

# Synthesis and Magnetic Properties of Chain Compounds of Dinuclear Copper(II) Complexes with Organic Radicals

関西学院大学大学院理工学研究科

化学専攻 御厨研究室 Renny Indrawati

The dinuclear paddle wheel copper(II) carboxylates with antiferromagnetic spin-exchange interaction have challenged numerous studies. Previous work of radical-containing copper(II) dimer systems have resulted in an attenuated antiferromagnetic interaction, in which the presence of 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (Hcaproxy) and 4-carboxy-2,2,6,6-tetramethylpiperidine-1-oxyl (Hcatempo) positioned as the bridging carboxylates fairly increase the entirety of paramagnetic components.<sup>1)</sup> As the parent complexes in the present work,  $[\text{Cu}_2(\text{caproxy})_4(\text{H}_2\text{O})_2]$  and  $[\text{Cu}_2(\text{catempo})_4(\text{H}_2\text{O})_2]$  were evolved into chain compounds by applying some *N,N'*-bidentate ligands. The objectives of this study are: (i) to synthesize and characterize new coordination polymer containing dinuclear copper(II) complexes with nitroxide radicals and (ii) to learn the magneto-structural properties of such complexes subsequent to the use of bidentate spacer ligands which control the distance of separation between the paddle wheel units.

The chain adducts were obtained through one-step synthesis reaction at room temperature. Six types of *N,N'*-bidentate ligands were applied, i.e. 4,4'-bipyridine (4,4'-bpy), 1,2-bis(4-pyridyl)ethane (bpe), *trans*-1,2-bis(4-pyridyl)ethylene (bpel), and 4,4'-dipyridyl disulfide (pds), 1,4-diazabicyclo[2.2.2]octane (dabco) and pyrazine (pyz). The precipitates were characterized by elementary analysis as well as spectroscopic studies. Single crystals of pds adduct from  $\text{Cu}_2(\text{caproxy})_4$  system and bpe adduct from  $\text{Cu}_2(\text{catempo})_4$  unit were determined by means of X-ray crystallography. The magnetic-susceptibility measurements were performed in the temperature range of 4.5-300 K.

Eleven chain adducts, formulated as  $[\text{Cu}_2(\text{caproxy})_4(\text{L})]_n$  (L = 4,4'-bpy (**3**), bpe (**4**), bpel (**5**), pds (**6**), dabco (**7**), pyz (**8**)) and  $[\text{Cu}_2(\text{catempo})_4(\text{L})]_n$  (L = 4,4'-bpy (**9**), bpe (**10**), bpel (**11**), pds (**12**), dabco (**13**)), were prepared in satisfactory yield. The *syn-syn* coordination mode of the  $\text{COO}^-$  group can be assumed from the  $\Delta$  value [ $\nu_{as}(\text{COO}) - \nu_s(\text{COO})$ ] of infrared spectra of all synthesis products, suggesting that the paddle wheel structure is maintained during the new complexation. The observed blue shift of pyridine ring ( $\nu(\text{CC/CN})$ ) and out-of-plane C-H vibration bands are indicative of metal coordination to the nitrogen atom of the bridging ligand. In the UV-Vis spectra, the maximum absorption of d-d transition bands shows a bathochromic shift upon the axial ligand substitution. The X-ray crystal structures of **6** and **10** revealed the integration of radical molecules in the dimeric copper(II) cores, in which each copper atoms adopts five-coordinated square pyramidal environment. The effective magnetic moments of all chain adducts are in harmony with the parent complexes. The inverses of magnetic susceptibility data in the thermal variation essentially follow the Curie-Weiss law. The two copper ions in the paddle wheel cage are antiferromagnetically coupled, while the inter-dimer interactions via the bridging *N,N'*-bidentate ligands are generally weak and antiferromagnetic.

1) M. Mikuriya, H. Azuma, J. Sun, D. Yoshioka, and M. Handa, *Chem. Lett.*, **2002**, 608-609.