Removal of Palladium(II) from Aqueous and Organic Solutions by Polystyrene-bound Trimercaptotriazine

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Polystyrene-bound 2,4,6-trimercapto-*s*-triazine was prepared from 2,4,6-trimercapto-*s*-triazine (TMT) and Merrifield resin in a single step. Treatment with polymer-bound TMT was highly effective for reducing the concentration of residual Pd(II) in aqueous and organic solutions.

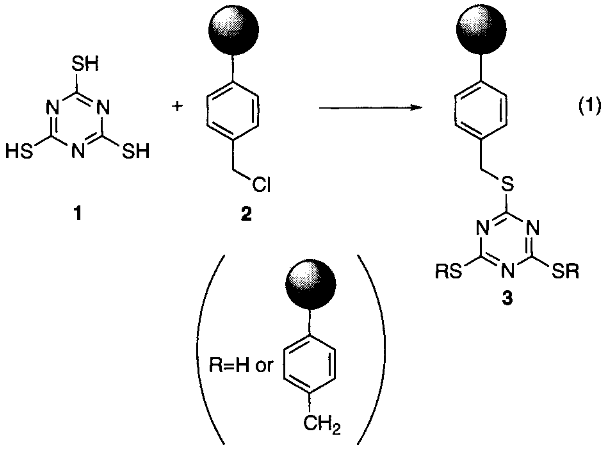
2,4,6-Trimercapto-*s*-triazine (TMT, **1**) has been used to precipitate heavy metals from wastewater,[1] flue gases,[2] and soil[3] and shows high affinity for cupric and palladium ions.[4,5] For example, TMT has been demonstrated to be very useful for removing residual palladium from potential drugs prepared by palladium-catalyzed indolization.[5]

TMT is commercially available as an un-ionized trithiol **1**, a solid trisodium salt (TMT-Na_3, undecahydrate, TMT 55), and a 15% aqueous solution of TMT-Na_3 (TMT 15). Studies have shown that **1** and TMT-Na_3 have low toxicity towards humans and animals.[6] TMT **1** is quite soluble in polar organic solvents such as 2-methoxyethanol, THF and dimethyl sulfoxide, but is only slightly soluble in water. On the other hand, its sodium salt, TMT-Na_3 is soluble not only in polar organic solvents such as methanol, 2-methoxyethanol, and dimethyl sulfoxide but also in water.[5] The high solubility of **1** and TMT-Na_3 makes it difficult to remove completely heavy metals by precipitation. In this report, we describe a single-step synthesis of polystyrene-bound TMT (**3**) and a simple filtration method for removing Pd(II) from aqueous and organic solutions.[7]

Polystyrene-bound TMT **3** was prepared by the substitution reaction of **1** with Merrifield resin (**2**, chloromethylated styrene-divinylbenzene copolymer, 100–200 mesh) as shown in eq 1. Low-loading resin **3** (0.32 mmol TMT unit/g resin) was prepared by heating the reaction mixture of **1** and **2** (substitution of Cl: 1.0 mmol/g) in methanol in the presence of potassium iodide and a neutral base such as triethylamine under reflux conditions (Method A).[8] On the other hand, high-loading resin **3** (0.60 mmol TMT unit/g resin) was prepared by heating the reaction mixture of TMT-Na_3 and **2** (substitution of Cl: 1.34 mmol/g) in *N*,*N*-dimethylformamide under reflux conditions (Method B). Loading of TMT was estimated based on nitrogen content as determined by elemental analysis.

In preliminary experiments concerning the adsorption of heavy metals with resin **3**, strong affinity was exhibited for Cr(VI), Cu(II), Pd(II), Cd(II), Pt(II), Pb(II), and U(VI). In this report, the affinity of resin **3** for Pd(II) was investigated in detail.

Using low-loading resin **3**, the removal of Pd(II) from several aqueous solutions of palladium dichloride was examined. After a mixture of an aqueous solution of Pd(II) (60.0 ppm, 10 mL) and **3** (67.7 mg, 0.32 mmol/g) was stirred at 23 °C for 1 day, the resin was removed by suction filtration through 1-µm filter paper. Residual Pd(II) levels in the filtrate were analyzed by inductively coupled plasma–mass spectroscopy (ICP-MS). The results are summarized in Table 1. The affinity of resin **3** for Pd(II) was enhanced as the acidity of the aqueous solution increased: 99.9% and 99.8% of the Pd(II) was removed from aqueous hydrogen chloride (pH = 0.1) and acetic acid (pH = 2.2) solutions, respectively. The aqueous solutions also changed from light brown to colorless, and **3** changed from light brown to dark brown. In contrast, insufficient Pd(II) was removed under weakly acidic (pH=3.8) or neutral (pH=6.9) conditions.



(1)

Method A: **1** (2 equiv), **2** (1.0 mmol Cl unit/g resin, 1 equiv), KI (1 equiv), Et_3N (6 equiv), MeOH, reflux for 1 day
→ **3** (0.32 mmol TMT unit/g resin)
Method B: **1** (2 equiv), **2** (1.34 mmol Cl unit/g resin, 1 equiv), NaH (6 equiv), DMF, reflux for 1 day
→ **3** (0.60 mmolTMT unit/g resin)

Table 1. Removal of Pd(II) from Aqueous Solution by **3** (3.8 equiv of **1**-component per Pd(II))[a]

Pd(II) aqueous solution[b] solvent	pH	Residual Pd(II) / ppb[c]	Adsorption / %
1M HCl	0.1	61	99.9
1M CH_3CO_2H	2.2	110	99.8
5 wt% NH_4Cl	3.8	19000	68.3
5 wt% NH_4OAc	6.9	33000	45.0

[a] A mixture of aqueous Pd(II) solution (60.0 ppm, 10 mL) and **3** (67.7 mg, loading: 0.32 mmol/g resin, based on nitrogen content, as determined by elemental analysis) was stirred at 23 °C for 1 day. [b] Palladium dichloride was homogeneously dissolved in aqueous solutions indicated in Table 1 (1 M = 1 mol dm^{-3}). [c] Pd(II) assayed by ICP-MS.

Next, similar experiments were carried out using three times as much resin **3** as was used in the above experiments: 99.7% and 96.7% of the Pd(II) was removed from aqueous solutions of ammonium chloride and ammonium acetate, respectively. Thus, resin **3** was effective for removing Pd(II) from aqueous solutions under a wide range of neutral to strongly acidic conditions.

Table 2. Removal of Pd(II) from Aqueous Solution by **3** (11.5 equiv of **1**-component per Pd(II))[a]

Pd(II) aqueous solution[b] solvent	pH	Residual Pd(II) / ppb[c]	Adsorption / %
5 wt% NH_4Cl	3.8	180	99.7
5 wt% NH_4OAc	6.9	2000	96.7

[a] A mixture of aqueous Pd(II) solution (60.0 ppm, 10 mL) and **3** (203.0 mg, loading: 0.32 mmol/g resin, based on nitrogen content, as determined by elemental analysis) was stirred at 23 °C for 20 h. [b] Palladium dichloride was homogeneously dissolved in aqueous solutions indicated in Table 2. [c] Pd(II) assayed by ICP-MS.

The removal of Pd(II) from organic solutions of palladium diacetate was also examined (Table 3). As expected, more than 99.9% of Pd(II) was removed from a 1 M (mol dm^{-3}) acetic acid solution in THF. Surprisingly, Pd(II) was almost completely removed even under neutral conditions.

Table 3. Removal of Pd(II) from Organic Solution by **3**[a]

Pd(II) organic solution[b] solvent	Pd(II) / ppm	Residual Pd(II) / ppb[c]	Adsorption / %
1M CH_3CO_2H in THF	47.4	45	99.91
THF	23.7	2	99.99

[a] A mixture of organic Pd(II) solution (10 mL) and **3** (67.7 mg, loading: 0.32 mmol/g resin, based on nitrogen content, as determined by elemental analysis) was stirred at 23 °C for 1 day. [b] Palladium diacetate was homogeneously dissolved in THF as indicated in Table 3 (1 M = 1 mol dm^{-3}). [c] Pd(II) assayed by ICP-MS.

Unfortunately, Pd(II) could not be completely dissociated from Pd(II)-containing **3** despite washing with several strong acidic and basic aqueous solutions.

In conclusion, we have demonstrated that treatment with polystyrene-bound TMT is highly effective for removing Pd(II) from aqueous and organic solutions. Due to the extremely strong affinity of TMT for heavy metals, it is expected that treatment with polymer-bound TMT could also be useful for reducing the concentrations of other metals.

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References and Notes

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8. Preparation of low-loading resin **3**: A reaction mixture of TMT **1** (2.5 g, 14 mmol), Merrifield resin **2** (7.0 g, 1.0 mmol/g), potassium iodide (1.2 g, 7 mmol), triethylamine (35 mL), and methanol (35 mL) was heated under reflux conditions (bath temperature: 97.5 °C) for 1 day. After cooling to ambient temperature, the resultant mixture was filtered, and resin **3** was washed with 2 M HCl (50 mL), dimethyl sulfoxide (100 mL), 2 M HCl (50 mL), and THF (100 mL) in this order. The resin **3** was dried under vacuum at 100 °C for 12 h. Loading of TMT was estimated based on nitrogen content as determined by elemental analysis. Anal. Found: C, 80.68; H, 7.84; N, 1.36%.