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SYNTHESIS OF NEW MACROCYCLIC COPPER(II) COMPLEX DERIVED FROM METHYL VINYL KETONE AND COPPER(II) COMPLEX OF N-SUBSTITUTED DIAMINE

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A new macrocyclic copper(II) complex was prepared by condensation reaction between methyl vinyl ketone and bis(3-(S)-ahaz)copper(II) complex (3-(S)-ahaz; 3(S)-3-aminohexahydroazepine). Sodium Borohydride could reduce the C=N bonds of the condensation product to a saturated mcrocyclic tetramine copper(II) complex.

In recent years, it has been pointed out that the high selectivity and specificity found in enzyme catalyzed reactions could be attributed to incorporation of organic molecules into cavities which surround active sites. Viewed in this light, molecules possessing the cavities such as cyclodextrins and crown ethers have been studied in the field of so-called host-gest chemistry. Here, we report on the preparation of macrocyclic tetramine with a chiral cavity by using template reaction.

The condensation reaction of acetone and bis(ethylenediamine)copper(II) complex yields macrocyclic complexes similar to nickel(II) analogues.[1,2] But in the case of copper(II) complexes, macrocycles could not be reduced to saturated compounds contrary to the case of nickel(II) analogues.[3] To introduce a chiral cavity on macrocycles, we used 3(S)-3-aminohexahydroazepine (3-(S)-ahaz), a N-substituted diamine as shown in Fig. 1-a, which has a medium size ring axially oriented with respect to the N-Cu-N five-membered chelate ring upon coordination (Fig. 1-b).

To a methanol solution of $[Cu(3\text{-}(S)\text{-}ahaz)_2](ClO_4)_2$, Complex A, (1 mole), was added methyl vinyl ketone (4 moles). After anhydrous ammonia had been bubbled through for ten minutes, the solution was refluxed for three hours, while the colour of the solution changed from blue to purple. Red crystals which deposited were collected and dried under vacuum. Anal. Calcd for $CuC_{20}H_{36}N_4O_8Cl_2$: C, 40.37; H, 6.09; N, 9.41 %. Found: C, 39.82; H, 5.99; N, 9.04 %.

Three structures can be anticipated for the condensation product, Complex B, as given in Fig. 2. Elemental analysis data show that two moles of methyl vinyl ketone reacted with one mole of $[Cu(3\text{-}(S)\text{-ahaz})_2]^{2+}$ and two moles of water were lost. These data agree with the changes of infrared spectra (nujol mull) summarized in Table. The N-H stretching absorptions at 3290, 3260 and 3150 cm^{-1} (νNH, νNH_2) and the vending absorption at 1585 cm^{-1} (δNH_2) disappeared in the spectrum of B, while a new band assignable to the C=N stretching absorption appeared at 1650 cm^{-1}. These features indicate the structure Fig. 2-a for the Complex B.

The filtrate after the removal of B was charged on a column of SP-Sephadex C-25 ion exchanger and eluted with 0.2 M aqueous solution of NaCl. Three bands, B-1, B-2 and B-3 were obtained and from each band crystalline product was isolated as its tetrachlorozincate salt. The infrared spectrum of B-1 is essentially same as that of B (the perchlorate salt) except the bands of ClO_4^-. Thus B-1 is assigned to the macrocyclic compound. The IR of B-3 is identical with that of tetrachlorozincate of the starting complex (A). B-2 has both features of A and B. The absorptions of amine protons (NH, NH_2) appear in the stretching modes at 3270, 3220 and 3130 cm^{-1} and in the vending mode at 1580 cm^{-1}. Elemental

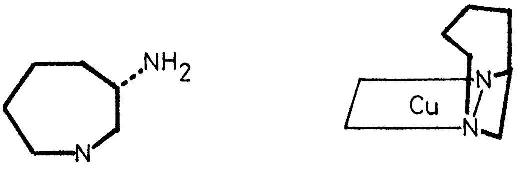

Figure 1 (a) (b)

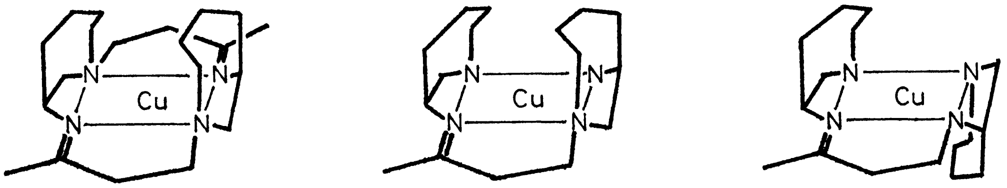

Figure 2 (a) (b) (c)

Table

Spectral Data of Cu(II) Complexes

Complex	IR (cm^{-1})			Visible*
	ν_{N-H}	$\nu_{C=N}$	δ_{NH_2}	max; nm (ε)
A	3290 3260 3150	--	1585	535 (80)
B	--	1650	--	507 (201)
B-2	3270 3220 3130	1655	1580	514 (114)
C	3240	--	--	485 (189)

* in aqueous solution

analysis data of B-2 show that one mole of methyl vinyl ketone reacted with one mole of $[Cu(3\text{-}(S)\text{-ahaz})_2]^{2+}$. Anal. Calcd for $CuC_{16}H_{32}N_4ZnCl_4$: C, 34.87; H, 5.85; N, 10.16 %. Found: C, 34.78; H, 6.02; N, 10.14 %. Consequently, the structure b in Fig. 2 is compatible with the data of B-2. We have no evidence suggesting the existence of complex which takes the structure c. This means that the specific selectivity distinguishing between the primary and secondary amino groups of the diamine emerged in the formation of the carbon-nitrogen single bond.

Reduction of the double bond (imine) with sodium borohydride generates the copper(II) complex with the saturated macrocyclic ligand (Complex C). It was isolated as its perchlorate salt. Anal. Calcd for $CuC_{20}H_{40}N_4Cl_2O_8$: C, 40.10; H, 6.73; N, 9.35 %. Found: C, 40.19; H, 6.60; N, 9.32 %. Infrared spectrum provides convincing evidence that the resulting product is the saturated macrocyclic copper(II) complex. The C=N stretching absorption at 1650 cm^{-1} in B was no longer observed and the N-H stretching band at 3240 cm^{-1} (ν_{N-H}) appeared in the IR of the product.

It was found that macrocyclization gives rise to a serious shift of absorption maxima of the d-d transition band. The maximum of copper(II) complex in water shifted from 535 nm for bis(diamine) type, A, to 507 nm and 485 nm for the unsaturated and the saturated compounds, respectively. As the ligands block one of two apical coordination sites by the 7-membered rings, an equilibrium between square planar and square pyramid species can be expected in coordinative solvents. A typical copper(II) complex of square planar coordination, $[Cu(daco)_2]^{2+}$ (daco; 1,5-diazacyclooctane), in which both of apical coordination sites are blocked completely by the ligands, has the d-d band maximum at 500 nm in water.5) On the other hand, $[Cu(dach)_2]^{2+}$ (dach; 1,4-diazacycoheptane), established to have the square pyramidal geometry on the basis of spectrophotometrical measurements and x-ray analysis data absorbs at 542 nm in water.5,6) Therefore, the shift of the absorption band in the complexes A, B and C should reflect change of the coordination number. The positions of the absorption maxima of B and C are comparable to those of related copper(II) complexes with 14-membered macrocyclic ligands.1,4) In x-ray data of copper(II) complexes with square pyramidal geometry, it was observed that the metal ion moves slightly into the inner sphere of the square pyramid by electronic repulsion towards the donner electrons of the apical ligand.6,7) So it is necessary for the ligands coordinated to the square pyramidal complexes to deform slightly towards the opposite side of the apical ligands. It is possible that linking the diamines to form the macrocyclic ligands make it hard for the complexes with rigid planar ligand as 14-membered macrocyclic tetramines to deform from the square planar geometry. Therefore, the copper(II) complexes with such quadridentate ligands would prefer the square planar coordination.

References

1) M. M. Blight and N. F. Curtis, J. Chem. Soc., 3016 (1962).
2) N. F. Curtis and D. A. House, Chem. and Ind., 1708 (1961).
3) N. F. Curtis, Coordin. Chem. Rev., 3, 3 (1968).
4) D. A. House and N. F. Curtis, J. Am. Chem. Soc., 84, 3248 (1962).
5) W. K. Musker and M. S. Hussain, Inorg. Chem., 8, 528 (1969).
6) M. S. Hussain and H. Hope, Acta Cryst., B25, 1866 (1969).
7) D. Hall, H. J. Morgan, and T. N. Waters, J. Chem. Soc. (A), 677 (1966).

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