1.48 (5)	C(22)-C(23)-C(24)	106 (3)
C(13)-C(14)	1.49 (4)	C(13)-C(14)-S(1)	107 (2)	C(23)-C(24)	1.58 (5)	C(23)-C(24)-S(2)	103 (2)
C(14)-S(1)	1.87 (3)	C(14)-S(1)-C(11)	93 (1)	C(24)-S(2)	1.82 (3)	C(24)-S(2)-C(21)	96 (1)

[a] See Figure 1 for atom-labeling scheme. Estimated standard deviations in the last significant digit(s) are given in parentheses. The gold atoms marked with a prime correspond to positions obtained by using the transformation $-x$, $^1/_2 + y$, $-z$.

of preparation, as was checked by determination of the unit cell dimensions.

In air at room temperature, the crystals stayed transparent for about 0.25 h; they then gradually darkened. Most probably, THT slowly evaporated, causing AuI to be formed on the surface.

For analysis, the compound was recrystallized from THT and then dried between filter papers. No suitable washing liquid could be found; even such seemingly innocent solvents as ether or carbon tetrachloride disintegrate the compound, presumably by extracting the THT. A weighed sample was then treated with a mixture of concentrated nitric acid (10 mL) and hydrochloric acid (1 mL). The solution was evaporated almost to dryness, some dilute sulfuric acid added, and the gold then determined electrolytically at 70 °C: Au(THT)I, 47.8%; found, 49.0%.

Crystal Data and Intensity Measurements. A single crystal with the dimensions 0.07 × 0.09 × 0.38 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer employing graphite-monochromatized Mo Kα radiation ($\lambda = 0.7107$ Å). Since the crystal decomposes when exposed to air at room temperature, all data were collected at 200 K with the aid of a nitrogen gas blower device.[11] Laue symmetry, *mmm*, and systematic extinctions ($0kl$, l odd; $hk0$, $h + k$ odd) are consistent with the space groups $Pc2_1n$ and $Pcmn$. Cell dimensions (Table I) were obtained by least-squares calculations from 25 θ values determined as $\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$, with the diffractometer in the bisecting mode and measuring $\omega_{\bar{h}\bar{k}\bar{l}}$ at a negative θ angle. The intensities of 2078 reflections in one octant of the reflection sphere obeying $3° \leqslant \theta \leqslant 28°$ were measured with the ω–2θ scan technique ($\Delta\omega = 1.1 + 0.5 \tan \theta$). The scan interval was extended 25% at both ends for the background measurement. The ratio $\sigma(I)/I$ requested in a scan was 0.028, and the maximum recording time was 150 s. Three standard reflections were recorded at regular intervals; no systematic variation in their intensities were observed. I and $\sigma(I)$ were corrected for Lorentz, polarization, and absorption effects. The transmission factors evaluated by numerical integration[12] varied from 0.212 to 0.501. Only the 1541 reflections with $I > 2\sigma(I)$ were considered significantly different from the background to be used in the calculations.

Structure Solution and Refinement. The structure was solved by vector and difference Fourier methods. Of the two space groups, $Pc2_1n$ and $Pcmn$, the noncentrosymmetric $Pc2_1n$ was considered the best choice from the distribution of the largest maxima in the Patterson map. The parameters of the non-hydrogen atoms were refined by full-matrix least squares. The positions of the H atoms were calculated from geometrical criteria and included in the structure factor calculations. Neither positional nor temperature parameters ($B_{\text{iso}} = 3.0$ Å^2) were refined for the H atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = [(\sigma^2/4|F_o|)^2 + (0.065|F_o|)^2 + 0.5]^{-1}$. In the final refinement, anisotropic temperature factors were applied to Au, I, and S. Scattering factors with corrections for anomalous dispersion were taken from ref 13. The final agreement indices $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - F_c|)^2/\sum w|F_o|^2]^{1/2}$ were 0.062 and 0.075, respectively. A δR plot resulted in an approximately straight line with slope 1.02 and intercept −0.08. Computer programs used are those compiled and amended by Lundgren.[12] Tables of $|F_o|$, $\sigma(|F_o|)$, and $|F_c|$ are available as supplementary material. The final positional and thermal parameters are given in Table II and selected interatomic distances and angles in Table III.

Description of the Structure

The asymmetric unit contains two monovalent gold atoms. Of these, Au(1) coordinates two I$^-$ while Au(2) coordinates two THT. Both arrangements are almost linear. The distances Au–I are both the same, while the Au–S distances differ slightly (Table IIIA). Au(1) and Au(2) alternate along *b* through the 2_1 axis, forming an infinite zigzag chain, with the angles Au(2)–Au-

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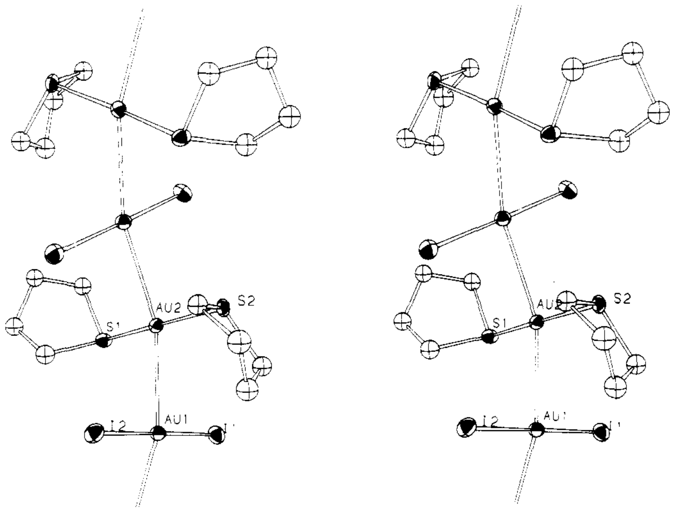

Figure 1. Coordination around Au(1) and Au(2). The infinite Au–Au chain is running along the *b* axis.

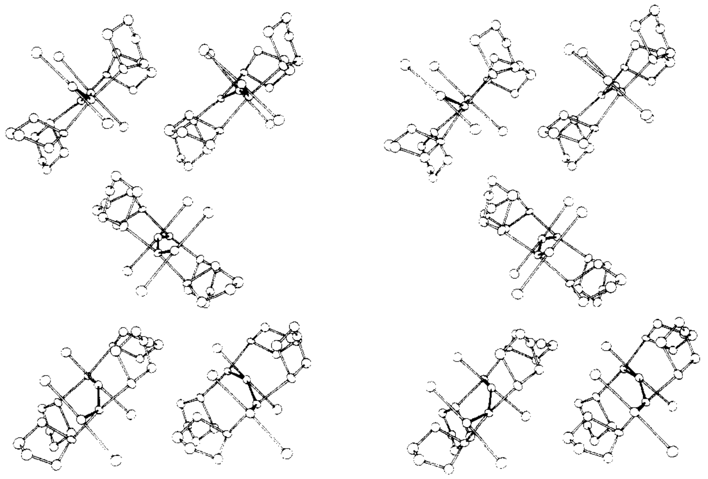

Figure 2. Structure viewed along the *b* axis.

(1)–Au(2)′ = 161.3° and Au(1)–Au(2)–Au(1)′ = 155.5° (Table IIIA; Figure 1). The units AuI_2 and AuS_2 are arranged so that the LS planes through Au(2)′, Au(1), Au(2), I(1), I(2) and Au(1), Au(2), Au(1)′, S(1), S(2) are at almost right angles (88°) (Figure 2).

The distances between adjacent gold atoms in the chain are short, and not very different, alternately 2.967 and 2.980 Å. They are in fact not much longer than in metallic gold, 2.877 Å.[14] As the gold atoms are not forced together by any bridging ligand, these short Au–Au distances are evidently due to fairly strong metal–metal bonds. Both Au(1) and Au(2) are thus four-coordinated. From what has been said above, it follows that the coordination is not far from planar. The following deviations are obtained for the previously mentioned LS planes (Å): 0.31, –0.17, 0.31, –0.21, –0.23; 0.44, –0.19, 0.44, –0.35, –0.34. The figures are given in the same order as the atoms are listed above. The coordination geometries around the two gold atoms could alternatively be described as very compressed tetrahedra.

The bond angles around S(1) and S(2) in the two THT ligands are in the range 93–111 and 96–110°, respectively (Table IIIB). Evidently the bonding around the S atoms is close to tetrahedral, as is also found in bis(tetrahydrothiophene)silver(I) tetrafluoroborate.[15]

The bond lengths and angles of the coordinated THT molecules (Table IIIC) do not differ significantly from those found in the molecule in the gaseous phase.[16]

The two different gold atoms should have fairly different charges that ought to show up in the ESCA spectrum. Unfortunately, however, even at such a low temperature as 125 K, the THT evaporates at the low pressure ($\approx 10^{-7}$ torr) applied at the ESCA measurements. This is indicated, first, by the virtual absence of the sulfur signal and, second, by the fact that only one gold signal is observed.

Discussion

The infinite chain of gold atoms held together by uniformly short metal–metal bonds is the most distinctive feature of the present structure. To our knowledge, it is so far unique. Presumably the compound is a one-dimensional conductor in the direction of the chains. So far, we have not been able to confirm this experimentally, however. Another striking characteristic is that the gold atoms along the chain are alternately present in a solvate and in a diiodo complex, both almost linear. Formally, cations $Au(THT)_2^+$ and anions AuI_2^- thus alternate along the chain. In reality, the charges are certainly much equalized via the metallic bonds.

Also, in the pyridine solvates of gold(I) iodide and chloride of analogous stochiometry Au:I:py and Au:Cl:py = 1:1:1, the gold is present alternately as a solvate and as a dihalo complex, both linear.[17] The structures formed are quite different from that of the THT compound, however. In the py–iodide, one $Au(py)_2^+$ is bonded to one AuI_2^- by a short metal–metal bond. The distance

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is much the same as in the THT-iodide (2.99 Å); the two complexes stand perpendicular to each other, but the similarity ends there. No infinite chains are formed; instead the units mentioned are joined by a fairly long (3.29 Å) metal–metal bond between the gold atoms of the solvates, forming a discrete tetrameric complex. The py–chloride has also a tetrameric structure of a similar type, though the two solvate units are differently arranged and the Au–Au distances are much longer.

The short Au–Au bonds in these solvates present new examples of close interactions between d^{10} centers, as discussed for other systems by Mehrotra and Hoffmann[18] (Cu(I)) and by Dedieu and Hoffmann[19] (Pt(0)).

An infinite chain of gold atoms has been found also in the complex $[[\mathrm{Au}(i\text{-}\mathrm{C_3H_7O})_2\mathrm{PS_2}]_2]_\infty$, but in this case every second Au–Au pair is joined also via two S–P–S bridges.[20] A really short Au–Au distance, 2.914 Å, is found only between such ligand-bridged pairs; the distances between gold atoms joined only by metal–metal interactions are considerably longer, 3.050 and 3.109 Å.

In cases where gold atoms are forced together by strongly bonding ligand bridges, very short Au–Au distances have in fact been observed. Thus, in the dimer $[(\mathrm{C_3H_7})_2\mathrm{NCS_2Au}]_2$ the Au–Au distance is only 2.76 Å, evidently very much due to the two S–C–S bridges between the gold atoms.[21]

Recently, a most remarkable compound containing alternate Au–Au and Au–Ag bonds, the latter in a branched arrangement, has been prepared,[22] viz. $[(\mathrm{C_6F_5})_2\mathrm{Au}(\mu\text{-}\mathrm{AgSC_4H_8})_2]_\infty$. There are no ligand bridges; still, the distances between the metal atoms are all very short: Au–Au = 2.889 Å, Au–Ag = 2.717, 2.726 Å.

The tetramers found in the solid pyridine solvates do not exist in the dilute pyridine solutions recently investigated by potentiometric measurements.[23] At gold(I) concentration around 1 mM, only mononuclear species are formed, viz. $\mathrm{Au^+}$, AuX, and $\mathrm{AuX_2^-}$, solvated in a manner that is still unknown. The intermediate complex AuX thus exists in solution though its range of existence is fairly narrow, especially in the iodide system.

Certainly the chains present in solid Au(THT)I do not persist in THT solutions. The solubility is low at room temperature, only a few millimolar, but increases steeply with the temperature, exceeding 0.1 M at the boiling point. This can be reasonably interpreted by assuming that the chains have to be broken in order that the compound should be dissolved; such a process is evidently favored by increasing temperature.

A most striking difference also exists between the structure of Au(THT)I and that of the corresponding silver compound Ag(THT)I, of the same stochiometry. The silver compound is a tetramer of the cubane type, with each iodine bonding to three silver atoms and one THT bonded to each silver.[10] The steric arrangement around silver is, however, close to tetrahedral; the cubane angles of 90° are thus considerably distorted. A better description of the coordination geometry is a starlike structure, a stella quadrangula, which can be described as a central, empty tetrahedron sharing all its faces with four silver tetrahedra.[24]

It is also most remarkable that the bonds Au–S and Au–I are much shorter, 0.22 and 0.33 Å, then the bonds Ag–S and Ag–I. An analogous difference has previously been found in the case of three-coordinate phosphine complexes[25] where the bonds Au–P are 0.10–0.15 Å shorter than the bonds Ag–P. Gold moreover tends to coordinate the two P linearly whereas P–Ag–P is considerably bent (with an angle ≃140°).

It may be argued that the coordination geometries around Au and Ag are so different (though the coordination numbers are, after all, the same) that the bond distances cannot be strictly compared. But even when the geometries are identical, as is the case for the short-lived gaseous hydrides, the same relation persists. In these, the distances are[26] Au–H = 1.524 and Ag–H = 1.617 Å.

Several factors presumably combine in order to bring about this bond shortening.[27] The classical interpretation is based on the lanthanoid contraction; the main reason would thus be the large increase of nuclear charge between $_{47}\mathrm{Ag}$ and $_{79}\mathrm{Au}$. The effect of this change is considerably enhanced, however, by the large increase of the relativistic contraction of the s and p shells that takes place between the fifth and sixth period. The outermost d shell, on the other hand, becomes better shielded from the nuclear charge the higher the period. As a result, the energies and geometries of the orbitals of the gold 5d electrons are much more favorable for covalent bond formation than those of the silver 4d electrons, in concordance with the experimental fact that Au(I) is a much softer acceptor than Ag(I).[28-32] If the ligand is also prone to covalent bonding, the bond formed with Au(I) thus becomes especially strong and, consequently, short. Relative to the Ag(I) bonds, the Au(I) bonds should thus be shorter, the softer the ligand. This is borne out by the bond length variations found in the phosphine halides discussed above[25] and also by a comparison of the bond lengths in the Ag(I) and Au(I) halides. Among the latter ones, AgCl and AgBr crystallize, at ordinary temperature and pressure, in a rock salt structure,[33,34] with the distances Ag–Cl = 2.78 Å and Ag–Br = 2.89 Å. Under these conditions AgI has, on the other hand, quite a different structure[35] so this compound cannot be included in the comparison. As might be expected from the experience quoted above, the structures of AuCl and AuBr are completely different from those of AgCl and AgBr. They contain infinite zigzag chains of gold and halogen atoms, in the case of AuBr even in two different arrangements.[36] One of these is isostructural with AuCl, however, so a comparison between the two silver and two gold halides should therefore be possible. The gold–halogen distances are Au–Cl = 2.36 Å and Au–Br = 2.40 Å, i.e. as expected much shorter than the corresponding silver–halogen distances. The differences are 0.42 Å between the chlorides and 0.49 Å between the bromides. Relative to the bonds Ag–X, the bonds Au–X are thus shortened more, the softer the ligand, just as has been postulated above.

Registry No. $[\mathrm{Au}[\overline{\mathrm{S(CH_2)_3CH_2}}]\mathrm{I}]_\infty$, 95344-34-6; Au, 7440-57-5.

Supplementary Material Available: Tables of observed and calculated structure factors, atomic parameters (including the H atoms), anisotropic thermal parameters, and the least-squares planes through the coordination polyhedra (16 pages). Ordering information is given on any current masthead page.

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