

Dichlorotetrakis[3-(4-pyridyl)-1H-pyrazole]cobalt(II) acetonitrile tetrasolvate: an infinite hydrogen-bonded network, in an instant

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Received 7 September 2005

Accepted 5 October 2005

Online 22 October 2005

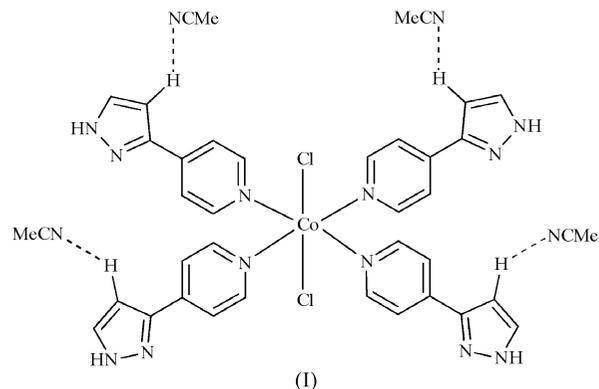
Reaction of 3-(4-pyridyl)pyrazole (4ppyz) with cobalt(II) chloride in acetonitrile affords the title complex, $[\text{CoCl}_2(\text{C}_8\text{H}_7\text{N}_3)_4] \cdot 4\text{CH}_3\text{CN}$, within seconds of addition, as purple X-ray quality crystals. The molecule has C_4 symmetry. The metal ion exhibits a *trans*- N_4Cl_2 octahedral geometry, with the four 3-(4-pyridyl)-1H-pyrazole ligands coordinating through their pyridyl N-atom donors; one coordinated chloride ion forms hydrogen bonds with the pyrazole rings from four separate units. This configuration creates an infinite three-dimensional coordination network containing channels that are filled with acetonitrile solvent molecules.

Comment

We have extensively studied the structural and photophysical properties of metal complexes with the scorpionate ligand hydrotris[3-(2-pyridyl)pyrazol-1-yl]borate ($\text{Tp}^{2\text{py}}$) (Davies, Adams, Pope *et al.*, 2005; Davies, Adams & Ward, 2005; Davies *et al.*, 2004; Beeby *et al.*, 2002; Ward *et al.*, 2001; Jones, Amoroso *et al.*, 1997; Amoroso *et al.*, 1994). The potentially tridentate ligand 3-(2-pyridyl)pyrazole (2ppyz), a precursor to ($\text{Tp}^{2\text{py}}$), has also proven to be of interest, with a range of coordination modes being displayed depending on whether the pyrazole unit is neutral or deprotonated (Ward, Fleming *et al.*, 1998; Ward, Mann *et al.*, 1998; Jones, Jeffery *et al.*, 1997). Accordingly, we have prepared the isomeric ligand 3-(4-pyridyl)pyrazole (4ppyz) (Adams *et al.*, 2005), which can no longer act as a chelate but in principle can act as a bridging ligand whose coordination mode will again depend on whether the pyrazole unit is deprotonated.

Linear bridging ligands commonly give rise to infinite coordination polymers (Fujita *et al.*, 1996; Choudhury *et al.*, 2002; Zheng *et al.*, 2005; Subramanian & Zaworotko, 1995); 'bent' bridging ligands, arising here from the combination of six- and five-membered rings, are less explored. As a result, we decided to explore the coordination chemistry of the 4ppyz ligand. In this paper, we describe the synthesis and structure of

the title complex, $[\text{CoCl}_2(4\text{ppyz})_4] \cdot 4\text{MeCN}$, (I), a new hydrogen-bonded coordination network based on 4ppyz, in which the 4ppyz ligand combines a metal coordination site and a hydrogen-bond donor site. Mulyana *et al.* (2005) recently described complexes of the isomeric ligand 4-(4-pyridyl)pyrazole, in which the ligand could be either cationic (protonated) and monodentate or anionic (deprotonated) and tridentate; in the former case, the network structure is propagated by hydrogen bonding between mononuclear units, whereas in the latter case, the ligand coordinates to three metal ions, resulting in a genuine coordination network.



Reaction of 4ppyz with anhydrous cobalt(II) chloride in acetonitrile afforded a blue solution from which, a few seconds after addition, purple X-ray quality crystals of complex (I) began to appear. In contrast to the behaviour displayed by 4-(4-pyridyl)pyrazole (Mulyana *et al.*, 2005), 3-(4-pyridyl)pyrazole remains neutral upon coordination. The cobalt(II) centre retains both chloride ions in a *trans* arrangement and coordinates to the pyridyl termini of four separate 4ppyz ligands around the equatorial plane (Fig. 1), giving a *trans*-

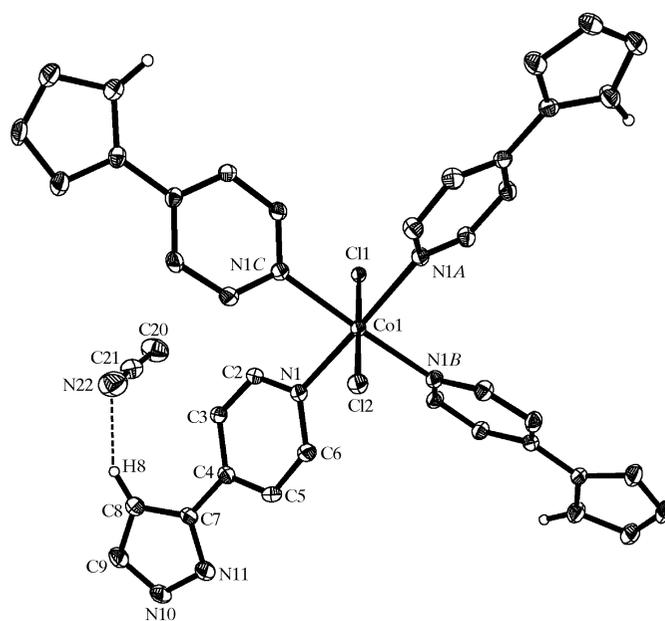


Figure 1

A view of $[\text{CoCl}_2(4\text{ppyz})_4] \cdot 4\text{MeCN}$; displacement ellipsoids are shown at the 40% probability level. [Symmetry codes: (A) $1 - x, 1 - y, -z$; (B) $1 - y, x, z$; (C) $y, 1 - x, z$.]

N_4Cl_2 pseudo-octahedral coordination geometry. Only one 4pypz arm is located in the asymmetric unit, the Cl—Co—Cl axis (parallel to the c axis) being a fourfold rotation axis such that the Co and Cl atoms have 25% occupancy in the asymmetric unit. The Co1—N1 bond length of 2.1648 (12) Å is typical of pyridyl—cobalt(II) coordination (Long & Clarke, 1978). One Co—Cl bond is significantly longer than the other, *viz.* Co1—Cl1 = 2.5775 (11) Å and Co1—Cl2 = 2.3962 (12) Å.

In relation to the mean plane of the four pyridyl N atoms (N_{py}), the pyridyl and pyrazole rings are twisted by 46.3 and 26.6°, respectively, and by 20.0° with respect to each other. Pyrrolic N10 atoms form the vertices of a perfect square parallel to the ab plane, with a side length of 11.935 Å and rotated by 7° about the c axis with respect to the square face of the unit cell. The mean plane of the four N10 donors lies 0.27 Å below that of the four pyridyl donors because of the twist between the pyridyl and pyrazolyl rings.

Each pyrrolic H atom, H10, is hydrogen bonded to one of the chloride ions of a separate $[CoCl_2(4pypz)]$ unit [$N10 \cdots Cl1 = 3.260$ (2) Å, $H10 \cdots Cl1 = 2.41$ Å and $N10-H10 \cdots Cl1 = 164^\circ$]; there is a square array of four such hydrogen bonds to each Cl1 atom (Fig. 2), generating a hydrogen-bonded sheet of complex molecules in the ab plane. Each Cl1 atom is therefore in a 'square-pyramidal' coordination environment, with four equivalent N—H \cdots Cl hydrogen bonds in the basal plane and an axial dative bond to atom Co1. Owing to the orientation of the pyrazole rings, the network of hydrogen bonds also extends down the c axis, giving an overall three-dimensional coordination network.

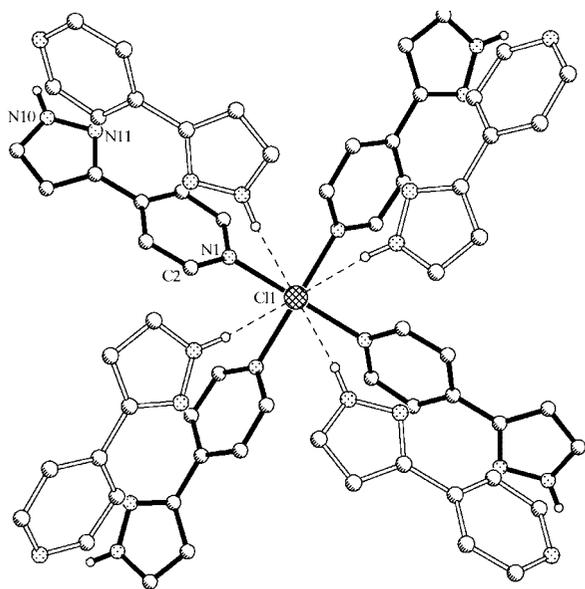


Figure 2

A view down the c axis, showing the arrangement of four N—H \cdots Cl hydrogen bonds (dashed lines) to atom Cl1 at the centre of the figure. The four ligands coordinated to atom Co1 (observed beneath Cl1) are shown with solid bonds; the four ligands with hollow bonds are coordinated *via* their pyridyl N-atom donors to separate metal atoms but act as hydrogen-bond donors to the central complex molecule (see *Comment*).

Hydrogen-bonding interactions between NH donors and Cl acceptors have been studied extensively as a tool for crystal engineering (Brammer *et al.*, 2002; Angeloni & Orpen, 2001; Angeloni *et al.*, 2004).

In addition, the network contains square channels with a cross-section area of 71 Å², whose perimeters are defined by the ligands. These channels contain four columns of acetonitrile solvent molecules, each of which interacts weakly *via* a C—H \cdots N hydrogen bond between atom H8 of a pyrazole ring and atom N22 of the acetonitrile molecule ($H8 \cdots N22 = 2.61$ Å). These solvent molecules are easily lost from the lattice on drying, as shown by loss of weight on drying and elemental analysis of the dried material.

Finally, we note that the Flack (1983) parameter for this chiral crystal is indicative of racemic twinning.

Experimental

3-(4-Pyridyl)-1*H*-pyrazole was prepared according to the published method of Davies *et al.* (2003) and a solution (100 mg, 0.69 mmol) in MeCN (10 ml) was added to a solution of anhydrous $CoCl_2$ (22.4 mg, 0.17 mmol) in MeCN (10 ml); the resulting solution was stirred once and filtered through celite. Upon being left to stand for a few moments, purple X-ray quality crystals began to precipitate out of the blue solution. After the mixture had been left to stand for a few hours, the purple crystals were filtered off and dried, giving opaque pink crystals of $[CoCl_2(4pypz)_4] \cdot 4MeCN$ in 30% yield. Analysis found: C 53.4, H 4.2, N 23.4%; calculated for $C_{32}H_{28}Cl_2CoN_{12} \cdot 4MeCN$: C 53.4, H 4.1, N 23.4%. IR (cm⁻¹): 3287 (*m*), 1614 (*s*), 1556 (*w*), 1496 (*w*), 1456 (*m*), 1424 (*m*), 1356 (*w*), 1290 (*w*), 1216 (*m*), 1178 (*m*), 1122 (*w*), 1079 (*w*), 1039 (*m*), 1014 (*m*), 947 (*m*), 843 (*s*), 758 (*s*), 740 (*s*), 701 (*s*), 663 (*w*), 622 (*m*). A crystal for X-ray diffraction analysis was removed directly from the mother liquor, coated in engine oil to clean it of subsidiary grains, and quickly (to prevent loss of MeCN) mounted in a stream of cold N_2 (150 K) on the diffractometer for subsequent analysis.

Crystal data

$[CoCl_2(C_8H_7N_3)_4] \cdot 4C_2H_3N$
 $M_r = 874.71$
 Tetragonal, $I4$
 $a = 15.649$ (2) Å
 $c = 8.653$ (2) Å
 $V = 2119.0$ (6) Å³
 $Z = 2$
 $D_x = 1.371$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 1005 reflections
 $\theta = 5.4$ – 53.8°
 $\mu = 0.58$ mm⁻¹
 $T = 150$ (2) K
 Block, purple
 $0.31 \times 0.31 \times 0.19$ mm

Data collection

Bruker SMART 1000 diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{min} = 0.840$, $T_{max} = 0.898$
 11871 measured reflections

2407 independent reflections
 2197 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.032$
 $\theta_{max} = 27.5^\circ$
 $h = -20 \rightarrow 19$
 $k = -20 \rightarrow 20$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.069$
 $S = 0.97$
 2407 reflections
 138 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2 + 0.1612P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.27$ e Å⁻³
 $\Delta\rho_{min} = -0.16$ e Å⁻³
 Absolute structure: Flack (1983),
 1094 Friedel pairs
 Flack parameter: 0.418 (14)

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors thank the University of Sheffield for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF1015). Services for accessing these data are described at the back of the journal.

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