

Pyridinethiol-assisted dissolution of elemental gold in organic solutions

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Dissolution of elemental Au in organic solutions is a contemporary approach to lower environmental burden related to gold recycling. Here we describe fundamental studies on a highly efficient method for dissolution of Au which is based on DMF solutions containing pyridine-4-thiol (4-PSH) as a reactive ligand and hydrogen peroxide as an oxidant. Dissolution of Au proceeds mechanistically through several elementary steps: isomerization of 4-PSH to pyridine-4-thione (4-PS); coordination with Au⁰; then oxidation of Au⁰ thione species to Au^I simultaneously with the oxidation of free pyridine thione to elementary S and further to sulfuric acid. The final dissolution product is an Au^I complex bearing two 4-PS ligands and SO₄²⁻ as a counter ion. The role of the ligand is, therefore, crucial as it assists the oxidation process and stabilizes and solubilizes the formed Au cations. The generality of the designed method was successfully highlighted with other Group 11 metals and its applicability to the circular economy was further demonstrated with printed circuit board samples.

Noble metals, including Au, Ag and Pt, are scarce elements in earth's crust and greatly needed in high-tech applications.¹⁻⁴ They are, therefore, precious and their demand is continuously growing. The possibility to recycle the elements from multi-metal materials such as printed circuit boards (PCBs) is crucial when sustainability and the circular economy are considered.⁵ In general, recovery of Au in the mining industry is mostly based on the hydrometallurgical cyanidation process, which relies on the use of stoichiometric amounts of cyanide salts and produces large amounts of hazardous waste.^{6,7} Consequently, a new and fairly unexploited concept known as dissolution of noble metals in organic solvents is highly attractive – it offers the possibility to develop benign and selective dissolution methods.⁸⁻¹⁶

Three different methods for dissolution of Au⁰ in organic solutions have been reported up to date (Fig. 1). One approach is based on pyridine, dimethylformamide or imidazole solutions of thionyl chloride (SOCl₂) called organic *aqua regia* (Fig. 1a) which, regardless of the toxicity of SOCl₂,

benefits from high selectivity towards Pt/Au/Pd and Au/Pd mixtures.⁸⁻¹⁰ The second method is based on somewhat toxic I₂ using dithioxamides or tetraalkylthiuram disulfides as donors to oxidize Au⁰ to Au^{III} (Fig. 1b).¹¹⁻¹⁵ The third concept is a pyridine-4-thiol (4-PSH) based method developed by us, characterized by slow dissolution of Au in ethanol solutions (0.06×10⁻³ mol/(m²*h)) at room temperature (Fig. 1c).¹⁶ Interestingly, by fine-tuning the reaction conditions, this method can also be used in selective preparation of self-supporting nanometer-thick gold foils.¹⁶ As thiols are commonly used as etch resists for Au⁰ surfaces, the results were intriguing and counterintuitive. Therefore, we took an initiative to carry out further studies and reveal mechanistic details related to the 4-PSH-assisted dissolution.

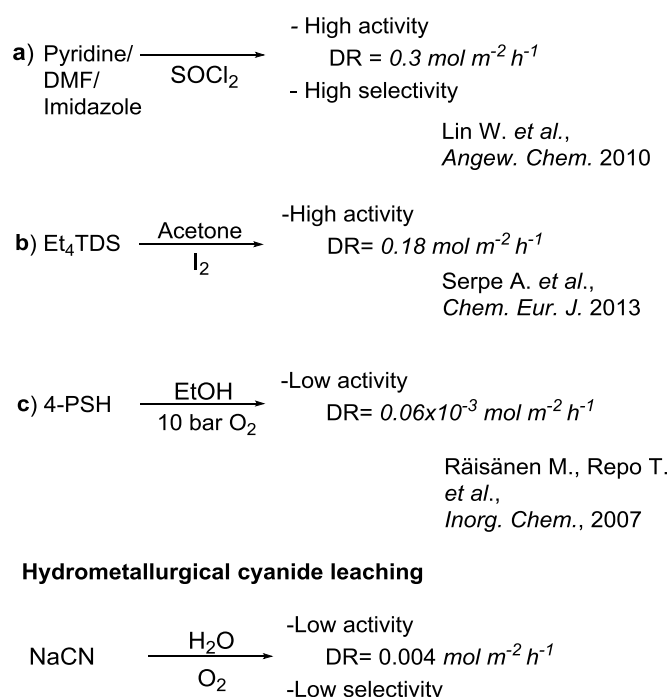


Fig. 1 | Organic solvent-based methods for dissolution of elemental gold. a, SOCl₂ with py/Im/DMF b, Et₄TDS/I₂ c, 4-PSH/EtOH/O₂ and comparison with common hydrometallurgical cyanide leaching. DR stands for dissolution rate.

Here we report a new dissolution method for elemental Au that rapidly and quantitatively dissolves Au upon heating in DMF solution of 4-PSH and H₂O₂. The achieved rate, 0.10 mol/(m²*h), is 1,600-fold higher than that measured for the published 4-PSH protocol¹⁶, and comparable in efficiency to the other two non-conventional methods.^{8,15} Experimental and computational studies revealed mechanistic insights for the dissolution of Au, particularly the role for 4-PSH and the selectivity of the system towards metals with the stable oxidation state +1. In terms of the circular economy, the study opens opportunities to develop technologically and economically viable dissolution of elemental gold.

Results and discussion

New dissolution method for Au powder. The study was initiated by conducting Au dissolution experiments using our previously published protocol¹⁶ as follows: a small amount of fine Au powder was added to 16 mM EtOH solution of 4-PSH and the mixture was stirred for 23 h under 10 bar of O₂ at 22 °C. This resulted in only 14% of dissolved Au (Table 1, entry 1). To increase Au dissolution, a series of optimization reactions was carried out varying the solvent, oxidant, ligand concentration and temperature (see Supplementary Section 2). As a result, we found that Au could be quantitatively dissolved upon heating at 60°C in DMF solutions of 4-PSH using H₂O₂ as an oxidant (Table 1, entry 2). A noteworthy interdependence between solvent and oxidant was observed, since a similar increase in the dissolution efficiency could not be achieved by changing either the solvent or oxidant alone. Next, a series of experiments was performed with gold powder in DMF solutions with 4-PSH concentrations of 20, 102, 203 and 406 mM, resulting in 1%, 50%, 67% and 84% of dissolved Au in only 8 min (Table 1, entries 3-6) showing that the dissolution efficiency correlates directly with the 4-PSH concentration. Importantly, complete dissolution of Au sample was achieved either with extended reaction time (23h) and low 4-PSH concentration or within 25 min using 203 mM 4-PSH concentration (Table 1, entries 2 and 7). The latter result is equivalent to an Au dissolution rate of 0.06 mol/(m²*h), which is 1,000-fold higher than that obtained under the initial conditions which utilized O₂ (10 bar) as oxidant in EtOH solution at RT¹⁶.

To obtain an understanding of the reaction mechanism, the partial composition of the reaction solution was studied during the dissolution. According to ¹H NMR studies, pyridine-4-thiol (4-PSH) is prone to isomerize to pyridine-4-thione (4-PS) which is the major component in the studied d₇-DMF solutions (Fig. 2, Step I, Supplementary Figs. S4-S5). This is in accordance with our previous studies on 4-PSH in alcohol solutions¹⁶ where a similar equilibrium was observed. We assume that the isomerization of 4-PSH is highly beneficial for 4-PS coordination to Au⁰ surfaces and, in this way, for initiating the dissolution. Upon heating the solution to 60°C and introducing H₂O₂ as an oxidant, signals belonging to 4-PS disappear and signals belonging to 4,4'-dipyridyl sulfide **2**, 4,4'-dipyridyl disulfide **3** and 4,4'-dipyridyl trisulfide **4** appear in the ¹H NMR spectrum (Fig. 2, step II, Supplementary Figs. S6-S7). This was also confirmed by HRMS studies wherein transformation of 4-PSH to **2**, **3** and **4** was clearly established (Supplementary Figs. S28-S33). At the same time, HRMS analysis of the reaction mixture revealed that [Au^I(4-PS)₂]⁺ **1** is the main gold cation in the solution. In addition to **1**, Au^I complexes **5** and **6** bearing **2** and 4-PS ligands were identified with HRMS (Fig. 2, step III, Supplementary Figs. S34-S37).

We were able to isolate **1** in crystalline form with the SO₄²⁻ as the counter anion and use XRD for structural analysis (see Supplementary Section 3.3 for details). Accordingly, the Au^I centers coordinate two neutral 4-PS ligands and SO₄²⁻ balances the overall charge of two adjacent Au^I complexes (Fig. 2). In the solid state, the dimeric structure is further stabilized by a weak aurophilic

interaction (3.1314 Å). Together with formation of **1** in the dissolution reaction, a significant amount of yellow crystals also precipitate from the DMF solution after prolonged storage. Upon XRD analysis, the crystals were identified as elemental sulfur (S₈). In fact, it is known that oxidized sulfur species are formed during the self-assembly of 4-PSH¹⁶ or alkane thiols¹⁷⁻¹⁸ on gold surfaces. As strongly oxidizing conditions are needed for efficient dissolution of elementary gold, S₈ might have an important role; it can react with H₂O₂ and form SO₂ and successively SO₃, which then generates sulfuric acid in contact with H₂O (Fig. 2, step IV). The combination of sulfuric acid and H₂O₂ is thought to form a strong enough oxidant, an *in situ* made Piranha-like solution, to assist the oxidation of Au⁰ to Au^I, where the generated SO₄²⁻ anions serve as a counter ion (Fig. 2).

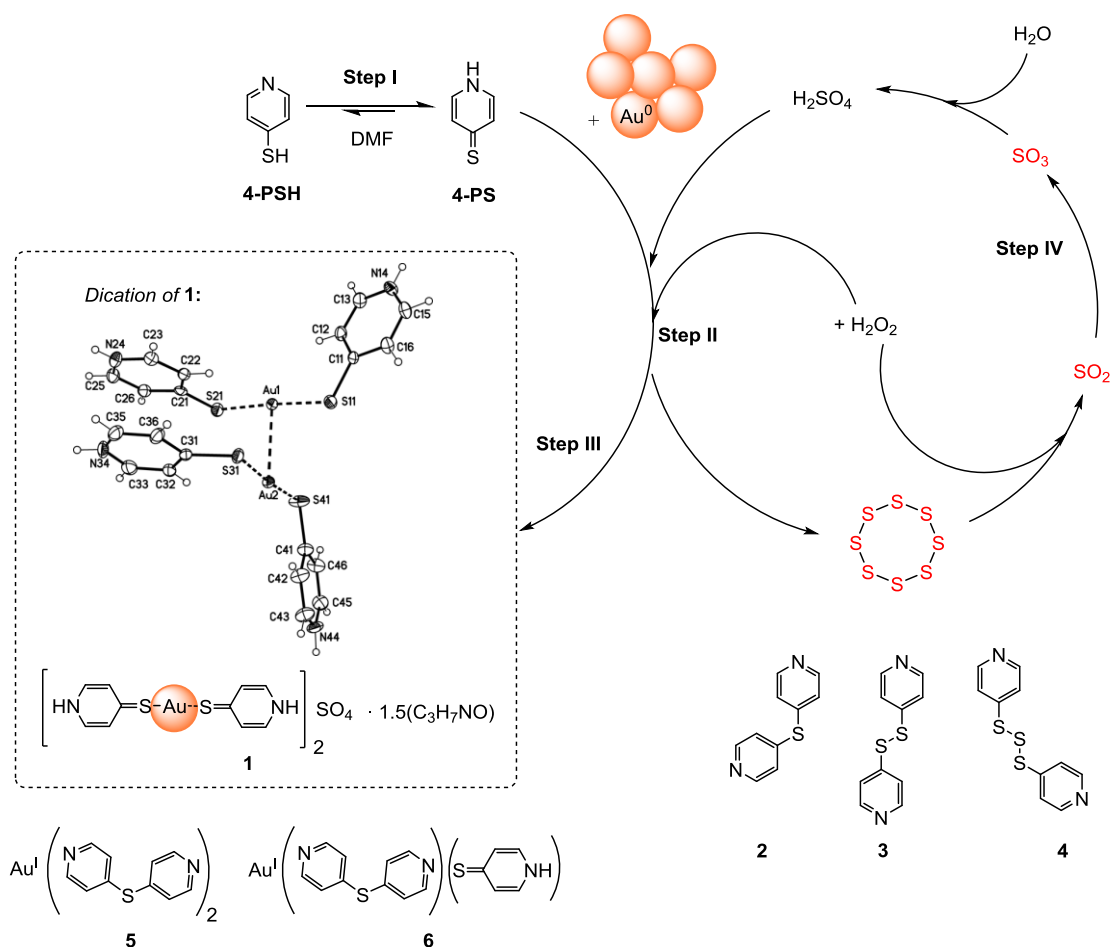


Fig. 2 Elementary reaction steps during the dissolution of elemental Au. Step I: isomerization of pyridine-4-thiol to pyridine-4-thione and coordination with the Au⁰ surface, Step II/III: oxidation of Au⁰ to Au^I and simultaneous oxidation of free pyridine-4-thione. Au^I species detected in HRMS during the dissolution are Au^I(pyridine-4-thione)₂⁺ **1**, (Au^I(dipyridyl sulfide)₂)⁺ **5** and (Au^I(dipyridyl sulfide)(pyridine-4-thione))⁺ **6**. A solid-state structure of **1** [bis(pyridine-4-thione)Au]₂SO₄ illustrates a linear coordination sphere of Au^I and a weak aurophilic interaction. The sulfate anion and DMF molecules are omitted from the X-ray structure. Several 4-PSH derived products were detected simultaneously with oxidized Au^I species including 4,4'-dipyridyl sulfide **2**, 4,4'-dipyridyl disulfide **3**, 4,4'-dipyridyl trisulfide **4** and elemental sulfur (S₈). Step IV: further oxidation of S₈ to sulfuric acid.

Evidently, due to the marked excess of 4-PSH needed for efficient dissolution and the observed sulfate counter anion of the Au^I complex – the relation between *in situ* formed S₈ and the dissolution rate of Au appeared to be important. To confirm this hypothesis, we attempted to use external S₈ as an accelerator by introducing one equivalent of S₈ into the reaction. With this approach, the dissolution of Au powder with high 4-PSH concentrations (406 and 203 mM) and external S₈ had a minor effect on the dissolution efficiency (Table 1, entries 8 and 9). In contrast, when the concentration of 4-PSH was markedly reduced (20 mM), the added S₈ greatly enhanced the dissolution of Au (Table 1, entries 3 and 4 vs. 10 and 11). These results imply that the dissolution reaction depends strongly on the presence of S₈. With low 4-PSH concentrations there is less free ligand and *in situ* formation of S₈ is the rate limiting factor. Notably, no rise in the dissolution efficiency was observed with the above stoichiometric amounts of S₈ (see Supplementary Section 3.4 for details).

Table 1| Optimization of dissolution conditions for Au powder by varying the 4-PSH concentration, oxidant, solvent, time and additive S₈.

Entry	Solvent	Oxidant	c[4-PSH] (mM)	Time	Temperature (°C)	Dissolved Au (%) [*]
1	EtOH	O ₂	16	23h	22	14 ^a
2	DMF	H ₂ O ₂	16	23h	60	99 ^a
3	DMF	H ₂ O ₂	20	8 min	60	1 ^b
4	DMF	H ₂ O ₂	102	8 min	60	50 ^b
5	DMF	H ₂ O ₂	203	8 min	60	67 ^b
6	DMF	H ₂ O ₂	406	8 min	60	84 ^b
7	DMF	H ₂ O ₂	203	25 min	60	99 ^c
With added S ₈						
8	DMF	H ₂ O ₂	406	8 min	60	86 ^d
9	DMF	H ₂ O ₂	203	8 min	60	73 ^d
10	DMF	H ₂ O ₂	102	8 min	60	61 ^d
11	DMF	H ₂ O ₂	20	8 min	60	33 ^d
12	DMF	H ₂ O ₂	20	8 min	60	30 ^e

^{*} Au concentration analyzed by flame atom absorption spectroscopy (FAAS).

^aConditions: 1 mg of Au powder (5 μmol, particle size 1.5-3.0 μm), 27 mg of 4-PSH (243 μmol, c[4-PSH] = 16 mM), H₂O₂ (46,4 μl, when applicable), O₂ (10 bar, when applicable) DMF (15 ml), 23 h.

^bConditions: 2 mg of Au powder (10 μmol, particle size 1.5-3.0 μm), H₂O₂ (92.8 μl), DMF (5 ml), 8 min. c[4-PSH] = 102, 203 or 406 mM.

^cConditions: Au thin film (300 nm), 294 mg of 4-PSH (c[4-PS] = 203 mM), 1.7 mg of S₈, H₂O₂ (61 μl), DMF (13 ml). Mass of Au ca. 1.3 mg.

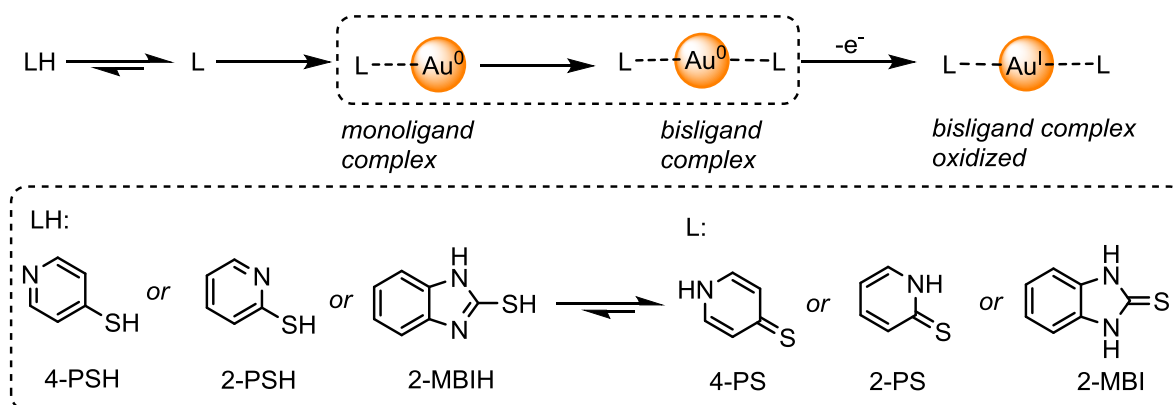
^dConditions: as in b, but Au : S₈ = 1:1.

^eConditions: as in b, but Au : S₈ = 1:4.

Insights into the dissolution mechanism. The dissolution mechanism was further investigated in a combined experimental/theoretical study. To determine the ligand dependence of the gold dissolution, experiments with 4-PSH, 2-pyridinethiol (2-PSH), 4,4'-dipyridyl disulfide (**3**) and 2-mercaptobenzimidazole (2-MBIH) were conducted under the same reaction conditions. At 60 °C and with 200-fold excess of the ligand, 4-PSH dissolves 81%, both 2-PSH and **3** dissolve 11% and 2-MBIH dissolves 8% of Au. According to ¹H NMR and HRMS analysis of the reaction mixtures, with 2-PSH the thione/thiol equilibrium resides on the thione side. In the presence of the oxidant, 2-PSH is readily oxidized to 2,2'-dipyridyl disulfide which is the major component in the solution (Supplementary Figs. S15-S20). Interestingly, in the presence of H₂O₂, neither **3** nor 2-MBIH produce sulfides in amounts that are detectable by ¹H NMR (see Supplementary Section 3.1.2 for details). The slow formation of S₈ from thiol ligands could partially explain the very low dissolution capability of 2-PSH, **3** and 2-MBIH; but the use of S₈ as an additive does not improve the Au dissolution rate (Supplementary Section 3.4). For example, 2-MBIH gives a similar 8% Au dissolution with and without S₈ in otherwise similar reaction conditions. This result implies that the dissolution of Au with 2-MBIH does not rely on rapid oxidation of thiol ligand to S₈. Instead, it seems likely that the dissolution rate is dependent on the coordination ability of the thione isomer of the ligands to the gold surface and on the oxidation potential of the formed reactive intermediate.

The ligand influence on the one electron oxidation of Au⁰ was computationally rationalized following the suggested mechanism that the dissolution is initiated by ligand coordination (Table 2). In principle, gold could be present in solution as mono- or bisligand complexes, although only the latter is experimentally observed. According to the DFT calculations, the coordination of the second ligand to the monoligand Au complex lowers the oxidation potential of Au⁰, 1.2 V with 4-PSH and 1.6 V with 2-MBIH (Table 2, entries **1** and **3**, Supplementary Section 8.1). Thus it seems that the formation of bisligand Au⁰ centers is crucial for the oxidation reaction. Such Au⁰ species are most likely formed at the corners and edges of the gold surface, thus rationalizing a similar etching order observed in experiments with Au thin films (Supplementary Section 4). According to the calculations, the significant lowering of the oxidation potential of bisligand Au⁰ species is caused by delocalization of the 6s¹ electron on the ligands, thus allowing the one-electron oxidation of the ligand instead of the metal. This theoretical insight further supports the experimental results which show that Pd and Pt were not dissolved with pyridinethiol ligands as their dissolution would require two-electron oxidation (Supplementary Section 5.2).

Table 2| Calculated oxidation potentials for mono- and bisligand Au complexes and the formation energies of bisligand complexes from monoligand ones.^c



Entry	Ligand	Monoligand complex (L-M) oxidation potential (V) ^b	Bisligand complex (L-M-L) oxidation potential (V) ^b	Formation energy of bisligand complex (kcal/mol) ^c $\Delta G(L-M \rightarrow L-M-L)$	Dissolved metal (%) [*]
1	4-PSH	4.1	2.9	-11.2	84 ^a
2	2-PSH	4.3	3.0	-10.6	11 ^a
3	2-MBIH	4.3	2.7	1.3	8 ^a

^{*} Experimental reaction conditions: DMF (5 ml), 60°C, 8 min, molar ratio: M⁰/LH/H₂O₂ 1:200:100. Metal concentrations analyzed by FAAS.

^a Au⁰ (2 mg, 0.010 mmol), 4-PSH (226 mg, 2.033 mmol) or 2-PSH (226 mg, 2.033 mmol) or 2-MBIH (305 mg, 2.033 mmol), H₂O₂ (92.6 μl), DMF (5 ml).

^b Computed absolute oxidation potentials (in V) at TPSS-D3/def2-TZVP/COSMO levels.

^c Formation free energies of the bisligand metal complexes from the monoligand complexes at TPSS-D3/def2-TZVP/COSMO (left) levels. Energies are in kcal/mol.

The calculations also give an interesting insight into the markedly lower reactivity of 2-PSH and 2-MBIH in comparison to 4-PSH in the dissolution of Au. The oxidation potentials of reactive intermediates increase in the order (2-MBI)₂Au⁰ < (4-PS)₂Au⁰ < (2-PS)₂Au⁰ and the significantly lower reactivity of 2-PSH in the dissolution of Au can be rationalized by considering the 0.1 V higher oxidation potential of (2-PS)₂Au⁰ compared with the (4-PS)₂Au⁰ complex (Table 2, entries 1-3). On the other hand, the (2-MBI)₂Au⁰ complex exhibits a 0.2 V lower oxidation potential than (4-PS)₂Au⁰ but its endothermic formation energies hamper the overall dissolution reaction (Table 2, entry 3). Unambiguously, the rate of dissolution is dependent on the formation energy of the bisligand intermediate and its oxidation potential.

Dissolution of other coinage metals. 4-PSH assisted dissolution can also be successfully applied to other coinage metals, namely silver and copper, i.e. metals with the stable oxidation state of +1. Using a high 4-PSH concentration ($c[4\text{PSH}] = 742 \text{ mM}$) at $60 \text{ }^\circ\text{C}$, the reaction was very fast and after 8 min 61% of Ag and 72% of Cu were dissolved (Table 3, entries 1 and 3). When 4-PSH loading was reduced, the reaction slowed down and with 10-fold ligand excess only minor amounts of the metals dissolved (4% Cu, 17% Ag). Yet a significant accelerating effect was observed for Cu when the experiment were repeated with S_8 additive in otherwise similar dissolution conditions (20% Cu, see Supplementary Section 5.4). To identify the structures of the resulting Ag^{I} and Cu^{I} complexes, the products were isolated and analyzed with FTIR, TGA and elemental analysis (EA). Based on the results, the structures of Cu^{I} complex **9** and Ag^{I} complex **10** resemble that of **1**. The counter anion in **9** and **10** can be clearly identified from FTIR spectra as the observed broad peaks around wave numbers 1100 cm^{-1} (strong) and 600 cm^{-1} are characteristic of the ν_3 and ν_4 vibrational modes of SO_4^{2-} , respectively¹⁹⁻²² (Supplementary Section 5.5). According to EA (CHNS) and TGA, the Cu^{I} center binds two 4-PS ligands and a sulfate anion stabilizes the overall charge of the dimeric structure, while each Ag^{I} center binds only one 4-PS ligand and SO_4^{2-} serves as the counter anion.

Next, dissolution experiments with 2-PSH and 2-MBIH were performed for Cu^0 and Ag^0 similarly as before for Au^0 ; Cu and Ag powders were hardly affected by 2-PSH solutions while reactions with high 2-MBIH concentration dissolved Ag 15% and Cu 78% in 8 min reaction time. When the ratio of 2-MBIH to Cu^0 was reduced from 200:1 to 10:1 and S_8 was used as an additive, Cu^0 was dissolved 48% in 8 min reaction time and quantitatively in elongated 30 min reaction time (Supplementary Section 5.4).

The reactivity differences between 2-MBIH with Cu^0 and Au^0 demonstrate a preferred dissolution selectivity among the coinage metals. This was further investigated with theoretical studies on the dissolution of Cu^0 and Ag^0 with 4-PSH and 2-MBIH ligands. As observed with the Au complexes, the coordination of the second 4-PS ligand markedly lowers the oxidation potential of Cu^0 and Ag^0 and delocalization of the $4s^1/5s^1$ electron on the ligands favors the one-electron oxidation of the metal (Table 3, entries 1 and 3). Due to the 0.1 V lower oxidation potential of $(4\text{-PS})_2\text{Cu}^0$ and $(4\text{-PS})_2\text{Ag}^0$ species compared to $(4\text{-PS})_2\text{Au}^0$, they are predicted to be oxidized slightly faster. Although the theoretical results support the fast dissolution of metallic Ag and Cu, it seems that the true efficiency of the dissolution method is hampered e.g. by formation of an oxide layer on the metal surface. This leads unexpectedly to a higher experimental dissolution efficiency with Au. From the extended ligand series, $(2\text{-MBI})_2\text{Cu}^0$ and $(2\text{-MBI})_2\text{Ag}^0$ species exhibit lower oxidation potentials than their 4-PS analogues, but the dissolution reactivity towards Ag^0 (as with Au^0 above) is reduced by endothermic complex formation energies (Table 3, entry 2). $(2\text{-MBI})_2\text{Cu}^0$ has an exothermic formation energy and shows a high dissolution rate. This rationalized the experimentally observed minor dissolution of Ag^0 with 2-MBIH assisted reactions while Cu^0 is efficiently dissolved.

Table 3| Calculated oxidation potentials for mono- and bisligand Ag and Cu complexes and the formation energies of bisligand complexes from monoligand ones.^d

Entry	Ligand	Metal	Monoligand complex (L-M) oxidation potential (V) ^c	Bisligand complex (L-M-L) oxidation potential (V) ^c	Formation energy of bisligand complex (kcal/mol) ^d $\Delta G(L-M \rightarrow L-M-L)$	Dissolved metal (%) [*]
1	4-PSH	Ag	3.5	2.8	-8.5	61 ^a
2	2-MBIH	Ag	3.6	2.7	3.0	15 ^a
3	4-PSH	Cu	3.4	2.8	-19.6	72 ^b
4	2-MBIH	Cu	3.6	2.5	-5.6	78 ^b

^{*} Reaction conditions: DMF (5 ml), 60°C, 8 min, molar ratio: M⁰/LH/H₂O₂ 1:200:100. Metal concentrations analyzed by FAAS.

^a Ag⁰ (2 mg, 0.019 mmol), 4-PSH (412 mg, 3.709 mmol) or 2-PSH (412 mg, 3.709 mmol) or 2-MBIH (557 mg, 3.709 mmol), H₂O₂ (172 μ l), DMF (5 ml).

^b Cu⁰ (2 mg, 0.032 mmol), 4-PSH (700 mg, 6.297 mmol) or 2-PSH (700 mg, 6.297 mmol) or 2-MBIH (945 mg, 6.297 mmol), H₂O₂ (292 μ l), DMF (5 ml).

^c Computed absolute oxidation potentials (in V) at TPSS-D3/def2-TZVP/COSMO levels.

^d Formation free energies of the bisligand metal complexes from the monoligand complexes at TPSS-D3/def2-TZVP/COSMO (left) levels. Energies are in kcal/mol.

Dissolution of Au in thin films and printed circuit boards (PCB). Recycling of noble metals from secondary sources including electronic waste is becoming increasingly important when modern societies are heading towards a circular economy. In this respect, dissolution of Au films is essential and methods other than cyanidation or Hg/Au amalgam extractions are also needed to fulfill the criteria of green chemistry and sustainability.²³ Due to their lower surface area, Au films are more challenging substrates than powders. We studied the dissolution of 300 nm thick Au films (1 cm \times 2.2 cm on mica substrate) and noted that etching began at the edges and then steadily progressed towards the center of the film (Fig. 3a). The studied Au film was fully dissolved in a DMF solution of 4-PSH/H₂O₂ (c[PSH]=203 mM) in 18 min, which corresponds to an Au dissolution rate of 0.06 mol/(m²*h). Remarkably, with added S₈, an even more efficient dissolution rate was achieved (0.10 mol/(m²*h) corresponding to a 1,600-fold enhancement when compared to our previous 4-PSH/EtOH method (0.06 \times 10⁻³ mol/(m²*h))¹⁶.

Because of their multi-metallic composition, we considered PCBs as one of the most challenging substrates and identified the so-called 'Au finger' part suitable for dissolution studies. Accordingly, this type of sample contains 23.4 m-% of Cu and only 0.25 m-% of Au (and 0.008 m-% of Ag) (see Supplementary Section 6 for details). In this regard, a direct 4-PSH leaching of Au is not rational due

to the high Cu content compared to that of Au. Therefore, we treated the sample first with $\text{NH}_3/(\text{NH}_4)_2\text{SO}_4$ and H_2O_2 to extract Cu and Ag^{24} (Fig. 3b, step I). The residue was then filtered and immersed in a DMF solution of 4-PSH/ H_2O_2 resulting in a significant 84% of dissolved Au (Fig. 3b, step II). As the 4-PSH-assisted dissolution method is selective for Group 11 metals, the recovery of these metals from Pt and Pd mixtures is also possible.

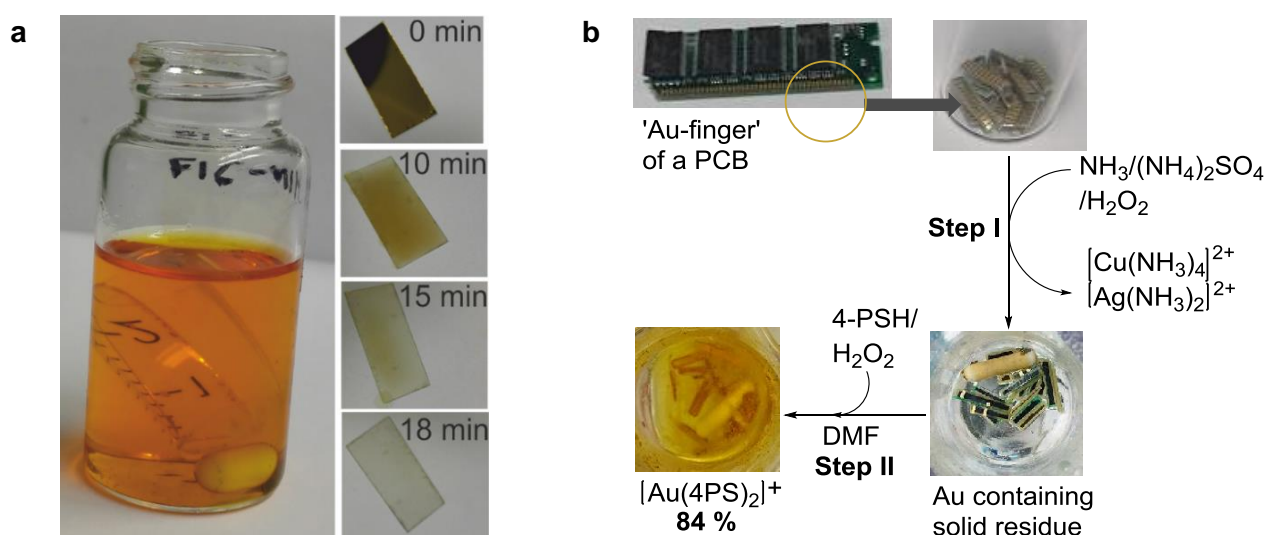


Fig. 3| Dissolution of Au from thin film substrates and PCB samples. a, Progress of Au thin film etching. On the left; a reaction setup used to protect the Au film from mechanical peeling and, on the right; the progress of the etching process from edges towards center of the film. **b,** Dissolution of Au in PCB samples. Step I: extraction of Cu and Ag with $\text{NH}_3/(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}_2$ and Step II: dissolution of Au with 4-PSH/ H_2O_2 method.

Conclusions

4-PSH as a reactive ligand and hydrogen peroxide as an oxidant forms together a highly efficient combination for dissolution of metallic gold. The reaction is driven by the ability of a thione isomer of 4-PSH to coordinate to a gold surface and to lower oxidation potentials of the gold atoms on the surface. Simultaneously, a part of 4-PSH is oxidized to S_8 and to the sulfate anions needed in the reaction to solubilize the generated Au^{I} species. As shown here, the excess of 4-PSH can be significantly reduced and the reaction rate markedly accelerated by adding external S_8 , which under optimized conditions leads to very fast and quantitative dissolution of Au ($0.10 \text{ mol}/(\text{m}^2 \cdot \text{h})$).

The reaction mechanism is supported by identification of intermediate species and rationalized by quantum-chemical calculations. The success with 4-PSH ligand is a balanced combination of its good coordinative ability with respect to Au^0 and the low oxidation potential of the generated bisligand intermediate. As a result of one-electron oxidation, a soluble Au^{I} complex is formed with sulfate counter anion. Notably, the studies with 2-PSH and 2-MBIH ligands illustrate how the dissolution of

Au⁰ is markedly hindered either by higher formation energies of the reactive bisligand intermediates or by their higher oxidation potentials.

The 4-PSH dissolution method was also applied to Cu⁰ and Ag⁰ substrates resulting in high dissolution efficiencies. The method possesses inherent selectivity towards metals which undergo one-electron oxidation; Pt and Pd thin films remain intact during the 4-PSH treatment. Furthermore, selectivity within Group 11 was demonstrated by changing the ligand; 2-MBI as a reactive ligand prefers only Cu⁰. This selectivity results from the remarkably lower formation energy of the bisligand intermediate Cu(2-MBI)₂ in comparison to the Au and Ag species. The possibility to dissolve coinage metals with benign and mild methods is highly important for human endeavors towards sustainable society and circular economy. In this respect, the dissolution was further implemented as an efficient method for Au films and printed circuit board samples. Thus, the principles learned from the studies reported herein could find future applications in sustainable dissolution pathways for noble metals.

Methods

Standard Au dissolution reaction. Au powder (2 mg, 10 μmol) and 4-PSH (226 mg, 2 mmol) were weighted in a glass vial (20 ml) followed by addition of DMF (5 ml). The reaction mixture was stirred at RT for a few minutes to dissolve all 4-PSH. Then H₂O₂ (33% in water, 92.8 μL, 1 mmol) was added (Au/4-PSH/H₂O₂ molar ratio 1:200:100) and the reaction was placed in an oil bath set to 60 °C and stirred for 8 min. Samples for FAAS analysis were prepared by diluting the reaction mixture in DMF (300 μl/9.5 ml).

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Author contributions

M.T.R. and E.H. contributed equally and produced most of the experimental results and analyzed the data. M.M. performed computational studies. M.K. prepared Ag and Pd substrates and carried out the FESEM-EDS measurements and J.H. prepared Pt substrates. M.T.R. and M.N. carried out the crystallographic characterization and K.M. performed ESI-MS experiments. F.A.-Q., A.E. and H.L. contributed to dissolution experiments and K.L. assisted in preparation of the manuscript. T.R. supervised the project. All the authors have agreed to all the content of the manuscript.

Data availability

Supplementary information and chemical compound information are available in the online version of the paper. Correspondence and requests for material should be addressed to T.R. and those related to computational studies to M.M. CCDC 1852214 (1) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Competing financial interests

The authors declare no competing financial interests.