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SPECIFIC BEHAVIOR OF KBF_3OH OBSERVED IN PMR ON THE INTERACTION* BETWEEN La(III)-NITRILOTRIACETATE CHELATE AND FLUOROBORATES

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The effects of NaF, KBF_3OH and $NaBF_4$ on the proton magnetic resonance spectra of La(III)-NTA chelate were investigated in 1:2 molar ratio of La to NTA in H_2O solution at 35°C. The remarkable change of PMR spectra occurs in the presence of KBF_3OH, which is not explained by simple effect of free F^- formed by hydrolysis from BF_4^- and BF_3OH^-.

In a previous paper[1], the author reported the remarkable effect of potassium monohydroxotrifluoroborate(KBF_3OH)on the visible absorption spectra of lanthanum(III) -alizarin complexon(La-ALC)and reports in this paper that the remarkable effect of KBF_3OH is also found on PMR spectra of lanthanum(III) chelate(La-NTA) of nitrilotriacetic acid(NTA) same quadridentate ligand as ALC.

The pH dependence of chemical shift and that of half width are shown in Figs.1 and 2. In the absence of La, a sharp peak corresponding to dissolve species, HL^{2-}, at pH region 3 - 9 appears at τ value 6.2 and a sharp peak corresponding to L^- at high pH region appears at τ value 6.9. The pH dependence of these half width is little. In the presence of 1:2 molar ratio La to NTA, a peak with remarkable pH dependence of half width appears at τ value 6.6, and it is assumed that the broadening of this peak is based on the intermolecular ligand exchange between free NTA and La-NTA.

Effects of NaF, $NaBF_4$ and KBF_3OH on PMR spectra of La-NTA are summarized in Table I with other data for comparative experiments. In spite of equimolar addition of fluorine to La-NTA, the remarkable change occurs only in the presence of KBF_3OH, i. e., a strong peak at τ value 6.6 separates from two weak broad peaks, which are an original peak and a new peak corresponding to free NTA. NaF and $NaBF_4$ bring about same effect as KBF_3OH only by rising reaction temperature, rising concentration of fluorine or prolonging reaction time. Thus, it is assumed that the effective species on these spectrum changes is not F^- or BF_4^- but one or more species of hydrolysis products of BF_4^- as described by following equations[2]

$$BF_4^- \underset{+F^-}{\overset{+OH^-}{\rightleftharpoons}} BF_3OH^- \underset{+F^-}{\overset{+OH^-}{\rightleftharpoons}} BF_2(OH)_2^- \underset{+F^-}{\overset{+OH^-}{\rightleftharpoons}} BF(OH)_3^-$$

The spectrum change of La-NTA from a sharp single peak to two broad peaks in the presence of KBF_3OH may indicate that the interaction between one of three hydroxofluoroborates as described above and either NTA or La-NTA slows down ligand exchange rate between NTA and La-NTA. As is evident from Table I in comparison with Figs. 1 and

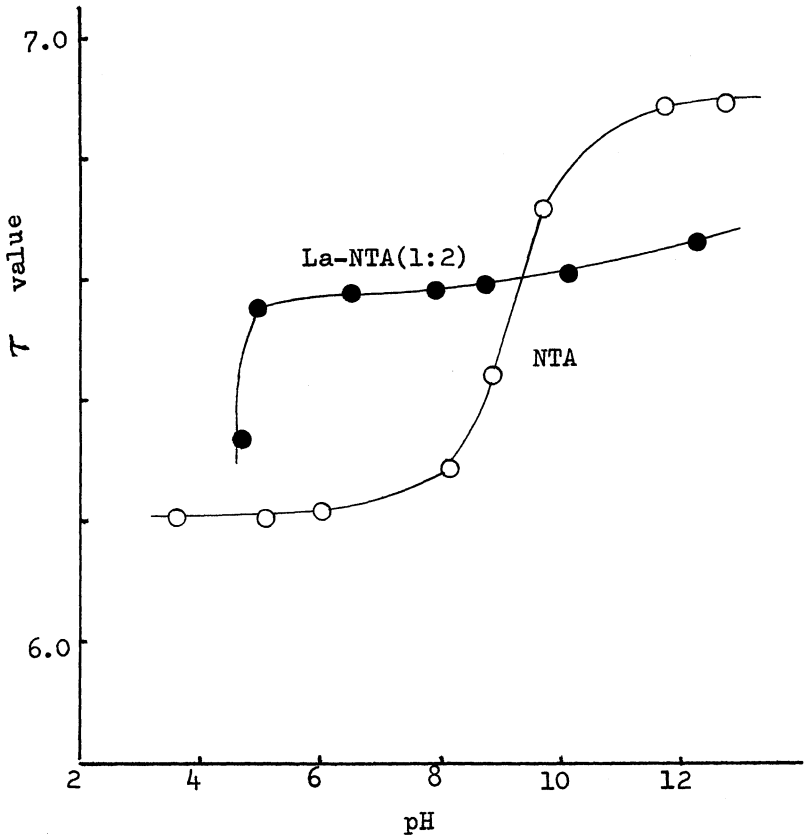


Fig.1 The pH dependence of methylene proton chemical shift in NTA

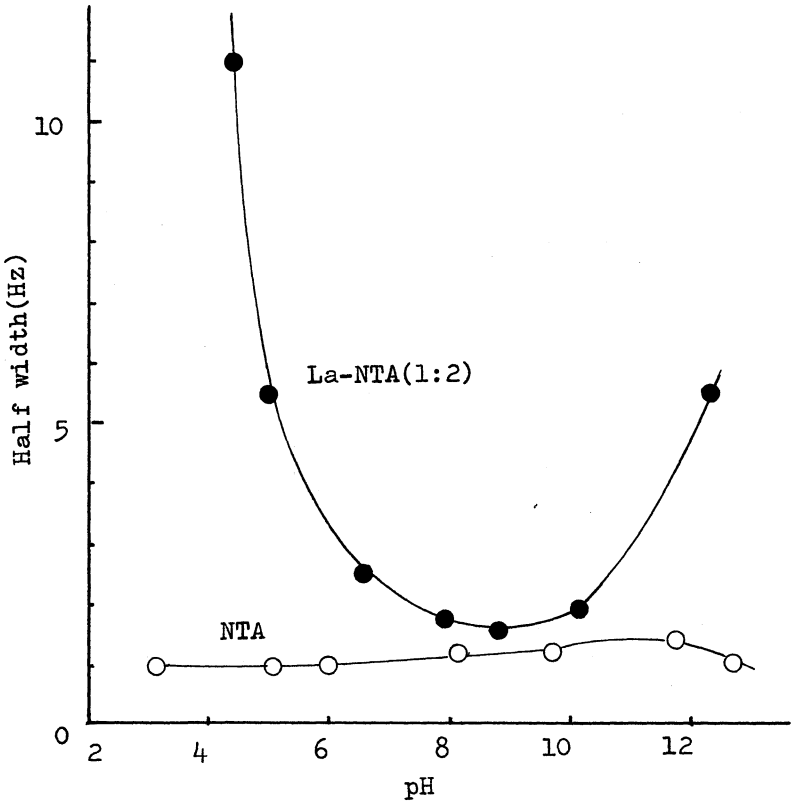
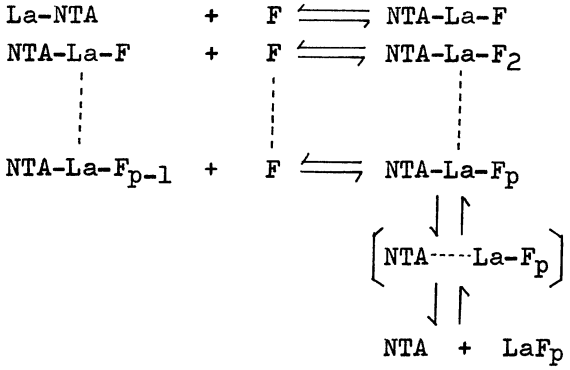
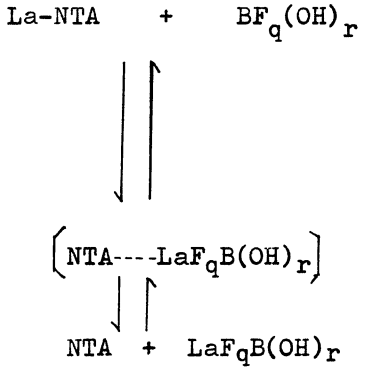


Fig. 2 The pH dependence of half width of methylene proton signal in NTA

2, each spectrum change when $B(OH)_3$ or KBF_3OH is added to NTA corresponds to the pH dependence of NTA spectrum itself, and a signal peak when $B(OH)_3$ is added to La-NTA remains single without separating two peaks. Thus, we assumed that most effective species of three hydroxofluoroborates which brings about the remarkable spectrum change is not a high OH-containing $BF_2(OH)_2^-$ or $BF(OH)_3^-$ but a high fluorine-containing BF_3OH^- because the effect of $B(OH)_3$ on La-NTA spectrum is a little, and that reaction mechanism of BF_3OH^- and La-NTA is as described by following schemes(the charge on ions is omitted for purpose of simplicity).



Scheme I



most probable effective species; q=3, r=1

Scheme II

The reaction of NaF and La-NTA in scheme I is stepwise attacking of fluoride ion to La-NTA chelate, on the other hand, the reaction of BF_3OH^- and La-NTA in scheme II is an effective elimination of La from La-NTA chelate by direct attacking of three fluorines to La-NTA chelate. In view of the fact that the effect of regular tetrahedral BF_4^- on La-NTA is little, the effect of BF_3OH^- on La-NTA may be related to its distort tetrahedral structure.

Experimentals

The PMR spectra were taken on Hitachi R-22 high resolution spectrometer operating at 90 MHz for proton. Chemical shifts were measured relative to t-buthylalcohol as an internal reference(τ value 8.78). Reagent grade 0.22 M and 1.1 M lanthanum nitrate were used to prepare sample solutions of lanthanum-free NTA and 1:2 lanthanum-NTA in water and the pH of these solutions is previously controled by adding nitric acid or sodium hydroxide water solution. The effects of fluoride and fluoroborates on La-NTA PMR spectra were observed after adding solid NaF, $NaBF_4$ or KBF_3OH to above La-NTA water solution and standing for prescribed time at 35°C.

Potassium hydroxotrifluoroborate, KBF_3OH, was prepared by Wamser's method[3] and its purity was confirmed by B, F, K, elementary analyses and X-ray analysis.

Table I

	X	X/NTA (molar ratio)	pH before adding X	pH after adding X[a)]	^{1}H NMR[a) d)] Peak I τ value	Peak I half width (Hz)	Peak II τ value	Peak II half width (Hz)	
NTA + X	$B(OH)_3$	0.5	5.70	5.50	6.23	1.3			
	$B(OH)_3$	0.5	9.31	8.96			6.54	1.5	
	KBF_3OH	0.5	5.70	4.02	6.22	1.6			
	KBF_3OH	0.5	9.22	6.00	6.24	1.0			
La-NTA[e)] + X	$B(OH)_3$	0.5	5.71	5.66			6.51	8.0	
	$B(OH)_3$	0.5	9.38	8.15			6.59	5.0	
	NaF	0.5	5.69	7.50			6.55	6.1	
	NaF	0.5	9.21	9.22			6.60	1.5	
	NaF	1.4	6.44		6.25	9.0	6.59	8.0	
	$NaBF_4$	0.5/4	5.68	5.60			6.57	6.4	
	$NaBF_4$	0.5/4	9.19	9.10			6.60	1.4	
	$NaBF_4$[b)]	2.0	9.20	6.65	6.26	4.5	6.59	8.0	pptn.[c)]
	KBF_3OH	0.5/3	5.61	5.40	6.23	9.2	6.66	10.5	
	KBF_3OH	0.5/3	9.10	6.28	6.25	11.0	6.59	9.0	
	KBF_3OH	0.6	9.10	4.85	6.22	4.0			pptn.

a) Values allowed to stand for 30 min. after adding X except b)
b) Values allowed to stand for 6 days after adding X
c) Forming precipitation
d) On NMR data in the absence of X, refer to Figs. 1 and 2.
e) 1:2 molar ratio of La to NTA mixture

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