The Crystal Structure of the Gold(III) Complex, Tribromo(dibenzyl sulfide)gold(III)

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Synopsis. The crystal structure of tribromo(dibenzyl sulfide) gold(III) has been determined. The crystal belongs to the triclinic system, with a=7.002(1), b=7.949(1), c=17.244(2) Å, α=88.83(1), β=79.52(1), and γ=66.35(1)°, with the space group $P\bar{1}$ and with Z=2. The complex has a square-planar coordination geometry with 3Br1S donor atoms. The bond lengths of the three Au-Br coordinations are in the range of 2.41—2.43 Å.

Since the gold complexes of dibenzyl sulfide (DBS) were first reported by Herrmann,[1] more than ten species of gold(I), gold(III), and mixed-valence gold(I)-gold(III) complexes have been synthesized and characterized.[2]

We have begun to study the structures and electronic states of a series of halogen-gold-DBS ternaly complexes, taking special interest in the coordination mode of the alkyl sulfide and the correlation between the structure and the valence of the gold ion.[3] However, the molecular structures of most of the gold-DBS complexes have not yet been revealed. Though detailed structural studies of the above compounds are much to be desired, the crystal structure determinations of only two DBS-gold(I) complexes have thus far been reported.[4]

In order to obtain details of the molecular structure and the coordination mode of DBS, we have in this study prepared good single crystals of the gold(III) compound, [$AuBr_3$(DBS)], and determined its molecular structure by the use of the X-ray diffraction method.

Experimental

The [$AuBr_3$(DBS)] was prepared by Brain's method.[2] The deep brown prismatic crystals were obtained by recrystallization from a 1,2-dibromoethane/diethyl ether solution (Found: C, 25.62; H, 2.10%) at ca. 5 °C. The intensity data were collected at room temperature with a Rigaku AFC-3 four-circle diffractometer using graphite monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). The unit cell parameters were determined from 47 reflections with $15<2\theta<30°$.

Crystal Data: $C_{14}H_{14}SBr_3Au$, M=651.0; triclinic; space group $P\bar{1}$; a=7.002(1), b=7.949(1), c=17.244(2) Å, α=88.83(1), β=79.52(1), γ=66.35(1)°, V=863.0(2) Å^3; D_m=2.47 (by floatation), D_c=2.51 g cm^{-3}; Z=2; μ=130 cm^{-1}; crystal size 0.1×0.2×0.2 mm^3. A total of 5039 reflections were collected by the ω scan ($2\theta\leqq30°$) and ω-2θ scan techniques ($30\leqq2\theta\leqq60°$), with a 2θ scan rate for 4° min^{-1}, and by monitoring 5 check reflections after each 50 measurements. The check reflections showed a max. 14.2% (on F_o) intensity drop during the course of the data collection. The intensity data were corrected for Lorents-polarization effects, decay, and absorption using 10 crystal faces.[5] 3866 independent reflections with $|F_o|\geqq3\sigma(|F_o|)$ were used for the structure analysis. The structure was solved by the direct method, and was then refined by the full-matrix least-squares procedure. Anisotropic thermal parameters were adopted for the non-hydrogen atoms. Fourteen hydrogens were placed at the calculated positions and were included in the last cycle of the final refinements with B_{eq}=8.0 Å^2 (fix). The final $R_1(=\sum||F_o|-|F_c||/\sum|F_o|)$ and $R_2(=\{\sum||F_o|-|F_c||^2/\sum|F_o|^2\}^{1/2})$ values are 0.041 and 0.043, respectively. All the calculations were carried out on a FACOM M-340S computer at the NIRIM, using UNICS III computing systems.[6] The final atomic positional and isotropic thermal parameters of the non-hydrogen atoms are given in Table 1.††

Results and Discussion

An ORTEP drawing of the complex molecule is shown in Fig. 1. Table 1 lists the final atomic coordinates of the non-hydrogen atoms.

As is shown in Fig. 1, the Au atom is four-coordinated, with the square-planar coordination geometry normally observed in mononuclear Au(III) complexes. The square plane consists of three bromine atoms and the sulfur atom of DBS. The

Table 1. Atomic Positional(×10^4) and Isotropic Thermal Parameters for Non-Hydrogen Atoms, with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å$^{2a)}$
Au	−1222(1)	1470.7(5)	7517.0(2)	2.30
Br(1)	1981(2)	−1326(1)	7352(1)	4.10
Br(2)	−4390(2)	4285(2)	7578(1)	4.77
Br(3)	−3368(2)	−302(2)	7692(1)	4.40
S	985(4)	3068(3)	7448(1)	2.97
C(1)	360(19)	4676(14)	6657(6)	3.91
C(2)	1414(18)	3629(14)	5876(6)	3.77
C(3)	3458(21)	3495(19)	5531(8)	5.36
C(4)	4421(26)	2526(24)	4785(9)	6.84
C(5)	3376(31)	1755(23)	4399(9)	7.09
C(6)	1354(29)	1909(19)	4738(8)	6.05
C(7)	310(23)	2880(17)	5493(7)	5.05
C(8)	−211(18)	4712(13)	8329(6)	3.65
C(9)	−104(19)	3656(13)	9062(6)	3.68
C(10)	−1997(23)	3600(18)	9490(7)	5.21
C(11)	−1922(33)	2663(22)	10217(8)	7.05
C(12)	−27(36)	1854(19)	10471(9)	7.10
C(13)	1874(31)	1905(19)	10039(9)	6.79
C(14)	1786(22)	2821(16)	9321(7)	4.87

a) $B_{eq}=4/3\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\boldsymbol{a}_j$.

†† Lists of structure factors, the anisotropic thermal parameters, the coordinates of the hydrogen atoms, the bond distances and angles, and the results of the least-squares plane calculations are deposited at the office of the Chemical Society of Japan as Document No. 8775.

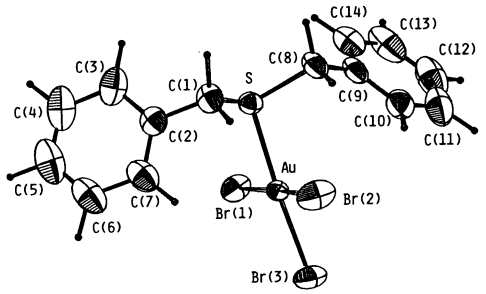

Fig. 1. ORTEP drawing of the molecule with atom numbering scheme for non-hydrogen atoms(thermal ellipsoids are drawn at 50% probability level). Hydrogen atoms are drawn at an arbitraty small size. Selected interatomic distances(l/Å) and angles(ϕ/°) around the coordination sphere of Au are: Au-Br(1) 2.418(1), Au-Br(2) 2.425(1), Au-Br(3) 2.419(2), Au-S 2.349(3), Br(1)-Au-Br(2) 175.78(5), Br(1)-Au-Br(3) 90.54(4), Br-(1)-Au-S 86.88(6), Br(2)-Au-Br(3) 90.21(5), Br(2)-Au-S 92.70(6), Br(3)-Au-S 174.78(7).

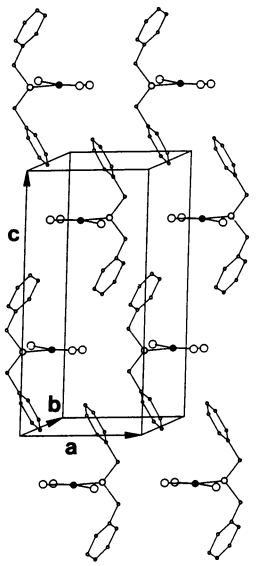

Fig. 2. Perspective view of the crystal structure.

deviations of the Au and donor atoms from the least-squares plane (through Br(1), Br(2), Br(3), and S) are less than 0.1 Å. The bond lengths of the three Au–Br coordinations are in the range from 2.418 to 2.425 Å, and Au–S is 2.349(3) Å. The values of the Au–Br bonds fall within the range observed for the previously reported gold(III) tribromide complexes (2.40—2.47 Å).[7] The Au–S bond length could not be compared with those of other sulfide-coordinated gold(III) complexes because of the lack of any structural study of similar complexes. The dihedral angles of coordination bonds across the Au atom are in the 86—93° range, deviating slightly from the ideal angle, 90°. These results indicate that the first coordination sphere of Au is little affected sterically by the bulky benzyl groups of DBS.

In the case of trihalogeno(phosphine)gold(III) complexes, which possess a coordination structure similar to that of [$AuBr_3$(DBS)], the Au–halogen bond trans to the Au–P bond is appreciably longer than the other two Au–halogen bonds (ca. 0.05 Å). This is due to the strong trans influence of the coordinated phosphine.[7] In the present complex, however, no such strong effect of the trans ligand DBS is observed on the Au–Br(3) bond. The above remarkable difference in the effect from the trans donor species, phosphine and sulfide, seems to reflect the order of the electronegativities of coorddinated sulfur and phosphorus atoms in each ligand (Phosphine$<Au^{3+}$ (2.7)[8]$<$DBS).

The crystal structure of [$AuBr_3$(DBS)] is shown in Fig. 2. The significant intermolecular distances less than 3.5 Å are: Br(1)–Br(2)(symmetry code: $x+1$, $y-1$,z; 3.460(2) Å), C(11)–C(12)($-x$,$-y$,$2-z$; 3.44(2) Å) and C(12)–C(12)($-x$,$-y$,$2-z$; 3.38(3) Å). In the crystal structure of the two-coordinated gold(I)–DBS complex, [AuBr(DBS)], the short intermolecular distance of Au^+–Au^+ (3.30 Å) is observed.[4] No such adjacency of gold atoms is observed in the crystal structure of [$AuBr_3$(DBS)](the shortest distance of Au^{3+}–Au^{3+} (x,y,$z+1$); 7.002(1) Å).

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