CHEMISTRY LETTERS, pp. 483-484, 1981.

COPPER(II) AND NICKEL(II) COMPLEXES OF A "STRATI-BIS" LIGAND, 1,2,3,4-TETRAKIS(SALICYLIDENEAMINO)-2,3-DIMETHYLBUTANE[1)]

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Copper(II) and nickel(II) complexes of a new binucleating ligand 1,2,3,4-tetrakis(salicylideneamino)-2,3-dimethylbutane (H_4sata), Cu_2(sata)2.5H_2O and Ni_2(sata)2H_2O, have been prepared and characterized. Electronic and ESR spectra indicated that there operates a magnetic interaction between the copper ions in Cu_2(sata)2.5H_2O, suggesting a stacking between the two CuN_2O_2 planes.

Synthesis of binucleating ligands whose donating sites are separated by 3-7 Å from each other is of importance for model study on bimetallic enzymes. As one of such ligands, we have prepared 1,2,3,4-tetrakis(salicylideneamino)-2,3-dimethylbutane (abbreviated as H_4sata) which contains two "salen"-like moieties combined at the carbon atom of the bridging chain. This ligand formed binuclear complexes, Cu_2(sata)2.5H_2O and Ni_2(sata)2H_2O.

1,2,3,4-Tetraamino-2,3-dimethylbutane was synthesized by the $LiAlH_4$ reduction of 2,3-diamino-2,3-dimethylsuccinonitrile, which was obtained by the reaction of 2,3-dihydroxy-2,3-dimethylsuccinonitrile and ammonia. The tetramine is either meso- or dl-isomer, but its configuration is unknown at present. Reaction of the tetramine and salicylaldehyde in a 1:4 mole ratio gave H_4sata as yellow crystals. Metal complexes were synthesized by reacting H_4sata and a metal(II) acetate in a 1:2 mole ratio in ethanol. Cu_2(sata)2.5H_2O formed brownish purple needles. Found: C, 55.70; H, 4.61; N, 7.54%. Calcd: C, 55.88; H, 4.83; N, 7.67%. Ni_2(sata)-2H_2O formed orange needles. Found: C, 57.20; H, 4.72; N, 7.90%. Calcd: C, 57.35; H, 4.81; N, 7.87%. These complexes may have either the "en"-chelated or the "tn"-chelated structure given in Fig. 1.

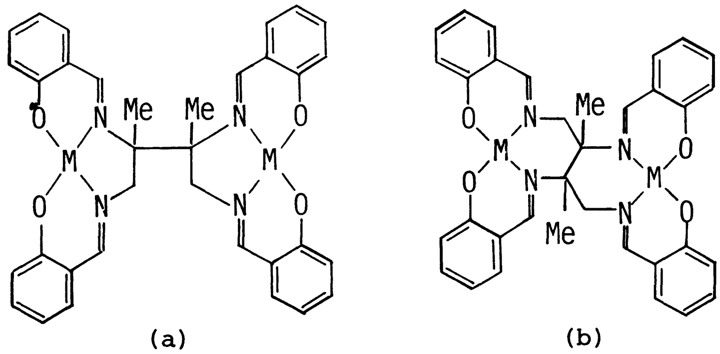

Fig. 1. Possible structures for M_2(sata): (a) "en"-chelated and (b) "tn"-chelated structures.

Electronic spectra of $Cu_2(sata)2.5H_2O$ and $Ni_2(sata)2H_2O$ are given in Fig. 2. The figure also includes the spectra of Cu(salpn) and Ni(salpn)[2,3] ($salpn^{2-}$= N,N'-disalicylidene-1,2-propylenediamine anion) for comparison. The contour and frequency of the spectrum of $Cu_2(sata)2.5H_2O$ much resemble those of Cu(salpn), demonstrating the "en"-chelated structure for $Cu_2(sata)2.5H_2O$. The π-π^* transition originating from the azomethine group[2,4] of $Cu_2(sata)2.5H_2O$ is found at 26,100 cm^{-1}, which is lower by 1,200 cm^{-1} than that of Cu(salpn). This suggests that two CuN_2O_2 moieties are in a close proximity so as to cause an interaction between them. ESR spectrum of $Cu_2(sata)2.5H_2O$ in tetrachloroethane at room temperature differs from that of Cu(salpn) and showed a band around 3360 G ($G=10^{-4}T$) and a sharp band at 1630 G. The intensity of the latter band observed at ca. 80K is much higher than that at room temperature. Hence, it is likely that the band at 1630 G is due to the transition of $\Delta M_s=\pm 2$ within the spin-triplet state generated by a ferromagnetic spin-spin coupling between the two copper(II) ions.[5] Cryomagnetic measurement added a strong support to this assumption, i.e., the magnetic moment per one copper atom for $Cu_2(sata)2.5H_2O$ increased from 1.87 BM to 1.94 BM as lowering temperature from room temperature to liquid nitrogen temperature. On the basis of these facts, we assume that $Cu_2(sata)2.5H_2O$ has a structure in which two CuN_2O_2 planes are stacked, in spite of possible rotation of these planes about the C_2-C_3 bond of the tetramine.

$Ni_2(sata)2H_2O$ is diamagnetic and shows a very similar electronic spectrum to that of Ni(salpn). This indicates that the complex takes the "en"-chelated structure but not "tn"-chelated structure.

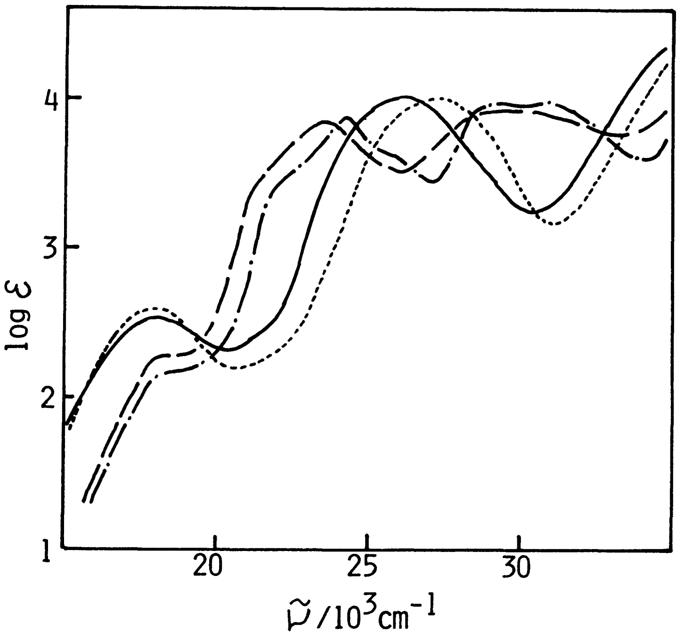

Fig. 2. Electronic spectra of
(———)$Cu_2(sata)2.5H_2O$,
(— —)$Ni_2(sata)2H_2O$,
(-------)Cu(salpn), and
(—·—)Ni(salpn)

References

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(Received January 29, 1981)