Synthesis and Crystal Structures of Copper(I) and Gold(I) Complexes $[C(NH_2)_3]_2[M_2(1,2\text{-dithiosquarate})_2]$, M = Cu, Au, Containing Short M···M Distances, and of the Gold(III) Complex $(^{cyclo}PrPh_3P)[Au(1,2\text{-dithiosquarate})_2]$

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The new compounds $[C(NH_2)_3]_2[Cu_2(dtsq)_2]$ (**1**), $[C(NH_2)_3]_2[Au_2(dtsq)_2] \cdot H_2O$ (**2**), and $(^{cyclo}PrPh_3P)[Au(dtsq)_2]$ (**3**, $^{cyclo}Pr$ = cyclopropyl) have been prepared from $CuSO_4 \cdot 5\ H_2O$, $KAuCl_4$, and $K_2dtsq \cdot H_2O$ (dtsq = dianion of 1,2-dithiosquaric acid, $C_4O_2S_2^{2-}$). Compounds **1** and **2** contain pairs of metal atoms with short intermetallic distances of 2.587(2) (Cu···Cu) and 2.846(2) Å (Au···Au). Cu(I) is trigonally coordinated to three sulfur atoms of three different ligands and lies 0.51 Å above the S_3 plane. It is oriented towards the copper atom of a second CuS_3 unit related to the first one by a center of inversion. Au(I) shows a linear coordination, leading to the formation of $Au_2(dtsq)_2^{2-}$ dimers. These have intermolecular Au···Au distances of 3.259(2) Å. Compound **3** contains isolated $Au(dtsq)_2^-$ ions with square planar coordination geometry stacked along the *a* axis at 4.708 Å distance.

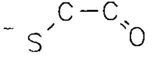
The 1,2-dithiosquarate dianion, $C_4O_2S_2^{2-}$ (dtsq), is a very attractive ligand in many respects. It contains two pairs of different, hard and soft, donor centers and a delocalized π system. Many discrete 2:1 complexes of the transition elements are known. Among the structurally characterized examples are several salts of $[Ni(dtsq)_2]^{2-}$ [1,2] and $[Pd(dtsq)_2]^{2-}$ [3], $(Ph_4P)_2[Fe(dtsq)_2]$[4], and $(\mu\text{-}O)(\mu\text{-}S)[MoO(dtsq)]_2$[5]. The series of copper(I) and copper(II) complexes show interesting structural and magnetic properties: $(Ph_4P)_4[Cu_8(dtsq)_6]$ exhibits a metallocubane structure[6]. $[Cu^{II}(en)_2][Cu^{II}(dtsq)_2]$ contains planar CuN_4 and flattened tetrahedral CuS_4 moieties; cations and anions interact strongly, leading to a chain structure having antiferromagnetic and ferromagnetic behavior, depending on the temperature[7]. The anions in $(Ph_4P)_2[Cu(dtsq)_2]$[8] and (18-crown-6)$K_2[Cu(dtsq)_2]$[9] are square planar. $[Cu^{II}(en)_2(H_2O)]_2[Cu^{I}_4(dtsq)_4] \cdot 2\ H_2O$[7] contains tetrameric and $(pyH)[Cu^{I}(dtsq)]$[10] polymeric moieties of sulfur-coordinated Cu(I), which have short Cu···Cu distances in the range from 2.55 to 2.76 Å.

The structures of compounds containing metal ions such as Cu(I), Ag(I), Au(I), and Hg(II) have been investigated recently under the aspect of homoatomic interactions between the d^{10} configurated ions, which result in shorter metal-metal distances than that in the elements[11]. Several theoretical models have been proposed; nevertheless, the presence of substantial M–M bonding and the nature of possible bonding interactions are discussed still controversely[7]. In order to add further experimental data, we continued our search for compounds which might exhibit these types of interactions. Salts of anionic M(I) dithiosquarate complexes [M(I) = Cu, Ag, Au] with flat or planar polyatomic cations as counterions appeared to be suitable candidates. In this paper we report on the synthesis and the structures of $\{[C(NH_2)_3]_2[Cu_2(dtsq)_2]\}$ (**1**) and $\{[C(NH_2)_3]_2[Au_2(dtsq)_2]\} \cdot H_2O$ (**2**). The Au(III) compound $(^{cyclo}PrPh_3P)[Au(dtsq)_2]$ (**3**, $^{cyclo}Pr$ = Cyclopropyl) has also been prepared during our studies. For the purpose of comparison its structure is also included.

Results and Discussion

The dithiosquarate complexes **1** and **2** could be prepared only in small quantities. These compounds are insoluble in all widely used solvents. Therefore, no NMR spectra could be measured. On prolonged times of storage the compounds change their color and decompose into metal sulfides. For the preparation of **2**, the convenient precursor complex $ClAu[S(CH_2CH_2OH)_2]$ for studies of gold(I) chemistry was used[13]. $(^{cyclo}PrPh_3P)[Au(dtsq)_2]$ (**3**), a gold(III) compound, was synthesized serendipitiously during the search for a polynuclear type $Au^{I}(dtsq)$ complex. The IR spectra of **1**–**3** exhibit absorption bands which are characteristic of *S,S'*-coordinated dithiosquarate complexes. But no structural information can be inferred from the spectra.

dtsq =



1: $[C(NH_2)_3]_2[Cu_2(dtsq)_2]$

2: $[C(NH_2)_3]_2[Au_2(dtsq)_2] \cdot H_2O$

3: $(^{cyclo}PrPh_3)[Au(dtsq)_2]$

0009–2940/94/0404–0605 $ 10.00+.25/0

Structure of $[C(NH_2)_3]_2[Cu_2(dtsq)_2]$ (1)

The $[Cu_2(dtsq)_2]^{2-}$ anion forms an infinite chain structure which contains one pair of Cu(I) atoms per repeating unit. The repeating distance, 3.89(2) Å, is identical with the crystallographic *a* axis. Figure 2 shows a view of two chain segments, Figure 1 the asymmetric unit with part of the hydrogen bonding, and Figure 3 the coordination of a pair of copper atoms. Copper is coordinated in a distorted trigonal, nonplanar coordination geometry to three sulfur atoms, which belong to three different dithiosquarate ions. The Cu−S distances fall in the small range from 2.254(2) to 2.296(2) Å, the S−Cu−S angles in the range between 113.0(1) and 117.5(1)°. Cu(I) lies 0.513 Å above the S_3 plane and is oriented towards the copper atom of a second CuS_3 unit, which is related to the first one by a center of inversion, halfway between the copper atoms [Cu and Cu(a) in Figure 2]. The (unbridged) distance Cu···Cu(a) is only 2.587(2) Å. The copper-copper vector is inclined by 60.5° towards the plane containing the S atoms. In an alternative description, six sulfur atoms (from four different dithiosquarate ions) form a trigonal antiprism with two long [4.841 Å, S(1)···S(2a)] and ten short (3.723 to 3.890 Å) edges. The copper pair consisting of Cu and Cu(a) lies inside this polyhedron (see Figure 3).

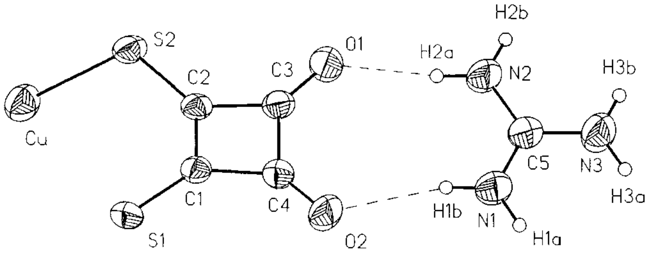


Figure 1. Asymmetric unit and atom labeling scheme for **1**. Selected bond lengths [Å] and angles [°]: Cu−S(1b) 2.262(2), Cu−S(2) 2.254(2), Cu−S(2a) 2.296(2), Cu···Cu(c) 3.890(1), Cu···Cu(a) 2.587(2), S(1)···S(2) 3.723(3), C(1)−S(1) 1.683(6), C(1)−C(2) 1.385(7), C(1)−C(4) 1.481(8), C(3)−O(1) 1.206(7), C(2)−S(2) 1.704(5), C(2)−C(3) 1.465(8), C(3)−C(4) 1.514(7), C(4)−O(2) 1.213(7); S(1b)−Cu−S(2) 114.7(1), S(1b)−Cu−S(2a) 113.0(1), S(2)−Cu−S(2a) 117.5(1), Cu−S(2)−C(2) 118.1(2), Cu−S(2)−Cu(c) 117.5(1)

The dithiosquarate ion is completely planar (mean deviation 0.032 Å). From its two sulfur atoms S(1) is bound to one and S(2) to two metal atoms. These metal atoms are situated at +0.53 [Cu(a)], −1.19 (Cu), and +2.24 Å [Cu(c) in Figure 2] with respect to the ligand plane. The C−S bond distances, 1.683(6) and 1.704(5) Å, differ slightly. The C−C bond distances vary from 1.385(7) Å for C(S)−C(S) to 1.514(7) Å for C(O)−C(O). They are of the same magnitude as in other dithiosquarate *S,S'* complexes[1−10]. As shown in Figure 1, the guanidinium ion $C(NH_2)_3^+$ is linked to the oxygen atoms of the dithiosquarate by two hydrogen bonds like a chelate. Their lengths are 2.829(4) [N(2)···O(1)] and 3.080(5) Å. In the crystal lattice the cations are stacked parallel to the anions along *a*. Further hydrogen bonds, N(2)···O(1) and N(3)···O(2), connect the stacks in the (100) plane.

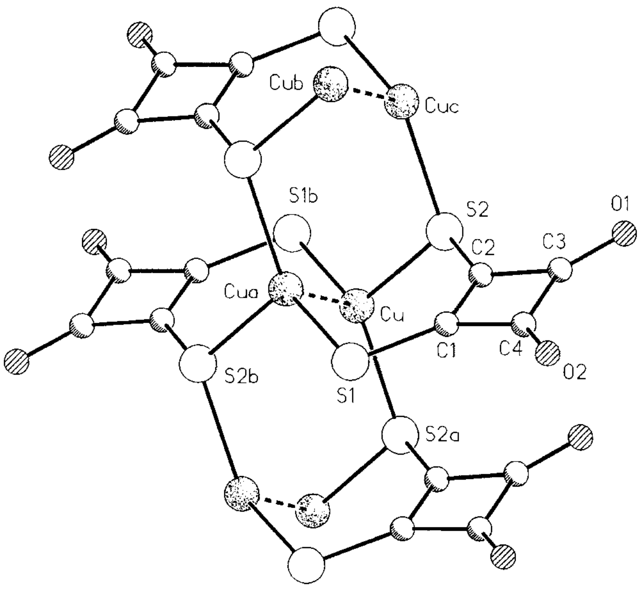


Figure 2. Stacking sequence of the dithiosquarate ions and the pairs of Cu(I) atoms in the structure of **1**

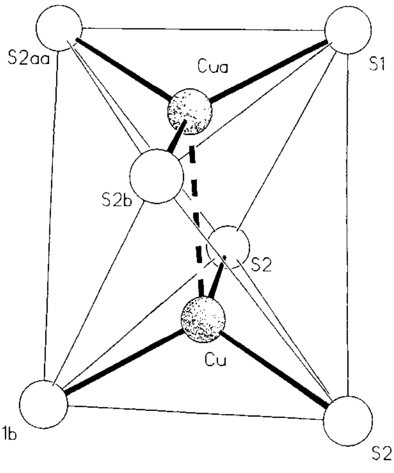


Figure 3. A copper pair in **1** within the polyhedron of six sulfur atoms

The present structure is to be compared with the structures of (pyH)[Cu(dtsq)][10] and $[Cu^{II}(en)_2(H_2O)]_2[Cu^I_4(dtsq)_4]$[7], which have been determined earlier by us. Both compounds contain Cu(I) and dithiosquarate in a ratio of 1:1; Cu(I) is exclusively coordinated to the *S*-donor atoms and possesses short contacts to neighboring copper centers. $[Cu^{II}(en)_2(H_2O)]_2[Cu^I_4(dtsq)_4]$ contains a centrosymmetric, slightly bent chain of four Cu(I) with Cu···Cu distances of 2.552(1) and 2.579(1) Å. In the middle of the chain two adjacent Cu(I) are tetrahedrally coordinated to four sulfur atoms from three different dithiosquarate ions. The tetrahedra are considerably distorted and share a common edge, or, in other words, the copper atoms are bridged by a $(\mu - S)_2$ group. The end atoms of the four-atomic chain are in a nonplanar trigonal environment with a mean Cu−S distance of 2.268(1) Å. One S atom is shared between the tetrahedrally and trigonally coordinated Cu(I). The latter is situated 0.26 Å above the plane containing the S atoms and is oriented towards a more distant sulfur donor at 3.145(1) Å.

(pyH)[Cu(dtsq)] contains an infinite zigzag chain of Cu(I), which extends through a stack of dithiosquarate ions, to which the pyH^+ ions are attached by hydrogen bonds. Cu(I) is again tetrahedrally and trigonally coordinated. The Cu···Cu distances are 2.573(8) [$(\mu - S)_2$-bridged], 2.764(8) [$(\mu - S)$-bridged], and 2.621(8) Å (unbridged). The bonding situation of the unbridged copper atoms is completely analogous to the situation in compound **1**: the mean Cu−S distance is 2.30 Å, copper is lying 0.47 Å above the S_3 plane and is oriented towards the copper center of a second CuS_3 unit, related to the first one by a center of inversion.

Compounds with short $Cu^I \cdots Cu^I$ contacts, in the range of the sum of r_{cov} of copper have been recently reviewed by Strähle[14]. Results of theoretical investigations seem to be contradictory. It is still an open question, whether any bonding interactions exist at all. In the classical theory, d^{10}-configurated metal ions are unable to form metal-to-metal bonds. Therefore, hybridization of the filled $3d_{z^2}$ orbital with the empty 4s and $4p_z$ orbitals has been suggested to explain bonding. But in all structures determined so far, bridging between the metal centers seems to be important. Two types of bridging can be distinguished, and both occur in the structures discussed above: (i) bridging by a single donor atom, e.g. $(\mu - S)$ or $(\mu - S)_2$ bridges, and (ii) bridging by a chelate ligand along unsaturated bonds, e.g. Cu−S−C−C−S−Cu′. For the structures discussed here the Cu···Cu distance seems roughly to be independent of the type of bridging. The distances range from 2.55 to 2.76 Å, with the distances of type (ii) bridges, surprisingly, at 2.621(3) and 2.587(2) Å. It has been suggested that these short distances are caused by the stereochemical and electronic requirements of the ligands involved. But an inspection of the structures with type (ii) bridges gives no hint that the mutual approach of the copper atoms might be forced by the requirements of the dithiosquarate ligands. On the contrary, their modes of coordination seem to be very variable. In the structures discussed the ligand bites, the Cu−S−Cu angles, and the directions of the S−Cu vectors with respect to the ligand plane vary greatly. We think, therefore, that these short Cu···Cu distances may indeed be caused by attractive forces.

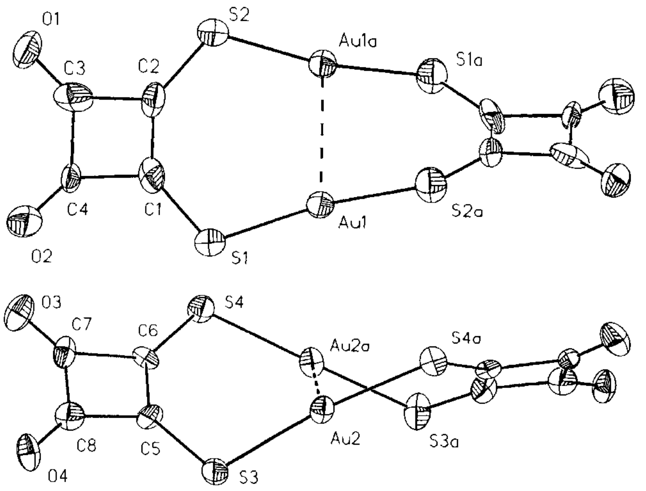


Figure 4. The two crystallographically independent $Au_2(dtsq)_2^{2-}$ ions from different perspectives in the structure of **2**. Selected bond lengths [Å] and angles [°]: Au(1)−S(1) 2.297(5), Au(1)−S(2) 2.292(5), Au(1)···Au(1a) 2.927(2), Au(1)···Au(1b) 3.259(2), Au(2)−S(3) 2.271(6), Au(2)−S(4) 2.294(6), Au(2)···Au(2a) 2.846(2), C(1)−S(1) 1.707(19), C(2)−S(2) 1.655(2), S(1)···S(2) 3.967, C(5)−S(3) 1.710(2), C(6)−S(4) 1.671(18), S(3)···S(4) 3.940; S(1)−Au(1)−S(2) 170.1(2), S(3)−Au(2)−S(4) 167.9(2), Au(1b)−Au(1)−Au(1a) 143.8(0), C−S−Au 107.3(7) to 110.3(7)

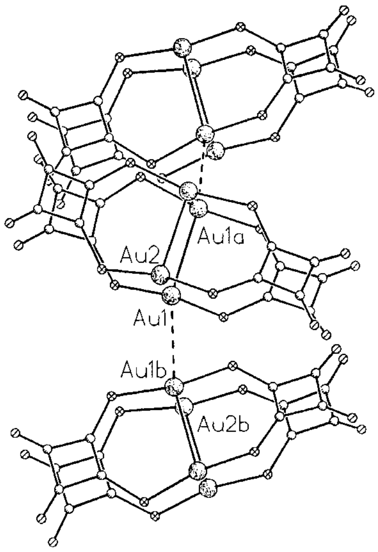


Figure 5. Section of the crystal lattice showing the arrangement of the $Au_2(dtsq)_2^{2-}$ dimers in the structure of **2**

Structure of $[C(NH_2)_3]_2[Au_2(dtsq)_2] \cdot H_2O$ (2)

Figure 4 shows the atom labeling scheme within the two independent $[Au_2(dtsq)_2]^{2-}$ groups in the asymmetric part of the unit cell. They are projected from different views to give an impression of their three-dimensional structure. Figure 5 shows the packing within the crystal lattice.

The structure of **2** bears no relationship to any of the Cu(I) compounds discussed in the last paragraph. In the dimers, which possess crystallographic twofold symmetry, each dithiosquarate is functioning as a bismonodentate ligand towards two Au(I). The gold atoms have rather short Au···Au distances of 2.927(2) and 2.846(2) Å. Each gold atom has a linear coordination geometry. The Au−S bond lengths vary from 2.271(6) to 2.297(5) Å; the S−Au−S angles are 170.1(2) at Au(1) and 167.9(2)° at Au(2). Recent work gives Au(I)−S distances of 2.285(3)−2.300(3) Å in $[Au_2(S_2CNEt_2)_2]$[15], 2.291(4) Å in $[BrAu(SC(NH_2)_2)]$[16] and 2.291(1) respectively 2.300(2) Å in $ClAu(PhNHC(S)SMe)_2$[17]. The C−S−Au angles of 107.3(7)−109.7(7)° exceed the C−S−Cu angles in **1** by 5−10°. In the dimers the dithiosquarate ligands are twisted against each other by 68°, while the S−Au−S groups remain linear (see Figure 4). This motion approaches the gold atoms towards each other. The ligands are essentially planar with mean deviations of 0.024 and 0.021 Å. The ligand bites increase to

3.967(9) and 3.940(8) Å, the highest values observed in dithiosquarate complexes so far.

It is interesting to note that Au(1) and Au(1a) as well as Au(2) and Au(2a) are differently spaced with respect to "their" ligand planes. Au(1) is situated 0.69 Å above the mean plane through the ligand containing S(1) and Au(1a) 0.95 Å below this ligand. The equivalent values for Au(2) and Au(2a) are +1.07 and −0.49 Å. The interatomic distances within the ligand are not further discussed due to their high standard deviations.

The dimers containing Au(1) and Au(1a) are oriented approximately side by side in the unit cell giving Au···Au intermolecular distances of 3.259(2) Å [Au(1)···Au(1b)] and Au−Au−Au angles of 143.8(0) Å (see Figure 5). The second dimers containing Au(2) and Au(2a), are situated alternatively above and below of the wave-like band formed by the Au(1) dimers. The interatomic distances between the superimposed dimers diminish slightly from the pairs of Au atoms at the center of the band (4.043 Å) to the pairs of oxygen atoms at the periphery (3.663 Å), giving an 8.6° interplanar angle between their ligand planes.

Schmidbaur has summarized recently the geometric forms of inter- and intramolecular interactions occurring in linearly coordinated gold(I) complexes[18]. The present structure fits well in the schemes given by him. Intramolecular Au−Au distances can be as short as 2.782(1) Å in $Au_2(S_2CNEt_2)_2$[15] or slightly larger as in several salts of $[Au_2(dppm)_2]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$)[19], although the van der Waals' radius of gold is 1.70 Å. Typical is the angular distortion of the $(XAuX)_2$ moieties, which results in X−Au−X angles greater than 180° on the side of the Au_2 pair. Short intermolecular distances arise from dimerization of compounds with linear P−Au−Cl moieties[20,21] or from alignment of dimeric units, so that continuous chains of Au−Au interactions result throughout the whole crystal lattice. Like in the present case, these distances are usually larger than the intramolecular contacts, but can be as short as 3.004(1) Å in $Au_2(S_2CNEt_2)_2$[15]. Recently, these interactions were called "aureophilic" interactions, because these phenomena are confined to gold[18].

Structure of (^{cyclo}PrPh$_3$P)[Au(dtsq)$_2$] (3)

As depicted in Figure 6, the unit cell contains two independent $[Au(dtsq)_2]^-$ ions. They are stacked along the *a* axis at 4.708 Å distance. Au(III) exhibits the expected square planar coordination geometry with Au−S distances ranging from 2.325(2) to 2.343(3) Å. These values are slightly larger than those observed in a number of other bis(1,2- and 1,3-dithiolato)gold(III) complexes[22,23]. This is probably caused in **3** by the electron-withdrawing carbonyl groups, which are part of the ligands. The C−S bond distances and the other bond lengths within the ligand are normal. The ligand bites, 3.403(4) and 3.388(4) Å, are slightly larger than the interligand S···S distances of 3.215(4) Å in the AuS_4 moiety. But unlike in $[Fe(C_5Me_5)_2][Au(C_3S_5)_2]$[23], there are no other short S···S contacts.

Very weak interactions occur between different complex ions, with Au(1)···S(4) at 3.750(2) and Au(2)···S(1) at 3.802(2) Å. The mean deviation from the molecular plane is considerably larger for the complex containing Au(2) (0.068 Å) than for the complex containing Au(1) (0.017 Å). The reason for this difference is unknown. The large $[^{cyclo}PrPh_3P]^+$ cations form pairs around the center of the unit cell.

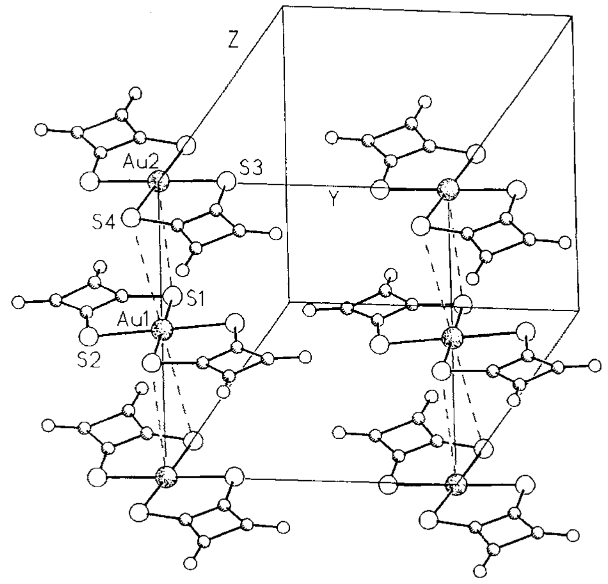


Figure 6. Arrangements of the Au(1,2-dtsq)$_2^-$ ions in the structure of **3**. Selected bond lengths [Å] and angles [°]: Au(1)−S(1) 2.340(3), Au(1)−S(2) 2.341(2), Au(2)−S(3) 2.325(2), Au(2)−S(4) 2.343(3), S(1)···S(2) 3.403(4), S(1)···S(2a) 3.215(4), S(3)···S(4) 3.388(4), S(3)···S(4a) 3.212(5); S(1)−Au(1)−S(2) 93.2(1), S(3)−Au(2)−S(4) 93.1(1)

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Experimental

Commercial chemicals were used without purification. − IR (KBr pellets): Perkin-Elmer 683. − Microanalyses: performed by using standard techniques.

$[C(NH_2)_3]_2[Cu_2(dtsq)_2]$ (**1**): To a solution of $CuSO_4 \cdot 5\ H_2O$ (0.25 g, 1.0 mmol) in H_2O (10 ml) was added an aqueous solution (10 ml) of $K_2dtsq \cdot H_2O$[24] (0.24 g, 1.0 mmol) and guanidinium chloride (0.573 g, 6.0 mmol). A dark-green precipitate was formed immediately, from which dark-brown needle-like crystals were grown during 1−2 d. They were mechanically separated. Yield 0.08 g (30%). − IR: ṽ = 3415 cm^{-1} (s), 1730 (s), 1680 (m, b), 1400 (w), 1370 (m), 1215 (m), 1110 (w), 945 (w), 905 (w), 545 (w), 510 (w). − $C_5H_6CuN_3O_2S_2$ (267.8): calcd. C 22.4, H 2.18, N 15.7; found C 22.0, H 2.3, N 15.0.

$[C(NH_2)_3]_2[Au_2(dtsq)_2] \cdot H_2O$ (**2**): $KAuCl_4$ (0.10 g, 0.26 mmol) was dissolved in water/acetone (1:1, 4 ml) at 0°C. A solution of $(HOCH_2CH_2)_2S$ (0.065 g, 0.52 mmol) in acetone (1 ml) was added. After 30 min a colorless solution had formed. Then a solution of guanidinium chloride (0.17 g, 0.156 mmol) and $K_2dtsq \cdot H_2O$ (0.068 g, 0.26 mmol) in H_2O (5 ml) was added. The colour turned to yellow. The solution was slowly concentrated at room temp., and a small quantity (11 mg) of red-brown needles was obtained. − IR: ṽ = 3400 cm^{-1} (m), 1720 (vs), 1645 (vs, b), 1360 (s), 1160 (m), 1090 (w), 910 (m), 530 (w), 500 (w). − $C_5H_7AuN_3O_{2.5}S_2$

Table 1. Crystal data of **1**–**3**

Compound	**1**	**2**	**3**
formula	$C_5H_6N_3O_2S_2Cu$	$C_5H_7N_3O_{2.5}S_2Au$	$C_{29}H_{20}O_4PS_4Au$
mol mass	267.8	410.3	788.6
crystal system	monoclinic	orthorhombic	triclinic
space group	$P2_1/n$	Pnna	$P\bar{1}$
a (Å)	3.890(0)	14.570(3)	9.415(2)
b (Å)	11.811(2)	11.098(2)	12.055(2)
c (Å)	19.830(4)	25.038(5)	14.297(3)
α (°)	90	90	101.91(3)
β (°)	91.62(3)	90	101.87(3)
γ (°)	90	90	94.73(3)
V (Å^3)	910.5	4048.5	1450.4
Z	2	8	2
d_{calc}(g·cm^{-3})	1.95	2.69	1.81
d_{meas}(g·cm^{-3})	1.96	2.65	1.82
cryst.dimensions (mm)	0.3x0.1x0.8	0.4x0.05x0.05	0.4x0.2x0.2
abs.coeff.(mm^{-1})	2.8	14.9	5.5
transm.coeff.	0.86-1	0.66-1	0.83-1
2θ-range (°)	4-54	4-54	4-50
reflections measured	2360	4954	2361
unique $I \geq 2\sigma(I)$	1485	3175	1949
octants	h,k,±l	h,k,l	h,±k,±l
variables	118	234	265
g(weighting)	0.0004	0.00025	0.0003
R	0.056	0.041	0.029
R_w	0.072	0.040	0.031

(410.3): calcd. C 15.0, H 1.5, N 10.5; found C 15.8, H 1.8, N 7.7.

$(^{cyclo}PrPh_3P)[Au(dtsq)_2]$ (**3**): A solution of $KAuCl_4$ (0.10 g, 0.26 mmol) in H_2O (5 ml) was added to a solution of $(^{cyclo}PrPh_3P)$dtsq (0.397 g, 5.3 mmol) in EtOH (5 ml). Compound **3** was obtained within a short time as a red microcrystalline solid. Single crystals of X-ray quality could be obtained by slow interdiffusion of these solution; yield 102 mg (51%). – IR: $\tilde{\nu}$ = 1800 cm^{-1} (w), 1750 (s), 1720 (s), 1480 (m), 1460 (s), 1430 (m), 1110 (w), 845 (w), 530 (w), 520 (w). – $C_{29}H_{20}AuO_4PS_4$ (788.6): calcd. C 44.4, H 2.51; found C 44.2, H 2.55.

Crystal Structure Determinations: The quality of the crystals mounted on a glass fiber was checked by oscillation and Weissenberg photographs. Using the same crystals, we collected diffraction data for **1**–**3** on a CAD 4 single-crystal diffractometer at room temp. with graphite-monochromated Mo-K_α radiation, λ = 0.71069 Å. Crystallographic data are presented in Table 1. The lattice parameters were determined by using 25 high-angle reflections. The data were corrected for Lorentz and polarization effects and for intensity fluctuations in the standards. Only random fluctuations were observed. Absorption corrections were made empirically on the basis of azimuthal scans. The structures were determined by using Patterson and difference Fourier techniques with the aid of the SHELXTL package[12]. The weighting scheme $w^{-1} = \sigma(F)^2 + g \cdot F^2$ (for g see Table 1) was used. Final refinement was performed with hydrogen atoms placed in idealized positions (C–H = 0.96, N–H = 0.85 Å). Carbon atoms of phenyl rings in compound **3** were refined isotropically. In compound **2** one $C(NH_2)_3^+$ ion is disordered [on both sides of a pseudo mirror plane through N(4) and N(5)]. Disordered atoms are refined isotropically. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57935, the names of the authors, and the journal citation.

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