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Studies on β-Type Binuclear Chelates of Lanthanides with Chlorophosphonazo-mA*

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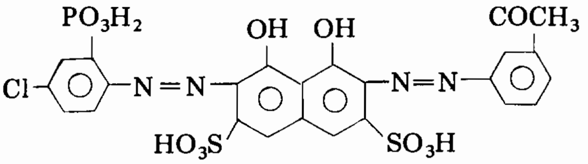
Some 2,7-bis(arylazo) derivatives of chromotropic acid react with heavier lanthanoid ions giving two kinds of chelate: one with an absorption band near 670 nm, defined as the α-type; the other having a maximum absorption in the region of 700–800 nm, defined as the β-type [1]. In our previous studies [2, 3], it has been pointed out that light and heavy rare earth β-type binuclear chelates can be formed with some azo-dyes and their absorption increases remarkably. As a part of a systematic study, this paper discusses a color reaction of chlorophosphonazo-mA (CPA-mA), *i.e.*, 2-(4-chloro-2-phosphonophenylazo)-7-(3-acetylphenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid, with rare earth ions (see Scheme 1).



Scheme 1. Structure of chlorophosphonazo-mA.

Experimental

All absorption spectra were measured with a model UV-300 automatic recording spectrophotometer (Shimadzu, Japan). The hydrogen ion concentration was determined by a pHs-2 model meter (Shanghai, China).

Standard solutions of lanthanoid chlorides were prepared from the respective oxides with a purity of 99.99%. Chlorophosphonazo-mA, purchased from The East China Normal University, was used without further purification. All other chemicals used were of analytical reagent grade. The experimental details may be found in ref. 2.

Results and Discussion

Figure 1 shows the absorption spectra of Ln^{3+}–CPA-mA β-type mononuclear chelates (may be homobinuclear) (left) and Ln^{3+}–CPA-mA–Er^{3+} β-type isobinuclear chelates (right). Most of the light rare earth ions did not form β-type chelates. Only samarium gives a weak peak. Among the heavy rare earth ions, also absorbance of erbium is not strong. From Fig. 1 (right) a hyperchromic effect can be found when the other lanthanoid ions are added respectively into the above Er^{3+}–CPA-mA chelate solution. It follows that a new β-type isobinuclear chelate is formed. In other systems of Ln–CPA-mA–Ln′ (Ln and Ln′ are different lanthanoids) the hyperchromic effect can also be found. As an example, the results of the Ln–CPA-mA–Sm system are given in Table I.

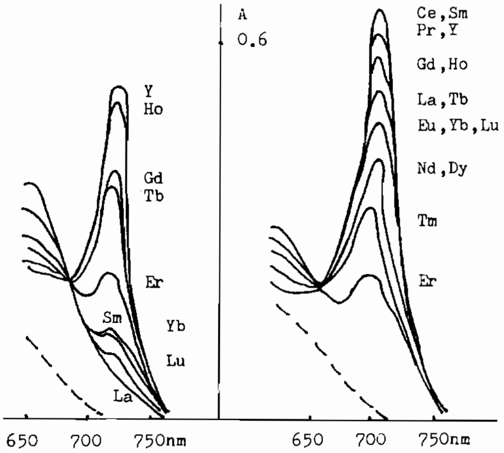


Fig. 1. Left: Ln^{3+}–CPA-mA β-type mononuclear chelates. Right: Ln^{3+}–CPA-mA–Er^{3+} β-type binuclear chelates [Ln^{3+}] = [Er^{3+}] = 6.0 × 10^{-6} M; [CPA-mA] = 2 × 10^{-5} M; pH = 1.5.

TABLE I. Absorption Characteristics of the β-Type Binuclear Chelates in the Sm^{3+}–CPA-mA–Ln^{3+} System

System	λ_{max}	*A*	$\epsilon \times 10^5$
Sm–CPA-mA	712	0.086	0.22
Sm–CPA-mA–La	714.5	0.482	1.21
Sm–CPA-mA–Ce	714	0.614	1.54
Sm–CPA-mA–Pr	714	0.605	1.51
Sm–CPA-mA–Nd	714	0.442	1.11
Sm–CPA-mA–Eu	713	0.489	1.22
Sm–CPA-mA–Gd	712	0.624	1.56
Sm–CPA-mA–Tb	712	0.620	1.56
Sm–CPA-mA–Dy	712	0.477	1.19
Sm–CPA-mA–Ho	712	0.659	1.65
Sm–CPA-mA–Er	712	0.616	1.54
Sm–CPA-mA–Tm	712	0.417	1.04
Sm–CPA-mA–Yb	712	0.559	1.40
Sm–CPA-mA–Lu	712	0.512	1.30
Sm–CPA-mA–Y	712.5	0.604	1.51

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In general, the molar absorptivity of the β-type isobinuclear chelates is higher than those of the β-type mononuclear chelates and the maximum is up to 1.5×10^5 l mol^{-1} cm^{-1}.

TABLE II. Molar Absorptivity of β-Type Binuclear Chelates ($\epsilon \times 10^5$ l mol^{-1} cm^{-1})

Ln + CPA-mA Ln	Sm	Gd	Tb	Ho	Er	Yb	Lu
	0.22	0.33	0.30	1.21	0.33	0.23	0.18
La	1.21	1.38	1.41	1.72	1.39	1.07	0.75
Ce	1.54	1.64	1.56	1.79	1.53	1.30	1.07
Pr	1.51	1.53	1.51	1.70	1.45	1.21	1.01
Nd	1.11	1.15	1.09	1.50	1.01	0.70	0.44
Sm		1.56	1.57	1.65	1.54	1.40	1.30
Eu	1.22	1.18	1.14	1.44	1.13	0.91	0.76
Gd	1.56		1.41	1.56	1.41	1.28	1.21
Tb	1.57	1.41		1.52	1.34	1.45	1.15
Dy	1.19	1.15	1.05	1.31	1.02	0.82	0.65
Ho	1.65	1.56	1.52		1.43	1.35	1.33
Er	1.54	1.41	1.34	1.43		1.15	1.10
Tm	1.04	1.06	0.93	1.23	0.86	0.66	0.41
Yb	1.40	1.28	1.25	1.35	1.15		0.89
Lu	1.30	1.21	1.15	1.33	1.10	0.89	

These isobinuclear chelates are stable in the pH range 1.2–1.8 and the color reaction was completed in 4 h at room temperature. Constant absorbance was obtained with a 8:1:1 ratio of CPA-mA to light and heavy rare earth ion.

All the results of the Ln–CPA-mA–Ln′ system are listed in Table II.

These colored reactions can be used to determine the traces of light rare earths in the presence of heavy rare earths. Beer's law is obeyed over a concentration range of 0–6.0×10^{-6} M for the light rare earths and 0–3.0×10^{-6} M for heavy rare earths. Fifty-fold quantities of K^+, Na^+, Cu^{2+}, $SO_4{}^{2-}$, $PO_4{}^{3-}$, Cl^- and F^- do not interfere. Twenty-fold quantities of Ca^{2+}, Mg^{2+}, Zn^{2+} and Hg^{2+} are permitted. Fe^{3+}, Al^{3+} and Th^{4+} can destroy the formation of a β-type isobinuclear chelate.

References

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