

References

- ASHIDA, T. (1973). *The Universal Crystallographic Computing System—Osaka*. The Computation Center, Osaka Univ., Japan.
- ASHWORTH, R. S., PROUT, C. K., DOMENICANO, A. & VACIAGO, A. (1968). *J. Chem. Soc. A*, pp. 93–104.
- BARNES, J. C., BLYTH, C. S. & PATON, J. D. (1982). *J. Chem. Soc. Pak. A*, 103–113.
- DALZIEL, J. A. W., HITCH, M. J. & ROSS, S. D. (1969). *Spectrochim. Acta, Part A*, **25**, 1061–1066.
- DOMENICANO, A., SCARAMUZZA, L., VACIAGO, A., ASHWORTH, R. S. & PROUT, C. K. (1968). *J. Chem. Soc. A*, pp. 866–869.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- LINDLEY, P. F. & WOODWARD, P. (1966). *J. Chem. Soc. A*, pp. 123–126.
- MOTHERWELL, S. & CLEGG, W. (1978). *PLUTO*. Program for molecular drawings. Univ. of Cambridge, England.
- PROSEN, R. J. & TRUEBLOOD, K. N. (1956). *Acta Cryst.* **9**, 741–746.
- ROBERTS, P. & SHELDRIK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- WALTON, R. A. (1966). *Inorg. Chem.* **5**, 643–649.

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Dichloro[phenyldi(2-pyridyl)phosphine-*N,N'*]cobalt(II) Hemiethanolate, [Co(C₁₆H₁₃N₂P)Cl₂]_½C₂H₆O

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Abstract. $M_r = 417.1$, monoclinic, $P2_1/c$, $a = 16.249$ (3), $b = 12.078$ (2), $c = 19.642$ (2) Å, $\beta = 99.21$ (2)°, $V = 3805$ (1) Å³, $Z = 8$, $D_x = 1.456$ g cm⁻³, $T = 294$ K, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 12.69$ cm⁻¹, $F(000) = 1672$, final $R = 0.029$ over 2425 reflections. Crystals of this synthetic organometallic compound contain disordered ethanol solvate molecules and monomeric Co^{II} complex molecules. The Co atom is tetrahedrally coordinated to two Cl atoms [average Co–Cl = 2.221 (1) Å] and two pyridines [average Co–N = 2.031 (2) Å]. The dipyridylphosphine forms a six-membered chelate ring in the boat conformation.

Introduction. Phenyldi(2-pyridyl)phosphine (Phpy₂P) is one member of a series of heterocyclic compounds synthesized (Newkome & Hager, 1978*a,b,c*) specifically as sequestering agents for transition-metal ions. The analogous Ph₂pyP has been shown (Inoguchi, Mahrle, Neugebauer, Jones & Schmidbauer, 1983) to coordinate through the P atom, although N-monodentate and P,N-bidentate coordinations are conceivable. Likewise, Phpy₂P might be expected to participate in a number of binding modes: N- or P-monodentate, N,N'- or N,P-bidentate, or even tridentate ligation. The crystal structure reported herein illustrates the N,N'-bidentate bonding mode of Phpy₂P with CoCl₂.

Experimental. Blue crystals grown by slow evaporation from ethanol, D_m not determined, well formed crystal ca 0.54 × 0.20 × 0.22 mm glued to a glass fiber

mounted on an Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; preliminary survey of reflections revealed systematic absences ($0k0$, k odd, $h0l$, l odd) which uniquely define monoclinic space group $P2_1/c$; lattice parameters derived from least-squares refinement of 25 well centered reflections ($26^\circ \leq 2\theta \leq 30^\circ$); total of 4809 intensity data measured ($\omega/2\theta$ scans) in one quadrant: $2^\circ \leq 2\theta \leq 43^\circ$, $0 \leq h \leq 16$, $0 \leq k \leq 12$, $-20 \leq l \leq 20$; no systematic variation in three periodically remeasured intensities; empirical absorption correction (ψ scans) applied to 4361 unique reflections, minimum relative transmission coefficient 0.918. Positions of two Co and two Cl atoms determined by direct methods, and those of all other atoms in the two independent organometallic molecules from successive Fourier difference syntheses. From residual electron density in an otherwise anomalous void, the existence of a highly disordered molecule of ethanol was deduced. Model refined by weighted full-matrix least squares of the 2425 structure amplitudes which met the criterion $|F| > 6\sigma(|F|)$; $\sum w(\Delta F)^2$ minimized, $w = [\sigma^2(|F|) + 0.05|F|^2]^{-1}$. The disordered ethanol model assumed thirteen orientations and eight distinct non-hydrogen sites, with assigned occupancy factors [C(1S) to C(8S)] 8/13, 7/13, 4/13, 4/13, 5/13, 4/13, 4/13, and 3/13. All disordered atoms treated as thermally isotropic C atoms, and disordered H atoms ignored. All non-hydrogen atoms of the organometallic molecules treated anisotropically, and H atoms placed in calculated positions with a common fixed thermal parameter ($B = 5.0$ Å²). A total of 429 variables

yielded $R = 0.029$, $wR = 0.046$, and error-of-fit = 1.486. In final cycle $(\Delta/\sigma)_{\max} = 0.56$, and maximum residual in final difference synthesis $0.31 \text{ e } \text{\AA}^{-3}$; scattering factors from Cromer & Mann (1968); no correction for secondary extinction. Computer programs used: *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), the Enraf-Nonius *Structure Determination Package* (Frenz, 1980), and the *PROPHET* computing system.

Discussion. Atomic coordinates are given in Table 1.* A view of the molecule is shown in Fig. 1, and the packing is illustrated in Fig. 2.

The crystallographically independent unit contains one highly disordered $\text{C}_2\text{H}_5\text{OH}$ molecule, and two Co^{II} complex molecules in which two Cl and two pyridyl-*N* ligands are tetrahedrally disposed about each central Co. Tetrahedral coordination has been rarely observed in dipyridylcobalt dihalide complexes since such complexes tend to polymerize in an octahedral environment (Gill & Nyholm, 1961). Known tetrahedral structures include (4-vinylpyridine) $_2\text{CoCl}_2$ (Admiraal & Gafner, 1968), (4-methylpyridine) $_2\text{CoCl}_2$ (Laing, & Carr, 1975), (2-methoxypyridine) $_2\text{CoCl}_2$ (Allan, Jones & Sawyer, 1981), and [bis(2-pyridyl) disulfide]CoCl $_2$ (Kadooka, Warner & Seff, 1976). In the latter molecule, a seven-membered chelate ring is formed.

In the complex reported in this paper, the two pyridines are linked (*ortho* to N) in a tertiary phosphine and form a six-membered metallocyclic chelate ring in

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, interatomic distances and angles, torsion angles and mean-plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38853 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the boat conformation. With Co in the bow and P in the stern, the two Cl atoms occupy the bowsprit and flagpole (Eliel, 1962), the two pyridine rings form port and starboard outriggers, and the phenyl ring is in the rudder position. The entire molecule has approximate *m*

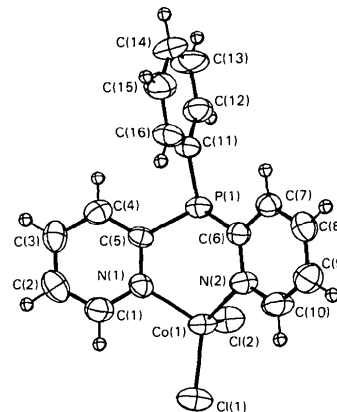


Fig. 1. $(\text{Phy}_2\text{P-N,N}')\text{CoCl}_2$ showing 50% thermal ellipsoids.

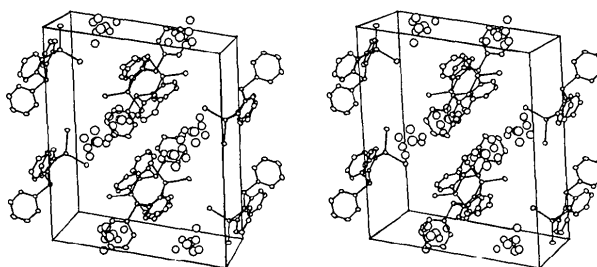


Fig. 2. Packing diagram of the title compound showing disordered ethanol (unconnected circles).

Table 1. Coordinates and isotropic or equivalent isotropic thermal parameters (\AA^2)

	x	y	z	B or B _{eq}		x	y	z	B or B _{eq}
Co	0.94585 (5)	0.22249 (6)	0.11509 (4)	3.81 (2)	C(8)	1.0930 (3)	0.5580 (4)	0.1814 (2)	4.3 (1)
Co'	0.36382 (5)	0.27231 (7)	0.17228 (4)	4.27 (2)	C(8')	0.4471 (4)	0.0331 (5)	0.3647 (3)	6.2 (2)
Cl(1)	0.93524 (9)	0.2020 (1)	0.00118 (7)	5.39 (4)	C(9)	1.0504 (4)	0.5449 (5)	0.1161 (3)	5.1 (2)
Cl(1')	0.22771 (9)	0.2456 (2)	0.13957 (8)	6.14 (4)	C(9')	0.3779 (3)	0.0095 (5)	0.3180 (3)	6.3 (2)
Cl(2)	0.82666 (9)	0.2111 (1)	0.15658 (7)	5.60 (4)	C(10)	1.0097 (3)	0.4479 (5)	0.1000 (2)	4.7 (1)
Cl(2')	0.44337 (9)	0.2621 (1)	0.09136 (7)	5.42 (4)	C(10')	0.3568 (4)	0.0807 (5)	0.2635 (3)	5.3 (2)
P	1.04113 (8)	0.2648 (1)	0.27117 (7)	3.49 (3)	C(11)	1.1296 (3)	0.2878 (4)	0.3386 (2)	3.6 (1)
P'	0.52503 (9)	0.3247 (1)	0.28985 (8)	4.06 (3)	C(11')	0.5811 (3)	0.3546 (5)	0.3757 (2)	4.0 (1)
N(1)	1.0341 (2)	0.1185 (3)	0.1644 (2)	3.35 (9)	C(12)	1.1123 (3)	0.3005 (5)	0.4047 (3)	4.7 (2)
N(1')	0.3784 (2)	0.4156 (4)	0.2270 (2)	3.7 (1)	C(12')	0.6665 (3)	0.3714 (6)	0.3813 (3)	5.7 (2)
N(2)	1.0088 (2)	0.3635 (3)	0.1448 (2)	3.7 (1)	C(13)	1.1763 (4)	0.3168 (6)	0.4588 (3)	6.8 (2)
N(2')	0.4003 (2)	0.1750 (4)	0.2565 (2)	4.1 (1)	C(13')	0.7129 (4)	0.3961 (7)	0.4456 (4)	8.2 (2)
C(1)	1.0521 (3)	0.0244 (5)	0.1330 (3)	4.5 (1)	C(14)	1.2578 (4)	0.3206 (6)	0.4489 (3)	6.5 (2)
C(1')	0.3205 (3)	0.4940 (5)	0.2144 (3)	4.3 (1)	C(14')	0.6759 (4)	0.4026 (6)	0.5023 (3)	7.4 (2)
C(2)	1.1038 (3)	-0.0547 (5)	0.1649 (3)	4.9 (1)	C(15)	1.2747 (3)	0.3090 (5)	0.3828 (3)	5.6 (2)
C(2')	0.3238 (3)	0.5895 (4)	0.2506 (3)	5.1 (2)	C(15')	0.5918 (4)	0.3848 (6)	0.4983 (3)	6.3 (2)
C(3)	1.1402 (3)	-0.0372 (4)	0.2324 (3)	4.6 (2)	C(16)	1.2120 (3)	0.2928 (5)	0.3276 (2)	4.3 (1)
C(3')	0.3888 (3)	0.6078 (5)	0.3025 (3)	4.4 (1)	C(16')	0.5454 (3)	0.3626 (5)	0.4347 (3)	5.0 (1)
C(4)	1.1253 (3)	0.0608 (4)	0.2640 (2)	4.0 (1)	C(15S)	0.715 (1)	0.025 (2)	0.501 (1)	20.3 (8)
C(4')	0.4498 (3)	0.5287 (4)	0.3171 (3)	4.1 (1)	C(2S)	0.230 (1)	0.001 (2)	0.467 (1)	15.3 (7)
C(5)	1.0729 (3)	0.1386 (4)	0.2289 (2)	3.1 (1)	C(3S)	0.650 (2)	0.004 (3)	0.471 (2)	11.4 (8)
C(5')	0.4427 (3)	0.4317 (4)	0.2793 (2)	3.5 (1)	C(4S)	0.770 (2)	0.066 (3)	0.582 (1)	13.2 (10)
C(6)	1.0523 (3)	0.3752 (4)	0.2084 (2)	3.2 (1)	C(5S)	0.743 (2)	0.102 (3)	0.458 (2)	16.7 (11)
C(6')	0.4657 (3)	0.2008 (5)	0.3053 (3)	4.2 (1)	C(6S)	0.788 (2)	0.009 (3)	0.489 (2)	14.2 (10)
C(7)	1.0938 (3)	0.4725 (4)	0.2280 (2)	3.6 (1)	C(7S)	0.734 (3)	0.077 (4)	0.507 (2)	19.4 (16)
C(7')	0.4911 (4)	0.1284 (5)	0.3594 (3)	5.5 (1)	C(8S)	0.678 (2)	0.097 (3)	0.510 (2)	10.4 (10)

(C_s) symmetry, and the two independent molecules are essentially identical. In fact, a least-squares fit (Rohrer & Smith, 1980) of the relative positions of equivalent atoms in the two molecules yields an average separation of 0.09 (5) Å, with maximum separation 0.23 Å at C(3)···C(3'). Thus, although some small, statistically significant differences in 'chemically equivalent' geometric measures can be found,* only weighted averages are reported herein (Table 2).

The four pyridine rings are planar (r.m.s. deviation 0.01 Å)* with dihedral angles 48 and 55° (molecules 1 and 2 respectively). Each P atom is out-of-plane by *ca* 0.1 Å, and the two Co atoms are within 0.08 Å of three of the pyridine planes. Co(1) is 0.2 Å from the plane containing N(1), a distortion due perhaps to intermolecular forces in the disordered structure. Each phenyl ring is planar (r.m.s. deviation 0.004 Å) and locked into an orientation parallel to the mean molecular plane through very close contact with pyridine H atoms: H···C = 2.75 Å (calculated 2.9 Å; Pauling, 1960). Torsion angles have been deposited.

Most of the bond lengths and angles are similar to those previously reported. However, the N—Co—N angle varies considerably and seems to depend largely on the stereochemical requirements of the substituted pyridine ring. Thus, in the unrestricted 4-substituted complexes (Admiraal & Gafner, 1968; Laing & Carr, 1975) the N—Co—N angle is near the tetrahedral value. With a bulkier 2-substituent (Allan, Jones & Sawyer, 1981), this angle is slightly expanded to 114°, while in the seven-membered chelate ring (Kadooka, Warner & Seff, 1976) the angle is greatly expanded to 118°. In the current six-membered chelate ring, the angle is reduced to 95°.

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* See deposition footnote.

Table 2. *Average geometry*

Co—Cl	2.221 (1) Å	Cl—Co—Cl	116.2 (1)°
Co—N	2.031 (2)	Cl(1)—Co—N	108.7 (1)
P—C(Ph)	1.816 (4)	Cl(2)—Co—N	113.2 (1)
P—C(ph)	1.843 (3)	N—Co—N	94.8 (1)
N—C	1.347 (2)	C—P—C	102.3 (1)
C—C(py)	1.371 (2)	C—N—C	118.5 (3)
C—C(Ph)	1.379 (2)	C(1)—N—Co	119.4 (2)
		C(5)—N—Co	122.0 (2)
		N—C(1)—C(2)	123.1 (3)
		N—C(5)—C(4)	120.7 (3)
		P—C—N	116.6 (2)
		P—C—C(py)	122.2 (2)
		P—C(11)—C(12)	116.6 (3)
		P—C(11)—C(16)	124.7 (3)
		C—C—C(py)	119.2 (2)
		C—C—C(Ph)	119.9 (2)

References

- ADMIRAAL, L. J. & GAFNER, G. (1968). *J. Chem. Soc. Chem. Commun.* pp. 1221–1222.
- ALLAN, J. R., JONES, C. L. & SAWYER, L. (1981). *J. Inorg. Nucl. Chem.* **43**, 2707–2711.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- ELIEL, E. L. (1962). *Stereochemistry of Carbon Compounds*, p. 205. New York: McGraw-Hill.
- FRENZ, B. A. (1980). *SDP User's Guide*. Enraf–Nonius, Delft.
- GILL, N. S. & NYHOLM, R. S. (1961). *J. Inorg. Nucl. Chem.* **18**, 88–97.
- INOBUCHI, Y., MAHRLA, M. B., NEUGEBAUER, D., JONES, P. G. & SCHMIDBAUR, H. (1983). *Chem. Ber.* **116**, 1487–1493.
- KADOOKA, M. M., WARNER, L. G. & SEFF, K. (1976). *Inorg. Chem.* **15**, 812–816.
- LAING, M. & CARR, G. (1975). *Acta Cryst.* **B31**, 2683–2684.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- NEWKOME, G. R. & HAGER, D. C. (1978a). *J. Am. Chem. Soc.* **100**, 5567–5568.
- NEWKOME, G. R. & HAGER, D. C. (1978b). *J. Org. Chem.* **43**, 947–949.
- NEWKOME, G. R. & HAGER, D. C. (1978c). Unpublished results.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 261. Ithaca: Cornell Univ. Press.
- ROHRER, D. & SMITH, G. D. (1980). *FITMOL in PROPHET Molecules*, edited by W. P. RINDONE & T. KUSH. Cambridge, MA: Bolt Beranek and Newman.

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Monopotassium Salt of 4-Methyl[1,2,5]thiadiazolo[3,4-c][1,2,6]thiadiazine-7(6H)-one 5,5-Dioxide, C₄H₃N₄O₃S₂·K⁺

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Abstract. $M_r = 258.33$, monoclinic, $C2/c$, $a = 0.026$ for 1714 observed reflexions. The thiadiazine ring shows the expected envelope conformation. The K⁺ ion is mainly surrounded by seven neighbours at distances ranging from 2.72 (4) to 3.10 (1) Å forming a laterally capped trigonal prism.

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