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FIVE-COORDINATE COPPER(II) COMPLEXES OF GEM-$N_3P_3Ph_2(dmpz)_4$

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Abstract—2,2-Diphenyl-4,4,6,6-tetrakis(3,5-dimethyl-1-pyrazolyl)cyclotriphosphazene, $N_3P_3Ph_2(dmpz)_4$ (**2**), forms mononuclear five-coordinate complexes $N_3P_3Ph_2(dmpz)_4 \cdot CuX_2$ [X = Cl (**3**) and Br (**4**)] with copper(II) halides. The structure of dichloromethane solvate of the chloro derivative, $N_3P_3Ph_2(dmpz)_4 \cdot CuCl_2$, has been determined by single crystal X-ray diffraction. The metal exists in a distorted trigonal bipyramidal geometry and the ligand **2** acts as an N_3 capping tridentate ligand with two non-geminal pyrazolyl pyridine and one cyclotriphosphazene ring nitrogen and two chloride ions complete the trigonal bipyramidal environment. The spectroscopic (IR, UV–vis and EPR) characterization of the complexes is also reported.

Pyrazolylcyclotriphosphazenes are multisite dual coordination response ligands containing both organic (pyrazolyl) and inorganic (cyclophosphazene) nitrogen ligators. They act, depending upon the number and geometrical disposition of the pyrazolyl groups and the nature of the transition metal, either as an N_3 capping ligand or an N_2 donor (Scheme 1). We have recently shown that the hexakis(3,5-dimethyl-l-pyrazolyl)cyclotriphosphazene, $N_3P_3(dmpz)_6$ (**1**), forms both mono- and d-nuclear complexes with copper halides in which the ligand acts as an N_3 donor.[1,2] Two pyrazolyl groups attached to two different phosphorus atoms (non-geminal) were found to be involved in coordination. However, the same ligand had been reported earlier by Paddock to yield six-membered 'metallaphosphapyrazaboles' with palladium and platinum.[3] Also, Krishnamurthy and co-workers have identified a novel N_3 coordination mode arising from two geminal pyrazolyl pyridine and one cyclophosphazene ring nitrogen.[4,5] In view of this we have studied the coordination behaviour of 2,2-diphenyl-4,4,6,6-tetrakis(3,5-dimethyl-1-pyrazolyl)-cyclotriphosphazene, $N_3P_3Ph_2(dmpz)_4$ (**2**), which possesses only four pyrazolyl substituents instead of six as in $N_3P_3(dmpz)_6$. Herein, we report the synthesis and spectroscopy of the copper complexes $N_3P_3Ph_2(dmpz)_4 \cdot CuX_2$ [X = Cl (**3**) and Br (**4**)]. The X-ray crystal structure of the dichloromethane solvate of **3** is also determined.

EXPERIMENTAL

Preparations

The synthesis of 2,2-diphenyl-4,4,6,6-tetrakis (3,5-dimethyl-l-pyrazolyl)cyclotriphosphazene (**2**) has been described previously.[6] The complexes **3** and **4** were obtained by reacting one equivalent of $Cu^{II}X_2$ (X = Cl, Br) with **2** in dichloromethane

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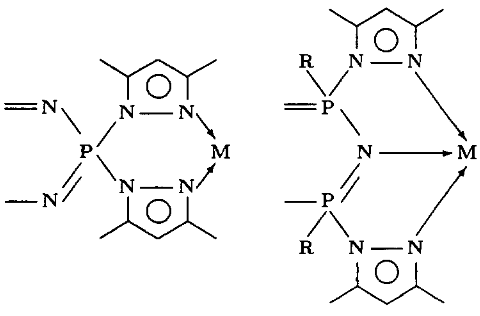
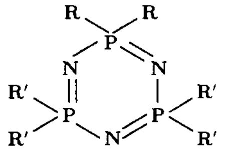


'*geminal coordination*' '*nongeminal coordination*'



1; R = R' = 3,5-dimethyl-1-pyrazolyl

2; R = phenyl, R' = 3,5-dimethyl-1-pyrazolyl

Scheme 1.

and precipitation using hexane. The pertinent data are listed in Table 1.

Physical measurements

Microanalyses were obtained from the microanalytical service centre of the Central Drug Research Institute, Lucknow. Metal content was determined complexometrically by indirect titration with Na_2H_2edta and zinc acetate after destruction of the sample with conc. HNO_3[7]. The IR (as KBr pellets) and UV–vis spectra were performed on Perkin–Elmer 1320 and Shimadzu UV-160 spectrophotometers, respectively. The EPR spectra were obtained on a Varian spectrometer at x-band frequency, and the magnetic field strength was calibrated with diphenylpicrylhydrazyl (dpph, $g = 2.0036$). The spin Hamiltonian parameters were deduced from the theoretical simulation of the EPR spectra.[8]

X-ray structure determination

A green single crystal, with dimension $0.36 \times 0.16 \times 0.55$ mm, was mounted on an Enraf–Nonius CAD-4 diffractometer which uses graphite monochromatized Mo$-K_\alpha$ radiation. The unit cell dimensions were refined from 25 reflections in the range $18 < 2\theta < 19$. Intensities were measured using an $\theta - 2\theta$ scan technique (2θ range, 4–50°). Among the 7107 unique reflections, only 3850 with $I > 6\sigma(I)$ were used for solving and refining the structure. Data were corrected for Lorentz and polarization factors and an absorption correction was applied by psi scans. Refinement of the structure was by full-matrix least-squares procedures.[9] Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model at their calculated positions (C—H, 0.95 Å). The weighting scheme was $w^{-1} = [\sigma^2(I) + PI^2]/4f^2$. Scattering factors were from ref. 10. The final agreement parameters were $R = 0.065$ and $R_w = 0.080$. Crystal data are compiled in Table 2. All calculations were performed using NRC386 (personal computer version of NRCVAX)[11] in the Department of Chemistry and Biochemistry of Arkansas University.

Table 1. Analytical and IR data

Compound	M.p. (°C)	Yield (%)	Found (Calc.) % C	H	N	Cu	IR (cm^{-1}) ν(P=N)	ν(C=N)
3[a]	207d	95	44.5 (44.6)	4.4 (4.5)	17.5 (17.3)	7.1 (7.2)	1225 1180	1568
4	209d	90	43.0 (43.0)	4.3 (4.3)	17.1 (17.3)	7.2 (7.1)	1230 1180	1565
2							1220 1175	1560

[a] Includes one molecule of dichloromethane.

Table 2. Crystallographic information for **3**

Chemical formula	$CuCl_4P_3N_{11}C_{33}H_{40}$
M_r	889.03
Space group	$P\text{–}1$
a (Å)	9.784 (4)
b (Å)	11.666 (4)
c (Å)	18.061 (6)
α (°)	91.52 (3)
β (°)	97.24 (3)
γ (°)	98.26 (3)
U (Å^3)	2021.7 (13)
D_{calc} (g cm^{-3})	1.46
μ (mm^{-1})	0.96
λ (Å)	0.71073
Z	2
Temperature (K)	293
F(000)	914
Scan speed (° min^{-1})	4–16
Scan width (°)	$1.0+0.35\tan\theta$
No. of refined parameters	469
GOF	1.45
Maximum Δ/σ	0.005

RESULTS AND DISCUSSION

Synthesis and spectroscopic investigations

The ligand **2** forms mononuclear complexes with copper(II) halides in excellent yields. No dinuclear complexes could be isolated with this ligand. It is interesting to note that the hexakis analogue of **2** (**1**) formed both mononuclear and di(homo and hetero)nuclear complexes. However, similar behaviour has been observed in the reactions of **2** with nickel(II) and cobalt(II) salts.[6] The complexes **3** and **4** are non-electrolytes in acetonitrile solution. The ν(C=N) band in the IR spectra of the complexes are shifted *ca* 5–8 cm^{-1} to a higher wave number with respect to the free ligand. Similarly, P=N stretching vibrations change slightly (Table 1). These alterations are consistent with the involvement of both pyrazolyl pyridine and cyclophosphazene skeletal nitrogens in coordination to the metal.[12,13]

The UV–vis spectra of the complexes in dichloromethane are typical for a distorted trigonal bipyramidal environment with the *d–d* transitions at around 940 nm. The bands at *ca* 360 and 270 nm are due to $pz \rightarrow Cu$ charge transfer transitions,[14] while the intense band at 230 nm is attributed to the intra-ligand π–π^* transitions. On changing the solvent from dichloromethane to acetonitrile, the *d–d* band is shifted 20–30 nm to low energy (Table 3). This probably indicates that in acetonitrile the metal experiences a weaker ligand field. The solution magnetic moment values calculated from measurements using Evans' method[15] lie in the usual range (Table 3) and rule out any significant magnetic interactions between metallic centres.

The EPR spectra of the complexes exhibit a rhombic pattern in the solid state. The relevant parameters derived from the computer simulation of the spectra are given in Table 4, along with those of related complexes. The theoretical and experimental spectra are displayed in Fig. 1. From these it is evident that the geometry about copper is considerably distorted from the regular trigonal bipyramid.[16,17] The large anisotropies of the two lower g-values (g_1 and g_2) indicate a geometry intermediate between a square pyramid and a trigonal bipyramid for the CuN_3X_2 polyhedra. This is analogous to the observation of copper(II) complexes derived from terpyridine ligand.[18,19]

Crystal structure of 3

The crystal structure of **3** consists of monomeric units, in which the copper atom lies in a distorted trigonal bipyramidal geometry with an N_3Cl_2 donor set of two chloride ions and a cyclotriphosphazene ring nitrogen defining the equatorial plane and two non-geminal pyrazolyl pyridine nitrogens in the

Table 3. EPR data[a]

Compound	g_1	g_2	g_3	g_{av}[b]	Ref.
3	2.018	2.124	2.290	2.147	This work
4	2.007	2.146	2.238	2.132	This work
terpy · $CuCl_2$	2.070	2.135	2.188	2.132	18
terpy · $CuBr_2$	2.032	2.126	2.239	2.134	19
terpy · CuI_2	2.066	2.110	2.206	2.128	18
$CuCl_2(dmIm)_3$	2.060	2.160	2.210	2.144	20

[a] For polycrystalline powder samples at room temperature.

[b] $g_{av} = [\frac{1}{3}(g_1^2+g_2^2+g_3^2)]^{1/2}$.

Table 4. Optical absorption data

Compound	Solvent	λ_{max} (ε_{max})[a]	Assignments
3	CH_2Cl_2	931 (0.21)	*d–d*
		359 (1.24), 279sh (3.22)	*pz* → Cu LMCT[b]
		259 (4.59), 241 (12.32)	π–π^* (intraligand)
	CH_3CN	961 (0.27)	*d–d*
		460 (0.18)	*d–d*
		353 (1.40), 285sh (3.67)	*pz* → Cu LMCT
		267 (5.02), 224 (13.78)	π–π^* (intraligand)
4	CH_2Cl_2	926 (0.36)	*d–d*
		413 (1.05)	Br → Cu LMCT
		360 (1.25), 304 (2.92)	*pz* → Cu LMCT
		273 (2.76), 240 (11.85)	π–π^* (intraligand)
	CH_3CN	948 (0.41)	*d–d*
		414 (2.04)	Br → Cu LMCT
		365sh (1.89), 304 (3.42)	*pz* → Cu LMCT
		267 (4.01), 223 (15.14)	π–π^* (intraligand)

[a] sh = shoulder, units: nm(mol^{-1} cm^{-1} × 10^3).

[b] Ligand to metal charge transfer.

axial positions (Fig. 2). The copper, Cl(1), Cl(2) and N(1) atoms have very small deviations of −0.003(10), 0.001(3), 0.0005(27) and 0.003(5) Å respectively from the least-squares plane passing through these atoms. This plane makes an angle of 87.92(7)° with the cyclotriphosphazene P_3N_3 ring plane. The Cu—N$_{CTP}$ bond distance is longer [2.320(5) Å] and the average Cu—N$_{pz}$ bond length is normal [1.979(5) Å]. The inequivalence in the Cu—N bond distances is similar to that observed for $N_3P_3(dmpz)_6 \cdot CuCl_2$, but all three Ni—N bond lengths are in fact equivalent in the nickel analogue $N_3P_3Ph_2(dmpz)_4 \cdot NiCl_2$. The mean Cu—Cl bond distance is 2.27 Å. The main axis of the trigonal bipyramid constituted by N(12), copper and N(62) deviates greatly [159.39(20)°] from the required angle of 180° for a regular trigonal bipyramid. The Cl(1)—Cu—Cl(2) angle is increased to 132.21(8)° which is reflected in the constriction of the bond angle Cl(2)—Cu—N(1) [104.26(13)°]. These deviations result in an intermediate geometry between

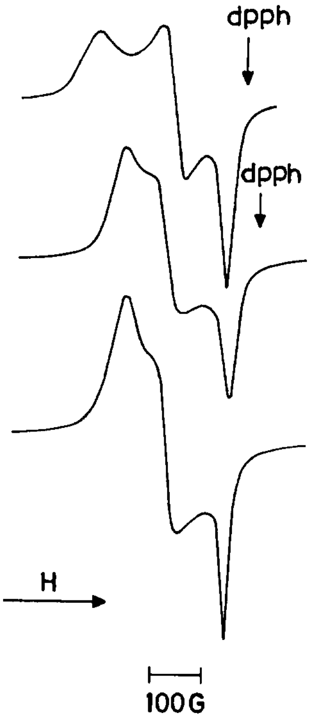


Fig. 1. EPR spectra of: (a) **3** and **4**; (b) experimental; (c) simulated.

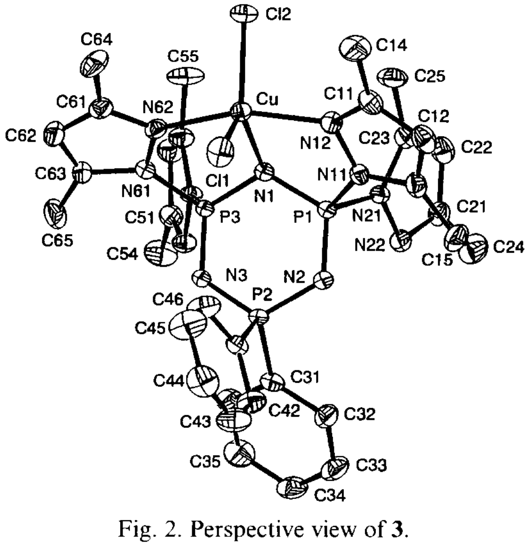


Fig. 2. Perspective view of **3**.

Table 5. Selected bond distances (Å) and angles (°)

Cu—Cl(1)	2.2639(21)	P(1)—N(1)	1.601(5)
Cu—Cl(2)	2.2822(14)	P(1)—N(2)	1.561(5)
Cu—N(1)	2.320(5)	P(2)—N(2)	1.614(5)
Cu—N(12)	1.984(5)	P(2)—N(3)	1.610(5)
Cu—N(62)	1.974(5)	P(3)—N(1)	1.600(5)
Mean distances		P(3)—N(3)	1.552(5)
P—N_{exo}	1.692(5)		
P—C_{exo}	1.794(6)		
Cl(1)—Cu—Cl(2)	132.21(8)	N(1)—P(1)—N(2)	119.1(3)
Cl(1)—Cu—N(1)	123.54(14)	N(2)—P(2)—N(3)	114.9(3)
Cl(1)—Cu—N(12)	90.59(17)	N(1)—P(3)—N(3)	118.4(3)
Cl(1)—Cu—N(62)	92.19(17)	P(1)—N(1)—P(3)	117.6(3)
Cl(2)—Cu—N(1)	104.26(13)	P(1)—N(2)—P(2)	122.1(3)
Cl(2)—Cu—N(12)	97.59(17)	P(2)—N(3)—P(3)	123.1(3)
Cl(2)—Cu—N(62)	95.62(16)	N(11)—P(1)—N(21)	100.9(3)
N(1)—Cu—N(12)	80.86(19)	N(51)—P(3)—N(61)	100.2(3)
N(1)—Cu—N(62)	80.60(19)	C(31)—P(2)—C(41)	106.0(3)
N(12)—Cu—N(62)	159.39(20)		

the square pyramid and trigonal bipyramid and account for the rhombic EPR spectral pattern observed for the powder sample.

The effect imparted on the cyclotriphosphazene skeletal bonding parameters due to the ring nitrogen participation in coordination is as follows. The P—N bonds flanking N(1) are longer (1.60 Å) than the adjacent P—N bond lengths (1.55 Å). However, the depletion of skeletal π-bond is more severe in the N—P(Ph_2)—N segment owing to the presence of electron-withdrawing phenyl substituents (Table 5). The cyclotriphosphazene ring adopts a slightly distorted planar conformation. The coordinated skeletal nitrogen atom N(1) is 0.319(5) Å away from the mean plane defined by P(1), P(2), P(3), N(2) and N(3).

Finally, the difference in the bonding interactions of the cyclophosphazene skeletal nitrogen with nickel and copper suggests that besides the basicity of the cyclophosphazene ligand the nature of the transition metal is also pivotal.

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