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# Crystal structure of bis(4-nitroaniline-$\kappa N^1$)(5,10,15,20-tetraphenylporphyrinato-$\kappa^4 N$)cobalt(III) chloride dichloromethane monosolvate

**Yassine Belghith,[a]* Anissa Mansour[b] and Habib Nasri[a]**

[a]Laboratoire de Physico-chimie des Matériaux, Faculté des Sciences de Monastir, Avenue de l'environnement, 5019 Monastir, University of Monastir, Tunisia, and [b]University of Dammam, PO Box 1982, Dammam, Kingdom of Saudi Arabia. *Correspondence e-mail: yassinbelghith@gmail.com

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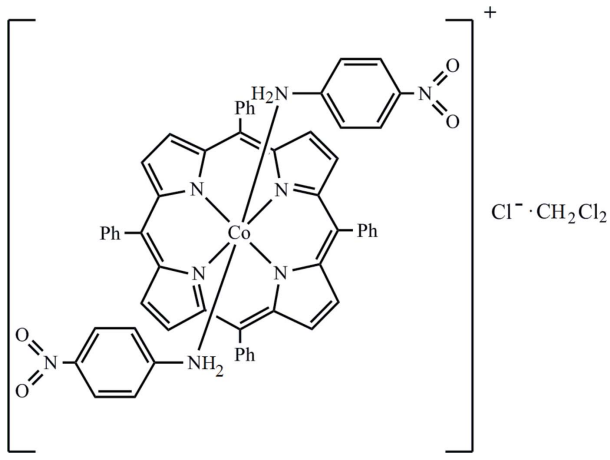
The reaction of [Co$^{III}$(TPP)Cl] (TPP is the dianion of 5,10,15,20-tetraphenylporphyrin) with an excess of 4-nitroaniline in dichloromethane leads to the title compound, [Co$^{III}$($C_{44}H_{28}N_4$)($C_6H_6N_2O_2$)$_2$]Cl·$CH_2Cl_2$. The Co$^{III}$ ion lies on an inversion centre and is octahedrally coordinated by two N atoms of the $NH_2$ groups of the two 4-nitroaniline *trans*-axial ligands and four pyrrole N atoms of the porphyrin. The asymmetric unit contains one half of the [Co$^{III}$(TPP)(4-nitroaniline)$_2$]$^+$ ion complex, one chloride counter-ion (lying on a twofold rotation axis) and one half dichloromethane solvent molecule, where the C atom lies on a twofold rotation axis. The average equatorial Co—N(pyrrole) distance (Co—Np) is 1.982 (2) Å and the axial Co—N(4-nitroaniline) bond length
is 2.006 (2) Å. The crystal packing is stabilized by an N—H···Cl hydrogen bond between the N atom of the amino group of the 4-nitroaniline axial ligand and the chloride counter-ion. The supramolecular architecture is further stabilized by weak C—H···$\pi$ interactions.

**Keywords:** crystal structure; cobalt(III) complex; 5,10,15,20-tetraphenylporphyrin ligand.

**CCDC reference**: 1013796

## 1. Related literature

For the synthesis of the title compound, see: Madure & Scheidt (1976). For related structures, see: Dhifet *et al.* (2010); Konarev *et al.* (2003); Jentzen *et al.* (1995); Mansour *et al.* (2013); Zhang *et al.* (2005); Feng (2012). For a description of the Cambridge Structural Database, see: Allen (2002).




## 2. Experimental

### 2.1. Crystal data

$[Co(C_{44}H_{28}N_4)(C_6H_6N_2O_2)_2]Cl\cdot CH_2Cl_2$
$M_r$ = 1068.30
Monoclinic, $P2/c$
$a$ = 13.3527 (9) Å
$b$ = 12.4492 (10) Å
$c$ = 14.8935 (14) Å
$\beta$ = 95.604 (4)°
$V$ = 2463.9 (3) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.57 mm$^{-1}$
$T$ = 150 K
0.40 × 0.24 × 0.11 mm

### 2.2. Data collection

Bruker APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
$T_{min}$ = 0.819, $T_{max}$ = 0.939
20514 measured reflections
4853 independent reflections
4083 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.038

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.097
$S$ = 1.04
4853 reflections
338 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.63 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.96 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

*Cg*7 and *Cg*8 are the centroids of the C11/C12–C16 and C17/C18–C22 rings, respectively.

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N3—H3*B*···Cl2 | 0.88 (4) | 2.32 (3) | 3.174 (2) | 164 (3) |
| C13—H13···*Cg*8$^{i}$ | 0.95 | 3.00 | 3.723 (3) | 134 |
| C20—H20···*Cg*7$^{ii}$ | 0.95 | 2.94 | 3.788 (2) | 150 |

Symmetry codes: (i) $x, y-1, z$; (ii) $-x-1, -y, -z+1$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

## Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: XU5802).

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# supporting information

*Acta Cryst.* (2014). E**70**, m312–m313 [doi:10.1107/S1600536814016274]

# Crystal structure of bis(4-nitroaniline-$\kappa N^1$)(5,10,15,20-tetraphenylporphyrinato-$\kappa^4 N$)cobalt(III) chloride dichloromethane monosolvate

**Yassine Belghith, Anissa Mansour and Habib Nasri**

## S1. Comment

In continuation of our research on the crystal structures of porphyrin complexes (Dhifet *et al.*, 2010) we herein report the crystal structure of the title compound. The coordination geometry around the $Co^{III}$ is octahedral where the N-donor atoms from the four pyrrole moieties of the *meso*-tetraphenylporphyrin (TPP) occupy equatorial positions along the porphyrin core. The nitrogen atoms of the amino groups of the two 4-nitroaniline trans axial ligands occupy the axial positions (Fig. 1).

The average equatorial cobalt–pyrrole N atom distance [Co—Np = 1.982 (2) Å] is (i) longer than the one of the [$Co^{II}$(TPP)] complex (Konarev *et al.*, 2003) [Co—Np = 1.923 (4) Å which presents a very ruffled porphyrin core (Jentzen *et al.*, 1995), (ii) very close the Co—Np bond length [1.9885 (5) Å] of the dimer {[$Co^{II}$(TPP)($\mu$-4,4′-bipy)].2bipy}$_n$ (Mansour *et al.*, 2013) which exhibits a practically planar porphyrin core. Thus, our synthetic derivative should display a planar conformation of the porphyrin core which is confirmed by the very small desplacements of the atoms of the porphyrin core with respect to the $CoN_4C_{20}$ mean plane [between -0.052 (1) Å and 0.041 (1) Å].

The distance between the cobalt cation and the nitrogen of the amino group of the 4-nitroaniline is 2.006 (2) Å. It is noteworthy that in the Cambridge Structural Database (CSD, Version 5.35; Allen, 2002) there are only one reported structure of a N-bonded 4-nitroaniline complex [$PdCl_2$(*p*-$NO_2C_6H_4NH_2)_2$] (Feng, 2012) and one reported structure of a N-bonded 4-nitroanilinato coordination compound [$Os^{IV}$(Br-salch)(*p*-$NO_2C_6H_4NH)_2$] (Zhang *et al.*, 2005) (Br-salch = (3,5-dibromosalicylidene)-1,2-cyclohexane-diamine].

The crystal packing of the title compound is stabilized by N—H···Cl intermolecular hydrogen bonding between the nitrogen N5 of amino group of the 4-nitroaniline and the Cl2 counterion and by weak C—H···$\pi$ intermolecular interactions involving Cg pyrrole and phenyl rings (Table 1 and Fig. 2).

## S2. Experimental

To a solution of [$Co^{III}$(TPP)Cl] (100 mg, 0.141 mmol) (Madure & Scheidt, 1976) in dichloromethane (10 mL) was added an excess of 4-nitroaniline (80 mg, 0.579 mmol). The reaction mixture was stirred at room temperature and at the end of the reaction, the color of the solution changed from red-orange to dark–red. Crystals of the title complex were obtained by diffusion of hexanes through the dichloromethane solution.

## S3. Refinement

All H atoms attached to C atoms were fixed geometrically and treated as riding with C—H = 0.99 Å (methylene) and 0.95 Å (aromatic) with $U_{iso}(H) = 1.2U_{eq}(C_{aromatic,\ methylene})$. The two H atoms of the amino group of the 4-nitroaniline axial ligand were found in the difference Fourier map and were refined independently with fixed isotropic displacement parameters.

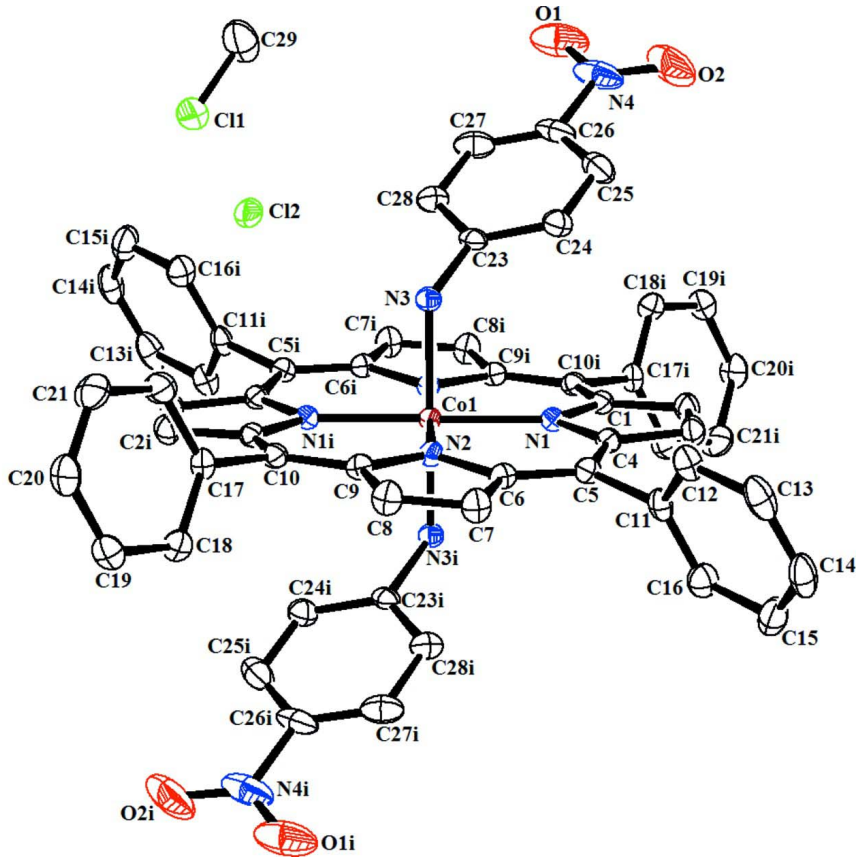


**Figure 1**

An *ORTEP* view of the molecular structure of the title molecule with the atom-numbering. Displacement ellipsoids are drawn at 50%. The H atoms have been omitted for clarity.

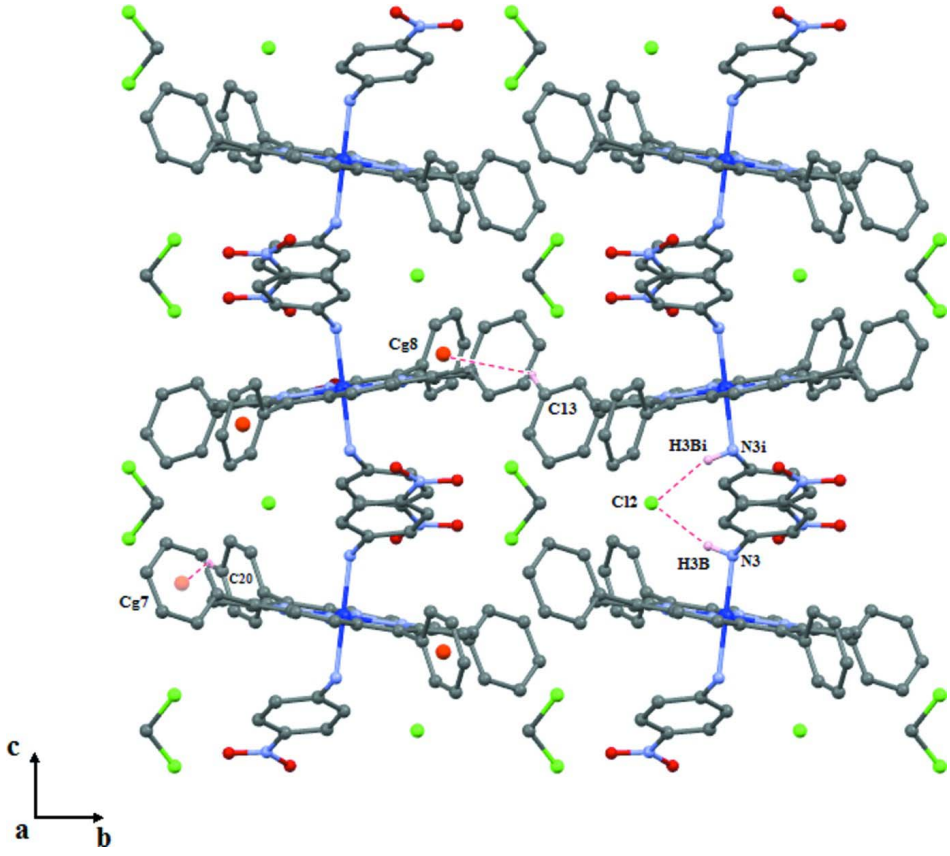


**Figure 2**

The crystal structure of the title compound plotted in projection along [100]. H atoms have been omitted.

## Bis(4-nitroaniline-$\kappa N^1$)(5,10,15,20-tetraphenylporphyrinato-$\kappa^4 N$)cobalt(III) chloride dichloromethane monosolvate

*Crystal data*

$[Co(C_{44}H_{28}N_4)(C_6H_6N_2O_2)_2]Cl\cdot CH_2Cl_2$
$M_r = 1068.30$
Monoclinic, $P2/c$
Hall symbol: -P 2yC
$a = 13.3527\ (9)$ Å
$b = 12.4492\ (10)$ Å
$c = 14.8935\ (14)$ Å
$\beta = 95.604\ (4)°$
$V = 2463.9\ (3)$ Å$^3$
$Z = 2$
$F(000) = 1100$
$D_x = 1.440$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 22812 reflections
$\theta = 3.0–26.0°$
$\mu = 0.57$ mm$^{-1}$
$T = 150$ K
Prism, black
0.40 × 0.24 × 0.11 mm

*Data collection*

Bruker APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
CCD rotation images, thin slices scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
$T_{min} = 0.819$, $T_{max} = 0.939$
20514 measured reflections
4853 independent reflections
4083 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 26.0°$, $\theta_{min} = 3.0°$
$h = -15\rightarrow16$
$k = -15\rightarrow13$
$l = -18\rightarrow18$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.097$
$S = 1.04$
4853 reflections
338 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 2.4863P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.63$ e Å$^{-3}$
$\Delta\rho_{min} = -0.96$ e Å$^{-3}$

*Special details*

**Geometry**. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2$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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Co1 | 0.0000 | 0.0000 | 0.5000 | 0.01228 (11) | |
| N1 | 0.02932 (12) | −0.15405 (13) | 0.48224 (11) | 0.0141 (4) | |
| N2 | −0.14475 (12) | −0.03522 (14) | 0.50284 (11) | 0.0151 (4) | |
| N3 | 0.01549 (13) | −0.01847 (15) | 0.63444 (12) | 0.0163 (4) | |
| H3A | −0.034 (2) | −0.061 (3) | 0.640 (2) | 0.050* | |
| H3B | 0.007 (2) | 0.046 (3) | 0.656 (2) | 0.050* | |
| N4 | 0.37671 (17) | −0.1997 (2) | 0.79687 (15) | 0.0439 (6) | |
| O1 | 0.44300 (15) | −0.1385 (2) | 0.82761 (14) | 0.0564 (6) | |
| O2 | 0.38324 (17) | −0.2986 (2) | 0.79970 (15) | 0.0616 (7) | |
| C1 | −0.03818 (15) | −0.23849 (16) | 0.47479 (13) | 0.0161 (4) | |
| C2 | −0.14203 (15) | −0.23050 (17) | 0.47355 (14) | 0.0170 (4) | |
| C3 | −0.19067 (15) | −0.13424 (17) | 0.48748 (14) | 0.0164 (4) | |
| C4 | −0.29731 (16) | −0.12384 (18) | 0.48996 (15) | 0.0218 (5) | |
| H4 | −0.3456 | −0.1796 | 0.4797 | 0.026* | |
| C5 | −0.31655 (16) | −0.02085 (18) | 0.50949 (15) | 0.0215 (5) | |
| H5 | −0.3805 | 0.0090 | 0.5176 | 0.026* | |
| C6 | −0.22209 (15) | 0.03581 (17) | 0.51590 (14) | 0.0160 (4) | |
| C7 | −0.21196 (15) | 0.14533 (17) | 0.53055 (14) | 0.0168 (4) | |
| C8 | −0.12188 (15) | 0.19990 (17) | 0.52819 (14) | 0.0163 (4) | |
| C9 | −0.11209 (16) | 0.31445 (17) | 0.53702 (15) | 0.0206 (5) | |
| H9 | −0.1649 | 0.3642 | 0.5434 | 0.025* | |
| C10 | −0.01374 (16) | 0.33815 (17) | 0.53458 (15) | 0.0200 (5) | |
| H10 | 0.0156 | 0.4077 | 0.5384 | 0.024* | |
| C11 | −0.20377 (15) | −0.32921 (17) | 0.45060 (15) | 0.0188 (4) | |

| | | | | | |
|---|---|---|---|---|---|
| C12 | −0.25842 (16) | −0.38074 (18) | 0.51311 (16) | 0.0236 (5) | |
| H12 | −0.2578 | −0.3531 | 0.5726 | 0.028* | |
| C13 | −0.31392 (17) | −0.47253 (19) | 0.48862 (19) | 0.0305 (6) | |
| H13 | −0.3504 | −0.5076 | 0.5318 | 0.037* | |
| C14 | −0.31641 (18) | −0.51302 (19) | 0.40228 (19) | 0.0321 (6) | |
| H14 | −0.3542 | −0.5759 | 0.3861 | 0.038* | |
| C15 | −0.26382 (18) | −0.46183 (19) | 0.33937 (18) | 0.0313 (6) | |
| H15 | −0.2661 | −0.4890 | 0.2796 | 0.038* | |
| C16 | −0.20733 (17) | −0.37009 (18) | 0.36355 (16) | 0.0253 (5) | |
| H16 | −0.1710 | −0.3353 | 0.3201 | 0.030* | |
| C17 | −0.30262 (15) | 0.20696 (16) | 0.55320 (14) | 0.0172 (4) | |
| C18 | −0.38252 (15) | 0.22896 (18) | 0.48905 (15) | 0.0203 (5) | |
| H18 | −0.3799 | 0.2061 | 0.4285 | 0.024* | |
| C19 | −0.46643 (16) | 0.28433 (18) | 0.51305 (16) | 0.0232 (5) | |
| H19 | −0.5203 | 0.3001 | 0.4685 | 0.028* | |
| C20 | −0.47187 (16) | 0.31632 (19) | 0.60080 (17) | 0.0267 (5) | |
| H20 | −0.5298 | 0.3531 | 0.6171 | 0.032* | |
| C21 | −0.39250 (18) | 0.2947 (2) | 0.66542 (17) | 0.0313 (6) | |
| H21 | −0.3961 | 0.3163 | 0.7262 | 0.038* | |
| C22 | −0.30775 (17) | 0.24141 (19) | 0.64141 (16) | 0.0262 (5) | |
| H22 | −0.2528 | 0.2284 | 0.6856 | 0.031* | |
| C23 | 0.10649 (15) | −0.06513 (17) | 0.67693 (13) | 0.0179 (4) | |
| C24 | 0.11492 (17) | −0.17626 (19) | 0.68680 (15) | 0.0232 (5) | |
| H24 | 0.0600 | −0.2215 | 0.6668 | 0.028* | |
| C25 | 0.20399 (19) | −0.2201 (2) | 0.72605 (16) | 0.0311 (6) | |
| H25 | 0.2110 | −0.2957 | 0.7331 | 0.037* | |
| C26 | 0.28217 (18) | −0.1523 (2) | 0.75473 (15) | 0.0307 (6) | |
| C27 | 0.27532 (17) | −0.0420 (2) | 0.74682 (16) | 0.0304 (6) | |
| H27 | 0.3302 | 0.0028 | 0.7679 | 0.036* | |
| C28 | 0.18596 (17) | 0.00184 (19) | 0.70711 (15) | 0.0237 (5) | |
| H28 | 0.1793 | 0.0775 | 0.7006 | 0.028* | |
| Cl2 | 0.0000 | 0.19408 (6) | 0.7500 | 0.02607 (19) | |
| Cl1 | −0.07442 (8) | 0.55949 (7) | 0.67168 (6) | 0.0712 (3) | |
| C29 | 0.0000 | 0.4862 (4) | 0.7500 | 0.0670 (15) | |
| H29A | −0.0441 | 0.4391 | 0.7825 | 0.080* | 0.50 |
| H29B | 0.0441 | 0.4391 | 0.7175 | 0.080* | 0.50 |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Co1 | 0.01021 (19) | 0.0130 (2) | 0.0136 (2) | 0.00020 (14) | 0.00090 (14) | −0.00036 (15) |
| N1 | 0.0125 (8) | 0.0149 (9) | 0.0149 (9) | −0.0002 (7) | 0.0015 (6) | 0.0006 (7) |
| N2 | 0.0136 (8) | 0.0149 (9) | 0.0170 (9) | 0.0001 (7) | 0.0018 (7) | −0.0012 (7) |
| N3 | 0.0151 (9) | 0.0171 (10) | 0.0164 (9) | −0.0001 (7) | 0.0007 (7) | 0.0000 (7) |
| N4 | 0.0283 (13) | 0.078 (2) | 0.0256 (12) | 0.0227 (13) | 0.0045 (10) | 0.0145 (12) |
| O1 | 0.0248 (10) | 0.106 (2) | 0.0370 (12) | 0.0146 (12) | −0.0023 (9) | 0.0107 (12) |
| O2 | 0.0546 (14) | 0.0739 (18) | 0.0554 (14) | 0.0394 (12) | 0.0005 (11) | 0.0199 (12) |
| C1 | 0.0178 (10) | 0.0154 (10) | 0.0151 (10) | −0.0008 (8) | 0.0015 (8) | 0.0008 (8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2 | 0.0158 (10) | 0.0172 (11) | 0.0177 (11) | −0.0016 (8) | 0.0011 (8) | 0.0009 (8) |
| C3 | 0.0161 (10) | 0.0174 (11) | 0.0157 (10) | −0.0028 (8) | 0.0018 (8) | 0.0005 (8) |
| C4 | 0.0148 (10) | 0.0199 (12) | 0.0306 (13) | −0.0030 (9) | 0.0020 (9) | −0.0009 (9) |
| C5 | 0.0123 (10) | 0.0228 (12) | 0.0298 (12) | −0.0004 (8) | 0.0043 (9) | −0.0022 (9) |
| C6 | 0.0127 (10) | 0.0194 (11) | 0.0160 (10) | 0.0007 (8) | 0.0021 (8) | −0.0006 (8) |
| C7 | 0.0144 (10) | 0.0195 (11) | 0.0163 (10) | 0.0031 (8) | −0.0002 (8) | −0.0012 (8) |
| C8 | 0.0159 (10) | 0.0173 (11) | 0.0154 (10) | 0.0020 (8) | 0.0005 (8) | −0.0005 (8) |
| C9 | 0.0177 (10) | 0.0179 (11) | 0.0257 (12) | 0.0038 (9) | 0.0000 (9) | −0.0002 (9) |
| C10 | 0.0212 (11) | 0.0136 (11) | 0.0250 (12) | −0.0002 (8) | 0.0002 (9) | 0.0009 (9) |
| C11 | 0.0122 (10) | 0.0149 (11) | 0.0289 (12) | 0.0021 (8) | 0.0003 (8) | 0.0015 (9) |
| C12 | 0.0198 (11) | 0.0193 (12) | 0.0317 (13) | 0.0011 (9) | 0.0025 (9) | 0.0035 (9) |
| C13 | 0.0183 (11) | 0.0211 (12) | 0.0517 (17) | −0.0021 (9) | 0.0024 (11) | 0.0121 (11) |
| C14 | 0.0210 (12) | 0.0164 (12) | 0.0570 (18) | −0.0022 (9) | −0.0058 (11) | 0.0011 (11) |
| C15 | 0.0285 (13) | 0.0226 (13) | 0.0416 (15) | 0.0005 (10) | −0.0034 (11) | −0.0092 (11) |
| C16 | 0.0227 (11) | 0.0231 (12) | 0.0300 (13) | −0.0020 (9) | 0.0017 (9) | −0.0003 (10) |
| C17 | 0.0134 (10) | 0.0139 (10) | 0.0245 (11) | −0.0003 (8) | 0.0031 (8) | −0.0007 (8) |
| C18 | 0.0157 (10) | 0.0212 (11) | 0.0241 (12) | −0.0018 (9) | 0.0018 (8) | −0.0025 (9) |
| C19 | 0.0140 (10) | 0.0232 (12) | 0.0319 (13) | −0.0010 (9) | 0.0000 (9) | 0.0026 (10) |
| C20 | 0.0172 (11) | 0.0263 (13) | 0.0377 (14) | 0.0061 (9) | 0.0089 (10) | −0.0027 (10) |
| C21 | 0.0320 (13) | 0.0371 (15) | 0.0256 (13) | 0.0085 (11) | 0.0073 (10) | −0.0076 (11) |
| C22 | 0.0220 (11) | 0.0306 (13) | 0.0253 (12) | 0.0069 (10) | −0.0012 (9) | −0.0026 (10) |
| C23 | 0.0188 (10) | 0.0233 (12) | 0.0116 (10) | 0.0043 (9) | 0.0020 (8) | 0.0021 (8) |
| C24 | 0.0265 (12) | 0.0240 (12) | 0.0190 (11) | 0.0021 (9) | 0.0020 (9) | 0.0023 (9) |
| C25 | 0.0378 (14) | 0.0310 (14) | 0.0251 (13) | 0.0130 (11) | 0.0061 (10) | 0.0081 (10) |
| C26 | 0.0245 (12) | 0.0509 (17) | 0.0165 (12) | 0.0146 (11) | 0.0011 (9) | 0.0084 (11) |
| C27 | 0.0204 (12) | 0.0479 (16) | 0.0222 (12) | −0.0027 (11) | −0.0011 (9) | 0.0022 (11) |
| C28 | 0.0233 (11) | 0.0276 (12) | 0.0197 (11) | −0.0018 (9) | −0.0009 (9) | 0.0004 (9) |
| Cl2 | 0.0409 (5) | 0.0192 (4) | 0.0185 (4) | 0.000 | 0.0051 (3) | 0.000 |
| Cl1 | 0.1153 (8) | 0.0558 (5) | 0.0398 (5) | 0.0400 (5) | −0.0065 (5) | −0.0044 (4) |
| C29 | 0.059 (3) | 0.045 (3) | 0.089 (4) | 0.000 | −0.033 (3) | 0.000 |

*Geometric parameters (Å, º)*

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| Co1—N1$^{i}$ | 1.9802 (17) | C11—C12 | 1.394 (3) |
| Co1—N1 | 1.9802 (17) | C12—C13 | 1.391 (3) |
| Co1—N2$^{i}$ | 1.9863 (16) | C12—H12 | 0.9500 |
| Co1—N2 | 1.9863 (16) | C13—C14 | 1.379 (4) |
| Co1—N3$^{i}$ | 2.0060 (17) | C13—H13 | 0.9500 |
| Co1—N3 | 2.0060 (17) | C14—C15 | 1.380 (4) |
| N1—C1 | 1.382 (3) | C14—H14 | 0.9500 |
| N1—C8$^{i}$ | 1.384 (3) | C15—C16 | 1.396 (3) |
| N2—C3 | 1.386 (3) | C15—H15 | 0.9500 |
| N2—C6 | 1.388 (3) | C16—H16 | 0.9500 |
| N3—C23 | 1.437 (3) | C17—C22 | 1.390 (3) |
| N3—H3A | 0.86 (3) | C17—C18 | 1.388 (3) |
| N3—H3B | 0.87 (3) | C18—C19 | 1.392 (3) |
| N4—O1 | 1.223 (3) | C18—H18 | 0.9500 |
| N4—O2 | 1.234 (4) | C19—C20 | 1.375 (3) |

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| N4—C26 | 1.477 (3) | C19—H19 | 0.9500 |
| C1—C2 | 1.389 (3) | C20—C21 | 1.387 (3) |
| C1—C10$^{i}$ | 1.435 (3) | C20—H20 | 0.9500 |
| C2—C3 | 1.388 (3) | C21—C22 | 1.388 (3) |
| C2—C11 | 1.500 (3) | C21—H21 | 0.9500 |
| C3—C4 | 1.434 (3) | C22—H22 | 0.9500 |
| C4—C5 | 1.345 (3) | C23—C28 | 1.389 (3) |
| C4—H4 | 0.9500 | C23—C24 | 1.395 (3) |
| C5—C6 | 1.440 (3) | C24—C25 | 1.385 (3) |
| C5—H5 | 0.9500 | C24—H24 | 0.9500 |
| C6—C7 | 1.385 (3) | C25—C26 | 1.378 (4) |
| C7—C8 | 1.385 (3) | C25—H25 | 0.9500 |
| C7—C17 | 1.499 (3) | C26—C27 | 1.380 (4) |
| C8—N1$^{i}$ | 1.384 (3) | C27—C28 | 1.391 (3) |
| C8—C9 | 1.437 (3) | C27—H27 | 0.9500 |
| C9—C10 | 1.350 (3) | C28—H28 | 0.9500 |
| C9—H9 | 0.9500 | Cl1—C29 | 1.719 (3) |
| C10—C1$^{i}$ | 1.435 (3) | C29—Cl1$^{ii}$ | 1.719 (3) |
| C10—H10 | 0.9500 | C29—H29A | 0.9900 |
| C11—C16 | 1.389 (3) | C29—H29B | 0.9900 |

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|---|---|---|---|
| N1$^{i}$—Co1—N1 | 180.0 | C16—C11—C12 | 118.8 (2) |
| N1$^{i}$—Co1—N2$^{i}$ | 89.69 (7) | C16—C11—C2 | 118.72 (19) |
| N1—Co1—N2$^{i}$ | 90.31 (7) | C12—C11—C2 | 122.5 (2) |
| N1$^{i}$—Co1—N2 | 90.31 (7) | C13—C12—C11 | 120.2 (2) |
| N1—Co1—N2 | 89.69 (7) | C13—C12—H12 | 119.9 |
| N2$^{i}$—Co1—N2 | 180.0 | C11—C12—H12 | 119.9 |
| N1$^{i}$—Co1—N3$^{i}$ | 91.14 (7) | C14—C13—C12 | 120.6 (2) |
| N1—Co1—N3$^{i}$ | 88.86 (7) | C14—C13—H13 | 119.7 |
| N2$^{i}$—Co1—N3$^{i}$ | 87.66 (7) | C12—C13—H13 | 119.7 |
| N2—Co1—N3$^{i}$ | 92.34 (7) | C13—C14—C15 | 119.8 (2) |
| N1$^{i}$—Co1—N3 | 88.86 (7) | C13—C14—H14 | 120.1 |
| N1—Co1—N3 | 91.14 (7) | C15—C14—H14 | 120.1 |
| N2$^{i}$—Co1—N3 | 92.34 (7) | C14—C15—C16 | 120.0 (2) |
| N2—Co1—N3 | 87.66 (7) | C14—C15—H15 | 120.0 |
| N3$^{i}$—Co1—N3 | 180.000 (15) | C16—C15—H15 | 120.0 |
| C1—N1—C8$^{i}$ | 105.06 (16) | C11—C16—C15 | 120.6 (2) |
| C1—N1—Co1 | 127.70 (13) | C11—C16—H16 | 119.7 |
| C8$^{i}$—N1—Co1 | 127.22 (14) | C15—C16—H16 | 119.7 |
| C3—N2—C6 | 105.46 (16) | C22—C17—C18 | 118.96 (19) |
| C3—N2—Co1 | 127.49 (13) | C22—C17—C7 | 119.08 (19) |
| C6—N2—Co1 | 126.97 (14) | C18—C17—C7 | 121.95 (19) |
| C23—N3—Co1 | 119.10 (13) | C17—C18—C19 | 120.3 (2) |
| C23—N3—H3A | 110 (2) | C17—C18—H18 | 119.8 |
| Co1—N3—H3A | 100 (2) | C19—C18—H18 | 119.8 |
| C23—N3—H3B | 111 (2) | C20—C19—C18 | 120.4 (2) |
| Co1—N3—H3B | 105 (2) | C20—C19—H19 | 119.8 |
| H3A—N3—H3B | 113 (3) | C18—C19—H19 | 119.8 |

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| O1—N4—O2 | 124.2 (2) | C19—C20—C21 | 119.7 (2) |
| O1—N4—C26 | 117.9 (3) | C19—C20—H20 | 120.1 |
| O2—N4—C26 | 117.9 (3) | C21—C20—H20 | 120.1 |
| N1—C1—C2 | 126.09 (19) | C22—C21—C20 | 120.1 (2) |
| N1—C1—C10$^{i}$ | 110.37 (17) | C22—C21—H21 | 120.0 |
| C2—C1—C10$^{i}$ | 123.51 (19) | C20—C21—H21 | 120.0 |
| C3—C2—C1 | 122.76 (19) | C17—C22—C21 | 120.5 (2) |
| C3—C2—C11 | 119.10 (17) | C17—C22—H22 | 119.8 |
| C1—C2—C11 | 118.04 (18) | C21—C22—H22 | 119.8 |
| C2—C3—N2 | 125.91 (18) | C28—C23—C24 | 120.7 (2) |
| C2—C3—C4 | 124.20 (19) | C28—C23—N3 | 119.1 (2) |
| N2—C3—C4 | 109.87 (18) | C24—C23—N3 | 120.2 (2) |
| C5—C4—C3 | 107.63 (19) | C25—C24—C23 | 119.5 (2) |
| C5—C4—H4 | 126.2 | C25—C24—H24 | 120.2 |
| C3—C4—H4 | 126.2 | C23—C24—H24 | 120.2 |
| C4—C5—C6 | 107.25 (18) | C26—C25—C24 | 118.8 (2) |
| C4—C5—H5 | 126.4 | C26—C25—H25 | 120.6 |
| C6—C5—H5 | 126.4 | C24—C25—H25 | 120.6 |
| C7—C6—N2 | 125.92 (18) | C25—C26—C27 | 122.8 (2) |
| C7—C6—C5 | 124.32 (19) | C25—C26—N4 | 118.5 (2) |
| N2—C6—C5 | 109.74 (18) | C27—C26—N4 | 118.7 (2) |
| C6—C7—C8 | 123.40 (19) | C26—C27—C28 | 118.3 (2) |
| C6—C7—C17 | 118.07 (18) | C26—C27—H27 | 120.9 |
| C8—C7—C17 | 118.49 (19) | C28—C27—H27 | 120.9 |
| C7—C8—N1$^{i}$ | 126.01 (19) | C23—C28—C27 | 119.9 (2) |
| C7—C8—C9 | 123.79 (19) | C23—C28—H28 | 120.0 |
| N1$^{i}$—C8—C9 | 110.20 (18) | C27—C28—H28 | 120.0 |
| C10—C9—C8 | 107.13 (19) | Cl1$^{ii}$—C29—Cl1 | 115.8 (3) |
| C10—C9—H9 | 126.4 | Cl1$^{ii}$—C29—H29A | 108.3 |
| C8—C9—H9 | 126.4 | Cl1—C29—H29A | 108.3 |
| C9—C10—C1$^{i}$ | 107.11 (19) | Cl1$^{ii}$—C29—H29B | 108.3 |
| C9—C10—H10 | 126.4 | Cl1—C29—H29B | 108.3 |
| C1$^{i}$—C10—H10 | 126.4 | H29A—C29—H29B | 107.4 |

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| N1$^{i}$—Co1—N1—C1 | 32 (100) | C5—C6—C7—C8 | −173.8 (2) |
| N2$^{i}$—Co1—N1—C1 | −178.83 (17) | N2—C6—C7—C17 | −173.47 (19) |
| N2—Co1—N1—C1 | 1.17 (17) | C5—C6—C7—C17 | 8.3 (3) |
| N3$^{i}$—Co1—N1—C1 | −91.18 (17) | C6—C7—C8—N1$^{i}$ | −4.9 (3) |
| N3—Co1—N1—C1 | 88.82 (17) | C17—C7—C8—N1$^{i}$ | 172.92 (19) |
| N1$^{i}$—Co1—N1—C8$^{i}$ | −150 (100) | C6—C7—C8—C9 | 175.5 (2) |
| N2$^{i}$—Co1—N1—C8$^{i}$ | −1.01 (17) | C17—C7—C8—C9 | −6.7 (3) |
| N2—Co1—N1—C8$^{i}$ | 178.99 (17) | C7—C8—C9—C10 | 178.0 (2) |
| N3$^{i}$—Co1—N1—C8$^{i}$ | 86.64 (17) | N1$^{i}$—C8—C9—C10 | −1.7 (2) |
| N3—Co1—N1—C8$^{i}$ | −93.36 (17) | C8—C9—C10—C1$^{i}$ | −0.6 (2) |
| N1$^{i}$—Co1—N2—C3 | 174.74 (17) | C3—C2—C11—C16 | 108.9 (2) |
| N1—Co1—N2—C3 | −5.26 (17) | C1—C2—C11—C16 | −67.5 (3) |
| N2$^{i}$—Co1—N2—C3 | −10 (11) | C3—C2—C11—C12 | −70.5 (3) |
| N3$^{i}$—Co1—N2—C3 | 83.59 (17) | C1—C2—C11—C12 | 113.2 (2) |

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| N3—Co1—N2—C3 | −96.41 (17) | C16—C11—C12—C13 | 1.1 (3) |
| N1$^{i}$—Co1—N2—C6 | −1.48 (17) | C2—C11—C12—C13 | −179.5 (2) |
| N1—Co1—N2—C6 | 178.52 (17) | C11—C12—C13—C14 | −0.6 (3) |
| N2$^{i}$—Co1—N2—C6 | 173 (11) | C12—C13—C14—C15 | −0.3 (4) |
| N3$^{i}$—Co1—N2—C6 | −92.63 (17) | C13—C14—C15—C16 | 0.8 (4) |
| N3—Co1—N2—C6 | 87.37 (17) | C12—C11—C16—C15 | −0.7 (3) |
| N1$^{i}$—Co1—N3—C23 | −125.89 (16) | C2—C11—C16—C15 | 180.0 (2) |
| N1—Co1—N3—C23 | 54.11 (16) | C14—C15—C16—C11 | −0.3 (4) |
| N2$^{i}$—Co1—N3—C23 | −36.25 (16) | C6—C7—C17—C22 | 105.9 (2) |
| N2—Co1—N3—C23 | 143.75 (16) | C8—C7—C17—C22 | −72.1 (3) |
| N3$^{i}$—Co1—N3—C23 | 88 (33) | C6—C7—C17—C18 | −72.9 (3) |
| C8$^{i}$—N1—C1—C2 | −174.5 (2) | C8—C7—C17—C18 | 109.1 (2) |
| Co1—N1—C1—C2 | 3.7 (3) | C22—C17—C18—C19 | −0.2 (3) |
| C8$^{i}$—N1—C1—C10$^{i}$ | 3.7 (2) | C7—C17—C18—C19 | 178.6 (2) |
| Co1—N1—C1—C10$^{i}$ | −178.12 (14) | C17—C18—C19—C20 | −1.1 (3) |
| N1—C1—C2—C3 | −5.6 (3) | C18—C19—C20—C21 | 1.0 (4) |
| C10$^{i}$—C1—C2—C3 | 176.5 (2) | C19—C20—C21—C22 | 0.3 (4) |
| N1—C1—C2—C11 | 170.66 (19) | C18—C17—C22—C21 | 1.6 (3) |
| C10$^{i}$—C1—C2—C11 | −7.3 (3) | C7—C17—C22—C21 | −177.3 (2) |
| C1—C2—C3—N2 | 0.9 (3) | C20—C21—C22—C17 | −1.6 (4) |
| C11—C2—C3—N2 | −175.24 (19) | Co1—N3—C23—C28 | 91.4 (2) |
| C1—C2—C3—C4 | −177.6 (2) | Co1—N3—C23—C24 | −88.0 (2) |
| C11—C2—C3—C4 | 6.2 (3) | C28—C23—C24—C25 | −0.8 (3) |
| C6—N2—C3—C2 | −178.0 (2) | N3—C23—C24—C25 | 178.53 (19) |
| Co1—N2—C3—C2 | 5.2 (3) | C23—C24—C25—C26 | 0.2 (3) |
| C6—N2—C3—C4 | 0.7 (2) | C24—C25—C26—C27 | 0.6 (4) |
| Co1—N2—C3—C4 | −176.13 (14) | C24—C25—C26—N4 | 179.7 (2) |
| C2—C3—C4—C5 | 176.8 (2) | O1—N4—C26—C25 | −175.1 (2) |
| N2—C3—C4—C5 | −2.0 (3) | O2—N4—C26—C25 | 4.1 (3) |
| C3—C4—C5—C6 | 2.3 (3) | O1—N4—C26—C27 | 4.0 (3) |
| C3—N2—C6—C7 | −177.7 (2) | O2—N4—C26—C27 | −176.8 (2) |
| Co1—N2—C6—C7 | −0.8 (3) | C25—C26—C27—C28 | −0.9 (4) |
| C3—N2—C6—C5 | 0.7 (2) | N4—C26—C27—C28 | −179.9 (2) |
| Co1—N2—C6—C5 | 177.58 (14) | C24—C23—C28—C27 | 0.6 (3) |
| C4—C5—C6—C7 | 176.5 (2) | N3—C23—C28—C27 | −178.75 (19) |
| C4—C5—C6—N2 | −1.9 (3) | C26—C27—C28—C23 | 0.2 (3) |
| N2—C6—C7—C8 | 4.4 (3) | | |

Symmetry codes: (i) −*x*, −*y*, −*z*+1; (ii) −*x*, *y*, −*z*+3/2.

*Hydrogen-bond geometry (Å, º)*

Cg7 and Cg8 are the centroids of the C11/C12–C16 and C17/C18–C22 rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3*B*···Cl2 | 0.88 (4) | 2.32 (3) | 3.174 (2) | 164 (3) |
| C13—H13···*Cg*8$^{iii}$ | 0.95 | 3.00 | 3.723 (3) | 134 |
| C20—H20···*Cg*7$^{iv}$ | 0.95 | 2.94 | 3.788 (2) | 150 |

Symmetry codes: (iii) *x*, *y*−1, *z*; (iv) −*x*−1, −*y*, −*z*+1.