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Bis(μ-3,5-dimethyl-1,2,4-triazol-4-amine-κ²N¹:N²)bis[dichloridocobalt(II)]

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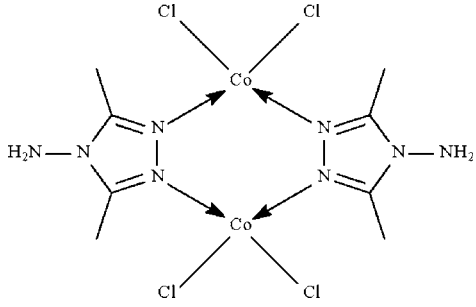
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.032; wR factor = 0.085; data-to-parameter ratio = 16.1.

In the centrosymmetric dinuclear compound, $[Co_2Cl_4(C_4H_8N_4)_2]$, the Co^{II} atom is coordinated by N atoms from two 3,5-dimethyl-1,2,4-triazol-4-amine ligands and two Cl atoms in a distorted tetrahedral geometry. A six-membered ring is formed by four N atoms from two ligands and the two Co^{II} centers; the Co···Co distance is 3.756 (9) Å.

Related literature

For related compounds, see: Cheng *et al.* (2007); Lavrenova *et al.* (1992); Liu *et al.* (2003); Nockemann & Meyer (2007).



Experimental

Crystal data

$[Co_2Cl_4(C_4H_8N_4)_2]$
M_r = 483.95
Monoclinic, $P2_1/c$
a = 6.7412 (10) Å
b = 12.2094 (16) Å
c = 11.4423 (14) Å
β = 97.8270 (10)°
V = 933.0 (2) Å³
Z = 2
Mo $K\alpha$ radiation
μ = 2.36 mm⁻¹
T = 298 K
0.34 × 0.33 × 0.17 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.46, T_{max} = 0.67
4733 measured reflections
1638 independent reflections
1304 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.085
S = 1.07
1638 reflections
102 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.43 e Å⁻³
$\Delta\rho_{min}$ = −0.58 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Co1—N2^{i}	2.023 (3)	Co1—Cl2	2.2154 (11)
Co1—N1	2.030 (3)	Co1—Cl1	2.2382 (11)
N2^{i}—Co1—N1	107.55 (11)	N2^{i}—Co1—Cl1	109.60 (9)
N2^{i}—Co1—Cl2	108.46 (9)	N1—Co1—Cl1	109.49 (9)
N1—Co1—Cl2	108.50 (9)	Cl2—Co1—Cl1	113.10 (5)

Symmetry code: (i) $-x+1, -y, -z+1$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 20008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2584).

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supporting information

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Bis(μ-3,5-dimethyl-1,2,4-triazol-4-amine-κ^2N^1:N^2)bis[dichloridocobalt(II)]

Yun Gong, Jinghua Li, Yuchao Zhou, Jianbo Qin and Xiaoxia Wu

S1. Comment

The rational design and synthesis of novel coordination polymers is of current interest in the field of supramolecular chemistry and crystal engineering, not only because of their intriguing structural motifs but also because of their potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics, and molecular sensing. 1,2,4-Triazole and its derivatives possess good coordination ability due to the hetercyclic nitrogen atoms in the structure. Many polymers of 3,5-dimethyl-1,2,4-triazol-4-amine (Dmatrz) have been synthesized. In 1992, Lavrenova reported a series of metal-Dmatrz complexes, such as $CuCl_2$(Dmatrz)(0.5H_2O), $CdCl_2$(Dmatrz), $Co(NO_3)_2(Dmatrz)_2(H_2O)$, $Cu(NO_3)_2$(Dmatrz)(0.5H_2O), $Ni(NO_3)_2(Dmatrz)_2(H_2O)$, $Zn(NO_3)_2(Dmatrz)_2$, $Cd(NO_3)_2(Dmatrz)_3$ (Lavrenova *et al.*, 1992). Other metal-Dmatrz complexes such as Cu(Dmatrz)SCN, $Zn_2(Dmatrz)_2Cl_4$, $Ag_3(Dmatrz)_2(NO_3)_3$ have also reported (Liu, *et al.*, 2003; Cheng, *et al.*, 2007; Nockemann, *et al.*, 2007). However, so far coordination polymer constructed from $CoCl_2$ and Dmatrz has never been reported. In the present word, we solvothermally synthesized a $CoCl_2$-Dmatrz complex and it is reported here.

The molecular structure of the complex (I) (Fig. 1) has one one Co(II), one Dmatrz and two chlorine anions in its asymmetric unit. The Co(II) center is four-coordinated by four nitrogen atoms from two Dmatrz ligands and two chlorine atoms in a tetrahedral geometry. Each Dmatrz ligand links two Co(II) centers *via* its two neighboring nitrogen atoms with a Co···Co separation of 3.756 (9) Å (Fig.1). A six membered ring is formed *via* four nitrogen atoms from two Dmatrz ligands and two cobalt centers. The chlorine atoms can form hydrogen bonds with nitrogen atom from the uncoordinated amino group of Dmatrz. For example, The H4B···Cl2(ii) and N4···Cl2(ii) distances are 2.514 and 3.277 Å, respectively [Symmetry codes: (ii) -*x* + 1,-*y*,-*z* + 1]. The N4—H4B··· Cl2(ii) angle is 148.39 °.

S2. Experimental

A mixture of Dmatrz(0.05 mmol, 0.006 g), $CoCl_2$(0.1 mmol, 0.024 g) and ethanol(5 mm l) was put into a Teflon-lined autoclave. The reaction mixture was heated at 120 centigrade for one and a half day, followed by slow cooling to room temperatrue and blue single crystals were collected. Elemental analyse found: C, 19.80; H, 3.39; N, 23.04; Cl, 29.28; Co, 24.45%.

S3. Refinement

H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.96Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms, N—H = 0.86Å and U_{iso}(H) = 1.2U_{eq}(C) for amino H atoms.

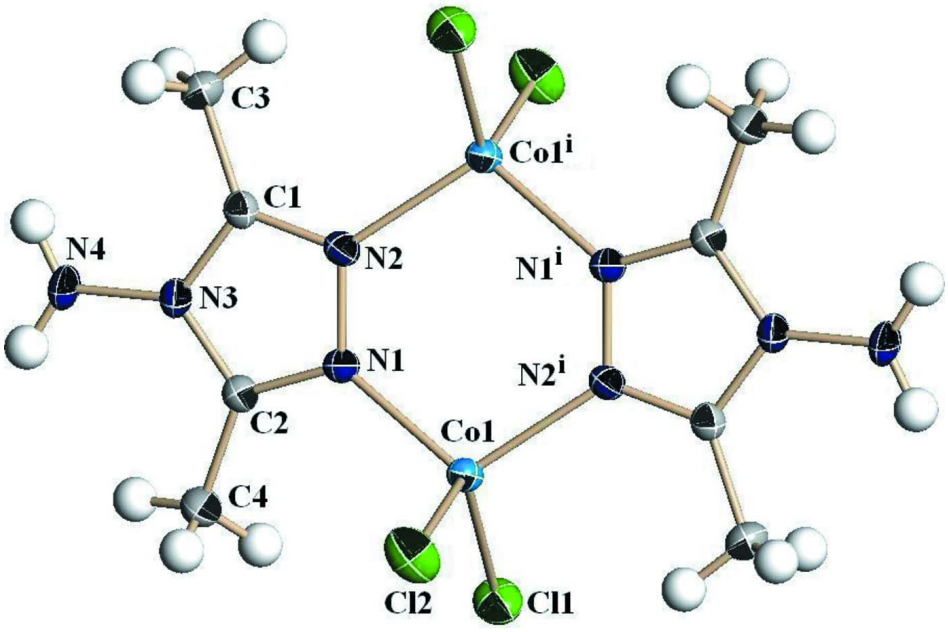

Figure 1

The structure of (I), with the atomic numbering scheme and displacement ellipsoids at the 30% probability level. [Symmetry codes: (i) -*x* + 1,-*y*,-*z* + 1.]

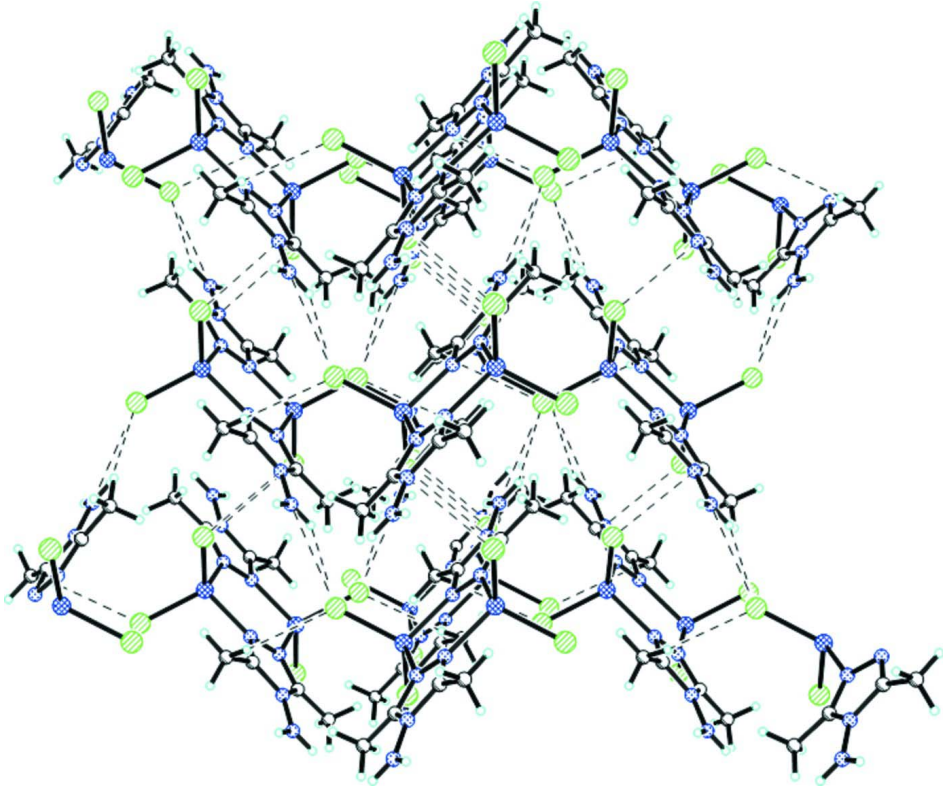

Figure 2

Three dimensional supramolecular architecture constructed by intermolecular hydrogen bonds. The dotted lines indicate the hydrogen bonds.

Bis(μ-3,5-dimethyl-1,2,4-triazol-4-amine-κ²N¹:N²)bis[dichloridocobalt(II)]

Crystal data

$[Co_2Cl_4(C_4H_8N_4)_2]$
$M_r = 483.95$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 6.7412$ (10) Å
$b = 12.2094$ (16) Å
$c = 11.4423$ (14) Å
$\beta = 97.827$ (1)°
$V = 933.0$ (2) Å^3
$Z = 2$
$F(000) = 484$
$D_x = 1.723$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4733 reflections
$\theta = 2.5$–$25.0°$
$\mu = 2.36$ mm^{-1}
$T = 298$ K
Block, blue
0.34 × 0.33 × 0.17 mm

Data collection

Siemens CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.46$, $T_{max} = 0.67$
4733 measured reflections
1638 independent reflections
1304 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.5°$
$h = -7 \rightarrow 7$
$k = -14 \rightarrow 14$
$l = -13 \rightarrow 8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.085$
$S = 1.07$
1638 reflections
102 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 1.1376P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ 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}
Co1	0.59569 (7)	0.10736 (4)	0.40423 (4)	0.03186 (17)
Cl1	0.84618 (15)	0.10010 (9)	0.29461 (10)	0.0545 (3)
Cl2	0.44352 (17)	0.26855 (9)	0.39618 (12)	0.0652 (3)
N1	0.7034 (4)	0.0747 (2)	0.5750 (2)	0.0360 (7)

N2	0.6098 (4)	0.0089 (2)	0.6507 (2)	0.0345 (7)
N3	0.8558 (4)	0.0937 (2)	0.7526 (2)	0.0341 (7)
N4	0.9948 (5)	0.1233 (3)	0.8494 (3)	0.0505 (9)
H4A	0.9879	0.0948	0.9174	0.061*
H4B	1.0872	0.1700	0.8409	0.061*
C1	0.7059 (5)	0.0212 (3)	0.7575 (3)	0.0328 (8)
C2	0.8540 (5)	0.1240 (3)	0.6382 (3)	0.0365 (8)
C3	0.6643 (6)	−0.0339 (3)	0.8663 (3)	0.0476 (10)
H3A	0.6222	0.0194	0.9195	0.071*
H3B	0.7834	−0.0698	0.9030	0.071*
H3C	0.5602	−0.0871	0.8471	0.071*
C4	1.0012 (7)	0.1982 (4)	0.5962 (4)	0.0576 (12)
H4C	1.0375	0.1709	0.5233	0.086*
H4D	1.1183	0.2022	0.6541	0.086*
H4E	0.9437	0.2699	0.5837	0.086*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0308 (3)	0.0312 (3)	0.0334 (3)	−0.00153 (19)	0.00350 (19)	0.0033 (2)
Cl1	0.0476 (6)	0.0600 (6)	0.0604 (6)	−0.0015 (5)	0.0239 (5)	−0.0066 (5)
Cl2	0.0540 (7)	0.0417 (6)	0.0976 (9)	0.0137 (5)	0.0018 (6)	0.0003 (6)
N1	0.0369 (17)	0.0385 (16)	0.0317 (16)	−0.0077 (13)	0.0015 (13)	0.0046 (13)
N2	0.0335 (16)	0.0330 (15)	0.0364 (16)	−0.0055 (12)	0.0026 (13)	0.0025 (13)
N3	0.0354 (16)	0.0355 (16)	0.0301 (15)	−0.0018 (13)	−0.0004 (12)	−0.0044 (12)
N4	0.051 (2)	0.067 (2)	0.0298 (16)	−0.0194 (17)	−0.0085 (14)	−0.0041 (15)
C1	0.0337 (19)	0.0314 (18)	0.0329 (19)	0.0008 (15)	0.0026 (14)	−0.0022 (14)
C2	0.0371 (19)	0.0365 (19)	0.0353 (19)	−0.0045 (15)	0.0030 (15)	0.0000 (15)
C3	0.058 (3)	0.049 (2)	0.036 (2)	−0.0039 (19)	0.0052 (18)	0.0071 (17)
C4	0.061 (3)	0.067 (3)	0.045 (2)	−0.029 (2)	0.007 (2)	0.000 (2)

Geometric parameters (Å, º)

Co1—N2^{i}	2.023 (3)	N4—H4A	0.8600
Co1—N1	2.030 (3)	N4—H4B	0.8600
Co1—Cl2	2.2154 (11)	C1—C3	1.475 (5)
Co1—Cl1	2.2382 (11)	C2—C4	1.472 (5)
N1—C2	1.310 (4)	C3—H3A	0.9600
N1—N2	1.394 (4)	C3—H3B	0.9600
N2—C1	1.312 (4)	C3—H3C	0.9600
N2—Co1^{i}	2.023 (3)	C4—H4C	0.9600
N3—C1	1.350 (4)	C4—H4D	0.9600
N3—C2	1.358 (4)	C4—H4E	0.9600
N3—N4	1.397 (4)		
N2^{i}—Co1—N1	107.55 (11)	N2—C1—N3	108.3 (3)
N2^{i}—Co1—Cl2	108.46 (9)	N2—C1—C3	127.4 (3)
N1—Co1—Cl2	108.50 (9)	N3—C1—C3	124.3 (3)

N2^{i}—Co1—Cl1	109.60 (9)	N1—C2—N3	108.1 (3)
N1—Co1—Cl1	109.49 (9)	N1—C2—C4	127.5 (3)
Cl2—Co1—Cl1	113.10 (5)	N3—C2—C4	124.4 (3)
C2—N1—N2	107.7 (3)	C1—C3—H3A	109.5
C2—N1—Co1	126.2 (2)	C1—C3—H3B	109.5
N2—N1—Co1	125.3 (2)	H3A—C3—H3B	109.5
C1—N2—N1	107.7 (3)	C1—C3—H3C	109.5
C1—N2—Co1^{i}	126.9 (2)	H3A—C3—H3C	109.5
N1—N2—Co1^{i}	124.1 (2)	H3B—C3—H3C	109.5
C1—N3—C2	108.1 (3)	C2—C4—H4C	109.5
C1—N3—N4	124.1 (3)	C2—C4—H4D	109.5
C2—N3—N4	127.6 (3)	H4C—C4—H4D	109.5
N3—N4—H4A	120.0	C2—C4—H4E	109.5
N3—N4—H4B	120.0	H4C—C4—H4E	109.5
H4A—N4—H4B	120.0	H4D—C4—H4E	109.5

Symmetry code: (i) $-x+1, -y, -z+1$.