Chlorocobalt complexes with pyridylethyl-derived diazacycloalkanes

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Syntheses are described for the blue/purple complexes of cobalt(II) chloride with the tetradeutate ligands 1,4-bis[2-(pyridin-2-yl)ethyl]piperazine (Ppz), 1,4-bis[2-(pyridin-2-y1)ethyl]homopiperazine (Phpz), trans-2,5-dimethyl-1,4-bis[2-(pyridin-2-yl)ethyl]piperazine (Pdmpz) and tridentate 4-methyl-1-[2-(pyridin-2-yl)ethyl]homopiperazine (Pmhpz). The CoCl₂ complexes with Ppz, namely, [μ-1,4-bis[2-(pyridin-2-yl)ethyl]piperazine]bis[dichloridocobalt(II)], [Co₂Cl₂(C₁₈H₂₄N₄)] or Co₂(Ppz)Cl₄, and Pdmpz (structure not reported as X-ray quality crystals were not obtained), are shown to be dinuclear, with the ligands bridging the two tetrahedrally coordinated CoCl₂ units. Co₂(Ppz)Cl₄ and [dichlorido{4-methyl-1-[2-(pyridin-2-yl)ethyl]-1,4-diazacycloheptane}cobalt(II)] [CoCl₂(C₁₃H₂₀N₃)] or Co(Pmhpz)Cl₂, crystallize in the monoclinic space group P2₁/n, while crystals of the pentacoordinate monochloro chelate 1,4-bis[2-(pyridin-2-yl)ethyl]piperazine|chloridocobalt(II) perchlorate, [CoCl(C₁₃H₂₀N₃)]ClO₄ or [Co(Ppz)Cl]ClO₄, are also monoclinic (P2₁). The complex [1,4-bis[2-(pyridin-2-yl)ethyl]-1,4-diazacycloheptane]dichloridocobalt(II) [CoCl₂(C₁₃H₂₀N₃)] or Co(Phpz)Cl₂ (P1) is mononuclear, with a pentacoordinated Co II ion, and entails a Phpz ligand acting in a tridentate fashion, with one of the pyridyl moieties dangling and non-coordinated; its displacement by Cl⁻ is attributed to the solvophobicity of Cl⁻ toward MeOH. The pentacoordinate Co atoms in Co(Phpz)Cl₂, [Co(Ppz)Cl]⁺ and Co(Pmhpz)Cl₂ have substantial trigonal–bipyramidal character in their stereochemistry. Visible- and near-infrared-region electronic spectra are used to differentiate the two types of coordination spheres. TDDFT calculations suggest that the visible/NIR region transitions contain contributions from MLCT and LMCT character, as well as their expected d–d nature. For Co(Pmhpz)Cl₂ and Co(Phpz)Cl₂, variable-temperature magnetic susceptibility data were obtained, and the observed decreases in moment with decreasing temperature were modelled with a zero-field-splitting approach, the D values being +28 and +39 cm⁻¹, respectively, with the S = 1/2 state at lower energy.

1. Chemical context

Pyridylethylation of amines has previously been used to prepare a variety of chelating agents (Phillip et al., 1970; Profft & Georgi, 1961; Profft & Lojack 1962; Gray et al., 1960; Kryatov et al., 2002; Kryatova et al., 2012; Marsich et al., 1998; Karlin et al., 1984; Anandababu et al., 2020; Muthuramalingam et al., 2019a,b), with an original driver being the generation of biomimetic molecules (Karlin et al., 1984). Examples immediately relevant to the present work (Fig. 1) include 1,4-bis[2-
(2′-pyridylethyl)piperazine (Ppz) and 1,4-bis[2′-(2′-pyridylethyl)]homo-piperazine, Phpz. Phpz was first prepared by Schmidt et al. (2013), while Jain and coworkers reported Ppz in 1967 (Jain et al., 1967). For Ppz, both copper(II) (Mautner et al., 2008, 2009; O’Connor et al., 2012) and nickel(II) (O’Connor et al., 2012) complexes have been described. In the case of Phpz, there are reports of copper(II) complexes (O’Connor et al., 2012), including their application as oxidation catalysts (Muthuramalingam et al., 2017, 2020). In addition, nickel(II) complexes of Phpz have been studied as catalysts (Muthuramalingam et al., 2019a,b) as has a recent cobalt(II) complex (Anandababu et al., 2020). For Pmhpz, copper and nickel complexes have been characterized (O’Connor et al., 2012), and Muthuramalingam and coworkers have recently examined oxidative catalysis by copper complexes including that of Pmhpz (Muthuramalingam et al., 2021), but there appears to be only the single prior report of Pdmpz (O’Connor et al., 2012). Four structures are described here. X-ray quality crystals of the Pdmzp complex were not obtained.

2. Structural commentary

The structures are not all entirely what was originally expected, based on previous work with these types of ligands. The Co–N(Pyr) bond lengths (Tables 1–4) range from 2.03 to 2.16 Å, which is within the usual span (Orpen et al., 1989), while the Co—Cl distances average 2.28 ± 0.03 Å, which is again common for cobalt(II) (Orpen et al., 1989). The Co—N amine bond lengths are generally longer than the Co—N pyridine ones, and quite variable (vide infra), with an average of 2.154 Å and covering a 0.153 Å range. The distances are unexceptional for CoII to tertiary amine linkages (Orpen et al., 1989), and indeed tertiary amine nitrogen atoms in tripodal ligands are often notably more distant from the CoII ion (2.44–3.27 Å; Brewer, 2020).

For the CoCl₂-Ppz combination, the dinuclear compound Co₂(Ppz)Cl₄ was obtained (Fig. 2), rather than the mono-nuclear Co(Ppz)Cl₂. The asymmetric unit in this P₂₁/n struc-
tecture is the half-molecule, related to the molecule’s other corresponding half by an inversion centre.

The piperazine moiety in Co(Ppz)Cl₂ does not chelate a cobalt ion, but instead bridges between two, so that each tetracoordinate Co is bound by a piperazine-N atom, a cobalt ion, but instead bridges between two, so that each A ligand has a larger (N₂—N₂)

Table 2
Selected geometric parameters (Å, °) for Co(Pmhpz)Cl₂.

| Bond | Value       |
|------|-------------|
| N₁—Co₁—N₂ | 2.0257 (15) |
| N₁—Co₁—N₃ | 2.0393 (15) |
| N₁—Co₁—Cl₁ | 2.3122 (4)  |
| N₂—Co₁—N₃ | 2.1498 (14) |
| N₂—Co₁—Cl₂ | 2.3110 (4)  |
| N₃—Co₁—Cl₂ | 2.2410 (6)  |

The piperazine moiety in Co(Ppz)Cl₂ does not chelate a cobalt ion, but instead bridges between two, so that each tetracoordinate Co is bound by a piperazine-N atom, a pyridyl-N atom and two chloride ions. The two identical coordination cores have \( \omega = 86^\circ \) (Sakaguchi & Addison, 1979) and \( \phi_i = 0.07 \) (Addison et al., 2004; Yang et al., 2007), so are fairly close to exactly tetrahedral in geometry.

As the same ligand behaves as a straightforward mononucleating quadridentate in the copper and nickel complexes (O’Connor et al., 2012; Muthuramalingam et al., 2017, 2019a,b), this led to the question as to whether the coordination is governed by the ligand bite vs the larger ionic radius of Co²⁺ vs Cu²⁺/Ni²⁺. This proposal was approached by synthesising the homopiperazine analogue, Phpz, whose ligand has a larger (N₂—N₂A) bite. The compound Co(Phpz)Cl₂ was indeed obtained as a mononuclear product (Fig. 3), crystallizing into a \( \text{P}_4 \text{I} \) lattice. The structure suffers some disorder, but one conformation is dominant, at 91% (the discussion below refers to that major component of the Co(Phpz)Cl₂ crystals). However, anticipatedly quadridentate Phpz is now seen to act as a tridentate ligand, with the cobalt(II) ion being pentacoordinate.

One of the pyridylethyl arms is now in the less-commonly observed dangling mode, pyridine being a consistent protagonist of this phenomenon (Reeves et al., 2014; Ball et al., 1981; Rajendiran et al., 2008; Camerano et al., 2011; Lonnon et al., 2006; Palaniandavar et al., 1996). The core geometry is marked toward the trigonal–bipyramidal (\( \tau = 0.62 \)) (Addison et al., 1984) with Cl₂ acting as the erstwhile reference tetragonal axial ligand. The bond from the cobalt ion to

Figure 3
Structure of Co(Phpz)Cl₂, with its dangling pyridine moiety. The dominant conformer is shown. Ellipsoids are drawn at the 50% level, and for clarity of presentation, H atoms are omitted.

Table 3
Selected geometric parameters (Å, °) for [Co(Ppz)Cl]ClO₄.

| Bond | Value       |
|------|-------------|
| Co₁—Cl₁ | 2.2057 (5)  |
| Co₁—Cl₂ | 2.2099 (5)  |
| Co₁—N₁ | 2.109 (5)   |
| N₁—Co₁—N₂ | 100.12 (6) |
| N₁—Co₁—N₃ | 107.46 (5) |
| N₁—Co₁—Cl₁ | 118.90 (3) |

As the same ligand behaves as a straightforward mononucleating quadridentate in the copper and nickel complexes (O’Connor et al., 2012; Muthuramalingam et al., 2017, 2019a,b), this led to the question as to whether the coordination is governed by the ligand bite vs the larger ionic radius of Co²⁺ vs Cu²⁺/Ni²⁺. This proposal was approached by synthesising the homopiperazine analogue, Phpz, whose ligand has a larger (N₂—N₂A) bite. The compound Co(Phpz)Cl₂ was indeed obtained as a mononuclear product (Fig. 3), crystallizing into a \( \text{P}_4 \text{I} \) lattice. The structure suffers some disorder, but one conformation is dominant, at 91% (the discussion below refers to that major component of the Co(Phpz)Cl₂ crystals). However, anticipatedly quadridentate Phpz is now seen to act as a tridentate ligand, with the cobalt(II) ion being pentacoordinate.

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Figure 4
Structural representation of [Co(Ppz)Cl]ClO₄ (major component). The perchlorate is disordered by a rocking motion along the O₂B–C₁₁B–O₄B direction, which may be related to weak C–H···O hydrogen-bonding interactions. Ellipsoids are drawn at the 50% level, and for clarity of presentation, H atoms are omitted.
the piperazine nitrogen atom (N3) holding the dangling arm is 0.08 (3) Å longer than the one associated with the coordinated pyridine arm. Inasmuch as the ability of Phpz to act as a tetradoentate toward CoII has recently been demonstrated in [Co(Phpz)Cl](BPh4) (Anandababu et al., 2020), it is clear that ligand bite is not the sole factor governing the structural outcome in Co(Phpz)Cl2. However, all the complexes herein were prepared in non-aqueous solvents – methanol or THF – and we propose that the chloride ion, with its substantial hydration energy, is solvofugic enough to displace a terminal pyridine in a complex involving cobalt(II). We hence prepared the compound of composition [Co(Ppz)Cl]ClO4, thus removing a chloride from the binding competition. The resulting structure bears out this hypothesis (Fig. 4).

[Co(Ppz)Cl]ClO4 crystallizes in the space group P21, and entails the [Co(Ppz)Cl]+ cation. This structure has \( \tau = 0.65 \), so is substantially trigonal–bipyramidal in its coordination geometry; the reference axis is Co1–Cl1A, and the (pseudo)-trigonal axis is N2A–Co1A–N4A. The cation is asymmetric, with non-matching Co–Npyridine bonds of 2.057 (5) and 2.109 (5) Å, while the Co–Namine distances are notably inequivalent, at 2.098 (5) for Co1A–N3A, but 2.238 (5) Å for Co1A–N2A – the longest Co–N bond in this set of four compounds. One might note that N3A is ‘trigonal–equatorial’, vs N2A being ‘trigonal–axial’, and suspect that this longer bond betokens an instability that leads to Co2(Ppz)Cl4. The perchlorate may be involved with quite weak C–H···O hydrogen-bonding interactions: e.g., C11A···O3B, C13A···O4B, and C11A···O4C are 3.28, 3.46 and 3.60 Å, respectively.

In a further experimental essay, we eliminated an otherwise dangling pyridyl arm by replacing it with a methyl group, as in the simpler tridentate ligand Pmhpz. The resulting molecule, Co(Pmhpz)Cl2 (Fig. 5) crystallizes in the P21/n space group.

The coordination core is somewhat trigonal–bipyramidal, with \( \tau = 0.57 \) and the reference axis being Co1–Cl1. The sole pyridine nitrogen N3 and the methylated piperazine nitrogen N1 form the pseudo-trigonal axis. Analogously to the [Co(Ppz)Cl]+ situation, the pseudo-equatorial Co–N2amine bond, at 2.097 (4) Å, is shorter that the Co–N1amine [2.232 (5) Å] and Co–N3pyridine [2.146 (4) Å] bonds in the trigonal directions. One may note that the same axial vs equatorial Co–N bond-length relationship also holds for Co(Phpz)Cl2, above.

Table 5
Principal absorption bands in the visible and near-IR regions.

| Compound               | \( \lambda_{\text{max}} \) (nm) |
|-----------------------|----------------------------------|
| Co2(Ppz)Cl4           | 580 620 1040 1335 1680           |
| Co2(Pdmaaz)Cl4        | 585 625 1055 1315 1680           |
| Co(Ppz)Cl2            | 540 565 635 783 975 1400 1664 1873 |
| Co(Pmhpz)Cl2          | 502 635 800 990 1700 1880        |
| [Co(Ppz)Cl]ClO4       | 540 610 810 1400 1710 1875       |

Figure 5
Molecular structure of the complex Co(Pmhpz)Cl2, with the ligand in which a pyridyl arm is replaced by a methyl group. Ellipsoids are drawn at the 50% level, and for clarity of presentation, H atoms are omitted.

Figure 6
Solid-state diffuse reflectance spectra of [Co2(Ppz)Cl4] (blue trace) and Co(Pmhpz)Cl2 (black trace).

Figure 7
Wavefunction density surface maps of MOs involved in several of the visible-NIR transitions in a CoN2Cl2 moiety of Co2(Ppz)Cl4, modelled with a 2-(dimethylaminoethyl)pyridine ligand. Lower left and right: originating HOMO(−3), HOMO(−4), respectively; upper left and right, the receiving LUMO and LUMO(+1), respectively. Blue indicates highest density. Note the translation of wavefunction density from the CoCl2 or CoN2Cl2 unit to the pyridine ring in the excitations.
Electronic spectra: Pseudotetrahedral species: The essentially identical UV–Vis–NIR spectra for \([\text{Co}_2(\text{Ppz})\text{Cl}_4]\) and \(\text{Co}(\text{Pdmpz})\text{Cl}_2\) (Fig. 6, Table 5) strongly implicate a tetrahedral CoN 2Cl2 coordination geometry for the latter, and its constitution as \([\text{Co}_2(\text{Pdmpz})\text{Cl}_4]\) is ultimately confirmed by the elemental analyses (vide infra).

Both might also be compared to \([\text{Co}(\text{Me}_4\text{en})\text{Cl}_2]\), which has maxima at ca 1670, 1380, 1000, 650 and 580 nm, attributed in a crystal-field model to \(4^A_2 \rightarrow 4^T_1\) (\(F\)) transitions (the first three) (Lever, 1984), and the latter two to \(4^A_2 \rightarrow 4^T_1\) (\(P\)). Though shifted slightly, these maxima are quite similar to the bands for \([\text{Co}_2(\text{Ppz})\text{Cl}_4]\) and \([\text{Co}_2(\text{Pdmpz})\text{Cl}_4]\). The DFT results for a CoN 2Cl2 chromophore of \([\text{Co}_2(\text{Ppz})\text{Cl}_4]\) suggest that even the low-energy transitions involve CT contributions from the CoCl2 moiety to the pyridine ring (Fig. 7).

Pentacoordinate Systems: Like \([\text{Co}_2(\text{ppz})\text{Cl}_4]\) and other CoN 2Cl2 chromophores, the roughly trigonal–bipyramidal archetypal CoN 3Cl2 systems \([\text{Co}(\text{Me}_5\text{dien})\text{Cl}_2]\) and \([\text{Co}(\text{Et}_4\text{-dien})\text{Cl}_2]\) also have strong ligand-field absorptions in the visible region near 500 and 650 nm, as well as NIR bands at ca 2500, 1140, and 950 nm (Ciampolini & Speroni, 1966; Lever, 1984). These transitions have been assigned as from \(4^A_2\) to \(4^E\), \(4^A_2\) (\(P\)) and \(4^E\) (\(P\)) (Lever, 1984). More recent examples of CoN 3Cl2 centres (Xiao et al., 2018) display similarly structured bands with maxima around 650–700 nm. The absorption bands for \([\text{Co}(\text{Ppz})\text{Cl}_2]\) resemble those of the above examples to various extents.

Magnetism analysis
Preliminary data indicated apparently reduced magnetic moments for some samples. However, the structures do not suggest the possibility of any pathway for significant super-exchange coupling. Inasmuch as there are pentacoordinate
cobalt(II) complexes that have recently been discovered to act as single-ion/single-molecule magnets (SIM/SMM) at reduced temperature (Reehkemmer et al., 2016; Świtlicka et al., 2018), we studied the temperature dependence of the magnetic behaviour of powdered samples of Co(Pmhpz)Cl₂ and Co(Phpz)Cl₂ (Figs. 10 and 11).

The magnetism as a function of temperature and applied field showed no evidence for SMM behaviour. In situations like this, the temperature dependence of the moments has been recognized as being due to zero-field splitting (Nemec et al., 2016; Cruz et al., 2018; Boča et al., 1999; Papánková et al., 2010; Rajnák et al., 2013; Žurowska et al., 2008) (see the supporting information for further discussion). We were able to fit the data through most of the temperature regime and the extracted $D$, $g_{\text{ave}}$, $\Delta$, $a$ and $b$ which are listed in Table 6, via:

$$\chi T = \frac{2\Delta}{2\Delta + \alpha} T + \frac{1}{2\Delta + \alpha} T + aTb$$

where $\chi$, $T$, $\Delta$, $\alpha$ and $\beta$ are the longitudinal and transverse modes of the anisotropic responses ($\Delta = S_x / S_z$), $a$ is the TIP and $b$ the total diamagnetic correction.

Both compounds have a positive axial single-ion anisotropy (SIA) term, and the anisotropy values also confirm the findings as self-consistent (e.g. $\Delta > 1$ for positive $D$ and $\Delta < 1$ for negative $D$, and larger $D$ leads to larger $\Delta$). The $D$ and $g_{\text{ave}}$ values appear to be in the normal ranges; $D$ values for Co$^{II}$ do cover a wide range, from $\sim -50$ to $+100 \text{ cm}^{-1}$ (Cruz et al., 2018; Nemec et al., 2016). While Co$^{II}$ $g$ values intrinsically also cover a wide range, applicable values for fitting ZFS data have been observed to be about 2.0–2.4 (Voronkova et al., 1974; Baum et al., 2016; Banci et al., 1980; Martinelli et al., 1989). Both compounds here show a faster drop in $\chi T$ and a distinct kink at temperatures below $ca 15$ K. These features have been seen in several other Co$^{II}$ systems (Žurowska et al., 2008; Papánková et al., 2010; Boča et al., 1999; Rajnák et al., 2013); however, no definitive accounting for this has been advanced as yet, apart from the not infrequently employed addition of a weak antiferromagnetism mean field term.

### Table 6

| Compound           | Co(Pmhpz)Cl₂ | Co(Phpz)Cl₂ |
|--------------------|-------------|-------------|
| $T$ window (K)     | 12.5–310    | 5–310       |
| $D/\hbar c$ (cm⁻¹) | +28 (1)     | +39 (1)     |
| $g_{\text{ave}}$  | 2.32 (2)    | 2.17 (2)    |
| $\Delta$           | 1.11 (6)    | 1.50 (10)   |
| $a^\prime$         | 0           | 0.00056 (21)|
| $b$                | 0.34 (5)    | 0.19 (2)    |

Note: ($a$) the $a$ value for Co(Pmhpz)Cl₂ was held at zero.

3. Supramolecular features

There are no true supramolecular structures formed by the compounds, whose crystal lattices containing individual molecules are defined mainly by weak, non-bonding interactions. Along with the absence of any solvation of these crystals, the only hydrogen-bonding interactions observed are in [Co(Ppz)Cl]ClO₄, which has weak C—H ⋅⋅⋅O hydrogen-bonds (numerical values are given in the CIF), likely of little energetic consequence.

Some lattice views of the compounds are displayed in the supporting information (Figs. S1–S8).

4. Database survey

Closely related compounds with similar $(pyridylethyl)$pyridylethylpiperazine), $X_2$, $M$(pyridylethylpiperazine),$X$⁺, $M$(pyridylethylhomopiperazine),$X_2$ or $M$(pyridylethylhomopiperazine)$X$⁺ structures include $[Co(Phpz)Cl]-$BP₄ (Anandababu et al., 2020) and Cu(Dpzp)(NC·N-CN)-ClO₄ (Mautner et al., 2008).

5. Synthesis and crystallization

**Methods**

Chemical ionization mass spectra were obtained on a Thermo-Electron LTQ–FT 7T FT–ICR instrument. UV–visible–near infrared spectra were obtained using PerkinElmer Lambda-35 or Shimadzu UV3600Plus spectrophotometers equipped with integrating spheres for solid-state spectroscopy. Magnetic susceptibility data between 1.8 and 310 K in an applied field of 1 kOe were collected using a Quantum Design MPMS-XL SQUID magnetometer. Crystals were powdered and packed into #3 gel capsules that were placed inside drinking straws attached to the sample rod. The magnetization was measured at 1.8 K as a function of increasing field from zero to five tesla and at selected fields returning to zero. The data were corrected for the contributions from the sample holders (measured independently) and the diamagnetism of the constituent atoms, as estimated using Pascal’s constants (Carlin, 1986). DFT calculations were performed using the $\omega$B97X-D/6-31G* method on an iMac16,2 with Spartan-18 software (Wavefunction Inc., Irvine CA, version 1.4.4), while structural diagrams were generated using the CrystalMaker-10 software and Preview-10. Reagents were used as received from TCI America, Sigma–Aldrich, MCB and Fisher Scientific. Elemental microanalyses were by Robertson Microlit Laboratories (Ledgewood, NJ).

Ligands were prepared by adaptations of the solventless method (Addison & Burke, 1981), typically using a 5–50% excess of 2-vinylpyridine plus a catalytic amount of acetic acid, and were then, in effect, purified as the metal complexes (Phillip et al., 1970); these ligand synthesis reactions are not necessarily stoichiometric or irreversible (Profft & Lojak, 1962). The procedure is exemplified by:

**1,4-Bis[2-(pyrid-2-yl)ethyl]piperazine (Ppz)**: A mixture of piperazine (0.86 g, 10 mmol), 2-vinylpyridine (3.15 g, 30 mmol), and 2 drops of glacial acetic acid was set to react at ca 368 K for 14 to 50 h in a capped tube. The reaction mixture was allowed to cool to room temperature, resulting in the...
formation of a brown solid mass. The mass spectrum indicated Ppz as the dominant component of the solid; \( m/z = 297.207 \), calculated for \((C_{19}H_{26}N_{4}+H)^+\), 297.208. The crude ligand was used without purification in the synthesis of the cobalt complexes.

**1,4-Bis[2-(pyridin-2-yl)ethyl]homopiperazine (Phpz):** From 2-vinylpyridine (6.32 g, 60 mmol) and homopiperazine (2.01 g, 30 mmol); crude ligand as a brown mass; \( m/z = 311.223 \), calculated for \((C_{19}H_{26}N_{4}+H)^+\), 311.224.

**trans-2,5-Dimethyl-1,4-bis[2-(pyridin-2-yl)ethyl]piperazine (Pdzp):** From trans-2,5-dimethylpiperazine (2.28 g, 20 mmol) and 2-vinylpyridine (6.32 g, 60 mmol) as a brown solid mass mingled with white crystals. \( m/z = 325.239 \), calculated for \((C_{20}H_{28}N_{4}+H)^+\), 325.239.

**4-Methyl-1-[2-(pyridin-2-yl)ethyl]homopiperazine (Pmpz):** N-methylhomopiperazine (1.14 g, 10 mmol) and 2-vinylpyridine (1.10 g, 10.5 mmol); heated at the boiling point (ca 433 K) for 3 min; as a viscous brown oil; \( m/z = 220.181 \), calculated for \((C_{13}H_{21}N_{3}+H)^+\), 220.181.

**Synthesis of cobalt complexes:** The cobalt(II) compounds were mainly prepared by the general method exemplified for \([Co_2(Ppz)Cl_4]\) below, using amounts of crude ligands equivalent to the molecular content of the diazacycloalkane used for the ligand synthesis.

\[ [Co_2(Ppz)Cl_4]: \text{Crude ligand equivalent to 12.0 mmol Ppz, in methanol (30 mL), was combined with 10.0 mmol (6.5 mL of 1.54 M) methanolic cobalt(II) chloride hydrate solution. Deep-blue crystals deposited, which were filtered off and recrystallized from nitromethane. The mass spectrum showed several elucidatory peaks, including } \frac{m}{z} = 518.975 \text{ for } (M-Cl)^+ = Co_2PpzCl_3^+, \text{ calculated } 518.973 \text{ as well as } \frac{m}{z} = 426.079 \text{ (CoPpzCl}_2^+ \text{), calculated 426.078} \text{ and } \frac{m}{z} = 390.102 \text{ (CoPpzCl}_2^+ \text{), calculated 390.102). Analysis C,H,N; found }, C \text{ 39.08, H 4.10, N 9.70} \text{; calculated for } C_{19}H_{24}Cl_4CoN_4: C 38.88, H 4.35, N 10.08.\]

\[ [Co(Phpz)Cl_2]: \text{In this case, the CoCl}_2 \text{ solution was added to the ligand in tetrahydrofuran. When the solution was allowed to stand for 4 d, purple crystalline clusters of product were} \]
obtained. This presumably THF-solvated efflorescent product was air-dried and recrystallized from nitromethane. MS m/z = 404.117 for (M – Cl)⁺, calculated 404.117. Analysis C₁₈H₂₄N₄CoCl₂O₄, C 44.1, H 4.93, N 11.4.

[C₉₆P₉z]ClO₄: This compound was obtained by dropwise addition of crude 1-(2’-pyridylethyl)-4-methylhomopiperazine in methanol to a warm solution of cobalt(II) chloride in methanol. After two days, the deep blue–purple solution yielded blue crystals in 55% yield. MS: observed m/z = 313.1, calculated for (M – Cl)⁺, 313.076. Analysis C₇H₁₅N₃Cl₂Co, C 44.72, 5.84, 11.79; calculated for C₁₃H₂₁N₃Cl₂Co, 44.72, 6.06, 12.03.

[C₉₆P₉z]ClO₄: The blue crystals produced were filtered off and recrystallized from acetonitrile. MS m/z = 390.102 (M – ClO₄)⁺ = C₁₉H₂₃N₄CoCl⁺, calculated 390.102. Analysis C₁₉H₂₃N₄CoCl₀: found %, C 44.3, H 4.78, N 11.4; calculated for C₁₉H₂₃N₄CoCl₀: C 44.1, H 4.83, N 11.4.

[C₉₆P₉mpz]ClO₄: This blue crystals produced were filtered off and recrystallized from nitromethane. MS m/z = 454.111, (M + H)⁺: calculated for C₃₀H₃₂Cl₂Co₄N₄⁺, 454.110; m/z = 418.133, (M – Cl)⁻, calculated for C₂₉H₂₉Cl₂Co₂N₄⁻, 418.133. Analysis C₁₈H₂₄N₄CoCl₀: found %, C 41.6, H 4.80, N 9.44; calculated for C₂₉H₂₉Cl₂Co₂N₄⁻: C 41.1, H 4.83, N 9.59.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 7. X-ray diffraction data were collected on a Rigaku Oxford Diffraction Gemini diffractometer via ω-scans using an Atlas CCD detector using Cu Kα radiation or a Bruker AXS D8 Quest diffractometer with a PhotonII charge-integrating pixel array detector (CPAD). Data for those structures were collected, scaled and corrected for absorption using the CrysAlis PRO 2015 software suite program package (Rigaku OD, 2015) or APEX4 and SAINT (Bruker, 2021) and SADABS (Krause et al., 2015). Crystal structures were solved using SHELXT (Sheldrick, 2015a), and refined using SHELXL (Sheldrick, 2015b) and ShelXle (Hübschle et al., 2011), with refinement by full-matrix least-squares on F². Further processing for the Ppz and Pmpz complexes utilized the OLEX software (Dolomanov et al., 2009).

The structure of Co(Phpz)Cl₂ contains an additional 121 Å³ of solvent-accessible voids filled by extensively disordered nitromethane recrystallization solvent. The residual electron density peaks are not arranged in an interpretable pattern. The structure factors were instead augmented via reverse-Fourier-transform methods using the SQUEEZE routine (van der Sluis & Spek, 1990; Spek, 2015) as implemented in PLATON. The resultant FAB file containing the structure-factor contribution from the electron content of the void space was used together with the original hkl file in the further refinement. (The FAB file with details of the SQUEEZE results is included in the CIF in the supporting information). The SQUEEZE procedure corrected for 69 electrons within the solvent-accessible voids, or around two nitromethane molecules. The central part of the metal complex (two of the Co-coordinated nitrogen atoms and the C atoms bridging between them) are disordered by a pseudo-mirror operation. Additional disorder that is vaguely recognizable (largest difference peak 0.78 electrons) was ignored. The two disordered moieties were restrained to have similar geometries. 69 components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions, the occupancy ratio refined to 0.914 (3):0.086 (3).

For all compounds, H atoms were placed in calculated positions (C—H = 0.95–0.99 Å) and refined as riding with Uiso(H) = 1.2Ueq(C).

Funding information

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Chlorocobalt complexes with pyridylethyl-derived diazacycloalkanes

Anthony W. Addison, Stephen J. Jaworski, Jerry P. Jasinski, Mark M. Turnbull, Fan Xiao, Matthias Zeller, Molly A. O’Connor and Elizabeth A. Brayman

Computing details
Data collection: CrysAlis PRO (Agilent, 2014) for ta-sa15-05; APEX4 (Bruker, 2021) for CoPhpzCl2_sq; CrysAlis PRO (Rigaku OD, 2015) for ta-eab1701-c, ta-eab1607. Cell refinement: CrysAlis PRO (Agilent, 2014) for ta-sa15-05; SAINT (Bruker, 2020) for CoPhpzCl2_sq; CrysAlis PRO (Rigaku OD, 2015) for ta-eab1701-c, ta-eab1607. Data reduction: CrysAlis PRO (Agilent, 2014) for ta-sa15-05; SAINT (Bruker, 2020) for CoPhpzCl2_sq; CrysAlis PRO (Rigaku OD, 2015) for ta-eab1701-c, ta-eab1607. Program(s) used to solve structure: ShelXT (Sheldrick, 2015a) for ta-sa15-05, ta-eab1607; SHELXT (Sheldrick, 2015a) for CoPhpzCl2_sq; ShelXT (Sheldrick, 2015b0) for ta-eab1701-c. Program(s) used to refine structure: SHELXL (Sheldrick, 2015b) for ta-sa15-05, ta-eab1607, SHELXL (Sheldrick, 2015b) for ta-sa15-05, ta-eab1607; SHELXL (Sheldrick, 2015b) for ta-eab1701-c. Molecular graphics: OLEX2 (Dolomanov et al., 2009) for ta-sa15-05, ta-eab1607. Software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009) for ta-sa15-05, ta-eab1607.

\( \mu\)-1,4-Bis[2-(pyridin-2-yl)ethyl]piperazine)bisdichloridocobalt(II) (ta-sa15-05)

Crystal data

\[
\begin{array}{ll}
[\text{Co}_{2}\text{Cl}_{4}(\text{C}_{18}\text{H}_{24}\text{N}_{4})] & F(000) = 564 \\
M_r = 556.07 & D_x = 1.654 \text{ Mg m}^{-3} \\
\text{Monoclinic, } P2_1/n & \text{Mo } K\alpha \text{ radiation, } \lambda = 0.71073 \text{ Å} \\
a = 11.6370 (5) \text{ Å} & \text{Cell parameters from 2820 reflections} \\
b = 7.4382 (2) \text{ Å} & \theta = 4.2–32.8^\circ \\
c = 13.3104 (5) \text{ Å} & \mu = 1.98 \text{ mm}^{-1} \\
\beta = 104.229 (4)^\circ & T = 173 \text{ K} \\
V = 1116.77 (7) \text{ Å}^3 & \text{Prism, blue} \\
Z = 2 & 0.32 \times 0.22 \times 0.11 \text{ mm} \\
\end{array}
\]

Data collection

Agilent, Eos, Gemini
diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.0416 pixels mm\(^{-1}\)
\(\omega\) scans
Absorption correction: multi-scan
(CrysAlisPro; Agilent, 2014)
\(T_{\text{min}} = 0.687, T_{\text{max}} = 1.000\)

\(7280\) measured reflections
\(3708\) independent reflections
\(3044\) reflections with \(I > 2\sigma(I)\)
\(R_{\text{int}} = 0.033\)
\(\theta_{\text{max}} = 33.0^\circ, \theta_{\text{min}} = 3.3^\circ\)
\(h = -17\rightarrow 13\)
\(k = -9\rightarrow 10\)
\(l = -19\rightarrow 18\)
Refinement

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.095$
$S = 1.04$
3708 reflections
127 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/\sigma^2(F_o^2) + (0.0428P)^2$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta \rho_{\text{max}} = 0.69 \text{ e} \AA^{-3}$
$\Delta \rho_{\text{min}} = -0.63 \text{ e} \AA^{-3}$

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)

|    | $x$        | $y$        | $z$        | $U_{iso}^{*}/U_{eq}$ |
|----|------------|------------|------------|----------------------|
| Co1| 0.48371 (2)| 0.39454 (3)| 0.78675 (2)| 0.01891 (8)         |
| Cl1| 0.66943 (5)| 0.29581 (7)| 0.80327 (4)| 0.03312 (13)        |
| Cl2| 0.34895 (5)| 0.17887 (6)| 0.77648 (4)| 0.02996 (13)        |
| N1 | 0.43498 (14)| 0.5445 (2) | 0.65615 (12)| 0.0208 (3)          |
| N2 | 0.48454 (14)| 0.59266 (18)| 0.89900 (12)| 0.0166 (3)          |
| C1 | 0.37081 (18)| 0.4753 (3) | 0.56620 (15)| 0.0259 (4)          |
| H1 | 0.3434     | 0.3549     | 0.5654     | 0.031*               |
| C2 | 0.34353 (18)| 0.5728 (3) | 0.47548 (16)| 0.0286 (4)          |
| H2 | 0.2999     | 0.5198     | 0.4127     | 0.034*               |
| C3 | 0.3809 (2) | 0.7490 (3) | 0.47777 (16)| 0.0300 (4)          |
| H3 | 0.3635     | 0.8195     | 0.4164     | 0.036*               |
| C4 | 0.44398 (19)| 0.8213 (3) | 0.57021 (16)| 0.0276 (4)          |
| H4 | 0.4691     | 0.9432     | 0.5731     | 0.033*               |
| C5 | 0.47084 (17)| 0.7165 (2) | 0.65901 (14)| 0.0206 (4)          |
| H5 | 0.43568 (13)| 0.7914 (2) | 0.7546     | 0.028*               |
| C6 | 0.47009 (18)| 0.7714 (2) | 0.84567 (14)| 0.0215 (4)          |
| H7A| 0.4966     | 0.8669     | 0.8981     | 0.026*               |
| H7B| 0.3849     | 0.7914     | 0.8133     | 0.026*               |
| C8 | 0.59897 (16)| 0.5912 (2) | 0.97969 (14)| 0.0198 (4)          |
| H8A| 0.6032     | 0.6989     | 1.0242     | 0.024*               |
| H8B| 0.6655     | 0.5973     | 0.9455     | 0.024*               |
| C9 | 0.38779 (16)| 0.5759 (2) | 0.95338 (14)| 0.0195 (3)          |
| H9A| 0.3106     | 0.5718     | 0.9015     | 0.023*               |
| H9B| 0.3880     | 0.6832     | 0.9974     | 0.023*               |

Atomic displacement parameters ($\AA^2$)

|    | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$    | $U^{13}$    | $U^{23}$    |
|----|-------------|-------------|-------------|-------------|-------------|-------------|
| Co1| 0.02127 (14)| 0.01542 (13)| 0.01850 (14)| 0.00189 (9) | 0.00194 (10)| 0.00053 (8) |

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|   |   |   |   |   |   |
|---|---|---|---|---|---|
| Cl1 | 0.0279 (3) | 0.0416 (3) | 0.0308 (3) | 0.0137 (2) | 0.0090 (2) | 0.0033 (2) |
| Cl2 | 0.0318 (3) | 0.0199 (2) | 0.0323 (3) | −0.00587 (19) | −0.0034 (2) | 0.00083 (17) |
| N1  | 0.0204 (7)  | 0.0207 (7)  | 0.0203 (8)  | 0.0012 (6)  | 0.0029 (6)  | 0.0011 (6)  |
| N2  | 0.0163 (7)  | 0.0165 (6)  | 0.0162 (7)  | −0.0008 (6) | 0.0025 (6)  | 0.0022 (5)  |
| C1  | 0.0247 (9)  | 0.0278 (9)  | 0.0239 (10) | 0.0026 (8)  | 0.0036 (8)  | −0.0013 (7) |
| C2  | 0.0231 (10) | 0.0396 (10) | 0.0203 (9)  | 0.0040 (9)  | 0.0001 (8)  | −0.0013 (8) |
| C3  | 0.0279 (10) | 0.0400 (11) | 0.0221 (9)  | 0.0066 (10) | 0.0061 (8)  | 0.0081 (8)  |
| C4  | 0.0306 (11) | 0.0268 (9)  | 0.0273 (10) | 0.0014 (8)  | 0.0107 (9)  | 0.0074 (8)  |
| C5  | 0.0209 (9)  | 0.0229 (8)  | 0.0192 (8)  | 0.0011 (7)  | 0.0070 (7)  | 0.0017 (7)  |
| C6  | 0.0281 (10) | 0.0199 (8)  | 0.0215 (9)  | −0.0063 (8) | 0.0053 (8)  | 0.0025 (7)  |
| C7  | 0.0281 (10) | 0.0167 (7)  | 0.0191 (8)  | 0.0019 (7)  | 0.0048 (7)  | 0.0030 (6)  |
| C8  | 0.0148 (8)  | 0.0236 (8)  | 0.0196 (9)  | −0.0045 (7) | 0.0019 (7)  | 0.0036 (6)  |
| C9  | 0.0156 (8)  | 0.0249 (8)  | 0.0177 (8)  | 0.0019 (7)  | 0.0035 (7)  | 0.0037 (6)  |

**Geometric parameters (Å, °)**

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| Co1—Cl1 | 2.2415 (6) | C4—H4 | 0.9500 |
| Co1—Cl2 | 2.2240 (6) | C4—C5 | 1.386 (3) |
| Co1—N1 | 2.0257 (15) | C5—C6 | 1.509 (3) |
| Co1—N2 | 2.0969 (15) | C6—H6A | 0.9900 |
| N1—C1 | 1.348 (2) | C6—H6B | 0.9900 |
| N1—C5 | 1.343 (2) | C6—H6C | 0.9900 |
| N2—C7 | 1.497 (2) | C7—H7A | 0.9900 |
| N2—C8 | 1.491 (2) | C7—H7B | 0.9900 |
| N2—C9 | 1.486 (2) | C8—H8A | 0.9900 |
| C1—H1 | 0.9500 | C8—H8B | 0.9900 |
| C1—C2 | 1.377 (3) | C8—C9 | 1.515 (2) |
| C2—H2 | 0.9500 | C9—C8 | 1.515 (2) |
| C2—C3 | 1.379 (3) | C9—H9A | 0.9900 |
| C3—H3 | 0.9500 | C9—H9B | 0.9900 |
| C3—C4 | 1.378 (3) |   |   |

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| Cl2—Co1—Cl1 | 114.71 (2) | N1—C5—C4 | 120.55 (17) |
| N1—Co1—Cl1 | 108.93 (5) | N1—C5—C6 | 117.07 (16) |
| N1—Co1—Cl2 | 107.46 (5) | C4—C5—C6 | 122.38 (17) |
| N1—Co1—N2 | 100.12 (6) | C5—C6—H6A | 109.2 |
| N2—Co1—Cl1 | 108.96 (5) | C5—C6—H6B | 109.2 |
| N2—Co1—Cl2 | 115.49 (5) | C5—C6—C7 | 111.99 (16) |
| C1—N1—Co1 | 121.94 (13) | H6A—C6—H6B | 107.9 |
| C5—N1—Co1 | 118.73 (12) | C7—C6—H6A | 109.2 |
| C5—N1—C1 | 119.31 (16) | C7—C6—H6B | 109.2 |
| C7—N2—Co1 | 107.82 (11) | N2—C7—C6 | 113.52 (15) |
| C8—N2—Co1 | 110.80 (11) | N2—C7—H7A | 108.9 |
| C8—N2—C7 | 108.92 (14) | N2—C7—H7B | 108.9 |
| C9—N2—Co1 | 114.63 (11) | C6—C7—H7A | 108.9 |
| C9—N2—C7 | 107.17 (14) | C6—C7—H7B | 108.9 |
| C9—N2—C8 | 107.34 (14) | H7A—C7—H7B | 107.7 |
| N1—C1—H1 | 118.8 | N2—C8—H8A | 109.2 |
N1—C1—C2 122.40 (19) N2—C8—H8B 109.2
C2—C1—H1 118.8 N2—C8—C9i 111.91 (14)
C1—C2—H2 120.7 C9i—C8—H8B 107.9
C1—C2—C3 118.52 (19) C9i—C8—H8A 109.2
C3—C2—H2 120.7 C9i—C8—H8B 107.9
C2—C3—H3 120.4 N2—C9—C8i 112.07 (15)
C4—C3—C2 119.14 (19) C9i—C8—H8A 109.2
C4—C3—H3 120.4 C9i—C8—H8B 109.2
C3—C4—H4 120.0 C8i—C9—H9A 109.2
C3—C4—C5 120.05 (19) C8i—C9—H9B 109.2
C5—C4—H4 120.0 C9i—C8—H8B 109.2
Co1—N1—C1—C2 −175.85 (15) C3—C4—C5—N1 −0.6 (3)
Co1—N1—C5—C4 177.07 (15) C3—C4—C5—C6 180.0 (2)
Co1—N1—C5—C6 −3.5 (2) C4—C5—C6—C7 122.0 (2)
Co1—N2—C7—C6 −39.88 (18) C5—N1—C1—C2 2.2 (3)
Co1—N2—C8—C9i −69.19 (16) C5—C6—C7—N2 86.0 (2)
Co1—N2—C9—C8i 66.77 (16) C7—N2—C8—C9i 172.37 (15)
N1—C1—C2—C3 −1.7 (3) C7—N2—C9—C8i −173.62 (15)
N1—C5—C6—C7 −57.4 (2) C8—N2—C7—C6 80.41 (18)
C1—N1—C5—C6 −1.0 (3) C8—N2—C9—C8i −56.8 (2)
C1—N1—C5—C4 178.43 (17) C9—N2—C7—C6 −163.77 (15)
C1—C2—C3—C4 0.0 (3) C9—N2—C8—C9i 56.7 (2)
C2—C3—C4—C5 1.1 (3)

Symmetry code: (i) −x+1, −y+1, −z+2.

{1,4-Bis[2-(pyridin-2-yl)ethyl]-1,4-diazacycloheptane}dichloridocobalt(II) (CoPhpzCl2_sq)

Crystal data

[CoCl2(C19H26N4)][+solvent]

Mr = 440.27
Triclinic, P

a = 7.2628 (3) Å
b = 11.5369 (4) Å
c = 12.6384 (5) Å

α = 86.9553 (19)°
β = 89.1996 (19)°

γ = 89.3798 (18)°
V = 1057.32 (7) Å³

Z = 2
F(000) = 458
Dx = 1.383 Mg m⁻³

Cell parameters from 9804 reflections

θ = 3.2–33.2°
μ = 1.07 mm⁻¹

Fragment, blue

Fragment, blue

Data collection

Bruker AXS D8 Quest

diffractometer with PhotonII charge-integrating pixel array detector (CPAD)

Radiation source: fine focus sealed tube X-ray source

Triumph curved graphite crystal monochromator

Detector resolution: 7.4074 pixels mm⁻¹

Absorption correction: multi-scan (SADABS; Krause et al., 2015)

Tmin = 0.660, Tmax = 0.747
43329 measured reflections
8042 independent reflections
7248 reflections with I > 2σ(I)
Rint = 0.035
θmax = 33.2°, θmin = 1.8°
h = −11→11
\[ k = -17 \rightarrow 17 \quad \text{and} \quad l = -19 \rightarrow 19 \]

**Refinement**

Refinement on \( F^2 \)

Least-squares matrix: full

\[ R(F^2 > 2\sigma(F^2)) = 0.037 \]

\[ wR(F^2) = 0.098 \]

\[ S = 1.12 \]

8042 reflections

317 parameters

298 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\[ w = 1/\left(\sigma^2(F_o^2) + (0.0309P)^2 + 1.165P\right) \]

\[ (\Delta/\sigma)_{\text{max}} = 0.002 \]

\[ \Delta \rho_{\text{max}} = 0.81 \text{ e Å}^{-3} \]

\[ \Delta \rho_{\text{min}} = -0.35 \text{ e Å}^{-3} \]

**Special details**

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

**Refinement.** The central part of the metal complex (two of the Co-coordinated nitrogen atoms and the C atoms bridging between them) are disordered by a pseudo-mirror operation. Additional disorder that is vaguely recognizable (largest difference peak 0.78 electrons) was ignored. The two disordered moieties were restrained to have similar geometries. Uij components of ADPs for disordered atoms closer to each other than 2.0 Ångstrom were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.914 (3) to 0.086 (3).

The structure contains additional 121 Ångstrom of solvent accessible voids filled by extensively disordered solvate molecules (presumably nitromethane, the solvate of crystallization). The residual electron density peaks are not arranged in an interpretable pattern. The structure factors were instead augmented via reverse Fourier transform methods using the SQUEEZE routine (P. van der Sluis & A.L. Spek (1990). Acta Cryst. A46, 194-201) as implemented in the program Platon. The resultant FAB file containing the structure factor contribution from the electron content of the void space was used in together with the original hkl file in the further refinement. (The FAB file with details of the Squeeze results is appended to this cif file). The Squeeze procedure corrected for 69 electrons within the solvent accessible voids, or around two nitromethane molecules.

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)**

|    | x     | y     | z     | Uiso*/Ueq | Occ. (<1) |
|----|-------|-------|-------|-----------|-----------|
| Co1 | 0.53192 (3) | 0.72356 (2) | 0.71546 (2) | 0.01491 (5) |
| Cl1 | 0.39576 (6) | 0.90464 (3) | 0.72682 (3) | 0.02551 (8) |
| Cl2 | 0.35412 (5) | 0.56244 (3) | 0.69120 (3) | 0.02233 (8) |
| N1  | 0.52808 (19) | 0.69410 (13) | 0.88487 (11) | 0.0210 (2) |
| N4  | 0.1556 (2) | 0.69189 (13) | 0.31011 (12) | 0.0236 (3) |
| C1  | 0.3612 (3) | 0.70540 (19) | 0.93121 (14) | 0.0299 (4) |
| H1  | 0.261957 | 0.733949 | 0.888753 | 0.036* |
| H2  | 0.3266 (3) | 0.6775 (2) | 1.03773 (15) | 0.0351 (4) |
| C3  | 0.4692 (3) | 0.63313 (18) | 1.09915 (14) | 0.0304 (4) |
| H3  | 0.449538 | 0.610848 | 1.171842 | 0.036* |
| C4  | 0.6422 (3) | 0.62179 (17) | 1.05229 (14) | 0.0285 (3) |
| H4  | 0.742296 | 0.591331 | 1.092985 | 0.034* |
| C5  | 0.6689 (2) | 0.65507 (16) | 0.94559 (13) | 0.0239 (3) |
| N2  | 0.8075 (2) | 0.67209 (14) | 0.69839 (12) | 0.0186 (3) | 0.914 (3) |
| N3  | 0.5951 (3) | 0.75652 (17) | 0.5435 (2) | 0.0161 (3) | 0.914 (3) |
| Atoms | x       | y       | z       | Ueq   | Ueq   |
|-------|---------|---------|---------|-------|-------|
| C6    | 0.8595  | 0.6501  | 0.8962  | 0.0278| 0.914 |
| H6A   | 0.9072  | 0.7302  | 0.8885  | 0.033 | 0.914 |
| H6B   | 0.9407  | 0.6056  | 0.9462  | 0.033 | 0.914 |
| C7    | 0.8759  | 0.5972  | 0.7900  | 0.0256| 0.914 |
| H7A   | 1.0070  | 0.5777  | 0.7767  | 0.031 | 0.914 |
| H7B   | 0.8066  | 0.5236  | 0.7933  | 0.031 | 0.914 |
| C8    | 0.8212  | 0.6019  | 0.6029  | 0.022 | 0.914 |
| H8A   | 0.7879  | 0.5206  | 0.6228  | 0.026 | 0.914 |
| H8B   | 0.9500  | 0.6022  | 0.5762  | 0.026 | 0.914 |
| C9    | 0.6934  | 0.6495  | 0.5141  | 0.0193| 0.914 |
| H9A   | 0.7673  | 0.6664  | 0.4488  | 0.023 | 0.914 |
| H9B   | 0.6023  | 0.5896  | 0.4988  | 0.023 | 0.914 |
| C10   | 0.7153  | 0.8598  | 0.5286  | 0.0203| 0.914 |
| H10A  | 0.6585  | 0.9253  | 0.5651  | 0.024 | 0.914 |
| H10B  | 0.7244  | 0.8827  | 0.4520  | 0.024 | 0.914 |
| C11   | 0.9089  | 0.8362  | 0.5717  | 0.0244| 0.914 |
| H11A  | 0.9753  | 0.7853  | 0.5230  | 0.029 | 0.914 |
| H11B  | 0.9753  | 0.9108  | 0.5704  | 0.029 | 0.914 |
| C12   | 0.9187  | 0.7802  | 0.6836  | 0.0239| 0.914 |
| H12A  | 1.0489  | 0.7614  | 0.7000  | 0.029 | 0.914 |
| H12B  | 0.8743  | 0.8368  | 0.7346  | 0.029 | 0.914 |
| N2B   | 0.817   | 0.7263  | 0.7020  | 0.0189| 0.086 |
| N3B   | 0.592   | 0.7352  | 0.539   | 0.018 | 0.086 |
| C6B   | 0.857   | 0.674   | 0.897   | 0.027 | 0.086 |
| H6C   | 0.9360  | 0.6986  | 0.9543  | 0.032 | 0.086 |
| H6D   | 0.9030  | 0.5959  | 0.8788  | 0.032 | 0.086 |
| C7B   | 0.903   | 0.7523  | 0.8028  | 0.028 | 0.086 |
| H7C   | 0.8677  | 0.8324  | 0.8195  | 0.033 | 0.086 |
| H7D   | 1.0389  | 0.7507  | 0.7919  | 0.033 | 0.086 |
| C8B   | 0.869   | 0.8190  | 0.6206  | 0.022 | 0.086 |
| H8C   | 0.9926  | 0.8008  | 0.5909  | 0.027 | 0.086 |
| H8D   | 0.8766  | 0.8942  | 0.6544  | 0.027 | 0.086 |
| C9B   | 0.727   | 0.829   | 0.529   | 0.021 | 0.086 |
| H9C   | 0.6624  | 0.9050  | 0.5308  | 0.026 | 0.086 |
| H9D   | 0.7930  | 0.8262  | 0.4603  | 0.026 | 0.086 |
| C10B  | 0.663   | 0.6218  | 0.508   | 0.020 | 0.086 |
| H10C  | 0.6624  | 0.6197  | 0.4295  | 0.025 | 0.086 |
| H10D  | 0.5808  | 0.5595  | 0.5370  | 0.025 | 0.086 |
| C11B  | 0.860   | 0.5997  | 0.5482  | 0.027 | 0.086 |
| H11C  | 0.9006  | 0.5208  | 0.5302  | 0.033 | 0.086 |
| H11D  | 0.9440  | 0.6561  | 0.5116  | 0.033 | 0.086 |
| C12B  | 0.873   | 0.6104  | 0.6666  | 0.027 | 0.086 |
| H12C  | 0.7939  | 0.5507  | 0.7028  | 0.032 | 0.086 |
| H12D  | 1.0014  | 0.5942  | 0.6882  | 0.032 | 0.086 |
| C13   | 0.4219  | 0.7729  | 0.4833  | 0.0197| 0.086 |
| H13A  | 0.3626  | 0.8463  | 0.5038  | 0.024 | 0.086 |
| H13B  | 0.3377  | 0.7089  | 0.5052  | 0.024 | 0.086 |
| C14   | 0.4423  | 0.7771  | 0.3617  | 0.0232| 0.086 |
### Table: Atomic displacement parameters (Å²)

|       | U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹³ |
|-------|-----|-----|-----|-----|-----|-----|
| Co1   | 0.01236 (9) | 0.01649 (9) | 0.01594 (9) | 0.00004 (6) | −0.00004 (6) | 0.00004 (6) |
| Cl1   | 0.02846 (19) | 0.02000 (16) | 0.02813 (19) | 0.00544 (14) | 0.00301 (14) | 0.00377 (14) |
| Cl2   | 0.02063 (16) | 0.02148 (16) | 0.02497 (17) | −0.00612 (13) | 0.00151 (13) | 0.00138 (13) |
| N1    | 0.0191 (6) | 0.0269 (7) | 0.0171 (6) | 0.0007 (5) | −0.0007 (4) | 0.00013 (4) |
| N4    | 0.0251 (7) | 0.0239 (6) | 0.0218 (6) | −0.0030 (5) | 0.00003 (5) | 0.0003 (5) |
| C1    | 0.0237 (8) | 0.0462 (11) | 0.0193 (7) | 0.0058 (7) | 0.0023 (6) | 0.0004 (7) |
| C2    | 0.0323 (10) | 0.0518 (12) | 0.0207 (8) | 0.0046 (8) | 0.0066 (7) | 0.00012 (8) |
| C3    | 0.0410 (10) | 0.0349 (9) | 0.0153 (7) | −0.0006 (8) | 0.00008 (6) | 0.00020 (6) |
| C4    | 0.0342 (9) | 0.0331 (9) | 0.0182 (7) | 0.0033 (7) | −0.0055 (6) | 0.00004 (6) |
| C5    | 0.0251 (7) | 0.0276 (8) | 0.0191 (7) | 0.0026 (6) | −0.0038 (6) | 0.00011 (6) |
| N2    | 0.0141 (6) | 0.0213 (7) | 0.0202 (6) | 0.0008 (5) | 0.0010 (5) | 0.00009 (5) |
| N3    | 0.0150 (6) | 0.0164 (8) | 0.0169 (7) | −0.0002 (6) | 0.00001 (5) | 0.00015 (6) |
| C6    | 0.0209 (9) | 0.0345 (16) | 0.0278 (10) | 0.0016 (8) | −0.0061 (7) | 0.0021 (9) |
| C7    | 0.0198 (8) | 0.0299 (9) | 0.0265 (8) | 0.0048 (6) | −0.0005 (6) | 0.00042 (7) |
| C8    | 0.0198 (7) | 0.0214 (7) | 0.0246 (8) | 0.0035 (6) | 0.0036 (6) | −0.0006 (6) |
| C9    | 0.0200 (8) | 0.0190 (8) | 0.0192 (7) | −0.0003 (6) | 0.0034 (6) | 0.00039 (7) |
| C10   | 0.0220 (8) | 0.0184 (9) | 0.0203 (7) | −0.0041 (8) | 0.00004 (6) | 0.00015 (7) |
| C11   | 0.0194 (8) | 0.0259 (8) | 0.0277 (9) | −0.0076 (6) | 0.0023 (6) | 0.0014 (7) |
| C12   | 0.0175 (7) | 0.0276 (8) | 0.0268 (8) | −0.0051 (6) | −0.0034 (6) | −0.0006 (7) |
| N2B   | 0.015 (3) | 0.019 (4) | 0.022 (3) | −0.008 (3) | −0.002 (3) | 0.002 (3) |
| N3B   | 0.018 (4) | 0.020 (5) | 0.017 (4) | −0.006 (4) | 0.001 (4) | 0.001 (4) |
| C6B   | 0.020 (5) | 0.035 (6) | 0.025 (5) | 0.003 (5) | −0.008 (5) | 0.001 (5) |
| C7B   | 0.019 (4) | 0.036 (4) | 0.028 (4) | −0.002 (4) | −0.004 (4) | 0.003 (4) |
| C8B   | 0.020 (4) | 0.023 (4) | 0.023 (4) | −0.008 (4) | 0.002 (4) | 0.004 (4) |
| C9B   | 0.023 (4) | 0.022 (5) | 0.019 (4) | 0.001 (4) | 0.003 (4) | 0.005 (4) |
| C10B  | 0.020 (4) | 0.020 (5) | 0.021 (4) | 0.000 (4) | 0.002 (4) | −0.003 (4) |
| C11B  | 0.027 (5) | 0.028 (5) | 0.026 (5) | 0.001 (4) | 0.006 (4) | 0.001 (4) |
| C12B  | 0.022 (4) | 0.030 (4) | 0.028 (4) | 0.000 (4) | 0.006 (4) | 0.002 (4) |
| C13   | 0.0177 (6) | 0.0252 (7) | 0.0161 (6) | 0.0001 (5) | −0.006 (5) | −0.0006 (5) |
| C14   | 0.0203 (7) | 0.0324 (8) | 0.0169 (6) | −0.0006 (6) | −0.0014 (5) | −0.0014 (6) |
| C15   | 0.0223 (7) | 0.0241 (7) | 0.0145 (6) | −0.0007 (5) | −0.0016 (5) | −0.0023 (5) |
| C16   | 0.0237 (7) | 0.0312 (8) | 0.0225 (7) | −0.0067 (6) | 0.0024 (6) | −0.0030 (6) |
| C17   | 0.0225 (8) | 0.0384 (10) | 0.0305 (9) | 0.0027 (8) | −0.0042 (6) | −0.0042 (7) |
Geometric parameters (Å, º)

|   |   |   |   |   |   |
|---|---|---|---|---|---|
|   |   |   |   |   |   |
| Co1—N2B | 2.072 (15) | C11—H11B | 0.9900 |
| Co1—N2  | 2.0933 (15) | C12—H12A | 0.9900 |
| Co1—N1  | 2.1498 (14) | C12—H12B | 0.9900 |
| Co1—N3  | 2.228 (3)   | N2B—C7B  | 1.475 (15) |
| Co1—N3B | 2.26 (3)    | N2B—C12B | 1.493 (15) |
| Co1—Cl2 | 2.31 (4)    | N2B—C8B  | 1.493 (15) |
| Co1—Cl1 | 2.3122 (4)  | N3B—C9B  | 1.471 (18) |
| N1—C5  | 1.347 (2)   | N3B—C10B | 1.473 (18) |
| N1—C1  | 1.347 (2)   | N3B—C13  | 1.481 (15) |
| N4—C15 | 1.341 (2)   | C6B—C7B  | 1.489 (18) |
| N4—C16 | 1.341 (2)   | C6B—H6C  | 0.9900 |
| C1—C2  | 1.388 (3)   | C6B—H6D  | 0.9900 |
| C1—H1  | 0.9500     | C7B—H7C  | 0.9900 |
| C2—C3  | 1.381 (3)   | C7B—H7D  | 0.9900 |
| C2—H2  | 0.9500     | C8B—C9B  | 1.557 (17) |
| C3—C4  | 1.389 (3)   | C8B—H8C  | 0.9900 |
| C3—H3  | 0.9500     | C8B—H8D  | 0.9900 |
| C4—C5  | 1.394 (2)   | C9B—H9C  | 0.9900 |
| C4—H4  | 0.9500     | C9B—H9D  | 0.9900 |
| C5—C6B | 1.508 (18)  | C10B—C11B| 1.542 (17) |
| C5—C6  | 1.512 (3)   | C10B—H10C| 0.9900 |
| N2—C8  | 1.490 (2)   | C10B—H10D| 0.9900 |
| N2—C7  | 1.496 (2)   | C11B—C12B| 1.512 (17) |
| N2—C12 | 1.496 (2)   | C11B—H11C| 0.9900 |
| N3—C9  | 1.481 (3)   | C11B—H11D| 0.9900 |
| N3—C13 | 1.484 (2)   | C12B—H12C| 0.9900 |
| N3—C10 | 1.487 (3)   | C12B—H12D| 0.9900 |
| C6—C7  | 1.505 (4)   | C13—C14  | 1.540 (2) |
| C6—H6A | 0.9900     | C13—H13A | 0.9900 |
| C6—H6B | 0.9900     | C13—H13B | 0.9900 |
| C7—H7A | 0.9900     | C14—C15  | 1.506 (2) |
| C7—H7B | 0.9900     | C14—H14A | 0.9900 |
| C8—C9  | 1.541 (3)   | C14—H14B | 0.9900 |
| C8—H8A | 0.9900     | C15—C19  | 1.390 (2) |
| C8—H8B | 0.9900     | C16—C17  | 1.379 (3) |
| C9—H9A | 0.9900     | C16—H16  | 0.9500 |
| C9—H9B | 0.9900     | C17—C18  | 1.385 (3) |
| C10—C11| 1.532 (3)   | C17—H17  | 0.9500 |
| C10—H10A| 0.9900   | C18—C19  | 1.389 (3) |
| C10—H10B| 0.9900   | C18—H18  | 0.9500 |
| C11—C12| 1.526 (3)   | C19—H19  | 0.9500 |
| C11—H11A| 0.9900 |   |   |   |   |
supporting information

N2B—Co1—N1 94.8 (4) N2—C12—H12A 108.9
N2—Co1—N1 94.16 (6) C11—C12—H12A 108.9
N2—Co1—N3 75.49 (6) N2—C12—H12B 108.9
N1—Co1—N3B 168.7 (4) C7B—N2B—C12B 108.9
N2B—Co1—C12 142.4 (4) C7B—N2B—C8B 108.1 (13)
N2—Co1—C12 107.08 (5) C12B—N2B—C8B 110.4 (13)
N1—Co1—C12 92.63 (4) C7B—N2B—Co1 106.0 (11)
N3—Co1—C12 94.48 (5) C8B—N2B—Co1 108.6 (10)
N3B—Co1—C12 88.7 (6) C9B—N3B—C10B 114 (2)
N2B—Co1—Cl2 114.2 (4) C9B—N3B—Co1 108.7 (16)
N1—Co1—Cl2 131.72 (5) C7B—C6B—C5 126 (2)
N2—Co1—Cl2 91.92 (4) C7B—C6B—H6C 105.7
N1—Co1—Cl2 91.92 (5) C5—C6B—H6C 105.7
N3—Co1—Cl2 97.4 (5) C7B—C6B—H6D 108.1
N3B—Co1—Cl2 92.63 (4) C6B—C7B—H7C 108.1
C12—N2—Co1 124.4 (4) C6B—C7B—H7D 108.1
N2B—Co1—Cl1 74.9 (6) C9B—N3B—C10B 111.9 (14)
N1—Co1—Cl1 168.81 (6) C7B—N2B—Co1 111.9 (14)
N2—Co1—Cl1 74.9 (6) C12B—N2B—Co1 106.0 (11)
N1—Co1—Cl1 74.9 (6) N3B—C9B—C10B 108.6 (10)
N3—Co1—Cl1 74.9 (6) C13—N3B—Co1 108.7 (16)
N3B—Co1—Cl1 74.9 (6) C7B—C6B—H6C 105.7
C12—N2—Co1 124.4 (4) C7B—C6B—H6D 108.1
N1—Co1—Cl1 124.4 (4) C6B—C7B—H7C 108.1
N2—Co1—Cl1 124.4 (4) C6B—C7B—H7D 108.1
N1—Co1—Cl1 74.9 (6) N2B—C7B—C6B 117 (2)
C1—Co1—Cl1 118.33 (15) N2B—C7B—H7C 108.1
C15—N4—C16 126.68 (12) N2B—C7B—H7D 108.1
N1—C1—C2 118.33 (15) N2B—C8B—C9B 111.2 (13)
N1—C1—H1 118.33 (15) N2B—C8B—H8C 109.4
C2—C1—H1 118.33 (15) C9B—C8B—H8C 109.4
C3—C2—C1 118.69 (18) C5—C6B—H6D 108.4
C3—C2—H2 120.8 C7B—C6B—H6D 108.4
C1—C2—H2 120.8 N2B—C8B—C9B 111.2 (13)
C2—C3—C4 120.0 C8B—C9B—H9C 109.4
C2—C3—H3 120.7 C8B—C9B—H9D 109.4
C3—C4—C5 120.0 C8B—C9B—H9C 109.4
C3—C4—H4 120.7 C8B—C9B—H9D 109.4
C5—C4—H4 120.0 C9B—C8B—H8D 109.4
C9—N3—Co1 121.30 (17) C9B—C8B—H8D 109.4
C9—N3—C13 114.8 (10) H8C—C8B—H8D 108.0
C4—C5—C6 122.7 (11) N3B—C9B—C8B 111.3 (15)
C4—C5—C6 122.7 (11) N3B—C9B—H9C 109.4
C8—N2—Co1 120.10 (18) C8B—C9B—H9C 109.4
C8—N2—C7 118.52 (17) N3B—C9B—H9D 109.4
C8—N2—C12 118.52 (17) N3B—C10B—C11B 110.9 (15)
C7—N2—C12 118.52 (17) N3B—C10B—H10C 109.5
C8—N2—C7 118.52 (17) C11B—C10B—H10C 109.5
C7—N2—Co1 118.52 (17) N3B—C10B—H10D 109.5
C13—N3—C10 118.52 (17) C11B—C10B—H10D 109.5
C9—N3—Co1 118.52 (17) H10C—C10B—H10D 108.1
C9—N3—C13 118.52 (17) C12B—C11B—C10B 112.3 (16)

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| Bond          | Value (Std. Err.) | Bond          | Value (Std. Err.) | Bond          | Value (Std. Err.) |
|--------------|------------------|--------------|------------------|--------------|------------------|
| C13—N3—Co1  | 110.15 (16)      | C12B—C11B—H11C | 109.2          | C12B—C11B—H11C | 109.2           |
| C10—N3—Co1  | 109.47 (14)      | C10B—C11B—H11D | 109.2          | C10B—C11B—H11D | 109.2           |
| C7—C6—C5    | 116.7 (2)        | C7—C6—H6A    | 108.1           | N2B—C12B—C11B | 113.6 (14)      |
| C7—C6—H6A   | 108.1            | C5—C6—H6B    | 108.1           | N2B—C12B—H12C | 108.8           |
| H6A—C6—H6B  | 107.3            | C10—N3—Co1   | 109.47 (14)     | C1—C2—C3—C4  | 2.0 (3)          |
| N2—C7—C6    | 115.13 (18)      | H7A—C7—H7B   | 107.5           | H8B—C8—H8A   | 109.9           |
| N2—C7—H7A   | 108.5            | N3—C9—C8     | 111.81 (15)     | C9—C8—H8B    | 109.3           |
| C6—C7—H7A   | 108.5            | C9—C8—H8A    | 109.3           | H8A—C8—H8B   | 107.9           |
| H7A—C7—H7B  | 108.5            | C8—C9—H9A    | 109.2           | N3—C9—C8     | 111.89 (17)     |
| N2—C7—H7B   | 108.5            | C8—C9—H9A    | 109.2           | N3—C9—H9A    | 109.2           |
| N2—C7—H7B   | 108.5            | C3—C4—C5     | 0.1 (3)         | C5—N1—C1—C2  | -0.9 (3)         |
| C6—C7—H7B   | 108.5            | C1—C2—C3—C4  | 2.0 (3)         | C5—N1—C1—C2  | 172.64 (18)     |
| N2—C7—C6    | 115.13 (18)      | C5—C6—C7     | 116.03 (17)     | N1—C1—C2—C3  | -1.7 (4)         |
| N2—C8—C9    | 111.81 (15)      | C10B—N3—C9B  | 115.4 (14)      | C5—N1—C1—C2  | 172.64 (18)     |
| N2—C8—H8A   | 109.3            | C9B—C8B—C9B  | 118.2 (15)      | Co1—N1—C1—C2 | -169.60 (14)    |
| C9—C8—H8A   | 109.3            | N4—C15—C19   | 122.17 (16)     | N1—C1—C2—C3  | -1.7 (4)         |
| N2—C8—H8B   | 109.3            | C4—C14—H14A  | 108.9           | C1—C2—C3—C4  | 2.0 (3)          |
| C9—C8—H8B   | 109.3            | C4—C14—H14B  | 109.8           | C2—C3—C4—C5  | 0.1 (3)          |
| H8B—C8—H8B  | 107.9            | C4—C14—H14B  | 109.8           | C1—N1—C5—C4  | 3.0 (3)          |
| N3—C9—C8    | 111.89 (17)      | C4—C14—H14B  | 109.8           | Co1—N1—C5—C4 | -169.60 (14)    |
| N3—C9—H9A   | 109.2            | H9B—C9B—C10A | 115.4 (14)      | C1—N1—C5—C4  | -169.60 (14)    |
| C8—C9—H9A   | 109.2            | C10B—N3B—C9B | 115.92 (16)     | C1—N1—C5—C6B | -165 (2)         |
| H9A—C9—H9B  | 107.9            | C9B—C8B—C9B  | 116.69 (15)     | C1—N1—C5—C6B | -165 (2)         |
| N3—C10—C11  | 112.12 (17)      | H10A—C10—H10B | 107.9         | H11A—C11—H11B | 107.4          |
| N3—C10—H10A | 109.2            | C10—C11—H11A | 108.3           | N2—C12—C11   | 113.26 (15)     |
| C11—C10—H10A | 109.2         | C10—C11—H11A | 108.3           |              |                 |
| C11—C10—H10B | 109.2        | C10—C11—H11B | 108.3           |              |                 |
| H10A—C10—H10B | 107.9        | H11A—C11—H11B | 107.4      |              |                 |
| C5—N1—C1—C2 | -0.9 (3)        | C12B—N2B—C7B—C6B | -62 (2)  |              |                 |
| Co1—N1—C1—C2 | 172.64 (18)    | C8B—N2B—C7B—C6B | 176 (2)   |              |                 |
| N1—C1—C2—C3 | -1.7 (4)        | Co1—N2B—C7B—C6B | 57 (2)    |              |                 |
| C1—C2—C3—C4 | 2.0 (3)         | C5—C6B—C7B—N2B | -62 (4)   |              |                 |
| C2—C3—C4—C5 | 0.1 (3)         | C7B—N2B—C8B—C9B | -156.5 (19)|              |                 |
| C1—N1—C5—C4 | 3.0 (3)         | C12B—N2B—C8B—C9B | 81 (2)   |              |                 |
| Co1—N1—C5—C4 | -169.60 (14)   | Co1—N2B—C8B—C9B | -35 (2)  |              |                 |
| C1—N1—C5—C6B | -165 (2)       | C10B—N3B—C9B—C8B | -76 (3)  |              |                 |
sup-11

Co1—N1—C5—C6B 23 (2)  C13—N3B—C9B—C8B 156 (2)
C1—N1—C5—C6 −175.7 (2)  Co1—N3B—C9B—C8B 41 (2)
Co1—N1—C5—C6B 11.6 (3)  N2B—C8B—C9B—N3B −8 (3)
C3—C4—C5—N1 −2.7 (3)  C9B—N3B—C10B—C11B 41 (3)
C3—C4—C5—C6B 164 (2)  C13—N3B—C10B—C11B 167 (2)
C3—C4—C5—C6 176.0 (2)  Co1—N3B—C10B—C11B −72 (2)
N1—C5—C6—C7 −46.8 (3)  N3B—C10B—C11B—C12B 55 (3)
C4—C5—C6—C7B 134.4 (2)  C7B—N2B—C12B—C11B −154.9 (16)
N1—C5—C6B—C7B 15 (4)  C8B—N2B—C12B—C11B −34 (2)
C4—C5—C6B—C7B −153 (3)  C10B—N3B—C13—C14 73 (2)
C8—N2—C7—C6 −175.57 (18)  C9—N3—C13—C14 −56.5 (2)
C12—N2—C7—C6 −175.57 (18)  N3—C10—C11—C12 −59 (2)
C1—N1—C5—C6B −175.57 (18)  C9—N3—C10—C11 67.8 (2)
C9—N2—C8—C9 2.7 (2)  Co1—N3—C10—C11 −176.5 (5)
C9—N3—C10—C11 −44.7 (3)  C9—N2—C8—C9 67.8 (2)
C13—N3—C9—C8 −155.72 (19)  C10—N3—C9—C8 79.9 (2)
C10—N3—C9—C8 −155.72 (19)  C10—N3—C9—C8 −170.61 (12)
C1—N1—C5—C6 −15.6 (3)  Co1—N2—C8—C9 83.0 (16)
C9—N2—C8—C9 36.99 (17)  C9—N2—C8—C9 −56.5 (2)
C12—N2—C8—C9 36.99 (17)  C10—N3—C9—C8 79.9 (2)
C13—N3—C9—C8 −155.72 (19)  Co1—N2—C8—C9 −176.5 (5)
C10—N3—C9—C8 −155.72 (19)  C9—N2—C12—C11 0.8 (3)
Co1—N2—C8—C9 −79.80 (18)  C10—N3—C9—C8 −170.61 (12)
C1—N1—C5—C6B −15.6 (3)  C10—N3—C10—C11 67.8 (2)
C4—C5—C6—C7B 134.4 (2)  C10—N3—C10—C11 −176.5 (5)
N1—C5—C6B—C7B 15 (4)  N3B—C13—C14—C15 −176.65 (19)
C8—N2—C7—C6 −175.57 (18)  N3—C10—C11—C12 97.9 (2)
C12—N2—C7—C6 63.2 (2)  C8—N2—C7—C6 −34 (2)
C10—N3—C9—C8 −155.72 (19)  Co1—N2—C7—C6 83.0 (16)
C10—N3—C9—C8 −155.72 (19)  C9—N2—C7—C6 −59 (2)
C7—N2—C8—C9 74.9 (3)  C9—N2—C7—C6 59 (2)
C7—N2—C8—C9 −159.07 (16)  C10—N3—C9—C8 79.9 (2)
N1—C5—C6B—C7B −15.6 (3)  Co1—N2—C8—C9 −176.5 (5)
C4—C5—C6B—C7B −153 (3)  C10—N3—C9—C8 −170.61 (12)

(1,4-Bis[2-(pyridin-2-yl)ethyl]piperazine)chloridocobalt(II) perchlorate (ta-eab1701-c)

Crystal data

$[\text{CoCl(C₁₈H₂₄N₄)}]\text{ClO}_₄$

$M_ᵣ = 490.24$

Monoclinic, $P2₁$

$a = 8.3952$ (3) Å

$b = 10.9341$ (4) Å

$c = 11.3643$ (4) Å

$β = 92.125$ (3)°

$V = 1042.46$ (6) Å³

$Z = 2$

$F(000) = 506$

$D_ᵣ = 1.562$ Mg m⁻³

Cell parameters from 2470 reflections

$θ = 3.9–71.3°$

$μ = 9.10$ mm⁻¹

$T = 293$ K

Prism, violet

0.18 × 0.14 × 0.12 mm

Data collection

Rigaku, Oxford diffraction
diffractometer

Radiation source: fine-focus sealed X-ray tube,
Enhance (Cu) X-ray Source

Graphite monochromator

Detector resolution: 16.0416 pixels mm⁻¹

$ω$ scans

Absorption correction: multi-scan
(ChargeAlisPro; Rigaku OD, 2015)

$T_{min} = 0.378$, $T_{max} = 1.000$

6624 measured reflections

3274 independent reflections

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2877 reflections with $I > 2\sigma(I)$

$R_{int} = 0.052$

$\theta_{max} = 71.5^\circ$, $\theta_{min} = 3.9^\circ$

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.116$

$S = 1.03$

3274 reflections

308 parameters

155 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(Fo^2) + (0.0576P)^2]$

where $P = (Fo^2 + 2Fc^2)/3$

$\Delta/\sigma$ max = 0.002

$\Delta rho_{max} = 0.77 e \AA^{-3}$

$\Delta rho_{min} = -0.40 e \AA^{-3}$

Absolute structure: Classical Flack method preferred over Parsons because s.u. lower

Absolute structure parameter: −0.021 (7)

Special details

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

Refinement. The perchlorate ion was refined as disordered by a slight rotation. The two disordered moieties were restrained to have similar geometries. Uij components of ADPs for disordered atoms closer to each other than 2.0 Ångstrom were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.540 (19) to 0.460 (19).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)

| Atom | x     | y     | z     | Uiso* Ueq | Occ. (<1) |
|------|-------|-------|-------|-----------|-----------|
| Co1A | 0.55461 (10) | 0.55297 (7) | 0.83474 (7) | 0.0299 (2) |
| Cl1A | 0.4381 (2) | 0.5403 (2) | 1.01221 (12) | 0.0572 (5) |
| N1A  | 0.6426 (6) | 0.3908 (5) | 0.7724 (4) | 0.0328 (11) |
| N2A  | 0.3341 (5) | 0.5009 (5) | 0.7303 (5) | 0.0378 (12) |
| N3A  | 0.4779 (6) | 0.6982 (5) | 0.7259 (5) | 0.0369 (12) |
| N4A  | 0.7676 (6) | 0.6407 (5) | 0.8916 (5) | 0.0362 (11) |
| C1A  | 0.7876 (7) | 0.3864 (6) | 0.7261 (6) | 0.0363 (13) |
| H1A  | 0.850157 | 0.456584 | 0.728812 | 0.044* |
| C2A  | 0.8478 (8) | 0.2833 (7) | 0.6751 (6) | 0.0462 (17) |
| H2A  | 0.948525 | 0.284273 | 0.643694 | 0.055* |
| C3A  | 0.7578 (9) | 0.1795 (7) | 0.6710 (6) | 0.0476 (17) |
| H3A  | 0.797059 | 0.108202 | 0.638103 | 0.057* |
| C4A  | 0.6069 (9) | 0.1819 (6) | 0.7166 (6) | 0.0418 (15) |
| H4A  | 0.543737 | 0.112018 | 0.714020 | 0.050* |
| C5A  | 0.5508 (8) | 0.2878 (6) | 0.7657 (6) | 0.0335 (14) |
| C6A  | 0.3877 (8) | 0.2942 (7) | 0.8161 (6) | 0.0437 (15) |
| H6AA | 0.398062 | 0.323980 | 0.896421 | 0.052* |
| H6AB | 0.343464 | 0.212291 | 0.818602 | 0.052* |
| C7A  | 0.2709 (8) | 0.3772 (8) | 0.7460 (7) | 0.0485 (17) |
| H7AA | 0.247778 | 0.341021 | 0.669318 | 0.058* |
| H7AB | 0.171676 | 0.382148 | 0.786883 | 0.058* |

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C8A  0.2215 (8)  0.5989 (8)  0.7598 (7)  0.0505 (17)
H8AA  0.175124  0.581761  0.834998  0.061*
H8AB  0.135983  0.603416  0.700176  0.061*
C9A  0.3123 (9)  0.7207 (7)  0.7661 (8)  0.053 (2)
H9AA  0.259024  0.780907  0.715770  0.064*
H9AB  0.316132  0.751531  0.846192  0.064*
C10A  0.3831 (7)  0.5229 (7)  0.6094 (5)  0.0427 (16)
H10A  0.290829  0.520504  0.555489  0.051*
C11A  0.5736 (9)  0.8108 (7)  0.7317 (7)  0.0449 (17)
H11A  0.553124  0.853475  0.804460  0.054*
H11B  0.541105  0.863798  0.666230  0.054*
C12A  0.806884  0.858794  0.702779  0.054*
C14A  0.8280 (7)  0.7406 (6)  0.8409 (5)  0.0347 (13)
C15A  0.9611 (8)  0.8001 (7)  0.8921 (7)  0.0449 (16)
C13A  0.7532 (9)  0.7846 (7)  0.7263 (6)  0.0454 (16)
C16A  1.10294 (8)  0.7562 (8)  0.9948 (7)  0.0511 (19)
C17A  1.117969  0.795338  1.028881  0.061*
C18A  0.9692 (8)  0.6564 (8)  1.0469 (6)  0.0496 (18)
C19A  1.015624  0.625491  1.116260  0.060*
C11B  0.8515 (11)  0.5211 (9)  0.4162 (9)  0.041 (2)  0.540 (19)
O1B  0.9721 (18)  0.4337 (16)  0.4341 (17)  0.081 (4)  0.540 (19)
O2B  0.841 (2)  0.551 (2)  0.2956 (13)  0.082 (4)  0.540 (19)
O3B  0.698 (2)  0.477 (2)  0.450 (3)  0.064 (5)  0.540 (19)
O4B  0.891 (2)  0.6189 (19)  0.4913 (17)  0.098 (5)  0.540 (19)
C11C  0.8480 (15)  0.5254 (12)  0.4181 (12)  0.050 (3)  0.460 (19)
O1C  0.9811 (19)  0.495 (2)  0.4894 (18)  0.089 (5)  0.460 (19)
O2C  0.891 (3)  0.510 (2)  0.3011 (16)  0.078 (5)  0.460 (19)
O3C  0.721 (2)  0.446 (2)  0.447 (3)  0.056 (5)  0.460 (19)
O4C  0.822 (2)  0.6509 (13)  0.4417 (18)  0.069 (4)  0.460 (19)

Atomic displacement parameters (Å²)

|   | U¹¹   | U²²   | U³³   | U¹²   | U¹³   | U²³   |
|---|-------|-------|-------|-------|-------|-------|
| Co1A | 0.0308 (4) | 0.0292 (5) | 0.0295 (4) | −0.0003 (4) | −0.0008 (3) | 0.0007 (4) |
| C11A | 0.0685 (9) | 0.0720 (12) | 0.0319 (6) | −0.0196 (11) | 0.0101 (6) | −0.0027 (9) |
| N1A  | 0.030 (2) | 0.034 (3) | 0.033 (2) | 0.000 (2) | −0.0033 (19) | −0.001 (2) |
| N2A  | 0.023 (2) | 0.048 (3) | 0.042 (3) | 0.001 (2) | −0.0016 (18) | −0.001 (2) |
| N3A  | 0.037 (3) | 0.037 (3) | 0.037 (3) | 0.008 (2) | −0.002 (2) | 0.002 (2) |
| N4A  | 0.037 (3) | 0.034 (3) | 0.037 (3) | −0.006 (2) | −0.001 (2) | −0.002 (2) |
| C1A  | 0.027 (3) | 0.039 (4) | 0.043 (3) | 0.003 (3) | −0.002 (2) | 0.001 (3) |

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| Atom   | U11 | U22 | U33 | U12 | U13 | U23 |
|--------|-----|-----|-----|-----|-----|-----|
| C2A    | 0.032 (3) | 0.060 (5) | 0.046 (4) | 0.010 (3) | −0.004 (3) | −0.005 (3) |
| C3A    | 0.052 (4) | 0.049 (4) | 0.041 (3) | 0.014 (3) | −0.007 (3) | −0.011 (3) |
| C4A    | 0.052 (4) | 0.030 (3) | 0.043 (3) | −0.001 (3) | −0.004 (3) | −0.005 (3) |
| C5A    | 0.037 (3) | 0.029 (3) | 0.035 (3) | 0.001 (3) | 0.002 (3) | 0.009 (2) |
| C6A    | 0.043 (3) | 0.037 (4) | 0.051 (4) | −0.014 (3) | 0.008 (3) | 0.002 (3) |
| C7A    | 0.032 (3) | 0.054 (5) | 0.059 (4) | −0.011 (3) | 0.001 (3) | −0.002 (4) |
| C8A    | 0.028 (3) | 0.054 (4) | 0.070 (5) | 0.006 (3) | 0.006 (3) | −0.001 (4) |
| C9A    | 0.041 (4) | 0.041 (4) | 0.077 (5) | 0.016 (3) | 0.010 (4) | 0.005 (4) |
| C10A   | 0.038 (3) | 0.053 (5) | 0.036 (3) | 0.000 (3) | −0.006 (2) | −0.008 (3) |
| C11A   | 0.050 (4) | 0.061 (5) | 0.031 (3) | −0.005 (3) | −0.002 (3) | 0.008 (3) |
| C12A   | 0.051 (4) | 0.034 (4) | 0.050 (4) | 0.006 (3) | −0.004 (3) | 0.001 (3) |
| C13A   | 0.051 (4) | 0.041 (4) | 0.045 (4) | −0.017 (3) | 0.004 (3) | 0.009 (3) |
| C14A   | 0.032 (3) | 0.034 (3) | 0.038 (3) | −0.001 (2) | 0.003 (2) | −0.009 (3) |
| C15A   | 0.042 (3) | 0.041 (4) | 0.052 (4) | −0.016 (3) | 0.007 (3) | −0.008 (3) |
| C16A   | 0.040 (4) | 0.061 (5) | 0.051 (4) | −0.016 (3) | −0.006 (3) | −0.018 (4) |
| C17A   | 0.041 (4) | 0.063 (5) | 0.044 (4) | −0.004 (3) | −0.008 (3) | −0.005 (3) |
| C18A   | 0.040 (3) | 0.045 (4) | 0.039 (3) | −0.003 (3) | −0.008 (3) | 0.001 (3) |
| C11B   | 0.039 (3) | 0.043 (3) | 0.044 (3) | −0.017 (3) | 0.012 (3) | −0.007 (3) |
| O1B    | 0.069 (7) | 0.078 (9) | 0.099 (9) | 0.024 (7) | 0.016 (7) | 0.012 (7) |
| O2B    | 0.099 (9) | 0.086 (10) | 0.061 (6) | 0.018 (8) | 0.015 (6) | 0.016 (7) |
| O3B    | 0.053 (7) | 0.059 (11) | 0.082 (8) | −0.004 (7) | 0.026 (6) | −0.011 (8) |
| O4B    | 0.098 (10) | 0.097 (10) | 0.099 (9) | −0.042 (8) | 0.011 (8) | −0.043 (8) |
| C11C   | 0.047 (5) | 0.053 (5) | 0.049 (5) | 0.010 (4) | 0.006 (4) | 0.014 (4) |
| O1C    | 0.059 (7) | 0.121 (11) | 0.087 (9) | −0.020 (8) | −0.029 (7) | 0.031 (8) |
| O2C    | 0.088 (10) | 0.081 (10) | 0.069 (8) | 0.004 (8) | 0.031 (7) | −0.013 (8) |
| O3C    | 0.050 (8) | 0.046 (10) | 0.073 (8) | −0.021 (8) | 0.005 (8) | −0.014 (8) |
| O4C    | 0.075 (9) | 0.046 (7) | 0.088 (9) | −0.005 (7) | 0.021 (7) | −0.009 (7) |

**Geometric parameters (Å, °)**

| Bond            | Length (Å) | Angle (°) |
|-----------------|------------|-----------|
| Co1A—N1A        | 2.057 (5)  |           |
| Co1A—N3A        | 2.099 (5)  |           |
| Co1A—N4A        | 2.109 (5)  |           |
| Co1A—N2A        | 2.236 (5)  |           |
| Co1A—C11A       | 2.2780 (16)|           |
| N1A—C1A         | 1.344 (8)  |           |
| N1A—C5A         | 1.366 (8)  |           |
| N2A—C7A         | 1.467 (10) |           |
| N2A—C10A        | 1.468 (8)  |           |
| N2A—C8A         | 1.476 (9)  |           |
| N3A—C12A        | 1.470 (9)  |           |
| N3A—C11A        | 1.480 (8)  |           |
| N3A—C9A         | 1.500 (9)  |           |
| N4A—C14A        | 1.344 (9)  |           |
| N4A—C18A        | 1.352 (8)  |           |
| C1A—C2A         | 1.372 (10) |           |
| C1A—H1A         | 0.9300     |           |
| C2A—C3A         | 1.363 (11) |           |
| Bond                  | Distance | Bond                  | Distance |
|----------------------|----------|----------------------|----------|
| C2A—H2A              | 0.9300   | C16A—H16A            | 0.9300   |
| C3A—C4A              | 1.387 (11)| C17A—C18A           | 1.386 (9) |
| C3A—H3A              | 0.9300   | C17A—H17A           | 0.9300   |
| C4A—C5A              | 1.376 (10)| C18A—H18A           | 0.9300   |
| C4A—H4A              | 0.9300   | Cl1B—O4B            | 1.400 (13)|
| C5A—C6A              | 1.506 (9) | Cl1B—O1B            | 1.401 (13)|
| C6A—C7A              | 1.537 (10)| Cl1B—O2B            | 1.409 (13)|
| C6A—H6AA             | 0.9700   | CI1C—O1C            | 1.395 (14)|
| C6A—H6AB             | 0.9700   | CI1C—O2C            | 1.400 (15)|
| C7A—H7AA             | 0.9700   | CI1C—O4C            | 1.417 (15)|
| C7A—H7AB             | 0.9700   | CI1C—O3C            | 1.425 (15)|
| C8A—C9A              | 1.535 (11)| N1A—Co1A—N3A        | 123.7 (2) |
| C8A—H8AA             | 0.9700   | C9A—C8A—H8AB        | 110.0    |
| N1A—Co1A—N3A         | 123.7 (2)| N1A—C1A—N3A         | 100.7 (2) |
| N1A—Co1A—N4A         | 100.7 (2)| N3A—C9A—C8A         | 107.9 (6) |
| N3A—Co1A—N4A         | 94.3 (2) | N3A—C9A—H9AA        | 110.1    |
| N1A—Co1A—N2A         | 84.2 (2) | N3A—C9A—H9AA        | 110.1    |
| N3A—Co1A—N2A         | 69.5 (2) | N2A—C10A—C11A       | 110.0    |
| N4A—Co1A—N2A         | 162.6 (2)| N3A—C9A—H9AB        | 110.1    |
| N1A—Co1A—Cl1A        | 115.11 (16)| N2A—C10A—C11A      | 110.0    |
| N3A—Co1A—Cl1A        | 115.81 (17)| C8A—C9A—H8AA        | 110.1    |
| N4A—Co1A—Cl1A        | 98.25 (16)| C9A—C8A—H8AB        | 110.0    |
| N2A—Co1A—Cl1A        | 94.62 (15)| N2A—C10A—C11A      | 110.0    |
| C1A—N1A—C5A          | 117.7 (6) | C11A—C10A—H10A      | 110.0    |
| C1A—N1A—Co1A         | 120.5 (4) | N2A—C10A—C11A      | 110.0    |
| C5A—N1A—Co1A         | 121.4 (4) | N2A—C10A—H10B       | 110.0    |
| C7A—N2A—C10A         | 112.4 (6) | C11A—C10A—H10B      | 110.0    |
| C7A—N2A—C8A          | 113.8 (6) | H10A—C10A—H10B      | 108.4    |
| C10A—N2A—C8A         | 107.3 (6) | N3A—C11A—C10A       | 108.8 (5) |
| C7A—N2A—Co1A         | 117.8 (4) | C10A—C11A—H11A      | 109.9    |
| C10A—N2A—Co1A        | 101.5 (3) | N3A—C11A—H11B       | 109.9    |
| C8A—N2A—Co1A         | 102.7 (4) | C10A—C11A—H11B      | 109.9    |
| C12A—N3A—C11A        | 112.3 (6) | H11A—C11A—H11B      | 108.3    |
| C12A—N3A—C9A         | 111.1 (6) | N3A—C12A—C13A       | 112.2 (6) |
| C11A—N3A—C9A         | 107.0 (6) | N3A—C12A—H12A       | 109.2    |
| C12A—N3A—Co1A        | 116.8 (4) | C13A—C12A—H12A      | 109.2    |
| C11A—N3A—Co1A        | 106.5 (4) | N3A—C12A—H12B       | 109.2    |
| C9A—N3A—Co1A         | 102.2 (4) | C13A—C12A—H12B      | 109.2    |
| C14A—N4A—C18A        | 118.3 (5) | H12A—C12A—H12B      | 107.9    |
| C14A—N4A—Co1A        | 124.6 (4) | C14A—C13A—C12A      | 113.8 (6) |
| C18A—N4A—Co1A        | 116.6 (4) | C14A—C13A—H13A      | 108.8    |
| N1A—C1A—C2A          | 123.2 (6) | C12A—C13A—H13A      | 108.8    |
| N1A—C1A—H1A          | 118.4    | C14A—C13A—H13B      | 108.8    |
| C2A—C1A—H1A          | 118.4    | C12A—C13A—H13B      | 108.8    |
| C3A—C2A—C1A          | 119.1 (7) | H13A—C13A—H13B      | 107.7    |
| C3A—C2A—H2A          | 120.5    | N4A—C14A—C15A       | 120.5 (6) |
| C1A—C2A—H2A          | 120.5    | N4A—C14A—C13A       | 118.6 (5) |
C2A—C3A—C4A 119.0 (7) C15A—C14A—C13A 120.8 (6)
C2A—C3A—H3A 120.5 C16A—C15A—C14A 119.6 (7)
C4A—C3A—H3A 120.5 C16A—C15A—H15A 120.2
C5A—C4A—C3A 119.9 (7) C14A—C15A—H15A 120.2
C5A—C4A—H4A 120.0 C17A—C16A—C15A 120.4 (6)
C3A—C4A—H4A 120.0 C17A—C16A—H16A 119.8
N1A—C5A—C4A 121.0 (6) C15A—C16A—H16A 119.8
N1A—C5A—C6A 117.4 (6) C16A—C17A—C18A 118.1 (7)
C4A—C5A—C3A 119.9 (7) C14A—C15A—C14A 119.8
C5A—C4A—H4A 120.0 C17A—C16A—H16A 119.8
N2A—C7A—C6A 112.4 (5) C18A—C17A—C18A 118.5
N2A—C7A—H7AA 109.1 C17A—C18A—H18A 118.5
C6A—C7A—H7AA 109.1 C18A—C17A—H17A 120.9
C5A—C6A—C7A 113.7 (6) C16A—C17A—H17A 120.9
C5A—C6A—H6AA 108.8 N4A—C18A—C17A 123.0 (7)
C7A—C6A—H6AA 108.8 N4A—C18A—H18A 118.5
C5A—C6A—H6AB 108.8 C17A—C18A—H18A 118.5
C7A—C6A—H6AB 108.8 O4B—Cl1B—O1B 106.3 (12)
H6AA—C6A—H6AB 107.7 O4B—Cl1B—O2B 114.9 (14)
N2A—C7A—C6A 112.4 (5) O1B—Cl1B—O2B 108.5 (11)
N2A—C7A—H7AA 109.1 O4B—Cl1B—O3B 106.6 (13)
C6A—C7A—H7AA 109.1 O1B—Cl1B—O3B 112.3 (13)
N2A—C7A—H7AB 109.1 O2B—Cl1B—O3B 108.4 (14)
C6A—C7A—H7AB 109.1 O1C—Cl1C—O2C 107.2 (15)
H7AA—C7A—H7AB 107.9 O1C—Cl1C—O4C 104.1 (15)
N2A—C8A—C9A 108.6 (5) O2C—Cl1C—O4C 110.1 (13)
N2A—C8A—H8AA 110.0 O2C—Cl1C—O3C 108.3 (15)
C9A—C8A—H8AA 110.0 O2C—Cl1C—O3C 111.6 (15)
N2A—C8A—H8AB 110.0 O4C—Cl1C—O3C 115.0 (15)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| C2A—H2A···O4Bii | 0.93 | 2.76 | 3.454 (19) | 133 |
| C2A—H2A···O4Ci | 0.93 | 2.63 | 3.439 (18) | 146 |
| C7A—H7A4···O4Cii | 0.97 | 2.49 | 3.34 (2) | 146 |
| C10A—H10B···O3B | 0.97 | 2.60 | 3.30 (2) | 129 |
| C11A—H11A···O3B | 0.97 | 2.54 | 3.28 (2) | 133 |
| C12A—H12B···O3Biii | 0.97 | 2.67 | 3.53 (3) | 147 |
| C13A—H13A···O4B | 0.97 | 2.54 | 3.461 (17) | 159 |
| C17A—H17A···O2Biv | 0.93 | 2.68 | 3.271 (17) | 122 |

Symmetry codes: (i) −x+2, y−1/2, −z+1; (ii) −x+1, y−1/2, −z+1; (iii) −x+1, y+1/2, −z+1; (iv) x, y, z+1.

Dichlorido{4-methyl-1-[2-(pyridin-2-yl)ethyl]-1,4-diazacycloheptane}cobalt(II) (ta-eab1607)

Crystal data

$[\text{CoCl}_2(C_{13}H_{21}N_3)]$

$M_r = 349.16$

Monoclinic, $P2_1/n$

$a = 10.3626$ (6) Å

$b = 11.5871$ (7) Å

$c = 13.7035$ (7) Å

$\beta = 108.308$ (6)$^\circ$

$V = 1562.12$ (16) Å$^3$

$Z = 4$

$\mu = 1.485$ Mg m$^{-3}$

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 1666 reflections

θ = 3.4–70.8°

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µ = 11.67 mm⁻¹
T = 273 K
0.42 × 0.08 × 0.06 mm

**Data collection**

Rigaku-OxfordDiffraction diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Cu) X-ray Source
Graphite monochromator
Detector resolution: 16.0416 pixels mm⁻¹
ω scans
Absorption correction: multi-scan

Tmin = 0.202, Tmax = 1.000
5711 measured reflections
2957 independent reflections
1805 reflections with I > 2σ(I)
Rmin = 0.054
θmax = 71.4°, θmin = 5.1°
h = −11→12
k = −9→14
l = −16→15

**Refinement**

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.056
wR(F²) = 0.139
S = 1.03

2957 reflections
173 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

w = 1/[σ²(Fo²) + (0.0523P)²]

where P = (Fo² + 2Fc²)/3

Δρmax = 0.54 e Å⁻³
Δρmin = −0.33 e Å⁻³

**Special details**

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

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)**

|     | x     | y     | z     | Uiso* / Ueq |
|-----|-------|-------|-------|-------------|
| Co1 | 0.47418 (8) | 0.55685 (8) | 0.71591 (6) | 0.0360 (2) |
| Cl1 | 0.42833 (17) | 0.63048 (14) | 0.85722 (11) | 0.0587 (4) |
| Cl2 | 0.69468 (13) | 0.55827 (16) | 0.71540 (11) | 0.0580 (4) |
| N1  | 0.4898 (6) | 0.3748 (4) | 0.7718 (4) | 0.0565 (13) |
| N2  | 0.2983 (5) | 0.4751 (4) | 0.6221 (4) | 0.0488 (12) |
| N3  | 0.4278 (4) | 0.7156 (4) | 0.6315 (3) | 0.0416 (10) |
| C1  | 0.5068 (6) | 0.8045 (5) | 0.6743 (4) | 0.0507 (15) |
| H1  | 0.5807 | 0.7900 | 0.7324 | 0.061* |
| C2  | 0.4869 (7) | 0.9154 (5) | 0.6387 (6) | 0.0643 (18) |
| H2  | 0.5442 | 0.9746 | 0.6726 | 0.077* |
| C3  | 0.3805 (7) | 0.9368 (6) | 0.5522 (6) | 0.0688 (18) |
| H3  | 0.3634 | 1.0112 | 0.5259 | 0.083* |
| C4  | 0.2996 (7) | 0.8472 (5) | 0.5049 (4) | 0.0566 (16) |
| H4  | 0.2275 | 0.8601 | 0.4453 | 0.068* |
| C5  | 0.3249 (5) | 0.7366 (5) | 0.5455 (4) | 0.0421 (12) |
| C6  | 0.2368 (6) | 0.6382 (6) | 0.4937 (4) | 0.0622 (18) |
| H6A | 0.1561 | 0.6695 | 0.4435 | 0.075* |
| H6B | 0.2854 | 0.5938 | 0.4564 | 0.075* |
### Atomic displacement parameters (Å²)

|       | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| Co1   | 0.0361 (4) | 0.0358 (4) | 0.0344 (4) | 0.0004 (4) | 0.0086 (3) | 0.0003 (4) |
| Cl1   | 0.0794 (10)| 0.0529 (9) | 0.0478 (8) | 0.0211 (8) | 0.0258 (7) | −0.0003 (7) |
| Cl2   | 0.0374 (6) | 0.0691 (10)| 0.0646 (9) | 0.0021 (7) | 0.0119 (6) | −0.0030 (8) |
| N1    | 0.083 (4)  | 0.040 (3)  | 0.052 (3)  | 0.011 (3)  | 0.029 (3)  | 0.010 (2)  |
| N2    | 0.045 (2)  | 0.034 (2)  | 0.064 (3)  | −0.006 (2) | 0.013 (2)  | −0.007 (2) |
| N3    | 0.040 (2)  | 0.040 (2)  | 0.039 (2)  | −0.003 (2) | 0.0042 (18)| 0.008 (2)  |
| C1    | 0.047 (3)  | 0.047 (3)  | 0.050 (3)  | −0.012 (3) | 0.004 (3)  | 0.005 (3)  |
| C2    | 0.065 (4)  | 0.041 (4)  | 0.090 (5)  | −0.011 (3) | 0.029 (4)  | 0.000 (3)  |
| C3    | 0.072 (4)  | 0.044 (4)  | 0.093 (5)  | 0.005 (4)  | 0.030 (4)  | 0.022 (4)  |
| C4    | 0.062 (4)  | 0.052 (4)  | 0.051 (3)  | 0.013 (3)  | 0.009 (3)  | 0.015 (3)  |
| C5    | 0.042 (3)  | 0.044 (3)  | 0.037 (3)  | 0.005 (3)  | 0.007 (2)  | 0.001 (2)  |
| C6    | 0.059 (4)  | 0.058 (4)  | 0.050 (3)  | 0.010 (3)  | −0.010 (3) | −0.004 (3) |
| C7    | 0.040 (3)  | 0.055 (4)  | 0.085 (5)  | −0.007 (3) | 0.005 (3)  | −0.009 (4) |
| C8    | 0.079 (5)  | 0.055 (4)  | 0.060 (4)  | −0.015 (4) | 0.013 (3)  | −0.015 (3) |
| C9    | 0.090 (5)  | 0.055 (4)  | 0.089 (5)  | −0.001 (4) | 0.041 (4)  | −0.022 (4) |
| C10   | 0.079 (5)  | 0.043 (4)  | 0.072 (4)  | 0.020 (3)  | 0.030 (4)  | 0.006 (3)  |
| C11   | 0.064 (4)  | 0.043 (4)  | 0.123 (6)  | −0.013 (3) | 0.055 (4)  | −0.001 (4) |
| C12   | 0.124 (6)  | 0.042 (4)  | 0.094 (5)  | −0.010 (4) | 0.071 (5)  | 0.019 (4)  |
| C13   | 0.125 (7)  | 0.068 (5)  | 0.063 (4)  | 0.032 (5)  | 0.024 (4)  | 0.033 (4)  |
### Geometric parameters (Å, °)

| Bond/Angle                        | Distance/Angle | Distance/Angle |
|-----------------------------------|----------------|----------------|
| Cl1—Co1—Cl2                       | 2.2981 (16)    | C6—H6A 0.9700 |
| Cl1—Co1—N1                        | 2.232 (5)      | C6—H6B 0.9700 |
| Cl1—Co1—N2                        | 2.097 (4)      | C7—H7A 0.9700 |
| Cl1—Co1—N3                        | 2.146 (4)      | C7—H7B 0.9700 |
| N1—Co1—Cl1                        | 1.473 (8)      | C8—H8A 0.9700 |
| N1—Co1—C10                        | 1.479 (9)      | C8—H8B 0.9700 |
| N1—Co1—C13                        | 1.482 (8)      | C8—C9 1.493 (9) |
| N2—Co1—Cl1                        | 1.494 (7)      | C9—H9A 0.9700 |
| N2—Co1—C12                        | 1.480 (8)      | C9—H9B 0.9700 |
| N2—Co1—C11                        | 1.465 (8)      | C9—C10 1.496 (9) |
| N3—Co1—Cl1                        | 1.331 (7)      | C10—H10A 0.9700 |
| N3—Co1—C5                         | 1.340 (6)      | C10—H10B 0.9700 |
| C1—H1                             | 0.9300         | C11—H11A 0.9700 |
| C1—C2                             | 1.367 (8)      | C11—H11B 0.9700 |
| C2—H2                             | 0.9300         | C11—C12 1.535 (10) |
| C2—C3                             | 1.365 (9)      | C12—H12A 0.9700 |
| C3—H3                             | 0.9300         | C12—H12B 0.9700 |
| C3—C4                             | 1.363 (9)      | C13—H13A 0.9600 |
| C4—H4                             | 0.9300         | C13—H13B 0.9600 |
| C4—C5                             | 1.389 (8)      | C13—H13C 0.9600 |
| C5—C6                             | 1.493 (8)      |                 |

| Bond/Angle                        | Distance/Angle | Distance/Angle |
|-----------------------------------|----------------|----------------|
| Cl2—Co1—Cl1                       | 118.10 (7)     | C7—C6—H6A 108.3 |
| N1—Co1—Cl1                        | 94.21 (14)     | C7—C6—H6B 108.3 |
| N1—Co1—C12                        | 92.47 (15)     | N2—C7—H7A 108.3 |
| N2—Co1—Cl1                        | 108.33 (15)    | N2—C7—H7B 108.3 |
| N2—Co1—Cl12                       | 132.67 (15)    | C6—C7—N2 115.8 (5) |
| N2—Co1—N1                         | 74.86 (19)     | C6—C7—H7A 108.3 |
| N2—Co1—N3                         | 93.00 (17)     | C6—C7—H7B 108.3 |
| N3—Co1—Cl1                        | 93.75 (13)     | H7A—C7—H7B 107.4 |
| N3—Co1—Cl2                        | 92.70 (13)     | N2—C8—H8A 108.4 |
| N3—Co1—N1                         | 167.11 (18)    | N2—C8—H8B 108.4 |
| C10—N1—Co1                        | 110.9 (4)      | N2—C8—C9 115.7 (6) |
| C10—N1—C12                        | 110.3 (5)      | H8A—C8—H8B 107.4 |
| C10—N1—C13                        | 109.6 (5)      | C9—C8—H8A 108.4 |
| C12—N1—Co1                        | 102.4 (4)      | C9—C8—H8B 108.4 |
| C12—N1—C13                        | 110.8 (6)      | C8—C9—H9A 108.2 |
| C13—N1—Co1                        | 112.6 (4)      | C8—C9—H9B 108.2 |
| C7—N2—Co1                         | 112.9 (3)      | C8—C9—C10 116.2 (6) |
| C8—N2—Co1                         | 108.2 (4)      | H9A—C9—H9B 107.4 |
| C8—N2—C7                          | 110.2 (5)      | C10—C9—H9A 108.2 |
| C11—N2—Co1                        | 105.9 (4)      | C10—C9—H9B 108.2 |
| C11—N2—C7                         | 107.8 (5)      | N1—C10—C9 114.0 (5) |
| C11—N2—C8                         | 111.8 (5)      | N1—C10—H10A 108.8 |
| C1—N3—Co1                         | 115.0 (3)      | N1—C10—H10B 108.8 |
| Bond                  | Bond Angle (°) | Bond Angle (°) | Bond Angle (°) |
|----------------------|---------------|---------------|---------------|
| C1—N3—C5            | 117.2 (5)     | C9—C10—H10A  | 108.8         |
| C5—N3—Co1           | 127.7 (4)     | C9—C10—H10B  | 108.8         |
| N3—C1—H1            | 117.7         | H10A—C10—H10B| 107.6         |
| N3—C1—C2            | 124.5 (5)     | N2—C11—H11A  | 109.2         |
| C2—C1—H1            | 117.7         | N2—C11—H11B  | 109.2         |
| C1—C2—H2            | 121.0         | N2—C11—C12   | 111.9 (5)     |
| C3—C2—C1            | 118.1 (6)     | H11A—C11—H11B| 107.9         |
| C3—C2—H2            | 121.0         | C12—C11—H11A | 109.2         |
| C2—C3—H3            | 120.6         | C12—C11—H11B | 109.2         |
| C4—C3—C2            | 118.9 (6)     | N1—C12—C11   | 111.9 (5)     |
| C4—C3—H3            | 120.6         | N1—C12—H12A  | 109.2         |
| C3—C4—H4            | 119.9         | N1—C12—H12B  | 109.2         |
| C3—C4—C5            | 120.1 (5)     | C11—C12—H12A | 109.2         |
| C5—C4—H4            | 119.9         | C11—C12—H12B | 109.2         |
| N3—C5—C4            | 121.2 (5)     | H12A—C12—H12B| 107.9         |
| N3—C5—C6            | 118.6 (5)     | N1—C13—H13A  | 109.5         |
| C4—C5—C6            | 120.2 (5)     | N1—C13—H13B  | 109.5         |
| C5—C6—H6A           | 108.3         | N1—C13—H13C  | 109.5         |
| C5—C6—H6B           | 108.3         | H13A—C13—H13B| 109.5         |
| H6A—C6—H6B          | 107.4         | H13A—C13—H13C| 109.5         |
| C7—C6—C5            | 115.9 (5)     | H13B—C13—H13C| 109.5         |