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PREPARATION OF 18- AND 22-MEMBERED TETRAAZA MACROCYCLES AND THEIR COPPER(II) COMPLEXES

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18- and 22-membered tetraaza macrocycles were prepared from acetylacetone and 1,4-diaminobutane or 1,6-diaminohexane, respectively. Their copper(II) complexes were characterized by electronic spectroscopy and the copper(II) complex of the 18-membered macrocycle was found to be pseudo-tetrahedral.

Recently, many tetraaza macrocycles and their metal complexes have been prepared and characterized.1) These ligands have also been applied as solvent extractants,2) selective reagents for the colorimetric determination of transition metals3) and chelate adsorbents.4) The saturated macrocycles have produced much interesting information on the stabilities and structures of metal complexes.5) Of the various tetraaza macrocycles the 14-membered Schiff base compounds have received most attention with few studies on 15- and 16-membered compounds reported.6) We now wish to report the preparation of 18- and 22-membered tetraaza macrocycles derived from acetylacetone and linear diamines, and the characterization of their copper(II) complexes.

These tetraaza macrocycles (see Fig. 1), 7,9,16,18-tetramethyl-1,6,10,15-tetraazacyclooctadeca-1,7,9,16-tetraene (N_4[18]) and 9,11,20,22-tetramethyl-1,8,12,19-tetraazacyclodocosa-1,9,11,20-tetraene (N_4[22]) were prepared by refluxing a benzene solution (500 cm^3) of N,N'-bis(1-methyl-3-thioxo-1-butenyl)-ethylenediamine7) (0.097 mol) and the diamine (0.195 mol) for 5 and 8 d, respectively. The solvent was evaporated at reduced pressure and the dark-

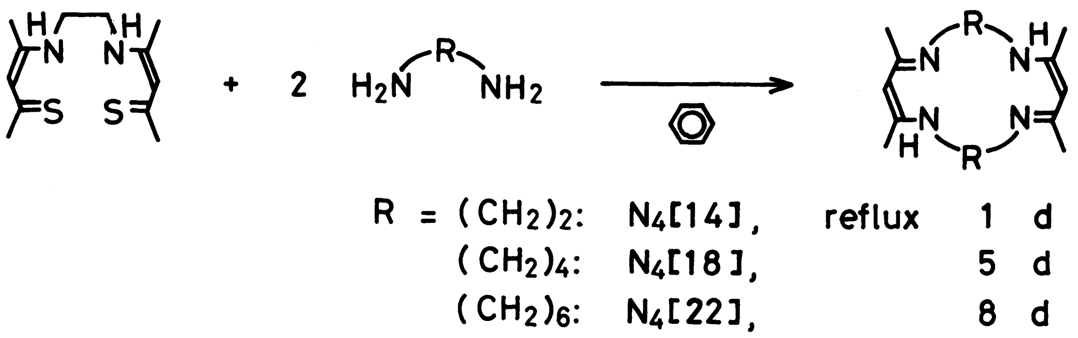

Fig. 1. Scheme of preparation of macrocycles.

brown residue was recrystallized twice from ethanol. The pale yellow needles were obtained in 20% yields. The macrocyclic ligands were identified by elemental analysis, IR and UV spectroscopy, MS, ^1H and ^{13}C NMR spectroscopy.[8)]

Figure 2 shows the electronic spectra of the copper(II) complexes with three macrocyclic ligands, which were obtained by the mixture of N,N-dimethylformamide (DMF) solutions of the ligand and copper(II) acetate monohydrate. The copper(II) complexes with $N_4[18]$ and $N_4[22]$ have not been isolated yet. The electronic spectra exhibited differences, particularly in the visible and near infrared regions. The spectrum of $[Cu(N_4[14])]$[9)] shows an absorption band with moderate intensity at 16700 cm^{-1} assigned to the ligand field transitions and no absorption band in the near infrared region. These results suggest that $[Cu(N_4[14])]$ is planar.[10)] The spectrum of $Cu(N_4[18])$ has characteristic absorption bands at 8570, 12800, and 20200 cm^{-1}. The third band is very intense, and can be assigned to the charge transfer transitions, while the first two bands are moderately intense and can be assigned to the

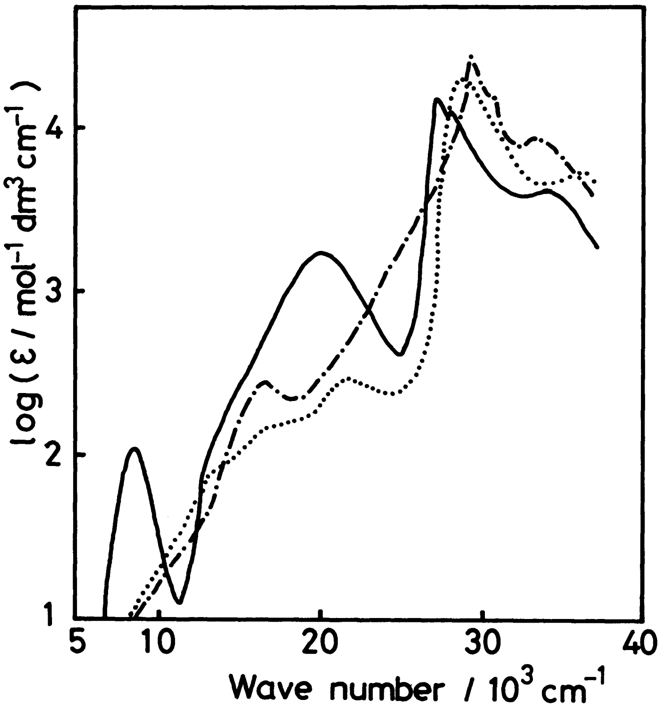

Fig. 2. Electronic spectra of copper(II) complexes in DMF.

(—·—·—): $[Cu(N_4[14])]$; (———): $Cu(N_4[18])$; (·········): $[Cu_2(N_4[22])]^{2+}$.

ligand field transitions. These results indicate that $Cu(N_4[18])$ is not planar but pseudo-tetrahedral.[10)]

The 22-membered macrocyclic ligand has so large a cavity that it can coordinate two metal ions in one cyclic system. In fact, the absorption maxima of the mixtures of DMF solutions of $N_4[22]$ and copper(II) ion were shifted from 564 to 462 nm in the visible region with increasing the ratio of copper(II) to $N_4[22]$. The absorption band at 462 nm should be arised from the formation of the bimetallic complex, $[Cu_2(N_4[22])]^{2+}$. This result was spectrophotometrically obtained by the mole ratio method. The spectrum of $[Cu_2(N_4[18])]^{2+}$ has three absorption bands at 13400, 17600, and 21600 cm^{-1} in the visible region, which can be assigned to the ligand field transitions, and no absorption band in the near infrared region. In addition, the greenish precipitate was produced by mixing each DMF solution of $N_4[22]$ and a large excess of copper(II) ion. It was identified with the formula, $Cu_3(N_4[22])\cdot(OCOCH_3)_4$, by elemental analysis. This trimetallic complex was slightly soluble in the ordinary organic solvents and every copper(II) ion may not keep in the tetraaza cycle but be bridged by the acetate ions. However, the structural information of the copper(II) complexes with $N_4[22]$ is still insufficient.

The electronic spectroscopic data for the ligands and their copper(II) complexes are summarized in Table 1. The electronic spectra of 14-, 18-, and 22-membered tetraaza macrocycles are similar to each other and have an intense absorption band ($\log \varepsilon$ = ca. 4.5) centered around 310 nm, which can be assigned to the π-π^* transition.

Table 1. Absorption maxima of macrocycles and their copper(II) complexes in DMF

Compound	λ_{max} / nm (log (ε/mol^{-1} dm^3 cm^{-1}))
$N_4[14]$	305 (4.53)
$[Cu(N_4[14])]$	341 (4.40), 598 (2.41)
$N_4[18]$	308 (4.47)
$Cu(N_4[18])$	354 (4.11), 494 (3.23), 1167 (2.05)
$N_4[22]$	315 (4.47)
$[Cu_2(N_4[22])]^{2+}$	349 (4.31), 462 (2.46), 568^{sh}(2.18)

In conclusion, the 18-membered macrocyclic ligand is not able to coordinate with metal ions in a planar fashion due to the steric demand of the methylene chains. The effect of the size of the macrocyclic ligands on the structure of metal complexes and their spectroscopic properties will be the subject of future investigations.

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8) N_4[18] Found: C, 71.14; H, 10.67; N, 18.26%. Calcd for $C_{18}N_4H_{32}$: C, 70.99; H, 10.61; N, 18.40%. IR(in KBr disk): 3400, 2910, 1620, 1555, 1440, 1330, 1260, 1025, and 735 cm^{-1}. MS: M^+ 304. ^1H NMR(in $CDCl_3$): 1.79 (8H, $C\underline{H}_2$, m), 1.88(12H, $C\underline{H}_3$, s), 3.31(8H, $C\underline{H}_2$, m), and 4.50(2H, $C\underline{H}$, s)ppm. ^{13}C NMR(in $CDCl_3$): 19.39(4C, $\underline{C}H_3$, s), 29.46(4C, $\underline{C}H_2$, s), 46.73(4C, $\underline{C}H_2$, s), 94.07(2C, $\underline{C}H$, s), and 160.57(4C, $\underline{C}$=N, s)ppm.

N_4[22] Found: C, 73.31; H, 11.28; N, 15.64%. Calcd for $C_{22}N_4H_{40}$: 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. ^1H NMR(in $CDCl_3$): 1.56 (8H, $C\underline{H}_2$, m), 1.67(8H, $C\underline{H}_2$, m), 1.87(12H, $C\underline{H}_3$, s), 3.22(8H, $C\underline{H}_2$, m), and 4.50(2H, $C\underline{H}$, s)ppm. ^{13}C NMR(in $CDCl_3$): 20.00(4C, $\underline{C}H_3$, s), 29.05(4C, $\underline{C}H_2$, s), 31.75(4C, $\underline{C}H_2$, s), 47.54(4C, $\underline{C}H_2$, s), 94.29(2C, $\underline{C}H$, s), and 161.35(4C, $\underline{C}$=N, s)ppm.

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