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Dichloridobis(3,5-dimethyl-1*H*-pyrazol-4-amine-κN^2)cobalt(II)

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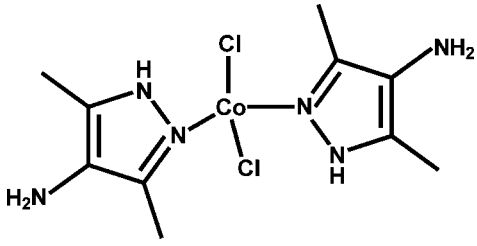
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.043; wR factor = 0.102; data-to-parameter ratio = 19.6.

In the title compound, $[CoCl_2(C_5H_9N_3)_2]$, the Co^{II} atom adopts a slightly distorted tetrahedral coordination geometry provided by two chloride anions and two N atoms from the organic ligands. The dihedral angle between the pyrazole rings is 85.91 (10)°. In the crystal structure, molecules are linked into a three-dimensional network by intermolecular N—H···N and N—H···Cl hydrogen-bonding interactions.

Related literature

For the crystal structures of related pyrazole compounds, see: Francisco *et al.* (1980); Murray *et al.* (1988); Zhao & Eichhorn (2005).



Experimental

Crystal data

$[CoCl_2(C_5H_9N_3)_2]$
M_r = 352.13
Triclinic, $P\overline{1}$
a = 9.182 (3) Å
b = 9.191 (4) Å
c = 10.085 (3) Å
α = 94.807 (13)°
β = 106.105 (4)°
γ = 107.814 (12)°
V = 765.1 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.47 mm^{-1}
T = 293 (2) K
0.25 × 0.15 × 0.04 mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.836, T_{max} = 0.940
7916 measured reflections
3456 independent reflections
2579 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.102
S = 0.98
3456 reflections
176 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9A···Cl1	0.96	2.67	3.570 (5)	157
N2—H2A···N6^{i}	0.86	1.98	2.835 (3)	175
N5—H5D···N3^{ii}	0.86	2.08	2.919 (4)	164
N3—H3A···Cl2^{iii}	0.90	2.56	3.452 (3)	169
N6—H6B···Cl1^{iv}	0.90	2.72	3.457 (3)	140

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $x, y+1, z$; (iv) $-x+1, -y, -z$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2230).

References

Francisco, R. H. P., Lechat, J. R., Massabni, A. C., Melios, C. B. & Molina, M. (1980). *J. Coord. Chem.* **10**, 149–153.
Murray, J. J., Raptis, R. G. & Fackler, J. P. Jr (1988). *Inorg. Chem.* **27**, 26–33.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Zhao, N. & Eichhorn, D. M. (2005). *Acta Cryst.* E**61**, m822–m823.

supporting information

Acta Cryst. (2008). E**64**, m1012 [doi:10.1107/S1600536808020461]

Dichloridobis(3,5-dimethyl-1*H*-pyrazol-4-amine-κN^2)cobalt(II)

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S1. Comment

Pyrazolylmethane late-transition-metal complexes of the first row have shown great potential for the construction of magnetic devices. In the course of our studies of the coordination chemistry of these ligands with cobalt, the title compound was synthesized and we report its crystal structure here.

There have been a few crystal structures reported to date for four-coordinate metal complexes containing two coordinated pyrazoles and two coordinated halides, for examples, dichlorobis(1- phenyl-3,5-dimethylpyrazole)copper(II) (Francisco *et al.*, 1980;), dibromobis(3,5-diphenylpyrazole)copper(II) (Murray *et al.*, 1988) and dichlorobis(3,5-dimethyl-pyrazole) copper(II) (Zhao & Eichhorn, 2005). The Co—N (2.003 (2) and 2.006 (2) Å) and Co—Cl bond lengths (2.2373 (10) and 2.2829 (11) Å) are within the ranges expected. The dihedral angle formed by the pyrazole rings is 85.91 (10)°. An intramolecular C—H···Cl hydrogen bond (Table 1) helps to stabilzie the molecular conformation. In the crystal structure, molecules are linked by intermolecular N—H···N and N—H···Cl hydrogen bonding interactions to form a three-dimensional network (Table 1).

S2. Experimental

3,5-Dimethyl-1*H*-pyrazol-4-amine (0.111 g, 1 mmol) was dissolved in ethanol (5 ml) and $CoCl_2$ (0.127 g, 1 mmol) in aqueous solution (5 ml) was added with stirring. Colourless crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature over several days

S3. Refinement

All H atoms were located in a difference Fourier map and refined using the riding-atom approximation, with C—H = 0.96 Å, N—H = 0.86-0.90 Å, and with U_{iso}(H) = 1.2 U_{eq} (N) or 1.5 U_{eq} (C).

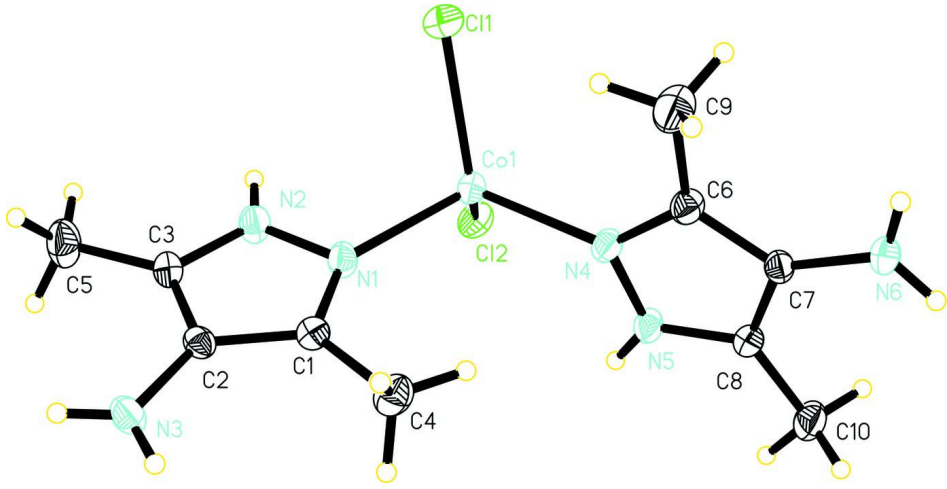

Figure 1

The molecular structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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V = 765.1 (5) Å^3
Z = 2
F(000) = 362
D_x = 1.528 Mg m^{-3}
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Cell parameters from 2030 reflections
θ = 2.7–27.5°
μ = 1.47 mm^{-1}
T = 293 K
Plate, colourless
0.25 × 0.15 × 0.04 mm

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CCD_Profile_fitting scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.836, T_{max} = 0.940
7916 measured reflections
3456 independent reflections
2579 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 27.5°, θ_{min} = 2.8°
h = −11→11
k = −11→11
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.102
S = 0.98
3456 reflections
176 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.36013 (4)	0.23415 (4)	0.15884 (4)	0.03042 (13)
Cl1	0.21996 (10)	0.22767 (10)	−0.06317 (8)	0.0469 (2)
Cl2	0.24095 (9)	0.03437 (9)	0.25653 (8)	0.0412 (2)
C1	0.4561 (3)	0.5640 (3)	0.3357 (3)	0.0286 (6)
C2	0.3704 (3)	0.6573 (3)	0.3698 (3)	0.0287 (6)
C3	0.2086 (4)	0.5675 (3)	0.3138 (3)	0.0343 (7)
C4	0.6339 (4)	0.6063 (4)	0.3676 (3)	0.0423 (8)
H4A	0.6603	0.5134	0.3594	0.064*
H4B	0.6879	0.6646	0.4615	0.064*
H4C	0.6681	0.6683	0.3025	0.064*
C5	0.0604 (4)	0.6012 (4)	0.3138 (4)	0.0548 (10)
H5A	−0.0320	0.5235	0.2461	0.082*
H5B	0.0687	0.7017	0.2900	0.082*
H5C	0.0486	0.6001	0.4054	0.082*
C6	0.6694 (3)	0.2278 (3)	0.0980 (3)	0.0328 (6)
C7	0.7967 (3)	0.1765 (3)	0.1557 (3)	0.0289 (6)
C8	0.7838 (3)	0.1407 (3)	0.2824 (3)	0.0322 (6)
C9	0.6290 (5)	0.2806 (5)	−0.0382 (4)	0.0587 (10)
H9A	0.5146	0.2584	−0.0741	0.088*
H9B	0.6621	0.2270	−0.1039	0.088*
H9C	0.6841	0.3905	−0.0249	0.088*
C10	0.8851 (4)	0.0783 (4)	0.3884 (3)	0.0491 (9)
H10A	0.8390	0.0580	0.4624	0.074*
H10B	0.9923	0.1532	0.4267	0.074*
H10C	0.8894	−0.0164	0.3445	0.074*
N1	0.3517 (3)	0.4248 (3)	0.2644 (2)	0.0325 (5)
N2	0.2026 (3)	0.4300 (3)	0.2516 (3)	0.0382 (6)
H2A	0.1144	0.3540	0.2085	0.046*
N3	0.4325 (3)	0.8117 (3)	0.4457 (3)	0.0368 (6)
H3A	0.3934	0.8723	0.3907	0.044*
H3B	0.5407	0.8473	0.4675	0.044*
N4	0.5806 (3)	0.2228 (3)	0.1851 (2)	0.0335 (6)

N5	0.6537 (3)	0.1685 (3)	0.2974 (2)	0.0342 (6)
H5D	0.6207	0.1541	0.3687	0.041*
N6	0.9218 (3)	0.1729 (3)	0.1011 (3)	0.0362 (6)
H6A	0.8924	0.1782	0.0093	0.043*
H6B	0.9413	0.0835	0.1104	0.043*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0280 (2)	0.0327 (2)	0.0333 (2)	0.01479 (17)	0.00943 (16)	0.00507 (16)
Cl1	0.0451 (5)	0.0591 (5)	0.0349 (4)	0.0222 (4)	0.0057 (3)	0.0085 (4)
Cl2	0.0346 (4)	0.0415 (4)	0.0474 (5)	0.0122 (3)	0.0119 (3)	0.0154 (3)
C1	0.0293 (15)	0.0267 (15)	0.0297 (15)	0.0091 (11)	0.0094 (11)	0.0068 (11)
C2	0.0342 (16)	0.0288 (15)	0.0249 (14)	0.0114 (12)	0.0116 (11)	0.0057 (11)
C3	0.0357 (17)	0.0332 (17)	0.0374 (17)	0.0173 (13)	0.0117 (13)	0.0038 (13)
C4	0.0331 (17)	0.0422 (19)	0.049 (2)	0.0115 (14)	0.0106 (14)	0.0073 (15)
C5	0.039 (2)	0.048 (2)	0.078 (3)	0.0178 (16)	0.0199 (18)	−0.0025 (18)
C6	0.0285 (16)	0.0401 (17)	0.0332 (16)	0.0120 (12)	0.0133 (12)	0.0117 (13)
C7	0.0249 (14)	0.0283 (15)	0.0322 (15)	0.0085 (11)	0.0090 (11)	0.0005 (11)
C8	0.0262 (15)	0.0392 (17)	0.0314 (16)	0.0140 (12)	0.0075 (11)	0.0031 (12)
C9	0.056 (2)	0.096 (3)	0.053 (2)	0.045 (2)	0.0306 (18)	0.044 (2)
C10	0.049 (2)	0.070 (3)	0.0416 (19)	0.0387 (18)	0.0132 (15)	0.0163 (17)
N1	0.0281 (13)	0.0320 (14)	0.0392 (14)	0.0123 (10)	0.0121 (10)	0.0027 (11)
N2	0.0237 (13)	0.0328 (14)	0.0517 (17)	0.0064 (10)	0.0092 (11)	−0.0040 (12)
N3	0.0401 (15)	0.0314 (14)	0.0364 (14)	0.0109 (11)	0.0113 (11)	0.0016 (11)
N4	0.0322 (14)	0.0442 (15)	0.0313 (14)	0.0198 (11)	0.0122 (10)	0.0122 (11)
N5	0.0347 (14)	0.0486 (16)	0.0309 (13)	0.0232 (12)	0.0165 (10)	0.0146 (11)
N6	0.0297 (14)	0.0422 (15)	0.0398 (15)	0.0145 (11)	0.0148 (11)	0.0033 (11)

Geometric parameters (Å, º)

Co1—N4	2.003 (2)	C6—C9	1.483 (4)
Co1—N1	2.006 (2)	C7—C8	1.373 (4)
Co1—Cl1	2.2373 (10)	C7—N6	1.412 (3)
Co1—Cl2	2.2829 (11)	C8—N5	1.340 (3)
C1—N1	1.337 (3)	C8—C10	1.488 (4)
C1—C2	1.409 (4)	C9—H9A	0.9600
C1—C4	1.490 (4)	C9—H9B	0.9600
C2—C3	1.384 (4)	C9—H9C	0.9600
C2—N3	1.416 (3)	C10—H10A	0.9600
C3—N2	1.341 (4)	C10—H10B	0.9600
C3—C5	1.486 (4)	C10—H10C	0.9600
C4—H4A	0.9600	N1—N2	1.355 (3)
C4—H4B	0.9600	N2—H2A	0.8600
C4—H4C	0.9600	N3—H3A	0.9000
C5—H5A	0.9600	N3—H3B	0.9000
C5—H5B	0.9600	N4—N5	1.364 (3)
C5—H5C	0.9600	N5—H5D	0.8600

C6—N4	1.349 (3)	N6—H6A	0.9001
C6—C7	1.391 (4)	N6—H6B	0.9000
N4—Co1—N1	116.07 (10)	N5—C8—C7	107.2 (2)
N4—Co1—Cl1	114.54 (7)	N5—C8—C10	122.7 (3)
N1—Co1—Cl1	103.32 (8)	C7—C8—C10	130.0 (3)
N4—Co1—Cl2	103.72 (7)	C6—C9—H9A	109.5
N1—Co1—Cl2	104.88 (8)	C6—C9—H9B	109.5
Cl1—Co1—Cl2	114.26 (4)	H9A—C9—H9B	109.5
N1—C1—C2	109.4 (2)	C6—C9—H9C	109.5
N1—C1—C4	122.5 (2)	H9A—C9—H9C	109.5
C2—C1—C4	128.1 (3)	H9B—C9—H9C	109.5
C3—C2—C1	106.1 (2)	C8—C10—H10A	109.5
C3—C2—N3	125.5 (2)	C8—C10—H10B	109.5
C1—C2—N3	128.4 (3)	H10A—C10—H10B	109.5
N2—C3—C2	106.3 (2)	C8—C10—H10C	109.5
N2—C3—C5	122.1 (3)	H10A—C10—H10C	109.5
C2—C3—C5	131.6 (3)	H10B—C10—H10C	109.5
C1—C4—H4A	109.5	C1—N1—N2	106.1 (2)
C1—C4—H4B	109.5	C1—N1—Co1	137.05 (19)
H4A—C4—H4B	109.5	N2—N1—Co1	116.27 (17)
C1—C4—H4C	109.5	C3—N2—N1	112.1 (2)
H4A—C4—H4C	109.5	C3—N2—H2A	124.0
H4B—C4—H4C	109.5	N1—N2—H2A	124.0
C3—C5—H5A	109.5	C2—N3—H3A	109.0
C3—C5—H5B	109.5	C2—N3—H3B	109.1
H5A—C5—H5B	109.5	H3A—N3—H3B	108.0
C3—C5—H5C	109.5	C6—N4—N5	105.4 (2)
H5A—C5—H5C	109.5	C6—N4—Co1	132.8 (2)
H5B—C5—H5C	109.5	N5—N4—Co1	120.26 (18)
N4—C6—C7	109.9 (3)	C8—N5—N4	111.3 (2)
N4—C6—C9	122.4 (3)	C8—N5—H5D	124.3
C7—C6—C9	127.7 (3)	N4—N5—H5D	124.3
C8—C7—C6	106.2 (2)	C7—N6—H6A	109.9
C8—C7—N6	126.4 (3)	C7—N6—H6B	109.9
C6—C7—N6	127.3 (3)	H6A—N6—H6B	108.5

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N2—H2*A*···N6^{i}	0.86	1.98	2.835 (3)	175
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