December, 1990] © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 3443—3449 (1990) 3443

Preparation of 14-, 18-, and 22-Membered Tetraaza Macrocycles and Their Complexing Ability for Copper(II) and Nickel(II) Ions

Manabu Fujiwara, Hisanobu Wakita, Takayuki Matsushita,*,† and Toshiyuki Shono††
Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814-01
†Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520-21
††Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565

(Received June 8, 1990)

14-,18-, and 22-membered tetraaza macrocycles have been prepared by the reaction of acetylacetone with ethylenediamine, 1,4-butanediamine, or 1,6-hexanediamine, respectively. Their copper(II) and nickel(II) complexes were characterized by electronic and infrared spectroscopies. The 14-membered macrocycle forms a mononuclear copper(II) complex with a planar structure, whereas the 18-membered macrocycle forms a mononuclear copper(II) complex with a pseudo-tetrahedral structure, and the 22-membered macrocycle forms di- and trinuclear copper(II) complexes. The complexation and extraction abilities of these macrocycles toward copper(II) and nickel(II) ions are discussed.

Tetraaza macrocycles and their metal complexes have been studied extensively in connection with their resemblance to naturally occuring porphyrins.[1] Of them, saturated macrocycles with various numbers of their ring members have been synthesized consistently; these compounds have produced much interesting information concerning both the stabilities and structures of their metal complexes.[2] On the other hand, for unsaturated macrocycles, 14-membered Schiff base compounds have received much attention, with few studies on 15- and 16-membered compounds.[3] Recently, Lippard et al.[4] have prepared mononuclear copper(II) complexes with 14-, 16-, 18-, and 20-membered tetraaza macrocycles derived from two aminotropone imine moieties connected with two polymethylene groups. They have reported that the conformation around the central metal ion in the copper(II) complexes is distorted from planar toward tetrahedral with an increase in the methylene chain lengths.

In this paper, the preparation of 14-, 18-, and 22-membered tetraaza macrocycles derived from acetylacetone and linear diamines, and the characterization of their copper(II) and nickel(II) complexes is described. In addition, the complexation and extraction abilities of these macrocycles toward copper(II) and nickel(II) are also described.

Experimental

Materials. All reagents were of reagent grade. *N,N*-dimethylformamide (DMF) was distilled over CaH_2 under reduced pressure before use. Other solvents were purified in the usual manner.

Measurements. UV and visible absorption spectra were recorded on a Hitachi 340 recording spectrophotometer. IR spectra were recorded on a Hitachi 215 grating spectrophotometer. ^1H and ^{13}C NMR spectra were taken with a JEOL FX-90 spectrometer, using $CDCl_3$ as a solvent and TMS as the internal standard. The ^{13}C relaxation time measurements were carried out by applying an inversion recovery method in a $CDCl_3$ solution. Mass spectra were measured at 70 eV with a Hitachi RMU-6E instrument. Magnetic susceptibilities were measured by a Gouy method at room temperature.

Preparation of Tetraaza Macrocycles. The synthetic scheme is shown in Fig. 1. The 14-membered macrocycle, N_4[14], was prepared according to a method described in the literature.[6]

The 18-membered macrocycle, N_4[18], (Fig. 2) was prepared in the following manner. To a benzene solution (500 cm^3) of *N,N'*-bis(1-methyl-3-thioxo-1-butenyl)ethylenediamine[6] (25.0 g, 0.097 mol) was added 1,4-butanediamine (17.2 g, 0.195 mol). The mixture was refluxed for 5 days. The solution was evaporated under reduced pressure and the residue recrystallized from ethanol twice. Pale-yellow needles were obtained in 20% yield.

Found: C, 71.14; H, 10.67; N, 18.26%. Calcd for $C_{18}H_{32}N_4$: C, 70.99; H, 10.61; N, 18.40%. IR (in KBr disk): 3400, 2910,

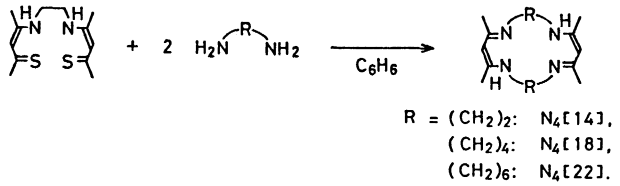
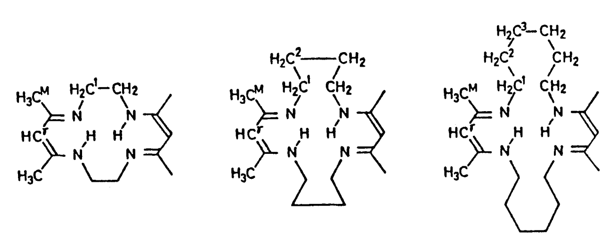


Fig. 1. Synthetic scheme of tetraaza macrocycles.



N$_4$[14] N$_4$[18] N$_4$[22]

Fig. 2. Chemical structure of tetraaza macrocycles.

---

†† Present address: Department of Applied Chemistry, Osaka Institute of Technology, Omiya, Asahi-ku, Osaka 535.

1620, 1555, 1440, 1330, 1260, 1025, and 735 cm^{-1}. MS; M$^+$ 304.

The 22-membered macrocycle, N$_4$[22], (Fig. 2) was prepared in a similar manner to that described for N$_4$[18], using 1,6-hexanediamine in place of 1,4-butanediamine. The mixed solution was refluxed for 8 days. The resulting product was recrystallized twice from a small amount of ethanol. White needles were obtained in 25% yield.

Found: C, 73.13; H, 11.28; N, 15.64%. Calcd for $C_{22}H_{40}N_4$: C, 73.26; H, 11.20; N, 15.54%. IR (in KBr disk): 3400, 2925, 1615, 1550, 1440, 1340, 1260, 1020, and 735 cm^{-1}. MS: M$^+$ 360.

Preparation of Metal(II) Complexes with Tetraaza Macrocycles. A copper(II) complex with a 14-membered macrocycle, Cu(N$_4$[14](2−)), was prepared by a method described in the literature.[7] A copper(II) complex with an 18-membered macrocycle, Cu(N$_4$[18](2−)), was prepared by the following method. To an ethanol solution (100 cm^3) of N$_4$[18] (3.0 g, 0.01 mol) was added copper(II) acetate monohydrate (1.5 g, 7.5 mmol). The solution was refluxed for 30 min under a nitrogen atmosphere, and then cooled on an ice-water bath. The resulting precipitate was collected on a glass filter, washed with a cold ethanol, and dried in vacuo. No further purification was made. Red-brown crystals were obtained in 65% yield.

Found: C, 58.82; H, 8.34; N, 15.17%. Calcd for $CuC_{18}H_{30}N_4$: C, 59.05; H, 8.28; N, 15.31%. IR (in KBr disk): 2920, 1570, 1490, 1420, 1395, 1020, 995, and 720 cm^{-1}. Magnetic moment: μ_{eff}=1.85 BM.

A trinuclear complex with a 22-membered macrocycle, Cu$_3$(N$_4$[22](2−))·(OCOCH$_3$)$_4$, was prepared as follows. To an ethanol solution (200 cm^3) of N$_4$[22] (3.0 g, 8.3 mmol) was added copper(II) acetate monohydrate (3.0 g, 15 mmol). The solution was refluxed for 2 h under a nitrogen atmosphere, and then cooled to room temperature. The resulting precipitate was collected on a glass filter, washed with ethanol several times, and then dried in vacuo. No further purification was made. Green solid matter was obtained in 70% yield. This copper(II) complex is slightly soluble in chloroform but insoluble in methanol, ethanol, and DMF.

Found: C, 45,69; H, 6.54; N, 7.15%. Calcd for $Cu_3C_{30}H_{50}N_4O_8$: C, 45.87; H, 6.42; N, 7.13%. IR (in KBr disk): 2925, 1565, 1540, 1465, 1420, 1345, 1020, 750, and 680 cm^{-1}. Magnetic moment: μ_{eff}=1.71 BM.

The nickel(II) complex with the 14-membered macrocycle, Ni(N$_4$[14](2−)), was prepared by the method described in the literature.[7]

The isolation of other complexes such as Ni(N$_4$[18](2−), Ni(N$_4$[22](2−)), and binuclear Cu$_2$(N$_4$[22](2−))·(OCOCH$_3$)$_2$ was examined but could not be achieved by the method described above.

Results and Discussion

Electronic Spectra. Figure 3 shows the electronic spectra of the copper(II) complexes with the 14-, 18-, and 22-membered macrocycles in DMF. A DMF solution of a copper(II) complex with a 22-membered macrocycle was prepared by mixing a DMF solution of N$_4$[22] and a DMF solution of copper(II) acetate monohydrate. It was found that a binuclear complex, [Cu$_2$(N$_4$[22](2−))]$^{2+}$, was formed in this solution. This was confirmed spectrophotometrically using a mole-ratio method. Details will be described in a later section.

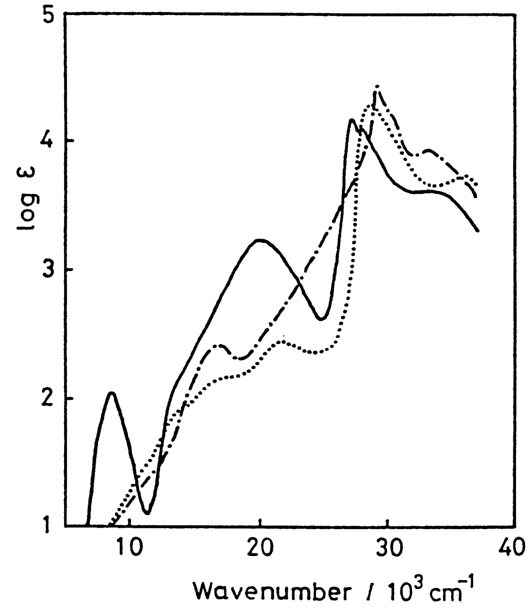


Fig. 3. Electronic spectra of copper(II) complexes in DMF.
(— - —): Cu(N$_4$[14](2−)), (——): Cu(N$_4$[18](2−)), (······): [Cu$_2$(N$_4$[22](2−))]$^{2+}$.

The electronic spectral feature of three complexes is different, particularly in the visible and near-infrared regions. The spectrum of Cu(N$_4$[14](2−)) shows an absorption band with moderate intensity at 16700 cm^{-1}, which was assigned to ligand-field transitions; no absorption band exists in the near-infrared region. This suggests that this complex may adopt a planar structure around the central copper(II) ion.[8] The spectrum of Cu(N$_4$[18](2−)) has the characteristic absorption bands at 8570, 12800, and 20200 cm^{-1}. The highest-energy band is so intense that it can be assigned to charge-transfer transitions, while the other two bands are moderately intense and can be assigned to ligand-field transitions. These results indicate that the conformation around the copper(II) ion may distort from planar to pseudo-tetrahedral.[8] The spectrum of [Cu$_2$(N$_4$[22](2−))]$^{2+}$ has three absorption bands at 13400, 17600, and 21600 cm^{-1} in the visible region, which can be assigned to ligand-field transitions; no absorption band exists in the near-infrared region. In this binuclear copper(II) complex, each copper(II) ion may be coordinated with a N$_2$O$_2$ donor set of two nitrogen atoms of N$_4$[22] and two oxygen atoms of acetate groups. Although structural information concerning this binuclear copper(II) complex is still insufficient, the copper(II) ions may be bridged with two acetate groups, as in a binuclear copper(II) complex with a 22-membered homologue of Curtis-type tetraaza macrocycles.[9]

Table 1. Absorption Maxima of Macrocycles and Their Copper(II) and Nickel(II) Complexes in DMF

Compound	$\frac{\lambda_{max}}{nm}$ (log ε)			
$N_4[14]$	305(4.53)			
$Cu(N_4[14](2-))$	299(3.92),	340(4.40),	598(2.41)	
$Ni(N_4[14](2-))$	286(4.26),	396(3.91),	562(2.32)	
$N_4[18]$	308(4.47)			
$Cu(N_4[18](2-))$	354(4.18),	368(4.25),	494(3.23),	1167(2.05)
$Ni(N_4[18](2-))$	328	520		
$N_4[22]$	315(4.47)			
$[Cu_2(N_4[22](2-))]^{2+}$	297(3.72),	349(4.31),	462(2.46),	568^{sh}(2.18)
$Cu_3(N_4[22](2-))(OAc)_4$[a)]	316,	372,	474^{sh},	604
$Ni\text{-}N_4[22]$[b)]	324^{sh},	460		

a) Measured by reflectance spectroscopy. b) The molar ratio between metal(II) ion and macrocycle is uncertain.

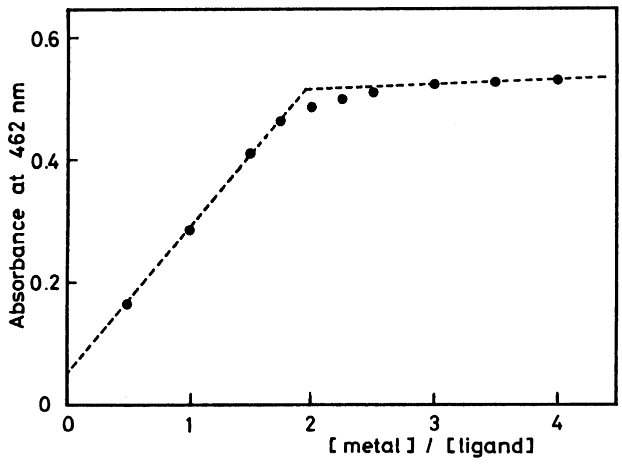


Fig. 4. Absorbance at 462 nm in the various ratios of concentration of copper(II) ion to that of $N_4[22]$ in DMF.
$[N_4[22]]=2.00\times10^{-3}$ mol dm^{-3}; cell length: 1 cm.

The electronic spectroscopic data for the three macrocycles and their copper(II) and nickel(II) complexes are summarized in Table 1. The absorption spectra of the macrocycles and their copper(II) and nickel(II) complexes were measured in DMF, except for $Cu_3(N_4[22](2-))\cdot(OCOCH_3)_4$, the spectrum of which was measured in solid reflectance. All of the electronic spectra of the macrocycles are similar to each other and have an intense absorption band (log ε = ca. 4.5) centered around 32300 cm^{-1}, which can be assigned to the π—π^* transition.

The spectrum of $Ni(N_4[14](2-))$ has an absorption band at 17800 cm^{-1} in the visible region, which can be assigned to ligand-field transitions; this complex may adopt a planar configuration.[8)] Since other nickel(II) complexes with $N_4[18]$ and $N_4[22]$ could not be isolated, their absorption spectra were measured by mixing a DMF solution of each macrocycle and a DMF solution of nickel(II) acetate tetrahydrate under a nitrogen atmosphere. Thus, their molar extinction coefficients could not be determined. The spectrum of nickel(II) complex with $N_4[18]$ has two absorption bands at 19200 and 22300 cm^{-1}, and that of the nickel(II) complex with $N_4[22]$ has an absorption band at 21700 cm^{-1} in the visible region. The structural properties of these nickel(II) complexes can not be argued only from the spectroscopic data.

Determination of Molar Ratio of Copper(II) Ion to 22-Membered Macrocycle. A 22-membered macrocycle has such a large cavity that it might coordinate with two metal ions in one cyclic system. In fact, the absorption maximum of a mixed DMF solution of $N_4[22]$ and copper(II) ion was shifted from 564 to 462 nm upon increasing the molar ratio of copper(II) ion to $N_4[22]$. The absorption band at 462 nm should arise from the formation of binuclear complex, $[Cu_2(N_4[22](2-))]^{2+}$. This was confirmed spectrophotometrically by the mole-ratio method (Fig. 4). The absorbances at 462 nm increased with an increase in the molar ratio of copper(II) ion to $N_4[22]$ and was kept constant at a ratio of 2.0 and above. This result clearly indicates that one molecule of $N_4[22]$ can complex with two copper(II) ions in a DMF solution.

On the other hand, a green precipitate was obtained by allowing a mixed DMF solution of copper(II) ion and $N_4[22]$ to stand for several hours, or using a DMF solution of $N_4[22]$ containing excess amounts of copper(II) ion. This precipitate was identified to be a trinuclear complex with the formula $Cu_3(N_4[22](2-))\cdot(OCOCH_3)_4$ by elemental analysis. Figure 5 shows the reflectance spectrum of this complex; numeral data are included in Table 1. In the visible region, three absorption bands are observed at 15200, 16600, and 21100 cm^{-1}, which can be assigned to ligand-field transitions. The absorption bands at 15200 and 16600 cm^{-1} may be attributed to a copper(II) moiety coordinated by the O_4 donor set of two bridged acetate groups and two copper(II) moieties coordinated by the N_2O_2 donor set of two nitrogen atoms in the macrocy-

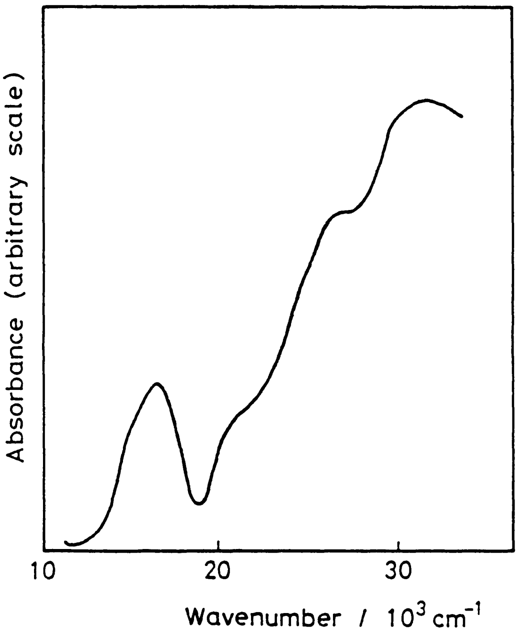


Fig. 5. A reflectance spectrum of trinuclear copper(II) complex with $N_4[22]$.

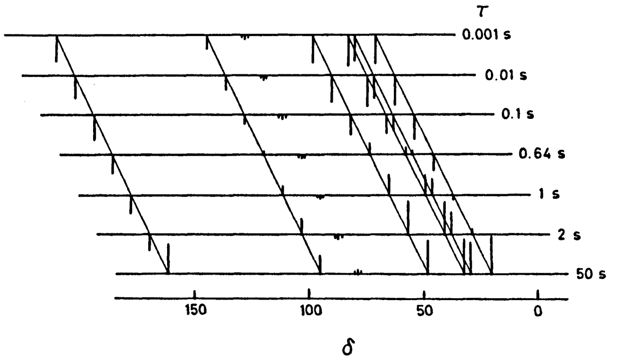


Fig. 6. Relaxation time measurements for ^{13}C atoms of $N_4[22]$ in $CDCl_3$.

cle and two oxygen atoms of the bridged acetate groups, respectively. Although the structural aspects of copper(II) complexes with $N_4[22]$ have not been clarified yet, the copper(II) ions in trinuclear copper(II) complex may be forced out of the cavity of $N_4[22]$ and linked by the acetate groups, since the cavity size of $N_4[22]$ might not be sufficiently large to hold all three copper(II) ions.

A slightly lower magnetic moment ($\mu_{eff}=1.71$ BM) of this trinuclear complex than those of Cu($N_4[18](2-)$) (1.85 BM) and Cu($N_4[14](2-)$) (1.78 BM) is consistent with the trinuclear structure bridged with acetate groups.

^{13}C Relaxation Time Measurement. Carbon-13 spin-lattice relaxation measurements[10)] were carried out in order to reveal the internal motion of the tetraaza macrocycles. A 90° rf pulse was 9.80 μs.

Table 2. ^1H and ^{13}C NMR Spectral Data and ^{13}C Relaxation Times (T_1) of Macrocyclic Ligands in $CDCl_3$ at 25 °C

Compound		^1H/ppm	^{13}C/ppm	T_1/s
$N_4[14]$	C^MH_3	1.80	19.6	4.22
	C^1H_2	3.44	46.8	0.98
	$C^\gamma H$	4.51	94.4	2.09
	C(=N)	—	160.8	(10.8)
$N_4[18]$	C^MH_3	1.88	19.4	2.73
	C^1H_2	3.31	46.7	0.79
	C^2H_2	1.79	29.5	0.93
	$C^\gamma H$	4.50	94.1	0.93
	C(=N)	—	160.6	(10.5)
$N_4[22]$	C^MH_3	1.87	20.0	2.50
	C^1H_2	3.22	47.5	0.59
	C^2H_2	1.67	29.1	0.73
	C^3H_2	1.56	31.8	0.59
	$C^\gamma H$	4.50	94.3	0.68
	C(=N)	—	161.4	(10.8)

Figure 6 shows the results obtained for $N_4[22]$. When the pulse interval, τ, was 0.001 s, all of the peaks were inverted. The time required for a recovery increased according to the order of the carbon atoms: $C^1 \simeq C^3 < C^\gamma < C^2 \ll C^M$. The T_1 value of the indivisual carbon atom can be obtained as the reciprocal slope of a straight line of $\log(I_\infty - I_\tau)$ vs. τ plot, where I_∞ is the equilibrium intensity of a resonance peak, and I_τ is the peak intensity at each τ value. The above plots for all of the ^{13}C resonance peaks of the tetraaza macrocycles gave good linear relations. The T_1 data, thus obtained, are listed in Table 2, together with ^1H and ^{13}C NMR spectral data for the macrocycles.

Because the molecular weight of $N_4[22]$ is the highest among them, $N_4[22]$ should exhibit a slow overall motional behavior of molecules in a solution, such as translation and rotation. Therefore, all of the T_1 values of the carbon atoms in $N_4[22]$ are smaller than those of the corresponding carbon atoms in $N_4[14]$ and $N_4[18]$. However, the internal motion of the $N_4[22]$ molecule differs from those of $N_4[14]$ and $N_4[18]$ molecules. It should be predictable that the deformation and distortion (or reorientation) of macrocycles take place more easily in the order $N_4[14] < N_4[18] < N_4[22]$. If the ratios of the T_1 values of methyl (C^M) and methylene (C^1, C^2, and C^3) carbons to that of methine (C^γ) carbon in a macrocycle are given, respectively, they may represent the degree of internal motility of each macrocyclic molecule. The ratios of $T_1(C^M)/T_1(C^\gamma)$ are 2.0, 2.6, and 3.7 for $N_4[14]$, $N_4[18]$, and $N_4[22]$, respectively. The ratios of $T_1(C^1)/T_1(C^\gamma)$ are 0.5, 0.7, 0.9 for $N_4[14]$, $N_4[18]$, and $N_4[22]$, respectively. These values increase with an increase in the size of the macrocycles. These results lead to the idea that the conformation changes of the macrocycles for coordination with a given metal(II) ion may occur easier in the order $N_4[14] < N_4[18] < N_4[22]$.

Complexation of Copper(II) and Nickel(II) with Macrocycles. The complexation rates of copper(II) and nickel(II) ions with the macrocycles were determined spectrophotometrically in a homogeneous DMF solution at 25 °C. A DMF solution of each macrocycle (8.0×10^{-5} mol dm^{-3}) and a DMF solution of equimolar amount of each metal ion were mixed under a nitrogen atmosphere. In the case of $N_4[22]$, a DMF solution of twice the molar amount of copper(II) ion (1.6×10^{-4} mol dm^{-3}) was used. Their absorption spectra were measured over the range 270—500 nm at regular time intervals. The results are shown in Fig. 7.

In a system of copper(II) ion with $N_4[14]$, the absorption spectrum remarkably changes within an initial 2 min, and then gradually for 20 min: the absorption peak due to $N_4[14]$ at 305 nm decreased in intensity and a new absorption band which appeared at 341 nm increased in intensity, having an isosbestic point at 322 nm (Fig. 7A). The spectral changes clearly indicate that the $Cu(N_4[14](2-))$ complex is formed, since the absorption maximum (341 nm) agrees to that of isolated $Cu(N_4[14](2-))$.

Similar spectral changes were observed for other cases. For a system of copper(II) ion with $N_4[18]$, the absorption maximum of the macrocycle was shifted from 308 to 354 and 368 nm, having an isosbestic point at 338 nm (Fig. 7B). In the case of copper(II) ion with $N_4[22]$, the spectral change was slight and the absorption maximum of the macrocycle was shifted from 315 to 349 nm, having an isosbestic point at 330 nm (Fig. 7C).

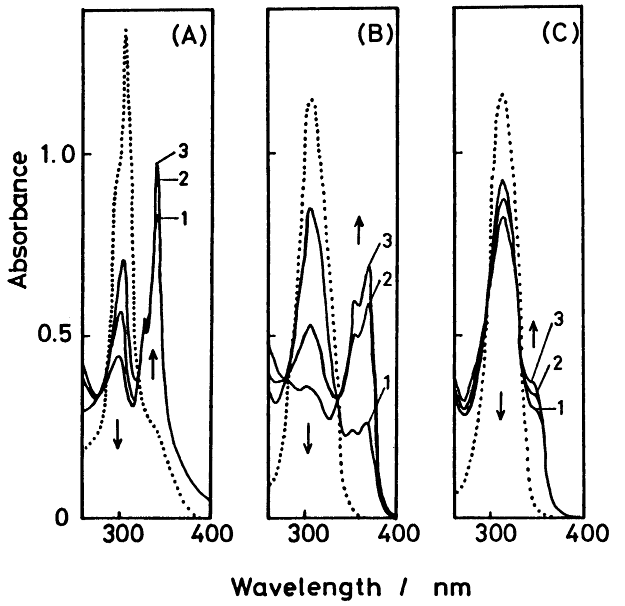


Fig. 7. Absorption spectral changes caused by complexation of copper(II) with $N_4[14]$(A), $N_4[18]$(B), and $N_4[22]$(C) in DMF at 25 °C.
[ligand]=4.00×10^{-5} mol dm^{-3}; cell length: 1 cm. (A) (⋯⋯): $N_4[14]$; (——): 1, 2, and 3, after 2, 10, and 20 min, respectively. (B) (⋯⋯): $N_4[18]$; (——): 1, 2, and 3, after 2, 10, and 60 min, respectively. (C) (⋯⋯): $N_4[22]$; (——): 1, 2, and 3, after 2, 10, and 15 min, respectively.

In the case of nickel(II) ion with $N_4[14]$, the absorption spectrum changed gradually for over 7 h. The absorption maximum of $N_4[14]$ was shifted from 305 to 396 nm, having an isosbestic point at 348 nm. In this case, the spectral changes indicate that the $Ni(N_4[14](2-))$ complex is formed in solution, on the basis of the absorption maximum. For the cases of nickel(II) ion with $N_4[18]$ and $N_4[22]$, though the absorption maxima of the macrocycles at 308 and 315 nm, respectively, decreased in intensity, new absorption bands could not be observed, indicating the formation of their nickel(II) complexes. In these cases, only the decomposition of the macrocycles may occur, since the complexation rates are very slow.

The extents of complexation for the four systems were calculated from their spectral changes. The results are shown in Fig. 8. With $N_4[14]$, the rate of complexation of the copper(II) ion was found to be much faster than that of the nickel(II) ion. The extent of complexation of the copper(II) ion with $N_4[14]$ reached nearly 90% after 20 min, and decreased gradually after 120 min due to decomposition of the complex.[7] On the other hand, the extent of complexation of the nickel(II) ion with $N_4[14]$ increased slowly with time, and reached about 20% after 130 min. For the case of the copper(II) ion with $N_4[18]$, its extent reached 98% after 70 min, although the rate of complexation was slightly lower than that with $N_4[14]$. For the copper(II) ion with $N_4[22]$, the extent of complexation reached about 45% after 15 min, and then decreased.

Solvent-Extraction of Copper(II) and Nickel(II) Ions with Macrocycles. Solvent extractions were carried out by using a 10-cm^3 test tube with a stopper in which an aqueous solution (5.0 cm^3) of metal acetate

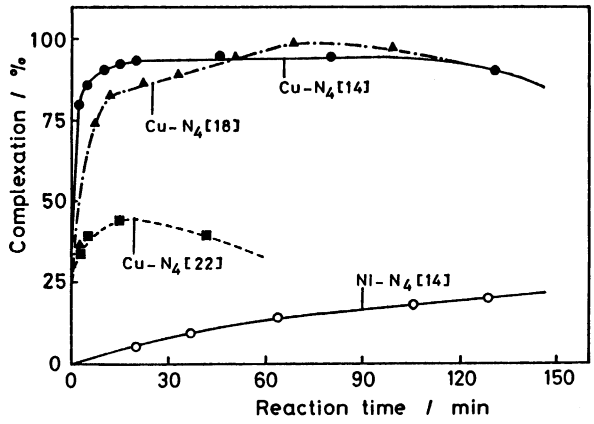


Fig. 8. Time-courses of complexation of copper(II) and nickel(II) with tetraaza macrocycles in DMF at 25 °C.

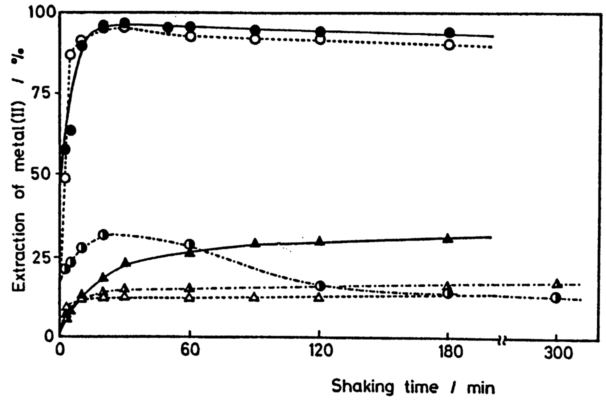


Fig. 9. Extractability of tetraaza macrocycles for copper(II) and nickel(II).
[metal(II)]=2.00×10^{-4} mol dm^{-3}; [extractant]=2.00×10^{-3} mol dm^{-3}. (—●—): Cu(II)-N$_4$[14]; (···○···): Cu(II)-N$_4$[18]; (-·-◐-·-): Cu(II)-N$_4$[22]; (—▲—): Ni(II)-N$_4$[14]; (···△···): Ni(II)-N$_4$[18]; (-·-▲-·-): Ni(II)-N$_4$[22].

(copper(II) or nickel(II)) and a chloroform solution (5.0 cm^3) of the macrocycles were contained as aqueous and organic phases, respectively. The concentrations of metal(II) ion in the aqueous solution and of macrocycles in the chloroform solution were 2.00×10^{-4} and 2.00×10^{-3} mol dm^{-3}, respectively. The test tube was shaken for an adequate time (from 2 to 300 min) at room temperature using a shaker. After shaking, the concentration of the metal(II) ion remaining in the aqueous phase was determined by atomic absorption spectrometry. Figure 9 shows plots of the percentages of the above-mentioned metal(II) ions extracted with the macrocycles against the shaking time. The rates of extraction of the copper(II) ion with these macrocycles were found to be much faster than those of the nickel(II) ion.

With N$_4$[14], 95% of the copper(II) ions in the aqueous phase could be extracted within 20 min; its value was almost constant over 180 min. With N$_4$[18], its extractability for the copper(II) ion was similar to that of N$_4$[14], though the percentage of extracted copper(II) ion decreased gradually. In more detail, 49% of the copper(II) ions was transferred into the organic phase after 2 min. Its value was smaller than that with N$_4$[14] (57%). However, after 5 min the percentage of extracted copper(II) ions with N$_4$[18] (87%) was larger than that with N$_4$[14] (63%). With N$_4$[22], the extractability for the copper(II) ion was low and only 31% of the copper(II) ions was extracted after 20 min; then, the percentage of extracted copper(II) ions gradually decreased with the shaking time. This may have been caused by an instability of the copper(II) complex with N$_4$[22].

As for the nickel(II) ion, the extraction rates with these macrocycles became faster in the order N$_4$[18]$<$N$_4$[22]$\ll$N$_4$[14]. No decreases in the percentages of extracted nickel(II) ions with them were observed within 300 min. These results may have arisen from the extremely slow complexation rates of the nickel(II) ion. It should be noticed that with N$_4$[22], the percentage of extracted nickel(II) ions became higher than that of copper(II) ions after 300 min. In this case, the copper(II) ions may be transferred into the organic phase during the initial stage (30 min) as a mixture of complexes which consist of compositions of 1 : 1, 2 : 1, and/or 3 : 1 copper(II)/N$_4$[22] ratios. Because these complexes are labile, they may decompose during shaking of the organic phase with the aqueous phase; free copper(II) ions may be back-transferred into the aqueous phase. This may cause a decrease in the percentage of extracted copper(II) ions with the shaking time.

The results obtained in the solvent-extraction experiments are almost parallel with those in the complexation measurements. However, these results are not consistent with those expected from NMR relaxation time measurements of the macrocycles. The absorption spectral changes and the percentage of extraction may reflect the degree of complete complexation of metal(II) ions with macrocycles, rather than the degree of weakly bound metal(II) ions with them. On the other hand, the NMR relaxation time measurements should reflect the degree of weakly bound metal(II) ions at the initial complexation step: at which time they are coordinated with one or two donor atoms (nitrogen atom) of the macrocycles. In fact, polyaza macrocyclic ligands have been reported to form a coordination bond between a metal ion and one donor atom (N atom) of the macrocyclic molecule during the initial step of complexation.[11] Therefore, the NMR relaxation time measurements of ligands, themselves, may be very effective for judging their complexation abilities toward metal ions when they are unidentate and/or bidentate ligands.

References

1) See, for example, a) D. H. Busch, *Helv. Chim. Acta Special Issue*, 174 (1967); b) D. H. Busch, *Acc. Chem. Res.*, **11**, 392 (1978); c) K. Henrick, P. A. Tasker, and L. F. Lindoy, *Prog. Inorg. Chem.*, **33**, 1 (1985).

2) M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, **1978**, 1081.

3) a) S. C. Tang, S. Koch, G. N. Weinstein, R. W. Lane, and R. H. Holm, *Inorg. Chem.*, **12**, 2589 (1973); b) D. P. Riley, J. A. Stone, and D. H. Busch, *J. Am. Chem. Soc.*, **98**, 1752 (1976).

4) W. M. Davis, A. Zask, K. Nakanishi, and S. J. Lippard, *Inorg. Chem.*, **24**, 3737 (1985).

5) This work was partly reported previously in *Chem. Lett.*, **1986**, 907.

6) T. Tokumitsu and T. Hayashi, *Bull. Chem. Soc. Jpn.*, **54**, 2348 (1981).

7) T. J. Truex and R. H. Holm, *J. Am. Chem. Soc.*, **93**, 285 (1972).

8) a) L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, **1964**,

276; b) S. Yamada and H. Nishikawa, *Bull. Chem. Soc. Jpn.*, **36**, 755 (1963).

9) M. Yamashita, H. Ito, and T. Ito, *Inorg. Chem.*, **22**, 2101 (1983).

10) a) K. Müllen and P. S. Pregosin, "Fourier Transform NMR Techniques-A Practical Approach," Academic Press, London (1976); b) S. Kinoshita and I. Masuda, *Polyhedron*, **4**, 1245 (1985).

11) a) E. Kimura and M. Kodama, *Yuki Gosei Kagaku Kyokai Shi*, **35**, 632 (1977); b) T. Kaden, *Helv.Chim. Acta*, **53**, 619 (1970).