Unusual Tridentate N_3 Capping Coordination Behavior of Hexakis(3,5-dimethylpyrazolyl)cyclotriphosphazene, $N_3P_3(3,5\text{-}Me_2Pz)_6$: Synthesis, Spectroscopy, and Electrochemistry of Mono- and Dinuclear Copper(II) Complexes and the X-ray Structure of $N_3P_3(3,5\text{-}Me_2Pz)_6\cdot CuCl_2$

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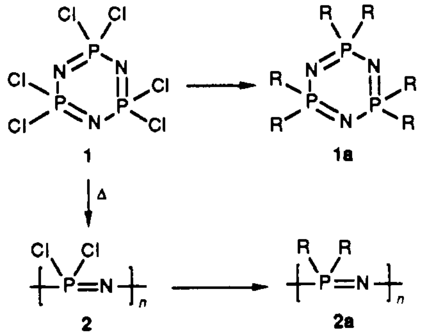
Received June 11, 1992

The reactions of hexakis(3,5-dimethylpyrazolyl)cyclotriphosphazene, $N_3P_3(3,5\text{-}Me_2Pz)_6$ (HPCTP) (**3**), with copper(II) halides afford mononuclear HPCTP·CuX_2 (X = Cl, **3a**; X = Br, **3b**) and dinuclear HPCTP·2CuX_2 (X = Cl, **3c**; X = Br, **3d**) coordination complexes. Optical absorption spectra and ESR spectra of these complexes suggest a distorted trigonal bipyramidal geometry around copper in all of the compounds **3a**–**3d**. The structure of HPCTP·$CuCl_2$ (**3a**) was determined by X-ray crystallography. The crystals of **3a** are monoclinic, space group $P2_1/n$, with a = 21.338 (4) Å, b = 11.43 (3) Å, c = 18.285 (3) Å, β = 104.37 (2)°, V = 4321(2) Å^3, and Z = 4. The structure shows that the cyclophosphazene ligand functions as an unprecedented N_3 capping ligand: coordination to copper is through two nongeminal pyrazolyl pyridinic nitrogen atoms and one cyclophosphazene ring nitrogen atom, and the geometry around copper is distorted trigonal bipyramidal. Cyclic voltammetric studies have been carried out on complexes **3a**–**3d**.

The chemistry of the inorganic heterocyclic cyclophosphazenes has developed extensively on two main themes (1) nucleophilic substitution reactions at phosphorus in the six-membered and eight-membered ring systems $N_3P_3Cl_6$ and $N_4P_4Cl_8$[2] and (2) ring-opening polymerization of $N_3P_3Cl_6$ to the linear dichlorophosphazene and subsequent nucleophilic reactions at phosphorus on the polymer.[3]



R = amino, alkyl (aryloxy), etc.

The possibility of using cyclophosphazenes as ligands toward transition metals has also been attracting the attention of research workers in this area. There are at least three ways in which cyclophosphazenes can interact with transition metals: (a) coordination by skeletal (ring) nitrogen atoms, (b) ring phosphorus–transition metal covalent bond formation, and (c) coordination by an exocyclic group substituted on ring phosphorus. Of these the method c is the most versatile as it offers the advantage of designing and assembling appropriate cyclophosphazene ligands by a proper choice of substituent. Second, this method has the advantage of being adapted to linear macromolecules by the protocol developed by Allcock and co-workers to generate new types of polymeric ligands.[3] Therefore, we have embarked upon a program of developing cyclophosphazene-based ligands containing exocyclic nitrogen coordination sites. Previous choice of exocyclic coordination groups included acetylinic units,[4] phosphines,[5,6] carboranyl moieties,[7] etc.

Paddock and co-workers have shown that in pyrazolyl cyclophosphazenes $N_3P_3(Pz)_6$ and $N_4P_4(Pz)_8$ (Pz = pyrazolyl or 3,5-dimethylpyrazolyl) the pyridinic nitrogen atom of the exocyclic organic heterocycle is more basic than the cyclophosphazene ring nitrogen atom and coordination to metals occurs exclusively through the exocyclic units.[8] In this investigation we report an unusual N_3 coordination to Cu(II) involving pyridinic nitrogen atoms of two nongeminal pyrazole substituents and one cyclotriphosphazene ring nitrogen atom. We describe here the details of an investigation on the reactions of hexakis(3,5-dimethylpyrazolyl)cyclotriphosphazene, $N_3P_3(3,5\text{-}Me_2Pz)_6$ (**3**) (HPCTP) with copper(II) halides. The synthesis, spectroscopic and electrochemical studies on the copper(II) complexes **3a**–**d** are described. An X-ray structure on **3a** has also been carried out.

Experimental Section

Reagents and General Procedures. The solvents were dried by heating under reflux with the appropriate drying agents: methylenedichloride and acetonitrile, P_4O_{10}; benzene, P_4O_{10} or Na/benzophenone; hexane, CaH_2; petroleum ether (60–80 °C), sodium metal; ether, sodium metal. The solvents were distilled and stored over molecular sieves in stoppered flasks.

Hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, was obtained from Aldrich and purified by recrystallization from hexane. 3,5-Dimeth-

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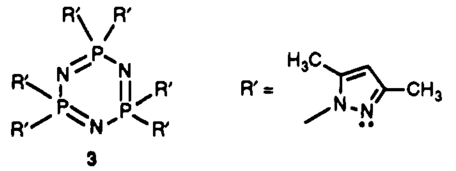

3

HPCTP

3a = HPCTP·$CuCl_2$
3b = HPCTP·2$CuCl_2$
3c = HPCTP·$CuBr_2$
3d = HPCTP·2$CuBr_2$

ylpyrazole was prepared according to standard literature procedure as described in ref 30 and recrystallized from petroleum ether (60–80 °C). Triethylamine (Qualigens) was dried over KOH by heating under reflux and only freshly distilled samples were used. $CuBr_2$ (BDH) and $CuCl_2$ (Qualigens) were heated in a vacuum oven at 120 °C for 4 h immediately before using. Tetrabutylammonium perchlorate was prepared from perchloric acid and tetrabutylammonium bromide (Aldrich) and recrystallized three times from hexane–ethylacetate (1:1). Tetraethyl ammonium perchlorate (BDH) was used as such.

Instrumentation. Infrared spectra were recorded as KBr or CsI pellets on KBr windows by using a Perkin-Elmer IR 1320 spectrophotometer and a Shimadzu FT-IR spectrophotometer. ^1H NMR spectra were obtained on a Bruker spectrometer operating at 80 MHz, and chemical shifts are reported with reference to internal TMS. ^{31}P NMR were recorded on a Jeol Fx 90Q spectrometer operating at 36.43 MHz. Chemical shifts are reported with reference to ext 85% H_3PO_4; upfield shifts are negative. Optical absorption spectra were obtained by using 1-cm quartz cells in a Shimadzu UV-160 spectrophotometer. Solid state electronic spectra were obtained on Nujol mulls adhered to Whatman filter paper strips. EPR spectra were recorded on a Varian spectrometer at X-band frequency, and the magnetic field strength was calibrated with DPPH. Solution magnetic susceptibilities were measured at 27 °C by the NMR method.[9] Conductivity studies were made in acetonitrile solutions on a Century digital conductivity bridge. Cyclic voltammetric measurements were performed with a BAS Bioanalytical equipment. For methylenedichloride solutions, tetrabutyl ammonium perchlorate was used as a supporting electrolyte and for dimethyl formamide (DMF) solutions tetraethylammonium perchlorate was used as the supporting electrolyte. Pt wire served as the ancillary electrode while the reference electrode and working electrode were Ag/AgCl and glassy carbon electrodes respectively. Before each experiment the solutions were thoroughly purged with dry argon. Chemical analysis (C,H,N) were obtained from Central Drug Research Institute's (Lucknow, India) regional instrumentation facility. Metal analysis were carried out by standard optical absorption methods.[10] All melting points reported were obtained in sealed glass capillaries and are uncorrected.

Synthesis of Hexakis(3,5-dimethylpyrazolyl)cyclotriphosphazene, $N_3P_3(3,5\text{-}Me_2\,Pz)_6$ (HPCTP) (3). A modified synthesis of HPCTP giving better yields than reported earlier[8] is given below.

A solution of $N_3P_3Cl_6$ (3.48 g, 0.01 mol) in benzene (25 cm^3) [*Caution*! benzene is a known carcinogen] was added dropwise to a solution of 3,5-dimethylpyrazole (5.8 g, 0.0603 mol) and triethylamine (6.4 g, 0.063 mol) in benzene (50 cm^3) at 20 °C with constant stirring. The reaction flask was equipped with a calcium chloride guard tube to prevent ingress of moisture. After the addition was complete (20 min) the reaction temperature was raised to 80 °C in an hour's time, and the reaction was allowed to proceed at this temperature for 4 h. It was cooled and filtered. The precipitate was rapidly washed with water (3 × 30 cm^3), benzene (2 × 20 cm^3) and ether (2 × 20 cm^3) and dried under vacuum. A white solid was obtained which was recrystallized from methylene dichloride/hexane (1:1) (6.76 g, 96%). This product was identified as HPCTP. Mp: 255–256 °C (lit[8] mp 253.5–254.5 °C). ^{31}P NMR ($CDCl_3$, ppm): –3.37. ^1H NMR ($CDCl_3$, ppm): 2.20 (s, 3H), 2.30 (s, 3H), 5.50 (s, 1H). IR (KBr, cm^{-1}): 3142 (m), 2950 (s), 1574 (vs), 1450 (s), 1410 (s), 1371 (vs), 1296 (vs), 1220 (vs), 1170 (vs), 1084 (vs), 1030 (m), 966 (vs), 902 (m), 828 (m), 802 (s), 756 (s), 611 (s), 636 (m), 510 (vs), 475 (s).

Synthesis of HPCTP·$CuCl_2$ (3a). Anhydrous $CuCl_2$ (0.04 g, 0.30 mmol) and HPCTP (0.21 g, 0.3 mmol) were taken together in methylene dichloride (30 cm^3) and stirred for 30 min, at about 25 °C. The solution was filtered and concentrated to about 5 cm^3. Dry benzene (5 cm^3) followed by diethylether (30 cm^3) was added to the concentrated solution precipitating **3a** as a light green solid (0.24 g, 96% yield). It was recrystallized by slow diffusion of *n*-hexane into a methylene dichloride solution of **3a** at room temperature. Mp: 207 °C. Anal. Calcd for $C_{31}H_{44}N_{15}Cl_4CuP_3$ (including 1 molecule of CH_2Cl_2 of crystallization): C, 40.25; H, 4.79; N, 22.71, Cu, 6.87. Found: C, 40.11; H, 4.82; N, 22.54; Cu, 6.64. Conductivity (mho cm^2 mol^{-1} in CH_3CN): 7.454. IR (cm^{-1}, CsI): 2950 (m), 1573 (s), 1460 (m), 1440 (sh), 1405 (s), 1370 (m), 1310 (sh), 1293 (s), 1240 (vs), 1200 (sh), 1170 (sh), 1142 (s), 1080 (m), 1042 (sh), 1030 (m), 1015 (m), 957 (m), 890 (m), 800 (m), 770 (m), 620 (m), 577 (vs), 520 (sh), 510 (s), 460 (m), 440 (m). ^1H NMR ($CDCl_3$, ppm): 6.2 (br), 2.30 (br), 2.27 (s), 2.22 (s), 2.14 (s). ^{31}P NMR ($CDCl_3$, ppm): –0.59, –1.45 (broad signals).

Synthesis of HPCTP·2$CuCl_2$ (3b). Anhydrous $CuCl_2$ (0.09 g, 0.67 mmol) and HPCTP (0.21 g, 0.30 mmol) were taken together in methylene dichloride (20 cm^3). After being stirred at 25 °C for 2 h the reaction mixture was filtered and concentrated in vacuo to 5 cm^3. Excess *n*-hexane (~30 cm^3) was added. A green precipitate was obtained. This was washed with benzene (4 × 10 cm^3) and dried in vacuo to afford a green residue identified as **3b**. Mp: 164 °C (0.24 g, 80%). Anal. Calcd for $C_{31}H_{44}N_{15}P_3Cu_2Cl_6$: C, 35.14; H, 4.19; N, 19.83, Cu, 11.99. Found: C, 34.87; H, 4.41; N, 19.60; Cu, 11.42. Conductivity (mho cm^2 mol^{-1}, CH_3CN): 4.164. IR (cm^{-1}, CsI): 2950 (m), 1570 (s), 1450 (m), 1410 (m), 1375 (m), 1300 (m), 1240 (vs), 1190 (vs), 1142 (vs), 1110 (m), 1080 (m), 1042 (m), 970 (m), 870 (m), 800 (m), 770 (m), 615 (m), 570 (vs), 512 (vs), 450 (m), ^1H NMR ($CDCl_3$, ppm), 5.9 (br), 2.17 (br). ^{31}P ($CDCl_3$, ppm): no signal could be detected, presumably due to the large line widths of the signals.

Synthesis of HPCTP·$CuBr_2$ (3c). HPCTP (0.21 g, 0.3 mmol) and anhydrous $CuBr_2$ (0.067 g, 0.3 mmol) were taken together in 30 cm^3 of methylene dichloride and stirred at 25 °C for 30 min. The solution was concentrated to 5 cm^3 and anhydrous diethyl ether (30 cm^3) added. This was filtered to discard a small amount of HPCTP·2$CuBr_2$ (**3d**) and the filtrate was again concentrated to 5 cm^3 and addition of *n*-hexane (30 cm^3) afforded the yellowish green compound (**3c**) (0.46 g, 95% yield). Mp: 168 °C. Anal. Calcd for $C_{30}H_{42}N_{15}P_3\,CuBr_2$: C, 38.79; H, 4.56; N, 22.62; Cu, 6.84. Found, C, 38.42, H, 4.25; N, 22.30; Cu, 6.50. Conductivity (mho cm^2 mol^{-1}, CH_3CN): 4.114. IR (cm^{-1}, (CsI): 2950 (m), 1572 (s), 1460 (s), 1410 (s), 1370 (m), 1292 (s), 1231 (vs), 1200 (vs), 1171 (sh), 1143 (s), 1080 (m), 1040 (m), 1018 (m), 960 (s), 900 (m), 800 (m), 770 (m), 620 (m), 578 (vs), 520 (sh), 505 (s), 470 (m), 940 (m). ^1H NMR ($CDCl_3$, ppm): 5.91 (br), 2.41 (br), 2.20, 2.19. ^{31}P NMR ($CDCl_3$, ppm): –0.85, –2.55 (br).

Synthesis of HPCTP·2$CuBr_2$ (3d). HPCTP (0.21 g, 0.29 mmol) and anhydrous $CuBr_2$ (0.13 g, 0.6 mmol) were reacted as above in methylene dichloride. Addition of diethyl ether (30 cm^3) to the concentrated reaction mixture afforded **3d** as a brown powder (0.30 g, 90% yield). Mp: 173 °C. Anal. Calcd for $C_{30}H_{42}N_{15}P_3Cu_2Br_4$: C, 31.27; H, 3.67; N, 18.23, Cu, 11.03. Found: C, 30.96; H, 3.42, N, 18.01; Cu, 10.83. Conductivity (mho cm^2 mol^{-1}): 6.224. IR (cm^{-1}, CsI): 2950 (m), 1560 (s), 1450 (m), 1410 (m), 1370 (m), 1340 (m), 1295 (m), 1245 (vs), 1160 (vs), 1140 (sh), 1047 (s), 975 (m), 840 (s), 570 (s), 520 (s). ^1H NMR ($CDCl_3$, ppm): 5.89 (br), 2.63 (br). ^{31}P NMR ($CDCl_3$, ppm): –0.17, –4.2 (br).

Reactions of HPCTP with an excess of $CuCl_2$ or $CuBr_2$ in the above reaction conditions or in more forcing conditions (heating under reflux in methylene dichloride) always afforded either **3b** or **3d**. No complexes could be isolated incorporating more than two copper atoms per mole of the cyclophosphazene ligand.

X-ray Analysis of HPCTP·$CuCl_2$ (3a). A suitable green-colored crystal with approximate dimensions of 0.14 × 0.36 × 0.50 mm obtained by recrystallization from CH_2Cl_2–hexane, was glued on the top of a glass fiber and mounted on an Enraf-Nonius CAD-4 diffractometer. Unit cell dimensions and their standard deviations were determined from 25 reflections with 2θ angles in the range 16.00–17.5°. Intensity data were collected by the $\omega/2\theta$ scan method using variable scan sweep (4–16° min^{-1}) scan width $(1.0 + 0.35 \tan\theta)°$ and monochromatic Mo Kα radiation in the 2θ range 2–47.8° with $h = -24$ to $+23$, $k = 0$ to 13 and $l = 0$ to 20. Three reflections were monitored every 2 h of exposure time and showed insignificant variations. The intensities of 6945 reflections were measured of which 3486 had $I \geq 3\sigma(I)$. Data were corrected for Lorentz, polarization and absorption effects,[11] the correction range for absorption being 0.76–0.70. Crystal data are given in Table I.

The structure was solved by direct methods (SHELX). Refinement of the structure was by the full-matrix least-squares method, first with

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Table I. Crystallographic Data for HPCTP·$CuCl_2$ (**3a**)

chem formula: $C_{31}H_{44}N_{15}CuCl_4P_3$	fw = 925.06
a = 21.338 (4) Å	space group: $P2_1/n$
b = 11.432 (3) Å	λ = 0.7093 Å
c = 18.285 (3) Å	ρ_{calcd} = 1.422 Mg m^{-3}
β = 104.37 (2)°	μ = 0.78 mm^{-1}
V = 4321 (2) $Å^3$	R = 0.0409
Z = 4	R_w = 0.049

isotropic and subsequently with anisotropic temperature factors for the non-hydrogen atoms. Most hydrogen atom positions were located on a difference Fourier map. The hydrogen atoms were ultimately included with their positions calculated using sp^2 or sp^3 hybridization at the appropriate C atom with a fixed C–H distance of 0.95 Å, the H atoms found served to determine the conformation of the methyl groups. These were included in the subsequent cycles of refinement with isotropic temperature factors. Refinement converged with R = 0.049 and R_w = 0.049. In the refinement cycles, weights were derived from the counting statistics. Scattering factors were from ref 31. A final difference map calculated at the conclusion of the refinement had no chemically significant features. The computer program used was NRC 386[12] (PC version of NRC VAX).

Results and Discussion

Synthesis. Basicity studies on several cyclophosphazenes have shown that the ring nitrogen atoms are considerably more basic than exocyclic nitrogen atoms.[13] Therefore, protonation or complexation with metals is expected to occur preferably at the ring nitrogen site. This has been verified in many examples such as $[N_3P_3(NMe_2)_6H]_2^+[Mo_6O_{19}]^{2-}$,[14] $N_4P_4(NHMe_8)\cdot PtCl_2$,[15] $[HN_4P_4(CH_3)_8\cdot CuCl_3]$,[16] etc. However, in the case of pyrazolyl phosphazenes the geminal exocyclic pyridinic nitrogen atoms have been shown to coordinate to metals such as Pd and Pt.[8] In contrast, recently Krishnamurthy[17] and co-workers have demonstrated that in the complex *gem*-$N_3P_3(C_6H_5)_4(3,5\text{-}Me_2Pz)_2\cdot Mo(CO)_3$, two geminal exocyclic nitrogen atoms and one adjacent ring nitrogen atom are involved in coordination to the metal. It is clear that the mode of complexation must also be dependent on the nature of the transition metal ion involved. In order to gain a better understanding of these systems, we have investigated the reactions of HPCTP with copper(II) halides in several molar ratios.

The mono- and dimetallated derivatives HPCTP·CuX_2 [X = Cl, **3a**; X = Br, **3b**) and HPCTP·$2CuX_2$ (X = Cl, **3c**; X = Br, **3d**) are readily obtained as crystallizable solids from the reactions of HPCTP with copper(II) halides in a 1:1 or a 1:2 molar ratio in methylene dichloride at 25 °C. Compounds of the type HPCTP·$3CuX_2$ could not be isolated under any reaction conditions, suggesting that a purely geminal mode of coordination from two exocyclic nitrogens as observed earlier[8] with PdX_2 or PtX_2 might not be present in compounds **3a**–**3d**. Conductivity data for **3a**–**3d** in acetonitrile clearly indicates that the chlorides are bound to copper in the coordination sphere while magnetic susceptibility data rule out any significant magnetic interaction between the copper atoms in the 1:2 compounds **3c** and **3d**.

It is known that metallation and protonation of ring nitrogen atoms in cyclophosphazenes leads to a splitting of ring P–N stretching frequency which is observed usually between 1190 and 1300 cm^{-1}.[2d] On the contrary, if coordination is exclusively through exocyclic nitrogen atoms the ring P–N stretching frequency remains largely unaffected.[8] In the free ligand HPCTP the ring P–N stretching frequency is seen around 1220 cm^{-1}. In compounds **3a**–**3d** a splitting of the parent P-N stretching frequency is seen and two peaks, one between 1230 and 1243 cm^{-1}, and another between 1190 and 1200 cm^{-1} are observed. This suggests the possibility that the ring nitrogen atoms are also involved in coordination to the copper atom. NMR data (^1H and ^{31}P) are not very informative since the spectra show poorly resolved and broad peaks.

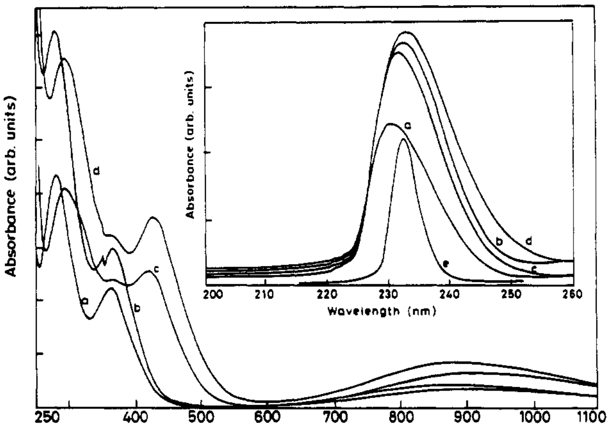

Figure 1. UV–vis spectra of complexes **3a**–**3d** (a–d) along with the ligand HPCTP **3** (inset) in methylene dichloride solution.

Optical Spectra. The electronic spectra of the complexes (**3a**–**3d**) and the free ligand HPCTP are shown in Figure 1. The data are presented in Table II.

Two strong and well-resolved transitions near 277 and 360 nm are seen for all of the complexes (**3a**–**3d**). On the basis of earlier work by Schugar and co-workers[18] on Cu(II)–pyrazole complexes, these absorptions could be assigned as predominantly due to π_2(pyrazole) → Cu(II) and π_1(pyrazole) → Cu(II) charge transfer conditions. The band at around 230 nm is attributed to the π–π^* intraligand transition with some contribution from n(pyrazole) → Cu(II) charge transfer. This overlap results in the broadness of this peak. In the chloro derivatives **3a** and **3b** the chloride → Cu(II) LMCT are probably buried in the high-energy transition at 277 nm. However, in the bromo complexes **3c** and **3d** a new low-energy absorption at 420 nm is seen which is assigned to a bromide → Cu(II) LMCT based on data available for similar bromo derivatives.[19] In acetonitrile, complexes **3a** and **3b** exhibit a new band at 457 nm with low extinction coefficients (Table II). At present the origin of this peak is not clear.

It is generally accepted that the presence of a single d–d absorption with a high-energy shoulder for copper complexes is suggestive of a trigonal bipyramidal geometry around copper,[20] although the absence of such a high-energy shoulder is not necessarily indicative of alternate geometries.[21] The copper complexes of HPCTP (**3a**–**3d**) show a single broad absorption between 870 and 950 nm. In acetonitrile, **3d** exhibits a high-energy shoulder at 641 nm indicating a TBP geometry around copper. The spectrum remains virtually unchanged in methylene dichloride and in the mull transmittance suggesting that the solution structures are retained in the solid state as well.

Electron Spin Resonance. ESR spectra of trigonal bipyramidal copper(II) complexes are characterized by an axial symmetry with $g_\perp > g_\parallel \simeq 2.0$. Usually a hyperfine structure is seen in the $g_\parallel$ region with $A_\parallel$ being in the range (60–100) × 10^{-4} cm^{-1}. The

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Table II. Electronic Spectral Data (λ, nm (ε, M^{-1} cm^{-1}))

				CT			
no.	compound		d–d	$\pi_2(p_z) \rightarrow Cu(II)$	$\pi_1(p_z) \rightarrow Cu(II)$	others	$\pi-\pi^*$ intraligand or $n(p_z) \rightarrow Cu(II)$
3	HPCTP	*a*					234.2 (7830)
3a	HPCTP·$CuCl_2$	*a*	902 (237)	279 (2860)	361 (1458)		230.7 (23 998)
		b	949 (246.7)	276 (2790)	358 (1243)	458 (166.7)	224.6 (26 869)
		c	909	300	390		251
3b	HPCTP·$2CuCl_2$	*a*	877 (472)	277 (7734)	364 (3269)		232.6 (39 878)
		b	905 (486.7)	277 (5643)	363 (3093)	457 (443.3)	225.2 (50 920)
		c	876	300	395		249
3c	HPCTP·$CuBr_2$	*a*	902 (426)	293 (2645)	364 (1547)	419 (1651)	231.7 (34 244)
		b	930 (380)	295 (2107)	365 (1267)	412 (1320)	223.2 (50 133)
		c	900	299	423	464	246
3d	HPCTP·$3CuBr_2$	*a*	885 (729)	291 (5686)	361 (2801)	427 (3090)	233 (41 363)
		b	905 (797) 641 (250)	295 (4740)	360 (3020)	424 (3227)	223.6 (68 500)
		c	876	299	431	465	248
4	$Cu(Im)_3Cl_2$[f]	*d*	952, 758				
5	$[Cu_2(bpeac)OAc]^{2+}$[g]	*e*	778 (163)	290 (7400)			~300
6	$Cu(Pz)_4(ClO_4)_2$[h]	*e*	629 (73)	311 (1490)	353.4 (1570)		218 (41 200)

[a] Methylene chloride solution. [b] Acetonitrile solution. [c] Mull transmittance. [d] Diffuse reflectance. [e] Methanol solution. [f] Taken from ref 23. [g] Taken from: Sorrell, T. N.; O'Connor, C. J. O.; Anderson, O. P.; Ribenspies, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 4199. [h] Taken from ref 18; Pz = 3,5-dimethylpyrazole.

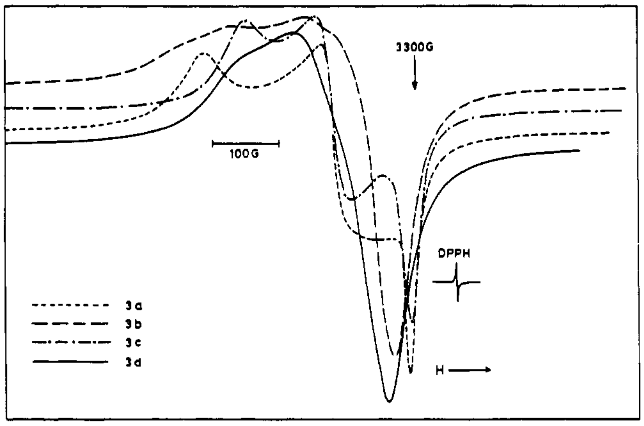

Figure 2. ESR spectra of complexes **3a**–**3d**.

Table III. ESR and Magnetic Moment Data

compound	g_1	g_2	g_3	$g_\parallel$	$g_\perp$	μ_{eff}, μ_B
HPCTP·$CuCl_2$[a]	2.255	2.119	2.046			1.733
HPCTP·$2CuCl_2$[a,b]				2.223	2.059	1.672
HPCTP·$CuBr_2$[a]	2.210	2.119	2.048			1.758
HPCTP·$2CuBr_2$[a]				2.211	2.065	1.634
$Cu(Im)_3Cl_2$[c]	2.21	2.16	2.06			1.76
$[Cu(NTB)Cl]PF_6 \cdot H_2O$[d]				1.996	2.233	1.9

[a] g_{iso} values in CH_3CN solution at room temperature are 2.138, 2.135, 2.128, and 2.124 respectively. [b] $A_\parallel$ observed in this case is 117×10^{-4} cm^{-1}. [c] Im = 1,2-dimethylimidazole; taken from ref 23. [d] NTB = tris(2-benzimidazolylmethyl)amine; $A_\parallel = 69 \times 10^{-4}$ cm^{-1}: Addision, A. W.; Hendriks, K. M. J.; Reedijk, J.; Thompson, L. K. *Inorg. Chem.* **1981**, *201*, 103.

reversed pattern of $g_\parallel > g_\perp \simeq 2.0$ observed for compounds **3b** and **3d** (Figure 2, Table III) indicates a distorted TBP geometry around copper.[22] The $A_\parallel$ value calculated from the resolved hyperfine structure for **3b** is 117×10^{-4} cm^{-1}. Compounds **3a** and **3c** show a rhombic symmetry in the ESR spectrum, and the lowest principal *g* values are 2.040 and 2.048, respectively. These are closely related to the values observed for the structurally analogous compounds $Cu(Im)_3Cl_2$[23] and $[Cu(nnss')Br]ClO_4$[22b] where the geometry around copper has been shown to be trigonal bipyramidal by single-crystal X-ray studies.[22b,23] It is also clear from the ESR spectra of the dinuclear complexes **3c** and **3d** that both copper atoms are present in identical coordination environments. Thus, the above facts clearly suggest that the coordination geometry around Cu in the complexes (**3a**–**3d**) is distorted trigonal bipyramidal. This estimate is confirmed by an X-ray analysis of **3a**.

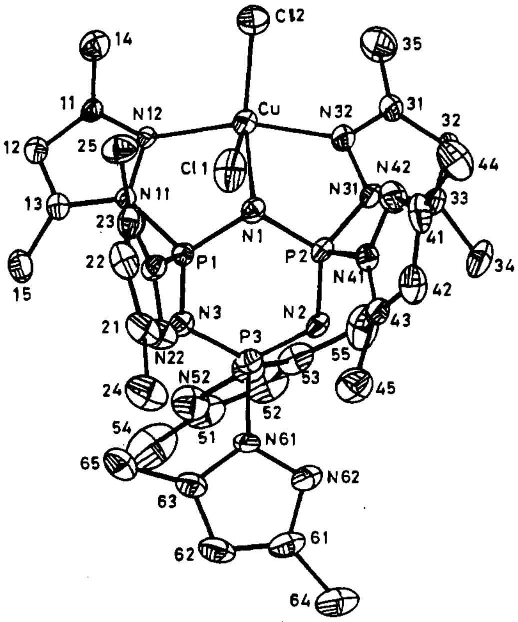

Figure 3. Ortep diagram of **3a** with hydrogen atoms omitted for clarity.

X-ray Structure of HPCTP·$CuCl_2$ (3a). An ortep diagram of **3a** with atomic numbering scheme is given in Figure 3. Selected bond lengths and angles are given in Table IV. Atomic positional parameters are given in Table V.

The X-ray determination of HPCTP·$CuCl_2$ (**3a**) indicates that the molecule consists of the cyclophosphazene ring functioning as an unprecedented N_3 ligand. The copper metal atom is coordinated to two pyridinic atoms from the nongeminal 3,5-dimethylpyrazolyl substituents on P(1) and P(2), to one cyclophosphazene ring nitrogen atom, N(1), and to two chloride ligands. The geometry around copper atom is distorted trigonal bipyramidal with the two chlorides and the ring nitrogen atom occupying the equatorial positions. The axial sites are taken by the nitrogens of the pyrazole (N(12) and N(32)). The distortion in the geometry is as a result of the steric constraints imposed by the coordination behavior of the ligand. This is reflected in the narrowing of the axial N(12)–Cu–N(32) (160.74°) and the equatorial N(1)–Cu–

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(22) (a) Barbacu, R.; Bencini, A.; Gatteschi, D. *Inorg. Chem.* **1977**, *16*, 2117. (b) nnss' = *N*-(2-pyridylmethyl)-*N*,*N*-bis(2-methylthioethyl)amine: Takahashi, K.; Ogawa, E.; Osihi, N.; Nishida, Y.; Kida, S. *Inorg. Chim. Acta.* **1982**, *66*, 97.

(23) Hug, F.; Skapski, A. C. *J. Chem. Soc., A* **1971**, 1927.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for HPCTP·CuCl$_2$ **3a**

Bond Lengths			
Cu–Cl(1)	2.2676 (21)	P(3)–N(2)	1.575 (5)
Cu–Cl(2)	2.2429 (19)	P(3)–N(3)	1.578 (5)
Cu–N(1)	2.360 (5)	P(1)–N(11)	1.693 (5)
Cu–N(12)	1.988 (5)	P(1)–N(21)	1.676 (5)
Cu–N(32)	1.974 (5)	P(2)–N(31)	1.690 (5)
P(1)–N(1)	1.596 (5)	P(2)–N(41)	1.672 (6)
P(1)–N(3)	1.564 (5)	P(3)–N(51)	1.680 (6)
P(2)–N(1)	1.589 (5)	P(3)–N(61)	1.679 (5)
P(2)–N(2)	1.574 (5)		
Bond Angles			
Cl(1)–Cu–Cl(2)	142.28 (10)	N(1)–P(1)–N(3)	118.22 (24)
Cl(1)–Cu–N(1)	108.32 (13)	N(1)–P(2)–N(2)	117.7 (3)
Cl(2)–Cu–N(1)	109.40 (13)	N(2)–P(3)–N(3)	117.2 (3)
Cl(1)–Cu–N(12)	88.85 (15)	P(1)–N(1)–P(2)	118.4 (3)
Cl(2)–Cu–N(12)	96.53 (14)	P(2)–N(2)–P(3)	122.5 (3)
Cl(1)–Cu–N(32)	91.30 (16)	P(1)–N(3)–P(3)	121.3 (3)
Cl(2)–Cu–N(32)	95.09 (16)	N(11)–P(1)–N(21)	101.07 (25)
N(12)–Cu–N(32)	160.74 (21)	N(17)–P(2)–N(41)	101.4 (3)
N(1)–Cu–N(12)	81.00 (18)	N(51)–P(3)–N(61)	102.7 (3)
N(1)–Cu–N(32)	80.68 (19)		

Table V. Atomic Parameters *x*, *y*, *z* and B_{iso}, Where Esd's Refer to the Last Digit Printed

	x	*y*	*z*	B_{iso},[a] Å^2
Cu	0.10654 (4)	0.14626 (7)	0.38555 (4)	2.75 (4)
P(1)	0.16584 (8)	0.32642 (14)	0.52101 (9)	2.44 (7)
P(2)	0.17183 (8)	0.40237 (15)	0.38102 (9)	2.59 (8)
P(3)	0.28382 (8)	0.37279 (16)	0.49355 (9)	2.73 (8)
Cl(1)	0.19920 (10)	0.04098 (19)	0.40381 (11)	5.45 (11)
Cl(2)	–0.00089 (8)	0.13260 (22)	0.33950 (10)	6.02 (12)
Cl(3)	0.80174 (19)	0.5155 (3)	0.18509 (19)	13.2 (3)
Cl(4)	0.83296 (18)	0.6525 (4)	0.0697 (3)	15.9 (3)
N(1)	0.13313 (21)	0.3368 (4)	0.43272 (24)	2.33 (24)
N(2)	0.24685 (23)	0.4188 (4)	0.4132 (3)	2.68 (24)
N(3)	0.24133 (22)	0.3301 (4)	0.54780 (25)	2.73 (25)
N(11)	0.13732 (23)	0.1991 (4)	0.5473 (3)	2.47 (25)
N(12)	0.10699 (22)	0.1186 (4)	0.4930 (3)	2.47 (23)
N(21)	0.1344 (3)	0.4232 (4)	0.5708 (3)	2.7 (3)
N(22)	0.1718 (3)	0.5211 (5)	0.5974 (3)	3.7 (3)
N(31)	0.15432 (23)	0.3264 (4)	0.2992 (3)	2.64 (24)
N(32)	0.12267 (24)	0.2200 (5)	0.2943 (3)	3.0 (3)
N(41)	0.1406 (3)	0.5334 (5)	0.3520 (3)	3.2 (3)
N(42)	0.0791 (3)	0.5320 (6)	0.3017 (3)	4.3 (3)
N(51)	0.3349 (3)	0.2663 (5)	0.4823 (3)	3.7 (3)
N(52)	0.3721 (3)	0.2261 (6)	0.5506 (4)	5.4 (4)
N(61)	0.33415 (24)	0.4771 (5)	0.5387 (3)	3.1 (3)
N(62)	0.3700 (3)	0.5327 (5)	0.4953 (3)	3.9 (3)
C(1)	0.7914 (5)	0.5339 (9)	0.0915 (6)	8.6 (6)
C(11)	0.0979 (3)	0.0248 (6)	0.5307 (3)	2.6 (3)
C(12)	0.1206 (3)	0.0428 (6)	0.6088 (3)	3.4 (3)
C(13)	0.1458 (3)	0.1529 (6)	0.6186 (3)	3.1 (3)
C(14)	0.0687 (3)	–0.0836 (6)	0.4909 (4)	4.1 (4)
C(15)	0.1776 (4)	0.2173 (7)	0.6887 (4)	5.0 (4)
C(21)	0.1336 (4)	0.5885 (6)	0.6248 (4)	3.9 (4)
C(22)	0.0727 (4)	0.5396 (7)	0.6169 (4)	4.3 (4)
C(23)	0.0725 (3)	0.4350 (6)	0.5822 (4)	3.5 (4)
C(24)	0.1585 (4)	0.7046 (7)	0.6591 (5)	7.0 (5)
C(25)	0.0211 (3)	0.3462 (7)	0.5570 (4)	4.8 (4)
C(31)	0.1193 (3)	0.1798 (7)	0.2249 (4)	3.9 (4)
C(32)	0.1481 (3)	0.2588 (7)	0.1859 (4)	4.0 (4)
C(33)	0.1700 (3)	0.3490 (7)	0.2319 (3)	3.6 (3)
C(34)	0.2040 (4)	0.4592 (8)	0.2195 (4)	7.0 (5)
C(35)	0.0891 (5)	0.0640 (8)	0.2013 (4)	6.6 (5)
C(41)	0.0620 (4)	0.6437 (8)	0.2914 (4)	4.6 (4)
C(42)	0.1102 (4)	0.7162 (6)	0.3349 (4)	4.4 (4)
C(43)	0.1583 (3)	0.6474 (7)	0.3730 (4)	3.5 (4)
C(44)	–0.0008 (4)	0.6760 (8)	0.2403 (5)	7.1 (5)
C(45)	0.2193 (4)	0.6786 (7)	0.4291 (5)	5.7 (5)
C(51)	0.4143 (4)	0.1546 (8)	0.5309 (7)	6.3 (5)
C(52)	0.4040 (4)	0.1501 (8)	0.4530 (7)	6.4 (6)
C(53)	0.3555 (4)	0.2216 (7)	0.4222 (5)	4.5 (4)
C(54)	0.4631 (5)	0.0939 (10)	0.5911 (7)	10.6 (8)
C(55)	0.3267 (5)	0.2531 (8)	0.3427 (5)	6.7 (5)
C(61)	0.4178 (4)	0.5816 (7)	0.5457 (5)	4.5 (4)
C(62)	0.4145 (4)	0.5576 (7)	0.6196 (4)	4.6 (4)
C(63)	0.3617 (3)	0.4890 (6)	0.6147 (4)	3.5 (3)
C(64)	0.4671 (4)	0.6529 (8)	0.5214 (5)	7.4 (5)
C(65)	0.3387 (4)	0.4359 (8)	0.6768 (4)	5.3 (4)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Cl(1) (108.3°), N(1)–Cu–Cl(2) (109.4°) bond angles and a widening of the equatorial Cl(1)–Cu–Cl(2) (142.28°) angle. The Cu–N axial bond distances (average: 1.981 Å) are smaller than the equatorial Cu–N distance (2.360 Å); the ring nitrogen to copper coordination is much weaker than the pyridinic nitrogen interaction. In a related structure the observed bond distances are Cu–N$_{eq}$ = 2.145 Å, Cu–N$_{ax}$ = 2.005 Å, and Cu–Cl$_{eq}$ = 2.414 and 2.170 Å, respectively.[23] The coordination to the copper metal atom by the cyclophosphazene ring undoubtedly affects the structure of the inorganic heterocyclic system. The six membered ring adopts a distorted conformation with the ring nitrogens N(2) (+0.130 Å) and N(1) (–0.265 Å) displaced away from a mean plane defined by P(1), P(3), P(2), and N(3). This kind of a distortion of the ring structure upon coordination to metals is seen in many other examples.[24,25]

Complex formation with copper also affects the bond lengths and bond angles of the cyclophosphazene ligand. Several structural studies on cyclophosphazenes have conclusively shown that either protonation or coordination of a metal to the ring nitrogen atom increases the P–N bond distances involved with that nitrogen atom.[2d] This feature has been interpreted as due to a nonavailability of the lone pair on the nitrogen concerned for participation in skeletal π-bonding, thereby resulting in a decrease in the π-bond character.[26] In the present structure these are longer (average 1.593 Å) in comparison with other P–N bond lengths (average 1.573 Å). These differences are much smaller, however, than those observed in many instances. Thus in $N_4P_4(NHMe)_8 \cdot PtCl_2$, where the coordination to platinum metal atom occurs through the antipodal ring nitrogen atoms, the P–N distances observed are 1.64 and 1.58 Å, respectively. Similarly in $N_4P_4(CH_3)_8 \cdot H \cdot CuCl_3$ the coordination to the metal occurs through the ring nitrogen. The P–N bond lengths involved (1.635 Å average) are again longer than observed for **3a**. This indicates clearly that in **3a** the interaction between the ring nitrogen and the copper atom is weaker as is reflected in the Cu–N(1) bond distance as well. The ring bond angles are unexceptional. Exocyclic P–N bond distances involving the coordinating pyrazolyl group are slightly longer (average 1.692 Å) than those involving the noncoordinating pyrazolyl group (1.667 Å).

Electrochemical Studies. There are no earlier reports of electrochemical studies on any cyclophosphazene metal complexes except certain ferrocenyl-substituted derivatives.[27] In view of the interest in the redox chemistry of copper complexes containing pyrazolyl or imidazolyl residues,[28] we have carried out a cyclic voltammetric investigation on compounds **3a**–**3d**. The cyclic voltammograms recorded for complexes **3a**–**3c** are shown in Figure 4. Table VI summarizes the electrochemical parameters. Analysis of the cyclic voltammetric responses for mononuclear complexes **3a** and **3c** with scan rates varying from 0.02 to 51.2 V s^{-1} showed a simple quasi-reversible one-electron charge transfer for the Cu(II)/Cu(I) couple which is located at a relatively positive potential, 0.204 and 0.501 V, respectively: the anodic to cathodic peak current ratio i_{p_a}/i_{p_c} is constantly equal to one. The ratio between the cathodic peak current and the square root of the scan rate i_{p_c} and $V^{-1/2}$ is practically constant. The difference between

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[24] Allcock, H. R.; Suszko, P. R.; Wayner, L. J.; Whittle, R. R.; Boso, B. *Organometallics* **1985**, *4*, 446.

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[28] Zanello, P. *Comments Inorg. Chem.* **1988**, *8* (1 & 2) 45.

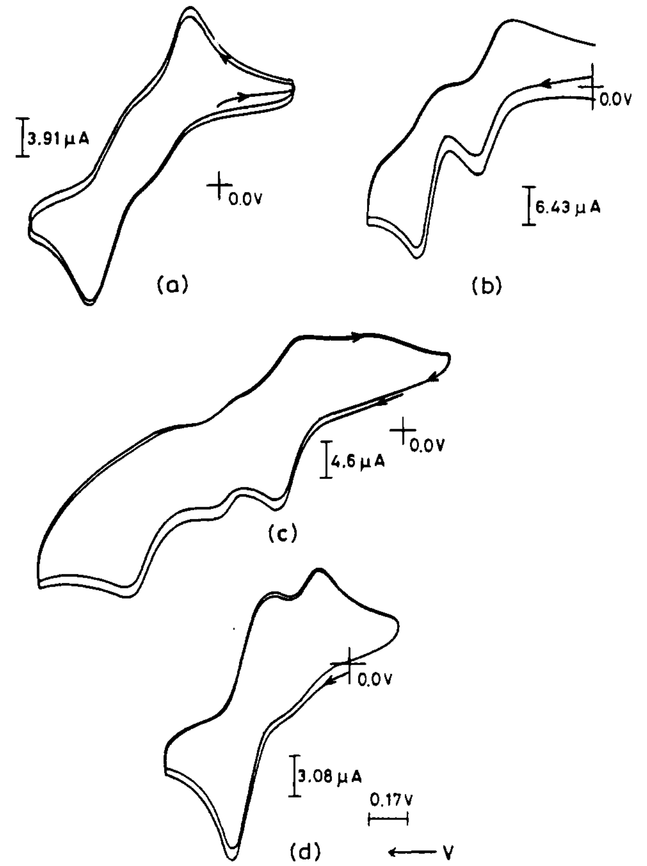


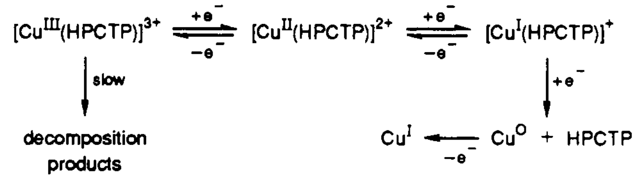
Figure 4. Cyclic voltammograms of complexes **3a** in CH_2Cl_2 (a), **3b** in DMF (b), **3b** in CH_2Cl_2 (c) and **3c** in DMF (d).

Table VI. Redox Properties of HPCTP Complexes

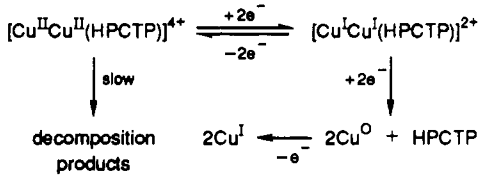
compound	solvent	potential[a]	ΔE_p[b]	processes[c]
HPCTP·$CuCl_2$ (**3a**)	CH_2Cl_2	+0.204	160	q, R
		+0.453	160	q, O
		+1.580		i, O
HPCTP·$2CuCl_2$ (**3b**)	CH_2Cl_2	+0.499	221	q, R
		+1.612		i, O
		-1.287		i, R
	DMF	+0.451	158	q, R
		+1.591		i, O
		-0.756		i, R
HPCTP·$CuBr_2$ (**3c**)	CH_2Cl_2	+0.501	124	q, R
		+1.125	141	q, O
		+1.680		i, O
		-1.336		i, R
	DMF	+0.435	130	q, R
		+0.727	111	q, O
		+1.620		i, O
		-1.456		i, R
HPCTP·$2CuBr_2$ (**3d**)	CH_2Cl_2	+0.591	103	q, R
		+1.181		q, O
		+1.594		i, O
		-1.275		i, R

[a] In volts vs Ag/AgCl reference electrode; $E_{1/2} = (E_c + E_a)/2$. [b] ΔE_p values for 100 mV/s scan rate in volts. [c] q = quasireversible; i = irreversible; R = reduction; O = oxidation.

the potential of the anodic peak and that of the cathodic peak ΔE_p gradually increases. However, the corresponding process in the dinuclear complexes **3b** and **3d** is indicative of a simultaneous two-electron transfer (Cu(II)–Cu(II) $\leftrightarrow$ Cu(I)–Cu(I)) and does not proceed by a stepwise process [Cu(II)–Cu(II) $\overset{e}{\leftrightarrow}$ Cu(II)–Cu(I) $\overset{e}{\leftrightarrow}$ Cu(I)–Cu(I)]. The quasi reversibility of this electrode process is probably due to the stereochemical changes accompanying the Cu(II) $\overset{e}{\leftrightarrow}$ Cu(I) redox step from a trigonal bipyramid to a distorted tetrahedral geometry.[29] Since the highest Cu(II)/Cu(I) potentials are in principle expected for the reversible tetrahedral copper(II)/tetrahedral copper(I) redox change, it is likely that both the nonplanar geometries of the copper(II)–copper(I) couples and the electronic effects of the pyrazolyl groups act in concert to produce the notably positive location of the redox potentials of these complexes. The second cathodic step, Cu(I)–Cu(0), proceeds always in an irreversible manner, because of the extreme lability of the copper(0) complex. This is confirmed by the appearance of a strong characteristic stripping peak due to the reoxidation of electrodeposited copper metal to free copper ion. Nonplanar geometry around Cu(II) ion inhibits accessibility to a planar copper(III) assembly. This is reflected by the potentials of the Cu(III)/Cu(II) couples. An irreversible multielectron ligand centered anodic process is located at about +1.59 V invariably for all complexes. The redox behavior of mononuclear copper(II) complexes can be summarized as follows:



For dinuclear complexes the valid redox equation is



Conclusions

The coordination response of the pyrazolyl cyclophosphazenes is significantly dependent on the nature of the interacting metal ion. HPCTP behaves as an unusual capping tridentate N_3 ligand toward copper leading to mononuclear and dinuclear complexes. The X-ray structure of the mononuclear derivative **3a** shows that one face of the cyclophosphazene ligand is completely free. Evidently, it is this coordination sphere which interacts with the second metal atom, producing dinuclear complexes. This raises the possibility of the HPCTP ligand serving as a host for heterobimetallic systems.

Acknowledgment. V.C., K.R.J.T. and P.S.P. thank DST (India) for financial support. K.R.J.T. thanks IIT Kanpur for a fellowship. We are thankful to Prof. S. Sarkar (IIT Kanpur, India) for allowing use of cyclic voltammetric instrument.

Supplementary Material Available: Listing of anisotropic thermal parameters, hydrogen atom parameters, interatomic parameters, and mean plane information (Tables S(1)–S(4)) (9 pages). Ordering information is given on any current masthead page.

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