Crystal and Molecular Structure of 1,5-Dihydrodecamethylcyclopentaphosphonitrilium Tetrachlorocuprate(II) Monohydrate

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Crystals of the title compound are triclinic, a = 9·034(6), b = 14·390(8), c = 10·924(8) Å, α = 91·66(7), β = 96·52(9), γ = 109·77(5)°, Z = 2, space group $P\bar{1}$. The structure was determined from diffractometer data by a combination of direct methods and electron-density maps, and refined by full-matrix least-squares methods to R 0·072 for 2707 observed reflexions. The structure consists of a distorted tetrahedral $CuCl_4^{2-}$ anion and a ten-membered phosphonitrilic ring with two nitrogen atoms protonated. Bond-length inequalities in the phosphonitrilic ring are explained in terms of π-bonding theory. The conformation of the phosphonitrilic ring appears to be influenced primarily by N–H · · · Cl hydrogen bonding to the anion and N–H · · · O hydrogen bonding to the water molecule of crystallization.

THE structures of the three protonated phosphonitrilic derivatives have been determined. In $N_3P_3Cl_2(NHPr^i)_4$-HCl protonation occurs[1] on a ring nitrogen atom instead of a nitrogen atom of an exocyclic isopropylamido-group. The structure $[(NPMe_2)_4H]_2CoCl_4$ shows the effect of protonation of a ring nitrogen atom of a homogeneously substituted tetrameric phosphonitrilic derivative.[2] Finally the structure $[(NPMe_2)_4H]CuCl_3$ demonstrates[3] that the base strength of $(NPMe_2)_4$ is sufficiently large to allow the protonated molecule to donate to a transition metal. These structures demonstrate that protonation of a ring nitrogen atom produces inequalities in the ring P–N bond lengths, which in the unprotonated phosphonitrilic derivatives with similar substituents on the phosphorus atoms are equal.[4]

In the $[NPMe_2]_n$ (n = 3—5) series there is a steady increase in base strength with ring size, and in the case of $(NPMe_2)_5$, pK_{a2} is sufficiently large to be measured.[5]

We now report the structure of $[(NPMe_2)_5H_2][CuCl_4]$,H_2O. Protonation of the phosphonitrilic ring at two sites produces variations in the P–N bond lengths in the ring which are explained in terms of π-bonding theory.[4] In addition the conformation adopted by the ten-membered phosphonitrilic ring is of interest.

EXPERIMENTAL

Orange crystals from acetonitrile were of varying shape, with a large number of exposed crystal faces.

Crystal Data.—$C_{10}H_{34}Cl_4CuN_5OP_5$, M = 600·64, Triclinic, a = 9·034(6), b = 14·390(8), c = 10·924(8) Å, α = 91·66(7), β = 96·52(9), γ = 109·77(5)°, U = 1324·3 Å^3, D_m = 1·504 g cm^{-3} (flotation), Z = 2, D_c = 1·506 g cm^{-3}, $F(000)$ = 622. No systematically absent reflexions. Space group $P\bar{1}$ from the distribution of the normalized structure factors and the structure analysis. Mo-K_α radiation, λ = 0·71069 Å; μ(Mo-K_α) = 15·7 cm^{-1}.

The space group and initial unit-cell parameters were determined from precession and Weissenberg films. Accurate unit-cell parameters were obtained by least-squares refinement of $\sin^2\theta$ values for 30 reflexions measured on a General Electric XRD 6 diffractometer.

Intensity data were collected on a Datex-automated General Electric XRD 6 diffractometer with a scintillation counter, Mo-K_α radiation (zirconium filter and pulse-height analyser) and a θ—2θ scan. The scan width in 2θ was $(1·80 + 0·86 \tan\theta)°$, and 20 s background counts were taken on either side of every scan. All reflexions with 2θ(Mo-K_α) $\leq 45°$ were measured. A check reflexion was monitored every 30 reflexions throughout data collection and its intensity used put the data on the same relative scale. Lorentz and polarization corrections were applied and structure amplitudes derived. The crystal used for data collection had dimensions $0·3 \times 0·3_5 \times 0·2_5$ mm. No corrections were made for absorption. Of 3462 independent reflexions measured, 2707 (78·2%) were considered observed, having intensities $>3\sigma(I)$ above background, where $\sigma^2(I) = S + B + (0·03S)^2$ with S = scan count and B = background count.

Structure Analysis.—The structure was solved by a combination of direct methods and electron-density maps. The distribution of normalized structure factors $|E|$ is compared with the theoretical values[6] for centrosymmetric and non-centrosymmetric structures in Table 1. The centrosymmetric space group $P\bar{1}$ is shown to be highly probable. For the 261 reflexions for which $|E| > 1·83$ all triplets of reflexions to be used in the Σ_2 relationship, $S(E_{hkl}) \sim \Sigma_{h'k'l'}S(E_{h'k'l'}) \,.\, S(E_{h-h',\ k-k',\ l-l'})$, were calculated. The origin-determining reflexions and reflexions to which a symbolic sign was given are listed in Table 2. With a computer program[7] which uses the symbolic addition method[8] it was possible to give probable signs to

TABLE 1

Distribution of the normalized structure factors

		Calc.	
	Obs.	Centro-symmetric	Noncentro-symmetric
$\langle\|E\|^2\rangle$	0·804	0·798	0·886
$\langle\|E^2 - 1\|\rangle$	1·026	1·000	1·000
$\langle\|E\|\rangle$	0·980	0·968	0·736
$\|E\| > 1$	0·19%	0·3%	0·01%
$\|E\| > 2$	4·88%	5·0%	1·8%
$\|E\| > 3$	32·61%	32·0%	37·0%

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[2] J. Trotter and S. H. Whitlow, *J. Chem. Soc.* (*A*), 1970, 460.

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all 261 reflexions for which $|E| > 1{\cdot}83$ ($a = b = -$; $c = +$), and from these an E map was calculated. The copper, four chlorine, and five phosphorus atoms accounted for the ten largest peaks on the map. A structure-factor calculation based on the positions of these 10 atoms gave

TABLE 2

Starting set for phase determination

Reflexion			$\|E\|$	Sign	
$\bar{6}$	3	0	3·555	+	Origin-determining
$\bar{3}$	2	7	2·977	+	
2	7	$\bar{9}$	3·061	+	
$\bar{4}$	2	6	2·955	*a*	
0	10	0	3·544	*b*	
1	2	$\bar{8}$	2·799	*c*	

R 0·304. One cycle of full-matrix least-squares refinement of positional and isotropic thermal parameters of these atoms reduced R to 0·278. Initially B was set at 3·5 Å^2 for all atoms. The positions of the 16 remaining non-hydrogen atoms were obtained from a three-dimensional difference map. Although the elemental analysis agreed with the presence of one water molecule of crystallization, and there was a peak on the difference map in a reasonable position to account for the oxygen atom, the oxygen atom was not included at this stage. With the nitrogen and carbon atoms included, R was 0·160. Two cycles of isotropic refinement reduced R to 0·146. A difference map confirmed the presence of the oxygen atom and showed that only one water molecule of crystallization was present. Refinement was continued, initially with the copper, chlorine, and phosphorus atoms having anisotropic thermal parameters, and finally with all atoms being refined anisotropically. Convergence was reached at R 0·072 for 2707 observed reflexions. On the final cycle of refinement no parameter shift was $> 0{\cdot}3\sigma$.

The least-squares refinement was based on the minimization of $\Sigma w(|F_o| - |F_c|)^2$. The anisotropic thermal parameters are U_{ij} in the expression: $f = f_0 \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$. Scattering factors ($f_0$) for all atoms were obtained from ref. 9. Correction for anomalous dispersion was included for copper. The weighting scheme $\sqrt{w} = 1{\cdot}0$ when $|F_o| \leq 24{\cdot}0$ and $\sqrt{w} = 24{\cdot}0/|F_o|$ when $|F_o| > 24{\cdot}0$, gave approximately constant average values of $w(|F_o| - |F_c|)^2$ over ranges of $|F_o|$ and was used in the last cycles of refinement. Unobserved reflexions were given zero weight.

A final difference map showed maximum fluctuations of up to $\pm 1{\cdot}0$ eÅ^{-3}, but the hydrogen atoms could not be located with certainty and were not included in the least-squares refinement. There was also a peak of 1·7 eÅ^{-3} close to the copper atom.

Final atomic positions and thermal parameters are given in Table 3. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 20874 (5 pp.).*

DISCUSSION

The structure consists of a $CuCl_4^{2-}$ anion, a $[(NPMe_2)_5H_2]^{2+}$ cation, and a water molecule of crystallization. Bond lengths and angles are given in Table 4 and a general view of the structure in Figure 1. Hydrogen atoms bonded to N(1) and N(3) could not be located,

TABLE 3

Final positional parameters (fractional $\times 10^4$) and anisotropic thermal parameters (U_{ij}, Å$^2 \times 10^4$) with standard deviations in parentheses

Atom	x	y	z
Cu	2763(1)	2391(1)	3510(1)
Cl(1)	1663(3)	3516(2)	4070(2)
Cl(2)	4680(3)	3383(2)	2512(3)
Cl(3)	0540(3)	1051(2)	2894(2)
Cl(4)	4125(3)	1585(2)	4569(3)
O	5493(10)	5668(6)	3558(8)
P(1)	3229(3)	9409(1)	1544(2)
P(2)	1031(3)	8381(2)	3358(2)
P(3)	1500(3)	6424(2)	3186(2)
P(4)	3125(3)	6260(2)	0996(2)
P(5)	1786(2)	7609(2)	−0206(2)
N(1)	1711(9)	9240(5)	2380(6)
N(2)	1227(11)	7422(6)	2883(7)
N(3)	2987(9)	6300(6)	2509(6)
N(4)	1816(8)	6558(5)	0229(6)
N(5)	3070(8)	8560(5)	0579(7)
C(1)	3301(14)	0539(7)	0845(10)
C(2)	5043(12)	6938(9)	2586(10)
C(3)	2045(12)	8849(8)	4884(8)
C(4)	−0990(11)	8300(8)	3349(10)
C(5)	2047(12)	6292(7)	4780(8)
C(6)	−0281(12)	5394(8)	2633(10)
C(7)	2845(15)	4989(8)	0522(10)
C(8)	5173(11)	6983(8)	0898(10)
C(9)	−0216(10)	7800(7)	−0212(8)
C(10)	2161(11)	7698(7)	−1785(8)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	508(7)	416(7)	501(7)	254(5)	107(5)	130(5)
Cl(1)	520(14)	404(13)	716(17)	260(11)	65(12)	18(12)
Cl(2)	672(17)	627(17)	672(17)	292(14)	303(14)	238(13)
Cl(3)	516(14)	397(13)	729(17)	249(11)	121(12)	110(12)
Cl(4)	574(16)	561(16)	908(20)	290(13)	−12(14)	268(14)
O	869(59)	638(51)	920(59)	348(45)	−223(46)	110(43)
P(1)	363(12)	244(11)	355(12)	77(9)	119(9)	79(9)
P(2)	397(13)	311(12)	335(12)	150(10)	129(9)	142(9)
P(3)	415(13)	256(11)	360(12)	134(10)	69(9)	125(9)
P(4)	444(13)	306(12)	335(12)	175(10)	18(10)	64(9)
P(5)	358(12)	271(11)	307(11)	120(9)	34(9)	78(9)
N(1)	541(45)	307(38)	432(40)	227(34)	235(34)	217(32)
N(2)	945(65)	440(47)	403(43)	353(46)	160(42)	196(36)
N(3)	480(44)	507(45)	367(39)	222(36)	104(33)	124(34)
N(4)	475(42)	296(38)	397(39)	148(33)	−48(32)	32(31)
N(5)	402(41)	308(39)	495(43)	84(32)	125(33)	24(32)
C(1)	1012(86)	315(52)	719(69)	251(54)	507(63)	319(49)
C(2)	476(60)	872(83)	555(64)	145(57)	−35(49)	−63(58)
C(3)	645(64)	638(65)	305(48)	232(52)	35(43)	42(43)
C(4)	353(53)	793(76)	724(68)	197(51)	169(48)	341(58)
C(5)	609(61)	606(62)	367(50)	272(51)	96(44)	220(44)
C(6)	550(64)	475(61)	670(67)	−26(50)	37(51)	171(52)
C(7)	939(86)	534(66)	629(67)	424(62)	−93(59)	−63(53)
C(8)	344(52)	686(68)	738(70)	176(48)	147(47)	242(55)
C(9)	326(48)	514(56)	542(56)	174(42)	95(41)	169(45)
C(10)	564(57)	473(54)	336(47)	229(46)	69(41)	95(40)

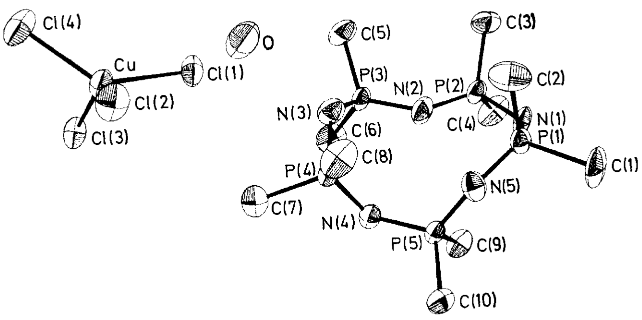

FIGURE 1 General view of the structure, showing 50% probability thermal ellipsoids

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. Items less than 10 pp. are sent as full size copies.

[9] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

TABLE 4

Bond lengths (Å) and angles (deg.) with standard deviations in parentheses *

(*a*) Distances

Cu–Cl(1)	2·270(3)	P(1)–C(1)	1·801(9)
Cu–Cl(2)	2·251(3)	P(1)–C(2)	1·811(10)
Cu–Cl(3)	2·281(3)	P(2)–C(3)	1·800(9)
Cu–Cl(4)	2·218(3)	P(2)–C(4)	1·788(9)
		P(3)–C(5)	1·790(9)
N(2)–P(2)	1·533(8)	P(3)–C(6)	1·807(10)
P(2)–N(1)	1·661(6)	P(4)–C(7)	1·812(11)
N(1)–P(1)	1·687(7)	P(4)–C(8)	1·808(9)
P(1)–N(5)	1·548(7)	P(5)–C(9)	1·803(9)
N(5)–P(5)	1·608(7)	P(5)–C(10)	1·796(9)
P(5)–N(4)	1·606(7)		
N(4)–P(4)	1·557(7)	Mean P–C	1·802(8)
P(4)–N(3)	1·672(7)		
N(3)–P(3)	1·663(8)		
P(3)–N(2)	1·574(8)		

(*b*) Angles

Cl(1)–Cu–Cl(2)	98·6(1)	C(1)–P(1)–N(1)	101·3(4)
Cl(1)–Cu–Cl(3)	100·6(1)	C(2)–P(1)–N(1)	109·0(4)
Cl(1)–Cu–Cl(4)	133·2(1)	C(1)–P(1)–N(5)	112·5(4)
Cl(2)–Cu–Cl(3)	133·7(1)	C(2)–P(1)–N(5)	108·3(5)
Cl(2)–Cu–Cl(4)	99·9(1)	C(3)–P(2)–N(1)	108·6(4)
Cl(3)–Cu–Cl(4)	96·8(1)	C(3)–P(2)–N(2)	114·6(5)
		C(4)–P(2)–N(1)	103·5(4)
P(1)–N(1)–P(2)	129·0(4)	C(4)–P(2)–N(2)	113·9(5)
P(2)–N(2)–P(3)	148·3(5)	C(5)–P(3)–N(2)	116·0(4)
P(3)–N(3)–P(4)	127·3(5)	C(5)–P(3)–N(3)	103·4(4)
P(4)–N(4)–P(5)	131·7(5)	C(6)–P(3)–N(2)	109·3(5)
P(5)–N(5)–P(1)	142·4(5)	C(6)–P(3)–N(3)	108·5(5)
		C(7)–P(4)–N(3)	106·7(5)
N(5)–P(1)–N(1)	116·6(4)	C(7)–P(4)–N(4)	108·2(4)
N(1)–P(2)–N(2)	108·2(4)	C(8)–P(4)–N(3)	104·1(4)
N(2)–P(3)–N(3)	111·3(4)	C(8)–P(4)–N(4)	117·9(4)
N(3)–P(4)–N(4)	112·2(4)	C(9)–P(5)–N(4)	107·3(4)
N(4)–P(5)–N(5)	115·1(4)	C(9)–P(5)–N(5)	112·4(4)
		C(10)–P(5)–N(4)	108·6(4)
C(1)–P(1)–C(2)	108·8(6)	C(10)–P(5)–N(5)	107·3(4)
C(3)–P(2)–C(4)	107·4(5)		
C(5)–P(3)–C(6)	108·0(5)		
C(7)–P(4)–C(8)	107·2(6)		
C(9)–P(5)–C(10)	105·7(4)		
Mean C–P–C	107·4(11)		

* For the mean values the number in parentheses is the root-mean-square deviation from the mean.

but their presence is confirmed by bond-length variations in the ring and by the presence of likely $\overset{+}{\mathrm{N}}\text{–H}\cdots\mathrm{Cl}$ and $\overset{+}{\mathrm{N}}\text{–H}\cdots\mathrm{O}$ hydrogen bonds (see later). In addition there appears to be O–H ⋯ Cl hydrogen bonds linking the water molecule to the $\mathrm{CuCl_4}^{2-}$ anion producing a chain-like structure.

The conformation of the ten-membered phosphonitrilic ring can be seen in Figure 1. Although the structure of $\mathrm{(NPMe_2)_5}$ has not yet been investigated the structures of two other pentameric phosphonitrilic derivatives, $\mathrm{(NPCl_2)_5}$ and $\mathrm{(NPBr_2)_5}$, have been reported. In $\mathrm{(NPCl_2)_5}$ [10] the ring is nearly planar with two re-entrant angles at nitrogen and approximate C_{2v} symmetry. In $\mathrm{(NPBr_2)_5}$,[11] however, a different conformation is found, with one phosphorus atom deviating by 0·75 Å from the mean plane through the remaining nine atoms. There is one re-entrant angle at nitrogen, and a pseudo-mirror plane normal to the $\mathrm{N_5P_5}$ ring passing through this nitrogen atom and the opposite phosphorus atom. The conformation found in the $\mathrm{[(NPMe_2)_5H_2]^{2+}}$ ion resembles that in $\mathrm{(NPBr_2)_5}$ rather than that in $\mathrm{(NPCl_2)_5}$. However, the pseudo-mirror plane found in $\mathrm{(NPBr_2)_5}$ is not present, probably because of distortions of the ring so that $\overset{+}{\mathrm{N}}\text{–H}\cdots\mathrm{O}$ and $\overset{+}{\mathrm{N}}\text{–H}\cdots\mathrm{Cl}$ hydrogen bonds can be formed (see later). Table 5 gives distances of ring atoms from a mean plane passing through P(1)—(4). N(1) is displaced from the mean plane by 0·37 Å while N(3) is displaced by 0·72 Å in the opposite direction. This distortion has further effects on the conformation of the ring. There appears to be twisting about P(4), so that N(4) is displaced much more than N(5) from the mean plane. There is one re-entrant angle at N(2), and the opposite phosphorus atom, P(5), is displaced by 1·80 Å from the mean plane through the other four phosphorus atoms.

TABLE 5

Mean plane through four phosphorus atoms, P(1)—(4)

Equation: $0{\cdot}7177X + 0{\cdot}2125Y + 0{\cdot}6632Z = 2{\cdot}3656$

X, *Y*, *Z* are orthogonal co-ordinates (Å) with respect to axes *a*, *b′*, and *c**

Distances (Å) of ring atoms from the plane:

P(1) −0·094, P(2) 0·157, P(3) −0·162, P(4) 0·115, P(5) 1·802, N(1) 0·368, N(2) 0·261, N(3) −0·720, N(4) 1·452, N(5) 0·547

There are substantial inequalities in the ring P–N bond lengths, in contrast to the equality of ring bond lengths in homogeneously substituted unprotonated phosphonitrilic derivatives.[4] Protonation of $\mathrm{(NPMe_2)_5}$ results in appreciable changes in the π-electron distribution in the ring. Variations in P–N bond lengths can be explained in terms of the π-bonding theory of Craig and Paddock[4] for phosphonitrilic compounds. The longest are those meeting at the protonated nitrogen atoms, N(1) and N(3), mean 1·671 Å. Complete localization of the lone-pair electrons at the protonated nitrogen atoms removes the π_s system in these bonds, decreasing the π-bond order. However the π_a system is still present, and the bonds are shorter than a P–N single bond (1·77 Å)[12] but longer than a normal phosphonitrilic P–N bond (*e.g.* 1·596 Å in $\mathrm{N_4P_4Me_8}$[13]). The length is similar to that in the metaphosphimate and oxophosphazane structures $\mathrm{Na_3(NHPO_2)_3,4H_2O}$,[14] $\mathrm{(NH)_4P_4O_8H_4,2H_2O}$,[15] and $\mathrm{N_3Me_3P_3O_3(OMe)_3}$,[16] where only a single π-system can exist, and to the exocyclic P–N bond length in dimethylamidophosphonitriles.[17,18] Similar lengths are found for corresponding bonds in other protonated phosphonitrilic derivatives: $\mathrm{[(NPMe_2)_4H]_2CoCl_4}$ 1·695, $\mathrm{[(NPMe_2)_4H]CuCl_3}$ 1·670, and $\mathrm{N_3P_3Cl_2}$-

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(NHPr^i)$_4$HCl 1·666 Å. These long bonds are followed by short P–N bonds, mean 1·553 Å. Localization of the lone-pair electrons at the protonated nitrogen atom and the formal positive charge increases the effective electronegativity of the adjacent phosphorus atoms, making these phosphorus atoms more receptive to d_π–p_π bonding. The short bonds are the result of increased donation of lone-pair electrons from N(2), N(4), and N(5) into the π_s system of these bonds thereby increasing the double-bond character. The length can be compared with that of corresponding bonds in [(NPMe$_2$)$_4$H]$_2$CoCl$_4$ (1·538 Å) and [(NPMe$_2$)$_4$H]CuCl$_3$ (1·559 Å). The P–N bonds meeting at P(5), mean 1·607 Å, are intermediate between these long and short bonds and are closer to the value for unperturbed methylphosphonitriles.

Variations among P–C bond lengths are not significant. The mean value [1·802(8) Å] is similar to that in N$_4$P$_4$Me$_8$ [1·805(4) Å].[13]

The smallest endocyclic angles at nitrogen are to the protonated nitrogens, 127·3° at N(3) and 129·0° at N(1), mean 128·2°. Corresponding angles in (NPBr$_2$)$_5$ are *ca.* 3° larger (129·7 and 132·6, mean 131·2°). Endocyclic angles at N$^+$ are 127·3 in [(NPMe$_2$)$_4$H]CuCl$_3$ and 126·2° in [(NPMe$_2$)$_4$H]$_2$CoCl$_4$. The small angles at N$^+$ are consistent with less electron-density in the P–N bonds meeting at these nitrogen atoms, and hence weaker interbond repulsions. The endocyclic angle at N(4) [131·7(5)°] is significantly smaller than at N(5) [142·4(5)°]. However, their mean (137·0°) is the same as for corresponding angles in (NPBr$_2$)$_5$ (136·6°) where the two angles are equal. The re-entrant angle at N(2) [148·3(5)°] is larger than that at nitrogen in (NPBr$_2$)$_5$ [143·8(10)°] but smaller than at nitrogen in (NPCl$_2$)$_5$, mean 158·1°. The endocyclic angles at phosphorus are smaller than in (NPBr$_2$)$_5$, except at P(5), where the corresponding angles in the two compounds are nearly equal. In addition, the angles at phosphorus are not equal in pairs about a pseudo-mirror plane, as in (NPBr$_2$)$_5$.

There are now many structures which demonstrate the flexibility of phosphonitrilic derivatives. The two similar molecules (NPCl$_2$)$_5$ and (NPBr$_2$)$_5$ have quite different conformations, even though there are no steric reasons for the difference.[11] In [(NPMe$_2$)$_4$H]$_2$CoCl$_4$ the two [(NPMe$_2$)$_4$H]$^+$ ions have different conformations,[2] one with the saddle and one with the tub conformation. These structures suggest that the energy differences between conformations in phosphonitrilic derivatives are small and that the particular conformation adopted depends on a delicate balance of a number of intra- and inter-molecular factors. This is consistent with the dual π-system model[4] for phosphonitrilic derivatives since the total π-overlap in a P–N bond would be independent of the dihedral angle if the π_a and π_s systems are equivalent. Thus it is not surprising that the phosphonitrilic ring in the [(NPMe$_2$)$_5$H$_2$]$^{2+}$ ion assumes an unusual conformation influenced primarily by $\overset{+}{\text{N}}$–H · · · O and $\overset{+}{\text{N}}$–H · · · Cl hydrogen bonding.

The co-ordination geometry about copper is distorted tetrahedral. The distortion from tetrahedral geometry is much greater than in Cs$_2$CuCl$_4$[19] where the angles around copper are 124·9, 123·3, 102·5, 102·5, 102·9, and 102·9°. Corresponding angles in the present compound are 133·2, 133·7, 100·6, 96·8, 99·9, and 98·6° indicating that the tetrahedron is much more flattened. The distortion is similar to that found in other structures having a CuCl$_4$$^{2-}$ anion together with a large cation.[20] Three of the Cl atoms are involved in hydrogen bonding (see later). The fourth Cl atom, Cl(4), is not involved in hydrogen bonding and the Cu–Cl(4) distance [2·218(3) Å] is similar to the Cu–Cl distances to Cl atoms not involved in hydrogen bonding in the compounds [(NPMe$_2$)$_4$H]CuCl$_3$ [2·22(1) Å][3] and (C$_{13}$H$_{19}$N$_2$OS$^+$)$_2$[CuCl$_4$]$^{2-}$ [2·220(2) Å].[20a] However, as in these other structures, the remaining Cu–Cl distances are significantly longer [2·251(3), 2·270(3), and 2·281(3) Å], giving further evidence for O–H · · · Cl hydrogen bonding.

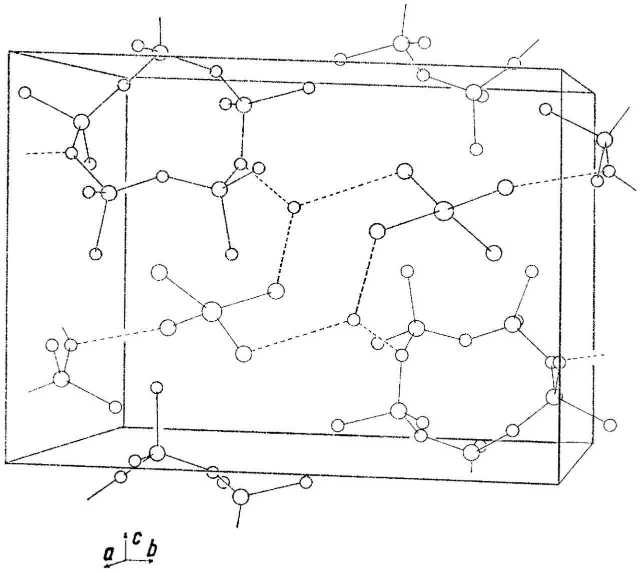

FIGURE 2 View of the unit-cell contents down a^*. Hydrogen bonds are indicated by dashed lines

The [(NPMe$_2$)$_5$H$_2$]$^{2+}$ cation is linked to the CuCl$_4$$^{2-}$ anion and water molecule by intermolecular hydrogen bonds. In addition, there appears to be hydrogen bonding from the water molecule to the CuCl$_4$$^{2-}$ anion, so that a chain-like structure is produced (Figure 2). Although the hydrogen atoms could not be located there are other indications of hydrogen bonding; N · · · O, N · · · Cl, and O · · · Cl distances and relevant angles are given in Table 6. The N(3) · · · O and

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[20] (*a*) A. C. Bonamartini, M. Nardelli, C. Palmieri, and C. Pelizzi, *Acta Cryst.*, 1971, **B27**, 1775; (*b*) J. H. Russel and S. C. Wallwork, *ibid.*, 1969, **B25**, 1691; (*c*) J. Lamotte-Brasseur, L. Dupont, and O. Dideberg, *ibid.*, 1973, **B29**, 241; (*d*) M. Bonamico and G. Dessy, *Theoret. chim. Acta*, 1967, **7**, 367.

N(1) . . . Cl(3) distances are in the expected range for $\overset{+}{\mathrm{N}}$–H ··· O and $\overset{+}{\mathrm{N}}$–H ··· Cl hydrogen bonds,[21] and the angles around these nitrogen atoms are favourable for the formation of hydrogen bonds. The O ··· Cl distances are slightly larger than usually found [21] for H–O–H ··· Cl⁻ hydrogen bonds but are probably still in the range for hydrogen bonding. The geometry is favourable for such hydrogen bonds to form, the Cl(2) ··· O ··· Cl(1) angle being 116°.

TABLE 6

Probable hydrogen bonds

(*a*) A ··· B Lengths (Å)			
N(3) ··· O	2·85	Cl(2) ··· O	3·26
Cl(1) ··· O	3·31	N(1) ··· Cl(3)	3·19
(*b*) Angles (deg.)			
P(3)–N(3) ··· O	127·9	Cl(1) ··· O ··· N(3)	134·6
P(4)–N(3) ··· O	103·5		
Cl(1) ··· O ··· Cl(2)	116·0	P(2)–N(1) ··· Cl(3)	109·5
Cl(2) ··· O ··· N(3)	107·4	P(1)–N(1) ··· Cl(3)	118·8

Aside from the close intermolecular contacts assigned to hydrogen-bonded atoms, intermolecular contacts are of the normal van der Waals type. The closest Cl ··· C distance is 3·59 and the closest C ··· C distance is 3·66 Å. Methyl–methyl contacts are frequently <4·0 Å, and the Cl ··· C distance of 3·59 Å is not unusually small.

We thank Professor N. L. Paddock, Dr. T. N. Ranganathan, and Dr. J. N. Wingfield for providing the crystals and for much helpful discussion, the National Research Council of Canada for financial support and for a scholarship (to H. P. C.) and the staff of the University of British Columbia Computing Centre for assistance.

[3/1451 *Received*, 11*th July*, 1973]

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