

Letters to the Editor

Synthesis and structure of the first dinuclear gold complex with the Au—Au bond containing no bridging ligands*

S. A. Yurin,^{a*} D. A. Lemenovskii,^a K. I. Grandberg,^a I. G. Il'ina,^a and L. G. Kuz'mina^b

^aDepartment of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory, 119992 Moscow, Russian Federation.

Fax: +7 (095) 932 8846. E-mail: YSA@yandex.ru

^bN. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation

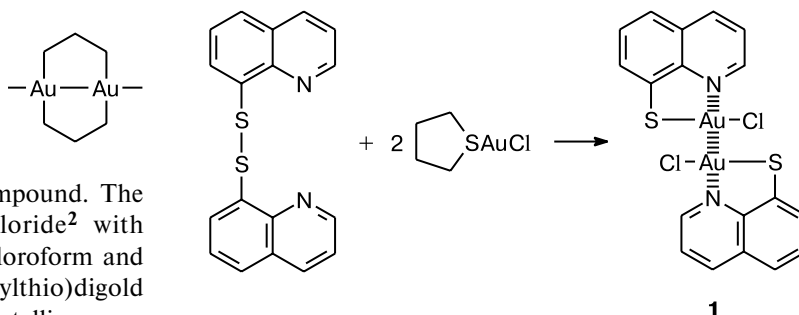
Analysis of the published data demonstrated that the oxidation state +2 is very rare for gold. It was established that gold(II) compounds are formed as intermediates in redox reactions involving complexes of gold in stable oxidation states, viz., gold(I) and gold(III). Divalent gold compounds synthesized earlier are unstable,¹ except for compounds in which two Au atoms are not only involved in the Au—Au bond but are also linked via a pair of bridging ligands (for example, diphosphine ligands).

We prepared a stable divalent gold compound. The reaction of tetrahydrothiophenegold chloride² with di(8-quinolyl) disulfide in a mixture of chloroform and dichloromethane afforded bis(quinolin-8-ylthio)digold dichloride (**1**) as an air-stable dark-brown crystalline compound. Complex **1** melts with decomposition at 230 °C and is very poorly soluble in all organic solvents. The latter fact did not allow us to study **1** by NMR spectroscopy.

* Materials were presented at the Mark Vol'pin Memorial International Symposium "Modern Trends in Organometallic and Catalytic Chemistry" dedicated to his 80th anniversary.

Found (%): C, 27.50; H, 1.56; Au, 50.16; Cl, 9.04. C₉H₆AuCl₂NS. Calculated (%): C, 27.53; H, 1.54; Au, 50.17; Cl, 9.03.

The ESR study demonstrated that the reaction product is diamagnetic.



According to the results of X-ray diffraction study, complex **1** has a dinuclear structure. In the crystal, molecules **1** occupy special positions on twofold symmetry axes (molecular symmetry of the complex is C₂). The Au atoms have a planar-square coordination formed by the Au—Cl bonds as well as by the Au—S and Au—N bonds of the mercaptoquinoline ligand. The Au—N bond is in a

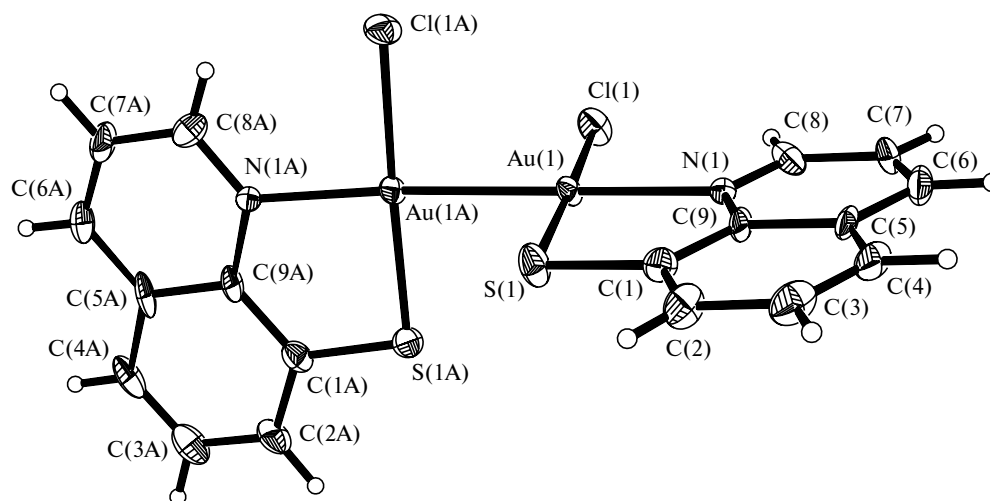


Fig. 1. Structure of complex 1.

trans position with respect to the Au—Au bond (Fig. 1). Therefore, although complex 1 contains formally divalent gold, the coordination environment of each metal atom in this complex is typical of Au^{III}.

X-ray diffraction study was carried out on a Bruker SMART CCD diffractometer. The crystals of [C₉H₆AuClNS]₂ are monoclinic, space group *C2/c*, *a* = 13.8678(4) Å, *b* = 10.3657(4) Å, *c* = 13.4957(5) Å, α = 90.000(2)°, β = 96.259(1)°, γ = 90.000(2)°, *V* = 1928.4(1) Å³, ρ = 2.705 g cm⁻³, *Z* = 4, *T* = 153.0(2) K, *R*₁ = 0.0445, *wR*₂ = 0.1064.

The pairs of the Au(1)—Cl(1) and Au(1a)—Cl(1a), Au(1)—S(1) and Au(1a)—S(1a), Au(1)—N(1) and Au(1a)—N(1a) bonds have equal lengths (2.328(2), 2.265(2), and 2.186(8) Å, respectively), which is consistent with the published data³ on gold compounds in different oxidation states.

The Au—Au bond lengths in Au^{II} complexes vary in the range of 2.52—2.69 Å. The Au—Au bond length in the complex under consideration (2.5355(5) Å) is close to the

lower limit of this range. Apparently, this short Au—Au bond additionally stabilizes the complex. The structure of the complex under consideration is the only example of complexes with formally divalent gold without bridging ligands.

Based on the geometry of the complex, the hybridization of the gold atoms can be represented as sp_xd_{x²-y²}.

References

1. R. J. Puddephatt, *The Chemistry of Gold*, Elsevier Scientific Publishing Company, Oxford, 1987, 71.
2. C. K. Mirabeli, R. K. Johnson, and D. T. Hill, *J. Med. Chem.*, 1986, **29**, 218.
3. F. H. Allen and O. Kennard, *Chem. Design Autom. News*, 1993, **8**, 1.

Received April 10, 2003;
in revised form September 8, 2003