Diamide Derivatives of α-Amino Acids with a Quinolyl Group as Cu(II) Ionophores

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Several new *N*-(8-quinolyl)-substituted diamide compounds were synthesized from α-amino acids and their Cu(II) transport abilities as carriers through liquid membranes were investigated. The Cu(II) transport ability of the carrier is affected by the α-substituent of the amino acid. Diamides derived from alanine and phenylalanine have good Cu(II) transport abilities.

Much attention has been paid to the selective extraction and transport of metal cations by synthetic ionophores through liquid membranes because of their potential applications in the fields of separation and analytical sciences as well as biological and medical studies.[1] New synthetic ionophores for heavy or transition metal ions and for alkali and alkaline earth metal ions have been developed.[2] However, most of those artificial ion carriers are macrocyclic compounds and some cannot be easily prepared. During our study of the synthesis of new ionophores,[3] we found that simple acyclic amide compounds with one or two quinolyl groups are effective for selective Cu(II) extraction or transport.[4—8] For example, *N*,*N*′-di-8-quinolyldibutylmalonamide (**1**) (R=R′=*n*−Bu) is a selective Cu(II)-extractant although its Cu(II) transport ability is poor.[4] By contrast, *N*,*N*′-di-8-quinolylglutaramide (**2**) has high selectivity and efficiency towards Cu(II) in transport experiments but extracts few metal ions (Chart 1).[6] In Cu(II) transport experiments using methyl-substituted glutaramide derivatives, we found that slight changes in the structure of a carrier affect its transport ability.[7,8] For increased transport ability by **2**, several *N*,*N*′-[2-(acylamino)glutamoyl]bis[8-quinolylamine]s **3** with a triamide structure were prepared from glutamic acid and their transport ability was investigated.[9] The Cu(II) transport ability of the carrier **3** was affected by the acyl group on the 2-acylamino substituent. Derivatives with a small acyl group (acetyl and butyryl) had high efficiency in Cu(II) transport. Thus, the participation of the 2-acylamino substituent, as well as the 8-quinolylcarbamoyl part, in the complexation of the carrier **3** with Cu(II) seems likely. We next examined the part of the structure of **3** encircled by dotted lines in the diagram and synthesized new diamide compounds **4a**—**f** derived from α-amino acids to clarify the role of the acylamino group in Cu(II) transport.

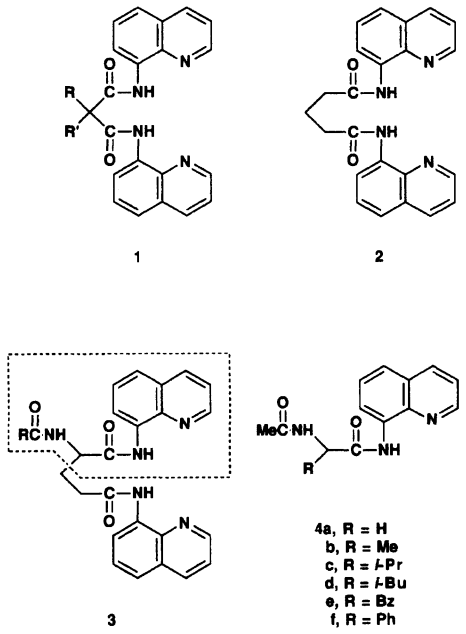


Chart 1.

Results and Discussion

Six diamide compounds **4a**—**f** were synthesized from α-amino acids and their structures were confirmed by elemental analyses and, NMR and IR spectra.

In an experiment on single Cu(II) ion transport under standard conditions (see Table 1), diamide **4e**, derived from phenylalanine, could transport 82% of Cu(II) after 1 d, and the transport was almost complete by 48 h. With excess Cu(II) ions (Cu(II)/**4e**=1.5 in molar ratio), 97% of Cu(II) was transported by 72 h. In the competitive transport of transition metal ions (Cu(II), Ni(II), Co(II), and Zn(II)), 99% of Cu(II) was transported by **4e** by 48 h. Ni(II), Co(II), and Zn(II) were not transported. For Ni(II) and Co(II) ions, single ion transport by **4e** was also attempted under the same conditions. Neither was transported at all by 48 h. These results indicate that diamide **4e** transports Cu(II) ion with high selectivity.

The transport ability of **4e** was compared with the abilities of *N*,*N*′-di-8-quinolylglutaramide (**2**) and triamide **3** (R=Me), which are effective and selective Cu(II) carriers.[6,9] Figure 1 shows the time-dependence of Cu(II) transport by **2**,**3**, and **4e**. The Cu(II) transport rate of **4e** is faster than that of **2**. In the first stage of transport, **4e** transports Cu(II) faster than **3**. These results show that the part of the structure of triamide **3** encircled by dotted lines is sufficient for effective Cu(II) ion transport. In Fig. 1, two curves for carrier **4e**, that correspond to the increasing amount of Cu(II) in the receiving phase and the decreasing amont in the source phase, seem to be almost symmetrical along the line

Table 1. Amount of Cu(II) Transported through $CHCl_3$ Phase after 24 h[a)]

Carrier		Cu(II) transported into the receiving phase/%	Cu(II) remaining in the source phase/%
2		38[b)]	61[b)]
3	(R=Me)	68[c)]	28[c)]
4a	(R=H)	25	46
4b	(R=Me)	84	14
4c	(R=*i*-Pr)	65	34
4d	(R=*i*-Bu)	61	37
4e	(R=Bz)	82	12
4f	(R=Ph)	37	53
5		0	100

a) Initial transport conditions (25 °C); (Source phase) 10 mmol dm^{-3} Cu(OAc)$_2$, pH 6.2, 15 ml/(Liquid membrane) 0.3 mmol of carrier in 30 ml of chloroform/(Receiving phase) 0.05 mol dm^{-3} sulfuric acid 15 ml. b) Ref. 6. c) Ref. 9.

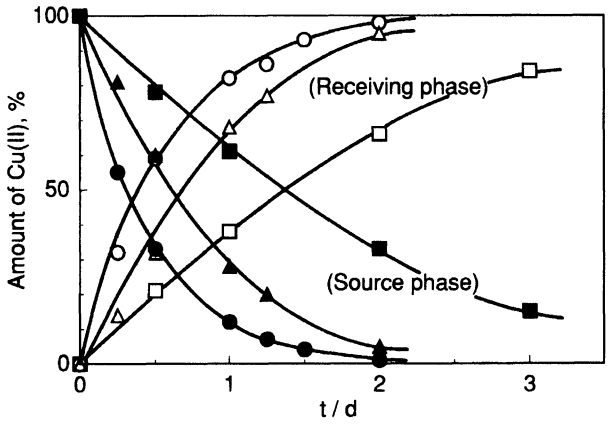


Fig. 1. Time dependence of Cu(II) transport through a $CHCl_3$ liquid membrane: For transport conditions, see Table 1. Receiving phase, **2**, -□-; **3** (R=Me), -△-; **4e**, -○-; Source phase, **2**, -■-; **3** (R=Me), -▲-; **4e**, -●-.

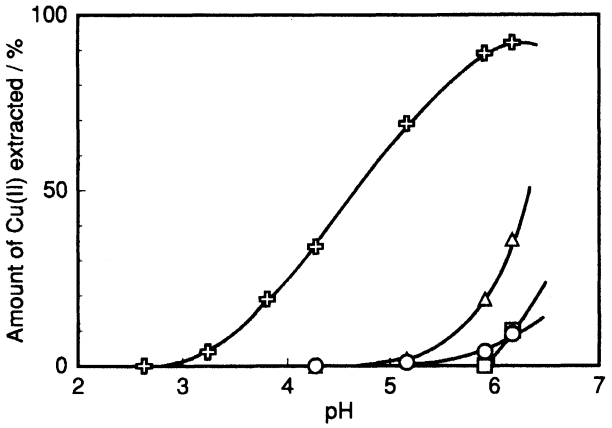


Fig. 2. pH-dependence on Cu(II) extraction with carriers. **1** (R=R′=*n*−Bu), -✣-; **2**, -□-; **3** (R=Me), -△-; **4e**, -○-.

of nearly 50% Cu(II), as with carriers **2** and **3**. This finding means that the rates of uptake of Cu(II) and its release by **4e** are almost the same; that is, Cu(II) taken into the chloroform phase could easily be released into the receiving phase.

This conclusion was supported by the results of extraction experiments. Figure 2 shows the pH dependence of the amount of Cu(II) (%) extracted by carriers. The extraction ability of carrier **4e** is inferior to that of **1** (R=R′=*n*−Bu), which is a good Cu(II) extractant, as already mentioned. In the acidic pH range (<6), carrier **4e** extracted no Cu(II) ion, as with carrier **2**. This result means that a Cu(II) complex of **4e** could release Cu(II) ions easily even under the weak acidic conditions of the receiving phase. This tendency is different from that of **1**. As mentioned before,[5)] the carriers must satisfy two requirements: One is rapid extraction of the metal ion and the other is its rapid release. Malonamide **1** has good Cu(II) extraction ability (Fig. 2). However, the rate of release of Cu(II) ion is slow because of the stability of the Cu(II) complex. Hence, the transport ability of malonamide **1** is low. With **4e**, the uptake of the ion and its release seem to be balanced, although extractability of **4e** is lower than that of **1** even at nearly neutral pH. Consequently, diamide **4e** is superior to **1** as a carrier.

Next, the effect of the α-substituent of the parent amino acids on Cu(II) transport ability was investigated. Table 1 shows the amounts of Cu(II) transported after 24 h by carriers, that differ in their substituent (R). Carrier **4a**, derived from glycine, gave poor results. As the uptake of Cu(II) by the carrier proceeded, a Cu(II) complex of **4a** appeared at the interface between the source and the organic phases because of the low solubility of the complex in the organic phase. Consequently, transport efficiency was lowered. The alanine derivative **4b** showed the best results among the carriers synthesized. The transport abilities of the carriers with bulky substituents (**4c**, **d**, and **f**) were inferior to the ability of **4b**. However, as already mentioned, carrier **4e**, which has also a bulky benzyl group as its α-substituent, had the transport ability as good as that of **4b**. Therefore, it is difficult to explain differences in Cu(II) transport abilities of carriers **4a**—**f** by the steric effects of the substituent alone. By inspection of a molecular

model (Corey–Pauling–Koltun) for the Cu(II) complex of **4e**, it was found that the phenyl ring and Cu metal can come close enough to interact by so-called π-metal interaction[10] if the formation of a 1 : 1 complex is postulated as shown in Fig. 3. The contribution of π-metal interactions in the formation of stable metal complexes has been mentioned in our earlier study of malonamide derivatives.[5] In that study, one reason for the high Cu(II)-extraction ability of malonamide derivatives **1** with a benzyl or *p*-methylbenzyl group was suggested to be the stabilization by π-metal interactions of the metal complex. Therefore, in the Cu(II) complex of **4e**, the phenyl ring of the carrier **4e** might help to stabilize the complex via π-metal interactions. On the other hand, carrier **4f**, which has also a phenyl ring, could not take on this conformation in its Cu(II) complex and stabilization effects could not be expected. Hence the transport ability of **4f** was predicted to be lower than that of **4e** because of the negative steric effect of the phenyl group.

Figure 4 shows changes in the UV-visible spectrum of **4e** in chloroform by complexation with Cu(II) ions. A 1 : 1 complex of **4e** with Cu(II) was obtained from

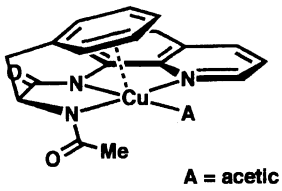


Fig. 3. Possible structure of the Cu(II) complex of **4e**.

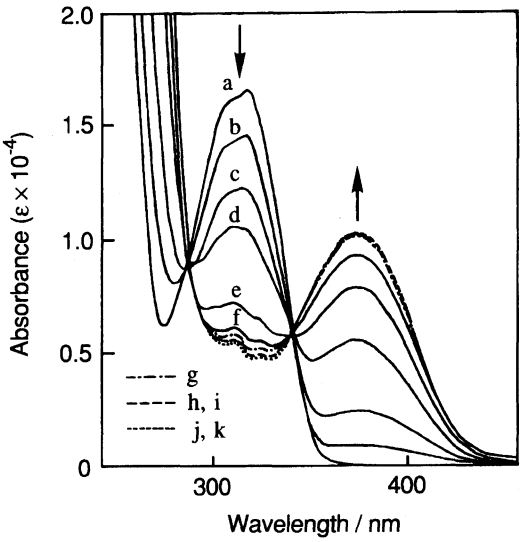


Fig. 4. Changes in the absorption spectra of **4e** (2.5×10^{-4} mol dm^{-3}) in $CHCl_3$ by complexation with Cu(II). a, **4e**; b, Cu(II)/**4e**=0.1; c, Cu(II)/**4e**=0.25; d, Cu(II)/**4e**=0.5; e, Cu(II)/**4e**=0.75; f, Cu(II)/**4e**=0.9; g, Cu(II)/**4e**=1.0; h, Cu(II)/**4e**=1.25; i, Cu(II)/**4e**=1.5; j, Cu(II)/**4e**=1.75; k, Cu(II)/**4e**=2.0. The values of Cu(II)/**4e** indicate molar ratios of metal/carrier.

the reaction of **4e** with powdered copper(II) acetate in chloroform. And this complex was recrystallized from benzene–cyclohexane. This 1 : 1 complex has the same absorption spectrum in chloroform as that in the range over the ratio of metal/ligand=1 in Fig. 4. Therefore, **4e** presumably forms a 1 : 1 complex with Cu(II) in chloroform. Although the mode of the coordination is unknown, a 4-coordinate structure of the complex with one molecule of acetic acid as a ligand can be postulated from these results.

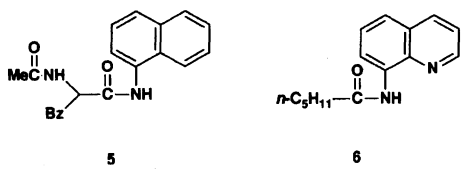
The structural requirement of diamides **4** for effective uptake of Cu(II) ions was investigated. Cu(II)-transport experiments with carrier **5**, which has a naphthyl group instead of a quinolyl group, were carried out. Carrier **5** was found to transport no Cu(II) ion at all by 24 h. *N*-quinolyl amide **6** cannot transport Cu(II) ions under the same conditions (Chart 2).[8] Hence, in these diamide compounds **4a**—**f** derived from α-amino acids, the acetamido group at the α-position, the 8-quinolylcarbamoyl group, and the proper arrangement of these two amide moieties seem to be indispensable for Cu(II) ion uptake. In other words, the size of the cavity formed by the pseudocyclic structure of **4** and the relative positions of three donor nitrogen atoms in **4** are suitable for the selective and efficient incorporation of Cu(II) ions.

In conclusion, the diamide compounds **4** were effective for selective transport of Cu(II) through liquid membranes. Of these compounds, the alanine and phenylalanine derivatives **4b** and **4e**, had the greatest Cu(II) transport ability. These compounds might be used as carriers for Cu(II) separation.

Experimental

General. Melting points were determined on a Mettler FP62 melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ with a Bruker MSL-300 spectrometer. Proton chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as the internal standard. The positions of the proton on the quinolyl group are shown as Q-H^n. IR spectra (KBr disk) were recorded on a JASCO A-3 spectrophotometer. UV-visible spectra were obtained in chloroform on a Hitachi 330 spectrophotometer. Analytical TLC was performed on Merck aluminum plate coated with silica gel 60 F_{254}. Wakogel C-300 (silica gel, 200—300 mesh) was used for column chromatography. Elemental analyses were done with a Perkin–Elmer 2400 CHN elemental analyzer.

N-Acetyl-DL-valine and *N*-acetyl-DL-leucine were purchased from Tokyo Kasei Co., Ltd. and *N*-acetylglycine was purchased from Wako Pure Chemical Ind., Ltd. Other *N*-acetyl amino acids were prepared as described in the



5 6

Chart 2.

literature.[11] Dry tetrahydrofuran (THF) was stored over 4-Å molecular sieves. Other reagents and solvents of high-purity grade were obtained from commercial suppliers and were used without further purification.

8-(*N*-Acetylglycylamino)quinoline (4a). To a solution of *N*-acetylglycine (1.85 g, 15.8 mmol) and *N*-methylmorphorine (1.60 g, 15.8 mmol) in dry THF (20 ml), pivaroyl chloride (1.90 g, 15.8 mmol) was added dropwise at temperatures between −10 and −15 °C under nitrogen atmosphere with stirring. The resulting solution was stirred for 1 h at 0 to −5 °C. To this solution was added dropwise a solution of 8-aminoquinoline (2.28 g, 15.8 mmol) and *N*-methylmorphorine (1.60 g, 15.8 mmol) in THF (5 ml) at 0 to −5 °C. The reaction mixture was stirred overnight at room temperature. The mixture was diluted with chloroform (200 ml), washed with water, 5% aqueous $NaHCO_3$, water, and brine, in this order, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was column-chromatographed on silica gel, with hexane–ethyl acetate (3:2) used for elution. The separated diamine **4a** was recrystallized from hexane–ethyl acetate to afford colorless fine needles (1.95 g, 51%): Mp 160—160.5 °C; ^{1}H NMR δ=2.14 (3H, s, CH_3), 4.30 (2H, d, J=5.0 Hz, CH_2), 6.35 (1H, bt, J=5.0 Hz, N<u>H</u>CH_2), 7.47 (1H, dd, J=4.2, 8.3 Hz, Q-H^3), 7.55 (2H, d, J=4.5 Hz, Q-H^5, H^7), 8.18 (1H, dd, J=1.6, 8.2 Hz, Q-H^4), 8.70 (1H, t, J=4.5 Hz, Q-H^6), 8.77 (1H, dd, J=1.6, 4.2 Hz, Q-H^2), 10.07 (1H, s, NHQ); IR (KBr) 3300 (NH), 1670, 1650 (C=O) cm^{-1}. Found: C, 72.04; H, 5.66; N, 12.70%. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.61%.

8-(*N*-Acetyl-DL-alanylamino)quinoline (4b). Diamide **4b** was prepared from 1.01 g (10 mmol) of *N*-acetyl-DL-alanine by the same procedure as described for **4a**. Recrystallization from hexane–ethyl acetate afforded pure **4b** as colorless plates (0.69 g, 27%): Mp 152—153 °C; ^{1}H NMR δ=1.57 (3H, d, J=7.0 Hz, CH_3), 2.09 (3H, s, CH_3CO), 4.87 (1H, q, J=7.05 Hz, CH), 6.48 (1H, d, J=6.5 Hz, N<u>H</u>CH), 7.46 (1H, dd, J=4.2, 8.3 Hz, Q-H^3), 7.53 (2H, d, J=4.4 Hz, Q-H^5, H^7), 8.15 (1H, dd, J=1.6, 8.3 Hz, Q-H^4), 8.70 (1H, t, J=4.4 Hz, Q-H^6), 8.82 (1H, dd, J=1.6, 4.2 Hz, Q-H^2), 10.17 (1H, s, NH-Q); IR (KBr) 3270 (NH), 1650 (C=O) cm^{-1}. Found: C, 65.52; H, 5.83; N, 16.47%. Calcd for $C_{14}H_{15}N_3O_2$: C, 65.35; H, 5.88; N, 16.33%.

8-(*N*-Acetyl-DL-valylamino)quinoline (4c). Diamide **4c** was prepared from 1.59 g (10 mmol) of *N*-acetyl-DL-valine by the procedure described for **4a**. Recrystallization from hexane–ethyl acetate afforded pure **4c** as colorless fine powder (1.09 g, 38%): Mp 163—164.5 °C; ^{1}H NMR δ=1.06 (3H, d, J=6.8 Hz, CH_3), 1.07 (3H, d, J=6.8 Hz, CH_3), 2.28 (1H, m, $(CH_3)_2$C<u>H</u>), 4.70 (1H, dd, J=5.9, 9.0 Hz, NHC<u>H</u>), 6.36 (1H, d, J=8.5 Hz, N<u>H</u>CH), 7.47 (1H, dd, J=4.2, 8.3 Hz, Q-H^3), 7.54 (2H, d, J=4.4 Hz, Q-H^5, H^7), 8.17 (1H, dd, J=1.7, 8.3 Hz, Q-H^4), 8.72 (1H, t, J=4.5 Hz, Q-H^6), 8.82 (1H, dd, J=1.7, 4.2 Hz, Q-H^2); IR (KBr) 3330, 3240 (NH), 1690, 1650 (C=O) cm^{-1}. Found: C, 67.25; H, 6.76 N, 14.53%. Calcd for $C_{16}H_{19}N_3O_2$: C, 67.34; H, 6.71; N, 14.73%.

8-(*N*-Acetyl-DL-leucylamino)quinoline (4d). Diamide **4d** was prepared from 1.00 g (5.78 mmol) of *N*-acetyl-DL-leucine by the procedure described for **4a**. Recrystallization from hexane–ethyl acetate afforded pure **4d** as colorless plates (1.34 g, 78%): Mp 129—130 °C; ^{1}H NMR δ=1.02 (6H, d, J=5.7 Hz, $(CH_3)_2$C), 1.66—1.89 (3H, m, CH_2), 2.09 (3H, s, CH_3CO), 4.85 (1H, dt, J=5.8, 8.0 Hz, C<u>H</u>NH), 6.14 (1H, d, J=8.0 Hz, N<u>H</u>CH), 7.46 (1H, dd, J=4.2, 8.3 Hz, Q-H^3), 7.53 (2H, d, J=4.6 Hz, Q-H^5, H^7), 8.16 (1H, dd, J=1.5, 8.3 Hz, Q-H^4), 8.71 (1H, t, J=4.6 Hz, Q-H^6), 8.84 (1H, dd, J=1.5, 4.2 Hz, Q-H^2), IR (KBr) 3290 (NH), 1690, 1650 (C=O) cm^{-1}. Found: C, 68.33; H, 7.11; N, 14.14%. Calcd for $C_{17}H_{21}N_3O_2$: C, 68.20; H, 7.07; N, 14.04%.

8-(*N*-Acetyl-DL-phenylalanylamino)quinoline (4e). Diamide **4e** was prepared from 3.00 g (14.5 mmol) of *N*-acetyl-DL-phenylalanine by the same procedure as described for **4a**. Recrystallization from hexane–ethyl acetate afforded pure **4e** as colorless fine plates (1.81 g, 37%): Mp 160—162 °C; ^{1}H NMR δ=2.06 (3H, s, CH_3), 5.07 (1H, q, J=6.8, 14.3 Hz, CH), 6.38 (1H, d, J=1.7 Hz, N<u>H</u>CH), 7.16—7.28 (5H, m, phenyl), 7.31 (1H, dd, J=4.2, 8.3 Hz, Q-H^3), 7.51—7.53 (2H, m, Q-H^5, H^7), 8.13 (1H, dd, J=1.6, 8.3 Hz, Q-H^4), 8.68 (1H, t, J=4.2 Hz, Q-H^6), 8.71 (1H, dd, J=1.6, 4.2 Hz, Q-H^2), 9.98 (1H, s, NH-Q); IR (KBr) 3330 (NH), 1650 (C=O) cm^{-1}. Found: C, 72.04; H, 5.66; N, 12.70%. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.6%.

8-(*N*-Acetyl-DL-phenylglycylamino)quinoline (4f). Diamide **4f** was prepared from 1.20 g (7.25 mmol) of *N*-acetyl-DL-phenylglycine by the procedure described for **4a**. Recrystallization from hexane–ethyl acetate afforded pure **4f** as colorless needles (0.28 g, 12%): Mp 252 °C (decomp); ^{1}H NMR δ=2.11 (3H, s, CH_3), 5.83 (1H, d, J=7.0 Hz, CH), 6.95 (1H, d, J=7.0 Hz, N<u>H</u>CH), 7.29—7.42 (3H, m, phenyl), 7.44 (1H, dd, J=4.3, 8.2 Hz, Q-H^3), 7.53 (2H, d, J=5.3 Hz, Q-H^5, H^7), 7.53—7.57 (2H, m, phenyl), 8.14 (1H, dd, J=1.4, 8.6 Hz, Q-H^4), 8.69 (1H, dd, J=3.8, 5.1 Hz, Q-H^6), 8.76 (1H, dd, J=1.4, 4.3 Hz, Q-H^2), 10.11 (1H, s, NHQ); IR (KBr) 3350 (NH), 1690, 1650 (C=O) cm^{-1}. Found: C, 71.07; H, 5.23; N, 13.05%. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.45; H, 5.37; N, 13.16%.

1-(*N*-Acetyl-DL-phenylalanylamino)naphthalene (5). Diamide **5** was prepared from 1.50 g (7.25 mmol) of *N*-acetyl-DL-phenylalanine and 1.04 g (7.25 mmol) of 1-naphthylamine by the procedure described for **4a**. Recrystallization from hexane–ethyl acetate afforded pure **5** as colorless fine powder (0.94 g, 39%): Mp 211—212 °C; ^{1}H NMR δ=2.03 (3H, s, CH_3), 3.21 (2H, d, J=7.4 Hz, CH_2), 5.05 (1H, q, J=7.5 Hz, CH), 5.99 (1H, d, J=8.1 Hz, N<u>H</u>CH), 7.26—7.32 (5H, m, phenyl), 7.37—7.48 (4H, m, naphthyl), 7.65 (1H, d, J=8.3 Hz, naphthyl), 7.79—7.84 (2H, m, naphthyl), 8.47 (1H, s, NH-naphthyl); IR (KBr) 3280 (NH), 1650 (C=O) cm^{-1}. Found: C, 75.76; H, 6.08; N, 8.21%. Calcd for $C_{21}H_{20}N_2O_2$: C, 75.88; H, 6.07; N, 8.43%.

Preparation of the Cu(II) Complex of 8-(*N*-Acetyl-DL-phenylalanylamino)quinoline (4e). Copper (II) acetate monohydrate (0.30 g, 1.50 mmol) was added to a solution of 8-(*N*-acetyl-DL-phenylalanylamino)quinoline (**4e**) (0.25 g, 0.75 mmol) in $CHCl_3$ (10 ml). The resulting mixture was stirred at room temperature for 48 h. Then the mixture was filtered through celite and the filtrate was concentrated under reduced pressure. The deep-green solid obtained was recrystallized by diffusion of cyclohexane into benzene solution to give 0.25 g (yield 58%) of the Cu(II) complex of **4e**: Mp 213 °C (decomp); UV ($CHCl_3$) λ_{max}=372 nm, ε=4240; IR (KBr) 3280 (NH), 1650 (C=O) cm^{-1}. Found: C, 48.45; H, 3.86; N, 7.22%. Calcd for $C_{23}H_{22}N_3O_4Cu$: C, 48.10; H, 3.86; N, 7.32%.

Transport Experiments. The transport experiments were done with a U-type glass cell across a chloroform liquid membrane from a buffered aqueous source phase (pH 6.2) containing one or several kinds of metal ions [Cu(II), Ni(II), Co(II), and Zn(II)] into a receiving phase containing 0.05 M (M=mol dm^{-3}) sulfuric acid. The cell was kept at 25 °C and each phase was mechanically agitated at 200 rpm.[6] Other transport conditions are described in Table 1. At regular intervals, the aqueous phase was sampled. The sample was suitably diluted, and the concentration of metal ion was assayed with an atomic absorption spectrometer (Shimadzu A-340). Standard deviation of the results were ±5% or better.

Extraction Experiments. Solvent extraction of Cu(II) ion by the compounds **1**—**4** was done as follows. An aqueous solution (5 ml, pH 6.2) containing 1 mM of Cu(II) was shaken vigorously for 24 h at 25 °C with 5 ml of chloroform containing the compound at the concentration of 1 mM. After separation of the aqueous phase, the concentration of Cu(II) remaining in it was found by atomic absorption spectroscopy.

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