Dalton Transactions

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Gold oxidative dissolution by (thioamide)–I_2 adducts†

Cite this: *Dalton Trans.*, 2013, **42**, 492

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Received 14th August 2012,
Accepted 4th October 2012

DOI: 10.1039/c2dt31855e

www.rsc.org/dalton

Elemental gold powder is easily oxidised under mild reaction conditions with 1 : 1 I_2-adducts of the thioamides 3-methyl-benzothiazole-2-thione (mbtt) and 1-methyl-1*H*-benzimidazole-2(3*H*)-thione (mbit) with separation of the ionic complexes $[Au^I(mbtt)_2]I_3$ (**1**) and $[(mtbiH)_2](AuI_4)I_3$ (**2**) [mtbiH = the imido protonated form of 2-(methylthio)benzimidazole] (gold oxidation yield >78% and 45%, respectively). The X-ray crystal structure of **1** shows the Au(I) centre linearly bound by two neutral ligands *via* the sulphur atom, whereas the X-ray crystal structure of **2** shows the Au(III) centre surrounded by four iodides in a square-planar arrangement. The oxidising/complexing properties of the mbtt·I_2 and mbit·I_2 adducts were interpreted considering the S-donor to I_2 interaction that leads to a charge separation between the I_b and I_t iodine atoms in the fragment S–I_b–I_t. The oxidation of gold in a non-aqueous solvent by thioamide–I_2 adducts could be a promising alternative process to the numerous hydrometallurgical ones for the recovery of gold from secondary sources.

Introduction

The use of iodine or inter-halogen charge-transfer adducts of sulphur donor molecules[1a] (DS···IX, X = I, Br) as oxidising/complexing agents towards zero-valent metals has attracted some interest in recent years because of their possible applications in the recovery of precious metals from waste industrial materials, in the recovery of toxic metals for the environment,[2] and in nanotechnology.

An interesting aspect offered by this synthetic procedure is related to the possibility of dissolving elemental metals in non-aqueous solvents using mild reaction conditions through a one-step reaction. Notwithstanding the great number of iodine adducts with ligands containing sulphur donors synthesised to date,[1a] only a few of them have been shown to be active reagents in the oxidative dissolution of metals of low and high standard reduction potential, as summarised in Table 1.

Previous studies on the general reaction (1) carried out on a wide selection of S-donors (DS) and metals (M^0) have allowed us to understand a dual role for the donor. In fact, in addition to polarising the bound I_2 molecule, DS also acts as a good coordinating agent toward the oxidised metal ion. Moreover, we have identified some factors that limit the success of reaction (1).

$$DS \cdot I_2 + M^0 \xrightarrow[1-14\ \text{days/r.t.}]{Et_2O\ \text{or}\ CH_2Cl_2} \text{products} \qquad (1)$$

Firstly, the DS·I_2 adduct can be inherently unstable over time, causing the oxidation of the donor and the formation of (poly)iodides; secondly, the oxidation/complexation of metals whose ions are "hard" is not observed under the experimental conditions outlined in eqn (1) since the "soft" S-donor atom is intrinsically a poor coordinating agent towards these ions; thirdly, the oxidation of the metal may occur with the formation of oily compounds; in this case, changing the solvent or varying the DS·I_2 to M^0 molar ratio can often favour the formation of solid compounds; lastly, if the adduct DS·I_2 is in equilibrium with species DS and I_2, due to a low value of the constant formation of the adduct (K_f),[1b] the outcome of reaction (1) becomes very unpredictable since the donor DS and I_2 can react with the oxidised/complexed metal. Recovery of gold from secondary sources has become an important subject not only from the point of monetary and increasing demand, but also from waste treatment management.[15]

An analysis of the data reported in Table 1 shows that gold dissolution was achieved by employing the I_2-adduct of the chelating S,S′-donors Me_2dazdt in THF and $HN(SPPh_2)_2$ in Et_2O with the synthesis of the square planar Au(III) complexes $[Au(Me_2dazdt)I_2]I_3$ and $[Au(N(SPPh_2)_2)I_2]$, respectively.[2a,9]

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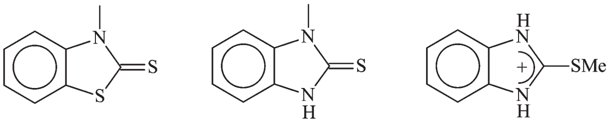
† Electronic supplementary information (ESI) available: Chemical structures of the compounds discussed in this paper (Fig. S1); Packing view of $[(mtbiH)_2](AuI_4)I_3$ (Fig. S2). ^{13}C NMR data of complex **1** (Table S1). CCDC 892460 and 892461. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31855e

Table 1 Structurally characterised metal complexes obtained by using IX-adducts (X = I, Br) of S-donor molecules as oxidising reagents towards metal powders and liquid mercury

Adduct[a]	Metal	Solvent	Main product/s	Complex geometry	Ref.
$\mathrm{bmitm{\cdot}2I_2}$	Sn	$\mathrm{Et_2O}$	$\mathrm{[Sn(bmitm)_2I_2](I_3)_2{\cdot}2/3I_2}$	Octahedral	3
$\mathrm{Me_2dazdt{\cdot}2I_2}$	Au	THF	$\mathrm{[Au(Me_2dazdt)I_2]I_3}$	Square planar	2*a*
$\mathrm{Me_2dazdt{\cdot}2IBr}$	Au	THF	$\mathrm{[Au(Me_2dazdt)Br_2]IBr_2}$	Square planar	4
$\mathrm{Me_2dazdt{\cdot}2I_2}$	Hg	THF	$\mathrm{[Hg(Me_2dazdt)I_2]}$	Tetrahedral	2*b*
$\mathrm{Me_2dazdt{\cdot}2I_2}$	Pd	THF	$\mathrm{[Pd(Me_2dazdt)_2](I_3)_2}$	Square planar	5
$\mathrm{HN(SPPh_2)_2{\cdot}I_2}$	Sb	$\mathrm{Et_2O}$	$\mathrm{[(N(SPPh_2)_2)Sb(\mu\text{-}S)(\mu\text{-}I)_2Sb(N(SPPh_2)_2)]}$	Octahedral	6
$\mathrm{HN(SPPh_2)_2{\cdot}I_2}$	Co	$\mathrm{Et_2O}$	$\mathrm{[Co(N(SPPh_2)_2)_2]}$	Tetrahedral	7
$\mathrm{HN(SPPh_2)_2{\cdot}I_2}$	Cu	$\mathrm{Et_2O}$	$\mathrm{[Cu(HN(SPPh_2)_2)_2]I_3{\cdot}MeCN}$	Tetrahedral	8
			$\mathrm{[Cu_4(N(SPPh_2)_2)_3]I_3}$	$\mathrm{Cu_4S_6}$ core	8
$\mathrm{HN(SPPh_2)_2{\cdot}I_2}$	Au	$\mathrm{Et_2O}$	$\mathrm{[Au(N(SPPh_2)_2)I_2]}$	Square planar	9
$\mathrm{HN(SPPh_2)_2{\cdot}I_2}$	In	$\mathrm{Et_2O}$	$\mathrm{[In(N(SPPh_2)_2)I_2]}$	Tetrahedral	10
$\mathrm{HN(SPPh_2)_2{\cdot}I_2}$	Hg	$\mathrm{Et_2O}$	$\mathrm{[Hg(HN(SPPh_2)_2)I_2]}$	Tetrahedral	11
			$\mathrm{[Hg(N(SPPh_2)_2)_2]}$	Tetrahedral	11
$\mathrm{HN(SPPh_2)_2{\cdot}I_2}$	Pd	$\mathrm{Et_2O}$	$\mathrm{[Pd(HN(SPPh_2)_2)I_2]}$	Square planar	12
			$\mathrm{[Pd(N(SPPh_2)_2)_2]}$	Square planar	12
$\mathrm{HN(SPPh_2)(OPPh_2){\cdot}I_2}$	Co	$\mathrm{Et_2O}$	$\mathrm{[Co(\{HN(SPPh_2)(OPPh_2)\}_2I_2]}$	Tetrahedral	13
			$\mathrm{[Co(N(SPPh_2)(OPPh_2))_2]}$	Tetrahedral	13
$\mathrm{MeImSH{\cdot}I_2}$	Hg	$\mathrm{CH_2Cl_2}$	$\mathrm{[Hg_2I_4(MeImSH)_2]}$	Tetrahedral	14
$\mathrm{PTU{\cdot}I_2}$	Hg	$\mathrm{CH_2Cl_2}$	$\mathrm{[Hg(PTU)_2I_2{\cdot}HgI_2]}$	Tetrahedral	14

[a] bmitm = 1,1′-bis(3-methyl-4-imidazoline-2-thione)methane; $\mathrm{Me_2dazdt}$ = *N*,*N*′-dimethylperhydro-1,4-diazepine-2,3-dithione; $\mathrm{HN(SPPh_2)_2}$ = tetraphenyldithioimidodiphosphine; $\mathrm{HN(SPPh_2)(OPPh_2)}$ = tetraphenylthiooxoimidodiphosphine; MeImSH = methimazole, 1-methyl-3*H*-imidazole-2-thione; PTU = propylthiouracil, 6-propyl-2-sulfanylpyrimidin-4-one. See Fig. S1† for the chemical structure of donors.



mbtt mbit mtbiH

Fig. 1 Chemical structures of 3-methyl-benzothiazole-2-thione (mbtt), 1-methyl-1*H*-benzimidazole-2(3*H*)-thione (mbit), and the 2-methylthiobenzimidazolium cation (mtbiH).

Although these donors are very effective in stabilising the Au(III) oxidation state, they are unfortunately very expensive to synthesise, thereby preventing any practical use. In this context, we have exploited this synthetic route using the I_2-adducts of two thioamide donors easily available in large quantities, *i.e.* the 3-methyl-benzothiazole-2-thione[16a] (mbtt) and 1-methyl-1*H*-benzimidazole-2(3*H*)-thione[16b] (mbit) (Fig. 1). Both donors are promising reagents for reaction (1) since they form stable complexes with I_2 [K_f ($\mathrm{dm^3\ mol^{-1}}$) = 6.26×10^2 and 1.08×10^4, respectively, 25 °C, $\mathrm{CH_2Cl_2}$],[16c] and the thioamide sulphur atom has proven to be a good Lewis base donor in the synthesis of gold complexes.[17] mbtt and mbit feature a different heteroatom in the penta-atomic ring; in the latter donor, the presence of the imido group (NH) can favour the formation of hydrogen bond interactions.

This manuscript is concerned with the reactivity in diethyl ether at room temperature of I_2-adducts of mbtt and mbit with gold powder to test the oxidative process in a non-aqueous solvent according to reaction (1); based on the NBO charge distribution, we also provide an explanation on the oxidising properties of the mbtt·I_2 and mbit·I_2 adducts. The structures of the isolated ionic complexes $\mathrm{[Au^I(mbtt)_2]I_3}$ and $\mathrm{[(mtbiH)_2](Au^{III}I_4)I_3}$ [mtbiH = the imido protonated form of 2-(methylthio)benzimidazole, Fig. 1] were determined by single-crystal X-ray diffraction analysis.

Results and discussion

Synthesis and crystal structure determination of $\mathrm{[Au^I(mbtt)_2]I_3}$ and $\mathrm{[(mtbiH)_2](Au^{III}I_4)I_3}$

The adduct mbtt·I_2 and gold powder (2 : 1 molar ratio, 25 °C) were left to react for three days in anhydrous diethyl ether. In the course of the reaction, the initial dark red colour of the solution, typical of the n → σ* charge-transfer transition between the mbtt S-donor molecule and I_2, turned to pale brown and the compound $\mathrm{[Au(mbtt)_2]I_3}$ (**1**) was obtained in good yield (78%) as an air-stable dark red powder. No unreacted gold dust was recoverable from the reaction vessel, demonstrating the almost complete oxidation of the gold. Single crystals of $\mathrm{[Au(mbtt)_2]I_3}$ (**1**) suitable for X-ray crystallography were obtained by slow evaporation of a $\mathrm{CHCl_3}$–MeCN solution. The crystallographic data and selected bond lengths and angles are reported in Tables 2 and 3, respectively. Compound **1** consists of the gold(I) cationic unit $\mathrm{[Au(mbtt)_2]^+}$ having an asymmetric I_3^- as the counter ion (Fig. 2a). The Au^+ is located on a crystallographic mirror and the two mbtt ligands interact with the metal ion through the exocyclic sulphur atom S1. The Au–S and S–C distances are comparable with those found in analogous linear gold(I) cations like bis(1,3-thiazolidine-2-thione)gold(I) and bis(1-methylimidazolidine-2-thione)-gold(I).[18] Au–S bond lengths in the range 2.27–2.33 Å have been reported for analogous gold(I) complexes. The S1–Au–S1′ system is almost linear [175.9(1)°] as is the triiodide anion [179.45(6)°]. The gold atom of the $\mathrm{[Au(mbtt)_2]^+}$ cation displays two interactions with two different adjacent

Table 2 Crystallographic data and structure refinement details

Compound	$[Au^I(mbtt)_2]I_3$ (**1**)	$[(mbtiH)_2](Au^{III}I_4)I_3$ (**2**)
Formula	$C_{16}H_{14}AuI_3N_2S_4$	$C_{16}H_{18}AuI_7N_4S_2$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/m$ (no. 11)	$P2_1/n$ (no. 14)
M.W.	940.20	1415.73
a (Å)	7.315(1)	12.715(1)
b (Å)	18.345(2)	9.257(1)
c (Å)	9.067(1)	13.666(1)
β (°)	109.02(1)	107.36(1)
V (Å^3)	1150.3(2)	1535.3(2)
Z	2	2
D_c (Mg m^{-3})	2.174	3.062
μ (mm^{-1})	10.788	11.978
Measured reflections	11 715	14 539
Unique reflections, R_{int}	2737, 0.026	3037, 0.034
Observed reflections [$I > 2\sigma(I)$]	1728	2317
Min–max transmission factors	0.331, 1.000	0.468, 1.000
R [observed reflections]	0.0487	0.0385
wR_2 [all data]	0.1187	0.1315
S	0.842	1.044
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0400\,q)^2]$	$w = 1/[\sigma^2(F_o^2) + (0.0921q)^2]$
Min–max electron density residual (e Å^{-3})	−3.86–4.80	−2.32–2.49

Notes: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $q = [\max(0, F_o^2) + 2F_c^2]/3$; $S = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

Table 3 Selected interatomic distances (Å) and angles (°) for compounds **1** and **2**

$[Au^I(mbtt)_2]I_3$ (**1**)			
I1–I2	2.942(2)	I1–I2–I3	179.45(6)
I2–I3	2.839(2)	Au–S1–C1	104.8(3)
Au–S1	2.308(3)	S1–Au–S1′	175.9(1)
S1–C1	1.698(10)	S1–C1–S3	123.8(6)
S3–C1	1.712(9)	C1–S3–C2	91.6(5)
S3–C2	1.742(9)	C1–N1–C7	113.9(8)
N1–C1	1.343(12)	C1–N1–C8	123.2(9)
N1–C7	1.399(12)	C7–N1–C8	123.0(8)
N1–C8	1.464(12)	N1–C1–S1	123.9(7)
C2–C3	1.384(12)	N1–C1–S3	112.3(7)
C2–C7	1.396(13)	N1–C7–C2	112.5(8)
C3–C4	1.393(15)	C7–C2–S3	109.8(7)
C4–C5	1.393(16)		
C5–C6	1.367(16)		
C6–C7	1.402(13)		
Symmetry code: ′ = x, 3/2 − y, z			
$[(mbtiH)_2](Au^{III}I_4)I_3$ (**2**)			
I1–I2	2.8420(8)	I1–I2–I1′	180
Au–I3	2.6294(7)	I3–Au–I3′	180
Au–I4	2.6305(7)	I4–Au–I4″	180
S1–C7	1.707(9)	I3–Au–I4	89.37(2)
S1–C8	1.801(9)	I3–Au–I4″	90.63(2)
N1–C1	1.393(10)	C7–S1–C8	101.7(4)
N1–C7	1.342(10)	C7–N1–C1	110.1(6)
N2–C2	1.410(10)	C7–N2–C2	107.8(7)
N2–C7	1.348(10)	S1–C7–N1	129.6(6)
C1–C2	1.394(12)	S1–C7–N2	121.4(6)
		N1–C7–N2	109.1(8)
		C1–C2–N2	107.5(6)
		C2–C1–N1	105.5(6)
Hydrogen bonds			
N1–HN1 3.626(7)	HN1···I1 2.71(7)	N1–HN1···I1	157(5)
N2–HN2 3.599(7)	HN2···I1′ 2.75(7)	N2–HN2···I1′	155(6)
Symmetry code: ′ = 1 − x, 1 − y, 2 − z; ″ = −x, −y, −z.			

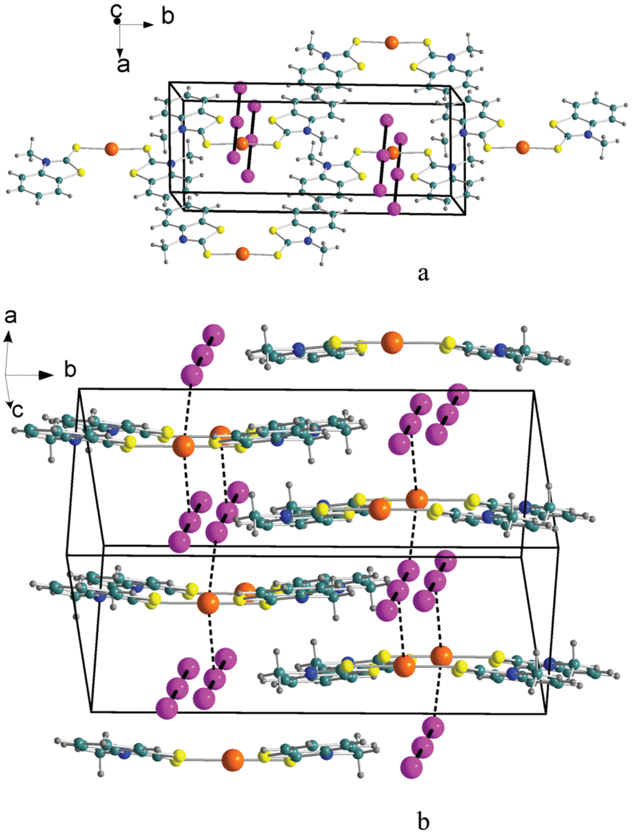


Fig. 2 Views of the crystal packing of $[Au(mbtt)_2]I_3$.

triiodide anions, only slightly below the sum of the van der Waals radii (≈3.6 Å), as shown in Fig. 2b: Au···I2 (x, y, z − 1) 3.525(2) Å and Au···I3 (x − 1, y, z − 1) 3.524(1) Å. One interaction takes place at the central I atom of the anion, while the other takes place at the terminal I atom. The ^{13}C NMR data for complex **1** along with that of donor mbtt are listed in Table S1.† As a consequence of complex formation $[Au(mbtt)_2]^+$ the CS carbon is expected to be the most sensitive to coordination since it is two bonds away from bonded gold. The CS carbon in the complex shows an upfield shift of 10.1 ppm as compared to the CS in donor mbtt. The CS shielding is in keeping with the reduction of the π-electron density in the C═S bond, and shortening of the N–C(═S)–S bonds of the penta-atomic ring due to the donor-gold(I) coordination [mbtt: d(C═S) = 1.63, d(CS–NMe) = 1.43, d(CS–S) = 1.77 Å].[16a] Conversely, the NCH_3 and the other carbons are slightly downfield shifted.

When gold powder was reacted with the adduct mbit·I_2 (1 : 2 molar ratio, Et_2O, 25 °C), only partial disappearance of the gold powder was observed in the course of three days. Evaporation of the solution led to the separation of a sticky dark red solid, which was dissolved in a $CHCl_3$–CH_3CN mixture to separate small well-shaped crystals upon solvent evaporation. Single crystal X-ray diffraction analysis allowed us to formulate the resulting compound as $[(mbtiH)_2](Au^{III}I_4)I_3$ (**2**), in which the gold ion, in the +3 oxidation state, is not bound to any cationic mbtiH unit, but rather to iodides to

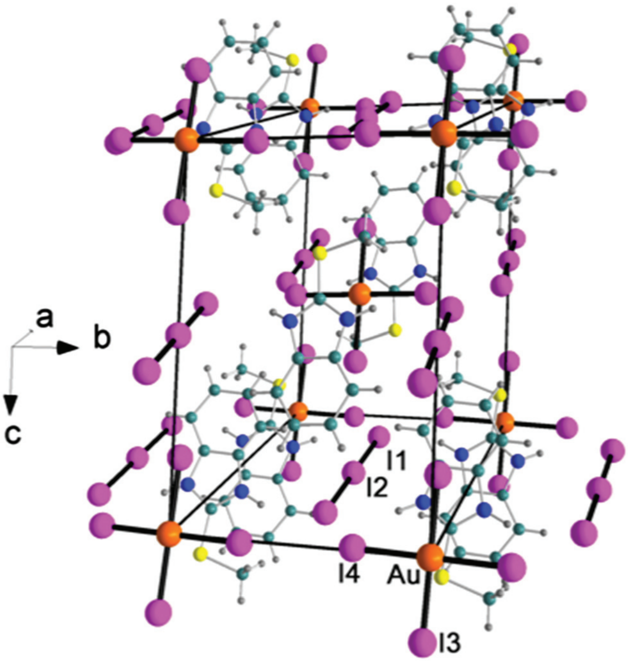


Fig. 3 View of the crystal packing of $[(mtbiH)_2](AuI_4)I_3$.

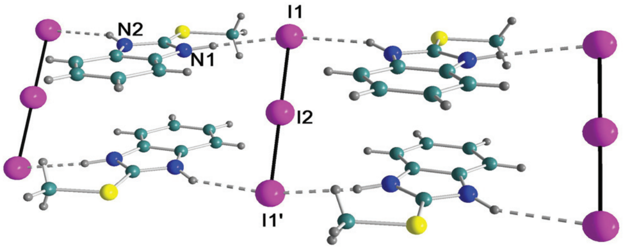


Fig. 4 A portion of the crystal packing of $[(mtbiH)_2](AuI_4)I_3$ with the hydrogen bond interactions between the triiodides and the mtbiH cations.

form the square planar AuI_4^- anion; the asymmetric unit also features a triiodide anion with the charge balanced by cationic units of mtbiH (Fig. 3). The crystallographic data and selected bond lengths and angles are reported in Tables 2 and 3, respectively. The AuI_4^- and I_3^- anions are located about two different crystallographic inversion centres. Hydrogen-bond interactions (Table 3) between the triiodides and the mtbiH cationic units give rise to molecular ribbons as shown in Fig. 4. In these moieties the mtbiH molecules are stacked face-to-face in an antiparallel way, and each carbon atom bonded to the exocyclic sulphur points towards the center of the phenyl ring of an adjacent molecule. All the I⋯I interactions between the triiodides and the AuI_4^- are not shorter than the sum of the van der Waals radii. The Au–I bond lengths in the AuI_4^- anion compare well with those reported by other authors.[19,20] In the crystal packing, the AuI_4^- anions are connected to the mtbiH cationic units through weak C8″–H8c⋯I4 interactions in the expected range (H⋯I, 3.32 Å; C–H⋯I, 164°; Fig. S2†).[21]

The experimental data show that, under mild reaction conditions, both I_2-adducts of the thioamides mbtt and mbit can effectively dissolve gold powder according to the overall reactions (2) and (3), respectively, to yield in the case of mbit·I_2 the formation of a compound of unusual and unexpected stoichiometry.

$$2\ \text{mbtt}\cdot I_2 + Au \rightarrow [Au(mbtt)_2]I_3 + \frac{1}{2}\ I_2 \qquad (2)$$

$$4\ \text{mbit}\cdot I_2 + Au \rightarrow [(mtbiH)_2](AuI_4)I_3 + \text{products} \qquad (3)$$

The process of oxidative dissolution of metals by I_2-adducts of S-donors molecules is yet to be understood at this time. Recently, in an attempt to find an explanation for the greater oxidising ability of I_2-adducts of S-donor molecules as compared to that of I_2 (E° = +0.54 V *vs.* SHE), the electrochemical behaviour of adducts $Me_2dazdt\cdot I_2$[4] and $HN(SPPh_2)_2\cdot I_2$[12] was investigated by cyclic voltammetry measurements. Unexpectedly, no significant increase in the reduction potentials of the S-bound I_2 was observed. Studies have also excluded the formation of reactive species between the I_2-adduct and a solvent with the ability to bind the electrons of the metal, thereby facilitating its oxidation.[22]

In a previous paper concerning the oxidative dissolution of liquid mercury by I_2-adducts of the antithyroid drugs MeImSH and PTU to yield the complexes $[Hg^{II}(MeImSH)I_2]$ and $[Hg^{II}(PTU)_2I_2]$,[14] we reported that oxidation to the mercuric ion requires a two-electron transfer process accomplished by oxidative addition from the "activated" iodine moiety. We also inferred that the intrinsic oxidising/complexing properties of MeImSH·I_2 and PTU·I_2 could be related to the charge-transfer interaction between the S-donor and I_2 that leads to a $(DS\text{-}I)^{\delta+}\cdots I^{\delta-}$ polarised system with a charge separation between the iodine atoms that we calculated as 0.348 and 0.175 e, respectively.

In the case of the mbtt·I_2 adduct, analysis of the X-ray crystal structure highlighted the mutual donor–acceptor interaction that results both in a marked elongation of the I–I bond compared to that observed in solid I_2, 2.7914 *vs.* 2.715 Å,[1a] respectively, and in the formation of an S–I bond whose length of 2.803 Å corresponds to an approximate 26% reduction in the sum of the van der Waals radii of the interacting atoms (3.78 Å). Natural charges calculated at the optimised geometry show that the net charge transferred from the donor mbtt to the acceptor I_2 is 0.215 e,[1a] which results in a charge separation between the iodine atoms of 0.131 e. According to the calculated NBO charge values in the fragment $DS\text{–}I_b\text{–}I_t$ (I_b −0.042, I_t −0.173 e, respectively), the I_b atom becomes nearly neutral, such that we can describe the adduct as a polarised system with a partial positive charge δ^+ associated to the whole mbtt donor and the terminal I atom carrying a partial negative charge δ^-, *i.e.* $(DS)^{\delta+}\cdots I\text{–}I^{\delta-}$. Because of the intrinsic experimental difficulties, studies concerning the adsorption of I_2-adducts on gold powder are not reported in the literature. Recently, Repo *et al.*[23] reported on the oxidation of elemental gold by 4-pyridinethiol (4-PS) in ethyl alcohol, suggesting that the chemiadsorption and S-bonding of 4-PS to form Au/SAM (SAM = self-assembled monolayers) is facilitated by its zwitterionic nature. Since neither I_2 nor mbtt can oxidise gold in Et_2O, it is reasonable to assume that the oxidation of gold to the +1 oxidation state proceeds *via* the breakage of the polarised I–I bond of the adsorbed adduct(s) on the gold surface and the generation of an iodide anion that does not bind to the metal. Based on the stoichiometry of the isolated complex $[Au(mbtt)_2]I_3$, a second unit of mbtt binding the gold (I) centre accomplishes a coordination number of 2, and the triiodide anion will stay at the outer sphere to balance the charge, as described in eqn (4) and (5).

$$\begin{aligned}(\mathrm{DS})^{\delta+}\cdots\mathrm{I{-}I}^{\delta-}+\mathrm{Au}^0 &\rightarrow \mathrm{Au}^0[(\mathrm{DS})^{\delta+}\cdots\mathrm{I{-}I}^{\delta-}]\\ &\rightarrow [\mathrm{DS{-}Au}]^+ + \frac{1}{2}\ \mathrm{I}_2 + \mathrm{I}^- \qquad (4)\end{aligned}$$

$$[\mathrm{DS{-}Au}]^+ + \mathrm{I}^- + (\mathrm{DS})\cdots\mathrm{I{-}I} \rightarrow [\mathrm{DS{-}Au{-}SD}]^+ + {\mathrm{I}_3}^- \qquad (5)$$

Compared to the formation of $[Au(mbtt)_2]I_3$, the stoichiometry of the complex $[(mtbiH)_2](AuI_4)I_3$ reveals that the oxidation/complexation process of gold by mbit·I_2 is a much more complex process than expected. The natural charges calculated at the optimised geometry of mbit·I_2 show that the net charge transferred from the donor mbit to the acceptor I_2 is 0.244 e, with a charge separation between the iodine atoms of 0.131 e (I_b −0.044, I_t −0.200 e, respectively). A comparison of the electronic charge distribution in adducts mbtt·I_2 and mbit·I_2 does not show significant differences to justify such a different reactivity. Puzzling points concerning reaction (3) are both the oxidation of gold to the +3 oxidation state with the formation of the anion ${AuI_4}^-$ and the presence of the cation mtbiH, which may be derived from the transfer in mbit of the N(3)–Me methyl to the thiocarbonyl sulphur atom and *N*-protonation. This cation is sparingly mentioned in the literature, and was not observed in the reaction of mbit with iodine.[16c] Hinrichs *et al.* reported on this cation in the compound bis(2-methylmercapto-benzimidazolium)hexachloro-tellurium(IV) tetrahydrofuran solvate;[24] only small differences in bond distances and angles were found between the two cations, except that in **1**, both N(H) groups are engaged in hydrogen bonding.

At the moment, we can only speculate that the different reactivity in the oxidation of gold(0) by the mbit·I_2 and mbtt·I_2 adducts may depend on the presence of the imido group. In fact, it is well-documented in the literature[25] that in the I_2-adducts of many penta-atomic rings containing a thioamido group, the S-bonded iodine atom (I_b) acts as a hydrogen bond acceptor site, forming an intramolecular hydrogen bond N–H⋯I_b. This increases the stability of the $[(DS)^{\delta+}\cdots I]$ moiety and therefore, in our opinion, somewhat modifies its reactivity on the gold surface. Complex $[(mtbiH)_2](AuI_4)I_3$ is insoluble in apolar solvents.

Conclusions

From the results of the present study, it appears that the oxidative dissolution in Et_2O of gold powder formed by I_2-adducts of the thioamides mbtt and mbit is easily accomplished. Very little gold dust is still present in the reaction mixtures after three days in the case of mbtt·I_2 (gold oxidation yield >78%). From the reaction of the mbtt·I_2 adduct with gold, the complex $[Au(mbtt)_2]I_3$ was separated, the X-ray crystal structure of which shows Au(I) ion binding *via* the S-atoms of two neutral ligands in a linear fashion. Conversely, the mbit·I_2 adduct reacted with gold (2 : 1 molar ratio) in an unexpected way; in fact, the separated complex $[(mtbiH)_2](AuI_4)I_3$ features an Au(III) ion binding four iodides in a square planar fashion with the charge balanced by an unusual cation originating from the transfer in the mbit donor of the N(3)–Me methyl to the sulphur atom. In this case, the complexity of the reaction strongly limits the yield of gold oxidation (≈45%), with the consequence of making the use of mbit·I_2 unsatisfactory. Conversely, the oxidant "reagent" mbtt·I_2 represents a significant improvement over the previously reported $Me_2dazdt{\cdot}2I_2$ or $HN(SPPh_2)_2{\cdot}I_2$. In fact, in addition to ensuring a better reaction yield and limiting the oxidation of gold to the +1 oxidation state, the mbtt donor is easily and widely available on the market.

The valuable results observed provide a challenging task for further investigations (*e.g.* the use of green solvents) which are beyond the object of the present study.

Experimental

Materials and instrumentation

Reagents were used as purchased from Aldrich. Diethyl ether was distilled over $LiAlH_4$ shortly before use. Elemental analyses were obtained using a Fisons Instruments 1108 CHNS elemental analyser. Infrared spectra (4000–400 cm^{-1}) were recorded on a Thermo-Nicolet 5700 spectrometer. ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer, chemical shifts are reported in ppm (δ) downfield from TMS using the same solvent as an internal reference. The samples were dissolved in DMSO-d_6 and measured at 25 °C. Concentrations of the samples were 0.02 M.

Synthesis of complexes

$[Au(mbtt)_2]I_3$ (1). A mixture of mbtt·I_2 (0.100 g, 0.230 mmol) and powdered gold (<10 μm) (0.023 g, 0.117 mmol) in diethyl ether (70 cm^3) was stirred at 20 °C for three days. The resultant dark red solid was collected by suction filtration, washed with a mixture of CH_2Cl_2–*n*-hexane (1 : 5 v : v) and dried *in vacuo* (0.086 g, 0.0915 mmol, yield 78.2% referring to gold). The crude product was recrystallised from a warm $CHCl_3$–MeCN mixture (3 : 1 v : v) allowing the solution to stand at 5 °C for 48 h to yield 0.070 g of dark red crystals of **1**. Anal. Calcd for $C_{16}H_{14}AuI_3N_2S_4$: C 20.43; H 1.50; N 2.98; S 13.61. Found: C 20.6; H 1.4; N 3.0; S 13.9%. δ_c (75.4 MHz, DMSO-d_6, Me_4Si) 178.0 (*C*S), 145.1, 129.3, 127.3, 125.1, 122.0, 113.6, 34.3 (NMe). IR (KBr, ν/cm^{-1}): 2960w, 2782vw, 1459m, 1429m, 1364s, 1317m, 1263m, 1093m, 1053m, 981m, 936w, 879vw, 802m, 762m, 749s, 715m, 633m, 534w, 508vw.

$[(mtbiH)_2](AuI_4)I_3$ (2). A mixture of mbit·I_2 (0.100 g, 0.239 mmol) and powdered gold (<10 μm) (0.0236 g, 0.120 mmol) in diethyl ether (70 cm^3) was stirred at 20 °C under N_2 for three days. The resultant red solution was slowly concentrated to dryness and the sticky solid was sonicated in 10 mL of $CHCl_3–CH_3CN$ (9 : 1 v : v). The solution was filtered and allowed to stand to −15 °C for 24 h to separate the dark red crystals of complex **2** that were washed with *n*-hexane and stored in a desiccator. Obtained 0.076 g, 0.054 mmol; yield 45% referring to gold. The reaction yield did not increase by increasing the reaction time to seven days. Complex **2** is virtually insoluble in most common organic solvents, and in water. Anal. Calcd for $C_{16}H_{18}AuI_7N_4S_2$: C 13.57; H 1.28; N 3.96; S 4.52. Found: C 13.7; H 1.3; N 4.1; S 4.7. IR (KBr, ν/cm^{-1}, selected bands): 3195m, 1621m, 1507s, 1456s, 1437m, 1417m, 1360m, 754vs, 671m, 633m, 620m, 591w, 483w.

X-ray structure determination of complexes 1 and 2

A summary of the crystal data and refinement details for complexes **1** and **2** is given in Table 2. Intensity data were collected at room temperature for complexes **1** and **2** on a Bruker Apex II CCD diffractometer using graphite-monochromatised Mo-Kα radiation (λ = 0.71073 Å). Datasets were corrected for Lorentz polarisation effects and for absorption (*SADABS*[26]). All structures were solved by direct methods (*SIR-97*[27]) and completed by iterative cycles of full-matrix least squares refinement on F_o^2 and Δ*F* synthesis using the *SHELXL-97*[28] program (*WinGX* suite).[29] Hydrogen atoms, located on the Δ*F* maps, were allowed to ride on their carbon and nitrogen atoms. Crystallographic data for compounds **1** and **2** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC- 892460 and 892461, respectively.

Computational studies

Quantum chemical calculations were carried out on mbtt·I_2, and mbit·I_2, by means of the commercially available suite of programs, Gaussian 03.[30] Based on the encouraging results reported recently on related diiodine adducts,[31] density functional calculations (DFT) were performed using the hybrid mPW1PW functional.[32] For all calculations, Schafer, Horn and Ahlrichs pVDZ[33] basis sets (BS) were used for C, H, N, O, and S, while the recently reported completely uncontracted LANL08 BS[34] supplemented with d-polarisation functions, together with effective core potentials (ECP), were adopted for iodine. Numerical integration was performed using the FineGrid option, which indicates that a total of 7500 points are used for each atom. NBO calculations[35] were performed for each molecule. Kohn–Sham orbital drawings were elaborated with Molden 4.7.[36] All calculations were performed on an E4 workstation equipped with four AMD Opteron quad-core processors and 16 GB of RAM.

References

1 (*a*) The interaction between the S-donor Lewis base (DS) and I_2 to give 1 : 1 adducts containing an almost linear S–I–I fragment can be seen as a charge-transfer process. It occurs via the transfer of charge density from a lone pair of electrons (n) on the donor atom to the empty σ* antibonding orbital of the iodine species. Depending on the charge density transferred by the DS donor molecule and the nature of the solvent, this can result in lengthening of the I–I bond length (I_2(s), *d*(I–I) = 2.715 Å, at −163.1 °C) W. T. Pennington, T. W. Hanks and H. D. Arman, in *Halogen Bonding: Fundamentals and Applications*, ed. P. Metrangolo and G. Resnati, Spinger-Verlag, Berlin, 2008, pp. 65–104, and references therein(*b*) Compounds containing S-donor atoms generally form only 1 : 1 charge-transfer complexes with I_2 in apolar solvents according to the equilibrium DS + I_2 = DS·I_2. The formation constant of the 1 : 1 complex is related to the equilibrium molar concentrations by the equation $K_f = [DS·I_2]/[DS][I_2]$. The calculated K_f values spread over a very wide range of values depending on the nature of the donor, *i.e.* 1 : 1 adduct methimazole-I_2, K_f = 92 433 L mol^{-1}, CH_2Cl_2, 25 °C; 1 : 1 adduct dimethyl sulfide-I_2, K_f = 74.0 L mol^{-1}, CCl_4, 25 °C M. C. Aragoni, M. Arca, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis and G. Verani, *Coord. Chem. Rev.*, 1999, **184**, 271–290, and references therein.

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