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Crystal Engineering of Gold(I) Thiolate Based Compounds via Cooperative Auophilic and Hydrogen-Bonding Interactions

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Treatment of sodium 2-amino-5-mercapto-1,3,4-thiadiazolate (NaSSNH₂) with monophosphines (triphenylphosphine and trimethylphosphine) and diphosphines [bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), and *trans*-1,2-bis(diphenylphosphino)ethene (dppee)] affords a series of gold(I) thiolates with the respective stabilizing phosphine ligands [Au(PR₃)(SSNH₂)] (R = Ph **1** and Me **2**) and [PP(Au(SSNH₂))₂] (PP = dppm **3**, dppe **4** and dppee **5**). The crystal structures of the complexes have been determined by single-crystal X-ray diffraction studies, confirming hydrogen-bonded frameworks in the crystal lattices based on the functions of the SSNH₂ ligands. The triphenylphosphine complex **1** (with crystal diethyl ether, 1·0.5Et₂O) forms a dimer solely via bifurcated hydrogen bonds. In the presence of crystal methanol (1·MeOH) it gives rise to a one-dimensional ladder structure via intermolecular hydrogen-bonding interactions with molecules of crystal methanol as bridges. With a reduced steric effect of the auxiliary ligand, the trimethylphosphine analogue **2** forms a novel two-dimensional sheet structure via cooperative intermolecular auophilic [Au(I)···Au(I) 3.0581(6) Å] and hydrogen-bonding interactions. The bis(diphenylphosphino)methane complex **3**·2DMF features dinuclear units associated into a meandering chain structure via intramolecular auophilic and intermolecular hydrogen bonding interactions. Further aggregation is terminated by hydrogen-bonding to crystal solvent molecules. **4**·0.5MeOH forms a complicated network via cooperative intermolecular auophilic [Au(I)···Au(I) 3.0675(7) Å] and hydrogen-bonding interactions. With DMF as a chain-terminating solvent molecule, the *trans*-1,2-bis(diphenylphosphino)ethylene complex **5**·4DMF can only form isolated dinuclear units hydrogen bonded to these solvent molecules. Complexes **2** and **4** are rare examples of two-dimensional frameworks built on cooperative intermolecular auophilic and hydrogen-bonding interactions in the solid state.

Introduction

The propensity for closed-shell d¹⁰ gold(I) centers to form weakly bonding interactions leading to a large variety of dimers, oligomers, and polymers (molecular solids) is an interesting phenomenon in gold chemistry and has intrigued both theoretical and experimental chemists.^{1–7} These interactions are typically identified by means of X-ray diffraction studies in all cases

where Au(I)···Au(I) distances are less than the sum of the van der Waals radii. The energies involved have been measured⁸ or estimated⁹ and were found to be in the same order as the energies of standard hydrogen bonds (ca. 6–12 kcal/Au(I)···Au(I) at Au(I)···Au(I) distances of 2.8–3.2 Å). Auophilic Au(I)···Au(I) interactions have also been suggested to be responsible for the excited state properties of some luminescent gold(I) compounds.¹⁰

For over 60 years, gold(I) thiolates have been important in the formulation of gold drugs,¹¹ and the binding of gold(I) to thiolate functions in proteins is expected to play a key role in the molecular pharmacology of gold. Pastes known as “liquid

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Table 1. Crystallographic Data for Compounds **1**•MeOH, **1**•0.5Et₂O, and **2**

	1 •MeOH	1 •0.5Et ₂ O	2
empirical formula	C ₂₁ H ₂₁ AuN ₃ OPS ₂	C ₂₂ H ₂₂ AuN ₃ O _{0.5} PS ₂	C ₅ H ₁₁ AuN ₃ PS ₂
fw	623.46	628.48	405.22
cryst syst	monoclinic	monoclinic	monoclinic
space group (No.)	<i>P</i> 2 ₁ / <i>n</i> (14)	<i>P</i> 2 ₁ / <i>c</i> (13)	<i>C</i> 2/ <i>c</i> (15)
<i>a</i> (Å)	6.299(1)	18.012(2)	13.047(1)
<i>b</i> (Å)	14.073(1)	9.750(1)	15.074(1)
<i>c</i> (Å)	24.659(3)	26.806(3)	12.576(1)
α (deg)			
β (deg)	95.90(1)	99.94(1)	109.96(1)
γ (deg)			
<i>V</i> (Å ³)	2174.3(5)	4636.9(9)	2324.8(3)
ρ _{calc} (g cm ⁻³)	1.905	1.801	2.316
<i>Z</i>	4	8	8
<i>F</i> (000) (e)	1208	2440	1504
μ(Mo Kα) (cm ⁻¹)	70.49	66.11	131.10
<i>T</i> (K)	148(2)	164(2)	190(2)
measd rflns	5111	9426	4237
unique rflns	4683 (<i>R</i> _{int} = 0.0133)	9068 (<i>R</i> _{int} = 0.0362)	2703 (<i>R</i> _{int} = 0.0779)
obsd rflns (<i>F</i> _o ≥ 4σ(<i>F</i> _o))	4384	7987	2659
refined params	274	532	110
<i>R</i> ^a	0.0204	0.0333	0.0465
<i>R</i> _w ^b	0.0485	0.0742	0.1193
ρ _{fin} (max/min) (e Å ⁻³)	0.738/−1.283	1.17/−1.006	2.516/−2.297
abs corr	DIFABS	DIFABS	ψ-scans

^a *R* = Σ||*F*_o| − |*F*_c||/Σ|*F*_o|. ^b *wR*₂ = {[Σ*w*(*F*_o² − *F*_c²)/Σ[*w*(*F*_o²)²]}^{1/2}; *w* = 1/[σ²(*F*_o²) + (*ap*)² + *bp*]; *p* = (*F*_o² + 2*F*_c²)/3; *a* = 0.0221 (**1**•MeOH), 0.0460 (**1**•1/2Et₂O), 0.0545 (**2**); *b* = 4.29 (**1**•MeOH), 3.44 (**1**•1/2Et₂O), 28.55 (**2**).

Table 2. Crystallographic Data for Compounds **3**•2DMF, **4**•0.5MeOH, and **5**•4DMF

	3 •2DMF	4 •0.5MeOH	5 •4DMF
empirical formula	C ₃₅ H ₄₀ Au ₂ N ₈ O ₂ P ₂ S ₄	C _{30.5} H ₃₀ Au ₂ N ₆ O _{0.5} P ₂ S ₂	C ₄₂ H ₅₄ Au ₂ N ₁₀ O ₄ P ₂ S ₄
fw	1188.86	1072.72	1347.06
cryst syst	triclinic	monoclinic	triclinic
space group (No.)	<i>P</i> 1̄ (2)	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1̄ (2)
<i>a</i> (Å)	10.244(1)	11.749(3)	8.410(1)
<i>b</i> (Å)	13.350(2)	19.959(6)	8.772(1)
<i>c</i> (Å)	18.411(3)	15.387(3)	18.797(2)
α (deg)	99.54(1)	90	98.30(1)
β (deg)	101.73(1)	106.38(1)	93.40(1)
γ (deg)	110.97(1)	90	112.54(1)
<i>V</i> (Å ³)	2222.3(5)	3462(2)	1257.3(2)
ρ _{calc} (g cm ⁻³)	1.777	2.058	1.779
<i>Z</i>	2	4	1
<i>F</i> (000) (e)	1148	2044	660
μ(Mo Kα) (cm ⁻¹)	68.94	88.34	61.07
<i>T</i> (K)	177(2)	159(2)	177(2)
measd rflns	4440	7512	5464
unique rflns	3474 (<i>R</i> _{int} = 0.0551)	7512	5462
obsd rflns (<i>F</i> _o ≥ 4σ(<i>F</i> _o))	3453	6937	5441
refined params	265	405	324
<i>R</i> ^a	0.0381	0.0308	0.0210
<i>R</i> _w ^b	0.0958	0.0725	0.0520
ρ _{fin} (max/min) (e Å ⁻³)	1.252/−0.663	1.833/−2.203	0.989/−1.103
abs corr	ψ-scans	DIFABS	ψ-scans

^a *R* = Σ||*F*_o| − |*F*_c||/Σ|*F*_o|. ^b *wR*₂ = {[Σ*w*(*F*_o² − *F*_c²)/Σ[*w*(*F*_o²)²]}^{1/2}; *w* = 1/[σ²(*F*_o²) + (*ap*)² + *bp*]; *p* = (*F*_o² + 2*F*_c²)/3; *a* = 0.0490 (**3**•2DMF), 0.0399 (**4**•0.5MeOH), 0.0315 (**5**•4DMF); *b* = 11.69 (**3**•2DMF), 8.89 (**4**•0.5MeOH), 1.05 (**5**•4DMF).

gold” used for gold-plating of glass and ceramics¹² are also mixtures of gold(I) thiolates, often derived from natural products. Furthermore, advanced gold thin film technology¹³ is relying mainly on the special properties of gold(I)–sulfur systems.

In a new approach to the obviously very broad area of applications of gold(I) thiolates, we have recently tried to take advantage of phenomena based on cooperative aurophilic and hydrogen-bonding interactions.¹⁴ Significantly, the metal...metal interactions are expected to strongly influence not only the

crystal properties but also the pharmacological effects. Following the theoretical predictions of Pykkö^{1c} and Balch^{3c} and their co-workers, it is anticipated that aurophilic interactions between the Au(I)–X units would be strengthened in the order X = Cl < Br < I < thiolate. As a first contribution to this topic,^{14a} this laboratory has recently reported two novel supramolecular structures of (isocyanide)gold(I) thiosalicylates [2-[(RNC)AuS]–C₆H₄COOH, R = *tert*-butyl and mesityl]. The crystal structures of both compounds are governed by aurophilic (R = *tert*-butyl, Au(I)···Au(I) 3.157(2) Å; R = mesityl, Au(I)···Au(I) 3.3186–

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Table 3. Hydrogen Bonds in the Structures of Compounds **1**·MeOH, **1**·0.5Et₂O, **2**, **3**·2DMF, **4**·0.5MeOH, and **5**·4DMF

compd	D—H···A ^a (Å)	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (deg)
1 ·MeOH	O—H···N(1) ^(a)	0.955	1.863	2.816	175.6
	N(3)—H(1)···N(2) ^(b)	0.900	2.307	3.169	160.2
	N(3)—H(2)···O ^(c)	0.637	2.235	2.855	164.7
1 ·0.5Et ₂ O	N(3)—H(32)···N(2a) ^(d)	0.917	2.152	3.053	167.4
	N(6)—H(61)···N(5a) ^(e)	0.950	2.156	2.943	139.5
2	N(3)—H(1)···S(1) ^(f)	1.115	2.687	3.505	129.69
	N(3)—H(1)···N(1) ^(f)	1.115	2.078	3.161	163.01
	N(3)—H(2)···N(2) ^(g)	0.855	2.127	2.950	161.23
3 ·2DMF	N(23')—H(23c)···O(2') ^(a)	0.900	2.083	2.878	146.7
	N(13')—H(13c)···O(1) ^(a)	0.900	2.237	2.958	136.8
	N(13)—H(13b)···N(12') ^(a)	0.900	2.037	2.921	167.3
4 ·0.5MeOH	N(13)—H(1)···N(21) ^(h)	0.843	2.178	3.005	166.9
	N(13)—H(2)···N(22) ⁽ⁱ⁾	0.885	2.310	3.136	155.3
	N(23)—H(3)···N(11) ^(j)	1.063	1.929	2.957	161.6
5 ·4DMF	N(3)—H(31)···O(1) ^(k)	0.715	2.189	2.897	170.2
	N(3)—H(32)···O(2) ^(k)	0.815	2.014	2.815	166.8

^a Symmetry positions of atoms A: (a) $-x, -y, -z$; (b) $x + 2, y, z$; (c) $x, y - 2, z$; (d) $-x + 1, -y, -z + 1$; (e) $-x + 1, -y + 1$; (f) $x, -y, z + 0.5$; (g) $-x + 2, y, -z + 0.5$; (h) $0.5 - x, 0.5 + y, 1.5 - z$; (i) $-0.5 + x, 0.5 - y, 0.5 + z$; (j) $0.5 + x, 0.5 - y, -0.5 + z$; (k) $-x, -y + 1, -z + 1$.

(5) Å) and hydrogen-bonding interactions via the carboxylic acid groups. Au(I)···Au(I) associated dimers are further aggregated to give one-dimensional polymers. This result has prompted the present study with the novel combination of phosphine and amino/thiolate ligands. In extending these earlier studies, 2-amino-5-mercapto-1,3,4-thiadiazol (HSSNH₂) was chosen as a building block for the construction of hydrogen-bonded frameworks. This ligand has both soft (S) and hard (N) donor atoms and potential hydrogen-bonding functions and should induce a strengthening of aurophilic interactions of the Au(I)—X units in the solid state.

We now report on the synthesis and structural studies of a series of corresponding gold(I) thiolates with monophosphines and diphosphines as systematically tuned auxiliary phosphine ligands: The triphenylphosphine complex forms a hydrogen-bonded dimer, but **1**·MeOH gives rise to a one-dimensional ladder structure via intermolecular hydrogen-bonding interactions, whereas the trimethylphosphine complex **2** forms a novel two-dimensional sheet structure via cooperative intermolecular aurophilic and hydrogen-bonding interactions in the solid state. The bis(diphenylphosphino)methane complex **3**·2DMF features dinuclear units associated into a one-dimensional meandering chain structure via intramolecular aurophilic and intermolecular hydrogen-bonding interactions. The bis(diphenylphosphino)ethane complex **4**·0.5MeOH aggregates into chains via Au···Au bonding and is also further associated via hydrogen bonding. With DMF as a chain-terminating solvent molecule, the *trans*-1,2-bis(diphenylphosphino)ethylene complex **5**·4DMF only forms isolated dinuclear units hydrogen bonded to these solvent molecules.

Experimental Section

General Information. The experiments were carried out routinely under an atmosphere of dry and pure nitrogen. Glassware and solvents were dried and filled/saturated with nitrogen. NMR: JEOL GX 400 spectrometer; deuterated solvents with the usual standards. MS: Varian MAT 311A instrument (FAB, *p*-nitrobenzyl alcohol). IR: Perkin-Elmer (type 1600 series FTIR) using KBr pellets. HSSNH₂ is commercially available. [AuCl(PR₃)] (R = Ph and Me) and [PP(AuCl)₂] [PP = dppe, bis(diphenylphosphino)methane; dppe, *trans*-1,2-bis(diphenylphosphino)ethylene] were prepared following the literature procedures.¹⁵

[Au(PPh₃)(SSNH₂)]·MeOH, **1·MeOH.** The reaction of NaSSNH₂ [155 mg, 1 mmol, obtained from HSSNH₂ (133 mg, 1 mmol) and NaOMe (57 mg, 1.05 mmol) in MeOH (25 mL)] with [AuCl(PPh₃)] (495 mg, 1 mmol) in CH₂Cl₂/MeOH (1:1, 50 mL) at room temperature

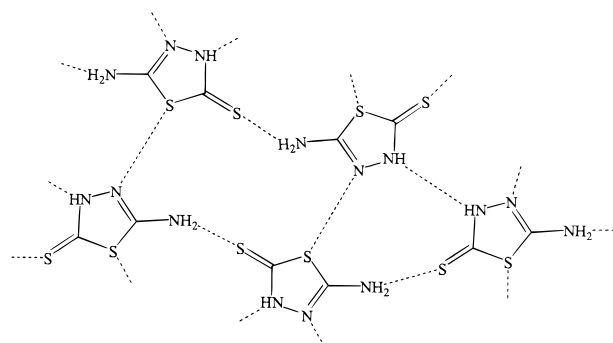


Figure 1. Molecular packing diagram of HSSNH₂ showing S···S, S···N, N···N, and weak N—H···S hydrogen-bonding contacts.¹⁶

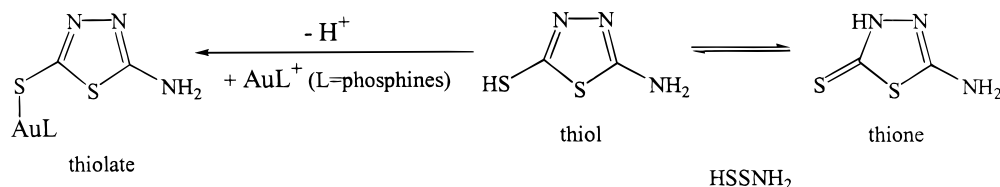
for 4 h gave a colorless solution. The solution was concentrated in a vacuum to give a crystalline solid, which was recrystallized by slow evaporation of a CH₂Cl₂/MeOH solution. Colorless single crystals of [Au(PPh₃)(SSNH₂)]·MeOH were obtained in 75% yield. MS (FAB): [Au(PPh₃)(SSNH₂)], *m/e* = 591, 74%. {¹H} ³¹P NMR (CDCl₃, 25 °C): δ 37.02 (s). ¹H NMR (CDCl₃, 25 °C): δ 7.44–7.57 (m, 17H, NH₂ + PPh₃). IR (KBr) ν_{NH₂} 3299 and 3123, ν_{C=N} 1624 and 1514 cm⁻¹. Anal. Calcd for AuC₂₀H₁₇N₃PS₂·CH₃OH: C, 40.42; H, 3.37; N, 6.74; Au, 31.60. Found: C, 40.59; H, 3.05; N, 6.51; Au, 31.97. Crystals of Au-(PPh₃)(SSNH₂)·0.5Et₂O (**1**·0.5Et₂O) were obtained from solutions in dichloromethane/diethyl ether.

[Au(PMe₃)(SSNH₂)]₂, **2,** was prepared in 85% yield in a similar way except that [AuCl(PMe₃)] was used instead of [AuCl(PPh₃)]. Single crystals of **2** grown from CH₂Cl₂/MeOH contain no crystal solvent. MS (FAB): [Au(PMe₃)(SSNH₂)], *m/e* = 405, 46%. {¹H} ³¹P NMR (DMSO-*d*₆, 25 °C): δ -1.54 (s). ¹H NMR (DMSO-*d*₆, 25 °C): δ 1.62 (d, *J*_{PH} = 11.52 Hz, 9H, PMe₃), 6.68 (s, 2H, NH₂). IR (KBr) ν_{NH₂} 3258 and 3095, ν_{C=N} 1614 and 1506 cm⁻¹. Anal. Calcd for AuC₅H₁₁N₃PS₂: C, 14.81; H, 2.71; N, 10.36; Au, 48.62. Found: C, 14.69; H, 2.95; N, 10.21; Au, 48.18.

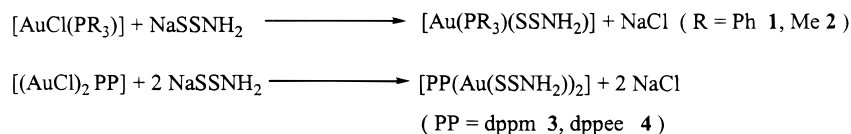
[dppm(Au(SSNH₂))]₂·2DMF, **3·2DMF.** The reaction of NaSSNH₂ (155 mg, 1 mmol) with [dppm(AuCl)₂] (425 mg, 0.5 mmol) in CH₂Cl₂/MeOH (1:1, 50 mL) at room temperature for 4 h gave a pale-yellow precipitate. The precipitate was filtered off in a vacuum and recrystallized by slow evaporation of a Et₂O/DMF solution. Pale-yellow single crystals of [dppm(Au(SSNH₂))]₂·2DMF were obtained in 72% yield. Single crystals of **3** grown from Et₂O/DMF contain 2 equiv of crystal DMF. MS (FAB): [dppm(Au(SSNH₂))Au], *m/e* = 910, 24%. {¹H} ³¹P NMR (DMSO-*d*₆, 25 °C): δ 32.01 (s). ¹H NMR (DMSO-*d*₆,

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Scheme 1



Scheme 2



25 °C): δ 4.68 (t, $^2J_{\text{PCH}} = 12.02$ Hz, 2H, CH₂), 6.71 (s, 4H, NH₂), 7.38–7.96 (m, 20H, PPh₂). IR (KBr) ν_{NH_2} 3279 and 3092, $\nu_{\text{C=O}}$ 1665, $\nu_{\text{C=N}}$ 1518 cm⁻¹. Anal. Calcd for Au₂C₂₉H₂₆N₆P₂S₄·2C₃H₇NO: C, 35.35; H, 3.37; N, 9.43; Au, 33.16. Found: C, 35.02; H, 3.48; N, 9.18; Au, 33.29.

[dppee(Au(SSNH₂))₂]**4**·0.5MeOH was prepared in 77% yield in a similar way except that [dppee(AuCl)₂] was used instead of [dpmm-(AuCl)₂]. Single crystals were grown from MeOH/DMF. MS (FAB): [dppee(Au(SSNH₂))Au], $m/e = 924$, 18%. $\{^1\text{H}\}$ ^{31}P NMR (DMSO-*d*₆, 25 °C): δ 38.72 (s). ^1H NMR (DMSO-*d*₆, 25 °C): δ 2.65 (s, 4H, CH₂CH₂), 7.44–7.89 (m, 24H, NH₂ + Ph₂P). IR (KBr) ν_{NH_2} 3276 and 3148, $\nu_{\text{C=N}}$ 1618 and 1506 cm⁻¹. Anal. Calcd for Au₂C₃₀H₂₈N₆P₂S₄: C, 34.09; H, 2.56; N, 7.95; Au, 37.31. Found: C, 34.21; H, 2.35; N, 7.61; Au, 37.58.

[dppee(Au(SSNH₂))₂]**4**·DMF, **5**·4DMF was prepared in 82% yield in a similar way except that [dppee(AuCl)₂] was used instead of [dpmm-(AuCl)₂]. Single crystals of **5** grown from Et₂O/DMF contain 4 equiv of crystal DMF. MS (FAB): [dppee(Au(SSNH₂))₂], $m/e = 922$, 33%. $\{^1\text{H}\}$ ^{31}P NMR (DMSO-*d*₆, 25 °C): δ 30.25 (s). ^1H NMR (DMSO-*d*₆, 25 °C): δ 6.95 (s, 2H, =CH), 7.76–8.11 (m, 24H, NH₂ + PPh₂). IR (KBr) ν_{NH_2} 3281 and 3158, $\nu_{\text{C=O}}$ 1665, $\nu_{\text{C=N}}$ 1620 and 1511 cm⁻¹. Anal. Calcd for Au₂C₃₀H₂₆N₆P₂S₄·4C₃H₇NO: C, 37.41; H, 4.01; N, 10.39; Au, 29.25. Found: C, 37.69; H, 4.35; N, 10.51; Au, 28.97.

Crystal Structure Determinations. Suitable single crystals of **1**·MeOH, **1**·0.5Et₂O, **2**, **3**·2DMF, **4**·0.5MeOH, and **5**·4DMF were sealed under argon into glass capillaries and examined directly on the diffractometer. Data were corrected for Lorentz, polarization, and absorption effects. Structures were solved by direct methods and refined by full-matrix least-squares calculations on F^2 . The thermal motion was treated anisotropically for all non-hydrogen atoms, except for those of one DMF molecule in the lattice of **3**·2DMF, the solvent methanol in the lattice of **4**, and the phenyl C atoms of **3**, which were included as rigid groups in the refinement. One of the two independent DMF molecules in the lattice of **5**·4DMF was disordered and was refined in split positions (SOFs: 70/30). Due to the size of the U values of the solvent MeOH in the lattice of **4**, the SOFs were reduced to 0.5, and the H atoms were neglected. All phenyl and methyl/methylene hydrogen atoms were calculated and allowed to ride on their corresponding C atoms, whereas all N–H atoms were located and included with isotropic contributions. The MeO–H atoms in the lattice of **1** were also located. Details of crystal parameters, data collection, and structure refinement are summarized in Tables 1 and 2. Hydrogen bonds in the structures of compounds **1**·MeOH, **1**·0.5Et₂O, **2**, **3**·2DMF, **4**·0.5MeOH and **5**·4DMF are given in Table 3.

Results and Discussion

The crystal structure of HSSNH₂ was reported by Downie and co-workers¹⁶ in 1972. It features a supramolecular aggregate via S···S, S···N, N···N, and weak N–H···S hydrogen-bonding contacts (Figure 1). The bond distances indicate that this compound exists in the thione rather than in the thiol form (Scheme 1). It is expected to retain its hydrogen-bonding functions after coordination to metal centers, although it may

be converted into its thiol isomer or into a thiolate depending on the affinity of the metal. There is no precedent study in the literature about the coordination chemistry of this ligand.

In this work, five related gold(I) thiolates with stabilizing phosphine ligands have been readily prepared by reaction of NaSSNH₂ with 1 equiv of [AuCl(PR₃)] or 1/2 equiv of [PP-(AuCl)₂], respectively, in a CH₂Cl₂/MeOH solution (Scheme 2). Colorless crystalline solids were obtained for **1**·MeOH, **1**·0.5Et₂O, and **4**·0.5MeOH and pale-yellow solids for **2**, **3**·2DMF, and **5**·4DMF. The products were obtained in high yields (72–85%) and identified by elemental analysis, FAB mass spectrometry, and NMR and IR spectroscopy (Experimental Section). The X-ray crystal structures have also been determined. These structures show that upon coordination to the gold(I) centers the SSNH₂ ligands exclusively exist in the thiolate form.

Perspective views of **1**·MeOH, **1**·0.5Et₂O, **2**, **3**·2DMF, **4**·0.5MeOH, and **5**·4DMF and their extended structures are shown in Figures 2–7. The Au(I) centers are all two-coordinate and adopt an almost linear geometry with P–Au–S angles ranging from 172.8(2)° to 177.80(14)°. Au–P [2.247(2)–2.2630(8) Å] and Au–S [2.295(5)–2.323(4) Å] distances fall in a normal range.

In **1**·0.5Et₂O and **1**·MeOH, any close Au(I)···Au(I) contacts are prevented by the bulky PPh₃ ligand. However, in **1**·0.5Et₂O the complexes are associated into dimers via bifurcated hydrogen bonds (Figure 2a). The diethyl ether molecules are neither coordinated to the metal atoms nor involved in hydrogen bonding. By contrast, for **1**·MeOH the crystal structure features an interesting ribbon pattern with the molecules linked only through weak intermolecular hydrogen-bonding interactions N(3)–H(1)···N(2) [N(3)···N(2) 3.169 Å] (Figure 2b), but with the chains further connected by molecules of crystal methanol to give a one-dimensional ladder structure [N(3)–H(2)···O–H···N(1) interactions [O···N(1) 2.816 Å, N(3)···O 2.855 Å]]. The bridging methanol molecules act as dual hydrogen-bonding donors and acceptors.

Crystals of **1**·0.5Et₂O contain two crystallographically independent molecules (**1A** and **1B**), which are almost superimposable (Figure 2c), except for the orientation of the phenyl groups. However, the conformation of **1A,B** in **1**·0.5Et₂O is different from that in **1**·MeOH regarding the dihedral angle S2–C1–S1–Au1: In the former the gold atom is in an in-plane trans position while it is in the in-plane cis position in the MeOH solvate (Figure 2d).

Crystals of complex **2** contain no solvent molecules. A ladder structure of SSNH₂ moieties is generated by direct slipped head-

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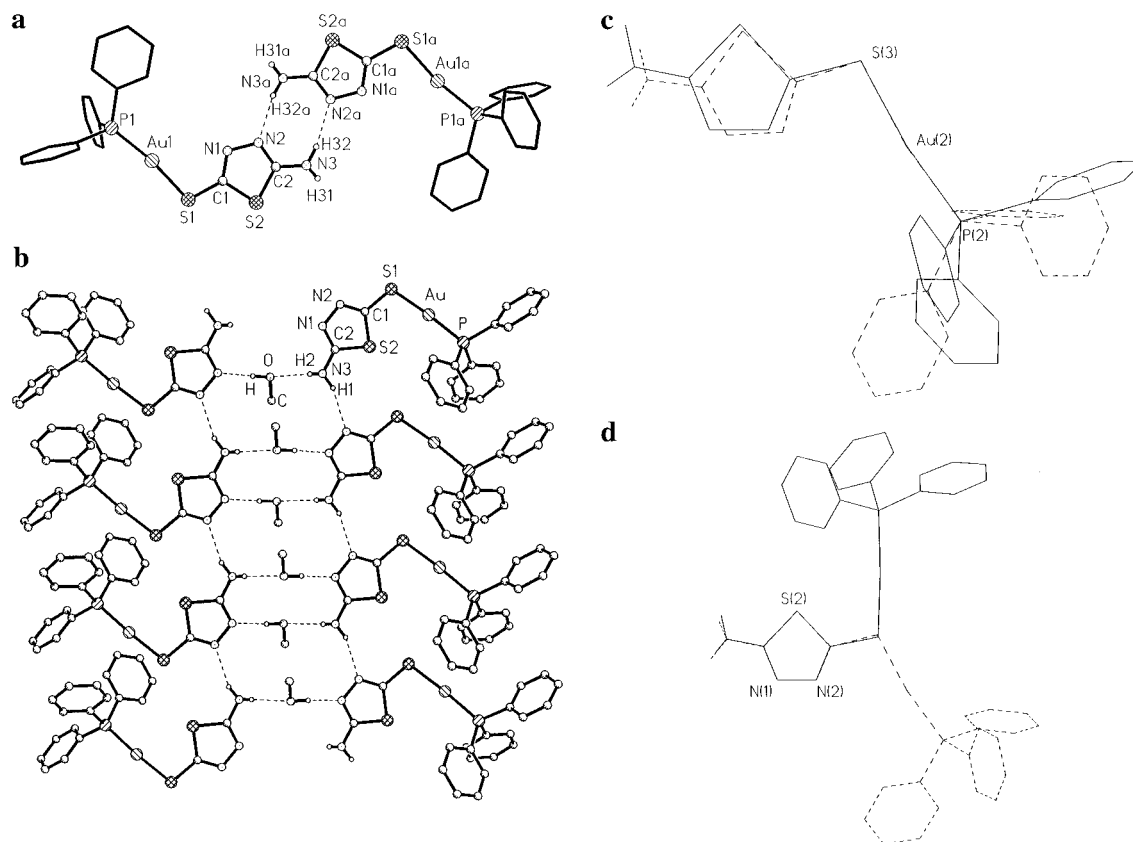


Figure 2. (a) Dimeric structure of **1**·0.5Et₂O with hydrogen-bonding interactions. Selected bond lengths (Å) and angles (deg). (only one of the two independent pairs is shown; the corresponding values are given in square brackets): Au(1)–P(1) 2.260(2) [2.260(2)], Au(1)–S(1) 2.311(2) [2.303(2)], S(1)–C(1) 1.717(6) [1.720(6)], S(2)–C(1) 1.755(6) [1.741(6)], S(2)–C(2) 1.746(6) [1.729(7)], N(1)–N(2) 1.402(7) [1.392(7)]; P(1)–Au(1)–S(1) 171.60(6) [172.62(6)], C(1)–S(1)–Au(1) 103.5(2) [104.4(2)], S(2)–C(1)–S(1) 119.7(3) [119.0(3)], N(1)–C(1)–S(1) 127.3(4) [127.1(5)], N(1)–C(1)–S(2) 113.0(4) [113.9(5)]. (b) One-dimensional ladder structure of complex **1**·MeOH with hydrogen-bonding interactions with molecules of crystal methanol. Selected bond lengths (Å) and angles (deg): Au–S(1) 2.3135(8), Au–P 2.2630(8), S(1)–C(1) 1.744(3), S(2)–C(1) 1.744(3), S(2)–C(2) 1.744(3), N(1)–N(2) 1.394(4); P–Au–S(1) 176.18(3), C(1)–S(1)–Au 102.67(10), S(2)–C(1)–S(1) 122.3(2), N(2)–C(1)–S(1) 123.7(2), N(2)–C(1)–S(2) 113.9(2). (c) Superposition of the two crystallographically independent molecules of **1**·0.5Et₂O (**1A** and **1B**), showing the different orientations of the phenyl groups. (d) Superposition of **1**·MeOH and **1A** (see part c), showing the different conformations of the molecules.

to-tail hydrogen-bonding interactions [N(3)–H(2)···N(2), N(3)···N(2) 2.950 Å; N(3)–H(1)···N(1), N(3)···N(1) 3.161 Å]. Due to the less bulky PMe₃ ligands, as compared to PPh₃, auriphilic interactions are also present in the crystal packing as expected (Figure 3a). The ladders are associated via these Au(I)···Au(I') contacts into a novel two-dimensional sheet structure. The torsion angle P–Au–Au'–P' is 68.4°, and the Au(I)···Au(I') distance of 3.0581(6) Å is significantly shorter than those in the one-dimensional reference polymers 2–[(RNC)AuS]C₆H₄–COOH.^{14a} In addition, **2** also shows weak N(3)–H(1)···S(1) [N(3)···S(1) 3.505 Å] and weak Au(I)···S (3.72 Å) contacts. From another point of view, **2** can also be illustrated as dinuclear units based on auriphilic interactions and further associated into a two-dimensional hydrogen-bonded framework through multiple hydrogen-bonding and weak Au(I)···S contacts (Figure 3b).

Single crystals of complex **3** containing two crystal DMF molecules in the lattice feature dinuclear units with an intramolecular auriphilic interaction at a distance of 3.0987(10) Å (Figure 4a), which is somewhat shorter than the reference in [dppm(AuCl)₂].^{15a} These dinuclear units are further associated into a one-dimensional meandering chain via hydrogen bonding. One of the two N–H functions of each NH₂ group is engaged in hydrogen bonding to one DMF molecule [N(23')–H(23C)···O(2'), N(23')···O(2') 2.878 Å; N(13')–H(13C)···O(1), N(13')···O(1) 2.958 Å], and therefore neighboring SSNH₂ pairs

can only form bifurcated hydrogen bonds through N(13)–H(13b)···N(12') [N(13)···N(12') 2.921 Å] contacts. Due to the steric effect of the dppm ligands, the N(11) and (N11') atoms are unable to become involved in the hydrogen-bonding aggregation, and this phenomenon is different from those of **1**·MeOH and **2**, where all the hydrogen-bonding donors and acceptors participate in the hydrogen-bonded aggregation. DMF plays a terminating role blocking further hydrogen-bonded aggregation (Figure 4b).

The molecules in the crystals of complex **4** (Figure 5), which contain some disordered methanol, are associated via intermolecular Au···Au contacts [Au(1)···Au(2') 3.06757(7) Å] into parallel chains (Figure 6a). These are interconnected through multiple hydrogen-bonding to give a layer structure [Figure 6b, N(13)–H(2)···N(22'), N(13)···N(22') 3.136 Å; N(23)–H(3)···N(11'), N(23)···N(11') 2.957 Å], which is further aggregated into a complicated network [N(13)–H(1)···N(21'), N(13)···N(11') 3.005 Å]. In addition, weak Au···S contacts between the layers can be detected [Au(2)···S(2') 3.823 Å]. The resulting hydrogen-bonding pattern resembles that observed in the crystals of complex **2**. However, in the latter all available H atoms are involved in network formation, whereas in **4** one hydrogen (H4) is left without any contacts. Surprisingly, the solvent methanol, which played an essential role in the structure of **1**·MeOH through hydrogen bonding, does not participate in network formation in the structure of **4**·0.5MeOH.

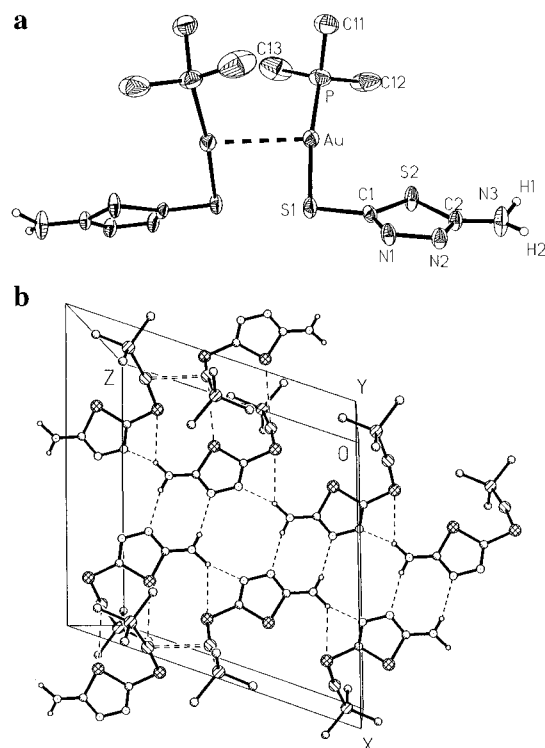


Figure 3. (a) Molecular structure of complex **2** in the crystal. The ORTEP diagram shows 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Au...Au' 3.0581(6), Au–S(1) 2.311(2), Au–P 2.247(2), S(1)–C(1) 1.731(7), S(2)–C(1) 1.758(7), S(2)–C(2) 1.757(8), N(1)–N(2) 1.389(8); P–Au–S(1) 173.67(8), P–Au–Au' 104.28(7), S(1)–Au–Au' 82.05(5), C(1)–S(1)–Au 100.0(3), S(1)–C(1)–S(2) 123.4(4). (b) Extended two-dimensional sheet structure of complex **2** with cooperative intermolecular aurophilic and hydrogen-bonding interactions.

Unlike the chains of [dppee(AuX)₂] (X = Cl,^{15b} SPh¹⁷), where the dinuclear units are associated to give one-dimensional structures via aurophilic interactions of 3.043(1) and 3.023(2) Å, respectively, **5**·4DMF features isolated dinuclear units with four solvating DMF molecules hydrogen-bonded to each N–H function of the NH₂ groups [N(3)–H(31)···O(1), N(3)···O(1) 2.897 Å; N(3)–H(32)···O(2), N(3)···O(2) 2.815 Å]. An inversion center is imposed at the midpoint of the C–C' bond (Figure 7). The DMF molecules can only act as hydrogen-bonding acceptors and prevent any further aggregation in the crystal lattice. The potential hydrogen-bonding acceptors (the N atoms) in the SSNH₂ moieties remain unengaged, probably due to the lack of flexibility and bulkiness of the dppee ligand. It thus appears that the hydrogen-bonding interactions between [dppee(Au(SSNH₂))₂] and four DMF molecules compensate for the loss of Au(I)···Au(I) and N–H···N interactions in **5**·4DMF and lend stabilization to the molecular array in the lattice.

The structural studies of four related phosphine gold(I) thiolates in this work have shown that the hydrogen-bonding functions of the SSNH₂ ligands govern all aggregations in the lattices. By reducing the steric effect of the phosphine auxiliary ligands (from PPh₃ to PMe₃), a two-dimensional framework is formed from the hydrogen-bonded ladder components by taking advantage of intermolecular aurophilic interactions. When dpmm is used instead of PPh₃, a one-dimensional meandering chain structure is formed with intramolecular aurophilic and inter-

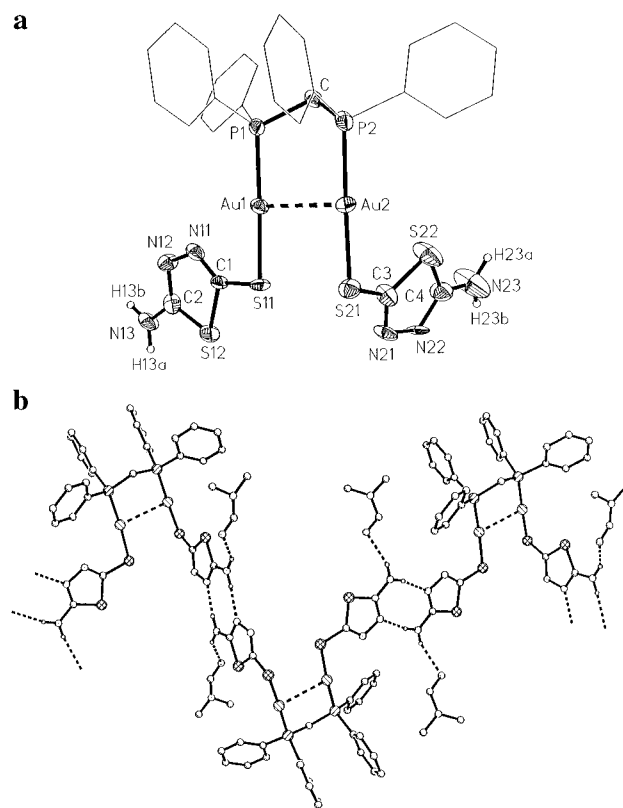


Figure 4. (a) Molecular structure of complex **3**·2DMF in the crystal. The ORTEP diagram shows 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Au(1)···Au(2) 3.0987(10), Au(1)–S(11) 2.323(4), Au(2)–S(21) 2.295(5), Au(1)–P(1) 2.255(4), Au(2)–P(2) 2.259(5), S(11)–C(1) 1.79(2), S(21)–C(3) 1.745(11), N(11)–N(12) 1.41(2), N(21)–N(22) 1.407(13); P(1)–Au(1)–S(11) 172.8(2), P(2)–Au(2)–S(21) 177.80(14), P(1)–Au(1)–Au(2) 88.73(9), P(2)–Au(2)–Au(1) 90.29(10), S(11)–Au(1)–Au(2) 96.96(11), S(21)–Au(2)–Au(1) 91.91(11). (b) Extended one-dimensional chain structure of complex **3**·2DMF with intramolecular aurophilic and intermolecular hydrogen-bonding interactions.

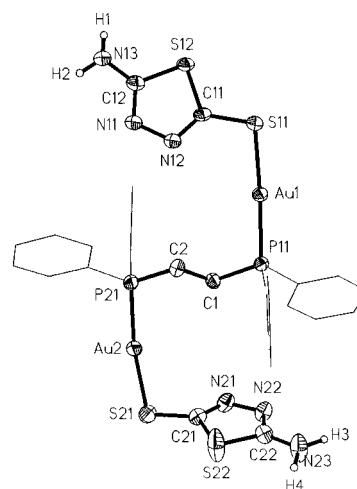


Figure 5. Molecular structure of complex **4** in the crystal. The ORTEP diagram shows 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Au(1)–S(11) 2.315(2), Au(1)–P(11) 2.266(2), S(11)–C(11) 1.739(6), P(11)–C(1) 1.821(5), C(1)–C(2) 1.532(7), C(1)–P(21) 1.823(5), P(21)–Au(2) 2.258(2), Au(2)–S(21) 2.213(2), S(21)–C(21) 1.740(6); S(11)–Au(1)–P(11) 175.46(5), Au(1)–S(11)–C(11) 104.3(2), S(21)–Au(2)–P(21) 171.43(5), Au(2)–S(21)–C(21) 100.0(2).

molecular hydrogen-bonding interactions in the crystal lattice. Any further aggregation is terminated by hydrogen bonding to

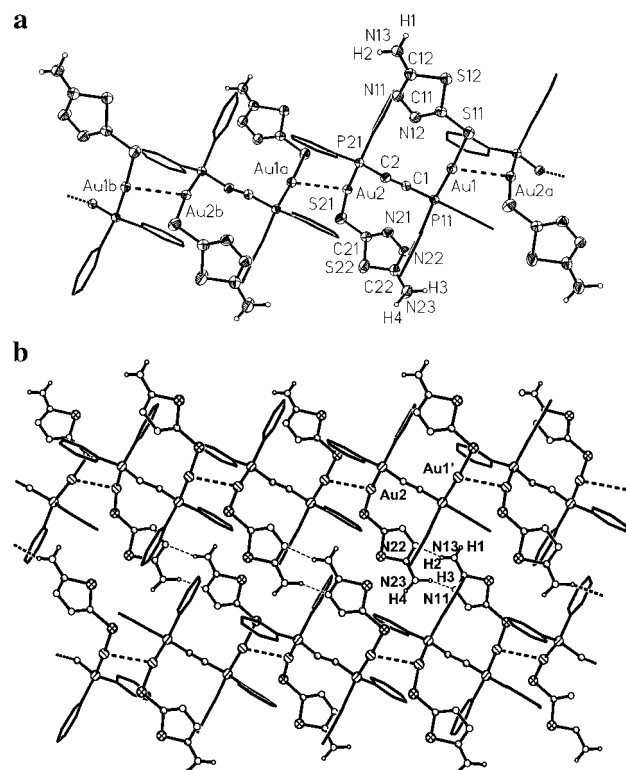


Figure 6. (a) One-dimensional chain structure of **4** with intramolecular aurophilic interactions and (b) extended two-dimensional sheet structure of **4** with cooperative intermolecular aurophilic and hydrogen-bonding interactions.

crystal solvent molecules. The highly flexible dppe complex also permits intermolecular contacts through both aurophilic and hydrogen-bonding interactions. The more rigid *trans*-1,2-bis-(diphenylphosphino)ethene complex, however, appears as isolated dinuclear units owing to the presence DMF as a chain-terminating solvent molecule.

Conclusion

To construct novel molecular solids that utilize cooperative aurophilic and hydrogen-bonding interactions as weak intermolecular forces facilitating self-assembly of the components is a current synthetic challenge.^{14,18} In this work, we have successfully prepared and characterized a series of related phosphine gold(I) thiolates with hydrogen-bonding capability. As a new approach to molecular solids through formation of complementary multiple hydrogen-bonding interactions, preorganized dimeric [SSNH₂]₂ moieties (with or without solvent

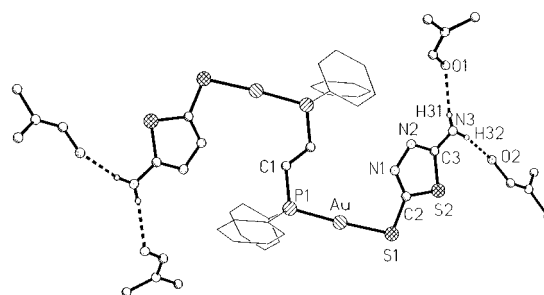


Figure 7. Molecular structure of complex **5**·4DMF in the crystal. Selected bond lengths (Å) and angles (deg): Au–S(1) 2.3046(9), Au–P(1) 2.2536(8), S(1)–C(2) 1.744(3), S(2)–C(3) 1.740(3), S(2)–C(2) 1.744(3), N(1)–N(2) 1.389(4); P(1)–Au–S(1) 176.69(3), C(2)–S(1)–Au 98.96(11), S(1)–C(2)–S(2) 118.9(2), N(1)–C(2)–S(2) 113.5(3), N(3)–C(3)–S(2) 122.1(3).

molecules as bridges) have been further associated into ladder or chain structures through Au(I)···Au(I) contacts. By reducing the steric effect of the phosphine units novel two-dimensional frameworks are built via cooperative intermolecular aurophilic and hydrogen-bonding interactions in the solid state. In this context, the new ladder or chain components may generally be good building blocks for the construction of interesting molecular solids by a judicious choice of (phosphine)Au(I) units. In addition, it is anticipated that the introduction of paramagnetic metal ions and transition metal chromophores into the system of the hydrogen-bonded frameworks may lead to new materials with interesting magnetic and electrooptical properties.

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Supporting Information Available: Listing of crystallographic data, data collection and refinement details, atomic positional and thermal parameters, anisotropic thermal parameters, bond distances, and bond angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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