

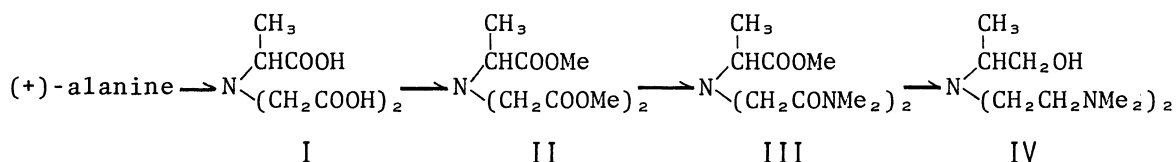
FIVE-COORDINATED COMPLEXES CONTAINING
AN OPTICALLY ACTIVE LIGAND

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Copper(II), nickel(II), and cobalt(II) complexes containing (+)₅₄₆-2-[bis(dimethylaminoethyl)amino]-1-propanol were prepared. The CD spectra of these complexes in nitromethane were measured between 10000-26000 cm⁻¹.

Many reports on five-coordinated complexes have been published, but few ones have been found on the five coordinated complexes containing a chiral ligand. Recently, we prepared a tripodal ligand, (+)₅₄₆-2-[bis(dimethylaminoethyl)amino]-1-propanol (abbreviated as "HL") and found that it formed five-coordinated complexes with divalent transition-metal ions.

The ligand was prepared through the preparation scheme given below. The compounds, I and II, were prepared by the reported methods.^{1,2)} The diamide, III, was obtained by heating the solution of II and (CH₃)₂NH in CH₃OH at 40°C for 4 days. Prolonged heating or heating at elevated temperature (60-70°C) gave some undefined substances. Reduction of III with LiAlH₄ afforded IV; bp 60-61.5°C/130 Pa; [α]₅₄₆ = +16.0 (2% H₂O); ¹³C-NMR (H₂O, 30°C) δ(rel intensity) = 12.45(23), 45.49(100), 49.10(42), 58.11(45), 58.68(28), and 64.32(25).



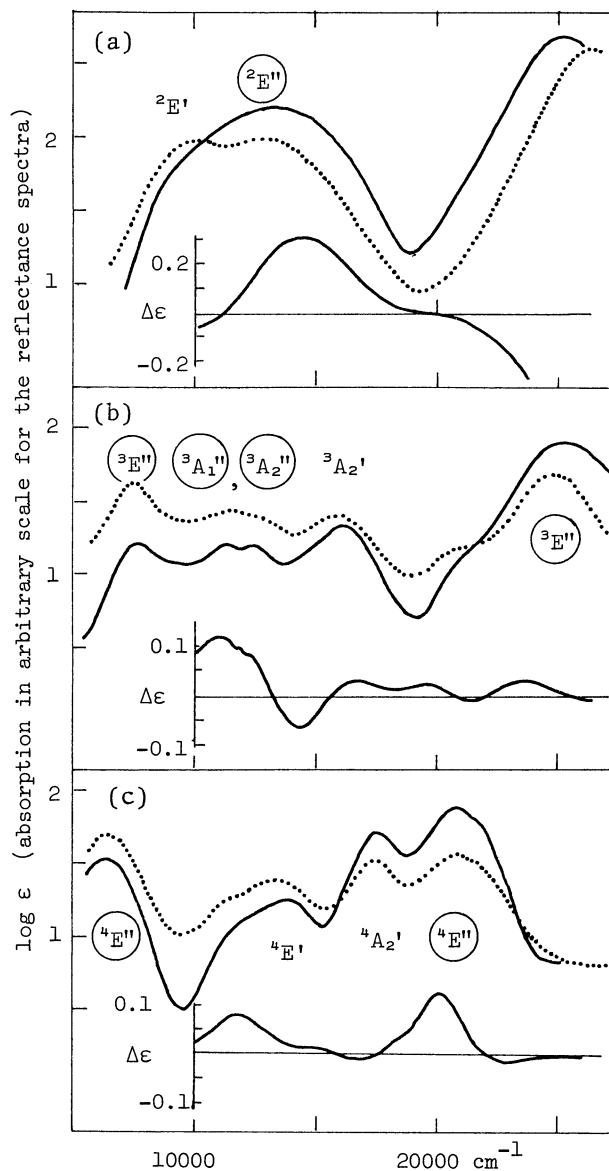
Copper(II), nickel(II), and cobalt(II) complexes were prepared by adding sodium hydroxide solution to the mixture of metal perchlorate and IV in water with a molar ratio of 1:1:1. Copper and cobalt complexes were recrystallized from hot acetonitrile and nickel complex from hot nitromethane. [Cu(L)]₂(ClO₄)₂. Found: Cu, 16.72; C, 36.63; H, 7.02; N, 10.98%. Calcd for C₂₂H₅₂N₆O₁₀Cl₂Cu₂: Cu, 16.75; C, 34.83; H, 6.91; N, 11.08%. μ_{eff} = 1.30 BM (18°C). [α]₅₈₉ = -190 (0.2% CH₃NO₂). [Ni(L)]₂(ClO₄)₂. Found: Ni, 15.50; C, 34.94; H, 6.99; N, 11.28%. Calcd for C₂₂H₅₂N₆O₁₀Cl₂Ni₂: Ni, 15.68; C, 35.28; H, 7.00; N, 11.22%. μ_{eff} = 3.05 BM (18°C). [α]₅₈₉ = -9.0 (0.2% CH₃NO₂). [Co(L)]₂(ClO₄)₂. Found: Co, 15.68; C, 34.78; H, 6.99; N, 11.33%. Calcd for C₂₂H₅₂N₆O₁₀Cl₂Co₂: Co, 15.73; C, 35.26, H, 6.99; N, 11.21%. μ_{eff} = 4.28 BM (18°C). [α]₅₈₉ = +34.4 (0.2% CH₃NO₂).

Each complex ion was also isolated as tetraphenylborate, magnetic and spectral properties of which were very similar to those of corresponding perchlorate. Thus, coordination of perchlorate ion can be excluded. Nevertheless, these complexes exhibit the solid reflectance spectra typical of five-coordinated complexes, as is shown in Fig. 1. Therefore, dimeric structure is assumed for each complex. This is consistent with the low magnetic moment of them, especially of the copper complex.

Fig. 1 also shows the AB and CD spectra of the complexes in nitromethane. The AB spectra reveal that these complexes are also five-coordinated in solution. Moreover, trigonal-bipyramidal geometry should be assigned to these complexes.³⁾ Each transition is assigned on the basis of D_{3h} symmetry.⁴⁾ The circled states on the figure are the excited states, to which magnetic dipole transitions are allowed from the ground state under D_{3h} symmetry. The observed CD spectra do not correspond well with the expected transitions. This should mainly be due to low symmetry of the complex ions.

Preparation of more symmetrical ligand and its complexes is now in progress.

Fig. 1. AB and CD spectra of $[ML]_2(ClO_4)_2$ in nitromethane: a, Cu; b, Ni; and c, Co. Dotted lines are the reflectance spectra.



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References and Note

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