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A Novel Cu(II) Carrier with High Efficiency and Selectivity for Proton-driven Uphill Transport through Liquid Membranes

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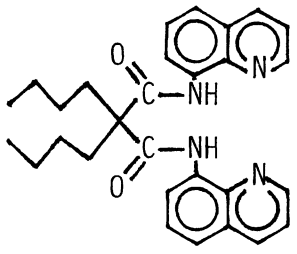
N-(8-Quinolyl)-N'-(2-pyridylmethyl)malonamide derivative, which has been synthesized as carrier for transition metal ions, can transport Cu(II) with high selectivity against its concentration gradient through liquid membranes.

Selective transport of transition metal ions through liquid membranes has become increasingly important and noteworthy as well as that of alkali and alkaline earth metal ions. So far, a number of carriers for heavy metal ions have been reported, but there were a few which can transport them not only selectively but also efficiently.[1-4]

Recently, we have found that N,N'-di(8-quinolyl)malonamide derivative(1) can selectively extract Cu(II) among transition metal ions from the aqueous phase buffered at pH 6.2 into the chloroform phase although the Cu(II) transport ability of 1 is low.[5] On the contrary, N,N'-di(8-quinolyl)glutaramide(2) has been reported to transport Cu(II) with high selectivity but hardly to extract any metal ion.[6]



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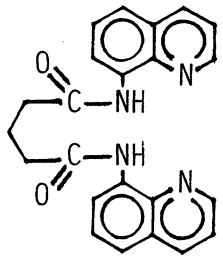

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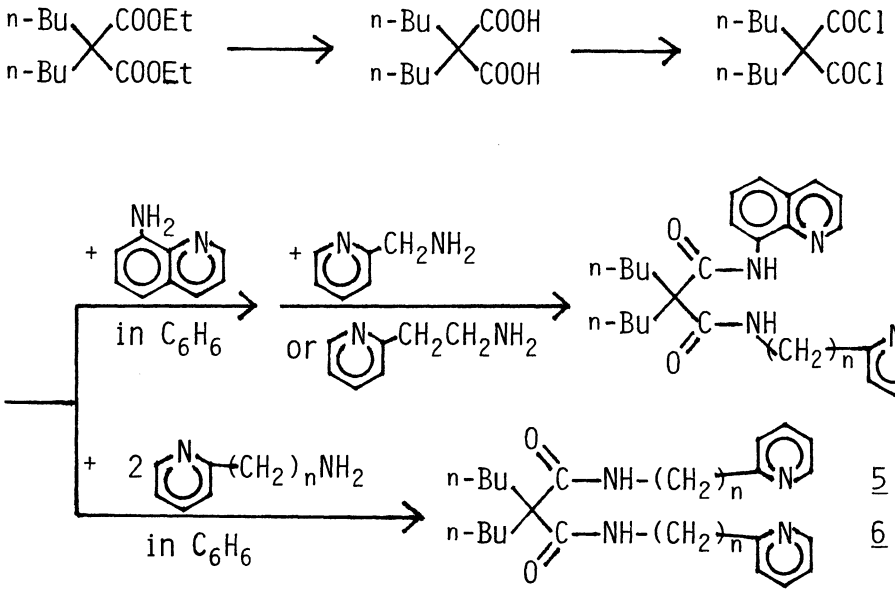
To design a better Cu(II) carrier, we have elaborated that it is essentially important to realize the following concepts: 1) carriers should have such structures as that of malonamide 1, which could extract ions rapidly and selectively; 2) on the contrary, they should have comparably small stability of the complex like glutaramide 2 so that they could release ions from the liquid membrane phase into the aqueous phase easily and rapidly.

In this study we report a novel carrier which can exhibit highly selective and efficient Cu(II)-transport through liquid membranes. Based on the hypothesis that the potential carrier could be designed by weakening the coordination ability of nitrogen atoms on malonamide skeleton, compounds 3 and 4, which substitute 2-pyridylmethyl and 2-pyridyl-2-ethyl groups respectively for the 8-quinolyl group of 1, have been synthesized stepwise starting from malonic ethyl ester.[7] For comparison, 2,2-dibutyl-N,N'-di(2-pyridylmethyl)malonamide(5) and 2,2-dibutyl-N,N'-di(2-pyridyl-2-ethyl)malonamide(6) were also prepared.[8]



The transport experiments were carried out by using a U-type glass cell across the cloroform liquid membrane from the buffered aqueous source phase (pH 6.2) containing one or several kinds of metal ions of Cu(II), Ni(II), Co(II), and Zn(II) to the receiving phase containing 0.05 M(= mol dm^{-3}) sulfuric acid. The cell was kept at 25.0 ± 0.2 °C and each phase was mechanically agitated at 200 rpm.[9]

Table 1 shows the amounts of Cu(II) transported after 2 days, along with the transport conditions. These results show that 3 has the greatest ability of Cu(II) transport among these carriers. In the carriers, 1, 3 - 6, the Cu(II) transport ability largely depends on the kinds of N-substituent, that is, the order of the ability decreases as follows: 3 > 5 > 4 >> 1 = 6. Noticeably 3 can efficiently transport Cu(II) against its concentration gradient.

Figure 1 shows the pH-dependence of the Cu(II) amount(%) extracted by these carriers. Carrier 3, of which the extraction ability is considerably inferior to that of 1, can exhibit greater transport ability than the latter. This fact implies that the balance between uptake and release of Cu(II) is of substantial importance. Figure 2 shows the time-dependence of

the Cu(II) transport by 3, 4, and 5. Under the same conditions, 3 apparently transports Cu(II) at an appreciable rate compared with 4 and 5. In these cases, the curves of decreasing amount with time in the source phase are almost symmetrical about the lines corresponding to the increasing amount with time in the receiving phase where proton plays an important role to the enforced ion release due to prptonation of the nitrogen atoms.[4,5] It is presumed that the releasing rate is very rapid and the rate-determining step is the uptake process.

The single ion-transport of Ni(II), Co(II), and Zn(II) by 3 was attempted under the same conditions, but none of them could be transported

Table 1. Amount of Cu(II) transported through $CHCl_3$ phase after 2 days[a)]

Carrier	Cu(II) transported in the receiving phase, %	Cu(II) remaining in the source phase, %
1	0.2	94
2	63	35
3	93	4
4	15	85
5	56	43
6	0	100

a) Initial transport conditions(25 °C): (Source phase) 10 mM $Cu(OAc)_2$, pH 6.2, 15 ml / (Liquid membrane) 0.3 mmol of carrier in 30 ml of chloroform / (Receiving phase) 0.05 M sulfuric acid 15 ml.

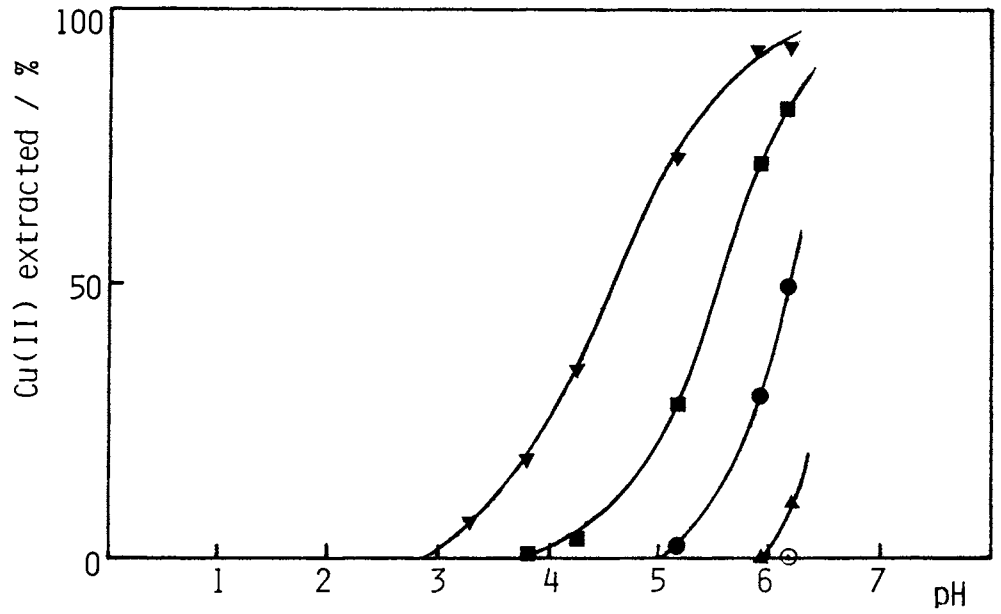


Fig. 1. pH-dependence on Cu(II) extraction with carriers, 1 :—▼—, 2 :—▲—, 3 :—■—, 5 :—●—, and 6 :—○—. Shaking time 1 day, 25 °C.

at all even after 2 days. In the competitive transport of transition metal ions by 3, only Cu(II) could be transported with high selectivity and efficiency against its concentration gradient through liquid membranes.

Thus, it is elucidated that asymmetric malonamide derivative having two different N-substituents (8-quinolyl and 2-pyridylmethyl groups) would be an excellent carrier for ion transport and could be a potential candidate for the practical use of Cu(II)-separation.

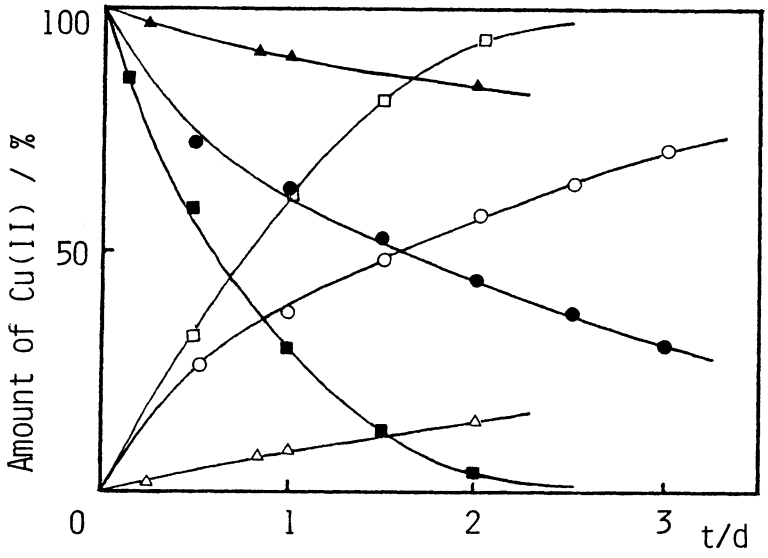


Fig. 2. Plots of amount of Cu(II) transported vs. time. (Receiving phase) 3: —□—, 4: —△— ,and 5: —○—, (Source phase) 3: —■—, 4: —▲— ,and 5: —●— . Initial transport conditions : see in Table 1.

References

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6) K. Hiratani and K. Taguchi, Chem. Lett., 1990, 725.
7) 3: Yield 27%, colorless oil, Precise Mass, Found 432.254, Calcd 432.252 for $C_{26}H_{32}N_4O_2$; 4: Yield 29%, colorless oil, Precise Mass, Found 446.264, Calcd 446.268 for $C_{27}H_{34}N_4O_2$.
8) 5: Yield 75%, colorless oil, Precise Mass, Found 396.253, Calcd 396.252 for $C_{23}H_{32}N_4O_2$; 6: Yield 71%, colorless oil, Precise Mass, Found 424.282, Calcd 424.284 for $C_{25}H_{36}N_4O_2$.
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