Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Poly[tris(μ-di-4-pyridylamine-κ²*N*:*N*′)-tetrathiocyanato-κ⁴*N*-dicobalt(II)]

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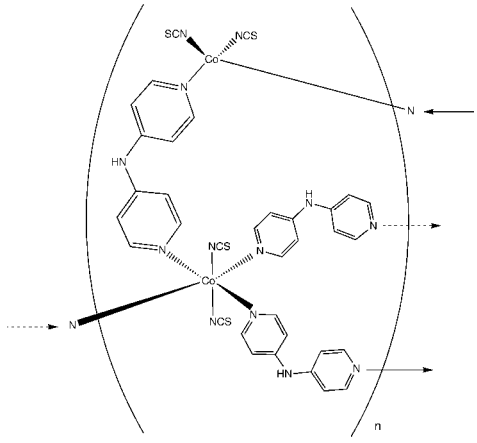
Received 4 October 2007; accepted 12 October 2007

Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.011 Å; R factor = 0.066; wR factor = 0.168; data-to-parameter ratio = 17.0.

In the title compound, $[Co_2(NCS)_4(C_{10}H_9N_3)_3]_n$, 4,4′-dipyridylamine (dpa) ligands link octahedrally and tetrahedrally coordinated Co^{II} atoms with pendant isothiocyanate ligands into $[Co_2(NCS)_4(dpa)_3]_n$ chains that propagate along the *c* axis. These form sinusoidal pseudo-layers coincident with the *ac* plane via N—H···S hydrogen bonding.

Related literature

For literature on complexes of 4,4′-dipyridylamine, see: Mallika Krishnan *et al.* (2007); Montney *et al.* (2007). For the synthesis of 4,4′-dipyridylamine, see Zapf *et al.* (1998). For the radii of cobalt ions, see: Shannon (1976).



Experimental

Crystal data

$[Co_2(NCS)_4(C_{10}H_9N_3)_3]$
M_r = 863.79
Orthorhombic, $P2_12_12_1$
a = 7.9245 (2) Å
b = 21.7051 (5) Å
c = 22.8134 (5) Å
V = 3923.95 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.10 mm^{-1}
T = 173 (2) K
0.24 × 0.16 × 0.04 mm

Data collection

Bruker APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.769, T_{max} = 0.957
21566 measured reflections
8215 independent reflections
3888 reflections with $I > 2\sigma(I)$
R_{int} = 0.087

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.168
S = 1.00
8215 reflections
484 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}
Absolute structure: Flack (1983), with 4324 Friedel pairs
Flack parameter: 0.07 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···S1^{i}	0.89 (2)	2.59 (5)	3.366 (7)	147 (7)
N5—H5A···S3^{ii}	0.88	2.55	3.355 (7)	153
N8—H8N···S4^{iii}	0.88 (2)	2.53 (3)	3.382 (7)	162 (7)

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

Data collection: *COSMO* (Bruker, 2006); cell refinement: *APEX2* (Bruker, 2006); data reduction: *SAINT* (Bruker, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalMaker* (Palmer, 2005); software used to prepare material for publication: *SHELXL97*.

The authors gratefully acknowledge Michigan State University for the funding of this work. WRK thanks the MSU Freshman Honors Chemistry program for his participation in the research.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2333).

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supplementary materials

Acta Cryst. (2007). E**63**, m2745 [**doi:10.1107/S160053680705057X**]

Poly[tris(μ-di-4-pyridylamine-κ^2N:N')tetrathiocyanato-κ^4N-dicobalt(II)]

W. R. Knapp, D. P. Martin and R. L. LaDuca

Comment

One of the most common tethering ligands for the generation of functional coordination polymers is 4,4'-bipyridine. By comparison, similar materials based on 4,4'-dipyridylamine (dpa) are much less common (Montney *et al.*, 2007). The title compound was prepared during continued attempts to investigate the effect of the counteranion on the structure of dpa-containing cobalt coordination polymers (Mallika Krishnan *et al.*, 2007).

The title compound crystallizes in the non-centrosymmetric space group $P2_12_12_1$ with an asymmetric unit (Fig. 1) comprised of two cobalt atoms, four ligated *N*-bound isothiocyanate anions and three crystallographically distinct dpa ligands. The two crystallographically distinct cobalt atoms have differing coordination geometries, with Co1 displaying an octahedral [CoN_6] arrangement and Co2 possessing a tetrahedral [CoN_4] coordination sphere. The longer bond distances about the octahedrally coordinated Co atom are consistent with the well known trend towards larger ionic radii for higher coordination numbers (Shannon, 1976).

Propagation of the asymmetric unit *via* the 2_1 screw axis coincident with the *c* crystal direction generates a 1-D coordination polymeric ribbon with a formulation of [$Co_2(SCN)_4(dpa)_3$] (Fig. 2). Each octahedrally coordinated Co1 atom connects to two other neighboring Co1 atoms and two tetrahedrally coordinated Co2 atoms through tethering dpa ligands. In turn, each Co2 atom is linked to two neighboring Co1 atoms in the same fashion. The Co1–Co1 distance measures 11.409 (1) Å, while the two distinct through-ligand Co1–Co2 distances are 11.160 (1) Å and 11.234 (1) Å.

The 1-D ribbon motifs construct sinusoidal *pseudo* 2-D layers coincident with the *ac* crystal planess *via* N—H···S hydrogen bonding between dpa amines and S2 atoms of isothiocyanate ligands bound to Co2, within the next-nearest neighbor ribbon motif (Fig. 3). Neighboring ribbons within the *pseudo* 2-D layer do not engage in hydrogen bonding. The closest Co—Co distance between neighboring ribbons within the same pseudo 2-D layer is 7.924 (1) Å, defining the *a* lattice parameter. These layers in turn link together *via* three different N–H···S hydrogen bonding interactions to afford the full *pseudo* 3-D structure of the title compound.

Experimental

Cobalt thiocyanate was obtained commercially. 4,4'-Dipyridylamine (dpa) was prepared *via* a published procedure (Zapf *et al.*, 1998). Cobalt thiocyanate (58 mg, 0.33 mmol) and dpa (57 mg, 0.33 mmol) were added to 10 ml water in a 23 ml a Teflon-lined Parr acid digestion bomb. The mixture was then heated under autogenous pressure at 423 K for 48 h, whereupon it was cooled slowly to 293 K. Dark blue crystals (78 mg, 0.27 mmol, 82% yield base on dpa) of the title compound were produced.

Refinement

All H atoms bound to C atoms were placed in calculated positions, with C—H = 0.95 (2) Å and refined in riding mode with U_{iso} = 1.2U_{eq}(C). Two of the H atoms bound to N within dpa ligands were found *via* Fourier difference map, restrained with N—H = 0.88 (2) Å, and refined with U_{iso} = 1.2U_{eq}(N). The third dpa amine H atom was placed in a calculated position, with N—H = 0.88 (2) Å and refined in riding mode with U_{iso} = 1.2U_{eq}(N).

Figures

Fig. 1. Asymmetric unit of the title compound, showing 50% probability ellipsoids and partial atom numbering scheme. H atom positions are shown as gray sticks. Color codes: light-blue N, yellow S, black C, dark blue Co.

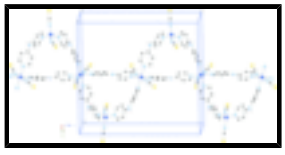


Fig. 2. A single $[Co_2(NCS)_4(dpa)_3]_n$ chain viewed down *c*.

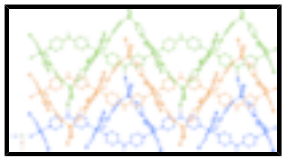


Fig. 3. A *pseudo* two-dimensional layer formed by N—H···S hydrogen bonding interactions (shown as dashed lines) between next-nearest neighbor $[Co_2(NCS)_4(dpa)_3]_n$ chains.

Poly[tris(μ-di-4-pyridylamine-$\kappa^2N:N'$)tetrathiocyanato-κ^4Ndicobalt(II)]

Crystal data

$[Co_2(NCS)_4(C_{10}H_9N_3)_3]$	D_x = 1.462 Mg m^{-3}
M_r = 863.79	Mo *K*α radiation λ = 0.71073 Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 21566 reflections
a = 7.9245 (2) Å	θ = 1.3–27.5°
b = 21.7051 (5) Å	μ = 1.10 mm^{-1}
c = 22.8134 (5) Å	*T* = 173 (2) K
V = 3923.95 (16) Å^3	Plate, blue
Z = 4	0.24 × 0.16 × 0.04 mm
F_{000} = 1760	

Data collection

Bruker APEXII diffractometer	8215 independent reflections
Radiation source: fine-focus sealed tube	3888 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.087
T = 173(2) K	θ_{max} = 27.5°
ω/φ scans	θ_{min} = 1.3°

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.769, T_{max} = 0.957
21566 measured reflections

h = −10→10
k = −23→27
l = −29→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.168
S = 1.00
8215 reflections
484 parameters
2 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
$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}
Extinction correction: none
Absolute structure: Flack (1983), with 4324 Friedel pairs
Flack parameter: 0.07 (3)

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 $F^2 > 2\sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Co1	0.72244 (11)	0.50638 (5)	0.98492 (4)	0.0355 (3)
Co2	−0.19707 (13)	0.77752 (6)	1.25735 (5)	0.0601 (4)
S1	0.3044 (3)	0.36061 (11)	1.04968 (12)	0.0650 (7)
S2	−0.5888 (6)	0.6243 (2)	1.22905 (16)	0.1580 (19)
S3	1.1421 (3)	0.63571 (12)	0.89090 (10)	0.0585 (7)
S4	−0.4974 (3)	0.95834 (18)	1.28237 (18)	0.1299 (16)
N1	1.5164 (8)	0.2278 (4)	0.8190 (3)	0.059 (2)
N2	1.0726 (9)	0.2531 (3)	0.9131 (3)	0.0503 (19)
H2N	1.023 (9)	0.2168 (19)	0.909 (3)	0.060*
N3	0.8455 (7)	0.4207 (3)	0.9616 (2)	0.0360 (16)
N4	0.6024 (7)	0.5921 (3)	1.0081 (3)	0.0397 (16)

N5	0.3715 (8)	0.7490 (3)	1.0815 (3)	0.054 (2)
H5A	0.4276	0.7837	1.0770	0.064*
N6	−0.0573 (8)	0.7694 (4)	1.1858 (3)	0.0530 (19)
N7	0.5961 (6)	0.5045 (3)	0.8987 (2)	0.0332 (15)
N8	0.3962 (7)	0.4829 (4)	0.7301 (3)	0.057 (2)
H8N	0.287 (3)	0.491 (4)	0.731 (3)	0.069*
N9	0.6494 (7)	0.4914 (3)	0.5685 (2)	0.0378 (16)
N10	0.9299 (8)	0.5549 (3)	0.9507 (3)	0.0414 (17)
N11	0.5209 (8)	0.4570 (3)	1.0222 (3)	0.0441 (17)
N12	−0.3452 (10)	0.7073 (4)	1.2577 (4)	0.080 (3)
N13	−0.3002 (10)	0.8556 (4)	1.2636 (3)	0.074 (2)
C1	1.3997 (12)	0.1836 (5)	0.8223 (4)	0.066 (3)
H1	1.4220	0.1459	0.8026	0.080*
C2	1.2493 (11)	0.1886 (4)	0.8523 (3)	0.056 (2)
H2	1.1687	0.1562	0.8527	0.068*
C3	1.2216 (10)	0.2452 (4)	0.8826 (3)	0.047 (2)
C4	1.3462 (10)	0.2899 (4)	0.8809 (3)	0.050 (2)
H4	1.3341	0.3273	0.9021	0.059*
C5	1.4861 (11)	0.2789 (5)	0.8482 (4)	0.063 (3)
H5	1.5686	0.3106	0.8463	0.075*
C6	0.9431 (10)	0.4146 (4)	0.9130 (3)	0.043 (2)
H6	0.9600	0.4506	0.8900	0.052*
C7	1.0190 (10)	0.3622 (4)	0.8941 (4)	0.047 (2)
H7	1.0827	0.3615	0.8589	0.057*
C8	1.0000 (9)	0.3095 (4)	0.9282 (3)	0.038 (2)
C9	0.8950 (9)	0.3134 (4)	0.9768 (3)	0.045 (2)
H9	0.8728	0.2778	0.9997	0.054*
C10	0.8250 (9)	0.3675 (4)	0.9915 (3)	0.048 (2)
H10	0.7558	0.3684	1.0255	0.058*
C11	0.6909 (10)	0.6408 (4)	1.0275 (3)	0.046 (2)
H11	0.8104	0.6396	1.0243	0.055*
C12	0.6186 (10)	0.6920 (4)	1.0517 (3)	0.051 (2)
H12	0.6877	0.7248	1.0653	0.061*
C13	0.4435 (10)	0.6962 (4)	1.0565 (3)	0.048 (2)
C14	0.3538 (11)	0.6476 (4)	1.0330 (4)	0.058 (3)
H14	0.2340	0.6489	1.0330	0.069*
C15	0.4360 (10)	0.5969 (4)	1.0094 (4)	0.053 (2)
H15	0.3702	0.5644	0.9935	0.064*
C16	0.0310 (10)	0.8176 (4)	1.1639 (3)	0.048 (2)
H16	−0.0047	0.8580	1.1738	0.058*
C17	0.1659 (9)	0.8114 (4)	1.1290 (3)	0.048 (2)
H17	0.2243	0.8469	1.1154	0.058*
C18	0.2204 (11)	0.7526 (4)	1.1128 (3)	0.052 (2)
C19	0.1268 (11)	0.7033 (4)	1.1330 (4)	0.069 (3)
H19	0.1571	0.6624	1.1224	0.082*
C20	−0.0092 (12)	0.7135 (5)	1.1683 (4)	0.065 (3)
H20	−0.0730	0.6790	1.1811	0.078*
C21	0.4854 (9)	0.5064 (4)	0.5748 (3)	0.042 (2)
H21	0.4260	0.5194	0.5408	0.051*

C22	0.3991 (9)	0.5044 (4)	0.6259 (3)	0.055 (2)
H22	0.2839	0.5164	0.6272	0.066*
C23	0.4817 (8)	0.4843 (4)	0.6772 (3)	0.042 (2)
C24	0.6493 (9)	0.4671 (4)	0.6714 (3)	0.0362 (19)
H24	0.7102	0.4514	0.7040	0.043*
C25	0.7255 (9)	0.4729 (3)	0.6180 (3)	0.041 (2)
H25	0.8421	0.4631	0.6157	0.049*
C26	0.4431 (9)	0.4811 (4)	0.8876 (3)	0.046 (2)
H26	0.3776	0.4683	0.9202	0.055*
C27	0.3730 (10)	0.4740 (4)	0.8332 (3)	0.055 (3)
H27	0.2634	0.4568	0.8290	0.066*
C28	0.4634 (9)	0.4922 (4)	0.7844 (3)	0.046 (2)
C29	0.6197 (9)	0.5176 (4)	0.7943 (3)	0.046 (2)
H29	0.6863	0.5312	0.7622	0.055*
C30	0.6785 (9)	0.5234 (3)	0.8494 (3)	0.038 (2)
H30	0.7860	0.5421	0.8543	0.045*
C31	1.0209 (9)	0.5889 (4)	0.9264 (3)	0.035 (2)
C32	0.4329 (9)	0.4177 (4)	1.0336 (3)	0.039 (2)
C33	−0.4444 (13)	0.6725 (5)	1.2456 (4)	0.068 (3)
C34	−0.3839 (11)	0.8982 (5)	1.2716 (4)	0.072 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0386 (5)	0.0427 (7)	0.0253 (5)	0.0015 (5)	0.0051 (5)	−0.0005 (5)
Co2	0.0419 (6)	0.0872 (10)	0.0514 (7)	0.0058 (7)	−0.0016 (6)	0.0045 (7)
S1	0.0450 (11)	0.0500 (16)	0.1002 (18)	−0.0023 (12)	−0.0013 (14)	0.0113 (15)
S2	0.189 (4)	0.178 (4)	0.107 (3)	−0.109 (4)	−0.042 (3)	0.019 (3)
S3	0.0443 (11)	0.0676 (18)	0.0634 (15)	−0.0119 (12)	0.0110 (12)	0.0117 (14)
S4	0.0483 (15)	0.141 (3)	0.200 (4)	0.0435 (18)	−0.040 (2)	−0.094 (3)
N1	0.048 (4)	0.063 (6)	0.066 (5)	0.005 (4)	0.006 (4)	−0.013 (5)
N2	0.060 (4)	0.028 (5)	0.063 (5)	0.000 (4)	0.016 (4)	−0.002 (4)
N3	0.038 (3)	0.037 (4)	0.032 (3)	0.003 (3)	0.002 (3)	0.002 (3)
N4	0.035 (3)	0.052 (5)	0.032 (4)	0.007 (3)	0.001 (3)	−0.006 (4)
N5	0.056 (4)	0.039 (5)	0.065 (5)	0.004 (4)	0.011 (4)	−0.012 (4)
N6	0.042 (4)	0.060 (6)	0.057 (5)	0.002 (4)	0.002 (4)	0.003 (5)
N7	0.037 (3)	0.034 (4)	0.029 (3)	0.001 (3)	0.003 (3)	−0.009 (3)
N8	0.036 (3)	0.105 (7)	0.031 (4)	−0.023 (4)	0.004 (3)	0.001 (4)
N9	0.034 (3)	0.050 (5)	0.029 (3)	0.004 (3)	−0.003 (3)	−0.005 (3)
N10	0.042 (4)	0.046 (5)	0.036 (4)	0.001 (3)	−0.005 (3)	−0.006 (4)
N11	0.045 (4)	0.052 (5)	0.035 (4)	0.001 (4)	0.001 (3)	−0.004 (4)
N12	0.072 (5)	0.097 (8)	0.071 (6)	−0.021 (5)	0.000 (5)	−0.001 (5)
N13	0.063 (4)	0.102 (7)	0.057 (5)	0.047 (5)	−0.003 (5)	−0.011 (5)
C1	0.067 (6)	0.058 (7)	0.074 (7)	0.003 (6)	0.027 (6)	−0.018 (6)
C2	0.069 (6)	0.048 (6)	0.052 (5)	0.008 (5)	0.015 (5)	0.000 (5)
C3	0.041 (4)	0.057 (6)	0.044 (5)	0.005 (5)	0.010 (4)	0.006 (5)
C4	0.051 (5)	0.058 (7)	0.039 (5)	0.014 (5)	0.007 (4)	−0.006 (5)
C5	0.053 (5)	0.060 (7)	0.075 (6)	−0.014 (5)	0.015 (5)	−0.022 (6)

C6	0.053 (5)	0.041 (6)	0.035 (4)	0.000 (4)	0.011 (4)	0.008 (4)
C7	0.051 (5)	0.037 (6)	0.054 (5)	0.001 (4)	0.023 (4)	0.001 (5)
C8	0.048 (4)	0.041 (6)	0.026 (4)	0.001 (4)	0.003 (4)	−0.003 (4)
C9	0.051 (4)	0.036 (5)	0.047 (5)	0.008 (4)	0.008 (4)	0.007 (5)
C10	0.049 (5)	0.051 (6)	0.044 (5)	0.011 (4)	0.017 (4)	0.007 (5)
C11	0.045 (4)	0.053 (6)	0.039 (5)	0.004 (5)	0.011 (4)	0.003 (5)
C12	0.060 (5)	0.042 (6)	0.051 (5)	−0.004 (5)	0.005 (5)	0.004 (5)
C13	0.051 (5)	0.054 (7)	0.040 (5)	0.012 (5)	0.006 (4)	−0.009 (5)
C14	0.048 (5)	0.063 (7)	0.062 (6)	0.006 (5)	−0.018 (5)	−0.005 (5)
C15	0.060 (5)	0.053 (6)	0.046 (5)	0.012 (5)	−0.013 (5)	−0.006 (5)
C16	0.038 (4)	0.055 (7)	0.051 (5)	0.012 (5)	0.001 (4)	−0.011 (5)
C17	0.036 (4)	0.042 (6)	0.066 (6)	0.004 (4)	−0.002 (4)	−0.005 (5)
C18	0.054 (5)	0.060 (7)	0.043 (5)	0.017 (5)	0.000 (5)	0.005 (5)
C19	0.066 (6)	0.037 (6)	0.102 (8)	0.007 (5)	0.014 (6)	0.012 (6)
C20	0.073 (7)	0.055 (8)	0.068 (7)	−0.005 (6)	0.022 (6)	0.004 (6)
C21	0.045 (4)	0.054 (6)	0.029 (4)	0.007 (4)	−0.005 (4)	0.000 (5)
C22	0.035 (4)	0.100 (8)	0.031 (4)	0.001 (5)	0.000 (4)	−0.006 (5)
C23	0.036 (4)	0.063 (7)	0.026 (4)	−0.016 (4)	0.002 (4)	−0.007 (4)
C24	0.037 (4)	0.048 (6)	0.024 (4)	−0.002 (4)	−0.005 (3)	0.001 (4)
C25	0.036 (4)	0.053 (6)	0.033 (4)	0.008 (4)	−0.005 (4)	−0.003 (4)
C26	0.043 (4)	0.063 (7)	0.032 (4)	−0.015 (4)	0.012 (4)	−0.007 (5)
C27	0.052 (5)	0.092 (8)	0.022 (4)	−0.026 (5)	0.004 (4)	−0.004 (5)
C28	0.043 (4)	0.072 (7)	0.023 (4)	−0.010 (5)	−0.009 (4)	−0.009 (5)
C29	0.044 (4)	0.071 (7)	0.023 (4)	−0.009 (4)	−0.002 (4)	−0.004 (4)
C30	0.036 (4)	0.048 (6)	0.029 (4)	−0.010 (4)	0.008 (4)	−0.001 (4)
C31	0.028 (4)	0.052 (6)	0.026 (4)	0.007 (4)	−0.007 (4)	−0.009 (4)
C32	0.032 (4)	0.049 (6)	0.036 (5)	0.004 (4)	−0.004 (4)	0.002 (4)
C33	0.080 (7)	0.076 (8)	0.049 (6)	−0.011 (6)	0.004 (6)	0.005 (6)
C34	0.050 (5)	0.116 (10)	0.050 (6)	0.005 (6)	−0.011 (5)	−0.037 (7)

Geometric parameters (Å, °)

Co1—N10	2.103 (7)	C3—C4	1.385 (11)
Co1—N11	2.103 (7)	C4—C5	1.357 (10)
Co1—N4	2.155 (6)	C4—H4	0.9500
Co1—N9^{i}	2.161 (5)	C5—H5	0.9500
Co1—N3	2.165 (6)	C6—C7	1.357 (10)
Co1—N7	2.207 (5)	C6—H6	0.9500
Co2—N13	1.888 (8)	C7—C8	1.390 (10)
Co2—N12	1.924 (9)	C7—H7	0.9500
Co2—N6	1.981 (7)	C8—C9	1.390 (10)
Co2—N1^{i}	2.010 (7)	C9—C10	1.340 (10)
S1—C32	1.645 (9)	C9—H9	0.9500
S2—C33	1.596 (12)	C10—H10	0.9500
S3—C31	1.615 (9)	C11—C12	1.366 (11)
S4—C34	1.605 (11)	C11—H11	0.9500
N1—C5	1.317 (11)	C12—C13	1.394 (11)
N1—C1	1.334 (11)	C12—H12	0.9500

N1—Co2^{ii}	2.010 (7)	C13—C14	1.380 (11)
N2—C3	1.380 (10)	C14—C15	1.387 (11)
N2—C8	1.396 (10)	C14—H14	0.9500
N2—H2N	0.89 (2)	C15—H15	0.9500
N3—C10	1.352 (9)	C16—C17	1.339 (10)
N3—C6	1.358 (9)	C16—H16	0.9500
N4—C15	1.323 (10)	C17—C18	1.398 (11)
N4—C11	1.344 (9)	C17—H17	0.9500
N5—C18	1.396 (10)	C18—C19	1.381 (12)
N5—C13	1.402 (10)	C19—C20	1.363 (12)
N5—H5A	0.8800	C19—H19	0.9500
N6—C20	1.332 (11)	C20—H20	0.9500
N6—C16	1.354 (10)	C21—C22	1.353 (9)
N7—C26	1.339 (9)	C21—H21	0.9500
N7—C30	1.365 (8)	C22—C23	1.409 (10)
N8—C28	1.364 (9)	C22—H22	0.9500
N8—C23	1.383 (9)	C23—C24	1.387 (10)
N8—H8N	0.88 (2)	C24—C25	1.365 (9)
N9—C25	1.341 (8)	C24—H24	0.9500
N9—C21	1.348 (8)	C25—H25	0.9500
N9—Co1^{ii}	2.161 (5)	C26—C27	1.367 (9)
N10—C31	1.171 (9)	C26—H26	0.9500
N11—C32	1.131 (9)	C27—C28	1.381 (10)
N12—C33	1.124 (10)	C27—H27	0.9500
N13—C34	1.151 (11)	C28—C29	1.375 (10)
C1—C2	1.378 (11)	C29—C30	1.346 (9)
C1—H1	0.9500	C29—H29	0.9500
C2—C3	1.429 (11)	C30—H30	0.9500
C2—H2	0.9500		
N10—Co1—N11	177.7 (2)	C9—C8—C7	117.4 (8)
N10—Co1—N4	90.2 (2)	C9—C8—N2	119.9 (8)
N11—Co1—N4	90.3 (2)	C7—C8—N2	122.5 (7)
N10—Co1—N9^{i}	87.1 (2)	C10—C9—C8	120.1 (8)
N11—Co1—N9^{i}	90.7 (2)	C10—C9—H9	120.0
N4—Co1—N9^{i}	88.4 (2)	C8—C9—H9	120.0
N10—Co1—N3	89.2 (2)	C9—C10—N3	124.9 (7)
N11—Co1—N3	90.2 (2)	C9—C10—H10	117.5
N4—Co1—N3	179.4 (2)	N3—C10—H10	117.5
N9^{i}—Co1—N3	91.4 (2)	N4—C11—C12	123.6 (8)
N10—Co1—N7	91.9 (2)	N4—C11—H11	118.2
N11—Co1—N7	90.3 (2)	C12—C11—H11	118.2
N4—Co1—N7	92.0 (2)	C11—C12—C13	120.2 (8)
N9^{i}—Co1—N7	178.9 (2)	C11—C12—H12	119.9
N3—Co1—N7	88.3 (2)	C13—C12—H12	119.9
N13—Co2—N12	116.6 (4)	C14—C13—C12	115.6 (8)
N13—Co2—N6	112.6 (3)	C14—C13—N5	125.0 (7)
N12—Co2—N6	105.9 (3)	C12—C13—N5	119.4 (8)

N13—Co2—N1^{i}	107.9 (3)	C13—C14—C15	121.0 (8)
N12—Co2—N1^{i}	112.7 (3)	C13—C14—H14	119.5
N6—Co2—N1^{i}	100.0 (3)	C15—C14—H14	119.5
C5—N1—C1	116.8 (8)	N4—C15—C14	122.6 (8)
C5—N1—Co2^{ii}	122.1 (7)	N4—C15—H15	118.7
C1—N1—Co2^{ii}	119.5 (7)	C14—C15—H15	118.7
C3—N2—C8	125.8 (7)	C17—C16—N6	123.7 (9)
C3—N2—H2N	103 (5)	C17—C16—H16	118.1
C8—N2—H2N	128 (5)	N6—C16—H16	118.1
C10—N3—C6	113.4 (6)	C16—C17—C18	119.7 (9)
C10—N3—Co1	123.8 (5)	C16—C17—H17	120.2
C6—N3—Co1	122.7 (5)	C18—C17—H17	120.2
C15—N4—C11	116.8 (7)	C19—C18—N5	126.0 (9)
C15—N4—Co1	120.9 (6)	C19—C18—C17	117.0 (8)
C11—N4—Co1	122.0 (5)	N5—C18—C17	116.8 (8)
C18—N5—C13	127.1 (8)	C20—C19—C18	119.6 (9)
C18—N5—H5A	116.5	C20—C19—H19	120.2
C13—N5—H5A	116.5	C18—C19—H19	120.2
C20—N6—C16	116.4 (7)	N6—C20—C19	123.5 (9)
C20—N6—Co2	119.2 (7)	N6—C20—H20	118.2
C16—N6—Co2	121.6 (6)	C19—C20—H20	118.2
C26—N7—C30	113.0 (6)	N9—C21—C22	124.8 (7)
C26—N7—Co1	126.0 (5)	N9—C21—H21	117.6
C30—N7—Co1	120.8 (4)	C22—C21—H21	117.6
C28—N8—C23	126.7 (6)	C21—C22—C23	119.4 (7)
C28—N8—H8N	109 (5)	C21—C22—H22	120.3
C23—N8—H8N	121 (5)	C23—C22—H22	120.3
C25—N9—C21	114.6 (6)	N8—C23—C24	123.1 (7)
C25—N9—Co1^{ii}	122.6 (4)	N8—C23—C22	120.2 (6)
C21—N9—Co1^{ii}	122.8 (5)	C24—C23—C22	116.6 (6)
C31—N10—Co1	166.6 (6)	C25—C24—C23	119.0 (7)
C32—N11—Co1	161.0 (7)	C25—C24—H24	120.5
C33—N12—Co2	163.1 (9)	C23—C24—H24	120.5
C34—N13—Co2	169.0 (9)	N9—C25—C24	125.5 (6)
N1—C1—C2	124.8 (9)	N9—C25—H25	117.3
N1—C1—H1	117.6	C24—C25—H25	117.3
C2—C1—H1	117.6	N7—C26—C27	125.6 (7)
C1—C2—C3	116.2 (9)	N7—C26—H26	117.2
C1—C2—H2	121.9	C27—C26—H26	117.2
C3—C2—H2	121.9	C26—C27—C28	119.3 (7)
N2—C3—C4	122.5 (8)	C26—C27—H27	120.4
N2—C3—C2	118.8 (8)	C28—C27—H27	120.4
C4—C3—C2	118.7 (8)	N8—C28—C29	124.1 (7)
C5—C4—C3	118.4 (8)	N8—C28—C27	119.2 (6)
C5—C4—H4	120.8	C29—C28—C27	116.7 (6)
C3—C4—H4	120.8	C30—C29—C28	120.2 (7)
N1—C5—C4	125.1 (9)	C30—C29—H29	119.9

N1—C5—H5	117.5	C28—C29—H29	119.9
C4—C5—H5	117.5	C29—C30—N7	125.2 (7)
C7—C6—N3	126.4 (8)	C29—C30—H30	117.4
C7—C6—H6	116.8	N7—C30—H30	117.4
N3—C6—H6	116.8	N10—C31—S3	178.0 (6)
C6—C7—C8	117.6 (7)	N11—C32—S1	179.5 (8)
C6—C7—H7	121.2	N12—C33—S2	178.6 (11)
C8—C7—H7	121.2	N13—C34—S4	178.9 (11)
N10—Co1—N3—C10	149.6 (6)	C6—C7—C8—C9	4.4 (11)
N11—Co1—N3—C10	−28.1 (6)	C6—C7—C8—N2	−179.9 (7)
N9^{i}—Co1—N3—C10	62.5 (6)	C3—N2—C8—C9	−153.7 (8)
N7—Co1—N3—C10	−118.5 (6)	C3—N2—C8—C7	30.8 (12)
N10—Co1—N3—C6	−34.6 (6)	C7—C8—C9—C10	−4.2 (11)
N11—Co1—N3—C6	147.6 (6)	N2—C8—C9—C10	180.0 (7)
N9^{i}—Co1—N3—C6	−121.7 (5)	C8—C9—C10—N3	1.2 (12)
N7—Co1—N3—C6	57.3 (5)	C6—N3—C10—C9	1.4 (11)
N10—Co1—N4—C15	150.3 (6)	Co1—N3—C10—C9	177.5 (6)
N11—Co1—N4—C15	−31.9 (6)	C15—N4—C11—C12	4.7 (11)
N9^{i}—Co1—N4—C15	−122.6 (6)	Co1—N4—C11—C12	−168.7 (6)
N7—Co1—N4—C15	58.4 (6)	N4—C11—C12—C13	−1.1 (12)
N10—Co1—N4—C11	−36.5 (6)	C11—C12—C13—C14	−2.9 (12)
N11—Co1—N4—C11	141.3 (6)	C11—C12—C13—N5	179.8 (7)
N9^{i}—Co1—N4—C11	50.6 (6)	C18—N5—C13—C14	33.3 (13)
N7—Co1—N4—C11	−128.4 (6)	C18—N5—C13—C12	−149.8 (8)
N13—Co2—N6—C20	−164.5 (7)	C12—C13—C14—C15	3.4 (12)
N12—Co2—N6—C20	−36.0 (8)	N5—C13—C14—C15	−179.5 (8)
N1^{i}—Co2—N6—C20	81.2 (7)	C11—N4—C15—C14	−4.2 (12)
N13—Co2—N6—C16	35.0 (7)	Co1—N4—C15—C14	169.3 (6)
N12—Co2—N6—C16	163.6 (6)	C13—C14—C15—N4	0.2 (14)
N1^{i}—Co2—N6—C16	−79.2 (6)	C20—N6—C16—C17	−3.6 (12)
N10—Co1—N7—C26	−177.1 (6)	Co2—N6—C16—C17	157.4 (6)
N11—Co1—N7—C26	3.6 (7)	N6—C16—C17—C18	1.0 (12)
N4—Co1—N7—C26	−86.8 (6)	C13—N5—C18—C19	11.1 (13)
N3—Co1—N7—C26	93.8 (6)	C13—N5—C18—C17	−174.2 (8)
N10—Co1—N7—C30	8.9 (6)	C16—C17—C18—C19	1.7 (12)
N11—Co1—N7—C30	−170.5 (6)	C16—C17—C18—N5	−173.6 (7)
N4—Co1—N7—C30	99.2 (6)	N5—C18—C19—C20	173.2 (8)
N4—Co1—N10—C31	−47 (3)	C17—C18—C19—C20	−1.6 (13)
N9^{i}—Co1—N10—C31	−135 (3)	C16—N6—C20—C19	3.7 (14)
N3—Co1—N10—C31	134 (3)	Co2—N6—C20—C19	−157.8 (7)
N7—Co1—N10—C31	45 (3)	C18—C19—C20—N6	−1.2 (15)
N4—Co1—N11—C32	165 (2)	C25—N9—C21—C22	0.6 (13)
N9^{i}—Co1—N11—C32	−106 (2)	Co1^{ii}—N9—C21—C22	178.4 (7)
N3—Co1—N11—C32	−15 (2)	N9—C21—C22—C23	−1.1 (15)
N7—Co1—N11—C32	73 (2)	C28—N8—C23—C24	31.3 (14)
N13—Co2—N12—C33	65 (3)	C28—N8—C23—C22	−148.2 (10)
N6—Co2—N12—C33	−61 (3)	C21—C22—C23—N8	179.0 (8)

N1^{i}—Co2—N12—C33	−170 (3)	C21—C22—C23—C24	−0.6 (13)
N12—Co2—N13—C34	24 (4)	N8—C23—C24—C25	−176.8 (7)
N6—Co2—N13—C34	147 (4)	C22—C23—C24—C25	2.8 (12)
N1^{i}—Co2—N13—C34	−104 (4)	C21—N9—C25—C24	1.9 (12)
C5—N1—C1—C2	2.2 (15)	Co1^{ii}—N9—C25—C24	−176.0 (6)
Co2^{ii}—N1—C1—C2	−163.8 (7)	C23—C24—C25—N9	−3.6 (12)
N1—C1—C2—C3	−1.5 (14)	C30—N7—C26—C27	2.0 (12)
C8—N2—C3—C4	23.3 (13)	Co1—N7—C26—C27	−172.5 (7)
C8—N2—C3—C2	−157.5 (8)	N7—C26—C27—C28	−0.2 (14)
C1—C2—C3—N2	179.6 (8)	C23—N8—C28—C29	14.9 (15)
C1—C2—C3—C4	−1.2 (11)	C23—N8—C28—C27	−163.6 (9)
N2—C3—C4—C5	−177.9 (8)	C26—C27—C28—N8	177.4 (9)
C2—C3—C4—C5	3.0 (12)	C26—C27—C28—C29	−1.2 (13)
C1—N1—C5—C4	−0.3 (14)	N8—C28—C29—C30	−177.9 (8)
Co2^{ii}—N1—C5—C4	165.4 (7)	C27—C28—C29—C30	0.6 (13)
C3—C4—C5—N1	−2.3 (14)	C28—C29—C30—N7	1.4 (13)
C10—N3—C6—C7	−1.1 (11)	C26—N7—C30—C29	−2.6 (11)
Co1—N3—C6—C7	−177.2 (6)	Co1—N7—C30—C29	172.2 (6)
N3—C6—C7—C8	−1.9 (12)		

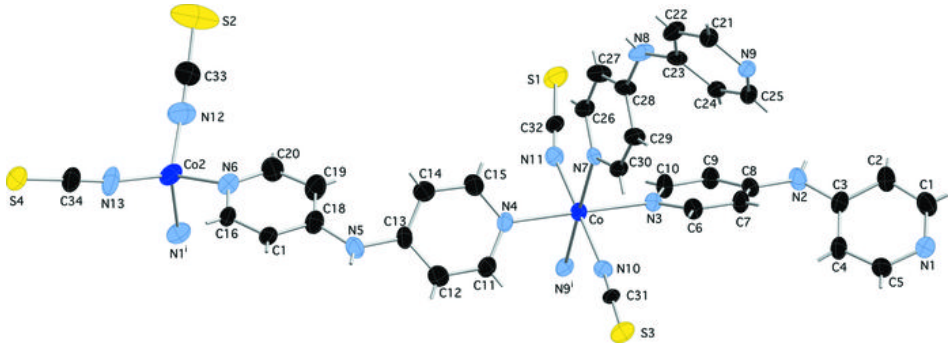
Symmetry codes: (i) −*x*+3/2, −*y*+1, *z*+1/2; (ii) −*x*+3/2, −*y*+1, *z*−1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···S1^{iii}	0.89 (2)	2.59 (5)	3.366 (7)	147 (7)
N5—H5A···S3^{iv}	0.88	2.55	3.355 (7)	153
N8—H8N···S4^{v}	0.88 (2)	2.53 (3)	3.382 (7)	162 (7)

Symmetry codes: (iii) *x*+1/2, −*y*+1/2, −*z*+2; (iv) *x*−1/2, −*y*+3/2, −*z*+2; (v) *x*+1/2, −*y*+3/2, −*z*+2.

Fig. 1


S2
C33
N12
Co2
N6
C20
C19
C18
C16
C1
N5
C13
C14
C15
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C12
C11
N1i
S4
C34
N13
S1
C32
N11
N7
C27
C28
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C30
C22
C21
N8
C23
N9
C24
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Co
N3
C10
C9
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N2
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C2
C1
C4
C5
N1
N9i
N10
C31
S3

Fig. 2

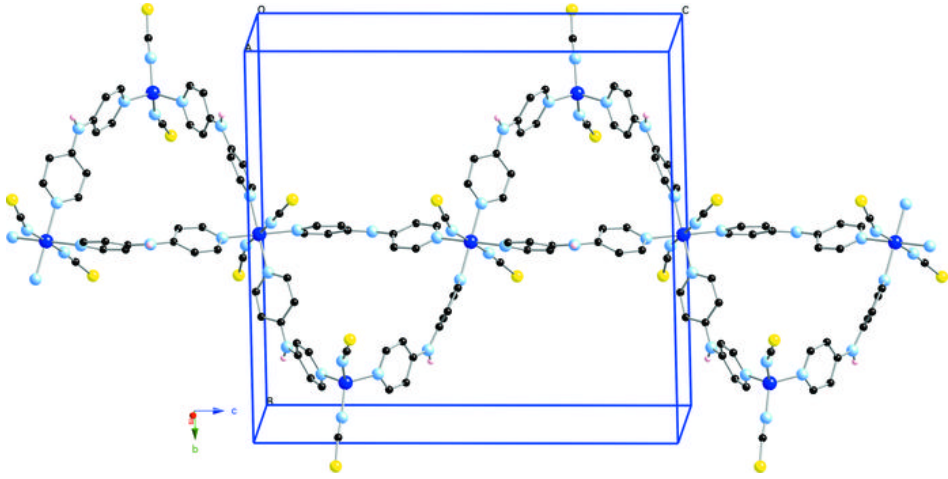

Fig. 3