Gold(I) Complexes with Amine Ligands, 6[+]

Hydrogen Bonding Networks in Bis(amine)gold(I) Complexes with Disulfonylamide Anions

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The use of disulfonylamines as counter-ions allows the synthesis of stable ionic gold(I) complexes with the amine ligands cyclohexylamine, benzylamine, 3-iodobenzylamine, morpholine, pyrrolidine, and piperidine. There is a considerable increase in stability for the morpholine complex compared to the previously synthesised chloro derivative; the benzylamine derivatives displayed better solubility and crystallinity than their chloro analogues. The use of silver disulfonylamine derivatives in the syntheses led in two cases to the incorporation of silver into the products, with concomitantly poor yields. Crystal structure determinations of eight complexes revealed, as expected, extensive systems of N–H···O hydrogen bonds. Amines with NH functions tend to form hydrogen-bonded chain motifs, those with NH_2 as donor group form layers of linked ring patterns. It thus seems that the packing can more easily be classified in terms of influence of the cation than of the anion. Some C–H···O hydrogen bonds were also observed, but play a less important role. Aurophilic contacts were not observed, although one mixed gold/silver complex displayed short Au···Ag contacts. Of the two compounds containing iodine, only one showed short I···I contacts.

Introduction

Our studies of gold(I) complexes with amine ligands have involved a detailed investigation of the role of secondary bonds in these compounds.[1] Two types of secondary contacts are most frequently observed: aurophilic interactions[2] and hydrogen bonds. Gold(I) complexes of aliphatic amines had previously been regarded as relatively unstable − a viewpoint easily rationalised in terms of incompatibility of the soft metal centre gold(I) and the hard nitrogen donor − in the absence of stabilising ligands, such as phosphanes. We believe that hydrogen bonds are particularly important in stabilising such complexes.

Until now we have generally used chloride as counter-ion or second ligand, because of the convenience of using chloro precursors such as chloro(tetrahydrothiophene)gold(I). The use of more versatile hydrogen bond acceptors might be expected to increase the stability of gold(I)−amine complexes still further, at least in the solid state; we have therefore started to exchange the sterically and geometrically undemanding halogen anion for disulfonylamides, using as reagent the silver disulfonylamides in acetonitrile solution. For a similar recent example with the ligand (dppm)Se, see ref.[3]

Here we report the synthesis and structure of gold(I) compounds with cyclohexylamine (**1**, **6**, **8**), benzylamine (**2**), 3-iodobenzylamine (**3**), morpholine (**4**; this was not stable as a chloro complex), pyrrolidine (**5**), and piperidine (**9**) as the amine ligands and bis(methanesulfonyl)amide (**1**, **2**, **3**, **4**, **5**), bis(*p*-chlorobenzenesulfonyl)amide (**7**), bis(*p*-iodobenzenesulfonyl)amide (**8**), and *o*-benzenedisulfonylamide (= 1,1,3,3-tetraoxo-1,3,2-benzodithiazole; **6**) as the anions. The corresponding chloro derivatives of **2** and **3** were highly insoluble and at best microcrystalline, whereas that of **4** was unstable.[1]

Our previously studied chloride derivatives involved three chemically distinct types of complexes: LAuCl (e.g. L = 2-methylpyridine, piperidine),[4,5] $[L_2Au^+]Cl^-$ (e.g. L = piperidine, cyclohexylamine)[1] and $[L_2Au^+][AuCl_2^-]$ (e.g. L = pyridine,[6] 3-bromopyridine[7]). Some crystal structures showed more than one structural type in the same crystal. With L = pyrrolidine a by-product was obtained in which two molecules of LAuCl crystallised together with one ionic complex $[L_2Au^+]Cl^-$;[8] other workers have shown that with L = 2-aminopyridine, one molecule LAuCl crystallised together with one ionic complex $[L_2Au^+]$ $[AuCl_2]^-$.[9] However, none of the compounds we examined showed appreciable conductivity in acetone solution, hence an equilibrium favouring the molecular over the ionic form was proposed.[1] After exchanging the chloride for a disulfonyla-

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mide, in the presence of additional amine ligand, only ionic structures are observed. These complexes do conduct in acetone solution, although not very strongly, e.g. Λ_c = 79 cm^2 Ω^{-1} mol^{-1} for $[(cyNH_2)_2{}^+]NMs_2{}^-$; cf. Λ_c = 140 cm^2 Ω^{-1} mol^{-1} in the case of 1:1 electrolytes such as PPN^+Cl^-. It is conceivable that some form of ionic association occurs in solution.

All crystallographically characterised complexes described here display hydrogen bonding. As would be expected, the resulting networks become more complex with increasing numbers of donor hydrogen atoms. Comparison of the resulting patterns shows a seemingly greater contribution to the packing from the cation than from the anion.

None of the complexes shows aurophilic interactions, although the unexpected complex **5** involves an Au···Ag contact (see below).

Within those complexes where iodine is present, either in the ligand or the anion, I···I ("soft-soft") interactions were expected. However, only in one case were I···I contacts observed [3.723(4) Å in **3**, cf. 4.3804(10) Å in **8**; sum of the van der Waals radii 3.96 Å].[10] This further supports the conclusion that the hydrogen bonds contribute most to the three-dimensional pattern in these complexes.

Results and Discussion

Complexes with Bis(methanesulfonyl)amide as Anion and Cyclohexylamine, Benzylamine, 3-Iodobenzylamine, Morpholine or Pyrrolidine as Ligand

$[(CyNH_2)_2Au^+]NMs_2{}^-$ [**1**, cyNH$_2$ = cyclohexylamine, NMs$_2$ = bis(methanesulfonyl)amide, Figure 1, Table 1] crystallised with two independent molecules in the asymmetric unit. $[(Benzylamine)_2Au^+]NMs_2{}^-$ (**2**, Figure 2, Table 2), $[(3\text{-iodobenzylamine})_2Au^+]NMs_2{}^-$ (**3**, Figure 3, Table 3) and $[(morpholine)_2Au^+]NMs_2{}^-$ (**4**, Figure 4, Table 4) crystallised with one formula unit in the asymmetric unit. With pyrrolidine as the ligand, the "non-innocence" of the silver reagent was demonstrated by the formation of a different complex (**5**): instead of a single NMs$_2{}^-$ anion this complex contains the anion $[Ag(NMs_2)_2{}^-]$, and involves a d^{10}−d^{10} interaction between Ag and the gold atom of the $[(pyrrolidine)_2Au^+]$ cation (Figure 5, Table 5). Even under exact stoichiometric conditions for the expected reaction, only this complex was obtained. We assume that the d^{10}−d^{10} interaction, in addition to the hydrogen bonding, stabilises the complex. Its length [3.309(3) Å] lies in the typical range of purely aurophilic interactions,[11] but much shorter Au···Ag contacts have been observed in $[Ag\{[Au(\mu\text{-}N^3,C^3\text{-bzim})]_3\}_2]^+BF_4{}^-$ [2.731(2) to 2.922(2) Å, bzim = 1-benzylimidazolate][12] or in $[Au_4Ag(CH_2SiMe_3)_4(\mu\text{-dppm})_2]SO_3CF_3$ [2.7179(13) to 2.7822(13) Å, dppm = bis(diphenylphosphanyl)methane].[13]

Table 1. Selected bond lengths and angles for **1**

Au1−N2	205.0(10)	Au1−N1	205.3(10)
Au2−N4	202.9(12)	Au2−N3	203.3(11)
S1−O2	144.2(9)	S1−O1	144.6(9)
S1−N5	162.1(9)	S1−C1	175.7(11)
S2−O4	143.6(9)	S2−O3	144.6(9)
S2−N5	157.3(11)	S2−C2	176.8(12)
S3−O6	145.1(9)	S3−O5	146.4(9)
S3−N6	158.0(12)	S3−C3	177.7(12)
S4−O7	145.7(11)	S4−O8	145.7(9)
S4−N6	159.1(11)	S4−C4	174.8(11)
N2−Au1−N1	177.9(4)	N4−Au2−N3	178.9(5)
O2−S1−O1	115.9(6)	N5−S1−C1	107.8(5)
O4−S2−O3	115.9(6)	N5−S2−C2	106.3(6)
O6−S3−O5	117.1(6)	N6−S3−C3	107.0(6)
O7−S4−O8	116.5(6)	N6−S4−C4	107.7(6)
S2−N5−S1	119.8(6)	S3−N6−S4	120.3(6)

All gold atoms are linearly coordinated [N1−Au1−N2 177.9(4), N3−Au2−N4 178.9(5)° (**1**), N1−Au−N2 177.66(10)° (**2**), N1−Au−N2 177.4(5)° (**3**), N1−Au−N2 177.19(8)° (**4**), and N1−Au−N2 178.0(6)° (**5**)]. The Au−N bond lengths of 2.053(10), 2.050(10) (at Au1), 2.033(11), 2.029(12) Å (at Au2) (**1**), 2.047(2), 2.045(3) Å (**2**), 2.037(13), 2.031(12) Å (**3**), 2.051(2), 2.055(2) Å (**4**), and 2.029(10), 2.044(12) Å (**5**) are similar to those in $(cyNH_2)_2Au^+Cl^-$ [Au−N 2.036(9) to 2.051(8) Å],[1] $(piperidine)_2Au^+Cl^-$ [Au−N 2.050(6), 2.055(6) Å][1] or in $(pyrrolidine)_2Au^+Cl^-$

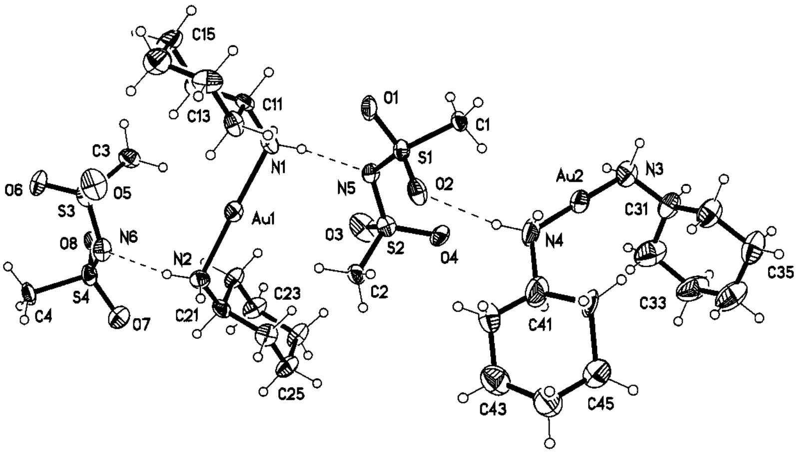

Figure 1. Bis(cyclohexylamine)gold(I) bis(methanesulfonyl)amide (**1**); asymmetric unit with numbering scheme; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds

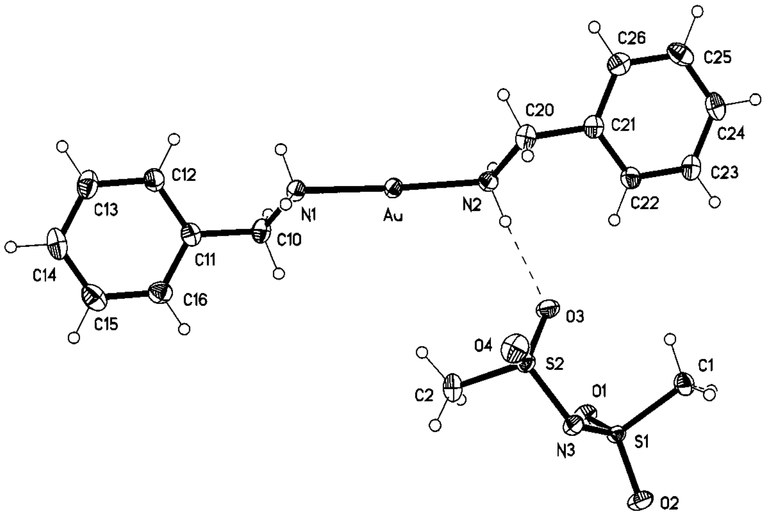

Figure 2. Bis(benzylamine)gold(I) di(methanesulfonyl)amide (**2**); asymmetric unit with numbering scheme; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds

Table 2. Selected bond lengths and angles for **2**

Au−N2	204.5(3)	Au−N1	204.7(2)
N1−C10	148.4(4)	C10−C11	151.1(4)
N2−C20	149.0(4)	C20−C21	151.2(4)
N3−S1	159.6(3)	N3−S2	159.8(3)
S1−O1	144.2(2)	S1−O2	145.1(2)
S1−C1	177.0(3)	S2−O4	144.5(2)
S2−O3	145.7(2)	S2−C2	175.0(3)
N2−Au−N1	177.66(10)	C10−N1−Au	117.36(19)
N1−C10−C11	113.1(3)	C20−N2−Au	115.15(19)
N2−C20−C21	113.4(2)	S1−N3−S2	120.96(15)
O1−S1−O2	115.54(14)	N3−S1−C1	106.34(15)
O4−S2−O3	116.30(15)	N3−S2−C2	105.88(15)

Table 3. Selected bond lengths and angles for **3**

Au−N2	203.1(12)	Au−N1	203.7(13)
I1−C13	215.0(17)	I2−C23	208.8(16)
N1−C10	150(2)	C10−C11	150(2)
N2−C20	150.8(19)	C20−C21	150(2)
N3−S2	156.9(14)	N3−S1	161.5(13)
C1−S1	178.3(17)	C2−S2	175.8(14)
S1−O2	144.3(11)	S1−O1	146.8(11)
S2−O3	144.1(11)	S2−O4	145.6(11)
N2−Au−N1	177.4(5)	C10−N1−Au	114.2(9)
C11−C10−N1	113.5(13)	C20−N2−Au	115.8(9)
C21−C20−N2	113.0(11)	S2−N3−S1	120.6(8)
O2−S1−O1	116.5(7)	N3−S1−C1	106.5(8)
O3−S2−O4	114.9(7)	N3−S2−C2	107.5(7)

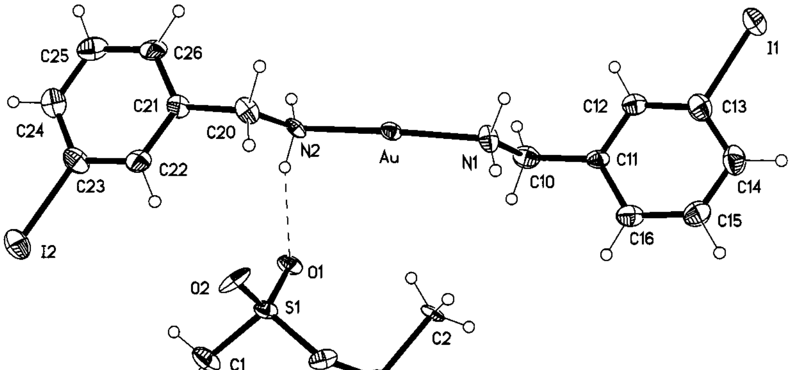

Figure 3. Bis(3-iodobenzylamine)gold(I) bis(methanesulfonyl)amide (**3**); asymmetric unit with numbering scheme; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds

[Au−N 2.052(5) to 2.055(7) Å].[1] The dimensions of **5** should however be interpreted with caution, because the cation is disordered over two positions (see Experimental Section; only the dimensions of the major component are discussed here) and because there is pseudosymmetry caused by the heavy atoms positioned approximately at 0.25,0.5,*z* in space group $Pna2_1$.[14]

The independent cations in **1** show different C−N···N−C torsion angles across the N−Au−N unit: The arrangement of the ligands at Au1 is antiperiplanar [C11−N1···N2−C21 169(1)°], and is eclipsed at Au2 [C31−N3···N4−C41 −18(1)°]. The former conformation is most common within this kind of cation, as in $[(cyNH_2)_2Au^+]Cl^-$ [C−N···N−C −174.2(9) and, because of inversion symmetry, 180°],[1] **2**

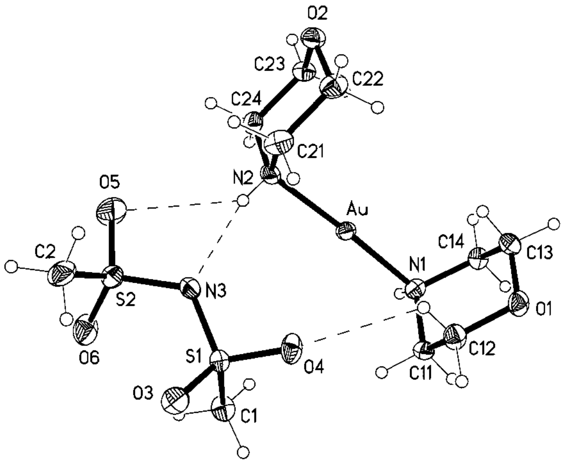

Figure 4. Bis(morpholine)gold(I) bis(methanesulfonyl)amide (**4**); asymmetric unit with numbering scheme; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds

Table 4. Selected bond lengths and angles for **4**

Au−N1	205.1(2)	Au−N2	205.5(2)
N3−S1	158.8(2)	N3−S2	159.9(2)
S1−O3	144.62(19)	S1−O4	145.66(19)
S1−C1	176.1(2)	S2−O5	144.5(2)
S2−O6	144.6(2)	S2−C2	176.5(3)
N1−Au−N2	177.19(8)	C11−N1−C14	108.0(2)
C11−N1−Au	112.24(16)	C14−N1−Au	114.52(16)
C21−N2−C24	108.3(2)	C21−N2−Au	114.35(18)
C24−N2−Au	114.55(17)	S1−N3−S2	122.47(14)
O3−S1−O4	115.56(12)	N3−S1−C1	108.29(13)
O5−S2−O6	117.06(15)	N3−S2−C2	107.08(14)

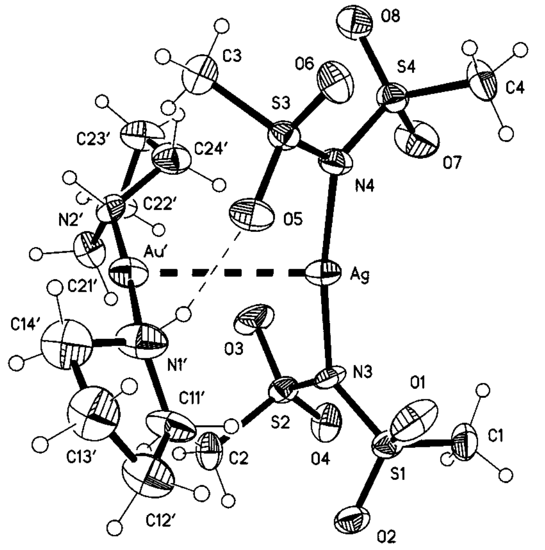

Figure 5. Bis(pyrrolidine)gold(I) bis[bis(methanesulfonyl)amide]argentate(I) (**5**); major disorder component with numbering scheme; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds; in the minor disorder component, the pyrrolidine ring involving N2 inverts to form an intramolecular hydrogen bond from N2 to O3; see also the corresponding packing diagrams in Figure 10

Table 5. Selected bond lengths and angles for **5** (only the major disorder component of the cation is given)

Au′−N2′	202.9(10)	Au′−N1′	204.4(10)
Au′−Ag	330.9(3)	Ag−N3	212.3(7)
Ag−N4	212.2(7)	S1−O1	143.8(6)
S1−O2	144.2(8)	S1−N3	162.7(7)
S1−C1	174.7(11)	S2−O4	142.9(7)
S2−O3	144.0(7)	S2−N3	162.3(8)
S2−C2	176.9(9)	S3−O5	143.5(7)
S3−O6	143.4(7)	S3−N4	162.3(8)
S3−C3	176.0(9)	S4−O8	143.1(7)
S4−O7	145.8(7)	S4−N4	162.7(8)
S4−C4	176.9(11)		
N2′−Au′−N1′	176.5(8)	N2′−Au′−Ag	100.5(4)
N1′−Au′−Ag	82.6(8)	N3−Ag−N4	171.1(3)
N3−Ag−Au′	95.5(2)	N4−Ag−Au′	93.4(2)
O1−S1−O2	117.8(4)	N3−S1−C1	106.8(5)
O4−S2−O3	116.6(4)	N3−S2−C2	106.9(4)
O5−S3−O6	116.9(4)	N4−S3−C3	107.5(5)
O8−S4−O7	118.4(4)	N4−S4−C4	107.5(5)
S2−N3−S1	120.5(4)	S3−N4−S4	120.5(4)

[C10−N1···N2−C20 179.5(2)°], and **3** [C10−N1···N2−C20 178.3(13)°].

The S−N bond lengths [1.569(14) to 1.627(8) Å, Table 6] in the NMs_2 anions of complexes **1** to **5** are similar to those in other metal complexes with bis(methanesulfonyl)amide {e.g. $[Ag_4(NMs_2)_4(H_2O)]$,[15] S−N 1.603(6) to 1.632(6) Å; S−N−S 118.0(4) to 120.6(4)°}. The corresponding S−N−S angles [119.8(6) to 122.47(14)°, Table 6] support the assumption of sp^2 hybridisation of the amide nitrogen atom.

The silver atom of the anion $[Ag(NMs_2)_2]^-$ in **5** is linearly coordinated [N3−Ag−N4 171.1(3)°]. The Ag−N bond lengths of 2.123(7) (Ag−N3) and 2.122(7) Å (Ag−N4) are similar to those in $[Ag(NCCH_3)_4][Ag(NMs_2)_2]$ of 2.129(2) Å.[16] The NMs_2 ligands at Ag in **5** are rotated with respect to each other across the N−Ag−N unit [S2−N3···N4−S3 101.4(6), S2−N3···N4−S4 −78.3(6)°], which may be in order to accommodate the hydrogen bonds. The N−Au−N and N−Ag−N bond axes in **5** are perpendicular to each other [N1′−Au′···Ag−N3 86.3(8), N1′−Au′···Ag−N4 −92.8(8)°].

One oxygen atom of every sulfonyl group of NMs_2 anions lies in or near the S−N−S bond plane. The resulting "W" shape is characteristic of the bis(methanesulfonyl)amide anion.[17] The two other oxygen atoms and the methyl groups lie above or below this plane and show a staggered conformation [absolute O−S−N−S torsion angles: 30.5(11) to 43.2(2), 159.1(9) to 171.5(7)°; Table 6]. Different signs are associated with the two different chirally frozen conformers of bis(methanesulfonyl)amide.

Within all bis(amine)gold(I) complexes with disulfonylamide as the anion, more hydrogen bond acceptors (A) are present than classical hydrogen bond donor groups (D) such as NH. Every disulfonylamide anion has five acceptor groups: the four oxygen atoms and the amide nitrogen atom. The cations of the complexes **1**, **2**, and **3** have four amine hydrogen atoms, the cations of **4** and **5** each have two amine hydrogen atoms. Logically, therefore, not all of the hydrogen bond acceptors can be involved in classical hydrogen bonding, whereas every amine hydrogen atom in the complexes **1** to **5** *is* involved in hydrogen bonding. Associated H bond dimensions H···A, D···A and D−H···A are shown in Table 7.

Table 6. Geometrical parameters of the bis(methanesulfonyl)amide anions

Compound		S−N [Å]	S−N−S [°]	O′−S−N−S [°]	O“−S−N−S [°]
1	S1−N5	1.621(9)	119.8(6)	−163.0(6)	−34.8(8)
	S2−N5	1.573(11)			
	S3−N6	1.580(12)	120.3(6)	168.0(6)	37.7(9)
	S4−N6	1.591(11)			
2	S1−N3	1.596(3)	120.96(15)	−166.8(2)	−38.5(2)
	S2−N3	1.598(3)			
3	S1−N3	1.615(13)	120.6(8)	−159.1(9)	−30.5(11)
	S2−N3	1.569(14)			
4	S1−N3	1.588(2)	122.47(14)	−170.7(2)	−43.2(2)
	S2−N3	1.599(2)			
5	S1−N3	1.627(7)	120.5(4)	−171.3(6)	−43.1(7)
	S2−N3	1.623(8)			
	S3−N4	1.623(8)	120.5(4)	−168.1(5)	−41.1(7)
	S4−N4	1.627(8)			

Table 7. N−H···X hydrogen bonds and unitary graph sets (N_1)

Comp.	Bond	H···A [Å][a]	H···A [Å][b]	D···A [Å][c]	D−HA [°]	N_1
1	N1−H1A···N5 *(a)*	2.05	1.95	2.962(14)	171.1	D
	N1−H1B···O3^{i} *(b)*	2.27	2.18	3.163(13)	163.3	D
	N2−H2A···O5^{ii} *(c)*	2.09	2.00	2.995(13)	166.2	D
	N2−H2B···N6 *(d)*	2.18	2.09	3.064(14)	160.1	D
	N3−H3A···O6^{i} *(e)*	2.27	2.18	3.161(13)	161.9	D
	N3−H3B···O1^{iii} *(f)*	2.12	2.02	3.030(14)	169.6	D
	N4−H4A···O7^{iv} *(g)*	2.13	2.03	3.040(19)	169.6	D
	N4−H4B···O2 *(h)*	2.18	2.09	3.008(14)	149.5	D
2	N1−H1A···N3^{v} *(j)*	2.06	1.96	2.974(3)	171.9	D
	N1−H1B···O2^{vi} *(k)*	2.03	1.96	2.827(3)	143.5	D
	N2−H2A···O3 *(l)*	2.08	1.98	2.990(3)	171.3	D
	N2−H2B···O1^{ii} *(m)*	2.35	2.30	2.974(3)	124.9	D
3	N1−H1A···O3^{vii} *(n)*	2.02	1.94	2.867(18)	151.9	D
	N1−H1B···N3^{viii} *(o)*	2.21	2.11	3.085(19)	159.9	D
	N2−H2A···O4^{ix} *(p)*	2.06	1.97	2.978(17)	172.2	D
	N2−H2B···O1 *(q)*	2.06	1.98	2.894(17)	149.4	D
4	N1−H1···O4^{x}	1.98(3)	1.88	2.857(3)	162(3)	D
	N2−H2···N3	2.18(4)	1.96	2.894(3)	154(4)	D
5	N1−H1···O5	2.08	2.00	2.94(5)	154	$R_2^2(12)$
	N2−H2···O3	1.79	1.71	2.68(3)	158	$R_2^2(12)$
	N1′−H1′···O5	1.99	1.71	2.86(3)	148	D
	N2′−H2′···O7^{xi}	2.23	2.15	3.12(2)	158	D
6	N1−H1A···O2	2.28	2.19	3.125(10)	154.5	$R_2^2(10)$
	N1−H1B···O2^{xii}	2.57	2.77	3.013(10)	110.3	$R_2^2(10)$
	N1−H1B···O1^{xiii}	2.49	2.43	3.141(9)	128.0	$C_2^2(10)$
8	N10−H10A···O2^{xi}	2.16(7)	1.89	2.896(10)	169(6)	D *or*[d]
	N10−H10A···O2′^{xi}	2.28(7)	2.06	2.948(11)	148(6)	$C_2^2(10)$
	N10−H10B···O1^{ix}	2.01(8)	1.89	2.883(9)	163(7)	D *or*[d]
	N10−H10B···O1′^{ix}	2.08(8)	1.97	2.964(10)	166(7)	$C_2^2(10)$
9	N1−H1···Cl1	2.39	2.32	3.245(10)	152.0	D
	N2−H2···Cl1^{xiv}	2.30	2.22	3.171(10)	155.3	D

[a] Hydrogen bonds without a standard deviation were based on a riding model. − [b] Distances with normalised N−H 1.02 Å.[30]. − [c] Cf. van der Waals radii: N 1.55, O 1.53, H 1.20, Cl 1.75 Å.[10] − [d] The assignment depends on whether the two hydrogen bonds to the two positions of the disordered oxygen atoms are considered as different [D] or identical [$C_2^2(10)$] for the graph theoretical analysis. − Operators: i: −*x*, 1 − *y*, −*z*; ii: 1 − *x*, 1 − *y*, −*z*; iii: −*x*, 1 − *y*, 1 − *z*; iv: *x*, *y*, 1 + *z*; v: 2 − *x*, 1 − *y*, −*z*; vi: *x*, 1 + *y*, *z* − 1; vii: *x* − 1, *y*, *z*; viii: 1 − *x*, 1 − *y*, 1 − *z*; ix: 1 − *x*, −*y*, 1 − *z*; x: *x* + 1, *y*, *z*; xi: *x*, *y*, *z* − 1; xii: 1 − *x*, *y*, 1 − *z*; xiii: 0.5 + *x*, 0.5 − *y*, *z*; xiv: 1 − *x*, 3 − *y*, 1 − *z*.

In complexes **1**, **2**, and **3**, with four amine hydrogen atoms per formula unit, layers are formed, containing rings of hydrogen bonds. In complex **4** and **5** (major component), with two amine hydrogen atoms per formula moiety, the molecules are arranged in chains.

Graph theoretical analysis[18] of the hydrogen bond patterns led to the following conclusions: Each individual hydrogen bond forms a distinct pattern. Rings were formed by combining two (binary level, N_2) or four hydrogen bonds (quaternary level, N_4). In **1,** the combination of four different rings forms the layers parallel to (1 0 1), see Figure 6. The rings are described by the graph sets $R_4^4(12)$, $R_4^4(16)$, $R_4^4(20)$ [all N_2] and $R_4^4(18)$ [N_4]. In **2** and **3**, the layers are formed parallel to (1 1 0) from rings on binary level [N_2] (Figure 7 and Figure 8). In **2**, these rings are described by the graph sets $R_4^4(12)$ and $R_4^4(16)$ and in **3** by $R_4^4(8)$, $R_4^4(12)$, $R_4^4(16)$. The different ring pattern in the layers of the two complexes with benzylamine ligands, **2** and **3,** is presumably influenced by the iodine substitution of the benzylamine in **3**. Apart from the obvious steric effects, the iodine atom shows, as mentioned above, a short contact of 3.723(4) Å to an iodine atom of the next layer.

The chains in **4** (parallel to the *x* axis) and **5** (parallel to the *z* axis) are formed by combination of the two independent hydrogen bonds present in these complexes (Figure 9 and Figure 10a). The chain in **4** is described by the graph set $C_2^2(8)$, in **5** by $C_2^2(10)$. The minor disorder component of **5**, in which the ring at N2 is inverted, involves solely intra-

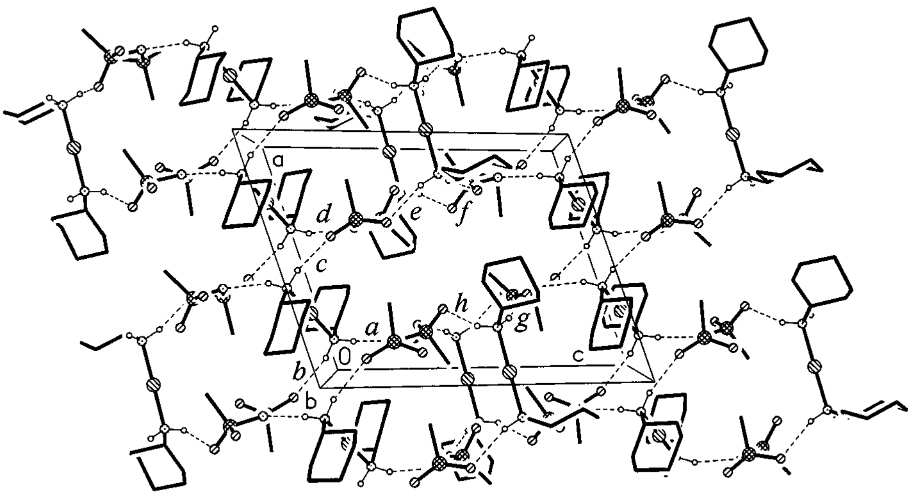

Figure 6. Bis(cyclohexylamine)gold(I) bis(methanesulfonyl)amide (**1**); layer structure; atom radii are arbitrary; dashed lines represent hydrogen bonds (Table 7); carbon-bonded hydrogen atoms are omitted for clarity

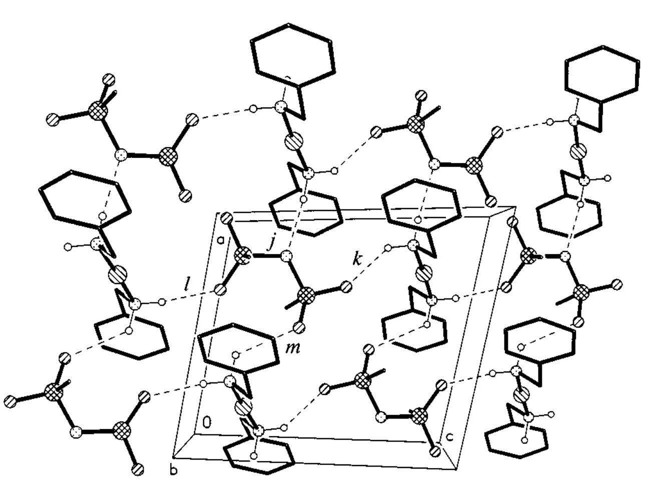

Figure 7. Bis(benzylamine)gold(I) bis(methanesulfonyl)amide (**2**); layer structure; atom radii are arbitrary; dashed lines represent hydrogen bonds (Table 7); carbon-bonded hydrogen atoms are omitted for clarity

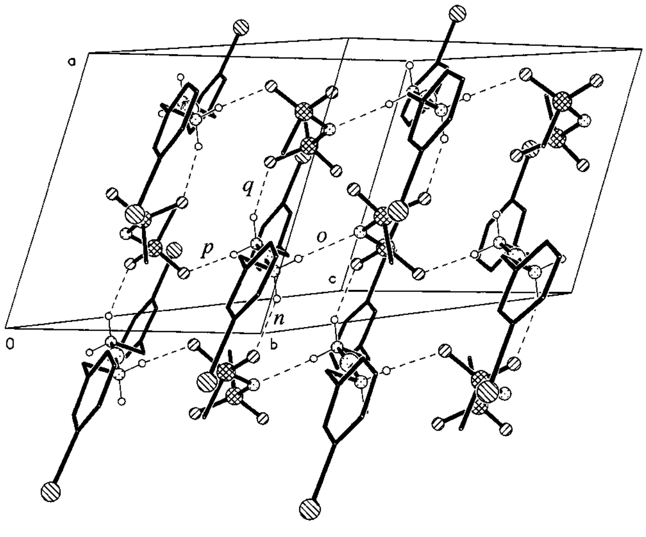

Figure 8. Bis(3-iodobenzylamine)gold(I) bis(methanesulfonyl)amide (**3**); layer structure; atom radii are arbitrary; dashed lines represent hydrogen bonds (Table 7); carbon-bonded hydrogen atoms are omitted for clarity; short I···I contacts are formed between layers and thus are not shown here

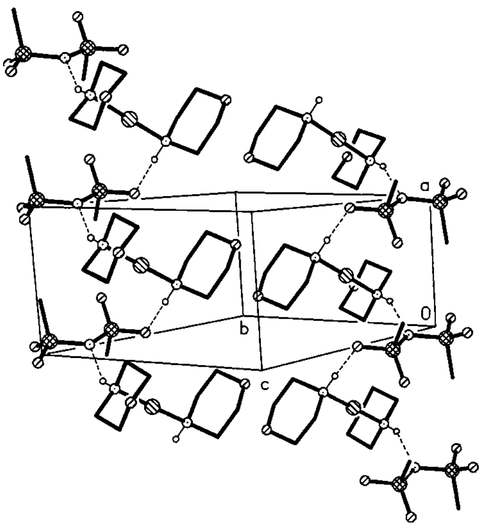

Figure 9. Bis(morpholine)gold(I) bis(methanesulfonyl)amide (**4**); chain structure; atom radii are arbitrary; dashed lines represent hydrogen bonds (Table 7); carbon-bonded hydrogen atoms are omitted for clarity

molecular hydrogen bonds; clearly the alternative direction of the N2−H2 vector presents a viable alternative hydrogen bonding system.

Complexes with Cyclohexylamine as Ligand and *o*-Benzenedisulfonylamide or Bis(*p*-halobenzenesulfonyl)amide as Anion

$[(CyNH_2)_2Au^+]$−*o*-benzodisulfonylamide (**6**, Figure 11) crystallised with half a formula unit in the asymmetric unit, together with dichloromethane (overall composition **6**/dichloromethane of 2:3). The gold and the amide nitrogen atom lie on a mirror plane; the gold atom is linearly coordinated [N1−Au−N1′ 177.1(4)°]. The Au−N bond length of 2.045(7) Å is similar to those in complex **1** [2.020(12) to 2.053(10) Å].

The *o*-benzenedisulfonylamide anion in **6** is conformationally more constrained than the other disulfonylamide anions, leading to a different arrangement of the acceptor groups. The S−N bond length of 1.554(5) Å is slightly shorter than in the NMs_2 anions in complexes **1** to **5** [1.569(14) to 1.638(9) Å] and also shorter than in the silver complexes of this anion {1.613(2) Å in $[Ag(H_2O)\{N(SO_2)_2C_6H_4\}]$,[19] 1.614(1) Å in $[Ag(NCCH_3)\{N(SO_2)_2C_6H_4\}]\}$.[16] The S−N−S angle in **6** [119.7(7)°] is larger than in the silver complexes [111.6(2) and 116.7(1)°]. Hence, the shorter S−N bond length in **6** could be attributed to a greater sp^2 hybridisation of the amide nitrogen atom. This is in good agreement with the assumption of a greater degree of backbonding caused by the additional charge in the non-coordinating anion of **6**. The *o*-benzenedisulfonylamide anion is also present solely as a counter-ion in the structures of $[Ca(H_2O)_7][N(SO_2)_2C_6H_4]_2$[20] and $[Me_2Sn(H_2O)_4][N(SO_2)_2C_6H_4]_2$,[21] and here the situation is not so clear-cut; in both cases the S−N bond lengths [1.574(3) to 1.587(3) Å] are longer than in **6**, and the S−N−S bond angles [115.7(2), 114.9(2)°] are smaller than in **6**.

The five- and the six-membered ring of the anion are coplanar; the interplanar angle is 2.4(7)°. The oxygen atoms lie above or below the S−N−S′ plane. This conformation has an influence on the packing in the crystal, resulting in a cation showing the more unusual eclipsed conformation (C11−N1···N1′−C11′ 0°, by symmetry). Nevertheless, layers are also formed in **6** by combination of hydrogen-bonded rings (Figure 12, Table 8). The two crystallographically independent oxygen atoms of the anion are involved in hydrogen bonding (see Table 7). The amide nitrogen atom shows a long contact to the gold atom [Au···N2 3.382(10) Å; cf. sum of the van-der-Waals radii 3.21 Å][10] and is not involved in hydrogen bonding; a shorter Au···N contact of 3.009(7) Å was observed in the related complex bis(tetrahydrothiophene)gold(I) *o*-benzenedisulfonylamide.[22] Overall there are three independent hydrogen bonds present in **6**: N1−H1A···O2, N1−H1B···O2^{xii} and N1−H1B···O1^{xiii} (for symmetry operators see Table 7). H1B is the donor atom of a three-centre hydrogen bond, and O2 the acceptor atom of a bifurcated hydrogen bond.

The layers in **6** are in fact double layers, with the cations on the outside and the anions inside (Figure 12). The rings within the layers in **6** can be described with the graph sets $R_2^2(10)$ (combination of the two hydrogen bonds involving O2 with themselves), $R_4^2(8)$ and $R_2^4(8)$ (combination of two different hydrogen bonds).

Unfortunately, no crystals could be obtained from complex **7** with bis(*p*-chlorobenzenesulfonyl)amide as anion. $[(CyNH_2)_2Au^+]$−bis(*p*-iodobenzenesulfonyl)amide (**8**, Figure 13) crystallised with half a formula unit in the asymmetric unit. The gold atom lies on an inversion centre and the bis(sulfonyl)amide group of the anion is disordered over an inversion centre.

The gold atom in **8** is linearly coordinated by symmetry, with an N−Au bond length of 2.034(5) Å similar to those in $[(cyNH_2)Au^+]Cl^-$ [1] and complexes **1** to **3** [2.029(12) to 2.053(10) Å]. The ligands at Au are antiperiplanar (C−NN−C 180° by symmetry). The S−N bond lengths [1.569(9), 1.571(9) Å] are similar to those in the bis(methanesulfonyl)amide anions of complexes **1** to **5** [1.569(14) to 1.638(9) Å]. The S−N−S angle of 127.3(7)° in **8** is slightly larger [cf. 119.8(6) to 122.57(14)° in **1** to **5**], but this should be interpreted with caution because of the disorder of the anion.

Changing the anion from bis(methanesulfonyl)amide to bis(*p*-halobenzensulfonyl)amide should result in a greater influence of the anion on the crystal packing. With the latter anions, more secondary interactions, apart from hydrogen bonding, should be observable, e.g. halogen−halogen or even π···π interactions. However, none of these was observed in the crystal structure of **8**.

The disorder of the anion in **8** makes the bond lengths of the hydrogen bonds less precise, but the overall pattern, a layer parallel to (1 1 0), formed by combination of hydrogen-bonded rings, is similar to that in complexes **1** to **3** (Figure 14, Table 9). The rings in **8** can be described with the graph sets $R_4^4(12)$ and $R_4^4(20)$. Because of the disorder, assignment of a distinct level (N_2 or N_4) is not meaningful.

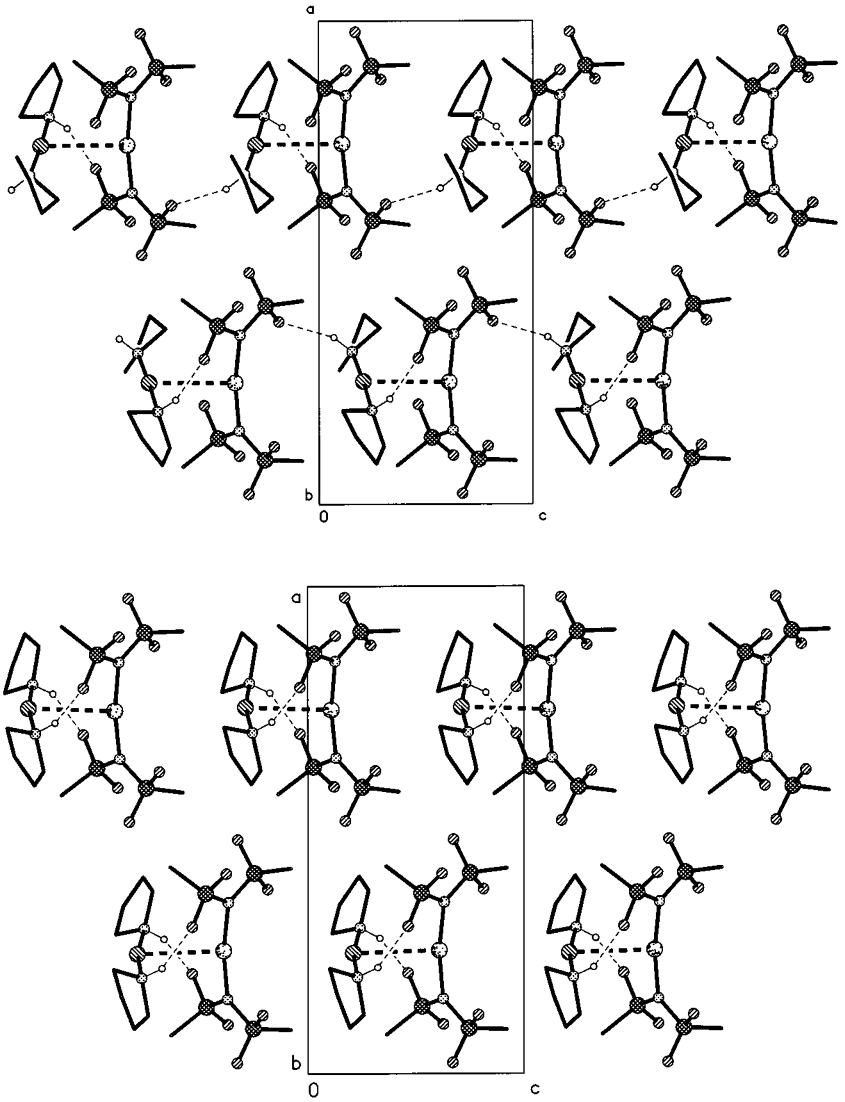

Figure 10. (a) Bis(pyrrolidine)gold(I) bis[bis(methanesulfonyl)amide]argentate(I) (**5**); projection of the chain structure involving the major disorder component; atom radii are arbitrary; dashed lines represent hydrogen bonds (Table 7); carbon-bonded hydrogen atoms are omitted for clarity; (b) an equivalent view of the minor disorder component showing the purely intramolecular hydrogen bonds

Non-Classical Hydrogen Bonding

Non-classical hydrogen bonds, i.e. hydrogen bonds with C−H as donor group, were previously the subject of controversial discussion, but are nowadays of accepted validity and the subject of great interest.[23] In complexes **1** to **4** the oxygen atoms not involved in classical hydrogen bonding showed hydrogen bonds of the type C−H···O, with uncorrected H···O in the range 2.35 to 2.73 Å (see Table 10). These hydrogen bonds can link neighbouring layers (complexes **1** to **3**) or chains (complex **4**); others connect molecules within the layer or chain. We do not discuss the disordered complexes, in which the alternative positions of the C−H functions render meaningful discussion impossible.

An Unexpected Complex with Piperidine as Ligand

Attempts to replace the chloride anion in [(piperidine)$_2$Au$^+$]Cl$^-$ [1] by NMs$_2$$^-$, as in the reactions described above, led not to the desired complex but to one with AgCl$_2$$^-$ as anion, again showing that silver can play an active (but undesired) role in such reactions. In the crystal structure of [(piperidine)$_2$Au$^+$][AgCl$_2$$^-$] (**9**, Figure 15), the anion is not a discrete moiety, but forms polymeric chains, containing Ag$_2$Cl$_2$ squares [Ag−Cl 2.598(4) to 2.631(3) Å, Cl−Ag−Cl 96.96(9) to 113.78(12)°, see Table 11]. A search of the Cambridge structural database[24] revealed only two other complexes with this [AgCl$_2$$^-$]$_n$ chain, namely [(CH$_3$)$_4$N$^+$][AgCl$_2$$^-$][25] and [(CH$_3$C(O)CH$_2$C(O)CH$_3$)$_3Si^+$][AgCl$_2$$^-$].[26]

The cations in **9** lie above and below the Ag$_2$Cl$_2$ squares and form hydrogen bonds to the chlorine atoms (Figure 16). The conformation of the cation in **9** is slightly different from that of the (piperidine)$_2$Au$^+$ cation in the chloride complex.[1] The gold atom in **9** is, as usual, linearly coordinated [N1−Au−N2 179.3(4)°]. The N−Au bond lengths are slightly longer than in complexes **1** to **3** and in the chloride complex [N1−Au 2.104(10), N2−Au 2.098(11) Å, cf.

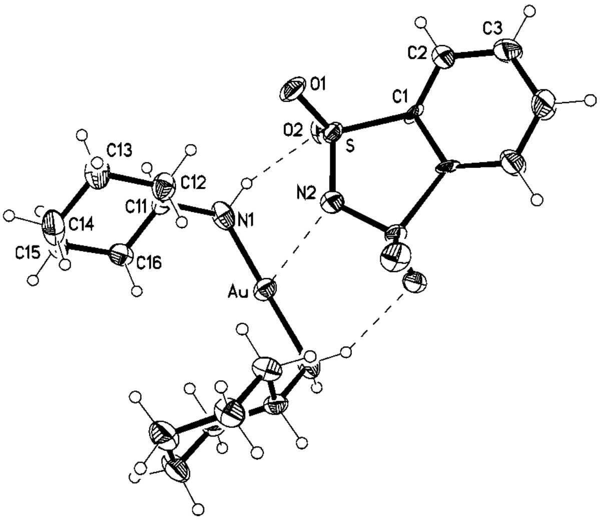

Figure 11. Bis(cyclohexylamine)gold(I) *o*-benzenedisulfonylamide dichloromethane solvate (2/3) (**6**); asymmetric unit with numbering scheme; solvent omitted; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds; one H atom at N1 is eclipsed

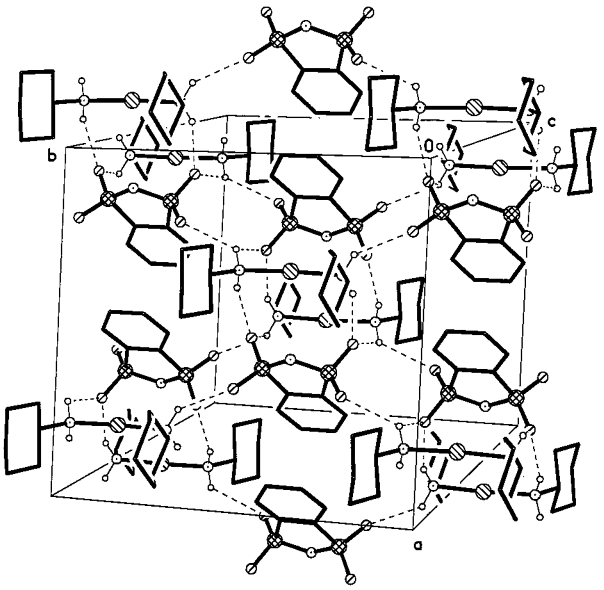

Figure 12. Bis(cyclohexylamine)gold(I) *o*-benzenedisulfonylamide dichloromethane solvate (2/3) (**6**); layer structure; atom radii are arbitrary; dashed lines represent hydrogen bonds (Table 7); carbon-bonded hydrogen atoms and dichloromethane molecules are omitted for clarity

Table 8. Selected bond lengths and angles for **6**

Au−N1	204.5(7)	S−O1	143.6(6)
S−O2	144.5(6)	S−N2	155.4(5)
S−C1	177.0(8)		
N1−Au−N1^{xxiii} [a]	177.1(4)	O1−S−O2	113.2(4)
N2−S−C1	99.0(4)	S−N2−S^{xxiii}	119.7(7)

[a] Symmetry transformations for equivalent atoms: xxiii: *x*, −*y* + 1, *z*.

N−Au 2.029(12) to 2.055(6) Å], but are similar to those in [(pyridine)$_2$Au$^+$][AuCl$_2^-$] [N−Au 2.08(3), 2.10(4) Å]. The main difference of the conformation of the cation, compared to the chloride complex, is the arrangement of the ligands at Au. In **9** it is a more eclipsed arrangement, in the chloride complex the arrangement is better described as staggered [C11−N1···N2−C21 1.1(12), C11−N1···N2−C25 127.1(11)°, cf. C11−N1···N2−C21 −68.6(7), C11−N1···N2−C25 164.0(6)° in the chloride]. This change in the conformation is probably due to the restricted conformation of the anion in **9**; in both complexes $R^2_4(12)$ rings are formed, but in **9** the chloride anions are fixed by the AgCl$_2$ chain.

Conclusion

Considerable similarities were found between all structures containing either N−H or NH$_2$ as hydrogen donor groups. The complexes with N−H as donor groups and NMs$_2$ as the anion (**4**, **5**) displayed a secondary structure consisting of chains. The gold complexes with pyrrolidine as ligand and chloride as anion had also been found to involve mainly chains as secondary pattern.[1,8]

Those complexes with piperidine as ligand and chloride as the anion behaved somewhat differently, showing either dimeric (L$_2$Au$^+$Cl$^-$)$_2$[1] or tetrameric (LAuCl)$_4$[5] structures. In both structures ring systems of hydrogen bonds could be recognised. The ring pattern of the dimeric structure is again found in **9**, but now with polymeric AgCl$_2^-$ as anion.

In all complexes with NH$_2$ as donor group (**1**, **2**, **3**, **6**, and **8**) layers containing ring patterns were formed; evidently the "extra" H donor facilitates the formation of two-dimensional hydrogen bond systems. These ring patterns are topologically closely related to those in [(cyNH$_2$)$_2$Au$^+$]Cl$^-$ [1] and even to those in the metal-free cyclohexylamine hemihydrochloride.[27]

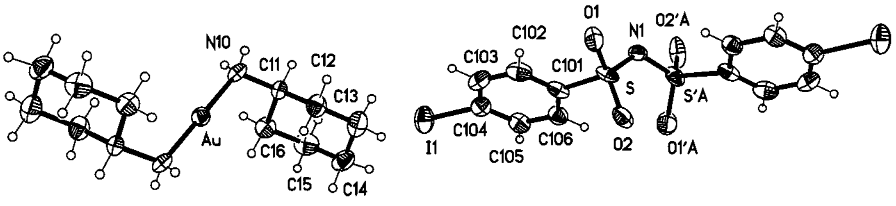

Figure 13. Bis(cyclohexylamine)gold(I) bis(*p*-iodobenzenesulfonyl)amide (**8**); asymmetric unit with numbering scheme; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds; only one position of the disordered anion is shown

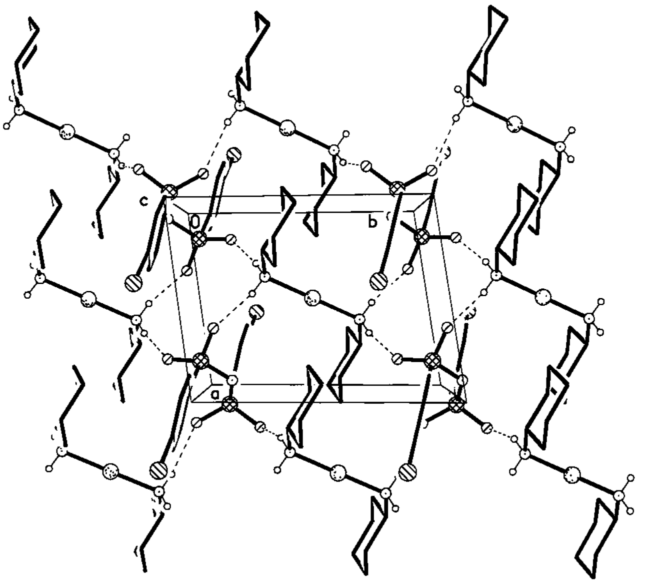

Figure 14. Bis(cyclohexylamine)gold(I) bis(*p*-iodobenzenesulfonyl)amide (**8**); layer structure; atom radii are arbitrary; dashed lines represent hydrogen bonds (Table 7); carbon-bonded hydrogen atoms are omitted for clarity; only one position of the disordered anion is shown

Table 9. Selected bond lengths and angles for **8**

Au−N10	203.4(5)	N1−S	156.9(9)
N1−S′$^{\text{xxiv}}$ [a]	157.1(9)	S−O2	143.9(9)
S−O1	144.1(10)	S−C101	177.4(11)
S′−O2′	145.6(10)	S′−O1′	146.0(9)
S′−C101	179.1(11)	C104−I1	210.2(6)
N10−Au−N10$^{\text{ii}}$	180.0(3)	C11−N10−Au	119.3(3)
S−N1−S′$^{\text{xxiv}}$	127.2(7)	O2−S−O1	117.2(8)
N1−S−C101	104.0(6)	O2′−S′−O1′	114.4(8)
N1$^{\text{xxiv}}$−S′−C101	111.5(6)		

Symmetry transformations for equivalent atoms: xxiv: $-x$, $-y$, $-z + 2$; ii: $-x + 1$, $-y + 1$, $-z$.

Table 10. Selected C−H···O hydrogen bonds, with H···O < 2.7 Å, not normalised

Compound	Bond	H···O [Å]	C···O [Å]	C−H···O [°]
1	C1−H1C···O8$^{\text{iv}}$ [a]	2.41	3.295(14)	150
	C33−H33···O4$^{\text{xv}}$	2.66	3.36(2)	128
2	C2−H2E···O4$^{\text{v}}$	2.50	3.209(4)	129
	C15−H15···O4$^{\text{xvi}}$	2.69	3.453(4)	138
3	C22−H22···O2	2.44	3.339(19)	158
4	C1−H1B···O3$^{\text{x}}$	2.41	3.288(3)	149
	C1−H1C···O1$^{\text{xvii}}$	2.64	3.453(2)	141
	C2−H2A···O2$^{\text{xviii}}$	2.63	3.489(4)	146
	C12−H12A···O4	2.69	3.312(3)	121

[a] Operators: xv: $-x$, $2 - y$, $1 - z$; xvi: x, $y + 1$, z; xvii: x, $y - 1$, z; xviii: $-x$, $-y$, $-z$. For operators up to xiv, see Table 7.

We thus conclude that the packing influence of the cation, as exercised through the NH functions of the ligands, is greater than that of the anion.

Experimental Section

General: NMR spectra were measured with a Bruker AC 200 spectrometer in $CDCl_3$ solution with TMS as the internal standard (if not otherwise stated). Frequencies: 200.1 MHz (^1H), 50.3 MHz (^{13}C). − Mass spectra were recorded with a Finnigan MAT 8430. − All complexes were prepared as follows: 0.5 mmol of $L_2Au^+Cl^-$

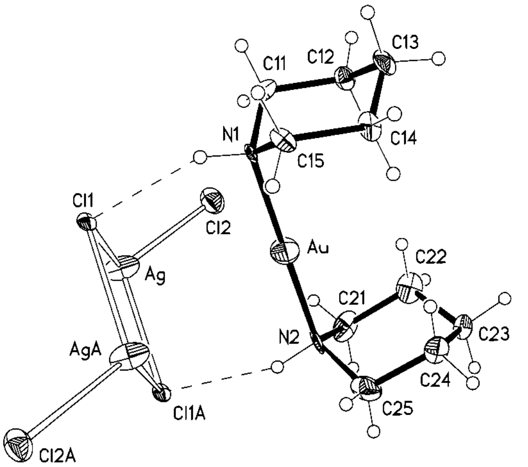

Figure 15. Bis(piperidine)gold(I) dichloroargentate(I), **9**, asymmetric unit with numbering scheme, extended by one $AgCl_2^-$ unit; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds

Table 11. Selected bond lengths and angles for **9**

Au−N2	209.8(11)	Au−N1	210.4(10)
Ag−Cl2	259.8(4)	Ag−Cl2$^{\text{xxv}}$	260.2(4)
Ag−Cl1$^{\text{xiv}}$	262.9(3)	Ag−Cl1	263.1(3)
Ag···Ag$^{\text{xxv}}$ [a]	313.1(2)		
N2−Au−N1	179.3(4)	C(11)−N(1)−C(15)	110.5(9)
C11−N1−Au	113.6(8)	C15−N1−Au	112.7(7)
C21−N2−C25	108.8(10)	C21−N2−Au	114.8(10)
C25−N2−Au	113.7(10)	Cl2−Ag−Cl2$^{\text{xxv}}$	105.95(10)
Cl2−Ag−Cl1$^{\text{xiv}}$	113.31(12)	Cl2$^{\text{xxv}}$−Ag−Cl1$^{\text{xiv}}$	113.73(12)
Cl2−Ag−Cl1	113.78(11)	Cl2$^{\text{xxv}}$−Ag−Cl1	113.28(12)
Cl1$^{\text{xiv}}$−Ag−Cl1	96.96(9)	Ag$^{\text{xiv}}$−Cl1−Ag	83.04(9)
Ag−Cl2−Ag$^{\text{xxv}}$	74.05(10)		

[a] Symmetry transformations for equivalent atoms: xxv: $-x + 2$, $-y + 3$, $-z + 1$; xiv: $-x + 1$, $-y + 3$, $-z + 1$.

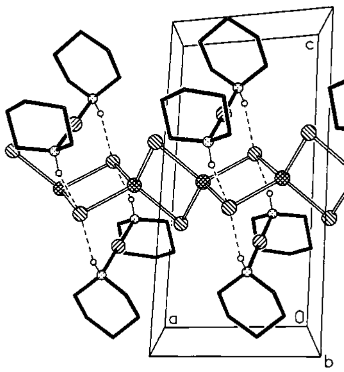

Figure 16. Bis(piperidine)gold(I) dichloroargentate (**9**); chain structure; atom radii are arbitrary; dashed lines represent hydrogen bonds (Table 7); carbon-bonded hydrogen atoms are omitted for clarity

(L = amine) was suspended in acetonitrile (10 mL). The silver salt of the disulfonylamide, kindly provided by Prof. A. Blaschette, TU Braunschweig, was added in 10% excess (0.55 mmol). The reaction mixture was stirred for 2 h at room temperature with exclusion of light. The precipitated AgCl was filtered off and washed with acetonitrile. The combined solutions were concentrated in vacuo and the white residue was recrystallised from CH_2Cl_2/petroleum ether (40:60) to obtain colourless crystals.

Bis(cyclohexylamine)gold(I) Bis(methanesulfonyl)amide (1): Yield 59%, dec. > 123 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.29, m, 10 H, CH_2 (ax.); 1.66, m, 2 H, 4-CH_2 (eq.); 1.80, m, 4 H, 3-, 3′-CH_2 (eq.); 2.08, m, 4 H, 2-, 2′-CH_2 (eq.); 3.00, m, 2 H, CH; 3.08, s, 6 H, CH_3; 4.5, br., NH_2. − MS (FAB pos.): *m/z* = 395 (100% $[K]^+$); MS (FAB neg.): *m/z* = 172 (100% $[A]^-$). − Conductivity: Λ_c = 79 $cm^2\ \Omega^{-1}\ mol^{-1}$. − $C_{14}H_{32}AuN_3O_4S_2$ (567.52): calcd. C 29.63, H 5.68, N 7.40, S 11.30; found C 27.26, H 5.44, N 7.09, S 12.74.

Bis(benzylamine)gold(I) Bis(methanesulfonyl)amide (2): Yield 76%, dec. > 109°C. − ^{1}H NMR ($CDCl_3$): δ = 2.87, s, 6 H, CH_3; 3.96, br., 4 H, CH_2; 4.68, br., 4 H, NH_2; 7.32, m, 20 H, Ph. − $C_{16}H_{24}AuN_3O_4S_2$ (583.48): calcd. C 32.94, H 4.15, N 7.20, S 10.99; found C 33.03, H 4.21, N 7.29, S 11.03.

Bis(3-iodobenzylamine)gold(I) Bis(methanesulfonyl)amide (3): Dec. > 108°C. − ^{1}H NMR ($CDCl_3$): δ = 2.95, s, 6 H, CH_3; 4.11, s, 4 H, CH_2; 7.48, m, 8 H, Ph. − $C_{16}H_{22}AuI_2N_3O_4S_2$ (835.28): calcd. C 23.00, H 2.66, N 5.03, S 7.68; found C 22.94, H 2.61, N 4.82, S 7.61.

Bis(morpholine)gold(I) Bis(methanesulfonyl)amide (4): Yield 41%, dec. > 50°C. − ^{1}H NMR ($CDCl_3$): δ = 3.05, s, 6 H, CH_3; 3.27, m, 8 H, α-CH_2; 3.86, m, 12 H, β-CH_2. − $C_{10}H_{24}AuN_3O_6S_2$ (543.42): calcd. C 22.10, H 4.45, N 7.73, S 11.80; found C 21.39, H 4.33, N 7.43, S 10.86.

Bis(pyrrolidine)gold(I) Bis[bis(methanesulfonyl)amido-*N*]argentate(I) (5): Yield 81%, dec. > 104 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.87, m, 8 H, β-CH_2; 2.99, m, 4 H, α-CH_2; 3.12, s, 12 H, CH_3; 3.54, m, 4 H, α-CH_2. − MS (FAB pos.): *m/z* = 72 (18% $[K\text{-}C_4H_8NAu]^+$); 339 (100% $[K]^+$); MS (FAB neg.): *m/z* (%) = 172 (100) $[A - C_2H_6AgO_4S_2]^-$; 450 (52) $[A - H]^-$; 452 (58) $[A + H]^-$. − $C_{12}H_{30}AgAuN_4O_8S_4$ (791.49): calcd. C 18.21, H 3.82, N 7.08 S, 16.21; found C 17.28, H 3.74, N 6.78, S 17.38.

Bis(cyclohexylamine)gold(I) *o*-Benzenedisulfonylamide (6): Yield 57%, dec. > 73°C. − ^{1}H NMR ($CDCl_3$): δ = 1.22, m, 10 H, CH_2 (ax.); 1.58, m, 2 H, 4-CH_2 (eq.); 1.73, m, 4 H, 3-, 3′-CH_2 (eq.); 2.02, m, 4 H, 2-, 2′-CH_2 (eq.); 3.08, m, 2 H, CH; 4.4, br., NH_2, 5.30, s, 2 H, CH_2Cl_2; 7.71, m, 2 H, β-Ph; 7.86, m, 2 H, α-Ph. − MS (FAB pos.): *m/z* (%) = 100 (100) $[K - C_6H_{12}NAu]^+$; 395 (71) $[K]^+$; MS (FAB neg.): *m/z* (%) = 218 (100) $[A]^-$. − $C_{18}H_{30}AuN_3O_4S_2$ (613.55) × 0.75 CH_2Cl_2: calcd. C 33.25, H 4.69, N 6.20, S 9.47; found C, 33.24 H, 4.65 N 6.25, S 10.90.

Bis(cyclohexylamine)gold(I) Bis(*p*-chlorobenzenesulfonyl)amide (7): Yield 57%, dec. > 88°C. ^{1}H NMR ([D$_6$]DMSO): δ = 1.17, m, 10 H, CH_2 (ax.); 1.58, m, 2 H, 4-CH_2 (eq.); 1.70, m, 4 H, 3-, 3′-CH_2 (eq.); 1.96, m, 4 H, 2-, 2′-CH_2 (eq.); 2.81, m, 2 H, CH; 5.4, br., NH_2; 7.42, m, 4 H, *m*-Ph; 7.63, m, 4 H, *o*-Ph. − MS (FAB pos.): *m/z* (%) = 100 (44) $[K - C_6H_{12}NAu]^+$; MS (FAB neg.): *m/z* (%) = 363 (100) $[A - H]^-$. − $C_{24}H_{34}AuCl_2N_3O_4S_2$ (760.56): calcd. C 37.90, H 4.51, N 5.52, Cl 9.32, S 8.43; found C 32.30, H 4.05, N 4.58, Cl 10.73, S 8.14.

Bis(cyclohexylamine)gold(I) Bis(*p*-iodobenzenesulfonyl)amide (8): Yield: very low (few crystals), dec. > 97°C. − $C_{24}H_{34}AuI_2N_3O_4S_2$ (943.49): calcd. C 30.55 H 3.63 N 4.45 S 6.80; found C 26.77 H 2.52 N 2.91 S 6.84.

Bis(piperidine)gold(I) Dichloroargentate(I) (9): Compound **9** was unexpectedly obtained following the general procedure using (piperidine)$_2$AuCl and $AgNMs_2$. − Yield: very low (few crystals), dec. > 87°C. − ^{1}H NMR ($CDCl_3$): δ = 1.76, br., 4 H, α-CH_2; 3.24, 6 H, β-, γ-CH_2. − $C_{10}H_{22}AgAuCl_2N_2$ (546.04): calcd. C 22.00, H 4.06, N 5.13; found C 22.58, H 4.24, N 5.11.

X-ray Structure Determinations: For crystal data, see Table 12 and Table 13. − *Data collection and reduction*: The crystals were mounted in inert oil on a glass fibre. Data were measured using Mo-K_α radiation (λ = 0.71073 Å) with a Siemens P4 diffractometer (**1**, **5**, **6**, **8**) or a Bruker Smart area detector (**2**, **3**, **4**, **9**), fitted with an LT-2 (P4) or LT-3 (Smart) low-temperature attachment. Semiempirical absorption corrections were based on ψ-scans (XEMP) or on multiple scans (SADABS). *Structure solution and refinement*: Structures were solved by direct (**3**, **5**, **8**, **9**) or Patterson (**1**, **2**, **4**, **6**) methods and subjected to full-matrix least-squares refinement on F^2 (program SHELXL-97).[28] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using rigid methyl groups or a riding model, except that those bonded to a nitrogen atom were refined freely in **4** and with restrained bond lengths in **8**. For several structures (see Table 12 and 13), particularly the disordered **5** and **8**, an extensive system of restraints to displacement parameters was employed to improve refinement stability of light atoms in the presence of gold. The Flack *x* parameter for the noncentrosymmetric structure **5** refined to −0.001(7).[29] The complete cation of **5** is disordered over two positions with occupation factors 0.37 (unprimed atoms) and 0.63 (primed atoms). The gold and silver atom positions correspond closely to space group *Aba*2, in which a doubly disordered model can also be refined, but too many reflections are observed that should be systematically absent. By lowering the symmetry, it was hoped to find an ordered model, but this proved impossible even in *P*1. It is unlikely that X-ray methods alone can resolve the space group ambiguity. The central $N(SO_2)_2$ moiety of the anion of **8** is disordered over two positions with occupation factors 0.5. Clearly the dimensions of both disordered structures should be interpreted with caution. The high *R* values and high residual electron densities of structures **3** and **9** may be attributed to poor crystal quality, and unsatisfactory absorption correction with SADABS, associated with extreme crystal forms (thin plate, needle).

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre

Table 13. Crystallographic data

Compound	**1**	**2**	**3**	**4**
Formula	$C_{14}H_{32}AuN_3O_4S_2$	$C_{16}H_{24}AuN_3O_4S_2$	$C_{16}H_{22}AuI_2N_3O_4S_2$	$C_{10}H_{24}AuN_3O_6S_2$
M_r	567.51	583.47	835.25	543.41
Crystal habit	Colourless plate	Colourless prism	Colourless plate	Colourless prism
Crystal size [mm]	0.24×0.20×0.04	0.19×0.07×0.05	0.20×0.08×0.01	0.29×0.12×0.09
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P-1$	$P-1$	$P-1$	$P-1$
Cell dimensions				
a [Å]	11.227(3)	9.6578(10)	8.978(14)	5.8123(6)
b [Å]	13.649(4)	10.5065(12)	9.084(15)	9.5145(10)
c [Å]	14.550(4)	11.3968(12)	15.556(18)	15.5486(16)
α [°]	105.62(2)	65.651(2)	74.49(7)	88.212(2)
β [°]	107.30(2)	73.539(2)	73.95(7)	82.518(2)
γ [°]	93.915(19)	74.447(2)	76.53(8)	89.669(2)
V [Å^3]	2023.2(10)	995.12(19)	1157(3)	852.12(15)
Z	4	2	2	2
D_x [Mg m^{-3}]	1.863	1.947	2.397	2.118
μ [mm^{-1}]	7.500	7.628	9.229	8.907
F(000)	1120	568	776	528
T [°C]	−100	−130	−130	−130
$2\theta_{max}$ [°]	50	61	57	61
Transmission	0.30−0.86	0.58−0.96	0.66−0.96	0.41−0.70
No. of reflections				
Measured	6958	12254	12367	10503
Independent	6919	6004	5839	5140
R_{Int}	0.023	0.049	0.099	0.038
Parameters	458	237	255	209
Restraints	550	16	142	0
$wR2(F^2$, all refl.)	0.135	0.055	0.196	0.049
$R1[F>2\sigma(F)]$	0.053	0.027	0.077	0.021
S	0.91	0.98	1.02	1.02
Max. Δ/σ	< 0.001	0.002	< 0.001	0.001
Max. $\Delta\rho$ [eÅ^{-3}]	1.41	1.89	4.36	1.21

Table 13. *(Continued)*

Compound	**5**	**6**	**8**	**9**
Formula	$C_{12}H_{30}AgAuN_4O_8S_4$	$C_{19.5}H_{33}AuCl_3N_3O_4S_2$	$C_{24}H_{34}AuI_2N_3O_4S_2$	$C_{10}H_{22}AgAuCl_2N_2$
M_r	457.33	740.93	943.43	546.03
Crystal habit	Colourless tablet	Colourless plate	Colourless plate	Colourless needle
Crystal size [mm]	0.60×0.30×0.10	0.24×0.14×0.04	0.40×0.40×0.03	0.30×0.03×0.02
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	$Pna2_1$	$C2/m$	$P-1$	$P-1$
Cell dimensions				
a [Å]	18.545(2)	12.572(2)	6.6744(6)	6.618(3)
b [Å]	15.970(2)	13.593(3)	8.6880(8)	9.394(4)
c [Å]	8.221(2)	15.988(3)	13.2291(12)	13.250(6)
α [°]	90	90	81.622(8)	104.488(10)
β [°]	90	98.301(16)	80.386(8)	90.033(10)
γ [°]	90	90	80.471(8)	110.571(8)
V [Å^3]	2434.9(7)	2703.7(10)	740.39(12)	743.1(5)
Z	4	4	1	2
D_x [Mg m^{-3}]	2.159	1.820	2.166	2.440
μ [mm^{-1}]	7.209	5.923	7.227	11.515
F(000)	1536	1460	448	512
T [°C]	−100	−74	−100	−130
$2\theta_{max}$ [°]	50	50	50	57
Transmission	0.37−0.95	0.58−0.89	0.24−0.86	0.74−0.96
No. of reflections				
Measured	7094	2521	5179	8050
Independent	4132	2406	2589	3753
R_{Int}	0.028	0.058	0.019	0.076
Parameters	373	156	204	145
Restraints	548	96	208	0
$wR2(F^2$, all refl.)	0.106	0.087	0.076	0.219
$R1[F>2\sigma(F)]$	0.043	0.047	0.029	0.074
S	1.07	0.83	0.98	1.05
Max. Δ/σ	0.001	0.001	< 0.001	< 0.001
Max. $\Delta\rho$ [eÅ^{-3}]	0.97	1.39	1.05	5.6

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[1] B. Ahrens, P. G. Jones, A. K. Fischer, *Eur. J. Inorg. Chem.* **1999**, 1103−1110.

[2] [2a] H. Schmidbaur, *Gold Bull.* **1990**, *23*, 11−21. − [2b]H. Schmidbaur, *Chem. Soc. Rev.* **1995**, 391−400.

[3] B. Ahrens, P. G. Jones, *Z. Naturforsch., Sect. B* **1999**, *54*, 1474−1477.

[4] P. G. Jones, B. Ahrens, *Z. Naturforsch., Sect. B* **1998**, *53*, 653−662.

[5] J. J. Guy, P. G. Jones, M. J. Mays, G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.* **1977**, 8−10.

[6] H. N. Adams, W. Hiller, J. Strähle, *Z. Anorg. Allg. Chem.* **1982**, 485, 81−91.

[7] P. G. Jones, M. Freytag, *Chem. Commun.* **2000**, 277−278.

[8] P. G. Jones, B. Ahrens, *Chem. Ber.* **1997**, *130*, 1813−1814.

[9] J. H. K. Yip, R. Feng, J. J. Vittal, *Inorg. Chem.* **1999**, *38*, 3586−3589.

[10] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441−451.

[11] S. S. Panthaneni, G. R. Desiraju, *J. Chem. Soc., Dalton Trans.* **1993**, 319−322.

[12] A. Burini, J. P. Fackler, Jr., R. Galassi, B. R. Pietroni, R. J. Stapler, *Chem. Commun.* **1998**, 95−96.

[13] M. Contel, J. Garrido, M. C. Gimeno, M. Laguna, *J. Chem. Soc., Dalton Trans.* **1998**, 1083−1084.

[14] R. E. Marsh, V. Schomaker, F. H. Herbstein, *Acta Crystallogr., Sect. B* **1998**, *54*, 921−924.

[15] M. Näveke, P. G. Jones, A. Blaschette, D. Schomburg, H. K. Cammenga, M. Epple, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1027−1036.

[16] A. Blaschette, P. G. Jones, T. Hamann, M. Näveke, D. Schomburg, H. K. Cammenga, M. Epple, I. Steppuhn, *Z. Anorg. Allg. Chem.* **1993**, *619*, 912−922.

[17] A long series of dimesylamide structures has been published by Prof. A. Blaschette and co-workers; for a recent example, see: K. Wijaya, O. Moers, A. Blaschette, P. G. Jones, *Z. Naturforsch., Sect. B* **1999**, *54*, 1441−1449.

[18] J. Bernstein, R. E. Davis, L. Shimoni, N.-L. Chang, *Angew. Chem.* **1995**, *107*, 1689−1708; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1545−1554.

[19] P. G. Jones, T. Hamann, A. Blaschette, H. K. Cammenga, M. Epple, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1441−1445.

[20] O. Moers, A. Blaschette, P. G. Jones, *Acta Crystallogr., Sect. C* **1997**, *53*, 845−848.

[21] I. Hippel, P. G. Jones, A. Blaschette, *J. Organotmet. Chem.* **1993**, *448*, 63−67.

[22] S. Friedrichs, P. G. Jones, *Acta Crystallogr., Sect. C*, in press.

[23] [23a] G. A. Jeffrey, *J. Mol. Struct.* **1999**, *485−486*, 293−298. − [23b] T. Steiner, *New J. Chem.* **1998**, 1099−1103. − [23c] G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond*, Oxford University Press, Oxford, **1999**.

[24] F. H. Allen, O. Kennard, *Chem. Des. Autom. News* **1993**, *8*, 31−37.

[25] G. Helgesson, M. Josefsson, S. Jagner, *Acta Crystallogr., Sect. C* **1988**, *44*, 1729−1731.

[26] D. Hogerle, V. Link, U. Thewalt, *Z. Naturforsch., Sect. B* **1993**, *48,* 691−693.

[27] P. G. Jones, B. Ahrens, *Eur. J. Org. Chem.* **1998**, 1687−1688.

[28] G. M. Sheldrick, *SHELXL-97, Program for crystal structure refinement*, University of Göttingen, **1997**.

[29] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876−881.

[30] T. Steiner, *Acta Crystallogr. Sect. B* **1998**, *54*, 456−463.

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