Cooperative Ligands in Dissolution of Gold

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Abstract: Development of new, environmentally benign dissolution methods for metallic gold is driven by needs in the circular economy. Gold is widely used in consumer electronics, but sustainable and selective dissolution methods for Au are scarce. Herein, we describe a quantitative dissolution of gold in organic solution under mild conditions by using hydrogen peroxide as an oxidant. In the dissolution reaction, two thiol ligands, pyridine-4-thiol and 2-mercaptobenzimidazole, work in a cooperative manner. The mechanistic investigations suggest that two pyridine-4-thiol molecules form a complex with Au^0 that can be oxidized, whereas the role of inexpensive 2-mercaptobenzimidazole is to stabilize the formed Au^I species through a ligand exchange process. Under optimized conditions, the reaction proceeds vigorously and gold dissolves quantitatively in two hours. The demonstrated ligand-exchange mechanism with two thiols allows to drastically reduce the thiol consumption and may lead to even more effective gold dissolution methods in the future.

Recycling of precious metals is at the core of the circular economy. Gold is a valuable component in electronic waste, but one major barrier toward its efficient recycling is the inability to selectively dissolve Au under mild and benign conditions.[1–4] Among the classical methods; *aqua regia*,[5] chlorine gas,[5] amalgam formation,[5] and cyanide leaching,[6,7] which is particularly widely used. Unfortunately, these methods require harsh reaction conditions or hazardous reagents,[5–7] or both, in addition they are also unselectively dissolving all metals simultaneously. Recently, a new approach based on organic solvents and reactive ligand systems has been introduced.[8–25] These methods are mainly based on *S*-donor ligands[8–13,17,18] such as dithioxamides,[10] tetraethylthiuram disulfides,[8–13] pyridinethiols,[17,18] and/or halides.[19–24] However, for efficient dissolution of gold, powerful and aggressive oxidants, such as fairly toxic I$_2$[8–13] or corrosive SOCl$_2$,[14–16] are needed. Understanding the dissolution mechanism of gold is essential to learning how to design sustainable dissolution methods for other precious metals.

Oxidation of gold is a thermodynamically uphill and challenging task. However, it is envisioned that if the energy cost is small enough, facile dissolution of gold can take place even with mild oxidants. We reported recently a pyridine-4-thiol (**4-PS**) -assisted dissolution of Au in *N,N*-dimethylformamide (DMF) solutions using H$_2$O$_2$ as a benign oxidant (Figure 1).[18] We concluded that the dissolution with thiols depends on three parameters: (i) ability of thiol to undergo thiol–thione tautomerization, (ii) ability of thione to coordinate with Au^0 and form bisliganded Au^0 species, and (iii) the oxidation potential of this bisliganded species. The oxidation potential (iii) was observed to be highly ligand dependent, which is because gold's 6 s^1 electron should be delocalized on the ligands to reduce the oxidation potential significantly, while item (ii) was found to be the most important parameter to rationalize the ligand dependence between different ligands and gold. Even though **4-PS** coordinates well with the gold surface in the thione form, for efficient dissolution high concentrations are needed to shift the complexation equilibrium toward bisliganded Au^0 and to stabilize the dissolved bisliganded Au^I species. While the dissolution with **4-PS** proceeds in mild reaction conditions, its limitation is the high consumption of the expensive ligand under the oxidative stress. Here we describe a novel ligand-assisted dissolution mechanism and demonstrate that a cooperative two-ligand method provides an alternative, more atom-economic approach to quantitatively dissolve gold in DMF solution.

A series of different aromatic thiols capable of thiol–thione tautomerism were selected for the background study, namely, 2-mercapto-benzimidazole (**1**), 2-mercaptobenzothiazole (**2**), thiobenzamide (**3**), 2-thio-2-thiazoline (**4**) and pyridine-2-thiol (**5**) (Table 1). We initiated the study by immersing Au powder (with particle size of 1.5–3 μm) into DMF solutions of a thiol in 200-fold excess. Hydrogen peroxide was used as an oxidant, and the reaction time was set for 20 min. Under these reaction conditions the Au powder was dissolved nearly quantitatively with **4-PS** while the other thiols could only dissolve trace amounts of gold (see Supporting Information Section S2.1 for details). However, the ability of **1** to dissolve 40% of the gold under these conditions during the first 20 min is noteworthy. The key difference between the two ligands able to dissolve gold is their affinity to form bisliganded Au^0 species that can be

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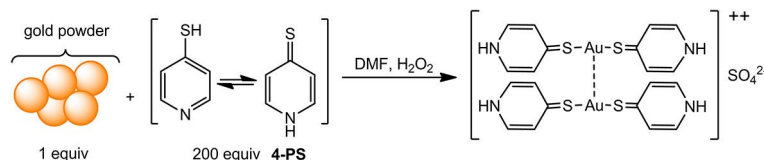BASF SE
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Figure 1. The concept of 4-PS-assisted gold dissolution. The thione form of 4-PS coordinates to the Au[0] surface, and the formed bisliganded Au[0] species assist the one-electron oxidation and dissolution of Au[I]. The *in situ* formed sulfate anion balances the charge.[18]

Table 1. Effect of 4-PS and thiol ligands (SL) on Au dissolution.

Entry	SL (No.)	SL (equiv)	4-PS (equiv)	Time (min)	Dissolved Au (%)[*]
1	none	none	200	20	85[a]18
2	1	200	none	20	40[a]
3	none	none	2	120	ND[b]
4	2	20	2	120	5[c]
5	3	20	2	120	6[c]
6	4	20	2	120	6[c]
7	5	20	2	120	9[c]
8	1	20	2	120	60[c]
9	1	20	none	120	20[d]
10	1	4	4	120	8[e]
11	1	50	2	120	99[f]
12	1	100	2	120	>97[f]
13	1	100	none	120	76[g]
14	1	20	4	120	20[h]
15	1	20	1	120	40[i]

[*] Au concentration analyzed by flame atomic absorption spectroscopy (FAAS). All measurements were carried out in air/acetylene flame by using a Au hollow cathode lamp (see the Supporting Information for details). [a] Au powder (2 mg, 10 μmol, particle size 1.5–3.0 μm), 4-PS (226 mg, when applicable), 1 (306 mg, when applicable), S$_8$ (20 μmol, 5.2 mg), H$_2$O$_2$ (33 w% in water, 92.8 μl), DMF (5 ml), 60 °C, 20 min. [b] Au powder (2 mg, 10 μmol), 4-PS (2.3 mg), H$_2$O$_2$ (92.8 μl), DMF (5 ml), 60 °C, 120 min. [c] As in [a], but 1 (31 mg, when applicable), 2 (34 mg, when applicable), 3 (28 mg, when applicable), 4 (24 mg, when applicable), 5 (22.6 mg, when applicable), 120 min. [d] As in [c], but no 4-PS. [e] As in [c], but 4-PS (4.5 mg) and 1 (6.2 mg). [f] As in [c], but 1 (155 or 77.5 mg). [g] As in [f], but no 4-PS. [h] As in [c], but 4-PS (4.5 mg, 4 equiv). [i] As in [c], but 4-PS (1.1 mg, 1 equiv).

oxidized.[18] Accordingly, the formation energy of Au[0] bisliganded species from monoliganded Au[0] species is clearly exergonic with **4-PS** when computed at DFT level ($\Delta G = -11.2$ kcal/mol) and slightly endergonic with **1** ($\Delta G = 1.3$ kcal/mol),[18] while the oxidation potentials of both Au[0]L$_2$ species are nearly same (L = thione ligand). Indeed, the ability of **4-PS** to

form bisliganded complexes with gold drives the one-electron oxidation and is superior among the thiols studied so far.

Au[I] complexes are coordinatively labile and have an intriguing propensity to undergo ligand-exchange reactions.[27,28] This directed us to investigate the ligand-exchange reactions, that is to design a novel, two-ligand method for dissolution of gold. On the basis of the above, **4-PS** was an obvious choice as one of the ligands, while ideally an excess of inexpensive thiols **1**–**4** (collectively **SL**; see Table 1) could be used to stabilize the generated Au[I] centers. In this respect, we focused on reactions where **4-PS** was used in 2-fold excess compared to Au[0]. As an expected result, there was no dissolution of gold, even in extended 120 min reactions when **4-PS** was used alone (Table 1, entry 3). Next, we repeated the experiment, but now added thiols **1**–**5** in a small, 20-fold excess to the reaction mixture (Table 1, entries 4–8). While the addition of thiols **2**–**5** had no influence on the dissolution, thiol **1** provided an impressive 60% of dissolved gold. Further enhancement in the dissolution of Au was observed by increasing the amount of **1**. Gratifyingly, using 50-fold or higher excess of **1** gave quantitative dissolution reactions (Table 1, entries 11 and 12).

We continued the study to identify the role of **4-PS** in these reactions. A clear inhibition in the dissolution efficiency was observed when decreasing the **4-PS** concentration to 1 equiv. (Table 1, entry 15). When repeating the reaction without **4-PS**, low yields were obtained (Table 1, entry 9). The acceleration effect is nicely demonstrated in entries 8 and 9, which show a three-fold increase in dissolution when 4-PS is used as an initiator. Based on that, **4-PS** can account for the reactive species needed to initiate the dissolution in the two-ligand system. Experiments showed that with longer reaction times Au[I] is reduced back to Au[0] and that the optimal reaction time is 2 h. Overall, the results emphasize the cooperativity of these two ligands and that high concentrations of **1** shift the complexation equilibrium toward the bisliganded Au[I] species in short time periods. The reactivity with the two-ligand method is unprecedented, as **4-PS** alone does not dissolve Au in the low ligand concentrations used and **1** alone does so to only a minor extent (Table 1, entries 8 versus 9). Full details of reaction optimization can be found in Supporting Information Section S2.

To continue our experimental investigations, thiol **1** was studied with ^{1}H NMR under the dissolution conditions. It seems to occur in its thione form, as a characteristic S–H signal is absent in DMF-d_7/H$_2$O$_2$ solution (see Supporting Information Figures S5-S12). Also, the number of signals (equivalent car-

Chemistry–A European Journal

Communication
doi.org/10.1002/chem.202101028

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bons) in the ^{13}C NMR spectrum further implies that **1** is present in a C_2-symmetric thione form; if otherwise, the absence of a NH group would destroy the symmetry of the molecule. A similar tendency was observed earlier for **4-PS**.[18] Unavoidably, aromatic thiols are easily oxidized in the DMF-d_7/H$_2$O$_2$ solution, and accordingly, a new singlet appears at $\delta 9.5$ in the aromatic region of the spectrum, indicating the formation *1H*-benzimidazole (Figure 2, **7**, 7%), an oxidized derivative of **1**. The formation of **7** and **8**, as well as the presence of 4′,4′-dipyridylsulfide (**4-DPS**) as a second major oxidation product of **4-PS**, were also confirmed by HRMS analysis (Figure 2, **7** and **8**; Supporting Information Figures S17 and S18).

When Au powder was introduced to DMF-d_7 solution containing **4-PS** and **1** in a 1:10 ratio (reaction molar ratio Au/**4-PS**/**1**/S$_8$/H$_2$O$_2$ 1:2:20:2:100), the ^{1}H NMR spectrum is dominated by signals arising from thione **1** (4:1 ratio of thione; see Supporting Information Figures S13–S15). Because of the overlapping peaks in ^{1}H NMR, the assignment of the formed gold species is not unambiguous, whereas high resolution ESI-TOF mass spectrometry turned out be a highly useful analytical method for their identification. With high **4-PS** loadings, 200 equiv. (Table 1, entry 1), the main dissolved Au^I species was [Au(**4-PS**)$_2$]$^+$ (Figure 2, **9**), along with minor amounts of [Au(**4-PS**)(**4-DPS**)]$^+$ (Figure 2, **10**). After the completion of the dissolution reaction, we added an equimolar amount of **1** (200 equiv) into the same reaction solution. During 15 min stirring, the mass peak at *m/z* 419 attributed to [Au(**4-PS**)$_2$]$^+$ decreased, and the peak assigned to [Au(**1**)$_2$]$^+$ simultaneously increased (Figure 2, **11**, Supporting Information Figures S22–S28). After a 15 min interval, the main Au^I complex detected was [Au(**1**)$_2$]$^+$ (Figure 2, **11**). Interestingly, a new mass peak at *m/z* 458 formed soon after adding **1** to the solution. It is assigned to a novel mixed-ligand species [Au(**4-PS**)(**1**)]$^+$ (Figure 2, **12**, Supporting Information Figure S29), which is likely a fingerprint of the hypothesized ligand-exchange reaction between **4-PS** and **1** on the Au^I cation.
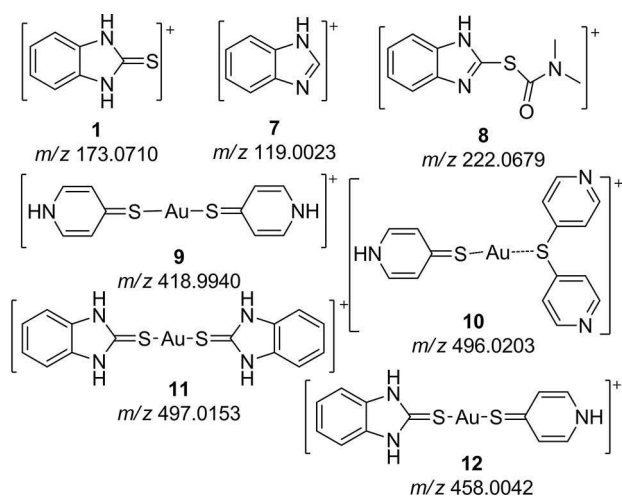
We further studied the two-ligand method with low loadings of **4-PS** and **1**, 2 and 20 equiv, respectively (Table 1, entry 8). The formation of the mixed-ligand species [Au(**4-PS**)(**1**)]$^+$ together with [Au(**1**)$_2$]$^+$ was again identified by ESI-MS (see Supporting Information Figure S52). Additional efforts were made to confirm the formation of the mixed-ligand complex. We synthesized Au(**4-PS**)$_2$Cl as a model complex and studied the isolated complex under the dissolution conditions. When a slight excess (2.5-fold) of **1** was added, the mass peak *m/z* 419 attributed to the original [Au(**4-PS**)$_2$]$^+$ slowly decreased, simultaneously as the peak *m/z* 458 assigned to a mixed-ligand complex [Au(**4-PS**)(**1**)]$^+$ appeared (SI Figs. S81-S84). When a 10-fold excess of **1** was used instead, the equilibrium shifted from [Au(**4-PS**)$_2$]$^+$ toward the mixed-ligand complex and further on toward [Au(**1**)$_2$]$^+$. An indicator of the ligand-exchange on Au^I is also the appearance of free **4-PS** sulfide in the mass spectrum (*m/z* 221, SI Figures S85–S87). These results give insight into a spontaneous, step-wise ligand-exchange reaction between **4-PS** and **1** on the coordination sphere of Au^I. As importantly, when the dissolution reaction was started in the reverse order, by addition of **1**, the [Au(**1**)$_2$]$^+$ complex was formed. Now, the addition of **4-PS** to the solution also generated the formation of the [Au(**4-PS**)(**1**)]$^+$ complex. This result underlines the reversibility of the ligand-exchange reaction on Au^I and the central role of the mixed-ligand complex in the process (Figure 4). Accordingly, the bisliganded Au^I complexes are present in equilibria determined by the applied reaction conditions.

To gain further insight into the ligand-exchange reaction and gold complexes, we studied theoretically their structures and energetics (TPSS-D3/def2-TZVP/COSMO in DMF). The computed free energies for step-wise ligand exchange reactions to form the Au(**1**)$_2$ complex from the corresponding Au(**4-PS**)$_2$ complex in both redox states are shown in Figure 4: **4-PS** clearly has the greatest affinity to form bisliganded complex with Au^0; the Au^0(**4-PS**)$_2$ complex is 17.6 kcal/mol more stable than the corresponding Au^0(**1**)$_2$ complex, thus rationalizing the higher affinity of **4-PS** to dissolve gold. This is also an important parameter, as the Au^0(**1**)$_2$ complex is easier oxidized than the Au^0(**4-PS**)$_2$ complex. The ligand preference is still the same for the oxidized complexes, but the relative stability of the Au^I(**1**)$_2$ complex is increased by 4 kcal/mol, going from 17.6 to 13.2 kcal/mol, while the absolute computed values are susceptible to errors rising especially from solvation. The observed trend indicates that bisliganded **1** gold complexes can exist after one-electron oxidation, especially when considering that Au^I has an overall higher tendency to form liganded complexes than Au^0. The mixed-ligand systems have the complexation free energies and oxidation potentials between homocoordinating gold, implying that these mixed complexes can also be active species in the dissolution process.

We extended our dissolution studies to cover other group 11 metals. In our preliminary experiments, copper and silver were dissolved under mild conditions with **1** as the only ligand (see Supporting Information S2.2 and S3.2.3). The main Ag^I species identified in HRMS analysis was bisliganded analogue of [Au(**1**)$_2$]$^+$, [Ag(**1**)$_2$]$^+$, respectively (Figure 3, **13**, Supporting Information Figure S72). DMF/H$_2$O$_2$ solutions of **1** contain a

Figure 2. Species found in high-resolution ESI-TOF mass spectra when dissolving Au^0 with 4-PS and 1.

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doi.org/10.1002/chem.202101028

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mass peak at m/z 222 in HRMS, which is attributed to an in situ C—S coupled side-product between **1** and the solvent DMF ($[C_{10}H_{11}N_3OS+H]^+$, Figure 3, **8**). This coupling product is also supported by HRMS of Cu^I species containing two **8** molecules coordinated to Cu^I centers ($[Cu(\mathbf{8})_2]^+$, m/z 505, Figure 3, **16**, see Supporting Information S3.2.3 for details).

In summary, we described a conceptually new gold dissolution method. It benefits from the use of two cooperative thiol ligands: 2-mercaptobenzimidazole (**1**) and pyridine-4-thiol (**4-PS**), which together form a reactive ligand mixture and give a quantitative dissolution of Au under mild conditions. The reaction benefits from the favorable formation energy for the bisliganded Au^0 complex with **4-PS**. After initial complexation, the dissolution proceeds by ligand-assisted oxidation of Au^0(**4-PS**)$_2$ to Au^I(**4-PS**)$_2$. The formed Au^I centers are prone toward ligand-exchange reactions (Figure 4a, steps III and IV), and by using an excess of ligand **1** the dissolution reaction results in the Au(**1**)$_2^+$ complex. Overall, the ability to exploit the dynamic

coordination sphere of Au^I species enables use of commercially available, inexpensive ligands in the dissolution. The conceptual findings are substantial, as the reported two-ligand method overcomes limitations of our previous ligand-assisted method,[16] including the excessive use of valuable **4-PS** ligand, as well as its predominance in reactivity over other aromatic thiones. The principles reported herein enable future development of sustainable dissolution methods for gold and other high-value metals.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: gold · gold dissolution · ligand exchange · reaction mechanisms · S ligands
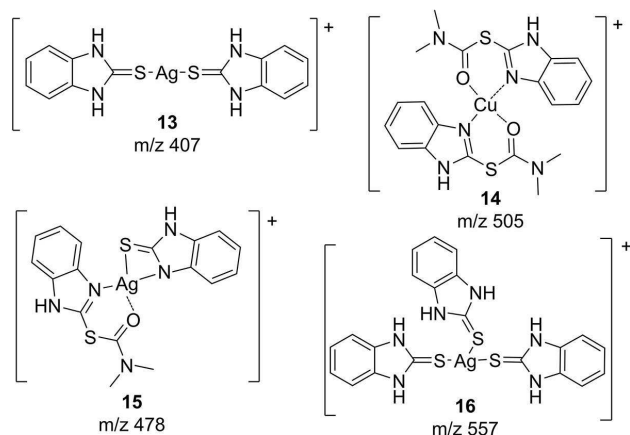
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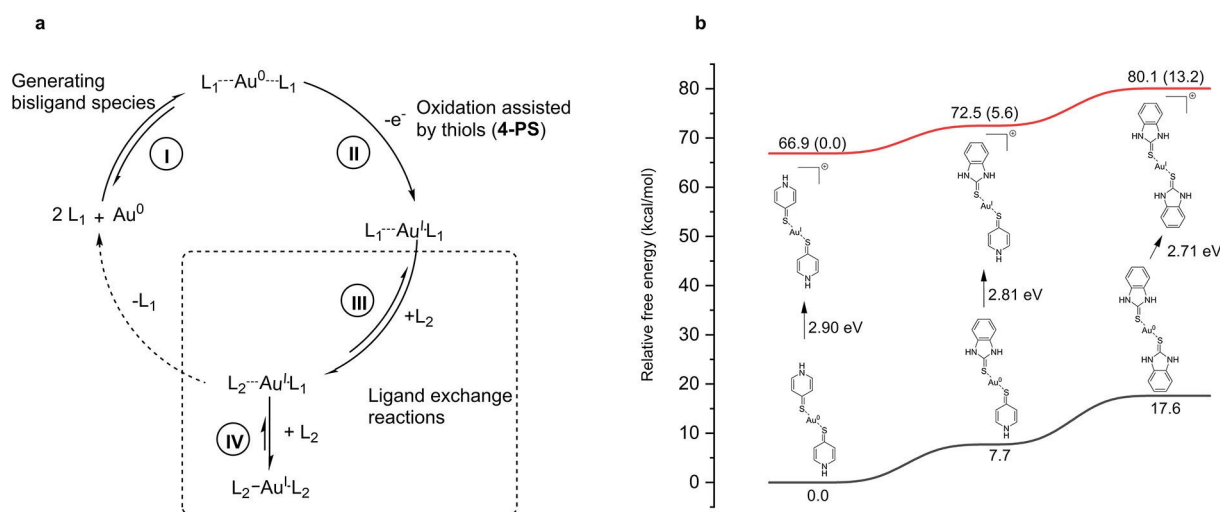[7] A. Birich, S. Stopic, B. Friedrich, *Sci. Rep.* **2019**, *9*, 1–10.

Figure 3. Cu^I and Ag^I species found in high-resolution ESI-TOF mass spectra in dissolution experiments with **1**.

Figure 4. (a) Schematic picture of the cooperative two-ligand dissolution of Au^0; **Step I**: Generation of Au^0 bisliganded species, **Step II**: Oxidation of Au^0(L1)$_2$ to Au^I(L$_1$)$_2$, **Step III**: Ligand-exchange reaction and formation of mixed-ligand species Au^I(L$_1$)(L$_2$), **Step IV**: Formation of bisliganded Au^I(L$_2$)$_2$. (b) Complexation free energies for Au^0 and Au^I and the corresponding oxidation potentials of **9**, **11** and **12**.

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