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Study on synthesis, structure, and DNA-binding of lanthanide complexes with 2-carboxylbenzaldehyde thiosemicarbazone

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Abstract—2-Carboxylbenzaldehyde thiosemicarbazone (HL), and its three lanthanide (III) complexes, $LnL_3{\cdot}4H_2O$ [Ln(III) = La, Sm, Eu], have been synthesized in water. The complexes were characterized by elemental analyses, molar conductivity and IR spectra. The crystal structure of $[Sm_2L_6(CH_3OH)_4]{\cdot}7.5CH_3OH{\cdot}0.5H_2O$ obtained from methanol solution was determined by X-ray diffraction analysis, crystallized in the triclinic system, space group $P-1$, $Z = 1$, $a = 12.217$ (2) Å, $b = 14.706$ (2) Å, $c = 15.035$ (2) Å, $\alpha = 111.84(1)°$, $\beta = 103.47(1)°$, $\gamma = 104.24(1)°$, $R_1 = 0.0290$. It has symmetrical $(\mu\text{-OCO})_2$, $(\mu\text{-O})_2$ and disamarium(III) units. The coordination geometry of each Sm(III) ion is a distorted tetradecahedron with nine oxygen atoms. In addition, the DNA-binding properties of the ligand and its complexes have been investigated by absorption, fluorescence, and viscosity measurements. The experimental results indicate that the ligand and the Sm-complex can bind to DNA, but the other two complexes cannot; the binding affinity of the Sm-complex is higher than that of the ligand and the intrinsic binding constant K_b of the complex is $3.22 \times 10^5\ M^{-1}$.

Since the 50s of last century, a great many thiosemicarbazones have provoked wide interest for their biological and pharmaceutical activities, such as antimalarial and antineoplastic as well as anticancer activity.[1–3] Subsequent interests were focused on the redox properties, structures, and biological activity of their transition metal complexes.[4–9] In particular, some copper (II) complexes of thiosemicarbazones were reported to be anticancer agents.[10] More recently, the lanthanide (III) complexes of thiosemicarbazones increasingly attracted attention because of their certain antibacterial activities.[11,12] Yet it is noticed that the DNA-binding investigations of such complexes have been relatively few. Because the interaction between metal complexes and DNA is in close relationship with their potential biological and pharmaceutical activities,[13,14] studies on DNA-binding of metal complexes are very important in the development of new therapeutic regents and DNA molecular probes. Therefore, DNA-binding property of three lanthanide (III) complexes with 2-carboxyl benzaldehyde thiosemicarbazone is reported in the paper. But what interests us most is relationship between the structure of complexes and their pharmaceutical activities. The two Sm(III) ions for Sm-complex are surrounded by 10 ligands and bridged by four groups, two of which are bidentate bridges (μ-OCO), and the other two oxygen bridges (μ-O), but the azomethine N atom and S atom of the ligand do not take part in the coordination. That is to say, the ligand acts as a carboxylate ligand rather than a thiosemicarbazone one.[10–12] This conforms to the rule that hard samarium ion binds to benzoate which is a hard base much more tightly than soft thiosemicarbazone ligand.

In this experiment 2-carboxylbenzaldehyde thiosemicarbazone (0.223 g, 1 mmol) was added to water (20 mL) and then was heated at 50 °C with stirring. The pH was adjusted to 7–8 by an aqueous solution of NaOH (0.01 mol/L). After all of the ligand was dissolved, a solution of $La(NO_3)_3{\cdot}6H_2O$ (0.235 g, 0.5 mmol) in water (10 mL) was added dropwise to the system. A white precipitate immediately appeared in the solution. After stirring for 4 h at 50 °C, the precipitate was separated. The centrifugal was washed six times with water and one time with ether, and finally dried in vacuo. All the complexes were synthesized by the same way.

Keywords: 2-Carboxylbenzaldehyde thiosemicarbazone; Lanthanide complexes; DNA interaction.
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All of complexes are soluble in DMF and DMSO, slightly soluble in ethanol and acetone, insoluble in water and ether, and may be kept in air for a long time. The molar conductivities of the complexes are around 11.0–19.9 S cm^2 mol^{-1} in DMF (Table 1), showing that all complexes are non-electrolytes in DMF.[12] The elemental analyses (Table 1) show that the formulas of the powder complexes are $LnL_3{\cdot}4H_2O$ (Ln = La, Sm, and Eu), which are different from the crystal composition of the Sm-complex, $[Sm_2L_6(CH_3OH)_4]{\cdot}7.5CH_3OH{\cdot}0.5H_2O$ confirmed by the X-ray diffraction analysis.

The main stretching frequencies of the IR spectra of the ligand (HL), its sodium salt (NaL), and three lanthanide (III) complexes are tabulated in Table 2. It can be found that the characteristic absorption peaks of all complexes are similar. The spectra of the ligand exhibit bands of the νOH(COOH) vibrations at the 2600–2850 cm^{-1} range, while the νOH(H_2O) vibrations for its complexes are at the 3200–3430 cm^{-1} range. The ν(C=O) vibration of free ligand appears at 1678 cm^{-1}, but it is absent in the complexes. The new absorptions for the complexes at around 1580, 1602 cm^{-1}, and 1390, 1477 cm^{-1} are ascribed to $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$, respectively.[12,15,16] These indicate that the carboxy groups of the ligand take part in the coordination, and the carboxy hydrogens are substituted by the metals. The $\Delta\nu$ values (92–224 cm^{-1}) are less than that (229 cm^{-1}) of NaL. These

Table 1. Elemental analyses and molar conductivity

Compound	Yield (%)	C% (Cal)%	N% (Cal)%	H% (Cal)%	Ln% (Cal)%	Λ (S cm^2 mol^{-1})
$LaL_3{\cdot}4H_2O$	70.5	37.41	14.24	3.37	15.9	11.0
$C_{27}H_{32}N_9S_3O_{10}La$		(36.95)	(14.36)	(3.67)	(15.8)	
$SmL_3{\cdot}4H_2O$	85.4	36.36	14.24	3.57	17.3	19.9
$C_{27}H_{32}N_9S_3O_{10}Sm$		(36.47)	(14.18)	(3.63)	(16.9)	
$EuL_3{\cdot}4H_2O$	76.9	36.77	13.95	3.25	17.5	12.6
$C_{27}H_{32}N_9S_3O_{10}Eu$		(36.41)	(14.15)	(3.62)	(17.1)	

Table 2. Some main IR data of the ligand and its complexes

Compound	HL	NaL	$LaL_3{\cdot}4H_2O$	$SmL_3{\cdot}4H_2O$	$EuL_3{\cdot}4H_2O$
ν(OH)(COOH H_2O)	2600–2850		3421	3406	3424
$\nu(NH_2)$	3268	3208	3278	3278	3284
ν(C=O)(COOH)	1678				
ν(C=S)	822	820	815	816	815
ν(C=N)	1549	1555	1546	1547	1543
$\nu_{as1}(CO_2^-)$		1615	1602	1613	1601
$\nu_{as2}(CO_2^-)$			1580	1591	1569
$\nu_{s1}(CO_2^-)$		1386	1390	1389	1399
$\nu_{s2}(CO_2^-)$			1477	1478	1477
$\Delta\nu_1(\nu_{s1}-\nu_{s2})$		229	212	224	202
$\Delta\nu_2(\nu_{s1}-\nu_{s2})$			103	113	92
ν(Ln–O)			459	456	455

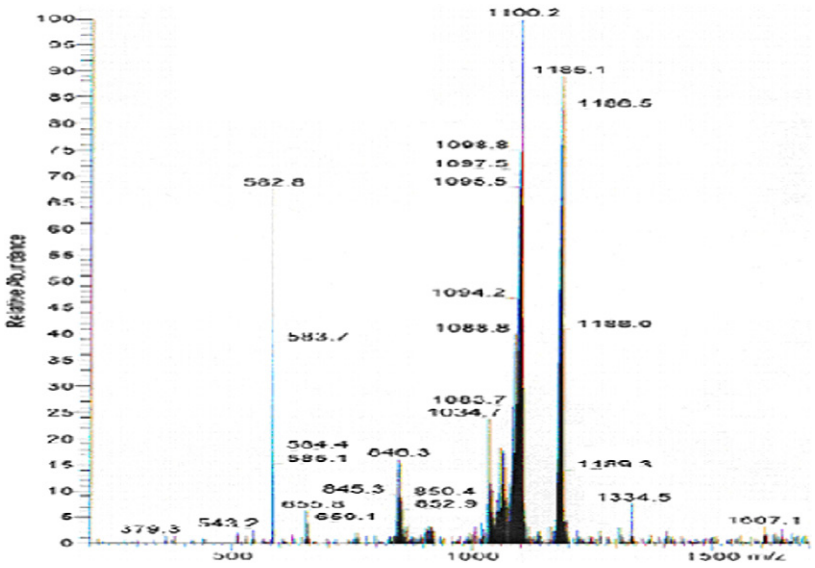

Figure 1. The mass spectrum for the La-complex.

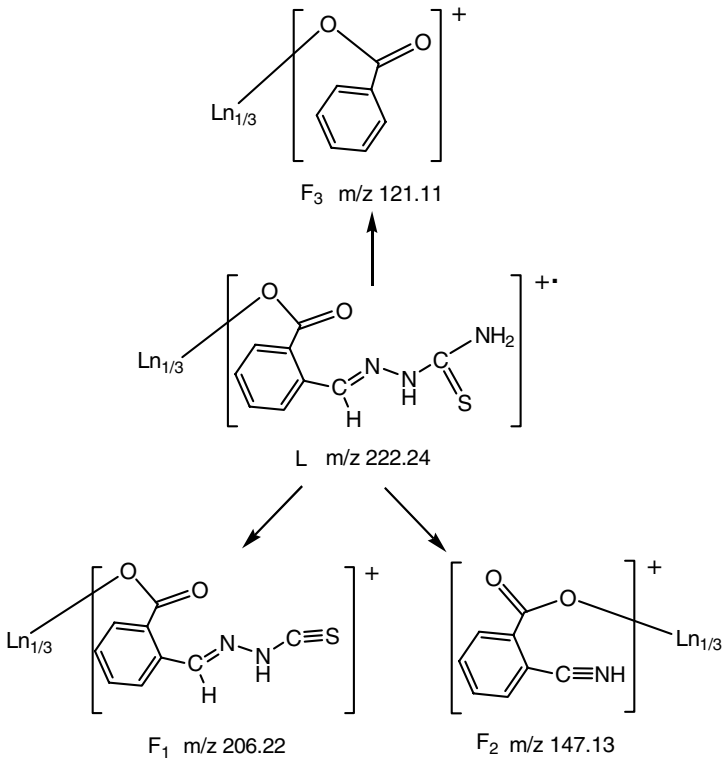

Figure 2. The proposed degradation of the ligand in the complexes.

indicate that there are bridged and chelated carboxy groups in the complexes.[15] It is also confirmed by the crystal structure of $[Sm_2L_6(CH_3OH)_4]\cdot 7.5CH_3OH\cdot 0.5H_2O$. The ν(C=N) and ν(C=S) bands of the ligand at 1549 and 822 cm^{-1} are similar to ones of the complexes at 1545 and 815 cm^{-1},[7,12] respectively. It indicates that the azomethine N atom and S atom of the ligand do not coordinate to lanthanide (III) ions. Weak bands at 460 cm^{-1} are assigned to ν(Ln–O).[10,11] Above-mentioned facts show that the powder complex structures may be similar to the crystal.

The mass spectra of the three complexes are similar and confirm the binuclear structures of the complexes (see Figure 1 for the La-complex, other mass spectra were left out). The spectrum shows numerous peaks representing successive degradation of the molecule. Figure 2 demonstrates the proposed fragments of the ligand in the complexes. The La-complex has five significant peaks at 1607 $[La_2L_6]^+$, 1186.5 $[La_2L_3F^3{}_2]^+$, 1094.2 $[La_2LF^1F^2F^3{}_2]^+$, 852.9 $[La_2LF^1F^2]^+$, and 584.4 $[LaL_2]^+$. The other two complexes occur the same degradation. For the Sm-complex, the peaks appear at 1634 $[Sm_2L_6]^+$ (lost), 1210.9 $[Sm_2L_3F^3{}_2]^+$, 1117.0 $[Sm_2LF^1F^2F^3{}_2$, and 595.8 $[SmL_2]^+$. For the Eu-complex the peaks appear at 1637 $[Eu_2L_6]^+$ (lost), 1212.4 $[Eu_2L_3F^3{}_2]^+$, 1121.3 $[Eu_2LF^1F^2F^3{}_2]^+$, and 597.9 $[EuL_2]^+$.

The X-ray diffraction data for $[Sm_2L_6(CH_3OH)_4]\cdot 7.5CH_3OH\cdot 0.5H_2O$ are given in Table 3. Selected bond lengths and angles are summarized in Table 4. The crystal structure, as shown in Figure 3, consists of two symmetrical Sm(III) ions and each of them is surrounded by five ligand anions. The coordination geometry of each Sm(III) ion is a distorted tetradecahedron with nine oxygen atoms. Full molecule is a binuclear complex bridged by symmetrical two μ-OCO and two μ-O. Its molecular structure is similar to that of $[Sm_2(benzoate)_6(bipyridine)_2]$,[17] $[\{Nd[C_{10}H_6(OH)(COO)]_3(H_2O)(C_2H_6O)\}_2]\cdot 2H_2O\cdot 2C_2H_6O$[16] and $[Ho_2(o\text{-}HOC_6H_4CO_2)_6(H_2O)_4]\cdot 4H_2O$[18]. But 'tridentate' carboxy groups with μ-O in the Sm-complex are rather unique.

A pair of ligand anions bridge two Sm(III) ions via *syn-syn* mode through both oxygen atoms of each carboxy group. The C(1)–O(1) (1.245 Å) and C(1)–O(2)

Table 3. Crystal data and experimental data

Formula: $C_{65.50}H_{95}N_{18}O_{24}S_6Sm_2$	V = 2266.72(77) Å^3
Formula weight = 2011.66	D_{calc} = 1.474 g/cm^3
Crystal color: yellow	Radiation: 0.71073 Å (Mo K_a)
Crystal size: 0.58 × 0.54 × 0.40 mm	R_1 = 0.0290 [7799 reflections, $I > 2\sigma(I)$]
Crystal system: Triclinic	wR_2 = 0.0814
Space group: $P-1$ Z = 1	$(\Delta/\sigma)_{max}$: 0.0018
T = 289(2) K	$(\Delta\rho)_{max}$ = 1.326 eÅ^{-3}
a = 12.217(2) Å	$(\Delta\rho)_{min}$ = −0.653 eÅ^{-3}
b = 14.706(2) Å	Measurement: Siemens P4
c = 15.035(2) Å	Monochromator: graphite
α = 111.84(1)°	Structure determination: SHELXS-97 and SHELXL-97
β = 103.47(1)°	
γ = 104.24(1)°	Refinement: Full-matrix least-squares on F^2

Table 4. Selected bond lengths (Å) and angles (°)

Bond lengths (Å)			
Sm–O(1)#1	2.380(2)	O(1)–Sm#1	2.380(2)
Sm–O(2)	2.368(2)	O(5)–Sm#1	2.381(2)
Sm–O(3)	2.507(2)	Sm–Sm#1	4.0914(10)
Sm–O(4)	2.495(2)	O(1)–C(1)	1.245(4)
Sm–O(5)	2.740(3)	O(2)–C(1)	1.263(4)
Sm–O(5)#1	2.381(2)	O(3)–C(10)	1.268(4)
Sm–O(6)	2.462(2)	O(4)–C(10)	1.260(4)
Sm–O(7)	2.462(3)	O(5)–C(19)	1.265(4)
Sm–O(8)	2.516(3)	O(6)–C(19)	1.250(4)
Bond angles (°)			
O(2)–Sm–O(3)	83.84(8)	O(5)–Sm–O(5)#1	74.15(9)
O(2)–Sm–O(4)	125.77(9)	O(6)–Sm–O(7)	80.85(9)
O(2)–Sm–O(5)	71.53(8)	O(6)–Sm–O(8)	69.49(9)
O(2)–Sm–O(6)	85.23(9)	O(6)–Sm–O(1)#1	84.44(10)
O(2)–Sm–O(7)	147.62(9)	O(6)–Sm–O(5)#1	123.41(8)
O(2)–Sm–O(8)	75.26(10)	O(7)–Sm–O(8)	72.50(10)
O(2)–Sm–O(1)#1	133.29(9)	O(7)–Sm–O(1)#1	74.30(10)
O(2)–Sm–O(5)#1	72.07(9)	O(7)–Sm–O(5)#1	139.32(9)
O(3)–Sm–O(4)	51.99(8)	O(8)–Sm–O(1)#1	140.34(11)
O(3)–Sm–O(5)	153.70(8)	O(8)–Sm–O(5)#1	143.08(10)
O(3)–Sm–O(6)	139.28(8)	O(1)#1–Sm–O(5)#1	76.29(9)
O(3)–Sm–O(7)	87.88(9)	O(2)–Sm–Sm#1	66.96(6)
O(3)–Sm–O(8)	69.80(9)	O(3)–Sm–Sm#1	126.81(6)
O(3)–Sm–O(1)#1	129.81(9)	O(4)–Sm–Sm#1	112.37(6)
O(3)–Sm–O(5)#1	89.87(8)	O(5)–Sm–Sm#1	34.04(5)
O(4)–Sm–O(5)	139.13(8)	O(6)–Sm–Sm#1	83.37(6)
O(4)–Sm–O(6)	148.42(9)	O(7)–Sm–Sm#1	138.99(7)
O(4)–Sm–O(7)	69.33(9)	O(8)–Sm–Sm#1	134.91(7)
O(4)–Sm–O(8)	109.33(9)	O(1)#1–Sm–Sm#1	66.65(6)
O(4)–Sm–O(1)#1	77.85(9)	O(5)#1–Sm–Sm#1	40.11(6)
O(4)–Sm–O(5)#1	77.51(9)	Sm#1–O(5)–Sm	105.85(8)
O(5)–Sm–O(6)	49.39(8)	O(1)–C(1)–O(2)	125.6(3)
O(5)–Sm–O(7)	117.89(9)	O(4)–C(10)–O(3)	120.3(3)
O(5)–Sm–O(8)	111.07(8)	O(6)–C(19)–O(5)	120.9(3)
O(5)–Sm–O(1)#1	67.30(8)	C(1)–O(1)–Sm#1	139.8(2)

(1.263 Å) of this type of carboxy group ligand are not equal, this shows that its C=O double bond is localized. This results in difference between O(1)–Sm (2.380 Å) and O(2)–Sm#1 (2.369 Å) forming μ-OCO. It is clear that the O for the longer C–O bond forms the shorter Sm–O bond. The other pair of ligand anions act as a 'tridentate' bridge, which is coordinated to Sm(III) as bidentate, and one oxygen atom of the carboxy group bridges two Sm(III) ions to form μ-O. Both O(5)–Sm (2.740 Å) and O(5)–Sm#1 (2.381 Å) for μ-O are evidently different, the C(19)–O(6) (1.250 Å) and C(19)–O(5) (1.265 Å) for the carnoxy groups are different, too. But the C(10)–O(4) (1.260Å) and the C(10)–O(3) (1.268Å) for other bidentate carboxy groups are similar, which show that the carboxy groups are evidently delocalized. So the O(3)–Sm (2.507 Å) and O(4)–Sm (2.495 Å) forming chelate bidentate are similar. The bond lengths between the oxygen atoms of the methanol molecules and the Sm atom are not equal, too, which are Sm–O(7) (2.462 Å) and Sm–O(8) (2.516 Å). Furthermore, the average distance of Sm–O is shorter than that of $[Sm_2(benzoate)_6(bipyridine)_2]$,[17] while the distance of Sm–Sm#1 [4.0914 Å] is somewhat longer than that of $[Sm_2(benzoate)_6(bipyridine)_2]$ (4.05 Å).[17] It is clear that Sm-complex in crystal is a strange double nuclear structure.

The DNA-binding properties of the ligand and its complexes have been investigated by absorption, fluorescence, and viscosity measurements. The experimental results indicate that the intrinsic binding constant of the Sm-complex with CT-DNA is $3.22 \times 10^5\ M^{-1}$. The Sm-benzoate complex which was prepared from benzoic acid and $Sm_2(CO_3)_3$ in water was used as contrast, the experiment results show that it is not responsible for affinity to DNA. These testify to the facts that the basic structure of the Sm-complex and the thiosemicarbazone moieties may be together responsible for affinity to DNA.

It is a general observation that a hypochromicity in the absorption spectra accompanies the binding of molecules to DNA. The extent of spectral change is related to the strength of binding.[19] The La(O) and Eu(O) complexes display weak hypochromicity indicating that they cannot bind to DNA. The absorption spectra of the ligand and the Sm-complex in the absence and presence of CT-DNA (at a constant concentration of the compounds) are given in Figure 4. Addition of increasing amounts of CT-DNA results in observation of notable hypochromicities. The Sm-complex at 222 and 308 nm exhibits hypochromicity of around 81.6% and 11.8%,

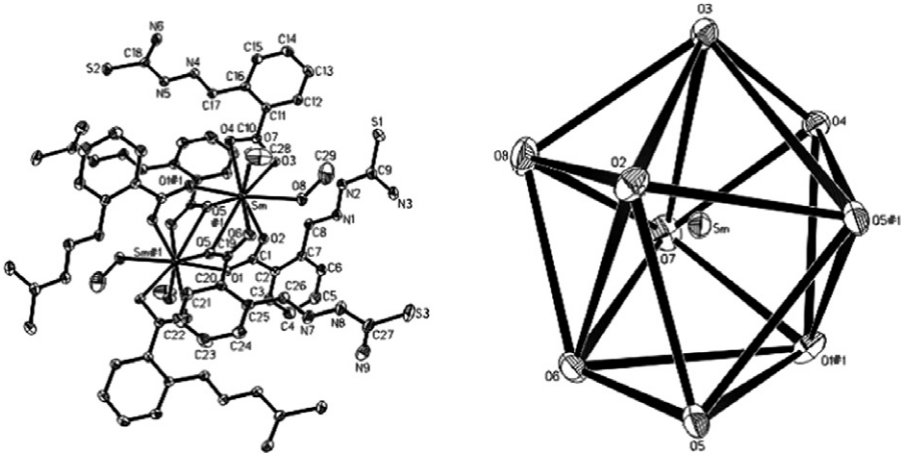

Figure 3. Structure and the coordination polyhedron of the $[Sm_2L_6(CH_3OH)_4]\cdot 7.5CH_3OH\cdot 0.5H_2O$.

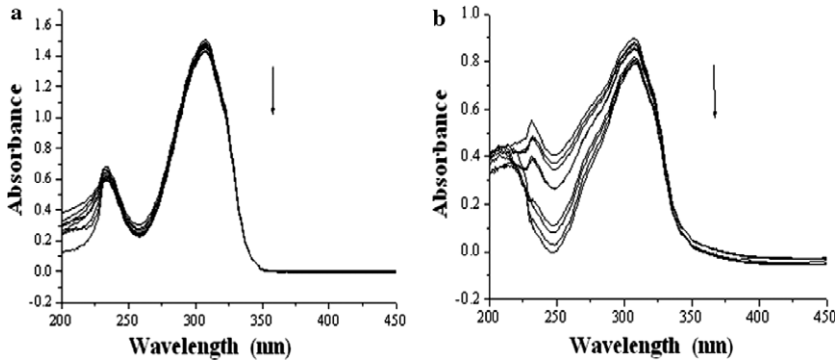

Figure 4. (a) Electronic spectra of the ligand (10 μM) in the presence of CT-DNA. [CT-DNA] = 0–40 μM. Arrow shows the absorbance changes upon increasing CT-DNA concentration (the concentration of CT-DNA is expressed nucleotide). (b) Electronic spectra of the Sm-complex (10 μM) in the presence of CT-DNA. [CT-DNA] = 0–40 μM. Arrow shows the absorbance changes upon increasing CT-DNA concentration.

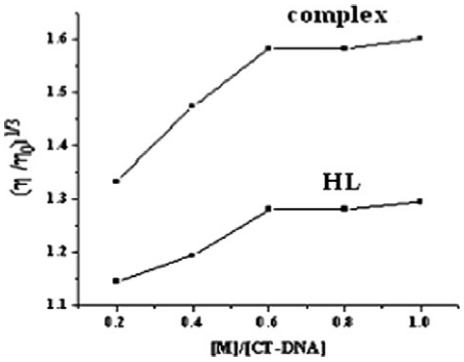

Figure 5. Effect of increasing amounts of the ligand and the Sm-complex on the relative viscosity of CT-DNA at 25.0 °C.

respectively. The ligand at 233 and 308 nm exhibits hypochromicity of around 12.8% and 5.1%, respectively. These results show an association of the compounds with CT-DNA. The Sm-complex gives somewhat more serious hypochromicity than the ligand, indicating that the binding strength of the Sm-complex is stronger than that of the ligand.

The interaction of the compounds could bend the DNA helix, and reduce its effective length, concomitantly, its viscosity.[20] The effects of the ligand and the Sm-complex on the viscosity of CT-DNA at 25.0 °C are shown in Figure 5. With an increasing amount of compounds, the relative viscosity of CT-DNA increased, which suggests that the ligand and the Sm-complex can bind to DNA. Other complexes have no effect.

The enhancements in the emission intensity of the ligand and the Sm-complex with increasing CT-DNA concentration are shown in Figure 6. It can be seen that the emission intensity enhancement of the ligand is obscure, so its binding constant is not calculated. What's more, in the absence of CT-DNA, the Sm-complex emits luminescence in the tris buffer at ambient temperature, with a maximum appearing at 450 nm. Upon addition of CT-DNA, the emission intensity enhancement for the Sm-complex may be largely due to the increase of the molecular planarity of the complex and the decrease of the collisional frequency solvent molecules with the complex.[21] According to the Scatchard equation, a plot of r/C_f versus r gave the binding constant $3.22 \times 10^5\ M^{-1}$ from the fluorescence data for the Sm-complex. Figure 7 shows the emission spectra of DNA–EB system upon the increasing amounts of the Sm-complex. The emission intensity of the DNA–EB system (λ = 587 nm) decreased apparently as the concentration of the Sm-complex increased, which indicated that the Sm-complex replaced EB from the DNA–EB

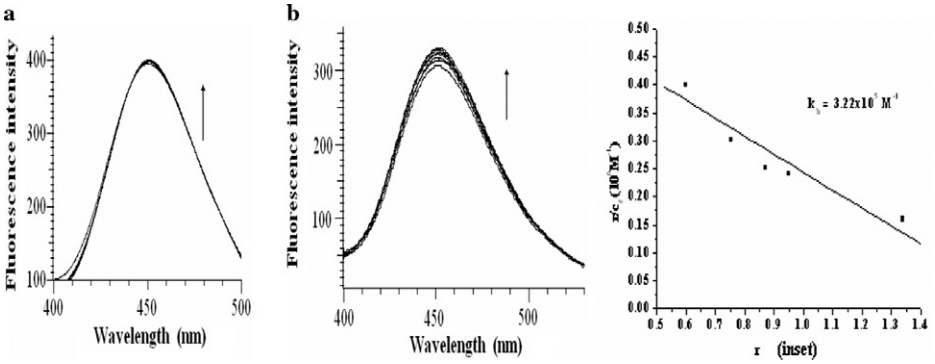

Figure 6. (a) The emission enhancement spectra of the ligand (1 μM) in the presence of 0, 2.5, 5, 7.5, 10, 12.5, 15, and 17.5 μM CT-DNA. Arrow shows the absorbance changes upon increasing DNA concentration. (b) The emission enhancement spectra of the Sm-complex (1 μM) in the presence of 0, 2.5, 5, 7.5, 10, 12.5, 15, and 17.5 μM CT-DNA. Arrow shows the absorbance changes upon increasing DNA concentration. Inset: Scatchard plot of the fluorescence titration data of the Sm-complex, $K_b = 3.22 \times 10^5\ M^{-1}$.

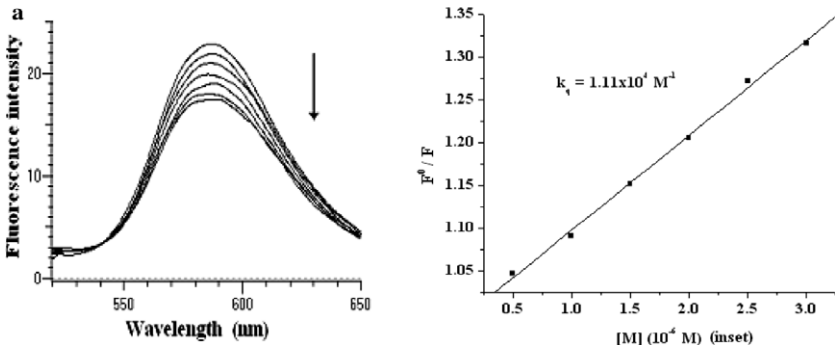

Figure 7. (a) The emission spectra of CT-DNA—EB system (10 μM and 0.32 μM EB) in the presence of the Sm-complex (0, 5, 10, 15, 20, 25 and 30 μM). Arrow shows the absorbance changes upon increasing the Sm-complex concentration. Inset: Stern–Volmer plot of the fluorescence titration data of the Sm-complex, $K_q = 1.11 \times 10^4\ M^{-1}$.

system and EB changed from a hydrophobic environment to water solution.[22] According to the classical Stern–Volmer equation, the quenching plot illustrates that the quenching of EB bound to DNA by the Sm-complex is in good agreement with the linear Stern–Volmer equation, which also proves that Sm-complex can bind to DNA. In the plots of F_0/F versus [complex], K_q is given by the ratio of the slope to intercept. The K_q value for the Sm-complex is $1.11 \times 10^4\ M^{-1}$. It may be concluded that Sm-complex bind with CT-DNA via intercalation mode.

Acknowledgments

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Supplementary data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, on request, quoting the deposition number CCDC 605778. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bmcl.2006.10.049.

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