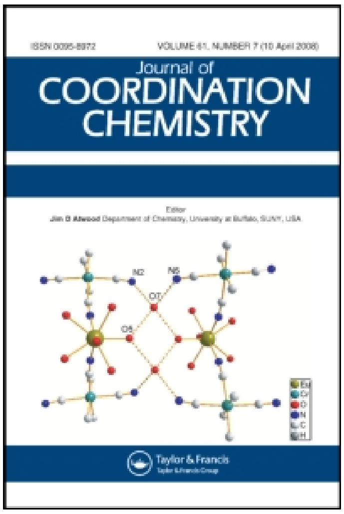

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Copper(II)-Lanthanoid(III) Hetero-Metal Binuclear Complexes of Compartmental Ligand, N, N'-Bis(3-Carboxy-Salicylidene) Ethylenediamine

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COPPER(II)-LANTHANOID(III) HETERO-METAL BINUCLEAR COMPLEXES OF COMPARTMENTAL LIGAND, N,N'-BIS(3-CARBOXYSALICYLIDENE)ETHYLENEDIAMINE

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Abstract The title complexes have been newly synthesized for the lanthanoid ions except for Ce and Pm. The effect of lanthanoid ions on the ligand field of copper(II) ion are discussed on the basis of electronic spectra.

Keywords: Lanthanoid ions, electronic spectra

INTRODUCTION

Although many studies have been reported on the hetero-metal binuclear complexes of compartmental ligands containing two different d-transition metal ions,[1-11] there are few investigations on the hetero-metal binuclear complexes containing a d-transition metal ion and a lanthanoid ion.[12]

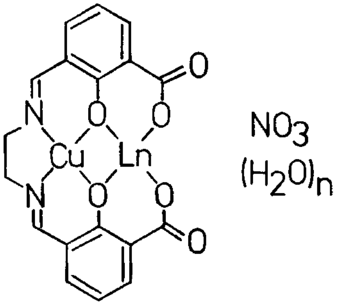

FIGURE 1 The chemical structure of CuLn(fsaen)$(NO_3)(H_2O)_n$.

In this work we have prepared copper(II)-lanthanoid(III) complexes of N,N'-bis(3-carboxysalicylidene)ethylenediamine (H_4fsaen) which was reported as a binucleating ligand possessing dissimilar coordination sites by Okawa et al.[1] (Fig. 1). The optical property of the copper(II) ion bound at the N_2O_2-site was examined using a series of lanthanoid ions as the second metal ion at the O_4-site.

PREPARATION

Copper(II)-lanthanoid(III) hetero-metal binuclear complexes were obtained by the addition of lanthanoid(III) nitrate hydrate in methanol to a methanolic solution of the mononuclear copper(II) complex,[13] $[Cu(H_2fsaen)](H_2O)_{0.5}$, and lithium hydroxide monohydrate. Elemental analyses demonstrated the compositions of the binuclear complexes obtained to be $CuLn(fsaen)(NO_3)(H_2O)_4$ for Ln = La - Gd and $CuLn(fsaen)(NO_3)(H_2O)_5$ for Ln = Tb - Lu, respectively.

ELECTRONIC SPECTRA

The absorption maximum of the ligand field band due to copper(II) ion is summarized in Fig. 2. The nujol mull spectra show the band at $(18.6 - 19.5) \times 10^3$ cm^{-1} for the binuclear complexes; the frequency is higher than that for the mononuclear copper(II) complex (18.2×10^3 cm^{-1}). Such a blue shift of the d-d band may be attributed to the enhanced planarity of the $[CuN_2O_2]$ chromophore on forming a binuclear complex with a second lanthanoid ion at the O_4-site.[2]

When the mononuclear copper(II) complex was dissolved in pyridine(Py), dimethylsulfoxide(DMSO), or N,N-dimethylformamide(DMF), the frequencies of the band maxima are in the following order: DMF > DMSO > Py. This order is reverse to that of the affinity of the solvent molecule as the apical ligand to the copper(II) ion. The frequencies are, on the other hand, in the order of DMSO > DMF > Py for the binuclear complexes. Since pyridine has a high affinity for copper(II) ion but probably a low affinity for lanthanoid(III) ions, the pyridine molecule coordinates selectively to the copper (II) ion to result in the shift of the d-d band toward lowest wave number side. On the other hand, DMSO and DMF are considered to coordinate preferentially to the lanthanoid ions rather than the copper(II) ion. The coordinated solvent molecules may hinder the approach of other solvent molecules to the copper(II) ion due to high coordination number of lanthanoid ions. Such a shielding must be more effective in DMSO than in DMF because the former solvent coordinates more strongly to lanthanoid(III) ions.

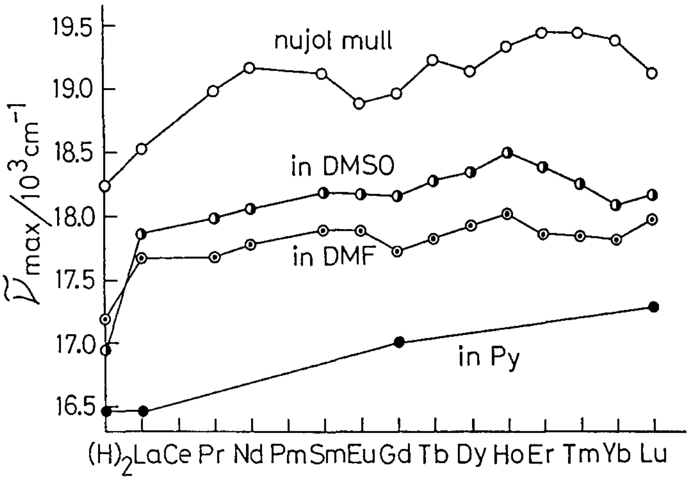

FIGURE 2 The d-d band absorption maxima of $[Cu(H_2fsaen)](H_2O)_{0.5}$ and $CuLn(fsaen)(NO_3)(H_2O)_n$. $(H)_2$, La, ..., and Lu of abscissa denote the mononuclear copper(II), copper(II)-lanthanum(III), ..., and copper(II)-lutetium(III) binuclear complexes, respectively.

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