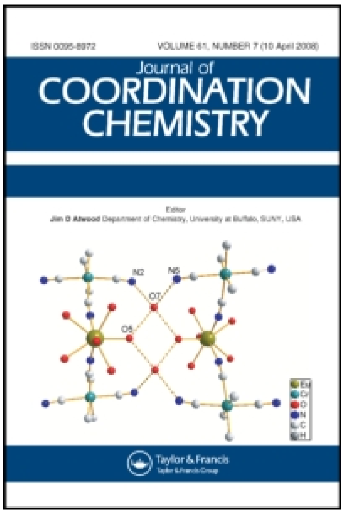

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COMPLEXATION OF ZINC(II) AND CALCIUM(II) IONS WITH ORGANIC MONOPHOSPHATE ESTERS

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The complexation of zinc(II) and calcium(II) ions with the phosphate esters methyl phosphate, glyceryl-2-phosphate, α-*D*-glucose-1′-phosphate, 1-naphthyl phosphate, phenyl phosphate and *p*-nitrophenyl phosphate has been studied by potentiometry at 25°C and an ionic strength of 0.15 M in chloride medium. A linear relationship between the pK_as of the phosphates and the stability constants is found for complexation with zinc(II) ions, but not with calcium(II) ions. The differing behaviour is explained by assuming inner sphere coordination for the zinc complexes, while calcium forms loose ion pairs with the ligands.

Keywords: Organic phosphates, complexes, stability constants, zinc(II), calcium(II)

INTRODUCTION

The importance of the presence of metal ions to many vital biochemical reactions has stimulated a lot of research concerning the interactions of metal ions with biologically relevant or structurally related compounds. In many of these reactions complex formation between the metal ion and a ligand is the prerequisite of a reaction. For example, hydrolytic reactions of phosphorus esters are often mediated by divalent metal ions.[1] In a recent study[2] we investigated complexation between copper(II) ions and a set of monophosphate esters by potentiometry and calorimetry. Complexation was found to be governed by two effects. The first is an electronic induction effect and depends on the electron-donating or electron-withdrawing power of the ester group. The second is the desolvation of metal ion and ligand during complexation. Formation and alteration of hydrogen bonds of the ester group with water or within itself also proved to be of importance for glucose phosphate and glyceryl phosphate.

In this paper we report potentiometric results for the complexation of zinc(II) and calcium(II) ions with the same set of phosphorus esters. Both zinc(II) and calcium(II) ions are esssential to numerous biochemical processes, calcium(II) ions being particularly important in phosphate transfer reactions.[3]

EXPERIMENTAL

The potentiometric method used has been described in detail.[4] The conditions used were a temperature of 25.0±0.1°C and an ionic strength of 0.15 M, which was

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achieved by the addition of sodium chloride (BDH "Aristar") to obtain solutions 0.15 M in chloride ion. Sodium hydroxide solutions and hydrochloric acid solutions were prepared from Merck ampoules and standardized against potassium hydrogen phthalate and sodium hydroxide, respectively. Zinc chloride solutions were prepared by dissolving accurately weighed zinc granules (Merck p.a.) in concentrated hydrochloric acid and subsequent dilution in a calibrated flask. The acid content was standardized *via* Gran titration.[5] Calcium chloride solutions were prepared from anhydrous $CaCl_2$ (ROC/RIC). Metal concentrations of stock solutions were determined by titration against ethylenediaminetetraacetate, EDTA.[6] *p*-Nitrophenyl phosphate (disodium salt, Sigma 104), phenyl phosphate (disodium salt, Aldrich), 1-naphthyl phosphate (synthesized by M. M. Armstrong[4]), α-*D*-glucose-1′-phosphate (disodium salt, Sigma) and glyceryl-2-phosphate (disodium salt, Sigma) were used as supplied after examination of the compounds by proton and phosphorus nmr as well as microanalysis. Methyl phosphate was synthesized.[2] Because of slow hydrolysis reactions, solutions were discarded after 6 hours. During the titrations the ligand and metal ion concentrations varied between 1 and 15 mM. The potentiometric data were analyzed using the program library ESTA[7] to obtain overall formation constants β_{pqr} for the complexes $M_pL_qH_r$

$$\beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$$

by a procedure described earlier.[4] The appropriate metal ion hydrolyses[8] were accounted for in all the refinements.

RESULTS

The formation constants calculated from the potentiometric data are presented in Table I. Complexation could only be studied in the lower pH region because at alkaline pH precipitation occurred. The reproducibility of identical titrations was good or excellent in some cases, but poor for the weakly complexing systems zinc(II)–*p*-nitrophenyl phosphate and calcium(II)–phenyl phosphate.

Overlapping sets of formation curves were obtained only for the complexation of phenyl phosphate with zinc(II) and calcium(II) ions. This suggests that only mononuclear complexes occur and the best refinements were indeed found by assuming one single complex, ML. For all other systems the formation curves show backfanning patterns. In most cases they could successfully be accounted for by postulating the complex MLH_{-1} in addition to ML.

The constants obtained for the calcium complexes $CaLH_{-1}$ of 1-naphthyl phosphate and of methyl phosphate, however, should be regarded as good estimates rather than precise values because the agreement between experimental and theoretical fanning is rather poor despite reasonable statistics. In the case of calcium and glucose phosphate the fanning could not be accounted for at all. It is not possible to decide whether the (reproducible) fanning patterns are real or just a manifestation of experimental error in these weakly complexing systems. Formation curves are particularly sensitive to small errors of the hydrogen ion concentration at higher pH,[9,10] which is also the region of formation of hydroxo complexes. Nevertheless, the values reported for the complex ML for these systems can be regarded as reliable. They were obtained separately from the data in the lower pH region where no fanning occurs and had been kept fixed in the search for additional complexes to explain the fanning.

TABLE I

Logarithms of formation constants, β_{pqr}; d = standard deviation in $\lg\beta$, n_t = number of titrations, n_p = number of data points, R = Hamilton factor; the ligands are: 1 = *p*-nitrophenyl phosphate, 2 = 1-naphthyl phosphate, 3 = phenyl phosphate, 4 = α-*D*-glucose-1′-phosphate, 5 = glyceryl phosphate, 6 = methyl phosphate.

ligand	cation	pqr	$\lg\beta_{pqr}$	d	n_t	n_p	pH-range	R	T/°C	I/(mol/l)	Ref.
1	Zn^{2+}	110	1.758	0.004	6	233	2.4–5.8	0.006	25	0.15 NaCl	*
	Ca^{2+}	110	0.88								11
	H^+	011	4.987	0.001	5	275	2.2–8.5	0.005	25	0.15 NaCl	2
2	Zn^{2+}	110	2.01	0.01	14	400	2.0–6.0	0.005	25	0.15 NaCl	4
		11-1	−4.73	0.03							4
	Ca^{2+}	110	1.223	0.006	7	203	5.2–6.8	0.030	25	0.15 NaCl	*
		11-1	−6.1 to −6.8 suspect								
	H^+	011	5.740	0.005	4	301	2.0–8.0	0.002	25	0.15 NaCl	4
3	Zn^{2+}	110	2.146	0.004	9	191	2.3–6.2	0.014	25	0.15 NaCl	*
	Ca^{2+}	110	1.44	0.03	9	161	3.0–6.0	0.033	25	0.15 NaCl	*
	H^+	011	5.827	0.002	9	394	2.2–10.0	0.012	25	0.15 NaCl	2
4	Zn^{2+}	110	2.34						25	0.1 KNO_3	15
		110	2.37						25	0.1 KNO_3	15
		110	2.118	0.003	9	521	2.5–7.5	0.003	25	0.15 NaCl	*
		11-1	−5.818	0.009							*
	Ca^{2+}	110	2.495							−> 0	16
		110	1.773	0.007	10	429	2.4–8.0	0.003	25	0.15 NaCl	*
	H^+	011	5.9767	0.0003	5	245	2.5–8.6	0.001	25	0.15 NaCl	2
5	Zn^{2+}	110	2.137	0.007	9	737	2.2–7.3	0.006	25	0.15 NaCl	*
		11-1	−5.63	0.02							*
	Ca^{2+}	no complexation									
	H^+	011	6.1054	0.0005	7	366	2.0–11.0	0.001	25	0.15 NaCl	2
6	Zn^{2+}	110	2.16						20	0.1 Cl^-	12
		110	2.175	0.008	8	189	2.7–7.3	0.024	25	0.15 NaCl	*
		11-1	−5.12	0.01							*
	Ca^{2+}	110	1.49						20	0.1 Cl^-	12
		110	1.394	0.009	7	435	3.0–8.0	0.037	25	0.15 NaCl	*
		11-1	−7.09	0.02							*
	H^+	011	6.251	0.001	5	261	2.5–9.5	0.018	25	0.15 NaCl	2

* This work.

Despite the accumulation of a large number of experiments under various conditions, we could not detect any complexation between calcium(II) and glyceryl phosphate. This is rather remarkable because of the comparatively strong complexation of glyceryl phosphate with zinc(II) ions. No attempt was made to study the complexation between *p*-nitrophenyl phosphate and calcium(II) ions because complexation was thought to be too weak ($\lg\beta = 0.88$)[11] to obtain reliable data by potentiometry.

DISCUSSION

Figure 1 shows a plot of $\lg\beta_{ML}$ against pK_a for the protonated ligands. In the case of zinc the points fit a straight line suggesting a linear free energy relationship. This is analogous to complexation with copper(II) ions.[2] It has been demonstrated by spectrophotometry that both copper(II) and zinc(II) form inner sphere complexes with methyl phosphate.[12] Independently, it has been shown by a comparison of the entropy changes accompanying complex formation, that one water molecule is displaced from the inner coordination shell of the zinc(II) ion[13] while at least two water molecules are displaced from the coordination shell of the copper(II) ion.[2] If we assume that inner sphere coordination takes place in the coordination equilibria of the whole series of phosphate esters with zinc(II) ions, we indeed expect to obtain a linear relation between pK_a and $\lg\beta_{ZnL}$. The reason for this is that both complexation and protonation are similar processes in the sense that direct coordination occurs between ligand and cation.

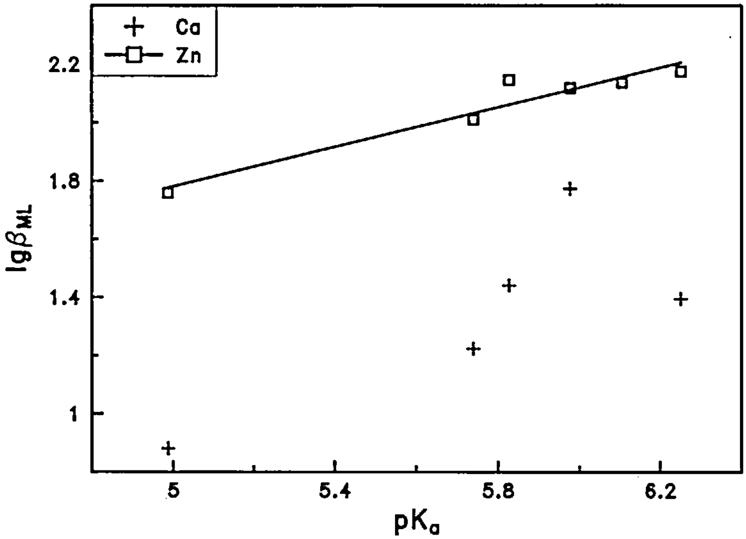

FIGURE 1 Plot of $\lg\beta_{ML}$ against pK_a for zinc(II) and calcium(II) ions.

The points obtained for calcium(II) complexation do not fall on a line in Figure 1. We suggest that, in contrast to zinc(II), calcium(II) does not form inner sphere complexes with phosphate esters, but that loosely associated ion pairs are formed. This again is supported by spectrophotometric measurements[12] of the calcium(II)–

methyl phosphate complex. In addition, the small magnitude of the stability constants ($\lg\beta < 1.8$) points to outer sphere complexation. Any stability constant can be divided into an inner sphere and an outer sphere contribution, $\beta = \beta_{is} + \beta_{os}$. The term β_{os} can be estimated by use of the Fuoss equation.[14] For complexes of divalent metal ions with di-negative ligands we calculate $\lg\beta_{os}$ to be in the range 1.8 to 2.3 if the centre-to-centre distance of the ions in a pair is assumed to be 6–8Å. This result indicates that for both zinc(II) and calcium(II) outer sphere complexation is significant, but that for calcium(II) it may be the only contribution. Thus we do not obtain a linear relation between pK_a and $\lg\beta_{CaL}$.

Entropy considerations[13] led to the contrary result that two water molecules are displaced from the inner hydration sphere of calcium(II) upon complexation with methyl phosphate. We feel that this conclusion needs confirmation by redetermination of the respective stability constants as well as direct calorimetric measurements, preferably of the whole series of phosphate esters, in order to identify the factors that give rise to the unexpectedly high complexation entropy of the calcium(II)–methyl phosphate complex.

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REFERENCES

1. B.S. Cooperman, in "Metal Ions in Biological Systems", ed. H. Sigel, (Marcel Dekker Inc., New York and Basel, 1976), vol. 5, p. 79.
2. U. Kramer-Schnabel and P.W. Linder, submitted for publication.
3. D.R. Williams, "The Metals of Life", (Van Nostrand Reinhold Company, London, 1971).
4. M.M. Armstrong, U. Kramer, P.W. Linder, R.G. Torrington and T.A. Modro, *J. Coord. Chem.*, **20**, 81 (1989).
5. G. Gran, *Analyst*, **77**, 611 (1952).
6. Vogel's Textbook of Quantitative Inorganic Analysis, 4th edition, (Longman Group Limited, New York, 1981).
7. P.M. May, K. Murray and D.R. Williams, *Talanta*, **32**, 483 (1985); **35**, 825 (1988); **35**, 927 (1988); **35**, 933 (1988).
8. C.F. Baes, Jr. and R. Mesmer, "The Hydrolysis of Cations", (Wiley, New York, 1976).
9. S. Cabani, *J. Chem. Soc.*, 5271 (1962).
10. A. Avdeef, D. L. Kearney, J.A. Brown, and A.R. Chemotti, *Anal. Chem.*, **54**, 2322 (1982).
11. D. Herschlag and W.P. Jencks, *J. Am. Chem. Soc.*, **109**, 4665 (1987).
12. H. Brintzinger, *Helv. Chim. Acta*, **48**, 47 (1965).
13. R. Aruga, *J. Inorg. Nucl. Chem.*, **43**, 3414 (1981).
14. R.M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).
15. B.E. Doody, E.R. Tucci, R. Scruggs and N.C. Lee, *J. Inorg. Nucl. Chem.*, **28**, 833 (1966).
16. H.B. Clarke and S.P. Datta, *Biochem. J.*, **64**, 604 (1956).