Complexing properties of phosphinic analogues of glycine

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A series of aminomethylphosphinic acids $H_2NCH_2PRO_2H$ (R = H, Me, Bu^t or Ph) was synthesized and the acid–base and complexing properties with Co^{II}, Ni^{II} and Cu^{II} were determined pH-metrically (25 °C, 0.1 mol dm^{-3} KNO_3). The pK_a values were found to increase from R = H to Ph, Me and Bu^t, as the $-I$ effect decreases. The complex stability constants lie in the same order, except for R = H. The compound $H_2NCH_2PHO_2H$ (HL^1) exhibits higher values than the ligands with methyl or phenyl substituents, probably due to better deformability of the PHO_2^- group and its better ability to form chelate rings. The complexes of $H_2NCH_2P(Ph)O_2H$ (HL^4), $H_2NCH_2P(Me)O_2H$ (HL^2) and $H_2NCH_2P(Bu^t)O_2H$ (HL^3) with several transition metals were prepared and the crystal structures of $[CuL^4_2]$ **1** and $[Cu_3L^2_4][ClO_4]_2$ **2** were determined. The formation of chelate rings was observed in both structures; **1** forms dimers and **2** polymeric layers *via* the phosphinates.

Polyazamacrocycles bearing CH_2PRO_2H pendant group at N are of considerable interest as potential therapeutic and diagnostic agents.[1–3] Since these applications generally involve complexation with metal ions, the complexing abilities of such compounds have been studied both in solution[2–4] and in the solid state.[3,5] We recently reported the results for the transition-metal complexes of 1,4,7-triazacyclononane-1,4,7-triyltrimethylenetrisphosphinic and 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayltetramethylenetetrakisphosphinic acids in solution.[6] Comparison of our solution[6] results with the literature[2–4] has shown that the complexing properties should be significantly influenced by R in the $>NCH_2PRO_2H$ part of the ligand. However, the influence on the acid–base and complexing properties of the more simple aminomethylphosphinic acids have not been systematically studied; only some information is available for solutions[7–12] and for the solid state.[8b,13–16]

Therefore, we decided to study the detailed complexation chemistry of the simplest series of the phosphinic analogues of glycine. As R we chose H, Me, Bu^t and Ph. Thus the substituents have various sizes and in $-I$ effects. This paper describes the synthesis, acid–base properties and formation constants of the following acids: $H_2NCH_2P(H)O_2H$ (HL^1), $H_2NCH_2P(Me)O_2H$ (HL^2), $H_2NCH_2P(Bu^t)O_2H$ (HL^3) and $H_2NCH_2P(Ph)O_2H$ (HL^4). A series of complexes was prepared in crystalline form but only two were obtained as single crystals.

Results and Discussion

Synthesis

All the phosphinic acids studied were prepared previously: HL^3 by a modification of the procedure of Tyka and Haegele[17] which was also used for HL^2 and HL^4. The synthesis of HL^2 and HL^4 was found to be more facile and with better yields than that described earlier.[18] According to our experience the reaction between an alkyl- or aryl-dihalogophosphine and *N*-(hydroxymethyl)benzamide in glacial acetic acid may be a general procedure for the preparation of alkyl or aryl aminomethylphosphinic acids. The compound HL^1 was synthesized by a modification of the procedure of McCleery and Tuck.[19] The protected ester was hydrolysed at room temperature under an argon atmosphere. We tested several hydrolysis procedures;[19,20] however, only under these conditions oxidation of the phosphinic to the phosphonic group was not observed. The purity of all the compounds prepared was checked by TLC and NMR techniques. No impurities were found. The NMR data together with the analytical results are summarized in Table 1.

Potentiometry

The calculated values of the protonation and dissociation constants are given in Table 2. Calibration of the glass electrode in a wide pH region from 1.7 to 12 by the method described in the Experimental section and use of our program permitted determination of the log β_1 values with an accuracy of three decimal places and estimation of log β_2 or pK_a lower than 1. The accuracy points to the good reproducibility and precision of the measurements under our experimental conditions. However, the real accuracy would be lower and, according to ref. 21, we estimate that of log β to be at least ±0.05 log unit.

The present phosphinic acids, similarly to earlier results,[7–12] are less basic than aminomethylphosphonic acids or amino acids. The basicity decreases in the order HL^3, HL^2, HL^4 and HL^1, *i.e.* from R = Bu^t to Me, Ph and H for both the amino and phosphinic groups. The same trend from Me to Ph and H was observed in the 1-aminoethylphosphinic series for the amino group[10] (dissociation of the phosphinic groups was not calculated) or for the carboxyl group in the simple carboxylic acid series[22] from pivalic to acetic, benzoic and formic acid. The log β_1 values found indicate that they are not influenced by the size of the substituent on the phosphorus atom and increase as the $-I$ effect decreases.

The values of the stability constants of the metal complexes are listed in Table 2 and selected distribution diagrams in Fig. 1. The metal, proton, ligand species 111, 101, 102, 103, 1−11, 1−21, 112 and, owing to the stoichiometry of the compound prepared, 304 were taken into account for the models. However, all the systems studied were described by a relatively simple chemical model which roughly corresponds to that considered for 1-aminoethylphosphinic acids.[10]

In the acidic region pH 1.8–4, as for 1-aminoethylphosphinic acids,[10] no protonated ML(HL) or MHL_2 species were observed. The complexes start to form at neutral pH. The cation ML^+ found in all the systems studied is predominant in the region pH 5–8.0. At pH about 8 we observed non-reproducibility and slow drift of the *E* values measured and at pH > 8.5 precipitation. Therefore, species such as 102, 103 or

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Table 1 Characterization of the phosphinic acids

Acid	NMR (δ, J/Hz) ^{1}H	^{31}P-{^{1}H}	M.p./°C (decomp.)	Yield (%)	Analysis (%)* C	H	N
HL^1	3.04 (2 H, dd, $^2J_{PH}$ = 11.1, $^3J_{HH}$ = 2.2, CH_2), 7.16 (1 H, dt, $^1J_{PH}$ = 540.5, $^3J_{HH}$ = 2.2)	16.67(s)	272	76	12.5 (12.65)	6.25 (6.35)	14.9 (14.75)
HL^2	3.06 (2 H, d, $^2J_{PH}$ = 9.9, CH_2), 1.39 (3 H, d, $^2J_{PH}$ = 13.9, Me)	33.67(s)	296	25	21.8 (22.0)	7.45 (7.40)	13.0 (12.85)
HL^3	3.13 (2 H, d, $^2J_{PH}$ = 7.0, CH_2), 139 (9 H, d, $^3J_{PH}$ = 15.4, Me)	42.98(s)	> 300	89	39.5 (39.75)	9.25 (9.35)	9.15 (9.25)
HL^4	3.06 (2 H, d, $^2J_{PH}$ = 10.1, CH_2), 7.47 (5 H, m, Ph)	24.60(s)	286	56	49.6 (49.15)	5.90 (5.90)	8.20 (8.20)

* Calculated values in parentheses.

Table 2 Protonation constants of HL^1, HL^2, HL^3 and HL^4 and stability constants of their complexes at 25 °C and I = 0.1 mol dm^{-3}; $\beta_{pqr} = [M_pH_qL_r]/[M]^p[H]^q[L]^r$

	p	q	r	HL^3	HL^2	HL^4	HL^1
H^+	0	1	1	8.427(1)	8.403(4)	8.082(5)	8.066(4)
	0	2	1	9.631(4)	9.29(1)	< 8.5	—
Co^{2+}	1	0	1	3.17(7)	2.62(2)	2.39(1)	2.96(2)
	1	−1	1	—	−6.66(6)	−6.50(1)	−5.64(1)
Ni^{2+}	1	0	1	3.62(2)	3.22(1)	2.93(1)	3.95(2)
	1	0	2	6.27(2)	5.68(9)	5.20(2)	6.14(4)
	1	0	3	8.45(8)*	—	—	—
	1	−1	1	−5.18(3)*	—	−5.82(5)*	−3.73(2)
	1	−2	1	−14.80(5)*	—	−15.18(7)*	−14.0(1)*
Cu^{2+}	1	0	1	5.37(1)	4.60(2)	4.411(5)	4.97(2)
	1	0	2	6.27(9)	—	—	7.64(3)
	1	−1	1	−4.95(1)*	—	−5.55(9)*	−3.47(3)*
	1	−2	1	—	—	−14.50(8)*	—

* Low abundance.

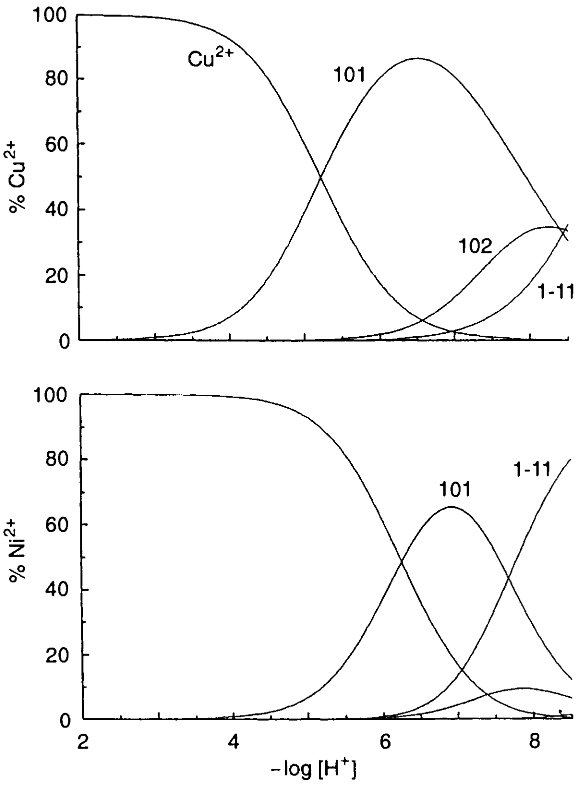

Fig. 1 Concentration distribution of the complexes formed in the Cu^{2+}- and Ni^{2+}-HL^1 systems as a function of pH (c_{Cu} = 0.005, c_{Ni} = 0.005, c_L = 0.01 mol dm^{-3})

hydroxo-complexes 1 − 11 and 1 − 21 could not be determined in all these systems. All these species were found only in systems with HL^3, probably due to the higher complexing ability and/or hydrophobicity of the acid and its complexes. Even when the abundance of hydroxo-complexes was lower than 10%, the statistics required inclusion of the species in the chemical model.

From Table 2 it is evident that the log β_{101} values increase in the order Co^{II}, Ni^{II} and Cu^{II} for each phosphinic acid, and for Co^{II} and Cu^{II} the log β_{101} values increase in the order HL^4, HL^2, HL^1 and HL^3 and for Ni^{II} in the order HL^4, HL^2, HL^3 and HL^1. Except for HL^1, this order follows, as was expected, the order found for the pK_a values. The log β_{101} values of HL^1 are surprisingly high and we assume that this is probably caused by the greater deformability of the $P(H)O_2^-$ group and consequently better ability to form a chelate ring and/or to the softer character of the group.

Comparison of the log β_1 values of 1-aminoethylphosphinic acids $H_2NCH(Me)PRO_2H$ where R = H (HL^5), Me(HL^6) or Ph(HL^7) and their stability constants for the copper(II) systems found by Kiss *et al.*[10] show a similar trend to our values for HL^1, HL^2 and HL^4 and thus the protonation constants log β_1 of HL^1 and HL^5, HL^2 and HL^6, and HL^4 and HL^7 are very similar. The stability constants log β_{101} for HL^1 and HL^5 with Cu^{II} are also very similar. However, these values for HL^6 and HL^7 are higher (5.45 and 5.13) than for HL^2 and HL^4 probably due to hydrophobic interaction of the methyl group on the α-carbon with the substituent on the phosphorus atom. A similar increase in the stability constants as a result of hydrophobic interaction of the substituents was observed for phosphonodipeptides.[23]

Comparison of the log β_1 and stability constant values log β_{101} found with those for glycine confirmed the higher acidity and lower ability to form complexes for aminomethylphosphinic acids.

As was mentioned above, at pH about 8 a drift in E values was observed and at pH about 8.5 precipitation. The complexes $[CuL^4{}_2]$ **1** and $[Cu_3L^2{}_4][ClO_4]_2$ **2** exhibit a polymeric character and were prepared by slow neutralization of the

Table 3 Characterization of the complexes

Complex	Yield (%)	Analysis (%)* C	H	N	M	Reflectance spectra λ/nm	Assignment
$[CoL^4_2]\cdot4.5H_2O$	78	35.0	5.30	5.75	12.5	1150	${}^4T_{2g} \leftarrow {}^4T_{1g}$
		(35.0)	(5.65)	(5.85)	(12.3)		
						580 (sh)	
						495	${}^4T_{1g}(P) \leftarrow {}^4T_{1g}$
						380 (sh)	
						270	${}^1L_b$
						230	${}^1L_a$
$[NiL^4_2]\cdot4H_2O$	63	35.9	5.10	5.85	12.4	980	${}^3T_{2g} \leftarrow {}^3A_{2g}$
		(35.7)	(5.55)	(5.95)	(12.5)		
						740	${}^1E_g \leftarrow {}^3A_{2g}$
						640	${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$
						380	${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$
						271	${}^1L_b$
						230	${}^1L_a$
$[CuL^4_2]$	74	40.8	4.25	6.80	15.3	710	${}^2T_{2g} \leftarrow {}^2E_g$
		(41.6)	(4.50)	(6.95)	(15.7)		
						265	${}^1L_b$
$[ZnL^4_2]$	46	41.0	4.35	6.75	15.8		
		(41.4)	(4.45)	(6.90)	(16.1)		
$[CdL^4_2]$	57	37.0	3.65	6.05	24.5		
		(37.1)	(4.00)	(6.20)	(24.8)		
$[CoL^3_2]\cdot4H_2O$	51	27.5	7.45	6.25	13.8	1150	${}^4T_{2g} \leftarrow {}^4T_{1g}$
		(27.8)	(7.95)	(6.50)	(13.7)		
						575 (sh)	
						500	${}^4T_{1g}(P) \leftarrow {}^4T_{1g}$
$[NiL^3_2]\cdot5H_2O$	49	26.9	7.55	6.15	13.5	1050	${}^3T_{2g} \leftarrow {}^3A_{2g}$
		(27.7)	(8.10)	(6.25)	(13.1)		
						650	${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$
						385	${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$
$[CuL^3_2]\cdot5H_2O$	27	26.8	7.55	6.20	14.2	720	${}^2T_{2g} \leftarrow {}^2E_g$
		(26.4)	(8.00)	(6.15)	(14.0)		
$[ZnL^3_2]\cdot4H_2O$	40	27.7	7.80	6.30	15.1		
		(27.4)	(7.80)	(6.40)	(14.9)		
$[CdL^3_2]\cdot4H_2O$	49	24.8	7.05	5.70	23.0		
		(24.7)	(7.05)	(5.75)	(23.2)		
$[Cu_3L^2_4][ClO_4]_2$	23	12.3	3.80	6.55	23.2	725	${}^2T_{2g} \leftarrow {}^2E_g$
		(12.7)	(3.45)	(6.80)	(23.2)		

* Calculated values in parentheses.

diluted $Cu(ClO_4)_2$ solutions with HL^4 or HL^2 to pH about 7. Analysis of the precipitates pointed to compositions that were found in the complexes prepared. Therefore, we assume dimerization and polymerization during potentiometric titration in the neutral pH region and the complexes analogous to the systems with glycine, *i.e.* with higher metal : ligand molar ratio could not be determined.

Preparation of the complexes

Complexes of HL^3 and HL^4 with a molar ratio M : L = 1 : 2 were prepared according to the procedure described in the Experimental section by very slow neutralization of a solution containing $M(ClO_4)_2$ and the phosphinic acid with diluted (1%) NaOH. Only this route led to reproducible results. The analysis and the spectroscopic data determined are listed in Table 3. The compounds form microcrystalline powders and are sparingly soluble in water. The crystalline character was confirmed by orientative X-ray powder patterns. Crystals of $[CuL^4_2]$ were used for X-ray analysis, in spite of the fact that their shape was not convenient.

Complexes of HL^1 and HL^2 were more soluble in water and easily form supersaturated solutions. Diffusion of ethanol or acetone into their aqueous solutions led only to precipitates with higher metal : ligand ratio. The molar ratio of the precipitates was not exactly reproducible, except for $[Cu_3L^2_4][ClO_4]_2$ which was also employed in X-ray analysis. For this reason the other complexes of HL^1 and HL^2 were not studied. Bands in the reflectance spectra of the solid substances are shown in Table 3. Comparison of the Jørgensen parameter

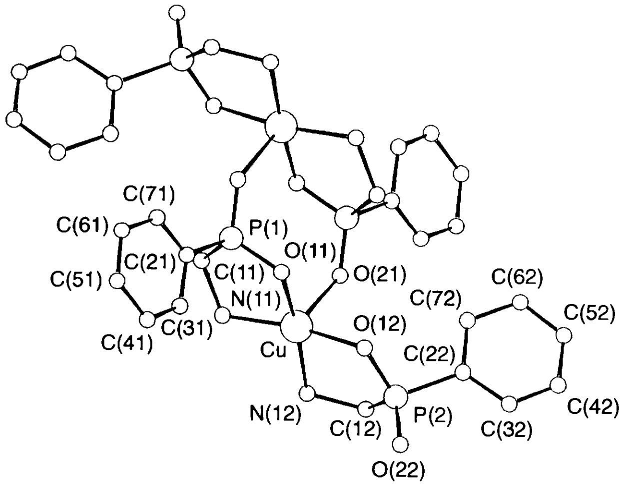

Fig. 2 View of the structure of $[CuL^4_2]$ with the atom numbering scheme

f_L calculated for the acids investigated with those tabulated[24] for other ligands shows that it is similar to that of water.

Structures of $[CuL^4_2]$ and $[Cu_3L^2_4][ClO_4]_2$

The structure of $[CuL^4_2]$ **1** in the dimer form is shown in Fig. 2; Table 4 lists selected bond distances and angles. This is the first structure published for a complex of an aminoalkyl- or

Table 4 Selected bond lengths (Å) and angles (°) in $[CuL^4{}_2]$

Cu–O(11)	1.956(13)	P(1)–C(21)	1.817(21)
Cu–N(11)	1.989(16)	P(2)–O(12)	1.533(14)
Cu–O(21)	2.311(14)	P(2)–O(22)	1.467(16)
Cu–O(12)	1.998(12)	P(2)–C(12)	1.833(20)
Cu–N(12)	2.004(16)	P(2)–C(22)	1.832(23)
P(1)–O(11)	1.521(14)	N(11)–C(11)	1.480(25)
P(1)–O(21$^{\text{I}}$)	1.468(14)	N(12)–C(12)	1.477(28)
P(1)–C(11)	1.802(17)		
N(11)–Cu–O(11)	87.8(6)	O(11)–P(1)–O(21$^{\text{I}}$)	118.7(6)
O(21)–Cu–O(11)	98.5(5)	C(11)–P(1)–O(21$^{\text{I}}$)	110.9(7)
O(21)–Cu–N(11)	97.3(7)	C(21)–P(1)–O(21$^{\text{I}}$)	108.2(6)
O(12)–Cu–O(11)	91.1(5)	C(12)–P(2)–O(12)	102.9(8)
O(12)–Cu–N(11)	169.2(7)	C(22)–P(2)–O(12)	106.3(9)
O(12)–Cu–O(21)	93.5(6)	C(22)–P(2)–C(12)	103.5(10)
N(12)–Cu–O(11)	170.6(7)	O(12)–P(2)–O(22)	116.9(8)
N(12)–Cu–N(11)	93.0(7)	C(12)–P(2)–O(22)	115.0(9)
N(12)–Cu–O(21)	90.7(6)	C(22)–P(2)–O(22)	111.0(10)
N(12)–Cu–O(12)	86.3(6)	Cu–O(11)–P(1)	119.3(7)
C(11)–P(1)–O(11)	102.0(8)	Cu–O(12)–P(2)	117.9(6)
C(21)–P(1)–O(11)	107.5(9)	Cu–N(11)–C(11)	109.9(11)
C(21)–P(1)–C(11)	109.0(9)	Cu–N(12)–C(12)	112.5(11)

Symmetry relation: I $-x, -y, -z$.

aminoaryl-phosphinic acid with the ratio M : L = 1 : 2 and the first reported for an aminoalkylphosphinic acid bearing R different from methyl. Owing to the mentioned shape and poor quality of the crystals (thin plates and broad reflections and low ratio of observed : measured reflections) the *R* factor determined is rather high.

The co-ordination number of the copper atoms is five and the square-based pyramidal co-ordination sphere is formed by chelation of both ligand molecules and by an oxygen atom of the neighbouring phosphinate. The chelation through the amino groups and oxygen atoms of the phosphinates gives rise to five-membered rings (see Fig. 2). The nitrogen atoms of the amino groups are bonded to copper in the *cis* position. The donor atoms of both chelating rings O(11), N(11), O(12), N(12) lie in the equatorial plane and the copper atom is slightly above this plane (about 0.18 Å). The apical position is occupied by an oxygen atom of the neighbouring phosphinate, O(21), and, thus two co-ordination tetragons are connected by P(1) and P(2) phosphinates. In this way, an eight-membered ring with a crystallographic inversion centre is formed.

The dimers are connected through the O(22) oxygen and copper atoms to the polymeric chain. The O(22) • • • Cu distance is too long (2.94 Å) for bonding and also, according to Brunner's criterion,[25] the crystallochemical co-ordination number of Cu is five and the co-ordination polyhedron at Cu is square-based pyramidal. Nevertheless, interaction of the copper and O(22) atoms and formation of the polymeric chain is evident. The structure is similar to that of $[Cu(GlyO)_2]{\cdot}H_2O$ GlyO = glycinate).[26] In both of these substances the same co-ordination polyhedron at the Cu, *i.e.* means of chelation, *cis* position of the N atoms and linkage of the units into a polymeric chain, was found. Furthermore, the Cu–N or Cu–O bond lengths of atoms in the equatorial plane are almost identical. The Cu • • • O(22) bond length (linkage of units into chain) is also similar to that in the structures $[Cu(GlyO)_2]{\cdot}H_2O$[26] and $[Cu(AlaO)_2]{\cdot}H_2O$ (AlaO = alaninate),[27] although the co-ordination polyhedra are connected only through the oxygen atom of one carboxylic group.

An eight-membered ring is not commonly found in copper(II) complexes of the simple α-aminocarboxylic acids; however, it is a dominant and characteristic feature of transition-metal complexes with simple phosphinic acids.[28] Thus, the structure of $[CuL^4{}_2]$ represents a combination of typical features of the transition-metal complexes with both α-aminocarboxylic and phosphinic acids.

Table 5 Selected bond lengths (Å) and angles (°) in $[Cu_3L^2{}_4][ClO_4]_2$

Cu(1)–N(1)	2.000(6)	P(2)–O(21)	1.528(5)
Cu(1)–O(11)	1.947(5)	P(2)–O(22)	1.499(6)
Cu(1)–O(12)	1.928(6)	P(2)–C(21)	1.805(9)
Cu(1)–O(22)	1.931(5)	P(2)–C(22)	1.784(8)
Cu(2)–N(2)	1.999(6)	N(1)–C(11)	1.472(11)
Cu(2)–O(2)	1.941(5)	N(2)–C(21)	1.433(12)
P(1)–O(11)	1.512(5)	Cl–O(3)	1.411(7)
P(1)–O(12$^{\text{I}}$)	1.492(6)	Cl–O(4)	1.392(7)
P(1)–C(11)	1.811(10)	Cl–O(5)	1.371(8)
P(1)–C(12)	1.787(8)	Cl–O(6)	1.456(8)
N(1)–Cu(1)–O(11)	89.1(2)	O(21)–P(2)–C(22)	112.3(4)
N(1)–Cu(1)–O(12)	175.5(3)	O(22)–P(2)–C(21)	110.3(6)
N(1)–Cu(1)–O(22)	89.5(2)	O(22)–P(2)–C(22)	106.9(4)
O(11)–Cu(1)–O(12)	91.5(2)	C(21)–P(2)–C(22)	107.0(6)
O(11)–Cu(1)–O(22)	166.2(2)	N(1)–C(11)–P(1)	110.0(5)
O(12)–Cu(1)–O(22)	91.0(2)	N(2)–C(21)–P(2)	112.6(6)
N(2)–Cu(2)–O(21)	89.1(2)	Cu(1)–N(1)–C(11)	114.1(5)
N(2)–Cu(2)–O(21$^{\text{II}}$)	91.0(3)	Cu(2)–N(2)–C(21)	114.2(5)
O(21)–Cu(2)–N(21$^{\text{II}}$)	91.0(3)	Cu(1)–O(11)–P(1)	115.8(3)
O(11)–P(1)–O(12$^{\text{I}}$)	115.1(4)	Cu(1)–O(12$^{\text{I}}$)–P(1$^{\text{I}}$)	132.2(4)
O(11)–P(1)–C(11)	104.9(4)	Cu(2)–O(21)–P(2)	117.8(3)
O(11)–P(1)–C(12)	109.1(4)	O(3)–Cl–O(4)	111.0(5)
C(11)–P(1)–O(12$^{\text{I}}$)	111.4(4)	O(3)–Cl–O(5)	114.3(6)
C(11)–P(1)–C(12)	108.4(4)	O(3)–Cl–O(6)	103.7(6)
O(12$^{\text{I}}$)–P(1)–C(12)	108.0(4)	O(4)–Cl–O(5)	112.9(6)
O(21)–P(2)–O(22)	115.3(3)	O(4)–Cl–O(6)	107.1(5)
O(21)–P(2)–C(21)	104.7(4)	O(5)–Cl–O(6)	107.0(7)

Symmetry relations: I $x, y - 1, z$; II $-x, -y, -z$.

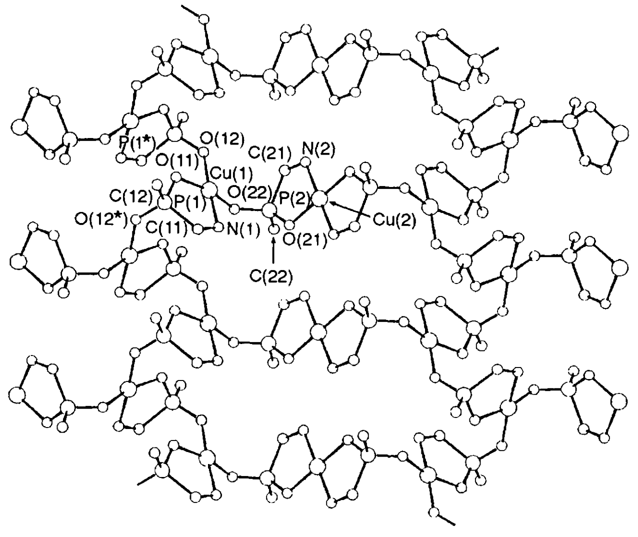

Fig. 3 View of the structure of $[Cu_3L^2{}_4][ClO_4]_2$ with the atom numbering scheme

The structure of $[Cu_3L^2{}_4][ClO_4]_2$ **2** forms polymeric layers in the *x,y* plane. (Fig. 3). Two crystallographically and chemically different copper atoms with co-ordination numbers of four and square co-ordination spheres connect the ligands in the layers. The Cu(2) atoms occupy special positions (0, ½, ½; a crystallographic centre of symmetry), and their co-ordination spheres are formed by chelation of two ligand molecules through the amino groups and the oxygen atoms of the phosphinates. This gives rise to two five-membered rings. The nitrogen atoms are bonded to copper in the *trans* position. The co-ordination sphere of Cu(1) is formed by chelation of only one ligand molecule through the nitrogen and oxygen of phosphinate. Two remaining positions are occupied by two oxygen atoms of two different neighbouring phosphinates. Thus, the phosphinates form both five-membered chelate rings and bridges between the co-ordination polyhedra. The Cu(1) co-ordination sphere is virtually planar [deviation of Cu(1) from the N(1), O(11), O(12), O(22) plane is 0.076(6) Å].

Selected bond lengths and angles are listed in Table 5. All Cu–O distances are within 3σ the same as the Cu–N distances and in good agreement with literature values[26,27,29] and, of course, with the values found for complex **1**. The axial positions of the copper atoms are occupied by oxygen atoms of perchlorates with non-bonding distances Cu(1)···O(6) 2.653(7) and Cu(2)···O(3) 2.759(7) Å. This non-bonding character of O(3) and O(6) was confirmed by Brunner's criterion.[25] Nevertheless, we assume a weak interaction to the copper atoms similar to that in **1** for O(22). All donor atoms (both oxygens and nitrogen) of $(L^4)^-$ are co-ordinated to copper atoms, through nitrogen and one oxygen as a chelate, and to the next copper atom and thus the phosphinate group forms Cu(1)–O–P–O–Cu(2) bridges. This structural motif is common for compounds of phosphinic acids with transition metals.[28] All P–O distances lie in a narrow range from 1.492(6) to 1.528(5) Å. The values of the O–P–O angles are higher than for a regular tetrahedron, probably due to the formation of the bridges.

As was mentioned above, the structure of complex **2** forms polymeric layers. The layers are linked through hydrophobic interaction of the CH_3 groups. The density found is higher than that for complexes of this type and is probably caused by the close packing of these layers. In this structure we again observe the typical features both of complexes of the simple α-aminocarboxylic acids and those of the simple phosphinic acids.

Experimental

Instrumentation

Melting points were determined with a Boeithus apparatus and are uncorrected. Proton and ^{31}P NMR spectra were taken on a Varian Unity 200 MHz spectrometer, using approximately 0.1 mol dm^{-3} solutions in D_2O or $CDCl_3$, with chemical shifts reported in ppm from sodium 4,4-dimethyl-4-silapentane-1-sulfonate or $SiMe_4$ (internal) and 85% H_3PO_4 (external) standards. The IPAV eluent for TLC (silica gel sheets) contained propan-2-ol, concentrated ammonia and water in a volume ratio of 7 : 3 : 3.

Preparations of HL^1, HL^2, HL^3, HL^4

The starting compounds $RPCl_2$ (R = Me,[30] Bu^t,[31] Ph[32]) and $HPO(OEt)[CH(OEt)_2]$[33] were prepared according to previously described procedures and all the reactions were carried out under a dry argon atmosphere. Their purity was checked by conventional methods (^1H and ^{31}P NMR spectra and elemental analysis). Solvents were purified and dried using established procedures.

HL^1. The compound $Ph_3CN{=}CH_2$ (11.98 g, 44 mmol) synthesized according to Soroka and Zygmund[34] was dissolved in dry toluene (75 cm^3) and ethyl diethoxymethylphosphinate (8.85 g, 45.1 mmol) was added in one portion. The solution was stirred for 20 min at ambient temperature, then refluxed for 2 h. Toluene was evaporated and a clear, almost colourless oil of ethyl diethoxymethyl[(triphenylmethylamino)methyl]phosphinate (**I**) was obtained in almost quantitative yield and sufficient purity for the next reaction step. It was purified by chromatography on silica (mobile phase $CHCl_3$–MeOH), is stable in the air and can be stored in a refrigerator for at least 1 year without decomposition, as was confirmed by ^{31}P NMR spectroscopy.

Hydrolysis of compound I. Compound **I** (44 mmol) was dissolved in glacial acetic acid (100 cm^3) and azeotropic hydrochloric acid (100 cm^3) were added to the stirred solution under an argon atmosphere. The mixture was allowed to stand under Ar at room temperature until ^{31}P NMR spectroscopy showed the completion of the hydrolysis (*ca.* 14 d). The reaction can be followed by TLC (IPAV, silica, ninhydrin). The solid residue was filtered off and the filtrate evaporated to dryness on a rotary evaporator. The temperature of the water-bath did not exceed 30 °C. The residue was co-evaporated three times with water (3 cm^3), dissolved in the minimum of methanol and treated with propylene oxide. After standing in a refrigerator overnight, the product was filtered off, washed with cold methanol and dried in vacuum.

HL^2, HL^3, HL^4. These compounds were prepared from dichloromethyl-, *tert*-butyldichloro- or dichlorophenyl-phosphine according to the following general procedure. A suspension of *N*-(hydroxymethyl)benzamide (9.6 g, 63.5 mmol) in dry acetic acid (15 cm^3) was cooled to 10 °C, and the appropriate phosphine (63.1 mmol) was added dropwise over 60 min under stirring, while maintaining the temperature at 10 °C. The clear solution was then stirred for 60 min at 25 °C. The reaction was completed by gentle refluxing for 60 min (*ca.* 120 °C). The solution was allowed to cool to 80 °C, and water (10 cm^3) and concentrated hydrochloric acid (25 cm^3) were added. The mixture was refluxed overnight, cooled to 0 °C, crystals of benzoic acid were filtered off and washed with cold water (8 cm^3). The filtrate was evaporated to dryness, the residue was dissolved in the smallest possible volume of methanol, and aminomethylphosphinic acid was released using propylene oxide (*ca.* 2 cm^3). Acetone (50 cm^3) was added to the suspension and the crystallisation was completed by leaving the mixture to stand at 0 °C overnight. The white crystals of the product were filtered off, washed with acetone (20 cm^3) and dried. To obtain analytical samples of sufficient purity for pH-metric titrations, the products were recrystallized twice from hot water.

Complexes $[ML^3_2]\cdot xH_2O$ and $[ML^4_2]\cdot xH_2O$ (M=Cu, Zn, Cd, Co or Ni)

These were prepared in a similar way, mixing stoichiometric amounts of the transition-metal perchlorate with an appropriate acid in water, and extremely slow neutralization of this mixture by stirring. In a typical procedure, the transition-metal perchlorate hexahydrate (0.15 mmol) was dissolved in water (1 cm^3) and 0.30 mmol of HL^3 or HL^4 dissolved in water (1 cm^3) was added in one portion. The stirred mixture was slowly neutralized using 1% NaOH. After the mixture had reached pH *ca.* 7 the desired complexes started to separate in the form of a microcrystalline precipitate. At the same time the pH decreased. It was carefully readjusted to 7 several times, and the mixture left to stand at ambient temperature overnight. The yields, UV/VIS spectra and analyses are given in Table 3. Using the same procedure as for HL^2, $[Cu_3L^2_4][ClO_4]_2$ was isolated and materials with this stoichiometry were obtained for the other metals and with both HL^1 and HL^2.

Potentiometric titrations

Stock solutions for potentiometric titrations of the individual metal cations were acidified solutions of the nitrates, recrystallized from aqueous solutions. Their metal contents were determined by titration with ethylenedinitrilotetraacetate solution and excess of nitric acid was determined by pH-metric acid–base titration using Gran's method. The nitric acid was prepared from recrystallized potassium nitrate on a column with Dowex 50 (H$^+$ form).

Potentiometric measurements were carried out using a PHM 84 pH-meter, ABU 80 automatic burette and a GK 2401 B combined electrode (Radiometer) in a glass vessel (10 cm^3) thermostatted at 25 ± 0.1 °C at an ionic strength of I (KNO_3) × 0.1 mol dm^{-3}. An inert atmosphere was ensured by constant passage of argon saturated with the solvent vapour. The initial solution volume was 5 cm^3 and the concentration of aminomethylphosphinic acid was 0.01 mol dm^{-3} for determin-

Table 6 Experimental data for the X-ray diffraction studies of $[CuL^4{}_2]$ and $[Cu_3L^2{}_4][ClO_4]_2$

	$[CuL^4{}_2]$	$[Cu_3L^2{}_4][ClO_4]_2$
Formula	$C_{14}H_{18}CuN_2O_4P_2$	$C_8H_{28}Cl_2Cu_3N_4O_{16}P_4$
M	403.8	821.74
Crystal dimensions/mm	0.24 × 0.32 × 0.06	0.58 × 0.13 × 0.13
Shape and colour	Blue thin flake	Bright blue prism
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a/Å	5.606(1)	8.9946(8)
b/Å	10.427(5)	5.7452(7)
c/Å	14.864(5)	25.443(3)
α/°	81.77(4)	
β/°	79.20(3)	92.641(9)
γ/°	89.35(3)	
Z	2	2
U/Å^3	844.6(2)	1313.4(3)
D_c/g cm^{-3}	1.572	2.078
$D_m{}^a$/g cm^{-3}	—	2.066(7)
μ/mm^{-1}	1.501	2.930
R^b	0.1219	0.0698
R'^b	0.1117	0.0697
S^b	1.882	2.257
Number of reflections measured	3221	2311
Number of reflections observed [$I > 2\sigma(I)$]	1702	1909
Largest difference peak and hold e Å^{-3}	1.31, −1.10	1.58, −1.17

[a] Flotation in $CHCl_3$–$CHBr_3$. [b] $R = \Sigma(F_o - F_c)/\Sigma F_o$, $R' = \Sigma w^2(F_o - F_c)/\Sigma w^2 F_o$ (SHELX 76, ref. 37).

ation of the protonation and of the stability constants. The metal : ligand ratio was 1 : 1, 1 : 2 or 1 : 4. Total number of data points: >200. Calibration was carried out by titration of 0.05 mol dm^{-3} HNO_3 with 0.17 mol dm^{-3} KOH in 0.1 mol dm^{-3} KNO_3 in the region pH 1.8–12.0, with the pH-meter yielding *E* values.

The protonation and stability constants β_{pqr} are concentration constants defined by $\beta_{pqr} = [M_pH_qL_r]/[M]^p[H]^q[L]^r$. They were refined by our program[35] which minimizes the criterion of the generalized least-squares method. The program includes the calibration function (1) where the additive term E_0 contains the

$$E = E_0 - S(-\log[H^+]) + j_a[H^+] + j_b(K_w/[H^+]) \quad (1)$$

standard potentials of the electrodes used and contributions of inert ions to the liquid-junction potential, *S* corresponds to the Nernstian slope, the value of which should be close to the theoretical value and $j_a[H^+]$ and $j_b[OH^-]$ are contributions of the H^+ and OH^- ions to the liquid-junction potential. It is clear that j_a and j_b cause deviation from a linear dependence between *E* and $-\log$ $[H^+]$ only in strong acid and strong base. The procedure was tested by the 'glycine test'.[36]

Crystallography

Crystals of $[CuL^4{}_2]$ **1** suitable for X-ray diffraction were obtained by crystallization from water, while those of $[Cu_3L^2{}_4][ClO_4]_2$ **2** were obtained from water–ethanol. Air-stable crystals of both compounds were mounted on glass fibres at random orientations for unit-cell and space-group determination and for data collection. An Enraf–Nonius CAD 4 and a Hilger & Watts diffractometer were used for measurements of **2** and **1**, respectively, at 293 (2) K with Mo-Kα radiation (λ = 0.710 69 Å). Unit-cell dimensions were obtained by least-squares fits of the 2θ values of 25 high-order (θ = 17–18°) reflections using the CAD 4 centring routines for **2**. For **1** the unit-cell dimensions were obtained using 28 high-order (θ = 9–13°) reflections. Selected crystallographic and other relevant data are listed in Table 6.

Intensities were collected using variable scan speed to assure constant statistical precision. Three standard reflections measured every hour were used to check the stability of the crystal and of the experimental conditions. The orientation of the crystal were checked by measuring three standards every 200 reflections.

The structures were solved by a combination of Patterson and Fourier methods and refined by full-matrix least-squares techniques (SHELX 76).[37] Scattering factors for neutral atoms used were taken from ref. 38. The weighting scheme was $w = 1/[\sigma^2(F_o) + 0.0009F_o{}^2]$ in both cases.[37] Hydrogen atoms in CH_3, CH_2 and CH fragments were included in the calculated positions and only their isotropic thermal parameters (one for every type of hydrogen atom) were refined on F^2 (SHELX 76).[37]

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/75.

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