Novel Structural Transformation around Ln(III) and Unusual Bending of Acetylacetonato Chelate in A Series of New 3d–4f Dinuclear Complexes [(hfac)$_3$Ln(μ-bpypz)Cr(acac)$_2$]

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A new series of discrete [(hfac)$_3$Ln(μ-bpypz)Cr(acac)$_2$] dinuclear complexes has demonstrated the novel Ln^{III} ion size depedent structural transformation around Ln^{III} as well as diastereospecifically assembled chiral configuration along with the unusual bending of the acetylacetonate chelate ring in Cr^{III}.

In general, isoleptic Ln^{III} complexes exhibit the ion size dependent change of the coordination number (CN) as found for [Ln(hfac)$_3$(bpy or phen)$_n$] (hfac = hexafluoromethylacetylacetonate: from $n = 1$ (Yb) to 2 (La)).[1] However, some examples for the structural modification by the ion size in mononuclear complexes with the identical CN have recently been reported. Mizukami et al. postulated possibility of fine adjustment of helical structure of a series of isostructural Ln^{III} complexes by the Ln ion size leading to intentional control of helices or sheets in nanostructures.[2] Further Bombieri et al. demonstrated the structural variations of macrocyclic Ln^{III}(DOTA) complexes.[3] We have found subtle polyhedral change in a series of [Ln(hfac)$_3$(IM2py)],[4] but currently discovered polyhedral variation with CN change from 7 to pseudo 8 in a series of 4f–4f dinuclear complexes [(HBpz$_3$)Ln(μ-pba)$_4$Ln(HBpz$_3$)] (pba = *S*- and *R*-phenylbutyrate).[5] On the other hand, the 3d–4f heteropolymetallic complexes[6] have been extensively studied to improve physicochemical properties with much interest. There seem to be little Ln ion size dependent structural variations not only in kinetically inert optically active Cr^{III}–Ln^{III} self-assembled triple-stranded podates,[7] but also in the podate Fe^{II}–Ln^{III} complexes even associated with the fine control of the iron(II) spin-state equilibria.[8] No significant structural change was found in our three series of 3d–4f tri- and dinuclear [Ni(μ-tdo or -edo){Ln(HBpz$_3$)$_2$}$_2$][9] and [(acac)$_2$Cr(μ-ox)Ln(HBpz$_3$)$_2$].[10–12]

It could be invaluable to explore structural transformation between different configurations along a series of 3d–4f dinuclear complexes, since it is expected to provide invaluable information on integrated intramolecular interactions in relation with physicochemical properties including chiroptical spectra.

This letter will report novel stereochemistry and emission properties of new discrete bpypz bridged Ln–Cr dinuclear complexes [(hfac)$_3$Ln(μ-bpypz)Cr(acac)$_2$] (Ln = Ce (**1**), Er (**2**), Yb (**3**)) which were prepared from [Ln(hfac)$_3$(H$_2$O)$_2$] and a "complex ligand" [Cr(acac)$_2$(bpypz)].[14] As shown in Figure 1, the X-ray structural analysis[15] of the complexes **1** and **3** demonstrated a distorted six coordinate octahedral *OC*-6 Cr^{III} and an eight coordinate bicapped trigonal prismatic *TPRS*-8 Ln^{III} configuration comprising two caps (O5 and O10) on the lateral faces (O7–O8–O6–O9 and O7–O9–N3–N4). One of three hfac chelates (O9–O10) and bpypz chelate (N3–N4) occupy the almost same positions in the TPRS for the complexes **1**, **2**, and **3**, whereas the connections of the remaining two hfac chelates in **1** are different from those in **2** and **3**, demonstrating two kinds of the *TPRS*-8 Ln^{III} configuration which are classified into the A and B forms (schematic views in Figure 1). Although the four oxygen ligators (O5,O6,O7,O8) of the two hfac chelates are located at the same vertices of the TPRS, the chelations between the O5 and O8 are interchanged: O6–O8 and O7–O5 for two hfac's in the complex **1** (A form). O6–O5 and O7–O8 for two hfac's in the complexes **2** and **3** (B form). The preliminary X-ray analysis revealed a mixture of two disordered A and B forms in the Sm^{III}–Cr^{III} and Nd^{III}–Cr^{III} complexes with medium Ln size.[16] Thus, it is seen that the smaller the Ln ionic radius becomes, the more dominant the B form in the Ln^{III}–Cr^{III} complexes becomes. In other words, there occurs an unique ion size dependent structural transformation with configurational changes along the present series of Ln–Cr complexes. As for the absolute configurations around the Yb^{III} or Er^{III} and Cr^{III} of which the definitions (Figure 1) are proposed for convenience assuming the pseudo square antiprism and for the octahedron, respectively, each two of four molecules in the unit cell have the Δ_{Ln}–Λ_{Cr} and Λ_{Ln}–Δ_{Cr} diastereomeric pairs, but not the (Δ_{Ln}–Δ_{Cr}) and (Λ_{Ln}–Λ_{Cr}) ones, indicating diastereospecific assembly with configurational chilarity without asymmetric carbon as found for (Λ_{Ln}–Δ_{Cr})-[(acac)$_2$Cr(μ-ox)Ln(HBpz$_3$)$_2$].[10–12] The similar situation is encountered for the complex **1**, though the definition for the absolute configuration around the Ce ion is somewhat different from that around the Yb ion (Figure 1). It is anticipated to synthesize inert chiral Ln moiety of the present Ln–Cr complexes in solutions by using optically resolved [Cr(acac)$_2$-

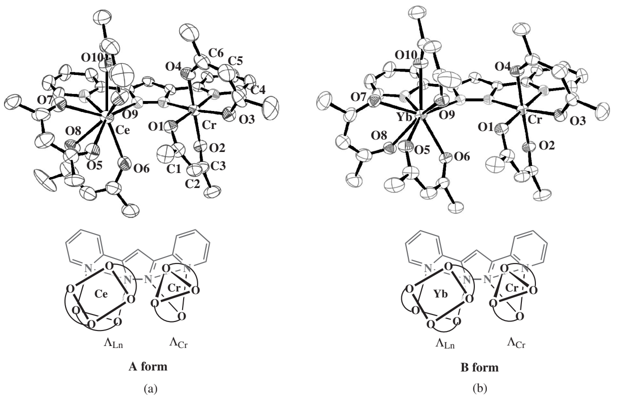

Figure 1. ORTEP drawings and schematic views of the complex **1** a (A form) and **2** b (B form) with the configuraional chirality difinition.

(bpypz)] as revealed for the Cr(μ-ox)Ln complexes.[11,12]

Another structural characteristic is found for stereochemistry around the acetylacetonate chelate ring. That is, one of the two acac chelates around Cr bends away from the proximate hfac chelate with an unusually larger torsion angle (Cr–O1–C1–C2) as compared with that(ca. 4°) for the other acac chelate (Cr–O3–C4–C5). The torsion angles are $-21.1(10)^\circ$ and $-21.9(8)^\circ$ for the complexes **3** and **2**, respectively, and $-29.4(11)^\circ$ for the complex **1**, which is the largest to our knowledge. In view of the bond distances and angles in the bent acac chelate, the π-conjugated system seems to retain. Moreover, it is seen that the torsion angles become the larger with increasing the Ln^{III} ion size in the Ln(μ-bpypz)Cr complexes, suggesting to synchronize the structural transformation from B to A form. Such a large bending in the acac chelate or structural transformation may result from steric requirement in the bridging moieties as inferred from shortening of nonbonding Ln$\cdots$O1 distances (from 3. 86 Å (**3**) to 3.16 Å (**1**)) and/or triangular van der Waals contacts among O1, O6, and O9 or a π–π stacking (C$\cdots$C = 3.45–3.7 Å) between the hfac and acac in complexes **2** and **3** of the B form. Since there is no π–π stacking in the complex **1** of the A form even with the largest acac bending, this stacking does not necessarily bring about the bending. Therefore, the steric congestion due to shortening of the interatomic distances or contacts plays an important role for such structural specificity of the acac chelate and/or structural transformation. It is noted that the Ln$\cdots$O1 distance shortening reflects the increasing tendency of the CN with increasing the Ln^{III} ion size as if there were an attractive force between Ln and O1 as found for [(HBpz$_3$)Ln(μ-*RS*-pba)$_4$Ln(HBpz$_3$)].[5] More understanding must wait systematic X-ray and spectroscopic (NMR and chiroptical) examinations for a series of the Ln–Cr complexes, which are in progress in our laboratory.

As presumed from the fact that the Yb^{III}–Cr^{III} distance (4.65 Å) in the complex **3** is shorter than that (5.63 Å) in [(acac)$_2$Cr(μ-ox)Yb(HBpz$_3$)$_2$],[9] the luminescence behaviors are different from each other. The complex **3** gives only the strong 4f–4f emission near 1000 nm even at 10 K with the excitation at 488 nm (Ar^+ laser), showing the fast energy transfer, in contrast to [(acac)$_2$Cr(μ-ox)Yb(HBpz$_3$)$_2$] which exhibits the low temperature simultaneous 3d–3d and 4f–4f emissions with the energy transfer from Cr^{III} to Yb^{III}.[13]

In conclusion, a series of the discrete Ln(μ-bpypz)Cr complexes exhibits the Ln ion size dependent structural transformation and acac bending due to subtle interplay between the intraligand interactions, leading to characteristic physicochemical properties.

References and Notes

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14 Preparation of [Cr(acac)$_2$(bpypz)]$\cdot$C$_2$H$_5$OH: The reaction of an equimolar mixture of [Cr(acac)$_2$(H$_2$O)$_2$]Cl and Hbpypz in ethanol at room temperature followed by adding acetonitrile gave pink powder. Orange precipitate was obtained by the addition of Et$_3$N to the solution of the pink powder. Calcd (Found) for $C_{23}H_{29}O_5N_4Cr$: C, 58.02 (57.53); H, 5.65 (5.52); N, 10.83 (10.88)%. Preparation of [(hfac)$_3$Ln(μ-bpypz)Cr(acac)$_2$](Ln = Ce (**1**), Er (**2**), Yb (**3**)) : To a chloroform solution (10 mL) of [Cr(acac)$_2$(bpypz)]$\cdot$C$_2$H$_5$OH (0.2 mmol) was added [Ln(hfac)$_3$(H$_2$O)$_2$] (0.2 mmol) and the mixed solution was stirred for a day. Slow evaporation after addition of a small amount of hexane to this solution gave violet crystals except for the brown complex **1**. Calcd (Found) for $C_{38}H_{26}N_4O_{10}F_{18}CeCr$: C, 37.03 (37.21); H, 2.13 (2.04); N, 4.55 (4.63)%. $C_{38}H_{26}N_4O_{10}F_{18}ErCr$: C, 36.23 (36.28); H, 2.08 (1.99); N,4.45 (4.49)%. $C_{38}H_{26}N_4O_{10}F_{18}YbCr$: C, 36.06 (36.05); H, 2.07 (1.99); N, 4.43 (4.49)%.

15 All measurements were made on a Rigaku Mercury CCD area detector with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71070$) at 300 ± 1 K. Chemical formula, crystal systems, space group, and No. of formula units in unit cell for the **1**, **2**, and **3** complexes are all identical; $C_{38}H_{26}N_4O_{10}F_{18}Ln_1Cr_1$, monoclinic, $P2_1/c$ (No. 14), $Z = 4$, respectively. The other data as follows: for **1**, $M_r = 1232.73$, $a = 12.289$ (1) Å, $b = 17.472$ (2) Å, $c = 22.450$ (2) Å, $\beta = 95.020$ (4)°, $V = 4801.9$ (7) Å^3. 62643 reflections measured, 10893 unique used in all calculations. Final $R_1 = 0.0669$; for **2**, $M_r = 1259.87$, $a = 12.4546$ (9) Å, $b = 17.268$ (1) Å, $c = 22.126$ (2) Å, $\beta = 98.299$ (3)°, $V = 4708.7$ (6) Å^3. 62744 reflections measured, 10405 unique used in all calculations. Final $R_1 = 0.0445$; for **3**, $M_r = 1265.65$, $a = 12.4407$ (8) Å, $b = 17.230$ (1) Å, $c = 22.013$ (2) Å, $\beta = 98.322$ (3)°, $V = 4668.9$ (5) Å^3. 62472 reflections measured, 10650 unique used in all calculations. Final $R_1 = 0.0393$.

16 Occupancies of the A and B forms were estimated to be about 70% and 30%, respectively, for the Cr–Sm complex. The 50% occupancy for both forms was found for the Cr–Nd complex.

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