

Bis(dialkylaminomethyl)phosphinic Acids and Their Addition Compounds with Tetrahedral $[MCl_4]^{2-}$ Ions ($M = Cu^{II}, Co^{II}$)

by F. Kašpárek¹, Z. Trávníček¹, V. Bekárek² and J. Marek³

¹Department of Inorganic and Physical Chemistry, Palacký University, 771 47 Olomouc, Czech Republic; trav@aix.upol.cz

²Department of Organic Chemistry, Palacký University, 771 46 Olomouc, Czech Republic

³X-ray Laboratory of Faculty of Science, Masaryk University, 611 37 Brno, Czech Republic

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Monohydrate monohydrochloride of bis(dialkylaminomethyl)phosphinic acids of the composition, $[(R_1HCH_2)_2PO_2]Cl \cdot H_2O$ $\{R_1 = Me_2N, Et_2N, (n-Bu)_2N, C_5H_{10}N, OC_4H_8N\}$, dihydrate dihydrochloride of bis(dialkylaminomethyl)phosphinic acids, $[(R_2HCH_2)_2P(O)OH]Cl_2 \cdot 2H_2O$ $\{R_2 = Me_2N, C_4H_8N, C_5H_{10}N, OC_4H_8N\}$, and their copper(II) and cobalt(II) addition compounds with tetrahedral $[MCl_4]^{2-}$ ions $\{M = Cu^{II}, Co^{II}\}$ have been prepared and characterized by elemental analyses, effective magnetic moments, IR, VIS, and 1H and ^{31}P -NMR spectra. Crystal and molecular structures of $[(OC_4H_8NHCH_2)_2PO_2]Cl \cdot H_2O$ and $[(OC_4H_8NHCH_2)_2PO_2]_2CuCl_4$ have also been determined.

Key words: bis(dialkylaminomethyl)phosphinic acids, synthesis, X-ray structure

Aminoderivatives of organophosphinic/phosphonic acids are in forefront of chemist publicity for a long time. A special attention is focused on alpha-amino-phosphonic/phosphinic or phosphonous acids. These compounds are phosphorus analogues of amino acids and for this reason they should exhibit both physiological and complexation properties [1], which enable wide range of application in industry. Whereas aminoalkylorganophosphorus compounds have attracted considerable attention and have been extensively studied [2–4], literature data concerning bis(aminomethyl)phosphinic acids are somewhat limited sketchy. Aminomethylation reactions of hypophosphorous acid, as the simplest method for preparation of these compounds, can proceed *via* either one or both hydrogens bonded to phosphorus [5–9]. Bis(dialkylaminomethyl)phosphinic acids were not satisfactory characterized yet in comparison with dialkylaminomethylphosphonous acids. To date, Maier *et al.* synthesized and characterized bis(N-hydroxycarbonylmethyl-aminomethyl)phosphinic acids [10] and Varga described the synthesis of N,N,N',N'-tetrasubstituted bis(aminomethyl)phosphinic acids *via* a Mannich reaction [11]. Bis(dialkylaminomethyl)phosphinic acids have also been prepared and studied by Prishchenko *et al.* [12]. A betaine structure has been proposed for these compounds on the basis of 1H , ^{13}C and ^{31}P -NMR spectra and was unambiguously confirmed by a single crystal X-ray analysis in the case of bis(imidazol-2-yl)phosphinic acid hemihydrate [13]. The structural features of metal complexes with 1-hydroxyethylidenediphosphonic acid

[14], di(hydroxymethyl)phosphinic and di(chloromethyl)phosphinic acids [15] have been reviewed by Sergienko. From the review it is evident that these variously substituted alkyl- and aminoalkyl(aryl)phosphinic acids form a wide range of complexes with 3d transition metals such as Cu, Zn, Co and Ni. The derivatives of alkylphosphinic acids may act on the metal centres as bidentate and often as bridging ligands. In connection with considerable coordination variability of substituted alkyl- and aminoalkyl(aryl)phosphinic acids their transition metal complexes may exist as monomers, dimers, polymeric chains or three-dimensional frameworks.

Here, we describe the preparation and characterization of bis(alkylaminomethyl)phosphinic acids and their addition compounds with $[\text{CoCl}_4]^{2-}$ or $[\text{CuCl}_4]^{2-}$ complex anions.

EXPERIMENTAL

Syntheses: *Bis(dialkylaminomethyl)phosphinic acid monohydrochloride monohydrate*, $[(R_1\text{HCH}_2)_2\text{PO}_2]\text{Cl}\cdot\text{H}_2\text{O}$ $\{R_1 = \text{Me}_2\text{N}, \text{Et}_2\text{N}, (n\text{-Bu})_2\text{N}, \text{C}_5\text{H}_{10}\text{N}, \text{OC}_4\text{H}_8\text{N}\}$. 9 cm³ of 35% HCl (0.1 mol) was added to a mixture of 6.6 g H₃PO₂ (0.1 mol, 50% water solution) and dialkylamine (0.2 mol), with stirring and surface cooling. (Note: When we used dialkylamine hydrochloride as the starting compound, it was not necessary to add concentrated HCl). The reaction mixture was boiled under reflux for 1 h. Then, we added 30.6 cm³ of formaldehyde (0.4 mol, 36% water solution) dropwise during this period and the mixture was still refluxed for 1 h. An excess of water and formaldehyde was vacuum fully evaporated. The solid was dissolved in water and concentrated to crystallization on water bath. A soft solution colouring was eliminated by addition of an active carbon. This procedure was repeated twice. Formed crystals were separated by filtration and dried on air. Yield: 70–85%. M.p's (°C): 248 (Me₂N), 92–3 (Et₂N), oil ((n-Bu)₂N), 258 (C₅H₁₀N) and 215 (OC₄H₈N). The analytical data (C, H, N, Cl) of the compounds were within the limits of experimental error (± 0.4%).

Bis(dialkylaminomethyl)phosphinic acid dihydrochloride dihydrate, $[(R_2\text{HCH}_2)_2\text{P(O)OH}]\text{Cl}_2\cdot 2\text{H}_2\text{O}$ $\{R_2 = \text{Me}_2\text{N}, \text{C}_4\text{H}_8\text{N}, \text{C}_5\text{H}_{10}\text{N}, \text{OC}_4\text{H}_8\text{N}\}$. Monohydrate monohydrochloride of bis(dialkylaminomethyl)phosphinic acid (0.01 mol) was dissolved in 10 cm³ of concentrated hydrochloric acid. The solution was evaporated to dryness on water bath. Yield: nearly quantitative. M.p's (°C): 215 (Me₂N), 264 (C₄H₈), 240 (C₅H₁₀N) and 210 (OC₄H₈N). The analytical data (C, H, N, Cl) of the compounds were within the limits of experimental error (± 0.4%).

Caution: A precipitation using ethanol led only to formation of monohydrate monohydrochloride of bis(dialkylaminomethyl)phosphinic acid.

Addition compounds of bis(dialkylaminomethyl)phosphinic acid with $[\text{CuCl}_4]^{2-}$ and $[\text{CoCl}_4]^{2-}$. Bis(dialkylaminomethyl)phosphinic acid monohydrochloride monohydrate (0.01 mol) and 0.85 g CuCl₂·2H₂O (0.005 mol) or 1.19 g CoCl₂·6H₂O (0.005 mol) was dissolved in hot water (20 cm³). The reaction mixture was stirred for 1 h and subsequently filtered. Then, the solution was left to crystallization. Dark yellow (adducts with CuCl₄²⁻) or blue crystals (adducts with CoCl₄²⁻) formed were filtered off and dried on air.

Physical and spectral techniques: Elemental analyses (C, H, N) were performed using an analyser EA1108 (Fisons Instruments). The chlorine content was determined by the Schöniger method. Electronic absorption spectra (diffuse-reflectance) were recorded on a SPECORD M40 (Carl Zeiss Jena) within the 30000–11000 cm⁻¹ range. IR spectra were recorded on an ATI Mattson Genesis Series FT IR spectrometer by KBr technique (diffuse-reflectance) within the 4000–400 cm⁻¹ range. The susceptibility studies of copper and cobalt complexes were performed on powdered samples using the Faraday's method with Hg[Co(NCS)₄] as a calibrant. Measurements were made in the room temperature and molar susceptibilities were corrected for diamagnetism using Pascal's constants [16]. ¹H-NMR and ³¹P-NMR spectra (in D₂O) were recorded with a Tesla BS-587 UG instrument with HDMS as internal standard at 80 MHz (¹H) or 85% H₃PO₄ as external standard at 32 MHz (³¹P).

X-ray data collection and structure refinements for [(OC₄H₈NHCH₂)₂PO₂]Cl·H₂O (1) and [(OC₄H₈NHCH₂)₂PO₂]₂CuCl₄ (2). X-ray data were collected at 150 K on a four-circle κ -axis KUMA KM-4 diffractometer equipped with an Oxford Cryostream cooler using graphite-monochromated MoK α radiation. Data collections for both compounds were performed using a CCD detector (KUMA Diffraction, Wrocław). KUMA KM4RED software was used for data reduction. The structures were solved using the direct methods [SHELXS-97] [17] and refined on F^2 using full-matrix least-squares procedure [SHELXL-97] [18] with weight: $w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 1.0027P]$ for [(OC₄H₈NHCH₂)₂PO₂]Cl·H₂O (1), and $w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 7.5217P]$ for [(OC₄H₈NHCH₂)₂PO₂]₂CuCl₄ (2), where $P = (F_o^2 + 2F_c^2)/3$. All hydrogens in both structures were located in difference Fourier maps and all their parameters were refined. The O(5) atom of water molecule in (1) is disordered over two positions with the occupancy factors fixed at 0.5000. The largest peak and hole on the final difference map were 0.36 [0.92 Å from C(6)] and -0.37 [0.88 Å from P(1)] e Å⁻³ for (1), and 1.01 [2.26 Å from H(6B)] and -0.73 [0.97 Å from Cu(1)] e Å⁻³ for (2), respectively. Summaries of crystal data and structure refinements for (1) and (2) are given in Table 1.

Table 1. Crystal data and structure refinements for [(OC₄H₈NHCH₂)₂PO₂]Cl·H₂O (1) and [(OC₄H₈NHCH₂)₂PO₂]₂CuCl₄ (2).

Compound	(1)	(2)
Formula	C ₁₀ H ₂₄ ClN ₂ O ₅ P	C ₂₀ H ₄₄ Cl ₄ CuN ₄ O ₈ P ₂
Formula weight	318.73	735.87
Temperature (K)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>Cc</i>
Unit cell dimensions		
<i>a</i> (Å)	9.748(2)	17.2309(15)
<i>b</i> (Å)	9.805(2)	9.8066(7)
<i>c</i> (Å)	10.495(2)	18.741(2)
α (°)	114.96(3)	90.00
β (°)	92.06(3)	94.463(9)
γ (°)	119.78(3)	90.00
Volume (Å ³)	749.9(3)	3157.2(5)
<i>Z</i>	2	4
D_{calcd} (g cm ⁻³)	1.412	1.548
μ (mm ⁻¹)	0.379	1.179
$F(000)$	340	1532
Crystal size (mm)	0.80 × 0.30 × 0.30	0.60 × 0.50 × 0.30
Reflections collected	3601	11003
Independent reflections	2236 [$R_{\text{int}} = 0.0460$]	4274 [$R_{\text{int}} = 0.0626$]
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2236 / 0 / 276	4274 / 2 / 528
Goodness-of-fit on F^2	1.030	1.090
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0411$, $wR2 = 0.0977$	$R1 = 0.0355$, $wR2 = 0.0910$
R indices (all data)	$R1 = 0.0569$, $wR2 = 0.1093$	$R1 = 0.0364$, $wR2 = 0.0927$
Extinction coefficient	0.018(3)	none
Absolute structure parameter	none	0.341(14)
Largest diff. peak and hole (e Å ⁻³)	0.362 and -0.368	1.008 and -0.734

RESULTS AND DISCUSSION

The prepared bis(alkylaminomethyl)phosphinic acids contain two strong basic alkylamino groups in the molecule. Owing to the fact that the syntheses proceed in strong acidic medium, the products exclude the form of betaine and hydrochloride. The betaine structure of bis(alkylaminomethyl)phosphinic acids was already confirmed by single crystal X-ray analysis as described in [12,13]. The betaine structure was also proved by NMR spectra for monohydrate hydrochloride of bis(morpholinomethyl)phosphinic acids presented in this paper. Moreover, this was also unambiguously confirmed by single crystal X-ray analysis in the case of the morpholine derivative $[(OC_4H_8NHCH_2)_2PO_2]Cl \cdot H_2O$ (*1*) (see Figure 1). ^{31}P -NMR chemical shifts observed in the spectra are ranging from 15.32 ppm (for morpholine derivative) to 17.23 ppm (for ethyl derivative). In the ^{31}P -NMR spectra, doublets belonging to the CH_2 group connecting nitrogen and phosphorus atoms lie in the range of 3.42–3.54 ppm. Chemical shifts of other hydrogens bonded to methyl and methylene groups are summarized in Table 2. The spin-spin interaction between nucleus ^{31}P and 1H of the methylene group exhibits by a shape both the ^{31}P signal (quintet) and 1H signal (doublet). The spin-spin interaction constant ($^2J_{P-H}$), determined from difference between peaks of these quintets and doublets, is equal to 8.7 ± 0.1 Hz.

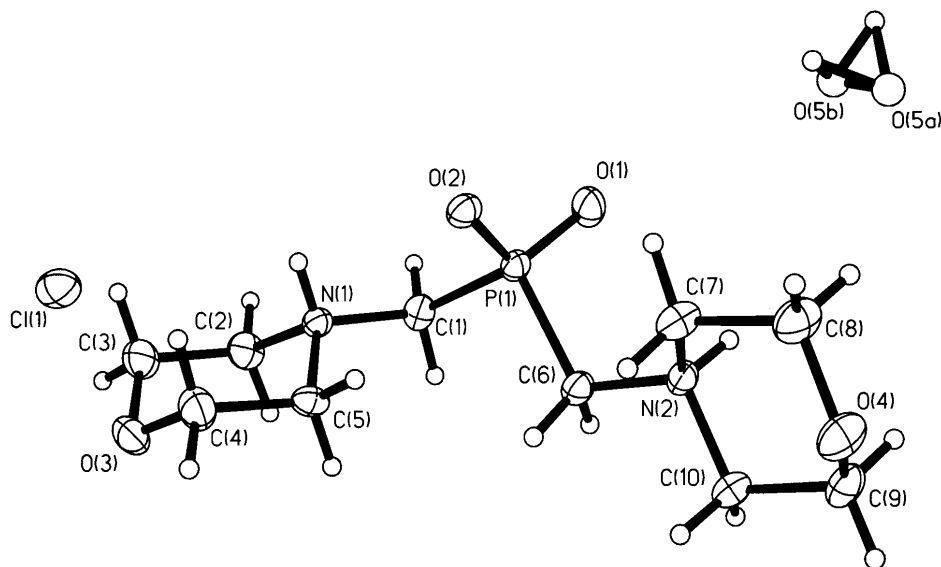


Figure 1. The molecular structure of (*1*) showing the atom labelling scheme. Thermal ellipsoids are drawn at the 30% probability level with the exception of the O(5) atom.

Table 2. ^{31}P and ^1H -NMR data (δ , ppm) for monohydrate monohydrochloride of bis(alkylaminomethyl)-phosphinic acids.

Compound	^{31}P -NMR δ (quintet)	^1H -NMR, (δ , splitting)	
		N-CH ₂ -P	Other signals
[(Me ₂ NHCH ₂) ₂ PO ₂]Cl·H ₂ O	16.005	3.49, d, 4H	3.06, s, 6H (CH ₃)
[(Et ₂ NHCH ₂) ₂ PO ₂]Cl·H ₂ O	17.23	3.42, d, 4H	1.36, t, 6H (CH ₃) 3.40, q, 4H (CH ₂)
[(Bu ₂ NHCH ₂) ₂ PO ₂]Cl·H ₂ O	16.94	3.43, d, 4H	0.97, t, 6H (CH ₃) 1.41, sextet, 4H (CH ₂) 1.74, quintet, 4H (CH ₂) 3.34, t, 4H (CH ₂)
[(C ₄ H ₈ NHCH ₂) ₂ PO ₂]Cl·H ₂ O	16.72	3.54, d, 4H	2.09, t, 4H (CH ₂) 3.85, t, 4H (CH ₂)
[(C ₅ H ₁₀ NHCH ₂) ₂ PO ₂]Cl·H ₂ O	16.35	3.42, d, 4H	1.84, quintet, 2H (CH ₂) 1.97, quintet, 2H (CH ₂) 3.14, t, 2H (CH ₂)
[(OC ₄ H ₈ NHCH ₂) ₂ PO ₂]Cl·H ₂ O	15.32	3.53, d, 4H	3.57, t, 4H (CH ₂) 4.04, t, 4H (CH ₂)

All reaction products exhibit ionic nature and their composition may be formulated as hydrochlorides of bis(alkylaminomethyl)phosphinic acids as can be deduced from somewhat higher melting points or temperatures of decomposition (see Experimental section). A decrease in the melting point values of diethyl- and dibutyl- derivatives can be probably caused by a presence of aliphatic chains in the molecule. Surprisingly, a complexation ability of these compounds is very low and their addition compounds with CuCl₂ and CoCl₂ may be formulated as ionic pairs of protonated bis(alkylaminomethyl)phosphinic acids with [CuCl₄]²⁻ or [CoCl₄]²⁻ complex anions. Analytical data point on such formulae for these compounds. A coordination geometry around Cu(II) and Co(II) ions is tetrahedral as can be deduced both from effective magnetic moment values and maxima displayed in electronic spectra (see Table 3).

Table 3. Composition, effective magnetic moments and electronic spectra of the ionic pairs between bis(dialkylaminomethyl)phosphinic acids and [CuCl₄]²⁻ and [CoCl₄]²⁻ complex anions.

Compound	Composition	$\mu_{\text{eff}}/\mu_{\text{B}}$	VIS [cm ⁻¹]
[(Me ₂ NHCH ₂) ₂ PO ₂] ₂ CoCl ₄	C ₁₂ H ₃₆ Cl ₄ CoN ₄ O ₄ P ₂	4.68	14500
[(Et ₂ NHCH ₂) ₂ PO ₂] ₂ CoCl ₄	C ₂₀ H ₅₂ Cl ₄ CoN ₄ O ₄ P ₂	5.06	14700
[(C ₅ H ₁₀ NHCH ₂) ₂ PO ₂] ₂ CoCl ₄ ·2H ₂ O	C ₂₄ H ₅₆ Cl ₄ CoN ₄ O ₆ P ₂	4.87	14400
[(OC ₄ H ₈ NHCH ₂) ₂ PO ₂] ₂ CoCl ₄	C ₂₀ H ₄₄ Cl ₄ CoN ₄ O ₈ P ₂	4.66	14600
[(Me ₂ NHCH ₂) ₂ PO ₂] ₂ CuCl ₄	C ₁₂ H ₃₆ Cl ₄ CuN ₄ O ₄ P ₂	2.01	24400
[(Et ₂ NHCH ₂) ₂ PO ₂] ₂ CuCl ₄	C ₂₀ H ₅₂ Cl ₄ CuN ₄ O ₄ P ₂	2.19	23700
[(OC ₄ H ₈ NHCH ₂) ₂ PO ₂] ₂ CuCl ₄	C ₂₀ H ₄₄ Cl ₄ CuN ₄ O ₈ P ₂	2.05	24600

The blue cobalt compounds exhibited effective magnetic moments between 4.66 and 5.06 $\mu_{\text{eff}}/\mu_{\text{B}}$. These facts may show on tetrahedral coordination in [CoCl₄]²⁻ complex ions [16]. The tetrahedral surrounding can be also supported by maxima observed at 14500 cm⁻¹ in diffuse-reflectance spectra of cobalt(II) compounds, which were relatively displaced to lower energy, in contrast to octahedrally coordinated Co(II) ions.

These maxima are assigned to the ${}^4A_2(F) \rightarrow {}^4T_1(F)$ transition [19]. The effective magnetic moments found for copper(II) compounds are ranging from 2.01 to 2.19 $\mu_{\text{eff}}/\mu_{\text{B}}$. Their electronic absorption spectra exhibited broad bands in the range of 23700–24600 cm^{-1} belonging to $d-d$ transitions with a 2T ground state. This may indicate that the complex anion has a tetrahedral structure. The distorted tetrahedral coordination in $[\text{CuCl}_4]^{2-}$ was also unambiguously confirmed by results of a single crystal X-ray analysis of $[(\text{OC}_4\text{H}_8\text{NHCH}_2)_2\text{PO}_2]_2\text{CuCl}_4$ (see Figure 2).

IR spectra of all prepared compounds are similar and were not studied in detail. Strong maxima observed in the region 1228–1260 cm^{-1} belong to $\nu(\text{P}=\text{O})$, while less intense absorptions in the range 730–778 cm^{-1} can be assigned to P–C stretching vibrations [20,21]. The CH_2 deformation vibration of the P– CH_2 group appears in the range of 1440–1470 cm^{-1} , although it can be overlapped by the C–H bending absorption, which may also be revealed near this frequency. The phosphorus attached to the P– CH_2 group also affects the CH_2 stretch band by displaying weak shoulders observed between 2810–2820 cm^{-1} in IR spectra of all compounds.

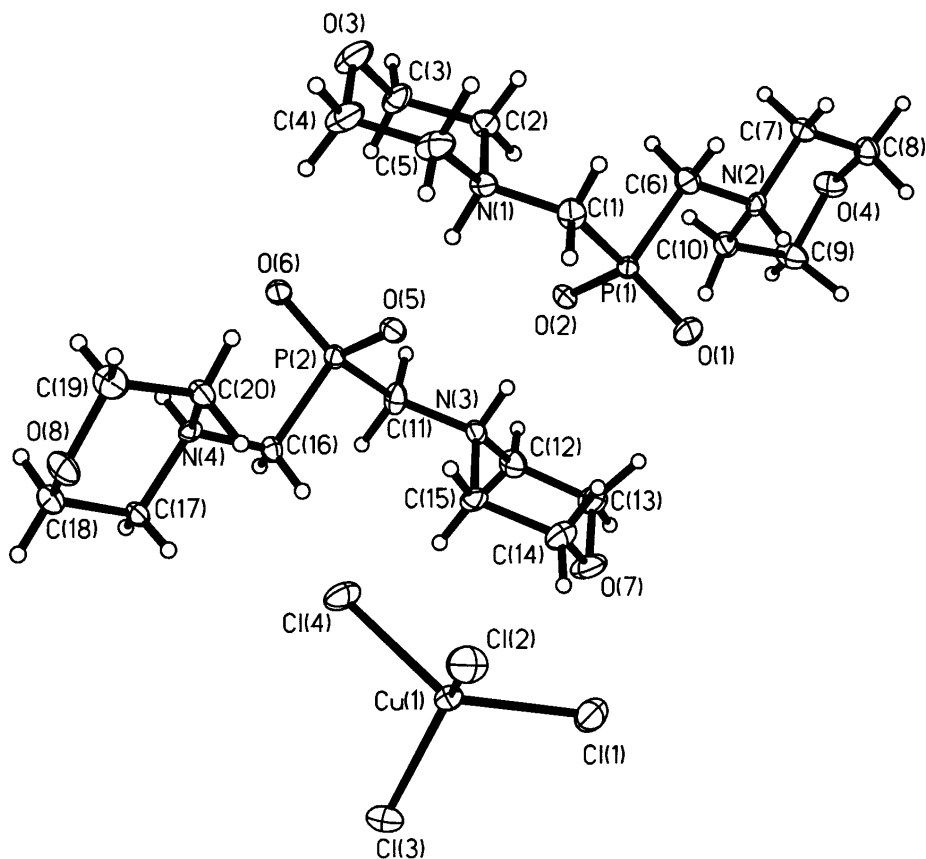


Figure 2. The molecular structure of (2) showing the atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level.

Molecular structures. Summaries of the crystal data, intensity collection and structure refinement parameters for $[(OC_4H_8NHCH_2)_2PO_2]Cl \cdot H_2O$ (*1*) and $[(OC_4H_8NHCH_2)_2PO_2]_2CuCl_4$ (*2*) are summarized in Table 1, as well as in the Experimental section. Selected bond lengths and angles for both are given in Tables 4 and 5, while perspective views of the molecules are shown in Figures 1 and 2. As can be seen from Figure 1, the structure of (*1*) consists of the $[(OC_4H_8NHCH_2)_2PO_2]^+$ cation, chloride anion and water molecule. The cation is composed of two morpholinomethyl groups and two oxygen atoms tetrahedrally arranged around the central phosphorus atom and possess the usual bond lengths and angles. The structure of (*2*), as presented in Figure 2, consists of two $[(OC_4H_8NHCH_2)_2PO_2]^+$ cations and one $[CuCl_4]^{2-}$ complex ion. Bond lengths and angles found in (*1*) and (*2*) for the cations are quite comparable. This points on the fact that a presence of $[CuCl_4]^{2-}$ in the structure has no influence on distortion of interatomic parameters in the cations. On the other hand, a degree of deformation in $[CuCl_4]^{2-}$ can be deduced from interatomic Cu–Cl parameters (see Table 5).

Table 4. Bond lengths (Å) and angles (°) for $[(OC_4H_8NHCH_2)_2PO_2]Cl \cdot H_2O$ (*1*).

P(1)-O(1)	1.491(2)	N(1)-C(1)	1.502(3)
P(1)-O(2)	1.5000(19)	N(1)-C(2)	1.513(4)
P(1)-C(1)	1.829(3)	N(2)-C(7)	1.500(4)
P(1)-C(6)	1.832(3)	N(2)-C(6)	1.499(3)
O(3)-C(3)	1.427(4)	N(2)-C(10)	1.503(4)
O(3)-C(4)	1.430(4)	C(2)-C(3)	1.518(4)
O(4)-C(9)	1.425(4)	C(4)-C(5)	1.514(4)
O(4)-C(8)	1.425(4)	C(7)-C(8)	1.518(4)
N(1)-C(5)	1.494(4)	C(9)-C(10)	1.514(4)
O(1)-P(1)-O(2)	117.75(12)	C(7)-N(2)-C(10)	109.3(2)
O(1)-P(1)-C(1)	109.14(13)	C(6)-N(2)-C(10)	109.1(2)
O(2)-P(1)-C(1)	108.19(11)	N(1)-C(1)-P(1)	113.45(19)
O(1)-P(1)-C(6)	108.10(13)	N(1)-C(2)-C(3)	109.5(3)
O(2)-P(1)-C(6)	110.88(13)	O(3)-C(3)-C(2)	111.4(3)
C(1)-P(1)-C(6)	101.55(14)	O(3)-C(4)-C(5)	111.9(3)
C(3)-O(3)-C(4)	110.1(2)	N(1)-C(5)-C(4)	109.5(2)
C(9)-O(4)-C(8)	109.5(2)	N(2)-C(6)-P(1)	115.36(19)
C(5)-N(1)-C(1)	113.0(2)	N(2)-C(7)-C(8)	109.3(2)
C(5)-N(1)-C(2)	109.1(2)	O(4)-C(8)-C(7)	111.7(3)
C(1)-N(1)-C(2)	111.2(2)	O(4)-C(9)-C(10)	110.6(2)
C(7)-N(2)-C(6)	113.0(2)	N(2)-C(10)-C(9)	110.6(2)

Table 5. Bond lengths (Å) and angles (°) for [(OC₄H₈NHCH₂)₂PO₂]₂CuCl₄ (2).

Cu(1)-Cl(2)	2.2428(13)	C(7)-C(8)	1.515(6)
Cu(1)-Cl(4)	2.2558(11)	C(9)-C(10)	1.517(6)
Cu(1)-Cl(1)	2.2577(12)	P(2)-O(6)	1.500(3)
Cu(1)-Cl(3)	2.2650(12)	P(2)-O(5)	1.507(3)
P(1)-O(1)	1.499(3)	P(2)-C(16)	1.843(4)
P(1)-O(2)	1.500(3)	P(2)-C(11)	1.848(4)
P(1)-C(6)	1.835(4)	O(7)-C(14)	1.425(6)
P(1)-C(1)	1.845(5)	O(7)-C(13)	1.438(6)
O(3)-C(3)	1.427(6)	O(8)-C(18)	1.427(5)
O(3)-C(4)	1.446(6)	O(8)-C(19)	1.443(6)
O(4)-C(8)	1.426(5)	N(3)-C(15)	1.506(5)
O(4)-C(9)	1.435(5)	N(3)-C(11)	1.501(5)
N(1)-C(5)	1.494(5)	N(3)-C(12)	1.505(5)
N(1)-C(1)	1.502(5)	N(4)-C(16)	1.498(5)
N(1)-C(2)	1.508(5)	N(4)-C(20)	1.496(5)
N(2)-C(7)	1.501(5)	N(4)-C(17)	1.519(5)
N(2)-C(6)	1.498(5)	C(12)-C(13)	1.517(6)
N(2)-C(10)	1.504(5)	C(14)-C(15)	1.530(6)
C(2)-C(3)	1.523(6)	C(17)-C(18)	1.519(5)
C(4)-C(5)	1.538(7)	C(19)-C(20)	1.524(6)
Cl(2)-Cu(1)-Cl(4)	98.38(5)	O(4)-C(8)-C(7)	110.5(3)
Cl(2)-Cu(1)-Cl(1)	100.94(6)	O(4)-C(9)-C(10)	111.6(4)
Cl(4)-Cu(1)-Cl(1)	134.16(5)	N(2)-C(10)-C(9)	110.6(3)
Cl(2)-Cu(1)-Cl(3)	129.58(5)	O(6)-P(2)-O(5)	117.67(19)
Cl(4)-Cu(1)-Cl(3)	97.63(4)	O(6)-P(2)-C(16)	108.36(18)
Cl(1)-Cu(1)-Cl(3)	101.16(5)	O(5)-P(2)-C(16)	111.27(18)
O(1)-P(1)-O(2)	118.82(19)	O(6)-P(2)-C(11)	108.50(19)
O(1)-P(1)-C(6)	108.44(19)	O(5)-P(2)-C(11)	108.56(17)
O(2)-P(1)-C(6)	110.83(18)	C(16)-P(2)-C(11)	101.2(2)
O(1)-P(1)-C(1)	107.6(2)	C(14)-O(7)-C(13)	109.1(4)
O(2)-P(1)-C(1)	108.21(18)	C(18)-O(8)-C(19)	109.5(3)
C(6)-P(1)-C(1)	101.5(2)	C(15)-N(3)-C(11)	113.2(3)
C(3)-O(3)-C(4)	109.5(3)	C(15)-N(3)-C(12)	109.8(3)
C(8)-O(4)-C(9)	109.4(3)	C(11)-N(3)-C(12)	109.4(3)
C(5)-N(1)-C(1)	110.8(3)	C(16)-N(4)-C(20)	113.0(3)
C(5)-N(1)-C(2)	110.2(3)	C(16)-N(4)-C(17)	108.9(3)
C(1)-N(1)-C(2)	113.3(3)	C(20)-N(4)-C(17)	109.4(3)
C(7)-N(2)-C(6)	108.9(3)	N(3)-C(11)-P(2)	115.2(3)
C(7)-N(2)-C(10)	110.0(3)	N(3)-C(12)-C(13)	109.9(4)
C(6)-N(2)-C(10)	112.7(3)	O(7)-C(13)-C(12)	111.6(4)
N(1)-C(1)-P(1)	114.2(3)	O(7)-C(14)-C(15)	110.7(4)
N(1)-C(2)-C(3)	109.3(3)	N(3)-C(15)-C(14)	109.7(3)
O(3)-C(3)-C(2)	111.2(4)	N(4)-C(16)-P(2)	114.8(3)
O(3)-C(4)-C(5)	110.6(4)	C(18)-C(17)-N(4)	110.0(4)
N(1)-C(5)-C(4)	109.7(4)	O(8)-C(18)-C(17)	110.9(3)
N(2)-C(6)-P(1)	116.6(3)	O(8)-C(19)-C(20)	110.4(4)
N(2)-C(7)-C(8)	110.4(4)	N(4)-C(20)-C(19)	110.5(3)

Supplementary data. Crystallographic data for structures $[(OC_4H_8NHCH_2)_2PO_2]Cl \cdot H_2O$ (1) and $[(OC_4H_8NHCH_2)_2PO_2]_2CuCl_4$ (2) have been deposited with Cambridge Crystallographic Data Centre under deposition numbers CCDC-171581 and CCDC-171582, respectively. Further details on the structure determinations can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336-0363; e-mail: deposit@ccdc.cam.ac.uk).

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REFERENCES

1. Lukeš I., Kotek J., Vojtišek P. and Hermann P., *Coord. Chem. Rev.*, **216–217**, 287 (2001).
2. Petrov K.A., Tchazov V.A. and Erochina T.S., *Usp. Khim.*, **43**, 2045 (1974).
3. Redmore D., in *Topics in Phosphorus Chemistry*, **8**, 515 (1976), Editors: E.J. Griffith and M. Grayson, Wiley-Interscience, NY, 1976.
4. Kuchar V.P. and Solodenko V.A., *Usp. Khim.*, **56**, 1504 (1987).
5. Schmidt H., *Chem. Ber.*, **81**, 477 (1948).
6. Maier L., *Helv. Chim. Acta*, **50**, 1742 (1967).
7. Kreutzkamp N., Schimpfky C. and Storck K., *Arch. Pharmaz.*, **300**, 868 (1967).
8. Maier L., *Swiss Pat.*, Nr. 475 287 (1969).
9. Kapura A.A. and Shermergom E., *Zh. Obsh. Khim.*, **59**, 1283 (1989).
10. Maier L. and Smith M.J., *Phosphorus sulfur*, **8(1)**, 67 (1980).
11. Varga T.R., *Synth. Commun.*, **27(17)**, 2899 (1997).
12. Prishchenko A.A., Pisarnitzkii D.A., Livantsov M.V. and Petrosyan V.S., *Zh. Obsh. Khim.*, **63**, 1899 (1993).
13. Howard-Lock H.E., Lock C.J.L., Penny S. and Turner M.A., *Can. J. Chem.*, **67**, 1051 (1989).
14. Sergienko V.S., *Koord. Khim.*, **27**, 723 (2001).
15. Sergienko V.S. and Aleksandrov G.G., *Koord. Khim.*, **27**, 351 (2001).
16. König E., *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds*, Springer, Berlin, 1966.
17. Sheldrick G.M., SHELXS-97, *Acta Cryst.*, **A46**, 467 (1990).
18. Sheldrick G.M., SHELXL-97, Program for crystal structure refinement. University of Göttingen, Germany, 1997.
19. Lever A.B.P., *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1968.
20. Corbridge D.E.C., *The Infrared Spectra of Phosphorus Compounds*, **6**, 235 (1969), *Topics in Phosphorus Chemistry*, Eds. M. Grayson and E.J. Griffith, NY, Interscience, 1969.
21. Pouchert C.J., *The Aldrich Library of Infrared Spectra*, Edition III, Aldrich Chemical Company, Wisconsin, 1981.