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# *cis*-Dichloridobis(1,10-phenanthroline)-cobalt(II) dimethylformamide solvate

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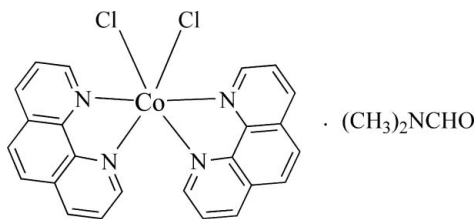
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å; disorder in solvent or counterion;  $R$  factor = 0.026;  $wR$  factor = 0.063; data-to-parameter ratio = 12.2.

In the title complex,  $[\text{CoCl}_2(\text{C}_{12}\text{H}_8\text{N}_2)_2] \cdot \text{C}_3\text{H}_7\text{NO}$ , which has twofold rotation symmetry, the  $\text{Co}^{\text{II}}$  cation is coordinated by two 1,10-phenanthroline (phen) molecules and two chloride ligands in a distorted octahedral geometry. In the crystal structure, a cavity is created by six complex molecules connected by  $\text{C}-\text{H} \cdots \pi$  interactions and non-classical  $\text{C}-\text{H} \cdots \text{Cl}$  hydrogen bonds. The cavities are occupied by the disordered dimethylformamide solvent molecule. The C and N atoms of the C—N bond in the solvent molecule also lie on a crystallographic twofold rotation axis; the remaining atoms of the solvent are statistically disordered (ratio 0.5:0.5) about this axis.

## Related literature

For general background, see: Forster *et al.* (2000); Holder *et al.* (2007); Ma *et al.* (2002). Matsumoto *et al.* (2002); Xie *et al.* (2006). For a related structure, see: Hazell *et al.* (1997).



## Experimental

### Crystal data

 $[\text{CoCl}_2(\text{C}_{12}\text{H}_8\text{N}_2)_2] \cdot \text{C}_3\text{H}_7\text{NO}$ 
 $M_r = 563.33$ Orthorhombic, *Pbcn* $a = 16.345$  (3) Å $b = 12.342$  (2) Å $c = 12.342$  (2) Å $V = 2489.8$  (8) Å<sup>3</sup> $Z = 4$ Mo  $K\alpha$  radiation $\mu = 0.94$  mm<sup>-1</sup> $T = 293$  (2) K

0.20 × 0.20 × 0.20 mm

### Data collection

Rigaku Mercury70 CCD diffractometer  
Absorption correction: multi-scan (*CrystalClear*; Rigaku & Molecular Structure Corporation,

2000)  
 $T_{\text{min}} = 0.829$ ,  $T_{\text{max}} = 0.829$   
14711 measured reflections  
2204 independent reflections  
2168 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.017$

### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.026$  $wR(F^2) = 0.063$  $S = 1.09$ 

2204 reflections

180 parameters

2 restraints

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.34$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.21$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

|                        |             |                          |            |
|------------------------|-------------|--------------------------|------------|
| Co1—N2                 | 2.1517 (13) | Co1—Cl1                  | 2.4099 (5) |
| Co1—N1                 | 2.1636 (13) |                          |            |
| N2—Co1—N2 <sup>i</sup> | 176.70 (7)  | N2 <sup>i</sup> —Co1—Cl1 | 90.43 (4)  |
| N2—Co1—N1              | 76.81 (5)   | N1—Co1—Cl1               | 162.67 (4) |
| N2—Co1—N1 <sup>i</sup> | 100.65 (5)  | N1 <sup>i</sup> —Co1—Cl1 | 87.23 (4)  |
| N1—Co1—N1 <sup>i</sup> | 82.44 (7)   | Cl1—Co1—Cl1 <sup>i</sup> | 105.91 (2) |
| N2—Co1—Cl1             | 91.56 (4)   |                          |            |

Symmetry code: (i)  $-x + 1, y, -z + \frac{1}{2}$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

| $D-\text{H} \cdots A$                     | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|---|--------------|---------------------|--------------|-----------------------|
| C10—H10A <sup>·</sup> ···Cl1              | 0.93         | 2.74                | 3.3408 (17)  | 124                   |
| C6—H6A <sup>·</sup> ···Cl1 <sup>ii</sup>  | 0.93         | 2.80                | 3.6743 (18)  | 158                   |
| C5—H5A <sup>·</sup> ···Cl1 <sup>iii</sup> | 0.93         | 2.85                | 3.6375 (17)  | 144                   |
| C2—H2A <sup>·</sup> ···Cg1 <sup>iv</sup>  | 0.93         | 2.99                | 3.768 (2)    | 142                   |
| C8—H8A <sup>·</sup> ···Cg2 <sup>v</sup>   | 0.93         | 2.90                | 3.608 (2)    | 134                   |

Symmetry codes: (ii)  $x + \frac{1}{2}, -y + \frac{3}{2}, -z$ ; (iii)  $x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iv)  $x, -y + 1, z - \frac{1}{2}$ ; (v)  $-x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ .

Data collection: *CrystalClear* (Rigaku & Molecular Structure Corporation, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear* program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek; 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2538).

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**supplementary materials**

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## ***cis*-Dichloridobis(1,10-phenanthroline)cobalt(II) dimethylformamide solvate**

**S.-L. Cai, S.-M. Ying, H. Li and Y. Chen**

### **Comment**

$ML_mX_n$  coordination compounds ( $L = \alpha, \alpha'$ -diimine chelate ligands, such as 2,2'-bipyridine, 1,10-phenanthroline, and their derivatives;  $X =$  halide or pseudohalide ligands) have been receiving extensive attention due to their importance in crystal engineering and supramolecular chemistry. They also serve as models to aid the understanding of phenomena such as photosensitization and crystallization (Forster *et al.*, 2000; Holder *et al.*, 2007; Ma *et al.*, 2002). In such molecules a variety of weak intermolecular interactions involving the halide anions, aromatic ligands and solvent molecules can stabilise and regulate the supramolecular architecture in different aggregation states (Matsumoto *et al.*, 2002; Xie *et al.*, 2006). Herein, we report the crystal structure of a new cobalt(II) chloride complex with a phenanthroline ligand, Fig 1.

The crystallographic asymmetric unit of (I) consists of one half occupancy  $\text{Co}^{\text{II}}$  atom that lies on a two-fold rotation axis, one phenanthroline molecule, one  $\text{Cl}^-$  anion, and half a molecule of dimethylformamide. In the complex, the  $\text{Co}^{\text{II}}$  atom is in a distorted octahedral coordination environment provided by four N atoms from two bidentate phen ligands and two terminal  $\text{Cl}^-$  anions. The Co—N and Co—Cl bond lengths (Table 1) are normal, and are comparable to those found in a related octahedral cobalt(II) complex  $[\text{CoCl}_2(\text{C}_{12}\text{H}_8\text{N}_2)_2] \cdot 1.5\text{CH}_3\text{CN}$  [Hazell *et al.*, 1997].

Interestingly in the crystal structure, a cavity is created by six complex molecules connected by C—H $\cdots$  $\pi$  interactions and non-classical C—H $\cdots$ Cl hydrogen bonds (Table 2, Fig. 2) which is occupied by the disordered dmf solvate molecule. The solvate lies with the C14 and N3 on a crystallographic 2-fold rotation axis; the remaining atoms of the solvate are statistically disordered about this axis. The calculated void space of the cavity was estimated to be  $557.6 \text{ \AA}^3$  per unit cell, which corresponds to 23.2% of the total volume ( $2489.8 \text{ \AA}^3$ ) (Fig 2) (Spek, 2003).

### **Experimental**

$[\text{CoCl}_2 \cdot 6(\text{H}_2\text{O})]$  (238 mg) was dissolved in a mixture of dimethylformamide (10 ml) and tetrahydrofuran (10 ml) with stirring. A color change from blue to dark blue was observed after the phenanthroline (40 mg) was added to the solution. The mixture was cooled down to room temperature after stirring for 1 h at  $90^\circ\text{C}$ . The resulting mixture was then filtered, and the filtrate was concentrated to *ca* 13 ml by rotary evaporation and left in a refrigerator at  $4^\circ\text{C}$ . Transparent blue prismatic crystals suitable for X-ray diffraction were produced in a few days (yield 21%). Analysis calculated for  $\text{C}_{27}\text{H}_{23}\text{Cl}_2\text{CoN}_5\text{O}$ : C 57.57, N 12.43, H 4.12%; found: C 57.72, N 12.56, H 3.97%.

### **Refinement**

The H atoms bonded to C atoms were placed in calculated positions and treated using a riding-model approximation (C—H =  $0.96 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for the methyl group; C—H =  $0.93 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for the 1,10-phenanthroline and aldehyde groups).

## Figures

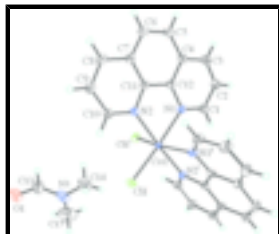


Fig. 1. The structure of the title compound showing the atom numbering. Thermal ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Only one of the disorder components of the dmf molecule is shown. [Symmetry codes: (i)  $1 - x + 1, y, 1/2 - z.$ ]

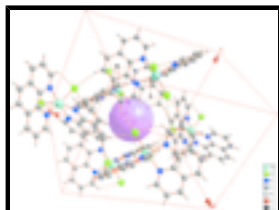


Fig. 2. Crystal packing of (I) showing the cavity (represented by the pink sphere) created by the C—H...Cl and C—H... $\pi$  interactions with hydrogen bonds drawn as dashed lines.

## *cis*-Dichloridobis(1,10-phenanthroline)cobalt(II) dimethylformamide solvate

### Crystal data

$[\text{CoCl}_2(\text{C}_{12}\text{H}_8\text{N}_2)_2] \cdot \text{C}_3\text{H}_7\text{NO}$

$M_r = 563.33$

Orthorhombic, *Pbcn*

Hall symbol:  $-P\ 2n\ 2ab$

$a = 16.345\ (3)\ \text{\AA}$

$b = 12.342\ (2)\ \text{\AA}$

$c = 12.342\ (2)\ \text{\AA}$

$V = 2489.8\ (8)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1156$

$D_x = 1.503\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 6370 reflections

$\theta = 2.1\text{--}25.0^\circ$

$\mu = 0.94\ \text{mm}^{-1}$

$T = 293\ (2)\ \text{K}$

Block, colorless

$0.20 \times 0.20 \times 0.20\ \text{mm}$

### Data collection

Rigaku Mercury70 CCD  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293\ (2)\ \text{K}$

$\omega$  scans

Absorption correction: multi-scan

(CrystalClear; Rigaku & Molecular Structure Corporation, 2000)

$T_{\min} = 0.829, T_{\max} = 0.829$

14711 measured reflections

2204 independent reflections

2168 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$

$\theta_{\max} = 25.0^\circ$

$\theta_{\min} = 2.1^\circ$

$h = -17 \rightarrow 19$

$k = -14 \rightarrow 14$

$l = -13 \rightarrow 14$

*Refinement*

|  |  |
|--|--|
| Refinement on $F^2$  | Secondary atom site location: difference Fourier map     |
| Least-squares matrix: full                                     | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.026$                                | H-atom parameters constrained                            |
| $wR(F^2) = 0.063$  | $w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 1.9948P]$        |
| $S = 1.09$   | where $P = (F_o^2 + 2F_c^2)/3$                           |
| 2204 reflections   | $(\Delta/\sigma)_{\max} < 0.001$                         |
| 180 parameters   | $\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$    |
| 2 restraints   | $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$   |
| Primary atom site location: structure-invariant direct methods | 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 ( $\text{\AA}^2$ )*

|      | <i>x</i>     | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|--------------|--------------|--------------|----------------------------------|-----------|
| Co1  | 0.5000       | 0.71666 (2)  | 0.2500       | 0.01272 (10)                     |           |
| Cl1  | 0.41390 (2)  | 0.59903 (3)  | 0.14376 (3)  | 0.01956 (11)                     |           |
| N2   | 0.59089 (8)  | 0.72168 (10) | 0.12398 (11) | 0.0151 (3)                       |           |
| C11  | 0.65206 (9)  | 0.79462 (12) | 0.14122 (12) | 0.0141 (3)                       |           |
| N1   | 0.57879 (8)  | 0.84851 (11) | 0.29957 (11) | 0.0162 (3)                       |           |
| C7   | 0.72069 (9)  | 0.80426 (13) | 0.07300 (13) | 0.0171 (3)                       |           |
| C12  | 0.64445 (9)  | 0.86417 (12) | 0.23421 (13) | 0.0148 (3)                       |           |
| C3   | 0.69394 (10) | 1.00860 (14) | 0.34665 (14) | 0.0228 (4)                       |           |
| H3A  | 0.7317       | 1.0626       | 0.3628       | 0.027*                           |           |
| C10  | 0.59726 (10) | 0.65659 (13) | 0.03895 (13) | 0.0187 (3)                       |           |
| H10A | 0.5558       | 0.6065       | 0.0264       | 0.022*                           |           |
| C1   | 0.57135 (10) | 0.91093 (14) | 0.38597 (14) | 0.0215 (4)                       |           |
| H1A  | 0.5264       | 0.9007       | 0.4311       | 0.026*                           |           |
| C6   | 0.78081 (10) | 0.88565 (14) | 0.09568 (14) | 0.0209 (4)                       |           |
| H6A  | 0.8261       | 0.8924       | 0.0507       | 0.025*                           |           |
| C5   | 0.77263 (10) | 0.95285 (14) | 0.18162 (14) | 0.0218 (4)                       |           |
| H5A  | 0.8120       | 1.0059       | 0.1940       | 0.026*                           |           |

## supplementary materials

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|      |              |              |               |             |      |
|------|--------------|--------------|---------------|-------------|------|
| C2   | 0.62797 (10) | 0.99184 (15) | 0.41280 (15)  | 0.0253 (4)  |      |
| H2A  | 0.6208       | 1.0336       | 0.4748        | 0.030*      |      |
| C8   | 0.72538 (11) | 0.73320 (13) | -0.01602 (14) | 0.0210 (4)  |      |
| H8A  | 0.7699       | 0.7360       | -0.0629       | 0.025*      |      |
| C9   | 0.66376 (10) | 0.65987 (14) | -0.03293 (14) | 0.0222 (4)  |      |
| H9A  | 0.6660       | 0.6126       | -0.0916       | 0.027*      |      |
| C4   | 0.70425 (10) | 0.94361 (13) | 0.25393 (13)  | 0.0176 (3)  |      |
| O1   | 0.5517 (2)   | 0.0842 (2)   | 0.1510 (3)    | 0.0433 (7)  | 0.50 |
| N3   | 0.5000       | 0.2344 (2)   | 0.2500        | 0.0453 (7)  |      |
| C13  | 0.5478 (6)   | 0.1828 (7)   | 0.1772 (8)    | 0.048 (3)   | 0.50 |
| H13A | 0.5840       | 0.2276       | 0.1400        | 0.057*      | 0.50 |
| C14  | 0.5000       | 0.3523 (3)   | 0.2500        | 0.0553 (10) |      |
| H14A | 0.5551       | 0.3783       | 0.2427        | 0.083*      | 0.50 |
| H14B | 0.4772       | 0.3783       | 0.3168        | 0.083*      | 0.50 |
| H14C | 0.4677       | 0.3783       | 0.1904        | 0.083*      | 0.50 |
| C15  | 0.5421 (7)   | 0.1760 (10)  | 0.1657 (9)    | 0.067 (4)   | 0.50 |
| H15A | 0.5375       | 0.2151       | 0.0987        | 0.100*      | 0.50 |
| H15B | 0.5180       | 0.1055       | 0.1575        | 0.100*      | 0.50 |
| H15C | 0.5988       | 0.1685       | 0.1846        | 0.100*      | 0.50 |

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

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$      | $U^{13}$      | $U^{23}$      |
|-----|--------------|--------------|--------------|---------------|---------------|---------------|
| Co1 | 0.01000 (16) | 0.01385 (16) | 0.01430 (17) | 0.000         | -0.00028 (11) | 0.000         |
| Cl1 | 0.0170 (2)   | 0.0213 (2)   | 0.0203 (2)   | -0.00516 (15) | -0.00274 (15) | -0.00162 (16) |
| N2  | 0.0134 (6)   | 0.0161 (6)   | 0.0159 (7)   | -0.0002 (5)   | -0.0015 (5)   | 0.0012 (5)    |
| C11 | 0.0124 (7)   | 0.0146 (7)   | 0.0152 (8)   | 0.0011 (6)    | -0.0018 (6)   | 0.0033 (6)    |
| N1  | 0.0131 (6)   | 0.0174 (7)   | 0.0181 (7)   | 0.0004 (5)    | -0.0004 (5)   | -0.0016 (6)   |
| C7  | 0.0148 (8)   | 0.0187 (8)   | 0.0177 (8)   | 0.0012 (6)    | 0.0003 (6)    | 0.0036 (6)    |
| C12 | 0.0130 (7)   | 0.0147 (7)   | 0.0168 (8)   | 0.0012 (6)    | -0.0027 (6)   | 0.0023 (6)    |
| C3  | 0.0203 (8)   | 0.0208 (8)   | 0.0272 (9)   | -0.0047 (7)   | -0.0045 (7)   | -0.0045 (7)   |
| C10 | 0.0185 (8)   | 0.0180 (8)   | 0.0195 (8)   | -0.0006 (6)   | -0.0012 (7)   | -0.0031 (7)   |
| C1  | 0.0176 (8)   | 0.0252 (9)   | 0.0218 (9)   | 0.0001 (7)    | 0.0035 (7)    | -0.0054 (7)   |
| C6  | 0.0156 (8)   | 0.0263 (8)   | 0.0208 (8)   | -0.0033 (7)   | 0.0022 (7)    | 0.0047 (7)    |
| C5  | 0.0181 (8)   | 0.0236 (8)   | 0.0238 (9)   | -0.0078 (7)   | -0.0018 (7)   | 0.0036 (7)    |
| C2  | 0.0227 (9)   | 0.0270 (9)   | 0.0262 (9)   | -0.0020 (7)   | 0.0003 (7)    | -0.0109 (8)   |
| C8  | 0.0185 (8)   | 0.0249 (8)   | 0.0197 (8)   | 0.0025 (7)    | 0.0055 (7)    | 0.0018 (7)    |
| C9  | 0.0240 (9)   | 0.0224 (8)   | 0.0203 (8)   | 0.0012 (7)    | 0.0022 (7)    | -0.0048 (7)   |
| C4  | 0.0155 (8)   | 0.0179 (8)   | 0.0194 (8)   | -0.0003 (7)   | -0.0034 (6)   | 0.0015 (6)    |
| O1  | 0.0492 (19)  | 0.0294 (16)  | 0.0512 (19)  | 0.0003 (14)   | -0.0046 (15)  | -0.0048 (14)  |
| N3  | 0.0390 (15)  | 0.0223 (12)  | 0.075 (2)    | 0.000         | -0.0214 (14)  | 0.000         |
| C13 | 0.065 (7)    | 0.018 (4)    | 0.060 (5)    | -0.007 (4)    | 0.030 (5)     | 0.001 (3)     |
| C14 | 0.049 (2)    | 0.0259 (16)  | 0.090 (3)    | 0.000         | -0.0091 (19)  | 0.000         |
| C15 | 0.047 (5)    | 0.057 (7)    | 0.095 (7)    | 0.001 (5)     | -0.041 (5)    | -0.028 (5)    |

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

|        |             |       |           |
|--------|-------------|-------|-----------|
| Co1—N2 | 2.1517 (13) | C6—C5 | 1.353 (2) |
|--------|-------------|-------|-----------|

|                                       |             |                          |             |
|---------------------------------------|-------------|--------------------------|-------------|
| Co1—N2 <sup>i</sup>                   | 2.1517 (13) | C6—H6A                   | 0.9300      |
| Co1—N1                                | 2.1636 (13) | C5—C4                    | 1.435 (2)   |
| Co1—N1 <sup>i</sup>                   | 2.1636 (13) | C5—H5A                   | 0.9300      |
| Co1—C11                               | 2.4099 (5)  | C2—H2A                   | 0.9300      |
| Co1—C11 <sup>i</sup>                  | 2.4099 (5)  | C8—C9                    | 1.370 (2)   |
| N2—C10                                | 1.326 (2)   | C8—H8A                   | 0.9300      |
| N2—C11                                | 1.362 (2)   | C9—H9A                   | 0.9300      |
| C11—C7                                | 1.408 (2)   | O1—C13                   | 1.260 (9)   |
| C11—C12                               | 1.439 (2)   | N3—C13                   | 1.351 (7)   |
| N1—C1                                 | 1.321 (2)   | N3—C15                   | 1.441 (8)   |
| N1—C12                                | 1.356 (2)   | N3—C14                   | 1.456 (4)   |
| C7—C8                                 | 1.408 (2)   | N3—C13 <sup>i</sup>      | 1.351 (7)   |
| C7—C6                                 | 1.433 (2)   | N3—C15 <sup>i</sup>      | 1.441 (8)   |
| C12—C4                                | 1.406 (2)   | C13—H13A                 | 0.9300      |
| C3—C2                                 | 1.368 (2)   | C14—H14A                 | 0.9600      |
| C3—C4                                 | 1.408 (2)   | C14—H14B                 | 0.9600      |
| C3—H3A                                | 0.9300      | C14—H14C                 | 0.9600      |
| C10—C9                                | 1.404 (2)   | C15—H15A                 | 0.9600      |
| C10—H10A                              | 0.9300      | C15—H15B                 | 0.9600      |
| C1—C2                                 | 1.401 (2)   | C15—H15C                 | 0.9600      |
| C1—H1A                                | 0.9300      |                          |             |
| N2—Co1—N2 <sup>i</sup>                | 176.70 (7)  | C5—C6—C7                 | 121.01 (15) |
| N2—Co1—N1                             | 76.81 (5)   | C5—C6—H6A                | 119.5       |
| N2 <sup>i</sup> —Co1—N1               | 100.65 (5)  | C7—C6—H6A                | 119.5       |
| N2—Co1—N1 <sup>i</sup>                | 100.65 (5)  | C6—C5—C4                 | 121.05 (15) |
| N2 <sup>i</sup> —Co1—N1 <sup>i</sup>  | 76.81 (5)   | C6—C5—H5A                | 119.5       |
| N1—Co1—N1 <sup>i</sup>                | 82.44 (7)   | C4—C5—H5A                | 119.5       |
| N2—Co1—C11                            | 91.56 (4)   | C3—C2—C1                 | 119.15 (16) |
| N2 <sup>i</sup> —Co1—C11              | 90.43 (4)   | C3—C2—H2A                | 120.4       |
| N1—Co1—C11                            | 162.67 (4)  | C1—C2—H2A                | 120.4       |
| N1 <sup>i</sup> —Co1—C11              | 87.23 (4)   | C9—C8—C7                 | 119.36 (15) |
| N2—Co1—C11 <sup>i</sup>               | 90.43 (4)   | C9—C8—H8A                | 120.3       |
| N2 <sup>i</sup> —Co1—C11 <sup>i</sup> | 91.56 (4)   | C7—C8—H8A                | 120.3       |
| N1—Co1—C11 <sup>i</sup>               | 87.23 (4)   | C8—C9—C10                | 119.48 (15) |
| N1 <sup>i</sup> —Co1—C11 <sup>i</sup> | 162.67 (4)  | C8—C9—H9A                | 120.3       |
| C11—Co1—C11 <sup>i</sup>              | 105.91 (2)  | C10—C9—H9A               | 120.3       |
| C10—N2—C11                            | 117.80 (14) | C12—C4—C3                | 117.06 (15) |
| C10—N2—Co1                            | 127.52 (11) | C12—C4—C5                | 119.30 (15) |
| C11—N2—Co1                            | 114.39 (10) | C3—C4—C5                 | 123.62 (15) |
| N2—C11—C7                             | 123.19 (14) | C13 <sup>i</sup> —N3—C13 | 123.8 (8)   |
| N2—C11—C12                            | 117.10 (14) | C13—N3—C15 <sup>i</sup>  | 121.4 (4)   |
| C7—C11—C12                            | 119.71 (14) | C13 <sup>i</sup> —N3—C15 | 121.4 (4)   |
| C1—N1—C12                             | 118.02 (14) | C15 <sup>i</sup> —N3—C15 | 120.0 (11)  |
| C1—N1—Co1                             | 127.74 (11) | C13—N3—C14               | 118.1 (4)   |

## supplementary materials

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|                              |              |                             |              |
|------------------------------|--------------|-----------------------------|--------------|
| C12—N1—Co1                   | 114.20 (10)  | C15—N3—C14                  | 120.0 (6)    |
| C11—C7—C8                    | 117.23 (15)  | O1—C13—N3                   | 130.9 (6)    |
| C11—C7—C6                    | 119.27 (15)  | O1—C13—H13A                 | 114.6        |
| C8—C7—C6                     | 123.49 (15)  | N3—C13—H13A                 | 114.6        |
| N1—C12—C4                    | 123.13 (14)  | N3—C14—H14A                 | 109.5        |
| N1—C12—C11                   | 117.25 (14)  | N3—C14—H14B                 | 109.5        |
| C4—C12—C11                   | 119.62 (14)  | H14A—C14—H14B               | 109.5        |
| C2—C3—C4                     | 119.56 (16)  | N3—C14—H14C                 | 109.5        |
| C2—C3—H3A                    | 120.2        | H14A—C14—H14C               | 109.5        |
| C4—C3—H3A                    | 120.2        | H14B—C14—H14C               | 109.5        |
| N2—C10—C9                    | 122.94 (15)  | N3—C15—H15A                 | 109.5        |
| N2—C10—H10A                  | 118.5        | N3—C15—H15B                 | 109.5        |
| C9—C10—H10A                  | 118.5        | H15A—C15—H15B               | 109.5        |
| N1—C1—C2                     | 123.06 (16)  | N3—C15—H15C                 | 109.5        |
| N1—C1—H1A                    | 118.5        | H15A—C15—H15C               | 109.5        |
| C2—C1—H1A                    | 118.5        | H15B—C15—H15C               | 109.5        |
| N1—Co1—N2—C10                | 178.15 (14)  | N2—C11—C12—N1               | 2.6 (2)      |
| N1 <sup>i</sup> —Co1—N2—C10  | -102.31 (13) | C7—C11—C12—N1               | -177.44 (14) |
| C11—Co1—N2—C10               | -14.83 (13)  | N2—C11—C12—C4               | -177.75 (14) |
| C11 <sup>i</sup> —Co1—N2—C10 | 91.10 (13)   | C7—C11—C12—C4               | 2.2 (2)      |
| N1—Co1—N2—C11                | 4.54 (10)    | C11—N2—C10—C9               | 0.1 (2)      |
| N1 <sup>i</sup> —Co1—N2—C11  | 84.08 (11)   | Co1—N2—C10—C9               | -173.37 (12) |
| C11—Co1—N2—C11               | 171.56 (10)  | C12—N1—C1—C2                | -0.1 (2)     |
| C11 <sup>i</sup> —Co1—N2—C11 | -82.51 (10)  | Co1—N1—C1—C2                | 177.45 (13)  |
| C10—N2—C11—C7                | 0.5 (2)      | C11—C7—C6—C5                | 0.2 (2)      |
| Co1—N2—C11—C7                | 174.73 (12)  | C8—C7—C6—C5                 | 179.06 (16)  |
| C10—N2—C11—C12               | -179.63 (14) | C7—C6—C5—C4                 | 1.1 (3)      |
| Co1—N2—C11—C12               | -5.35 (17)   | C4—C3—C2—C1                 | -0.8 (3)     |
| N2—Co1—N1—C1                 | 179.24 (15)  | N1—C1—C2—C3                 | 0.6 (3)      |
| N2 <sup>i</sup> —Co1—N1—C1   | 1.40 (15)    | C11—C7—C8—C9                | 0.7 (2)      |
| N1 <sup>i</sup> —Co1—N1—C1   | 76.37 (14)   | C6—C7—C8—C9                 | -178.19 (16) |
| C11—Co1—N1—C1                | 130.31 (14)  | C7—C8—C9—C10                | -0.2 (2)     |
| C11 <sup>i</sup> —Co1—N1—C1  | -89.67 (14)  | N2—C10—C9—C8                | -0.2 (3)     |
| N2—Co1—N1—C12                | -3.15 (10)   | N1—C12—C4—C3                | 0.1 (2)      |
| N2 <sup>i</sup> —Co1—N1—C12  | 179.00 (10)  | C11—C12—C4—C3               | -179.44 (14) |
| N1 <sup>i</sup> —Co1—N1—C12  | -106.02 (12) | N1—C12—C4—C5                | 178.67 (15)  |
| C11—Co1—N1—C12               | -52.08 (19)  | C11—C12—C4—C5               | -0.9 (2)     |
| C11 <sup>i</sup> —Co1—N1—C12 | 87.94 (10)   | C2—C3—C4—C12                | 0.4 (2)      |
| N2—C11—C7—C8                 | -0.8 (2)     | C2—C3—C4—C5                 | -178.04 (17) |
| C12—C11—C7—C8                | 179.25 (14)  | C6—C5—C4—C12                | -0.7 (2)     |
| N2—C11—C7—C6                 | 178.10 (14)  | C6—C5—C4—C3                 | 177.71 (16)  |
| C12—C11—C7—C6                | -1.8 (2)     | C13 <sup>i</sup> —N3—C13—O1 | 9.9 (10)     |
| C1—N1—C12—C4                 | -0.3 (2)     | C15 <sup>i</sup> —N3—C13—O1 | 18 (2)       |
| Co1—N1—C12—C4                | -178.17 (12) | C15—N3—C13—O1               | -62 (7)      |
| C1—N1—C12—C11                | 179.28 (14)  | C14—N3—C13—O1               | -170.1 (10)  |
| Co1—N1—C12—C11               | 1.42 (17)    |                             |              |

Symmetry codes: (i)  $-x+1, y, -z+1/2$ .

*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

| <i>D</i> —H $\cdots$ <i>A</i>      | <i>D</i> —H | H $\cdots$ <i>A</i> | <i>D</i> $\cdots$ <i>A</i> | <i>D</i> —H $\cdots$ <i>A</i> |
|------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| C10—H10A $\cdots$ C11              | 0.93        | 2.74                | 3.3408 (17)                | 124                           |
| C6—H6A $\cdots$ C11 <sup>ii</sup>  | 0.93        | 2.80                | 3.6743 (18)                | 158                           |
| C5—H5A $\cdots$ C11 <sup>iii</sup> | 0.93        | 2.85                | 3.6375 (17)                | 144                           |
| C2—H2A $\cdots$ Cg1 <sup>iv</sup>  | 0.93        | 2.99                | 3.768 (2)                  | 142                           |
| C8—H8A $\cdots$ Cg2 <sup>v</sup>   | 0.93        | 2.90                | 3.608 (2)                  | 134                           |

Symmetry codes: (ii)  $x+1/2, -y+3/2, -z$ ; (iii)  $x+1/2, y+1/2, -z+1/2$ ; (iv)  $x, -y+1, z-1/2$ ; (v)  $-x+3/2, -y+1/2, z-1/2$ .



Fig. 2

