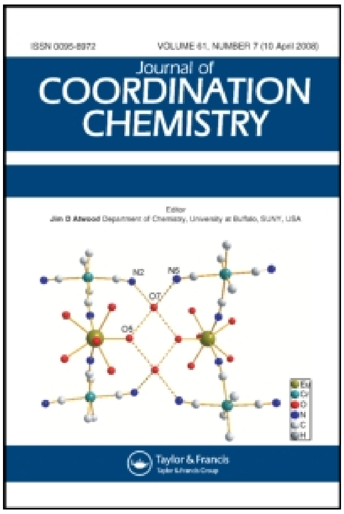

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HETEROBIMETALLIC (PD,PT,CU) COMPLEXES OF HEXAPYRAZOLYLCYCLOTRIPHOSPHAZENE *VIA* SIMULTANEOUS GEMINAL (N_2) AND NONGEMINAL (N_3) COORDINATION MODES

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HETEROBIMETALLIC (PD,PT,CU) COMPLEXES OF HEXAPYRAZOLYLCYCLOTRIPHOSPHAZENE *VIA* SIMULTANEOUS GEMINAL (N_2) AND NONGEMINAL (N_3) COORDINATION MODES

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Synthesis and spectroscopy of four heterobimetallic compounds containing the metal centres Cu(II)-Pd(II) and Cu(II)-Pt(II) with the multidentate nitrogen donor ligand hexakis (3,5-dimethylpyrazolyl)cyclotriphosphazene, (HPCTP) are reported. The complexes HPCTP·$CuCl_2$·MX_2 (M = Pd, X = Cl (3) or Br (4) and M = Pt, X = Cl (5) or Br (6)) were obtained by treating the metal-containing ligands HPCTP·CuX_2 X = Cl(1) or Br(2)) with $M(PhCN)_2Cl_2$(M = Pd or Pt). The electronic absorption spectra and electron paramagnetic resonance data indicate the copper in these compounds has a distorted trigonal bipyramidal geometry. A single crystal X-ray determination of 4 is reported. The crystals of 4 are monoclinic with a = 10.570(2), b = 28.863(4), c = 16.009(1)Å, β = 98.71(2)°, V = 4827(1)Å^3, Z = 4, D_c = 1.65 g cm^{-3} and space group $P2_1/c$. The geometry about copper is trigonal bipyramidal with mean distances of Cu-N(pz) = 1.987(13), Cu-N(ctp) = 2.352(11) and Cu-Cl = 2.315(10)Å while that of palladium is square planar with distances of Pd-N(pz) = 2.045(11) and Pd-Br = 2.384(6). While copper is coordinated through two nongeminal pyrazolyl nitrogen atoms and a cyclophosphazene ring nitrogen atom, coordination to palladium is through geminal pyrazolyl nitrogen atoms.

KEYWORDS: phosphazene, bimetallic, pyrazole, copper, palladium, complex

INTRODUCTION

There is continuing research in the synthesis and chemistry of metal-containing cyclophosphazene derivaties.[19] Several methodologies have been identified to attach metals to the cyclophosphazene skeleton; chief among them is using exocyclic donor groups bonded to the phosphorus atom.[6,7] Pyrazolycyclotriphosphazenes are potential multi-coordination ligands containing two different heterocyclic ring nitrogen donor atoms, the pyrazolyl and the cyclophosphazene skeletal nitrogen atoms.[8-10] The reaction of hexakis(3,5-dimethylpyrazolyl) cyclotriphosphazene

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(HPCTP) with $CuCl_2$ or $CuBr_2$ can be controlled to form 1:1 derivatives,[8] HPCTP·CuX_2(X = Cl(1) or Br(2)). In these complexes the copper is bound to HPCTP *via* two nongeminal pyrazolyl nitrogen atoms and one cyclophosphazene ring nitrogen atom in a distorted trigonal bipyramidal geometry (Scheme 1).[8] This leaves seveeral vacent coordination sites which can be utilized to bind additional metals. In order to test whether heterobimetallic compounds could be assembled with the metal-containing ligands 1 and 2 we have studied the reactions of these complexes with *trans*-$Pd(PhCN)_2Cl_2$ and *cis*-$Pt(PhCN)_2Cl_2$. This account describes the details of the synthesis and spectroscopic (IR, optical, EPR) studies on the heterobimetallic complexes HPCTP·$CuCl_2$·MX_2(M = Pd, X = Cl(3) or Br(4); M = Pt, X = Cl(5) or Br(6)). An X-ray crystal structure of the heterobimetallic complex HPCTP·$CuCl_2$·$PdBr_2$(4) has also been determined. It shows that copper retains its original coordination geometry as in 1 while palladium adopts a square planar geometry with coordination *via* the geminal pyrazolyl nitrogens which occupy *cis* positions.

EXPERIMENTAL

Materials

The precursor complexes HPCTP·CuX_2[X = Cl(1), X = Br(2)], *cis*-$Pt(PhCN)_2Cl_2$, and *trans*-$Pd(PhCN)_2Cl_2$ were made using known methods.[8,11] Dichloromethane, benzene, hexane and acetonitrile were distilled from P_2O_5 and stored over molecular sieves.

Synthesis of HPCTP·$CuCl_2$·$PdCl_2$·C_6H_6(3)

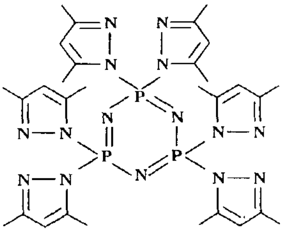
Solutions of HPCTP·$CuCl_2$ (168 mg, 0.2 mmol) in benzene (10 cm^3) and *trans*-$Pd(PhCN)_2Cl_2$ (76 mg, 0.2 mmol) in benzene (5 cm^3) were combined and stirred for 8 h at room temperature. The yellow precipitate formed was filtered off and washed with benzene and hexane. Crystallization from dichloromethane-benzene (1:1) afforded a yellow microcrystalline solid of 3. (190 mg, 93%), m.p. 209°C(dec), Λm (Scm^2 mol^{-1})5.5. *Anal.* Calcd. for $C_{36}H_{48}N_{15}$-P_3Cl_4CuPd(%): C, 39.5; H, 4.4; N, 19.2. Found: C, 39.65: H, 4.3; N, 19.2 IR(KBr, cm^{-1}): 1570m (C = N), 1460m, 1400 m, 1290 m, 1220 s(br) (P = N), 1140 s (P = N), 1100 m, 1050 m, 980 m, 970 m, 950 m, 800 w, 690 w and 680 w.

HPCTP·$CuCl_2$·$PdBr_2$·C_6H_6·H_2O (4)

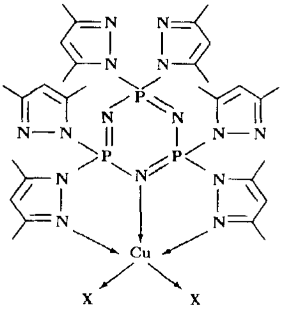
The compound was prepared in the form of brown crystals as described for 3 by using HPCTP·$CuBr_2$. Yield 85%, m.p. 192°C(dec), Λm (Scm^2 mol^{-1}) 8.5. *Anal.* Calcd.s for $C_{36}H_{50}N_{15}OP_3Cl_2Br_2CuPd$(%): C, 36.0; H, 4.2; N, 17.6. Found: C, 35.9; H, 4.2; N, 17.5 IR(KBr, cm^{-1}): 3450 w(br) (H_2O), 1570 m (C = N), 1460 m, 1410 m, 1290 m, 1220 s(br) (P = N), 1150 s (P = N), 1050 m, 985 m, 977 m, 960 m, 810 w and 690 w.

HPCTP·$CuCl_2$·$PtCl_2$·C_6H_6·H_2O (5)

To a solution of 1 (168 mg, 0.2 mmol) in benzene (10 cm^3) was added *cis*-$Pt(PhCN)_2Cl_2$ (94 mg, 0.2 mmol) and heated to reflux with stirring. After 24 h



HPCTP



1 X = Cl

2 X = Br

SCHEME 1

the mixture was filtered and concentrated to *ca*, 3 cm^3. Addition to 20 cm^3 of hexane yielded 220 mg (92%) of green microcrystalline solid. m.p. 142°C(dec), Λm (Scm^2mol^{-1}) 10.0. *Anal.* Calcd. for $C_{36}H_{50}N_{15}OP_3Cl_4CuPt$(%): C, 36.0; H, 4.2; N, 17.5. Found: C, 36.2; H, 4.15; N, 17.3 IR(KBr, cm^{-1}): 3450 m(br) (H_2O), 1555 m (C = N), 1450 m, 1390 m, 1280 m, 1215 s(br)(P = N), 1140 s (P = N), 1140 m, 940 m, 790 w and 670 m.

HPCTP·$CuCl_2$·$PtBr_2$·$1\frac{1}{2}C_6H_6$ (6)

This compound was prepared as described for 5. The reaction HPCTP·$CuBr_2$(186 mg, 0.2 mmol) and *cis*-$Pt(PhCN)_2Cl_2$(94 mg, 0.2 mmol) gave greenish yellow powder of 6 (250 mg, 95%), m.p. 148°C(dec), Λm $(Scm^2\ mol^{-1})$ 12.8: *Anal.* Calcd. for $C_{39}H_{51}N_{15}P_3Cl_2Br_2CuPt$(%): C, 35.7; H, 3.9; N, 16.0. Found: C, 35.5; H, 3.9; N, 15.95 IR(KBr, cm^{-1}): 1580 m (C = N), 1460 m, 1410 m, 1290 m, 1230s(br) (P = N), 1150 s (P = N), 960 m, 810 w, 765 m and 695 m.

Physical Measurements

Electronic absorption spectra in the 200–1100 nm range were recorded with a Shimadzu UV-160 spectrophotometer and infrared spectra (KBr pellets) with a Perkin Elmer model 1320 IR spectrophotometer. The solution conductivity was measured with a Century digital conductivity meter for solute concentrations of 10^{-3} M in acetonitrile. X-band EPR spectra were obtained with a Varian spectrometer, equipped with a variable temperature facility. The magnetic field strength was calibrated with dpph (g = 2.0036). The solution magnetic moments of the samples were obtained by the Evans NMR method.[12] Elemental analyses were obtained from the microanalytical laboratory situated at Central Drug Research Institute, Lucknow. Melting points were obtained using a hot plate and are uncorrected.

Structural Analysis and Refinements of 4

Crystals of 4 suitable for X-ray analysis were obtained from a 1:1 mixture of dichloromethane and benzene. A brown crystal (0.52 × 0.25 × 0.28 mm) 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 2σ in the range 17–20°. Data collection by the σ–2σ scan method using a variable scan sweep (4–16° min^{-1}) over the 2σ range 4–44° (h = 0 to 11, k = 0 to 30 and l = −16 to 16) yielded 3592 reflections with I >3.0σ(I). No decomposition of the crystal occurred during data collection. An absorption correction based on psi scans (0.85–1.0) was made. Table 1 summarizes the crystal formation. The fractional atomic coordinates are listed in Table 2.

Direct methods (SHELX)[13] were used for structure solution, and refinement was carried out by the full-matrix least-squares method using anisotropic thermal parameters for non-H, non-solvent atoms with $w = 4F^2/[\sigma^2(I) + 0.05I^2]$). Difference maps gave H atom orientations for methyl groups. H atoms bonded to C atoms were constrained to idealized (CH = 0.95Å) positions with isotropic thermal parameters 0.01 greaters than the U of the attached atom. The best model for the data set obtained included some disorder of the halogen atoms bonded to the Pd atom. For the final refinement two 0.4 Cl fragments were constrained to positions 2.33 Å from the Pd atom, along the Pd-Br vector, with fixed isotropic U values of

Table 1 Crystal and refinement data for 4

formula	$PdCuBr_{1.2}Cl_{2.8}P_3N_{15}C_{30}H_{42}\cdot C_6H_6\cdot H_2O$
fw	1166.9
space group	$P2_1/c$
a, Å	10.570(2)
b, Å	28.863(4)
c, Å	16.009(1)
β, deg	98.71(1)
V, $Å_3$	4827(1)
λ, Å	0.71073
Z	4
d(calcd), g cm^{-3}	1.61
temp, K	293
linear abs coeff, mm^{-1}	2.7
2Θ range, deg	4–44
data with I>3σ (I)	3592
parameters refined	505
$R(F^2)$, $Rw(F^2)$	0.059, 0.094

$R = [\Sigma\|F_o| - |F_c\|]/[\Sigma|F_o|]$

$R_w = \{[\Sigma w\|F_o| - |F_c\|^2]/[\Sigma(w|F_o|^2]\}^{1/2}$

Table 2 Positional parameters for 4 with e.s.d.'s in parentheses.

	x	*y*	*z*	Biso/Beq
Pd	0.08199(11)	0.87406(4)	0.03369(7)	2.72(5)
Cu	0.52420(18)	0.82988(6)	0.34877(12)	3.43(9)
Br1	0.1080(3)	0.93787(10)	-0.05733(17)	4.11(14)
Br2	0.2192(3)	0.82875(11)	-0.03852(19)	5.22(16)
Cl1	0.7185(3)	0.84174(13)	0.43284(22)	3.02(16)
Cl2	0.4016(3)	0.77474(12)	0.26720(22)	2.94(16)
Cl3	0.10730	0.93620	-0.05500	4.7
Cl4	0.21700	0.82960	-0.03690	4.7
P1	0.1307(4)	0.88170(12)	0.23349(22)	2.29(16)
P2	0.2835(4)	0.89309(13)	0.38557(22)	2.53(17)
P3	0.3769(4)	0.91330(13)	0.23867(23)	2.51(17)
O	0.2552(24)	0.6676(7)	0.2571(16)	15.1(7)
N1	-0.0298(11)	0.9119(4)	0.1031(6)	2.2(5)
N2	-0.0055(11)	0.9093(4)	0.1914(7)	2.7(6)
N3	0.1793(12)	0.9699(4)	0.4197(7)	3.4(6)
N4	0.2717(11)	0.9371(4)	0.4483(7)	2.8(6)
N5	0.3264(13)	0.8503(4)	0.4560(7)	3.2(6)
N6	0.4276(12)	0.8203(4)	0.4441(7)	3.3(6)
N7	0.0612(12)	0.8201(4)	0.1125(7)	2.8(6)
N8	0.0952(11)	0.8270(4)	0.2010(7)	2.8(6)
N9	0.5362(11)	0.9837(4)	0.2339(8)	3.2(6)
N10	0.4067(11)	0.9693(4)	0.2236(7)	2.7(5)
N11	0.4970(11)	0.8867(4)	0.1969(7)	2.8(5)
N12	0.5758(12)	0.8555(4)	0.2433(8)	3.2(6)
N13	0.1472(11)	0.8833(4)	0.3322(6)	2.6(6)
N14	0.4017(10)	0.8982(4)	0.3362(7)	2.7(5)
N15	0.2408(10)	0.9015(4)	0.1889(6)	2.5(5)
C1	-0.2025(15)	0.9428(6)	-0.0040(11)	4.3(9)
C2	-0.1385(15)	0.9338(5)	0.0848(9)	2.8(7)
C3	-0.1858(14)	0.9472(5)	0.1571(10)	3.5(7)
C4	-0.0996(14)	0.9302(4)	0.2246(9)	2.4(7)
C5	-0.1081(16)	0.9332(6)	0.3145(10)	4.3(8)
C6	0.1256(23)	1.0494(6)	0.4589(12)	7.0(13)
C7	0.2048(17)	1.0060(6)	0.4709(10)	4.0(9)
C8	0.3153(16)	0.9969(6)	0.5322(10)	4.0(8)
C9	0.3573(15)	0.9545(6)	0.5165(9)	3.5(8)
C10	0.4713(18)	0.9285(6)	0.5561(11)	5.5(10)
C11	0.1517(18)	0.8587(6)	0.5487(10)	4.7(9)
C12	0.2661(16)	0.8338(6)	0.5219(10)	4.1(9)
C13	0.3257(18)	0.7944(6)	0.5528(10)	4.5(9)
C14	0.4219(19)	0.7878(6)	0.5012(11)	4.7(9)
C15	0.5206(20)	0.7490(6)	0.5091(12)	5.9(10)
C16	-0.0257(18)	0.7582(5)	0.0163(11)	4.5(9)
C17	0.0215(14)	0.7776(6)	0.1007(9)	3.2(8)
C18	0.0303(16)	0.7553(5)	0.1793(10)	3.6(8)
C19	0.0770(14)	0.7862(5)	0.2419(9)	2.6(7)
C20	0.0919(17)	0.7806(6)	0.3334(10)	4.6(9)
C21	0.6548(18)	1.0554(7)	0.2297(13)	6.1(11)
C22	0.5328(16)	1.0277(6)	0.2259(9)	3.6(8)
C23	0.4055(17)	1.0439(5)	0.2143(10)	3.8(9)
C24	0.3240(15)	1.0065(6)	0.2117(9)	3.4(8)
C25	0.1800(16)	1.0031(5)	0.2019(10)	4.0(8)
C26	0.4528(17)	0.9212(6)	0.0470(10)	4.5(9)
C27	0.5215(15)	0.8899(5)	0.1134(10)	3.4(8)
C28	0.6157(15)	0.8591(5)	0.1105(11)	3.5(8)
C29	0.6463(15)	0.8383(5)	0.1907(11)	3.6(8)

Table 2 — *Continued*

C30	0.7420(19)	0.8040(8)	0.2196(13)	6.7(12)
C1B	0.857(3)	0.8495(15)	0.8100(25)	6.0(4)
C2B	0.841(3)	0.8546(14)	0.722(3)	6.0(4)
C3B	0.724(4)	0.8441(16)	0.6738(12)	6.0(4)
C4B	0.6224(25)	0.8285(15)	0.7129(24)	6.0(4)
C5B	0.638(3)	0.8234(14)	0.800(3)	6.0(4)
C6B	0.756(4)	0.8339(15)	0.8491(12)	6.0(4)
C7B	0.677(5)	0.8366(17)	0.6763(19)	7.6(5)
C8B	0.6263(25)	0.8229(16)	0.748(3)	7.6(5)
C9B	0.702(5)	0.8251(16)	0.8274(23)	7.6(5)
C10B	0.827(5)	0.8411(17)	0.8351(20)	7.6(5)
C11B	0.878(3)	0.8548(16)	0.763(4)	7.6(5)
C12B	0.803(5)	0.8526(16)	0.6840(24)	7.6(5)
HW1	0.23582	0.66915	0.30978	15.9
HW2	0.28058	0.69433	0.25974	15.9

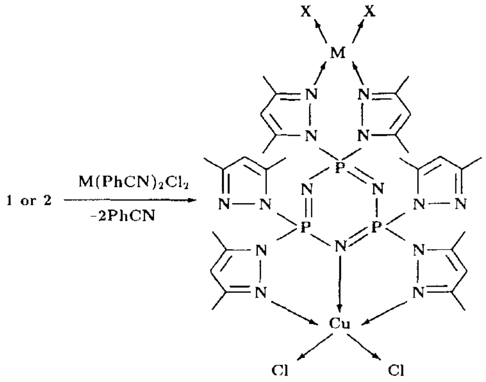
Beq is the mean of the principal axes of the thermal ellipsoid.

0.06. The benzene molecule was determined to occupy a cavity in two orientations in a 0.5:0.5 ratio. These orientations are nearly coplanar; the difference lies primarily in a rotation of about 30 degrees about the six-fold axis. The molecules were idealized and refined as individual rigid groups. A water molecule was found to occupy a cavity between halogens of adjacent molecules. The oxygen atom's position suggests a weak H-bond interaction with a bromine atom. Scattering factors were from ref. 14. A final difference map revealed no chemically significant features. The relatively high value of R is attributed to inability to exactly model the disorder of the included solvent molecules. The computer programs used were those of NRC386 (PC version of NRCVAX).[15]

RESULTS AND DISCUSSION

The reactions of the preformed complexes HPCTP·CuX$_2$ (X = Cl or Br 2) with M(PhCN)$_2$Cl$_2$ (M = Pd or Pt) in equimolar ratios in benzene give heterobimetallic compounds with the general formula HPCTP·CuCl$_2$·MX$_2$ (M = Pd, X = Cl(3) or Br (4); M = Pt, X = Cl(5) or Br(6)) in excellent yields (Scheme 2). All the bimetallic complexes are readily soluble in common organic solvents such as dichloromethane and acetonitrile. Conductivity measurements in acetonitrile suggest that compounds 3–6 behave as non-electrolytes indicating that the halide ions are intact in solution. The solution magnetic moments were obtained by Evans[12] NMR method and are given in Table 3. The magnetic moments of the compounds 3–6 are in the range of 1.81–1.84. Although these values are larger than the spin only value (1.73) for $S = 1/2$, they lie in the range of μ_{eff} values 1.8–2.0 generally observed for copper complexes at room temperature.[16] The larger values are attributed to a mixing-in of orbital angular momentum from excited states *via* spin-orbit coupling.[17]

An interesting aspect of these reactions is the facile halide exchange between copper and the heavy metal (Pt or Pd). The evidence for the attachment of bromide to platinum or palladium is obtained from the electronic absorption spectra (*vide infra*) and the crystal structure determination of 4. This spontaneous halide exchange reaction between copper and platinum or palladium can be easily explained on the basis of hard-soft interactions.[18] The IR spectra of the compounds are



M = Pd; X = Cl (3) or Br (4)

M = Pt; X = Cl (5) or Br (6)

SCHEME 2

Table 3 Magnetic moment and electronic spectral data.*

Compd	μ_{eff}	λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1})	Assignment
3 HPCTP·$CuCl_2$·$PdCl_2$	1.81	913(250)	d-d
		358(1930)	l.m.c.t. (N→Cu)
		280(7020)	l.m.c.t. (N→Cu)
		234(30750)	π-π*(ligand)
4 HPCTP·$CuCl_2$·$PdBr_2$	1.83	900(290)	d-d
		58(2500)	l.m.c.t. (N→Cu)
		280(sh)(5130)	l.m.c.t. (N→Cu)
		233(28840)	π-π*(ligand)
5 HPCTP·$CuCl_2$·$PtCl_2$	1.84	897(280)	d-d
		350(2450)	l.m.c.t. (N→Cu)
		275(15500)	l.m.c.t. (N→Cu)
		237(29450)	π-π*(ligand)
6 HPCTP·$CuCl_2$·$PtBr_2$	1.81	927(285)	d-d
		350(1960)	l.m.c.t. (N→Cu)
		270(13120)	l.m.c.t. (N→Cu)
		236(29860)	π-π*(ligand)
1 HPCTP·$CuCl_2$[†]	1.73	902(235)	d-d
		360(1460)	l.m.c.t. (N→Cu)
		279(2860)	l.m.c.t. (N→Cu)
		0230.7(24000)	π-π*(ligand)
2 HPCTP·$CuBr_2$[†]	1.76	902(425)	d-d
		419(1650)	l.m.c.t. (Br→Cu)
		364(1550)	l.m.c.t. (N→Cu)
		93(2645)	l.m.c.t. (N→Cu)
		231.7(34240)	π-π*(ligand)

*for dichlormethane solutions; sh = shoulder.
[†] from ref 8a.

analogous to those of the precursor complexes 1 and 2[8] suggesting that the cyclophosphazene ring nitrogen is coordinated to the copper in the heterobimetallic complexes as well. In view of the preference of square planar geometry by platinum and palladium and the X-ray structure of 4, it is reasonable to conclude that the remaining complexes 3, 5 and 6 also involve coordination to platinum or palladium *via* the geminal pyrazolyl nitrogen atoms.

Electronic Spectra

The electronic spectra of the compounds were recorded in dichloromethane solution. Absorption maxima and tentative assignments are reported in Table 3. The spectral assigments are based on our earlier reports. When compared with the mononuclear copper complexes 1 and 2 (Table 1) the heterobimetallic complexes show larger ε_{max} values for the band at *ca.* 275 nm indicating that it may have contributions from ligand-platinum or palladium charge transfer transitions. It is interesting to note that the UV-Vis spectral pattern for the heterobimetallic complexes closely resembles that of the HPCTP·$CuCl_2$ 1[8] rather than of the bromo analogue 2. No band could be identified attributable to the Br → Cu charge transfer. This also confirms that in the heterobimetallic complexes 4 and 6 the bromide is no longer bound to copper.

Electron Paramagnetic Resonance Spectroscopy

The EPR spectra of the heterobimetallic compounds were recorded at X-band frequency as polycrystalline solids and dichloromethane fluid and frozen solutions. The spin Hamiltonian parameters for them are presented in Table 4. At room temperature the powder samples of platinum derivatives show rhombic spectra while the palladium analogs exhibit very broad isotropic spectra with the g_{iso} values around 2.10. The observed g-parameters for the platinum complexes in the solid state are reminiscent of the mononuclear copper(II) chloride complex, which indicates a distorted N_3Cl_2 trigonal bipyramidal environment around copper. The

Table 4 Spin Hamiltonian Parameters of Cu-Pt and Cu-Pd complexes[a].

Compd		g_1	g_2	g_3	$A_\parallel$	g_{av}[b]	g_{iso}	A_{iso}	G[c]
3	d	–	–	–	–	–	2.140	–	–
	e	2.088	2.288	–	135	2.157	2.165	52	3.27
4	d	–	–	–	–	–	2.139	–	–
	e	2.084	2.291	–	126	2.155	2.161	55	3.46
5	d	2.043	2.130	2.244	–	2.141	–	–	–
	e	2.090	2.292	–	130	2.159	2.172	50	3.34
6	d	2.048	2.125	2.255	–	2.144	–	–	–
	e	2.078	2.285	–	121	2.149	2.168	45	3.65
1[f]	d	2.046	2.119	2.225	–	2.142	–	–	–
2[f]	d	2.048	2.119	2.210	–	2.127	–	–	–
$Cu(dmim)_3Cl_2$[g]	d	2.060	2.160	2.210	–	2.144	–	–	–

[a] for axial, $g_\parallel = g_2$ and $g_\perp = g_1$. A values are in $\times 10^{-4}$ cm^{-1} g_{iso} and A_{iso} values are from room temperature isotropic spectra. [b] from $[\frac{1}{3}(g_\parallel^2 + 2g_\perp^2)]^{1/2}$, $[\frac{1}{3}(g_1^2 + g_2^2 + g_3^2)]^{1/2}$ for axial and rhombic spectra respectively. [c] from $(g_\parallel - 2.0)/(g_\perp - 2.0)$. [d] polycrystalline powder, room temperature. [e] dichloromethane solution, room and liquid nitrogen temperatures. [f] from ref 8. [g] from ref 19; dmim = 1,2-dimethylimidazole.

deviant spectra of the palladium derivatives in the solid state may be attributed to the presence of a water molecule, which forms an intermolecular hydrogen bond and bridges the copper and palladium atoms of adjacent molecules *via* the halide ions in keeping with the X-ray structure of 4 (*vide infra*). In frozen dichlormethane solution the spectra of all the derivatives are similar, axial, with $g_{\parallel} > g_{\perp}$ and $A_{\parallel} \cong 121\text{–}135\ 10^{-4}\ \text{cm}^{-1}$ suggestive of a $d_{x^2-y^2}$ ground state[17] (Figure 1). Electron propagation between metal centres by the intervening hydrogen bonds are well documented in the literature.[20,21] No electronic transmittance between the metals through the bridging cyclotriphosphazene moiety is suggested. The $A_{\parallel}$ values are comparable to those observed for distorted trigonal bipyramidal copper complexes reported in the literature.[22] The observation of hyperfine coupling, in contrast to the mononuclear complexes HPCTP·CuX_2 (X = Cl, Br) is attributed to the diminished intermolecular metal-metal interactions in the heterobimetallic complexes as a result of the built-in diamagnetic dilution. In dichloromethane solution all the complexes, however, show only isotropic spectra with ill-resolved couplings due to copper (I = 3/2, 4 lines) at room temperature (Table 4).

Structural description of [HPCTP·$CuCl_2$·$PdBr_2$]·C_6H_6·H_2O (4)

An ORTEP drawing of the structure, with the atomic numbering scheme is shown in Figure 2. The unique feature of 4 is that in it HPCTP exhibits a dual coordination response towards copper and platinum. While copper engages in a nongeminal (N_3 donor set, five-membered chelate rings) coordination, palladium uses geminal (N_2) donors to form six-membered chelates. The copper ion is in a distorted trigonal bipyramidal geometry with the two chloride ions and a cyclotriphosphazene ring nitrogen N(14) in the equatorial plane. The two nongeminal *cis*-pyrazolyl nitrogens reside at the axial positions. The geometry around palladium is essentially square planar. Two geminal pyrazolyl nitrogen atoms occupy the *cis* positions with *trans* positions filled by two bromide ions. The halide exchange between copper and palladium or platinum estimated by UV-Vis and EPR spectra (*vide supra*) is confirmed, in general, by this structure. The water molecule bridging

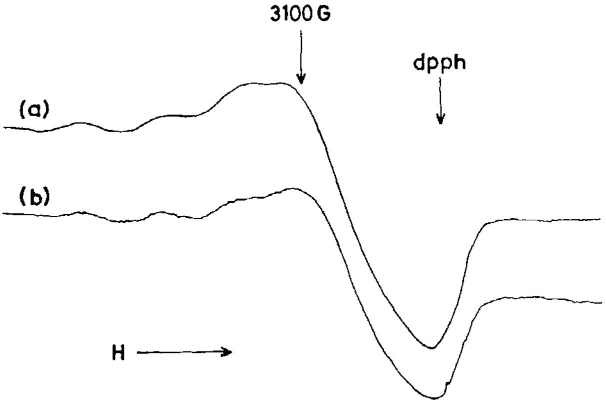


Figure 1 EPR spectra of 4(a) and 5(b) in frozen dicloromethane solution.

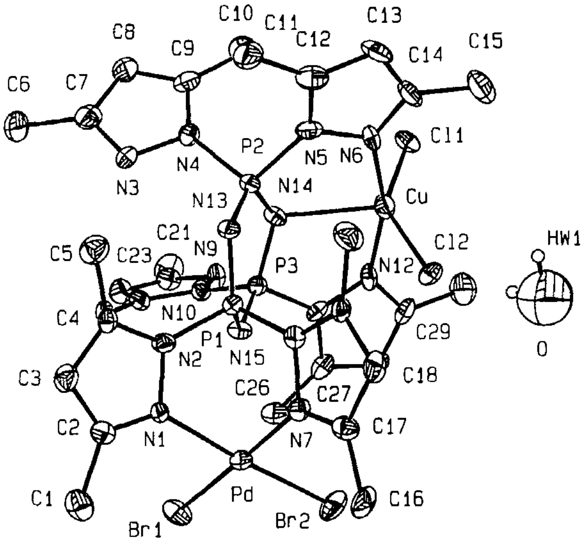


Figure 2 ORTEP plot (30% ellipsoids) of **4**.

the adjacent molecules *via* halogen H-bonding leads to a chain-like H-bonded polymer. The relevant structural parameters are given in Table 5.

Cu-N bond lengths in 4 are equal to those found for HPCTP·$CuCl_2$(1)[8], while the Cu-Cl bond lengths are somewhat shorter. The average Pd-N bond length

Table 5 Selected interatomic distances (A) and bond angles (deg) in 4.

Pd-Br1	2.390(3)	Br1-Pd-Br2	89.57(12)
Pd-Br2	2.378(3)	Br1-Pd-N1	92.8(3)
Pd-N1	2.054(11)	Br1-Pd-N7	179.3(3)
Pd-N7	2.036(11)	Br2-Pd-N1	176.4(3)
Cu-Cl1	2.304(4)	Br2-Pd-N7	90.7(3)
Cu-Cl2	2.325(4)	N1-Pd-N7	86.9(4)
Cu-N6	1.980(13)	Cl1-Cu-Cl2	143.28(16)
Cu-N14	2.352(11)	Cl1-Cu-N6	95.1(4)
Cu-N12	1.993(13)	Cl1-Cu-N12	96.1(4)
P1-N13	1.565(11)	Cl1-Cu-N14	110.8(3)
P1-N15	1.562(11)	Cl2-Cu-N6	91.6(4)
P2-N13	1.585(12)	Cl2-Cu-N12	88.8(4)
P2-N14	1.583(12)	Cl2-cu-N14	105.9(3)
P3-N14	1.604(11)	N6-Cu-N12	160.7(5)
P3-N15	1.572(11)	N6-Cu-N14	80.9(4)
Br2-O'	3.353(25)	N12-Cu-N14	80.4(4)
Cl2-O	3.452(23)	N13-P1-N15	118.3(6)
Br2-HW1	2.46	N13-P2-N14	118.0(6)
Cl2-HW2	2.64	N14-P3-N15	115.9(6)
		P1-N13-P2	120.2(7)
P-N(exo) 1.68(4) (ave)		P2-N14-P3	119.1(7)
		P1-N15-P3	122.4(7)
O' = O at x, 1.5-y, z-.5		Br2-HW1-O	171
		Cl2-HW2-O	170
		HW1-O-HW2	91.3

(2.045(11)Å is typical for organic heterocyclic bases[23] and the Pd-Br distances are slightly shorter (av. 2.384(6)Å) than those found in tetrabromo palladate anions[24] and related compounds.[25] As has been noted for other metal-HPCTP structures the P_3N_3 ring is non-planar: atoms N(13) (0.140(16)Å) and N(14) (-0.337(16) Å) are displaced significantly from the plane defined by P(1), P(2), P(3) and N(15).

CONCLUSIONS

The cyclotriphosphazene ligand hexakis(3,5-dimethl-1-pyrazolyl) cyclotriphosphazene, has been shown to be capable of forming heterodinuclear complexes. The coordination of this ligand gives copper with a N_3 donor set and palladium or platinum a N_2 donor set. Studies are on going to determine the effect of replacement of one or more pyrazolyl groups by other groups in order to alter the basicity of the cyclophosphazene skeletal nitrogen atoms and thereby influence the coordination behaviour.

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Supplementary Material Available

A complete listing of crystal and refinement data (S1), atomic coordinates (S2), anisotropic temperature factors (S3), bond distances (S4) and angles (S5), plane informations (S6) and torsion angles (S7) of 4 (12 pages) are available from the authors.

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