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COPPER(II) AND COBALT(II) COMPLEXES OF 2,2-DIPHENYL-4,4,6,6-TETRAKIS(1-PYRAZOLYL) CYCLOTRIPHOSPHAZENE, $N_3P_3Ph_2Pz_4$. X-RAY CRYSTAL STRUCTURE OF $N_3P_3Ph_2Pz_4 \cdot CoCl_2 \cdot 0.5CH_2Cl_2$

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Abstract—Synthesis and characterization of isotypical compounds $N_3P_3Ph_2Pz_4 \cdot MX_2$ (M = Cu, X = Cl or Br; M = Co, X = Cl) are reported. The X-ray crystal structure of $N_3P_3Ph_2Pz_4 \cdot CoCl_2 \cdot 0.5CH_2Cl_2$ is described. The structure is a distorted trigonal bipyramid in which the cobalt atom is coordinated by a ligand molecule through the two nongeminal pyrazolyl pyridinic nitrogens at the equatorial sites and a cyclophosphazene ring nitrogen at the axial position. The remaining axial and equatorial positions are occupied by the two chlorine atoms.

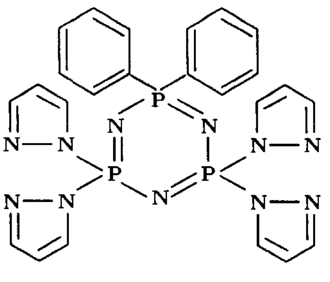
Interaction of inorganic heterocyclic compounds with transition metals has attracted widespread attention in recent years.[1–4] It was believed that such studies would yield important information regarding the bonding involved in these molecules. While the S—N and S—N—P heterocycles undergo skeletal degradation on reaction with transition metal reagents,[3,4] the cyclophosphazenes (P—N ring systems) form stable coordination compounds in which the P—N ring is intact.[1,2] Interest in cyclophosphazene based ligand systems also stems from the fact that such compounds would act as structural and functional models for the linear phosphazene polymers.[5]

As part of our investigations on the ligating properties of pyrazolyl substituted cyclophosphazenes[6–8] we report here the synthesis, magnetic moment, conductivity and spectral characterization of new cobalt(II) and copper(II) halide complexes of $N_3P_3Ph_2Pz_4$ (**1**). The crystal structure of $N_3P_3Ph_2Pz_4 \cdot CoCl_2 \cdot 0.5CH_2Cl_2$ has also been solved and results are compared with those of related compounds.

EXPERIMENTAL

Synthesis of ligand and complexes

The ligand was prepared by adopting the procedure reported previously for the 3,5-dimethyl



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$N_3P_3Ph_2Pz_2 \cdot CuCl_2$ (**2**)
$N_3P_3Ph_2Pz_2 \cdot CuCl_2$ (**3**)
$N_3P_3Ph_2Pz_2 \cdot CuCl_2$ (**4**)

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Table 1. Physical data of the complexes

Compound	Yield	Colour	Decomposition point (°C)	Found (Calc.) % C	H	N	Cu
2	65%	Blue–green	170	41.6	3.4	22.3	9.2
				(41.7)	(3.2)	(22.3)	(9.0)
3	71%	Yellow–brown	186	36.85	2.9	19.8	8.3
				(36.9)	(2.8)	(19.7)	(8.1)
4	85%	Blue	144	41.85	3.3	22.6	
				(41.9)	(3.2)	(22.4)	

pyrazole derivative.[8] The complexes were obtained by treating anhydrous metal salts with the ligand in 1 : 1 molar ratio using dichloromethane as solvent. The yield and physical data for the complexes are reported in Table 1. Apparatus and analytical procedures have been described previously.[8]

X-ray structure determination

A dark blue crystal of $N_3P_3Ph_2Pz_4 \cdot CoCl_2 \cdot 0.5CH_2Cl_2$ ($0.24 \times 0.28 \times 0.52$ mm) was mounted on a glass fibre with epoxy resin and used for data collection. Cell constants and orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 15 reflections in the 2θ range 8–20°. Data were collected on an Enraf–Nonius CAD4 diffractometer at 293 K using Mo-K_α radiation ($\lambda = 0.71073$ Å) and θ–2θ scan technique; 4066 unique reflections were measured in which 3038 data had $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization effects and an analytical absorption correction was applied. A summary of the crystal parameters, experimental details and refinement results are listed in Table 2.

The structure was solved by direct methods,[9] which revealed the position of all non-hydrogen atoms, and refined by a full-matrix least-squares procedure using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated with the fixed C—H distance of 0.95 Å and were included in the final refinement cycles. No extinction corrections were applied. The scattering factors were taken from Ref. 10.

RESULTS AND DISCUSSION

The three compounds reported are isomorphous in nature as indicated by the IR spectra. The infrared spectra indubitably demonstrates that in these complexes both the cyclotriphosphazene and pyrazolyl nitrogens participate in coordination. Thus, a band ascribed to P=N (*ca* 1220 cm^{-1}) is split into at least two components and the C=N stretching band is shifted to higher energy. The conductivity studies reveal that they are non-electrolytes in acetonitrile solutions.[11] The magnetic moment values (Table 3) are appropriate for $S = 1/2$ and $3/2$ spin systems of five-coordinate copper and cobalt complexes respectively.[12,13]

The electronic spectral data for the complexes are presented in Table 3 with probable assignment of each band. In general, they exhibit two bands attributable to the Pz→Cu charge transfer transitions at ~270 and ~360 nm. The *d–d* band of the copper(II) halide complexes, which is broad and extends into the near-IR region, is characteristic of copper chromophore with $d_{x^2-y^2}$ ground state.[14] The cobalt complex shows two *d—d* transitions in which the higher energy band displays a shoulder at the lower wavelength side. The band positions

Table 2. Crystal data and refinement parameters

Chemical formula	$C_{24}H_{22}P_3Cl_2CoN_{11} \cdot 0.5CH_2Cl_2$
M_r	729.74
Space group	P-1
a (Å)	11.002(3)
b (Å)	11.669(3)
c (Å)	12.941(2)
α (°)	92.46(2)
β (°)	94.96(2)
γ (°)	108.66(2)
V (Å^3)	1563.8(6)
Z	2
D_{calc} (g cm^{-3})	1.55
μ (mm^{-1})	0.993
$F(000)$	740
No. of parameters refined	383
R (F^2)	0.036
R_ω (F^2)	0.055
$(\Delta_\rho)_{max}$ (e Å^{-3})	0.88(6)

Table 3. Magnetic moment, conductivity and optical data

Compound	Band[a]	Assignment	μ_{eff}	Λ_m[b]
2	233(14.05)	π-λ^* ligand	1.78	17
	273(6.37)	pz→Cu l.m.c.t.		
	360(2.03)	pz→Cu l.m.c.t.		
	903(0.19)	*d*–*d*		
3	232(13.96)	λ-λ^* ligand	1.72	18
	276(3.89)	pz→Cu l.m.c.t.		
	364(2.82)	pz→Cu l.m.c.t.		
	425(3.26)	Br→Cu l.m.c.t.		
	562(0.34)	*d*–*d*		
	877(0.20)	*d*–*d*		
4	232(13.25)	λ-λ^* ligand	4.91	6
	266sh	pz→Co l.m.c.t.		
	554sh	*d*–*d*		
	599(0.07)	*d*–*d*		
	1040(0.008)	*d*–*d*		

[a] CH_2Cl_2 solution, units: nm (M^{-1} cm^{-1} × 10^3).
[b] CH_3CN solution, unit: ohm cm^2 mol^{-1}.

are acceptable for a high-spin trigonal bipyramidal chromophore.[13] The room temperature EPR spectra of the powder sample of the copper complexes are isotropic and broad and points the existence of weak exchange coupling between the metal ions in the coordination polyhedra.

Structure of $N_3P_3Ph_2Pz_4 \cdot CoCl_2 \cdot 0.5CH_2Cl_2$

The molecular structure and the atom labelling scheme of the complex is illustrated by Fig. 1. The selected bond distances and angles are listed in Table 4. The cobalt is five-coordinate, and best described as distorted trigonal bipyramid with two nitrogen atoms from the nongeminal *cis*-pyrazolyl groups, two chloride ions and one cyclotriphosphazene nitrogen. Interestingly, the equatorial plane is constituted by two nongeminal pyrazolyl nitrogens and one chlorine. The cobalt atom lies slightly out of the equatorial plane in the direction of the Cl(2) atom. The equatorial arrangement is in contradiction to the earlier observations with the ligands $N_3P_3Ph_2(dmpz)_4$[8] and $N_3P_3(dmpz)_6$.[6,7] In the copper complexes of $N_3P_3Ph_2(dmpz)_4$ and $N_3P_3(dmpz)_6$ the nongeminal pyrazolyl nitrogens occupied the axial positions thus leading to large N_{pz}—Cu—N_{pz} angle (~159°). In the present case the N_{pz}—Cu—N_{pz} angle is narrow and is significantly smaller [114.03(14)°]. This probably arises due to the absence of methyl groups at 3-position of pyrazolyl ring which prevent the formation of a smaller angle. The cyclotriphosphazene nitrogen–metal interaction is weak and is manifested in the long bond length of Co—N(1) [2.419(3) Å]. A significantly weak interaction of the cyclotriphosphazene nitrogen to the metal in the series of related complexes (Table 5) is in keeping with the basicity considerations. The environment of the metal ion is significantly distorted from that of a regular trigonal bipyramid. The main axis [N(1)—Co—Cl(2)] deviates [167.43(9)°] from the expected angle 180°. There is other evidence of distortion along the N(1)—Co—Cl(2) axis as the Co—Cl(2) bond is lengthened to 2.2859(15) Å for the equatorial Co—Cl(1) bond. The occurrence of two different cobalt–nitrogen distances, namely Co—N_{pz} and Co—N_{ctp}, makes more evident this distortion in comparison with similar structures (Tables 5–7). Significant deviations from idealized orthogonal geometry are found at the cobalt atom in the five-membered chelate rings CoN(1)P(1)N(51)N(52) and CoN(1)P(3)N(31)N(32), 77.30(13)° and 75.85(13)° for N(1)—Co—N(32) and N(1)—Co—N(52) respectively. The average Co—N_{pz} distance [2.050(4) Å] is shorter than that observed for nickel complex, $N_3P_3Ph_2(dmpz)_4 \cdot NiCl_2$[8] but greater than that of copper(II) complexes (Table 5).

The pyrazolyl rings of the $N_3P_3Ph_2Pz_4$ ligand are planar as expected with deviations from the mean planes not greater than 0.026 Å. However, the cyclotriphosphazene ring conformation is non-planar with the N(2) atom displaced −0.133 Å out of the plane defined by the remaining atoms, P(1), P(2), P(3), N(1) and N(3). The cyclo-

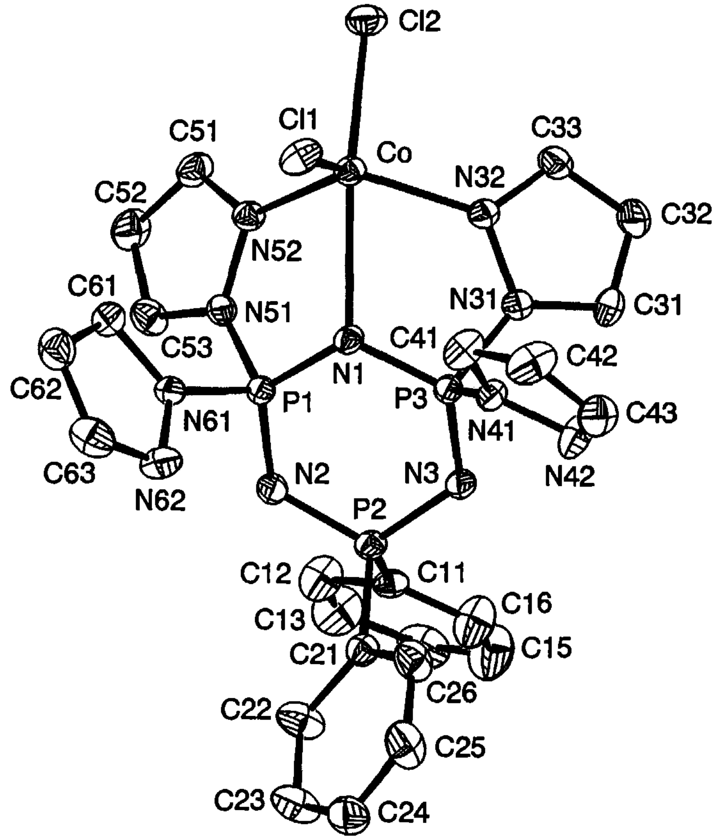

Fig. 1. Molecular structure and numbering of **4**.

Table 4. Selected bond distances (Å) and angles (°) in **4**

	Metal environment		
Co—Cl(1)	2.2709(14)	Cl(1)—Co—Cl(2)	106.44(5)
Co—Cl(2)	2.2859(14)	Cl(1)—Co—N(1)	85.98(9)
Co—N(1)	2.419(3)	Cl(1)—Co—N(32)	113.74(11)
Co—N(32)	2.038(4)	Cl(1)—Co—N(52)	122.90(11)
Co—N(52)	2.062(4)	Cl(2)—Co—N(1)	167.43(9)
Cl(2)—Co—N(32)	98.42(11)	Cl(2)—Co—N(52)	95.97(11)
N(1)—Co—N(32)	77.30(13)	N(1)—Co—N(52)	75.85(13)
N(32)—Co—N(52)	114.03(14)		
	Phosphazene ring		
P(1)—N(1)	1.586(3)	N(1)—P(1)—N(2)	121.16(19)
P(1)—N(2)	1.548(4)	N(2)—P(2)—N(3)	115.03(19)
P(2)—N(2)	1.621(4)	N(1)—P(3)—N(3)	119.94(18)
P(2)—N(3)	1.615(4)	P(1)—N(1)—P(3)	118.64(21)
P(3)—N(1)	1.592(4)	P(1)—N(2)—P(2)	121.25(22)
P(3)—N(3)	1.551(4)	P(2)—N(3)—P(3)	122.74(23)
mean values:		N(31)—P(3)—N(41)	99.58(17)
P—N_{exo}	1.687(4)	N(51)—P(1)—N(61)	101.47(18)
P—C_{exo}	1.791(5)	C(11)—P(2)—N(21)	105.78(20)

triphosphazene skeletal nitrogen participation in coordination affects the P—N bonds at the P(1)—N(1)Co—P(3) segment leading to the weakening of them as compared to the adjacent ones. The P—N bonds [P(2)—N(2) and P(2)—N(3)], associated with the phosphorus containing the

Table 5. Comparison of metal environment in the pyrazolylcyclotriphosphazene complexes[a]

Compound	N_{pz}—M—N_{pz}	N_{pz}—M—N_{ctp}	M—N_{ctp}	M—N_{pz}	M—Cl	Ref.
4	114.03(14)	77.30(13) 75.85(13)	2.419(3)	2.038(4) 2.062(4)	2.2709(14) 2.2859(14)	This work
5	159.39(20)	80.86(19) 80.60(19)	2.320(5)	1.984(5) 1.974(5)	2.2639(21) 2.2822(14)	15
6	160.0(1)	80.3(1) 80.5(1)	2.079(3)	2.080(4) 2.089(4)	2.258(1) 2.248(2)	8
7	160.74(21)	81.00(18) 80.68(19)	2.360(5)	1.984(5) 1.974(5)	2.2676(21) 2.2429(19)	6
8	159.3(6)	80.3(6) 79.6(6)	2.362(15)	2.003(16) 1.997(16)	2.312(5) 2.319(5)	16
9	—	—	2.394(2)	2.299(2) 2.312(3)		17
10		—	2.310(7)	2.250(7) 2.274(7)		17

[a] $N_3P_3Ph_2(dmpz)_4 \cdot CuCl_2$ (**5**), $N_3P_3Ph_2(dmpz)_4 \cdot NiCl_2$ (**6**), $N_3P_3(dmpz)_6 \cdot CuCl_2$ (**7**), $N_3P_3(dmpz)_6 \cdot CuCl_2 \cdot PdBr_2$ (**8**), $N_3P_3Ph_4(dmpz)_2 \cdot Mo(CO)_3$ (**9**), $N_3P_3[MeN(CH_2)_2O]_2(dmpz)_2 \cdot W(CO)_3$ (**10**).

Table 6. Comparison of the cyclotriphosphazene structural features

	P=N distance in		P—N—P angle in		
Compound	P—N(M)—P	P—N—P	P—N(M)—P	P—N—P	Ref.
4	1.586(3) 1.592(4)	1.548(4), 1.551(4) 1.615(4), 1.621(4)	118.64(21)	121.25(22) 122.74(23)	This work
5	1.601(5) 1.600(5)	1.552(5), 1.561(5) 1.614(5), 1.610(5)	117.6(3)	122.1(3) 123.1(3)	15
6	1.590(4) 1.591(4)	1.537(4), 1.537(4) 1.611(4), 1.591(4)	114.4(2)	120.9(2) 122.6(2)	8
7	1.596(5) 1.589(5)	1.564(5), 1.574(5) 1.575(5), 1.578(5)	118.4(3)	122.5(3) 121.3(3)	6
8	1.585(16) 1.586(15)	1.552(15), 1.554(15) 1.558(15), 1.591(16)	120.3(9)	120.2(10) 124.1(9)	16
9	1.594(2) 1.636(2)	1.557(2), 1.587(3) 1.598(3), 1.627(2)	120.2(3)	126.4(2) 120.1(3)	17
10	1.579(7) 1.628(7)	1.545(7), 1.569(7) 1.586(7), 1.593(8)	120.4(4)	130.0(5) 121.0(4)	17

phenyl groups are found to be longer [av. 1.618 Å] than the analogous bond in the coordination compounds derived from $N_3P_3Ph_2(dmpz)_4$ ligand (Table 6).[8]

The percentage of tbp has been calculated using the Goldschmied and Stephenson description.[26] The value obtained for **4** is 87% which indicates that the CoN_3Cl_2 is, as predicted, close to a trigonal pyramid. Also, from Table 7 it is evident that among the five-coordinate complexes of pyrazolylcyclotriphosphazenes, **4** has the high trigonal bipyramidal character. A similar estimation can be carried out from the structural parameter τ introduced by Addison *et al.*[27] to analyse the degree of distortion from square pyramidal ($\lambda = 0.00$) to trigonal bipyramidal ($\tau = 1.00$) geometries, given that τ value of **4** is 0.74.

On comparing the X—M—X angles observed for various complexes (Table 7) it is reasonable to suggest in the present case the small Cl—Co—Cl angle is mainly due to the absence of methyl substituents on the pyrazole nucleus. The steric influence, forcing the halogens apart to form a wider angle, has been observed for the 3,5-dimethyl pyrazole derived ligand complexes (**5–8** and **12** in Table 7).

Table 7. Comparison of geometries of selected five-coordinate complexes[a]

Complex	Geometry	X—M—X	M—N_{long}	M—N_{short}	τ_{value}	% tbp	Ref.
4	distorted tbp	106.44(5)	2.419(3)	2.038(4) 2.062(4)	0.74	87	This work
5	distorted tbp	132.21(8)	2.320(5)	1.984(5) 1.974(5)	0.45	74	15
6	distorted tbp	114.77(6)	2.089(4)	2.079(3) 2.080(4)	0.53	86	8
7	distorted tbp	142.28(10)	2.360(5)	1.988(5) 1.974(5)	0.31	63	6
8	distorted tbp	143.21(21)	2.362(15)	2.003(16) 1.997(16)	0.27	62	16
11	distorted sp	112.75(2)	2.191(2)	1.940(2) 1.957(2)	0.12	48	18
12	distorted tbp	131.32(4)	2.423(1)	1.988(5) 1.981(5)	0.40	81	19
13	distorted tbp	116.95(8)	2.131(9)	1.94(2) 1.983(9)	0.49	66	20
14	distorted tbp	115.89(6)	2.136(4)	1.975(4) 1.992(5)	0.45	63	20
15	distorted sp	103.2(9)	2.03(4)	2.01(5) 1.98(2)	0.13	28	21
16	sp	109.5(1)	2.148(15) 2.082(9)	2.114(14)	0.12	42	22
17	distorted sp	101.8(3)	2.21(1)	2.19(2) 2.16(2)	0.77	83	23
18	distorted tbp	149.2(1)	2.050(11)	2.042(10) 2.007(14)	0.23	51	24
19[b]	tbp	138.1(1)	2.145	2.005	0.64	69	25

[a] Cu(bpae)Br_2 (**11**), bpae = N,N-bis(1-pyrazolylmethyl)aminoethane; Cu(bdmpab)Br_2 (**12**), bdmpad = N,N-bis(3,5-dimethyl-1-pyrazolylmethyl)aminobenzene; Cu(PDAHP)Br_2 (**13**), PDAHP = 1-pyridine-2-yl-3-methyl-3,6-diazeheptane; Cu(PDAHP)Cl_2 (**14**); Cu(paphy)Br_2 (**15**), paphy = pyridine-2-aldehyde-2′-pyridyl hydrazone; Co (paphy)Cl_2 (**16**); Co(Et_4dien)Cl_2 (**17**), Et_4dien = N,N,N′,N′-tetraethyldiethylenetriamine; Ni(Me_2dpma)Br_2 (**18**), Me_2dpma = 6,6′-dimethyl-di(2-pyridylmethyl)amine; Cu(dmIm)Br_2 (**19**), dmIm = 1,2-dimethyl imidazole.

[b] Mean values from two crystallographically independent molecules.

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