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Highly Selective Solvent Extraction of Copper(II) from Transition Metal Ions with Dibutyl N,N'-Bis(8-quinolyl)malonamide

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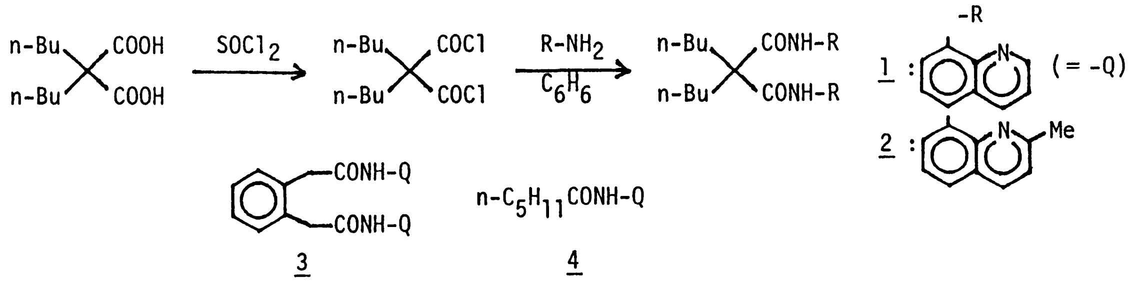
Dibutyl-N,N'-bis(8-quinolyl)malonamide can extract only Cu(II) with excellent selectivity among Cu(II), Ni(II), Co(II), and Zn(II) both in the competitive and single metal ion-extraction. It forms 1 : 1 complex with Cu(II) ion accompanied with the release of two protons from the amide groups.

Much attention has been paied to copper(II)-ionophores for extraction and transport in view of not only the metal ion-separation and detection but also biological interest.[1)] Recently, cyclic and noncyclic carriers, which contain plural nitrogen atoms as ligating ones, have been reported for Cu(II)-solvent extraction and transport through liquid membranes.[2-5)] In this paper we wish to report on a novel type of malonamide derivatives which can exhibit the specific Cu(II)-extraction.

The reaction processes for the synthesis of diamides 1 and 2 are shown below. In a similar manner, 3 and 4 were prepared for comparison in the extraction of heavy metal ions.[6)]



In the solvent extraction of transition metal ions with these compounds, aqueous solution(50 cm^3, pH 6.2) containing 10^{-2} mM(= $mmol/dm^3$) of each of metal ions(Cu(II), Ni(II), Co(II), and Zn(II)) was stirred vigorously for 24 h at 25 °C by a magnetic stirrer with 50 cm^3 of $CHCl_3$ phase containing either 1 mM of diamide compounds(1 - 3) or 2 mM of 4. After careful phase separation, the upper aqueous solution was analysed for the metal ion(s) remaining unextracted by atomic absorption spectroscopic method. The boundary layer kept completely clear before and after extraction in all cases, and thus it was observed that neither aqueous nor organic phase became foamy or turbid. It was also confirmed that the concentration of metal ion(s) extracted into $CHCl_3$ phase, which was determined after release of metal ion into 5 cm^3 of 0.05 M H_2SO_4 aqueous solution from $CHCl_3$, agreed very closely with that analysed previously. Table 1 shows the results of metal ion-extraction. One mM of malonamide drivative(1) extracted only Cu(II) ion from the aqueous solution containing 10^{-2} mM of each of four transition metal ions. Remarkable effect of the substituent at the 2-position of quinolyl group was observed in the comparison of 1 and 2. When inspecting the CPK model building, the 2-methyl groups on the quinoline rings of 2 could interfere with square-planar geometry composed of four nitrogen atoms which is favorable for Cu(II) ion. On the other hand, diamide (3) and monoamide(4) could not extract any metal ion used at all. From these results it is presumed that the appropriate configuration of two amide groups is one of the important factors for exhibiting Cu(II)-selective extraction.

Table 1. Solvent Extraction of Metal Ions(10^{-2} mM of Each) from the Aqueous Solution(50 cm^3, pH 6.2) into Chloroform Layer(50 cm^3) with Amide Extractants

Extractant	Concn. of amides in chloroform	Extraction percentage/%			
		Cu(II)	Ni(II)	Co(II)	Zn(II)
1	1 mM	96	0	0	0
2	1 mM	6	0	0	0
3	1 mM	0	0	0	0
4	2 mM	0	0	0	0

Table 2 shows the metal ion-extractability with 1 from the aqueous solution with the various concentration of metal ions. It was found that 1 could extract Cu(II) ion specifically under the conditions listed in Table 2. It is worth noting that only Cu(II) ion was extracted with 1(1 mM in $CHCl_3$) from a mixture of 10^{-2} mM Cu(II) and 1 mM of each of Ni(II), Co(II), and Zn(II) ions(Run 4). Even in the extraction from the aqueous solution containing single ion species(Ni(II), Co(II), or Zn(II)), neither of them could be extracted at all(Runs 5 - 7).

Figure 1 shows the spectroscopic change in the absorption spectrum of 1 in $CHCl_3$ by complexation with Cu(II) ion. Plots of the absorbance of the solution against the composition in Fig. 2 indicated that the composition of the complex of 1 with Cu(II) ion was 1 : 1. Besides, the 1 : 1 complex of deprotonated 1 with Cu(II)(line i in Fig. 1) was obtained from the reaction of 1 with powdered Cu(II) acetate in $CHCl_3$ and recrystallized from benzene-cyclohexane mixture.7) This complex shows the same absorption spectrum in $CHCl_3$ as that in the range over the ratio of metal/ligand = 1 in Fig. 2.

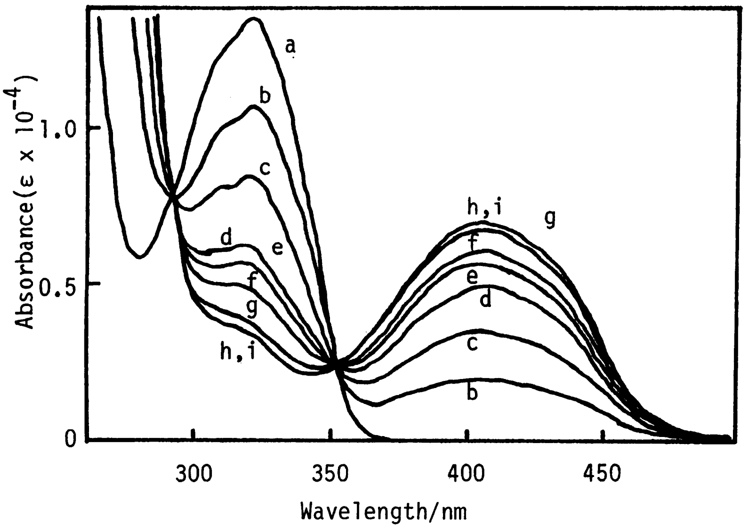
Furthermore, the influence of pH in aqueous solution on the solvent-extraction with 1 was investigated. As shown in Fig. 3, 1 could extract Cu(II) from the solution at pH above 3. Under the similar conditions, the relationship between the logarithm of distribution ratio(log D) and pH in the aqueous phase was investigated. The slope of 1.9 obtained from the plots of log D vs. pH suggested that two protons of 1 are participated in the extraction.8)

Table 2. Solvent Extraction of Metal Ions with 1(1 mM) from Aqueous Solution(50 cm^3, pH 6.2) into Chloroform Layer(50 cm^3)[a]

Run	Divalent metal ion(s) in the aqueous phase	Concentration of metal ion(s)	Extraction percentage/%			
			Cu(II)	Ni(II)	Co(II)	Zn(II)
1	Cu, Ni, Co, Zn	10 mM of each	10[b]	0	0	0
2	Cu, Ni, Co, Zn	0.1 mM of each	98	0	0	0
3	Cu, Ni, Co, Zn	0.01 mM of each	96	0	0	0
4	Cu, Ni, Co, Zn	0.01 mM of Cu and 1 mM of each of Ni, Co, and Zn	100	0	0	0
5	Ni	0.01 mM	-	0	-	-
6	Co	0.01 mM	-	-	0	-
7	Zn	0.01 mM	-	-	-	0

a) Other conditions are the same as those in Table 1.

b) The value means that 1 completely extracts equimolar Cu(II) as 1 : 1 complex.



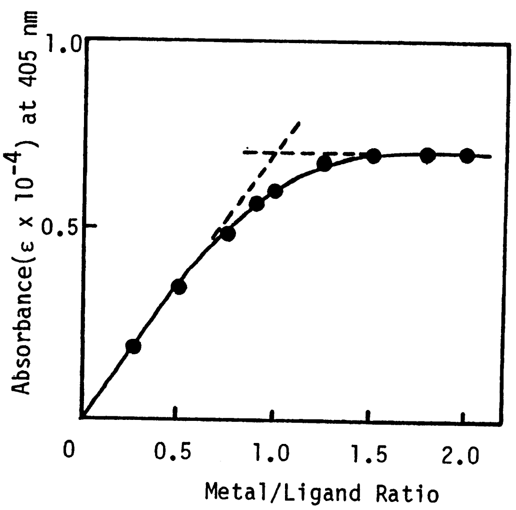
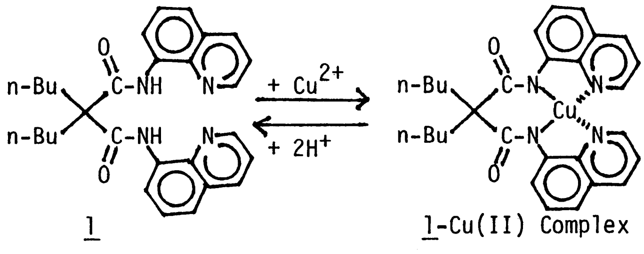


Fig. 1. Change in the absorption spectra of 1 in $CHCl_3$ by complexation with Cu(II); a: 1, b: Cu(II)/1=0.25, c: Cu(II)/1=0.5, d: Cu(II)/1=0.75, e: Cu(II)/1=0.9, f: Cu(II)/1 =1.0, g: Cu(II)/1=1.25, h: Cu(II)/1 ≥ 1.5, i: 1-Cu(II) complex(1 : 1). The values of Cu(II)/1 indicate molar ratio of metal ion/ligand.

Fig. 2. Plots of the absorbance of 1 in $CHCl_3$ vs. Cu(II)/1 ratio; wavelength used, 405 nm.

From these results, it may be concluded that 1 presumably forms 1 : 1 complex with Cu(II) accompanied with the release of two amide-protons in the solvent-extraction system as depicted in the following scheme.



Thus, it has been found that malonamide 1 can extract Cu(II) with excellent selectivity. In addition, it should be noted that 1 can extract only Cu(II) ion even in the nearly neutral range of pH. It is, therefore, expected that it could be a candidate for a selective Cu(II)-carrier in the proton-driven transport through liquid membranes under the mild conditions.

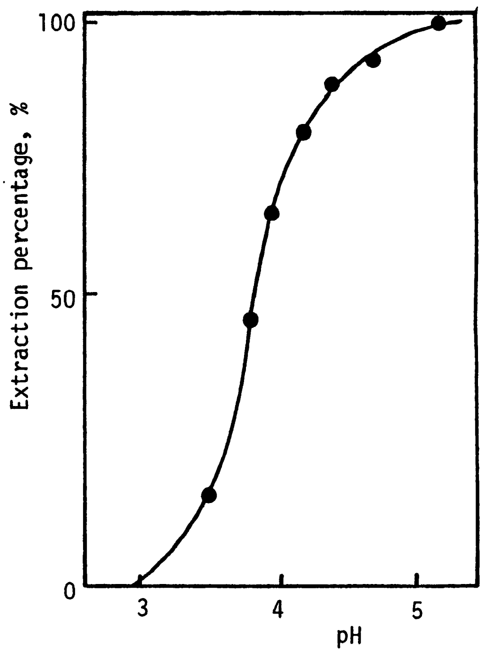


Fig. 3. Effect of pH on extraction of Cu(II)(5.0 mM) with 5.0 mM of 1 into chloroform. Shaking time, 52h; temp, 15 °C.

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6) 1 : Yield 81%, Mp 141.5-142.5 °C, Precise Mass, Found 468.251, Calcd 468.252; 2 : Y. 65%, Mp 96.5 - 98.5 °C, Precise Mass, F. 496.280, C. 496.284; 3 : Y. 91%, Mp 184-185 °C, Precise Mass, F. 446.171, C. 446.174; 4 : Y: 76%, liquid, Precise Mass, F. 242.144, C. 242.142.

7) Elemental analysis, Found: C,65.53; H,5.97; N,10.55%. Calcd for $C_{29}H_{30}O_2N_4Cu$: C,65.70; H,5.70; N 10.57%.

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