

COMPLEXATION OF METAL IONS BY 4-CHLOROBENZYLIDENEPYRUVATE IN AQUEOUS SOLUTION

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ABSTRACT: The protonation constant of 4-chlorobenzylidenepyruvate (4-Cl-BP) and the stability constants of its 1:1 complexes with Cu(II), La(III), Pr(III), Sm(III), Lu(III), Sc(III) and Th(IV) have been determined spectrophotometrically in aqueous solution, at 25°C and 0.500M ionic strength (NaClO₄). Coordination centres in 4-Cl-BP are suggested.

INTRODUCTION

In previous works from this laboratory several metal ion complexes of benzylidenepyruvate (BP, C₆H₅-CH=CH-COCOO⁻)¹ and three phenyl-substituted derivatives of BP, i.e., 4-dimethylaminobenzylidenepyruvate (DMBP)²⁻⁴, 2-chloro-4-dimethylaminobenzylidenepyruvate (2-Cl-DMBP)²⁻⁴ and 4-methoxybenzylidenepyruvate (4-MeO-BP)^{5,6} have been investigated in aqueous solution.

In an endeavour to extend the previous work, the present communication deals with preliminary results concerning complex formation equilibria in M-4-Cl-BP systems, where M = Cu(II), La(III), Pr(III), Sm(III), Lu(III), Sc(III) and Th(IV), studied spectrophotometrically in aqueous solution, at 25.0°C and ionic strength 0.500M, adjusted with NaClO₄.

EXPERIMENTAL

Distilled, de-ionized water was used throughout and all chemicals were of analytical-reagent grade. The 4-chlorobenzylidenepyruvic acid and its sodium salt were synthesised essentially as recommended by Stecher *et al.*⁷. Details concerning the synthesis of metal ion perchlorates, standardization of stock solutions of metal salts, standardization of stock solutions of 4-chlorobenzylidenepyruvic acid and its sodium salt, as well as instruments used and methods adopted for determination of stability constants from spectrophotometric data have been described elsewhere¹⁻⁴. The pKa value of 4-chlorobenzylidenepyruvic acid was also determined spectrophotometrically, following the directions given by Albert and Serjeant⁸.

RESULTS and DISCUSSION

The pKa values associated with 4-Cl-BP, BP, 4-MeO-BP, 2-Cl-DMBP and DMBP as well as the stability constants of their complexes are summarised in Table I. Only stability constants of 1:1 complexes species (β₁) were determined because the investigation of possible higher complexes (ML_n, n > 1) was prevented by solubility limitations.

The results given in Table I show, for all considered metal ions (except for Sc(III) complexes comprising BP and 4-Cl-BP, where logβ₁(4-Cl-BP) > logβ₁(BP)): logβ₁(4-Cl-BP) < logβ₁(BP) < logβ₁(4-MeO-BP) < logβ₁(2-Cl-DMBP) < logβ₁(DMBP), indicating that stability is governed, at least in part, by ligand basicity.

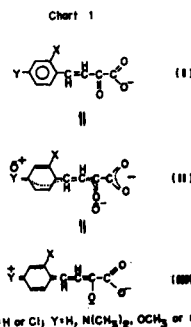
The stability constants of metal ion complexes of benzylidenepyruvates are consistently higher than those found for the corresponding alkyl-, aryl- and in some cases also for α-hydroxymonocarboxylates complexes^{1,3-6}. The source of this enhanced stabilization is tentatively rationalised by taking into account that conjugate π systems should show intraligand charge polarization, especially in the presence of multiply-charged cations, as firstly proposed by Choppin⁹. So, an increase in basicity of the ketonic carbonyl oxygen is expected. Also, a certain amount of electronic charge transfer to the bonding carboxylate site should occur (Chart 1).

The canonical structure II (Chart 1) is apparently the main

TABLE I - Binary Complexes of Metal Ions with BENZYLIDENEPYRUVATES. Stability Constants. I = 0.500M (NaClO₄) t = 25.0°C

ION	logβ ₁ (or pKa)				
	4-Cl-BP ^a	BP ^b	4-MeO-BP ^c	2-Cl-DMBP ^d	DMBP ^d
H ⁺	1413	1419	1473	308	379
Cu ²⁺	1081	1094	1283	1962	2207
La ³⁺	1279	1319	1442	1776	1885
Pr ³⁺	1524	1529	1705	2070	2173
Sm ³⁺	1619	1645	1813	2219	2313
Lu ³⁺	1427	1475	1687	2248	2367
Sc ³⁺	2258	2230	2608	3443	3707
Th ⁴⁺	2659	2740	3093	4714	5336

a - This work b - Ref. 1 c - Refs. 5 and 6 d - Refs. 2,3 and 4



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 10⁹, which is the β₁ value found for the Cu(II)-pyruvate enolate complex¹⁰.

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.

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REFERENCES

- 1 - Siqueira, O.S.; Melios, C.B.; Redigolo, H.; Ionashiro, M. and Molina, M., *Eclética Química* (1991), **16** (in press).
- 2 - Melios, C.B.; Torres, V.R.; Mota, M.H.A.; Tognolli, J.O. and Molina, M., *Analyst*, (1984), **109**, 385.
- 3 - Melios, C.B.; Campos, J.T.S.; Mazzeu, M.A.C.; Campos, L.L.; Molina, M. and Tognolli, J.O. *Inorg. Chim. Acta*, (1987), **139**, 163.
- 4 - Diniz, R.E.O., MSc Thesis, UNESP, Araraquara (SP), Brazil (1987).
- 5 - Redigolo, H., MSc Thesis, UNESP, Araraquara (SP), Brazil (1989).
- 6 - Melios, C.B.; Ionashiro, M.; Redigolo, H.; Miyano, M.H. and Molina, M., *Eur. J. Solid State Inorg. Chem.* (1991), **28**(supl.), 291.
- 7 - Stecher, E.D.; Incorvia, M.J.; Kerben, B.; Levine, D.; Oen, M. and Suhl, E., *J. Org. Chem.* (1973), **38**, 4453.
- 8 - Albert, A.; Serjeant, E.P., "The Determination of Ionization Constants", 3rd. Ed., Chapman & Hall, London (1984), pp. 70-85.
- 9 - Choppin, G.R., *J. Less-Common Met.* (1985), **112**, 193.
- 10 - Miller, B.A. and Leussing, D.L., *J. Amer. Chem. Soc.* (1985), **107**, 7146.