quite different conformations as observed in these two forms. The α-cyanoethyl group of [(*S*)-1-cyanoethyl](pyridine)cobaloxime (α-py complex) (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1982), which is a product of the β–α isomerization, is nearly parallel to the cobaloxime plane. The cyanoethyl group in form II bears closer resemblance in shape to that of the α-py complex than that in form I. This means that the atoms of the cyanoethyl group in form II move to a smaller extent than those in form I in β–α isomerization. The topochemical rule (Cohen & Schmidt, 1964) should be applicable when the reactive groups have such different conformations. This factor, the second factor, appears to control the reaction rate, in preference to the cavity size (the first factor), in the case of significantly different conformers of the reactive group.

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Structure of *cis*-Dichlorobis(3,5-diphenylpyrazole)platinum(II) Tetrahydrofuran Solvate: a Platinum Complex Containing Two Pyrazole Ligands

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Abstract. $[PtCl_2(C_{15}H_{12}N_2)_2].C_4H_8O$, $M_r = 778{\cdot}7$, triclinic, $P\overline{1}$, $a = 9{\cdot}954\,(3)$, $b = 11{\cdot}579\,(3)$, $c = 15{\cdot}141\,(3)$ Å, $\alpha = 70{\cdot}30\,(2)$, $\beta = 75{\cdot}79\,(2)$, $\gamma = 78{\cdot}54\,(2)^\circ$, $V = 1579{\cdot}8\,(7)$ Å^3, $Z = 2$, $D_x = 1{\cdot}637$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 4{\cdot}69$ mm^{-1}, $F(000) = 767{\cdot}8$, $T = 298$ K. The structure consists of a square-planar platinum(II) complex containing two chloride and two 3,5-diphenylpyrazole ligands in *cis* geometry along with an interstitial molecule of tetrahydrofuran. Convergence to final conventional R values of $R = 0{\cdot}0388$ and $wR = 0{\cdot}0406$ was obtained using 331 variable parameters and 3476 reflections with $F_o^2 > 3\sigma(F_o^2)$.

Introduction. Heterometallic doubly bridged complexes can be formed in a stepwise fashion from mononuclear compounds which contain two dangling ligands. Such compounds can be thought of as metal-containing ligands.

Focusing our attention on the heavier metals, we have synthesized the mononuclear complex $[Au\{(CH_2)P(C_6H_5)_2S)\}_2]$ containing two dangling S atoms. Using this as starting material, we have synthesized and structurally characterized some mixed metal complexes such as the ones containing AuPtAu (Murray, Briggs, Garzòn, Raptis, Porter & Fackler, 1987), AuTl (Wang, Fackler, King & Wang, 1988), AuPbAu (Wang, Garzòn, King, Wang & Fackler, 1989) and AuHg (Wang & Fackler, 1988) metal cores. We are extending these studies to complexes involving 3,5-diphenylpyrazole ligands.

Some transition-metal complexes of the general types $L_2M(\text{pz})_2$, $L_2M(\text{pzH})_2$, $L_2M[3,5\text{-}(CH_3)_2\text{pz}]$ and $L_2M[3,5\text{-}(CH_3)_2\text{pzH}]_2$, where L = Lewis base, M = Pt, Pd, pz = pyrazolato anion ($C_3H_3N_2$) and pzH = pyrazole ($C_3H_4N_2$), are known (Bonati & Clark,

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1978; Minghetti, Banditelli & Bonati, 1977, 1979). The deprotonated (pyrazolato) forms of these materials behave as five-membered bidentate ligands. A variety of metals, such as zinc, cadmium, mercury, cobalt, nickel and copper, can form adducts with such chelating ligands (Minghetti, Banditelli & Bonati, 1977; Bandini, Banditelli, Minghetti & Bonati, 1979; Cariati, Micera, Scozzafava, Minghetti & Banditelli, 1982). These heterobimetallic complexes, as well as their monomeric precursors, have been studied by spectroscopic techniques and to date no structural data are available on them. The crystal structure of $(CH_3)_2Ga(\mu\text{-pz})_2Ir(C_8H_8)$ has been reported (Nussbaum, Rettig, Storr & Trotter, 1985). Recently, *trans*-$PdCl_2(pzH)_2$ has been prepared and used for the synthesis of several heterometallic complexes (Pinillos, Tejel, Oro, Apreda, Foces-Foces & Cano, 1989).

Here, we report the crystal structure of *cis*-$PtCl_2[3,5\text{-}(C_6H_5)_2pzH]_2$ tetrahydrofuran solvate, a monomeric bispyrazole complex which, upon deprotonation, will form a dianionic platinum-containing bidentate ligand.

Experimental. Postassium tetrachloroplatinate and 3,5-diphenylpyrazole were purchased from Aesar, the Johnson Matthey Group plc and Lancaster Synthesis Ltd (N. H.), respectively, and were used as received. *cis*-Bis(3,5-diphenylpyrazole)platinum(II) dichloride was prepared by the addition of 3,5-diphenylpyrazole in an aqueous solution of potassium tetrachloroplatinate. Crystals were grown by slow diffusion of diethyl ether into a tetrahydrofuran solution of the product.

A single muliti-faceted light yellow crystal of approximate dimensions 0·10 × 0·30 × 0·30 mm was mounted in a random orientation on a glass fiber. Triclinic symmetry suggested on the basis of interaxial angles and confirmed by rotation photographs and $\bar{1}$ Laue symmetry. Axial lengths checked by comparison with the interlayer spacings observed in axial photographs. Refined cell parameters obtained from the setting angles of 25 reflections with $30 < 2\theta < 35°$. Data collection carried out at room temperature using the ω-scanning technique in bisecting geometry (Nicolet *R*3*m*/*E* diffractometer, graphite-monochromated Mo *Kα* radiation). Intensities measured for 4109 unique reflections ($|h| < 11$, $|k| < 13$, $+l < 7$) with $0 < 2\theta < 45°$, no symmetry equivalent reflections were collected. Scan rate variable, 3–30° min^{-1}; scan range ±0·9°. Backgrounds estimated from a 96-step peak profile. Three low-angle standards ($0\bar{3}\bar{1}$, $1\bar{3}\bar{1}$, $1\bar{1}1$) measured every 97 data reflections. The data were corrected for minor decay (less than 10%) by scaling on the three standards. Corrections for absorption applied empirically on the basis of azimuthal scans of ten reflections spanning a range of 2θ values (minimum and maximum transmission 0·117 and 0·208, respectively). Crystal-structure determination and refinement carried out using the *SHELXTL* collection of crystallographic software (Sheldrick, 1981). Pt-atom position determined from a sharpened Patterson map; all remaining non-H atoms located on difference Fourier maps. Phenyl rings refined as idealized polygons (C—C = 1·395 Å, C—C—C = 120°) using H atoms placed in calculated positions (C—H = 0·960 Å) with fixed thermal parameters [$U(\mathrm{H}) = 0{\cdot}08$ Å^2]. An interstitial molecule of tetrahydrofuran was found. All non-H atoms refined anisotropically. Refinement based on F with weights of the form $w^{-1} = [\sigma^2(F) + 0{\cdot}00727(F^2)]$. The value 0·00727, g, was refined by fitting $(F_o - F_c)^2$ to $[\sigma^2(F) + gF]/k$ (k scale factor) to put weights on an approximately absolute scale. Scattering factors, including terms for anomalous dispersion, taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Convergence to conventional R values of $R = 0{\cdot}0388$ and $wR = 0{\cdot}0406$ obtained using 331 variable parameters and 3476 reflections with $F_o^2 > 3\sigma(F_o^2)$. For final cycle, max. shift/σ = 0·011 with a goodness-of-fit indicator of 1·584. Max. and min. residual electron densities on final difference Fourier map of 1·29 and −2·04 e Å^{-3}, respectively, in the vicinity of the Pt atom.

Discussion. The product obtained from the reaction of K_2PtCl_4 and 3,5-diphenylpyrazole is a discrete mononuclear Pt$^{\mathrm{II}}$ complex containing two chloride and two 3,5-diphenylpyrazole ligands in *cis* geometry. The unit cell consists of two molecules of $PtCl_2(3,5\text{-}Ph_2pzH)_2$ and two interstitial molecules of tetrahydrofuran. A perspective view of the complex is shown in Fig. 1. A packing diagram of the cell contents projected down the *a* axis is shown in Fig. 2. Atomic positional and isotropic thermal parameters for all non-H atoms are presented in Table 1.* Bond angles and distances are summarized in Table 2.

The structure described here consists of a four-coordinate Pt$^{\mathrm{II}}$ center to which are bound two chloride and two 3,5-diphenylpyrazole ligands. The Pt—Cl bond lengths, 2·303 (2) and 2·287 (2) Å, as well as the Pt—N bond lengths, 1·994 (7) and 2·019 (7) Å, are typical of platinum square-planar complexes. The ligands are arranged in an almost ideal square-planar geometry around the metal center with all *cis* angles ranging between 88·3 (2)

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53749 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and 91·8 (2)° and *trans* angles of 177·0 (2) and 176·9 (2)°. To relieve the steric crowding, the two diphenylpyrazole ligands rotate to opposite directions so that they form 54·5 (2) and 58·4 (2)° dihedral angles with the best fit plane of the platinum coordination and a 57·3 (2)° dihedral angle with each other. In a similar Cu^{II} complex, $CuBr_2(3,5\text{-}Ph_2pzH)_2$ (Murray, Raptis & Fackler, 1988), the crowding of the bulky pyrazole groups is relieved by a large tetrahedral distortion of the metal coordination. The N—N, N—C and C—C bond lengths of the pyrazole rings, 1·355 (11)–1·361 (11), 1·330 (10)–1·360 (9) and 1·372 (13)–1·412 (13) Å, respectively, show no significant localization of the double bonds. The Pt—N—N angles, *ca* 120°, and the Pt—N—C angles, *ca* 134°, suggest a slight asymmetry of the ligand binding to the metal atoms. The tetrahydrofuran appears to be H bonded to the ring N atom at 2·85 (2) Å.

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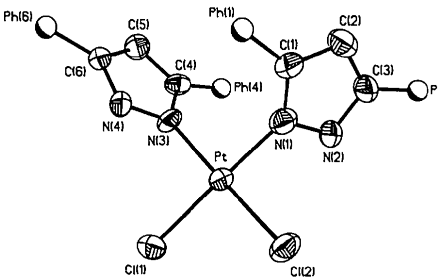

Fig. 1. A perspective view of the *cis*-$PtCl_2[3,5\text{-}(C_6H_5)_2C_3H_2N_2]_2$ structure. Thermal ellipsoids have been drawn at the 50% probability level. H atoms have not been included and phenyl groups are represented by their *ipso* C atoms for clarity (Ph1 = C11–C16, Ph3 = C31–C36, Ph4 = C41–C46, Ph6 = C61–C66). Solvent molecule not shown.

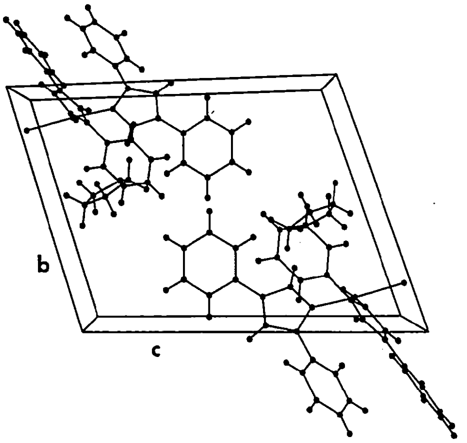

Fig. 2. A packing diagram viewed down the *a* axis.

Table 1. *Atomic coordinates* (× 10⁴) *and equivalent isotropic thermal parameters* (Å² × 10³) *for cis*-$PtCl_2[3,5\text{-}(C_6H_5)_2C_3H_3N_2]_2.C_4H_8O$

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Pt	4176 (1)	1099 (1)	1503 (1)	34 (1)
Cl(1)	4868 (2)	1633 (2)	−135 (1)	49 (1)
Cl(2)	6319 (2)	1315 (2)	1685 (2)	53 (1)
N(1)	3541 (7)	735 (6)	2914 (5)	45 (3)
N(2)	3646 (7)	1560 (6)	3342 (4)	42 (3)
N(3)	2295 (6)	817 (6)	1392 (4)	40 (2)
N(4)	2197 (6)	−113 (5)	1059 (4)	37 (2)
C(1)	2929 (8)	−190 (7)	3612 (6)	45 (3)
C(2)	2626 (10)	66 (8)	4494 (6)	54 (4)
C(3)	3086 (9)	1190 (7)	4293 (5)	48 (3)
C(4)	970 (7)	1172 (7)	1792 (5)	36 (3)
C(5)	86 (8)	473 (7)	1693 (5)	44 (3)
C(6)	890 (8)	−348 (7)	1217 (5)	37 (3)
C(11)	1272 (6)	−1658 (5)	3880 (4)	66 (4)
C(12)	933 (6)	−2705 (5)	3764 (4)	96 (7)
C(13)	1898 (6)	−3355 (5)	3207 (4)	90 (6)
C(14)	3202 (6)	−2959 (5)	2765 (4)	91 (6)
C(15)	3541 (6)	−1913 (5)	2880 (4)	64 (4)
C(16)	2576 (6)	−1263 (5)	3438 (4)	49 (3)
C(31)	3155 (8)	1260 (4)	5896 (4)	67 (4)
C(32)	3124 (8)	1912 (4)	6527 (4)	80 (5)
C(33)	3005 (8)	3201 (4)	6207 (4)	85 (6)
C(34)	2917 (8)	3838 (4)	5256 (4)	78 (5)
C(35)	2948 (8)	3186 (4)	4625 (4)	71 (5)
C(36)	3067 (8)	1897 (4)	4945 (4)	56 (4)
C(41)	−401 (6)	1995 (5)	3079 (4)	63 (4)
C(42)	−768 (6)	2903 (5)	3542 (4)	77 (5)
C(43)	−98 (6)	3963 (5)	3180 (4)	74 (5)
C(44)	939 (6)	4117 (5)	2355 (4)	64 (4)
C(45)	1306 (6)	3209 (5)	1893 (4)	56 (4)
C(46)	636 (6)	2148 (5)	2255 (4)	46 (3)
C(61)	−964 (4)	−1356 (4)	1070 (4)	50 (4)
C(62)	−1409 (4)	−2275 (4)	847 (4)	61 (4)
C(63)	−430 (4)	−3146 (4)	507 (4)	62 (4)
C(64)	995 (4)	−3099 (4)	390 (4)	69 (5)
C(65)	1440 (4)	−2180 (4)	613 (4)	58 (4)
C(66)	460 (4)	−1308 (4)	953 (4)	38 (3)
O*	4638 (7)	3904 (6)	2422 (4)	62 (3)
C(O1)*	5866 (12)	3904 (12)	2722 (8)	86 (6)
C(O2)*	6844 (18)	4594 (20)	1865 (11)	171 (12)
C(O3)*	6198 (13)	4910 (13)	1090 (9)	110 (7)
C(O4)*	4799 (13)	4525 (9)	1394 (7)	80 (5)

* Atoms of tetrahydrofuran.

Table 2. *Bond lengths* (Å) *and angles* (°) *for cis*-$PtCl_2[3,5\text{-}(C_6H_5)_2C_3H_3N_2]_2$

Pt—Cl(1)	2·303 (2)	N(4)—C(6)	1·330 (10)
Pt—Cl(2)	2·287 (2)	C(1)—C(2)	1·412 (13)
Pt—N(1)	1·994 (7)	C(2)—C(3)	1·377 (13)
Pt—N(3)	2·019 (7)	C(4)—C(5)	1·372 (13)
N(1)—N(2)	1·355 (11)	C(5)—C(6)	1·393 (11)
N(3)—N(4)	1·361 (11)	C(1)—C(16)	1·476 (12)
N(1)—C(1)	1·347 (9)	C(3)—C(36)	1·475 (12)
N(2)—C(3)	1·360 (9)	C(4)—C(46)	1·466 (11)
N(3)—C(4)	1·355 (9)	C(6)—C(66)	1·466 (11)

Cl(1)—Pt—Cl(2)	91·8 (1)	N(1)—N(2)—C(3)	111·3 (6)
Cl(1)—Pt—N(1)	176·9 (2)	N(4)—N(3)—C(4)	105·3 (7)
Cl(1)—Pt—N(3)	90·0 (2)	N(3)—N(4)—C(6)	112·7 (6)
Cl(2)—Pt—N(1)	88·3 (2)	N(1)—C(1)—C(2)	110·0 (8)
Cl(2)—Pt—N(3)	177·0 (2)	C(1)—C(2)—C(3)	105·4 (7)
N(1)—Pt—N(3)	90·1 (3)	C(2)—C(3)—N(2)	107·3 (7)
Pt—N(1)—N(2)	119·7 (4)	N(3)—C(4)—C(5)	109·1 (7)
Pt—N(3)—N(4)	120·1 (4)	C(4)—C(5)—C(6)	107·8 (7)
N(2)—N(1)—C(1)	106·0 (7)	C(5)—C(6)—N(4)	105·2 (8)

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Structure of Bis[2-methyl-1,1-di(2-pyridyl)-2-propanol]copper(II) Dichloride Dihydrate

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Abstract. $C_{28}H_{32}CuN_4O_2^{2+}.2Cl^-.2H_2O$, $M_r = 627·06$, monoclinic, $P2_1/c$, $a = 9·137\,(2)$, $b = 9·047\,(2)$, $c = 18·377\,(7)$ Å, $\beta = 99·10\,(3)°$, $V = 1500·4\,(9)$ Å^3, $Z = 4$, $D_x = 1·529$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·164$ mm^{-1}, $F(000) = 1308$, $T = 291$ K, $R = 0·028$ for 1768 unique observed reflections. The Cu atom displays an octahedral elongated (4 + 2) coordination. The four N atoms of two 2-methyl-1,1-di(2-pyridyl)-2-propanol molecules lie in a plane. The two out of plane bonds join the O atoms of the modified methane groups. The complex is monomeric with the Cl as counterions [Cu—Cl(1) = 6·105 (2) Å] and crystallizes with two H_2O molecules. The Cu atom is at an inversion center, so the two organic ligands are completely identical. Cu—N(1) = 2·016 (2), Cu—N(2) = 2·026 (2), Cu—O(2) = 2·294 Å.

Introduction. The methane group that bridges the two pyridines rings of the di(2-pyridyl)methane ligand can undergo different reactions. These reactions take place when the ligand is coordinated with copper(II). The oxidation reaction of the —CH_2— group to form an alcohol, which coordinates with the copper(II) through the O atom has been described (Garland, Le Marouille, Spodine & Manzur, 1986). The —CH_2— group can also be oxidized to a ketone group by molecular oxygen (Urbach, Knopp & Zuberbühler, 1978). The title compound results from the reaction of the —CH_2— group of the coordinated ligand with acetone: