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2,6-Bis[*N*-(8-quinolyl)carbamoyl]pyridine as a Highly Selective Extractant for Cu(II)

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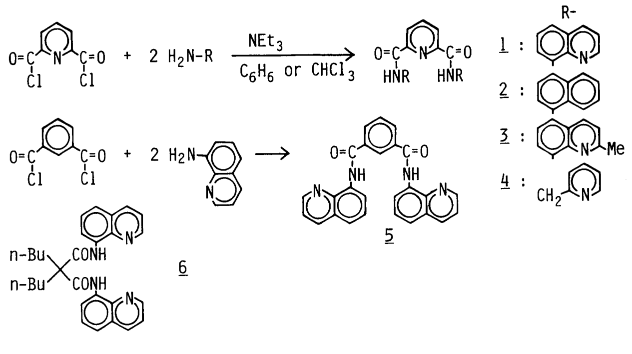
Synopsis. Pyridine derivatives containing two 8-quinolylamino groups were newly synthesized for heavy metal ion-cheletion. It was shown in solvent extraction that 2, 6-bis[*N*,N′-(8-quinolyl)aminocarbonyl]pyridine can extract only Cu(II) with excellent selectivity and efficiency from the aqueous phase(pH 6.2) containing Cu(II), Ni(II), Co(II), and Zn(II) into the chloroform phase.

Synthesis of highly selective extractants and carriers for available metal ions is of importance for the technology of both separation and detection.[1–6] We recently reported on 2,2-dibutyl *N*,*N*′-di(8-quinolyl)-malonamide(**6**), which can extract Cu(II) with excellent selectivity from aqueous solution (pH 6.2) into chloroform.[7] In this paper we wish to report on a new extractant which can extract Cu(II) more efficiently and selectively than the malonamide derivative (**6**).

Results and Discussion

The reactions of commercially available 2, 6-pyridinedicarbonyl dichloride with two equimolar amino compounds(8-aminoquinoline, 1-aminonaphthalene, 2-methyl-8-aminoquinoline, and 2-aminomethylpyridine) in the presence of triethylamine in anhydrous benzene or chloroform gave the corresponding 2,6-disubstituted derivatives (**1**—**4**) in high yields. The compound (**5**) was also obtained from the reaction of isophthaloyl dichloride with 8-aminoquinoline in the same manner.



Scheme 1.

In the solvent extraction of transition metal ions by these compounds, an aqueous solution(5 ml, pH 6.2) containing either 1 mM (=mmol dm^{-3}) of each of the metal ions(Cu(II), Ni(II), Co(II), and Zn(II)) or 1 mM of Cu(II) was shaken vigorously for 24 h at 25 °C with 5 ml of the CHCl$_3$ phase containing 1 mM of diamide compounds. After careful separation the upper aqueous solution was analysed for any metal ion(s) remaining unextracted by an atomic absorption spectroscopic method. The boundary layer was kept completely clear both before and after extraction in all cases.

Table 1 shows the results of metal ion extraction with diamide compounds, **1**—**5**. Among the diamides, **1**—**4** which can selectively extract Cu(II), the extractability of **1** for Cu(II) is superior to that of the others. That is, **1** in chloroform can quantitatively extract Cu(II) not only from an aqueous solution (pH 6.2) containing only Cu(II) but also from that containing plural transition metal ions. On the other hand, **5**, which has no pyridyl group, can not extract any metal ions under both experimental conditions. Additionally, **2**, which has 1-naphthyl groups instead of 8-quinoly ones, shows considerably less extractability than **1**. This means that the nitrogen atom of the 8-quinolyl group significantly contributes to the coordination and that the three nitrogen atoms of two amide groups and one pyridyl group alone are not sufficient to form its metal complex. Besides, since the extractability of **4**, having 2-pyridylmethyl groups, appreciably decreases, the 8-quinolyl group apparently plays a more important role in the metal coordination than does the 2-pyridinomethyl group. The methyl group at the

Table 1. Extraction of Heavy Metal Ions with Diamide Derivatives[a]

Extractant	Metal ion extracted/%							
	From the solution containing plural ions				From the solution containing single ion			
	Cu(II)	Ni(II)	Co(II)	Zn(II)	Cu(II)	Ni(II)	Co(II)	Zn(II)
1	95	0	0	0	97	0	0	0
2	4	0	0	0	3	0	0	0
3	52	0	0	0	56	0	0	0
4	23	0	0	0	26	0	0	0
5	0	0	0	0	0	0	0	0

a) Extraction conditions: 1 mM diamide in 5 ml chloroform/1 mM of each of Cu(II), Ni(II), Co(II), and/or Zn(II) in 5 ml of buffer aqueous solution (pH 6.2). Shaking vigorously at 25 °C, 1 d.

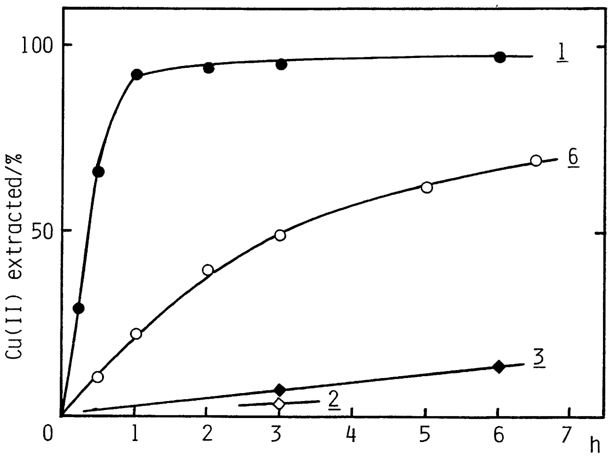


Fig. 1. Plots of amount of Cu(II) extracted vs. shaking time. Each number in the figure is corresponding to the compounds in the text.

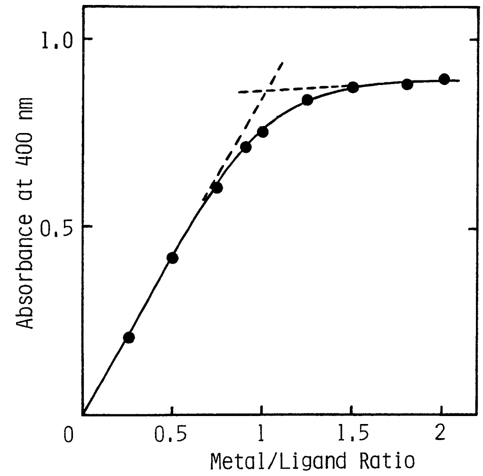


Fig. 3. Plots of the change of absorbance at 400 nm in $CHCl_3$ vs. Cu(II)/**1** ratio; concentration of **1**: 10^{-4} mol dm^{-3}.

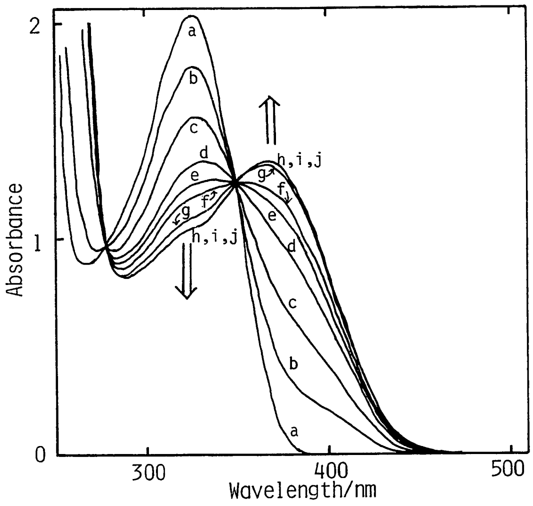


Fig. 2. Change in the absorption spectra of **1** ($=10^{-4}$ mol dm^{-3}) in $CHCl_3$ by Complepation with Cu(II); a: **1**, b: Cu(II)/**1**=0.25, c: Cu(II)/**1**=0.5, d: Cu(II)/**1**=0.75, e: Cu(II)/**1**=0.9, f: Cu(II)/**1**=1, g: Cu(II)/**1**=1.25, h: Cu(II)/**1**=1.5, i: Cu(II)/**1**=1.8, j: Cu(II)/**1**=2.0. The values of Cu(II)/**1** indicate molar ratio of metal ion/ligand.

2-position of the quinolyl group of **3** apparently decreases the Cu(II) extractability in comparison to **1** and **3** presumably because of a steric hindrance between the methyl groups for the formation of a metal complex.

The time dependence on the Cu(II) extractability of **1**—**3** and malonamide **6** was investigated. In Fig. 1, it can be seen that **1** can extract Cu(II) very rapidly compared to their extractability. Diamide **1** extracted more than 90% of the Cu(II) from the aqueous phase within 1 h, whereas the extraction rate with **2** and **3** were considerably low, compared with that with **1**. Noticeably, **1** can extract more efficiently than **6**.

Figure 2 shows the spectroscopic change in the absorption spectrum of **1** in chloroform by complexation with the Cu(II) ion. Plots of the absorbance of the solution against the composition in Fig. 3 indicates that the composition of the complex of **1** with the Cu(II) ion was 1:1. Besides, a 1:1 complex of deprotonated **1** with Cu(II) was obtained from the reaction of **1** with powdered Cu(II) acetate in chloroform and recrystallized from chloroform. Further, this complex shows the same absorption spectrum in chloroform as that in the range over the ratio of metal/ligand=1 in Fig. 3. From these results, it could be concluded that **1** presumably forms a 1:1 complex with Cu(II) followed by the release of two amide-protons in the solvent-extraction system.

It has thus been found that 2,6-pyridinecarboxamide **1**, which probably forms a pentacoordinated complex with Cu(II), can extract Cu(II) with excellent selectivity and efficiency. In this series, the effect of the structure on the extractability appears drastically as well as that in the series of malonamide derivatives. It should be noted that the Cu(II) extractability of **1** is apparently superior to that of tetradentate Cu(II) extractant (**6**).

Experimental

General. The IR and the UV sppectra were recorded with JASCO A-3 Infrared and Hitachi 330 spectrophotometers, respectively. The ^{1}H NMR spectrum was recorded with Bruker MSL-300 spectrometer. The chemical shifts for the $CDCl_3$ solution are reported from internal tetramethylsilane (TMS). The mass spectrum was recorded with a Hitachi M-80B mass spectrometer.

2,6-Bis[*N*-(8-quinolyl)carbamoyl]pyridine (1). 2,6-pyridinedicarbonyl dichloride (**7**) (1.0 g, 5 mmol) was dissolved in 50 ml of anhydrous benzene. To the solution was added dropwise 8-aminoquinoline(1.5 g, 10 mmol) and triethylamine(1.0 g, 10 mmol) in 20 ml of benzene; the mixture was then stirred at 70—80 °C for 5 h. After benzene was removed from the mixture by evaporation, the residue was dissolved in 100 ml of chloroform and washed with water. The chloroform solution was dried over anhydrous magnesium sulfate, and then concentrated in vacuo. The residual solid was recrystallized from benzene–chloroform; mp 290—292.5 °C, yield 1.8 g (86%); IR (KBr) 3300 (NH), 1680 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}=328 nm, ε=20400. ^{1}H NMR ($CDCl_3$) δ=7.33, 7.62, 7.67, 8.20, 8.26, 9.03 (2H each, q, d, t, d, d, and d, respectively, quinoline protons), 8.20 (1H, t, pyridine proton), 8.58 (2H, d, pyridine protons), 12.36 (2H, s, NH). Precise Mass Found: 419.139; Calcd for $C_{25}H_{17}N_5O_2$: 419.138.

2,6-Bis[*N*-(1-naphthyl)carbamoyl]pyridine (2). This compound was synthesized from the reaction of **7** with 1-aminonaphthalene in a similar manner to that described for **1**, and recrystallized from benzene–chloroform; mp 244—246 °C, yield 81%; IR (KBr) 3300 (NH), 3040 (C=C), 1660 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}=316 nm, ε=16300. ^{1}H NMR ($CDCl_3$) δ=7.36, 7.50, 7.57, 7.75, 7.91, 8.08, 8.32, (2H each, t, t, t, d, d, d, and d, respectively, 1-naphthalene protons), 8.19 (1H, t, pyridine proton), 8.58 (2H, d, pyridine protons), 10.26 (2H, s, NH). Precise Mass Found: 417.144; Calcd for $C_{27}H_{19}N_3O_2$: 417.148.

2,6-Bis[*N*-(2-methyl-8-quinolyl)carbamoyl]pyridine (3). In a similar manner, this compound was synthesized from the reaction of **7** with 8-amino-2-methylquinoline and recrystallized from benzene; mp 300—301.5 °C, yield 64%; IR (KBr) 3300 (NH), 3060 and 3020 (C=C), 1680 (C=O)cm^{-1}; UV ($CHCl_3$) λ_{max}=328 nm, ε=21400. ^{1}H NMR ($CDCl_3$) δ=1.70 (6H, s, CH_3), 7.14, 7.56, 7.59, 8.03, 8.98 (2H each, d, d, t, d, and d, respectively, quinoline protons), 8.19 (1H, t, pyridine proton), 8.55 (2H, d, pyridine protons), 12.48 (2H, s, NH). Precise Mass Found: 447.168; Calcd for $C_{27}H_{21}N_5O_2$: 447.169.

2,6-Bis[*N*-(2-pyridylmethyl)carbamoyl]pyridine (4). In a similar manner, this compound was synthesized from the reaction of **7** with 2-aminomethylpyridine, and recrystallized from benzene; mp 159—160 °C, yield 76%; IR (KBr) 3300 (NH), 3050 (C=C), 1670 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}=262 nm, ε=13300. ^{1}H NMR ($CDCl_3$) δ=4.74 (4H, d, CH_2), 7.16, 7.33, 7.64, 8.46 (2H each, q, d, t, and d, respectively, pyridine protons), 8.00 (1H, t, pyridine proton), 8.32 (2H, d, pyridine protons), 9.21 (2H, s, NH). Precise Mass Found: 347.136; Calcd for $C_{19}H_{17}N_5O_2$; 347.138.

***N*,*N*′-Bis(8-quinolyl)carbamoyl)isophthalamide (5).** In a similar manner, this compound was synthesized from the reaction of isophthaloyl dichloride with 8-aminoquinoline, and recrystallized from benzene; mp 190.5—191.5 °C, yield 71%; IR (KBr) 3340 and 3300 (NH), 1655 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}=328nm, ε=21200. ^{1}H NMR ($CDCl_3$) δ=7.51, 7.60, 7.64, 8.22, 8.88, 8.97 (2H each, q, d, t, d, d, and d, respectively, quinoline protons), 7.77 (1H, t, benzene proton), 8.31 (2H, d, benzene protons), 8.80 (1H, s, benzene proton), 10.88 (2H, s, NH). Precise Mass Found: 418.143; Calcd for $C_{26}H_{18}N_4O_2$; 418.143.

Preparation of Cu(II) Complex with 1. 2,6-pyridinedicarboxamide **1** (0.21 g, 0.5 mmol) and copper(II) acetate monohydrate(1.0 g, 5 mmol) were mixed in 50 ml of chloroform; the mixture was refluxed overnight. The chloroform solution was washed with water and dried over anhydrous magnesium sulfate. The solution was concentrated in vacuo and the residual dark-green solid was recrystallized from benzene–chloroform: mp>300 °C, yield 0.20 g, 83%; IR (KBr) no NH absorption band, 1620 (C=O) cm^{-1}, UV ($CHCl_3$) λ_{max}=370 nm, ε=13700. SIMS (M^+) Found: 480.7; Calcd for $C_{25}H_{15}N_5O_2Cu$: 480.7.

General Procedure of Solvent Extraction. In a 20 ml sample tube with screw cap was poured 5 ml of an aqueous solution containing either 1 mM (=mmol dm^{-3}) of each of transition metal ions (Cu(II), Ni(II), Co(II), and Zn(II)) or 1 mM of single transition metal ion (Cu(II), Ni(II), Co(II), or Zn(II)) and 5 ml of chloroform solution containing 1 mM of diamide compound. The aqueous solution was arranged at pH 6.2 by using both a 1 M sodium acetate and 0.2 M acetic acid. The mixture was shaken vigorously for 24 h at 25 °C. The concentration of the remaining metal ions in aqueous solution was determined by atomic absorption spectroscopy. The concentration of the extracted metal ions was calculated from the values.

References

1) *Chem. Eng. News*, Jan. 14, **1985**, 58.

2) R. W. Baker, M. E. Tuttle, D. J. Kelly, and H. K. Lonsdale, *J. Membr. Sci.*, **2**, 213 (1977).

3) E. L. Cussler and D. F. Evans, *J. Membr. Sci.*, **6**, 113 (1980).

4) K. Maruyama, H. Tsukube, and T. Araki, *J. Chem. Soc., Dalton Trans.*, **1981**, 1486.

5) E. Kimura, C. A. Dalimunte, A. Yamashita, and R. Machida, *J. Chem. Soc., Chem. Commun.*, **1985**, 1041.

6) N. Kishi, K. Araki, and S. Shiraishi, *J. Chem. Soc., Dalton Trans.*, **1985**, 373.

7) K. Hiratani, K. Taguchi, K. Ohashi, and H. Nakayama, *Chem. Lett.*, **1989**, 2073.