Letters to the Editor

Preparation of Tetraaza Macrocycles with Fluorescent Groups and Their Quenching Interactions with Copper(II) and Silver(I) Ions

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Macrocyclic polyamines form stable complexes with various metal ions. Since these ligands possess reactive secondary amines, their derivatives with appended side chains have also been prepared and their complexing abilities toward metal ions have been investigated.¹ Recently, macrocyclic ligands with chromophores have been synthesized and found to be useful for the determination of metal ions.² However, there are few reports on macrocyclic polyamines with fluorescent groups and on their applications as fluorescent reagents.³

In this paper, we describe the preparation and characterization of two novel type macrocyclic polyamines incorporating fluorescent groups: one of them contains the fluorescent groups attached directly to the nitrogen atoms of cyclam and the other contains groups attached on the terminal branches of 3-aminopropyl groups. The latter has been found to be superior to the former as a fluorescent reagent for the determination of copper(II) ion.

Experimental*Synthesis of fluorescent reagents*

Cyclam and its pendant-armed macrocycle, 1,4,8,11-tetrakis(3-aminopropyl)-1,4,8,11-tetraazacyclotetradecane, were prepared according to the methods described in the literature.^{4,5} Their dansyl, 5-dimethylaminonaphthalene-1-sulfonyl, derivatives were prepared as follows. To an aqueous solution (20 cm³) of cyclic amine (0.01 mol) and sodium hydroxide (1.6 g, 0.04 mol) was added an ether solution of dansyl chloride (16.2 g, 0.06 mol). The mixed solution was stirred vigorously for 24 h at room temperature. The resulting yellow precipitates were recrystallized from a mixture of chloroform and methanol (1:2). The products were obtained in about 50% yields, and were identified from spectroscopic methods and elemental analyses. The dansyl derivatives of cyclam and its pendant-armed macrocycle were found to involve two and four dansyl groups per each molecule, respectively, as shown in

Fig. 1 Chemical structure of macrocyclic polyamines with fluorescent groups.

Fig. 1. Hereafter, these are abbreviated as [14]aneN₄-dsl₂ and [14]aneN₄-(tnNH-dsl)₄.

Results and Discussion

Fluorescent intensities of dansyl derivatives are found to decrease in the presence of a copper(II) ion, which means that the copper(II) ion acts as a quencher.

As for [14]aneN₄-dsl₂, it was required to heat a sample solution to obtain a constant fluorescent intensity, because its reaction with a copper(II) ion is very slow at room temperature. The procedure for the determination of the copper(II) ion is as follows: a DMF solution containing a certain amount of copper(II) ion was added into a DMF solution of [14]aneN₄-dsl₂ (2.0×10⁻⁴ M, 5.0 cm³) (1 M=1 mol dm⁻³); the mixed solution was heated at 60 °C for 60 min, cooled to room temperature, diluted to 10 cm³ with DMF, and then the fluorescent intensity of the resulting DMF solution was measured against the reagent blank at 522 nm under the excitation at 345 nm. Under the above-mentioned conditions, a straight calibration curve was obtained in the range of 1×10⁻⁵ to 2×10⁻⁴ M of copper(II).

On the other hand, with [14]aneN₄-(tnNH-dsl)₄, its quenching reaction with copper(II) ion was found to be faster than that observed for [14]aneN₄-dsl₂, and a constant fluorescent intensity was obtained immediately after the addition of the copper(II) ion even at room temperature. The procedure for the determination of

copper(II) ion is almost the same as that conducted with [14]aneN₄-dsl₂, but heating of the sample solution is not needed and the concentration of the DMF solution of [14]aneN₄-(tnNH-dsl)₄ is 4.0×10^{-5} M. Under the above-mentioned conditions, a straight calibration curve was obtained in the range of 5×10^{-7} to 1×10^{-5} M of copper(II). The lower limit for the determination of copper(II) with [14]aneN₄-(tnNH-dsl)₄ is much better than that with [14]aneN₄-dsl₂. This may occur because the inherent fluorescent intensity of the former macrocycle is higher than that of the latter one.

Table 1 lists interferences of diverse metal ions for the determination of copper(II) ion with both the present fluorescent tetraaza macrocycles. These were determined from comparison between fluorescent intensities of the sample solutions of copper(II) in the presence and absence of an equimolar amount of a foreign metal ion. The conditions for the measurements are represented in Table 1. In the case of [14]aneN₄-dsl₂, magnesium(II), calcium(II) and nickel(II) ions interfered slightly with the determination of copper(II) ion, and chromium(III), manganese(II), cobalt(II), zinc(II), cadmium(II), platinum(II), mercury(II) and lead(II) ions interfered moderately. However, iron(III) and silver(I) ions interfered seriously with the determination of copper(II). Indeed, a remarkable interference from silver(I) ion was observed. This means that the fluorescent reagent, [14]aneN₄-dsl₂ can interact much more strongly with silver(I) ion than with copper(II) ion. In fact, the quenching reaction with silver(I) ion has been found to proceed faster than that with copper(II) ion even at room temperature. Therefore, this macrocycle was examined as a fluorescent reagent for the determination of silver(I) ion. Without heating treatment, a straight calibration curve for the silver(I) ion was obtained in the concentration range from 4×10^{-6} to 8×10^{-5} M. In addition, diverse metal ions including copper(II) have been found to interfere very slightly with the determination of silver(I) ion.

On the other hand, in the case of [14]aneN₄-

(tnNH-dsl)₄, extents of interferences of the foreign metal ions for the determination of copper(II) are considerably less than those observed with [14]aneN₄-dsl₂. Their trend is also different: magnesium(II), calcium(II), iron(III) and lead(II) ions did not interfere, whereas cobalt(II) and nickel(II) ions interfered seriously. Other metal ions such as zinc(II), silver(I), cadmium(II) and mercury(II) interfered slightly. Especially, it should be noticed that the extents of interferences from iron(III) and silver(I) ions are much smaller than those observed with [14]aneN₄-dsl₂.

The significant difference between the two macrocycles for interactions with various metal ions may arise from their structures: in the [14]aneN₄-dsl₂, the fluorescent groups are directly bonded to the donor nitrogen atoms, whereas in the [14]aneN₄-(tnNH-dsl)₄, they are spaced with the 3-aminopropyl groups. Moreover, these secondary amino groups should interact weakly with transition metal ions such as cobalt(II), nickel(II), and copper(II). It has been reported that incorporation of such additional donor functions might facilitate the complexation between metal ions and the macrocycle, itself, because metal ions are held near to the donor atoms and hence their "effective" concentration is greater than their bulk concentration.

In conclusion, two types of the tetraaza macrocycles having a fluorescent group, namely, [14]aneN₄-dsl₂ and [14]aneN₄-(tnNH-dsl)₄, have been synthesized. Their capabilities as a fluorescent reagent for the determination of copper(II) ion have been examined. The former has been found to interact strongly with the silver(I) ion rather than copper(II) ion as a fluorescent reagent. The latter macrocycle has been found to interact most strongly with copper(II) ion among the metal ions investigated. From these results, it can be concluded that the tetraaza macrocycle, [14]aneN₄-(tnNH-dsl)₄, may be applied to a fluorescent reagent for the determination of copper(II) ion.

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Table 1 Interferences of diverse metal ions for determination of copper(II)

Added ion	Error, %	
	[14]aneN ₄ -dsl ₂	[14]aneN ₄ -(tnNH-dsl) ₄
None	0	0
Mg(II)	8.7	0.3
Ca(II)	0.3	0
Fe(III)	-118.0	0
Co(II)	-27.0	-36.7
Ni(II)	6.6	-37.6
Zn(II)	-45.2	-4.8
Ag(I)	-140.6	-12.6
Cd(II)	-61.2	-13.6
Hg(II)	-59.1	-22.4
Pb(II)	-41.0	0
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[L]/M	1×10^{-4}	1×10^{-5}
[Metal]/M	1×10^{-4}	6×10^{-6}