

THE STABILITY CONSTANTS OF COPPER(I) PHOSPHINEACETATES*

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Systems containing univalent copper, phosphineacetic acid H_nL with the general formula $Ph_{3-n}P(CH_2COOH)_n$ ($n = 1-3$) and acetonitrile in a concentration necessary for stabilizing free copper(I) were studied by potentiometry with copper amalgam and glass indicating electrodes. The measurements were carried out in water and in 50 v/v % dioxan at 25°C and $I = 0.1$ (NaClO₄). Consecutive formation of complexes with $Cu^I : L^{n-} = 1 : 1, 1 : 2, 1 : 3$ and $1 : 4$, whose stability decreases slightly with an increasing number of acetate groups in the ligand and from 50% dioxan to water, was found in all systems. In these complexes the ligands are coordinated through the phosphorus atom alone. The acetonitrile completes the coordination sphere of copper in complexes with $L/Cu < 4$.

Phosphines are very good ligands for univalent copper, with which they form several types of complexes¹⁻³, which usually contain additional coordinated groups. Although the stabilizing effect of phosphine prevents disproportionation of $Cu(I)$ in aqueous media, practically all the chemistry of phosphine complexes of univalent copper is limited to the solid state and nonaqueous solutions, generally because of the insolubility of the initial components and/or products in water. The only exceptions are the complexes with *m*-diphenylphosphinebenzenesulphonic acid, studied by George and Bjerrum⁴. This monodentate P-donor displaces chloride ions from trichlorocuprate(I) yielding stable, water soluble complexes with metal : ligand ratios of 1 : 1 to 1 : 4.

Phosphineacetic acids with general composition $(C_6H_5)_3-nP(CH_2-COOH)_n$, prepared and studied in our previous works for $n = 1$ (HA) (ref.⁵), $n = 2$ (H_2R) (ref.⁶) and $n = 3$ (H_3X) (ref.⁷), have a similar character. In these substances, chelate bonding through phosphorus and carboxyl simultaneously, which could not occur with *m*-diphenylphosphinebenzenesulphonate, is, in principle, also possible in addition to monodentate coordination through the phosphorus. Although oxygen ligands are generally very poor donors for univalent copper, the possibility of chelate bonding through the phosphineacetate group cannot be excluded; *e.g.* the "soft" palladium (II) cation can form a chelate bond with diphenyl phosphineacetate under suitable conditions⁸.

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This work was carried out in order to investigate the phosphineacetate complexes of univalent copper in solution under various acidity and solvent conditions: in addition to water, 50% dioxan was employed in analogy to the previous study of phosphineacetates, as some ligands are insufficiently soluble in water. Acetonitrile was chosen as a reagent stabilizing univalent copper, as its complex with Cu(I) is much less stable than the chlorocomplexes and thus the possibility of competition with phosphineacetates is probably negligible.

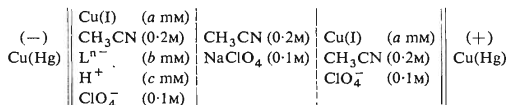
EXPERIMENTAL

The preparation and analysis of the ligands were described⁵⁻⁷. Their purity of $99.8 \pm 0.2\%$ was further checked by m.p. and TLC (silicagel, solvent CHCl_3 —*i*-PrOH— NH_3 — H_2O 10 : 10 : 1 : 1). The $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ complex was prepared according to the literature⁹; its purity was 99.5%. The two-phase copper amalgam was prepared electrolytically¹⁰ and its concentration was 1.55%. Before use it was diluted with an equal volume of redistilled mercury. As the two-phase amalgam exists in a broad range¹¹ and only the liquid part enters into the electrode process, the potentials are independent of the formal copper concentration in the two-phase amalgam. The amalgam was stored under 0.01M- HClO_4 and transferred into the electrode in an inert atmosphere using an apparatus functionally similar to that described by Ohtaki and coworkers¹². Acetonitrile (Mallinckrodt, *p.a.*) was fractionated under nitrogen and its purity was checked by gas chromatography. The purification of dioxan and sodium perchlorate has already been described⁵.

Copper was determined complexometrically using murexide indicator after sample oxidation with nitric acid. The absence of divalent copper in the initial solutions was verified by a negative color test with ammonia, carried out in the absence of air using a syringe technique¹³. The exact concentrations of solutions of acids and bases and the ligand alkalimetric equivalents were found by the Gran method¹⁴.

Apparatus and Measuring Method

The following concentration cell was used for the potentiometric measurements



The electromotive force of this cell was measured using a Radiometer PHM 64 instrument with a precision of 0.1 mV. Simultaneously, the pH of the solution in the left half-cell was measured with a combined Radiometer GK 2302 C electrode with a precision of 0.005 pH units. The electrode was calibrated⁵ so that the readings gave $-\log [\text{H}^+]$ directly. The solutions in both half-cells were placed in vessels fitted with a thermostating jacket permitting the temperature to be maintained with a precision of $25 \pm 0.02^\circ\text{C}$; joints for the electrodes, burettes, inert gas inlet and outlet and salt bridge fitted with S4 glass frits. The amalgam electrodes were of the J-type with a working surface of about 60 mm^2 .

The measurements were carried out in an inert atmosphere of pure nitrogen by two types of titration: *A*) From the stock solutions suitable amounts of NaClO_4 , solvent (water or dioxan) and acetonitrile solutions of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ were measured into both half-cells so that each contained 50 ml of identical solution ($b = c = 0$). The half-cells were connected by the salt bridge and the electrodes were introduced and left for 30–60 minutes for equilibration; the potential was then always less than ± 1 mV. Then the solution in the left-hand half-cell was titrated from a burette adapted for an inert atmosphere with a solution containing all components in the same concentrations as the titrated solution and also the ligand in an amount such that by addition of 10 ml of titrant (about 50 data points) a ratio of $b/a = 12$ was attained. This titration involves a constant copper concentration, which is advantageous in data handling. The potential values became constant after c. 5 minutes and were reproducible to ± 0.5 mV except when a precipitate was formed. In the first series of titrations, NaA , K_2R and Na_3X salts were used as ligands. No acid-base reaction took place in solution and the pH remained practically constant (± 0.2 pH). Under the experimental conditions the liquid-junction potentials compensated each other within experimental error. In some titrations the acetonitrile concentration was varied in the range 0.2–0.5M without any effect on the potential values. *B*) In the second group of titrations the left-half-cell contained a solution of sodium perchlorate, acetonitrile, copper and various fixed amounts of alkaline salts of the ligands with $b/a = 2, 4$ and 6. A perchloric acid solution containing the other components (except the ligand) in the same concentrations as the titrated solution was employed as the titrant. Thus the total copper concentration was constant during the titration, which is necessary for cell function. The concentration of HClO_4 was chosen so that, after addition of 10 ml (about 50 data points), values of $-\log [\text{H}^+]$ were obtained which corresponded to complete protonation of the ligand carboxyl groups. These values were found from distribution diagrams⁵⁻⁷. As the acidity of the solution in the left-half-cell changed during this titration, it was necessary to consider the shift of the liquid-junction potential. The appropriate correction was found using blanks: the titrant was added to the solution in the left half-cell (at $b = 0$) and appropriate corrections (not exceeding 7.5 mV) were then read from the $\text{mV}/-\log [\text{H}^+]$ curve.

Data Handling

Titration data from part *A* were first treated graphically. The equipotential fit method was used to find the corresponding solutions with the same potentials^{1,5} from the dependence of the potential on the ligand concentration; these then form straight lines in the c_{Cu} vs c_{L} coordinates, with slopes \bar{n} and intercepts on the c_{L} axis equal to $[\text{L}^{n-}]$. A section of the \bar{n} vs $-\log [\text{L}^{n-}]$ curve was constructed from the parameters of these straight lines, found by the least squares method. The $-\log [\text{L}^{n-}]$ values at low ligand concentrations could not be found graphically (as practically all the ligand was bound in the complex) and thus were calculated from the relationship^{15,16}:

$$\bar{n} = d \log X / d \log [L],$$

or

$$\log [L^*]/[L] = \int_{\log X(L)}^{\log X(L^*)} (1/\bar{n}) d \log X$$

where $X = c_{\text{Cu}}/[\text{Cu}]$ implies from the potential of the amalgam electrode and $[L^*]$ is an arbitrary reference value of the free ligand concentration, found from the intercept on the c_{L} axis by the above least squares method. The integral was solved numerically using the Simpson formula

on a Hewlett-Packard 9830A calculator. The composition of the complexes formed in the systems and their approximate stability constants were then found from the complete \bar{n} vs $-\log [L^{n-}]$ curve. The experimental values of the solution composition, titre and potentials were then treated statistically by the MINQUAD program¹⁷, which calculated the best stability constant values.

In treatment of type *B* titrations the data were assumed to define the protonation of the complexes, found in titration *A*. First the formal protonation curves of the ligands in the presence of univalent copper¹⁸ were orientatively calculated. The estimated constants were then refined by the MINQUAD program, where the input experimental quantities were the composition, consumption, $-\log [H^+]$ and amalgam electrode potentials. The stability constants of the unprotonated complexes found in titration *A* were considered invariant.

The computations were carried out on the ICL 4-72 computer in the University Computing Centre, Prague.

RESULTS AND DISCUSSION

The potential of the amalgam electrode during the first group of titrations in neutral solutions generally follows a sigmoid curve⁴, as is illustrated for the titration with a NaA solution in 50% dioxan (Fig. 1).^{*} The points of the corresponding solutions lie on a straight line in c_{Cu} vs c_L coordinates, indicating that no polynuclear complexes are formed in the systems. The stability constants and statistical parameters are given in Table I.

Study of complex protonation indicated that ligands coordinated to copper can bind protons practically as strongly as uncoordinated ligands. The formal dissociation

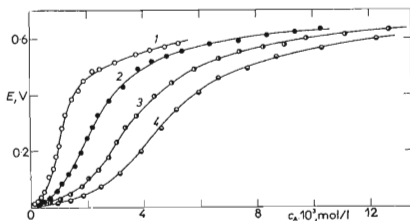


FIG. 1

Dependence of the Electromotive Force of the Concentration Cell on the NaA Concentration (50% dioxan)

$c_{Cu} \cdot 10^3$ M: curve 1 0.489; 2 0.977; 3 1.466; 4 1.955. Curves calculated from the stability constants are constructed through the experimental points.

* Numerical data for all the measurements are deposited with the authors.

constants of the ligands in the presence of univalent copper can be assumed as criteria of this bonding strength. It follows from Table II that the differences between the appropriate pK values for coordinated and free ligand do not exceed 0.4 pK units. This also corresponds to the finding that the potential of the amalgam electrode increases only slightly on solution acidification.

TABLE I
The Stability Constants of Complexes with Deprotonated Ligands
 $\beta_{n10} = [CuL_n]/([Cu][L]^n)$.

Constant	A ⁻		R ²⁻		X ³⁻	
	water	50% dioxan	water	50% dioxan	water	50% dioxan
	log β (3 σ)					
β_{110}	6.9(0.4) ^a	7.27(0.03)	6.6 ^b	7.01(0.10)	5.87(0.09)	6.49(0.09)
β_{210}	12.21(0.06)	12.89(0.04)	11.55(0.07)	11.84(0.02)	10.51(0.02)	10.87(0.05)
β_{310}	15.18(0.03)	16.89(0.02)	14.54(0.03)	15.51(0.04)	13.62(0.05)	14.30(0.03)
β_{410}	17.2(0.2)	19.37(0.06)	16.5(0.3)	17.8(0.2)	15.3(0.4)	15.7(0.4)
Number of exp. points (titrations)	178(6)	197(6)	142(4)	183(4)	190(8)	184(6)
R-factor ^c	0.013	0.011	0.040	0.032	0.029	0.022

^a 1:1 Complex poorly soluble; β_{110} calculated from values $\bar{n} > 0.8$; ^b 1:1 complex poorly soluble; β_{110} estimated from values of β_{410} to β_{210} ; ^c $R = [\sum(\Delta c_i)^2 / \sum c_i^2]^{1/2}$.

TABLE II
Decrease in the Formal Ligand Dissociation Constants Caused by the Presence of Univalent Copper

ΔpK	HA		H ₂ R		H ₃ X	
	water	50% dioxan	water	50% dioxan	water	50% dioxan
	$\Delta pK = pK_{cCu=0} - pK_{cCu=cL/4}$					
pK_1	0.31	0.38	0.22	0.26	0.14	0.19
pK_2			0.26	0.37	0.23	0.27
pK_3					0.35	0.40

It follows from the behaviour of the univalent copper-phosphineacetate systems that the ligands are bound to the copper through the phosphorus atom alone, as: 1) The maximum coordination number is 4 independent of the ligand type. 2) The stability constants in the A-R-X series, *i.e.* with increasing number of carboxyl groups, decrease slightly, corresponding to a decrease in the phosphorus basicity as a result of the inductive effect of the dissociated carboxyls; with chelate bonding through the phosphorus and the carboxyl, the constants would display the opposite trend. 3) The complexes are only slightly more stable in 50% dioxan than in water, which is typical for coordination through electroneutral donor groups¹⁹. 4) The carboxyl groups of the ligands undergo normal dissociation and the slight increase in their acidity compared with the free ligand corresponds to a decrease in the inductive effect of the lone electron pair caused by coordination through phosphorus. Chelate bonding through the phosphorus and the carboxyl would necessarily result in a marked increase in the acidity of the carboxyl groups.

The studied complexes probably have tetrahedral structure², supposed that in species with ratios less than 1 : 4 the coordination sphere is completed with acetonitrile molecules. It appears that the mechanism of phosphine complex formation consists of the following steps: 1) addition of one ligand to the $[\text{Cu}(\text{CH}_3\text{CN})_3]^+$ complex²⁰; 2) fast substitution of one labile acetonitrile molecule by a second ligand producing $\text{Cu}(\text{CH}_3\text{CN})_2\text{L}_2$; 3) slow substitution of the remaining two acetonitrile molecules in the kinetically relatively stable⁹ $\text{Cu}(\text{CH}_3\text{CN})_2^+$ species. The slow formation of the 1 : 3 and 1 : 4 complexes was reflected in the slower potential stabilization in the concentration range $4c_L > c_{\text{Cu}} > 2c_L$. At equilibrium, however, the acetonitrile is completely displaced as follows from the fact that the equilibrium potentials are independent of the acetonitrile concentration in the range 0.2–0.5M.

The stability constants can be tentatively corrected for aqueous media (in the absence of acetonitrile) by multiplying by the appropriate stability constant of the acetonitrile complex⁹ ($\log \beta_2 = 4.35$). The values obtained, which, *e.g.*, for the Cu-A system are $\log \beta_{110} = 11.3$, $\log \beta_{210} = 16.56$, $\log \beta_{310} = 19.53$, $\log \beta_{410} = 21.6$ indicate stability of the phosphineacetate complexes similar to that of the *m*-diphenylphosphinebenzenesulphonate complexes, in which the ligand is also coordinated through the phosphorus atom alone.

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