

# COMPOUNDS STRUCTURALLY RELATED TO COMPLEXONE I. TRIS(CARBOXYETHYL)PHOSPHINE

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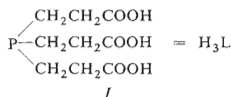
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Tris(carboxyethyl) phosphine was studied as a phosphorus complexone analogue. The acid dissociation constants were determined and the dissociation mechanism was elucidated. The complexes of cobalt, nickel and zinc were studied in aqueous solution. The corresponding stability constants were calculated and the electron spectra of these complexes were interpreted.

The term "complexones" is usually connected with the group of aminopolycarboxylic acids, containing carboxyl groups in  $\alpha$ - or  $\beta$ -positions to the tertiary nitrogen atom. The complexing ability of this type of compounds toward metal cations can be influenced to a certain degree by a change in the structural arrangement or type of donor atom. Aminopolyphosphonic acid<sup>1</sup>, ethylenediamine-bis(*o*-hydroxyphenylacetic) acid as a specific ligand for iron(III) (ref.<sup>2</sup>), and a series of other compounds<sup>3</sup> were also studied. In these compounds the polyamine skeleton remained unchanged and only the substituent type on the nitrogen atom was changed. Thus we have concentrated our attention on compounds derived from complexones by the replacement of the nitrogen atom with another hetero-atom, while the carbonyl substituent was not changed. In the previous papers<sup>4-6</sup> we studied the thiopolycarboxylic acids, containing the bidentate group  $-\text{SCH}_2\text{COOH}$  in different structural positions.

This work deals with a study of the complex forming properties of tris(carboxyethyl)phosphine (*I*) which contains three carboxyl groups in the  $\beta$ -position to the phosphorus atom:



This compound was prepared as the hydrochloride<sup>7</sup>, but its properties were not examined in detail.

## EXPERIMENTAL

### Chemicals

Tris(carboxyethyl)phosphine hydrochloride was prepared<sup>7</sup> by the cyanoethylation of phosphine and by the following alkaline hydrolysis of its trinitrile. Total yield of the preparation was

42 g (31% related to P) after crystallization from glacial acetic acid, to a constant m.p. of 170 to 171°C (the literature<sup>7</sup> gives 175–177°C). Analysis:  $C_9H_{16}ClO_6P$  (268.6) calculated: 37.70% C, 5.62% H, 12.37% Cl, 10.80% P; found: 37.75% C, 5.64% H, 11.85% Cl, 10.78% P.

Aluminium phosphide, necessary for the generation of phosphine, was prepared from aluminium powder and red phosphorus<sup>8</sup>. The acrylonitrile (pure, Lachema) was vacuum distilled before use. Solutions of metal perchlorates were prepared by the dissolution of the corresponding oxides or basic carbonates in a slight excess of 30%  $HClO_4$ . The solution of tetraethylammonium hydroxide was prepared from the chloride (r.g. Lachema) using an ion exchange column of Dowex 1 in the OH form. The NaOH solution used was free from carbonates. Deuterium oxide (99.7%  $D_2O$ ) was obtained from the Institute for Research, Production and Application of Radioisotopes, Prague.

### Apparatus

pH values were measured with Radiometer pH meter 26, using the electrodes, G 202 B and K 401. The measured solution was kept in a closed, jacketted vessel equipped with the electrodes, calibrated burette and inlet and outlet of nitrogen. The electrode system was calibrated with standard buffer solutions<sup>9</sup> in the pH range 1.65–9.16. The accuracy of the measurement was  $\pm 0.01$  pH units at the temperature,  $25 \pm 0.1^\circ C$  and at the ionic strength  $I 0.1$  ( $NaClO_4$ ). The concentration of hydrogen ions was calculated from the pH values using the tabulated value of the activity coefficient under these conditions<sup>10</sup>. Oxygen and carbon dioxide were removed from the nitrogen used, which was then saturated in  $0.1M-NaClO_4$  at  $25^\circ C$  before inlet into the titration vessel. The resulting titration curves represent the average of at least two titrations, which differ maximally by 0.02 pH units during the whole course. Electron spectra were measured with the instruments VSU-1 (Zeiss, Jena, GDR) and CF-4 (Optica, Milan, Italy). Infrared spectra were obtained with the instrument UR-20 (Zeiss, Jena, GDR) using silver chloride cells. Data processing was carried out with the computer IBM 7040.

### Analytical Methods

The content of the ligand was determined either as the tribasic acid by pH-metric titration to pH 6 or by titration with an iodine solution in neutral medium ( $NaHCO_3$ ) using starch as indicator, during which the ligand is oxidized to phosphine oxide. Both methods gave identical results to 0.5% rel. The solutions of metal perchlorates were analyzed by determination of the metal content by EDTA titration and the free perchloric acid content using Gran's method<sup>11</sup>.

## RESULTS AND DISCUSSION

### Acid-Base Dissociation

The titration curve of the ligand is presented in Fig. 1. The curves obtained in the tetraethylammonium chloride medium are identical with those obtained in sodium perchlorate medium. Sodium ions, therefore, do not form a complex with the ligand (in contrast to nitrilotriacetic acid<sup>12</sup>).

A computed transformation<sup>13</sup> of the titration curve to the  $\bar{n}_H$  vs  $-\log [H^+]$  curve (Fig. 2) and the linearization<sup>13</sup> of this function gave approximate values of the dissociation constants of  $H_4LCl$ . The final values of the constants given in Table I

were obtained by refinement by the nonlinear least squares method using the SCOGS programme<sup>14</sup>.

The step-wise dissociation mechanism of three medium acid and one weak acid hydrogen was elucidated by the measurement of UV and IR spectra of the solution at various pH values. The measurements were carried out in the absence of air to prevent oxidation of the ligand in alkaline media.

The pronounced increase in absorbance at 230 nm depends linearly on the concentration of the  $L^{3-}$  anion. In the IR spectrum, the intensity of the  $\nu_a(\text{COOH})$

TABLE I

The Dissociation Constants of  $H_4\text{LCI}$  at 25°C and 1.0 l

The given errors correspond to three times the standard deviation.

Constant	pK	3 $\sigma$
$K_1^H = [\text{H}^+][\text{H}_3\text{L}]/[\text{H}_4\text{L}]$	2.99	0.07
$K_2^H = [\text{H}^+][\text{H}_2\text{L}^-]/[\text{H}_3\text{L}]$	3.67	0.06
$K_3^H = [\text{H}^+][\text{HL}^{2-}]/[\text{H}_2\text{L}^-]$	4.36	0.06
$K_4^H = [\text{H}^+][\text{L}^{3-}]/[\text{HL}^{2-}]$	7.66	0.04

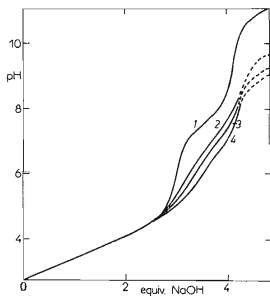


FIG. 1

The Titration Curve of  $5 \cdot 10^{-3}\text{M-H}_4\text{LCI}$  1 and Mixtures of  $5 \cdot 10^{-3}\text{M-H}_4\text{LCI}$  +  $5 \cdot 10^{-3}\text{M-Me}(\text{ClO}_4)_2$  2 Zn, 3 Co, 4 Ni.

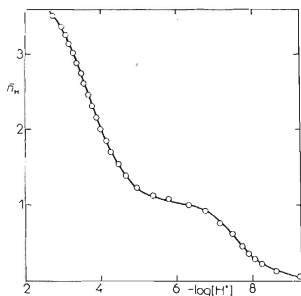


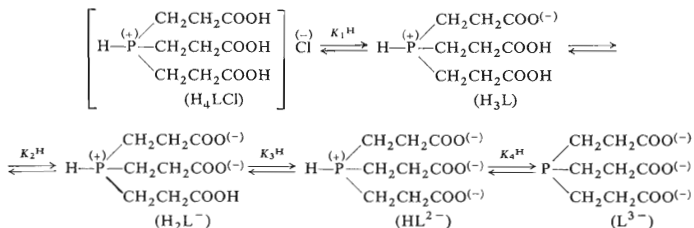
FIG. 2

The  $\bar{n}_H$  vs  $-\log [\text{H}^+]$  Curve for  $H_4\text{LCI}$

The points are the experimental values; the line was calculated from the dissociation constants.

band at  $1700\text{ cm}^{-1}$  decreases, and the intensity of the  $\nu_a(\text{COO})$  band at  $1575\text{ cm}^{-1}$  increases, with increasing pH. (Assignment of these maxima corresponds to the published data<sup>15</sup>.)

By measurement of the integral intensity of boths bands related to the background  $\text{D}_2\text{O}$  absorption, good agreement was found with the concentrations of  $-\text{COOH}$  and  $-\text{COO}^-$ , calculated using the dissociation constants (Fig. 3) under the supposition that the mechanism is:



In aqueous solution, tris(carboxyethyl)phosphine hydrochloride is therefore a quarternary phosphonium salt and the corresponding structure remains unchanged up to the pH value where the phosphonium hydrogen dissociates. Simultaneously the redox properties of the ligand also change. This indicates that the  $>\text{PCH}_2\text{CH}_2\cdot\text{COOH}$  group behaves similarly to its nitrogen analogue. The dissociation constant of the phosphonium hydrogen corresponds to the decrease in the electronegativity of phosphorus compared to nitrogen: for nitrilotripropionic acid<sup>16</sup>,  $\text{p}K_4^{\text{H}}$  is 9.30.

### Complexing Properties

On Fig. 1 are presented the titration curves of  $\text{H}_4\text{LCl}$  in the presence of metals in the ratio  $\text{L}/\text{Me} = 1/1$ . Reproducible results were obtained only with the  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions. Divalent manganese and trivalent lanthanum were partially precipitated as the hydroxides, divalent lead precipitated as an insoluble salt of the ligand, and  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  underwent a redox reaction with the ligand at  $\text{pH} > 6.5$ . The complexes of cobalt, nickel and zinc were studied in detail by the titration of solutions with different  $\text{Me} : \text{L}$  ratios at various  $\text{Me}$  concentrations. The  $\bar{n}$  vs  $-\log [\text{L}]$  curves, presented in Fig. 4, show that only  $\text{MeL}^-$  complexes were formed. The values of the corresponding stability constants, determined by the linearization of these curves and by the following statistical refinement using the SGOGS programme, are summarized in Table II. The metal to ligand ratios of these complexes were verified spectrophotometrically using Job's method, using wavelengths chosen according to the electronic spectra of the complexes. The spectra were measured in the solutions

containing the metal perchlorate and the ligand in 1 : 1 ratios; the pH was adjusted with sodium hydroxide solution. The  $d-d$  transition regions are presented and interpreted in Table III. The addition of nickel(II) to the ligand at pH > 6.5 results in a yellow solution. The colouration is more pronounced with increasing pH (the intensity of the band increases linearly with increasing  $\text{NiL}^-$  concentration) up to pH 9.5, where  $\text{Ni}(\text{OH})_2$  starts to precipitate. The electronic spectrum shows two bands, typical for low-spin square-planar  $d^8$  configuration<sup>17</sup>.

Under similar conditions, cobalt(II) yields an intensely red solution, stable in the pH range, 6.8–9.3, in the absence of air. The character of the corresponding spectrum

TABLE II

Stability Constants of  $\text{MeL}^-$  Complexes at 25°C and 1.0-1

The given errors correspond to three times the standard deviation.

Me	$\log \beta_1$	$3\sigma$	Residual <sup>14</sup> , ml
$\text{Co}^{2+}$	3.23	0.02	0.05
$\text{Ni}^{2+}$	3.80	0.03	0.10
$\text{Zn}^{2+}$	2.92	0.05	0.04

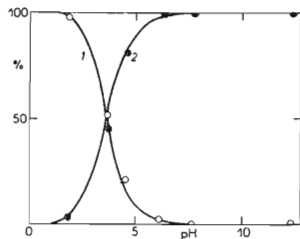


FIG. 3

The Fraction of Carboxyl Groups (%) Determined from IR Spectra

The curves are calculated using the dissociation constants; 1  $\text{COOH}$ , 2  $\text{COO}^-$ .

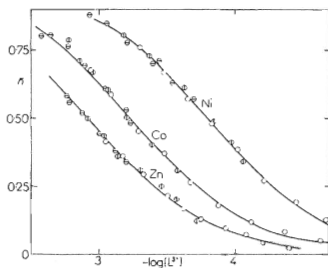


FIG. 4

The  $\bar{n}$  vs  $-\log [\text{L}^3]$  Curves

The points are the experimental values; the line was calculated from the dissociation constants:  $\circ$   $5 \cdot 10^{-3}\text{M-Me} + 5 \cdot 10^{-3}\text{M-L}$ ;  $\bullet$   $2.5 \cdot 10^{-3}\text{M-Me} + 5 \cdot 10^{-3}\text{M-L}$ ;  $\odot$   $2 \cdot 10^{-3}\text{M-Me} + 1 \cdot 10^{-2}\text{M-L}$ .

is typical for a high-spin octahedral configuration with the ligand field parameters<sup>18</sup>,  $Dq = 948 \text{ cm}^{-1}$ ,  $B = 857 \text{ cm}^{-1}$ . The band intensity is higher than the common value probably due to the covalent nature of the complex.

The colour of the solution of the cobalt(II) complex slowly changes to green in the presence of air. This change is practically instantaneous after the addition of hydrogen peroxide. At the ratio,  $\text{Co} : \text{L} = 1 : 1$ , a dark precipitate also appears while with a  $1 : 2$  ratio the solution remains clear. After filtration, the existence of a complex with the ratio  $\text{Co} : \text{L} = 1 : 2$  was verified in the filtrate using Job's curves. The green solution exhibits two maxima, typical for the low-spin octahedral cobalt(III) complex (for example, the spectrum of tris(oxalato)cobaltate(III) is very similar<sup>19</sup>). The corresponding ligand field parameters<sup>17</sup> are  $Dq = 1840 \text{ cm}^{-1}$ ,  $B = 325 \text{ cm}^{-1}$ .

### Redox Properties

If the ligand is present in an acidic solution as a phosphonium salt, it is stable towards weak oxidants (oxygen, solutions of iodine,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ). On the other hand, the  $\text{L}^{3-}$  anion is easily oxidized, evidently due to a free electron pair on the phosphorus atom. Oxidation in the air is slow even at pH 9 (half-time approx. 2 h) but reaction with  $\text{I}_2$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  is fast even at pH 6.8. Copper(II) ions are reduced to copper(I) and mercury(II) ions to the metal. The product of the oxidation of the ligand is tris(carboxyethyl)phosphine oxide or its complex with copper(I). After decomposition of this complex with hydrogen sulphide in acidic medium, the phosphine

TABLE III  
Electronic Spectra and their Interpretation

Wavenumber, $\text{cm}^{-1}$ ( $\epsilon_M$ )	Assignment
$\text{NiL}^-$ 10 000 (17) 22 700 (360) 25 300 sh	$\left. \begin{matrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{matrix} \right\} \text{ see }^{17}$
$\text{CoL}^-$ 8 690 (30) 17 500 (40) sh 20 400 (63)	$\begin{matrix} {}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{T}_{2g} \\ {}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g} \\ {}^4\text{T}_{1g}(\text{P}) \rightarrow {}^4\text{T}_{2g} \end{matrix}$
$\text{CoL}_2^{3-}$ 17 100 (115) 22 200 (140)	$\begin{matrix} {}^1\text{T}_{1g} \rightarrow {}^1\text{A}_{1g} \\ {}^1\text{T}_{2g} \rightarrow {}^1\text{A}_{1g} \end{matrix}$

oxide was obtained from the residue by evaporation of the acetic acid extract and was identified by a m.p. of 156°C (literature<sup>7</sup>, 155–156°C) and by its IR spectrum ( $\nu(\text{P}=\text{O})$  at 1078  $\text{cm}^{-1}$ ). On the other hand, the ligand is fully stabilized against oxidation in the complex with cobalt(III), probably due to the high stability of this complex related to the  $\text{P} \rightarrow \text{Co } \pi$ -bond.

## CONCLUSION

The tris(carboxyethyl)phosphine reacts with protons and metal ions of the first transition series similarly to the structural analogues containing nitrogen instead of phosphorus. Due to the lower electronegativity of phosphorus the stability constants, corresponding to the bond with a free electron pair, are lower than of nitrogen ligands. It can be expected that ions of the Cu(I) type, showing a higher affinity for heavier donor atoms, may form more stable complexes with this ligand.

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