Two-Coordinate Gold(I) Aliphatic Thiolate Complex: The Au-S Distance Is Smaller than the Ag-S One

Kiyoshi Fujisawa,* Sadako Imai, and Yoshihiko Moro-oka*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226

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We prepared the first example of two-coordinate aliphatic monothiolate gold(I) complex. Its structural parameter was compared with that of copper(I) and silver(I) derivatives. The physical properties may be used to differentiate the coordination mode of gold(I) complexes.

There is a continuing interest in d^{10} metal-thiolate complex, because of the relevance to cellular pharmacology in biological systems.[1] Especially importance in gold(I)-thiolate complexes arises from the potential use of these derivatives in medicine.[2] Gold(I) complexes (auranofin, sanachrysin, and myochrysine) are administered to rheumatoid arthritis patients.[3] Furthermore, these gold(I) ions accumulate in cysteine-rich tissues such as metallothionein in the kidney and liver.[3b] However, little attention has been given to the coordination chemistry of gold(I)-thiolate complex so far. We report herein the structure and properties of two-coordinate aliphatic thiolate complex $[NEt_4][Au(SAd)_2]$ (**1**) compared with those of the copper(I) and silver(I) derivatives (AdS^-: adamantyl thiolate anion).

In an analogous manner applied to the preparation of copper(I) thiolate complex $[NEt_4][Cu(SAd)_2]$ (**2**),[4] $[NEt_4][Au(SAd)_2]$ (**1**) was prepared by the reaction of a soluble salt $Au(I)Cl(SC_4H_8)$ with excess tetraethylammonium cation and excess NaSAd.[5]

The structure of the anion of the gold(I) complex **1** with its atomic numbering scheme is shown in Figure 1.[6] The coordination mode of the gold atom is linear as is expected for gold(I) complexes.[7] The anion has crystallographic C_2 symmetry. The S-Au-S' angle of 180.0° may be compared with those observed in the similar two-coordinate thiolate complexes, $[NEt_4][Au(S\text{-}C_6H_4\text{-}p\text{-}Cl)_2]$ (177°),[8] $[NH_4][Au(S\text{-}C_6H_2\text{-}2,4,6\text{-}iPr_3)_2]$(175.6(1)°),[9] $[PPh_4][Au(SC_6H_5)_2]$ (179.0(3)°),[10] and the clusters $Au_6(S\text{-}C_6H_2\text{-}2,4,6\text{-}iPr_3)_6$ (av. 176°),[9] $Au_4[SC(SiMe_3)_3]_4$(av. 178°).[11] Complex **1** is the first example of a two-coordinate aliphatic thiolate complex. The Au-S distance of 2.298(4) Å lies within the range (2.26 - 2.31 Å) observed in other gold(I) complexes with two thiolate donor.[8 - 11]

Surprisingly, the M-S distance of **1** (Au-S, 2.298(4) Å) is much smaller than that of silver(I) derivative $[NEt_4][Ag(SAd)_2]$ (**3**)[12] by 0.05 Å, namely between copper(I) derivative(2.147(4) Å) and silver(I) derivative(2.349(3) Å). It can be explained by "Lanthanide contraction". This phenomenon (only gold(I) and silver(I) derivatives) was reported by Schmidbaur and coworkers previously: $[Au(PMes_3)_2][BF_4]$($PMes_3$, trimesitylposphine) (Au-P, 2.353(1) Å) and $[Ag(PMes_3)_2][BF_4]$) (Ag-P, 2.441(1) Å).[13] To our knowledge, this is the first example of a comparison of M(I)-S(SAd) bond lengths in a series of complexes(Cu, Ag, and Au) involving the same ligands and counterions, the isomorphous crystal lattice, and the same experimental conditions. Selected crystal data of a series of $[NEt_4][M(SAd)_2]$ (**1** - **3**) are presented in Table 1.

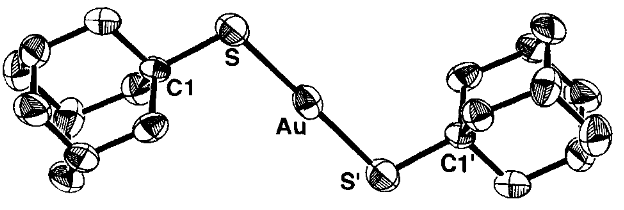

Figure 1. Molecular structure of the anion of **1** (ORTEP, 50 % parobability ellipsoids) with atomic numbering. Selected bond distances (Å) and angles (deg) are as follows. Au-S, 2.298(4); S-C1, 1.80(1); S-Au-S', 180.0; Au-S-C1, 106.0(4).

These differences reflect physical properties involving M-S stretching frequencies of far-IR and FT-Raman spectroscopy and MLCT (metal to ligand charge transfer) bands.

The M-S stretching frequencies are observed in low energy region, 50 - 500 cm^{-1}.[14] The higher wavenumber spectra of **1** could be assigned to internal vibrations of the thiolate group or to cation vibrations. The remaining bands are expected to arise from external bands. The vibrational spectra of **1** are similar to those of copper(I) derivative **2** and silver(I) one **3**, and can be assigned in the same way.[4] The very strong band at 317 cm^{-1} in far-IR spectrum can be assigned to ν_{asym}(Au-S) of the S-Au-S' group. By analogy with this result, the ν_{asym}(Au-Cl) in $[AuCl_2]^-$ occurs at 350 cm^{-1}.[15] This frequency was shifted to 333 cm^{-1} in copper(I) derivative **2** and to 313 cm^{-1} in silver(I) one **3**. The order of ν_{asym} (M-S) is as follows: Cu-S > Au-S > Ag-S.[16] This order is consistent with that of M-S distances. The Raman shift at 309 cm^{-1} is also assignable to ν_{sym}(Au-S).

Another example occurs in UV-vis spectrum. Complex **1** has characteristic absorption bands at 220 nm (ε, 33000 $M^{-1}cm^{-1}$) and 257 nm (ε, 15000 $M^{-1}cm^{-1}$). The latter band shifts to 253 nm (sh, ε, 8500 $M^{-1}cm^{-1}$) in the copper(I) analogue **2**[4] and 231 nm (ε, 34000 $M^{-1}cm^{-1}$) in silver(I) one **3**. Therefore, the absorption band at 257 nm is assigned to MLCT (two-coordinate

Table 1. Crystal Data for $[NEt_4][M(SAd)_2]$ with Au(**1**), Cu(**2**) and Ag(**3**) and Physical Properties

complex	**1**	**2**	**3**
space group	*Pbca*	*Pbca*	*Pbca*
a, Å	10.574(9)	10.681(2)	10.589(5)
b, Å	26.029(9)	25.524(3)	25.994(3)
c, Å	10.458(13)	10.516(1)	10.468(4)
v, Å^3	2878(4)	2867(1)	2881(1)
temperature, K	298	298	298
d (M-S), Å	2.298(4)	2.147(4)	2.349(3)
ν(M-S), cm^{-1}			
far-IR	317	333	313
FT-Raman	309	299	289
MLCT, nm	257	253	231

gold(I) to thiolate charge transfer) band. Because an aryl thiol has characteristic bands in UV region, these intense bands must obscure the assignment of MLCT bands. By the use of aliphatic thiolate gold(I) complex **1**, these MLCT bands can be distinguished clearly. Further research will focus on other useful methods for d^{10} metal complexes.

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5 Anal. Calcd for $C_{28}H_{50}NS_2Au$: C, 50.82; H, 7.62; N, 2.12; S, 9.69. Found : C, 50.75; H, 7.46; N, 2.50; S, 9.13 IR (KBr, cm^{-1}) : 2975, 2897, 2843, 1485, 1476, 1447, 1437, 1390, 1340, 1295, 1173, 1041, 999, 786, 686. ^{1}H-NMR (($(CD_3)_2CO$, 200 MHz): δ 1.41 (tt, $J_{N\text{-}H}$ = 2 Hz and $J_{H\text{-}H}$ = 7 Hz, 12 H, NCH_2CH_3), 1.60 (br, 12H, Ad), 1.88 (br, 6H, Ad), 2.00 (br, 12H, Ad), 3.52 (q, $J_{H\text{-}H}$ = 7 Hz, 8H, NCH_2CH_3). UV-vis (MeCN, r.t., nm (cm$^{-1}\cdot$ M^{-1}): 220 (s, 28000), 257 (12000).

6 **1** (fw 661.80, at 298 K) crystallized in the orthorhombic space group *Pbca* with a = 10.574(9) Å, b = 26.029(9) Å, c = 10.458(13) Å, V = 2878(4) Å^3, and Z = 4. The initial positional parameter of the Au atom was determined by the direct method SAPI 91. Subsequent difference Fourier synthesis easily locates all non-hydrogen atoms, which were refined anisotropically by TEXSAN. The hydrogen atoms were calculated and included in the final refinement. The high disorder of tetraethylammonium cation molecules was evident so was modeled with occupancies(0.5) for four methylene carbons (C111, C112. C211, and C212). The final cycle of full-matrix least-squares refinement was based on 1360 observed reflections ($I>3\sigma(I)$) with 136 variable parameters. The current R (R_w) factor is 4.85 (4.19)%.

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12 **3** (fw 572.70, at 298 K) crystallized in the orthorhombic space group *Pbca* with a = 10.589(5) Å, b = 25.994(3) Å, c = 10.468(4) Å, V = 2881(1) Å^3, and Z = 4. The final cycle of full-matrix least-squares refinement was based on 1313 observed reflections ($I>3\sigma(I)$) with 136 variable parameters. The current R (R_w) factor is 6.03 (5.42)%.

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