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Oxidant/complexing properties of the methimazole (MeImHS)/iodine system towards palladium and gold metals. Crystal structure of the complex cation [Pd^II(MeImHS)_4]^2+ balanced by a tetraiodide/iodide mixture†

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This paper reports on the oxidative dissolution ability in dichloromethane and water of the methimazole–iodine system towards gold and palladium in powder. This research has a potential application in the recovery process of these metals from electrical and electronic waste equipment (WEEE). The iodine-adduct of methimazole (1-methyl-3H-imidazole-2-thione; MeImHS) oxidises gold and palladium powders in dichloromethane to form the complexes $[Au^I(MeImHS)_2]I_3$ and $[Pd^{II}(MeImHS)_4](I_4)_{0.73} \cdot 2(I)_{0.27}$. The X-ray crystal structure of the palladium complex shows a square-planar Pd(II) ion S-coordinated to four MeImHS units with the charge essentially balanced by an unusual tetraiodide I_4^{2-} with minor amounts of iodide. The oxidative dissolution of palladium in water medium produces the cation $[Pd^{II}(MeImHS)_4]^{2+}$. Considering the reaction conditions under which the process was performed ($[I_2] = 1.14 \times 10^{-3}$ M, $T = 20\,^{\circ}C$, pH = 5, reaction time 24 h), the obtained value of 64% of oxidation yields from Pd(0) to Pd(II) is to be considered satisfactory. No appreciable oxidation was observed for the gold powder in water. The feasibility of recovering palladium from the triiodide salt of the complex cation $[Pd^{II}(MeImHS)_4]^{2+}$ was verified by carrying out a two-step reduction process using magnesium powder.

Introduction

Potential metal recovery processes from waste electrical and electronic equipment (WEEE) have been an intense area of research in recent decades. Indeed, the lifespan of EEE is subject to a rapid shortening due to obsolescence of technical features thus generating a large amount of industrial waste.[1] According to recent statistics, the production of WEEE has already exceeded 46 million metric tonnes, and is expected to reach 200 million metric tonnes in 2021, with an annual growth rate of 3 to 5%.[1] Although WEEE is a heterogeneous combination of materials (plastics, glass, ferrous and non-ferrous metals) the environmental and economic advantages of recycling metals are quite significant, at present and in the near future.[1] In fact, WEEE contains significant quantities of precious metals such as

gold, palladium, and silver with concentrations higher than in their respective ores, thus making their recycling important both from economic and environmental perspectives.[2,3] However, it should be borne in mind that many of the processes currently used to recover precious metals from WEEE have negative aspects such as the use of large amounts of water and energy, and what is worse, the simultaneous production of environmentally hazardous effluents.[4] For this reason, restrictions on waste disposal and stringent environmental regulations have motivated the development, over the past years, of both alternative processes to the cyanide one, and economically viable processes with reduced health risks.[5] In this context, we have been studying for several years alternative leaching agents based on the use of iodine adducts of thioamide derivatives ($DS \cdot I_2$) with the aim of recovering gold and palladium from WEEE.[6]

An interesting aspect offered by these oxidant/metal-complexing agents is related to the possible oxidative dissolution of selected metals through one-step reactions performed both in water and in non-aqueous solvents using mild reaction conditions, as summarized in reaction (1) (M^0 = elemental metal). In general, the metal oxidative dissolution process requires two essential components: an oxidant species to promote the metal oxidation,

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and a complexing ligand to stabilise/dissolve the metal ion.[7] We recently demonstrated that some selected 1:1 iodine adducts of thioamide derivatives DS·I_2 perform both functions simultaneously according to the general reaction (1). On this matter, we reported on the oxidative dissolution process in water of gold and

$$DS \cdot I_2 + M^0 \xrightarrow[\text{1–7 days/r.t.}]{CH_2Cl_2 - H_2O} \text{oxidised/complexed metal} \quad (1)$$
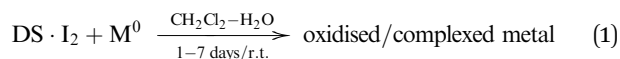
palladium powders based on the use of a mixture composed of the thioamide derivative 3-methyl-benzothiazole-2-thione (mbtt) and I_2. The insoluble complexes $[Au^I(mbtt)_2]I_3$ and $[Pd^{II}(mbtt)_3I]I_3$ were obtained under mild reaction conditions (H_2O, T = 21 °C, pH = 5, reaction time 24 h). The obtained oxidation yields of Au^0 and Pd^0 are to be considered satisfactory with values of 65% and 69%, respectively.[6b,c]

The main aim of the present study was devoted to the preliminary evaluation of the feasibility of the use of the I_2-adduct of thioamide methimazole (1-methyl-3H-imidazole-2-thione; MeImHS) (Fig. 1) as an oxidant/complexing system for the oxidative dissolution of pure gold and palladium metal powders. The reactions were performed both in dichloromethane and in water (pH 5.0) to determine the nature of the compounds that can be obtained in relation to the nature of the solvent. Although it is possible to develop an oxidative dissolution process for metals in non-aqueous solvents, it is also evident that this sets limits on its use when large quantities of material need to be treated. We have also checked whether there are grounds for considering the methimazole/iodine system in water as a potential alternative to the more common leaching agents used for the recovery of
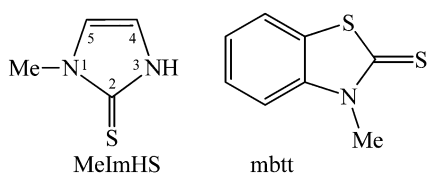
gold and palladium from the WEEE. Methimazole is a safe substance available in large quantities,[8] its choice stems from the fact that its iodine adduct (MeImHS·I_2) results very stable in nonpolar solvents featuring a high value of the formation constant.[9] This fact ensures that MeImHS·I_2 is the only "active" oxidant species acting in the reaction (1), moreover neither MeImHS nor I_2 alone can oxidise elemental palladium or gold in the reaction conditions considered. Methimazole, acting as a good Lewis base donor towards "soft" metal ions, may bind them in a variety of coordination modes, mainly as a neutral ligand as shown by its numerous metal-complexes reported in the literature.[10]

Results and discussion

Oxidative dissolution in dichloromethane of palladium powder

The oxidative dissolution process of metals reported in reaction (1) has been improved/refined over the years to achieve both the formation of pure metal-complexes, and high oxidation yields [see in ESI,† paragraph: Factors that influence the course of reaction (1)].[6] To this end, once the ability of the DS·I_2 adduct to oxidise the metal has been established, the necessary amounts of ligand DS and/or iodine and the reaction conditions need to be optimized. The reaction of palladium with a solution of I_2 and MeImHS in CH_2Cl_2 (1:2:4 molar ratio, T = 20 °C) was carried out in heterogeneous phase for 1 day.[11] During this period of time palladium powder was completely dissolved, a colour change of the solution from dark-red to orange-red was noticed, and no formation of solid products was observed in the reaction vessel. Slow evaporation of the solution in air resulted in red crystals which were shown by single crystal XRD to contain the $[Pd^{II}(MeImHS)_4]^{2+}$ cation and the tetraiodide I_4^{2-} partly substituted by minor amounts of iodide. Reactions carried out increasing either the molar ratio of iodine, or methimazole have led to the formation of sticky oils and to a marked decrease in the purity of the separated product, respectively.

Crystal structure of the complex $[Pd^{II}(MeImHS)_4](I_4)_{0.73} \cdot 2(I)_{0.27}$

A projection of the unit-cell content of the complex $[Pd^{II}(MeImHS)_4](I_4)_{0.73} \cdot 2(I)_{0.27}$ is shown in Fig. 2. The asymmetric

Fig. 1 Methimazole (MeImHS) and 3-methylbenzothiazole-2-thione (mbtt) structural formulas.
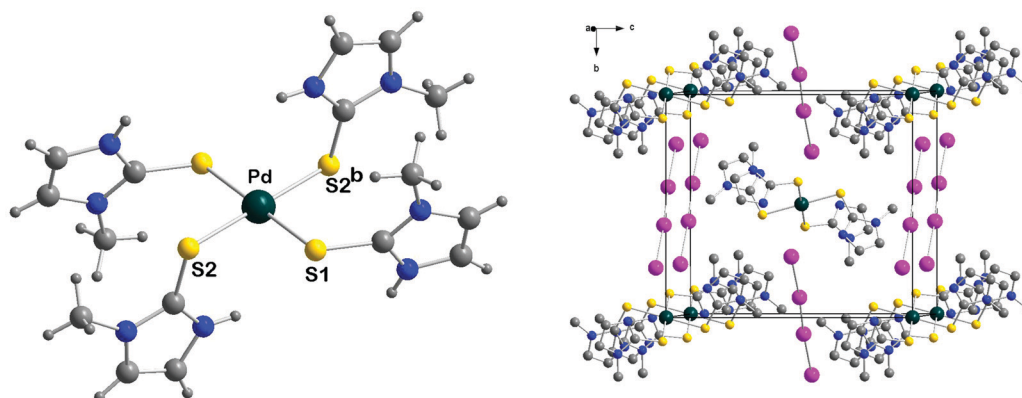
Fig. 2 The $[Pd^{II}(MeImHS)_4]^{2+}$ cation and a projection of the unit-cell content of the complex $[Pd^{II}(MeImHS)_4](I_4)_{0.73} \cdot 2(I)_{0.27}$ (only I_4^{2-} anions are shown). Selected bond distances (Å), angles (°) and hydrogen bond interactions are: Pd–S1 2.320(2), Pd–S(2) 2.334(2), S1–Pd–S2 84.61(9), S1–Pd–S2^b (b = −x, −y, −z) 95.39(9); N1–H1···I2 3.493(11), 158.8(6); N3–H3···I2 3.573(10), 150.8(6); N1–H1···I2^c (c = x − 1/2, 1/2 − y, z + 1/2) 3.604(15), 152.4(7); N3–H3···I2^c (c = x − 1/2, 1/2 − y, z + 1/2) 3.519(15), 150.9(6).

Fig. 3 View of the disorder of the iodine atoms. The pink atoms correspond to the I_4^{2-} anion with occupancy 0.73. The rose atoms correspond to the two I^- anions with occupancy 0.27. I1–I1^a (a = 1 − x, −y, −z − 1) 2.784(2) Å, I1–I2 3.292(4) Å.

Fig. 4 FT-Raman spectrum of complex $[Pd^{II}(MeImHS)_4](I_4)_{0.73}\cdot2(I)_{0.27}$ recorded in the 200–50 cm^{-1} region.

unit essentially consists of a square planar $[Pd^{II}(MeImHS)_4]^{2+}$ cation with the Pd atom located on a crystallographic inversion centre (2a Wyckoff position) and a mixture of the I_4^{2-} and I^- anions located about a different crystallographic inversion centre (2d Wyckoff position). The MeImHS molecules are arranged with their molecular plane almost normal to the coordination plane of the palladium ion. The situation corresponding to the positions of the iodine atoms is disordered and actually corresponds to the simultaneous presence of a I_4^{2-} and two I^- anions (Fig. 3). In fact, in the first stages of the refinement, the iodine atoms showed atomic displacement parameters that were higher than expected and the proposed model for the I_4^{2-} anion was not fully satisfactory because close to the terminal iodine atoms, a significant residual electron density still remained. The R factor was about 9%. An improvement of the model was obtained by refining the occupancies of the I_4^{2-} anion and introducing additional fractional I^- anions (I2′) to account for the residual electron density. As a matter of fact the arrangement of the iodine atoms can be interpreted as a system of four iodine atoms (I2–I1–I1^a–I2^a; a = 1 − x, −y, −z − 1) with occupancy 0.73 corresponding to the I_4^{2-} anion and two I^- anions (I2′ and I2′^{a}) with occupancy 0.27. This model is consistent with microanalytical data and also with the charge balance requirements since the occupancy of the I_4^{2-} anion is 0.73, thus corresponding to 1.46 negative charges and that of two I^- anions is 0.27 each, leading to a total of (1.46 + 2 × 0.27 = 2.00) negative charges required to balance the 2+ positive charge of the $[Pd^{II}(MeImHS)_4]^{2+}$ cation.

The central I1–I1^a distance in I_4^{2-} (2.784(2) Å) is only slightly elongated when compared to the distance observed in elemental iodine (2.667 Å and 2.715 Å for gaseous[12] and solid[12] iodine, respectively). The bond length between the central I1 and the terminal iodine atom I2 of 3.292(4) Å is markedly shorter than the sum of van der Waals and Pauli radii for I and I^-, respectively (4.04 Å), with an almost linear arrangement (I$^-\cdots$I–I angle 175.27°). In the crystal this dianion can be stabilised by intermolecular hydrogen bonds involving the terminal iodine atoms (I2/I2^a) and the N–H group of the MeImHS ligands [N1–H1$\cdots$I2 3.493(11) Å, 158.8(6)°].[13] The interatomic distances in I_4^{2-} suggest that this dianion can be represented as a week charge-transfer adduct consisting of two donating iodide anions and an iodine molecule as electron-density acceptor (I$^-\cdots$I$_2\cdots$I$^-$).[14]

Raman spectroscopy is a powerful tool for the investigation of polyiodide species,[15] especially when refers to structurally proved rare polyiodides such as I_4^{2-}. The FT-Raman spectrum of the complex in the region 200–50 cm^{-1} shows only one intense band at 167 cm^{-1} (Fig. 4), which can be attributed to the ν(I–I) stretching vibration of the slightly perturbed iodine
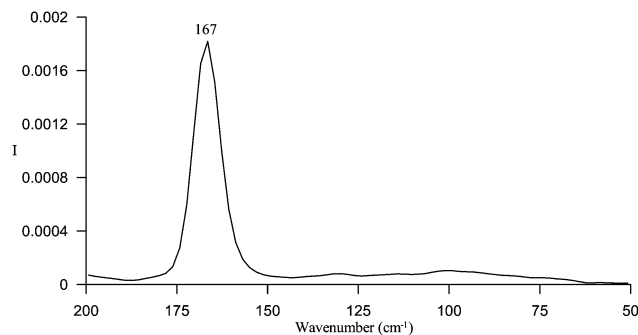
molecule as a consequence of the interaction with the two iodide electron donors.[16] This value is consistent with those reported for other I_4^{2-} structurally characterised polyiodides.[17] In general, the stretching ν(I–I) Raman band, observed at 180 cm^{-1} in I_2(s), is expected to move to lower frequencies (typically in the range of 180–140 cm^{-1}) when I_2 interacts with donors to form 1 : 1 charge-transfer complexes.[18]

The separation/identification of the Pd(II)-methimazole complex $[Pd^{II}(MeImHS)_4](I_4)_{0.73}\cdot2(I)_{0.27}$ from the reaction of palladium(0) with a solution of I_2 and MeImHS in CH_2Cl_2 (1 : 2 : 4 molar ratio, T = 20 °C) shows that the methimazole–I_2 adduct can successfully oxidise the palladium powder with a yield of 83% by a two-electron transfer process according to the overall reaction (2):

$$Pd^0 + 2I_2 + 4MeImHS \rightarrow [Pd^{II}(MeImHS)_4](I_4)_{0.73}\cdot2(I)_{0.27} + iodine \tag{2}$$
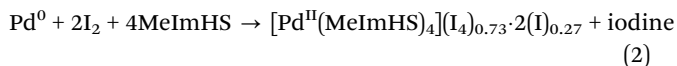
In previous studies, we recognised that the oxidising properties of DS·I_2 adducts towards zero-valent metals could be interpreted considering the charge separation along the S–I_b–I_t (I_b = bridging iodine, I_t = terminal iodine) moiety induced by the DS $\rightarrow$ I_2 charge-transfer interaction to form the reactive polarised system $[DS–I]^{\delta+}\cdots I^{\delta-}$.[6] In this regard, the calculated NBO charge distribution[6] for the adduct MeImHS·I_2 showed a sulphur atom that is slightly positive charged (0.078 e), and a marked charge separation between the iodine atoms of 0.348 e (NBO charges: I_b −0.19 e, I_t −0.367 e), which can be thought to be the basis of the increased reactivity of the MeImHS·I_2 adduct compared to that of molecular iodine.[6d] As similarly proposed for the oxidation/complexation of zinc(0) and mercury(0) by MeImHS·I_2 to yield the neutral complexes $[Zn^{II}(MeImHS)_2I_2]$,[6b] and $[Hg^{II}(MeImHS)_2I_4]$,[6d] it is reasonable to hypothesise that also the oxidation/complexation of palladium(0) proceeds via a mechanism of oxidative addition[19] with the $(MeImHS–I)^{\delta+}$ moiety acting as an electrophilic agent.

Oxidative dissolution of palladium powder in water

The reaction of palladium powder with a saturated solution of I_2 in water[20] and MeImHS (1 : 2 : 4 reaction molar ratio) was carried out in the heterogeneous phase at 20 °C for 1 day according to the general reaction (1). During this time, the palladium dissolved and the initial dark red colour of the mixture, due to the
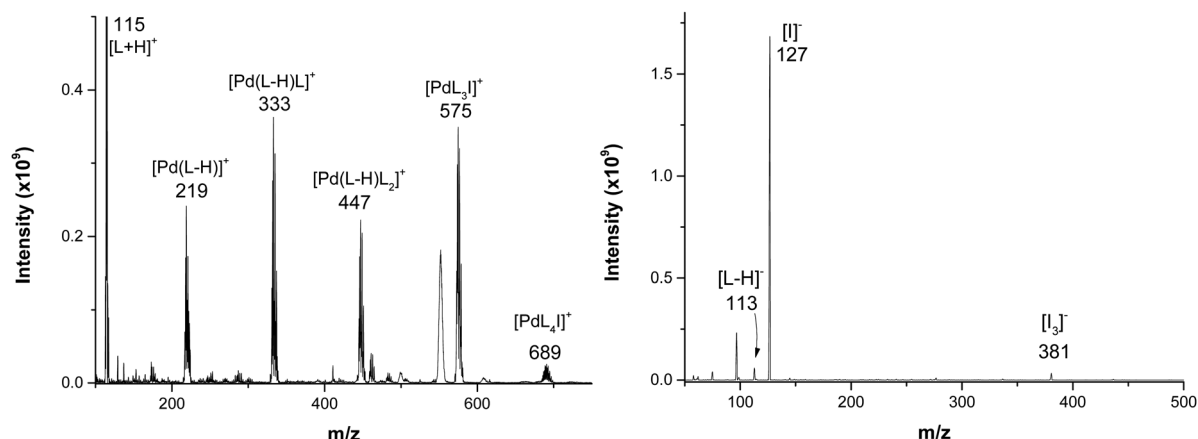
Fig. 5 ESI-MS spectra of the sample obtained from the reaction of MeImHS + I_2(aq) and Pd metal in powder, $Pd : I_2$: MeImHS reaction molar ratio of 1 : 2 : 4; positive ion mode (left) and negative ion mode (right), L = MeImHS.

visible absorption band of I_2(aq) at 460 nm,[20] turned to pale orange; after 24 hours, just a tiny amount of palladium dust or other formed solid species were observed in the reaction mixture. The determination of the concentration of the palladium ion in solution, carried out by the use of ICP atomic emission spectrometry, indicates a value of 20.8 ppm at 2 hours after the start of the reaction and 35.0 ppm at 24 hours. These values indicate a good oxidation yield from Pd(0) to Pd^{2+} of 47 and 64%, respectively. The nature of the palladium(II)-species in solution was investigated by electrospray ionisation mass spectrometry (ESI-MS), see Fig. 5, and ESI,† Fig. S1. In the positive ion mode the mass spectrum shows a signal at m/z 689 that is in agreement with the formation of the cation $[Pd^{II}(MeImHS)_4I]^+$, and signals at m/z 575 and m/z 447, which are related to the formation of the species $[Pd^{II}(MeImHS)_3I]^+$ and $[Pd^{II}-(MeImHS)_2(MeImHS–H)]^+$, respectively; MS–MS clarifies that the latter signal is originated from the fragmentation of complex $[Pd^{II}-(MeImHS)_4I]^+$. In the negative ion mode the most relevant signals are due to the presence of ions I_3^- (m/z 381) and I^- (m/z 127). These data confirm the oxidation of the palladium at its oxidation state 2+, and the complexation of the ion Pd^{2+} with four units of MeImHS as reported in reaction (3), a result that is similar to that obtained by carrying out the reaction in dichloromethane.

$$Pd^0 + 2I_2 + 4MeImHS \rightarrow [Pd^{II}(MeImHS)_4]^{2+} + I^- + I_3^- \quad (3)$$
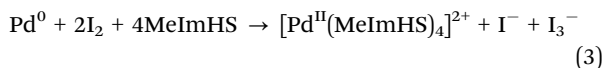
Palladium recovery process

There are numerous processes reported in the literature for the reduction of palladium(II) salt solutions by employing reducing agents in a variety of reaction conditions.[21] Among all these, the process we have applied for the recovery of palladium from complex $[Pd^{II}(MeImHS)_4]^{2+}$ involves the use of a non-toxic and inexpensive reducing agent such as magnesium powder.[6c,22]

The treatment of the water solution containing the Pd-complex with magnesium powder leads within 24 hours to complete discolouration of the solution and the formation/separation of a fine ochre-coloured powder. An analysis of the solution confirms both the absence of the palladium ion (ICP analysis: <0.1 ppm), and the presence of magnesium ions. The solid palladium complex is then dissolved in acetone before being treated with magnesium powder. The palladium(II) reduction process to palladium(0) occurs on the surface of the magnesium powder (ESI,† Fig. S2), the obtained palladium(II) reduction yield of 75% can be considered satisfactory. In Fig. 6 the flowsheet of the steps involving the Pd(II) recovery by magnesium powder is reported. The process steps involving the recovery of MeImHS, MgI_2, and $MgCl_2$ are also shown.

Oxidative dissolution in dichloromethane of gold powder

The reaction was initially performed under the same operating conditions as for palladium powder employing an $Au : I_2$: MeImHS reaction molar ratio of 1 : 2 : 4, $T = 20$ °C. After 24 h, the reaction mixture did not show traces of elemental gold, or related solid gold-complexes. Unlike the oxidative dissolution of palladium, no solid was separated by concentration of the solution, conversely the formation of a dark-red viscous oil was observed. The FT-Raman spectrum of this oil recorded in the region 250–50 cm^{-1} shows signals at 171, 135, and 112 cm^{-1} stating the presence of polyiodides and perturbed iodine molecules, Fig. 7.[15b,23] As suggested by the FT-Raman spectrum, the formation of oily compounds is to be related to an incorrect reaction molar ratio of the reagents, specifically an excess of iodine. To overcome this point, the same reaction was carried out changing the $Au : I_2$: MeImHS molar ratio to 1 : 1.5 : 2. We tentatively tailored the reagents molar ratio to accomplish the formation of a cationic Au(I)-complex of stoichiometry $[Au^I(MeImHS)_2]^+$ and a (poly)/iodide anion to balance the charge.[24] Under these experimental conditions we separated a brown powder that on the basis of the elementary analysis, and the intense Raman bands at 111 and 138 cm^{-1} was identified (Fig. 8) as the gold(I) complex $[Au^I(MeImHS)_2]I_3$.[25] We have failed, despite numerous attempts, to obtain crystalline samples suitable for structural investigation.
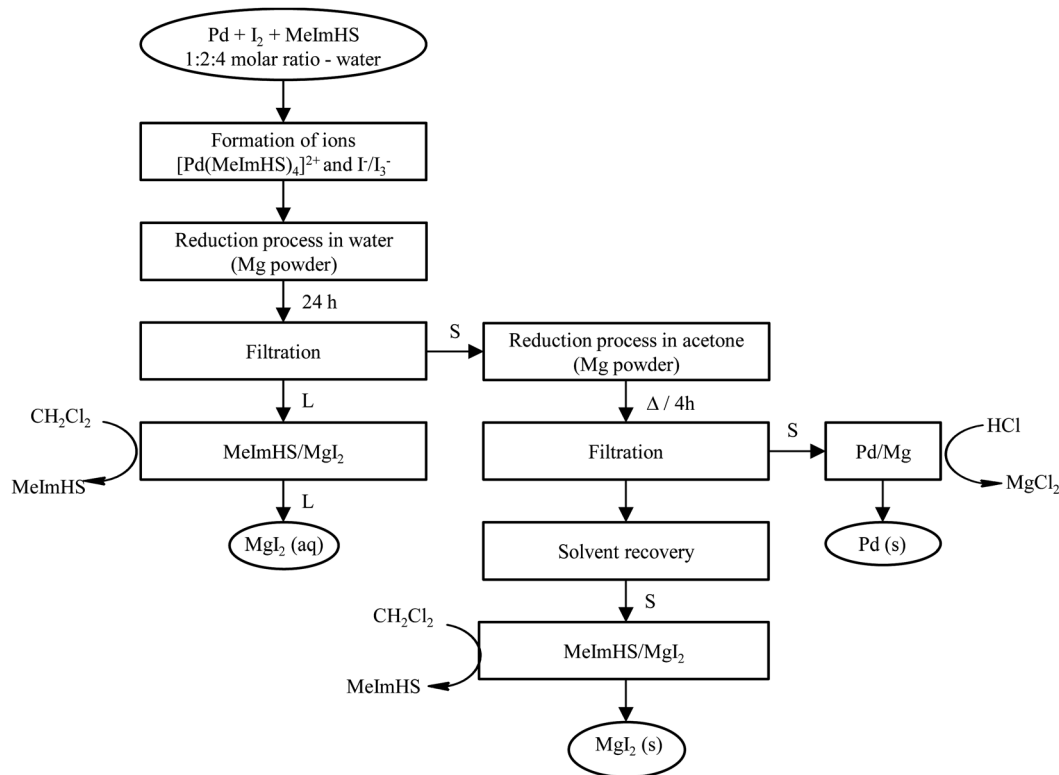
Fig. 6   Basic flowsheet showing the palladium recovery process applied to the reduction of complex in solution $[Pd^{II}(MeImHS)_4]^{2+}$ I^-/I_3^-. S, L = solid and liquid fractions, respectively.
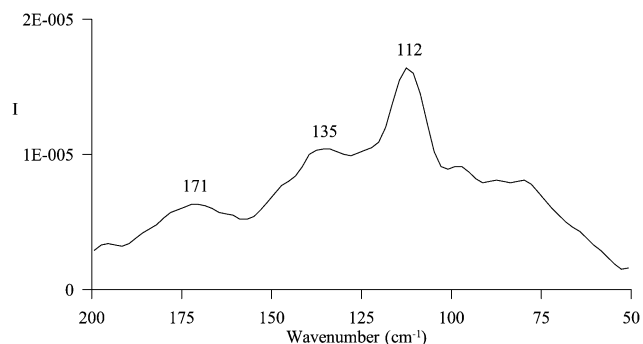

Fig. 7   FT-Raman spectrum recorded in the 200–50 cm^{-1} region of the oily compound obtained from the reaction of Au, I_2 and MeImHS, (1:2:4 molar ratio) in CH_2Cl_2; T = 20 °C, reaction time 1 day.
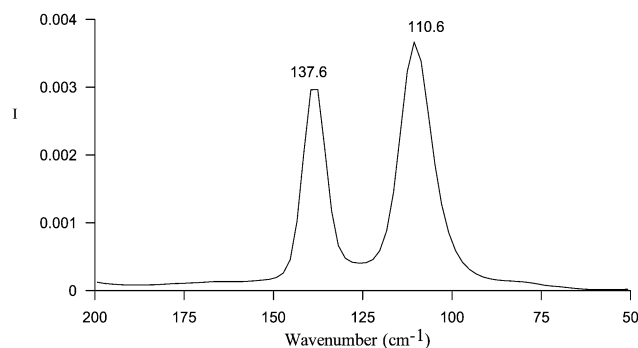

Fig. 8   FT-Raman spectrum recorded in the 200–50 cm^{-1} region of the solid compound obtained reacting Au, I_2, and MeImHS (1:1.5:2 molar ratio) in CH_2Cl_2; T = 20 °C, reaction time 1 day.

Oxidative dissolution in water of gold powder

Preliminary tests to evaluate the ability of the MeImHS·I_2 adduct to oxidise gold in water in its most common oxidation states +1 or +3 did not lead to satisfactory results. The reactions carried out using Au : MeImHS·I_2 molar ratios of 1:1, 1:2, and 1:3, (T = 20 °C, reaction time 24 hours) did not result in an appreciable oxidation of the gold powder. In the most favourable case (Au : MeImHS·I_2 1:3 molar ratio), an Au$^{I/III}$ ion content in the solution not exceeding 5.5 ppm was determined by ICP analysis, corresponding to a gold oxidation yield of 6.5%. The clear and colourless solution was analysed by ESI-MS to

highlight the nature of the ionic/soluble species formed. The ESI-MS spectrum recorded in positive ion mode, showed the presence of a peak at m/z 425 having an isotopic pattern consistent with the gold(ı)-containing species $[Au^I(MeImHS)_2]^+$ (Fig. 9); in the negative ion mode, the highest peak is found at m/z 127 related to the presence of iodide ion, other small signals at m/z 254, 381, and 451 are due to the species I_2, I_3^-, and $[AuI_2]^-$, respectively. It is noteworthy that neither oxidation species related to methimazole (i.e. dication or monocation methimazole-disulphide, and methimazole-disulphide) nor different gold-methimazole containing species were detected in the solution.
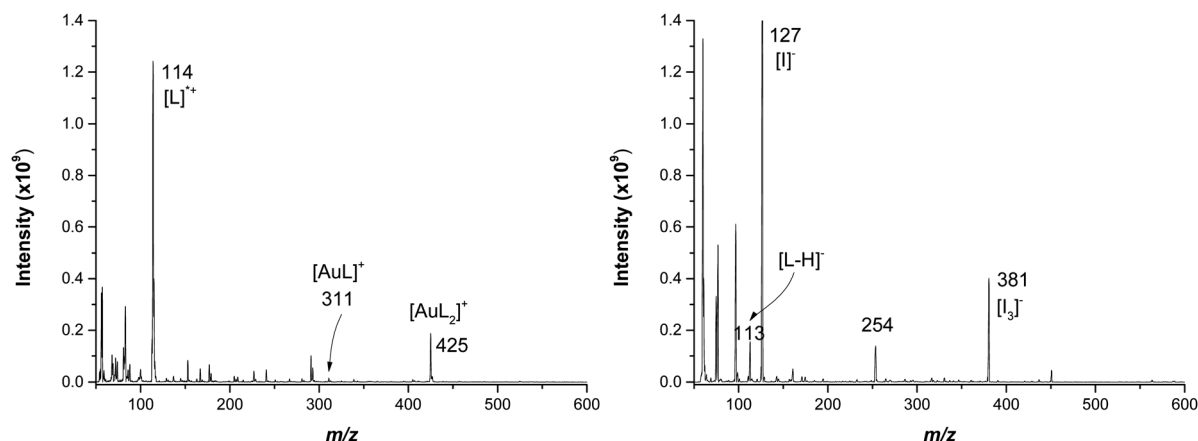
Fig. 9 ESI-MS spectra of the sample obtained from the reaction of MeImHS + I_2(aq) and Au metal in powder, Au:I_2:MeImHS reaction molar ratio 1 : 3 : 3; positive ion mode (left) and negative ion mode (right), L = MeImHS.

Conclusion

From the results of the present study, it appears that the oxidative dissolution process of palladium powder both in dichloromethane and water based on the oxidant/complexing mixture of methimazole (MeImHS) and I_2 is easily achievable by using mild and safe reaction conditions. On the contrary, the oxidative dissolution of gold was accomplished only in dichloromethane with the formation of the Au(I) complex [Au^I(MeImHS)$_2$]I_3. In dichloromethane, the palladium(II) complex [Pd^{II}(MeImHS)$_4$]-(I_4)$_{0.73}$(2I)$_{0.27}$ was separated. It features the metal ion bound to four MeImHS units in a square planar fashion *via* S-atoms; a mixture of tetraiodide I_4^{2-} and iodides balances the charge. The cation complex [Pd^{II}(MeImHS)$_4$]$^{2+}$ was also produced in the reaction carried out in water. Considering the conditions under which the process was performed in water ([I_2] = 1.14 × 10^{-3} M, T = 20 °C, pH = 5, reaction time 24 h), the obtained value of 64% of oxidation yields from Pd(0) to Pd(II) is to be considered satisfactory. The subsequent recovery of palladium from the cation [Pd^{II}(MeImHS)$_4$]$^{2+}$ in water solution was implemented by carrying out a two-step reduction process using magnesium powder. These results add further knowledge to the use of thioamide–iodine mixtures as oxidant/complexing agents. However, further studies to increase the potential of this oxidative-dissolution methodology towards noble metals are needed.

Experimental

Materials, instrumentation, and methods

Reagents were used as purchased from Aldrich. The concentration of iodine-saturated solution in water (20 °C) was standardized against sodium thiosulfate 0.05 M titration.[26] Elemental analyses were obtained using a PerkinElmer Series II – 2400. Metal concentration was determined with the atomic emission spectrophotometer ICP-OES 5110, Agilent. Palladium standard solution, traceable to SRM from NIST Pd(NO$_3$)$_2$ in HNO$_3$ 0.5 mol l^{-1} 1000 mg l^{-1} Pd Certipur® Aqua distillate MILLIPORE. Gold standard solution, traceable to SRM from NIST HAuCl$_4$

in HCl 2 mol l^{-1} 1000 mg l^{-1} Au Certipur®. Infrared spectra (4000–400 cm^{-1}) of samples were recorded on a Bruker Vector 22 FT-IR spectrometer equipped with ATR accessory. FT-Raman spectra were recorded on a Bruker FRS 100/S transform Raman spectrometer, operating with a diode-pumped Nd:YAG exciting laser emitting at 1064 nm. MAS ^{13}C NMR spectra were recorded at 298.1 K on a Varian 500 MHz spectrometer operating at 150.9 MHz; the spectra were calibrated such that the observed upfield peak in the spectrum of adamantane is set to δ = 31.47. Mass spectra were recorded in positive and negative ion mode on a triple quadruple 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 4500 V, shield voltage 600 V, housing temperature 60 °C, drying gas temperature 100 °C, nebuliser gas pressure 20 psi, drying gas pressure 20 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 40 V. The isotopic patterns of the peaks were analysed using the mMass 5.5.0 software package.[27] The sample solutions were infused directly into the ESI source using a programmable syringe pump at a flow rate of 1.00 mL h^{-1}. 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.

Oxidative dissolution of palladium powder in dichloromethane: synthesis of [Pd^{II}(MeImHS)$_4$](I_4)$_{0.73}$·2(I)$_{0.27}$. A suspension of palladium powder (1 μm) (0.0500 g, 0.4698 mmol) and MeImHS (0.2145 g 1.878 mmol) in 30 mL of CH$_2$Cl$_2$ was sonicated for 2 min and then added of iodine (0.2385 g, 0.9396 mmol) dissolved in 20 mL of CH$_2$Cl$_2$. The mixture was stirred at a constant stirring rate of 500 rpm for one day at 20 °C. After that, the solution was filtered (polyester syringe filter Chromafil-Xtra PET 0.45 μm) in order to separate any traces of unreacted metal powder, and then slowly concentrated to separate air stable ruby red crystals of complex [Pd^{II}(MeImHS)$_4$](I_4)$_{0.73}$·2(I)$_{0.27}$ which were washed with a mixture *n*-hexane–CH$_2$Cl$_2$ 9/1 v/v and dried in an oven at 30 °C for 1 hour. Yield 0.390 g, 83%; C$_{16}$H$_{24}$I$_{3.46}$N$_8$PdS$_4$, M (1002.14 g mol^{-1}): calcd C 19.17, H 2.41, N 11.17, S 12.79.

Found: C 18.4, H 2.3, N 10.9. MAS ^{13}C-NMR, δ_C 152.5 (CS), 125.8 (C5), 116.1 (C4), 34.6 (N-Me). IR (ν/cm^{-1}): 3151m, 3100m, 2998w, 1571s, 1472s, 1441s, 1275w, 1149w, 922w, 729vs, 680s, 661vs, 509m, 428w; ESI,† Fig. S3. With regard to the amount of iodine present, the value of I$_{3.46}$ depends both on the simultaneous presence in the compound of the I$_4{}^{2-}$ and I$^-$ anions, and the occupancy value (0.73 and 0.27, respectively). The four iodine atoms of the species I$_4{}^{2-}$ contribute 2.92 units of iodine atoms (4 × 0.73) while the two iodide contribute 0.54 units of iodine atoms (2 × 0.27). So, the total units of iodine atoms in the compound are 2.92 + 0.54 = 3.46.

Oxidative dissolution of palladium powder in water. A suspension of palladium powder (1 μm) (0.0435 g, 0.408 mmol) in 800 mL of solution of iodine in water (1.14 mM, 20 °C, 0.912 mmol) was sonicated for 2 min. Then MeImHS (0.2082 g, 1.824 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. After that, the solution was filtered to separate any traces of unreacted metal powder, and the molar concentration of the oxidised/complexed palladium in the solution determined by ICP analysis. The found value of 35.0 ppm was indicative of an oxidation yield of the 64.3%. ESI-MS m/z 689 [Pd^{II}(MeImHS)$_4$I]$^+$.

Palladium recovery process. 1600 mL of water solution containing ions [Pd^{II}(MeImHS)$_4$]$^{2+}$ and I$^-$/I$_3{}^-$ (0.056 g, 0.524 mmol of Pd^{2+}; 0.2678 g, 2.350 mmol of MeImHS) prepared as above, was added of magnesium powder 50 mesh (Pd/Mg 1 : 3 molar ratio) (0.0382 g, 1.572 mmol), sonicated for 5 min and then vigorously stirred for 1 day. In this time the deep red colour of the solution turned to pale yellow; the resulting reddish powder was collected by suction filtration, washed with water (500 mL, 50 °C) and dried in desiccator. To this powder dissolved in acetone (60 mL), it was added magnesium powder 50 mesh (0.0382 g, 1.572 mmol). The mixture was sonicated for 5 min and then refluxed under vigorous stirring for 4 h. In this time the deep red colour of the solution turned to pale yellow. The solution was hot filtered to separate the magnesium/palladium powder from MgI$_2$ and MeImHS dissolved in acetone. The recovery of the palladium was carried out dissolving the magnesium/palladium powder with HCl 0.5 M, and washing the residue with water. After drying *in vacuo*, 0.0420 g of palladium were obtained (yield 75.0%). MeImHS is recovered evaporating the CH$_2$Cl$_2$ solutions, after drying *in vacuo* 0.1869 g (yield 69.8%) of MeImHS was obtained.

Oxidative dissolution of gold powder in dichloromethane. A suspension of gold powder (<45 μm) (0.0500 g, 0.253 mmol) and MeImHS (0.0578 g, 0.506 mmol) in 30 mL of CH$_2$Cl$_2$ was sonicated for 2 min and then added of iodine (0.0963 g, 0.0379 mmol) dissolved in 20 mL of CH$_2$Cl$_2$. The mixture was stirred at a constant stirring rate of 500 rpm for one day at 20 °C. The solution was filtered (polyester syringe filter Chromafil-Xtra PET 0.45 μm) in order to separate any traces of unreacted metal powder, and then slowly concentrated until a solid sample was formed. Obtained 0.028 g. C$_8$H$_{12}$AuI$_3$N$_4$S$_2$ (805.73 g mol^{-1}): calcd C 11.91, H 1.50, N 6.95. Found: C 12.0, H 1.6, N 7.0. Yield 13.7%. IR (ν/cm^{-1}): 3314w, 3154w, 1570s, 1478m, 1384m, 1289m, 1253w, 1160w, 1094w, 775s, 665s, 656s; ESI,† Fig. S4.

Oxidative dissolution of gold powder in water. A suspension of gold powder (<45 μm) (0.0598 g, 0.304 mmol) in 800 mL of solution of iodine in water (1.14 mM, 20 °C, 0.912 mmol) was sonicated for 2 min. Then MeImHS (0.1041 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. Except for the gold powder that didn't react, there is no evidence of the formation of any solids. In the filtered solution the gold content, determined by ICP analysis, amounted to 5.5 ppm, indicative of an oxidation yield of 7.3%. ESI-MS m/z 425 [Au^I(MeImHS)$_2$]$^+$.

Crystallographic data for [Pd^{II}(MeImHS)$_4$](I$_4$)$_{0.73}$·2(I)$_{0.27}$. C$_{16}$H$_{24}$I$_{3.46}$N$_8$PdS$_4$, M = 1002.14, monoclinic, a = 8.721(2) Å, b = 12.844(3) Å, c = 14.190(34) Å, β = 99.62(3)°, U = 1567.1(6) Å^3, T = 294(2) K, space group $P2_1/n$ (no. 14), Z = 2, μ = (Mo-Kα) 4.287 mm^{-1}. 10 812 reflections (2824 unique; R_{int} = 0.028) were collected at room temperature, employing a 0.15 × 0.12 × 0.08 mm crystal mounted on a Bruker APEX II CCD diffracto-meter and using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). Final R_1 [wR_2] values are 0.0478 (0.0611) on I > 2$\sigma(I)$ (all data). Datasets were corrected for Lorentz-polarization effects and for absorption (SADABS).[28] The structure was solved by direct methods (SIR-97)[29] and completed by iterative cycles of full matrix least squares refinement on $F_o{}^2$ and ΔF synthesis using the SHELXL-2018[30] program (WinGX suite).[31] Hydrogen atoms, located on the ΔF maps, were allowed to ride on their carbon and nitrogen atoms. During the early stages of the structure refinement using a centro-symmetric (I–I–I–I)$^{2-}$ model for the anionic moiety of the complex in the asymmetric unit, anomalous displacement parameter were observed, thus suggest-ing that this moiety may be partially replaced by iodide atoms at the terminal iodine atom positions as indicated by microanalytical data. A competitive refinement was carried out to investigate this possibility and a final model with a mixed-site I$_4{}^{2-}$/2I$^-$ with occupancy of 0.73/0.27 was found to give the best fit to the data. Crystallographic data for compound [Pd^{II}(MeImHS)$_4$](I$_4$)$_{0.73}$·2(I)$_{0.27}$, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 1964288.†

Conflicts of interest

There are no conflict to declare.

Acknowledgements

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