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Polymer building blocks: a $CuCl_2$-bridged phosphazene dimer containing κ^5N coordinated Cu(II) †

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The reaction of a hexakis(2-pyridyloxy)cyclotriphosphazene (L) with $CuCl_2$ affords a novel $CuCl_2$-bridged dimer (1) with each monomeric unit also coordinated to Cu(II) *via* a κ^5N binding core; such a dimer represents a potentially new class of polymeric phosphazene–metal complexes.

Phosphazenes have been studied for many years, with particular emphasis being placed on designing polymers suitable for commercial applications. Although early research focused on the organic substitution chemistry of the phosphazene skeleton, the past 10–15 years has seen increasing interest in the synthesis of new phosphazene–metal complexes. These compounds, particularly at a polymeric level, potentially have desirable properties as catalysts, electrode mediators and electrode conductors.[1] The most accepted methodology to attain these complexes, is to attach suitable donor groups to the phosphazene skeleton.

Since there are inherent difficulties involved with accurately characterising polymeric compounds, cyclotriphosphazenes are commonly used as models for the higher polymer analogues. In the case of hexakis(2-pyridyloxy)cyclotriphosphazene (L), the presence of nine potential donor nitrogen atoms also makes this, and related cyclophosphazene ligands, very interesting and versatile multidentate ligands in their own right.

There are very few examples in the literature of multidentate ligands based on a cyclotriphosphazene core, although examples of cyclophosphazenes containing the 3,5-dimethylpyrazolyl group have been reported. Irrespective of whether the ligand contains four or six 3,5-dimethylpyrazolyl groups, for Co(II), Ni(II), Cu(I/II), Zn(II), Cd(II) and Hg(II), predominantly κ^3N tridentate binding (involving one phosphazene ring nitrogen atom) is observed.[2–9] In contrast, hexakis(2-pyridyloxy)cyclotriphosphazene (L) is capable of forming uni-, bi-, tri-, tetra- and penta-dentate complexes with first-row transition metal halides.[10] We report here on its reaction with $CuCl_2$, to yield a dimeric phosphazene–metal complex where each subunit features an uncoordinated pyridyloxy group, thereby offering the potential for higher order oligomerisation.

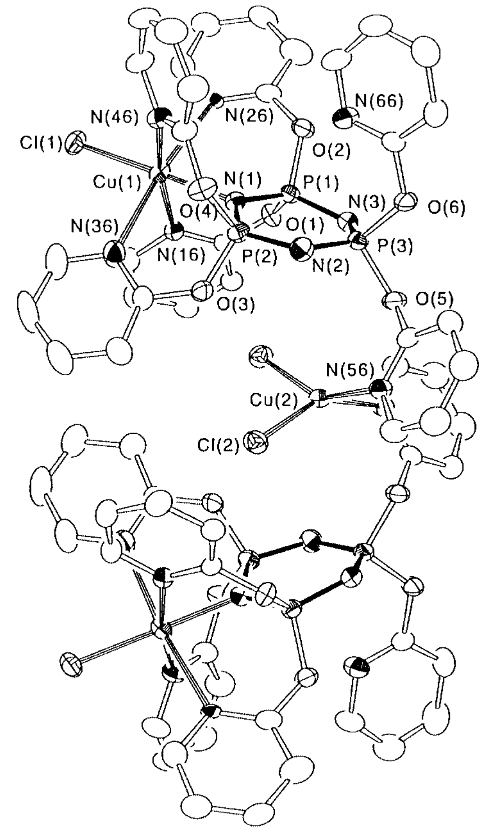

Fig. 1 ORTEP diagram of the dication of **1** (ellipsoids drawn at 50% probability level); the hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 1.988(2), Cu(1)–N(16) 2.093(2), Cu(1)–N(46) 2.090(3), Cu(1)–N(26) 2.509(3), Cu(1)–N(36) 2.559(3), Cu(1)–Cl(1) 2.2492(9), Cu(2)–N(56) 2.048(2), Cu(2)–Cl(2) 2.2204(8), P(1)–N(1), 1.603(2), P(2)–N(1) 1.597(2), P(2)–N(2) 1.565(3), P(3)–N(2) 1.584(3), P(1)–N(3) 1.567(2), P(3)–N(3) 1.584(3); N(1)–Cu(1)–Cl(1) 179.30(8), N(16)–Cu(1)–N(46) 169.84(10), N(26)–Cu(1)–N(36) 173.70(9).

Two mole equivalents of anhydrous $CuCl_2$ were allowed to react with L in CH_2Cl_2 for ≈17 hours at room temperature. Green crystals of **1** were grown *via* the slow diffusion of pentane into the CH_2Cl_2 solution (42% yield). Elemental analysis ‡ indicated a stoichiometry of 2.5 $CuCl_2$ per L which is inconsistent with the reaction stoichiometry. In the IR spectrum (KBr disc), changes to the bands assignable to the P–N stretching frequency of L on coordination are characteristic of the interaction of a phosphazene ring nitrogen with a metal ion (free ligand L: 1222 (vs), 1184 (vs); compound **1**: 1217 (sh), 1208 (vs), 1198 (sh) cm^{-1}). Both positive ion ES and FAB mass spectra § exhibit a peak assignable to $[Cu_2LCl]^+$ (*m*/*z* 862), which points to the coordination of more than one copper ion to L, as well as peaks due to $[CuLCl]^+$ (797) and $[CuL]^+$ (762). The detailed nature of the binding of copper to L was revealed by single-crystal X-ray crystallography ¶ which showed a dimeric dication coordinated to three Cu(II) ions (Fig. 1, Chart 1). The anomalous stoichiometry is the result of a $Cu_2Cl_6^{2-}$ counter ion [eqn. (1)].

$$5\mathrm{CuCl_2} + 2\mathrm{L} \longrightarrow \underset{\mathbf{1}}{[\mathrm{Cu_3L_2Cl_4}][\mathrm{Cu_2Cl_6}]} \qquad (1)$$

The two-fold symmetric dimeric cation consists of two κ^5N pentadentate Cu(II) complexes of L, that are bridged by a $CuCl_2$ [Cu(2)], which is coordinated to one pyridyloxy nitrogen [N(56)] from each monomeric unit. Pentadentate coordination by a phosphazene ligand has been previously reported only for eight-coordinate lanthanide complexes of 3,5-dimethylpyrazolylcyclotriphosphazene.[11] The six-coordinate Cu(1) ion binds to four pyridyloxy nitrogen atoms [N(16), N(26), N(36) and N(46)], one phosphazene ring nitrogen [N(1)] and a chlorine [Cl(1)]. The geometry about Cu(1) is best described as

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4123/

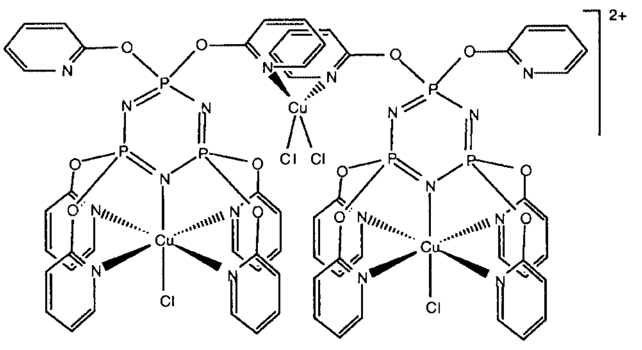

Chart 1 Dication of **1**.

elongated rhombic octahedral,[12] with N(16), N(46), N(1) and Cl(1) defining the equatorial, and N(26) and N(36) the axial positions, respectively. The shortest Cu–N interaction [1.988(2) Å] is to the phosphazene ring nitrogen N(1) *trans* to the chloro ligand. The axial Cu–N(pyridyloxy) bonds are ≈0.4 Å longer than the equatorial ones, which is consistent with other elongated octahedral Cu(II) complexes.[12] The compressed tetrahedral geometry of Cu(2) (dihedral angle of 43°) is unexceptional.[12]

Interpretation of spectroscopic data is complicated by the fact that **1** contains five copper(II) ions in three different environments: *viz.* distorted octahedral 'CuN_5Cl' and compressed tetrahedral 'CuN_2Cl_2' and '$CuCl_4$' chromophores. Hence overlapping d–d transitions appear in the solid state electronic spectrum as a broad band centred at 830 nm with a shoulder at *ca.* 700 nm and a strong tail into the near IR. In dichloromethane the d–d band envelope is centred at 875 nm ($\varepsilon = 120$ L mol^{-1} cm^{-1} per Cu) and a stronger band at 475 nm ($\varepsilon = 2050$ L mol^{-1} cm^{-1} per $[Cu_2Cl_6]^{2-}$) is seen which can be assigned to a Cl→Cu LMCT band for the dimeric anion. The ESR spectrum of **1** (dichloromethane, −160 °C) displays only a broad signal with $g_{iso} = 2.237$, hence no resolution of the expected three nonequivalent copper signals is observed. In powder form a similar g_{iso} value is found. Upon the addition of ethanol to the dichloromethane solution, solvolysis occurs as indicated by a change in the yellow-orange colour to light green. This is accompanied by the appearance of at least three Cu(II) signals in the ESR spectrum, one of the species has $g_{\parallel} = 2.398$ and $A_{\parallel} = 123 \times 10^{-4}$ cm^{-1} while the other has $g_{\parallel} = 2.421$ and $A_{\parallel} = 158 \times 10^{-4}$ cm^{-1}; the 'high' $g_{\parallel}$ values indicating oxygen donor (*e.g.* ethanol) coordination.[13] The room temperature magnetic moment for the complex averages over the five copper centres to be 1.81 μ_B, consistent with each Cu(II) having a normal magnetic moment.

Examples in the literature of metal-linked phosphazene dimers are sparse, and unlike the reported examples,[14–16] **1** is unique in that in addition to the coordinated metal ion linking the dimer, each monomeric unit also contains a coordinated metal ion. Certainly, no similar dimeric metal complexes have been reported from the much studied pyrazolyl class of phosphazene ligands. An appealing aspect of compounds such as **1** is the potential to synthesise larger oligomers *via* additional metal-ion linkages to the free pyridyloxy groups [*i.e.* N(66)]. Therefore, we are at present investigating this possibility through control of the Cu : Cl ratio, and if successful, such compounds would be an entirely new class of 'metal-rich' polyphosphazenes.

As previously alluded to, initial investigations of the coordination chemistry of L reveal that it forms a much more diverse range of coordination complexes with first-row transition metal halides, compared to the 3,5-dimethylpyrazolyl-based ligands. This may be attributable to greater ligand flexibility, on account of L forming six-membered chelate rings, as opposed to five-membered rings for pyrazolyl-based ligands.

Acknowledgements

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Notes and references

‡ Elemental analysis for **1**: Found: C, 34.74; H, 2.09; N, 12.17. $C_{60}H_{48}N_{18}O_{12}P_6Cl_{10}Cu_5$ Calc: C, 34.79; H, 2.34; N, 12.17%.

§ Given peaks correspond to the most abundant isotopomer; assignments were made by comparison of observed and simulated spectra.

¶ Crystal data for $C_{30}H_{24}Cl_5Cu_{2.5}N_9O_6P_3$: $M = 1035.59$, monoclinic, space group $C2/c$, $a = 25.205(6)$, $b = 20.141(4)$, $c = 17.587(4)$ Å, $\beta = 114.145(3)°$, $U = 8147(3)$ Å^3, $T = 168(2)$ K, $Z = 8$, $D_c = 1.689$ g cm^{-3}, $F(000) = 4140$; μ(Mo-K) = 1.797 mm^{-1}, 52215 reflections measured ($4.04 < 2\theta < 52.92°$), 8326 unique ($R_{int} = 0.0319$). Refinement of 501 parameters converged at $R_1 = 0.0377$ [observed data: 6782 $|F_o| > 4\sigma(F_o)$], $wR(F^2) = 0.0930$ (all data). CCDC reference number 186/1708. See http://www.rsc.org/suppdata/dt/1999/4123/ for crystallographic files in .cif format.

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