

Dichloridobis(3,5-dimethyl-1H-pyrazol-4-amine- κ N²)cobalt(II)

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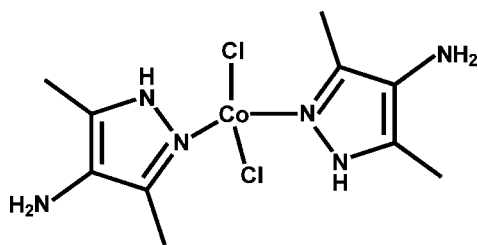
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.043; wR factor = 0.102; data-to-parameter ratio = 19.6.

In the title compound, $[\text{CoCl}_2(\text{C}_5\text{H}_9\text{N}_3)_2]$, 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 $\text{N}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{Cl}$ 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

$[\text{CoCl}_2(\text{C}_5\text{H}_9\text{N}_3)_2]$
 $M_r = 352.13$
Triclinic, $P\bar{1}$
 $a = 9.182$ (3) Å
 $b = 9.191$ (4) Å
 $c = 10.085$ (3) Å
 $\alpha = 94.807$ (13)°
 $\beta = 106.105$ (4)°

$\gamma = 107.814$ (12)°
 $V = 765.1$ (5) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 1.47$ mm⁻¹
 $T = 293$ (2) K
 $0.25 \times 0.15 \times 0.04$ mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)
 $T_{\text{min}} = 0.836$, $T_{\text{max}} = 0.940$

7916 measured reflections
3456 independent reflections
2579 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$

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

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C9}-\text{H9A}\cdots\text{Cl1}$	0.96	2.67	3.570 (5)	157
$\text{N2}-\text{H2A}\cdots\text{N6}^{\text{i}}$	0.86	1.98	2.835 (3)	175
$\text{N5}-\text{H5D}\cdots\text{N3}^{\text{ii}}$	0.86	2.08	2.919 (4)	164
$\text{N3}-\text{H3A}\cdots\text{Cl2}^{\text{iii}}$	0.90	2.56	3.452 (3)	169
$\text{N6}-\text{H6B}\cdots\text{Cl1}^{\text{iv}}$	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: RZ22230).

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.* **A64**, 112–122.
Zhao, N. & Eichhorn, D. M. (2005). *Acta Cryst.* **E61**, m822–m823.

supplementary materials

Acta Cryst. (2008). E64, m1012 [doi:10.1107/S1600536808020461]

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

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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-dimethylpyrazole)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 stabilize 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).

Experimental

3,5-Dimethyl-1*H*-pyrazol-4-amine (0.111 g, 1 mmol) was dissolved in ethanol (5 ml) and CoCl₂ (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

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 $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N})$ or $1.5 U_{\text{eq}}(\text{C})$.

Figures

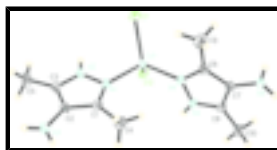


Fig. 1. The molecular structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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

Crystal data

[CoCl₂(C₅H₉N₃)₂]

$Z = 2$

supplementary materials

$M_r = 352.13$	$F_{000} = 362$
Triclinic, $P\bar{1}$	$D_x = 1.528 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation
$a = 9.182 (3) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 9.191 (4) \text{ \AA}$	Cell parameters from 2030 reflections
$c = 10.085 (3) \text{ \AA}$	$\theta = 2.7\text{--}27.5^\circ$
$\alpha = 94.807 (13)^\circ$	$\mu = 1.47 \text{ mm}^{-1}$
$\beta = 106.105 (4)^\circ$	$T = 293 (2) \text{ K}$
$\gamma = 107.814 (12)^\circ$	Plate, colourless
$V = 765.1 (5) \text{ \AA}^3$	$0.25 \times 0.15 \times 0.04 \text{ mm}$

Data collection

Rigaku Mercury2 (2x2 bin mode) diffractometer	3456 independent reflections
Radiation source: fine-focus sealed tube	2579 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.050$
Detector resolution: $13.6612 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 27.5^\circ$
$T = 293(2) \text{ K}$	$\theta_{\text{min}} = 2.8^\circ$
CCD_Profile_fitting scans	$h = -11 \rightarrow 11$
Absorption correction: multi-scan (CrystalClear; Rigaku, 2005)	$k = -11 \rightarrow 11$
$T_{\text{min}} = 0.836$, $T_{\text{max}} = 0.940$	$l = -13 \rightarrow 13$
7916 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.043$	H-atom parameters constrained
$wR(F^2) = 0.102$	$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2]$
$S = 0.98$	where $P = (F_o^2 + 2F_c^2)/3$
3456 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
176 parameters	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$
	Extinction correction: none

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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*

supplementary materials

Atomic displacement parameters (\AA^2)

	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 (\AA , $^\circ$)

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—C12	103.72 (7)	C6—C9—H9A	109.5
N1—Co1—C12	104.88 (8)	C6—C9—H9B	109.5
C11—Co1—C12	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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9—H9A \cdots C11	0.96	2.67	3.570 (5)	157
N2—H2A \cdots N6 ⁱ	0.86	1.98	2.835 (3)	175
N5—H5D \cdots N3 ⁱⁱ	0.86	2.08	2.919 (4)	164
N3—H3A \cdots C12 ⁱⁱⁱ	0.90	2.56	3.452 (3)	169
N6—H6B \cdots C11 ^{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) $-x+1, -y, -z$.

Fig. 1

