

The Formation of a Complex of Bivalent Gold by an Electron Exchange Reaction between Gold(I) and Gold(III)

By JAMES H. WATERS,*† TIMOTHY J. BERGENDAHL, and SANDRA ROSCOE LEWIS

(Department of Chemistry, University of Vermont, Burlington, Vermont 05401)

Summary The first example of the reaction $\text{gold(I)} + \text{gold(III)} \rightarrow 2\text{gold(II)}$ has been detected using the *cis*-1,2-dicyanoethylenedithiolate ligand.

DURING the last decade three complexes containing gold(II) were isolated and characterized.¹⁻³ Two of these compounds^{2,3} were prepared by reduction of gold(III) and the other¹ by oxidation of gold(I).

We now report that when equimolar amounts of gold(I) and gold(III) are treated with the ligand *cis*-1,2-dicyanoethylenedithiolate (mnt^{2-}) the gold(II) complex anion $\text{Au}(\text{mnt})_2^{2-}$ is formed. Starting materials were the gold(I)-gold(III) mixed-valence compounds $(\text{PhCH}_2)_2\text{SAuX} \cdot (\text{PhCH}_2)_2\text{SAuX}_3$ ($\text{X} = \text{Cl}^4$ or Br^5), tetra-*n*-butylammonium bromide, and the lithium salt of the *mnt* ligand. The latter was prepared in solution by cleavage of 4,5-dicyano-1,3-dithiol-2-one^{6,7} with lithium methoxide. The mole ratio of reactants was $\text{Au}:\text{mnt}:\text{Bu}^n_4\text{N} = 1:2:2$, and the solvent was carefully degassed 90% tetrahydrofuran-10% methanol. The light green precipitated product was shown by its elemental analysis (C, H, N, S), u.v.-visible spectrum, and e.s.r. g and $\langle a \rangle$ values to be identical with the previously reported complex $(\text{Bu}^n_4\text{N})_2\text{Au}(\text{mnt})_2$ prepared by borohydride reduction of the gold(III) complex of the same ligand.²

Yields of the gold(II) *mnt* complex are more consistently higher by the new procedure than by the borohydride reduction of $\text{Au}(\text{mnt})_2^-$, and the gold(I)-gold(III) reaction represents the method of choice for preparation of $(\text{Bu}^n_4\text{N})_2\text{Au}(\text{mnt})_2$.

As well as the *mnt* complex the phthalocyanine complex,¹ AuPc , and the π -carbollyl complex,³ $(\text{Et}_4\text{N})_2[\pi-(3)-1,2-\text{B}_9\text{C}_2\text{H}_{11}]_2\text{Au}$, have been isolated. Attempts to prepare these complexes by the analogous reaction of dilithium phthalocyanine or of $\text{Li}(\text{Bu}^n_4)_2\text{B}_9\text{C}_2\text{H}_{11}$ with the gold(I)-gold(III) mixed-valence complexes were unsuccessful.

E.s.r. survey experiments with other unsaturated sulphur-donor ligands were carried out in an effort to find further instances of the reaction $\text{Au}^I + \text{Au}^{III} \rightarrow 2\text{Au}^{II}$. Treatment of $(\text{PhCH}_2)_2\text{SAuCl} \cdot (\text{PhCH}_2)_2\text{SAuCl}_3$ in degassed tetrahydrofuran-methanol solution with toluene-3,4-dithiolate, 2,2-dicyanoethylene-1,1-dithiolate (*iso*-*mnt*), tetrachlorobenzene-1,2-dithiolate, *cis*-1,2-di(methoxycarbonyl)ethylenedithiolate,⁸ or cyanodithioformate gave homogeneous solutions that showed no e.s.r. signal. Thus, the reaction seems to be specific for the *mnt* ligand.

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† Present address: Missisquoi Valley Union Seven High School, Highgate, Vermont 05459.

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