

# Gold and palladium oxidation/complexation in water by the leaching thioamide-iodine system

Francesco Isaia,\*<sup>a</sup> Maria Carla Aragoni,<sup>a</sup> Massimiliano Arca,<sup>a</sup> Claudia Caltagirone,<sup>a</sup> Carlo Castellano<sup>b</sup> Greta De Filippo,<sup>a</sup> Alessandra Garau,<sup>a</sup> Vito Lippolis,<sup>a</sup> and Tiziana Pivetta<sup>a</sup>

<sup>a</sup>Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, Cittadella Universitaria, 09042 Monserrato (CA), Italy. Tel: +39 070 6754496. E-mail: [isaia@unica.it](mailto:isaia@unica.it)

<sup>b</sup>Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano. Italy.

This paper concerns the oxidative dissolution ability of a leaching thioamide/iodine system in water towards gold, palladium and silver metals in powder in view of a potential application in the recovery process of these metals from electrical and electronic waste equipment (E-waste). The leaching mixture composed by equimolar amounts of thioamide 3-methyl-benzothiazole-2-thione and I<sub>2</sub> in water can oxidize/complex gold and palladium metals in powder in order to form the complexes [Au<sup>I</sup>(mbtt)<sub>2</sub>]<sub>3</sub>I<sub>3</sub> and [Pd<sup>II</sup>(mbtt)<sub>3</sub>I]<sub>3</sub>I<sub>3</sub>. Considering the mild conditions in which the processes were performed ([I<sub>2</sub>] = 1.14x10<sup>-3</sup> M, T=20 °C, pH=5.0, leaching time = 24h), the obtained oxidation yield of Au<sup>0</sup> and Pd<sup>0</sup> are to be considered satisfactory with values of 65% and 69%, respectively. No oxidation was observed for the silver powder. The oxidising/complexing properties of the leaching mixture mbtt + I<sub>2</sub> were interpreted considering the formation of the mbtt-I<sub>2</sub> adduct that features, as a consequence of the S-donor to I<sub>2</sub> interaction, a charge separation between the bridging and terminal iodine atoms in the fragment S-I<sub>b</sub>-I<sub>t</sub>. The feasibility of recovering gold from the complex [Au<sup>I</sup>(mbtt)<sub>2</sub>]<sub>3</sub>I<sub>3</sub> was verified by performing a cementation with magnesium powder.

## 1. Introduction

Electrical and electronic waste equipment (E-waste) is one of the fastest growing waste streams on a global scale, with some 41.8 million tonnes generated in 2014, and expected to grow to 49.8 million tonnes in 2018, with an annual growth rate of 4 to 5 per cent.<sup>1-3</sup>

Rapid technology innovation and ever-shortening product lifespans are among the factors contributing to the growing amount of E-waste. Indeed, these facts pose a significant challenge to waste management in both developed and developing countries.

From the resource perspective, E-waste is to be considered a potential “urban mine” that could provide a significant amount of secondary resources for remanufacture, refurbishment and recycling.

For instance, the gold content from E-waste in 2014 was estimated at roughly 300 tonnes, which represents 11 per cent of the global gold production from mines in 2013 (2770 tonnes).<sup>4</sup> However, as it is shown in Table 1, the metal abundance is strongly dependent on the type of electronic waste

considered.<sup>5</sup> However, it should be taken into account that E-waste, since the intrinsic complexity of its composition, results in a difficult material being processed. In fact, in the case of hydrometallurgical processes, a sequence of two or three steps is in general necessary for the removal and/or recovery of base non-ferrous metals (mainly copper, tin, aluminium, nickel, and lead) to leave a residue enriched in gold and other precious metals to be processed with a specific leaching system. Nowadays, cyanide is still the most common leaching agent used in the recovery process of gold from primary and secondary resources.<sup>3,6-8</sup> In the presence of oxygen cyanides, metal gold is dissolved by forming the soluble anionic complex  $\text{Au}(\text{CN})_2^-$  (see Table 2); the pregnant solution is then processed to recover the solid gold (in general with one of the processes: zinc cementation, activated carbon adsorption, or ion-exchange resin extraction). However, the application of cyanide leaching has often resulted in a severe contamination of the environment from accidental leakages and exposures. For this reason, restrictions on waste disposal and stringent environmental regulations have motivated both the development of alternative lixivants to cyanide, and of economically viable processes that pose fewer health risks and are more eco-friendly in the past years.<sup>9,10</sup> In Table 2, alternative leaching systems for the recovery of precious metals are reported, the mbtt +  $\text{I}_2$  system has also been added for comparison purposes. In addition to leaching processes information, advantages and disadvantages in terms of their applicability and toxicity have been inserted in the table.

From the point of view of environmental impacts, thiosulfate leaching might be alternative to cyanide, but economic issues due to the high consumption of reagents do not render it suitable for large-scale applications. Also, a iodine/iodide leaching system is very promising from an ecological and technical point of view, however the big disadvantage of this system is its high reagent consumption and related cost issues. A reagent recovery process for iodine/iodide is still under investigation to fulfil the requirements to be an economic process. Thiourea is a viable alternative to cyanide; it features a high gold dissolution rate, but at the same time, a higher reagent consumption.

All these leaching processes have great potentiality, with thiourea and iodine/iodide leaching systems constituting the most promising alternative to cyanide.

**Table 1** Precious metals content in various types of E-waste.<sup>a</sup>

Types of E-waste	Metal content (g/ton)		
	Au	Ag	Pd
PC main board scrap	506	6.36	12.4
Mobile phone scrap	350	1340	210
PC board scrap	250	1000	110
Printed wiring board	110	280	-
Calculator scrap	50	260	5

<sup>a</sup>Adapted from Table 3 of ref. 5.

**Table 2** Comparison of leaching systems for gold<sup>a</sup>

Lixiviants	Leaching process	Leaching conditions <sup>b</sup>	Advantages	Disadvantages
Cyanide	$4\text{Au} + 8\text{CN}^- \rightarrow 4\text{Au}(\text{CN})_2^- + 4\text{e}^-$ $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	CN <sup>-</sup> 104 ppm O <sub>2</sub> 8.5 ppm pH 11, time 24h, T = 20 °C Gold recovery 93%	Very effective for leaching gold and silver. Use of cyanide is an effective low cost solution. Leaching parameters have been widely studied to optimize the performance of the cyanidation process.	Deadly poisonous chemical. Problematic for the health and environment. Long leaching time. Absence of reagent regeneration
Ammonium thiosulfate	$\text{Au} + 5\text{S}_2\text{O}_3^{2-} + \text{Cu}(\text{NH}_3)_4^{2+} \rightarrow$ $\text{Au}(\text{S}_2\text{O}_3)_2^{3-} + 4\text{NH}_3 +$ $\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$	thiosulfate 2M ammonia 4M copper sulphate 0.1 M pH 8.5-10.2, time 3h T = 25 °C Gold recovery: 80%	Non toxic. Leach gold faster than cyanide.	High consumption of reagents. High reagent consumption renders most thiosulfate systems non-economical. At present, no simple and affordable method for recovering gold from thiosulfate leach solutions exists.
Iodine/iodide	$\text{Au} + 2\text{I}^- \rightarrow \text{AuI}_2^- + \text{e}^-$ $\text{Au} + 4\text{I}^- \rightarrow \text{AuI}_4^- + 3\text{e}^-$  $\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$	iodine 2g/L - iodide 12 g/L pH 7, time 2h, T = 40 °C liquid-to-solid mass ratio 4:1 Gold recovery: 99%	Relatively healthy process. High chemical stability. High gold recovery	High cost of the reagents compared to cyanide. The regeneration process of iodine is carried out by means either of electrochemical oxidation, or chemical oxidation.
Thiourea	$\text{Au} + 2\text{CS}(\text{NH}_2)_2 \rightarrow$ $\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+ + \text{e}^-$  $\text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{+2}$	sample 1 kg thiourea 5 g ferric sulfate 0.5g H <sub>2</sub> SO <sub>4</sub> 5g pH 1-2, time 6h, T = 20 °C Gold recovery: 84%	Fast leaching rate	Low chemical stability of thiourea. Difficult recycling of the reagent. It is more expensive than cyanide. Its consumption in gold processing is high. The gold recovery step requires more development. Potential carcinogen.
mbtt/iodine	$\text{Au} + 2(\text{mbtt}-\text{I}_2) \rightarrow \text{Au}(\text{mbtt})_2^+ \text{I}_3^-$ $+ \frac{1}{2} \text{I}_2$	sample 0.090 g in 800 mL mbtt 0.165 g iodine 0.230 g pH 5, time 24h, T = 20 °C Gold recovery: 65%	Relatively healthy process. High chemical stability. Good reagent regeneration. Production of magnesium chloride, and magnesium iodide. The complex $\text{Au}(\text{mbtt})_2^+ \text{I}_3^-$ is a stable solid powder.	Relatively long reaction time. Gold oxidation yield is to be improved. High cost of the reagents compared to cyanide.

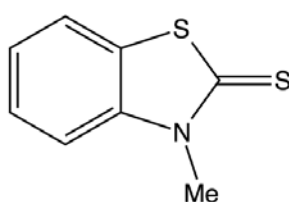
<sup>a</sup> Data from references 1, 3 and 5. <sup>b</sup> Leaching conditions as reported in references: cyanide 3m; ammonium thiosulfate 3n; iodine/iodide 3g; thiourea 3h; mbtt/iodine this work.

In this context, we have been involved for many years now in the study of metal/s oxidative dissolution aimed at the recovery of precious and toxic metals for the environment by employing iodine adducts of thioamide donor molecules<sup>11</sup> (DS·I<sub>2</sub>). Although the synthetic procedure we developed (eqn 1) has proved to be valuable in the oxidative dissolution of metals of low and high standard reduction potential (M<sup>0</sup>) (see ESI-Table S1), the use of non-aqueous solvents as diethyl ether or dichloromethane sets limits to the further development of this process.

Among the great number of (thioamide)-iodine adducts we tested,<sup>11</sup> good results were obtained with the use of the 3-methyl-benzothiazole-2-thione<sup>12</sup> (mbtt) (Fig. 1), that is a safe and easily available substance in large quantities. This is mainly due to the fact that mbtt is not oxidised by iodine, and act as the Lewis base donor towards “soft” metal ions binding them in a variety of coordination modes as a neutral ligand (Table 3).



As a further contribution to the development of the process of the oxidative dissolution of metals in view of a potential application in the recovery process of precious metals from E-waste, in the present study we have investigated at laboratory scale the potentiality of the lixiviant mixture mbtt + I<sub>2</sub> in water (pH 5.0) to oxidize pure gold, palladium, and silver powders, and verified whether it could be a potential alternative to the more common leaching agents used for the recovery of gold and other precious metals from the E-waste scrap.



**Fig. 1** Chemical structure of 3-methyl-benzothiazole-2-thione (mbtt).

**Table 3** Selection of structurally characterised metal complexes of 3-methyl-benzothiazole-2-thione (mbtt) with metal ions.

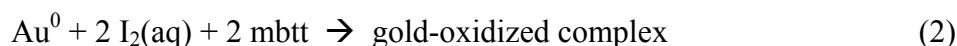
Complex	Reaction / Solvent	Geometry / Core	Ref.
[Ag <sub>2</sub> (mbtt) <sub>6</sub> ](NO <sub>3</sub> ) <sub>2</sub>	AgNO <sub>3</sub> + mbtt / CH <sub>3</sub> CN	T <sub>d</sub> / AgS <sub>4</sub>	13
[Ag(mbtt) <sub>3</sub> ](CF <sub>3</sub> SO <sub>3</sub> )	Ag(CF <sub>3</sub> SO <sub>3</sub> ) + mbtt / CH <sub>3</sub> CN	Trigonal planar / AgS <sub>3</sub>	13
[Ag <sub>2</sub> (mbtt) <sub>4</sub> (Cl) <sub>2</sub> ]	AgCl + mbtt / CH <sub>3</sub> CN	T <sub>d</sub> / AgS <sub>2</sub> Cl <sub>2</sub>	13
[Au(mbtt)Cl]	AuCl(tht) + mbtt / CH <sub>2</sub> Cl <sub>2</sub>	Linear / AuSCL	14
[Au(mbtt)Br]	AuBr <sub>3</sub> + mbtt / MeOH-CH <sub>2</sub> Cl <sub>2</sub>	Linear / AuSBr	14
[Au(mbtt) <sub>2</sub> ][AuI <sub>2</sub> ] <sub>1-n</sub> [I <sub>3</sub> ] <sub>n</sub>	AuI + mbtt / MeOH-CH <sub>2</sub> Cl <sub>2</sub>	Linear / AuS <sub>2</sub>	14
[Au(mbtt) <sub>2</sub> ][I <sub>3</sub> ]	Au + mbtt-I <sub>2</sub> / Et <sub>2</sub> O	Linear / AuS <sub>2</sub>	12
[Cu(mbtt)(xantphos)Br] <sup>b</sup>	CuBr + mbtt + xantphos / CH <sub>3</sub> CN-MeOH	T <sub>d</sub> / CuP <sub>2</sub> SBr	15
[Cu(mbtt)(xantphos)I] <sup>b</sup>	CuI + mbtt + xantphos / CH <sub>3</sub> CN-MeOH	T <sub>d</sub> / CuP <sub>2</sub> SI	15
[Cu(mbtt) <sub>2</sub> Cl] <sub>2</sub>	CuCl + mbtt / CH <sub>3</sub> CN-EtOH	T <sub>d</sub> / CuS <sub>3</sub> Cl <sub>2</sub>	16
[Cu(mbtt)(PPh <sub>3</sub> ) <sub>2</sub> I]	CuI + mbtt + PPh <sub>3</sub> / CH <sub>3</sub> CN-EtOH	T <sub>d</sub> / CuP <sub>2</sub> SI	16

<sup>a</sup>This work; <sup>b</sup>xantphos= (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(diphenylphosphine); tht = tetrahydrothiophene

## 2. Results and discussions

### 2.1 Oxidative dissolution of gold powder

The oxidative dissolution of noble metals requires two essential components: an oxidant species to promote the metal oxidation and the concomitant presence of a complexing ligand to stabilise/dissolve the metal ion.<sup>17</sup> A neutral ligand generally stabilises the metal ions in the lowest oxidation state, whereas in the case of anionic ligands different oxidation states are observed.<sup>17</sup> The reaction of the gold powder with a saturated solution of I<sub>2</sub> in water<sup>18,19</sup> and mbtt (1:2:2 molar ratio)<sup>20</sup> was carried out in the heterogeneous phase at 20 °C for 24 hours according to the general eqn. (2)



During this time, the initial reddish colour of the reaction mixture, due to the visible absorption band of I<sub>2</sub>(aq) at 460nm,<sup>21</sup> turned to colourless with the concomitant formation of a red-brownish powder. This crude material was firstly washed in hot water to dissolve the unreacted mbtt, and then crystallised from acetone or hot ethyl alcohol in order to separate any traces of unreacted metal powder.

The stoichiometry of the gold-complex was initially deduced from the elemental analysis data and the electrospray ionisation mass spectrometry (ESI-MS), and then it was definitely assessed by single crystal X-ray diffraction as the already described Au<sup>I</sup> complex [Au(mbtt)<sub>2</sub>]<sub>3</sub>.<sup>12</sup> The ESI-MS analysis is in agreement with the single crystal X-ray results: the presence of the [Au(mbtt)<sub>2</sub>]<sup>+</sup> (*m/z* 559) ion is

evident in the positive ion mode, whereas the  $[I_3]^-$  ion ( $m/z$  381) yields the most abundant peak in the negative ion mode (ESI-Fig. S1). The good yield of the conversion of gold(0) to gold(I) (65% at  $T=20$  °C) can be markedly improved by increasing the temperature of the reaction (74% at  $T=40$  °C).

Notably, the complex  $[Au(mbtt)_2]I_3$  is also synthesisable both by reacting the  $I_2$ -adduct of mbtt with gold in an apolar solvent,<sup>12</sup> and by reacting AuI with mbtt in a MeOH-CH<sub>2</sub>Cl<sub>2</sub> mixture. In the latter case the charge of cation  $[Au(mbtt)_2]^+$  is balanced by the  $[AuI_2]^-$  and  $[I_3]^-$  anions with an occupancy ratio varying from 0.87/0.13 to 0.28/0.72 in dependence of the reacting AuI/mbtt molar ratio.<sup>14</sup>

As far as the reaction solution is concerned, it is noteworthy that the presence of gold ions is negligible (<0.010 ppm – determined by the ICP analysis). This fact indicates that the complex  $[Au(mbtt)_2]I_3$  has a very poor solubility in water, and that no water-soluble gold-containing by-products are generated in the oxidative dissolution process. In Table 4, data concerning the oxidative dissolution of gold and other metals, the stoichiometry of the separated complexes, and the metals conversion yield are reported. The results obtained show that the oxidative-dissolution of gold in water using the mbtt +  $I_2$  mixture as a leaching system is possible under mild and safe reaction conditions. The use of chlorinated organic solvents and hydrocarbons in the workup, which are problematic both for the health and the environment, is not necessary, in contrast to the case of the oxidative process performed in diethyl ether.

As regards the yield of gold oxidation calculated after 24 h of reaction (65 % in water, 45 % in diethyl ether), the process carried out in water produces better results. This confirms that the oxidative dissolution of gold in water with the mbtt +  $I_2$  leaching system overall outperforms the one made in diethyl ether.

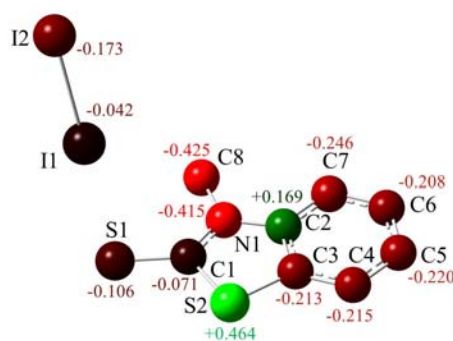
**Table 4** Oxidative dissolution process in water of gold, palladium, and silver powder ( $M^0$ ) by the leaching mbtt +  $I_2$ (aq) system. Reaction conditions:  $M^0:I_2:mbtt$  (1:2:2 molar ratio),  $T = 20$  °C, stirring rate 900 rpm.

$M^0$	Complex stoichiometry	Metal ions' concentration in the aqueous phase <sup>a</sup>	Oxidation reaction time = 6 h	yield % <sup>b</sup> reaction time = 24 h
Au	$[Au^I(mbtt)_2]I_3$	<0.010 ppm	50	66, 72 <sup>c</sup>
Pd	$[Pd^{II}(mbtt)_3I]I_3$	<0.019 ppm	47	69
Ag	no oxidation			

<sup>a</sup> Detected by the ICP analysis; <sup>b</sup> Based on the metal; <sup>c</sup> Reaction carried out at  $T= 40$ °C.

Since neither  $I_2$  nor mbtt can oxidise gold in water, it is reasonable to assume that the oxidation process proceeds *via* the initial formation of a reactive species between  $I_2$  and mbtt. Though the reactivity of thioamides with molecular iodine in polar and non-polar organic solvents is largely reported in the literature,<sup>22</sup> only a limited amount of information is reported for the reactivity in water.<sup>18</sup> We sought therefore to study the reaction between mbtt and  $I_2$  in order to evidence which

species is/are formed. The reaction of I<sub>2</sub> with mbtt (1:1 molar ratio) in water was monitored for 24 h, recording the changes of the visible absorption band of I<sub>2</sub>(aq) at 460nm.<sup>21</sup> In ESI-Fig. S5, the trend of the absorbance vs. time reveals that the initial iodine concentration was halved within 2 hours from the beginning of the reaction and reduced to ~70% in 24 hours. The solution became colourless within 48 h. During this time, a thin red-brown powder separated from the reaction mixture; its characterisation by elemental analyses and single crystal X-ray diffraction analysis confirms the formation of the adduct mbtt-I<sub>2</sub>.<sup>23,24</sup> Based on these data, we can infer that the values of the gold and palladium oxidation yield determined for the reactions of duration of 6 and 24 hours (Table 3) are very probably to be correlated with the amount of adduct<sup>23</sup> mbtt-I<sub>2</sub> formed in these periods of time ~62% and ~70%, respectively (ESI-Fig S6). The analysis of the X-ray crystal structure of the adduct mbtt-I<sub>2</sub> shows the effects of the mutual donor-acceptor interaction that results both in a marked elongation of the I–I bond compared to that observed in solid I<sub>2</sub> (2.7914 vs. 2.715 Å, respectively), and in the formation of an S–I bond whose length of 2.808Å corresponds to an approximate reduction of 26% in the sum of the van der Waals radii of the interacting atoms (3.78 Å).<sup>24</sup> Natural charges calculated at the optimised geometry show that the net charge of 0.215 e transferred from the donor mbtt to the acceptor I<sub>2</sub> causes a charge separation between the bridging and terminal iodine atoms of 0.131 e (DS–I<sub>b</sub>–I<sub>t</sub>; I<sub>b</sub> –0.042 e, I<sub>t</sub> –0.173 e). According to the calculated natural bond orbital (NBO) charge values,<sup>12</sup> the mbtt-I<sub>2</sub> adduct can be described as a polarised system with a partial positive charge δ<sup>+</sup> associated to the whole mbtt donor and the terminal iodine atom carrying a partial negative charge δ<sup>-</sup>, *i.e.* (DS)<sup>δ+</sup>⋯I<sub>b</sub>⋯I<sub>t</sub><sup>δ-</sup>

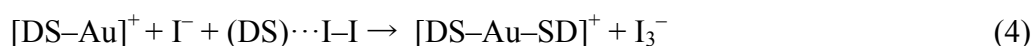
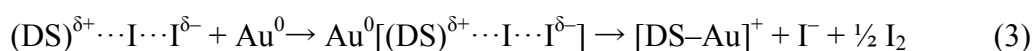


**Fig. 2** Natural charge distribution on the adduct mbtt-I<sub>2</sub>. Atoms are coloured based on a chromatic scale depending on the atomic charge (e) calculated at NBO level. Selected DFT-optimised bond distances (in parentheses the corresponding structural distances (Å) are reported).<sup>24</sup> I1–I2, 2.780 [2.7914(9)]; I1⋯S1, 2.972 [2.808(3)]; C1–S1, 1.673 [1.698(9)]; C1–N1, 1.357 [1.344(9)]; C1–S2, 1.742 [1.714(8)]; S2–C3, 1.743 [1.739(9)]; N1–C2, 1.390 [1.402(10)]; C2–C3, 1.404 [1.395(10)]; C3–C4, 1.397 [1.380(10)]; C4–C5, 1.393 [1.359(12)]; C5–C6, 1.400 [1.393(11)]; C6–C7, 1.391 [1.395(12)]; C2–C7, 1.380 [1.378(11)].

Because of the intrinsic experimental difficulties, studies concerning the adsorption of thioamide-I<sub>2</sub> adducts on gold powder are not reported in the literature. In the case of the oxidation of elemental

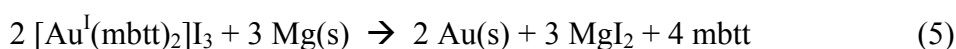
gold by 4-pyridinethiol in ethyl alcohol, Repo et al.<sup>25</sup> suggested that the chemisorption and *S*-bonding of 4-pyridinethiol to form Au/SAM (SAM = self-assembled monolayers) is facilitated by its zwitterionic nature.

Based on the stoichiometry of the isolated complex  $[\text{Au}(\text{mbtt})_2]\text{I}_3$ , it is reasonable to assume that the mbtt- $\text{I}_2$  assisted oxidation/complexation of gold(0) to +1 oxidation state proceeds *via* a) the breakage of the polarised I–I bond of the adsorbed adduct(s) on the metal surface with generation of an iodide anion, eqn. (3), and b) the intervention of a second unit of mbtt binding the gold(I) centre to accomplish the linear  $[\text{Au}(\text{mbtt})_2]^+$  coordination, eqn (4). The charge is balanced by a triiodide anion staying at the outer coordination sphere.

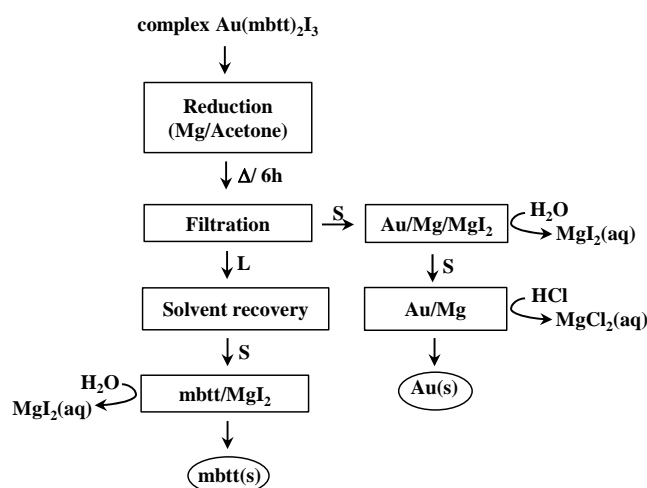


## 2.2 Gold and mbtt recovery

There are numerous processes reported in the literature for the reduction of gold(I) and gold(III) salt solutions by employing reducing agents in a variety of reaction conditions.<sup>26</sup> Among all these, for the recovery of gold from complex  $[\text{Au}^{\text{I}}(\text{mbtt})_2]\text{I}_3$ , the process we have applied, although entailing changes, involves the use of a non-toxic and inexpensive reducing agents as magnesium powder.<sup>27</sup> Magnesium powder in acetone reduces at its surface both the gold(I) ion (ESI-Fig. S7) and the iodine, consequently the formation of the salt  $\text{MgI}_2$  and the presence of free ligand mbtt in the solution are observed since the latter does not interact with the magnesium ion, eqn (5); in Figure 5 the flowsheet of the steps involving the Au(s) recovery by Mg-cementation and the recycling of reagents/solvent is reported. The amount of magnesium employed in this reaction is greater than the stoichiometric requirement, so that the reduction process can be nearly quantitative.







**Fig. 3** Flow sheet showing the gold recovery process applied to the reduction of complex  $[\text{Au}(\text{mbtt})_2\text{I}_3]$ . S, L = solid and liquid fractions, respectively.

### 2.3 Oxidative dissolution of palladium and silver powder

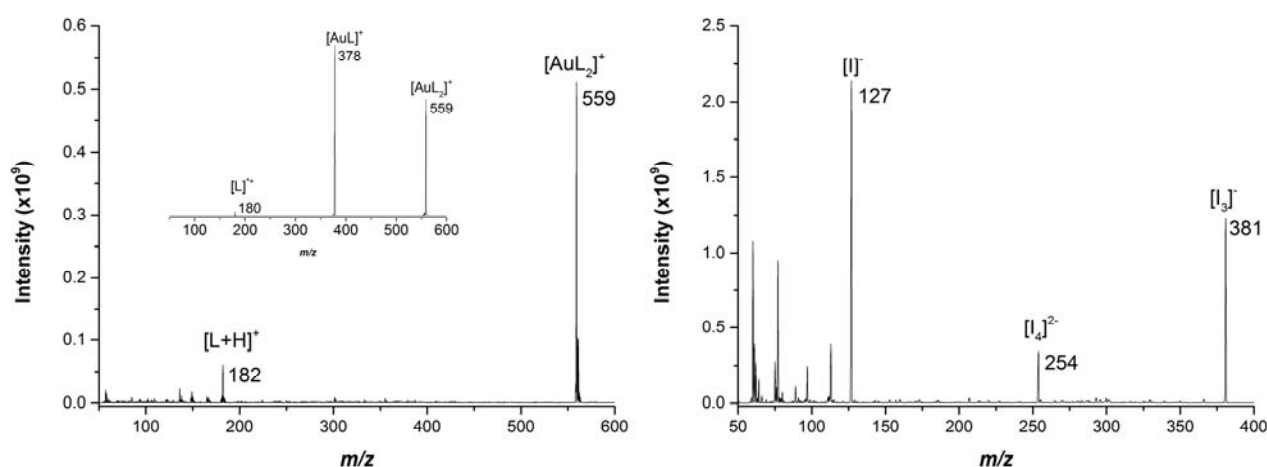
Considering the common presence in E-waste of other precious metals in addition to gold, we have also evaluated the oxidative dissolution ability of the leaching  $\text{mbtt} + \text{I}_2(\text{aq})$  system towards palladium and silver metal powders,  $\text{M}^0$ . The reaction was carried out with the same procedure previously reported for the gold powder  $[(\text{M}^0:\text{I}_2(\text{aq}):\text{mbtt}) \text{ reaction molar ratio of } 1:2:2; T = 20^\circ\text{C}, \text{ leaching time} = 24 \text{ h}]$ . In the case of the palladium powder, the leaching system oxidises palladium to a +2 oxidation state forming the complex  $[\text{Pd}(\text{mbtt})_3\text{I}]\text{I}_3$  (yield  $\sim 70\%$ ). The ESI-MS of the complex recorded in the positive ion mode, shows a signal at  $m/z$  777 that is in agreement with the formation of cation  $[\text{Pd}(\text{mbtt})_3\text{I}]^+$ , and a signal at  $m/z$  596 (related to the formation of the species  $[\text{Pd}(\text{mbtt})_2\text{I}]^+$ ) that MS-MS clarifies as originated by the fragmentation of complex  $[\text{Pd}(\text{mbtt})_3\text{I}]^+$ ; in the negative ion mode the highest signal is the one of  $\text{I}_3^-$  anion at  $m/z$  381. As far as the reaction solution is concerned, no relevant presence of Pd-containing species was detected (Table 4). The ESI mass spectrum of complex  $[\text{Pd}(\text{mbtt})_3\text{I}]\text{I}_3$  and the peak assignment are reported in ESI-Fig. S2. Compared to the formation of  $[\text{Au}(\text{mbtt})_2]\text{I}_3$ , the oxidation/complexation process by  $\text{mbtt}-\text{I}_2$  that lead to the formation of  $[\text{Pd}(\text{mbtt})_3\text{I}]\text{I}_3$  is more complex than expected, this fact depends both on the oxidation state of palladium ion, and on the stoichiometry of the complex. Unfortunately, we were not able to obtain crystals of this complex suitable for a single-crystals X-ray structure analysis. The recovery of palladium from the complex  $[\text{Pd}(\text{mbtt})_3\text{I}]\text{I}_3$  was performed by implementing the same procedure carried out for the gold complex.

In the case of the silver powder, the oxidative/complexing process was not observed and the metal was recovered un-reacted. The solid separated from the reaction mixture was analysed by the ESI-MS showing mode signals at  $m/z$  489 and  $m/z$  308 in the positive ion due to the species  $[(\text{mbtt})_2\text{I}]^+$  and

$[(\text{mbtt})\text{I}]^+$ , respectively, and a signal at  $m/z$  181  $(\text{mbtt})^*+$  related to the fragmentation of the main species. All of these signals are related to the leaching species  $\text{mbtt-I}_2$ .

#### 2.4 Competitivity of the leaching $\text{mbtt} + \text{I}_2(\text{aq})$ system towards gold and palladium

The reaction between  $\text{mbtt} + \text{I}_2(\text{aq})$  and a mixture of Au and Pd metals in powder was carried out so as to realise a  $(\text{Au}/\text{Pd}):\text{I}_2(\text{aq}):\text{mbtt}$  reaction molar ratio of  $(1/1):2:2$  in order to highlight which of the two metals shows the highest reactivity, at least under the experimental conditions employed. After 24 hours of stirring the reaction was interrupted. The colourless solution examined for the detection of metal ions by the ICP analysis showed only the presence of traces of gold ions (0.02 ppm). The separated solid was dissolved in dichloromethane. As a result of the evaporation of the solvent, a red-black crystalline solid was obtained. The ESI-MS analysis confirms both the formation of the Au-complex  $([\text{Au}(\text{mbtt})_2]^+ (m/z$  559)), and the absence of any signal attributable to the presence of palladium-complexes (Fig. 4). The yield of conversion of gold(0) to gold(I) is 66%, a value almost similar to the one reported (65%) for the oxidative-dissolution of gold alone carried out in the same reaction conditions. This result highlights the ability of the lixiviant  $\text{mbtt-I}_2$  to react preferentially with gold enabling therefore the possibility of separation of gold from a mixture gold-palladium.



**Fig. 4** ESI-MS spectrum of the sample obtained from the reaction  $\text{mbtt} + \text{I}_2(\text{aq})$  and a mixture of Au, and Pd metals in powder  $(\text{Au}/\text{Pd}):\text{I}_2(\text{aq}):\text{mbtt}$  reaction molar ratio of  $(1/1):2:2$ ; positive ion mode (left) and negative ion mode (right). In the inset, the MS-MS spectrum of the signal at  $m/z$  559 is shown, (L = mbtt).

### 3. Conclusion

From the results of the present study, it appears that the oxidative dissolution process in water of gold and palladium powders based on the lixiviant mixture of 3-methyl-benzothiazole-2-thione (mbtt) and  $I_2$  is easily accomplished by using process conditions that were safe for the health and the environment. However, no oxidation was observed in the case of silver powder.

Gold and palladium are oxidised to form the complexes  $[Au^I(mbtt)_2]I_3$  and  $[Pd^{II}(mbtt)_3I]I_3$ . Considering the mild conditions in which the process was performed ( $[I_2] = 1.14 \times 10^{-3} M$ ,  $T = 20^\circ C$ ,  $pH = 5.0$ , leaching time = 24h), the obtained oxidation yields to  $Au^I$  and  $Pd^{II}$  are to be considered satisfactory with values of 65% and 69%, respectively. Moreover, both complexes are easily separable from the leaching solution as they are poorly soluble in water. This makes it possible to store the product and allows the recovery process of gold at a later stage. This is not possible with cyanide as the separation of the  $Au(CN)_2^-$  as solid complex is not foreseen.

The process of recovering gold from the complexes  $[Au^I(mbtt)_2]I_3$  and  $[Pd^{II}(mbtt)_3I]I_3$  was implemented by carrying out the reduction of the complex with magnesium powder in acetone, while the purification of the reagent mbtt was accomplished with simple chemical operations. The production of  $MgCl_2$  and  $MgI_2$  can be considered as a resource rather than as a waste product.

The oxidising/complexing properties of the leaching mixture  $mbtt + I_2$  were interpreted considering the formation of the  $mbtt-I_2$  adduct that features a charge separation between the bridging and terminal iodine atoms in the fragment  $S-I_b-I_t$ .

In the light of the experimental data reported, the  $mbtt + I_2$  system can be considered a potential alternative to lixiviant cyanide. After using eco-friendly and mild reaction conditions, both the leaching, and the cementation steps are easy to implement and do not pose serious risks to human health and the environment. Non toxic solvents are used throughout the leaching and cementation processes, the reagent mbtt is easily recovered and reutilised while the iodine is recovered as magnesium iodide salt; in addition, magnesium chloride salt is also produced in the course of the cementation process.

The observed results provide a challenging task for further investigations (e.g. reduction of the leaching time and increase of the gold oxidation yield), which are beyond the object of the present study.

### 4. Experimental

#### 4.1 Materials, instrumentation, and methods

Reagents were used as purchased from Aldrich. Compound 3-methyl-benzothiazole-2-thione was finely ground before its use. The concentration of iodine-saturated solution in water ( $20^\circ C$ ) was

standardized against sodium thiosulfate 0.05 M titration.<sup>28</sup> Elemental analyses were obtained using a Perkin Elmer Series II – 2400. Infrared spectra (4000–400  $\text{cm}^{-1}$ ) of samples were recorded on a Bruker Vector 22 FT-IR spectrometer equipped with ATR accessory.  $^{13}\text{C}$  NMR spectra were recorded on a Varian 500 MHz spectrometer, chemical shift are reported in ppm ( $\delta$ ) downfield from TMS using the same solvent as internal reference. Absorption spectra were recorded on a Thermo-Nicolet Evolution 300 spectrophotometer (190 – 750 nm) at 23 °C using thermostated quartz cuvettes with an optical path length of 10.0 mm. Mass spectra were recorded in positive and negative ion mode on a triple quadrupole QqQ Varian 310-MS mass spectrometer using the Atmospheric-Pressure Electrospray Ionisation (ESI) technique in the  $m/z$  50–1000 range. The experimental conditions were the following: needle voltage 3500 V, shield voltage 600 V, housing temperature 60 °C, drying gas temperature 100 °C, nebuliser gas pressure 40 PSI, drying gas pressure 40 PSI, and detector voltage 1450 V. MS–MS experiments were performed with argon as the collision gas at 1.8 PSI. The collision energy was varied from 5 to 25 V. The isotopic patterns of the peaks were analysed using the mMass 5.5.0 software package.<sup>29</sup> The sample solutions were infused directly into the ESI source using a programmable syringe pump at a flow rate of 1.50 mL/h. A dwell time of 14 s was used and the spectra were accumulated for at least 10 min in order to increase the signal-to-noise ratio.

Metal ions concentrations of the aqueous solutions were determined, using an ICP-AES Varian Liberty 200 vacuum unit inductively coupled plasma emission spectrometer, with respect to five point calibration plot in the 0.5–5 ppm range for gold and palladium; The aqueous solutions were added of concentrated  $\text{HNO}_3$  to realize a 1% v/v acid solution.

#### 4.2 Oxidative dissolution of gold powder: synthesis of $[\text{Au}^{\text{I}}(\text{mbtt})_2]\text{I}_3$

A suspension of gold powder ( $<45 \mu\text{m}$ ) (0.0898 g, 0.456 mmol) in 800 mL of solution of iodine in water (1.14 mM, 20 °C, 0.912 mmol) was sonicated for 2 min. Then mbtt (0.1653 g, 0.912 mmol) was added and the heterogeneous solution was sonicated for 5 min and then stirred at a constant mixing rate of 900 rpm for one day. The resulting reddish powder was collected by suction filtration, washed with water (500 mL, 60 °C) and dried in desiccator. The crude product was recrystallised from hot ethyl alcohol (30 mL), or acetone (20 mL), then the solution left to stand at  $-15^\circ\text{C}$  for 24 h to yield a dark red powder. Obtained 0.2851 g, Yield 66.4 % referred to gold. Anal. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{AuI}_3\text{N}_2\text{S}_4$ : C 20.43; H 1.50; N 2.98; S 13.64. Found: C 20.6; H 1.4; N 3.0; S 13.9 %.  $\delta_{\text{c}}$  (75.4 MHz, DMSO- $d_6$ ,  $\text{Me}_4\text{Si}$ ) 178.0 (CS), 145.1, 129.3, 127.3, 125.1, 122.0, 113.6, 34.4 (NMe). IR ( $\nu/\text{cm}^{-1}$ ): 2960w, 2782vw, 1966vs, 1457m, 1422s, 1358m, 1314m, 1263m, 1131m, 1089m, 1052m, 981s, 817w, 749m, 718w, 638w. ESI-MS  $[\text{Au}(\text{mbtt})_2]^+$  exp.  $m/z$  559, found 559. Small crystals of complex  $[\text{Au}^{\text{I}}(\text{mbtt})_2]\text{I}_3$  were obtained dissolving a small amount of dark red powder in  $\text{CH}_2\text{Cl}_2$  and let the solution to stand at  $-15^\circ\text{C}$  for 48 h.

### 4.3 Oxidative dissolution of palladium powder: synthesis of $[\text{Pd}^{\text{II}}(\text{mbtt})_3\text{I}]\text{I}_3$

A suspension of palladium powder (1 $\mu\text{m}$ ) (0.0485g, 0.456 mmol) in 800 mL of solution of iodine in water (1.14 mM, 20 °C, 0.912 mmol) was sonicated for 2 min. Then mbtt (0.1653 g, 0.912 mmol) was added and the heterogeneous solution was sonicated for 5 min and then stirred for one day. The resulting brownish powder was collected by suction filtration, washed with water (500 mL, 60 °C) and dried in desiccator. The crude product was recrystallised from ethyl alcohol (40 mL). Obtained 0.3660 g. Yield 69.1% referring to palladium. Anal. Calcd. for  $\text{C}_{24}\text{H}_{21}\text{I}_4\text{N}_3\text{PdS}_6$ : C 24.9; H 1.83; N 3.63; S 16.62. Found: C 25.0; H 1.8; N 3.7; S 17.0 %. IR ( $\nu/\text{cm}^{-1}$ ): 1461w, 1429m, 1366m, 1266w, 1132wm, 1090m, 1052m, 981s, 937w, 817w, 749vs, 719w, 670w 638m. ESI-MS  $[\text{Pd}(\text{mbtt})_3\text{I}]^+$  exp.  $m/z$  777, found 777.

### 4.4 Oxidative dissolution of silver powder.

A suspension of silver powder (60 mesh) (0.0492 g, 0.456 mmol) in 800 mL of solution of iodine in water (1.14 mM, 20 °C, 0.912 mmol) was sonicated for 2 min. Then mbtt (0.1653 g, 0.912 mmol) was added and the heterogeneous solution was sonicated for 5 min and then stirred for one day. The resulting reddish powder was collected by suction filtration, washed with water (500 mL, 60 °C) and dried in desiccator. The crude product was recrystallised from  $\text{CH}_2\text{Cl}_2$  (25 mL). Obtained 0.322 g of compound that elemental analysis and ESI-MS spectroscopy confirm to be the adduct  $\text{mbtt-I}_2$ .

### 4.5 Gold and palladium recovery process

Complex  $[\text{Au}(\text{mbtt})_2]\text{I}_3$  (0.100 g, 0.106 mmol) was dissolved in acetone (20 mL) and added of magnesium powder 50 mesh (0.020g, 0.823 mmol), The mixture was refluxed under vigorous stirring for 6 h. In this time the deep red colour of the solution turned to pale yellow. The solution was hot filtered to separate unreacted Mg powder and the metallic gold adhering to the magnesium powder from  $\text{MgI}_2$  and mbtt dissolved in acetone. After evaporating the acetone at a reduced pressure, the solid residue was washed with water to dissolve  $\text{MgI}_2$ ; the solid residue of mbtt was dried in desiccator, obtained 0.0364 g (yield 94%). The recovery of the gold was carried out dissolving the magnesium with HCl 2M, and washing the residue with water and acetone. Dried in vacuo. Obtained 0.0167 g of gold (yield 79.9%).

The recovery of palladium from the complex  $[\text{Pd}(\text{mbtt})_3\text{I}]\text{I}_3$  was performed by implementing the same procedure carried out for the gold complex., the yield was 78%.

### 4.6 Reactivity of 3-methyl-benzothiazole-2-thione (mbtt) and $\text{I}_2$ in water; synthesis of the adduct $\text{mbtt-I}_2$ .

The reactivity of a solution of iodine in water (200 mL,  $1.28 \times 10^{-3}$  M, 23 °C) with mbtt (0.046 g, 0.256

mmol) was monitored by registering in a period of time of 48 hours the variation of absorbance of the band at 460 nm relative to the electronic transition  $\pi^* \rightarrow \sigma^*(I_2)$ . During the investigation aliquots of 3 mL were taken and analysed. After 48 h, the dark-reddish powder precipitated in the course of the reaction was collected and recrystallized from dichloromethane to yield crystals of the 1:1 adduct mbtt-I<sub>2</sub>. Obtained 0.102 g (yield 93 %). Anal. Calcd. for C<sub>8</sub>H<sub>7</sub>I<sub>2</sub>NS<sub>2</sub>: C 22.08; H 1.62; N 3.22; S 14.74. Found: C 22.0; H 1.6; N 3.3; S 14.9 %.  $\delta_c$  (75.4 MHz, CDCl<sub>3</sub>/DMSO v:v 1:1) 164.2 (CS), 140.6, 125.9, 125.7, 123.8, 120.3, 111.8, 32.1 (NMe). IR ( $\nu/cm^{-1}$ ): 1457m, 1425s, 1361s, 1316m, 1264m, 1160m, 1131m, 1090m, 1052m, 981s, 817w, 748s, 718m, 638w. ESI-MS for [(mbtt)<sub>2</sub>I]<sup>+</sup> exp. *m/z* 489. found 489; for [(mbtt)I]<sup>+</sup> exp. *m/z* 308, found 308.

#### 4.7 Computational studies

Quantum-mechanical calculations were performed on mbtt and the Charge-Transfer adduct mbtt-I<sub>2</sub> at Density Functional Theory (DFT) level<sup>30</sup> Gaussian 09 suite of programs<sup>31</sup> on a E4 workstation equipped with four 4-core processors and 16 Gb of RAM (OS: Ubuntu 14.04 Linux). By following the computational set-up recently adopted in strictly related systems,<sup>32,33</sup> the calculations were carried out by adopting the mPW1PW<sup>34</sup> hybrid functional, Schäfer, Horn and Ahlrichs pVDZ basis sets for C, H, N, and S,<sup>35</sup> and LANL08d<sup>36</sup> basis set for I. Notably, this set-up provides reliable results for CT adducts, with only slight overestimations (less than 6%) in the chalcogen-halogen distances.<sup>32</sup> In all cases, geometry optimizations were followed by frequency calculations aimed to verify the nature of the energy minima. A full NBO<sup>37</sup> analysis was carried out at the optimized geometries. The programs Gaussview 5.0.8<sup>38</sup> and Molden 5.2<sup>39</sup> were used to investigate the geometries, charge distributions, and molecular orbital shapes.

#### Acknowledgements

We would like to thank Regione Autonoma della Sardegna for financial support.

#### Notes and references

- 1 D. Pant, D. Joshi, M. K. Upreti and R. K. Kotnala, *Waste Manage.*, 2012, **32**, 979–990.
- 2 S. Needhidasan, M. Samuel and R. Chidambaram, *Journal of Environmental Science & Engineering*, 2014, **12**:36.
- 3 (a) A. Tuncuck, V. Stazi, A. Akcil, E. Y. Yazici and H. Deveci, *Mineral Engineering*, 2012, **25**, 28–37, and references cited therein; (b) S. Syed, *Hydrometallurgy*, 2012, **115-116**, 30–51, and references cited therein; (c) A. Akcil, C. Erust, C. Sekhar Gahan, M. Ozgun, M. Sahin, and L. A. Tuncuck, *Waste Manage.*, 2015, **45**, 258–271; (d) J. Cui, L. Zhang, *J. Hazard. Mater.*, 2008, **156**, 228–256; (e) U. Jadhav, H. Hocheng, *Sci. Rep.*, 2015, **5**, 14574; (f) S. S. Konyratbekova, A.

- Baikonurova, A. Akcil, *Mineral Processing & Extractive Metall. Rev.*, 2015, **36**, 198–212; (g)B. Altansukh, K. Haga, N. Ariunbolor, S. Kawamura, A. Shibayama, *Engineering Journal*, 2016,20(4), 29–40; (h) C-H Lee, L-W. Tang, S. R. Popuri, *Waste Management & Research*, 2001, **29**(7), 677–685; (i) T. Groenewald, *J. South African Institute of Mining and Metallurgy*, 1977, **77**(11), 217–223; (k) G. Hilson, A. J. Monhemius, *Journal of Cleaner Production*, 2006, **14**, (12-13), 1158–1167; (l) G. Senanayake, *Gold Bulletin*, 2005, 38(4), 170-179; (m) P. Ling, V. G. Papangelakis, S. A. Argyropoulos, P. D. Kondos, *Canadian Metallurgical Quarterly*, 1996, **35**(3), 225–234; (n) C. Abbruzzese, P. Fornari, R. Massidda, F. Vegliò, S. Ubaldini, *Hydrometallurgy*, 1995, **39**, 265–276; (o) S. Ubaldini, P. Fornari, R. Massidda, C. Abbruzzese, *Hydrometallurgy*, 1998, **48**, 113–124; (p) M Gokelma, A. Birich, S. Stopic, B. Friedrich, *Journal of Material Science and Chemical Engineering*, 2016, **4**, 8–17; (q) M. Sahin, A. Akcil, C. Erust, S. Altynbeck, C. S. Gahan, A. Tuncuk, *Separation Science and Technology*, 2015, **50**, 2587–2597.
- 4 C. P. Baldè, F. Wang, R. Kuehr and J. Huisman, 2015, The global E-waste monitor – 2014, United Nations University, IAS – SCYCLE, Bonn, Germany.
- 5 S. Needhidasan, M. Samuel and R. Chidambaram, *J. Environ. Health Sci. Eng.*, 2014, **12**:36
- 6 E. Y. Yazici and H. Deveci, *The Journal of the Chamber of the Mining Engineers of Turkey*, 2009, **48**(3), 3–18.
- 7 P. Quinet, J. Proost and A. L. Van, *Min. Metall. Process.*, 2005, **22**(1), 17–22.
- 8 P. P. Sheng and T. H. Etsell, *Waste Manage. Res.*, 2007, **25**, 380–383.
- 9 S. Syed, *Hydrometallurgy*, 2006, **82**, 48–53.
- 10 H. Gavin and A. J. Monhemius, *J. Cleaner Prod.*, 2006, **14**, 1158–1167.
- 11 F. Lippolis and F. Isaia, in *Handbook of Chalcogen Chemistry: New Perspectives in Sulfur, Selenium and Tellurium (2)*, ed. F. A. Devillanova and W. W. Du Mont, Royal Society of Chemistry, 2013, Chapter 8.2, 448–472.
- 12 F. Isaia, M. C. Aragoni, M. Arca, C. Caltagirone, F. Demartin, A. Garau and V. Lippolis, *Dalton Trans.*, 2013, **42**(2), 492–498.
- 13 Aslanidis, A. G. Hatzidimitriou, E. G. Andreadou, A. A. Pantazaki and N. Voulgarakis, *Materials Science and Engineering C*, 2015, **50**, 187–193.
- 14 L. Koskinen, S. Jääskeläinen, E. Kalenius, P. Hirva and M. Haukka, *Cryst. Growth Design.*, 2014, **14**, 1989–1997.
- 15 O. Evangelinou, A. G. Hatzidimitriou, E. Velali, A. A. Pantazaki, N. Voulgarakis and P. Aslanidis, *Polyhedron*, 2014, **72**, 122–129.
- 16 M. A. Tsiaggali, E. G. Andreadou, A. G. Hatzidimitriou, A. A. Pantazaki and P. Aslanidis, *J. Inorg. Biochem.*, 2013, **121**, 121–128.

- 17 (a) M. C. Gimeno and A. Laguna, *Comprehensive Coordination Chemistry II*, **2003**, Volume 6, chapter 6.6 Silver and Gold, ed. J. A. McCleverty and T. J. Meyer, Elsevier; (b) T. A. Green, *Gold Bull.*, 2014, **47**, 205–216.
- 18 (a) R. W. Ramette and R. W. Sandford, Jr., *J. Amer. Chem. Soc.*, 1965, **87**(22), 5001–5005; (b) J. S. McIndoe and D. G. Tuck, *Dalton Trans.*, 2003, 244–248; (c) G. Daniele, *Gazz. Chim. Ital.*, **1960**, *90*, 1068–1075; (d) W. Hirsch, J. Greenman and R. Pizer, *Can. J. Chem.*, 1993, **71**, 2171–2174; (e) F. A. Cotton and G. Wilkinson, in *Advanced Inorganic Chemistry Third edition*, Interscience Publishers, 1972, p 458–494, and references cited therein.
- 19 M. I. Bernal-Uruchurtu, G. Kerenskaya and K. C. Janda, *Int. Rev. Phys. Chem.*, 2009, **28**, 223–265.
- 20 The reagents molar ratio employed was chosen on the basis of the stoichiometry of complex  $[\text{Au}(\text{mbtt})_2]\text{I}_3$ .
- 21 A. D. Awtrey and R. E. Connick, *J. Am. Chem. Soc.*, 1951, **73**(4), 1842–1843.
- 22 (a) P. D. Boyle and S. M. Godfrey, *Coord. Chem. Rev.*, 2001, **223**(1), 265–299; (b) M. C. Aragoni, M. Arca, F. Demartin, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis and G. Verani. *Coord. Chem. Rev.*, 1999, **184**, 271–290; (c) M. C. Aragoni, M. Arca, F. A. Devillanova, F. Isaia, and V. Lippolis, *Cryst. Growth Des.*, 2012, **12**, 2769–2779
- 23 The interaction between *S*-donor Lewis base (DS) and  $\text{I}_2$  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  $\sigma^*$  antibonding orbital of the iodine species. Compound 3-methyl-benzothiazole-2-thione forms a stable adduct with  $\text{I}_2$  [ $K_f(\text{dm}^3 \text{mol}^{-1}) = 6.26 \times 10^2$ , 25 °C,  $\text{CH}_2\text{Cl}_2$ ]. F. Cristiani, F. A. Devillanova, A. Diaz, and G. Verani, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1383–1386. Depending on the charge density transferred by the DS donor molecule and solvent nature, this can result in lengthening of the I–I bond length up to breaking of the bond. W. T. Pennington, T. W. Hanks and H. D. Arman, in *Halogen Bonding: Fundamentals and Applications*, ed. P. Metrangolo and G. Resnati, Springer-Verlag, Berlin. 2008, pp 65–104, and references cited therein.
- 24 G. J. Corban, S. K. Hadjikakou, N. Hadjiliadis, M. Kubicki, E. R. T. Tiekink, I. S. Butler, E. Drouga and A. M. Kosmas, *Inorg. Chem.*, 2005, **44**, 8617–8623
- 25 M. T. Raisanen, M. Kemell, M. Leskela and T. Repo, *Inorg. Chem.*, 2007, **46**, 3251–3256.
- 26 K. Lutz and M. Golia, *US Patent*, US 3885955, 1975.
- 27 (a) P. Navarro, R. Alvarez, C. Vargas, and F. J. Alguacil, *Minerals Engineering*, 2004, **17**, 825–831; (b) M. Karavasteva, *Hydrometallurgy*, 2010, **104**, 119–112; (c) P. Deplano, M. L. Mercuri, L. Pilia, A. Serpe and M. Vanzi, *EU Patent*, EP 1964936, 2007.



- 28 J. Mendham, R. C. Denney, J. D. Barnes, M. J. K. Thomas, in *Vogel's Quantitative Chemical Analysis (6th ed)*, 2000, p 428–460, New York: Prentice Hall.
- 29 (a) M. Strohm, D. Kavan, P. Nova, M. Volny, *Anal. Chem.*, 2010, **82**, 4648–4651; (b) T.H.J. Niedermeyer, M. Strohm, *PLoS One.*, 2012, **7**, e44913.
- 30 W. Koch and M. C. Holthausen, in *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, Weinheim, Germany, 2nd edn, 2002.
- 31 Gaussian 09, Rev. D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- 32 A. Mancini, M. C. Aragoni, N. Bricklebank, C. Castellano, F. Demartin, F. Isaia, V. Lippolis, A. Pintus and M. Arca, *Chem. –Asian J.*, 2013, **8**, 639–647.
- 33 A. Mancini, L. Pala, M. C. Aragoni, M. Arca, F. A. Devillanova, M. B. Hursthouse, M. E. Light, P. J. Skabara and N. Bricklebank, *Eur. J. Inorg. Chem.*, 2012, 2373–2380.
- 34 C. Adamo and V. Barone, *J. Chem. Phys.*, 1998, **108**, 664–675.
- 35 A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571–2577.
- 36 L. E. Roy, P. J. Hay and R. L. Martin, *J. Chem. Theory Comput.*, 2008, **4**, 1029–1031.
- 37 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899–926.
- 38 Æ. Frisch, H.P. Hratchian, R.D. Dennington II, T.A. Keith, John Millam, A.B. Nielsen, A.J. Holder and J. Hiscocks. Gaussian, Inc. GaussView Version 5.0, 2009.
- 39 G. Schaftenaar and J. H. Noordik, *J. Comput.-Aided Mol. Des.*, 2000, **14**, 123–134.