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## Structure Reports

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# Dichloridobis(7-amino-2,4-dimethyl-1,8-naphthyridine- $\kappa^2N,N'$ )cobalt(II) methanol disolvate

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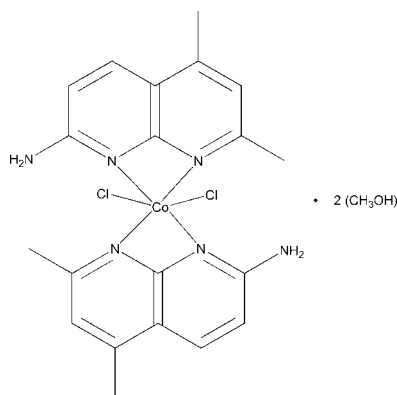
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å;  $R$  factor = 0.047;  $wR$  factor = 0.125; data-to-parameter ratio = 15.1.

The title compound,  $[\text{CoCl}_2(\text{C}_{10}\text{H}_{11}\text{N}_3)_2] \cdot 2\text{CH}_3\text{OH}$ , crystallizes with an elongated Co coordination polyhedron in a very distorted octahedral geometry. Both naphthyridine ligands coordinate to the Co atom *via* two N atoms in a bidentate chelating mode. The remaining coordination sites are occupied by two Cl atoms. Two uncoordinated solvent methanol molecules are hydrogen bonded to the Cl atoms. Additional  $\text{N}-\text{H} \cdots \text{O}$ ,  $\text{C}-\text{H} \cdots \text{Cl}$  and  $\text{N}-\text{H} \cdots \text{Cl}$  hydrogen bonds, and  $\pi-\pi$  stacking interactions [centroid-centroid distance 3.664 (4) Å], give rise to a three-dimensional network structure.

## Related literature

For related literature, see: Bayer (1979); Che *et al.* (2001); Gavrilova & Bosnich (2004); Harvey *et al.* (2004); Jin *et al.* (2007); Kukrek *et al.* (2006); Mintert & Sheldrick (1995*a,b*); Oskui *et al.* (1999); Oskui & Sheldrick (1999).



## Experimental

### Crystal data

$[\text{CoCl}_2(\text{C}_{10}\text{H}_{11}\text{N}_3)_2] \cdot 2\text{CH}_4\text{O}$   
 $M_r = 540.35$   
 Triclinic,  $P\bar{1}$   
 $a = 9.694$  (3) Å  
 $b = 10.651$  (3) Å  
 $c = 14.154$  (4) Å  
 $\alpha = 79.523$  (4)°  
 $\beta = 78.548$  (4)°  
 $\gamma = 65.697$  (4)°  
 $V = 1297.2$  (6) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.90$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
 $0.27 \times 0.21 \times 0.18$  mm

### Data collection

Bruker SMART APEX CCD diffractometer  
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)  
 $T_{\min} = 0.794$ ,  $T_{\max} = 0.855$   
 6885 measured reflections  
 4521 independent reflections  
 2999 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.021$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.125$   
 $S = 1.04$   
 4521 reflections  
 300 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.45$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.27$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$   | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|--|-------|--------------|--------------|----------------|
| $\text{O2}-\text{H2} \cdots \text{Cl1}^{\text{i}}$     | 0.82  | 2.35         | 3.162 (4)    | 172            |
| $\text{O1}-\text{H1} \cdots \text{Cl1}^{\text{ii}}$    | 0.82  | 2.44         | 3.194 (4)    | 154            |
| $\text{N6}-\text{H6B} \cdots \text{O2}^{\text{iii}}$   | 0.86  | 2.06         | 2.918 (4)    | 175            |
| $\text{N6}-\text{H6A} \cdots \text{Cl2}$               | 0.86  | 2.45         | 3.269 (4)    | 159            |
| $\text{N3}-\text{H3B} \cdots \text{O1}^{\text{iv}}$    | 0.86  | 2.09         | 2.947 (4)    | 175            |
| $\text{N3}-\text{H3A} \cdots \text{Cl1}$               | 0.86  | 2.51         | 3.309 (3)    | 156            |
| $\text{C22}-\text{H22B} \cdots \text{Cl1}^{\text{i}}$  | 0.96  | 2.91         | 3.789 (7)    | 154            |
| $\text{C22}-\text{H22B} \cdots \text{Cl1}^{\text{ii}}$ | 0.96  | 2.71         | 3.575 (6)    | 150            |
| $\text{C4}-\text{H4} \cdots \text{Cl2}^{\text{v}}$     | 0.93  | 2.85         | 3.705 (4)    | 153            |
| $\text{C7}-\text{H7} \cdots \text{Cl1}^{\text{vi}}$    | 0.93  | 2.87         | 3.757 (4)    | 160            |
| $\text{C13}-\text{H13} \cdots \text{Cl1}^{\text{ii}}$  | 0.93  | 2.88         | 3.733 (4)    | 152            |

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + 2, -y + 1, -z + 1$ ; (iii)  $x + 1, y, z$ ; (iv)  $x, y, z - 1$ ; (v)  $-x + 2, -y + 2, -z$ ; (vi)  $x, y + 1, z$ .

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

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2083).

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**supplementary materials**

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## Dichloridobis(7-amino-2,4-dimethyl-1,8-naphthyridine- $\kappa^2N,N'$ )cobalt(II) methanol disolvate

S. Jin and Y. Sun

### Comment

Molecular structures and chemical properties of transition metal complexes of 1,8-naphthyridine (napy) and its derivatives have received much attention (Kukrek *et al.*, 2006; Che *et al.*, 2001) as the ligands can link to metals *via* several coordination modes such as monodentate, chelating bidentate, and in a dinuclear bridging fashion (Gavrilova & Bosnich, 2004). 5,7-Dimethyl-1,8-naphthyridin-2-amine is a potentially tridentate ligand and is capable of linking two to four metal atoms together to form metal aggregates (Oskui *et al.*, 1999; Mintert & Sheldrick, 1995*a*; Oskui & Sheldrick, 1999; Mintert & Sheldrick, 1995*b*). The coordination chemistry of 5,7-dimethyl-1,8-naphthyridine-2-amine (*L*) has not been well studied before although a Co(II) complex (Co(*L*)<sub>2</sub>Cl<sub>2</sub>) was once described in a US patent (Bayer, 1979). As an extension of our study on naphthyridine coordination chemistry (Jin *et al.*, 2007), herein we report the synthesis and structure of the title complex as its bis methanol solvate, (Co(*L*)<sub>2</sub>(Cl)<sub>2</sub>).2(CH<sub>3</sub>OH).

The title compound was obtained as violet crystals by reacting cobalt chloride hexahydrate and *L* in methanol. The compound is air stable and light insensitive, and does not dissolve in water and most organic solvents. X-ray structural analysis shows that the complex is mononuclear, its molecular structure is shown in Fig. 1. The Co atom is positioned on an inversion center and is bonded to two *L* ligands and two chloride ions. Both of the two ligands coordinate to the metal center *via* two nitrogen atoms in a bidentate chelating fashion. The two chloride anions coordinated to the Co ion complete a very distorted octahedral geometry. With a N—Co—N bite angle of only 58.86 (11), and 60.39 (11) ° the structure can also be seen as a pseudotetrahedral complex with each of the naphthyridine ligands *L* counted as a singly bonded entity. The N—Co—N angle is of necessity quite small, thereby allowing for the Cl(2)—Co(1)—Cl(1) angle to expand to 96.99 (5) °. Perhaps as a result of the smaller spatial requirements of the chelating naphthyridine, the chloride ions are in *cis*-arrangement which is different from reported results (Harvey *et al.*, 2004).

The two naphthyridine rings are basically planar with an r.m.s. deviation of only 0.0098, and 0.0183 ° respectively, and both ligands are almost perpendicular to each other with an angle between the root mean square planes of the two ligands of 85.4 °.

The free methanol molecules are connected to the (Co(*L*)<sub>2</sub>(Cl)<sub>2</sub>) moieties *via* O—H...Cl and N—H...O hydrogen bonds, and the (Co(*L*)<sub>2</sub>(Cl)<sub>2</sub>) moieties themselves are connected with each other by N—H...Cl hydrogen bonds (see Table 1). The closest C—C distance between adjacent parallel naphthyridyl rings is 3.378 (4) Å, the corresponding centroid to centroid distance for the naphthyridyl rings is 3.664 Å, which implies the presence of  $\pi$ - $\pi$  stacking interactions between the naphthyridyl rings. Via all these interactions the compound forms a three-dimensional network structure as shown in Fig. 2.

### Experimental

All reagents and solvents were used as obtained without further purification. The CHN elemental analyses were performed on a Perkin-Elmer model 2400 elemental analyzer.

## supplementary materials

To a methanol solution of cobalt chloride hexahydrate (24 mg, 0.1 mmol), was added *L* (17.4 mg, 0.1 mmol) in 10 ml of methanol. The solution was stirred for three minutes, then the solution was filtered. The solution was left standing at room temperature for several days, and violet crystals were isolated after slow evaporation of the methanol solution in air. Yield: 38 mg, 70.3%. Anal. Calcd for  $C_{22}H_{30}Cl_2CoN_6O_2$ : C, 48.86; H, 5.55; N, 15.55; Found: C, 48.81; H, 5.52; N, 15.49.

### Refinement

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with aromatic C—H = 0.93 Å, and methyl C—H = 0.96 Å. Hydrogen atoms bound to methanol molecules and amine groups were fixed, and restrained to O—H = 0.85 (1) Å, and N—H = 0.86 (1) Å.

### Figures

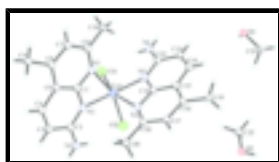


Fig. 1. The structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

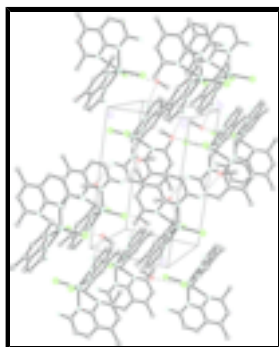


Fig. 2. The three dimensional network structure with  $\pi$ - $\pi$  interactions and hydrogen bonds. The dashed lines present hydrogen bonds, the hydrogen atoms were omitted for clarity.

### Dichloridobis(7-amino-2,4-dimethyl-1,8-naphthyridine- $\kappa^2N,N'$ )cobalt(II) methanol disolvate

#### Crystal data

$[CoCl_2(C_{10}H_{11}N_3)_2] \cdot 2CH_4O$

$M_r = 540.35$

Triclinic,  $P\bar{1}$

$a = 9.694$  (3) Å

$b = 10.651$  (3) Å

$c = 14.154$  (4) Å

$\alpha = 79.523$  (4)°

$\beta = 78.548$  (4)°

$\gamma = 65.697$  (4)°

$V = 1297.2$  (6) Å<sup>3</sup>

$Z = 2$

$F_{000} = 562$

$D_x = 1.383$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 2019 reflections

$\theta = 2.4$ – $24.7^\circ$

$\mu = 0.90$  mm<sup>-1</sup>

$T = 298$  (2) K

Block, violet

$0.27 \times 0.21 \times 0.18$  mm

*Data collection*

|   |  |
|---|--|
| Bruker SMART APEX CCD diffractometer                        | 4521 independent reflections           |
| Radiation source: fine-focus sealed tube                    | 2999 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite                                     | $R_{\text{int}} = 0.021$               |
| $T = 298(2)$ K  | $\theta_{\text{max}} = 25.0^\circ$     |
| phi and $\omega$ scans                                      | $\theta_{\text{min}} = 2.1^\circ$      |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h = -9 \rightarrow 11$                |
| $T_{\text{min}} = 0.794$ , $T_{\text{max}} = 0.855$         | $k = -12 \rightarrow 12$               |
| 6885 measured reflections                                   | $l = -15 \rightarrow 16$               |

*Refinement*

|  |  |
|--|--|
| Refinement on $F^2$  | Secondary atom site location: difference Fourier map         |
| Least-squares matrix: full                                     | Hydrogen site location: inferred from neighbouring sites     |
| $R[F^2 > 2\sigma(F^2)] = 0.047$                                | H-atom parameters constrained                                |
| $wR(F^2) = 0.125$  | $w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 0.2762P]$            |
| $S = 1.04$   | where $P = (F_o^2 + 2F_c^2)/3$                               |
| 4521 reflections   | $(\Delta/\sigma)_{\text{max}} < 0.001$                       |
| 300 parameters   | $\Delta\rho_{\text{max}} = 0.45 \text{ e } \text{\AA}^{-3}$  |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{\AA}^{-3}$ |
|  | Extinction correction: none                                  |

*Special details*

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

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

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

|     | $x$          | $y$          | $z$         | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|-------------|----------------------------------|
| Co1 | 0.96112 (6)  | 0.72223 (5)  | 0.23994 (3) | 0.04516 (18)                     |
| Cl1 | 0.94391 (12) | 0.51632 (9)  | 0.20816 (7) | 0.0583 (3)                       |
| Cl2 | 1.22929 (11) | 0.63991 (12) | 0.21805 (8) | 0.0690 (3)                       |
| N1  | 0.9345 (3)   | 0.9511 (3)   | 0.2182 (2)  | 0.0448 (7)                       |
| N2  | 0.8771 (3)   | 0.8510 (3)   | 0.1144 (2)  | 0.0426 (7)                       |

## supplementary materials

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|      |            |            |             |             |
|------|------------|------------|-------------|-------------|
| N3   | 0.8215 (4) | 0.7345 (3) | 0.0155 (2)  | 0.0671 (10) |
| H3A  | 0.8541     | 0.6596     | 0.0544      | 0.080*      |
| H3B  | 0.7872     | 0.7340     | -0.0359     | 0.080*      |
| N4   | 0.7015 (3) | 0.7946 (3) | 0.3218 (2)  | 0.0460 (7)  |
| N5   | 0.9139 (3) | 0.7129 (3) | 0.3919 (2)  | 0.0437 (7)  |
| N6   | 1.1406 (4) | 0.6339 (4) | 0.4536 (2)  | 0.0703 (10) |
| H6A  | 1.1885     | 0.6285     | 0.3955      | 0.084*      |
| H6B  | 1.1906     | 0.6110     | 0.5021      | 0.084*      |
| O1   | 0.7241 (4) | 0.7211 (4) | 0.8345 (2)  | 0.0855 (10) |
| H1   | 0.7914     | 0.6478     | 0.8186      | 0.089 (18)* |
| O2   | 0.2964 (4) | 0.5474 (4) | 0.6250 (2)  | 0.0891 (11) |
| H2   | 0.2413     | 0.5261     | 0.6713      | 0.12 (2)*   |
| C1   | 0.8775 (4) | 0.9703 (4) | 0.1350 (3)  | 0.0425 (9)  |
| C2   | 0.8242 (4) | 0.8508 (4) | 0.0350 (3)  | 0.0481 (9)  |
| C3   | 0.7689 (4) | 0.9765 (4) | -0.0293 (3) | 0.0545 (10) |
| H3   | 0.7321     | 0.9762     | -0.0851     | 0.065*      |
| C4   | 0.7702 (4) | 1.0942 (4) | -0.0091 (3) | 0.0544 (10) |
| H4   | 0.7348     | 1.1748     | -0.0513     | 0.065*      |
| C5   | 0.8252 (4) | 1.0972 (4) | 0.0763 (3)  | 0.0463 (9)  |
| C6   | 0.8331 (4) | 1.2114 (4) | 0.1076 (3)  | 0.0523 (10) |
| C7   | 0.8943 (5) | 1.1897 (4) | 0.1915 (3)  | 0.0584 (11) |
| H7   | 0.9018     | 1.2636     | 0.2132      | 0.070*      |
| C8   | 0.9459 (4) | 1.0583 (4) | 0.2454 (3)  | 0.0492 (9)  |
| C9   | 0.7767 (5) | 1.3537 (4) | 0.0519 (3)  | 0.0749 (13) |
| H9A  | 0.7672     | 1.4213     | 0.0919      | 0.112*      |
| H9B  | 0.6789     | 1.3739     | 0.0337      | 0.112*      |
| H9C  | 0.8481     | 1.3564     | -0.0053     | 0.112*      |
| C10  | 1.0178 (5) | 1.0346 (5) | 0.3348 (3)  | 0.0726 (13) |
| H10A | 1.0493     | 0.9387     | 0.3603      | 0.109*      |
| H10B | 0.9451     | 1.0909     | 0.3824      | 0.109*      |
| H10C | 1.1052     | 1.0592     | 0.3189      | 0.109*      |
| C11  | 0.7591 (4) | 0.7613 (3) | 0.4062 (3)  | 0.0423 (9)  |
| C12  | 0.9893 (5) | 0.6778 (4) | 0.4685 (3)  | 0.0499 (9)  |
| C13  | 0.9068 (5) | 0.6885 (4) | 0.5642 (3)  | 0.0590 (11) |
| H13  | 0.9596     | 0.6616     | 0.6174      | 0.071*      |
| C14  | 0.7540 (5) | 0.7371 (4) | 0.5777 (3)  | 0.0593 (11) |
| H14  | 0.7017     | 0.7442     | 0.6404      | 0.071*      |
| C15  | 0.6711 (4) | 0.7778 (4) | 0.4986 (3)  | 0.0486 (9)  |
| C16  | 0.5117 (5) | 0.8313 (4) | 0.5007 (3)  | 0.0578 (11) |
| C17  | 0.4541 (5) | 0.8647 (4) | 0.4146 (3)  | 0.0638 (12) |
| H17  | 0.3488     | 0.9014     | 0.4149      | 0.077*      |
| C18  | 0.5506 (5) | 0.8449 (4) | 0.3259 (3)  | 0.0548 (10) |
| C19  | 0.4055 (5) | 0.8563 (5) | 0.5956 (3)  | 0.0776 (14) |
| H19A | 0.3138     | 0.9365     | 0.5854      | 0.116*      |
| H19B | 0.4552     | 0.8713     | 0.6423      | 0.116*      |
| H19C | 0.3802     | 0.7769     | 0.6192      | 0.116*      |
| C20  | 0.4863 (5) | 0.8810 (5) | 0.2316 (3)  | 0.0796 (14) |
| H20A | 0.4401     | 0.9799     | 0.2175      | 0.119*      |
| H20B | 0.4107     | 0.8427     | 0.2367      | 0.119*      |

|      |            |            |            |             |
|------|------------|------------|------------|-------------|
| H20C | 0.5670     | 0.8432     | 0.1804     | 0.119*      |
| C21  | 0.5865 (6) | 0.7043 (6) | 0.8635 (4) | 0.1029 (18) |
| H21A | 0.5910     | 0.6461     | 0.9241     | 0.154*      |
| H21B | 0.5687     | 0.6620     | 0.8152     | 0.154*      |
| H21C | 0.5047     | 0.7932     | 0.8712     | 0.154*      |
| C22  | 0.4434 (6) | 0.4976 (5) | 0.6469 (5) | 0.107 (2)   |
| H22A | 0.5042     | 0.5342     | 0.5971     | 0.161*      |
| H22B | 0.4866     | 0.3982     | 0.6509     | 0.161*      |
| H22C | 0.4416     | 0.5256     | 0.7080     | 0.161*      |

*Atomic displacement parameters ( $\text{\AA}^2$ )*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Co1 | 0.0519 (3)  | 0.0477 (3)  | 0.0353 (3)  | -0.0186 (2)  | -0.0107 (2)  | -0.0001 (2)  |
| C11 | 0.0749 (7)  | 0.0444 (5)  | 0.0566 (6)  | -0.0238 (5)  | -0.0118 (5)  | -0.0039 (4)  |
| C12 | 0.0498 (6)  | 0.0887 (8)  | 0.0553 (6)  | -0.0175 (6)  | -0.0085 (5)  | 0.0021 (6)   |
| N1  | 0.0479 (18) | 0.0481 (18) | 0.0417 (18) | -0.0220 (15) | -0.0064 (14) | -0.0046 (14) |
| N2  | 0.0510 (19) | 0.0451 (17) | 0.0352 (17) | -0.0225 (15) | -0.0070 (14) | -0.0027 (13) |
| N3  | 0.100 (3)   | 0.064 (2)   | 0.056 (2)   | -0.043 (2)   | -0.032 (2)   | 0.0022 (17)  |
| N4  | 0.0452 (19) | 0.0450 (17) | 0.0464 (19) | -0.0159 (15) | -0.0101 (15) | -0.0016 (14) |
| N5  | 0.0458 (19) | 0.0458 (17) | 0.0383 (17) | -0.0171 (15) | -0.0091 (14) | -0.0001 (13) |
| N6  | 0.053 (2)   | 0.103 (3)   | 0.051 (2)   | -0.023 (2)   | -0.0185 (17) | -0.004 (2)   |
| O1  | 0.066 (2)   | 0.104 (3)   | 0.074 (2)   | -0.010 (2)   | -0.0108 (17) | -0.037 (2)   |
| O2  | 0.066 (2)   | 0.135 (3)   | 0.067 (2)   | -0.046 (2)   | -0.0200 (18) | 0.017 (2)    |
| C1  | 0.042 (2)   | 0.046 (2)   | 0.040 (2)   | -0.0202 (17) | 0.0012 (16)  | -0.0053 (17) |
| C2  | 0.053 (2)   | 0.055 (2)   | 0.041 (2)   | -0.027 (2)   | -0.0087 (18) | -0.0019 (18) |
| C3  | 0.057 (3)   | 0.067 (3)   | 0.039 (2)   | -0.023 (2)   | -0.0149 (18) | -0.0002 (19) |
| C4  | 0.057 (3)   | 0.048 (2)   | 0.047 (2)   | -0.015 (2)   | -0.0100 (19) | 0.0091 (19)  |
| C5  | 0.046 (2)   | 0.046 (2)   | 0.043 (2)   | -0.0183 (18) | -0.0006 (17) | -0.0012 (17) |
| C6  | 0.057 (2)   | 0.043 (2)   | 0.054 (3)   | -0.0209 (19) | 0.002 (2)    | -0.0043 (18) |
| C7  | 0.067 (3)   | 0.052 (2)   | 0.062 (3)   | -0.029 (2)   | 0.003 (2)    | -0.019 (2)   |
| C8  | 0.046 (2)   | 0.057 (2)   | 0.049 (2)   | -0.0237 (19) | -0.0045 (18) | -0.0111 (19) |
| C9  | 0.092 (4)   | 0.047 (2)   | 0.082 (3)   | -0.028 (2)   | -0.012 (3)   | 0.003 (2)    |
| C10 | 0.078 (3)   | 0.088 (3)   | 0.067 (3)   | -0.040 (3)   | -0.017 (2)   | -0.019 (3)   |
| C11 | 0.050 (2)   | 0.0359 (19) | 0.042 (2)   | -0.0175 (17) | -0.0092 (17) | -0.0023 (16) |
| C12 | 0.059 (3)   | 0.049 (2)   | 0.044 (2)   | -0.022 (2)   | -0.0132 (19) | -0.0022 (18) |
| C13 | 0.077 (3)   | 0.062 (3)   | 0.038 (2)   | -0.025 (2)   | -0.020 (2)   | 0.0027 (19)  |
| C14 | 0.076 (3)   | 0.059 (3)   | 0.041 (2)   | -0.027 (2)   | -0.002 (2)   | -0.0054 (19) |
| C15 | 0.059 (3)   | 0.043 (2)   | 0.043 (2)   | -0.0211 (19) | -0.0025 (19) | -0.0063 (17) |
| C16 | 0.061 (3)   | 0.052 (2)   | 0.057 (3)   | -0.024 (2)   | 0.006 (2)    | -0.011 (2)   |
| C17 | 0.043 (2)   | 0.065 (3)   | 0.077 (3)   | -0.016 (2)   | -0.003 (2)   | -0.012 (2)   |
| C18 | 0.054 (3)   | 0.053 (2)   | 0.058 (3)   | -0.020 (2)   | -0.016 (2)   | -0.0018 (19) |
| C19 | 0.070 (3)   | 0.082 (3)   | 0.070 (3)   | -0.029 (3)   | 0.019 (2)    | -0.015 (3)   |
| C20 | 0.066 (3)   | 0.093 (4)   | 0.076 (3)   | -0.025 (3)   | -0.033 (3)   | 0.010 (3)    |
| C21 | 0.081 (4)   | 0.111 (5)   | 0.113 (5)   | -0.030 (3)   | -0.013 (3)   | -0.024 (4)   |
| C22 | 0.083 (4)   | 0.075 (3)   | 0.168 (6)   | -0.034 (3)   | -0.036 (4)   | 0.009 (4)    |

## supplementary materials

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### Geometric parameters (Å, °)

|             |             |               |           |
|-------------|-------------|---------------|-----------|
| Co1—N5      | 2.100 (3)   | C7—C8         | 1.406 (5) |
| Co1—N2      | 2.115 (3)   | C7—H7         | 0.9300    |
| Co1—N1      | 2.312 (3)   | C8—C10        | 1.497 (5) |
| Co1—Cl2     | 2.3508 (13) | C9—H9A        | 0.9600    |
| Co1—Cl1     | 2.3936 (12) | C9—H9B        | 0.9600    |
| Co1—N4      | 2.417 (3)   | C9—H9C        | 0.9600    |
| N1—C8       | 1.321 (5)   | C10—H10A      | 0.9600    |
| N1—C1       | 1.345 (4)   | C10—H10B      | 0.9600    |
| N2—C2       | 1.325 (4)   | C10—H10C      | 0.9600    |
| N2—C1       | 1.356 (4)   | C11—C15       | 1.409 (5) |
| N3—C2       | 1.329 (5)   | C12—C13       | 1.428 (5) |
| N3—H3A      | 0.8600      | C13—C14       | 1.339 (6) |
| N3—H3B      | 0.8600      | C13—H13       | 0.9300    |
| N4—C18      | 1.328 (5)   | C14—C15       | 1.408 (5) |
| N4—C11      | 1.346 (4)   | C14—H14       | 0.9300    |
| N5—C12      | 1.339 (5)   | C15—C16       | 1.406 (5) |
| N5—C11      | 1.356 (4)   | C16—C17       | 1.368 (6) |
| N6—C12      | 1.327 (5)   | C16—C19       | 1.513 (5) |
| N6—H6A      | 0.8600      | C17—C18       | 1.401 (5) |
| N6—H6B      | 0.8600      | C17—H17       | 0.9300    |
| O1—C21      | 1.391 (6)   | C18—C20       | 1.505 (6) |
| O1—H1       | 0.8200      | C19—H19A      | 0.9600    |
| O2—C22      | 1.379 (5)   | C19—H19B      | 0.9600    |
| O2—H2       | 0.8200      | C19—H19C      | 0.9600    |
| C1—C5       | 1.403 (5)   | C20—H20A      | 0.9600    |
| C2—C3       | 1.439 (5)   | C20—H20B      | 0.9600    |
| C3—C4       | 1.341 (5)   | C20—H20C      | 0.9600    |
| C3—H3       | 0.9300      | C21—H21A      | 0.9600    |
| C4—C5       | 1.425 (5)   | C21—H21B      | 0.9600    |
| C4—H4       | 0.9300      | C21—H21C      | 0.9600    |
| C5—C6       | 1.403 (5)   | C22—H22A      | 0.9600    |
| C6—C7       | 1.372 (5)   | C22—H22B      | 0.9600    |
| C6—C9       | 1.507 (5)   | C22—H22C      | 0.9600    |
| N5—Co1—N2   | 140.51 (11) | C6—C9—H9B     | 109.5     |
| N5—Co1—N1   | 94.22 (11)  | H9A—C9—H9B    | 109.5     |
| N2—Co1—N1   | 60.40 (11)  | C6—C9—H9C     | 109.5     |
| N5—Co1—Cl2  | 100.61 (9)  | H9A—C9—H9C    | 109.5     |
| N2—Co1—Cl2  | 109.61 (8)  | H9B—C9—H9C    | 109.5     |
| N1—Co1—Cl2  | 92.55 (8)   | C8—C10—H10A   | 109.5     |
| N5—Co1—Cl1  | 103.03 (8)  | C8—C10—H10B   | 109.5     |
| N2—Co1—Cl1  | 97.99 (8)   | H10A—C10—H10B | 109.5     |
| N1—Co1—Cl1  | 158.32 (8)  | C8—C10—H10C   | 109.5     |
| Cl2—Co1—Cl1 | 96.99 (4)   | H10A—C10—H10C | 109.5     |
| N5—Co1—N4   | 58.85 (10)  | H10B—C10—H10C | 109.5     |
| N2—Co1—N4   | 88.79 (10)  | N4—C11—N5     | 111.7 (3) |
| N1—Co1—N4   | 88.66 (10)  | N4—C11—C15    | 124.9 (3) |

|              |            |               |           |
|--------------|------------|---------------|-----------|
| C12—Co1—N4   | 159.45 (8) | N5—C11—C15    | 123.4 (3) |
| C11—Co1—N4   | 89.14 (8)  | N6—C12—N5     | 118.9 (3) |
| C8—N1—C1     | 117.8 (3)  | N6—C12—C13    | 121.1 (4) |
| C8—N1—Co1    | 152.4 (3)  | N5—C12—C13    | 119.9 (4) |
| C1—N1—Co1    | 89.8 (2)   | C14—C13—C12   | 120.4 (4) |
| C2—N2—C1     | 119.8 (3)  | C14—C13—H13   | 119.8     |
| C2—N2—Co1    | 141.9 (3)  | C12—C13—H13   | 119.8     |
| C1—N2—Co1    | 98.2 (2)   | C13—C14—C15   | 121.1 (4) |
| C2—N3—H3A    | 120.0      | C13—C14—H14   | 119.5     |
| C2—N3—H3B    | 120.0      | C15—C14—H14   | 119.5     |
| H3A—N3—H3B   | 120.0      | C16—C15—C14   | 127.9 (4) |
| C18—N4—C11   | 117.6 (3)  | C16—C15—C11   | 116.2 (4) |
| C18—N4—Co1   | 154.6 (3)  | C14—C15—C11   | 115.9 (4) |
| C11—N4—Co1   | 87.8 (2)   | C17—C16—C15   | 118.5 (4) |
| C12—N5—C11   | 119.3 (3)  | C17—C16—C19   | 120.5 (4) |
| C12—N5—Co1   | 139.0 (3)  | C15—C16—C19   | 120.9 (4) |
| C11—N5—Co1   | 101.6 (2)  | C16—C17—C18   | 121.3 (4) |
| C12—N6—H6A   | 120.0      | C16—C17—H17   | 119.3     |
| C12—N6—H6B   | 120.0      | C18—C17—H17   | 119.3     |
| H6A—N6—H6B   | 120.0      | N4—C18—C17    | 121.5 (4) |
| C21—O1—H1    | 109.5      | N4—C18—C20    | 117.6 (4) |
| C22—O2—H2    | 109.5      | C17—C18—C20   | 120.9 (4) |
| N1—C1—N2     | 111.5 (3)  | C16—C19—H19A  | 109.5     |
| N1—C1—C5     | 124.7 (3)  | C16—C19—H19B  | 109.5     |
| N2—C1—C5     | 123.8 (3)  | H19A—C19—H19B | 109.5     |
| N2—C2—N3     | 119.8 (3)  | C16—C19—H19C  | 109.5     |
| N2—C2—C3     | 119.9 (4)  | H19A—C19—H19C | 109.5     |
| N3—C2—C3     | 120.3 (3)  | H19B—C19—H19C | 109.5     |
| C4—C3—C2     | 120.2 (4)  | C18—C20—H20A  | 109.5     |
| C4—C3—H3     | 119.9      | C18—C20—H20B  | 109.5     |
| C2—C3—H3     | 119.9      | H20A—C20—H20B | 109.5     |
| C3—C4—C5     | 120.8 (3)  | C18—C20—H20C  | 109.5     |
| C3—C4—H4     | 119.6      | H20A—C20—H20C | 109.5     |
| C5—C4—H4     | 119.6      | H20B—C20—H20C | 109.5     |
| C1—C5—C6     | 117.0 (3)  | O1—C21—H21A   | 109.5     |
| C1—C5—C4     | 115.5 (3)  | O1—C21—H21B   | 109.5     |
| C6—C5—C4     | 127.5 (3)  | H21A—C21—H21B | 109.5     |
| C7—C6—C5     | 117.7 (3)  | O1—C21—H21C   | 109.5     |
| C7—C6—C9     | 120.5 (4)  | H21A—C21—H21C | 109.5     |
| C5—C6—C9     | 121.8 (4)  | H21B—C21—H21C | 109.5     |
| C6—C7—C8     | 121.6 (4)  | O2—C22—H22A   | 109.5     |
| C6—C7—H7     | 119.2      | O2—C22—H22B   | 109.5     |
| C8—C7—H7     | 119.2      | H22A—C22—H22B | 109.5     |
| N1—C8—C7     | 121.2 (4)  | O2—C22—H22C   | 109.5     |
| N1—C8—C10    | 117.7 (4)  | H22A—C22—H22C | 109.5     |
| C7—C8—C10    | 121.1 (4)  | H22B—C22—H22C | 109.5     |
| C6—C9—H9A    | 109.5      |               |           |
| N5—Co1—N1—C8 | 32.8 (5)   | N3—C2—C3—C4   | 179.3 (4) |
| N2—Co1—N1—C8 | -179.2 (6) | C2—C3—C4—C5   | -0.4 (6)  |

## supplementary materials

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|                |             |                 |            |
|----------------|-------------|-----------------|------------|
| Cl2—Co1—N1—C8  | -68.0 (5)   | N1—C1—C5—C6     | -0.3 (5)   |
| Cl1—Co1—N1—C8  | 175.7 (4)   | N2—C1—C5—C6     | -180.0 (3) |
| N4—Co1—N1—C8   | 91.4 (5)    | N1—C1—C5—C4     | 179.6 (3)  |
| N5—Co1—N1—C1   | -146.2 (2)  | N2—C1—C5—C4     | -0.1 (5)   |
| N2—Co1—N1—C1   | 1.79 (19)   | C3—C4—C5—C1     | 0.6 (5)    |
| Cl2—Co1—N1—C1  | 112.95 (19) | C3—C4—C5—C6     | -179.6 (4) |
| Cl1—Co1—N1—C1  | -3.3 (3)    | C1—C5—C6—C7     | 1.5 (5)    |
| N4—Co1—N1—C1   | -87.6 (2)   | C4—C5—C6—C7     | -178.3 (4) |
| N5—Co1—N2—C2   | -121.2 (4)  | C1—C5—C6—C9     | -178.5 (3) |
| N1—Co1—N2—C2   | -177.4 (4)  | C4—C5—C6—C9     | 1.7 (6)    |
| Cl2—Co1—N2—C2  | 101.1 (4)   | C5—C6—C7—C8     | -0.8 (6)   |
| Cl1—Co1—N2—C2  | 0.7 (4)     | C9—C6—C7—C8     | 179.2 (4)  |
| N4—Co1—N2—C2   | -88.3 (4)   | C1—N1—C8—C7     | 2.6 (5)    |
| N5—Co1—N2—C1   | 54.4 (3)    | Co1—N1—C8—C7    | -176.3 (4) |
| N1—Co1—N2—C1   | -1.79 (19)  | C1—N1—C8—C10    | -176.5 (3) |
| Cl2—Co1—N2—C1  | -83.3 (2)   | Co1—N1—C8—C10   | 4.6 (7)    |
| Cl1—Co1—N2—C1  | 176.32 (19) | C6—C7—C8—N1     | -1.4 (6)   |
| N4—Co1—N2—C1   | 87.4 (2)    | C6—C7—C8—C10    | 177.7 (4)  |
| N5—Co1—N4—C18  | 178.9 (6)   | C18—N4—C11—N5   | -179.3 (3) |
| N2—Co1—N4—C18  | 22.7 (6)    | Co1—N4—C11—N5   | 0.3 (3)    |
| N1—Co1—N4—C18  | 83.1 (6)    | C18—N4—C11—C15  | -1.1 (5)   |
| Cl2—Co1—N4—C18 | 176.8 (5)   | Co1—N4—C11—C15  | 178.5 (3)  |
| Cl1—Co1—N4—C18 | -75.3 (6)   | C12—N5—C11—N4   | 178.6 (3)  |
| N5—Co1—N4—C11  | -0.21 (19)  | Co1—N5—C11—N4   | -0.4 (3)   |
| N2—Co1—N4—C11  | -156.4 (2)  | C12—N5—C11—C15  | 0.4 (5)    |
| N1—Co1—N4—C11  | -96.0 (2)   | Co1—N5—C11—C15  | -178.6 (3) |
| Cl2—Co1—N4—C11 | -2.3 (3)    | C11—N5—C12—N6   | -178.3 (3) |
| Cl1—Co1—N4—C11 | 105.60 (19) | Co1—N5—C12—N6   | 0.1 (6)    |
| N2—Co1—N5—C12  | -138.9 (3)  | C11—N5—C12—C13  | 1.4 (5)    |
| N1—Co1—N5—C12  | -92.5 (4)   | Co1—N5—C12—C13  | 179.8 (3)  |
| Cl2—Co1—N5—C12 | 0.9 (4)     | N6—C12—C13—C14  | 177.9 (4)  |
| Cl1—Co1—N5—C12 | 100.7 (4)   | N5—C12—C13—C14  | -1.8 (6)   |
| N4—Co1—N5—C12  | -178.4 (4)  | C12—C13—C14—C15 | 0.4 (6)    |
| N2—Co1—N5—C11  | 39.7 (3)    | C13—C14—C15—C16 | -179.6 (4) |
| N1—Co1—N5—C11  | 86.1 (2)    | C13—C14—C15—C11 | 1.2 (6)    |
| Cl2—Co1—N5—C11 | 179.49 (19) | N4—C11—C15—C16  | 1.0 (5)    |
| Cl1—Co1—N5—C11 | -80.7 (2)   | N5—C11—C15—C16  | 179.0 (3)  |
| N4—Co1—N5—C11  | 0.22 (19)   | N4—C11—C15—C14  | -179.6 (3) |
| C8—N1—C1—N2    | 177.9 (3)   | N5—C11—C15—C14  | -1.7 (5)   |
| Co1—N1—C1—N2   | -2.6 (3)    | C14—C15—C16—C17 | 179.9 (4)  |
| C8—N1—C1—C5    | -1.8 (5)    | C11—C15—C16—C17 | -0.9 (5)   |
| Co1—N1—C1—C5   | 177.6 (3)   | C14—C15—C16—C19 | 2.1 (6)    |
| C2—N2—C1—N1    | 179.8 (3)   | C11—C15—C16—C19 | -178.7 (3) |
| Co1—N2—C1—N1   | 2.9 (3)     | C15—C16—C17—C18 | 0.9 (6)    |
| C2—N2—C1—C5    | -0.5 (5)    | C19—C16—C17—C18 | 178.7 (4)  |
| Co1—N2—C1—C5   | -177.4 (3)  | C11—N4—C18—C17  | 0.9 (5)    |
| C1—N2—C2—N3    | -178.9 (3)  | Co1—N4—C18—C17  | -178.0 (4) |
| Co1—N2—C2—N3   | -3.9 (6)    | C11—N4—C18—C20  | -179.5 (4) |
| C1—N2—C2—C3    | 0.7 (5)     | Co1—N4—C18—C20  | 1.6 (8)    |

|              |           |                 |           |
|--------------|-----------|-----------------|-----------|
| Co1—N2—C2—C3 | 175.7 (3) | C16—C17—C18—N4  | -0.9 (6)  |
| N2—C2—C3—C4  | -0.2 (6)  | C16—C17—C18—C20 | 179.5 (4) |

*Hydrogen-bond geometry (Å, °)*

| <i>D</i> —H... <i>A</i>     | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| O2—H2...C11 <sup>i</sup>    | 0.82        | 2.35          | 3.162 (4)             | 172                     |
| O1—H1...C11 <sup>ii</sup>   | 0.82        | 2.44          | 3.194 (4)             | 154                     |
| N6—H6B...O2 <sup>iii</sup>  | 0.86        | 2.06          | 2.918 (4)             | 175                     |
| N6—H6A...C12                | 0.86        | 2.45          | 3.269 (4)             | 159                     |
| N3—H3B...O1 <sup>iv</sup>   | 0.86        | 2.09          | 2.947 (4)             | 175                     |
| N3—H3A...C11                | 0.86        | 2.51          | 3.309 (3)             | 156                     |
| C22—H22B...C17 <sup>i</sup> | 0.96        | 2.91          | 3.789 (7)             | 154                     |
| C22—H22B...C18 <sup>i</sup> | 0.96        | 2.71          | 3.575 (6)             | 150                     |
| C4—H4...C12 <sup>v</sup>    | 0.93        | 2.85          | 3.705 (4)             | 153                     |
| C7—H7...C11 <sup>vi</sup>   | 0.93        | 2.87          | 3.757 (4)             | 160                     |
| C13—H13...C11 <sup>ii</sup> | 0.93        | 2.88          | 3.733 (4)             | 152                     |

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $-x+2, -y+1, -z+1$ ; (iii)  $x+1, y, z$ ; (iv)  $x, y, z-1$ ; (v)  $-x+2, -y+2, -z$ ; (vi)  $x, y+1, z$ .



Fig. 2

