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New Dinucleating Ligand, N,N'-Ethylenebis(3-carboxysalicylamine), and Its Dinuclear Copper(II) and Nickel(II) Complexes

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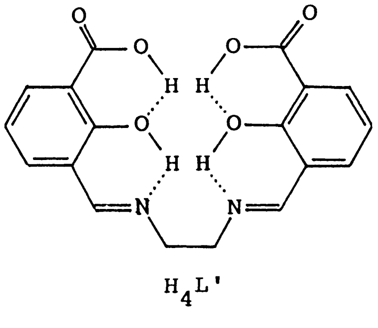
A new dinucleating ligand N,N'-ethylenebis(3-carboxysalicylamine) (H_4L) has been prepared and its copper(II) and nickel(II) complexes $[Cu_2(L)]2H_2O$ and $[Ni_2(L)(H_2O)_4]$, were obtained. A significant antiferromagnetic spin-exchange interaction operated in the copper complex through the phenolic bridge ($J=-270$ cm^{-1}), whereas no spin-exchange interaction was observed for the nickel complex.

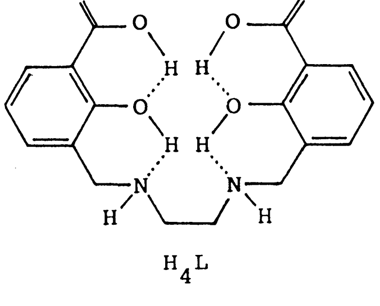
Discrete heterodinuclear complexes are of current interest in view of magnetic interaction between different metal ions and as models of active sites of some metalloenzymes.1) One of the most excellent dinucleating ligands is N,N'-ethylenebis(3-carboxysalicylideneimine) (H_4L'), which can form heterodinuclear and mixed-spin homodinuclear complexes bridged by the phenolic oxygens.2) In this study we have prepared a new ligand N,N'-ethylenebis(3-carboxysalicylamine) (H_4L), the reduced analog of H_4L'. It is expected that H_4L functions as a dinucleating ligand but forms metal complexes differing from those of H_4L' in coordination geometry and electronic configuration.

H_4L' was reduced with $NaBH_4$ in ethanol, and the resulted H_4L was separated as lead(II) salt. The salt was treated with 1 M (mol dm^{-3}) sulfuric acid, and the resulting precipitate ($PbSO_4$) was filtered. The aimed ligand was obtained from the filtrate as dihydrogensulfate.3)

The ligand salt was dissolved in an aqueous solution of LiOH. To this solution was added an aqueous solution of twice molar amount of copper(II) sulfate pentahydrate or nickel(II) sulfate hexahydrate to give greenish blue $[Cu_2(L)]2H_2O$ or $[Ni_2(L)(H_2O)_4]$, respectively.4)



H_4L'



H_4L

In the copper complex no coordination of the water molecules was inferred from the IR band at 3520 cm^{-1} (on nujol mull). The reflectance spectrum showed two bands at 16100 and 13400 cm^{-1}, which are attributable to the d-d bands of the CuN_2O_2 and CuO_4 chromophores, respectively. The corresponding bands for the copper(II) complex of H_4L', $[Cu_2(L')]2H_2O$,[2a] were found at 18100 and 13400 cm^{-1}. Thus, the reduction of the azomethine linkage of H_4L' resulted in the significant red-shift of the ligand field band of the copper(II) ion bound at the N_2O_2 site. The complex shows a subnormal magnetic moment (0.98 μ_B) at room temperature and is practically diamagnetic near liquid nitrogen temperature when the temperature-independent paramagnetism is taken into consideration. The temperature variation of the susceptibility was determined in the range 80-300 K. The result was well simulated with the Bleaney-Bowers equation,[5)]

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[\ 1 + \frac{1}{3}\exp(-2J/kT)\ \right]^{-1} + N\alpha,$$

where each symbol has its usual meaning. The magnetic parameters determined by the best-fit technique are $J=-270$ cm^{-1}, $g=2.10$, and $N\alpha=60\times10^{-6}$ $cm^3 mol^{-1}$. The result demonstrates a very strong antiferromagnetic spin-exchange interaction between the metal ions.

In $[Ni(L)(H_2O)_4]$ the coordination of the water molecules was suggested by the observation of ν(O-H) bands at 3380 and 3250 cm^{-1}, indicating a pseudo-octahedral configuration around the metal. In accord with this structure the reflectance spectrum showed two d-d bands centered at 15600 and 9700 cm^{-1}. Hence, both the metal ions are paramagnetic (3.19 μ_B), making a marked contrast with the nickel complex of H_4L', $[Ni_2(L')(H_2O)_2]2H_2O$,[2a)] where the nickel(II) ion at the N_2O_2 site is of low-spin. The magnetic moment of the present complex showed little temperature-dependence down to liquid nitrogen temperature.

From the above discussions it is expected that H_4L forms heterodinuclear complexes containing high-spin nickel(II) ion at the N_2O_2 site.

References
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2) a) M. Tanaka, M. Kitaoka, H. Ōkawa, and S. Kida, Bull. Chem. Soc. Jpn., 49, 2469 (1976); b) H. Ōkawa, Y. Nishida, M. Tanaka, and S. Kida, ibid., 50, 127 (1977); c) N. Torihara, H. Ōkawa, and S. Kida, Chem. Lett., 1978, 1269, and references therein.
3) Found: C, 42.25; H, 5.31; N, 5.32%. Calcd for $H_4L\cdot H_2SO_4\cdot 3H_2O$: C, 42.19; H, 5.51; N, 5.47%.
4) Copper complex. Found: C, 41.49; H, 3.91; N, 5.32%. Calcd for $[Cu_2(L)]2H_2O$: C, 41.62; H, 3.88; N, 5.39%. Nickel complex. Found: C, 39.96; H, 4.25; N, 5.08%. Calcd for $[Ni_2(L)(H_2O)_4]$: C, 39.61; H, 4.43; N, 5.13%.
5) B. Bleaney and K. D. Bowers, Proc. R. Soc. London, Ser. A, 214, 451 (1952).

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