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Coordination of Pyridinethiols in Gold(I) Complexes

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High-yield synthesis of gold(I) thionato complexes, bis(pyridine-2-thionato)gold(I) chloride (**1**) and bis(pyridine-4-thionato)gold(I) chloride (**2**), are described. According to their solid-state structures, a linear coordination of Au(I), equiplanar coordination of the ligands and two weak γ-agostic interactions are found in both of these complexes despite of different relative positions of N and S atoms in the pyridinethionato ligands. Density functional theory calculations on **1** and **2** reproduce the observed X-ray structures. Even though the C–H···Au interactions of Au(I) and two pyridine moieties (2.83 and 2.88 Å in **1** and 2.86 Å in **2**) are relatively weak, according to calculations they seem to provide further stabilization for the coordination and orientation of the ligands. In **1** the shortest Au···Au distances of 3.50 Å indicate that aurophilic interactions, even though weak, are present in the solid state, whereas in **2** these interactions are absent.

Introduction

Gold complexes bearing a gold−sulfur bond have been of interest for pharmacological, thin film, glass, and ceramic applications.[1] Coordination chemistry of gold complexes having both S and N functionalities in the same heterocycle has recently attracted considerable interest, and several Au(I) complexes containing pyridine-4-thione (4-PS),[2] pyridine-2-thione (2-PS),[2c,d,3] or similar ligands[2b,c,3b−d,f,g,4] have been reported. While coordinated to the Au atom through S, these ligands may coordinate to other transition metals through the N atom and thus form supramolecules, such as molecular dots or molecular wires.[2] Furthermore, different donor atoms within the same ligand can provide different coordination modes and thus tune both the stability and reactivity of a complex.[5]

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(1) See for example (a) Dash, K. C.; Schmidbaur, H. *Met. Ions Biol. Syst.* **1982**, *14*, 179−205. (b) Lorber, A.; Simon, T. M. *Gold Bull.* **1979**, *12*, 149−158. (c) Sutton, B. M.; McGusty, E.; Walz, D. T.; DiMartino, M. J. *J. Med. Chem.* **1972**, *15*, 1095−1098. (d) Shaw, C. F.; III; Beery, A.; Stocco, G. C. *Inorg. Chim. Acta* **1986**, *123*, 213−216. (e) Bain, C. D.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1989**, *28*, 506−512. (f) *Gold. Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; John Wiley and Sons Ltd.: London, 1999.

(2) (a) Nunokawa, K.; Onaka, S.; Mizuno, Y.; Okazaki, K.; Sunahara, T.; Ito, M.; Yaguchi, M.; Imai, H.; Inoue, K.; Ozeki, T.; Chiba, H.; Yosida, T. *J. Organomet. Chem.* **2005**, *690*, 48−56 and references therein. (b) Nunokawa, K.; Onaka, S.; Tatematsu, T.; Ito, M.; Sakai, J. *Inorg. Chim. Acta* **2001**, *322*, 56−64 and references therein. (c) Onaka, S.; Yaguchi, M.; Yamauchi, R.; Ozeki, T.; Ito, M.; Sunahara, T.; Sugiura, Y.; Shiotsuka, M.; Nunokawa, K.; Horibe, M.; Okazaki, K.; Iida, A.; Chiba, H.; Inoue, K.; Imai, H.; Sako, K. *J. Organomet. Chem.* **2005**, *690*, 57−68 and references therein. (d) Jia, G.; Puddephatt, R. J.; Vittal, J. J. *Polyhedron* **1992**, *11*, 2009−2014.

(3) (a) Bardají, M.; Connelly, N. G.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M. *J. Chem. Soc., Dalton Trans.* **1995**, 2245−2250 and references therein. (b) Abram, U.; Mack, J.; Ortner, K.; Müller, M. *J. Chem. Soc., Dalton Trans.* **1998**, 1011−1019. (c) Usón, R.; Laguna, A.; Laguna, M.; Jiménez, J.; Gómez, M. P.; Sainz, A. *J. Chem. Soc., Dalton Trans.* **1990**, 3457−3463. (d) Vicente, J.; Chicote, M.-T.; Rubio, C. *Chem. Ber.* **1996**, *129*, 327−330. (e) Vicente, J.; Chicote, M.-T.; Saura-Llamas, I.; Lagunas, M. C. *J. Chem. Soc., Chem. Commun.* **1992**, 915−916. (f) Akrivos, P. D.; Hadjikakou, S. K.; Karagiannidis, P. *Polyhedron* **1994**, *13*, 753−758. (g) Love, J. C.; Wolfe, D. B.; Chabinyc, M. L.; Paul, K. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 1576−1577. (h) Hao, L.; Mansour, M. A.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg R. *Inorg. Chem.* **2000**, *39*, 5520−5529. (i) Cookson, P. D.; Tiekink, E. R. T. *J. Chem. Soc., Dalton Trans.* **1993**, 259−263.

(4) (a) Colacio, E.; Romerosa, A.; Ruiz, J.; Román, P.; Gutiérrez-Zorilla, J. M.; Vegas, A.; Martínez-Ripoll, M. *Inorg. Chem.* **1991**, *30*, 3743−3749. (b) Tzeng, B.-C.; Huang, Y.-C.; Wu, W.-M.; Lee, S.-Y.; Lee, G.-H.; Peng, S.-M. *Cryst. Growth Des.* **2004**, *4*, 63−70. (c) Friedrichs, S.; Jones, P. G. *Z. Naturforsch.* **2004**, *59b*, 1429−1437. (d) Schulz Lang, E.; Marceli Fernandes, R., Jr.; Souza Lemos, S.; Schulz Lang, L.; Burrow, R. A. *Acta Crystallogr., Sect. E* **2002**, *58*, m469−m470. (e) Dodds, C. A.; Garner, M.; Reglinski, J.; Spicer, M. D. *Inorg. Chem.* **2006**, *45*, 2733−2741. (f) Ahmad, S.; Isab, A. A.; Perzanowski H. P. *Can. J. Chem.* **2002**, *80*, 1279−1284. (g) Isab, A. A.; Ahmad, S. *J. Inorg. Biochem.* **2002**, *88*, 53−60. (h) Dickson, P. N.; Wehrli, A.; Geier, G. *Inorg. Chem.* **1988**, *27*, 2921−2925. (i) Tzeng, B.-C.; Chan, C.-K.; Cheung, K.-K.; Che, C.-M.; Peng, S.-M. *J. Chem. Soc., Chem. Commun.* **1997**, 135−136.

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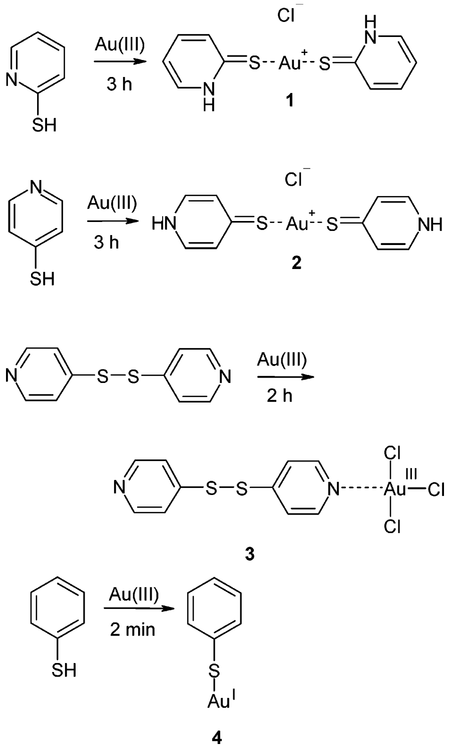
Characteristic of gold(I) complexes in the solid state are the short-range Au···Au contacts which arise from correlation and relativistic effects.[6] Such 'aurophilic' interactions have comparable strength with hydrogen bonding.[4b,6a,7] Agostic interactions[8] in gold complexes have not received as much attention as the other secondary interactions. In general, these are weak, short-range interactions that can be present in an electron-deficient metal complex with a free coordination site, assuming that the ligand framework is not sterically too hindered and the electronic effects do not prevent the interaction.[9] In an agostic interaction an intramolecular σ-bond, such as C−H, of the ligand orients toward a metal center. These kinds of interactions have an essential role for example in catalytic olefin polymerization.[10] Experimental evidence for the presence of the agostic interactions has been obtained by means of X-ray and neutron diffraction and NMR spectroscopy. Density functional theory (DFT) is the method most often applied in calculations.[9,11]

The presence of C−H···Au agostic interactions have been reported for only a few gold thione[12] and phosphine[13] complexes. In general, studies of C−H···metal agostic interactions including both crystallographic measurements and theoretical considerations are rare, and for Au complexes, such studies do not exist.[14] Herein, the syntheses and the solid-state structures of two Au(I) bis(pyridinethionato) complexes (**1**−**2**, Scheme 1) are described. These complexes are of particular interest, as they are considered to play a key role in the oxidation of elemental gold by O_2 in alcohol solutions.[15] Both complexes were modeled using the DFT method together with one additional gold species which was observed during the ionization of **1** and **2**. According to the calculations, agostic interactions are present in all of these complexes even though the interactions are inherently weak.[13a]

Scheme 1. Synthesis of Complexes **1**−**4**[a]



[a] All reactions were performed at room temperature in MeOH using $HAuCl_4 \cdot 4H_2O$ as a starting material. For the successful synthesis of **1**, **2**, and **4**, 4 equiv of the ligand were needed, while **3** formed with 2 equiv. The unambiguous structure of **3** remained unclear.

Experimental Section

General. ^1H and ^{13}C NMR spectra were measured with a Varian Gemini 200 apparatus and ESI$^+$-TOF MS with a Bruker micrOTOF mass spectrometer. IR spectra were recorded with a Perkin-Elmer Spectrum One, and elemental analyses were performed with an EA 1110 CHNS-O CE instrument. All chemicals were purchased from Aldrich and used as received. Crystals suitable for X-ray measurements were selected and mounted on a glass fiber using the oil drop method,[16] and the data were collected at 173 or 123 K using a Nonius KappaCCD diffractometer. The intensity data were corrected for Lorentz and polarization effects and for absorption by the multiscan method.[17] The crystal structures were solved using either SIR2002[18a] or SHELX97[18b] and refined with SHELX97.[18b] Graphics were obtained using the SHELXTL[19] program package. All nonhydrogen atoms were refined anisotropically except in 2-pyridinium disulfide dichloride, where a disordered methanol solvent was refined isotropically. The hydrogen atoms were

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(5) Crespo, O.; Fernández, E. J.; Jones, P. G.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Pérez, J. *Dalton Trans.* **2003**, 1076−1082.

(6) (a) Schmidbaur, H. *Gold. Bull.* **2000**, *33*, 3−10. (b) Pyykkö, P.; Zhao, Y. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 604−605. (c) Pyykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412−4456.

(7) (a) Schmidbaur, H. *Gold Bull.* **1990**, *23*, 11−21. (b) Schmidbaur, H.; Scherbaum, F.; Huber, B.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 419−421. (c) Tzeng, B.-C.; Schier, A.; Schmidbaur, H. *Inorg. Chem.* **1999**, *38*, 3978−3984.

(8) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395−408.

(9) (a) Clot, E.; Eisenstein, O. *Principles and Applications of Density Functional Theory in Inorganic Chemistry I*; Kaltsoyannis, N., McGrady, J. E., Eds.; Springer-Verlag: Berlin, Heidelberg, 2004; Vol. 112, pp 2−4. (b) Calhorda, M. J. *Chem. Commun.* **2000**, 801−809.

(10) see for example (a) Meier, R. J.; Aagaard, O. M.; Buda, F. *J. Mol. Catal. A* **2000**, *160*, 189−197. (b) Zeller, A.; Strassner, T. *J. Organomet. Chem.* **2006**, *691*, 4379−4385. (c) Mashima, K.; Nakamura, A. *J. Organomet. Chem.* **1992**, *428*, 49−58. (d) Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85−93.

(11) (a) Krüger, S.; Stener, M.; Mayer, M.; Nörtemann, F.; Rösch, N. *J. Mol. Struct. (Theochem)* **2000**, *527*, 63−74. (b) Popelier, P. L. A.; Logothetis, G. *J. Organomet. Chem.* **1998**, *555*, 101−111 and references therein.

(12) (a) Friedrichs, S.; Jones, P. G. *Z. Naturforsch.* **2004**, *59b*, 49−57. (b) Friedrichs, S.; Jones, P. G. *Z. Naturforsch.* **2004**, *59b*, 793−801. (c) Friedrichs, S.; Jones, P. G. *Z. Naturforsch.* **2004**, *59b*, 1429−1437.

(13) (a) Baukova, T. V.; Kuz'mina, L. G.; Oleinikova, N. A.; Lemenovskii, D. A.; Blumenfel'd, A. L. *J. Organomet. Chem.* **1997**, *530*, 27−38. (b) Baukova, T. V.; Kuz'mina, L. G.; Oleinikova, N. A.; Lemenoskii, D. A. *Izv. Akad. Nauk, Ser. Khim.* **1995**, 2023−2034.

(14) (a) Brady, E. D.; Clark, D. L.; Gordon, J. C.; Hay, P. J.; Keogh, D. W.; Poli, R.; Scott, B. L.; Watkin, J. G. *Inorg. Chem.* **2003**, *42*, 6682−6690. (b) Cooper, A. C.; Clot, E.; Huffman, J. C.; Streib, W. E.; Maseras, F.; Eisenstein, O.; Caulton K. G. *J. Am. Chem. Soc.* **1999**, *121*, 97−106. (c) Ujaque, G.; Cooper, A. C.; Maseras, F.; Eisenstein, O.; Caulton K. G. *J. Am. Chem. Soc.* **1998**, *120*, 361−365.

(15) Räisänen, M. T.; Kemell, M.; Leskelä, M.; Repo, T. *Inorg. Chem.* **2007**, *46*, 3251−3256.

(16) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615.

(17) *Nonius COLLECT*; Nonius BV: Delft, The Netherlands, 2002.

(18) (a) Burla, M. C.; Camalli, M.; Carrozzini, G. L.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2003**, *36*, 1103. (b) Sheldrick, G. M. *SHELX97 Program for the Solution and Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(19) Sheldrick, G. M. *SHELXTL Version 5.10*; Bruker AXS Inc.: Madison, WI, 1997.

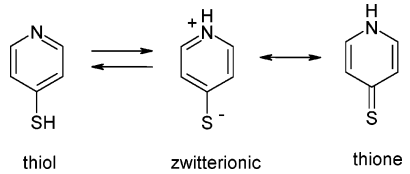

Figure 1. Tautomeric and mesomeric forms of pyridine-4-thiol. Pyridine-2-thiol has corresponding forms.

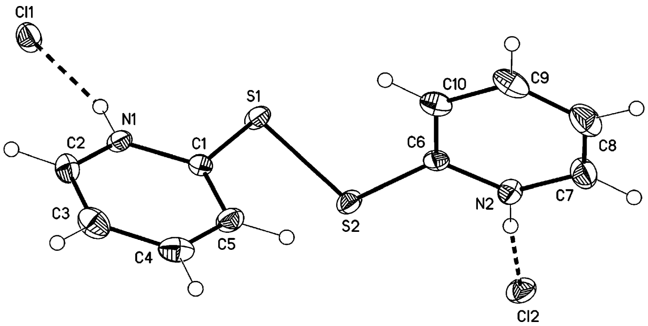

Figure 2. Solid-state structure of bis(2-pyridinium)disulfide dichloride which forms during the synthesis of **1**. Crystals suitable for X-ray measurement were obtained from a saturated MeOH solution. A disordered solvent molecule with a site occupation factor of 0.5 has been omitted for clarity. Displacement ellipsoids are depicted at the 30% probability level, and hydrogen bonds are represented by dashed lines. Selected bond lengths and angles are given in the Supporting Information.

introduced into their calculated positions or were picked from residual electron density map and refined with fixed geometry with respect to their carrier atoms.

Synthesis of Gold Complexes 1−4. Bis(pyridine-2-thionato)gold(I) chloride (**1**) was synthesized under Ar atmosphere using the standard Schlenk techniques. 2-PS (0.718 g, 6.46 mmol) and $HAuCl_4 \cdot 4H_2O$ (0.665 g, 1.61 mmol) were dissolved in dry MeOH (30 mL), and the immediately formed suspension was stirred for 3 h. The suspension was filtered in air and solvents were removed from the filtrate in a vacuum, yielding a crude product of **1** as a yellow powder that was purified by recrystallization from MeOH (0.51 g, 70%). Needles suitable for X-ray crystallographic measurement were obtained from $CHCl_3$ (Figure 3a). Anal. Calcd for $C_{10}H_{10}N_2S_2Cl_1Au_1$: C 26.41, H 2.22, N 6.16, S 14.10; Found: C 27.13, H 2.21, N 5.50, S 13.87%. ^1H NMR (200 MHz, $CDCl_3$): δ 7.21 (s, 2H, CH), 7.68 (s, 4H, CH), 8.30 (s, 2H, CH), 15.53 (s, 2H, NH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ 118.21, 130.23, 139.42, 141.04, 166.23 ppm. IR: $\nu = 750$ (CH), 1446 (pyridine ring), 1583 (pyridine ring), 1606 cm^{-1} (pyridine ring).[3d,20] HRMS (ESI$^+$-TOF) *m/z* (%):$[C_{10}H_{10}N_2S_2Au_1]^+$ 419 (100, calcd 418.995, found 418.993, error 4.49 ppm), 496 (34), 725 (15). A considerable amount (0.36 g) of a side-product was obtained as a yellow powder when the MeOH suspension was filtered. According to X-ray crystallographic measurement from the needles formed in MeOH, the side-product is a bis(2-pyridinium)disulfide dichloride (**5**, Figure 2).

Bis(pyridine-4-thionato)gold(I) chloride (**2**) was synthesized by a similar method as that for complex **1**, starting from $HAuCl_4 \cdot 4H_2O$ (0.100 g, 0.24 mmol) and 4-PS (0.110 g, 0.99 mmol) in 10 mL of MeOH. The yellow precipitate obtained was washed with MeOH and dried in a vacuum (0.068 g, 62%). Crystals suitable for X-ray analysis were obtained by a slow evaporation of solvents from the MeOH filtrate to which small amounts of EtOH, acetonitrile, and THF were added. Anal. Calcd for $C_{10}H_{10}N_2S_2Cl_1Au_1$: C 26.41, H 2.22, N 6.16, S 14.10; Found: C 26.79, H 2.27, N 6.08, S 13.52%. ^1H NMR (200 MHz, DMSO-d_6): δ 7.86 (s, 4H, CH), 8.22 (s, 4H, CH) ppm. ^{13}C NMR (50 MHz, DMSO-d_6): δ 127.39, 137.12, 174.17 ppm. IR: $\nu = 787$ (CH), 1461 (pyridine ring), 1589 (pyridine ring), 1613 cm^{-1} (pyridine ring).[3d,20] HRMS (ESI$^+$-TOF) *m/z* (%): $[C_{10}H_{10}N_2S_2Au_1]^+$ 419 (100, calcd 418.9945, found 418.9969, error 1.30 ppm), 496 (1), 726 (3).

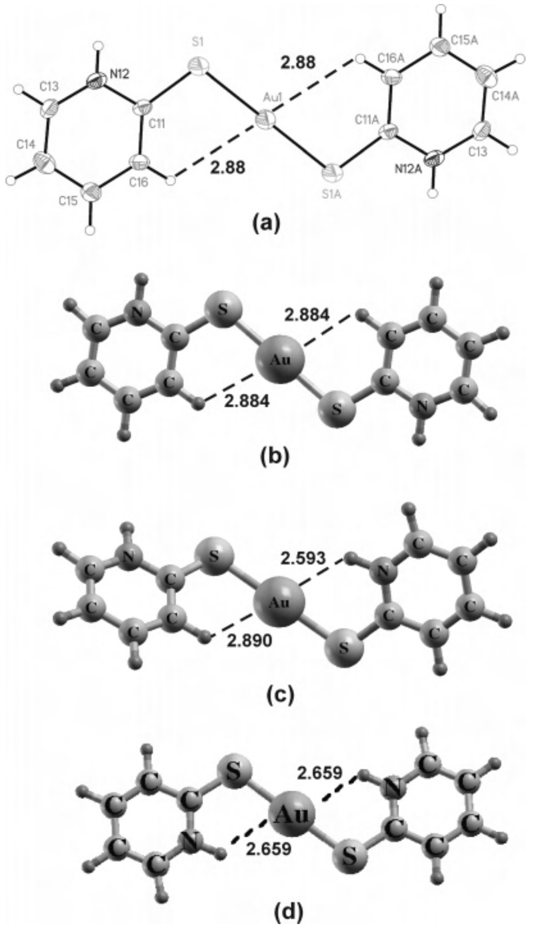

Figure 3. (a) Solid-state structure of Au(I) complex **1** bearing 2-PS ligands. Chloride as a counterion, disordered atoms, and hydrate are not shown for clarity. Displacement ellipsoids appear at the 30% probability level and hydrogen atoms are in their calculated positions. (b) The modeled structure of **1** with two C−H···Au (2.884 Å) agostic interactions. (c) The modeled structure of the unsymmetric conformer with one C−H···Au (2.890 Å) and one N−H···Au (2.593 Å) agostic interaction. (d) The modeled structure of the conformer with two N−H···Au (2.659 Å) agostic interactions. The γ-agostic interactions are represented by dashed lines.

Di(4-pyridyl)disulfide gold(III) trichloride (**3**) was prepared by adding MeOH (7 mL) and $CHCl_3$ (5 mL) to the Schlenk containing $HAuCl_4 \cdot 4H_2O$ (0.23 g, 0.57 mmol) and di(4-pyridyl)disulfide (0.25 g, 1.13 mmol). The bright yellow suspension which was formed immediately was stirred at room temperature for 2 h. The suspension was filtered and the obtained yellow powder was washed with MeOH and dried in a vacuum (0.23 g, 77%). Complex **3** is slightly soluble in DMSO. Anal. Calcd for $C_{10}H_8N_2S_2Cl_3Au_1$: C 22.94, H 1.54, N 5.35, S 12.25; Found: C 23.08, H 1.71, N 5.08, S 12.16%. ^1H NMR (200 MHz, DMSO-d_6): δ 8.01 (d, $^3J_{HH} = 6.4$ Hz, 4H, CH), 8.72 (s, 4H, CH) ppm. ^{13}C NMR (50 MHz, DMSO-d_6): δ 122.14, 144.23, 153.68 ppm. IR: $\nu = 793$ (CH), 1479 (pyridine ring), 1566 (pyridine ring), 1600 (pyridine ring), 1618 cm^{-1} (pyridine ring).[20] HRMS (ESI$^+$-TOF) MS *m/z* (%): 325 (34), 380

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(20) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*, 2nd ed.; Academic Press, Inc.: New York, 1975; p 322.

Table 1. Cell Parameters and Specific Data Collection Parameters for **1**, **2**, and **5**

	1	**2**	**5**
formula	$C_{10}H_{12}N_2OS_2ClAu$	$C_{10}H_{12}N_2OS_2ClAu$	$C_{10}H_{10}N_2S_2Cl_2\cdot\times baCH_3OH^a$
fw (g mol^{-1})	472.75	454.74	307.23
T (K)	173(2)	123(2)	173(2)
cryst syst	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$C2/c$	$P2_1/n$
unit cell dimens			
a (Å)	14.837(1)	10.030(2)	5.389(1)
b (Å)	13.797(1)	10.860(2)	11.128(1)
c (Å)	6.995(1)	11.787(2)	23.774(2)
β(°)	100.15(1)	98.04(1)	90.73(2)
V (Å^3)	1409.4(2)	1271.3(4)	1425.6(3)
Z	4	4	4
D_{calc} (Mg m^{-3})	2.228	2.376	1.436
abs coeff (mm^{-1})	10.908	12.083	0.730
cryst dimens (mm^3)	$0.50 \times 0.09 \times 0.07$	$0.25 \times 0.12 \times 0.06$	$0.50 \times 0.04 \times 0.03$
no. of data collected	9576	9164	8229
no. of data refined	1516	1448	2127
no. of params	135	78	154
R1^b [$I > 2\sigma(I)$]	0.0354	0.0176	0.0489
wR2^c (all data)	0.0964	0.0382	0.1409
residual density (e Å^{-3})	1.331	1.558	0.550

[a] Disordered methanol was refined isotropically using a site occupation factor 0.5. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

(48), 419 (72), 453 (100), $[C_{10}H_9N_2S_2Cl_3Au_1]^+$ 523 (46, calcd 522.8933, found 522.8942, error −1.70 ppm).

(Phenylthiolate)gold(I) (**4**) was synthesized by adding thiophenol (0.25 mL, 2.43 mmol) into a yellow MeOH (7 mL) solution of $HAuCl_4\cdot 4H_2O$ (0.25 g, 0.61 mmol). The yellow suspension immediately formed was stirred at room temperature for 2 min. After filtration, washing with MeOH, and drying in a vacuum, the complex was obtained as a yellow powder (0.09 g, 70%). The complex was insoluble in common solvents; therefore, NMR spectra could not be obtained.[21] Anal. Calcd for $C_6H_5S_1Au_1$: C 23.54, H 1.65, S 10.47; Found: C 23.34, H 1.40, S 10.27%. IR: $\nu = 733$ (CH), 1022 (benzene ring), 1437 (benzene ring), 1473 (benzene ring), 1576 (benzene ring), 3051 cm^{-1} (CH).[20] EI-MS m/z (%): $[C_6H_5S]^+$ 109 (100), $[C_{12}H_{10}]^+$ 154 (27), $[C_{12}H_9S]^+$ 185 (28), $[C_{12}H_{10}S_2]^+$ 218 (99). It is noteworthy that, if the reaction is continued for more than ca. 1 h, the color of the suspension begins to change: first to white, then to light gray, and finally to pale violet. After 22 h of stirring, the suspension was filtered and the pale violet powder was washed with MeOH and dried in a vacuum. This product was also completely insoluble in common solvents. According to elemental analysis, the product is a 1:1 mixture of (phenylthiolate)gold(I) and gold(I) chloride ($C_6H_5S_2Cl_1Au_2$, Calcd C 13.38, H 0.94, S 5.95; Found: C 13.42, H 0.93, S 5.85%). EI-MS m/z (%):$[C_6H_5S]^+$ 109 (92), $[C_{12}H_{10}S_2]^+$ 218 (100). When the solvent was evaporated from the MeOH filtrate, colorless needles, which were identified by X-ray crystallography as diphenyl disulfide, were crystallized as a side-product (Supporting Information).

Computational Methods. All quantum chemical calculations were performed with the TURBOMOLE program package[22] version 5.8. The geometric structures were optimized using the gradient-corrected functional BP86.[23] The resolution of the identity (RI) approximation of the Coulomb interaction[24] was used in the calculations. We employed the standard triple-ζ valence basis set augmented with double polarization functions, TZVPP, together with the corresponding auxiliary density-fitting (RI) basis set, as implemented in TURBOMOLE. On gold we employed a 19-valence electron scalar relativistic pseudopotential[25] together with a (9s7p5d2f)/[7s5p3d2f] basis set.[26] All geometries were fully optimized and they represent minimum structures, as confirmed by vibrational frequency calculations (Supporting Information).

Results and Discussion

The chemical reactivity of pyridinethiols and their coordination chemistry with Au is related to their tautomeric and mesomeric forms: thiol, thione, and zwitterionic form (Figure 1). Depending on the reaction, they can act as a typical anionic thiolato ligand or when in the thione form as a neutral ligand. The zwitterionic structure is an important intermediate having certain flexibility in the coordination mode. For example, in the recently reported oxidation of elemental gold the zwitterionic form of the 4-PS specifically has a crucial role.[15] In solution, pyridinethiols have a preference for the thione form[27] and according to ^{13}C NMR data, 2- and 4-PS favor the thione form in MeOH solution. While crystallizing from MeOH, this isomer remains.[28]

Au(I) thionato complexes **1** and **2** bearing 4-PS and 2-PS, respectively, were synthesized in MeOH at room temperature with high yields from corresponding thiols and $HAuCl_4\cdot$ $4H_2O$. From these complexes **1** was previously reported as

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(21) Bachman, R. E.; Bodolosky-Bettis, S. A.; Glennon, S. C.; Sirchio, S. A. *J. Am. Chem. Soc.* **2000**, *122*, 7146−7147.

(22) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165−169.

(23) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8824.

(24) (a) Eichkorn, K.; Treutler, H.; Öhm, O.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *242*, 652−660. (b) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, A. *Theor. Chem. Acc.* **1997**, *97*, 119−124.

(25) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123−141.

(26) (a) Gilb, S.; Weis, P.; Furche, F.; Ahlrichs, R.; Kappes, M. M. *J. Chem. Phys.* **2002**, *116*, 4094−4101. (b) Pyykkö, P.; Runeberg, N.; Mendizabal, F. *Chem. Eur. J.* **1997**, *3*, 1451−1457.

(27) Stoyanov, S.; Petkov, I.; Antonov, L.; Stoyanova, T.; Karagiannidis, P.; Aslanidis, P. *Can. J. Chem.* **1990**, *68*, 1482−1489.

(28) (a) Etter, M. C.; MacDonald, J. C.; Wanke, R. A. *J. Phys. Org. Chem.* **1992**, *5*, 191−200. (b) Flakus, H. T.; Tyl, A.; Jones, P. G. *Spectrochim. Acta Part A.* **2002**, *58*, 299−310. (c) Muthu, S.; Vittal, J. J. *Cryst. Growth Des.* **2004**, *4*, 1181−1184.

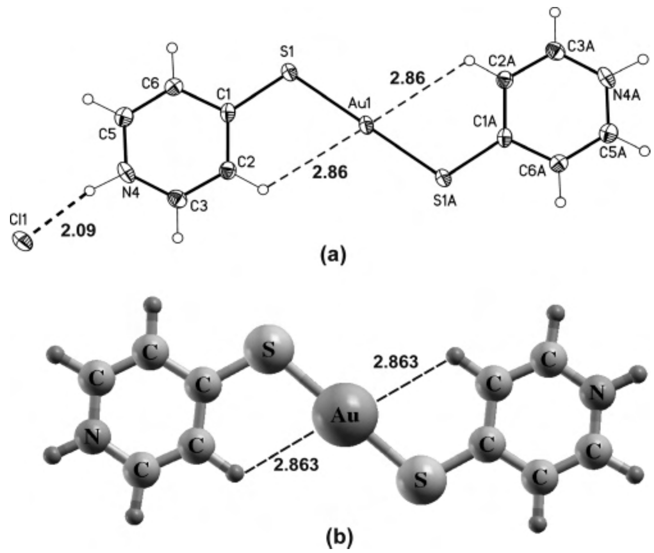

Figure 4. (a) Solid-state structure of complex **2** bearing 4-PS ligands. Displacement ellipsoids appear at the 50% probability level, and hydrogen atoms are in their calculated positions except the ones bonded to N atoms which were situated from the difference map. (b) Computationally optimized structure of cationic gold(I) complex **2**. The agostic interactions and the N−H···Cl hydrogen bond (Å) are represented by dashed lines.

a side-product during the synthesis of chloro-(2-(*N*,*N*-dimethylammoniummethyl)phenyl)-bis(2-mercaptopyridium)-gold(III) chloride when an excess of 2-PS was used.[3b] In complex synthesis a rapid reduction of Au(III) to Au(I) was observed when excess of thiol was present. Some thiol was oxidized simultaneously with the Au(III) reduction to disulfide. For example, bis(2-pyridinium)disulfide dichloride was formed as a side-product during the synthesis of **1** (Figure 2, Table 1). Although HAu(III)Cl_4 is commonly used as a starting material for the synthesis Au(I) complexes,[29] the mechanism for the Au(III) reduction with thiols is not unambiguously understood. According to the results above, it seems to be analogous with the classical organometallic chemistry. When HAu(III)Cl_4 is treated with an excess of 2- or 4-PS, bis(pyridinium-2-thiolato)gold(III) chloride or bis(pyridinium-4-thiolato)gold(III) chloride and two HCl molecules are presumably formed. The former can then undergo reductive elimination, and as a result disulfide and Au(I) are observed. Due to the reaction, disulfide was isolated as the HCl salt. On the basis of the results above, it is clear why, for example, complex **2** is not achievable when starting from di(4-pyridyl)disulfide. Instead, a gold(III) complex (**3**) with an intact S−S bond was obtained (Scheme 1). The reductive elimination of Au(III) and the formation of disulfide (Supporting Information) was observed also in the synthesis of **4** starting from HAu(III)Cl_4 and thiophenol.

As reported previously, gold complexes bearing 2-PS ligands are more soluble than their analogues bearing 4-PS ligands.[2d] In accordance with this, complex **1** is soluble in common solvents whereas **2** is only slightly soluble in DMSO and MeOH. Single crystals suitable for X-ray analysis were easily obtained for **1** in $CHCl_3$, while freshly prepared **2** was successfully recrystallized from MeOH. The crystal structure of **1** revealed two independent complex molecules with a site occupation factor of 0.5 (Figure 3a and Table 1). The structure is fully disordered, which implies that the −S1−Au−S1A− molecule occupies every second crystallographic site while the −S2−Au−S2A− molecule occupies the other sites. The latter is spatially approximately at a right angle to the former with the gold atom lying always at the center of the symmetry.[30] In general, Au(I) complexes prefer a linear geometry[3c,f] and due to symmetric reasons the S−Au−S angle in **1** is exactly 180.0°.

In the solid-state structure of **2**, the Au atom lies at the center of symmetry with equiplanar ligand coordination (Figure 4a and Table 1). The S−Au−S angle is 180° and the coordination sphere of the Au(I) is accomplished by two γ-agostic interactions (C−H···Au distances are 2.86 Å). In the structure Cl counterion forms a moderately strong N−H···Cl hydrogen bonding (2.09(4) Å)[31] that results in the ion lying practically in the same plane as the rest of the complex. In all, a variety of secondary interactions are present in the solid-state structure of **2** and it is clear that they are competing with each other and the resulting continuous supramolecular network is a compromise between them. In this structure aurophilic interactions are overruled by the other weak interactions.[32]

The Au−S bond lengths in **1** and **2** (2.305(3) and 2.312(4) Å for **1** and 2.2942(9) Å for **2**) are in the range reported for gold thiolato and thione complexes,[2a−d,3a−c,4a] but the C−S bonds (1.700(5) and 1.734(6) Å for **1** and 1.736(3) Å for **2**) possess significant double bond character, as they are noticeably shorter than the sum of covalent radii of C and S (1.81 Å),[33] and resemble the value measured for the free thione ligand (1.717(2) Å, see Supporting Information). This, together with two different trends in C−C bond distances (1.365−1.378 and 1.409−1.436 Å) in the pyridyl rings of the complexes, indicates that the ligands are coordinated in the thione form. Furthermore, ^{13}C NMR spectra support the thione form. In the spectrum of 4-PS, a shift of the C−S

Table 2. Selected Bond Lengths and Angles in the Measured and Modeled Structures of Complexes **1** and **2**

	measured **1**	modeled **1**	modeled **1**[a]	measured **2**	modeled **2**
Au−S (Å)	2.305(3) 2.312(4)	2.315 2.315	2.264 2.264	2.2942(9)	2.316 2.316
C−S (Å)	1.734(6) 1.700(5)	1.724 1.724	1.710 1.710	1.736(3)	1.717 1.717
C−N (Å)	1.37	1.361	1.350	1.355(4)	1.363
	1.40	1.377	1.360	1.356(4)	1.365
	1.37				
	1.41				
S−Au−S (deg)	180	180.0	180.0	180.00(4)	179.9
C−H···Au (Å)	2.83	2.884	2.768	2.86	2.863
	2.88				

[a] Results obtained at the MP2 level.

Table 3. Distances of C−H···Au Agostic Interactions in Gold(I) Complexes.

complex	C−H···Au (Å)	ref
bis(imidazolidine-2-thione)gold(I) di(methanesulfonyl)amide	2.95, 3.07	12c
bis(1-methyl-imidazolidine-2-thione)gold(I) di(methanesulfonyl)amide	2.83, 2.85, 2.91, 3.19	12c
bis(imidazolidine-2-thione)gold(I) camphor-10-sulfonate	3.07, 3.09	12b
bis(1-methyl-imidazolidine-2-thione)gold(I) camphor-10-sulfonate	3.16, 3.20	12b
bis(imidazolidine-2-thione)gold(I) chloride	2.93	12a
bis(1-methyl-imidazolidine-2-thione)gold(I) chloride	2.80, 3.09	12a
μ-diphenylphosphinoethane-bis-aurio(2,2′-diphenylmethane)	2.62	13a
(μ_2−1,2-bis(*o*-phenylene)ethane)-bis(triphenylphosphine-gold(I))	2.75, 3.00	13a
(μ_2−2,2′-bis(phenylene)methane)-(μ_2−1,2-bis(diphenylphosphino)ethane-di-gold(I)	2.92, 3.01, 3.06	13a
(μ_4−1,2-bis(phenylene)ethane)-tetrakis(triphenylphosphine-gold(I)) bis(tetrafluoroborate)	2.6, 3.0	13a
μ-diphenylphosphinoethane-bis-aurio(2,2′-diphenylmethane)	2.63	13b
1	2.83, 2.88	this work
2	2.86	this work

carbon appears at 190.34 ppm relative to DMSO-d_6 (in 2-PS at 176.23 ppm, relative to $CDCl_3$) and in the spectrum of **2** at 175.38 ppm in DMSO-d_6 (in **1** at 164.93 ppm in $CDCl_3$).

When the measured crystal structures of **1** and **2** are compared with their modeled structures, they appear to be very similar (Figures 3a,b and 4, Table 2). For both complexes, the energetic minimum (their energies are virtually the same) is achieved with an overall planar geometry and linear coordination of the gold(I) ion. In the modeled structures, the C−H···Au γ-agostic distances are 2.884 and 2.863 Å for **1** and **2**, respectively, whereas in the measured structures, which have hydrogen atoms in their calculated positions, these distances are 2.83 and 2.88 Å for **1** and 2.86 Å for **2**.[34] The agostic interaction with ca. 2.8 Å distance can be considered to be fairly weak.[13a] Nevertheless, they provide additional stabilization for the Au(I) complexes studied. For comparison, we calculated the optimized structures of two other possible conformers for **1** (Figure 3c,d). These conformers correspond to structures with one C−H···Au and one N−H···Au or two N−H···Au γ-agostic interactions, respectively. The calculated energies of these three conformers are virtually identical.

So far, the agostic interactions are known only for six other gold complexes bearing heterocyclic ligands.[12] The C−H···Au distances in **1** (2.83 and 2.88 Å) and **2** (2.86 Å) are in the middle of the range of agostic interactions previously reported for gold(I) complexes (Table 3). As weak interactions are competing with each other, even small modifications in complex structure can change the relative strength of the interactions. For example, the crystal structure of bis(pyridine-2-thionato)gold(I) perchlorate, differing from **1** only by the counterion, has been previously determined,[3c] but the structure of this complex appears to be different. In bis(pyridine-2-thionato)gold(I) perchlorate structure, aurophilicity is clearly present as pentameric clusters of the Au complex are formed having Au···Au distances of ca. 3.3 Å.[14b] Aurophilic interactions are weaker in **1**, as the shortest measured Au···Au distance is 3.50 Å. Instead, γ-agostic interactions, absent from the structure with the perchlorate counterion, provide additional stabilization for **1** and strengthen its overall planar geometry.

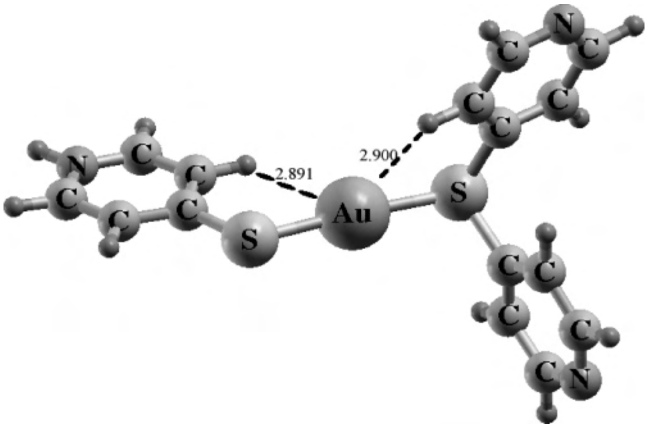

Figure 5. Computationally optimized structure of gold(I) cation (m/z = 496, $C_{15}H_{13}N_3S_2Au$) observed in the gas phase during ESI$^+$-MS measurements of **1** and **2**. The agostic interactions (Å) are represented by dashed lines.

During the ESI$^+$-MS analysis of gold(I) thione complexes **1** and **2**, the formation of several gold species (m/z = 496, 615, 692, 726, 803, and 922) was observed. Previously, similar behavior has been reported in FAB-MS measurements.[2d] On the basis of high-resolution MS identification, these species have either one of the following ligands or different combinations of them: pyridine-4-thione, pyridine-4-thiolato, and di(4-pyridyl)sulfide. It should be emphasized

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(29) (a) Li, C.-K.; Cheng, E. C.-C.; Zhu, N.; Yam, V. W.-W. *Inorg. Chim. Acta* **2005**, *358*, 4191−4200. (b) Steigelmann, O.; Bissinger, P.; Schmidbaur, H. *Angew. Chem.* **1990**, *102*, 1473−1475. (c) Schmidbaur, H.; Wohlleben, A.; Wagner, F.; Orama, O.; Huttner, G. *Chem. Ber.* **1977**, *110*, 1748−1754.

(30) It is probable that in the crystal of **1** several hydrogen bonds stabilize the internal structure (see Supporting Information). However, the intermolecular hydrogen bonding has to be studied very carefully because chloride ions, as well as water molecules with a site occupation factor of 0.5, occupy only every second site from the symmetry allowed sites deduced from the coordinates.

(31) Steiner, T., *Angew. Chem., Int. Ed.* **2002**, *41*, 48−76.

(32) Another polymorph of **2** was also obtained where the molecules are stacked one upon the other with Au···Au distances of ∼3.44 Å, which is an indication of aurophilic interactions. The polymorph was obtained in space group $P2_1/n$ by crystallization from MeOH or EtOH/2-propanol (3:1 v/v). Unit cell: a = 17.011(3) Å, b = 11.425(2) Å, c = 6.793(1) Å, β = 99.79(3)°, V = 1301.0(4) Å^3, Z = 4. The crystals were twins with at least three different domains. Due to the quality of the data, C and N atoms could be only refined isotropically (even after treatment as a twin).

(33) Robinson, W. R.; Odom, J. D.; Holtzclaw, H. F., Jr. *General Chemistry*, 10th ed.; Houghton Mifflin Company: Boston, 1997; p 172.

(34) It should be noted that in the measured structures of **1** and **2** C−H bond length used for aromatic hydrogens is 0.95 Å, whereas in the corresponding calculated structures the C−H bond length is 1.087 or 1.088 Å. Therefore, the similarity of the measured and modeled structure is better seen by comparing the $C_{agostic}$···Au distances. For **1** the measured distance is 3.432(6) and 3.374(6) Å vs 3.494 Å in the modeled structure and for **2** the 3.410(3) Å (measured) and 3.471 Å (modeled).

that these species are present only in the gas phase. The cation $m/z = 496$ was modeled, and its optimized structure is given in Figure 5. The ligands of the Au(I) cation are 4-PS and di(4-pyridyl)sulfide, both having a coordination bond to Au. Also in this structure the presence of two γ-agostic interactions with distances of 2.891 and 2.900 Å provide an energetic minimum. Calculated IR spectra of this species, together with the spectra of the cations of **1** and **2**, are given in the Supporting Information.

Conclusions

1 and **2** were synthesized from $HAuCl_4 \cdot 4H_2O$ and pyridine-2-thiol or pyridine-4-thiol, respectively. Simultaneous reduction of Au(III) and formation of disulfide indicate that the reaction proceeds via a reductive elimination mechanism. Due to the presence of the thione form of the ligand, N in the heterocycle carries a proton and loses its ability to coordinate with Au.

The solid-state and calculated structures of **1** and **2** revealed distinctive planar geometry and linear coordination for Au(I) complexes, regardless of the relative position of the nitrogen atom in the pyridine moiety. The distances of the C−H···Au agostic interactions observed are in accordance with the previously reported agostic interactions in Au(I) complexes. As Au(I) cannot be considered to be very electron deficient, it is reasonable that the γ-agostic interactions observed are relatively weak. In spite of this, they provide additional stabilization for the structures. Weak interactions are competing with each other in the packing of the complexes, which indicates their similar strength. For example, weak aurophilic interactions are present in **1**, whereas in **2** they are overruled by hydrogen bonding and agostic interactions.

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Supporting Information Available: Crystallographic data for complexes **1** and **2**, bis(2-pyridinium)disulfide dichloride methanol solvate, diphenyl disulfide, and pyridine-4-thione; calculated vibrational spectra for all the computationally studied species. This material is available free of charge via the Internet at http://pubs.acs.org.

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