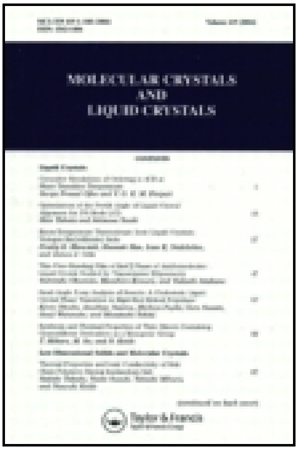

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Mono and Trinuclear Metal Complexes Containing an N_3O_3-Type Tripodal Ligand

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Mono and Trinuclear Metal Complexes Containing an N_3O_3- Type Tripodal Ligand

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Mononuclear and trinuclear nickel(II) and copper(II) complexes containing the N_3O_3-type ligand (H_3L), obtained by condensation of 1,1,1-tris(aminomethyl)ethane and salicylaldehyde (1 : 3), were synthesized. Two mononuclear nickel(II) complex units ([Ni(HL)]) are aggregated due to hydrogen bonding between the phenol group of one unit and the phenolate group of the other to give a dimer with homochirality. The trinuclear nickel(II) complex, $[Ni_3L_2]$ consists of three face-sharing octahedra. Three nickel(II) ions form a linear array. Two terminal nickel(II) ions are coordinated octahedrally by L. The central and two terminal nickel(II) ions are bridged by six phenolate oxygen atoms. In the mononuclear square-planar copper(II) complex, [Cu(HL)], one arm of the tripodal ligand is not coordinated to the metal. On the basis of the absorption spectra of the copper(II) complexes, the coordination geometry around each copper ion of the trinuclear complex is assigned to be square planar and copper ions will be bridged by L.

Keywords: tripodal ligand; trinuclear complex; homochiral pair; heterochiral pair

INTRODUCTION

The tripodal H_3L ligand (Fig. 1) prepared by condensation of 1,1,1-tris(aminomethyl)ethane and salicylaldehyde (1 : 3) has an *open-* or *half-cage* structure.[1] The ligand will afford six-coordinated octahedral complexes upon coordination.[2] The ligand also appears to be potentially suited to polynuclear binding through bridging by the phenolate oxygen atoms and this has led us to investigate its coordination chemistry. Herein we report three new findings on metal complexes of H_3L. The first finding is the formation of the dimeric nickel(II) complex, $[\{Ni(HL)\}_2]$; two mononuclear units aggregate due to hydrogen bonding between the phenol group of a unit and the phenolate group of the other one to give a dimeric complex with homochirality (Δ-Δ or Λ-Λ).[3] The second finding is the occurrence of the trinuclear nickel(II) complex, $[Ni_3L_2]$, which consists of three face-sharing octahedra. The last finding is the formation of the four-coordinated square-planar copper(II) complex, $[Cu(HL)]$ where one of the three arms of the tripodal ligand is not bound to the copper(II) ion.

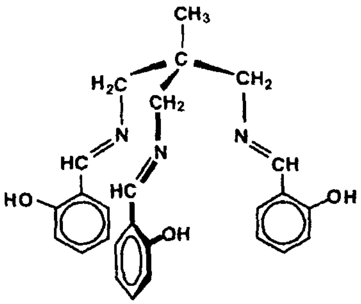

FIGURE 1. The H_3L ligand.

RESULTS AND DISCUSSION

Nickel(II) Complexes

We could obtain two kinds of nickel(II) complexes. When nickel(II) perchlorate hexahydrate in ethanol was allowed to react with the H_3L ligand (1 : 1) in chloroform, we obtained a bluish green complex. The complex was recrystallized from chloroform. The elemental analysis revealed that the ligand is not fully deprotonated, and that the complex involves both chloroform and water molecules as solvents of crystallization ([Ni(HL)]·$CHCl_3$·$2H_2O$).

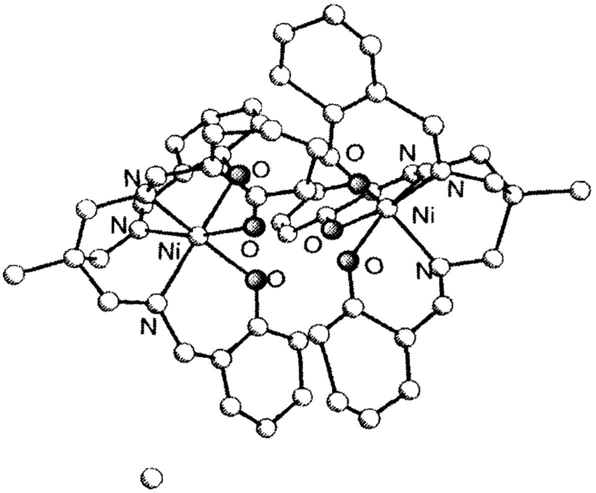

FIGURE 2. Dimeric structure of [Ni(HL)]·$CHCl_3$·$2H_2O$.

Figure 2 shows the molecular structure of the complex determined by the X-ray method. The coordination geometry around the nickel(II) ion is approximately octahedral. The complex has a dimeric structure, and the two molecules are linked by hydrogen bonding. The distance between the two hydrogen-bonding oxygen atoms is about 2.5 Å. When two chiral molecules associate to form a dimeric structure, homochiral (Δ-Δ or Λ-Λ) and heterochiral (Δ-Λ) pairs are possible. Both mononuclear units shown in Fig. 2 have the Δ configuration. Thus, this is a homochiral Δ-Δ pair. Examination of molecular models indicates that the heterochiral pair involves severe steric repulsion between the units. On the other hand, strong hydrogen bonding is possible in the homochiral pair. Moreover, in the homochiral pair, aromatic rings in two neighboring molecules can stack efficiently. Since the complex crystallizes in a centrosymmetric space group $P2_1/n$, molecules with the Δ-Δ pair and the Λ-Λ pair coexist in the crystal to form a racemic compound. In other words, this complex does not undergo spontaneous resolution.

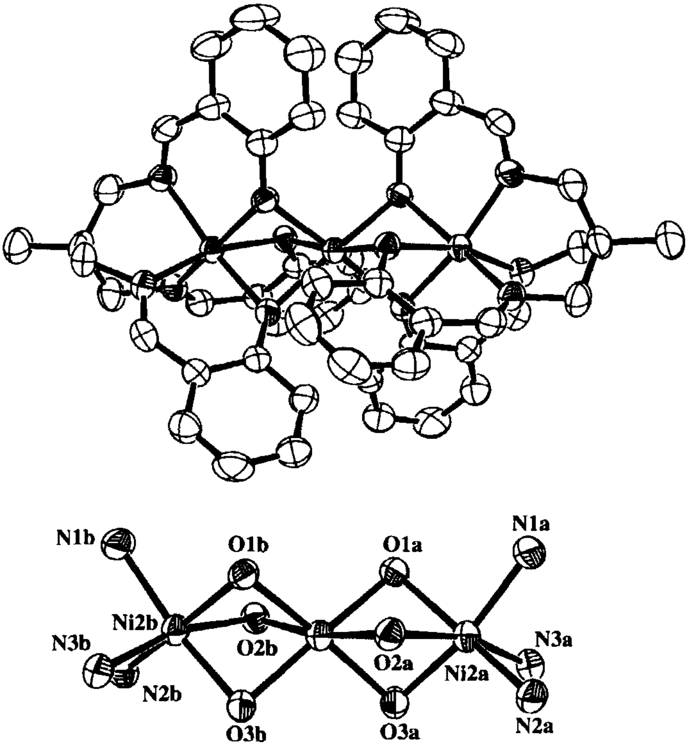

FIGURE 3. ORTEP drawing of [Ni_3L_2].

In addition to the bluish green mononuclear nickel(II) complex, we could obtain another kind of nickel(II) complex. The yellow nickel(II) complex was prepared by mixing nickel chloride with the ligand and triethylamine (3 : 2 : 6) in methanol. The complex was purified by silica gel column chromatography (eluent: ethyl acetate). At first, we expected that this yellow complex had a four-coordinated square planar structure. However, the complex was not diamagnetic as expected for the square planar complex. The mass spectrum (SIMS) showed a signal at m/z 1030.9, which indicates the trinuclear structure, $[Ni_3L_2]$. The elemental analysis was in accordance with this formulation. The magnetic moment at room temperature (5.05 μ_B) corresponds well to the spin-only value (4.90 μ_B). The trinuclear structure was confirmed by the X-ray method.

Figure 3 shows the molecular structure of the trinuclear complex, $[Ni_3L_2]$. The complex consists of three face-sharing octahedra. Three nickel(II) ions form a linear array. Two terminal nickel(II) ions are coordinated by the hexadentate tripodal ligands, and the central and terminal nickel(II) ions are bridged by six phenolate groups. Although the trinuclear molecule has a homochiral structure, the crystal contains both Δ–Δ and Λ–Λ pairs to give an achiral crystal (*C*2/*c*). The aromatic rings are stacked and the average distance between the paired rings is 3.94 Å.

Copper(II) Complexes

We prepared copper(II) complexes in the hope of obtaining

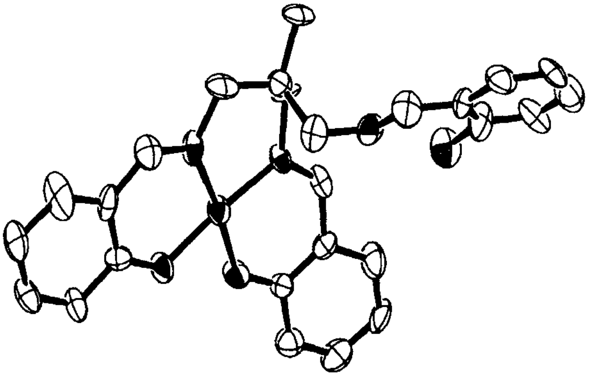

FIGURE 4. ORTEP drawing of [Cu(HL)].

complexes with other structures than six-coordinated octahedral one. A mononuclear copper(II) complex was prepared by the reaction of copper(II) perchlorate with the tripodal ligand in the presence of triethylamine (1 : 1 : 2) in ethanol. A green precipitate was purified by silica gel column chromatography (eluent: acetonitrile). The X-ray analysis (Fig. 4) revealed that the coordination geometry around the copper atom is square planar. The nitrogen and oxygen donor atoms of one arm are not coordinated to the copper atom.

In the following preparation we added more copper(II) ions than for preparation of the mononuclear complex, $CuCl_2 : H_3L : NEt_3 = 3 : 2 : 6$, and we obtained another kind of copper(II) complex. The elemental analysis was in accordance with the formulation, $[Cu_3L_2]$. The pattern of the absorption spectrum of the trinuclear complex is similar to that of the mononuclear complex. This suggests that the trinuclear copper(II) complex has a similar chromophore to that of the mononuclear complex. Although we have not determined the structure by the X-ray method, we assume that the coordination geometry around each copper ion is square planar and copper ions are bridged by the tripodal ligand.

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