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The Structure of Diaquatris(1,1,1-trifluoro-2,4-pentanedionato)neodymium(III)-Acetone (1/1)

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Synopsis. The crystal and molecular structure of the title complex was determined by means of the single-crystal X-ray diffraction method. The crystal of $NdC_{18}H_{22}O_9F_9$, F.W. 697.59, is orthorhombic, with a space group *Pbna*, a=22.068(5), b=22.293(4), c=11.020(2) Å, U=5421(2) Å^3, Z=8, D_m=1.72(3), D_x=1.71 Mg m^{-3}, and μ(Mo $K\alpha$)=20.46 cm^{-1}. The central metal atom is octa-coordinated, being ligated with six β-diketonato and two water oxygen atoms, and is in a dodecahedral geometry. Two configurational isomers co-exist in the crystal, with the respective occupancy factors of 74 and 26%. In these isomers, the two chelate rings span in different ways; although the positions of all ligating oxygen atoms are the same, the chelates span two m-edges in one isomer and two g-edges in the other one.

Although the structures of some β-diketonato complexes of lanthanoids(III) have already been reported, the coordination geometry and the spanned edges of the chelate rings have been found to be diverse. For example, in $M(acac)_3(H_2O)_2$ (where M=La, Pr, or Nd; Hacac=2,4-pentanedione), the central metal atom is in a square-antiprism geometry (octa-coordinated), and the chelate ligands span square edges.[1-3] On the other hand, in $Nd(tta)_3(Ph_3PO)_2$ (where Htta=4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione; Ph_3PO=triphenylphosphine oxide), the central metal is in a dodecahedral geometry (octa-coordinated), and the ligands span one m-edge and two g-edges.[a,4] In $NH_4Pr(tta)_4 \cdot H_2O$ and $(C_9H_8N)[Ce(tta)_4]$, all the ligands span g-edges and m-edges respectively.[5,6] Although 1,1,1,-trifluoro-2,4-pentanedione (Htfa) is a ligand which gives several interesting types of complexes,[7,8] few structural data about its lanthanoid complexes have yet been reported. Therefore, we have determined the structure of the title complex by the single-crystal X-ray diffraction technique.

Experimental

Single-Crystal X-Ray Analysis. The crystals of the title complex were obtained by the slow evaporation of the complex in an acetone–water mixed solvent (4:1=v/v). (The crude product was obtained by a reaction between the metal hydroxide and Htfa, as was the isomorphous lanthanum(III) complex.) Anal. ($MC_{18}H_{22}O_9F_9$, where M=La, or Nd), M, C, H. The crystal used for the structure determination was about 0.3×0.3×0.2 mm^3 in size, and was used without shaping. The reflections in the range of $3° < 2\theta < 60°$ were collected on a Rigaku AFC-6A automated four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation, by means of the ω—2θ scan technique (scan speed 4° min^{-1}; scan width, $1.30+0.5 \tan\theta°$). The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption and extinction. Among the 8731 independent reflections collected, 3611 with $|F_o| > 3\sigma(|F_o|)$ were used for the structure determination. All the calculations were carried out on a HITAC M-280H computer at the Computer Center of the University of Tokyo, using the local version of the UNICS.[9] The scattering factors were taken from Ref. 10.

The structure was solved by the heavy-atom method. It was found that the crystal is composed of mixture of two configurational isomers. As is shown in Fig. 2, except for the common ligand (**1**), the Type A complexes include the ligands of F(21, 22A, 23A), C(21, 22A, 23A, 24A, 25), and O(21, 22) (**2A**) and F(31A, 32, 33A), C(31, 32A, 33A, 34A, 35), and O(31, 32) (**3A**), while the Type B complexes include those of F(21, 22B, 23B), C(21, 22B, 23B, 34B, 35), and O(21, 32) (**2B**) and F(31B, 32, 33B), C(31, 32B, 33B, 24B, 25), and O(31, 22) (**3B**). The probabilities of the occupancy of both types of complexes were first approximately assigned from the intensities of the atoms belonging to the respective types of ligands, and were then refined by means of the full-matrix least-squares procedure; the final occupancy factors for the type A and B complexes are 73.6(18)% and 26.4% respectively.

At the final refinement process, the positions of the seven fluorine atoms as well as the two acetone carbon atoms were fixed assuming B_{iso}=11.0. For the other atoms, except for O(AC) and C(A1), the anisotropic temperature factors were applied; the final R value[11] thus obtained was 0.066.

NMR Measurements. ^{1}H-NMR and ^{13}C-NMR spectra of the isomorphous lanthanum(III) complex were obtained by means of a Varian EM 390 NMR spectrometer and a JEOL FX90Q Fourier Transform NMR spectrometer, using the acetone-d_6 solution and TMS as the internal standards.[a]

Results and Discussion

The selected interatomic distances and bond angles are shown in Table 1.[12] A perspective drawing of the complexes in Type A is shown in Fig. 1. The schematic presentation showing the positions of the ligating atoms and of the spanning ligands, together with the numbering scheme of the ligands is shown in Fig. 2.[12]

. The central metal atom is octa-coordinated and is in a little deformed dodecahedral geometry. The chelating ligand **1**, which spans an m-edge, is common to both types of the species, while the other two ligands span in different ways; in Type A species, the ligands, **2A** and **3A**, span m-edges, but in

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a) The isomorphism was checked from their powder X-ray diffraction patterns.

Table 1. Selected Bond Lengths and Bond Angles, with Estimated Standard Deviations in Parentheses

Bond length	l/Å	Bond length	l/Å	Bond length	l/Å
Nd-O(11)	2.411(8)	Nd-O(12)	2.393(8)	Nd-O(21)	2.366(9)
Nd-O(22)	2.460(8)	Nd-O(31)	2.372(8)	Nd-O(32)	2.455(8)
Nd-O(W1)	2.477(10)	Nd-O(W2)	2.498(9)	O(11)-C(12)	1.260(15)
O(12)-C(14)	1.264(15)	C(12)-C(13)	1.383(18)	C(13)-C(14)	1.386(15)
O(21)-C(22A)	1.20(2)	O(22)-C(24A)	1.32(2)	C(22A)-C(23A)	1.40(3)
C(23A)-C(24A)	1.43(3)	O(31)-C(32A)	1.23(2)	O(32)-C(34A)	1.283(19)
O(32A)-C(33A)	1.39(3)	C(33A)-C(34A)	1.40(2)	O(21)-C(22A)	1.11(4)
O(32)-C(34A)	1.30(4)	C(22B)-C(23B)	1.46(6)	C(23B)-C(34B)	1.27(6)
O(31)-C(32B)	1.17(5)	O(22)-C(24B)	1.32(4)	C(32B)-C(33B)	1.42(7)
C(33B)-C(24B)	1.36(6)	O(AC)···O(W1^i)	2.736(19)		
Bond angle	**ϕ/°**	**Bond angle**	**ϕ/°**	**Bond angle**	**ϕ/°**
O(11)-Nd-O(12)	70.5(3)	O(21)-Nd-O(22)	70.7(3)	O(31)-Nd-O(32)	70.5(3)
O(21)-Nd-O(32)	72.3(3)	O(31)-Nd-O(22)	72.7(3)	O(W1)-Nd-O(W2)	67.9(3)
O(11)-Nd-O(21)	97.9(3)	O(11)-Nd-O(31)	143.5(3)	O(11)-Nd-O(22)	74.9(3)
O(11)-Nd-O(32)	145.4(3)				

Key to the symmetry operation: i, x, y, $1+z$.

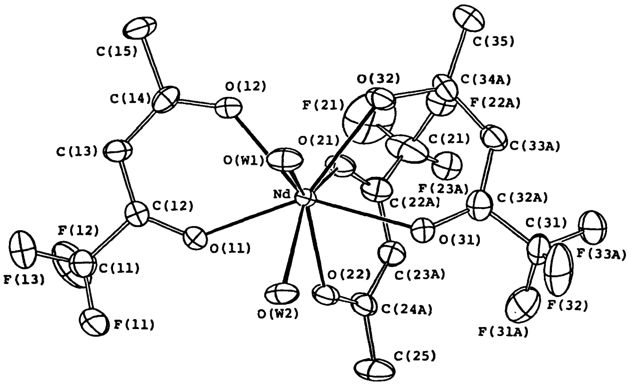

Fig. 1. A perspective drawing of Type A complex with the numbering scheme.

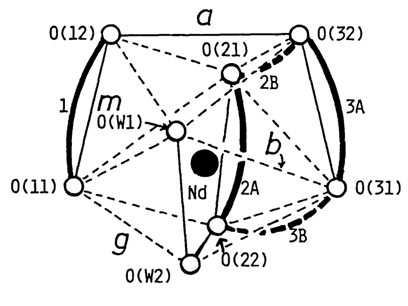

Fig. 2. Schematic presentation of the complex about the coordination geometry, with the numbering scheme of the chelating ligands (**1**, **2A**, and **3A** for Type A, and **1**, **2B**, and **3B** for Type B complex, respectively).

the Type B species, the ligands, **2B** and **3B**, span g-edges. In the chelate ring **1**, the two Nd-O bond lengths, 2.411(8) and 2.393(8) Å, are not much different from each other. On the other hand, in all the other chelate rings, the Nd-O(nl) lengths are shorter than the corresponding Nd-O(n2) ones. The Nd-O bond lengths to the coordinated water oxygen atoms are longer than those to the β-diketonato oxygen atoms. In view of the positions of O(11), O(21), and O(31), the trifluoromethyl groups of the ligands may be said to take the positions most separated from each other around the metal atom. Although the positions of all the atoms of the ligands were found, their thermal parameters, especially those of the fluorine atoms, were relatively large, probably because they are distributed around the most probable positions, respectively.

The NMR data of the isomorphous lanthanum(III) complex are as follows: ^{1}H-NMR (acetone d_6), δ=2.00 (9H, s, CH_3 of tfa), 2.10 (6H, s, CH_3 of acetone), 4.01 (4H, s, H_2O), 5.68 (3H, s, CH). ^{13}C-NMR (acetone-d_6), δ=28.8 (m, CH_3 in acetone), 29.9 (m, CH_3 in acetone-d_6), 96.1 (d, J_{CH}=146 Hz, CH), 169.1 (q, J_{CF}=31 Hz, CO(CF_3 side) of tfa), 197.3 (s, CO(CH_3 side) of tfa), 206.9 (s, CO of acetone), 120.1 (q, J_{CF}=290 Hz, CF_3). Judging from these data, the β-diketone in this complex can be said to be of the enol-type. As the peaks are all sharp, and as no splittings were found, a rapid exchange of the ligands can be expected between the two types of species in the solution at the ambient temperature (25 °C).

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11) $R=\sum||F_o|-|F_c||/\sum|F_o|$.

12) A perspective drawing of the complex B, the crystal packing diagram, the final atomic and thermal parameters, the final F_o-F_c table, and some additional data about the bond lengths and bond angles are deposited as Document No. 8602 at the Office of the Bull. Chem. Soc. Jpn.