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Dichloro[2,2-diphenyl-4,4,6,6-tetrakis(3,5-dimethylpyrazol-1-yl)cyclotriphosphazene]cobalt(II)

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The title compound, $[N_3P_3(C_5H_7N_2)_4(C_6H_5)_2]CoCl_2$ or $[CoCl_2(C_{32}H_{38}N_{11}P_3)]$, possesses a five-coordinated Co^{II} atom in an approximately trigonal-bipyramidal geometry. The N_3Cl_2 donor set of the metal environment comprises two non-geminal pyrazolyl N atoms, one cyclotriphosphazene N atom, and two Cl$^-$ ions. The coordination environment and bonding features of the compound are critically compared with related metal complexes of cyclotriphosphazene ligands.

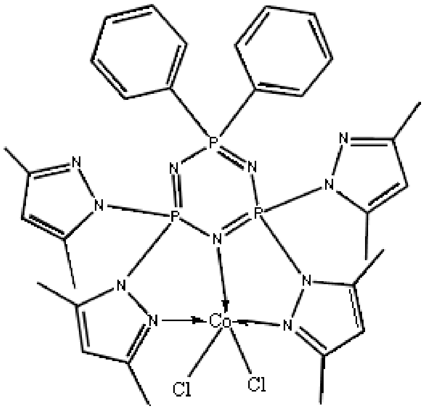
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.048
wR factor = 0.074
Data-to-parameter ratio = 20.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Pyrazolyl derivatives containing main group elements, such as boron (pyrazolylborates) and phosphorus, have received much attention in recent years due to their varying modes of interaction with transition metals (Trofimenko, 1993; Parkin, 1995; Reger, 1996; Kitajima & Tolman, 1995). The pyrazole (pz) moiety also occurs in some drug molecules such as antipyrine and celecoxib. We have been studying the coordination behaviour of pyrazolylcyclotriphosphazenes towards transition metals. Previously, we reported the synthesis and characterization of a series of transition metal complexes derived from the cyclotriphosphazene (ctp) ligands, hexakis(3,5-dimethylpyrazole-1-yl)cyclotriphosphazene (hdpctp) (Thomas, Chandrasekhar, Pal *et al.*, 1993; Thomas, Chandrasekhar, Scott *et al.*, 1993), 2,2-diphenyl-4,4,6,6-tetrakis(3,5-dimethylpyrazol-1-yl)cyclotriphosphazene (tdpctp) (Thomas *et al.*, 1994; Thomas, Tharmaraj *et al.*, 1995), and 2,2-diphenyl-4,4,6,6-tetrakis(1-pyrazolyl)cyclotriphosphazene (tpctp) (Thomas, Chandrasekhar *et al.*, 1995). The cyclotriphosphazene interaction varies with the nature of the transition metal in the tdpctp complexes. While the Cu—N$_{ctp}$ distance is longer, the Ni—N$_{ctp}$ distance is appreciably shorter and comparable to the Ni—N$_{pz}$ bond length. This discrepancy has prompted us to



(I)

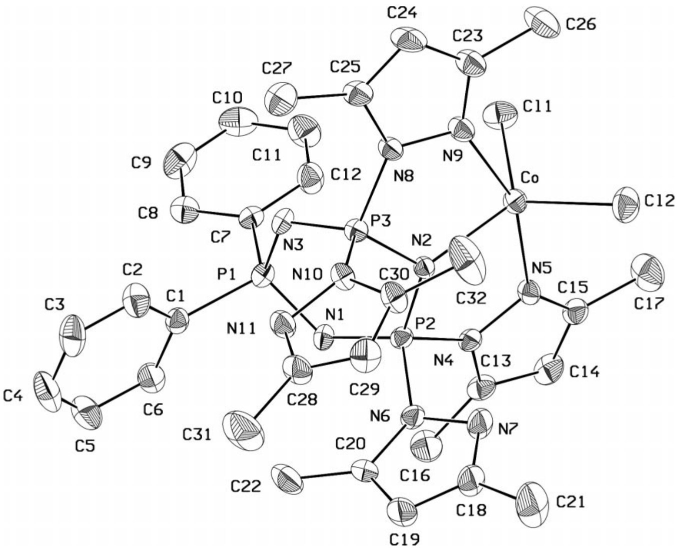


Figure 1
The title compound, (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

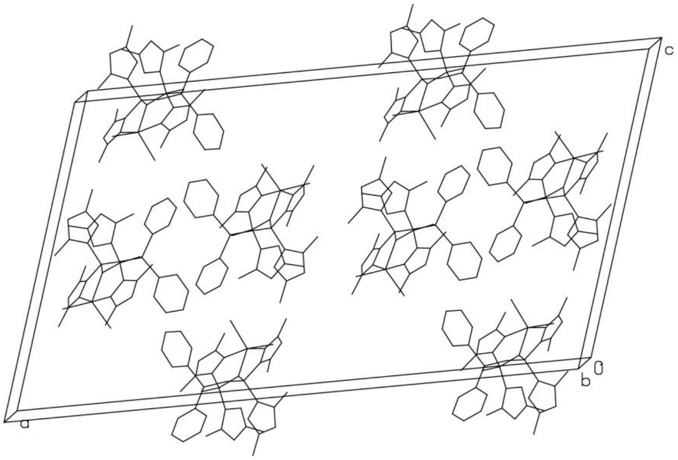


Figure 2
Packing diagram of the complex viewed down the *b* axis.

examine the crystal structure of the present cobalt complex, [tdpctp·CoCl$_2$], (I).

The N$_3$ donor set afforded by the potentially multidentate ligand, tdpctp, comprises two non-geminal pyrazolyl N atoms and one cyclotriphosphazene skeletal N atom. The coordination geometry of the Co atom is best described as a trigonal bipyramid with slight distortion. The trigonal plane of the coordination polyhedron is derived from the two Cl$^-$ ions and a cyclotriphosphazene ring N atom. The two non-geminal pyrazole N atoms fill the axial postions. For the title cobalt complex, (I), and the nickel complex [tdpctp·NiCl$_2$], (II) (Thomas *et al.*, 1994), the M—N$_{\rm ctp}$ and M—N$_{\rm pz}$ bond distances are comparable [2.106 (3) and 2.170 (3) Å for (I), and 2.079 (3) and 2.085 (4) Å for (II), respectively] and the small differences may arise from the difference in the basicity of the cyclophosphazene and pyrazole N atoms. On the other hand, for the related copper and cobalt complexes, [tdpctp·CuCl$_2$], (III) (Thomas, Chandrasekhar, Pal *et al.*, 1993), and [tpctp·CoCl$_2$], (IV) (Thomas *et al.*, 1994), these M—N$_{\rm ctp}$ and M—N$_{\rm pz}$ bond distances exhibit anomalous differences [2.320 (5) and 1.979 (5) Å for (III), and 2.419 (3) and 2.050 (4) Å for (IV), respectively], which may be due to the axial elongation induced by a Jahn–Teller effect in the copper complex and the resultant reduced basicity from the absence of methyl substituents on the pyrazole nucleus in the cobalt complex. Another striking difference between cobalt complexes (I) and (IV) is the N$_{\rm pz}$—Co—N$_{\rm pz}$ bond angle [158.67 (13) and 114.03 (14)° for (I) and (IV), respectively]. Although both the complexes have trigonal-bipyramidal geometry, the trigonal plane in (I) is composed of the N$_{\rm ctp}$ atom and two Cl$^-$ ions, whereas in (IV) it consists of two N$_{\rm pz}$ atoms and a Cl$^-$ ion. This difference in the spatial arrangement is mainly attributed to the enhanced steric effect exerted by the methyl substituents in the tdpctp ligand. The Cl—M—Cl angles are within the normal trigonal range for the cobalt and nickel complexes, (I) and (II) [117.15 (5) and 114.77 (6)°, respectively], and the corresponding Cl—M—Cl angle in copper complex (III) is widened [132.21 (8) Å]; probably the structure is approaching a square-based pyramidal one. This conclusion is also arrived at by comparing the trigonal distortion parameters (τ; Addison *et al.*, 1984), for which the values are 0.56, 0.53 and 0.45 for the complexes (I), (II) and (III), respectively. In the cyclophosphazene skeleton of (I), the P—N bond associated with the coordinating N atom is elongated [1.614(3 Å] and the adjacent P—N bond is shortened [1.564 (2) Å]. Even though a similar trend has been observed for the geminal N$_3$P$_3$$X_2$$Y_4$-type compounds (where X is an electron-withdrawing group; Chandrasekhar & Thomas, 1993), as well as in the related metal complexes (II), (III) and (IV), it is found that the metal interaction reinforces the effect. The P—N—P angles are normally around 120° and that for the N atom interacting with the metal is close to the value of the tetrahedral angle [113.67 (18);°]. This indicates that the N atom undergoes a hybridization change from sp^2 to sp^3 due to the metal coordination. The cyclotriphosphazene ring significantly deviates from planarity, while pyrazole groups do not show any noteworthy distortions.

Experimental

The title compound, (I), was prepared according to the reported procedure (Thomas *et al.*, 1994). Layering dry hexane over a dichloromethane solution of the compound yielded single crystals suitable for X-ray diffraction.

Crystal data

[CoCl$_2$(C$_{32}$H$_{38}$N$_{11}$P$_3$)]
M_r = 799.47
Monoclinic, $C2/c$
a = 38.755 (3) Å
b = 9.378 (3) Å
c = 22.043 (2) Å
β = 108.19 (3)°
V = 7611 (3) Å^3
Z = 8
D_x = 1.395 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 41 reflections
θ = 5.1–18.8°
μ = 0.76 mm^{-1}
T = 293 (2) K
Prism, blue
0.46 × 0.37 × 0.29 mm

m400 P. Prabakaran *et al.* • [CoCl$_2$(C$_{32}$H$_{38}$N$_{11}$P$_3$)] *Acta Cryst.* (2001). E**57**, m399–m401

Data collection

Philips PW11100 diffractometer
θ–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.673$, $T_{\max} = 0.803$
9394 measured reflections
9174 independent reflections
2983 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.062$
$\theta_{\max} = 28.0°$
$h = -51 \rightarrow 48$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 29$
1 standard reflection every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.074$
$S = 0.74$
9174 reflections
442 parameters
H-atom parameters constrained
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co—N2	2.106 (3)	P2—N2	1.612 (3)
Co—N5	2.162 (3)	N1—P1	1.624 (3)
Co—N9	2.177 (3)	P1—N3	1.618 (3)
Co—Cl2	2.2760 (13)	N3—P3	1.557 (3)
Co—Cl1	2.2917 (14)	P3—N2	1.622 (3)
P2—N1	1.567 (3)		
N2—Co—N5	79.45 (12)	N9—Co—Cl1	91.23 (9)
N2—Co—N9	79.90 (12)	Cl2—Co—Cl1	117.15 (5)
N5—Co—N9	158.67 (13)	N1—P2—N2	117.74 (17)
N2—Co—Cl2	125.08 (9)	P2—N1—P1	122.6 (2)
N5—Co—Cl2	99.48 (10)	N3—P1—N1	114.96 (17)
N9—Co—Cl2	96.72 (10)	P3—N3—P1	120.8 (2)
N2—Co—Cl1	117.71 (8)	N3—P3—N2	117.56 (17)
N5—Co—Cl1	93.63 (9)	P2—N2—P3	113.67 (18)

Data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *MolEN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *PLATON*.

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