A Novel Discrete d-f Heterobinuclear Complex Designed from Tetrahedrally Distorted [Cu(salabza)] (H_2salabza: *N,N'*-Bis(salicylidene)-2-aminobenzylamine) and [Gd(hfac)$_3$]

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(Received June 8, 1998; CL-980434)

Binuclear Cu(II)-Gd(III) complex, [Cu(salabza)Gd(hfac)$_3$], was synthesized by the combination of a tetrahedrally distorted Cu(II) complex, [Cu(salabza)] with [Gd(hfac)$_3$]·2H_2O, where H_2salabza and Hhfac denote *N,N'*-bis(salicylidene)-2-aminobenzylamine and *1,1,1,5,5,5*-hexafluoroacetylacetone, respectively. Structural analysis revealed that the complex has the long intermolecular metal-metal distances enough to be regarded as a discrete one.

Since heteronuclear Cu(II)-Ln(III) and Ni(II)-Ln(III) complexes (Ln: a family of lanthanides) were reported by Vidali and co-workers[1] and Abid and Fenton[2] in 1984, a number of d-f heteronuclear complexes comprising a d-transition metal ion and a lanthanide ion have been studied from the interests in developing the new functions and from the magnetic and structural interests. Most of such complexes structurally analyzed so far are polynuclear complexes including Cu_2Gd, Cu_2Gd_2, Cu_3Gd, Cu_4Gd_2, Cr_2Nd_3, Cr_3Nd, $NiYb_2$ or $NiLu_2$,[3-6] and very few reports are available on the structural determination of discrete d-f binuclear complex. Recently, two types of discrete complexes were structurally determined by two groups.[7-9] One is the Cu(II)-Gd(III) complexes reported by Costes and co-workers, where binucleating compartmental ligands possessing two dissimilar coordination sites were used.[7,8] The other is [Cu(salen)(Meim)Gd(hfac)$_3$] by Kahn and co-workers, where Meim (1-methylimidazole) coordinates to the Cu(II) of square planar [Cu(salen)] moiety as a fifth apical ligand to prevent the binuclear Cu(II)-Gd(III) units from being brought close together.[9] Thus, the number of the discrete d-f binuclear complexes is very limited. Here we report a new type of discrete binuclear complex, [Cu(salabza)Gd(hfac)$_3$], where the coordination geometry around the Cu(II) is tetrahedrally distorted so that the fifth apical ligand such as Meim is not necessary.

Complex was synthesized as follows: [Gd(hfac)$_3$]·2H_2O (0.408 g, 0.5 mmol) in a minimum quantity of methanol (1 cm^3) was added to an equivalent amount of [Cu(salabza)] (0.196 g, 0.5 mmol) in chloroform (40 cm^3). After the mixture was refluxed for 2 h and filtered, the filtrate was allowed to stand at room temperature for 5 days to give dark-green crystals suitable for X-ray analysis in 63% yield.[10,11]

The shortest intermolecular Cu-Cu, Cu-Gd, and Gd-Gd distances are 6.002(1), 7.522(1), and 8.507(1)Å, respectively, showing that the structure of the present complex consists of a discrete binuclear unit. An ORTEP view of the complex is given in Figure 1, together with the atomic numbering scheme. The Cu(II) and Gd(III) ions are bridged by the two phenolic oxygens. The Cu-Gd distance is 3.2481(8)Å which is close to that (3.252(4)Å)[9] of complex of Kahn and co-workers. However, it is shorter compared with those (3.428(1)~3.5231(4)Å)[7,8] of complexes of Costes and co-workers because of their employing the phenol-based binucleating ligands which are derived from 3-methoxysalicylaldehyde and diamines and thence are difficult to distort from the planar structure by their chemical structures. The Cu(II) ion is bound to the two imino nitrogens and the two phenolic oxygens of salabza^{2-}. The deviation of Cu(II) ion from the least-squares N_2O_2-plane formed by the four coordinating atoms is less than 0.06Å. However, the deviations of these coordinating atoms from the least-squares plane are -0.202(3)Å for O1, 0.190(3)Å for O2, 0.292(4)Å for N1, and -0.267 (4)Å for N2, and the dihedral angle between the CuO1N1 and CuO2N2 planes is 160.13°, indicating the relatively large tetrahedral distortion of the coordinating geometry around Cu(II) ion. The Gd(III) ion is of eight-coordination with six oxygens of three hfac$^-$ and two phenolic oxygens of salabza^{2-}. Four atoms

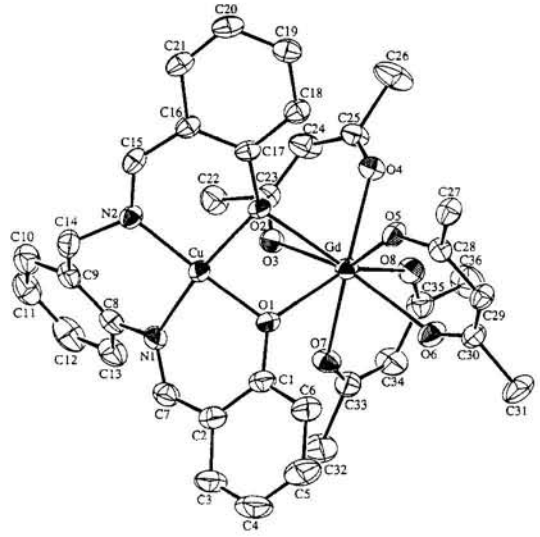

Figure 1. ORTEP view of [Cu(salabza)Gd(hfac)$_3$]. Fluorine and hydrogen atoms are ommited for clarity. Selected bond distances (Å) and angles (°): Cu-Gd 3.2481(8), Cu-O1 1.925(3), Cu-O2 1.923(3), Cu-N1 1.965(4), Cu-N2 1.914 (4), Gd-O1 2.345(3), Gd-O2 2.514(3), Gd-O3 2.369(3), Gd-O4 2.353(3), Gd-O5 2.369(3), Gd-06 2.383(3), Gd-O7 2.391(3), Gd-O8 2.367(4), O1-Cu-O2 81.5(1), O1-Cu-N1 92.1(2), O2-Cu-N2 95.7(1), N1-Cu-N2 93.9(2), O1-Gd-O2 62.2(1), O3-Gd-O4 74.1(1), O5-Gd-O6 70.6(1), O7-Gd-O8 71.1(1), Cu-O1-Gd 98.6(1), Cu-O2-Gd 93.2(1).

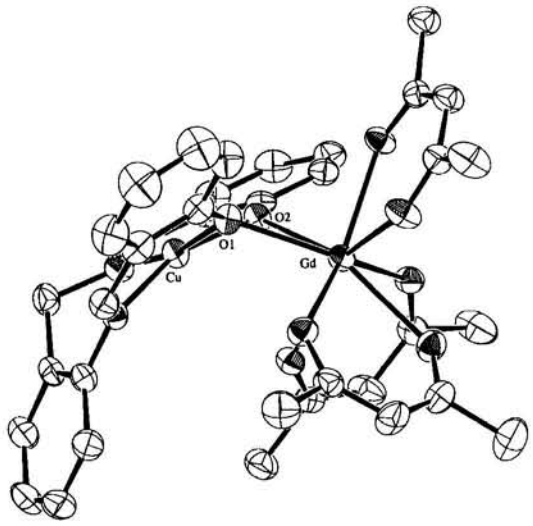

Figure 2. Side view of [Cu(salabza)Gd(hfac)$_3$].

of Cu, Gd, O1, and O2 do not lie on the same plane, as can be seen from Figure 2. The dihedral angle between the CuO1O2 and GdO1O2 planes is 132.61° .

From the above results, it is thought that the success in synthesis of a discrete binuclear complex without adding a fifth apical ligand may result from the larger distortion of the geometry around Cu(II) toward tetrahedral structure. Thus, the present work may give a new strategy for obtaining the discrete d-f binuclear complexes comprising a d-transition metal ion and a lanthanide ion. Magnetic property is under investigation. According to the preliminary data, the ferromagnetic spin-spin coupling may operate between Cu(II) and Gd(III) ions. Further syntheses are also in progress, using other d-transition metal and lanthanide ions.

References and Notes

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10 Anal. Found: C, 37.16; H, 1.73; N, 2.40%. Calcd for [Cu(salabza)Gd(hfac)$_3$], $C_{36}H_{19}N_2O_8F_{18}CuGd$: C, 36.95; H, 1.64; N, 2.39%.
11 Crystal data for [Cu(salabza)Gd(hfac)$_3$], $C_{36}H_{19}N_2O_8F_{18}$ CuGd, F.W. = 1170.32, monoclinic, space group $P2_1/n$ (#14), a = 17.354(3), b = 14.050(3), c = 17.780(3) Å, β = 105.45(1)° , V = 4178(1) Å^3, Z = 4, Dc = 1.860 g cm^{-3}, $F(000)$ = 2272, μ(MoKα) = 22.19 cm^{-1}. Cell parameters were defined by 25 reflections with $29.85 < 2\theta < 30.01$ ° 10007 unique reflections were measured with $2\theta_{max}$=55.0 ° All the measurements were made on a Rigaku AFC7R diffractometer with graphtite monochromated Mo-Kα radiation (λ=0.71069 Å) and a 12 kW rotation anode generator. The structure was solved by a direct method and refined by a full-matrix least-squares. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Final R = 0.034 and Rw = 0.040 for 6226 observed reflections ($I > 3.00\sigma(I)$).