

1 **Selective Separation of Palladium from Organic Solutions Containing** 2 **Nickel or Platinum Using Polythioamide as a Sorbent**

3
4 Shigehiro Kagaya,^{1*} Erika Tanaka,¹ Nobuhiro Kawai,¹ Ikumi Masore,¹ Emi Sato,¹ Kiyoshi
5 Hasegawa,¹ Masato Kishi,² Takaki Kanbara^{2,3*}

6
7 ¹ Graduate School of Science and Engineering for Research, University of Toyama, Gofuku
8 3190, Toyama 930-8555, Japan e-mail: kagaya@eng.u-toyama.ac.jp

9 ² Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku,
10 Yokohama 226-8503, Japan

11 ³ Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), University of
12 Tsukuba, Tennoudai 1-1-1, Tsukuba 305-8573, Japan e-mail: kanbara@ims.tsukuba.ac.jp

13
14 **Abstract** The feasibility of the selective recovery of Pd from organic liquid waste
15 using polythioamide (PTA) as a sorbent has been investigated. PTA effectively sorbed Pd(II)
16 in some organic solutions under not only acidic conditions but also basic conditions. PTA
17 was also able to sorb Pd from organic solutions containing PdCl₂(PhCN)₂ and Pd₂(dba)₃.
18 The results for the molecular structure of a model compound ([Pd(C₁₁H₁₅NS)₄]Cl₂) suggest
19 that the presence of a S donor plays an important role in the sorption of Pd(II) by PTA. The
20 sorbed Pd was quantitatively eluted using 1,3-bis(diphenylphosphino)propane in MeOH, and
21 the recovered PTA can be reused at least five times. The selective separation of Pd(II) was
22 achieved even from organic solutions containing a 100 times larger amount of Ni(II) or Pt(IV)
23 under acidic conditions or basic conditions, respectively.

24
25 **Keywords** Palladium separation, Polythioamide, Sorption, Elution with phosphine
26 compound

1 **1 Introduction**

2
3 The recovery of precious metals from aqueous and organic liquid waste arising from the
4 chemical, electronics, and plating industries has gained in importance from the viewpoint of
5 the effective utilization of resources. The group 10 metals (Ni, Pd, and Pt) are widely used
6 in these industries because of their specific physical and chemical properties. The catalytic
7 activity and nobility of these metals have resulted in a wide range of applications in many
8 fields in various chemical processes. The Pd-catalyzed carbon-carbon bond-forming
9 reactions such as the Mizoroki-Heck and Suzuki-Miyaura coupling reactions are used in the
10 production of fine chemicals [1]. However, the homogeneous catalytic systems usually
11 require tedious and expensive workups to obtain a pure fine chemical product; in other words,
12 the recovery of the precious metal is troublesome and time-consuming. Recently, several
13 Pd-immobilized heterogeneous catalyst systems have been investigated with the aim of
14 recovering the precious metal catalysts [2]; however, the durability of the catalysts and the
15 leaching of precious metals, which are due to the instability of the immobilized metal
16 complexes, still remain issues. Therefore, simple and selective techniques for recovering the
17 precious metals from aqueous and organic liquid waste are desired.

18 Sorption using polymer sorbents is one of the most practical techniques in the
19 recovery of metals from a solution. Although various sorbents have been developed and are
20 now commercially available as metal scavengers [3], highly selective and effective separation
21 techniques for organic liquid waste had limited success because of the interference by
22 coexisting organic and inorganic constituents. Ishihara *et al.* reported that
23 polystyrene-bound trimercaptotriazine is effective for removing Pd(II) from a THF solution
24 [4].

25 We previously prepared polythioamide (PTA) by the Willgerodt-Kindler reaction
26 [5]. The coordination chemistry of a secondary thioamide is intriguing because the

1 secondary thioamide group is involved in equilibrium with its amino-thione and imino-thiol
2 tautomers, which modulates the donor ability of the thioamide group via the N-to-S backbone
3 [6]. This situation prompted us to utilize PTA as a sorbent for group 10 metals in aqueous as
4 well as organic solutions, and we found that Pd(II) could be effectively separated. PTA was
5 able to sorb Pd(II) and its complexes in various aqueous and organic solutions under not only
6 acidic conditions but also basic conditions. We here report the feasibility of the selective
7 recovery of Pd(II) from organic liquid waste using PTA. Some of the results were reported
8 in a previous communication [7].

9

10 **2 Experimental**

11

12 2.1 Materials and General Procedures

13

14 All reagents were purchased from commercial suppliers and used without any further
15 purification. For the investigation of metal sorption in an aqueous solution and MeOH
16 solution, a standard solution of each metal (1000 mg L⁻¹) was purchased from Kanto
17 Chemical. In the standard solution, each metal was dissolved with 1 mol L⁻¹ HNO₃ for
18 Pd(II), 1 mol L⁻¹ HCl and trace amount of HNO₃ for Pt(IV) and Au(III), or 0.1 mol L⁻¹ HNO₃
19 for Co(II), Ni(II), Cu(II), and Zn(II). For Pt(II,IV), K₂PtCl₄ and Na₂PtCl₆ were also utilized.
20 Pd(OAc)₂ and some Pd complexes such as PdCl₂(PhCN)₂ [8], Pd₂(dba)₃ [9], PdCl₂(PEt₃)₂
21 [10], and PdCl₂(PPh₃)₂ [11], which were prepared in accordance with the literature, were used
22 to investigate Pd sorption in an organic solution.

23 IR, NMR, and mass spectra were recorded on a Jasco FT/IR-230 spectrometer, a
24 JEOL JNM-α400 or Bruker AVANCE-600 NMR spectrometer, and a Shimadzu LCMS-2010
25 mass spectrometer, respectively. Elemental analyses were carried out using a Yanaco CHN
26 Corder MT-5. To determine the metals in solutions, a Hitachi 180-80 polarized Zeeman

1 atomic absorption spectrometer and a PerkinElmer Optima 3000XL inductively coupled
2 plasma atomic emission spectrometer were used.

3

4 2.2 Preparation of PTA

5

6 The preparation of poly(iminoterephthalthioyliminohexamethylene) (69% yield) was carried
7 out in a manner analogous to that in our previous report (Scheme 1) [5]. The number
8 average molecular weight, M_n , was 8800.

9

10 2.3 Preparation of Model Compound

11

12 *N*-isobutylthiobenzamide was prepared by the Willgerodt-Kindler reaction (87% yield) in
13 accordance with the literature [12]. To a solution of *N*-isobutylthiobenzamide (386 mg, 2.0
14 mmol) in EtOH (5 mL), an aqueous solution (5 mL) of K_2PdCl_4 (162 mg, 0.5 mmol) was
15 added. The solution was stirred for 24 h at room temperature. The organic fraction was
16 evaporated, and the resulting orange precipitate was collected and thoroughly washed with
17 water, hexane, and ether to give an orange powder of
18 tetrakis(*N*-isobutylthiobenzamide- κS)palladium(II) dichloride (461 mg, 96% yield). Crystals
19 suitable for X-ray diffraction analysis were obtained after 3 days by slowly evaporating a
20 mixture of EtOH and H_2O solution of the complex. Analysis calculated for
21 $C_{44}H_{60}N_4Cl_2PdS_4 \cdot H_2O$: C 54.56, H 6.45, N 5.78%; found: C 54.35, H 6.28, N 5.69%.
22 ESI-MS: 915, 913 ($\{[Pd(C_{11}H_{15}NS)_4]Cl\}^+$), 720, 722 ($\{[Pd(C_{11}H_{15}NS)_3]Cl\}^+$), 529, 527
23 ($\{[Pd(C_{11}H_{15}NS)_2]Cl\}^+$). IR (KBr, cm^{-1}): 3368, 3134, 2959, 2926, 1559, 1489, 1462, 1387,
24 1338, 1290, 1227, 1155, 1053, 999, 952, 933, 889, 770, 696, 536, 453, 418. 1H NMR (500
25 MHz, CD_3OD): δ = 7.69 (t, 1H, J = 7.5 Hz), 7.51 (t, 2H, J = 7.5 Hz), 7.42 (t, J = 6.5 Hz), 3.42
26 (d, 2H, J = 7.2 Hz), 2.11 (sep, 1H, J = 6.7 Hz), 0.98 (d, J = 6.7 Hz). ^{13}C NMR (125 MHz,

1 CD₃OD): $\delta = 187.6, 131.1, 124.7, 120.6, 120.4, 47.2, 19.2, 5.69$.

2

3 2.4 Procedure for Sorption and Elution of Metal

4

5 The sorption of the metal was carried out in glass vials. To aqueous and organic solutions
6 (5-100 mL) containing an appropriate amount of metal or its complex (for Pd), HCl, NaOH
7 solution, or MeONa was added to control the acidity or basicity in the solution. Powdered
8 PTA was then added to the solution. After the solution was stirred vigorously using a
9 magnetic stirrer, it was filtered through a membrane filter (Nihon Millipore, Omnipore
10 membrane, 0.2 μm pore size). The percentage of metal sorption was calculated from the
11 difference in the amount of metal in the solution before and after the sorption.

12 For Pd elution, the Pd-sorbed PTA was placed a grass vial containing MeOH or the
13 other organic solvent (10-40 mL) with the filter. To the vial, a powdered tertiary phosphine
14 compound was added. After stirring vigorously, the solution was filtered. The percentage
15 of Pd elution was calculated from the amount of Pd in the filtrate.

16

17 2.5 X-ray Crystallographic Structure of Model Compound

18

19 The diffraction data were collected using a Rigaku Saturn CCD area detector with graphite
20 monochromated MoK α ($\lambda = 0.71070 \text{ \AA}$) at $-160 \text{ }^\circ\text{C}$. The data were corrected for Lorentz
21 and polarization effects, and an empirical absorption correction was applied. The structure
22 was solved by direct methods (SIR92) and expanded using Fourier techniques. The
23 non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined
24 isotropically. Crystal data of tetrakis(*N*-isobutylthiobenzamide- κ S)palladium(II) dichloride:
25 C₄₄H₆₄N₄Cl₂PdS₄O, $M = 986.56$, monoclinic, $P2_1/n$, $a = 10.642(4)$, $b = 17.138(6)$, $c =$
26 $13.856(4) \text{ \AA}$, $\beta = 92.2275(18)^\circ$, $V = 2525.1(14) \text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.297 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) =$

1 6.759 cm⁻¹, $T = 113$ K, $F(000) = 1032$, observed reflections 5561(all data), variables 387, $R_1 =$
2 0.0372, $R_w = 0.0213$, GOF = 0.884. Crystallographic data of the structural analysis have
3 been deposited with the Cambridge Crystallographic Data Centre; Publication Number CCDC
4 699162.

5

6 **3 Results and Discussion**

7

8 3.1 Sorption Behavior of Pd, Ni, and Pt in Aqueous and Organic Solutions

9

10 The sorption behavior of various metals including the group 10 metals, Ni(II), Pd(II), and
11 Pt(II,IV), was first investigated in aqueous solution to evaluate the potential of PTA for the
12 selective sorption of Pd(II). Figure 1 shows the sorption behavior of PTA toward the metals
13 at various pH. PTA exhibited excellent sorption behavior toward Pd(II); Pd(II) was
14 effectively sorbed on PTA under not only acidic conditions but also basic conditions. In
15 contrast, Ni(II) was hardly sorbed on PTA at a pH below 2. The percentage of Ni(II)
16 sorption increased with increasing pH and reached almost 100% at a pH above 6.3. Similar
17 sorption behavior was obtained for Co(II), Zn(II), and Cu(II); the percentages of sorption for
18 these metals were less than 0.4% at pH 2 and more than 90% at pH 9-10. For Au(III) and
19 Pt(II,IV), the opposite tendency was observed (Fig. 1). The quantitative sorption of Au(III),
20 Pt(II), and Pt(IV) was observed below pHs of 3.9, 6.9, and 2.0, respectively; the sorption
21 percentages decreased with increasing pH. These results indicate that PTA has the potential
22 to selectively separate Pd(II) from Ni(II), Co(II), Zn(II), and Cu(II) under acidic conditions as
23 well as from Pt(II,IV) and Au(III) under basic conditions.

24 Since PTA exhibited the attractive property of sorbing Pd(II), the sorption of Pd(II)
25 was investigated in detail. The sorption of Pd(II) on PTA at pH 1 followed the Langmuir
26 adsorption isotherm. The maximum amount of Pd(II) sorbable by 1 g of PTA was 1.03

1 mmol, corresponding to 0.287 mmol of Pd(II) sorbed by 1 mmol of the recurring unit in PTA
2 (Scheme 1). This amount was almost equal to the sorbable amount of Pt(IV) (1.04 mmol
3 g^{-1}) and approximately one-third of that of Au(III) (2.82 mmol g^{-1}).

4 As models of organic liquid waste, sorption tests on Pd(II), Ni(II), and Pt(II,IV) in
5 MeOH were carried out. As shown in Fig. 2, the sorption of Pd(II) was not affected by the
6 presence of HCl and MeONa; this tendency was similar to the sorption of Pd(II) in aqueous
7 solution. The results for Ni(II) and Pt(II,IV) were also consistent with those in aqueous
8 solution. The sorption was also investigated using various organic solutions of Pd(OAc)₂;
9 the results are summarized in Table 1. More than 76% of Pd(II) was sorbed from the various
10 model organic solutions, indicating that PTA has the ability to sorb Pd(II) from organic liquid
11 waste.

12

13 3.2 Structure of Model Pd Complex

14

15 Secondary thioamides are easily deprotonated to give their anionic thionate form, in which the
16 coordination potential is not only closer to that of a thiolate group but also further enhanced
17 by the donor capacity of the nitrogen atom via the S-to-N backbone [6]. To elucidate the
18 sorption capability of PTA toward Pd(II), we determined the molecular structure of a model
19 compound.

20 A model complex ($[\text{Pd}(\text{C}_{11}\text{H}_{15}\text{NS})_4]\text{Cl}_2$, **1**) was prepared from the reaction of
21 *N*-isobutylthiobenzamide with K_2PdCl_4 in a mixture of EtOH and H_2O in accordance with the
22 sorption experiments on PTA; reactions of K_2PdCl_4 with 2 and 4 equivalents of
23 *N*-isobutylthiobenzamide produced the same product (**1**).

24 Figure 3 shows the ORTEP drawing of **1**. As shown in Fig. 3, the Pd atom of **1** is
25 located at an inversion center, and the Pd(II) ion possesses a crystallographically imposed
26 square planar geometry. Four *N*-isobutylthiobenzamide molecules serve as a monodentate

1 S-donor ligand in its thione tautomeric form, as illustrated by the scheme in Fig. 3. The
2 thione form of the ligand has also been confirmed by ^{13}C NMR spectroscopy (δ 187.6).
3 These results coincide with those reported for thioamide-ligated palladium complexes [13].
4 These results suggest that the presence of a S donor plays an important role in the sorption of
5 Pd(II) by PTA.

6 7 3.3 Sorption Behavior of Various Pd Complexes in Organic Solutions

8
9 The sorption of various Pd complexes dissolved in organic solvents was attempted. The
10 obtained results are shown in Table 2. When $\text{PdCl}_2(\text{PhCN})_2$ was used for the test,
11 quantitative sorption of Pd(II) was achieved for various organic solutions and their mixtures.
12 In the case of $\text{Pd}_2(\text{dba})_3$, which is one of the popular Pd(0) complexes, Pd was almost
13 completely sorbed on PTA under acidic conditions; the sorption under neutral condition could
14 not be determined because of its poor solubility in MeOH. These results indicate that Pd can
15 be effectively sorbed from various organic solutions of these Pd complexes.

16 In contrast to $\text{PdCl}_2(\text{PhCN})_2$ and $\text{Pd}_2(\text{dba})_3$, low percentages of Pd sorption were
17 observed for $\text{PdCl}_2(\text{PEt}_3)_2$ and $\text{PdCl}_2(\text{PPh}_3)_2$. The ineffective sorption appears to be due to
18 the strong affinity of Pd(II) with phosphine ligands compared with that of the thioamide group.
19 Thus, we oxidized the phosphine ligand before the sorption experiment by the addition of
20 H_2O_2 to a CHCl_3 solution of $\text{PdCl}_2(\text{PPh}_3)_2$. The pretreatment was reasonably effective, and
21 the percentage of Pd sorption increased to 41% (last row in Table 2). Further work is
22 required to determine optimal conditions, but this result indicates that the vigorous oxidation
23 of phosphine to phosphine oxide efficiently improves the recovery of Pd from a solution
24 containing Pd complexes with phosphine ligands.

25

26 3.4 Elution and Reusability

1
2 The desorption of Pd(II) and the reuse of the sorbent are also crucial factors in the recovery
3 processes of precious metals. As mentioned above, PTA was able to sorb hardly any Pd(II)
4 from organic solutions of Pd-phosphine complexes. This result indicated to us that the
5 Pd(II) sorbed on PTA can be eluted by the phosphine ligands. Figure 4 shows the results for
6 the elution of Pd(II) sorbed on PTA using MeOH solutions containing various amounts of
7 triphenylphosphine (TPP) and 1,3-bis(diphenylphosphino)propane (DPPP). In this
8 experiment, the Pd(II)-sorbed PTA was prepared using MeOH solutions containing the Pd(II)
9 standard solution and 20 mmol L⁻¹ HCl. As shown in Fig. 4, TPP was able to elute up to
10 62% of the sorbed Pd(II), indicating that the P donor of TPP played an important role in the
11 elution of Pd(II) from PTA. When DPPP was used as an eluent, the chelating effect of DPPP
12 significantly improved the elution of Pd(II), and quantitative elution of Pd(II) was
13 accomplished. In addition, we found that the addition of a small amount of HCl to the
14 MeOH solution was efficient for achieving quantitative and reproducible elution of Pd(II) on
15 PTA using DPPP, although the effect of HCl on the elution process is not clear at present.
16 This elution technique was possible for every Pd-sorbed PTA sample prepared under various
17 conditions; the tested samples were prepared using MeOH containing PdCl₂(PhCN)₂ and
18 CHCl₃ containing PdCl₂(PhCN)₂ or Pd(OAc)₂. From these results, a combination of MeOH
19 containing 20 mmol L⁻¹ HCl and powdered DPPP was useful for the elution of Pd(II).

20 On the basis of these results, the reusability of PTA as a Pd sorbent was examined.
21 Pd(II) was sorbed in MeOH containing 20 mmol L⁻¹ HCl and then eluted using MeOH
22 containing 20 mmol L⁻¹ HCl and powdered DPPP; the sorption and elution were carried out
23 repeatedly. As shown in Fig. 5, the sorption capability of PTA remained almost constant,
24 and the quantitative sorption and elution can be achieved at least five times.

25

26 3.5 Demonstration of Separation of Pd from Ni or Pt

1

2 To evaluate the ability of PTA as a sorbent toward Pd(II), the selective separation of Pd(II)
3 from MeOH solution containing Ni(II) was carried out. Since Ni(II) was scarcely sorbed on
4 PTA from acidic MeOH solution (Fig. 2), the sorption was investigated using MeOH solutions
5 containing 20 mmol L⁻¹ HCl and both Pd(II) and Ni(II). As shown in Table 3, PTA only
6 sorbed Pd(II) from the solution; note that the selective separation of Pd(II) was achieved from
7 a MeOH solution containing a large amount of Ni(II) of up to 100 times higher than that of
8 Pd(II). Over 94% of the sorbed Pd(II) was recovered.

9 The separation of Pd(II) from MeOH solution containing Pt(IV) was also
10 investigated. Since Pt(IV) was hardly sorbed under basic conditions (Fig. 2), the sorption
11 was carried out using MeOH solutions containing 50 mmol L⁻¹ MeONa and both Pd(II) and
12 Pt(IV). The obtained results are summarized in Table 4. The quantitative sorption of Pd(II)
13 was observed for the solution containing a 10 times larger amount of Pt(IV) than that of Pd(II),
14 and 84% of Pd(II) was sorbed even from a solution containing 100 times more Pt(IV). In
15 these cases, Pt(IV) was hardly sorbed on PTA, and the elution of Pt(IV) was negligible. The
16 sorbed Pd(II) was quantitatively eluted. The separation of Pd(II) from Pt(II) was not
17 examined because a black precipitate was formed when both Pd(II) and Pt(II) were added to
18 MeOH solution containing MeONa. These results indicate that PTA is an effective sorbent
19 enabling the selective separation and recovery of Pd(II) from a solution also containing a
20 large amount of Ni(II) and Pt(IV).

21

22 **4 Conclusions**

23

24 PTA has the ability to sorb Pd in various organic solutions under not only acidic conditions
25 but also basic conditions. The Pd sorbed on PTA could be eluted quantitatively in MeOH
26 using DPPP as an eluent. Since Ni(II) and Pt(IV) were hardly sorbed under acidic conditions

1 and basic conditions, respectively, the selective separation of Pd(II) from Ni(II) or Pt(IV) was
2 achieved by controlling the acidity or basicity of the solution. To our knowledge, this is the
3 first example of the effective separation of Pd(II) from an organic solution containing a large
4 amount of Ni(II) and Pt(IV). PTA is thought to contribute to the separation and recovery of
5 Pd, which is utilized as a catalyst in various chemical processes.

6
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1

2 **Table 1** Sorption of Pd(II) in some organic solutions on PTA

Solution	Sorption / %
MeOH	100
CHCl ₃	98
Toluene	82
Acetone	76
MeCN	88
EtOAc	77

3 Pd(OAc)₂ (1 μmol) was added to 10 mL of the solution. PTA, 5 mg; stirring, 6 h.

4

1

2 **Table 2** Sorption of Pd complexes in some organic solution on PTA

Pd complex	Solution	Sorption / %
PdCl ₂ (PhCN) ₂	MeOH	100
	MeOH + HCl ^a	100
	CHCl ₃	100
	Toluene	100
	CHCl ₃ + Acetone (1 + 1)	100
	Toluene + Acetone (1 + 1)	100
Pd ₂ (dba) ₃	MeOH + HCl ^a	100
	CHCl ₃	69
	CHCl ₃ + Acetone (1 + 1)	96
PdCl ₂ (PEt ₃) ₂	MeOH	20
	MeOH + HCl ^a	24
	CHCl ₃	16
	Toluene	0
	CHCl ₃ + Acetone (1 + 1)	14
	Toluene + Acetone (1 + 1)	0
PdCl ₂ (PPh ₃) ₂	CHCl ₃	19
	CHCl ₃ ^b	41

3 Solution volume, 10 mL; Pd complex, 1 μmol; PTA, 5 mg; stirring, 6 h.

4 ^a MeOH containing 20 mmol L⁻¹ HCl.5 ^b CHCl₃ solution (20 mL) was stirred vigorously for 1 h with H₂O₂ (0.2 mL); 10 mL of the6 CHCl₃ solution was used for the sorption.

7

1

2 **Table 3** Separation of Pd(II) from Ni(II)

Initial amount / μmol		Sorption / μmol		Elution / μmol	
Pd(II)	Ni(II)	Pd(II)	Ni(II)	Pd(II)	Ni(II)
1	1	1.00	0	1.00	0
1	10	1.00	0	1.00	0
1	100	1.00	0	0.94	0

3 Sorption: Solution, 10 mL of MeOH containing 20 mmol L⁻¹ HCl; PTA, 5 mg; stirring, 15 h.4 Elution: Solution, 10 mL of MeOH containing 20 mmol L⁻¹ HCl; powdery DPPP, 5 μmol ;
5 stirring, 6 h.

6

1

2 **Table 4** Separation of Pd(II) from Pt(IV)

Initial amount / μmol		Sorption / μmol		Elution / μmol	
Pd(II)	Pt(IV)	Pd(II)	Pt(IV)	Pd(II)	Pt(IV)
1	1	0.98	0	1.00	0
1	10	0.97	0.00 ₈	0.99	0.00 ₄
1	100	0.84	0.03 ₈	0.83	0

3 Sorption: Solution, 10 mL of MeOH containing 50 mmol L⁻¹ MeONa; PTA, 5 mg; stirring, 154 h. Elution: Solution, 10 mL of MeOH containing 20 mmol L⁻¹ HCl; powdery DPPP, 5 μmol ;

5 stirring, 6 h.

1 **Scheme**

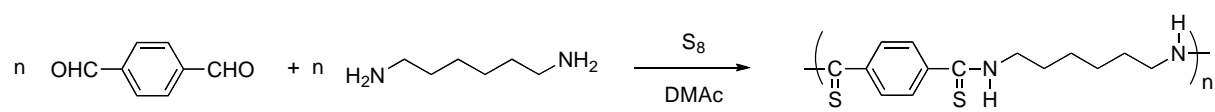
2

3

4

5 **Scheme 1** Preparation of PTA

6



1 **Figure captions**

2

3 **Fig. 1** Effect of pH on the sorption of some metals in aqueous solution.

4 Solution volume, 10 mL; each metal, 1 μmol ; PTA, 5 mg; stirring, 6 h.

5

6 **Fig. 2** Sorption of Pd(II), Ni(II), and Pt(II,IV) in MeOH on PTA. Solution volume, 10 mL;

7 Pd(II), Ni(II), or Pt(II,IV), 1 μmol ; PTA, 5 mg; stirring, 15 h. A: MeOH containing 20 mmol

8 L^{-1} HCl. B: MeOH only. C: MeOH containing 50 mmol L^{-1} MeONa.

9

10 **Fig. 3** Molecular structure of **1**.

11

12 **Fig. 4** Effect of the concentration of TPP (●) or DPPP (○) on the elution of Pd sorbed on

13 PTA. Sorption: Solution, 5 mL of MeOH containing 20 mmol L^{-1} HCl and 1 μmol of Pd(II);

14 PTA, 5 mg; stirring, 15 h. Elution: Solution, 10 mL of MeOH containing TPP and DPPP;

15 stirring, 6 h.

16

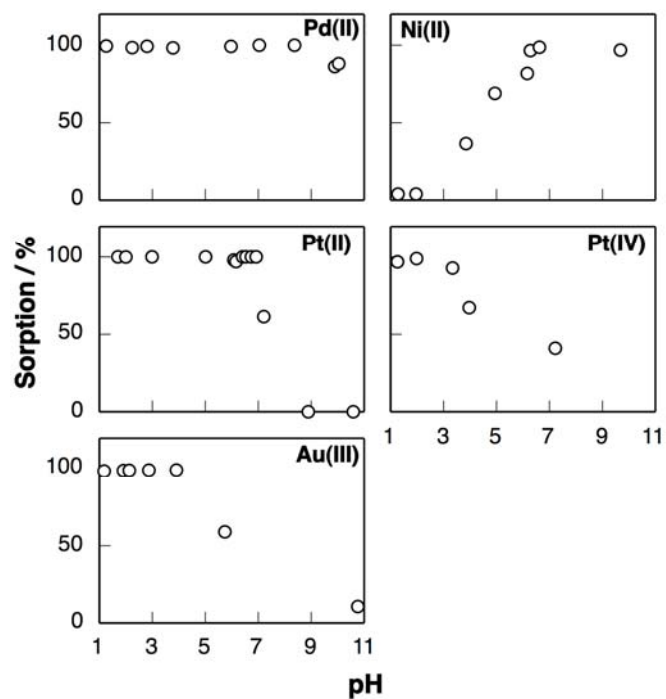
17 **Fig. 5** Reusability of PTA as Pd sorbent.

18 Sorption: Solution, 20 mL of MeOH containing 20 mmol L^{-1} HCl and 4 μmol of Pd(II); PTA,

19 20 mg; stirring, 15 h. Elution: Solution, 40 mL of MeOH containing 0.5 mmol L^{-1} DPPP;

20 stirring, 6 h.

1



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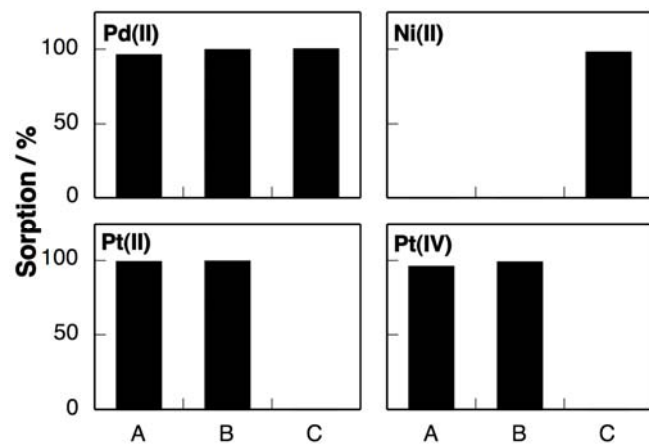
3

4 **Fig. 1** S. Kagaya, E. Tanaka, N. Kawai, I. Masore, E. Sato, K. Hasegawa, M. Kishi, T.

5 Kanbara

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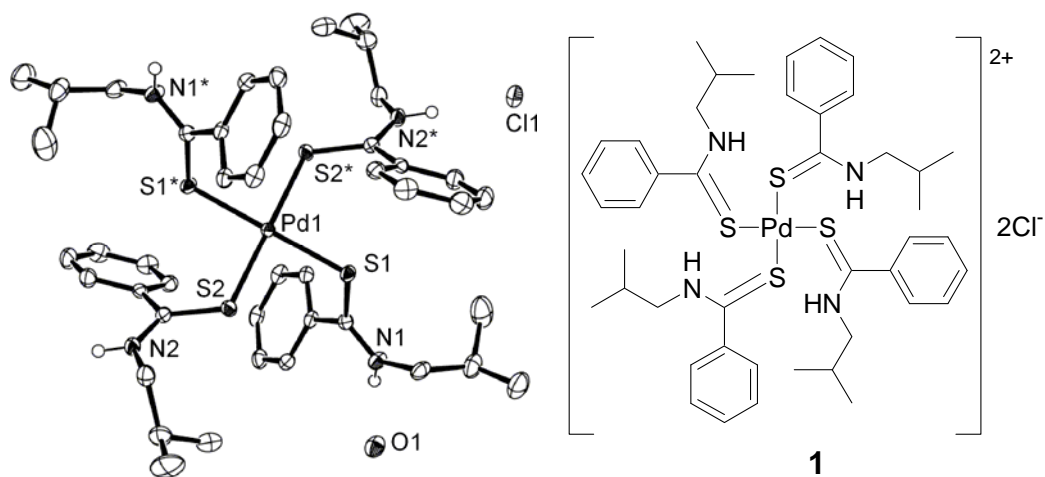
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4 **Fig. 2** S. Kagaya, E. Tanaka, N. Kawai, I. Masore, E. Sato, K. Hasegawa, M. Kishi, T.

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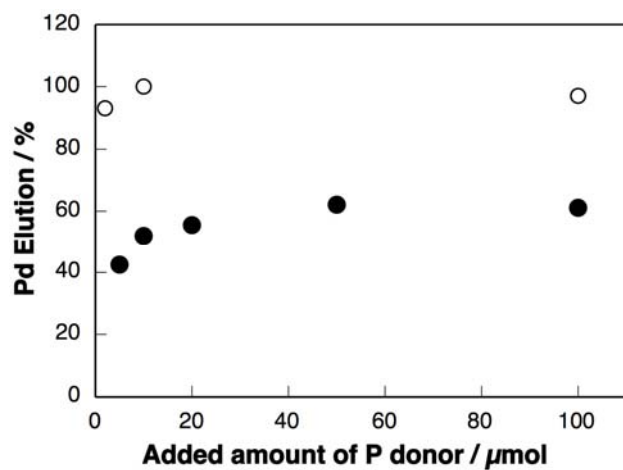
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4 **Fig. 3** S. Kagaya, E. Tanaka, N. Kawai, I. Masore, E. Sato, K. Hasegawa, M. Kishi, T.

5 Kanbara

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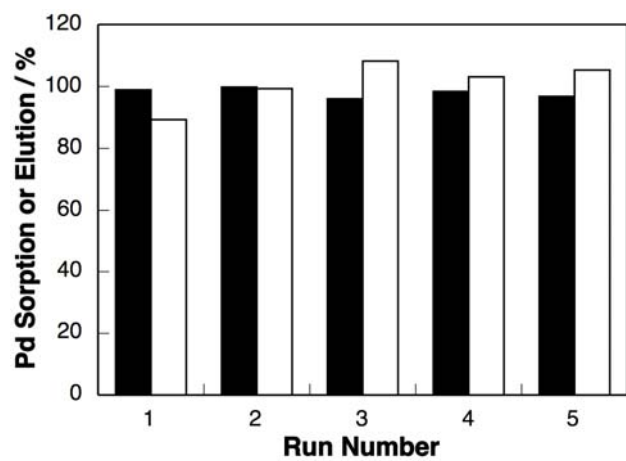
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4 **Fig. 4** S. Kagaya, E. Tanaka, N. Kawai, I. Masore, E. Sato, K. Hasegawa, M. Kishi, T.

5 Kanbara

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4 **Fig. 5** S. Kagaya, E. Tanaka, N. Kawai, I. Masore, E. Sato, K. Hasegawa, M. Kishi, T.

5 Kanbara