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

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Synopsis. The structure of the title complex has been determined. The crystal is orthorhombic, with the space group *Pnma*, $Z=4$, $a=13.331$ (2), $b=16.130$ (3), and $c=7.6949$ (9) Å. The complex has a square-planar coordination geometry. The Au and the 3Cl1S donor atoms are located on a crystallographic mirror plane. The length of the Au–Cl bond trans to the Au–S bond is slightly longer than those of the other two Au–Cl bonds.

Ever since two complexes consisting of halogen, gold, and dibenzyl sulfide (DBS) were first isolated in 1905,[1] many investigations for gold(I), gold(III), and mixed-valence gold(I)–gold(III) complexes of DBS have been undertaken in the fields of coordination chemistry and physical chemistry.[2–5] However, exact X-ray crystal structure analyses of these complexes, except for gold(I) complexes,[5] were not carried out until quite recently.

The author and collaborators have studied the DBS–gold complexes with interests in the coordination structures and a correlation between structures and physical properties. We have so far reported the structures of [$AuBr_3$(DBS)] and *catena*-[AuCl(DBS)]-[$AuCl_3$(DBS)],[6,7] and the optical properties of DBS–gold complexes.[8] In this study, the structure of the title complex, [$AuCl_3$(DBS)], has been determined by a single crystal X-ray diffraction method in order to reveal details of the coordination structure. Its structural features are compared with those of related gold(III) complexes, mainly focusing on the coordination structure and the trans influence of DBS. Further characterization has been carried out in terms of the electronic spectra.

Experimental

[$AuCl_3$(DBS)] was prepared according to the Ray and Sen's procedure,[2] using $HAuCl_4 \cdot 4H_2O$ as a metal source instead of $AuCl_3$. A yellow prismatic crystal was obtained by recrystallization from a benzene-toluene (95/5 v/v) solution at ca. 5 °C (Found: C, 32.70; H, 2.73%). The electronic spectra were recorded on a Shimadzu MPS-2000 spectrophotometer (280—800 nm). The intensity data were collected at 295±1 K, by use of an Enraf-Nonius CAD4 automated four-circle X-ray diffractometer (graphite monochromated Mo K_α radiation, $\lambda=0.71073$ Å). All the computations were carried out on a DEC MicroVAXII, using the programs in CAD4 Structure Determination Package (SDP, 4th ed). The unit cell parameters were determined from 25 reflections with $22<2\theta<31$ °.

Crystal Data: $C_{14}H_{14}SCl_3Au$; $M=517.7$; orthorhombic; *Pnma*; $a=13.331(2)$, $b=16.130(3)$, and $c=7.6949(9)$ Å; $V=1654.6(8)$ Å^3; $D_m=2.1$ (by floatation), $D_c=2.08$ g cm^{-3}; $Z=4$; $\mu=94.7$ cm^{-1}; crystal size=0.30×0.25×0.28 mm^3.

A total of 2191 reflections were collected (scan type: ω–2θ; scan range: $2\leqq 2\theta \leqq 55°$; scan width: $\Delta\omega=(0.8+0.35 \tan\theta)°$; ω scan rates: 2.75° min^{-1} for a preliminary scan, variable (1.18—2.75° min^{-1}, depending on intensity) for the final scan). The intensities of five standard reflections monitored at 90 min intervals showed good stability during data collection. The intensity data were corrected for the Lorentz-polarization effects, and for the absorption based on Ψ scans of the nine reflections ($80<\chi<88°$).[9] The structure was solved by the direct method (MULTAN in SDP) using 1314 independent reflections with $I>3\sigma(I)$, and was then refined by the full-matrix least-squares procedure. Anisotropic thermal parameters were adopted for non-hydrogen atoms. Hydrogen atoms were not included in the structure calculations. The final R values were $R=\sum||F_o|-|F_c||/\sum|F_o|=0.0319$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0.0435$, where the weighting scheme is $w=1/\sigma^2(|F_o|)=4|F_o|^2/\{\sigma(I)^2+(0.04|F_o|^2)^2\}$.

Results and Discussion

The final atomic coordinates are given in Table 1.[#] Figure 1 shows the molecular structure of [$AuCl_3$(DBS)]. The complex has a square-planar coordination geometry ordinarily observed in mononuclear four-coordinated Au(III) complexes. The Au and the four donor atoms form a perfectly planar coordination sphere since these atoms lie on the crystallographic mirror plane. The four bond angles subtended at the Au (86—92°) are slightly deviated from the ideal angle of 90°. These slight deviations are suggestive of very weak steric constraints of the bulky ligand, DBS. The lengths of three Au–Cl coordination bonds (2.27—2.29 Å) fall within the range observed for $[AuCl_4]^-$ (2.27—2.30 Å),[4,10] and for Au(III) complexes with 3Cl1L donor atom set (2.27—2.35 Å, L=P of triphenylphosphine,[11] and L=S of thianthrene[12]).

Table 1. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2 a)
Au	2915.4(3)	2500	3738.1(3)	3.572(7)
Cl(1)	4019(3)	2500	5988(4)	6.71(9)
Cl(2)	1597(3)	2500	5640(5)	6.89(8)
Cl(3)	1841(2)	2500	1447(4)	6.48(8)
S	4298(2)	2500	1927(3)	3.80(5)
C(1)	4100(7)	3367(5)	436(7)	4.7(2)
C(2)	4137(6)	4171(5)	1417(7)	4.3(1)
C(3)	5037(7)	4479(5)	2045(4)	5.1(2)
C(4)	5056(8)	5246(6)	2890(5)	5.6(2)
C(5)	4202(8)	5701(6)	3097(8)	6.1(2)
C(6)	3275(8)	5394(6)	2552(15)	6.8(2)
C(7)	3228(7)	4608(7)	1670(11)	5.6(2)

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

[#] Lists of structure factors, anisotropic thermal parameters, bond distances and angles, and the results of least-squares plane calculations are deposited as Document No. 8951 at the Office of the Editor of Bull. Chem. Soc. Jpn.

The Au–S bond length (2.310(3) Å) falls within the range observed for sulfur-coordinated square-planar Au(III) complexes (2.28—2.36 Å).[12,13] The molecular structure of [AuCl$_3$(DBS)] resembles the tribromo complex, [AuBr$_3$(DBS)].[6] The lengths of the three Au–Cl bonds are shorter than those of the corresponding Au–Br bonds in [AuBr$_3$(DBS)] (2.41—2.43 Å). A difference between Au–Cl and Au–Br distances (average 0.14 Å) is expected from a difference in the effective ionic radius between Cl^- (1.67 Å) and Br^- (1.82 Å), and also from that in the covalent radius between Cl (0.99 Å) and Br (1.14 Å).[14] Figure 2 shows the crystal structure of [AuCl$_3$(DBS)]. A significant intermolecular contact smaller than 3.5 Å is observed only between the phenyl rings of adjacent molecules (C(4)–C(4)' (symmetry code: $1-x,1-y,1-z$), 3.347(6) Å). The crystals of [AuCl$_3$(DBS)] and of [AuBr$_3$(DBS)] (triclinic) are not isomorphous. No close contact among chlorides less than the sum of the van der Waals radii is observed in the present crystal, in contrast to the close Br–Br contact (3.46 Å) observed in the [AuBr$_3$(DBS)] crystal.[6] The shortest Cl–Cl distance is 4.203(5) Å of the Cl(1)–Cl (3)″ ($1/2+x$, $1/2-y$ or $y,1/2-z$).

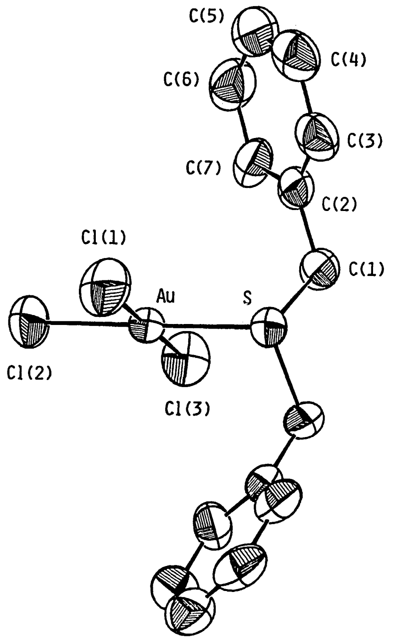

Fig. 1. ORTEP drawing of the [AuCl$_3$(DBS)] molecule with atom numbering scheme (thermal ellipsoids are drawn at 50% probability level). Selected interatomic distances (l/Å) and angles (ϕ/°) around the coordination sphere of the gold(III) ion are: Au–Cl(1) 2.272(3), Au–Cl(2) 2.287(4), Au–Cl(3) 2.272(3), Au–S 2.310(3) Å; Cl(1)–Au–Cl(2) 90.6(1), Cl(1)–Au–Cl(3) 178.8(1), Cl(1)–Au–S 86.7(2), Cl(2)–Au–Cl(3) 90.7(1), Cl(2)–Au–S 177.4(1), Cl(3)–Au–S 92.0(1)°.

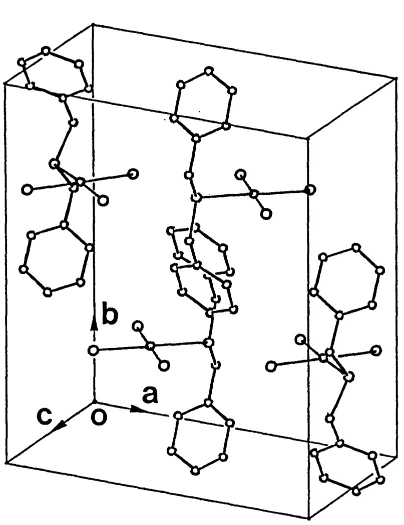

Fig. 2. Perspective view of the molecular arrangement in the unit cell.

In the molecules of square-planar trihalogeno(phosphine)gold(III) complexes, [AuCl$_3$(PPh$_3$)],[11] and [AuBr$_3${P(C$_2$H$_5$)$_3$}],[15] the Au–halogen bond trans to the Au–P bond is appreciably longer than the other two Au–halogen bonds. This lengthening is attributed to the electrostatic trans influence of phosphines.[11,15,16] A similar pattern is observed in the [AuCl$_3$(DBS)] molecule, i.e., the Au–Cl(2) bond (2.287(4) Å) trans to the Au–S is longer than the other two Au–Cl bonds (both 2.272(3) Å). It should be noted here that no such distinct lengthening is observed in the [AuBr$_3$(DBS)] molecule,[6] and that a difference in the length between the Au–Cl(2) bond and the other two Au–Cl bonds (0.01—0.02 Å, evaluated by considering their standard deviations) is smaller than those of the phosphine complexes (0.05—0.09 Å).[11,15] These facts indicate that the trans influence of DBS is very weak compared with the phosphine ligands in square-planar trihalogenogold(III) complexes. Taking into account the fact that the Au–S bond of the present complex is shorter than that in [AuBr$_3$(DBS)] (2.349(3) Å), the relative strength of the trans influence of ligands seem to be in the order, $Cl^- < Br^- \approx$ DBS, for the trihalogeno(DBS)gold(III) complexes.

The electronic spectra of [AuCl$_3$(DBS)] in CHCl$_3$ and Nujol mull are shown in Fig. 3. The solution and solid spectra show a single broad absorption band, with the absorption maxima at 29600 (ε=4860 mol^{-1} dm^3 cm^{-1})

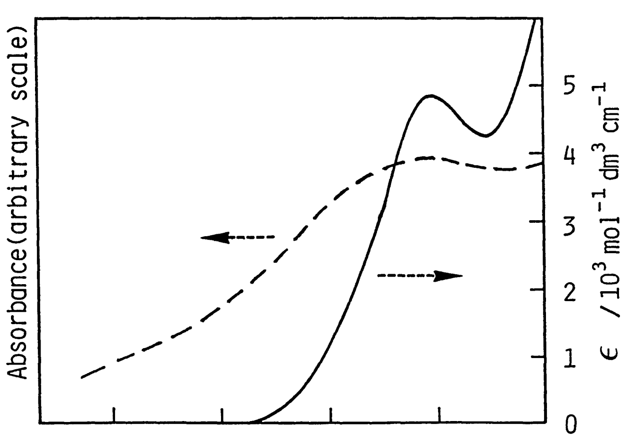

Fig. 3. Electronic spectra of [AuCl$_3$(DBS)].
———: CHCl$_3$ solution (5×10^{-4} mol dm^{-3}),
— — —: Nujol mull.

and 29400 cm^{-1}, respectively. This intense and broad band is attributable to a charge transfer interaction between Au^{3+} and ligands.[17] The d–d bands are presumably hidden in this intense band.

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