Temperature-Dependent Change of Extraction Performance of Soft Cadmium(II) Ion with TPEN-NIPA Gel. Studies on the Effect of the Ethylenediamine Skeleton

Maekawa, Tetsuya ; Kida, Tatsuya ; Miyazaki, Yuji ; Watanabe, Wataru ; Inaba, Yusuke ; Takeshita, Kenji ; Mori, Atsunori

(Citation)
Bulletin of the Chemical Society of Japan,84(1):122-124

(Issue Date)
2011-01-15

(Resource Type)
journal article

(Version)
Version of Record

(URL)
https://hdl.handle.net/20.500.14094/90003960

Temperature-Dependent Change of Extraction Performance of Soft Cadmium(II) Ion with TPEN–NIPA Gel. Studies on the Effect of the Ethylenediamine Skeleton

Tetsuya Maekawa,[1] Tatsuya Kida,[1] Yuji Miyazaki,[1] Wataru Watanabe,[1] Yusuke Inaba,[2] Kenji Takeshita,[2] and Atsunori Mori*[1]

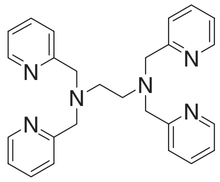
[1]Department of Chemical Science and Engineering,
Kobe University, 1-1 Rokkodai, Nada-ku, Kobe 657-8501

[2]Integrated Research Institute, Tokyo Institute of Technology,
4259 Nagatsuta, Yokohama 226-8503

Received May 31, 2010

E-mail: amori@kobe-u.ac.jp

TPEN (*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine) derivatives of different skeleton of the ethylene moiety are designed and synthesized. The obtained product is subjected to radical copolymerization with *N*-isopropylacrylamide (NIPA) to afford the polymer gel. Temperature-dependent extraction performance of TPEN derivatives and the corresponding polymer gels is compared at different temperatures and pH values.



TPEN

Chart 1.

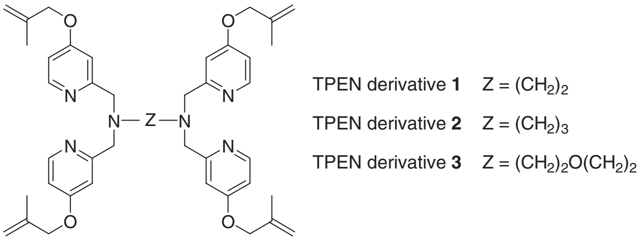


Figure 1. Structure of TPEN derivatives **1**–**3**.

We have recently shown that TPEN–(poly-NIPA) gel exhibits thermo-responsive extraction of soft metal ions. TPEN–NIPA gel was prepared by the copolymerization of *N*-isopropylacrylamide (NIPA) and TPEN (*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine) (Chart 1) derivatives bearing a polymerizable double bond on the subsituent of the pyridine ring.[1] TPEN, which is a hexadentate ligand bearing six nitrogen donors, efficiently extracts several soft metal ions and is recognized as a possible candidate for the separation of minor actinides (MA) such as Am and Cm from high-level waste during the reprocessing of fast breeder reactor nuclear fuel.[2–4] Since poly-NIPA gel shows thermo-responsive reversible swelling/shrinking in water at the LCST (lower critical solution temperature), extraction performance of the TPEN–NIPA gel, in which the TPEN derivatives are employed as a crosslinker, has shown to change depending on the temperature.[5] Concerning the relationship of the TPEN structure toward the extraction performance, we have studied the effect of the number of polymerizable double bond,[6] chain length of the spacer between double bond and the pyridine ring,[7] and branched structure on the spacer.[8] It is also intriguing to study the effect of the structure of ethylenediamine moiety. We herein report synthesis of several TPEN derivatives with different diamine structure, radical copolymerization of thus prepared TPEN derivatives and NIPA, and studies on the temperature-dependent extraction of cadmium(II) ion with thus obtained TPEN–NIPA gel derivatives.

TPEN derivatives we have designed are ethylenediamine (**1**), 1,3-propanediamine (**2**), and 1,5-diamino-3-oxapentane (**3**), whose amino group is substituted with 2-chloromethylpyridine bearing a 2-methyl-2-propenyloxy substituent at the 4-position of the pyridine ring (Figure 1). Synthesis of **1**–**3** was carried out in a similar manner to that of TPEN. NIPA gels composed of **1**–**3** as a crosslinker were prepared by radical polymerization with AIBN as an initiator in the presence of 2.5 mol % of **1**–**3** to give the corresponding gel compound in good yields. The obtained gels showed thermo-responsive swelling and shrinking in water around 30–35 °C. The volume change between swelling and shrinking of **1**–**3** was found to be 3.7, 3.6, and 3.8, respectively. Attempted spectroscopic characterization of gels **1**–**3** was unsuccessful. Since the obtained gels were completely insoluble in any solvents, it is difficult to characterize structure of the crosslinker by NMR analyses. Observation of characteristic absorptions of pyridine rings in IR spectra was also unsuccessful due to insufficient quantity.

Extraction performance of TPEN gels composed of **1**–**3** was examined with 1 mM solutions of $Cd(NO_3)_2$, whose pH was controlled to 2.0 or 5.0. The polymer gel was added to the aqueous cadmium solution, and stirring was continued for 1 h at 5 and 40 °C, respectively. Liquid–liquid extraction was also carried out with **1**–**3** using 1 mM solution of chloroform, at 5 and 40 °C at pH 2. Table 1 shows the results of the liquid–liquid extraction performance of TPEN derivative **3**, which possesses $(CH_2)_2O(CH_2)_2$ moiety instead of ethylenediamine. Excellent extraction performance was observed similarly to that of TPEN. It was also found that the performance was irrespective of the extraction temperature to observe mostly similar %extraction values at pH 5.0. Although the performance was slightly inferior at pH 2.0, Cd^{2+} ion was similarly extracted at both temperatures.

In contrast to the above results of the liquid–liquid extraction, temperature-dependent extraction performance was

Table 1. Extraction of Cd^{2+} with TPEN Derivative **3** at 5 and 40 °C at pH 2 and pH 5[a)]

TPEN derivative	%Extraction			
	pH 2		pH 5	
	5 °C	40 °C	5 °C	40 °C
3	55.7	57.5	89.8	87.2

a) Concentration of the cadmium ion was estimated by ICP-AES analysis in the aqueous phase.

Table 2. Extraction of Cd^{2+} with NIPA Gels Composed of **1**–**3** at 5 and 40 °C at pH 2 and pH 5

TPEN–NIPA gel	%Extraction			
	pH 2		pH 5	
	5 °C	40 °C	5 °C	40 °C
Gel **1**	47.9	18.2	85.0	11.1
Gel **2**	28.2	2.4	85.0	26.4
Gel **3**	23.0	10.5	79.3	7.1

observed in the extraction with TPEN–NIPA polymer gels **1**–**3**. Extraction was performed with 1 mM solutions of $Cd(NO_3)_2$, whose pH was controlled to 2.0 or 5.0, and TPEN–NIPA gels **1**–**3** at 5 and 40 °C, respectively. As summarized in Table 2, extraction with **1** at pH 5.0 showed that 85.0% of cadmium was incorporated in the polymer gel at 5 °C, while the performance decreased to 11.1% when the temperature was raised to 40 °C. Worthy of note is that such a temperature-dependent change was observed in the extraction at pH 2.0 although the %extraction values were slightly inferior to those at pH 5. Extraction with other polymer gels **2** and **3** also showed similar performance to that with **1**.

The results showed that different chain length in the ethylenediamine moiety of TPEN did not influence the extraction performance suggesting that all six nitrogen atoms of TPEN are not crucial for the incorporation of a metal ion. Subsequently, chelation with two nitrogen atoms of ethylenediamine leading to tight five-membered ring structure involving the cadmium atom is not a prerequisite for efficient extraction.

If the five-membered chelation with ethylenediamine moiety is not crucial for the extraction of cadmium ion, independent tridentate chelation with bis(2-pyridylmethyl)amino moiety is an alternative chelating structure, which may allow 1:2 complexation in **1**–**3**. Measurement of ^{1}H NMR spectra of a mixture of **3** and a cadmium ion was thus carried out. Figure 2 shows the spectra of the different ratio of **3** and $Cd(NO_3)_2$. The mixture of **3** and 0.5 equiv of $Cd(NO_3)_2$ (Figure 2b) indicated that several new signals that suggested formation of a metal complex were observed accompanied by characteristic signals, which were identical to those shown in Figure 2a. The 1:1 mixture of **3** and $Cd(NO_3)_2$ (Figure 2c) was completely identical to the new signals of Figure 2b. However, the NMR spectrum in the further addition of $Cd(NO_3)_2$ (1:10) also showed similar signals to Figure 2c. These results suggest that complexation of $Cd(NO_3)_2$ with **3** forms the 1:1 adduct.

In conclusion, several TEPN derivatives bearing a different number of spacer atoms from ethylenediamine were designed and synthesized. Extraction performance of these derivatives **1**–**3** and the corresponding polymer gels that are obtained by the radical copolymerization of **1**–**3** and NIPA was studied to reveal that the spacer structure was irrespective of the extraction of the cadmium ion in polymer gels as well as liquid–liquid system. Polymer gels of **1**–**3** showed temperature-dependent swelling and shrinking and thus induced change of the extraction performance, which was also irrespective of the spacer structures. These results suggest that the performance is not significantly influenced by the difference of the spacer structure, while all of these extractants form 1:1 chelation with cadmium.

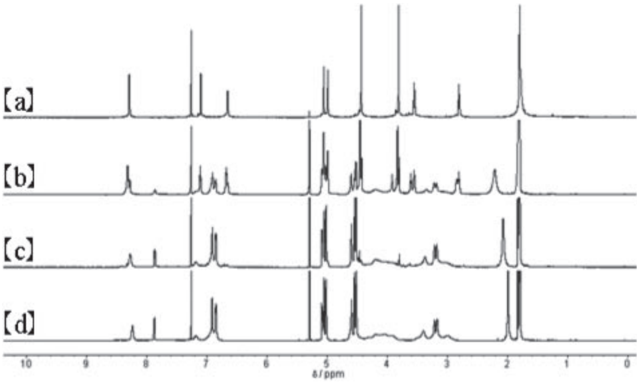


Figure 2. NMR spectra of uncomplexed **3** (a) and the mixture of **3** and Cd^{2+} (b–d). (b) 1:0.5, (c) 1:1, and (d) 1:10.

Experimental

General. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were measured in $CDCl_3$ with Bruker Avance 500. Chemical shifts are expressed in ppm using $CHCl_3$ (7.24 ppm) for ^{1}H NMR and the central signal of $CDCl_3$ (77 ppm) for ^{13}C NMR as internal standards. Coupling constants (*J*) are shown in Hertz (Hz). IR (ATR) spectra were measured with Bruker Optics Alpha with Ge. High-resolution mass spectra were measured at Nara Institute of Science and Technology with a JEOL JMS-700. ICP-AES analysis was carried out with a SII SPS3100. Column chromatography was performed using silica gel (Wakogel C200, Wako Chemicals Co., Ltd.) or basic alumina (Wako Chemicals Co., Ltd. or Merck).

Syntheses of 1–3. TPEN derivatives with a different spacer structure were prepared in a manner similar to those reported previously.

***N*,*N*,*N*′,*N*′-Tetrakis[4-(2-methyl-2-propenyloxy)-2-pyridylmethyl]ethylenediamine (1):** To a solution of ethylenediamine (26.1 µL, 0.39 mmol) in acetonitrile (3.12 mL) were successively added 4-(2-methyl-2-propenyloxy)-2-(chloromethyl)pyridine (0.309 g, 1.56 mmol), K_2CO_3 (0.431 mg, 3.12 mmol), and NaI (0.117 g, 0.708 mmol). The reaction mixture was stirred for 8 h at 80 °C. The suspension was filtered through a Celite pad. The filtrate was evaporated, and the resulting residue was purified by chromatography on aluminum oxide (chloroform/methanol = 30:1) to afford *N*,*N*,*N*′,*N*′-tetrakis[4-(2-methyl-2-propenyloxy)-2-pyridylmethyl]ethylenediamine as a brown oil. ^{1}H NMR: δ 8.27 (d, $J = 5.75$ Hz, 4H), 7.03 (d, $J = 2.45$ Hz, 4H), 6.60 (dd, $J = 2.50$, 5.65 Hz, 4H), 5.01 (d, $J = 29.5$ Hz, 12H), 4.39 (s, 8H), 2.79 (s, 4H), 1.79 (s, 12H). ^{13}C NMR: δ 5.1, 6.8, 38.3, 46.1, 57.3, 95.0, 99.2, 125.6, 135.8, 151.2, 162.6. IR: 2943, 1595, 1309, 1052 cm^{-1}. HRMS (EI) found: 704.4044, Calcd for $C_{42}H_{52}N_6O_4$: 704.4050.

***N,N,N′,N′*-Tetrakis[4-(2-methyl-2-propenyloxy)-2-pyridylmethyl]-1,3-propanediamine (2):** ^{1}H NMR: δ 8.27 (d, $J = 5.75$ Hz, 4H), 7.03 (d, $J = 2.45$ Hz, 4H), 6.64 (dd, $J =$ 2.55, 5.70 Hz, 4H), 5.30 (s, 2H), 5.02 (d, $J = 32.15$ Hz, 8H), 3.72 (s, 8H), 2.59 (s, 4H), 1.80 (s, 12H). ^{13}C NMR: δ 5.2, 10.8, 38.7, 46.3, 57.2, 94.7, 94.9, 99.3, 125.7, 136.0, 147.7, 151.3. IR: 2940, 1594, 1308, 1020 cm^{-1}. HRMS (EI) found: 718.4207, Calcd for $C_{43}H_{54}N_6O_4$: 718.4207.

***N,N,N′,N′*-Tetrakis[4-(2-methyl-2-propenyloxy)-2-pyridylmethyl]-1,5-diamino-3-oxapentane (3):** ^{1}H NMR: δ 8.29 (d, $J = 5.70$ Hz, 4H), 7.10 (d, $J = 2.35$ Hz, 4H), 6.65 (dd, $J = 2.45$, 7.95 Hz, 4H), 5.02 (d, $J = 33.8$ Hz, 8H), 4.43 (s, 8H), 3.81 (s, 8H), 3.55 (s, 4H), 2.81 (s, 4H), 1.80 (s, 12H). ^{13}C NMR: δ 5.1, 39.8, 46.7, 55.3, 57.2, 94.80, 94.8, 99.2, 125.6, 135.8, 147.5, 151.2. IR: 2942, 1594, 1308, 1020 cm^{-1}. HRMS (EI) found: 748.4318, Calcd for $C_{44}H_{56}N_6O_5$: 748.4318.

Radical Polymerization of NIPA with TPEN Derivatives. Poly-NIPA gels with 2.5 mol % of TPEN were synthesized in a similar manner described previously.[6] The obtained TPEN–NIPA gels were hardly soluble in organic solvents and water and showed swelling/shrinking change at 35 °C.

Extraction of Cadmium(II) Ion with TPEN–NIPA Gel. A 1 mM aqueous $Cd(NO_3)_2$ solution was prepared. The pH of the solution was controlled to 2.1 and 5.3 by the addition of 1 M aq NH_4NO_3 and 1 M HNO_3. TPEN–NIPA gel (2.5 mol % of TPEN contents), whose concentration of the TPEN moiety was controlled to 1.5 µmol, was added to 0.75 mL of the aqueous solution. Vigorous stirring of the mixture was continued for 60 min at 5 or 45 °C. An aliquot of the solution was taken, passed through a membrane filter (0.2 µm), and 0.2 mL of the filtrate was diluted with distilled water to 4 mL, which was subjected to ICP-AES analysis. The percent extraction value was calculated as

$$\%E = 100 \cdot D/(D+1), \{D = ([\mathrm{Cd}^{2+}]_{\mathrm{ini}} \cdot [\mathrm{Cd}^{2+}])/[\mathrm{Cd}^{2+}]\} \quad (1)$$

$[\mathrm{Cd}^{2+}]_{\mathrm{ini}}$: concentration of Cd^{2+} in water before extraction

$[\mathrm{Cd}^{2+}]$: concentration of Cd^{2+} in water after extraction

The authors thank the Support Network for Nanotechnology Research of Nara Institute of Science and Technology supported by MEXT for the measurement of high-resolution mass spectra.

References

1 K. Takeshita, K. Ishida, Y. Nakano, T. Matsumura, *Chem. Lett.* **2007**, *36*, 1032.

2 For a review: Z. Kolarik, *Chem. Rev.* **2008**, *108*, 4208.

3 a) M. P. Jensen, L. R. Morss, J. V. Beitz, D. D. Ensor, *J. Alloys Compd.* **2000**, *303–304*, 137. b) I. Cukrowski, E. Cukrowska, R. D. Hancock, G. Anderegg, *Anal. Chim. Acta* **1995**, *312*, 307. c) N. Hirayama, S. Iimuro, K. Kubono, H. Kokusen, T. Honjo, *Talanta* **1996**, *43*, 621. d) M. Watanabe, R. Mirvaliev, S. Tachimori, K. Takeshita, Y. Nakano, K. Morikawa, R. Mori, *Chem. Lett.* **2002**, 1230. e) R. Mirvaliev, M. Watanabe, T. Matsumura, S. Tachimori, K. Takeshita, *J. Nucl. Sci. Technol.* **2004**, *41*, 1122.

4 a) C. A. Blindauer, M. T. Razi, S. Parsons, P. Sadler, *Polyhedron* **2006**, *25*, 513. b) T. Ogata, K. Takeshita, G. A. Fugate, A. Mori, *Sep. Sci. Technol.* **2008**, *43*, 2630. c) T. Ogata, K. Takeshita, K. Tsuda, A. Mori, *Sep. Purif. Technol.* **2009**, *68*, 288. d) K. Shimojo, H. Naganawa, J. Noro, F. Kubota, M. Goto, *Anal. Sci.* **2007**, *23*, 1427. e) Y. Mikata, A. Yamanaka, A. Yamashita, S. Yano, *Inorg. Chem.* **2008**, *47*, 7295. f) M. Heitzmann, F. Bravard, C. Gateau, N. Boubals, C. Berthon, J. Pécaut, M.-C. Charbonnel, P. Delangle, *Inorg. Chem.* **2009**, *48*, 246. g) C. Ekberg, A. Fermvik, T. Retegan, G. Skarnemark, M. R. S. Foreman, M. J. Hudson, S. Englund, M. Nilsson, *Radiochim. Acta.* **2008**, *96*, 225. h) K. Takeshita, K. Watanabe, Y. Nakano, M. Watanabe, *Hydrometallurgy* **2003**, *70*, 63. i) K. Takeshita, K. Watanabe, Y. Nakano, M. Watanabe, *Chem. Lett.* **2003**, *32*, 96.

5 a) T. Tanaka, I. Nishio, S.-T. Sun, S. Ueno-Nishio, *Science* **1982**, *218*, 467. b) H. Tokuyama, T. Iwama, *Langmuir* **2003**, *26*, 13104, and references therein.

6 S. Fukuoka, T. Kida, Y. Nakajima, T. Tsumagari, W. Watanabe, Y. Inaba, A. Mori, T. Matsumura, Y. Nakano, K. Takeshita, *Tetrahedron* **2010**, *66*, 1721.

7 Y. Inaba, T. Tsumagari, T. Kida, K. Takeshita, A. Mori, unpublished results.

8 D. Kuwae, Thesis, Tokyo Institute of Technology, **2010**.