Template Synthesis of Phenol-based Heterodinucleating Macrocycles with Dissimilar N(amine)$_2$O$_2$ and N(imine)$_2$O$_2$ Metal-binding Sites

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Phenol-based dinucleating macrocycles possessing two dissimilar N(amine)$_2$O$_2$ and N(imine)$_2$O$_2$ metal-binding sites, sharing two phenolic oxygens, have been obtained as mononuclear Cu(II) complexes, capable of incorporating a second metal ion to provide homo- and hetero-dinuclear complexes.

Heterodinuclear metal complexes are of interest in the design of new functional molecules[1-3] and the study of mutual effects of dissimilar metal ions upon physicochemical properties of such heterodinuclear systems.[4-6] The use of macrocycles with dissimilar coordination sites for the purpose has a great advantage because such macrocycles can provide discrete heterodinuclear complexes and the resulting complexes can be stabilized by macrocyclic effect. Phenol-based dinucleating macrocycles have often been used for the study of heterodinuclear complexes.[7-10] The macrocycles of the type shown in Scheme 1, whose two metal-binding sites are dissimilar with respect to the nature of donor nitrogens (amine or imine), are very few[11,12] in spite of great interest in their heterodinuclear complexes. Fraser *et al.*[11] have reported a macrocycle of this type having a pyridyl pendant group at each amine nitrogen but their synthesis is based on many elaborate steps.[11] Thus, it is of value to establish a synthetic method applicable to a wide range of macrocycles of this type. Here we report a facile template synthesis of macrocycles of this type (X=Br; R=CH$_3$; m=n=2 (abbreviated as H$_2$L^1) or m=2 and n=3 (H$_2$L^2)).

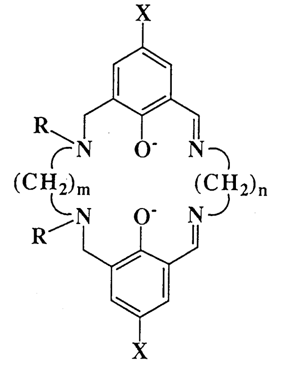
In order to prepare the unsymmetrical macrocycles H$_2$L^1 and H$_2$L^2, it is recommended that an appropriate acyclic precursor is used in the template reaction.[8,9] For the present purpose we adopt N,N'-dimethyl-N,N'-ethylenedi(5-bromo-3-formyl-2-hydroxybenzylamine) (H$_2$L') as the precursor, which was available by the Mannich reaction of 5-bromosalicylaldehyde, N,N'-dimethyletylenediamine and paraformaldehyde in ethanol at the refluxing temperature.[13]

The copper(II) complex of the acyclic ligand, [Cu(L')], was obtained as green microcrystals[14] by the reaction of H$_2$L' and copper(II) acetate monohydrate in an aqueous solution containing potassium hydroxide. Then, [Cu(L')] was reacted with ethylenediamine in hot DMF to give purple-colored [Cu(L^1)] as microcrystals.[15] A similar reaction with 1,3-diaminopropane in hot methanol gave brown-colored [Cu(L^2)], which was crystallized from a methanol/2-propanol mixture as [Cu(L^2)]·2-PrOH.[16]

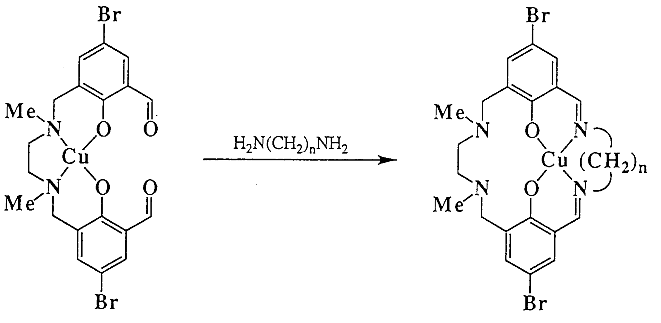
In the acyclic complex [Cu(L')] the Cu(II) ion may be bound at either the N(amine)$_2$O$_2$ site or the O$_4$ site of the ligand. The complex shows an intense IR band attributable to the ν(CO) vibration of the formyl group at 1650 cm^{-1}. In the visible spectrum in DMF a superposed d-d band is seen at 660 nm. The IR and visible spectral results indicate that the Cu(II) ion is bound at the N(amine)$_2$O$_2$ site of the acyclic ligand.

The macrocyclic complexes [Cu(L^1)] and [Cu(L^2)] show a ν(CN) vibration of the azomethine group at 1625 and 1610 cm^{-1}, respectively. A superposed d-d band is seen at 560 nm for [Cu(L^1)] (reflectance on powdered sample) and 600 nm for [Cu(L^2)] (in DMF). The d-d band of [Cu(L^1)] is compared to that of N,N'-ethylenedisalicylideneaminatocopper(II) (558 nm in chloroform)[17] and the d-d band of [Cu(L^2)] is compared to that of N,N'-1,3-trimethylenedisalicylideneaminatocopper(II) (602 in nujol mull[18] and 605 nm in acetonitrile[19]). This fact strongly suggests that the copper(II) ion shifts from the N(amine)$_2$O$_2$ site in $(L')^{2-}$ to the N(imine)$_2$O$_2$ site in $(L)^{2-}$ by the cyclization (see Scheme 2). This is proved by X-ray crystallography for [Cu(L^2)]·2-PrOH as described below.

An ORTEP drawing of the crystal is given in Figure 1 together with the numbering scheme.[20] The result clearly demonstrates the formation of the macrocyclic complex with the copper(II) ion at the N(imine)$_2$O$_2$ site. The 2-PrOH molecule is free from the coordination and captured in the crystal lattice. The geometry around the metal is essentially



Scheme 1. Unsymmetrical dinucleating macrocycles with dissimilar N(amine)$_2$O$_2$ and N(imine)$_2$O$_2$ coordination sites.



[Cu(L')] [Cu(L^i)]

Scheme 2. Synthetic scheme of [Cu(L^i)] (L^1 for n=2 and L^2 for n=3).

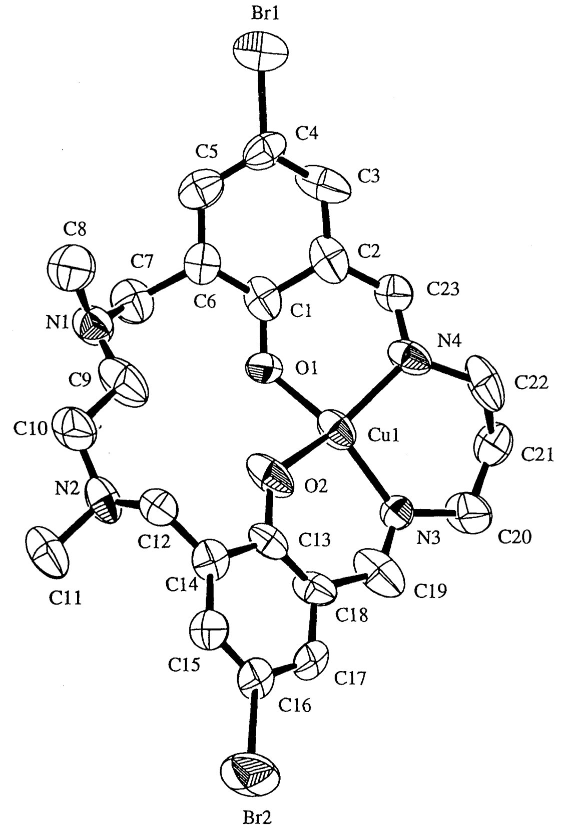


Figure 1. An ORTEP drawing of $[Cu(L^2)]\cdot$2-PrOH with the numbering scheme.

planar and similar to that of N,N'-1,3-trimethylenedisalicylideneaminatocopper(II).[19] The Cu-O1 and Cu-O2 bond distances are both 1.91(1) Å and the Cu-N3 and Cu-N4 bond distances are 1.93(1) and 1.99(1) Å, respectively. The O1-Cu-O2, O1-Cu-N4, O2-Cu-N3, and N3-Cu-N4 angles are 88.5(4), 91.9(5), 93.0(5), and 97.6(5)°, respectively, and the sum of the angles is ca. 371°. This fact means a slight distortion of the $\{CuN_2O_2\}$ chromophore to tetrahedron. The dihedral angle between the least-squares plane defined by O1, Cu and N4 and the plane defined by O2, Cu and N3 is 35.56°, which is slightly larger than the dihedral angle (28.36°) found for N,N'-1,3-trimethylenedisalicylideneaminatocopper(II).[19]

The trimethylene chain combining the imino nitrogens N3 and N4 assumes a chair conformation. The lateral chain involving the amino nitrogens N1 and N2 adopts a deformed conformation. The asymmetric nirogens N1 and N2 have *S* and *R* configuration, respectively.

The mononuclear complexes $[Cu(L^1)]$ and $[Cu(L^2)]$ can incorporate a second metal ion at the $N(amine)_2O_2$ site to form homo- and heterodinuclear complexes $[CuM(L)]X_2$ (L=L^1 or L^2; M=Mn, Co, Ni, Cu, Zn; X=Cl, ClO_4, etc.). Based on our preliminary study $[CuM(L^1)]X_2$ are rather unstable in solution, whereas $[CuM(L^2)]X_2$ are stable in DMF and DMSO. Further, we have found that coulometry of $[CuM(L^2)]X_2$ generates the corresponding Cu(I)M(II) and Cu(I)M(I) (M=Co, Ni, Cu) complexes which are significantly stable in solution. The details of the electrochemical and magnetic studies on the dinuclear complexes will be reported elsewhere.

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13 Found for H_2L': C, 46.81; H, 4.32; N, 5.30%. Calcd for $C_{20}H_{22}Br_2N_2O_4$: C, 46.72; H, 4.31; N, 5.45%. ^{1}H-NMR [δ/ppm] in $CDCl_3$: 2.30 (s, 6H), 2.70 (2, 4H), 3.68 (s, 4H), 7.71 (s, 2H), 7.72 (s, 2H), 10.18 (s, 2H).
14 Found for [Cu(L')]: C, 41.74; H, 3.49; N, 4.78; Cu, 11.03%. Calcd for $C_{20}H_{20}Br_2CuN_2O_4$: C, 41.72; H, 3.50; N, 4.87; Cu, 11.04%.
15 Found for $[Cu(L^1)]$: C, 44.04; H, 4.17; N, 9.33; Cu, 10.20%. Calcd for $C_{22}H_{24}Br_2CuN_4O_2$: C, 44.05; H, 4.03; N, 9.34; Cu, 10.59 %.
16 Found for $[Cu(L^2)]\cdot$2-PrOH: C, 46.27; H, 5.10; N, 8.28; Cu, 9.90%. Calcd for $C_{26}H_{34}Br_2CuN_4O_3$: C, 46.34; H, 5.09; N, 8.31; Cu, 9.43%.
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20 Crystal data for $[Cu(L^2)]\cdot$2-PrOH: $C_{26}H_{34}Br_2CuN_4O_3$, F.W.=673.93, triclinic, space group P1(#2), a = 11.621(6), b = 14.17(1), c = 9.390(4) Å, α = 96.59(6), β = 107.78(3), γ = 103.78(5)°, v = 1400(1) $Å^3$, Z = 2, D_c = 1.598 g cm^{-3}, μ(Mo-Kα) = 36.76 cm^{-1}, crystal dimensions 0.20 × 0.15 × 0.10 mm^3. Intensity data were collected on a Rigaku AFC-7R diffractometer with graphite monochromated Mo-Kα radiation (λ=0.71069 Å) at 293 K. The structure was solved, expanded and refined by the use of the teXsan crystallographic software package from Molecular Structure Corporation. Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement based on 2439 observed reflections ($I \geq 3\sigma(I)$) converged with R =0.084 and R_w =0.063.