DALTON
FULL PAPER

Reactions of dichloro[2-(dimethylaminomethyl)phenyl-C^1,N]gold(III), [Au(damp-C^1,N)Cl_2], with heterocyclic thiols. Evidence for Au–N bond cleavage and protonation of the dimethylamino group

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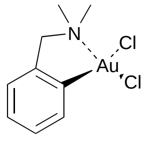
Dichloro[2-(dimethylaminomethyl)phenyl-C^1,N]gold(III), [Au(damp-C^1,N)Cl_2], reacts with 2-mercapto-1,3-thiazoline (HSthiaz), 2-mercaptopyridine (HSpy), sodium 1-methylmercaptotetrazolate (NaSmetetraz), 4-methyl-3-mercapto-1,2,4-triazole (HSmetriaz) or 6-mercaptopurine (HSpur) under cleavage of the Au–N bond and protonation of the dimethylamino group. Compounds of general formulae $[Au(Hdamp\text{-}C^1)Cl(HL)_2]^{2+}$ (HL = HSthiaz or HSpy), [Au(Hdamp-C^1)Cl(L)] (L = $Spur^-$) or [Au(Hdamp-C^1)$(L)_3$] (L = $Smetetraz^-$) have been isolated and characterized. The reaction with HSmetriaz leads to a rapid reduction of the metal and the formation of the gold(I) complex $[Au(HSmetriaz)_2]^+$. The crystal structures of [Au(Hdamp-C^1)Cl$(HSthiaz)_2$]$Cl_2\cdot Me_2CO$, [Au(Hdamp-C^1)Cl$(HSpy)_2$]$\cdot H_2O$, [Au(Hdamp-C^1)$(Smetetraz)_3$] and [Au(Hdamp-C^1)Cl(Spur)]Cl have been elucidated showing the gold atoms in distorted square-planar co-ordination environments. Generally, one or more hydrogen atoms of the heterocyclic ligands and/or the NMe_2H^+ group form hydrogen bonds in the solid-state structures. The reaction of Na[$AuCl_4$] with Na(Smetetraz) and [NEt_4]Br yields bright red crystals of [NEt_4][$Au(Smetetraz)_4$], the first structurally characterized gold(III) complex with four monodentate thiolate ligands. The structure of the complex shows well separated $[Au(Smetetraz)_4]^-$ anions with Au–S distances of 2.354(4) Å.

Square-planar gold(III) complexes containing 2-(dimethylaminomethyl)phenyl-C^1,N, (damp-C^1,N)$^-$, have been known since 1984.[1] Key compounds are the dichloro and diacetato complexes [Au(damp-C^1,N)Cl_2] (**1a**) and [Au(damp-C^1,N)$(CH_3CO_2)_2$][1] (**1b**) which recently have been studied by structural analysis[2] showing distorted square-planar co-ordination spheres for the gold atoms. During ligand exchange reactions the chloro or acetato ligands are preferably replaced.[2–9] Only a few examples are reported where the Au–N bond is cleaved.[9] However, to our knowledge, protonation of the liberated $N(CH_3)_2$ group has not yet been observed for gold compounds.



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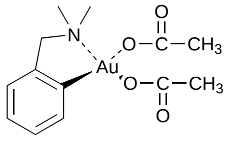


1b

In a recent paper, some tumour cell toxicity studies of [Au(damp-C^1,N)Cl_2], which has structural and electronic analogies to cisplatin, have been reported.[9] This makes further studies dealing with the ligand exchange behaviour of this complex and the biological activity of the products formed of interest.

Here, we present the synthesis and structural characterization of complexes which are obtained by the reaction of [Au(damp-C^1,N)Cl_2] with the heterocyclic thiols shown in Fig. 1. For almost all heterocycles used, tautomeric forms can be formulated involving thiol, thione or zwitterionic forms. Thus, different co-ordination modes may be expected for the ligands which are applied in their protonated form. 1-Methylmercaptotetrazole was used as its sodium salt. For this ligand the reaction with $[AuCl_4]^-$ was also studied.

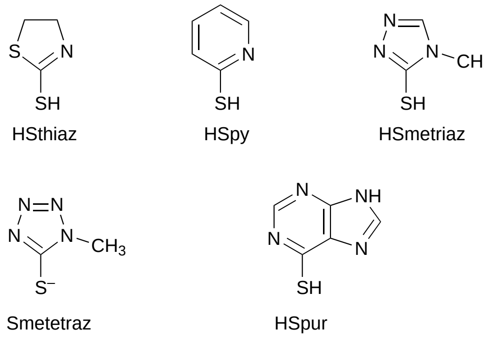


Fig. 1 Heterocyclic thiol ligands used throughout the experiments. All ligands are given in their thiol form despite some of them occurring mainly as thiones

Results and Discussion

All N-heterocyclic ligands summarized in Fig. 1 react with [Au(damp-C^1,N)Cl_2] under exchange of chloro ligands, cleavage of the Au–N bonds and protonation of the $N(CH_3)_2$ groups. This is a new reaction pattern for gold complexes. Almost all hitherto reported ligand exchange reactions starting from [Au(damp-C^1,N)Cl_2] and monodentate ligands L^1 resulted in the replacement of chloro ligands and the formation of neutral or cationic $[Au(damp\text{-}C^1,N)(X)L^1]^{0,+,2+}$ complexes (X = L^1 or Cl) depending on the net charge of L^1.[3–7] With chelating ligands L^2 in most cases $[Au(damp\text{-}C^1,N)L^2]^{0,+,2+}$ complexes are formed.[2,4,5,8,9] Cleavage of the Au–N bond has been reported for the reactions with CN^- or dialkyldithiocarbamates.[9] The liberated dimethylamino groups, however, are not protonated in the products and the structural characterization of [Au(damp-C^1)$(Et_2dtc)_2$][9] (Et_2dtc^- = diethyldithiocarbamate) shows the lone pair of the $N(CH_3)_2$ group strictly directed towards a free co-ordination position of the square-planar

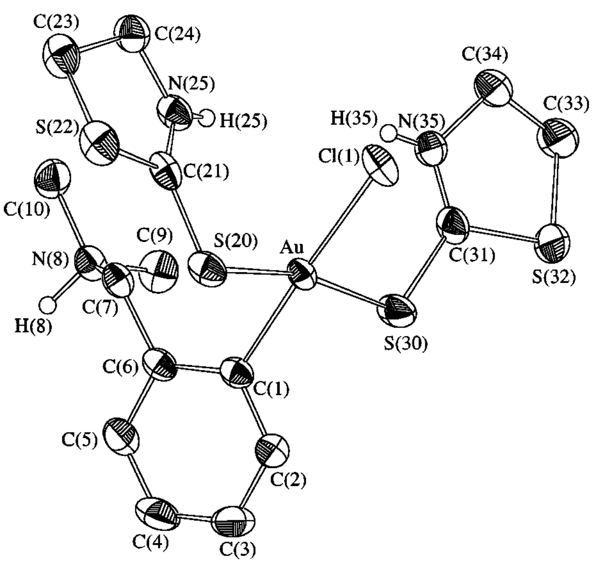


Fig. 2 A ZORTEP representation[13] of the [Au(Hdamp-C^1)Cl(HSthiaz)$_2$]$^{2+}$ complex cation. Thermal ellipsoids represent 40% probability. Carbon H atoms have been omitted for clarity

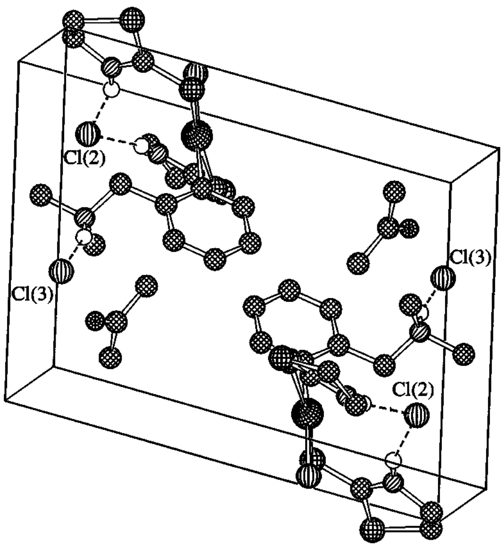


Fig. 3 Cell plot[14] of [Au(Hdamp-C^1)Cl(HSthiaz)$_2$]Cl$_2$·Me$_2$CO showing hydrogen bonds between H(25), H(35) and Cl(2) and H(8) and Cl(3), respectively

co-ordination sphere of the gold atom suggesting at least weak interactions with the metal.

All reactions of [Au(damp-C^1,N)Cl$_2$] with the heterocyclic thiols of Fig. 1 have been performed in acetone or methanol depending on the solubility of the ligands. In some cases slow diffusion of the ligand into [Au(damp-C^1,N)Cl$_2$] solutions gave the best results.

Pale yellow crystals of [Au(Hdamp-C^1)Cl(HSthiaz)$_2$]Cl$_2$ have been obtained by treating [Au(damp-C^1,N)Cl$_2$] with 2 equivalents of HSthiaz at room temperature. During the reaction reasonable amounts of side-products were formed. The colourless solid which precipitated was identified as [Au$^{\rm I}$(HSthiaz)$_2$]Cl while in the remaining filtrate the [Au(damp)$_2$]$^+$ cation could be detected mass spectrometrically. The amount of side-products increased with the excess of HSthiaz applied. Thus, for the preparation of analytically pure samples of [Au(Hdamp-C^1)Cl(HSthiaz)$_2$]Cl$_2$ a 1 : 1 ratio of the reactants was chosen despite the fact that the product contains two HSthiaz ligands. The resulting complex is only slightly soluble in acetone, but dissolves in dmso. In solution, however, the compound slowly decomposes. The ^{1}H NMR spectrum of [Au(Hdamp-C^1)Cl(HSthiaz)$_2$]Cl$_2$ in dmso shows the signal of the ammonium proton shifted downfield at δ 10.4. This value agrees with the chemical shift which has been found for the ammonium proton in [Pt{C$_6$H$_4$CH(Me)NMe-C^2,N_2}-C$_6$H$_4$CH(Me)NHMe$_2$-C^2)Br] at δ 10.9.[10,11] Protonation of the nitrogen atoms of the 1,3-thiazoline rings can be detected by signals at δ 7.5 {*cf.* δ 7.28 in [Au(HSthiaz)$_2$]ClO$_4$}.[12] The ^{13}C chemical shifts of the methyl and methylene carbon atoms are valuable indicators for the bonding mode of the damp ligand. In (damp-C^1,N)$^-$ chelates they are found at about δ 53 (CH$_3$) and 75 (CH$_2$).[1,2] The non-chelated, but non-protonated, (damp-C^1)$^-$ ligand in [Au(damp-C^1)(Et$_2$dtc)$_2$][9] shows these signals at δ 45 and 66, respectively. For the protonated CH$_2$NH(CH$_3$)$_2$ moiety in [Au(Hdamp-C^1)Cl(HSthiaz)$_2$]$^{2+}$ ^{13}C chemical shifts of δ 29.7 (CH$_3$) and 42.5 (CH$_2$) have been found.

The infrared spectrum of the complex shows NH vibrations at 3009, 2877 and 2616 cm^{-1}, indicating hydrogen bonds. The band at 2616 cm^{-1} can be assigned to NH$^+$ in the (Hdamp-C^1) unit and is in good agreement with the value in [Pt{C$_6$H$_4$-CH(Me)NMe$_2$-C^1,N}{C$_6$H$_4$CH(Me)NHMe$_2$-C^2}Br] (2670 cm^{-1}).[10,11] Both Au–C and Au–Cl stretching frequencies have been detected at 431 cm^{-1} and 301 cm^{-1}, respectively. The FAB$^+$ mass spectra show only monoionic fragments for the dicationic molecule.

Single crystals of [Au(Hdamp-C^1)Cl(Hthiaz)$_2$]Cl$_2$ suitable for X-ray crystallography have been obtained by slow evaporation of an acetone solution. The crystals contain one solvent molecule per complex. The gold atom possesses a slightly distorted square-planar co-ordination sphere (Au is out-of-plane by 0.15 Å) with the chloride *trans* to the σ-bonded phenyl ligand. A ZORTEP diagram[13] of the complex is given in Fig. 2. Table 1 contains selected bond lengths and angles. The heterocyclic ligands are co-ordinated in their neutral form. Hydrogen atoms have been located from Fourier maps at the atoms N(25) and N(35) suggesting co-ordination in the thione form (**b** shown below) as has been discussed for the gold(I) cation [Au(HSthiaz)$_2$]$^+$.[12] This, however, is not fully supported by the bond lengths found. The C–S bond lengths of about 1.71 Å range between carbon–sulfur single and double bonds (*cf.* carbon–sulfur bond lengths in the heterocyclic rings, Table 1) and the C(21)–N(25) and C(31)–N(35) distances of 1.294(6) Å and 1.275(6) Å are too short to represent C–N single bonds. Thus, the tautomeric form (**c**) of the heterocyclic ligand should dominate in [Au(Hdamp-C^1)Cl(HSthiaz)$_2$]Cl$_2$. This is mainly supported by the Au–S–C angles [which are 107.0(2) at S(20) and 110.6(2)° at S(30)], which clearly correspond to an sp^3 hybridization of the sulfur atom. This confirms the 'thiolate-type', zwitterionic co-ordination of the ligands. The differences in the Au–S–C angles (107 *vs.* 110°) suggests a larger extent of form **b** in the mercaptothiazoline ligand with the atoms S(30)–N(35). This, however, is not supported by the S(20)/S(30)–C(20)/C(31) and C(21)/C(31)–N(25)/N(35) bond distances and may be attributed to the torsion which is required to form a hydrogen bond [torsion angles Au–S(30)–C(31)–N(35) −32.66 *vs.* Au–S(20)–C(21)–N(25) 8.46°]. Both NH hydrogen atoms of the heterocycles form hydrogen bonds to the chloride anion Cl(2). Another hydrogen bond is evident between H(8) and Cl(3). This is illustrated in the cell plot given in Fig. 3. The phenyl ring of the mono-co-ordinated (Hdamp-C^1) ligand is twisted against the co-ordination plane by 58.3°. A distance of 4.51 Å has been found between Au and N(8) and H(8) is directed towards Cl(3). These two structural features represent the main differences

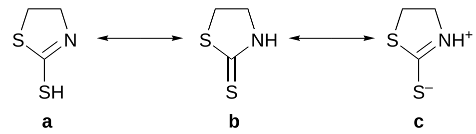
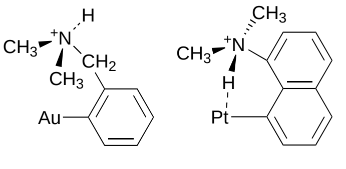


Table 1 Selected bond lengths (Å) and angles (°) in $[Au(Hdamp\text{-}C^1)Cl(HSthiaz)_2]Cl_2$ and $[Au(Hdamp\text{-}C^1)Cl(HSpy)_2]Cl_2$

	$[Au(Hdamp\text{-}C^1)Cl(HSthiaz)_2]Cl_2$		$[Au(Hdamp\text{-}C^1)Cl(HSpy)_2]Cl_2$	
Au–C(1)	2.045(5)		2.063(11)	
Au–S(30)	2.326(3)		2.337(3)	
Au–S(20)	2.331(3)		2.334(3)	
Au–Cl(1)	2.364(3)		2.365(3)	
S(20)–C(21)	1.709(5)		1.735(12)	
C(21)–N(25)/N(22)	1.294(6)		1.334(14)	
S(30)–C(31)	1.714(5)		1.741(12)	
C(31)–N(35)/N(32)	1.275(6)		1.35(2)	
C(1)–Au–S(30)	83.6(2)		83.5(3)	
C(1)–Au–S(20)	87.8(2)		86.9(3)	
S(30)–Au–S(20)	167.29(4)		169.99(12)	
C(1)–Au–Cl(1)	176.53(12)		171.8(3)	
S(30)–Au–Cl(1)	96.72(11)		96.83(12)	
S(20)–Au–Cl(1)	91.29(10)		92.24(12)	
C(21)–S(20)–Au	107.0(2)		108.7(4)	
N(25)–C(21)–S(20)	128.0(4)		122.5(9)	
C(31)–S(30)–Au	110.6(2)		108.1(4)	
	D–H	H···A	D···A	D–H···A
Hydrogen bonds in $[Au(Hdamp\text{-}C^1)Cl(HSthiaz)_2]Cl_2$				
N(8)–H(8)···Cl(3′)	0.99(6)	2.10(6)	3.055(6)	161(4)
N(25)–H(25)···Cl(2′)	0.94(6)	2.17(7)	3.074(5)	160(5)
N(35)–H(35)···Cl(2′)	0.75(6)	2.27(6)	3.010(6)	171(6)
Hydrogen bonds in $[Au(Hdamp\text{-}C^1)Cl(HSpy)_2]Cl_2$				
N(8)–H(8)···Cl(3)	0.97(14)	2.12(14)	3.066(13)	160(12)
N(22)–H(22)···Cl(2)	0.84(8)	2.32(9)	3.082(11)	152(7)
N(32)–H(32)···Cl(2)	0.71(13)	2.41(14)	3.108(12)	170(16)

Symmetry operations: ′ $x - 1, y - 1, z - 1$.

from the bonding situation in $[Pt(C_{10}H_6NMe_2\text{-}C^2,N)(C_{10}H_6\text{-}NHMe_2\text{-}C^2)Br]$ [10] where the hydrogen atom of the ammonium group interacts with the metal (see below).



A bonding situation similar to that found in $[Au(Hdamp\text{-}C^1)Cl(HSthiaz)_2]Cl_2$ has been realized for $[Au(Hdamp\text{-}C^1)Cl(HSpy)_2]Cl_2$. The compound was prepared by stirring a mixture of $[Au(damp\text{-}C^1,N)Cl_2]$ and 2-mercaptopyridine (HSpy) in a 1 : 2 ratio in acetone. During this reaction $[Au(HSpy)_2]Cl$ was formed as a side-product in amounts up to 20%. In the final filtrate $[Au(damp)_2]^+$ cations could be detected mass spectrometrically as already discussed for the reaction of $[Au(damp\text{-}C^1,N)Cl_2]$ and 2-mercapto-1,3-thiazoline.

Single crystals of $[Au(Hdamp\text{-}C^1)Cl(HSpy)_2]Cl_2\cdot H_2O$ have been obtained from overlayering an acetonic solution of $[Au(damp\text{-}C^1,N)Cl_2]$ containing *ca.* 5% water with a solution of the ligand in acetone. The co-crystallization of water seems to be essential since only a powdery product could be obtained from dry acetone. Similar results were found earlier for $[Au(damp\text{-}C^1,N)(CH_3CO_2)_2]\cdot 0.5H_2O$ where obviously the formation of hydrogen bonds to the solvent promoted the crystal growth.

Proton and ^{13}C NMR spectra of $[Au(Hdamp\text{-}C^1)Cl(HSpy)_2]Cl_2$ support a discussion which has been made for the corresponding HSthiaz complex (see above). The same holds true for IR results where a band at 2678 cm^{-1} represents the vibration of the hydrogen bonded $NMe_2H\cdots Cl$ unit. This H bond can also be detected in the crystal structure of the compound. Fig. 4 shows a ZORTEP diagram [13] of the complex cation along with the atomic numbering scheme. Selected bond lengths and angles are compared with the corresponding values in $[Au(Hdamp\text{-}C^1)Cl(HSthiaz)_2]^{2+}$ in Table 1 showing similar structural features for both complexes. The sulfur atoms are in a *trans* arrangement to each other and the square-planar co-ordination sphere of the gold atom is slightly distorted [with maximum deviations from the mean C(1),S(1),S(2),Cl(1) plane of 0.05 Å]. The neutral HSpy ligand co-ordinates rather in its zwitterionic form (**f**) than in the thione form (**e**). The mean S–C distance of 1.74 Å fits better with a carbon–sulfur single bond than with a double bond. This is supported by the Au–S–C angles of 108.7(4) and 108.1(4)° which confirm the ‘thiolate character’ of the donor atoms. As a consequence of protona-

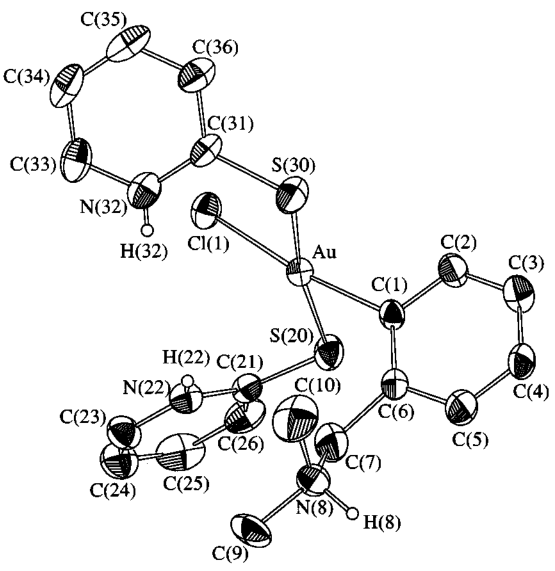
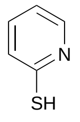


Fig. 4 A ZORTEP representation [13] of the $[Au(Hdamp\text{-}C^1)Cl(HSpy)_2]^{2+}$ complex cation. Thermal ellipsoids represent 30% probability. Carbon H atoms have been omitted for clarity

tion, the C–N–C angles within the pyridine rings are increased [123(1) and 125(1)°]. A comparison of the C–S bond distances with those in [Au(Hdamp-*C*^{1})Cl(HSthiaz)$_2$]$^{2+}$ shows that the zwitterionic tautomer plays a more dominating role in the structure of [Au(Hdamp-*C*^{1})Cl(HSpy)$_2$]Cl$_2$. The heterocyclic rings are twisted against the co-ordination plane of the metal by 52.21 and 60.87°. The larger value belongs to the C(21)–C(26) pyridinium ring which is influenced more strongly by the steric demands of the Hdamp ligand and the formation of the hydrogen bond to the chloride anion Cl(2). An additional hydrogen bridge is formed between H(8) and Cl(3) {comparable with the situation in [Au(Hdamp-*C*^{1})Cl(HSthiaz)$_2$]Cl$_2$ shown in Fig. 3}. The oxygen atom of the solvent water is only 2.37 Å from H(7B) and 2.43 Å from H(25). Thus, the co-crystallized water is also involved in the hydrogen-bond framework of the solid-state structure.



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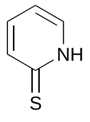

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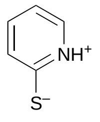


f

Whereas ligand exchange reactions between [Au(damp-*C*^{1},*N*)Cl$_2$] and 2-mercapto-1,3-thiazoline or 2-mercaptopyridine give one major product, the formation of gold(I) complexes becomes more important when 4-methyl-3-mercapto-1,2,4-triazole (HSmetriaz) is used. The reaction is complex and different products can be detected: (i) [Au(Hdamp-*C*^{1})-Cl(Smetriaz)$_2$] was obtained as pale yellow plates when the crude reaction mixture was overlayed with diethyl ether, (ii) from the remaining solution [Au^I(HSmetriaz)$_2$]Cl was isolated by slow evaporation and (iii) in the residual solution a compound of the composition [Au(damp)$_2$(Smetriaz)] was detected mass spectrometrically.

Solid [Au(Hdamp-*C*^{1})Cl(Smetriaz)$_2$] is pale yellow and is only sparingly soluble in acetone or alcohols but readily dissolves in water. The FAB$^+$ mass spectrum of the compound shows the ion [Au(damp)(Smetriaz)Cl]$^+$ at *m*/*z* 481 as base peak of the spectrum and [Au(damp)(Smetriaz)$_2$]$^+$ as an intense peak. The main fragmentation pattern is characterized by the loss of complete ligands. The cleavage of the Au–N bond and the protonation of the dimethylamino group is verified by the typical IR frequency at 2672 cm^{-1}.

The salt [Au^I(HSmetriaz)$_2$]Cl forms colourless crystals which are insoluble in water and readily soluble in acetone. The FAB$^+$ mass spectrum shows an intense molecular ion peak at *m*/*z* 427 and a fragment formed by the loss of one triazole ligand. Protonation of a ring nitrogen atom is evidenced by an IR band at 2725 cm^{-1}. The crystal structure of the compound has been solved[15] and confirms the spectroscopic results.

A clear reaction is obtained when the sodium salt of a heterocyclic thiol is used instead of the protonated compound. From sodium 1-methylmercaptotetrazolate (NaSmetetraz) and [Au(damp-*C*^{1},*N*)Cl$_2$] the neutral [Au(Hdamp-*C*^{1})(Smetetraz)$_3$] is obtained in good yields. The complex precipitates from the reaction mixture when acetone is used as solvent. The product can be recrystallized from methanol. Spectroscopic studies give evidence for singly bonded, protonated Hdamp-*C*^{1} ligands with an IR frequency of 2721 cm^{-1} for the ammonium proton and ^{13}C NMR chemical shifts at δ 34.6 (CH$_3$) and 43.7 (CH$_2$) for the CH$_2$NH(CH$_3$)$_2$ unit. Three Smetetraz$^-$ ligands complete the square-planar co-ordination sphere of gold. The heterocyclic ligands are bonded as thiols. Thus, [Au(Hdamp-*C*^{1})-(Smetetraz)$_3$] is the first neutral gold(III) complex with a Hdamp-*C*^{1} unit.

Crystals of [Au(Hdamp-*C*^{1})(Smetetraz)$_3$] suitable for X-ray crystallography have been obtained from methanol. A ZORTEP representation[13] of the molecule is given in Fig. 5. An intramolecular hydrogen bond between N(8) and N(32) is evident.

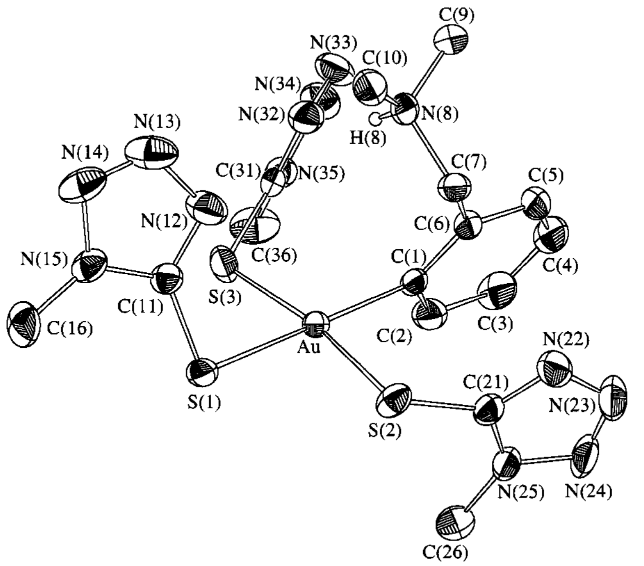


Fig. 5 A ZORTEP representation[13] of [Au(Hdamp-*C*^{1})(Smetetraz)$_3$]. Details as in Fig. 4

Table 2 Selected bond lengths (Å) and angles (°) in [Au(Hdamp-*C*^{1})-(Smetetraz)$_3$]

Au–C(1)	2.050(6)	S(1)–C(11)	1.723(7)
Au–S(3)	2.318(2)	S(2)–C(21)	1.732(7)
Au–S(2)	2.329(2)	S(3)–C(31)	1.728(7)
Au–S(1)	2.409(2)		
C(1)–Au–S(3)	93.4(2)	S(2)–Au–S(1)	85.26(8)
C(1)–Au–S(2)	93.8(2)	C(11)–S(1)–Au	98.4(2)
S(3)–Au–S(2)	171.42(7)	C(21)–S(2)–Au	106.1(2)
C(1)–Au–S(1)	178.3(2)	C(31)–S(3)–Au	106.8(2)
S(3)–Au–S(1)	87.70(8)		

	D–H	H···A	D···A	D–H···A
Hydrogen bond				
N(8)–H(8)···N(32)	0.73(7)	2.20(8)	2.881(9)	158(8)

Selected bond lengths and angles are summarized in Table 2. The mean value for the carbon–sulfur bonds of 1.728 Å fits with the range of single bonds between S and sp^3 and sp^2 hybridized carbon. The structural *trans* influence of the σ-bonded phenyl ligand is obvious. The Au–S(1) bond of 2.409(2) Å is larger than the sum of the Au and S covalency radii which is 2.36 Å. The heterocyclic rings are almost planar with a maximum deviation of 0.01 Å. The hydrogen atom which is linked to N(8) forms an intramolecular H bond to N(32). The phenyl ring forms a dihedral angle with the square-planar co-ordination sphere of gold of 69.4°. The neighbouring heterocyclic rings are directed towards the Hdamp-*C*^{1} ligand with C(21)–S(2)–Au and C(31)–S(3)–Au angles of 106.1 and 106.8°, respectively. This underlines the 'thiolate nature' of the co-ordinated ligands. The angle C(11)–S(1)–Au, however, is only 98.4° with the consequence of N(12) being only 3.25 Å from the gold atom.

In [Au(Hdamp-*C*^{1})(Smetetraz)$_3$] three monodentate thiolate ligands are present in a gold(III) complex. The higher oxidation state of the metal obviously is maintained by the presence of the σ-bonded Hdamp-*C*^{1} ligand. Nevertheless, the question remains, can the high oxidation state '+3' of gold be stabilized by the thiolate exclusively? Therefore, we studied the reaction of [AuCl$_4$]$^-$ with sodium 1-methylmercaptotetrazolate which resulted in the isolation of the first gold(III) anions with four monodentate thiolato ligands.

The salt [AsPh$_4$][Au(Smetetraz)$_4$] can be isolated as long red needles from the reaction of Na[AuCl$_4$] and NaSmetetraz in water. After addition of [AsPh$_4$]Cl a red precipitate is formed

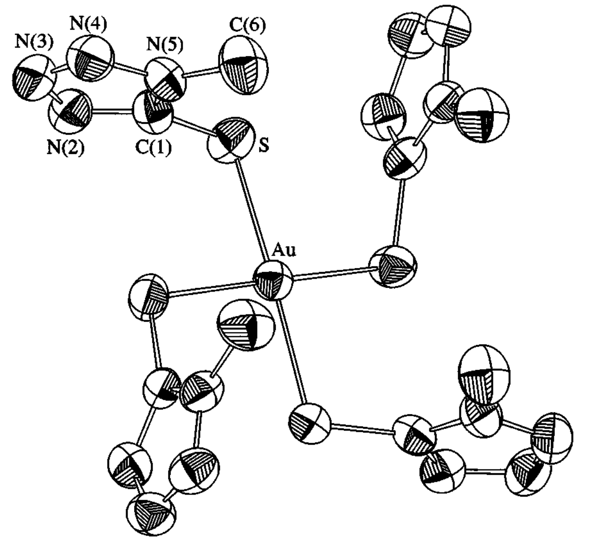


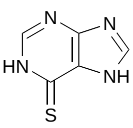
Fig. 6 A ZORTEP representation[13] of the $[Au(Smetetraz)_4]^-$ complex anion with exclusive labelling of the symmetry independent atoms. Thermal ellipsoids represent 50% probability. H atoms have been omitted for clarity

which can be recrystallized from acetonitrile. The molecular ion at *m*/*z* 657 is the base peak in the FAB^- mass spectrum. Main fragmentation products are due to the loss of $Smetetraz^-$ ligands.

A crystal-structure determination has been performed with the tetraethylammonium salt of $[Au(Smetetraz)_4]^-$ which was prepared analogously to the $AsPh_4^+$ salt with the exception that the aqueous solution was treated with CH_2Cl_2 after the addition of $[NEt_4]Cl$ to avoid reduction of the Au^{III} ions by an excess of the ligand. Recrystallization from CH_2Cl_2–methanol resulted in bright red cubes. The structure consists of well isolated complex anions and tetraethylammonium cations. The gold atom is located on a four-fold crystallographic axis of the tetragonal space group *P*4/*n*. Fig. 6 shows a ZORTEP diagram[13] of the complex anion. The thiolate character of the ligands is clearly indicated by the S–C bond length of 1.722(4) Å and the C–S–Au angle of 107.0(5)°. The gold atom deviates from the plane formed by the four sulfur atoms by 0.076 Å. The heterocyclic rings form angles of 88.29° to the plane of the donor atoms. Selected bond lengths and angles are summarized in Table 3.

Reactions of $[Au(damp\text{-}C^1,N)Cl_2]$ with chelating ligands have been reported previously and generally lead to the replacement of the chloro ligands.[2,4–9] With diethyldithiocarbamate, however, the introduction of a second Et_2dtc^- ligand resulted in the cleavage of the Au–N bond and the formation of a pseudo-octahedral gold(III) complex, $[Au(damp\text{-}C^1)(Et_2dtc)_2]$.[9]

6-Mercaptopurine is a biologically interesting ligand with a wide area of potential applications.[16,17] In metal complexes the ligand predominantely acts as chelate [*via* S and N(7), formula **j**] here or as monodentate thiolate.[18] The latter form has also been found in gold(I) compounds.[19,20]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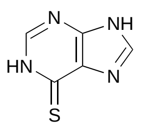
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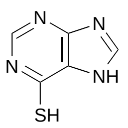
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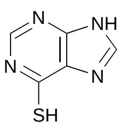

j

6-Mercaptopurine (HSpur) reacts with $[Au(damp\text{-}C^1,N)Cl_2]$ under chelate formation without adding a base. When a solution of the ligand in methanol is added to a $[Au(damp\text{-}C^1,N)Cl_2]$ solution in acetone, pale yellow plates of $[Au(Hdamp\text{-}C^1)Cl(Spur)]Cl$ crystallize from the reaction mixture. The complex is only sparingly soluble in all common solvents. Therefore, no NMR spectra of sufficient quality could be obtained. The FAB^+ mass spectra give evidence for the molecular ion at *m*/*z* 518. Fragmentaton occurs by the loss of Cl^- and degradation of the damp ligand. The IR frequency of the NH group in the Hdamp-C^1 ligand is found at 2666 cm^{-1} and suggests hydrogen bonds. The Au–C and Au–Cl bands for $[Au(Hdamp\text{-}C^1)Cl(Spur)]Cl$ have been found at 465 and 358 cm^{-1}. These values are shifted to higher energies by about 30 (Au–C) and 50 cm^{-1} (Au–Cl) with respect to values in $[Au(Hdamp\text{-}C^1)Cl(HSpy)_2]Cl_2$. This may be attributed to the different co-ordination spheres of the two complex types (shown below). In *trans* position to C and Cl we find in $[Au(Hdamp\text{-}C^1)Cl(Spur)]^+$ the donor atoms of mercaptopurine which should cause a smaller *trans* influence than Cl^- and the σ-bonded phenyl ligand. The effects should also be visible in the bond lengths.

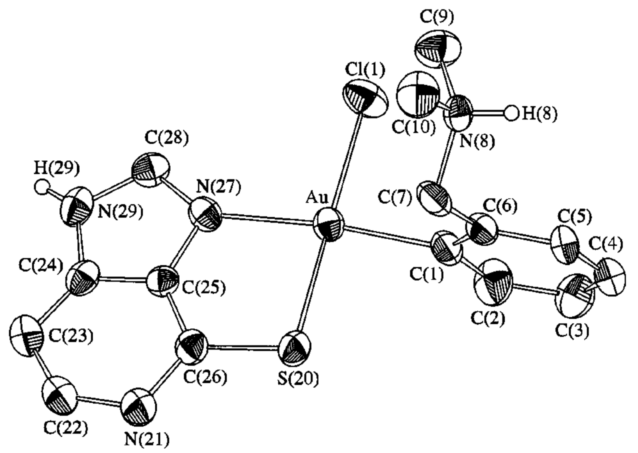
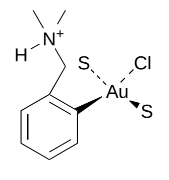


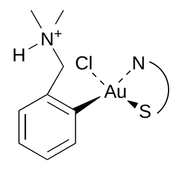
Fig. 7 A ZORTEP representation[13] of the $[Au(Hdamp\text{-}C^1)Cl(Spur)]^+$ complex cation. Details as in Fig. 4

Table 3 Selected bond lengths (Å) and angles (°) in $[NEt_4][Au(Smetetraz)_4]$

Au–S	2.354(4)	S–C(1)	1.722(4)
S–Au–S′	89.94(1)	C(1)–S–Au	107.0(5)
S–Au–S″	176.3(2)	N(2)–C(1)–N(5)	107.6(12)

Symmetry operations: ′ $0.5 - y, x, z$; ″ $0.5 - x, 0.5 - y, z$.





A ZORTEP representation of the $[Au(Hdamp\text{-}C^1)Cl(Spur)]^+$ cation is given in Fig. 7. Table 4 contains selected bond lengths and angles of the structure. The square-planar co-ordination sphere of gold is slightly distorted with a maximum deviation of 0.08 Å for the donor atoms. The gold atom is situated only 0.022(3) Å out of the mean plane formed by C(1),Cl(1),N(27) and S(20). The phenyl ring of the Hdamp-C^1 ligand is twisted against the co-ordination sphere by 84.07°. As expected from the IR results, the Au–C and Au–Cl bonds are somewhat shorter than in $[Au(Hdamp\text{-}C^1)Cl(Sthiaz)_2]^{2+}$ and $[Au(Hdamp\text{-}C^1)Cl(Spy)_2]^{2+}$. The hydrogen atom H(8) acts as a bridge to Cl(2) [N(8)–H(8) 0.88(7) Å, H(8)–Cl(2) 2.25(7) Å, N(8)–H(8)–Cl(2) 157(6)°]. Another hydrogen bond is formed between Cl(2) and N(29) of the neighbouring complex cations which leads to an infinite hydrogen-bonded chain of $[Au(Hdamp\text{-}C^1)Cl(Spur)]^+$ cations and chloride anions through the solid-state structure (see Fig. 8).

Table 4 Selected bond lengths (Å) and angles (°) in [Au(Hdamp-C^1)-Cl(Spur)]Cl

Au–C(1)	2.024(8)	Au–S(20)	2.328(2)
Au–N(27)	2.124(7)	S(20)–C(26)	1.747(8)
Au–Cl(1)	2.300(2)	N(21)–C(26)	1.34(1)
C(1)–Au–N(27)	172.9(3)	Cl(1)–Au–S(20)	176.65(8)
C(1)–Au–Cl(1)	90.4(2)	C(26)–S(20)–Au	96.4(3)
N(27)–Au–Cl(1)	94.0(2)	C(28)–N(27)–Au	145.9(6)
C(1)–Au–S(20)	88.1(2)	C(25)–N(27)–Au	109.5(5)
N(27)–Au–S(20)	87.8(2)		

	D–H	H···A	D···A	D–H···A
Hydrogen bonds				
N(8)–H(8)···Cl(2′)	0.88(7)	2.25(7)	3.080(7)	157(6)
N(29)–H(29)···Cl(2″)	0.73(8)	2.35(8)	3.086(8)	178(8)

Symmetry operations: ′ $0.5 - x, 0.5 + y, 0.5 - z$; ″ $1 - x, -y, -z$.

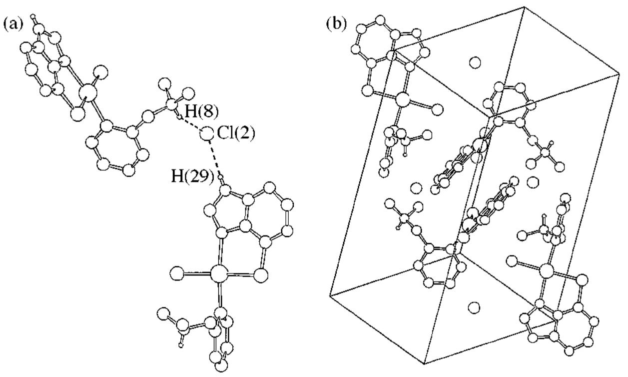


Fig. 8 Illustration of the hydrogen bond in [Au(Hdamp-C^1)Cl-(Spur)]Cl which leads to the formation of infinite ···[Au(Hdamp-C^1)Cl(Spur)]···Cl···[Au(Hdamp-C^1)Cl(Spur)]··· chains (a) and of the arrangement of the complex cations (b)

The purine ring system is planar within 0.022 Å. The angle between this plane and the co-ordination sphere of the gold atom is small (4.2°). A cell plot of the solid-state structure (Fig. 8) shows pairs of molecules stacked *via* their purine rings. This is often observed for chelate-bonded mercaptopurine complexes.[16]

Conclusion

Starting from [Au(damp-C^1,N)Cl$_2$] and heterocyclic thiols a variety of new gold complexes has been synthesized and structurally characterized. Scheme 1 summarizes the reactions performed and the products obtained. A main structural feature of the resulting gold(III) complexes is the formation of an ammonium function from the liberated N(CH$_3$)$_2$ group.

When an excess of thiol ligand is applied considerable amounts of gold(I) complex are formed. The use of the five-membered ring-forming chelate 6-mercaptopurine leads to the formation of [Au(Hdamp-C^1)Cl(Spur)]$^+$ rather than [Au(damp-C^1)(L)$_2$], as observed for the four-membered ring-forming chelate diethyldithiocarbamate.[9]

Experimental

The heterocyclic ligands were purchased from Fluka and used without further purification. The complex [Au(damp-C^1,N)Cl$_2$] was prepared by a literature procedure.[2] Infrared spectra have been recorded on a Bruker IFS 48 spectrometer. Proton and ^{13}C NMR spectra were measured on a DRX 250 instrument (Bruker) with SiMe$_4$ as internal standard. The FAB mass spectra were obtained using a TSQ 70 (FINNIGAN MAT) instrument with nitrobenzyl alcohol as matrix (8 keV ≈ 1.28×10^{-18} kJ, xenon).

Preparations

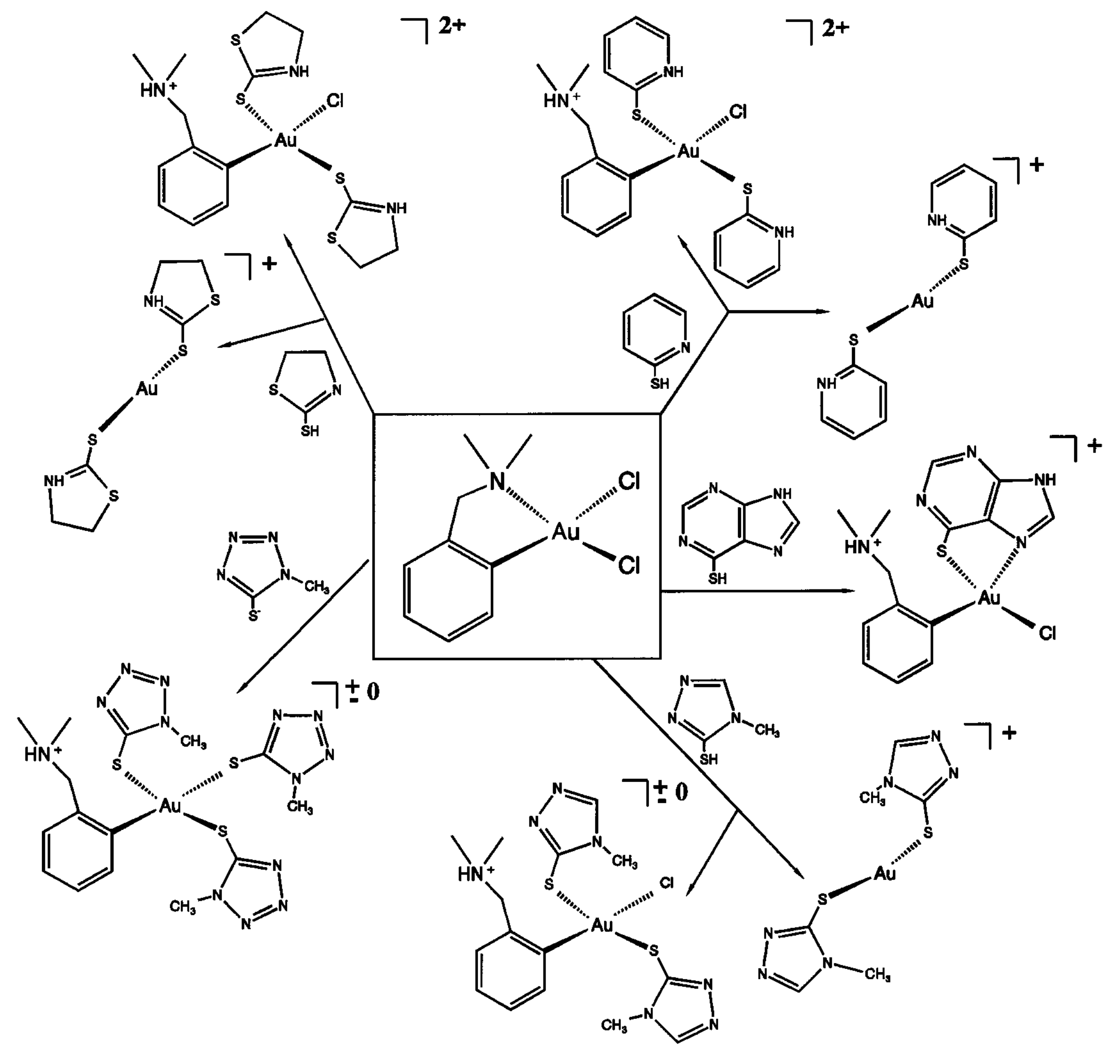
[Au(Hdamp-C^1)Cl(HSthiaz)$_2$]Cl$_2$. The complex [Au(damp-C^1,N)Cl$_2$] (40 mg, 0.1 mmol) was dissolved in acetone (*ca.* 3 ml) and added dropwise to a solution of HSthiaz (12 mg, 0.1 mmol) in acetone (1 ml). Upon standing for 1 d the intense yellow colour of the starting complex vanished and pale yellow crystals began to separate on the glass walls. About one third of the solvent was allowed to evaporate slowly producing more product, which was filtered off and dried carefully. This resulted in the formation of a pale yellow powder due to the loss of cocrystallized solvent. For the X-ray study a crystal of composition [Au(Hdamp-C^1)Cl(HSthiaz)$_2$]Cl$_2$·Me$_2$CO was taken directly from the reaction mixture upon slow evaporation. Yield 11 mg (32% based on HSthiaz) (Found: C, 26.4; H, 3.5; N, 5.8. Calc. for $C_{15}H_{23}AuCl_3N_3S_4$: C, 26.6; H, 3.4; N, 6.2%). IR ($\tilde{\nu}_{max}$/cm^{-1}): 3009m and 2877m (NH of HSthiaz), 2616m (NH of damp], 1560s, 1315s and 1023s (N–C–S), 431s (Au–C), 301s (Au–Cl). ^{1}H NMR [250 MHz, (CD$_3$)$_2$SO]: 10.4 (1 H, s, NH); 7.5 (2 H, s, NH); 7.13–7.53 (4 H, m, C$_6$H$_4$); 4.47–4.67, 3.87–3.94 (10 H, m, CH$_2$); 3.18 (6 H, s, CH$_3$). ^{13}C NMR (dmso): 198.9 (C=S), 130.9, 128.2, 127.8, 126.1, 125.8, 123.1 (C$_6$H$_4$); 42.5 (CH$_2$ of damp); 29.7 (CH$_3$); 53.2, 35.4 (CH$_2$ of HSthiaz). FAB$^+$ MS: *m*/*z* 486 {100, [Au(Hdamp-C^1)(HSthiaz)Cl]$^+$}, 449 {45%, [Au(Hdamp-C^1)(HSthiaz)]$^+$}.

[Au(Hdamp-C^1)Cl(HSpy)$_2$]Cl$_2$. The complex [Au(damp-C^1,N)Cl$_2$] (40 mg, 0.1 mmol) was dissolved in acetone (4 ml) and added dropwise to a solution of HSpy (22 mg, 0.2 mmol) in acetone (4 ml) containing about 5% water. The colour of the solution immediately turned to yellow brown and it became turbid. Acetone was added dropwise until a clear solution was obtained and the mixture was placed at 5 °C for 2 d. During this time yellow crystals deposited which were collected and washed with small amounts of acetone. Yield 25 mg (37%) (Found: C, 33.4; H, 3.9; Cl, 16.0; N, 6.2; S, 9.4. Calc. for $C_{19}H_{23}AuCl_3N_3OS_2$: C, 33.6; H, 3.7; Cl, 15.7; N, 6.2; S, 9.4%). IR ($\tilde{\nu}_{max}$/cm^{-1}): 3185w (NH of HSpy), 2678w (NH of damp), 1594s, 1580s, 1260m and 1026s (N–C–S), 438s (Au–C), 303s (Au–Cl). ^{1}H NMR [250 MHz, (CD$_3$)$_2$SO]: 10.65 (1 H, s, NH), 10.41 (1 H, s, NH), 7.63–8.48 (8 H, m, C$_5$*H*$_5$NH), 7.04–7.61 (4 H, C$_6$H$_5$), 4.37 (2 H, s, CH$_2$), 2.74 (6 H, s, CH$_3$). ^{13}C NMR [(CD$_3$)$_2$SO]: 160.4 (NCSH), 151.9, 151.6, 140.2, 136.9, 134.6, 133.5, 131.2, 124.0, 123.2, 121.6 (aromatic), 42.1 (CH$_2$), 30.6 (CH$_3$). FAB$^+$ MS: *m*/*z* 588 (5, M^+), 552 {15, [Au(Hdamp-C^1)(HSpy)(Spy)]$^+$}, 477 {71, [Au(Hdamp-C^1)Cl(HSpy)]$^+$}, 441 {60, [Au(Hdamp-C^1)(Spy)]$^+$}, 419 {38%, [Au(C$_6$H$_5$)Cl(Spy)]$^+$}.

[Au(Hdamp-C^1)Cl(Smetriaz)$_2$]. The complex [Au(damp-C^1,N)Cl$_2$] (120 mg, 0.3 mmol) was dissolved in acetone (*ca.* 4 ml) and mixed with a solution of HSmetriaz (174 mg, 1.5 mmol) in MeOH (2 ml). The colour changed to bright yellow after mixing the reactants. After standing for 1 h at room temperature, MeOH (5 ml) was added and the mixture overlayed with diethyl ether (10 ml). Upon standing yellow crystals of [Au(Hdamp-C^1)Cl(Striaz)$_2$] were filtered off, washed with diethyl ether and dried under vacuum. Yield 100 mg (56%). IR ($\tilde{\nu}_{max}$/cm^{-1}): 2672w (NH of damp), 759m (CH, disubstituted aromatic). ^{1}H NMR [250 MHz, (CD$_3$)$_2$SO]: 13.7 (1 H, br s, R$_3$N$^+$H), 7.1–7.5 (4 H, m, phenyl), 4.6 (2 H, s, CH$_2$). FAB$^+$ MS: *m*/*z* 481 {100, [Au(damp)(Smetriaz)Cl]$^+$}, 560 {5, [Au(damp)-(Smetriaz)$_2$]$^+$}, 445 {72, [Au(damp)(Smetriaz)]$^+$}, 427 {33, [Au(Smetriaz)$_2$]$^+$}, 312 {47%, [Au(Smetriaz)]$^+$}.

[Au(HSmetriaz)$_2$]Cl. *Method* (*a*). The filtrate from the above reaction mixture was brought to dryness and redissolved in MeOH. Upon standing in a refrigerator pale yellow crystals of [Au(HSmetriaz)$_2$]Cl precipitated. Yield 41 mg (32%).

Method (*b*): *from* [NBu$^n_4$][AuCl$_2$]. The salt [NBu$^n_4$][AuCl$_2$] (102 mg, 0.2 mmol) was dissolved in CH$_2$Cl$_2$ (*ca.* 2 ml) and



Scheme 1 Summary of the reactions studied starting from [Au(damp-C^1,*N*)Cl_2] and the structures of the isolated products

HSmetriaz (460 mg, 0.4 mmol) in MeOH (3 ml) added. The clear mixture became turbid after a few minutes and an almost colourless solid began to precipitate. After stirring for 1 h the solid was filtered off, washed with diethyl ether and recrystallized by diffusion of diethyl ether into a solution of the complex in acetone. Yield 74 mg (80%) (Found: C, 15.4; H, 2.1; N, 18.4. Calc. for $C_6H_{10}AuClN_6S_2$: C, 15.6; H, 2.2; N, 18.2%). IR ($\tilde{v}_{max}$/cm^{-1}): 2725s (br) (N^+H), 1500s (C=N). FAB$^+$ MS: *m*/*z* 427 (71, M^+), 312 {25%, [Au(HSmetriaz)]$^+$}.

[Au(Hdamp-C^1)(Smetetraz)$_3$]. The compound [Au(damp-C^1,*N*)Cl_2] (200 mg, 0.5 mmol) was dissolved in acetone (5 ml) and NaSmetetraz (210 mg, 1.5 mmol) in EtOH (2 ml) added. After stirring for 1 h at room temperature, the mixture was brought to dryness. The residue was redissolved in MeOH and filtered to remove NaCl. Slow evaporation of the solvent gave large yellow crystals. Yield 290 mg (86%) (Found: C, 26.6; H, 3.2; N, 26.7; S, 14.2. Calc. for $C_{15}H_{22}AuN_{13}S_3$: C, 26.6; H, 3.3; N, 26.9; S, 14.2%). IR ($\tilde{v}_{max}$/cm^{-1}): 2721w (N^+H), 1463s and 1442s (C=N). ^{1}H NMR [250 MHz, $(CD_3)_2SO$]: 9.54 (1 H, br s, Me_2NH), 6.9–7.3 (4 H, m, C_6H_4), 4.75 (2 H, s, CH_2), 3.9 (6 H, s, 2 CH_3), 3.8 (3 H, s, CH_3), 3.1 (6 H, s, 2 CH_3). ^{13}C NMR [$(CD_3)_2SO$]: 164.8 (Smetetraz), 157.9, 154.2, 132.7, 131.8, 129.9, 126.9 (C_6H_4), 43.7 (CH_2), 34.6 (CH_3 of damp), 34.0 (CH_3 of Smetetraz). FAB$^+$ MS: *m*/*z* 678 (5, M^+), *m*/*z* 562 {14, [Au(Hdamp)(Smetetraz)$_2$]$^+$}, 446 {100, [Au(Hdamp)(Smetetraz)]$^+$}, 332 {10%, [Au(Hdamp)]$^+$}.

[Au(Hdamp-C^1)Cl(Spur)]Cl. The complex [Au(damp-C^1,*N*)Cl_2] (20 mg, 0.05 mmol) in acetone (2 ml) was added dropwise to a solution of HSpur (8 mg, 0.05 mmol) in MeOH (2 ml). After stirring for 1 h the mixture was kept for 1 d in the refrigerator. During this time yellow crystals of the product precipitated which were collected, washed with acetone and dried. Single crystals of the compound have been obtained by overlaying the gold starting complex in acetone with the solution of the ligand and slow diffusion. Yield 9 mg (32%) (Found: C, 30.5; H, 3.0; Cl, 12.8; N, 12.4; S, 5.8. Calc. for $C_{14}H_{16}AuCl_2N_5S$: C, 30.3; H, 2.9; Cl, 12.8; N, 12.6; S, 5.8%). IR ($\tilde{v}_{max}$/cm^{-1}): 3081w, 3050w (NH, Spur), 2666m (NH^+), 1617s, 1589m, 1396s, 1033m (CNS), 465m (AuC), 358s (AuCl). FAB$^+$ MS: *m*/*z* 518 (23, M^+), 482 {48, [Au(damp)(Spur)]$^+$}, 391 {21%, [Au(NC_2H_5)(Spur)]$^+$}.

[$AsPh_4$][Au(Smetetraz)$_4$]. The salt Na[$AuCl_4$]·$2H_2O$ (38 mg, 0.1 mmol) was dissolved in water (5 ml) and a ten-fold excess of Na(Smetetraz) was added in water (1 ml). The solution immediately turned red. After stirring for 1 min an excess of [$AsPh_4$]Cl was added which resulted in the precipitation of a red solid. This was separated, dried and recrystallized from acetonitrile–xylene. Red needles. Yield 63 mg (72%) (Found: C, 36.6; H, 30.4; N, 21.2; S, 12.1. Calc. for $C_{32}H_{32}AsAuN_{16}S_4$: C, 36.9; H, 30.1; N, 21.5; S, 12.3%). FAB$^-$ MS: *m*/*z* 657 (100, M^-), 542 {100, [Au(Smetetraz)$_3$]$^-$}, 428 {40%, [Au(Smetetraz)$_2$]$^-$}.

Crystal-structure determinations

The intensities for the structure determinations were collected on an automated single crystal diffractometer of the type CAD4 (Enraf-Nonius, Delft) with Mo-Kα or Cu-Kα radiation.

Table 5 Crystal structure data collection and refinement parameters

	[Au(Hdamp-C^1)Cl(HSthiaz)$_2$]Cl$_2$·Me$_2$CO	[Au(Hdamp-C^1)Cl(HSpy)$_2$]Cl$_2$·H$_2$O	[Au(Hdamp-C^1)(Smetetraz)$_3$]	[NEt$_4$][Au(Smetetraz)$_4$]	[Au(Hdamp-C^1)Cl(Spur)]Cl
Crystal dimensions/mm	0.4 × 0.35 × 0.20	0.4 × 0.2 × 0.2	0.5 × 0.3 × 0.2	0.2 × 0.2 × 0.2	0.35 × 0.2 × 0.05
Formula	$C_{18}H_{29}AuCl_3N_3OS_4$	$C_{19}H_{23}AuCl_3N_3OS_2$	$C_{15}H_{22}AuN_{13}S_3$	$C_{16}H_{32}AuN_{17}S_4$	$C_{14}H_{16}AuCl_2N_5S$
M	735.0	676.84	677.60	787.79	524.24
Crystal system	Triclinic	Monoclinic	Triclinic	Tetragonal	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P4/n$	$P2_1/n$
a/Å	10.257(11)	15.910(6)	10.135(3)	15.218(1)	10.599(3)
b/Å	10.508(13)	11.036(3)	10.239(4)	15.218(1)	9.762(2)
c/Å	13.785(18)	14.650(5)	13.967(5)	6.511(1)	17.452(5)
α/°	107.23(7)		73.65(3)		
β/°	102.90(7)	71.22(2)	71.99(3)		101.71(1)
γ/°	97.84(7)		63.01(3)		
U/Å^3	1350(3)	2435(1)	1211.1(7)	1507.9(3)	1768.1(8)
Z	2	4	2	2	4
D_c/g cm^{-3}	1.808	1.846	1.858	1.735	2.082
T/°C	20	20	20	−40	20
Scan type	ω scans	ω scans	ω scans	ω scans	ω scans
μ/mm^{-1}	6.070	6.557	6.364	12.094	8.745
Absorption correction	ψ scans	DIFABS[23]	ψ scans	DIFABS[23]	DIFABS[23]
T_{min}	0.9093	0.732	0.7126	0.422	0.376
T_{max}	0.9996	0.999	0.9992	1.000	0.999
Weighting scheme [$P = (F_o^2 + 2F_c^2)/3$]	$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 1.1163P]$	$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 16.9761P]$	$w = 1/[\sigma^2(F_o^2) + (0.0628P)^2 + 0.2511P]$	$w = 1/[\sigma^2(F_o^2) + (0.0963P)^2 + 6.6817P]$	$w = 1/[\sigma^2(F_o^2) + (0.0622P)^2 + 1.4953P]$
Measured reflections	6203	5316	5054	1454	4897
Independent reflections	5291	4781	4266	1058	4231
Independent reflections [$I > 2\sigma(I)$]	4842	3460	3806	1002	3051
Refined parameters	387	272	293	87	216
$R1$ (F), $wR2$ (F^2)	0.0269, 0.0617	0.0558, 0.1148	0.0371, 0.0883	0.0614, 0.1738	0.0412, 0.0975
S	1.106	1.080	1.120	1.194	1.035
Programs used	SHELXS 86,[21] SHELXL 93,[22] PLATON,[24] HELENA[24]	SHELXS 86,[21] SHELXL 93,[22] PLATON,[24] HELENA[24]	SHELXS 86,[21] SHELXL 93,[22] PLATON,[24] HELENA[24]	SHELXS 86,[21] SHELXL 93,[22] PLATON,[24] HELENA[24]	SHELXS 86,[21] SHELXL 93,[22] PLATON,[24] SDP[25]

The unit cell dimensions were determined from the angular settings of 25 high-angle reflections. The structures were solved by Patterson synthesis using SHELXS 86.[21] Subsequent Fourier-difference map analysis yielded the positions of the non-hydrogen atoms. Refinement was performed using SHELXL 93.[22] The positions of all hydrogen atoms were derived from the final Fourier map and have been fully refined for [Au(Hdamp-C^1)Cl(HSthiaz)]. For the other structures only the H atoms which are involved in hydrogen bonds have been taken from the Fourier maps and fully refined. All other hydrogen atoms have been included at calculated positions and regarded using the 'riding model' option of SHELXL 93. Crystal data and more details of the data collections and refinements are contained in Table 5.

CCDC reference number 186/874.

See http://www.rsc.org/suppdata/dt/1998/1011/ for crystallographic files in .cif format.

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