Crystal Structure of a Luminescent Complex Sm(HTH)$_3$Phen

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The crystal structure of Sm(HTH)$_3$Phen [HTH: 4,4,5,5,6,6,6-heptafluoro-1-(2-thienyl)-1,3-hexanedione, Phen: 1,10-Phenanthroline] has been determined by single crystal X-ray diffraction and the coordination geometry of Sm atom is a dodecahedron. The complex can give the characteristic luminescence of Sm^{3+} upon UV excitation.

The design of complexes of lanthanide ions with organic ligands is an interesting field of research. The importance of lanthanide ions is related to the particularities of their luminescence emissions, which is characterized by long decay times and narrow band emission spectra.[1,2] Lanthanide β-diketonate chelates have long been known to give intense emission lines upon UV light irradiation due to the effective intramolecular energy transfer from the coordinating ligands to the central lanthanide ions. The structure of rare earth complexes is essential to understand the energy transfer from β-diketone to the central rare earth ions. Therefore, a considerable number of these complexes with various β-diketonates have been structurally characterized by X-ray crystallography since 1970's.[3,4]

Our interest concerned synthesis and characterization of a novel ternary lanthanide HTH complex with Phen (Sm(HTH)$_3$Phen, HTH: 4,4,5,5,6,6,6-heptafluoro-1-(2-thienyl)-1,3-hexanedione, Phen: 1,10-Phenanthroline) and the structure of the complex, in particular to determine whether the inductive effect of the ligand-fluorine atoms would be reflected in the structure of the complex in comparison to analogous β-diketone complexes. Therefore, in this study, the structure was determined and UV/Vis, luminescence spectra were measured. In addition, the difference in structure between the title complex and Eu(TTA)$_3$Phen was also compared.

The synthesis of Sm(HTH)$_3$Phen was referred to a previous report.[5] The complex was dissolved in ethanol solution. The crystal was formed in the resulting solution which stayed for two months at room temperature. The structure was solved by direct methods and difference Fourier methods using the program SHELXTL 5.01 and refined by full-matrix least-squares procedures based on F. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were located in a difference Fourier map. Final $R = 0.0709$, $wR2 = 0.1946$.

The projection of the structure of Sm(HTH)$_3$Phen is shown in Figure 1. Crystallographic parameters are listed in Note 9. The analysis of crystal structure indicates that the central Sm^{3+} is eight-coordinated. Six coordinated oxygen atoms are from three HTH ligands and two nitrogen atoms are from Phen. The samarium-oxygen bond distances vary between 2.339 Å and 2.396 Å. In each group, the samarium-oxygen bond distances adjacent to the thienyl ring are slightly longer than the other, however, as for Eu(TTA)$_3$Phen (TTA=thenoyltrifluoroacetone),[6] only one group is the case, the other two groups are contrary to this. This is probably due to more fluorine atoms in HTH than those in TTA, and therefore the inductive effect of fluorine atoms of the ligand HTH is stronger. The average samarium-oxygen distance is 2.374 Å and the average samarium-nitrogen distance is 2.608 Å. The carbon-carbon bond distances in the chelate ring vary between 1.350 Å and 1.426 Å, which are shorter than the single bond distance but longer than the double bond distance. It shows that there exists conjugated structure between thienyl ring and coordinated β-diketonate, which leads to the delocalization of electron density of the coordinated β-diketonate structure. However, the carbon-carbon bond distances near the fluorine atoms are close to the C=C bond, which is due to the inductive effect of the fluorine atom group. The central Sm^{3+} is surrounded by bulky anion ligands HTHs and synergistic ligand Phen and this encapsulated structure can meet the structural requirement of the samarium luminescent sensor:[7] protection metal ions from vibrational coupling and increase light absorption cross section by "antenna effects".

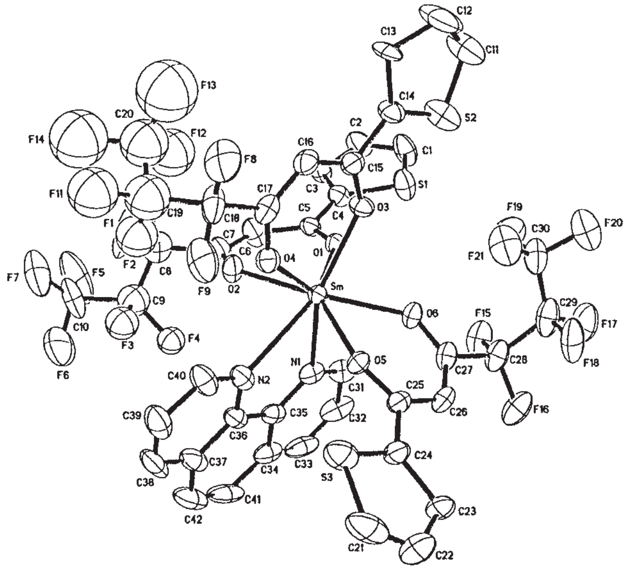

Figure 1. Projection of the structure of Sm(HTH)$_3$Phen with the used labeling scheme. Selected bond distances(Å): Sm–O(2), 2.339(5); Sm–O(4), 2.367(5); Sm–O(3), 2.378(5); Sm–O(6), 2.378(5); Sm–O(5), 2.395(5); Sm–O(1), 2.384(5); Sm–N(1), 2.601(6); Sm–N(2), 2.615(7); O(1)–C(5), 1.236(8); O(2)–C(7), 1.235(10); O(3)–C(15), 1.275(9); O(4)–C(17), 1.285(10); O(5)–C(25), 1.278(8); O(6)–C(27), 1.274(9); C(5)–C(6), 1.422(11); C(6)–C(7), 1.370(13); C(15)–C(16), 1.406(12); C(16)–C(17), 1.356(13); C(25)–C(26), 1.413(11); C(26)–C(27), 1.359(12).

Eight-coordinate polyhedron usually has two types: the square antiprism and the triangular dodecahedron. It is difficult to distinguish them because of their similarity. According to Hoard and Silverton,[8] for any given molecule which is thought to be dodecahedral, the best planes through the atoms comprising the two trapezoids may be calculated, and, from the direction cosines, the angle between these planes may be computed and compared to the ideal value of 90°. In Figure 2, the calculation of the best planes through the atoms of the Phen ring and the chelate ring shows that they are planar. Similarly, the calculation of the best planes through the chelate rings and the thenoyl rings shows that the chelate rings are approximately planar, while the thenoyl rings are planar within the experimental error. The appropriate planes for the dodecahedron contain the metal atom and either (1) the set of ligand atoms N1, N2, O3, O4 or (2) the set of ligand atoms O5, O6, O1, O2. The angle between the two planes is 89.5°, which is very close to the value of ideal dodecahedral angle 90°. Therefore, the eight-coordinate polyhedron is a dodecahedron.

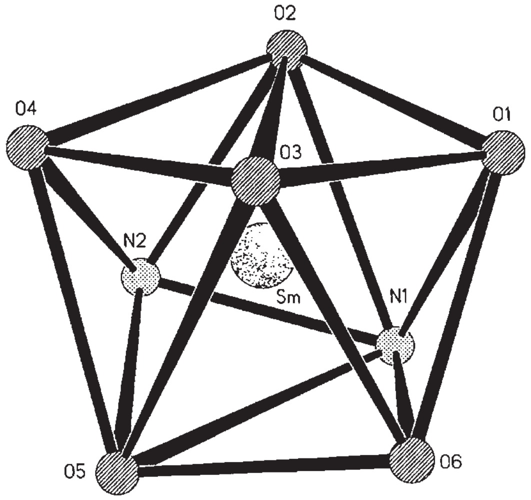

Figure 2. The coordination polyhedron.

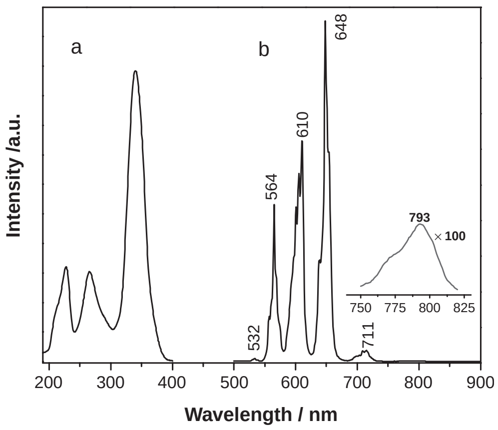

Figure 3. UV/Vis spectrum of the $Sm(HTH)_3Phen$ ethanol solution (a) and the emission spectrum of the complex (b).

Figure 3 shows the UV/Vis spectra of the $Sm(HTH)_3Phen$ ethanol solution and the emission spectra of the complex powder. The maximum peak belonging to $\pi \rightarrow \pi^*$ transition of the ligand of HTH appears at 340 nm and two weaker peaks due to the absorption of the second ligand (Phen) appear at 227 nm and 266 nm. λ_{max} is consistent with the excitation wavelength of $Sm(HTH)_3Phen$ fluorescence spectrum, which shows that the complex $Sm(HTH)_3Phen$ sheds fluorescence due to an intramolecular energy transfer from anion ligand HTH to the central Sm^{3+}. From the emission spectrum excited by 340 nm, it can be observed that the emission spectrum consists of the characteristic emission lines of Sm^{3+}, i.e., $^4G_{5/2} \rightarrow {}^6H_{3/2}$ (532 nm), $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (564 nm), $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (split at 600, 605 and 610 nm), $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (648 nm), $^4G_{5/2} \rightarrow {}^6H_{11/2}$ (711 nm) and $^4G_{5/2} \rightarrow {}^6H_{13/2}$ (793 nm). This indicates that an energy transfer occurs from the ligands to the central Sm^{3+} ion.

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References and Notes

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9 Crystal data: Formula, $C_{42}H_{20}F_{21}N_2O_6S_3Sm$, MW = 1294.13, Space group, $P2_1/n$, Unit cell dimensions, $a = 12.0092(6)$ Å, $b = 18.5580(10)$ Å, $c = 21.7652(13)$ Å, $\beta = 100.742(3)°$, $V = 4765.7(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.804$ g/cm^3, R (R_w) = 0.0709 (0.1946).