research communications

Crystal structure of bis(azido-*κN*)bis[2,5-bis-(pyridin-2-yl)-1,3,4-thiadiazole-*κ²N²*,*N³*]cobalt(II)

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In the mononuclear title complex, [Co(N₃)₂(C₁₂H₈N₄S)₂], the cobalt(II) atom is located on an inversion centre and displays an axially weakly compressed octahedral coordination geometry. The equatorial positions are occupied by the N atoms of two 2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole ligands, whereas the axial positions are occupied by N atoms of the azide anions. The thiadiazole and pyridine rings linked to the metal are almost coplanar, with a maximum deviation from the mean plane of 0.0273 (16) Å. The cohesion of the crystal is ensured by weak C—H⋯N hydrogen bonds and by π–π interactions between pyridine rings [intercentroid distance = 3.6356 (11) Å], forming a layered arrangement parallel to (001). The structure of the title compound is isotypic with that of the analogous nickel(II) complex [Laachir *et al.* (2013). *Acta Cryst.* E**69**, m351–m352].

1. Chemical context

In recent years, the use of the ligand 2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole has been studied for the synthesis of numerous complexes with transition-metal salts. An interesting feature of the metal–ligand chemistry of these compounds is that the resulting complexes can be mononuclear (Bentiss *et al.*, 2011*a*; 2012; Kaase *et al.*, 2014) or binuclear (Bentiss *et al.*, 2004; Laachir *et al.*, 2013). Another preparation method involves the use of the organic ligand and pseudohalide ions, especially the azide ion which is known to exhibit different coordination modes (Nath & Baruah, 2012; Ray *et al.*, 2011).
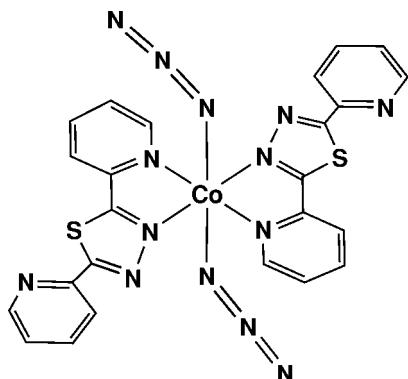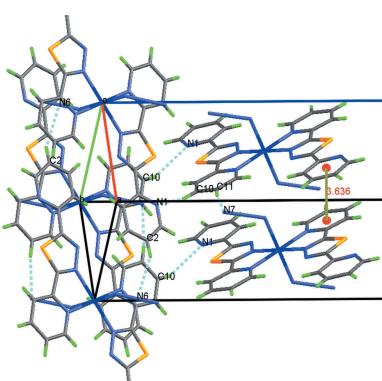

2. Structural commentary

The structure of the title compound (Fig. 1) is isotypic with its nickel(II) analogue (Laachir *et al.*, 2015) and similar to that of
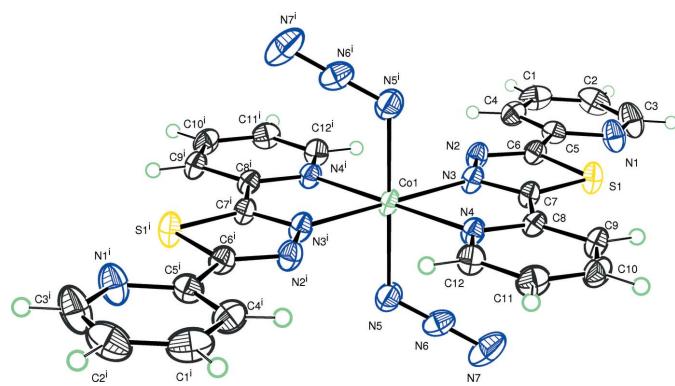
Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are represented as spheres of arbitrary radius. [Symmetry code: (i) $-x, -y, -z$.]

the homologous compound, $[Co(C_{12}H_8N_4S)_2(H_2O)_2] \cdot 2BF_4$, in which the water molecules are substituted by azide ions which at the same time neutralize the positive charge of Co^{2+} (Bentiss *et al.*, 2011*b*). The main difference between the two structures lies in the values of the dihedral angle between the two pyridine rings: this is 18.72 (6)° in the hydrated molecule, whereas it is 3.03 (2)° in the title molecule, (I). The dihedral angles formed by the thiadiazole ring and the pyridine rings N1/C1–C4 and N2/C8–C11 in (I) are 2.87 (9) and 1.1 (2)°, respectively. The cobalt cation, which is located on an inversion centre, shows an axially weakly compressed octahedral coordination geometry with the equatorial plane provided by four nitrogen atoms belonging to the pyridine and thiadiazole rings of two organic ligands [Co1—N3 = 2.1301 (14) and Co1—N4 = 2.1535 (14) Å] and the axial positions occupied by

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

D—H$\cdots$A	D—H	H$\cdots$A	$D\cdots$A	D—H$\cdots$A
C2—H2$\cdots$N6^i	0.93	2.59	3.432 (3)	151
C11—H11$\cdots$N7^{ii}	0.93	2.60	3.528 (3)	173
C10—H10$\cdots$N1^{iii}	0.93	2.63	3.438 (2)	146

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

two nitrogen atoms from azide anions [Co1—N5 = 2.1132 (17) Å].

3. Supramolecular features

In the crystal, the molecules are linked by π–π interactions between pyridine rings [intercentroid distance = 3.6356 (11) Å] and by weak C—H$\cdots$N hydrogen bonds (Table 1), forming a layered arrangement parallel to (001) (Fig. 2). The layers are connected by further C—H$\cdots$N hydrogen bonds into a three-dimensional network.

4. Synthesis and crystallization

The ligand 2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole (noted *L*) was synthesized as described previously by Lebrini *et al.* (2005). The complex $[CoL_2(N_3)_2]$ was synthesized in bulk quantity by dropwise addition with constant stirring at room temperature of an aqueous solution of NaN$_3$ (0.4 mmol, 26 mg) to an ethanol/water solution (1:1 *v/v*) of *L* (0.1 mmol,

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Co(N_3)_2(C_{12}H_8N_4S)_2]$
M_r	623.56
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	7.8004 (3), 8.2439 (3), 20.3222 (8)
β (°)	92.910 (2)
V (Å^3)	1305.15 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.86
Crystal size (mm)	0.39 × 0.31 × 0.18
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.640, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27415, 3667, 2884
R_{int}	0.043
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.694
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.088, 1.03
No. of reflections	3667
No. of parameters	187
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.70, −0.26

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012).
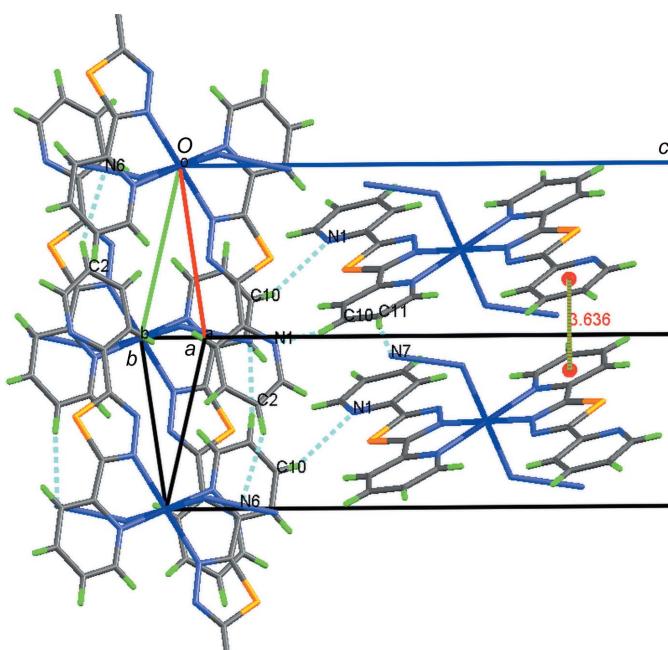
Figure 2
Partial crystal packing of the title compound, showing intermolecular π–π interactions between pyridine rings (dashed green lines) and intermolecular C—H$\cdots$N hydrogen bonds (dashed blue lines).

24 mg) and CoCl$_2$·6H$_2$O (0.1 mmol, 24 mg). The red-coloured solid precipitated was filtered and washed with cold ethanol. Single crystals of the title compound suitable for X-ray data collection were obtained by slow interdiffusion of a solution of CoCl$_2$·6H$_2$O and *L* in acetonitrile into NaN$_3$ dissolved in water. Red block-shaped single crystals appeared after one month. The crystals were washed with water and dried under vacuum (yield 60%). Analysis calculated for C$_{24}$H$_{16}$N$_{14}$CoS$_2$: C, 46.23; H, 2.59; N, 31.45 S, 10.28. Found: C, 46.42; H, 2.63; N, 31.35; S, 10.51.

CAUTION! Azide compounds are potentially explosive. Only a small amount of material should be prepared and handled with care.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were located in a difference Fourier map and treated as riding, with C—H = 0.93 Å, and with U_{iso}(H) = 1.2 U_{eq}(C). Two outliers (002 and $\overline{2}$24) were omitted in the last cycles of refinement.

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supporting information

Crystal structure of bis(azido-*κN*)bis[2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole-*κ²N²,N³*]cobalt(II)

Abdelhakim Laachir, Fouad Bentiss, Salaheddine Guesmi, Mohamed Saadi and Lahcen El Ammari

Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Bis(azido-*κN*)bis[2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole-*κ²N²,N³*]cobalt(II)

Crystal data

$[Co(N_3)_2(C_{12}H_8N_4S)_2]$	$F(000) = 634$
$M_r = 623.56$	$D_x = 1.587$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 3667 reflections
$a = 7.8004$ (3) Å	$\theta = 2.6$–29.6°
$b = 8.2439$ (3) Å	$\mu = 0.86$ mm^{-1}
$c = 20.3222$ (8) Å	$T = 296$ K
$\beta = 92.910$ (2)°	Block, red
$V = 1305.15$ (9) Å^3	$0.39 \times 0.31 \times 0.18$ mm
$Z = 2$	

Data collection

Bruker APEXII CCD diffractometer	27415 measured reflections
Radiation source: fine-focus sealed tube	3667 independent reflections
Graphite monochromator	2884 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.043$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$\theta_{max} = 29.6°$, $\theta_{min} = 2.6°$
	$h = -8 \rightarrow 10$
	$k = -11 \rightarrow 11$
$T_{min} = 0.640$, $T_{max} = 0.747$	$l = -28 \rightarrow 28$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.035$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.088$	
$S = 1.03$	Hydrogen site location: inferred from neighbouring sites
3667 reflections	
187 parameters	H-atom parameters constrained
0 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 0.5683P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.70$ e Å^{-3}

$\Delta\rho_{min} = -0.26$ e Å^{-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 $F^2 > \sigma(F^2)$ 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}
C1	0.7907 (3)	0.4986 (3)	0.07266 (12)	0.0486 (5)
H1	0.8731	0.5035	0.0412	0.058*
C2	0.8166 (3)	0.5770 (3)	0.13200 (13)	0.0540 (6)
H2	0.9169	0.6353	0.1416	0.065*
C3	0.6910 (3)	0.5672 (3)	0.17662 (13)	0.0568 (6)
H3	0.7097	0.6203	0.2167	0.068*
N1	0.5445 (2)	0.4873 (2)	0.16646 (9)	0.0448 (4)
C5	0.5212 (2)	0.4114 (2)	0.10851 (9)	0.0316 (4)
C6	0.3585 (2)	0.3225 (2)	0.10077 (8)	0.0298 (4)
C7	0.0891 (2)	0.1991 (2)	0.11550 (8)	0.0285 (3)
C8	−0.0761 (2)	0.1314 (2)	0.13257 (8)	0.0276 (3)
C9	−0.1510 (2)	0.1627 (2)	0.19143 (8)	0.0338 (4)
H9	−0.0963	0.2283	0.2233	0.041*
C10	−0.3087 (2)	0.0943 (2)	0.20186 (9)	0.0369 (4)
H10	−0.3623	0.1133	0.2410	0.044*
C11	−0.3856 (2)	−0.0022 (2)	0.15379 (10)	0.0382 (4)
H11	−0.4920	−0.0493	0.1599	0.046*
C12	−0.3022 (2)	−0.0285 (2)	0.09601 (9)	0.0348 (4)
H12	−0.3547	−0.0941	0.0637	0.042*
C4	0.6406 (2)	0.4123 (2)	0.06039 (10)	0.0383 (4)
H4	0.6204	0.3565	0.0210	0.046*
N2	0.30958 (18)	0.23430 (19)	0.05046 (7)	0.0314 (3)
N3	0.15296 (18)	0.16405 (19)	0.05884 (7)	0.0307 (3)
N4	−0.14945 (18)	0.03680 (18)	0.08497 (7)	0.0285 (3)
N5	0.1294 (2)	−0.1959 (2)	0.04761 (8)	0.0425 (4)
N6	0.1687 (2)	−0.1872 (2)	0.10472 (8)	0.0394 (4)
N7	0.2046 (3)	−0.1805 (3)	0.16093 (9)	0.0650 (6)
S1	0.21579 (6)	0.32700 (6)	0.16328 (2)	0.03604 (12)
Co1	0.0000	0.0000	0.0000	0.02677 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0316 (10)	0.0552 (13)	0.0600 (14)	−0.0009 (10)	0.0134 (9)	0.0183 (11)
C2	0.0366 (11)	0.0422 (12)	0.0829 (17)	−0.0157 (10)	0.0016 (11)	0.0003 (12)
C3	0.0475 (13)	0.0543 (14)	0.0687 (15)	−0.0162 (11)	0.0041 (11)	−0.0261 (12)
N1	0.0358 (9)	0.0484 (10)	0.0508 (10)	−0.0103 (8)	0.0086 (8)	−0.0184 (8)
C5	0.0270 (8)	0.0304 (9)	0.0371 (9)	−0.0022 (7)	0.0009 (7)	0.0008 (7)
C6	0.0269 (8)	0.0349 (9)	0.0278 (8)	−0.0020 (7)	0.0028 (7)	0.0002 (7)
C7	0.0292 (8)	0.0349 (9)	0.0213 (7)	−0.0025 (7)	0.0004 (6)	−0.0024 (6)
C8	0.0277 (8)	0.0330 (9)	0.0223 (7)	−0.0009 (7)	0.0028 (6)	0.0013 (6)
C9	0.0368 (9)	0.0432 (10)	0.0216 (8)	−0.0008 (8)	0.0040 (7)	−0.0026 (7)
C10	0.0371 (9)	0.0468 (11)	0.0280 (9)	0.0032 (9)	0.0118 (7)	0.0033 (8)
C11	0.0308 (9)	0.0445 (11)	0.0403 (10)	−0.0032 (8)	0.0112 (8)	0.0055 (8)
C12	0.0310 (9)	0.0393 (10)	0.0342 (9)	−0.0060 (8)	0.0042 (7)	−0.0026 (7)
C4	0.0353 (9)	0.0443 (11)	0.0355 (10)	0.0012 (8)	0.0029 (8)	0.0038 (8)
N2	0.0284 (7)	0.0407 (8)	0.0252 (7)	−0.0078 (6)	0.0032 (6)	−0.0028 (6)
N3	0.0281 (7)	0.0411 (8)	0.0229 (7)	−0.0064 (6)	0.0028 (6)	−0.0027 (6)
N4	0.0283 (7)	0.0340 (7)	0.0235 (7)	−0.0032 (6)	0.0034 (6)	−0.0012 (6)
N5	0.0489 (10)	0.0472 (10)	0.0316 (8)	0.0043 (8)	0.0037 (7)	0.0004 (7)
N6	0.0301 (8)	0.0476 (10)	0.0404 (9)	−0.0064 (7)	0.0010 (7)	0.0125 (7)
N7	0.0610 (13)	0.0935 (17)	0.0391 (10)	−0.0169 (12)	−0.0125 (9)	0.0198 (10)
S1	0.0322 (2)	0.0481 (3)	0.0282 (2)	−0.0092 (2)	0.00487 (17)	−0.01202 (19)
Co1	0.02599 (16)	0.03633 (19)	0.01818 (15)	−0.00561 (14)	0.00290 (11)	−0.00329 (13)

Geometric parameters (Å, º)

C1—C2	1.374 (3)	C9—H9	0.9300
C1—C4	1.382 (3)	C10—C11	1.374 (3)
C1—H1	0.9300	C10—H10	0.9300
C2—C3	1.371 (3)	C11—C12	1.388 (3)
C2—H2	0.9300	C11—H11	0.9300
C3—N1	1.326 (3)	C12—N4	1.337 (2)
C3—H3	0.9300	C12—H12	0.9300
N1—C5	1.338 (2)	C4—H4	0.9300
C5—C4	1.384 (3)	N2—N3	1.3704 (19)
C5—C6	1.467 (2)	N3—Co1	2.1301 (14)
C6—N2	1.297 (2)	N4—Co1	2.1535 (14)
C6—S1	1.7317 (16)	N5—N6	1.187 (2)
C7—N3	1.310 (2)	N5—Co1	2.1132 (17)
C7—C8	1.462 (2)	N6—N7	1.164 (2)
C7—S1	1.7128 (17)	Co1—N5^{i}	2.1132 (17)
C8—N4	1.347 (2)	Co1—N3^{i}	2.1301 (14)
C8—C9	1.382 (2)	Co1—N4^{i}	2.1535 (14)
C9—C10	1.380 (3)		
C2—C1—C4	119.10 (19)	N4—C12—C11	122.64 (17)
C2—C1—H1	120.5	N4—C12—H12	118.7

C4—C1—H1	120.5	C11—C12—H12	118.7
C3—C2—C1	118.31 (19)	C1—C4—C5	118.00 (19)
C3—C2—H2	120.8	C1—C4—H4	121.0
C1—C2—H2	120.8	C5—C4—H4	121.0
N1—C3—C2	124.4 (2)	C6—N2—N3	111.59 (13)
N1—C3—H3	117.8	C7—N3—N2	113.40 (14)
C2—C3—H3	117.8	C7—N3—Co1	113.97 (11)
C3—N1—C5	116.54 (18)	N2—N3—Co1	132.53 (10)
N1—C5—C4	123.60 (17)	C12—N4—C8	117.54 (15)
N1—C5—C6	113.95 (15)	C12—N4—Co1	126.96 (12)
C4—C5—C6	122.44 (17)	C8—N4—Co1	115.44 (11)
N2—C6—C5	125.69 (15)	N6—N5—Co1	119.66 (14)
N2—C6—S1	114.57 (12)	N7—N6—N5	178.7 (2)
C5—C6—S1	119.72 (13)	C7—S1—C6	86.85 (8)
N3—C7—C8	120.22 (15)	N5—Co1—N5^{i}	180.0
N3—C7—S1	113.57 (13)	N5—Co1—N3^{i}	90.73 (6)
C8—C7—S1	126.20 (12)	N5^{i}—Co1—N3^{i}	89.27 (6)
N4—C8—C9	123.13 (16)	N5—Co1—N3	89.27 (6)
N4—C8—C7	113.46 (14)	N5^{i}—Co1—N3	90.73 (6)
C9—C8—C7	123.40 (16)	N3^{i}—Co1—N3	180.0
C10—C9—C8	118.44 (17)	N5—Co1—N4	90.35 (6)
C10—C9—H9	120.8	N5^{i}—Co1—N4	89.65 (6)
C8—C9—H9	120.8	N3^{i}—Co1—N4	103.24 (5)
C11—C10—C9	119.22 (16)	N3—Co1—N4	76.76 (5)
C11—C10—H10	120.4	N5—Co1—N4^{i}	89.65 (6)
C9—C10—H10	120.4	N5^{i}—Co1—N4^{i}	90.34 (6)
C10—C11—C12	119.01 (17)	N3^{i}—Co1—N4^{i}	76.76 (5)
C10—C11—H11	120.5	N3—Co1—N4^{i}	103.24 (5)
C12—C11—H11	120.5	N4—Co1—N4^{i}	180.0

Symmetry code: (i) −*x*, −*y*, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···N6^{ii}	0.93	2.59	3.432 (3)	151
C11—H11···N7^{iii}	0.93	2.60	3.528 (3)	173
C10—H10···N1^{iv}	0.93	2.63	3.438 (2)	146

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