

La(III), Pr(III), Gd(III), Tb(III) & Dy(III) Complexes of Aryl Furyl & Aryl Thienyl β -Diketones

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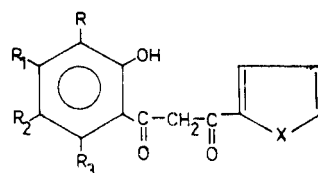
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Proton-ligand dissociation constants of aryl furyl and aryl thienyl β -diketones (I-VII) and stability constants of their complexes with La(III), Pr(III), Gd(III), Tb(III) and Dy(III) have been determined *pH*-metrically in 1:1 (v/v) water-dioxane at 30°C and at ionic strength = 0.1 M (NaClO₄). These ligands form complexes by the deprotonation of phenolic OH.

We report in this note the stability constants of the complexes of La(III), Pr(III), Gd(III), Tb(III) and Dy(III) with aryl furyl and aryl thienyl β -diketones (I-VII). The stability constants were determined by Calvin-Bjerrum *pH* titration technique in 1:1 (v/v) aqueous dioxane at 30°C and at ionic strength = 0.1 M (NaClO₄).

All the chemicals used were of AR grade. The various substituted aryl furyl and aryl thienyl β -diketones were prepared by the methods described earlier¹. 1,4-Dioxane was purified by standard method². The lanthanide ions, La(III), Pr(III), Gd(III), Tb(III) and Dy(III) were used in the form of their nitrates. A digital *pH* meter (Elico model LI-120) with an accuracy of ± 0.001 *pH* unit was used for *pH* titrations. The *pH* correction factor for the non-aqueous dioxane was applied according to the procedure of Van Uitert and Fernelius³.

The difference between $\log K_1$ and $\log K_2$ values of the lanthanide complexes under investigation was less than 2.5 indicating the simultaneous formation of both 1:1 and 1:2 complexes. It was therefore decided to calculate the $\log K_1$ and $\log K_2$ values employing the method of least squares⁴. These values along with thermodynamic dissociation of the ligands are presented in Table 1. There is a possibility of the $\log K_2$ values being less accurate due to hydrolysis of metal ions. The dissociation constants of various β -diketones



- I, R = R₁ = CH₃ ; R₂ = R₃ = H ; X = O
 II, R = R₂ = CH₃ ; R₁ = R₃ = H ; X = O
 III, R = R₃ = CH₃ ; R₁ = R₂ = H ; X = O
 IV, R = C₂H₅ ; R₂ = R₃ = H ; X = O
 V, R = R₂ = CH₃ ; R = R₃ = H ; X = S
 VI, R = R₂ = CH₃ ; R₁ = R₃ = H ; X = S

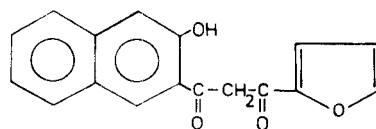


Table 1—Metal Ligand Stability Constants for Lanthanide (III) Complexes

Metal ions	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
	Ligand(I)		Ligand(II)		Ligand(III)		Ligand(IV)	
H ⁺	8.88	—	9.34	—	8.77	—	8.49	—
La ⁺³	6.65	5.00	6.50	—	7.30	5.84	6.19	—
Pr ⁺³	7.04	6.51	6.71	—	6.90	6.65	6.92	—
Gd ⁺³	7.12	7.56	6.84	—	7.67	6.58	7.17	—
Tb ⁺³	7.42	6.08	7.34	—	7.98	7.71	7.32	—
Dy ⁺³	7.57	7.10	7.47	—	6.87	6.57	7.46	—
	Ligand(V)		Ligand(VI)		Ligand(VII)			
H ⁺	8.45	—	9.20	—	8.85	—		
La ⁺³	6.87	5.09	7.10	6.23	6.99	6.25		
Pr ⁺³	6.57	5.98	7.23	6.30	6.36	5.72		
Gd ⁺³	8.00	6.45	7.67	6.58	8.00	5.75		
Tb ⁺³	7.48	6.95	7.50	7.24	7.84	6.62		
Dy ⁺³	7.49	6.98	7.77	7.06	7.35	6.66		

used in this study are well below 9.50 in 1:1 (v/v) water-dioxane indicating the dissociation of proton from phenolic OH. The dissociation of proton from enol tautomer could not be approached since the readings were erratic in this pH region. These ligands can be compared to the unsubstituted phenols and *o*-hydroxyacetophenone. The thermodynamic *pK* value of unsubstituted phenol in 1:1 (v/v) water-dioxane medium is 10.50 (ref. 5), which is higher than the *pK* values of the ligands mentioned above. The increase in acid strength of the ligands is due to the electron withdrawing substituents in the aryl part of the β -diketones.

A linear relationship between $\log K$ and *pK* values of the ligands suggests identical binding sites in all the ligands. In case of ligands (II) and (IV) the $\log K_2$ values could not be determined as the precipitation occurred after pH 5.85.

In the present investigation it has been observed that the Born relation holds good for the La(III) and Pr(III) complexes only, indicating the ionic nature of the complexes. There seems to be a fairly substantial entropy contribution towards the stability of the complexes of Gd(III), Tb(III) and Dy(III), which are non-ionic.

References

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