A powerful new oxidation agent towards metallic gold powder: *N*,*N′*-dimethylperhydrodiazepine-2,3-dithione (D) bis(diiodine). Synthesis and X-ray structure of $[AuDI_2]I_3$

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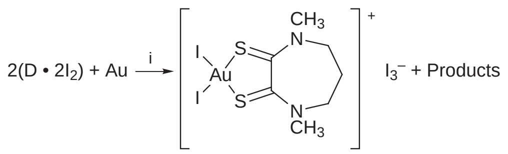
The oxidation of gold powder by a new safe and powerful oxidising reagent, the bis-diiodine adduct of *N*,*N′*-dimethylperhydrodiazepine-2,3-dithione (D), to produce $[AuI_2D]I_3$ under ambient conditions is described.

The potential of dihalogen or interhalogen adducts as new oxidising reagents towards elemental metals has been pointed out in recent years by the pioneering work of the McAuliffe group.[1] The used adducts were mainly halogeno-phosphoranes and -thioethers and a variety of complexes with unusual features (for stoichiometries, oxidation numbers and geometries) have been obtained. In particular in the reaction of $Me_3As{\cdot}I_2$ with the noble metal gold, the square-planar $[AuI_3\text{-}(Me_3As)]$ complex was obtained, while $[AuI_3(Me_3P)_2]$, where gold(III) shows a trigonal-bipyramidal geometry, was produced using $Me_3P{\cdot}I_2$.[2] The importance of these results, apart from their intrinsic interest in the field of inorganic chemistry, lies in the new perspectives opened by these reaction routes in many applications, such as in the recovery of noble metals from exhausted catalysts or in the metal refining industry. In the case of gold, treatments with cyanide are still in use.† The desirable reagents should fulfill the following requirements: they should be inexpensive, easy to handle, non polluting and hopefully also selective. Moreover, it is preferable that they react rapidly.

Based on our extensive past experience in the area of the dihalogen adducts of sulfur and selenium-rich donors, we are now investigating the above mentioned metal activation reaction using the adducts of polyfunctional thione donors.[3] Our working hypothesis is that the proper choice of polyfunctional donors, which can favour the preferred geometry required by the metal undergoing oxidation and give chelation, will add a favourable condition to the spontaneity and selectivity of the oxidation reaction.

Here we present the results obtained using the bis-diiodine adduct of *N*,*N′*-dimethylperhydrodiazepine-2,3-dithione[4] towards gold. This ligand is a cyclic dithio-oxamide where the two vicinal thioamido groups are suitable to accommodate the square-planar geometry demanded by Au^{III}. The adduct was prepared by mixing the donor and diiodine in a 1 : 2 molar ratio in $CHCl_3$ at room temperature. The orange-brown shiny crystals obtained by slow evaporation were characterized as $D{\cdot}2I_2$. The presence of a strong Raman peak at 146 cm^{-1} assignable to ν(I–I) suggests that the interaction strength in the adduct is medium–strong.[5,6]

The reaction of $D{\cdot}2I_2$ with gold powder is given in Scheme 1. The reaction is performed under mild conditions and without any protection from the air and/or moisture. The solution of the adduct turns from red-orange to red-brown on addition of the metal and after a relatively short time the gold powder disappears. This solution is allowed to stand and the obtained solid is recrystallized from THF–Et_2O giving well-shaped crystals of $[AuDI_2]I_3$. The molecular structure of the cation of $[AuDI_2]I_3$[7] is shown in Fig. 1. The gold atom has an approximately square-planar configuration [max. dev. −0.037(4) Å for S(1)]. *N*,*N′*-Dimethylperhydrodiazepine-2,3-dithione acts as an *S*,*S*-chelating ligand, and bond distances show that electron delocalization does not involve C(1)–C(2).



Scheme 1 i, THF, room temperature, 30 min to dissolve 14 mg of gold.

One of the iodides coordinated to the metal strongly interacts with the anion [I(1)···I(5) (x, $y - 1$, z) 3.582(2) Å], while the other participates in the formation of chains of monocationic complexes running parallel to *c* by interacting with a sulfur atom of another cation [I(2)···S(1) (x, y, $z - 1$) 3.790(5) Å].

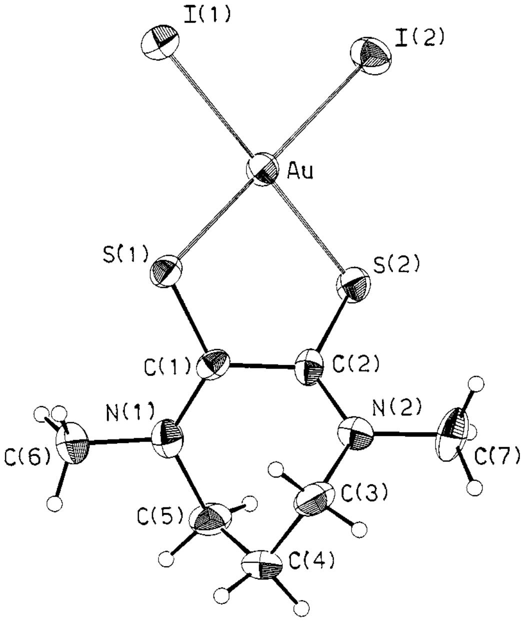


Fig. 1 Molecular structure of $[AuI_2(C_7H_{12}N_2S_2)]^+$. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: Au–I(1) 2.609(1), Au–I(2) 2.593(2), Au–S(1) 2.351(4), Au–S(2) 2.371(3), S(1)–C(1) 1.672(12), S(2)–C(2) 1.697(13), N(1)–C(1) 1.332(16), N(1)–C(5) 1.484(17), N(1)–C(6) 1.475(17), N(2)–C(2) 1.324(16), N(2)–C(3) 1.455(18), N(2)–C(7) 1.449(17), C(1)–C(2) 1.488(16), C(3)–C(4) 1.51(2), C(4)–C(5) 1.53(2). I(1)–Au–I(2) 92.24(4), I(1)–Au–S(1) 88.07(8), I(2)–Au–S(2) 88.71(9), S(1)–Au–S(2) 90.98(12), C(1)–S(1)–Au 98.3(4), C(2)–S(2)–Au 96.9(4).

The triiodide counterion is asymmetric and essentially linear: I(3)–I(4) 2.863(2), I(4)–I(5) 2.987(2) Å, I(3)–I(4)–I(5) 177.73(5)°. The Raman spectrum in the low frequency range shows peaks at 106s and 138m cm^{-1}, which are assigned to the symmetrical and antisymmetrical stretching of the triiodide units,[5a,b] and peaks at 153s, 166sh cm^{-1} which are likely to be related to the Au–I vibrations.

In conclusion a new oxidation reagent towards the noble metal gold has been synthesized. Since it reacts rapidly under ambient conditions in a one-step reaction and is scarcely polluting, inexpensive and easy to handle, this reagent can be used in practical applications. For the oxidation of noble metals, it represents a significant improvement over the previously reported reagents, $Me_3E\cdot I_2$ (E = P, As), which use polluting materials and are impractical since they require strictly anhydrous, anaerobic conditions and long reaction times.

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Notes and references

† The use of thiourea to accomplish gold dissolution from ore under oxidation conditions avoiding the cyanide process has been reported (see for example R. Schulze, *Ger. Offen. DE*. 3401961 (Cl. C22B3/00) 23 Aug. 1984).

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6 In fact the strong peak of uncoordinated diiodine (ν = 180 cm^{-1} in solid I_2 [d(I–I) = 2.715 Å, F. van Bolhuis, P. B. Koster and T. Migehelsen, *Acta Crystallogr*., 1967, **23**, 90]) is shifted to lower frequencies upon coordination as a consequence of the lowering of the force constant of the I–I vibration in a CT adduct.

7 Crystal data: $C_7H_{12}AuI_5N_2S_2$, M = 1019.77, crystal dimensions: 0.16 × 0.16 × 0.20 mm, triclinic, space group, $P\bar{1}$, a = 8.204(6), b = 15.994(5), c = 8.080(6) Å, α = 96.68(2), β = 112.40(2), γ = 92.20(2)°, V = 969.6(1.1) Å^3, Z = 2, D_c = 3.493 Mg m^{-3}, μ = 15.747 mm^{-1}, F(000) 888; 4249 reflections collected ($3.09 \leqslant \theta \leqslant 27.05°$) at T = 293(2) K, 4249 independent, R_1 = 0.0430 [$I > 2\sigma(I)$], wR_2 = 0.1172(all data), gof = 0.878 for 158 parameters, largest difference peak/hole 1.974/−1.286 e Å^{-3}, Data were collected from a Siemens AED diffractometer (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å) with θ–2θ scan technique. An empirical absorption correction[8] was applied (transmission coefficients: 0.8808, 1.2731). The structure was solved by direct methods using SIR92[9] and refined by full-matrix least-squares against F^2 (SHELXL-97[10]). Anisotropic refinement of all non-H atoms. R values $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

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