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New Dinucleating Macrocycle, 12,24-Dihydroxy-1,6-dioxo-2,5,14,17-tetraaza[6·6]metacyclophane-13,17-diene and Its Metal Complexes

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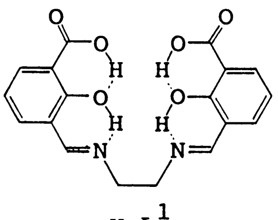
A dinucleating macrocycle with dissimilar coordination sites (imine and amide sites), 12,24-dihydroxy-1,6-dioxo-2,5,14,17-tetraaza[6·6]metacyclophane-13,17-diene, has been obtained and its complexing behavior was examined. It forms both mononuclear and dinuclear complexes with nickel(II) ion but only dinuclear complex with copper(II) ion. In the mononuclear nickel(II) complex the metal ion is bound at the imine site. In the dinuclear copper(II) complex an antiferromagnetic spin-exchange interaction (J=-355.2 cm^{-1}) occurred through the bridging phenolic oxygens.

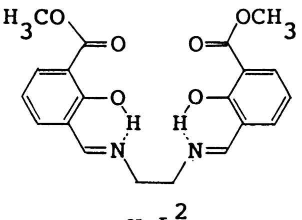
N,N'-Bis(3-carboxysalicylidene)ethylenediamine (H_4L^1)[1)] and N,N'-bis(3-methoxycarbonylsalicylidene)ethylenediamine (H_2L^2)[2)] are unique dinucleating ligands which can form discrete heterodinuclear complexes. We report here the synthesis, characterization, and complexing behavior of 12,24-dihydroxy-1,6-dioxo-2,5,14,17-tetraaza[6·6]metacyclophane-13,17-diene (H_4L^3), a macrocyclic analog of H_4L^1 and H_2L^1.

Attempts to obtain L^3-complexes by the reaction of ethylenediamine (en) and $[Cu(L^2)]$ or $[Cu_2(L^2)Cl_2]$ were all unsuccessful. The synthesis of H_4L^3 was eventually succeeded by non-template reaction of methyl 3-formylsalicylate and en. It was characterized by elemental analysis, mass spectra, and ^{1}H-NMR spectra.[3)]

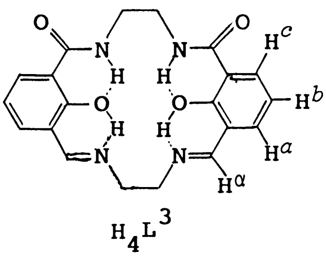
Complexing behaviors of H_4L^3 towards nickel(II) and copper(II) ions have been examined. Both mono- and dinuclear complexes, $[Ni(H_2L^3)]$ and $[Ni_2(L^3)]$,[4)] were isolated when a nickel(II) salt was allowed to react with H_4L^3 in ethanol in the 1:1 and 2:1 mole ratio, respectively. Orange $[Ni(H_2L^3)]$ is diamagnetic and



H_4L^1



H_2L^2



H_4L^3

shows a d-d band at 22.2×10^3 cm^{-1} characteristic of planar nickel(II) complex. Yellowish brown [$Ni_2(L^3)$] is also diamagnetic and shows d-d bands at 22.7×10^3 and 17.7×10^3 cm^{-1}. It is known that N,N'-ethylenedisalicylamidatoniccolate(II) shows two d-d bands at 21.8×10^3 and 18.4×10^3 cm^{-1}.$^{5)}$ Hence, it is evident that for [$Ni(H_2L^3)$] the metal ion is bound at the imine-site and for [$Ni_2(L^3)$] the second metal ion is bound at the amide-site with the deprotonated nitrogen atoms. [Ni(H_2L^3)] shows N-H vibration at 3200 cm^{-1} and C=O vibration at 1645 cm^{-1}. For [$Ni_2(L^3)$] the former band disappears and the latter band shifts to 1620 cm^{-1}. It is to be noted that H_4L^1 forms "mixed-spin" dinickel(II) complex (S=1),$^{6)}$ while H_4L^3 forms diamagnetic dinickel(II) complex.

With copper(II) ion H_4L^3 formed only dinuclear complex [$Cu_2(L^3)$]$^{7)}$ even when syntheses were carried out in the metal/ligand=1:1 stoichiometry. The band at 18.7×10^3 cm^{-1} observed for this complex must be the superposition of the d-d bands due to the copper(II) ions at the imine- amd amide sites, in view of the spectra of N,N'-ethylenedisalicylamidatocuprate(II)$^{5)}$ and N,N'-ethylenedisalicylideneaminatocopper(II).$^{8)}$ The magnetic moment of this complex is subnormal at room temperature (0.72 μ_B), suggesting an antiferromagnetic spin-exchange interaction within each molecule. Indeed, the magnetic susceptibility obeyed the Bleaney-Bowers equation$^{9)}$ in the range 80-300 K with the magnetic parameters, g=2.10, J=-355.2 cm^{-1}, and $N\alpha=60\times10^{-6}$ cm^{3}mol^{-1} (in cgs units). This complex exhibits a stronger antiferromagnetic interaction compared with dicopper(II) complexes of H_4L^1 and H_2L^2($J \approx -330$ cm^{-1}).$^{2,6)}$

It is very noticeable that the amide groups of H_4L^3 are readily deprotonated to bind metal ions even in a weakly acidic medium, whereas most amides generally undergo such a coordination under strongly alkaline conditions.

References

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3) Yellow needles (mp>240 °C). Anal. Found: C, 63.18; H, 5.27; N, 14.56%; MS, 381. Calcd for $C_{20}H_{20}N_4O_4$: C, 63.15; H, 5.30; N, 14.73%; MW, 380.41. NMR (400 MHz, $CDCl_3$): δ 3.87 (two $-CH_2CH_2-$; bd s), 6.91 (H^b; t, J=7.7 Hz), 7.72 (H^a; q, J_{ab}=7.7 and J_{ac}=1.8 Hz), 8.34 (H^c; q, J_{cb}=7.7 and J_{ca}=1.8 Hz), 8.45 (H^α; d, J=4.4 Hz), 10.15 (OH; bd s).

4) Anal. data. [$Ni(H_2L^3)$]$\cdot H_2O$. Found: C, 53.05; H, 4.39; N, 12.07%. Calcd: C, 53.02; H, 4.45; N, 12.34%. [$Ni_2(L^3)$]$\cdot\frac{3}{2}H_2O$. Found: C, 46.23; H, 4.01; N, 10.85%. Calcd: C, 46.13; H, 3.68; N, 10.76%.

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7) Found: C, 47.56; H, 3.24; N, 11.13%. Calcd: C, 47.71; H, 3.30; N, 11.13%.

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