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A New Class of Metal-Dependent Selective Anion Carrier. PH-Controlled Up-Hill Transport of SCN^- by Formation of Transition-Metal Complex

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In the presence of appropriate pH-gradient across an organic liquid membrane, selective up-hill transport of SCN^- through the membrane was efficiently mediated by 6,6'-bis(4-hexylbenzoylamino)-2,2'-bipyridine upon complex formation with Cu^{II}, in which the metal center served as an SCN^--selective binding site while pH-switched dissociation-association of the amide proton(s) of the ligand regulated uptake and release of SCN^-.

Physiological importance of selective ion carriers through membranes has been well recognized. Though there are wide variety of naturally-occurring and synthetic cation carriers,1) relatively few types of anion carrier have been known. Among them, macrocyclic amines have been used most frequently as a synthetic anion carrier.2) We wish to report here a new class of selective anion carrier, which, upon complexation with transition-metal, can transport anions as a counter or coordinated anion to the metal center. Binding of anion to the metal center was regulated by dissociation-association of amide proton(s) of the ligand moiety instead of a common anion-exchange mechanism, and the metal-complexed carrier mediated efficient and selective up-hill transport of SCN^- by coupling with the pH-gradient across an organic liquid membrane.

In our earlier paper,3) acidity of amide protons of 6,6'-bis(benzoylamino)-2,2'-bipyridine($babpH_2$) was shown to be greatly increased by formation of an amide-*O*-coordinated square-planar complex with Cu^{II}. Based on this result, we prepared more lipophilic derivative of $babpH_2$, h-$babpH_2$(LH_2) having 4-hexyl substituents, as an anion carrier.4) The carrier and its complex with $Cu(NO_3)_2$, $Cu(LH_2)(H_2O)_2(NO_3)_2$, dissolved

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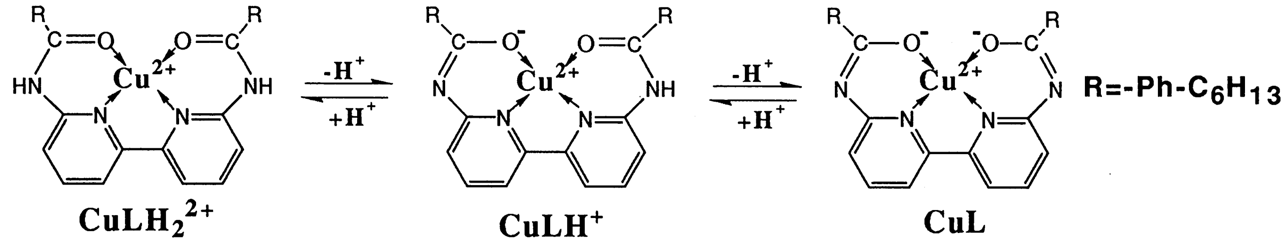


Scheme 1.

readily into organic solvents like CH_2Cl_2 and $CHCl_3$, but were insoluble to water at all. Addition of small amounts of methanolic NaOH solution to this non-deprotonated complex in CH_2Cl_2 showed the clear two-step spectral change(Fig.1(A) and (B)), which was ascribed to the step-wise deprotonation of the complex(Scheme 1) through a mono-deprotonated complex, $CuLH^+$ ([NaOH]/[complex] molar ratio = 0-1, Fig. 1(A)), into a fully deprotonated complex, CuL ([NaOH]/[complex]=1-2, Fig. 1(B)). The results are essentially the same as those observed for the Cu^{II} complex of $babpH_2$.$^{3)}$

Electronic spectra of LH_2/CH_2Cl_2 solutions ($1.11x10^{-4}$ mol dm^{-3}) after vigorous mixing with same volume of aqueous $Cu(NO_3)_2$ ($1.11x10^{-3}$ mol dm^{-3}) /Kolthoff's buffer solutions (mixtures of 0.05 mol dm^{-3} sodium succinate and 0.05 mol dm^{-3} sodium tetraborate, pH 3-6) are shown in Fig.1(C). When pH of the aqueous solution was 6.0, LH_2 formed the deprotonated complex quantitatively. While, the spectra after contact with the pH 3.0 buffer solution indicated the presence of uncomplexed LH_2, $CuLH_2{}^{2+}$, $CuLH^+$, and CuL in the organic layer. Use of $CuLH_2{}^{2+}$ in the organic layer instead of adding LH_2 and $Cu(NO_3)_2$ separately gave essentially the same

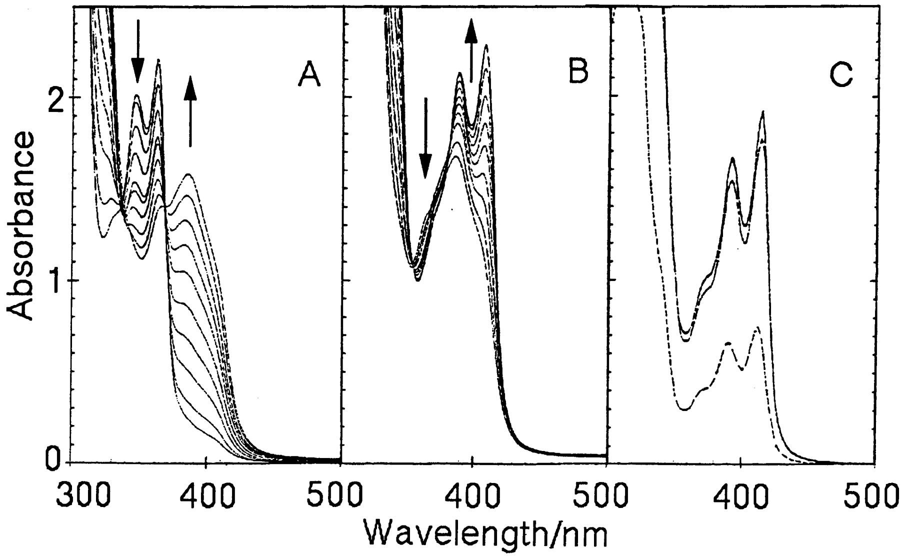


Fig. 1. Spectral change of $Cu(LH_2)(H_2O)_2(NO_3)_2$ ($6.67x10^{-5}$ mol dm^{-3}) in CH_2Cl_2 upon addition of small amounts of methanolic NaOH at 20 ℃, where [NaOH]/[complex] were (A) 0-1 and (B) 1-2. (C) Electronic spectra of the LH_2 ($1.11x10^{-4}$ mol dm^{-3})/CH_2Cl_2 solutions after contact with same volume of the aqueous $Cu(NO_3)_2$ ($1.11x10^{-3}$ mol dm^{-3}) solutions whose pH were adjusted to 3.0(---), 4.0(- -), 5.0(——), and 6.0(identical to that of pH 5.0).

results. Thus, it was confirmed that LH_2 in CH_2Cl_2 formed the CuII complex by incorporation of Cu^{II} from the aqueous layer, and deprotonation of its amide units could be controlled by the pH of the aqueous layer.

Transport experiments were carried out at 20 ℃ using a three phase system,[5)] where two aqueous buffer solutions I (pH 3-5, 10 ml) and II (pH 6.0, 10 ml) containing same concentration of NaSCN(1.00×10^{-2} mol dm^{-3}) were separated by a $CuLH_2^{2+}/CH_2Cl_2$ layer (1.11×10^{-3} mol dm^{-3}, 30 ml) and the organic layer was magnetically stirred. When the pH of the layer I was 4.0 or 3.0 (Fig. 2), SCN^- was transported efficiently from I to II against concentration gradient, but only a slow transport was observed when the pH of the layer I was 5.0. Use of LH_2 in the organic and $Cu(NO_3)_2$ in the aqueous layers separately instead of $CuLH_2^{2+}$ in the organic layer gave essentially the same results. No transport of SCN^- was observed in the absence of any one of $Cu(NO_3)_2$, LH_2, or pH difference between two aqueous layers. Therefore, the SCN^--carrier through the organic layer was not LH_2 nor Cu^{II} alone but the non-deprotonated or mono-deprotonated complex of LH_2, and SCN^- was transported as the counter or coordinated anion of these complexes.

To test anion-selectivity of this new class of carrier, we carried out the transport experiments in the presence of other anions (Table 1).

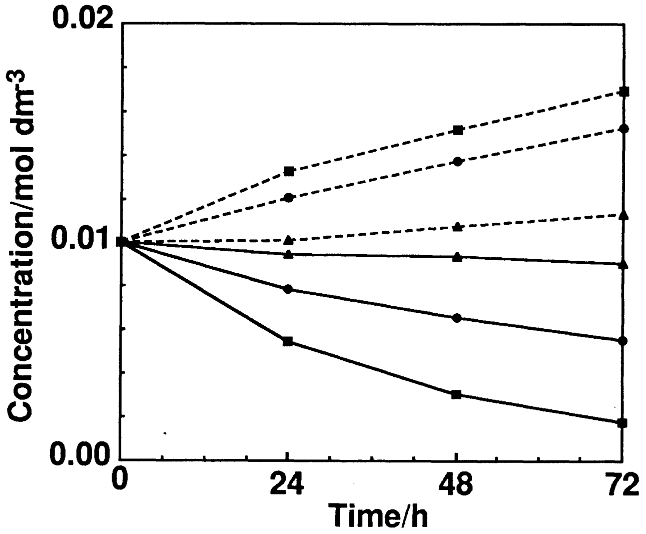


Fig. 2. Concentrations of SCN^- in the aqueous layers I (——) and II(---) during the up-hill transport across the CH_2Cl_2 layer mediated by $CuLH_2^{2+}$ (1.11×10^{-4} mol dm^{-3}) at 20 ℃. Initial concentrations of SCN^- in both aqueous layers were 1×10^{-2} mol dm^{-3}. The layer II was set at pH 6.0, while pH of the layer I was 3.0(■), 4.0(●), or 5.0 (▲).

Table 1. Anion transport from the aqueous layers I(pH 4.0, 10 ml) to II (pH 6.0, 10 ml) across the CH_2Cl_2 layer containing $CuLH_2^{2+}$ (1.11×10^{-4} mol dm^{-3}, 30 ml) at 20 ℃ a)

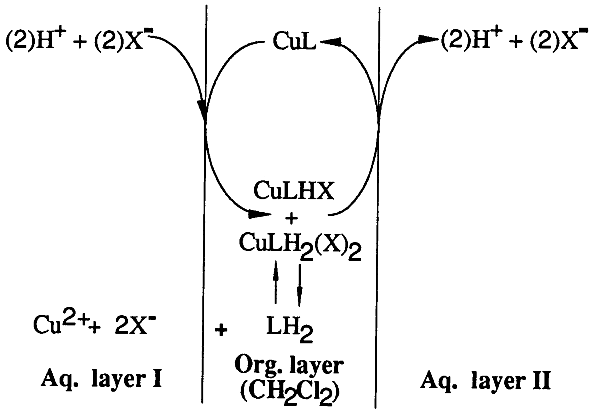
#	Anion	Concentration after 72 h /10^{-2} mol dm^{-3}	
		layer I (pH 4)	layer II (pH 6)
1	SCN^-	0.55	1.53
2	Br^-	1.00	1.00
3	p-tol	0.77	1.21
4b)	p-tol	0.88	1.03
	+		
	SCN^-	0.50	1.45

a) Initial anion concentrations in the aqueous layers I and II were 1.00×10^{-2} mol dm^{-3}.

b) The aqueous layers contained both p-tol and SCN^-.

It should be noted that no transport of the buffer anions (succinate and borate) was observed during the transport experiments. The carrier was ineffective for the transport of Br^-, but lipophilic anion, p-toluenesulfonate (p-tol), was transported through the liquid membrane. However, SCN^- having higher coordination ability was selectively transported when p-tol and SCN^- were present simultaneously in the aqueous layers(#4).[6) The results indicated that the coordination ability rather than the lipophilicity of anion is the important factor for determining the anion selectivity of the carrier.

Thus, the newly synthesized carrier, LH_2, is shown to serve as an efficient carrier for the up-hill transport of SCN^- when Cu^{II} is present in the system as a cofactor. Proposed mechanism of the transport is shown in Scheme 2. In the activated form of the carrier upon complexation, metal center is the binding site of anion, while the ligand moiety serves as the regulation site for uptake and release of anion by pH-switched dissociation-association of the amide, mediating the efficient up-hill transport.



Scheme 2.

References

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2) J.-M.Lehn, *Angew.Chem., Int.Ed.Engl.,* **27**, 90(1988).
3) M.Yamada, K.Araki, and S.Shiraishi, *Bull.Chem.Soc.Jpn.,* **60**,3149(1987); **61**, 2767(1988).
4) The carrier, h-babpH_2, was synthesized from 6,6'-diamino-2,2'-bipyridine and 4-hexylbenzoylchloride as white plates, yield 81%, mp 211-213 ℃, and the complex $Cu(LH_2)(NO_3)_2(H_2O)_2$ from LH_2 and $Cu(NO_3)_2$ as blue flakes; yield 50%. Anion concentrations were determined by following methods; SCN^- by colorimetric method according to the standard procedure, Br^- by an anion-selective electrode (Br-125, Toa Electronics Ltd., Tokyo), and p-tol by absorbance at 261 nm.
5) N.Kishii, K.Araki, and S.Shiraishi, *J.Chem.Soc., Dalton Trans.,***1985**, 373.
6) The d-d band of $Cu(LH_2)(NO_3)_2(H_2O)_2$ in CH_3OH shifted from 641.5 to 647.5 nm upon addition of NH_4SCN, but no shift was observed in the presence of p-tol supporting the selective coordination of SCN^- to the complex.

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