

## STRUCTURE OF THE COMPLEXES OF ETHYLENEDIPHOSPHINETETRAACETIC ACID IN SOLUTION\*

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Ethylenediphosphinetetraacetic acid is bonded to metal ions in aqueous solutions in four ways, depending on the type of metal ion: 1) through an ionic bond of the carboxylic groups to form weak complexes with a metal:ligand ratio of 1 : 1 (Ca(II), Mn(II), Zn(II), Pb(II), La(III)); 2) through type 1) bond with contributions from weak interaction with the phosphorus (Cd(II)); 3) through coordination of the ligand as a monodentate P-donor with the free carboxyl groups with formation of 2 : 1 and 1 : 1 complexes (Cu(I), Ag(I)); 4) through formation of square planar or, for Hg(II), tetrahedral complexes with a ratio of 1 : 2 with the ligand as a bidentate PP-donor with the free carboxyl groups (Fe(II), Co(II), Ni(II), Pd(II), Pt(II)). On acidification of the complex solution, the first two protons are bonded to the carboxyl groups. The behaviour during further protonation depends on the type of complex: in complexes of types 1) and 2) phosphorus is protonated and the complex dissociates; in complexes of types 3) and 4) the free carboxyl groups are protonated and the phosphorus-metal bond remains intact. The results are based on correlation of the stability constants, UV-visible, infrared,  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra and magnetic susceptibilities of the complexes in aqueous solution.

Ethylenediphosphinetetraacetic acid<sup>1,2</sup> ( $\text{H}_4\text{L}$ ) as a structural analogue of EDTA is a hybrid type ligand simultaneously containing soft and hard donor atoms. This combination leads to strong ligand selectivity compared with EDTA, reflected in the stability constants of the complexes<sup>3</sup>:  $\log \beta$  values lie in the range  $\log \beta_1 = 3.20$  (Ca(II)) to  $\log \beta_2 = 38.35$  (Hg(II)). It seems probable that, in contrast to the relatively uniform structure of the EDTA complexes, the great difference in the character of the two types of donor atoms in ethylenediphosphine-tetraacetic acid will result in a greater variety of structural types of complexes.

This work was carried out in order to study the coordination of  $\text{H}_4\text{L}$  and its anions to various metal ions in aqueous solutions. The infrared spectroscopic method was used in the region of antisymmetric stretching vibration of the carboxyl group<sup>2,4-7</sup>, along with the  $^1\text{H}$  NMR spectroscopy of nonlabile protons (for a summary see<sup>7-10</sup>) and  $^{31}\text{P}$  NMR spectroscopy<sup>11</sup>. Further information was obtained for the transition metal ions from UV-visible spectra and magnetic susceptibility measurements.

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## EXPERIMENTAL AND RESULTS

**Chemicals.** The preparation of  $\text{Na}_4\text{L}\cdot\text{H}_2\text{O}$  has been described previously<sup>1</sup>. For measurements in  $\text{D}_2\text{O}$  the salt was dehydrated by drying at  $150^\circ\text{C}/10\text{ Pa}$ . The stock solutions of the nitrates, chlorides or chlorocomplexes of the individual metals in  $\text{D}_2\text{O}$  were prepared from similarly dried anhydrous substances from Lachema, Merck and Alfa Inorganics:  $\text{CaCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{LaCl}_3$ ,  $\text{HgCl}_2$  (dried at  $80^\circ\text{C}$  over  $\text{P}_2\text{O}_5$ ),  $\text{AgNO}_3$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{K}_2\text{PdCl}_4$ ,  $\text{K}_2\text{PtCl}_4$ ,  $\text{K}_2\text{CuCl}_3$  (prepared in solution from  $\text{CuCl}$  and  $2\text{ KCl}$ ). The hydrates of the chlorides of  $\text{Mn}(\text{II})$ ,  $\text{Fe}(\text{II})$ ,  $\text{Co}(\text{II})$  and  $\text{Ni}(\text{II})$  were dehydrated by reaction with thionyl chloride<sup>12</sup>.

**Methods.** Solutions for measurement of the infrared and NMR spectra with ligand concentrations of  $0.1\text{ M}$  were prepared in a dry inert atmosphere from  $\text{Na}_4\text{L}$  and the metal salt in  $\text{D}_2\text{O}$  (isotopic purity 99.3%, ÚVVVR, Prague) and their  $pD$  values were adjusted with solutions of  $\text{DCl}$  and  $\text{NaOD}$  in  $\text{D}_2\text{O}$ . The combination GK 2301 electrode and the PHM 64 instrument manufactured by Radiometer were calibrated in  $\text{H}_2\text{O}$  and the correction<sup>13</sup>  $pD = \text{pH-meter reading} + 0.41$  was used for measurements in  $\text{D}_2\text{O}$ .

The samples were measured immediately after mixing or were stored at  $-78^\circ\text{C}$  in ampoules sealed in an argon atmosphere. No changes were observed in the spectra of these stored solutions compared to the fresh ones. The infrared spectra were measured on a Perkin Elmer 684 instrument in the region  $1500\text{--}1800\text{ cm}^{-1}$  in  $\text{CaF}_2$  cells with  $50\text{ }\mu\text{m}$  polyethylene spacers. The  $\text{D}_2\text{O}$  absorbance was subtracted during on-line spectra treatment by the Perkin Elmer 3 600 Data Station. The samples were transferred into the cells in a glove box in a nitrogen atmosphere. The  $^1\text{H}$  NMR spectra were measured at  $29^\circ\text{C}$  on a Tesla BS 487 A instrument at  $80\text{ MHz}$  using tert-butanol as an internal standard (the  $\delta$  values are recalculated to tetramethylsilane,  $\delta_{t\text{-BuOH}} = 1.25\text{ ppm}$ ). In some strongly acid solutions, comparative measurements were carried out in  $\text{H}_2\text{O}$  to eliminate the effect of possible deuteration<sup>2</sup> of the  $\text{CH}_2\text{COO}$  groups. In addition to measurements on solutions with a constant metal : ligand ratio, the limiting chemical shifts and kinetic behaviour of the complexes were found by NMR titrations: aliquots of concentrated solution of the metal salt were added to the  $\text{Na}_4\text{L}$  solution directly in the NMR tube and changes in the spectra were monitored. The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were measured using a Varian XL-200 instrument at  $80.8941\text{ MHz}$  and  $23^\circ\text{C}$ , with 85%  $\text{H}_3\text{PO}_4$  as an external standard. The spectra in the UV and visible regions were measured in  $\text{H}_2\text{O}$  on a Unicam SP 800 instrument. The magnetic susceptibility of solutions with composition  $0.05\text{ M-MCl}_2 + 0.2\text{ M-Na}_4\text{L}$  was measured by the modified Evans method<sup>14</sup>, calibrated using nickel chloride solutions.

Table I lists the results of measurement of the infrared and NMR spectra and magnetic susceptibility; Table II gives the ultraviolet and visible spectra. Typical infrared and NMR spectra are given in Figs 1–3.

## DISCUSSION

The type, amount and interpretability of information differs considerably in dependence on the type of method used.

The conclusions following from UV and visible spectra and the magnetic susceptibilities of complexes with metals with incompletely filled d-shells are unambiguous. Direct information was obtained on the electron structure of the central ion and geometry of the coordination sphere.

The infrared spectra of the ligand exhibit three separate bands<sup>2</sup> in the  $\nu(\text{COO} + \text{C}=\text{O})$  region, i.e.  $1500\text{--}1800\text{ cm}^{-1}$ , for the  $\text{PCH}_2\text{COO}^-$  (I),  $\text{HP}^+\text{CH}_2$ .

TABLE I  
The infrared and NMR spectra of the complexes

| Component ratio   | $pD$ | IR (relat. int., %) |                                                   |                   | NMR ( $\delta$ , ppm)                                                 |                                                             |                           |
|-------------------|------|---------------------|---------------------------------------------------|-------------------|-----------------------------------------------------------------------|-------------------------------------------------------------|---------------------------|
|                   |      | COO <sup>a</sup>    | HP <sup>+</sup> .CH <sub>2</sub> COO <sup>b</sup> | COOH <sup>c</sup> | <sup>1</sup> H<br>CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COO | <sup>31</sup> P{ <sup>1</sup> H}<br>( <sup>1</sup> J(P, M)) |                           |
| L                 | 9.20 | 1 562 (100)         |                                                   |                   | 1.71                                                                  | 2.53                                                        | —24.3                     |
|                   | 4.03 | 1 562 (29)          | 1 607 (35)                                        | 1 688 (36)        | 1.99                                                                  | 2.85                                                        | —20.6                     |
|                   | 2.46 |                     | 1 610 (6)                                         | 1 692 (94)        | 1.87                                                                  | 2.88                                                        | —23.8                     |
| CaL               | 8.40 | 1 562 (100)         |                                                   |                   | 1.91                                                                  | 2.84                                                        | —24.4                     |
|                   | 4.06 | 1 562 (23)          | 1 607 (44)                                        | 1 689 (33)        | 2.00                                                                  | 2.85                                                        | —20.5                     |
| MnL               | 8.38 | 1 562 (100)         |                                                   |                   |                                                                       | 5.95 <sup>d</sup>                                           |                           |
|                   | 3.99 | 1 561 (27)          | 1 607 (40)                                        | 1 688 (33)        |                                                                       |                                                             |                           |
| ZnL               | 8.03 | 1 562 (100)         |                                                   |                   | 2.09                                                                  | 2.81                                                        | —25.1                     |
|                   | 4.01 | 1 561 (20)          | 1 608 (49)                                        | 1 688 (31)        | 2.00                                                                  | 2.84                                                        | —22.7                     |
| PbL               | 8.54 | 1 564 (100)         |                                                   |                   | 2.14                                                                  | 2.92                                                        | 8.1                       |
|                   | 4.14 | 1 563 (26)          | 1 607 (53)                                        | 1 686 (21)        | 2.02                                                                  | 2.86                                                        | —7.0                      |
| LaL <sup>e</sup>  | 8.52 | 1 563 (100)         |                                                   |                   | 2.14                                                                  | 2.89                                                        | —26.1                     |
|                   | 4.10 | 1 563 (21)          | 1 606 (56)                                        | 1 686 (23)        | 2.01                                                                  | 2.87                                                        | —21.0                     |
| CdL <sup>f</sup>  | 7.98 | 1 575 (100)         |                                                   |                   | 2.15                                                                  | 2.85                                                        | —27.0                     |
|                   | 4.34 | 1 576 (69)          | 1 607 (10)                                        | 1 693 (21)        | 2.06                                                                  | 2.80                                                        | —24.4                     |
| Cu <sub>2</sub> L | 7.88 | 1 575 (100)         |                                                   |                   | 2.26                                                                  | 2.90                                                        | —20.4                     |
|                   | 2.73 | 1 573 (26)          |                                                   | 1 698 (74)        | 2.27                                                                  | 3.04                                                        | —20.2                     |
| CuL               | 7.90 | 1 569 (100)         |                                                   |                   | 1.98                                                                  | 2.73                                                        | —13.6                     |
|                   | 2.81 | 1 569 (28)          |                                                   | 1 696 (72)        | 1.98                                                                  | 2.79                                                        | —13.2                     |
| Ag <sub>2</sub> L | 7.80 | 1 579 (100)         |                                                   |                   | 2.28                                                                  | 2.93                                                        | —19.9 (261) <sup>g</sup>  |
|                   | 2.19 | 1 578 (14)          |                                                   | 1 699 (86)        | 2.29                                                                  | 3.07                                                        | —19.1 (255)               |
| AgL               | 7.23 | 1 572 (100)         |                                                   |                   | 1.99                                                                  | 2.76                                                        | —17.0 (529)               |
|                   | 2.30 | 1 571 (18)          |                                                   | 1 696 (82)        | 2.01                                                                  | 2.89                                                        | —17.2 (533)               |
| FeL <sub>2</sub>  | 7.50 | 1 584 (100)         |                                                   |                   |                                                                       | 3.82 <sup>d</sup>                                           |                           |
|                   | 2.98 | 1 585 (42)          |                                                   | 1 700 (58)        |                                                                       |                                                             |                           |
| CoL <sub>2</sub>  | 8.70 | 1 587 (100)         |                                                   |                   |                                                                       | 2.18 <sup>d</sup>                                           |                           |
|                   | 3.06 | 1 594 (39)          |                                                   | 1 705 (61)        |                                                                       |                                                             |                           |
| NiL <sub>2</sub>  | 8.68 | 1 590 (100)         |                                                   |                   | 2.36                                                                  | 3.14                                                        | 45.9                      |
|                   | 2.06 | 1 589 (25)          |                                                   | 1 702 (75)        | 2.61                                                                  | 3.48                                                        | 46.1                      |
| PdL <sub>2</sub>  | 8.00 | 1 592 (100)         |                                                   |                   | 2.36                                                                  | 3.18                                                        | 39.2                      |
|                   | 2.95 | 1 596 (31)          |                                                   | 1 700 (69)        | 2.61                                                                  | 3.62                                                        | 40.0                      |
| PtL <sub>2</sub>  | 7.98 | 1 594 (100)         |                                                   |                   | 2.46                                                                  | 3.22                                                        | 35.3 (2 377) <sup>h</sup> |
|                   | 2.40 | 1 593 (19)          |                                                   | 1 703 (81)        | 2.71                                                                  | 3.73                                                        | 35.7 (2 384)              |
| HgL <sub>2</sub>  | 8.63 | 1 585 (100)         |                                                   |                   | 2.56                                                                  | 3.55                                                        | 1.6 (2 504) <sup>i</sup>  |
|                   | 2.21 | 1 590 (10)          |                                                   | 1 701 (90)        | 2.84                                                                  | 3.86                                                        | 1.2 (2 507)               |

<sup>a</sup> PCH<sub>2</sub>COO<sup>−</sup>, <sup>b</sup> HP<sup>+</sup>CH<sub>2</sub>COO<sup>−</sup>, <sup>c</sup> PCH<sub>2</sub>COOH + HP<sup>+</sup>CH<sub>2</sub>COOH, <sup>d</sup> magnetic moment, B.M., <sup>e</sup> extrapolation from La<sub>0.8</sub>L, <sup>f</sup> extrapolation from Cd<sub>0.7</sub>L, <sup>g</sup> <sup>109</sup>Ag, <sup>h</sup> <sup>195</sup>Pt, <sup>i</sup> <sup>199</sup>Hg.

.COO<sup>-</sup> (II) and PCH<sub>2</sub>COOH + HP<sup>+</sup>CH<sub>2</sub>COOH (III) groups. The complex formation under constant conditions (concentration, acidity) is accompanied by changes in this spectral region, corresponding to various types of ligand coordination: 1) a decrease in the intensity or disappearance of band II as a result of competition of the metal ion with a proton on the phosphorus atom, indicating phosphorus-metal coordination; 2) an increase in the intensity of this band can be assigned to similar competition on the carboxyl group, forcing partial shift of the protons to the phosphorus atoms; this also indicates the presence of a carboxyl-metal bond. Band I is not shifted to higher wavenumbers during this process, as is common for the cations of divalent metals<sup>6</sup> and indicates ionic character of the carboxyl-metal bond.

TABLE II  
Ultraviolet and visible spectra of the complexes

| Solution composition            | Absorption bands, $\lambda_{\max} \cdot 10^3 \text{ cm}^{-1} (\epsilon_M)$               |
|---------------------------------|------------------------------------------------------------------------------------------|
| L <sup>4-</sup>                 | > 50 (> 4 000)                                                                           |
| H <sub>4</sub> L                | 43.8 sh (850), > 50 (> 2 000)                                                            |
| CaL <sup>2-</sup>               | > 50 (> 8 000)                                                                           |
| MnL <sup>2-</sup>               | > 50 (> 8 000)                                                                           |
| LaL <sup>-</sup>                | > 50 (> 8 000)                                                                           |
| ZnL <sup>2-</sup>               | 44.2 sh (5 000), > 50 (> 8 000)                                                          |
| PbL <sup>2-</sup>               | 39.2 (5 900), > 50 (> 8 000)                                                             |
| CdL <sup>2-</sup>               | 43.5 (5 200), > 50 (> 8 000)                                                             |
| CuL <sup>3-</sup>               | 42.5 sh (4 600), > 50 (> 10 000)                                                         |
| CuH <sub>3</sub> L              | 43.5 sh (6 100), > 50 (> 10 000)                                                         |
| AgL <sup>3-</sup>               | 37.3 (11 200), 44.8 sh (17 200), > 50 (> 10 000)                                         |
| AgH <sub>3</sub> L              | 32.6 sh (350), 43.5 sh (11 500), > 50 (> 15 000)                                         |
| FeL <sub>2</sub> <sup>6-</sup>  | 21.6 (460), 26.6 (215), 41.3 (23 000)                                                    |
| FeH <sub>6</sub> L <sub>2</sub> | 21.8 (510), 26.9 (230), 41.9 (24 600)                                                    |
| CoL <sub>2</sub> <sup>6-</sup>  | 11.0 sh (13), 17.5 (45), 26.3 (430), 37.6 (24 000)                                       |
| CoH <sub>6</sub> L <sub>2</sub> | 11.3 sh (12), 17.8 (42), 26.6 (410), 38.0 (21 500)                                       |
| NiL <sub>2</sub> <sup>6-</sup>  | 17.3 sh (7.5), 19.0 sh (25), 25.3 (510), 32.0 sh (2 700), 34.4 sh (8 070), 38.2 (39 100) |
| NiH <sub>6</sub> L <sub>2</sub> | 16.3 sh (9), 18.9 sh (48), 23.6 (560), 32.0 sh (2 720), 35.2 sh (8 500), 39.1 (29 500)   |
| PdL <sub>2</sub> <sup>6-</sup>  | 29.6 sh (360), 38.3 (24 600), 41.7 (20 000)                                              |
| PdH <sub>6</sub> L <sub>2</sub> | 29.4 sh (340), 39.1 (19 600), 41.5 (19 200)                                              |
| PtL <sub>2</sub> <sup>6-</sup>  | 34.0 sh (780), 38.0 (4 200), 44.4 sh (24 000)                                            |
| PtH <sub>6</sub> L <sub>2</sub> | 34.0 sh (700), 38.0 (3 400), 44.8 sh (20 000)                                            |
| HgL <sub>2</sub> <sup>6-</sup>  | 42.2 sh (23 000), > 50 (> 30 000)                                                        |
| HgH <sub>6</sub> L <sub>2</sub> | 42.5 sh (8 500), > 50 (> 10 000)                                                         |

Thus, in the studied complexes, coordinated carboxyl groups cannot be directly distinguished from free groups; this is mostly possible only for multivalent cations

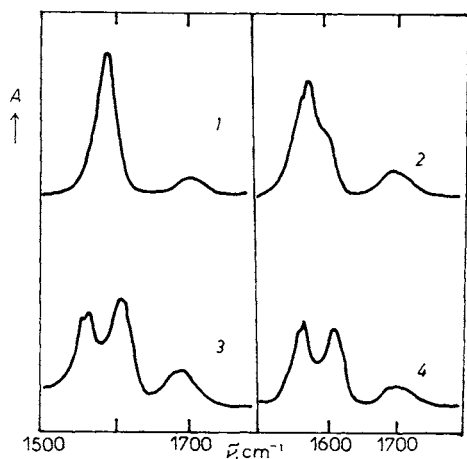


FIG. 1

The infrared spectra of the solutions in  $D_2O$  at  $pD = 4.4 \pm 0.1$ . Composition: 1  $HgL_2$ , 2  $Cd_{0.7}L$ , 3  $PbL$ , 4  $L$

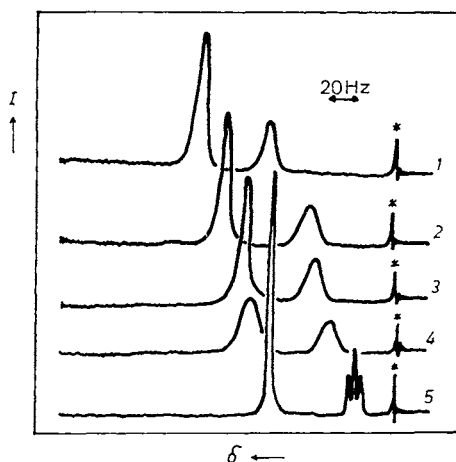


FIG. 2

The  $^1H$  NMR spectra of solutions in  $D_2O$  at  $pD = 8.0 \pm 0.5$ . Composition: 1  $HgL_2$ , 2  $NiL_2$ , 3  $PbL$ , 4  $ZnL$ , 5  $L$ . The  $t\text{-BuOH}$  band is designated by an asterisk

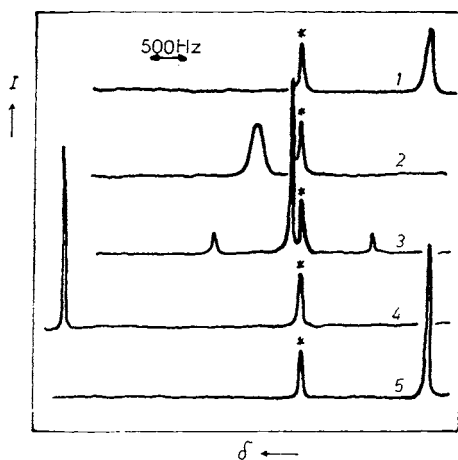


FIG. 3

The  $^{31}P \{^1H\}$  NMR spectra of solutions in  $D_2O$  at  $pD = 8.0 \pm 0.5$ . Composition: 1  $ZnL$ , 2  $PbL$ , 3  $HgL_2$ , 4  $NiL_2$ , 5  $L$ . The  $H_3PO_4$  band is designated by an asterisk

with strongly covalent metal-carboxyl bonds<sup>4,5</sup>. 3) In the presence of phosphorus-metal bonds, bands *I* and *III* are shifted to higher wavenumbers. As a similar shift was also observed for band *III* and the ratio of the shifts of bands *I* and *III* is roughly constant, this phenomenon must necessarily be only inductive in origin and probably reflects changes in the electron density on the phosphorus atoms as a result of their coordination. 4) The changes in the relative intensities of bands *I* and *III* with acidification of the complexes in which phosphorus is coordinated is in agreement with independent protonation of the free carboxyl groups in these complexes, described by the particular protonation constants<sup>3</sup>.

Further information can be obtained from the NMR spectra of diamagnetic systems, similarly as for analogous ligands<sup>8-11</sup>: 1) The spectra of all the complexes at laboratory temperature consists of characteristic broad bands (the half-width for the <sup>1</sup>H spectra is 5–20 Hz, for the <sup>31</sup>P{<sup>1</sup>H} spectra, 10–80 Hz), indicating kinetic lability of the complexes. This lability is intermolecular for the Ca(II), Zn(II), Pb(II), La(III) and Cd(II) complexes, i.e. involves exchange of whole ligand molecules; at lower metal : ligand ratios than 1 : 1 only an average signal appears in the spectrum, corresponding to the complex and excess ligand. The complexes of the other metals are kinetically inert in this respect and <sup>1</sup>J(M,P) coupling is apparent in the spectra of the Ag(I), Pt(II) and Hg(II) complexes. The lability of this type of complex, apparent here also from the band broadening, is thus intramolecular, probably of the conformational type and is connected with the uncoordinated

acetate groups and the  $\text{PCH}_2\text{CH}_2\text{PM}$  chelate rings or that part of the ligand bonded monovalently by phosphorus. 2) As usual<sup>11,15</sup>, the existence of the phosphorus metal bond cannot be simply related to the  $\delta_p$  value, due to the impossibility of separating the dominant paramagnetic contribution of the chemical shift of phosphorus from the minor diamagnetic contribution, which can primarily be expected to be affected by the coordination. Changes in  $\delta_p$  on acidification, however, clearly indicate the existence of phosphorus-metal bonds: if protons become bonded to uncoordinated phosphorus, the  $\delta_p$  values are shifted to regions typical for the protonated ligand; however, if the phosphorus is coordinated,  $\delta_p$  is not shifted substantially compared to the unprotonated complex. 3) The signals of the nonlabile protons during coordination of all the studied complexes are shifted to higher frequencies and the  $\delta_H$  values for the  $\text{PCH}_2\text{CH}_2\text{P}$  and  $\text{PCH}_2\text{COO}$  groups are roughly linearly correlated with the  $\log \beta_1 (1/2 \log \beta_2)$  values. A number of further semiquantitative dependences of this type follow from the spectra, especially for structurally identical complexes. However, because of a number of restricting effects, the  $\delta_H$  values cannot be correlated quantitatively with the relative number of coordinated and uncoordinated carboxyl groups, which would be very useful information for more exact description of the complex structure in solution. The main factors preventing such correlation include inductive effects (through bonds and through space), a strong effect of the metal

valency and deformability, the magnetic anisotropy of the COOH group and in some cases the nonavailability of the limiting shift values (for weak or poorly soluble complexes), as well as complications connected with non-equivalence of the equatorial and axial carboxyl groups. In addition it must be considered that a greater number of types of species are present in solutions of less stable complexes, with relative contents varying with concentration and exchange of  $\text{H}_2\text{O}$  for  $\text{D}_2\text{O}$ .

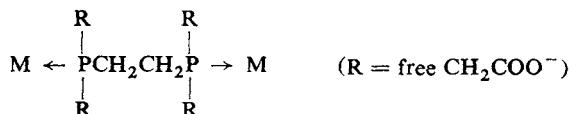
In spite of these restrictions, conclusions can be drawn from the measured data, dividing the complexes into four groups depending on the type of ligand coordination.

1) The  $\text{Ca(II)}$ ,  $\text{Mn(II)}$ ,  $\text{Zn(II)}$ ,  $\text{La(III)}$ , and  $\text{Pb(II)}$  cations form a limitedly stable 1 : 1 complex ( $\log \beta_1 = 3.20 - 6.67$ ), subject to rapid intermolecular exchange. It is apparent from the IR and NMR spectra that the metal–ligand interaction consists in bonding by the carboxyl groups. The ionic character of this bond decreases in the given series of metals, as follows from the decrease in the wavenumber of the  $n \rightarrow \pi^*$  band of the carboxyl group in the UV spectrum. The phosphorus atoms are not coordinated, as indicated simultaneously by all the above spectral criteria. As the  $\text{ML}$ ,  $\text{MHL}$  and  $\text{MH}_2\text{L}$  complexes are present in solution<sup>3</sup>, it is probable that two carboxyl groups of the ligand are bonded to the metal, while two are free and are readily protonated. The complex with  $\text{Pb(II)}$  which was assumed to involve coordination of phosphorus on the basis of the higher stability constant values<sup>3</sup>, also is of this type and its higher stability is connected with the general trend of stability of carboxylate complexes<sup>16</sup>. Low  $\text{Pb}_2\text{L}$  concentrations, found potentiometrically, are insufficient for spectral characterization of this species.

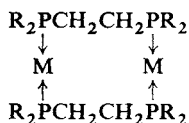
2) The  $\text{Cd}$  complex: The IR and NMR spectra clearly indicate simultaneous coordination of the carboxyl groups and weak  $\text{P} \rightarrow \text{Cd}$  interaction. Both bonds contribute to increased stability of the complex (compared to general trends<sup>16</sup>), but it decomposes in acid medium, as reflected in potentiometric data and especially in the appearance of a type II band and a shift in  $\delta_p$  on acidification of the solution into the region where  $\text{CdHL}$  and  $\text{CdH}_2\text{L}$  are present. On further acidification, the complexes decompose completely. The same conclusion is valid for the  $\text{Cd}_2\text{L}$  complex as for the  $\text{Pb}_2\text{L}$  complex; in addition, its low solubility so complicated measurements that some of the limiting spectra of the  $\text{CdL}$  composition had to be derived by extrapolation from solutions with a composition of maximally  $\text{Cd}_{0.7}\text{L}$ . On the NMR time scale,  $\text{Cd(II)}$  complexes also undergo intermolecular exchange.

3) The  $\text{Cu(I)}$  and  $\text{Ag(I)}$  complexes are structurally similar, as is indicated by their spectral behaviour and stability constants<sup>3</sup>. The similarity of the  $\beta$  value for the  $\text{Cu(I)}$  complex with monophosphine complexes<sup>17</sup> shows that the ligand acts as a monodentate P-donor towards these ions. It is apparent from the IR and NMR spectra that the ligand is bonded through phosphorus alone, while the carboxyl groups are uncoordinated and independently protonated. The complexes are stable

from the point of view of intermolecular exchange and  $^1J(\text{Ag}, \text{P})$  coupling can be observed; however, the band widths unambiguously indicate intramolecular kinetic lability. The structure of both types of complexes 2 : 1 and 1 : 1 can be a subject of speculation; none of the properties determined is contrary to the assumed bimetallic structure of the 2 : 1 complex:



or to dimeric arrangement of the 1 : 1 complex:



4) The Fe(II), Co(II), Ni(II), Pd(II), Pt(II) and Hg(II) cations form stable  $\text{ML}_2$  complexes that are kinetically inert to intermolecular exchange. The spectra and magnetic measurements unambiguously indicate bonding of two ligands through four phosphorus atoms with formation of a square planar low spin complex (tetrahedral for Hg(II), indicated by  $^1J(\text{Hg}, \text{P})$ , and analogous to the usual structure of tetracoordinated mercury complexes). The carboxyl groups are not coordinated and are protonated independently, in agreement with the stability of the complexes in acid medium. The square planar arrangement and the large *trans*-effect of the phosphine ligands explain why the 1 : 1 complex cannot be found in solution in the absence of other strongly coordinating species.

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