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PRELIMINARY NOTE

COMPLEXATION OF METAL IONS BY BENZYLIDENEPYRUVATE, IN AQUEOUS SOLUTION

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ABSTRACT: Complex formation equilibria involving M-BP binary systems in aqueous solution, where M = Cu(II), La(III), Pr(III), Sm(III), Lu(III), Sc(III) and Th(IV); BP = benzylidenepyruvate have been investigated spectrophotometrically at 25°C and ionic strenght 0.500 M. Coordination centres in BP are suggested.

KEYWORDS: Metal ions; benzylidenepyruvates; equilibria in solution.

INTRODUCTION

In previous works from this laboratory, several metal ion complexes of three phenyl-substituted derivatives of benzylidenepyruvate, $C_6H_5\text{-}CH{=}CH\text{-}COCOO^-$ (BP), i.e., 4-dimethylaminobenzylidenepyruvate (DMBP), 2-chloro-4-dimethylaminobenzylidenepyruvate (2-Cl-DMBP) and 4-methoxybenzylidenepyruvate (4-MeO-BP) have been investigated in aqueous solution[1,6]. The factors that govern the thermodynamic stability and the selectivity of these ligands towards metal ions, as well as analytical applications of the correspondent complexation reactions have been the main purposes of the aforementioned studies.

In an endeavour to extend the previous works, the present communication deals with complex formation equilibria involving M-BP systems, where M = Cu(II), La(III), Pr(III), Sm(III), Lu(III), Sc(III) and Th(IV), studied spectrophotometrically in aqueous solution. Preliminary results and conclusions associated with these systems are compared with those found for previously studied binary systems comprising the same metal ions and closely related ligands, i.e., DMBP, 2-Cl-DMBP and 4-MeO-BP.

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EXPERIMENTAL

Distilled, de-ionized water was used throughout and all chemicals were of analytical-reagent grade. Lanthanides(III), Sc(III) and Cu(II) perchlorates were prepared as previously described[1]. Thorium(IV) perchlorate was prepared from the correspondent nitrate as described by PORTANOVA et al.[7] Sodium benzylidenepyruvate was synthesized and purified essentially as recommended by REIMER[8] and its solutions were standardized by emission spectrophotometric determination of sodium. Details concerning the standardization of stock solutions of metal salts 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 features shown by the absorption spectra of M-BP binary mixtures in aqueous solution clearly indicate the occurrence of complex formation, pointing to the feasibility of a spectrophotometric study of the systems. The observed spectral changes are closely similar to those displayed by previously investigated systems[1,3,5]. 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 the pKa value for BP, are given in Table 1. The investigation of possible higher complexes (ML_n, $n > 1$) was prevented by solubility limitations.

TABLE 1 – Binary Complexes of Metal Ions with Benzylidenepyruvate. Stability Constants and Molar Absorptivities

I = 0.500 M ($NaClO_4$) t = 25.0 ± 0.1°C

ION	$\log \beta_1$(or pKa) $\pm \sigma^a$	λ^b(nm)	$\varepsilon_1^{\lambda}.10^{-4}(M^{-1}.cm^{-1})$
H^+	1.419 ± 0.007	345	0.851
Cu^{2+}	1.094 ± 0.005	350	1.17
La^{3+}	1.319 ± 0.003	350	1.25
Pr^{3+}	1.529 ± 0.003	350	1.51
Sm^{3+}	1.645 ± 0.003	350	1.49
Lu^{3+}	1.475 ± 0.003	350	1.56
Sc^{3+}	2.230 ± 0.001	350	2.38
Th^{4+}	2.740 ± 0.001	365	1.63

a – Standard deviation b – Analytical wavelength

The pKa values of BP, 4-MeO-BP, 2-Cl-DMBP and DMBP as well as the log β_1 of their complexes are summarised in Table 2. The results show, for all considered metal ions, $\log \beta_1(BP) < \log \beta_1(4\text{-MeO-BP}) < \log \beta_1(2\text{-Cl-DMBP}) < \log \beta_1(DMBP)$, indicating that the stability is governed, at least in part, by ligand basicity.

TABLE 2 – Stability Constants of binary complexes of Metal Ions with benzylidenepyruvates

I = 0.500 M ($NaClO_4$) t = 25.0 ± 0.1°C

ION	log β_1 (or pKa)			
	BP[a]	4-MeO-BP[b]	2-Cl-DMBP[c]	DMBP[c]
H^+	1.419	1.473	3.08	3.79
Cu^{2+}	1.094	1.283	1.962	2.207
La^{3+}	1.319	1.442	1.776	1.885
Pr^{3+}	1.529	1.705	2.070	2.173
Sm^{3+}	1.645	1.813	2.219	2.313
Lu^{3+}	1.475	1.687	2.248	2.367
Sc^{3+}	2.230	2.608	3.443	3.707
Th^{4+}	2.740	3.093	4.714	5.336

a – this work b – references 5 and 6 c – references 1, 2 and 3

Figure 1 shows the relationships between log β_1 values for a number of Th(IV) complexes with alkyl-, aryl- and -hydroxymonocarboxylates and pKa(s) of the ligand acids; the data were taken from refs. 9 and 10. 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.[11] and SMITH et al.[12] The log β_1 values associated with the benzylidenepyruvates show no correlation with the linear relationships displayed in Figure 1, in so far as alkyl-, aryl- and -hydroxymonocarboxylates are concerned; it has been noted that the stability constants associated with complexes of benzylidenepyruvates are consistently higher than those found for other monocarboxylates.

The source of the considerably enhanced stabilization is tentatively rationalized by taking into account, in addition to the possible bidentate nature of the BP ligands, that conjugate systems should show intraligand charge polarization, especially in the presence of multiply-charged cations[13]; the basicity of the ketonic carbonyl oxygen is thus reinforced (Chart 1). Also, a certain amount of electronic charge transfer to the bonding carboxylate site as well the occurrence of keto-enol tautomerism in BP ligands cannot be ruled out; in this last case, both metal ion keto- and enol- complexes should form, so $\beta_T = \beta_1(\text{keto}) + \beta_1(\text{enol})$. Regarding the keto form, the canonical structure II (Chart 1) is apparently the main one involved in the complexation. Participation of structure III must be small or negligible, as very high stabilities would be expected in that case; the order of magnitude should be of ~ 10^9, which is the β_1 value found for the complex[14].

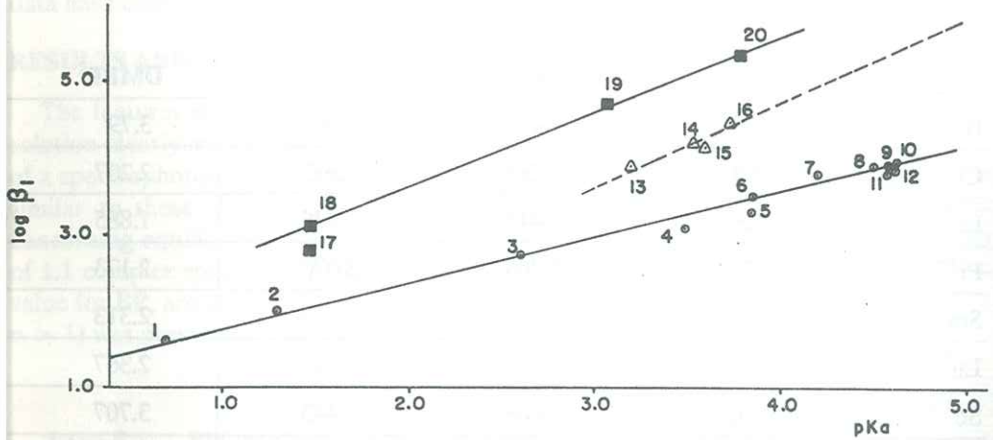
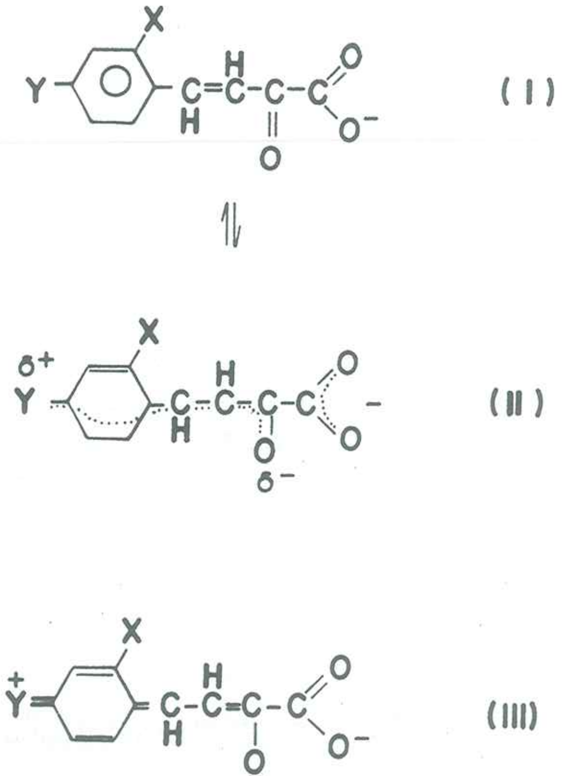


FIG. 1 – Relationships between stability constants, β_1, for formation of ThL^{3+} and the acid constants, pKa, of HL; I = 0.500M($NaClO_4$) t = 25.0°C. **Simple monocarboxylates:** (1) trichloroacetate; (2) dichloroacetate; chloroacetate; (4) formate; (5) 3-methoxybenzoate; (6) 3-chloropropionate; (7) cinnamate; (8) acetate; (9) butyrate; (10) propionate; (11) 4-hydroxybutyrate; (12) isobutyrate. **α-hydroxymonocarboxylates:** (13) mandelate; (14) glycolate; (15) lactate; (16) 2-hydroxyisobutyrate. **Benzylidenepyruvates:** (17) BP; (18) 4-MeO-BP; (19) 2-Cl-DMBP; (20) DMBP.

None of the above mentioned bonding modes of benzylidenepyruvates can be excluded, although there is no direct evidence concerning the existence of most of them at this stage. Multinuclear NMR could help sort out, so appropriate experiments are presently being planned and performed. Also, further studies on systems comprising metal ions and several other phenyl-substituted benzylidenepyruvates are under way in order to improve our understanding of metal ion binding to the aforementioned ligands.

Chart 1



X = H or Cl; Y=H, $N(CH_3)_2$ or OCH_3

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RESUMO: Os sistemas binários M-BP, onde M = Cu(II), La(III), Pr(III), Sm(III), Lu(III), Sc(III), Th(IV) e BP = benzalpiruvato, foram estudados espectrofotometricamente, em solução aquosa, a 25°C e força iônica 0,500 M. Sugerem-se os centros de coordenação do BP.

UNITERMOS: Íons metálicos; benzalpiruvatos; equilíbrios em solução.

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