STABILITY CONSTANTS OF PHOSPHINEACETATE COMPLEXES OF DIVALENT METALS*

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Anions of the phosphineacetic acids of the general formula $(C_6H_5)_{3-n}P(CH_2COOH)_n$ ($n = 1$—3) form with the cations Mn^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} in aqueous solutions complexes with the ratio M : L = 1 : 1 and in some cases also 1 : 2. In addition, the ligand with $n = 3$ exhibits the formation of the protonized complexes MHL. The stability constants of the complexes were calculated by statistical processing of the pH-metric titration curves, and the ligands were found to act as the O-donors to Mn^{2+} and Zn^{2+}, and as PO ($n = 1$) and POO ($n = 2, 3$) donors to the other cations.

Phosphineacetic acids of the general formula $(C_6H_5)_{3-n}P(CH_2COOH)_n$ (H_nL; $n = 1$, HA (ref.[1-3]); $n = 2$, H_2R (ref.[2,4]); $n = 3$, H_3X (ref.[5])) have been prepared and characterized in the works cited. From the study of their complexation properties with respect to divalent nickel[3,6,7] and some cations of the soft type[8-10] it follows that these compounds can operate as monovalent or chelating ligands in dependence on the conditions such as the metal ion type, solvent and acidity, the stability of the complexes formed being very different.

For the cations of the hard acid type, an increase of the number of the carboxylic groups in the ligand molecule can be expected to be accompanied by a lowered affinity of the phosphorus atom and, on the other hand, an increased stability of the complexes. In the present work, the complexation of the above ligands with some other divalent cations of transition as well as non-transition metals was studied, the ions representing a series changing in hardness from the divalent nickel to typical hard cations.

EXPERIMENTAL

The preparation of the ligands, purity testing, and purification of sodium perchlorate and dioxane have been reported[3-5]. The stock solutions of the metal perchlorates were prepared by dissolving the freshly precipitated and thoroughly washed oxides or basic carbonates in a slight excess

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of perchloric acid. The solutions did not contain detectable quantities of anions other than perchlorate.

The contents of the metals in the stock solutions were determined chelatometrically and the acid and base concentrations by employing the Gran's method. Bismuth metal (Alfa Inorganics, 99·999%), potassium hydrogen carbonate, and oxalic acid dihydrate (both *p.a.*, Merck) served as the primary standards; the mutual difference of the acid-base standards was below 0·2% rel.

The pH measurements were performed in a vessel fitted with a jacket for thermostatting to 25 ± ± 0·1°C and with ground joints for the inlet and outlet of pure nitrogen, the electrodes, and burette. A glass electrode G 202 C and a calomel electrode K 401 or a combined electrode GK 2302 C of Radiometer were used in conjunction with an instrument PHM 64 of the same manufacturer. The electrode systems were calibrated in aqueous medium[3] and in 50% (v/v) dioxan so[3,11] that the output values corresponded immediately to $-\log [H^+]$ with the precision of ±0·005. The calibration of the electrodes was checked prior to each series of measurements and between the individual titrations the stability of the system was checked with 0·05M potassium hydrogenphthalate solution.

For the measurements, 50 ml of the starting solution was prepared in inert atmosphere from the stock solvents and solutions (free from carbonates and from dissolved oxygen and carbon dioxide) and from weighed amounts of the ligand so that it contained the metal and the ligand in a ratio between 2 : 1 to 1 : 8, the total ligand concentration being 0·002 to 0·005 mol l^{-1} and ionic strength 0·1 (Na)ClO_4. In view of the insolubility of HA in water, all the measurements were accomplished also in 50% (v/v) dioxan. In the first measurement series, the starting solutions contained excess free perchloric acid and were titrated with 0·1M-NaOH from a calibrated burette (precise to ±0·002 ml) in 20—40 increments up to pH 12 or until the metal hydroxide precipitated. In the second series, the starting solutions were neutral or weakly basic and the titrating agent was 0·1M-$HClO_4$ (down to pH 2 or until HA precipitated in the aqueous solution). After each titration, the content of the trivalent phosphorus was re-checked iodometrically.

During the data processing, a tentative calculation[12] of the curves of the complex formation $\bar{n}$ *vs* $-\log [L]$ proved that no polynuclear complexes were formed in the systems and that the equilibria were reashed instantaneously since the two titration types were always completely consistent. The protonization constants of the ligand requisite for the calculation were taken from the previous works[3-5]. In the systems Co, Cd, Pb/H_3X a significant dependence of the curves of $\bar{n}$ *vs* $-\log [L]$ on the starting acidity of the solution was observed indicating the presence of protonized complexes.

The composition of the complexes and appropriate estimates of their stability constants, found from the formation curves, served then as the input parameters for the statistical program MINIQUAD (ref.[13]). The optimum parameters were sought by systematically varying the set the input complex compositions, any new complex being considered as acceptable if the overall error function decreased at least by 20%; this decrease corresponds approximately to twice of that caused by the total cumulation of the experimental errors, as verified by a tentative processing of one-sidedly biassed input values of the solution composition, consumption, and $-\log [H^+]$ for a typical data set. Some titrations were further processed by using the program[14] SCOGS, which employs a different statistical method; the resulting values of the constants agreed within their standard deviations.

The calculations were performed on an EMG 666 calculator and on an ICL 4-72 computer.

RESULTS AND DISCUSSION

In the system under study, the complexes are formed of the composition and stability constants as given in Table I. The ligand protonization constants and the stability constants of the nickel complexes found previously are shown in the table for a comparison, too.

In accordance with the expected low affinity of the phosphorus towards the cations concerned, the stability of the complexes studied is comparatively low. The stability constants for the various cations decrease independently of the ligand in the order Ni ≈ Pb > Cd > Co > Zn > Mn; the position of the transition metal cations complies with the Irving–Williams series, and the position of Pb and Cd is typical, too.

TABLE I

The log β Values of Phosphineacetate Complexes

25°C, I 0·1 (Na)ClO$_4$; $\beta_{pqr} = [M_qH_rL_p]/[M]^q[H]^r[L]^p$ (the charges are omitted); A = $(C_6H_5)_2P(CH_2COO^-)$, R = $C_6H_5P(CH_2COO^-)_2$, X = $P(CH_2COO^-)_3$; the 3σ values are given in parentheses.

Cation	pqr	A		R		X	
		H_2O	dioxan[a]	H_2O	dioxan[a]	H_2O	dioxan[a]
H^+[b]	101	3·82 (1)	6·05 (6)	4·76 (3)	6·59 (3)	5·43 (2)	7·16 (2)
	102	—	8·04 (7)	8·12 (3)	11·49 (4)	9·20 (2)	12·26 (4)
	103	—	—	—	13·29 (9)	11·93 (3)	16·37 (4)
Mn^{2+}	110	<1	1·9 (2)	<1	2·69 (2)	2·04 (3)	3·99 (2)
Co^{2+}	110	1·7 (1)	2·35 (3)	2·71 (3)	4·52 (6)	3·14 (1)	5·27 (2)
	111	—	—	—	—	7·21 (7)	10·21 (3)
	210	—	—	—	8·01 (9)	5·32 (9)	8·8 (1)
Ni^{2+}[c]	110	∼2·4[d]	∼3·5[d]	3·68 (4)	5·52 (2)	3·77 (1)	6·13 (1)
	111	—	—	—	—	7·18 (6)	10·44 (3)
	210	5·54 (4)	7·08 (3)	6·49 (8)	9·67 (3)	6·41 (9)	10·61 (7)
Zn^{2+}	110	1·3 (2)	2·54 (6)	1·69 (3)	3·64 (5)	2·50 (2)	4·97 (7)
Cd^{2+}	110	2·30 (8)	3·19 (6)	3·08 (3)	4·95 (8)	3·55 (1)	6·0 (3)[e]
	111	—	—	—	—	7·12 (4)	11·11 (4)
	210	—	—	—	8·6 (2)	—	—
Pb^{2+}	110	2·69 (2)	3·93 (5)	2·93 (3)	—	3·79 (3)	[e]
	111	—	—	—	[e]	7·82 (5)	12·75 (2)
	210	4·65 (6)	7·1 (1)	—	—	—	—

[a] 50% (v/v); [b] see[3–5]; [c] see[3,6,7]; [d] the system contains less than 10% of the complex; [e] precipitate formed.

If the ligands are varied, the stability of the complexes increases with the increasing number of the donor atoms, hence in the order A < R < X. The relative ratios of the stability constants of the first and the second or of the second and the third members of the series are, however, dependent on the metal ion involved. While the $\log \beta_{MR}/\log \beta_{MA}$ ratios are similar for all the cations, amounting to about 1·4, ratios of the cations studied can be divided into two groups according to the ratio $\log \beta_{MX}/\log \beta_{MR}$: with Mn^{2+} and Zn^{2+} the ratio is about 1·5, whereas with the remaining cations, including Ni^{2+}, it is only approximately 1·1. Similar relations were found to hold also for the complexes 1 : 2, so far as their stability constants could be measured. These different trends of the constants are obviously related with the different affinity of the cations towards phosphorus: as indicated by the absolute values of the stability constants and by their comparison with those of the nitrogen analogues[15], the Mn^{2+} and Zn^{2+} are probably coordinated by the carboxyl oxygens only and not by the phosphorus atom. This accounts for the gradual increase of the stability of their complexes in the order A < R < X, hence from the monodentate O-donor A^- (giving rise to complexes whose stability is comparable with that of, *e.g.*, the acetate complexes[15]) to the terdentate OOO-donor X^{3-}.

In the remaining group of cations, Ni^{2+}, Co^{2+}, Cd^{2+}, and Pb^{2+}, the absolute values of the stability constants (in accordance with some other properties of the nickel complexes[3,6,7] and in comparison with the nitrogen and arsenic analogues[15]) support the bonding of the ligands *via* both the carboxyl oxygens and the phosphorus atom. The logical increase of stability from the bidentate PO-donor A^- to the terdentate POO-donor R^{2-} is not, however, followed by an equivalent stabilization for the ligand X^{3-}. As can be seen from molecular models, the phosphorus-bonded phosphinetriacetate is, in fact, sterically unable to operate as a tetradentate POOO-donor, even towards the lead cation. The one carboxyl group that remains uncoordinated is easily protonized, and it is just Ni, Co, Pb, and Cd, and not Mn and Zn, that their MHX complexes are detectable. The type of the ligand bonding in these four protonized complexes is the same, as evidenced by the linear dependence of logarithms of their deprotonation constants ($[H][MX]/[MHX]$) on $\log \beta_1$.

The dividing of the cations involved into the two groups is supported also by the comparison of the corresponding stability constants in water and in 50% (v/v) dioxan: the higher stabilization of the Mn and Zn complexes is associated with the greater proportion of the ionically bonded donor atoms in the complex, whereas the stability of the complexes involving the covalent phosphorus atom is affected by the change of the dielectric constant of the medium less markedly[16].

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