Complexation of Trivalent Lanthanides and Yttrium by Benzylidenepyruvates in Aqueous Solution*

C. B. MELIOS**, J. T. SOUZA CAMPOS,
M. A. C. MAZZEU, L. L. CAMPOS, M. MOLINA**
and J. O. TOGNOLLI

Instituto de Química, UNESP, Caixa Postal 174, Araraquara (SP), 14.800, Brazil

In a previous work [1] the protonation of 4-dimethylaminobenzylidenepyruvate (DMBP) and 2-chloro-4-dimethylaminobenzylidenepyruvate (2Cl-DMBP), as well as their complex formation with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), Cd(II) and Al(III), have been studied by potentiometric and spectrophotometric methods at 25 °C and ionic strength 0.500 M. The equilibrium investigations were extended to include mixed ligand complexes formed in Cu(II)–B–BP systems, where B = 2,2′-bipyridyl, ethylenediamine or glycinate, and BP = DMBP or 2Cl-DMBP. The results reported were discussed mainly in connection with published stability constants for metal ion–pyruvate complexes. Analytical applications of the investigated ligands were outlined.

The present study deals mainly with complex formation equilibria in M–BP systems, where M = Y(III) and Ln(III) (La to Lu, except Pm), at 25.0 ± 0.1 °C and ionic strength (I) 0.500 M, adjusted by adding sodium perchlorate. The study is mostly concerned with the determination of formation constants and molar absorptivities.

Experimental

Distilled, de-ionised water was used throughout and chemicals were of analytical reagent grade unless indicated otherwise. Lanthanide(III) perchlorates were generally prepared by reaction of the oxides with perchloric acid, a slight excess of the oxides being employed. Cerium(III) perchlorate was synthesized by using the corresponding basic carbonate as starting material. Stock solutions of the metal ions were standardized by complexometric titration with EDTA [2]. Stock solutions of sodium perchlorate were analysed as previously described [1]. Details concerning synthesis of the sodium salts of DMBP and 2Cl-DMBP, standardization of their aqueous solutions, as well as instruments used and methods adopted for determination of formation constants from spectrophotometric data, have been described elsewhere [1].

Results and Discussion

The absorption spectra of $La(ClO_4)_3$ and mixtures of this salt with DMBP (C_M/C_L ratios from 0 to 800, where C_M and C_L are total metal and ligand concentrations, respectively), at constant C_L, covering the range 280–700 nm are given in Fig. 1. The features shown clearly indicate the occurrence of complex formation, pointing to the feasibility of a spectrophotometric study of the system. Addition of La(III) to 2Cl-DMBP, and of other metal ions considered in this work to DMBP or 2Cl-DMBP solutions, showed spectral changes similar to those displayed in Fig. 1. The main results concerning equilibrium studies on the aforementioned systems, *i.e.*, stability constants of 1:1 complex species (β_1) and associated molar absorptivities (ϵ_1), as well as pK_a values, are summarized in Table I. For all metal ions, $\log \beta_1$(DMBP) > $\log \beta_1$(2Cl·DMBP), indicating that the stability is governed, at least in part, by ligand basicity. This last order is also observed for ϵ_1 values. The β_1 values found for complexes involving benzylidenepyruvates are reasonably well correlated with Hancock's C_A parameter [3], suggesting the $-COCOO^-$ moiety as the metal binding site of the ligands. The investigation of possible higher binary complexes (ML_n,

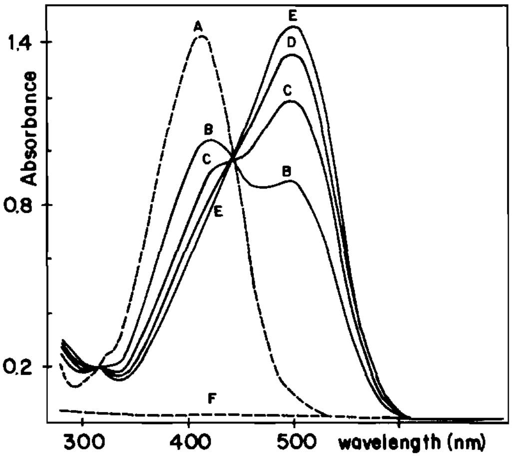

Fig. 1. $La(ClO_4)_3$–DMBP system: absorption spectra of DMBP (C_L = 0.050 mM) with various concentrations of added La(III). C_M = 0.00; 10.0; 20.0; 30.0 and 40.0 mM (Curves A to E, respectively). Curve F: 40.0 mM $La(ClO_4)_3$. (Conditions: pH = 5.18 ± 0.07; I = 0.500 M; t = 25 °C; path length = 1 cm; measurements were against 0.500 M $NaClO_4$.)

---

*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

**Authors to whom correspondence should be addressed.

0020-1693/87/$3.50

TABLE I. Stability Constants and Molar Absorptivities of Binary Complexes of Metal Ions with DMBP and 2Cl-DMBP

Ion	DMBP			2Cl-DMBP		
	$\log \beta_1$ (or pK_a) ± σ^a	λ_{max} (nm)	$\epsilon_{1(max)} \times 10^{-4}$ ($M^{-1}\,cm^{-1}$)	$\log \beta_1$ (or pK_a) ± σ^a	λ_{max} (nm)	$\epsilon_{1(max)} \times 10^{-4}$ ($M^{-1}\,cm^{-1}$)
H^+	3.79 ± 0.02[b]	414	2.90	3.08 ± 0.02[b]	414	2.89
La^{3+}	1.885 ± 0.005	500	3.85	1.776 ± 0.006	490	3.53
Ce^{3+}	2.073 ± 0.006	500	3.95	1.958 ± 0.006	495	3.64
Pr^{3+}	2.173 ± 0.004	505	4.04	2.070 ± 0.007	495	3.68
Nd^{3+}	2.249 ± 0.006	505	4.04	2.153 ± 0.007	500	3.63
Sm^{3+}	2.313 ± 0.003	505	4.08	2.219 ± 0.007	500	3.61
Eu^{3+}	2.286 ± 0.004	510	4.10	2.153 ± 0.003	500	3.73
Gd^{3+}	2.193 ± 0.003	510	4.17	2.077 ± 0.003	510	3.79
Tb^{3+}	2.173 ± 0.001	510	4.30	2.014 ± 0.004	510	4.02
Dy^{3+}	2.185 ± 0.003	515	4.59	2.024 ± 0.003	510	4.11
Ho^{3+}	2.200 ± 0.003	520	4.72	2.029 ± 0.001	510	4.29
Er^{3+}	2.239 ± 0.002	520	4.75	2.085 ± 0.004	510	4.20
Tm^{3+}	2.276 ± 0.002	520	5.00	2.128 ± 0.005	510	4.35
Yb^{3+}	2.269 ± 0.001	515	4.22	2.112 ± 0.001	510	4.14
Lu^{3+}	2.367 ± 0.008	520	5.14	2.248 ± 0.006	515	4.34
Y^{3+}	2.062 ± 0.003	515	4.69	1.942 ± 0.003	510	4.11

Conditions: $I = 0.500$ M ($NaClO_4$); $t = 25.0 \pm 0.1$ °C. [a] Standard deviation. [b] From ref. 1.

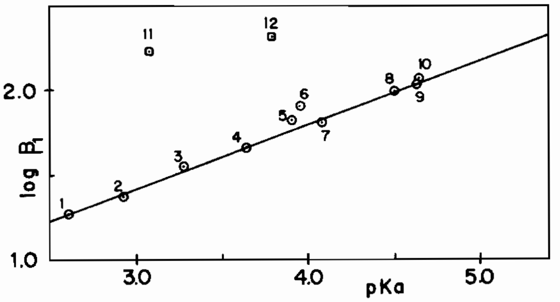

Fig. 2. Relationship between the stability constant, β_1, for formation of SmL^{2+} and the acid constant, pK_a, of HL: (1) chloroacetate; (2) iodoacetate; (3) 3-nitrobenzoate; (4) 3-fluorobenzoate; (5) 4-fluorobenzoate; (6) benzoate; (7) 3-mercaptopropionate; (8) acetate; (9) propionate; (10) isobutyrate; (11) 2Cl-DMBP; (12) DMBP ($I = 0.500$ M ($NaClO_4$); $t = 25$ °C).

$n > 1$) was prevented by solubility limitations; for most of the metal ions considered, working with $C_M = 0.025–0.050$ mM, precipitation takes place as soon as C_L/C_M is equal to or higher than 1.2.

Figure 2 shows the relationship between the $\log \beta_1$ values for a number of Sm(III) complexes with alkyl- and arylmonocarboxylates and pK_a values of the ligand acids. The values for the benzoate and phenyl-substituted benzoate complexes were taken from ref. 4; the remaining data are from ref. 5. The values have been adjusted when necessary to an ionic strength of 0.500 M in $NaClO_4$ medium by employing the conversion factors given by Choppin *et al.* [6] and Smith *et al.* [7]. The $\log \beta_1$ values associated with the benzylidenepyruvates show no correlation with the linear relationship displayed in Fig. 2. The source of the enhanced stabilization is tentatively rationalized by taking into account (in addition to the possible bidentate nature of the BP ligands) that conjugate π systems should show intraligand charge polarization, especially in the presence of multiply charged cations [8]; the basicity of the ketonic carbonyl oxygen is thus reinforced. Also, *keto–enol* tautomerism in BP ligands cannot be ruled out; both Ln^{3+}–*keto* and Ln^{3+}–*enol* complexes should form, so $\beta_T = \beta_1(keto) + \beta_1(enol)$.

Acknowledgements

The support of FAPESP and CNPq Foundations, Brazil, is gratefully acknowledged.

References

1 C. B. Melios, V. R. Torres, M. H. A. Mota, J. O. Tognolli and M. Molina, *Analyst, 109,* 385 (1984).
2 G. Schwarzenbach and H. Flaschka, 'Complexometric Titrations', Methuen, London, 1969.
3 R. D. Hancock and F. Marsicano, *Inorg. Chem., 19,* 2709 (1980).
4 G. R. Choppin and L. H. J. Lajunen, *Inorg. Chem., 25,* 3512 (1986).
5 A. E. Martell and R. M. Smith, 'Critical Stability Constants', Vol. 3, Plenum, New York, 1977.
6 G. R. Choppin, P. A. Bertrand, Y. Hasegawa and E. N. Rizkalla, *Inorg. Chem., 21,* 3722 (1982).
7 R. M. Smith, A. E. Martell and R. Motekaitis, *Inorg. Chim. Acta, 99,* 207 (1985).
8 G. R. Choppin, *J. Less-Common Met., 112,* 193 (1985).