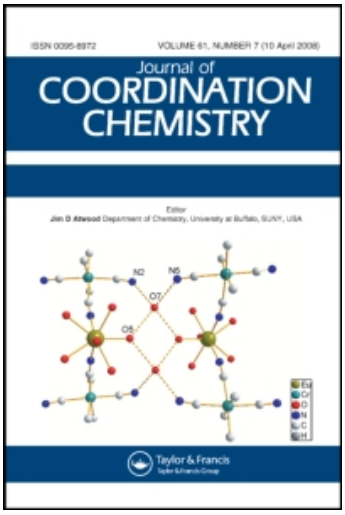

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SYNTHESIS, PROPERTIES AND BIOLOGICAL ACTIVITY OF RARE EARTH COMPLEXES OF 5-FLUOROURACIL-1-PROPIONIC ACID

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SYNTHESIS, PROPERTIES AND BIOLOGICAL ACTIVITY OF RARE EARTH COMPLEXES OF 5-FLUOROURACIL-1-PROPIONIC ACID

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Seven new solid complexes of 5-fluorouracil-1-propionic acid with rare earth metals have been synthesized. Elemental analyses, molar conductance, TG-DTA, IR, UV–Vis, fluorescence, XPS and ^{1}H NMR spectra have been used to characterize these complexes. The general formula of the complexes is $RE(FPA)_3 \cdot nH_2O$ where RE = Y(III), La(III), Pr(III), Sm(III), Eu(III), Dy(III), Er(III); $n = 3$ or 5. Prooxidative and antitumor activity of these complexes was tested. The results showed that these complexes augment free radical generation; especially the Pr^{3+} complex which obviously increased the $O_2^{-\bullet}$ and $OH^{\bullet}$ radicals. It was also found that La^{3+} and Y^{3+} complexes possess antitumor effects on human colon bladder HCT-B and human leukemia HL-60 cells *in vitro*.

Keywords: Prooxidative activity; antitumor activity; free radical; rare earth complexes; 5-fluorouracil-1-propionic acid

INTRODUCTION

Complexes of 5-fluorouracil (5-Fu) and its derivatives are receiving attention for their broad antitumor effects on many kinds of cancer.[1] It was reported that some of their metal complexes have antitumor activity.[2,3]

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There appear to be few reports on rare earth complexes of 5-fluorouracil-1-propionic acid (HFPA). Particularly, no studies have been done on the effect of the complexes on biochemical effects. Hence, seven complexes of HFPA with rare earth metals were prepared and their structures determined through many spectral measurements. The studies of antitumor and prooxidative activity of these complexes also are reported, for the first time, in this paper.

This paper is one of a series in our investigation of metal complexes with HFPA. Further studies on ternary complexes of rare earth metals with HFPA are in progress.

EXPERIMENTAL

Reagents

The chemicals used included RE_2O_3 (99.99%, Yulong Chemical Works, Shanghai, China) which were transformed into $RECl_3 \cdot nH_2O$; nitroblue tetrazolium (NBT); N-methylphenazine methosulfate (PMS); nicotinamide adenine dinucleotide (NADH); 3-(4,5-dimethylthianol-2-yl)-2,5-diphenyl-tetrazolium bromide (MTT); Malobialdehyde (MDA); thiobarbituric acid (TBA); all other reagents used were analytical grade. All biochemical reagents were obtained from Sigma Chemical Company.

Measurements

Carbon, hydrogen and nitrogen were determined using a Vario EL elemental analyzer. The amount of metals were determined by titration with EDTA. IR spectra were recorded on a Nicole FI-170SX IR spectrophotometer, using KBr discs in the range 4000–200 cm^{-1}. TG-DTA analyses were carried out with a DuPont 1090-B thermal analyzer. UV–Vis spectra were obtained on a Shimadzu UV-240 spectrophotometer. ^1H NMR spectra were recorded on a Varian FT-80A NMR spectrophotometer in d_6-DMSO with TMS as the internal reference. Electrolytic conductances were measured using a DDS-11A molar conductometer with DMF as the solvent at 25°C. Absorbencies were determined on a 751-spectrophotometer at 560/532 nm. Luminescence spectra were obtained with a Hitachi M-850 fluorescence spectrophotometer. The XPS were recorded on PHI550 universal X-ray photoelectron spectrometers, analyzed by the ESCALAB-210 process. The X-ray source was MGKα ($E_{h\nu} = 1253.6$ eV).

Synthesis of Complexes

HFPA · H_2O (0.3 mol) was dissolved in EtOH H_2O solution (50 mL, 1 : 1, v/v). After adding 5–6 drops of KOH saturated solution, $RECl_3 \cdot nH_2O$ (0.1 mol) was added to the mixture. The product precipitated immediately and stirring was continued for 24 h, keeping the temperature below 80°C. Then the precipitate was collected by filtration, washed with ethanol several times and dried in a vacuum dessicator to constant weight.

HFPA was made by an improved literature method.[1]

Test for Prooxidative Activity

The superoxide radicals ($O_2^{-\bullet}$) were produced by a system of NBT/PMS/O_2/NADH[4] and measured by the amount of NBT reduced by $O_2^{-\bullet}$ (tested at 560 nm). The 3 mL reaction mixture contained 73 μM NADH, 15 μM PMS, 50 μM NBT, 0.016 M tris–HCl buffer (pH = 8) and the compounds to be tested. The promotion ratio for $O_2^{-\bullet}$ was calculated from the following expression:

$$\text{Promotion ratio} = 100 \times (A_{\text{experiment}} - A_{\text{control}})/A_{\text{control}}.$$

The hydroxyl radicals (OH•) were produced by a system of MDA/TBA/$Fe^{2+} \rightarrow$ OH[5] and measured by the amount of TBA reduced by OH• (tested at 532 nm). The 3 mL reaction mixture contained 1.5 mM MDA, 3 mM X, 0.6 μM XO, 4.5 mmol $FeSO_4$, 0.225 M PBS buffer (pH = 7.4), 1.5% TBA (w/v) and the complexes to be tested. The promotion ratio for OH• was calculated as formulated above.

RESULTS AND DISCUSSION

Composition Properties of the Complexes

Elemental composition and molar conductance data are listed in Table I. The complexes are stable in air and soluble in DMSO, insoluble in water and other common organic solvents. The molar conductance of these complexes in DMF solution vary from 27.8 to 38.3 $S \cdot cm^2 \cdot mol^{-1}$, indicating that they are non-electrolytes.[6] Elemental analyses show that the formula of these complexes is $RE(FPA)_3 \cdot nH_2O$ (RE = Y, La, Pr, Sm, Eu, Dy, Er; $n = 3$ or 5).

TABLE I Elemental analyses and molar conductances for the complexes

No.	*Complex*	*RE%*		*C%*		*H%*		*N%*		Λ ($S \cdot cm^2 \cdot mol^{-1}$)
		Found	*Calc.*	*Found*	*Calc.*	*Found*	*Calc.*	*Found*	*Calc.*	
1.	$Y(FPA)_3 \cdot 5H_2O$	11.32	11.34	33.68	32.12	3.82	3.96	11.01	10.74	30.5
2.	$La(FPA)_3 \cdot 5H_2O$	16.55	16.71	30.06	30.29	3.35	3.73	9.97	10.10	32.6
3.	$Pr(FPA)_3 \cdot 3H_2O$	17.24	17.67	32.05	31.58	2.97	3.38	10.49	10.53	31.0
4.	$Sm(FPA)_3 \cdot 3H_2O$	18.82	18.63	31.24	31.21	3.10	3.34	10.44	10.40	36.0
5.	$Eu(FPA)_3 \cdot 3H_2O$	19.04	18.79	31.58	31.12	3.04	3.33	10.62	10.38	29.0
6.	$Dy(FPA)_3 \cdot 3H_2O$	20.03	19.83	30.43	30.75	2.97	3.29	10.39	10.25	27.8
7.	$Er(FPA)_3 \cdot 3H_2O$	19.93	20.29	30.25	30.58	3.11	3.28	10.01	10.19	38.3

Thermal Analysis

Two endothermic peaks appear in the DTA curve of La^{3+} and Y^{3+} complexes around 154°C and 70°C suggesting that the water molecules are either coordinated to the metal ions or present as waters of crystallization. The percent of weight loss, in the TGA curve, are 6.67% and 3.80%, total weight loss is 10.47% (calc. 10.82%), indicating three waters of coordination and two waters of crystallization, respectively. The other complexes only contain coordinated water (around 170°C). These results agree with the composition of the complexes determined by elemental analysis. Decomposition of the complexes starts around 290–321°C and occurs through more than one stage. After heating to about 650°C, the residues were rare earth oxides.

Infrared Spectra

The important IR data of the ligand and its complexes are given in Table II. Two vibrations at 750 and $\sim 550\,cm^{-1}$ suggest that the water molecules are coordinated to the rare earth ions.[7] A sharp peak at $3660\,cm^{-1}$ appears in the spectra of La(III) and Y(III) complexes, indicating that waters of crystallization exist.

The bands observed at ~ 3284 and $1416\,cm^{-1}$ in the spectra of HFPA assigned to ν (N^3–H) and δ (N^3–H) vibrations, respectively, disappear on complexation, except in the case of the La(III) complexes, for which the bands remain at 3283 and $1423\,cm^{-1}$. The new bands at about 1549, 1270 and $1035–1002\,cm^{-1}$, in the spectra of complexes, may be assigned to the ν (C=N) vibrations, δ (OH) of enol form and ν (C–O) vibrations, respectively.[8,9] The bands of ν (C^2=O) shift about $15\,cm^{-1}$. These results indicate that the free ligand HFPA has the following structure (Figure 1) when coordinated with rare earth metals (except La(III)).

TABLE II The important IR data (cm^{-1}) and their assignment for ligand and its complexes

	HFPA	1	2	3	4	5	6	7
ν_{OH} (H_2O)	3615	3599	3560					
$\nu_{C=O}$ (COOH)	1694							
δ_{N^3-H}	1416		1423					
$\nu_{as}(CO_2^-)$		1572	1564	1564	1564	1565	1570	1573
		1550		1551	1547	1549	1550	1551
$\nu_s(CO_2^-)$		1345	1446	1344	1346	1344	1346	1351
		1451		1450	1450	1450	1451	1451
$\Delta\nu$		227	108	220	218	221	224	222
		99		101	97	99	99	100
δ_{OH}		1270		1270	1270	1270	1272	1270
ν_{C-O}		1033		1038	1036	1035	1034	1034
		1001		999	1002	1001	1003	1003
ρ_r (H_2O)		750	749	752	751	752	750	751
ρ_ω (H_2O)		545	559	549	549	544	545	550
ν (RE–O)		466		464	467	466	465	466
		379	381	380	380	379	380	380

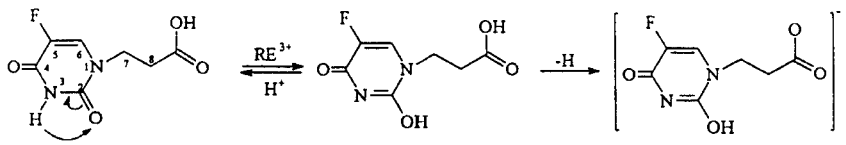

FIGURE 1 The proposed transformation of ligand.

Characteristic vibrations of ν (C–F) vary less, suggesting that the F atoms do not coordinate to RE^{3+}. The characteristic ν (C=O) mode of the ligand carboxyl group at 1694 cm^{-1} disappeared upon complexation. Subsequently, the complexes displayed both symmetric and asymmetric stretching vibrations of COO^- at *ca.* 1570/1550 and 1345/1450 cm^{-1}, respectively. $\Delta\nu = \nu_{as} - \nu_s = 227/99\ cm^{-1}$ is larger/smaller than that of sodium mandelate ($\Delta\nu = 1609 - 1437 = 172\ cm^{-1}$), which strongly suggests coordination of the ligand carboxyl group with rare earth ions in two fashions, monodentate or bidentate.[10]

New bands in far-IR spectra of the complexes at ~464 and 380 cm^{-1} due to ν (RE–O), further support the formation of RE–O bond.[10]

Visible Spectra

The electronic spectra of the Pr(III) and Er(III) solid complexes are summarized in Table III. By comparison with their hydrated cations, the absorption peaks of the rare earth complexes varied. The measured spectral parameters including Shiha's parameter (δ); the naphelauxetic ratio (β) and

TABLE III Electronic spectra parameters of the Pr(III) and Er(III) complexes

Complex	γ (cm^{-1})	*Assignment*	*Covalent parameters*
$Pr(FPA)_3 \cdot 3H_2O$	22 522	$^3H_4 \rightarrow {}^3P_2$	$\beta = 0.9988$
	21 322	$^3P_1$	$\delta = 0.1201$
	20 746	$^3P_0$	$b^{1/2} = 0.0245$
	16 978	$^1D_2$	
$Er(FPA)_3 \cdot 3H_2O$	20 555	$^4I_{15/2} \rightarrow {}^4F_{7/2}$	$\beta = 0.9978$
	19 230	$(^2H, {}^4Q)_{11/2}$	$\delta = 0.2205$
	18 450	$^4S_{3/2}$	$b^{1/2} = 0.0331$
	15 286	$^4F_{9/2}$	
	12 516	$^4I_{9/2}$	
	22 124	$^4F_{5/2}$	
	24 451	$^4H_{9/2}$	

the bonding parameter ($b^{1/2}$), were used to indicate the nature of the bonding between the metal and the ligand.[11,12] The small positive values of β, δ, and $b^{1/2}$ indicated that the bond between rare earth ions and the ligand is primarily ionic.

Fluorescence Spectra

Fluorescence spectra of the Eu(III) complex were obtained for the powered solid at room temperature (Figure 2). Since the Eu^{3+} ion is highly luminescent and environmentally sensitive, we analyzed the luminescence spectra of this complex to get more information on the structure. The complex exhibits red luminescence which arises from $^5D_0 \rightarrow {}^7F_{0-4}$ transitions. The single peak at 580 nm indicated the presence of only one site for the Eu^{3+} ion. Considering the electric transitions of $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ together with the steric hindrance, the coordination sphere about the Eu^{3+} may be viewed as a tricapped trigonal prism, the symmetry of which is D_{3h} under ideal conditions.[13]

^1H NMR Spectra of HFPA and $Y(FPA)_3 \cdot 5H_2O$

^1H NMR spectra of HFPA and Y(III) complexes were studied using d_6-DMSO as solvent and TMS as the internal reference.[1] The chemical shifts for HFPA are: δ 11.70 ppm (1H, s, ring N^3–H), 12.65 (1H, b, COOH), 7.85 (1H, d, ring C^6–H), 3.72 (2H, t, C^7–H), 2.54 (2H, t, C^8–H); and for $Y(FPA)_3 \cdot 5H_2O$: δ 7.92 ppm (1H, b, ring C^6–H), 3.81 (2H, t, C^7–H), 3.33 (br, H_2O). The N^3–H proton and carboxyl proton of the ligand disappeared upon complexation further proving the conjugate transformation and HFPA coordination with metal ion through the carboxyl group, in turn.

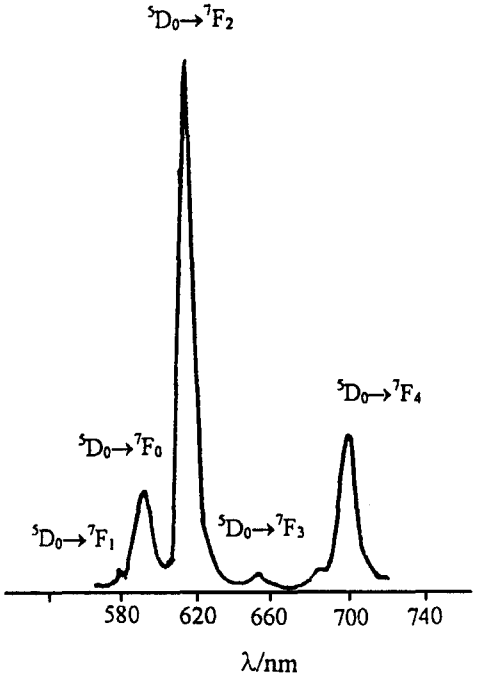

FIGURE 2 Luminescence spectra of $Eu(FPA)_3 \cdot 3H_2O$ in the solid state ($\lambda_{ex} = 395$ nm).

This is consistent with the IR spectra. The δ value of $C^{7,8}$–H shifted to highfield (C^8–H combined with DMSO) also results from the coordination.

XPS of $La(FPA)_3 \cdot 3H_2O$

XPS of the La^{3+} complex was obtained on PHI550 multifunction X-ray photoelectron spectrometers and analyzed by a ESCALAB210 processor. The X-ray source was MgKα mono. Range ($E_{h\nu} = 1253.6$ eV). The C1s binding energy of the ring-C and hydrocarbon-C was taken as the standard ($E_b = 284.6$ eV, CAE = 30 eV).

The XPS binding energy of HFPA and the lanthanum complex are shown in Figure 3(a). It can be seen that the FWHM of O1s of the free ligand is wider, since the carboxyl group contains two kinds of oxygen (C=O, C–OH). However, the peak of O1s is single, in the spectra of the complex, resulting from the charge transfer of carbonyl oxygen to the hydroxyl oxygen, suggesting that the ligand coordinates with La^{3+} ion in a bidentate fashion through carboxylic oxygen atoms. This result is consistent

with the IR studies above. The binding energies of N1s and F1s of the ligand vary less, indicating that N and F atom do not coordinate to the La^{3+} ion.

By comparison with lanthanum chloride, the binding energy of $La3d_{5/2}$ of the complex shifted lower (0.2 eV), as a result of the electron density of carboxyl HFPA transfer to La, which suggested coordination of the metal with ligand. XPS of the $La3d_{5/2}$ and its satellite are shown in Figure 3(b). As shown in this figure the satellite strength of the complex is weaker, indicating that the inter-effect of the 4f orbital with the bonding orbital

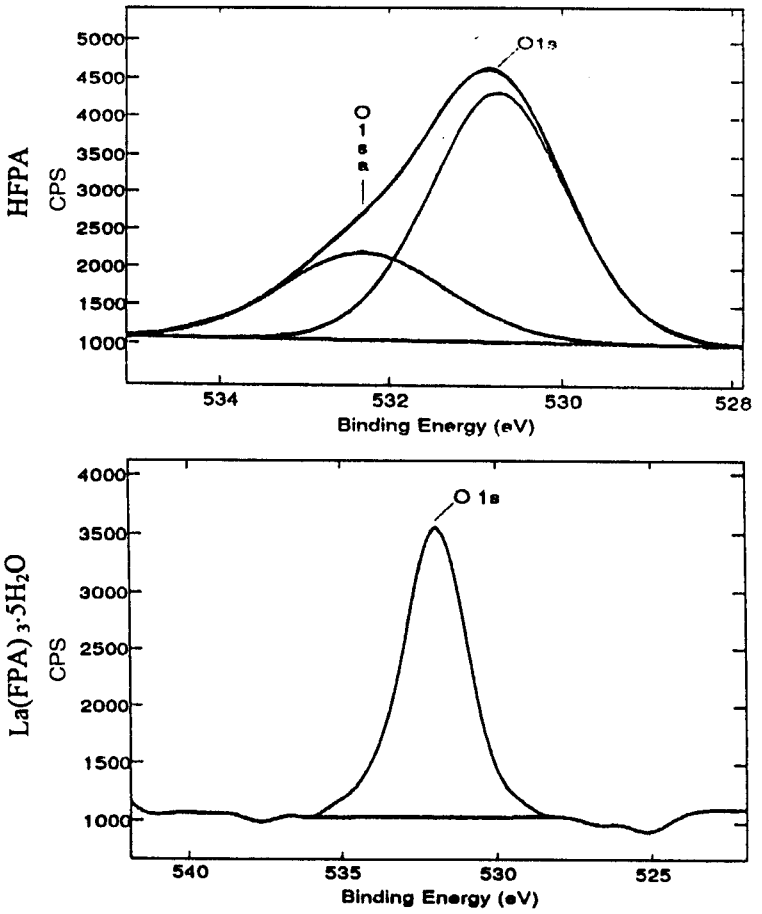

FIGURE 3(a) XPS of O1s of HFPA and $La(FPA)_3 \cdot 5H_2O$.

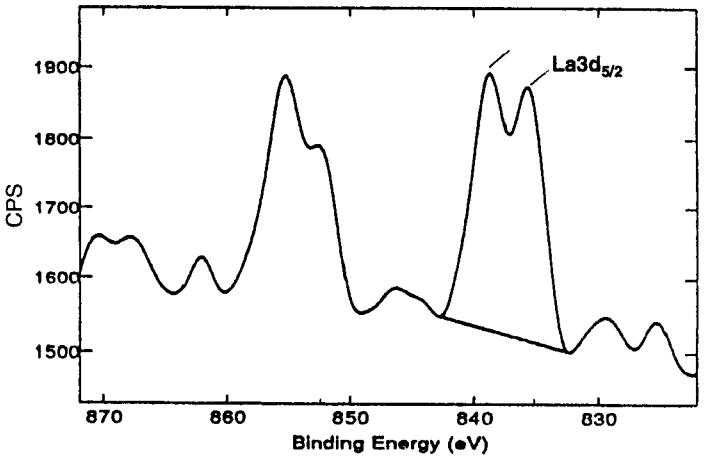

FIGURE 3(b) XPS of $La3d_{5/2}$ of $La(FPA)_3 \cdot 5H_2O$.

is poor. In other words that 4f orbital contributed little to the bonding of the complex. This result is consistent with the electronic spectral studies of the complexes.

Prooxidative Activity

The prooxidative activity of ligand and some complexes were determined. Data are summarized in Figures 4(a)–(c). As shown in Figure 4(a), by comparison of the experimental groups including the complexes and HFPA with the control group, we found that generation of $O_2^{-\bullet}$ radicals increased after treatment with experimental groups. The effects were obviously increased when the concentration increased. At 200 μM generation of $O_2^{-\bullet}$ radicals was increased 140% after treatment with the Pr^{3+} complex. In Figure 4(b), we can see the same, that at low concentration (25 μM) complexes cannot induce more $OH^\bullet$ radicals generation, but at higher concentration (200 μM), the generation of $OH^\bullet$ radicals was improved almost 165% by Pr^{3+} complex under the same conditions. In order to compare the effects of RE(III) complexes with the free ligand HFPA directly and clearly, the results presented in Figure 4(c) are pertinent. This figure illustrates that complexes have greater prooxidative effects than HFPA under the same conditions. Secondly this activity is greatly enhanced at higher concentration. Lastly the increased percent of $OH^\bullet$ radicals was higher than that of $O_2^{-\bullet}$ radicals, indicating more effects on $OH^\bullet$ than for $O_2^{-\bullet}$ radicals.

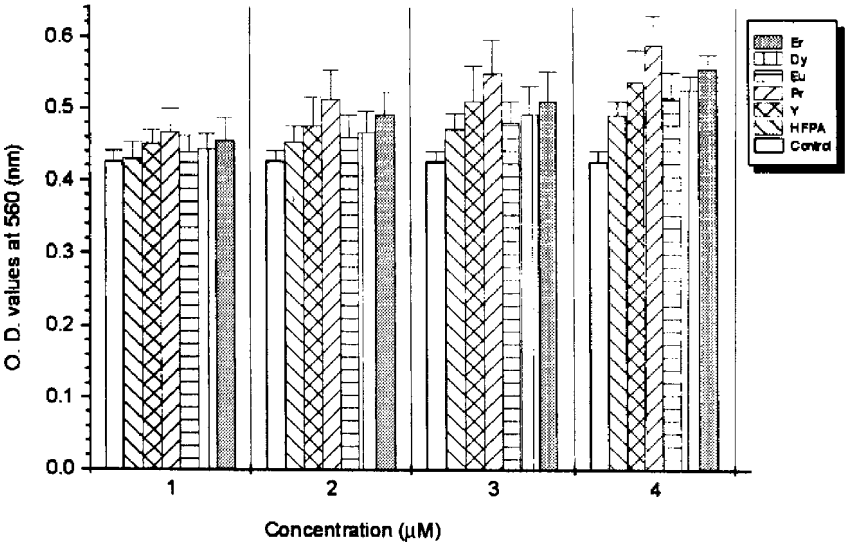

FIGURE 4(a) Effects of different compounds on $O_2^{-\bullet}$ radicals; 1–4 present the different concentration 25, 50, 100 and 200 μM, respectively.

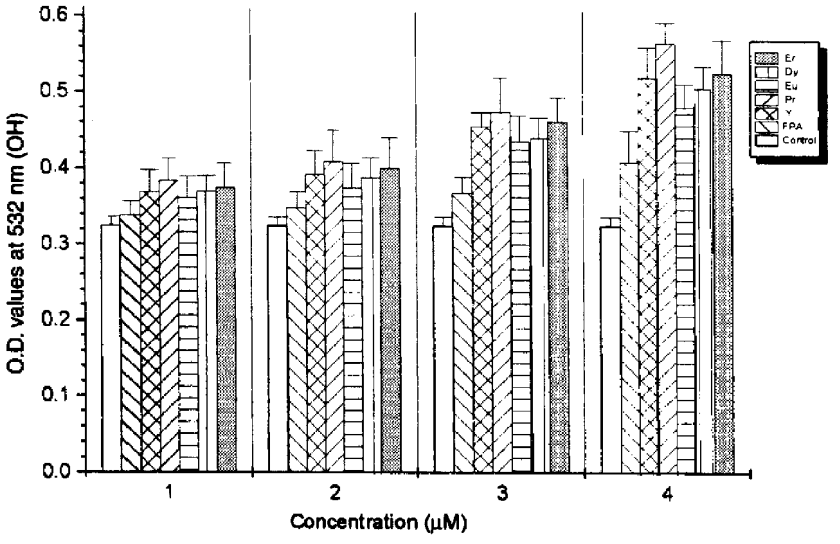

FIGURE 4(b) Effect of different compounds of $OH^{\bullet}$ radicals; 1–4 present the different concentration 25, 50, 100 and 200 μM, respectively.

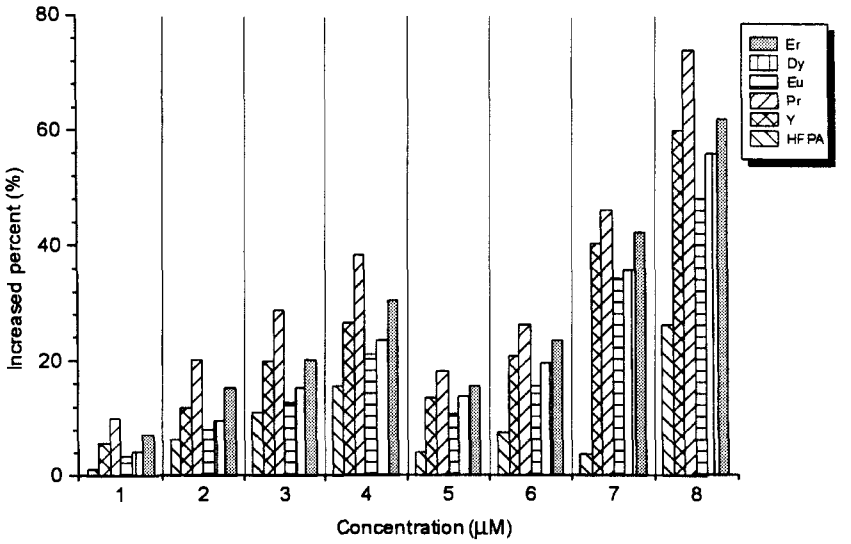

FIGURE 4(c) Increasing percent of different compound on the free radicals; 1–4 refer to the increasing effects on $O_2^{-\bullet}$ and the concentrations of the compounds vary from 25, 50, 100 to 200 μM, respectively; 5–8 refer to the increasing effects on $OH^{\bullet}$ radicals and the concentration of the compounds vary from 25, 50, 100 to 200 μM.

Antitumor Studies

Data on inhibitory effects of 5-FU, HFPA, Y(III) and La(III) complexes against human leukemia HL-60 and human colon bladder HCT-8 cells (tested in Key Lab. of Beijing Nat. and Bionic. Med.) are given in Table IV. In comparison of the complexes with HFPA, we found that $La(FPA)_3 \cdot 3H_2O$ and $Y(FPA)_3 \cdot 3H_2O$ greatly inhibit the proliferation of HCT-8 (Table V) and HL-60 cells, respectively, indicating that the antitumor effects of these complexes were better than the free ligand. Subsequently, the clinical medicine 5-FU was also used to compare with complexes, in order to get more biological information about the complexes. The results, as shown in the tables, indicate that the inhibitory effect of La^{3+} complex on HCT-8 cells is even great than that of 5-FU, indicating that $La(FPA)_3 \cdot 3H_2O$ may be the most promising medicine. In addition, the biochemical effect of Y^{3+} complex was not better than that of 5-FU, at the same conditions. The inhibiting effects of complexes on tumor cells may be due to their ability to generate more free radicals than HFPA.

Further studies on the detailed mechanism for the reaction of complexes with cancer line and oxygen free radical are in progress.

TABLE IV Inhibitory effects against HL-60 cells

Compound	*Concentration* (μM)	$OD = \bar{X} \pm SD$	*Inhibition ratio* (%)	*Evaluation*
Control		0.637 ± 0.041		
5-FU	0.1	0.660 ± 0.046	−3.6	+
	1	0.528 ± 0.037	17.1	
	10	0.316 ± 0.040	50.4	
HFPA	1	0.672 ± 0.102	−5.5	—
	0.1	0.832 ± 0.144	−30.6	
	10	0.505 ± 0.025	20.7	
La	0.1	0.606 ± 0.065	4.86	−
	1	0.525 ± 0.061	17.6	
	10	0.347 ± 0.100	45.5	
Y	0.1	0.686 ± 0.121	−7.7	+
	1	0.561 ± 0.089	11.9	
	10	0.275 ± 0.019	56.8	

'+' Presents compounds has killing effect on tumor cells; '−' presents no effect and tumor cells grow well.

TABLE V Inhibitory effects against HCT-8 cells

Compound	*Concentration* (μM)	$OD = \bar{X} \pm SD$	*Inhibition ratio* (%)	*Evaluation*
Control		0.916 ± 0.043		
5-FU	0.1	0.893 ± 0.011	2.5	—
	1	0.802 ± 0.011	12.5	
	10	0.556 ± 0.023	39.3	
HFPA	0.1	0.835 ± 0.036	8.8	−
	1	0.510 ± 0.046	44.3	
	10	0.544 ± 0.036	40.61	
La	0.1	0.750 ± 0.096	18.1	+
	1	0.438 ± 0.045	52.2	
	10	0.499 ± 0.016	45.52	
Y	0.1	0.727 ± 0.050	20.6	−
	1	0.485 ± 0.051	47.1	
	10	0.490 ± 0.016	46.5	

'+' Presents compound has killing effect on tumor cells; '−' presents no effect and tumor cells grow well.

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