# Polythioamide as a Collector for Valuable Metals from Aqueous and Organic Solutions

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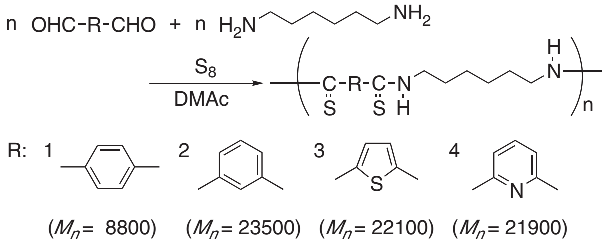
Polythioamides could effectively collect gold(III) and platinum(IV) from not only aqueous but also organic solutions. The collection of gold(III) from synthetic organic liquid waste was demonstrated.

Transition metals including gold[1,2] and platinum[2] are frequently used as catalysts for syntheses of various organic compounds. After organic-compound syntheses, the metals are often disposed with the organic liquid waste. In order to recycle the metals effectively, their recovery from the organic liquid waste is one of the most practical methods. Some materials have been proposed for this purpose; mesoporous silica materials containing functionalized organic monolayers are useful for the removal of mercury and other heavy metals from contaminated oil,[3] and polystyrene-bound trimercaptotriazine is also effective for removing palladium(II) from a tetrahydrofuran solution.[4] On the other hand, we have recently examined applications of the Willgerodt–Kindler type reaction to prepare various polythioamides.[5,6] Thioamides have the ability to coordinate with some transition metals[7–12] through S and/or N atoms in the thioamide unit. Chelating resins introduced thiourea,[13–15] isothiourea,[16] *N*-(hydroxymethyl)thioamide[17] and thiosemicarbazide[15] groups were proposed for the uptake of metals from aqueous solutions; however, the investigation of the metal recovery from organic solutions was not carried out. We here report the feasibility of the polythioamides for the collection of valuable metals from not only aqueous but also organic solutions.



**Scheme 1.**

Preparation of polythioamides **1**–**4** was carried out in a manner analogous to that in the previous report;[6,18] molecular structures of **1**–**4** and their number-average molecular weights ($M_n$, calibrated by GPC with polystyrene standards) are shown in Scheme 1. **1**–**4** were soluble in *N*,*N*-dimethylacetamide (DMAc) and *N*,*N*-dimethylformamide (DMF)[6] but insoluble in water and some organic solvents such as methanol, toluene, ethyl acetate, and chloroform.

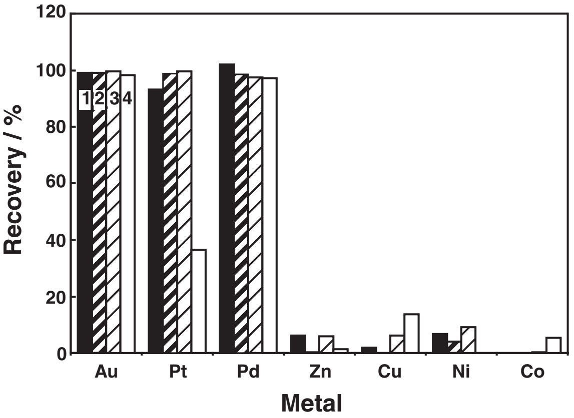


**Figure 1.** Recoveries of some metals from aqueous solutions at approximately pH 2 by powder polymers **1**-**4**. Sample volume, 10 mL; metal, $0.05\,\text{mmol}\,\text{L}^{-1}$; **1**-**4**, 5 mg; stirring time, 6 h.

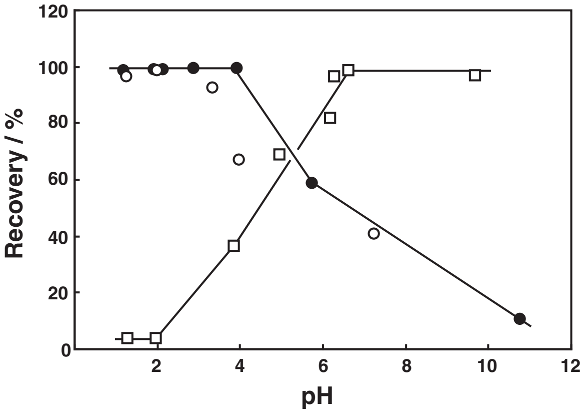


**Figure 2.** Effect of pH on the recoveries of gold(III) (●), platinum(IV) (○), and nickel(II) (☐) from aqueous solution by powder polymer **1**. Sample volume, 10 mL; metal, $0.05\,\text{mmol}\,\text{L}^{-1}$; **1**, 5 mg; stirring time, 6 h.

The sorption of some metals by **1**-**4** was investigated using 10 mL of an aqueous solution containing $0.05\,\text{mmol}\,\text{L}^{-1}$ of each metal and 5 mg of each polymer at approximately pH 2. The solution was prepared by diluting a commercially available metal stock solution (Kanto Chemical Co.) and, if necessary, adjusting the pH with a dilute hydrochloric acid or sodium hydroxide solution. The powdery polymer was then added to the solution, and the suspension was stirred vigorously for about 6 h at room temperature. After filtration, the concentration of the metal in the filtrate was measured using inductively coupled plasma atomic emission spectrometry. **1**–**4** could sorb gold(III) and palladium(II) efficiently, while more than 90% of platinum(IV) could be collected by **1**–**3** (Figure 1). On the contrary, the recoveries of zinc(II), copper(II), nickel(II), and cobalt(II) were less than 14% at this pH. Using **1**, the effect of pH on the recoveries of the metals was then examined, and the results for gold(III), platinum(IV), and nickel(II) are shown in Figure 2. Gold(III) was quantitatively collected by **1** over the pH range of 1 to 4; however, the recovery decreased with increasing pH above 4. A similar tendency was observed for platinum(IV). Nickel(II) was scarcely collected at a pH below 2, whereas the recovery increased with increasing pH and reached almost 100% at approximately pH 6.3. The sorption behavior of zinc(II), copper(II), and cobalt(II) was similar to that of nickel(II). These results indicate that **1** could sorb gold(III) and platinum(IV) effectively at a pH of less than 2. The sorption of gold(III) and platinum(IV) by **1** at approximately pH 1 followed the Langmuir adsorption isotherm. The amounts of gold(III) and platinum(IV) sorbable by 1 g of **1** were 2.82 mmol and 1.04 mmol, respectively, corresponding to 0.785 mmol of gold(III) or 0.291 mmol of platinum(IV) sorbed by 1 mmol of recurring unit in **1** (Scheme 1). It was reported that the complexes of gold(III) with dithiooxamides in acid media have S,S coordination.[9] The presence of S donor may play an important role in the sorption of gold(III) by the polythioamide.

**Table 1.** Recoveries of gold(III), platinum(IV), and nickel(II) from methanol solutions by **1–4**[a]

| Metal | Recovery/% | | | | | |
|---|---|---|---|---|---|---|
| | 1 | | 2 | | 3 | 4 |
| | A | B | A | B | B | B |
| Au(III) | 79.9 | 74.2 | 81.1 | 83.7 | 78.8 | 78.5 |
| Pt(IV) | 93.5 | 105.2 | 104.2 | 104.2 | 82.2 | 47.6 |
| Ni(II) | — | 0.0 | — | 0.0 | 7.5 | 54.4 |

[a] Sample volume, 10 mL; metal, 0.1 $\mathrm{mmol\,L^{-1}}$; acidity, 20 $\mathrm{mmol\,L^{-1}}$. Powder polymer (5 mg, A) or the DMF solution (0.5 mL) dissolving 5 mg of each polymer (B) was added. For B, 0.1 mmol of $CaCl_2$ was added to the methanol solution to improve flocculation of the precipitate.

We then investigated the recoveries of some metals by **1**-**4** using 10 mL of methanol solution containing 0.1 $\mathrm{mmol\,L^{-1}}$ of each metal. Gold(III) and platinum(IV) were recovered efficiently from the methanol solution at 20 $\mathrm{mmol\,L^{-1}}$ of acidity by adding powdery **1** and **2** after stirring for 10 h (Table 1, A). The collection of these metals was also evaluated by adding a DMF solution dissolving **1**-**4**. When 0.5 mL of the DMF solution, in which 5 mg of each **1**-**4** was dissolved, was added dropwise to the methanol solution containing each metal, a precipitate was formed and the metals were collected with the precipitate (Table 1, B). This procedure would also be feasible for the collection of metals. On the other hand, nickel(II) was slightly collected from the methanol solution by **1**–**3**; however, **4** was able to considerably collect nickel(II). Nickel complexes with *N*-alkylthiopicolinamides, which coordinate through the pyridine N and the thioamide S, have been prepared.[12] Therefore, the pyridine N in **4** would also contribute to the collection of nickel(II) from the methanol solution. These results suggest that control of the collection of metals in organic solution would be possible by selecting a polythioamide with an appropriate structure.

On the basis of the results mentioned above, we attempted to recover gold(III) from synthetic organic liquid waste using powder polymer **1**. A toluene solution containing gold(III) was prepared according to the Rhodamine B method[19,20] which was often used for the spectrophotometric determination of gold. When 5 mg of **1** was added to 10 mL of the toluene solution and the solution was then shaken for about 1 h at 25 °C, the absorbance at about 570 nm in the solution after centrifugation was not observed. Since the absorbance was not observed by further addition of Rhodamine B to the toluene solution after sorption, gold(III) appears to be recovered almost completely with **1**.

In conclusion, the polythioamides **1**–**4** could be used for the collection of gold(III) and platinum(IV) from not only aqueous but also organic solutions. By tuning the construction of the polythioamide, the collection of the metals from the organic solution could be modified. To apply polythioamides to recover metals from real organic liquid waste, further studies are in progress.

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