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Intramolecular hydrogen bonding in dichloridobis(3,5-di-*tert*-butyl-1*H*-pyrazole-κN^2)cobalt(II) as a consequence of ligand steric bulk

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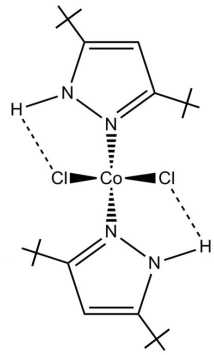
The title compound, $[CoCl_2(C_{11}H_{20}ClN_2)_2]$, forms two intramolecular hydrogen bonds [graph set $S(5)$] between the N atoms of the pyrazole ligands and the chloride ligands. This hydrogen-bonding motif is uncommon among related compounds but occurs here because of the bulk of *tert*-butyl substituents on the pyrazole ligands which shield the central metal atom to a significantly larger extent than pyrazole ligands with smaller 3,5-substituents.

Comment

Pyrazole and pyrazolyl transition metal complexes continue to be investigated as catalysts in ethylene oligomerization and polymerization reactions (Ojwach *et al.*, 2010). The ability of such metal complexes to catalyze the formation of polyethylene depends on the electrophilicity and steric bulk of the catalysts. Both of these factors are usually dictated by the nature and size of substituents on the pyrazolyl unit. However, in the polymer catalysts bis(pyrazole) nickel (Nelana *et al.*, 2004), pyrazole palladium (Li *et al.*, 2002) and pyrazolyl palladium complexes (Guzei *et al.*, 2003; Mohlala *et al.*, 2005) the high electrophilic metal centers ensure rapid insertion regardless of the steric bulk of these catalysts. In an extension of this study, we prepared the title compound, (I), which had appreciably lower catalytic activity than its nickel and palladium analogues.

The coordination geometry of the Co atom in (I) is distorted tetrahedral (Fig. 1). The metric parameters for bond distances and angles about the cobalt center are similar to those in six related compounds where a Co atom binds to two monodentate chloride ligands and two monodentate substituted pyrazole ligands (Table 1) [Cambridge Structural Database (CSD), Version 1.12, August 2010 update; Allen, 2002; the actual compounds are specified below]. However the N1—Co1—N3 angle in (I) is significantly larger and falls outside of the range of measurements for the related compounds in the CSD. This larger than expected angle can be attributed to the two intramolecular hydrogen bonds in (I) absent in similar compounds.



(I)

In complex (I), there are two intramolecular hydrogen bonds of the type N—H···Cl formed between the pyrazole and chloride ligands. It has been shown that Cl atoms coordinated to transition metals may act as moderately strong hydrogen-bond acceptors (Aullón *et al.*, 1998). But in the case of (I), the hydrogen bonds are considered weak because of the suboptimal N—H···Cl angles averaging 130.0 (13)° (Table 2). These intramolecular hydrogen-bonding interactions are described with the graph set $S(5)$ (Bernstein *et al.*, 1995). Compared to the six related compounds in the CSD, (I) is the only compound that forms exactly two intramolecular $S(5)$ N(pz)—H···Cl hydrogen bonds. Three compounds including dichlorobis(3,5-dimethylpyrazole)cobalt(II) (CSD refcode FUFVUX02; Guzei & Spencer, 2006), bis{dichloro[μ_2-bis(3,5-dimethyl-4-pyrazolyl)methane]cobalt(II)} ethanol solvate (CAFXIQ; Foces-Foces *et al.*, 1983) and dichlorobis(3,5-diethyl-4-methyl-1*H*-pyrazole)cobalt(II) (DEMPCO10; Agre *et al.*, 1978) form two intermolecular N(pz)—H···Cl hydrogen bonds with the graph set $R_2^2(10)$. Another related compound, dichlorobis(3-methyl-5-phenylpyrazol-2-yl)cobalt(II) (SEHTUU; Verweij *et al.*, 1989), forms only one intramolecular N(pz)—H···Cl $S(5)$ hydrogen bond but cannot form a second intramolecular hydrogen bond with the other pyrazole N-atom donor. The other N(pz)—Cl distance is too long and the N(pz)—H···Cl angle too acute for SEHTUU to form two $S(5)$ intramolecular bonds as in (I). The protonated pyrazole N atom on the two remaining related compounds forms inter- and intramolecular hydrogen bonds with O and N atoms in side chains of the pyrazole rings, respectively [CSD refcodes FOYWEW (Leovac *et al.*, 2007) and YOCYAR (Cai *et al.*, 2008)].

The fact that (I) forms two intramolecular N(pz)—H···Cl hydrogen bonds is likely responsible for the larger than average N—Co—N angle as the Cl—Co—N angles involved in the five-membered hydrogen-bonded rings are significantly smaller [99.93 (10) and 100.78 (11)°; ignoring the minor disordered position for Cl2] than the ideal tetrahedral angle. Compound (I) is believed to form the intramolecular rather than intermolecular N(pz)—H···Cl hydrogen bonds, seem-

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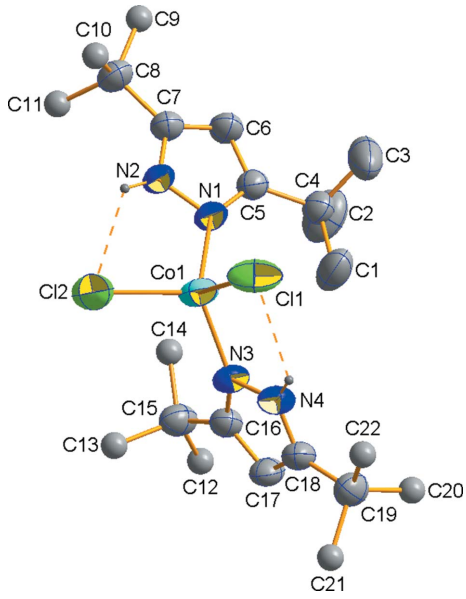

Figure 1
The molecular structure of (I) drawn with 50% probability displacement ellipsoids. All H atoms attached to C atoms and the minor components of disordered atoms have been omitted for clarity. Atoms C9–C14 and C20–C22 were refined isotropically. The two intramolecular hydrogen bonds are shown with dashed lines.

ingly more popular among related compounds, because the bulky *tert*-butyl pyrazole substituents in the 3,5-positions prevent molecules of (I) from approaching each other close enough to form intermolecular bonds. To substantiate this line of reasoning, we calculated the *G*-parameters and sizes of the pyrazole ligands in (I) and the six aforementioned complexes. The *G*-parameter (computed with the program *Solid-G*; Guzei, 2006) is the percentage of the coordination sphere of the central metal shielded by the ligand (Guzei & Wendt, 2006). This methodology is based on solid angles and is illustrated in Fig. 2. Each ligand 'casts a shadow' on a sphere of an arbitrary radius centered at the Co atom, and the percentage of the sphere shielded by each ligand is its *G*-parameter. It has been shown that even small (2–3%) changes in the *G*-parameters can lead to substantial changes in the mutual ligand arrangement (Fukin *et al.*, 2007). The ligand size is represented by the volume of the smallest parallelepiped circumscribing the free ligand as computed with the WBOX routine in the program *OLEX2* (Dolomanov *et al.*, 2009). This approach has been previously applied to alkali metal complexes of nonactin (Guzei *et al.*, 2009). Table 3 summarizes the geometric computations. The average *G*-parameter of the pyrazole ligands in (I) is significantly larger at 25.0 (5)% than that in any of the related compounds. Thus, the approach of adjacent complex molecules to the Cl ligands and formation of intermolecular bonds are hampered. The average pyrazole ligand volume in (I) is substantially larger than that for all related compounds, except for 3,5-dimethyl-4-pyrazolylmethane (Table 3). However, whereas the volume of 3,5-dimethyl-4-pyrazolylmethane is larger than that for (I), this ligand forms an elongated chain directed away from the central Co atom.

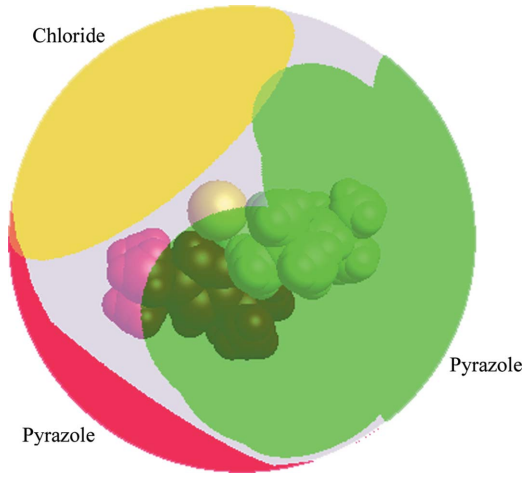

Figure 2
A diagram of the solid angles of (I), which shows the shielding of the Co atom by the various ligands. (Color key for the electronic version of the paper: pyrazole ligands are shown as red and green, and chloride ligands are yellow.)

Consequently, it does not crowd the central Co atom as much as 3,5-bis-*tert*-butylpyrazole does in (I), as evidenced by the larger *G*-parameter of the latter. It appears that the type of the hydrogen bonds in dipyrazole–dichloride complexes of Co^{II} is dictated by the ligand steric parameters.

Experimental

A solution of $CoCl_2$ (0.58 g, 4.45 mmol) and *tert*-butylpyrazole (1.60 g, 4.44 mmol) in CH_2Cl_2 (20 ml) was stirred at room temperature for 18 h. The resultant blue solution was reduced to about 10 ml, followed by the addition of about 5 ml of hexane. The solution was kept at 269 K for a day to produce blue crystals suitable for X-ray crystallography (yield 1.40 g, 64%). Analysis calculated for $C_{22}H_{40}Cl_2CoN_4$: C 62.99, H 9.61, N 13.36%; found: C 62.60, H 9.70, N 13.55%.

Crystal data

$[CoCl_2(C_{11}H_{20}ClN_2)_2]$
M_r = 490.41
Monoclinic, $P2_1/n$
a = 12.483 (4) Å
b = 17.516 (7) Å
c = 12.604 (4) Å
β = 90.22 (2)°
V = 2755.9 (17) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 6.76 mm^{-1}
T = 296 K
0.45 × 0.30 × 0.30 mm

Data collection

Bruker SMART APEXII area-detector diffractometer
Absorption correction: analytical (*SADABS*; Bruker, 2007)
T_{min} = 0.151, T_{max} = 0.236
44217 measured reflections
5156 independent reflections
4195 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.205
S = 1.06
5156 reflections
271 parameters
65 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Table 1
Comparison of bond lengths (Å) and angles (°) of (I) with six related compounds in the CSD.

	Co—Cl	Co—N	Cl—Co—Cl	N—Co—N	Cl—Co—N	Angle between pyrazole ring planes
Compound (I) average (including disordered atoms)	2.269 (2)	2.036 (15)	109 (9)	121.93 (13)	107 (8)	89.93 (13)
Six related compounds in CSD average	2.243 (14)	2.011 (14)	116 (4)	106 (5)	109 (7)	77 (11)
Six related compounds in CSD range	2.222–2.283	1.992–2.049	108.32–122.82	97.40–116.07	98.61–119.93	59.34–89.83

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···Cl2	0.86	2.52	3.131 (4)	129
N2—H2···Cl2A	0.86	2.46	3.099 (13)	131
N4—H4···Cl1	0.86	2.48	3.103 (4)	130

Table 3
Solid angle and WBOX volume measurements for the pyrazole ligands of (I) and related compounds.

See *Comment* for CSD refcode references.

Compound	*G*-parameter average (%)	WBOX volume average (Å^3)
3,5-Di-*tert*-butylpyrazole, (I)	25.0 (5)	487 (2)
3,5-Dimethylpyrazole, FUFVUX02	21.11 (18)	205 (6)
μ_2-Bis(3,5-dimethylpyrazol-4-yl)-methane, CAFXIQ	21.5 (7)	600 (40)
3,5-Diethyl-4-methyl-1*H*-pyrazole, DEMPCO10	22.35 (16)	400 (30)
3-Methyl-5-phenylpyrazol-2-yl, SEHTUU	20.7 (6)	317 (18)
1-(3-Amino-5-methyl-1*H*-pyrazol-4-yl)ethanone, FOYWEW	20.60	289.122
3,5-Dimethyl-1*H*-pyrazol-4-amine-κN^2, YOCYAR	20.69 (8)	241 (8)

The crystals of (I) do not survive thermal shock and shatter when immersed in a cold stream of nitrogen at either 100, 150, 200 or 250 K; thus, the crystal structure was determined at room temperature. There is positional disorder in the structure of (I). Atom Cl2 is disordered over two positions with a 79 (2)% major component contribution. The *tert*-butyl groups at atoms C8 and C15 are disordered over two positions with 60.8 (7) and 59.7 (13)% major component contributions. The *tert*-butyl group at atom C19 is disordered over three positions in a 40.9 (6):34.1 (7):25.0 (7)% ratio. In the disordered *tert*-butyl groups, all 1–2 distances were restrained to 1.538 (2) Å and 1–3 distances to 2.512 (2) Å. The isotropic displacement parameters of the methyl C atoms of each disordered *tert*-butyl group were constrained to be the same. The distances between the Co atom and both positions of the disordered Cl2 atom were restrained to be the same within 0.002 Å and the anisotropic displacement parameters of atoms Cl2 and Cl2A were constrained to be the same. All H atoms were placed in idealized positions, with N—H distances of 0.86 Å, Csp^2—H distances of 0.93 Å and Csp^3—H distances of 0.96 Å. All H atoms were refined as riding with displacement parameters of U_{iso}(H) = 1.2U_{eq}(parent atoms) for all N—H and Csp^2—H groups and 1.5U_{eq}(parent atoms) for all Csp^3—H groups.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* and *FCF_filter* (Guzei, 2007); molecular graphics: *SHELXTL*, *DIAMOND* (Brandenburg, 1999) and *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *SHELXTL*, *publCIF* (Westrip, 2010) and *modiCIFer* (Guzei, 2007).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3032). Services for accessing these data are described at the back of the journal.

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