Synthesis and Spectroscopy of Mono- and Di-nuclear Copper Complexes of a Pyrazolylcyclotriphosphazene. Crystal Structure of an Unusual Cyclotriphosphazene-bridged Dicopper Complex†

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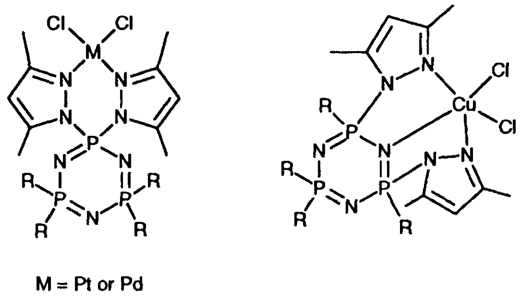
The mononuclear copper(II) complexes $[CuL(ClO_4)(H_2O)_2]ClO_4$ and $[CuL(bipy)(ClO_4)]ClO_4$ [L = 2,2,4,4,6,6-hexakis(3,5-dimethylpyrazolyl)-2λ^5,4λ^5,6λ^5-cyclotriphosphaza-1,3,5-triene] have been prepared and characterized by optical, EPR and IR spectral data. The crystal structure of an unusual cyclophosphazene-bridged dicopper complex $[H_2dmpz][(CuCl_2)_2\{N_3P_3O(dmpz)_5\}]$ (Hdmpz = 3,5-dimethylpyrazole) has been determined: space group $P\bar{1}$, $a = 11.640(3)$, $b = 14.497(14)$, $c = 14.775(3)$, $\alpha = 77.62(6)$, $\beta = 82.10(2)$, $\gamma = 74.88(6)°$, and $Z = 2$. The geometry around both copper atoms is a distorted trigonal bipyramidal with the axial positions occupied by pyrazolyl pyridinic nitrogens and the equatorial positions by one cyclophosphazene ring nitrogen and two chlorine atoms.

Although the chemistry of cyclophosphazenes has centred mainly on the substitution reactions of various nucleophiles at the ring phosphorus, there have been constant attempts to explore the co-ordination chemistry of these inorganic heterocyclic ring systems.[1,2] Three different modes of co-ordination behaviour have been recognized so far. (1) The ring nitrogen atoms of cyclophosphazenes possess a lone pair of electrons and these can participate in co-ordination to transition metals particularly when the substituents on phosphorus are electron releasing. Several complexes of this type have been isolated and characterized especially with four- and higher-membered cyclophosphazenes.[2,3] (2) The ring phosphorus atom also can interact with transition metals in certain favourable cases. Thus for example the hydridophosphazene, *gem*-$N_3P_3Ph_4(Me)H$ co-ordinates through a ring phosphorus(III) centre.[4] (3) An interesting mode of transition-metal interaction with cyclophosphazenes involves a suitable exocyclic donor group. Several exocyclic groups such as phosphine,[5] acetylene,[6] carborane[7] and Schiff base[8] have been incorporated in cyclophosphazenes. Although great opportunities exist for designing ligands of specific requirements this possibility has been explored to a smaller extent compared to the others. Keeping this in mind, we have recently initiated a program to study the co-ordination response of pyrazolylcyclophosphazenes with transition metals. We first chose to study 2,2,4,4,6,6-hexakis(3,5-dimethylpyrazolyl)-2λ^5,4λ^5,6λ^5-cyclotriphosphaza-1,3,5-ene (L). The co-ordination behaviour of which towards various transition metals is varied. Thus chlorides of Pd^{II} and Pt^{II} are reported[9] to form square-planar complexes through exclusive co-ordination by the geminal pyrazolyl pyridinic nitrogens (Scheme 1). In contrast, recently we have shown[10] that L co-ordinates *via* two non-geminal pyrazolyl pyridinic nitrogens and one cyclophosphazene ring nitrogen atom to copper(II) halides (Scheme 1). In continuation of this study, we report the reactions of copper(II) perchlorate hexahydrate with L. The synthesis and spectroscopic studies on complexes **1a** and **1b** are described. We also report the crystal structure of the unusual dinuclear copper(II) complex **2** of a pyrazolylcyclophosphazene oxide.



M = Pt or Pd

Scheme 1 R = 3,5-dimethylpyrazolyl

Experimental

Reagents and General Procedures.—Copper(II) perchlorate hexahydrate $Cu(ClO_4)_2\cdot6H_2O$ and hexachloro-λ^5-cyclotriphosphazene $N_3P_3Cl_6$ were obtained from Aldrich Chemical Co. 3,5-Dimethylpyrazole was synthesised using the literature method.[11] The ligand L was prepared by our improved procedure.[10] Reagent-grade dichloromethane, benzene and acetonitrile were dried (P_2O_5) and stored over molecular sieves. Diethyl ether and hexane were dried (Na) immediately before use.

Instrumentation.—Infrared spectra were recorded as KBr pellets on a Perkin Elmer 1320 spectrophotometer using polystyrene film as a calibrant, electronic spectra at 25 °C on a Shimadzu UV-160 spectrophotometer. The EPR spectra were recorded on a Varian E-series spectrometer with variable-temperature facility at X-band frequency. Diphenylpicrylhydrazyl (dpph, g = 2.0036) was used for magnetic field

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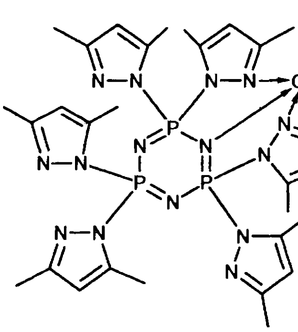
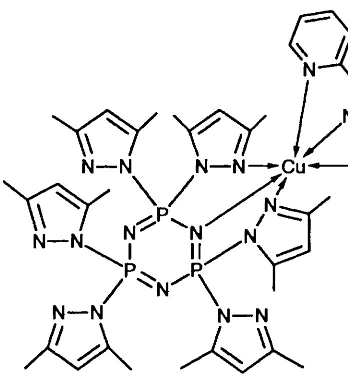
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, issue 1, pp. xxiii–xxviii.



1a

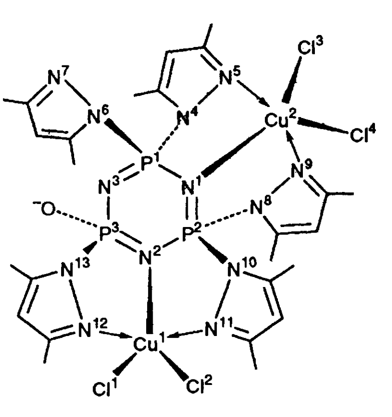


1b

strength calibration. Simulation was carried out using a FORTRAN romb[12] program on HP900 series 800 computers. Conductivity measurements were carried out in acetonitrile solutions on a Century Digital conductivity meter. The solution magnetic moments were obtained at 27 °C by the Evans NMR method using acetonitrile as the solvent[13] and are reported per copper. Metal analysis were carried out by complexometric titration with ethylenediaminetetraacetate (edta) after decomposing the complexes with concentrated H_2SO_4; C, H and N analyses were by the microanalytical centre at the Indian Institute of Technology, Kanpur and the Central Drug Research Institute, Lucknow.

Preparation of the Complexes.—$[CuL(ClO_4)(H_2O)_2]ClO_4$ **1a**. To a solution of L (0.141 g, 0.2 mmol) in dichloromethane (10 cm^3) was added copper(II) perchlorate hexahydrate (0.074 g, 0.2 mmol). The solution was stirred for 2 h and a bluish green solution was formed. It was filtered and concentrated to *ca.* 3 cm^3. Diethyl ether (10 cm^3) was added to obtain a blue precipitate which was dried over P_2O_5 and recrystallised from dichloromethane–benzene (1 : 1). Yield 0.162 g (80.71%), m.p. 165 °C, μ 1.82, Λ_M 227 S cm^2 mol^{-1}. IR(KBr, cm^{-1}): 1555s, 1450m, 1400s, 1320w, 1290s, 1240s (br), 1180 (sh), 1145 s (br), 1100 (sh), 1080 (sh), 1040 (sh), 955s and 620s (Found: C, 35.65; H, 5.05; Cu, 6.30; N, 20.80. Calc. for $C_{30}H_{46}Cl_2CuN_{15}O_{10}P_3N_{15}$: C, 35.90; H, 4.60, Cu, 6.35; N, 20.90%).

$[CuL(bipy)(ClO_4)]ClO_4{\cdot}CH_2Cl_2$ **1b**. 2,2′-Bipyridine (bipy) (0.0312 g, 0.2 mmol) dissolved in dichloromethane (5 cm^3) was added dropwise to a stirred solution of complex **1a** (0.2 g, 0.2 mmol) in dichloromethane (10 cm^3). The reaction mixture was stirred for 2 h, filtered and after concentrating the filtrate (*ca.* 3 cm^3) diethyl ether (10 cm^3) was added. A blue microcrystalline solid was formed. It was filtered off, washed with benzene and ether and dried over P_2O_5. The recrystallised product (dichloromethane–benzene) weighed 0.205 g (91%), m.p. 132 °C (decomp.), μ 1.98, Λ_M 220 S cm^2 mol^{-1}. IR(KBr, cm^{-1}): 1590m, 1560s, 1455m, 1430s, 1300s, 1280s, 1220s (br), 1170 (sh), 1080 (br), 950s and 610s (Found: C, 40.05; H, 4.85; Cu, 5.20; N, 19.30. Calc. for $C_{41}H_{52}Cl_4CuN_{17}O_8P_3$: C, 40.70; H, 4.35; Cu, 5.25; N, 19.70%).



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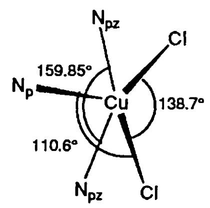

$[H_2dmpz][(CuCl_2)_2\{N_3P_3O(dmpz)_5\}]{\cdot}MeCN$ **2** (Hdmpz = 3,5-*dimethylpyrazole*). Attempts to obtain crystals of the dinuclear complex $[(CuCl_2)_2L]$ **3** by slow vapour diffusion of hexane into a solution of it in dichloromethane–acetonitrile (1 : 1) resulted in the formation of single crystals of **2** almost quantitatively, m.p. 132 °C, μ 1.68, Λ_M 120 S cm^2 mol^{-1}. IR(KBr, cm^{-1}): 3450m, 1560s, 1448m, 1400m, 1280s, 1242s (br), 954s and 630m (Found: C, 37.10; H, 4.60; Cu, 12.15; N, 21.55. Calc. for $C_{32}H_{47}Cl_4Cu_2N_{16}OP_3$: C, 37.20; H, 4.60; Cu, 12.30; N, 21.70%).

X-Ray Analysis of Complex **2**. A dark crystal (0.10 × 0.18 × 0.36 mm) of complex **2** was glued with epoxy on a glass fibre and mounted on an Enraf-Nonius CAD-4 diffractometer. Unit-cell dimensions and their standard deviations were determined from 25 reflections with 2θ in the range 14–16°. Intensity data were collected by the θ–2θ scan method using a variable scan sweep (4–16° min^{-1}). Monochromatic Mo-Kα radiation in the range 2θ 2–45.9° with $h = -12$ to 12, k = 0–15 and $l = -15$ to 16 was used. Three reflections were monitored every 2 h and showed insignificant variation. The intensities of 6785 reflections were measured of which 2762 had an $I > 3\sigma(I)$. The data were corrected for Lorentz, polarization and absorption effects, the corrections for the latter being 0.69–0.89. Table 1 summarizes the crystal information.

Direct methods (SHELX)[15a] were used for structure solution, and refinement was carried out by the full-matrix least-squares method using initially isotropic and subsequently anisotropic thermal parameters for non-hydrogen atoms. Most hydrogen atoms were found on a Fourier difference map. The positions of the remainder were calculated from idealized conformations using sp^2 or sp^3 hybridizations at the appropriate carbon atom with a fixed C–H distance. These were included in the subsequent cycles of refinement. Owing to the large thermal motion of the solvent molecule or perhaps since not all cavities contain the solvent, final refinement converged with rather high $R = 0.070$ and $R' = 0.091$. In the refinement cycles weights were derived from the counting statistics. Scattering factors were from ref. 16. A final difference map revealed no chemically significant features. The computer program used was NRC 386 (personal computer version of NRC VAX).[15b]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 1 Crystallographic information for compound **2** *

Formula	$C_{32}H_{47}Cl_4Cu_2N_{16}OP_3$
M	1033.66
Crystal colour	green
Space group	$P\bar{1}$
a/Å	11.640(3)
b/Å	14.497(14)
c/Å	14.775(3)
α/°	77.62(6)
β/°	82.10(2)
γ/°	74.88(6)
U/Å^3	2342.1(21)
D_c/g cm^{-3}	1.47
μ/cm^{-1}	12.9
Z	2
F(000)	1059.7
λ/Å	0.710 73
Scan width/°	1.0 + 0.35 tanθ
No. unique data	6482
No. of refined parameters	499
f	1.40
Maximum Δ/σ	0.003

* Weighting scheme $w^{-1} = [\sigma^2(I) + 0.05\,I^2]/4f^2$.

Table 2 Electronic spectral data for the complexes *

Compound	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	Assignment
1a	748 (49)	d–d
	311 (1089)	pz→Cu l.m.c.t.
	260 (2520)	pz→Cu l.m.c.t.
	225 (22 660)	π–π* intraligand
1b	670 (63)	d–d
	582 (78)	d–d
	308 (5460)	pz→Cu, bipy→Cu l.m.c.t.
	225 (40 075)	π–π* intraligand
2	905 (480)	d–d
	277 (5640)	pz→Cu l.m.c.t.
	363 (3050)	pz→Cu l.m.c.t.
	224 (23 500)	π–π* intraligand

* For acetonitrile solutions.

Table 3 Spin-Hamiltonian parameters for the complexes [a]

Compound	g_1	g_2	$A_{\parallel}$	g_{iso}	A_{iso}	g_{av} [b]	G [c]
1a	2.069 [d]	2.339	149	2.180	71	2.183	4.913
	2.072 [e]	2.351	131	—	—	2.169	4.875
	2.072 [f]	2.351	130	—	—	2.169	4.875
1b	2.042 [d]	2.232	173 [g]	2.137	78	2.138	5.524
	2.028 [h]	2.244	166 [g]	2.126	73	2.128	8.714
	2.060 [e]	2.250	173	—	—	2.125	4.167
	2.050 [f]	2.234	186	—	—	2.113	4.680
2	2.058 [d]	2.232	118	2.132	—	2.118	4.000
	2.054 [e]	2.220	116	—	—	2.111	4.074
	2.060 [h]	2.234	—	2.135	—	2.119	3.900

[a] A values are in $\times 10^{-4}$ cm^{-1}. [b] Computed using the formulae $[\frac{1}{3}(g_{\parallel}{}^2 + 2g_{\perp}^2)]^{\frac{1}{2}}$. [c] Obtained from $(g_{\parallel} - 2)/(g_{\perp} - 2)$. [d] Dichloromethane solution spectral data at room and liquid-nitrogen temperature. [e] Polycrystalline powder sample at room temperature. [f] Polycrystalline powder sample at liquid-nitrogen temperature. [g] a_N values are 12×10^{-4} and 13.5×10^{-4} cm^{-1} respectively. [h] For acetonitrile solution at room and liquid-nitrogen temperature.

Table 4 The EPR spectral parameters derived from computer simulation [a]

				Linewidth		
Compound	$A_{\parallel}$	$g_{\parallel}$	$g_{\perp}$	X	Y	Z
1a [b]	142	2.353	2.056	68	68	48
1a [c]	175	2.329	2.055	75	75	55
1b [b]	184	2.250	2.053	64	64	58
1b [c]	185	2.232	2.037	65	65	45

[a] $A_{\parallel}$ and linewidths are in G ($=0.9323 \times 10^{-4}$ cm^{-1}). [b] Polycrystalline sample at room temperature. [c] Frozen dichloromethane solution at liquid-nitrogen temperature.

Results and Discussion

Synthesis.—The reaction of ligand L with copper(II) perchlorate hexahydrate in various stoichiometries affords only complex **1a**. Failure to isolate stable di- and tri-nuclear complexes under all reaction conditions suggests strongly that co-ordination of L to copper cannot be exclusively through geminal exocyclic pyrazolyl nitrogen atoms. Conductivity data for **1a** and **1b** indicate that in solution they behave as 1:2 electrolytes and thus perchlorate remains outside the co-ordination sphere in acetonitrile. The facile reaction of **1a** with 2,2′-bipyridine to give **1b** evidently occurs *via* the expulsion of aqua ligands as reflected by the disappearance of the broad absorption at 3600–3520 cm^{-1} in the infrared spectra of the latter complex in contrast to the former. The P=N ring stretching frequency in cyclophosphazenes is quite diagnostic in indicating ring nitrogen interaction with transition metals. The splitting of the parent P=N stretching frequency (L, 1220 cm^{-1}) in the spectra of complexes **1a**, **1b** and **2**, to give bands between 1220 and 1250 and 1200 and 1170 cm^{-1}, is suggestive of co-ordination of cyclophosphazene ring nitrogen.[2] The splitting of the $\nu_3(ClO_4)$ band into two (1100 and 1040 cm^{-1}) is demonstrative of unidentate perchlorate, while observation of sharp singlets one slightly overlapped with the ν_3 doublet at 1080 cm^{-1} and another at 620 cm^{-1} confirms the presence of ionic perchlorate.[17] Magnetic moments were calculated by the Evans NMR method.[13] Those of **1a**, **1b** and **2** are consistent with widely accepted values.

Electronic Spectra.—The electronic spectral data are compiled in Table 2. All the complexes show one ligand-centred π–π* transition and two relatively intense charge-transfer bands. These are assigned to pyrazolyl→Cu ligand-to-metal charge transfer (l.m.c.t.) based on earlier work by Schugar and co-workers.[15] An additional charge-transfer band is identified at *ca.* 360 nm for **1b** and assigned to bipyridine→Cu l.m.c.t. The d–d transition of the complexes is seen as a broad and asymmetric band, that of the bipyridine adduct **1b** being shifted to higher energy compared to **1a** reflecting the difference in ligand strengths. The energies of these bands are appropriate for ligand-field transitions of tetragonal complexes with an equatorial CuN_4 environment of **1b** and N_2O_2 environment of **1a**.[19]

EPR Spectroscopy.—The EPR spectra of the complexes were recorded both as polycrystalline samples and in solution. The experimental and theoretical spectral data are summarized in Tables 3 and 4. Representative experimental spectra are given in Figs. 1 and 2. The polycrystalline spectra of mononuclear complexes **1a** and **1b** are typical of monomeric distorted tetragonal copper(II) complexes with a $d_{x^2-y^2}$ ground state ($g_{\parallel} > g_{\perp}$).[20] Replacement of aqua ligands by electron-rich 2,2′-bipyridine lowers the g values and simultaneously increases the $A_{\parallel}$ values. The $g_{\parallel}/A_{\parallel}$ quotients for **1a** and **1b** are 162 and 125 cm respectively. The larger value for the diaqua complex **1a** is suggested to reflect the increased distortion in the equatorial plane.[21] This complex shows all the four well resolved copper hyperfine lines in the $g_{\parallel}$ region at room temperature [Fig. 1(*c*)], while the bipyridine adduct **1b** shows only three lines in the parallel region and considerable broadening of the perpendicular component [Fig. 2(*c*)]. This clearly indicates a lower symmetry for **1b**.[20]

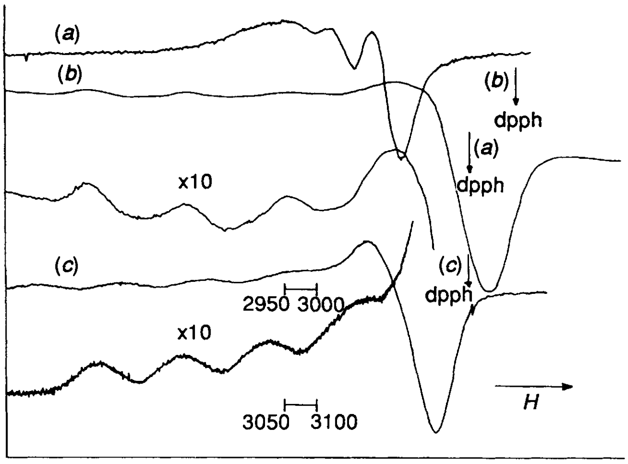

Fig. 1 The EPR spectra of complex **1a** in dichloromethane at room temperature (*a*) and in frozen dichloromethane solution at liquid-nitrogen temperature (*b*) and as the polycrystalline solid at room temperature (*c*)

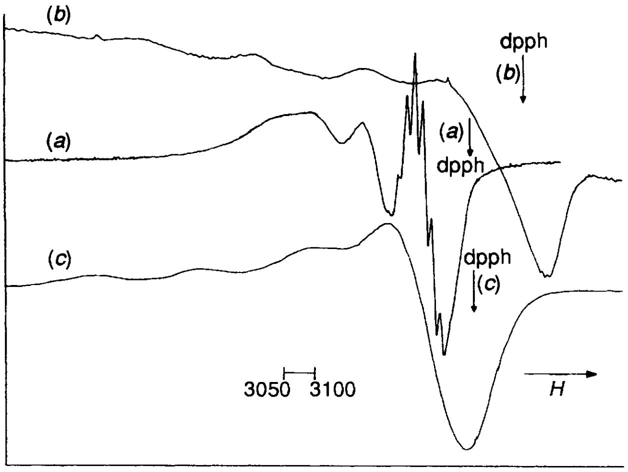

Fig. 2 The EPR spectra of complex **1b**. Details as in Fig. 1

The room-temperature EPR spectra of the mononuclear complexes in dichloromethane solution are isotropic [Figs. 1(*a*) and 2(*a*)]. The g_{iso} and A_{iso} values observed are very close to those for analogous complexes.[22,23] The spectrum of the bipyridine adduct **1b** exhibits eleven lines superimposed on the high-field copper hyperfine line [Fig. 2(*a*)]. The value of the isotropic nitrogen hyperfine splitting is 12×10^{-4} cm^{-1}.

The frozen-solution EPR spectra at liquid-nitrogen temperature for complexes **1a** and **1b** are also axial [Figs. 1(*b*) and 2(*b*)]. The change from solid state to solution does not affect the values of $g_{\parallel}$ and $A_{\perp}$ indicating that the copper environment is retained in solution. Similar spectra are obtained in acetonitrile solution. In Peisach and Blumberg plots[24] of $A_{\parallel}$ *vs.* $g_{\parallel}$, the present $A_{\parallel}$ and $g_{\parallel}$ values fit well for the N_3O_3 co-ordination environment of the diaqua complex **1a** and the N_5O donor set of the bipyridine adduct **1a**. This is consistent with the IR and electronic spectral data. On the basis of this accumulated evidence we prefer to assign an elongated-octahedral geometry for the mononuclear complexes **1a** and **1b**. Based on our earlier crystal structure determination of [CuCl$_2$L][10] we propose an N_3 co-ordination mode *via* two non-geminal pyrazolyl pyridinic nitrogens and one cyclophosphazene ring nitrogen. The EPR spectrum of the dinuclear complex **2** is analogous to that of [(CuCl$_2$)$_2$L] **3**.[10]

Crystal Structure of Complex **2**.—An ORTEP diagram of complex **2** with atomic numbering scheme is given in Fig. 3. Selected bond lengths and angles are given in Table 5, non-hydrogen atomic positional parameters in Table 6.

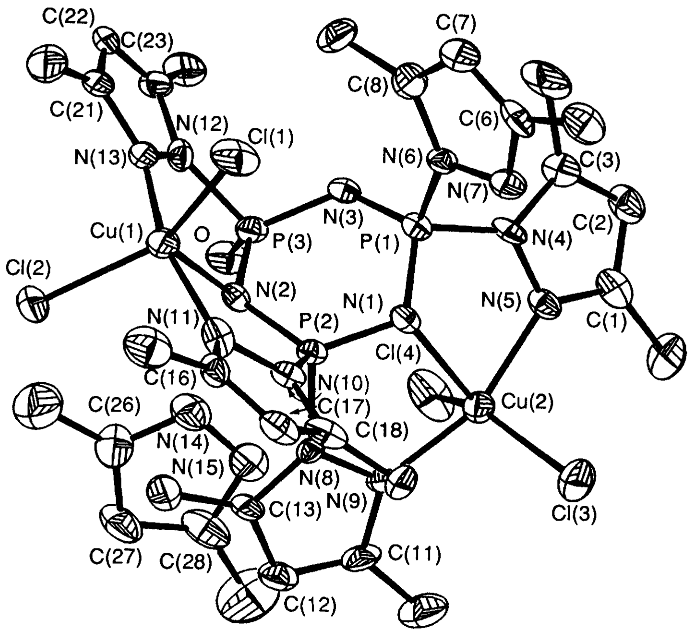

Fig. 3 An ORTEP[25] diagram of compound **2** showing the atomic numbering scheme

Table 5 Selected bond lengths (Å) and angles (°) for compound **2**

P(1)–N(1)	1.6014(12)	P(3)–O	1.505(11)
P(1)–N(3)	1.5222(12)	Cu(1)–Cl(1)	2.266(5)
P(2)–N(1)	1.576(12)	Cu(1)–Cl(2)	2.287(5)
P(2)–N(2)	1.577(12)	Cu(1)–N(2)	2.317(12)
P(3)–N(2)	1.630(12)	Cu(1)–N(11)	1.978(14)
P(3)–N(3)	1.600(13)	Cu(2)–N(13)	1.998(14)
P(1)–N(4)	1.677(14)	Cu(2)–Cl(3)	2.259(5)
P(1)–N(6)	1.672(12)	Cu(2)–Cl(4)	2.296(5)
P(2)–N(8)	1.712(12)	Cu(2)–N(1)	2.366(13)
P(2)–N(10)	1.661(13)	Cu(2)–N(5)	1.982(13)
P(3)–N(12)	1.708(13)	Cu(2)–N(9)	1.969(13)
Cl(1)–Cu(1)–Cl(2)	139.27(23)	Cl(4)–Cu(2)–N(5)	89.4(4)
Cl(1)–Cu(1)–N(2)	118.1(3)	Cl(4)–Cu(2)–N(9)	90.0(4)
Cl(1)–Cu(1)–N(11)	88.7(4)	N(1)–Cu(2)–N(5)	80.2(5)
Cl(1)–Cu(1)–N(13)	92.9(4)	N(1)–Cu(2)–N(9)	81.5(5)
Cl(2)–Cu(1)–N(2)	102.5(3)	N(5)–Cu(2)–N(9)	160.0(6)
Cl(2)–Cu(1)–N(11)	94.9(4)	N(1) – P(1)–N(3)	116.6(6)
Cl(2)–Cu(1)–N(13)	97.0(4)	N(1)–P(2)–N(2)	118.0(6)
N(2)–Cu(1)–N(11)	81.9(5)	N(2)–P(3)–N(3)	110.5(6)
N(2)–Cu(1)–N(13)	79.5(5)	P(1)–N(1)–P(2)	118.3(7)
N(11)–Cu(1)–N(13)	159.7(6)	P(2)–N(2)–P(3)	119.9(7)
Cl(3)–Cu(2)–Cl(4)	138.13(24)	P(1)–N(3)–P(3)	125.1(8)
Cl(3)–Cu(2)–N(1)	109.4(3)	N(4)–P(1)–N(6)	100.0(6)
Cl(3)–Cu(2)–N(5)	98.3(4)	N(8)–P(2)–N(10)	99.7(6)
Cl(3)–Cu(2)–N(9)	95.5(4)	N(8)–P(2)–O	105.5(6)
Cl(4)–Cu(2)–N(1)	112.4(3)		

The structure has many unprecedented features. This is the first example of a cyclophosphazene ring functioning as a bridging ligand system *via* two N_3 cores between copper atoms. Furthermore, it is unique in that two ring nitrogen atoms of a cyclophosphazene ring are involved in simultaneous co-ordination with two different copper atoms. The co-ordination of each copper is through two non-geminal pyrazolyl pyridinic nitrogen atoms and one cyclophosphazene ring nitrogen atom. This mode is in contrast to derivatives of L with Pd and Pt where only geminal pyrazolyl nitrogens are predicted to be involved in co-ordination to the metal with no interaction from the cyclophosphazene ring.[9] However, the crystal structure of the 1 : 1 complex [CuCl$_2$L] shows an analogous tridentate N_3 co-ordination pattern around copper.[10]

Table 6 Non-hydrogen-atom positional parameters for complex **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	0.248 10(18)	0.510 99(16)	0.278 93(13)	C(5)	0.163 8(20)	0.092 1(14)	0.123 2(17)
Cu(2)	0.597 37(18)	0.112 26(16)	0.198 80(14)	C(6)	0.196 6(18)	0.338 5(14)	−0.043 3(12)
Cl(1)	0.149 1(4)	0.554 6(4)	0.148 7(3)	C(7)	0.089 4(17)	0.366 4(15)	0.009 3(14)
Cl(2)	0.288 4(4)	0.580 6(4)	0.392 2(3)	C(8)	0.109 4(16)	0.337 9(14)	0.099 3(12)
Cl(3)	0.731 9(5)	0.109 8(4)	0.073 1(3)	C(9)	0.224 0(18)	0.359 8(15)	−0.147 1(12)
Cl(4)	0.569 6(6)	0.016 2(4)	0.341 4(3)	C(10)	0.023 3(15)	0.348 8(16)	0.184 5(13)
P(1)	0.320 0(4)	0.225 8(3)	0.183 6(3)	C(11)	0.767 0(14)	0.181 0(14)	0.296 8(12)
P(2)	0.457 1(3)	0.327 4(3)	0.238 0(3)	C(12)	0.762 1(16)	0.260 2(15)	0.339 2(12)
P(3)	0.268 4(4)	0.276 6(3)	0.357 7(3)	C(13)	0.653 2(15)	0.320 4(13)	0.329 8(11)
N(1)	0.444 3(10)	0.256 7(9)	0.174 5(7)	C(14)	0.864 0(17)	0.093 5(16)	0.288 5(16)
N(2)	0.354 8(10)	0.351 1(9)	0.317 5(7)	C(15)	0.601 3(16)	0.413 1(14)	0.361 3(13)
N(3)	0.245 8(11)	0.227 3(9)	0.276 8(8)	C(16)	0.438 6(16)	0.590 5(13)	0.147 7(13)
N(4)	0.361 6(12)	0.116 3(10)	0.152 5(8)	C(17)	0.540 6(17)	0.558 0(17)	0.090 4(11)
N(5)	0.477 7(12)	0.063 3(10)	0.151 5(9)	C(18)	0.567 8(16)	0.458 0(15)	0.111 9(11)
N(6)	0.232 9(11)	0.287 7(9)	0.098 7(8)	C(19)	0.380 5(19)	0.691 7(17)	0.150 8(14)
N(7)	0.287 2(12)	0.289 8(10)	0.010 4(9)	C(20)	0.665 1(16)	0.380 7(15)	0.078 8(12)
N(8)	0.594 4(10)	0.279 7(9)	0.280 1(8)	C(21)	0.005 0(16)	0.492 8(16)	0.377 7(12)
N(9)	0.665 2(11)	0.193 7(10)	0.257 3(8)	C(22)	−0.048 0(15)	0.420 5(16)	0.427 1(12)
N(10)	0.476 1(11)	0.434 8(10)	0.180 2(8)	C(23)	0.032 6(15)	0.333 7(15)	0.434 7(11)
N(11)	0.396 9(13)	0.522 3(11)	0.199 5(8)	C(24)	−0.043 3(17)	0.601 2(16)	0.354 6(13)
N(12)	0.137 1(12)	0.354 7(10)	0.386 1(9)	C(25)	0.025 3(16)	0.238 4(16)	0.476 4(14)
N(13)	0.120 8(11)	0.450 9(12)	0.353 9(8)	C(26)	0.528 2(19)	0.228 3(15)	0.579 2(13)
N(14)	0.506 9(14)	0.183 8(13)	0.516 6(10)	C(27)	0.641 4(20)	0.183 3(17)	0.608 1(14)
N(15)	0.599 6(15)	0.104 3(12)	0.506 9(10)	C(28)	0.680 3(20)	0.103 7(16)	0.563 8(15)
O	0.302 8(10)	0.208 3(9)	0.447 1(7)	C(29)	0.442 6(22)	0.318 9(21)	0.603 3(17)
C(1)	0.482 8(18)	−0.023 5(14)	0.132 0(11)	C(30)	0.790 2(25)	0.027 2(20)	0.571 8(19)
C(2)	0.368 5(19)	−0.028 8(13)	0.119 6(13)	C(97)	0.007 0(0)	0.809 4(0)	0.129 1(0)
C(3)	0.295 1(16)	0.057 4(12)	0.133 32(11)	C(98)	0.053 4(0)	0.836 6(0)	0.202 5(0)
C(4)	0.598 2(18)	−0.099 4(13)	0.128 1(15)	N(99)	0.090 5(0)	0.858 3(0)	0.261 1(0)

The local environment around each copper atom can be described as trigonal bipyramidal with the axial positions occupied by a pair of *cis* non-geminal pyrazolyl nitrogen atoms and the equatorial positions by one cyclophosphazene ring nitrogen. Only one cyclophosphazene ring nitrogen [N(3)] is not involved in any co-ordination. The N_3 core imposes a distortion around both copper atoms as reflected in the bond angle N_{ax}–Cu–N_{ax} (average 159.90) (Fig. 3). The Cu–N_{eq} bond length [average 2.342(13) Å] is longer than the Cu–N_{ax} [average 1.982(13) Å] reflecting the basicity differences between the two types of heterocyclic nitrogen atoms.

The co-ordination to the metal causes a severe distortion of the cyclophosphazene ring conformation with ring nitrogens N(2) (−0.373 Å) and N(1) (+0.294 Å) displaced from a mean plane defined by P(1), P(2), P(3) and N(3). This distortion is larger than that observed for [$CuCl_2L$]. The bond length and angle variations in the cyclophosphazene ring are in keeping with trends expected upon ring nitrogen co-ordination to transition metals and are easily accounted for by accepted theories of bonding in cyclophosphazenes.[2,3]

An interesting aspect of the structure of complex **2** is the unusual cleavage of one of the unco-ordinated pyrazolyl groups from the parent L ligand. This leads to the formation of a rare oxide-containing cyclophosphazene along with the liberated pyrazolium cation. The negative charge on oxygen is delocalized into the phosphazene ring as is reflected in the P–O bond length [1.505(11) Å], *cf.* those found in related systems: triphenylphosphine oxide [1.483(3) Å],[26] *gem*-$N_3P_3Ph_2(OMe)_3(OH)$ [1.456(1) Å][27] and *gem*-$N_3P_3Cl_3(NEt_2)_2(OH)$ (average 1.47 Å).[28] The cleavage of the pyrazolyl group is clearly a steric effect. This is also reflected in the inability of L to form trinuclear copper complexes.

Conclusion

The ligand L co-ordinates in a facial N_3 mode to copper(II) salts. The crystal structure determination of complex **2** reveals that the cyclophosphazene bridges the two copper atoms through two ring nitrogen atoms. Further studies are underway to explore the possibility of utilizing the mononuclear complexes to synthesise heterobimetallic compounds.

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