Synthesis and Structures of Novel Discrete Ni(Ⅱ)–Ln(Ⅲ) Heterodinuclear Complexes (Ln = Gd or Lu)

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The first discrete NiLn heteronuclear complexes, [Ni(salabza)Ln(hfac)$_3$] (Ln = Gd(Ⅲ) and Lu(Ⅲ)), were synthesized, where H$_2$salabza and Hhfac denote *N*,*N*′-bis(salicylidene)-2-aminobenzylamine and 1,1,1,5,5,5-hexafluoroacetylacetone, respectively. Structural analyses revealed that the Ni(Ⅱ) and Ln(Ⅲ) ions are bridged by the two phenolate oxygen atoms of salabza^{2-} and that the shortest intermolecular separation is > 5.9 Å for the Ni–Ni distance, indicating that the present complexes consist of a discrete dinuclear NiLn unit.

Metal complexes of tetradentate salen^{2-}-like Schiff bases are well-known to act as complex ligands toward a second metal, affording a large number of heteronuclear complexes comprising different d-transition metal ions.[1] This method has been applied for the preparation of so-called 3d–4f heteronuclear complexes comprising 3d-transition metal and 4f-transition metal (Ln) ions.[2–13] Most of them are obtained as trinuclear Cu$_2$Ln and Ni$_2$Ln or tetranuclear Cu$_2$Ln$_2$ complexes,[3–7] and discrete dinuclear 3d–4f complexes are very limited.[8–10] Apparent dinuclear [Cu(salen)Gd(hfac)$_3$],[8] [Cu(acacen)Gd(hfac)$_3$][10] and [Ni(salen)Gd(hfac)$_3$][11] have been obtained, but are regarded as ‘‘tetranuclear’’ because of a short inter–dimer separation. Previously we reported that [Cu(salabza)] (H$_2$salabza = *N*,*N*′-bis(salicylidene)-2-aminobenzylamine) produces discrete CuLn heterodinuclear complexes [Cu(salabza)Ln(hfac)$_3$] (Ln = Gd and Lu).[12,13] In this work, we report on the synthesis and structures of discrete NiLn heterodinuclear complexes [Ni(salabza)Ln(hfac)$_3$] (Ln = Gd (**1**) and Lu (**2**)).

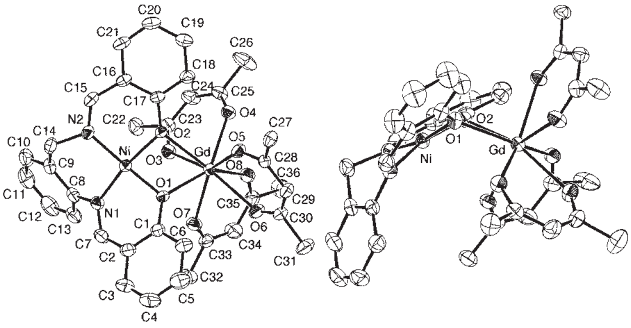

Fig. 1. ORTEP drawings of [Ni(salabza)Gd(hfac)$_3$] **1** with the atom numbering scheme. The drawing of right hand side is a side view. Selected bond lengths (Å) and angles (°): Ni–Gd 3.214(1), Ni–O1 1.869(2), Ni–O2 1.863(2), Ni–N1 1.886(3), Ni–N2 1.863(3), Gd–O1 2.347(2), Gd–O2 2.531(2), Gd–O3 2.355(3), Gd–O4 2.350(2), Gd–O5 2.370(2), Gd–O6 2.388(3), Gd–O7 2.386(2), Gd–O8 2.375(3), O1–Ni–O2 80.6(1), O1–Ni–N1 92.5(1), O2–Ni–N2 95.4(1), N1–Ni–N2 93.4(1), O1–Gd–O2 59.21(8), O3–Gd–O4 73.79(9), O5–Gd–O6 70.44(9), O7–Gd–O8 71.84(9).

ORTEP drawings of complex **1** are given in Fig. 1, together with the atomic numbering scheme. The Ni(Ⅱ) and Gd(Ⅲ) ions are bridged by two phenolate oxygen atoms, and the Ni–Gd distance is 3.214(1) Å, which is close to those (3.165(1) and 3.225(1) Å)[11] of [Ni(salen)Gd(hfac)$_3$]. The deviation of the Ni(Ⅱ) ion from the least-squares N$_2$O$_2$-plane formed by the four coordinating atoms is 0.036(2) Å, which is smaller than that (0.059 Å)[12,13] of the previous [Cu(salabza)Gd(hfac)$_3$]. The deviations of O(1) (0.156(1) Å), O(2) (−0.135(1) Å), N(1) (−0.209(2) Å) and N(2) (0.217(2) Å) coordinating atoms from the least-squares N$_2$O$_2$-plane are also smaller than the corresponding deviations (0.202(3) Å for O(1), −0.190(3) Å for O(2), −0.292(4) Å for N(1), and 0.267(4) Å for N(2)) of [Cu(salabza)Gd(hfac)$_3$]. The dihedral angle (164.91°) between the NiO(1)N(1) and NiO(2)N(2) planes is larger than the corresponding angle (160.13°) of [Cu(salabza)Gd(hfac)$_3$]. These observations are consistent with the general tendency of Ni(Ⅱ) to adopt a square-planar structure, compared with Cu(Ⅱ). The Gd(Ⅲ) ion is of eight-coordination, with six oxygen atoms of three hfac$^-$ and two phenolate oxygen atoms of salabza^{2-}. The four Ni, Gd, O(1), and O(2) atoms do not lie on the same plane, as was shown for [Cu(salabza)Gd(hfac)$_3$]. The dihedral angle between the NiO(1)O(2) and GdO(1)O(2) planes is 129.28°.

The structure of complex **2** is essentially similar to that of **1**.[14] The deviation of the Ni(Ⅱ) ion from the least-squares N$_2$O$_2$-plane formed by the four coordinating atoms is 0.042(2) Å. The deviations of atoms coordinating to Ni(Ⅱ) from the least-squares N$_2$O$_2$-plane are 0.153(1) Å for O(1), −0.138(1) Å for O(2), −0.207(2) Å for N(1) and 0.220(2) Å for N(2), and the dihedral angle between the NiO(1)N(1) and NiO(2)N(2) planes is 164.83°. All of the eight Lu–O distances are shorter than the corresponding Gd–O distances due to the lanthanide contraction. The dihedral angle between the NiO(1)O(2) and LuO(1)O(2) planes is 129.17°.

The shortest intermolecular Ni–Ni, Ni–Ln, and Ln–Ln distances are 5.945(1), 7.510(9) and 8.555(1) Å for **1** and 5.927(1), 7.455(1) and 8.635(1) Å for **2**, respectively. The intermolecular Ni–Ni distances are much longer compared with that (3.583(1) Å)[11] of [Ni(salen)Gd(hfac)$_3$] reported to be a dimer-of-dimers (NiGd)$_2$ by Gleizes et al., indicating that the structure of the present complexes consists of a isolated NiLn unit. This is the first discrete dinuclear NiLn complex synthesized using the Ni(II) complex of a tetradendate salen^{2-}-like Schiff base as a complex ligand.

Experimental

Preparation. [Ni(salabza)] was synthesized by a (1:1) reaction of nickel(II) acetate tetrahydrate and H$_2$salabza[13] in methanol.

[Ni(salabza)Gd(hfac)$_3$] 1. [Gd(hfac)$_3$]$\cdot$2H$_2$O[15] (0.408 g, 0.5 mmol) in methanol (1 cm^3) was added to an equivalent amount of [Ni(salabza)] (0.194 g, 0.5 mmol) in warm chloroform (40 cm^3). After the mixture was refluxed for 2 h and filtered, the filtrate was allowed to stand at room temperature for a few days to give dark-red crystals suitable for X-ray analysis. Yield: 0.204 g (35%) (Found: C, 37.10; H, 1.67; N, 2.33%. Calcd for $C_{36}H_{19}N_2O_8F_{18}NiGd$: C, 37.10; H, 1.64; N, 2.40%).

[Ni(salabza)Lu(hfac)$_3$] 2. The synthetic method was similar to that for **1**, except that [Lu(hfac)$_3$]$\cdot$2H$_2$O[15] was used instead of [Gd(hfac)$_3$]$\cdot$2H$_2$O. Yield: 0.237 g (40%) (Found: C, 36.75; H, 1.77; N, 2.42%. Calcd for $C_{36}H_{19}N_2O_8F_{18}NiLu$: C, 36.54; H, 1.62; N, 2.37%).

X-ray Crystallography. All of the measurements were made on a Rigaku AFC5S diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). The data were collected at 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 55.0° at a scan speed of 8.0°/min (in omega). The structures were solved by a direct method, and expanded using a Fourier technique. The non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the structure factor calculations, but not refined. The final cycle of the full-matrix least-squares refinement of **1** and **2** was based on 6477 and 6579 observed reflections ($I > 3.00\sigma(I)$), and 703 and 632 variable parameters, respectively. The crystallographic parameters are as follows: for **1**, $C_{36}H_{19}N_2O_8F_{18}NiGd$, MW = 1165.48, crystal size 0.25 × 0.20 × 0.25 mm, crystal system monoclinic, space group $P2_1/n$ (no. 14), $a = 17.259(2)$, $b = 14.037(2)$, $c = 17.917(3)$ Å, $\beta = 104.49(1)°$, $U = 4202(1)$ Å^3, $Z = 4$, μ(Mo-Kα) = 21.48 cm^{-1}, no. reflection collected 10367, no. unique reflection 10125, $R_{\text{int}} = 0.025$, $R = 0.031$, $R_{\text{w}} = 0.032$. For **2**, $C_{36}H_{19}N_2O_8F_{18}NiLu$, MW = 1183.19, crystal size 0.20 × 0.15 × 0.25 mm, crystal system monoclinic, space group $P2_1/n$ (no. 14), $a = 17.198(3)$, $b = 14.027(7)$, $c = 17.858(3)$ Å, $\beta = 105.24(1)°$, $U = 4156(2)$ Å^3, $Z = 4$, μ(Mo-Kα) = 29.47 cm^{-1}, no. reflection collected 10278, no. unique reflection 10010, $R_{\text{int}} = 0.018$, $R = 0.031$, $R_{\text{w}} = 0.034$. All calculations were performed using the TEXSAN crystallographic software package from Molecular Structure Corporation.[16] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 203153–203154.

Measurements. Elemental analyses of C, H and N were carried out at the Service Center of Elemental Analysis, Kyushu University.

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