Structure and Luminescence Properties of the Tetradentate β-Diketonate–Europium(III) Complexes

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The luminescence properties of Eu^{3+} complexes with a series of tetradentate β-diketones were compared and it was found that the Eu^{3+} complexes of bis(β-diketonyl)-*o*-terphenyl type ligands have stronger luminescence. The crystal structure determination of the Eu^{3+} complex with 4,4″-bis(4,4,4-trifluoro-1,3-dioxobutyl)-*o*-terphenyl (H_2btbt) showed that the complex is dinuclear having a unique cage structure.

Recently several new chlorosulfonylated tetradentate β-diketonate–Eu^{3+} luminescent complexes that can be directly bound to proteins were synthesized, and their applications in highly sensitive time-resolved fluoroimmunoassay were studied.[1] In the present work, a series of tetradentate β-diketones of the types bis(β-diketonyl)-1,1′-biphenyl, bis(β-diketonyl)dibenzothiophene and bis(β-diketonyl)-*o*-terphenyl, were synthesized (Figure 1).[2] The luminescence properties of their Eu^{3+} complexes were measured and summarized in Table 1. All of the complexes give the emission maximum wavelengths at 611 or 612 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} ion. In contrast to the almost identical emission maximum wavelengths, the excitation maximum wavelengths (330–360 nm) of the complexes are dependent on the ligand structures. In the 4,4′-bis(β-diketonyl)-1,1′-biphenyl and 4,4′-bis(β-diketonyl)-*o*-terphenyl complexes, substitution of CF_3 to C_2F_5 causes noticeable increase in the luminescence intensity, but further change of the C_2F_5 to C_3F_7 (or C_4F_9) does not increase the intensity.[3] Compared with the bidentate β-diketonate (TTA) and other tetradentate β-diketonate complexes, the Eu^{3+} complexes with 4,4′-bis(β-diketonyl)-*o*-terphenyl type ligands have stronger luminescence and long luminescence lifetime. Although the Eu^{3+} complex of 4,4″-bis(4,4,5,5,6,6,6-heptafluoro-1,3-dioxohexyl)-chloro-sulfo-*o*-terphenyl (BHHCT) is an excellent label in immunoassay,[1] its chlorosulfonyl group is unstable and the Eu^{3+} complex is not suitable for structural analysis. The crystal structure of the Eu^{3+} complex of BTBT, the analogue of BHHCT, was solved in the present study to examine the relation of the coordination structure with luminescence property and to help the ligand design.

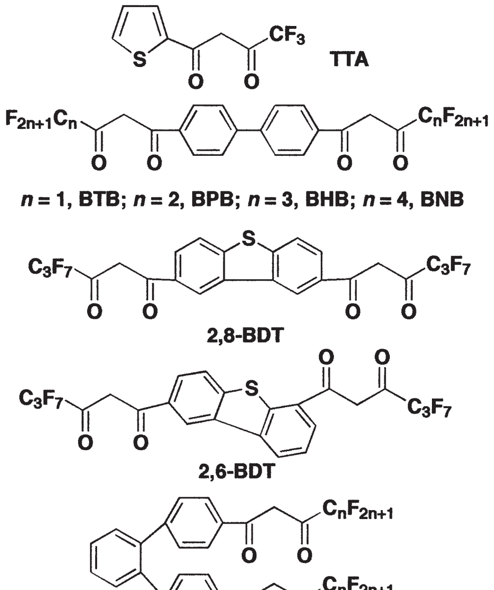

Figure 1. Structures and abbreviations of the β-diketones.

Table 1. Luminescence properties[a] of the Eu^{3+} complexes

Ligands	$\lambda_{ex,max}$/nm	$\lambda_{ex,max}$/nm	Normalized intensity	Lifetime /μs
TTA	340	612	30.6	624
BTB	349	612	29.5	267
BPB	349	612	38.2	301
BHB	349	612	37.7	300
BNB	349	612	37.3	302
2,8-BDT	350	612	32.0	495
2,6-BDT	356	611	38.9	508
BTBT	331	611	78.5	648
BPPT	333	612	100.0	655
BHHT	334	612	100.0	661

[a]Luminescence properties were measured with the concentration of [ligand] = $[Eu^{3+}] = 1.0 \times 10^{-5}$ mol dm^{-3} in acetonitrile-0.1% triethylamine.

After an acetone solution of $H_2[Eu_2(btbt)_4]\cdot C_2H_5OH$[4] was diffused against petroleum ether (30–60 °C fraction) containing 0.3% triethyl-amine, thin yellow plate crystals of the complex with the formula of $[HN(C_2H_5)_3]_2[Eu_2(btbt)_4]\cdot C_2H_5OH$ were obtained.[5] The crystal structure (Figure 2)[6] shows that the complex is dinuclear, and the four btbt^{2-} ligands bridge the two Eu^{3+} ions with bidentate coordination to each Eu^{3+}. Each Eu^{3+} ion is coordinated by eight oxygen atoms of the four btbt^{2-} ligands, and has a square antiprism coordination geometry. One $[HN(C_2H_5)_3]^+$ ion and an ethanol molecule are incorporated in the center of the cage formed by btbt^{2-} and Eu^{3+} ions, and another $[HN(C_2H_5)_3]^+$ ion exists in the crystal lattice.

In the structure, the oxygen atom of the ethanol molecule is disordered (O17A and O17B in Figure 2b), and is directed to N1 of $[HN(C_2H_5)_3]^+$ by an O···H–N hydrogen bonding (O17A-

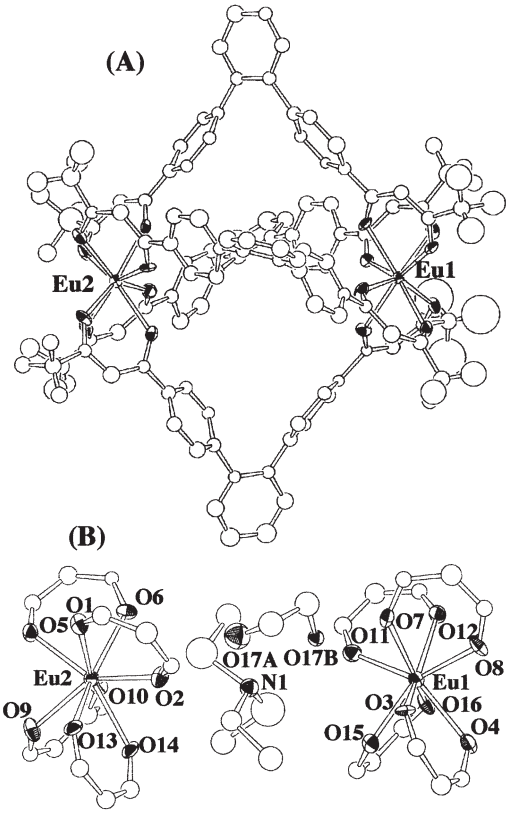

Figure 2. ORTEP drawing of $[HN(C_2H_5)_3]_2[Eu_2(btbt)_4]{\cdot}C_2H_5OH$. The ellipsoids are drawn at 30% probability level. (A) Overview. The disordered CF_3 groups, one $[HN(C_2H_5)_3]^+$ ion and an ethanol molecule are omitted for clarity. (B) The coordination environment of the Eu^{3+}, $[HN(C_2H_5)_3]^+$, and the ethanol molecule in the cage. The $btbt^{2-}$ ligands are omitted except the diketonate moiety for clarity.

N1, 2.80 (8) Å; O17B-N1, 2.76 (5) Å). The average distances of the C–O bonds in $btbt^{2-}$ are $\text{distance}_{\text{outer}} = 1.23$ (4) Å and $\text{distance}_{\text{inner}} = 1.28$ (4) Å. The average O–Eu bond distances are $\text{distance}_{\text{outer}} = 2.41$ (2) Å and $\text{distance}_{\text{inner}} = 2.38$ (2) Å. All the X-ray structures reported for Eu^{3+}-β-diketonate chelates are for monomeric complexes. The distinct angle of the two β-diketonate groups in $btbt^{2-}$ enables such a novel cage structure. Although the structure was determined at −50 °C, several disorders are observed in the lattice, and the R value is not very low.

The Eu–O (β-diketonato ligand) distance is reported to affect the luminescence efficiency;[7] the luminescence quantum yield is increased as the distance of the triplet energy donor (β-diketonato ligand) and Eu^{3+}, i.e. the Eu–O distance, is decreased. The present Eu–O distances are comparable to those reported in other [Eu(β-diketonato)$_3$(diamine)] type complexes.[7,8] All of the previously reported structures are of this tris(β-diketonato) formula type, and the present complex is the first tetrakis(β-diketonato) complex, in which the Eu^{3+} is surrounded only by β-diketonato oxygen atoms. The site symmetry of Eu^{3+} is often related to the relative intensities of $^5D_0 \rightarrow {}^7F_0$ (ca. 580 nm), $^5D_0 \rightarrow {}^7F_1$ (ca. 595 nm), and $^5D_0 \rightarrow {}^7F_2$ (ca. 610 nm).[7] Both [Eu(β-diketonato)$_3$(diamine)] type complexes and the present Eu_2(β-diketonato)$_4$ complex and others in Table 1 have the same emission spectral pattern with the dominantly strong $^5D_0 \rightarrow {}^7F_2$ single peak without splitting. This fact suggests that in both types of complexes, the site symmetry is C_1 and the emission is based on electric dipole transition.

References and Notes

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2 All β-diketones were synthesized by the Claisen condensation reaction in dry ether in the presence of $NaOCH_3$. The products were recrystallized from ethanol or 1,4-dioxane. Anal. Calcd for $C_{20}H_{12}F_6O_4$ (BTB): C 55.82, H 2.81. Found: C 55.74, H 2.85. Anal. Calcd for $C_{22}H_{12}F_{10}O_4$ (BPB): C 49.82, H 2.28. Found: C 49.95, H 2.11. Anal. Calcd for $C_{24}H_{12}F_{14}O_4$ (BHB): C 45.73, H 1.92. Found: C 45.72, H 1.91. Anal. Calcd for $C_{26}H_{12}F_{18}O_4$ (BNB): C 42.76, H 1.66. Found: C 42.76, H 1.41. Anal. Calcd for $C_{24}H_{10}F_{14}O_4S$ (2,8-BDT): C 43.65, H 1.53. Found: C 43.91, H 1.40. ^{1}H NMR ($CDCl_3$): δ 8.88 (d, $J = 1.65$ Hz, 2H), 8.09 (dd, $J = 1.65$, 8.58 Hz, 2H), 8.03 (d, $J = 8.58$ Hz, 2H), 6.80 (s, 2H). Anal. Calcd for $C_{26}H_{14}F_{14}O_5S$ [2,6-BDT(1,4-dioxane)$_{0.5}$]: C 44.33, H 2.00. Found: C 44.69, H 1.81. ^{1}H NMR ($CDCl_3$): δ 8.84 (s, 1H), 8.60 (dd, $J = 0.99$, 7.58 Hz, 1H), 8.20 (d, $J = 7.59$ Hz, 1H), 8.09 (s, 2H), 7.74 (t, $J = 7.45$ Hz, 1H), 6.93 (s, 1H), 6.78 (s, 1H), 3.71 (s, 4H, 1,4-dioxane). Anal. Calcd for $C_{26}H_{16}F_6O_4$ (BTBT): C 61.60, H 3.19. Found: C 61.68, H 3.32. Calcd for $C_{28}H_{16}F_{10}O_4$ (BPPT): C 55.46, H 2.66. Found: C 55.71, H 2.54. Calcd for $C_{30}H_{16}F_{14}O_4$ (BHHT): C 51.00, H 2.28. Found: C 51.20, H 2.41.

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4 Prepared by reacting H_2btbt with $EuCl_3$ (1:1) in ethanol.

5 Anal. Calacd for $Eu_2C_{118}H_{94}F_{24}N_2O_{17}$: C 55.10, H 3.68, N 1.09. Found: C 55.31, H 3.47, N 0.99.

6 Crystal data for $[HN(C_2H_5)_3]_2[Eu_2(btbt)_4]{\cdot}C_2H_5OH$: $Eu_2C_{118}H_{94}F_{24}N_2O_{17}$, Mr = 2571.91, monoclinic, space group $P2_1/c$ (no. 14), $a = 25.546$ (6) Å, $b = 19.84$ (2) Å, $c = 24.96$ (1) Å, $\beta = 107.02$ (2)°, $V = 12094$ (13) Å^3, Z = 4, $D_{\text{calcd}} = 1.417$ g/cm^3, $T = -50 \pm 1$ °C, $R = 0.139$, $R_w = 0.320$, GOF = 2.24. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-194988. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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