

# Dichloridobis(methanol- $\kappa$ O)bis(6-methyl-3-phenyl-1,2,4-triazolo[3,4-*b*]-[1,3,4]thiadiazole- $\kappa$ N<sup>1</sup>)cadmium(II)

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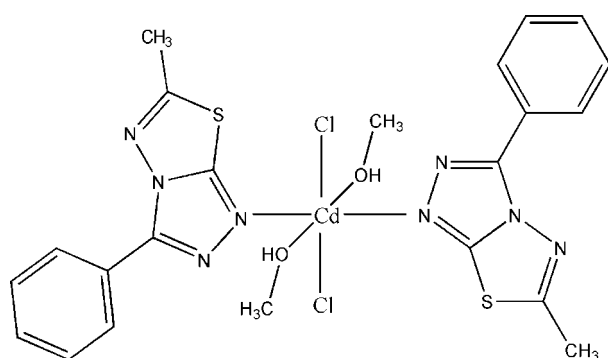
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Key indicators: single-crystal X-ray study;  $T = 291$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.019;  $wR$  factor = 0.051; data-to-parameter ratio = 14.0.

The title complex,  $[\text{CdCl}_2(\text{C}_{10}\text{H}_8\text{N}_4\text{S})_2(\text{CH}_4\text{O})_2]$ , a neutral mononuclear molecule, consists of a  $\text{Cd}^{\text{II}}$  ion, two 6-methyl-3-phenyl-1,2,4-triazolo[3,4-*b*]-[1,3,4]thiadiazole ligands, two chloride ligands and two coordinated methanol molecules. The  $\text{Cd}^{\text{II}}$  ion, located on a center of symmetry, displays a distorted octahedral coordination geometry. A supramolecular network structure is formed by intermolecular  $\text{O}-\text{H}\cdots\text{Cl}$  hydrogen bonds and  $\pi-\pi$  contacts [centroid-centroid distance 3.613 (7) Å].

## Related literature

For related literature, see: Fornies-Marquina *et al.* (1974); Huang *et al.* (2005); Molina *et al.* (1989); Naveen *et al.* (2006).



## Experimental

### Crystal data

$[\text{CdCl}_2(\text{C}_{10}\text{H}_8\text{N}_4\text{S})_2(\text{CH}_4\text{O})_2]$	$c = 12.1019$ (15) Å
$M_r = 679.91$	$\alpha = 95.588$ (1)°
Triclinic, $P\bar{1}$	$\beta = 104.037$ (1)°
$a = 6.7576$ (9) Å	$\gamma = 102.496$ (1)°
$b = 8.6138$ (11) Å	$V = 658.81$ (15) Å <sup>3</sup>

$Z = 1$   
Mo  $K\alpha$  radiation  
 $\mu = 1.23$  mm<sup>-1</sup>

$T = 291$  (2) K  
 $0.44 \times 0.31 \times 0.22$  mm

### Data collection

Bruker APEXII area-detector diffractometer	4509 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2386 independent reflections
$T_{\text{min}} = 0.633$ , $T_{\text{max}} = 0.764$	2327 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.011$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$	171 parameters
$wR(F^2) = 0.051$	H-atom parameters constrained
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.46$ e Å <sup>-3</sup>
2386 reflections	$\Delta\rho_{\text{min}} = -0.45$ e Å <sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Cd1—N1	2.3438 (16)	Cd1—Cl1	2.5721 (5)
Cd1—O1	2.3785 (14)		
N1 <sup>i</sup> —Cd1—O1	86.91 (6)	N1—Cd1—Cl1	86.68 (4)
N1—Cd1—O1	93.09 (6)	O1 <sup>i</sup> —Cd1—Cl1	92.17 (4)
N1 <sup>i</sup> —Cd1—Cl1	93.32 (4)	O1—Cd1—Cl1	87.83 (4)

Symmetry code: (i)  $-x, -y + 2, -z$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1A}\cdots\text{Cl1}^{\text{ii}}$	0.93	2.57	3.2005 (16)	126

Symmetry code: (ii)  $-x + 1, -y + 2, -z$ .

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2004); 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: ZL2054).

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**supplementary materials**

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## Dichloridobis(methanol- $\kappa$ O)bis(6-methyl-3-phenyl-1,2,4-triazolo[3,4-*b*][1,3,4]thiadiazole- $\kappa$ N<sup>1</sup>)cadmium(II)

P.-Z. Hong, W.-D. Song and Z.-H. Wu

### Comment

The molecular structure of 6-methyl-3-phenyl-[1,2,4]triazolo(3,4-*b*)-1,3,4-thiadiazole (Fornies-Marquina *et al.*, 1974) and its substituted derivatives (Molina *et al.*, 1989; Huang *et al.*, 2005; Naveen *et al.*, 2006) have been reported, however, no metal complexes of these ligands have so far been reported. In this paper, we report the crystal structure of the title compound, (I), a Cd complex obtained by the reaction of 6-methyl-3-phenyl-[1,2,4]triazolo(3,4-*b*)-1,3,4-thiadiazole with cadmium chloride in methanol solution.

As illustrated in Fig. 1, the Cd<sup>II</sup> atom, which is a neutral mononuclear molecule, lies on a centre of symmetry and has a distorted octahedral geometry with six coordinating atoms: two N atoms from two 6-methyl-3-phenyl-[1,2,4]triazolo(3,4-*b*)-1,3,4-thiadiazole, two O from two methanol molecules and two chlorine atoms (Table 1). The structural components are connected through O—H...Cl hydrogen bonding involving the coordinating methanol molecules as donors and the Cl atoms as acceptors and  $\pi$ - $\pi$  stacking interactions between the phenyl and triazolo rings, thus forming a supramolecular network structure (Fig. 2; Table 2). The centroid-centroid distance of adjacent phenyl and triazolo rings (at  $1-x, -y, 1-z$ ) is 3.613 (7) Å, indicating a normal  $\pi$ - $\pi$  interaction.

### Experimental

The title complex was prepared by the addition of a stoichiometric amount of cadmium chloride (1 mmol) to a hot methanol solution (10 ml) of 2-methyl-5-phenyl-s-triazolo(3,4-*b*)-1,3,4-thiadiazole (1 mmol). The resulting solution was filtered, and yellow blocky crystals were obtained on slow evaporation of the solvent over several days at room temperature.

### Refinement

Carbon-bound and hydroxyl H atoms were placed at calculated positions and were treated as riding on the parent C atoms with C—H = 0.93–0.97 or O—H = 0.82 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2$  or  $1.5 U_{\text{eq}}(\text{C}, \text{O})$ . The terminal methyl and hydroxyl groups were also allowed free rotation.

### Figures

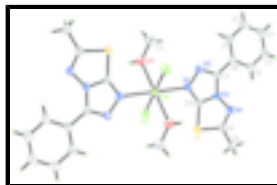


Fig. 1. The structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. Unlabelled atoms are related to the labelled atoms by the symmetry operator  $(-x, 2-y, -z)$ .

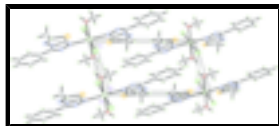


Fig. 2. A packing view of (I), showing the intermolecular hydrogen bonding interactions as broken lines.

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### Crystal data

[CdCl<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>4</sub>S)<sub>2</sub>(CH<sub>4</sub>O)<sub>2</sub>]

$M_r = 679.91$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$a = 6.7576$  (9) Å

$b = 8.6138$  (11) Å

$c = 12.1019$  (15) Å

$\alpha = 95.5880$  (10)°

$\beta = 104.0370$  (10)°

$\gamma = 102.4960$  (10)°

$V = 658.81$  (15) Å<sup>3</sup>

$Z = 1$

$F_{000} = 342$

$D_x = 1.714$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 2400 reflections

$\theta = 1.4$ – $28.0$ °

$\mu = 1.23$  mm<sup>-1</sup>

$T = 291$  (2) K

Block, yellow

$0.44 \times 0.31 \times 0.22$  mm

### Data collection

Bruker APEX II area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 291$ (2) K

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.633$ ,  $T_{\max} = 0.764$

4509 measured reflections

2386 independent reflections

2327 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.011$

$\theta_{\text{max}} = 25.5$ °

$\theta_{\text{min}} = 2.5$ °

$h = -8 \rightarrow 8$

$k = -10 \rightarrow 10$

$l = -14 \rightarrow 14$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.019$

$wR(F^2) = 0.051$

$S = 1.12$

2386 reflections

171 parameters

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2 + 0.3405P]$$

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

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

$\Delta\rho_{\text{max}} = 0.46$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.45$  e Å<sup>-3</sup>

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd1	0.0000	1.0000	0.0000	0.02382 (7)
Cl1	0.21045 (8)	0.79569 (6)	-0.04065 (4)	0.03678 (13)
S1	-0.03252 (8)	0.61793 (6)	0.16761 (4)	0.03174 (12)
O1	0.3105 (2)	1.20734 (17)	0.02416 (13)	0.0378 (3)
H1A	0.3961	1.1971	-0.0245	0.057*
N1	0.0945 (3)	0.9611 (2)	0.19295 (13)	0.0293 (4)
N2	0.1805 (3)	1.0753 (2)	0.29327 (14)	0.0287 (3)
C7	0.1962 (3)	0.9992 (2)	0.38328 (16)	0.0257 (4)
N3	0.1205 (2)	0.83616 (18)	0.34395 (13)	0.0249 (3)
N4	0.0906 (3)	0.69736 (19)	0.39330 (14)	0.0280 (3)
C1	0.3662 (3)	1.2428 (3)	0.52946 (18)	0.0343 (4)
H1	0.3696	1.3028	0.4698	0.041*
C2	0.4460 (4)	1.3187 (3)	0.6438 (2)	0.0411 (5)
H2	0.5006	1.4298	0.6600	0.049*
C3	0.4446 (3)	1.2307 (3)	0.73328 (18)	0.0410 (5)
H3	0.4988	1.2822	0.8093	0.049*
C4	0.3625 (4)	1.0656 (3)	0.70944 (18)	0.0400 (5)
H4	0.3622	1.0061	0.7696	0.048*
C5	0.2802 (3)	0.9882 (3)	0.59548 (17)	0.0336 (4)
H5	0.2244	0.8773	0.5797	0.040*
C6	0.2815 (3)	1.0772 (2)	0.50492 (16)	0.0266 (4)
C10	0.0617 (3)	0.8198 (2)	0.22672 (15)	0.0265 (4)
C8	0.0103 (3)	0.5756 (2)	0.31026 (16)	0.0292 (4)
C9	-0.0456 (4)	0.4066 (3)	0.33259 (19)	0.0425 (5)
H9A	0.0025	0.4046	0.4138	0.064*
H9B	0.0203	0.3415	0.2915	0.064*
H9C	-0.1957	0.3649	0.3069	0.064*
C11	0.3701 (4)	1.3467 (3)	0.1099 (2)	0.0519 (6)
H10A	0.2510	1.3914	0.1077	0.078*
H10B	0.4814	1.4250	0.0953	0.078*
H10C	0.4179	1.3176	0.1846	0.078*

## supplementary materials

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cd1	0.02905 (11)	0.02292 (11)	0.01872 (10)	0.00580 (8)	0.00528 (7)	0.00425 (7)
Cl1	0.0386 (3)	0.0388 (3)	0.0361 (3)	0.0168 (2)	0.0112 (2)	0.0022 (2)
S1	0.0461 (3)	0.0253 (2)	0.0220 (2)	0.0082 (2)	0.0065 (2)	0.00352 (19)
O1	0.0324 (8)	0.0315 (8)	0.0454 (9)	0.0019 (6)	0.0123 (7)	-0.0034 (6)
N1	0.0398 (9)	0.0263 (8)	0.0215 (8)	0.0093 (7)	0.0066 (7)	0.0040 (6)
N2	0.0361 (9)	0.0262 (8)	0.0229 (8)	0.0077 (7)	0.0067 (7)	0.0024 (6)
C7	0.0270 (9)	0.0270 (9)	0.0240 (9)	0.0083 (8)	0.0077 (7)	0.0036 (7)
N3	0.0309 (8)	0.0254 (8)	0.0193 (7)	0.0085 (7)	0.0066 (6)	0.0058 (6)
N4	0.0349 (9)	0.0270 (8)	0.0247 (8)	0.0095 (7)	0.0094 (7)	0.0091 (7)
C1	0.0363 (11)	0.0329 (11)	0.0320 (10)	0.0079 (9)	0.0070 (9)	0.0042 (9)
C2	0.0391 (12)	0.0353 (11)	0.0410 (12)	0.0058 (9)	0.0046 (9)	-0.0075 (10)
C3	0.0365 (11)	0.0537 (14)	0.0268 (10)	0.0108 (10)	0.0036 (9)	-0.0089 (10)
C4	0.0432 (12)	0.0532 (14)	0.0242 (10)	0.0129 (11)	0.0091 (9)	0.0072 (9)
C5	0.0380 (11)	0.0349 (11)	0.0267 (10)	0.0073 (9)	0.0081 (8)	0.0042 (8)
C6	0.0240 (9)	0.0323 (10)	0.0230 (9)	0.0089 (8)	0.0055 (7)	0.0006 (8)
C10	0.0328 (10)	0.0279 (10)	0.0200 (9)	0.0097 (8)	0.0068 (7)	0.0049 (7)
C8	0.0353 (10)	0.0297 (10)	0.0247 (9)	0.0105 (8)	0.0082 (8)	0.0084 (8)
C9	0.0642 (15)	0.0284 (11)	0.0323 (11)	0.0081 (10)	0.0096 (10)	0.0089 (9)
C11	0.0438 (13)	0.0419 (14)	0.0585 (16)	0.0012 (11)	0.0091 (11)	-0.0136 (11)

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

Cd1—N1 <sup>i</sup>	2.3438 (16)	C1—C6	1.390 (3)
Cd1—N1	2.3438 (16)	C1—C2	1.394 (3)
Cd1—O1 <sup>i</sup>	2.3785 (14)	C1—H1	0.9300
Cd1—O1	2.3785 (14)	C2—C3	1.382 (3)
Cd1—Cl1	2.5721 (5)	C2—H2	0.9300
Cd1—Cl1 <sup>i</sup>	2.5721 (5)	C3—C4	1.383 (3)
S1—C10	1.731 (2)	C3—H3	0.9300
S1—C8	1.7672 (19)	C4—C5	1.394 (3)
O1—C11	1.423 (3)	C4—H4	0.9300
O1—H1A	0.9300	C5—C6	1.398 (3)
N1—C10	1.313 (3)	C5—H5	0.9300
N1—N2	1.399 (2)	C8—C9	1.491 (3)
N2—C7	1.319 (3)	C9—H9A	0.9600
C7—N3	1.379 (2)	C9—H9B	0.9600
C7—C6	1.476 (2)	C9—H9C	0.9600
N3—C10	1.362 (2)	C11—H10A	0.9600
N3—N4	1.386 (2)	C11—H10B	0.9600
N4—C8	1.299 (3)	C11—H10C	0.9600
N1 <sup>i</sup> —Cd1—N1	180.00 (8)	C3—C2—C1	120.7 (2)
N1 <sup>i</sup> —Cd1—O1 <sup>i</sup>	93.09 (6)	C3—C2—H2	119.7
N1—Cd1—O1 <sup>i</sup>	86.91 (6)	C1—C2—H2	119.7

N1 <sup>i</sup> —Cd1—O1	86.91 (6)	C2—C3—C4	119.8 (2)
N1—Cd1—O1	93.09 (6)	C2—C3—H3	120.1
O1 <sup>i</sup> —Cd1—O1	180.0	C4—C3—H3	120.1
N1 <sup>i</sup> —Cd1—Cl1	93.32 (4)	C3—C4—C5	120.1 (2)
N1—Cd1—Cl1	86.68 (4)	C3—C4—H4	119.9
O1 <sup>i</sup> —Cd1—Cl1	92.17 (4)	C5—C4—H4	119.9
O1—Cd1—Cl1	87.83 (4)	C4—C5—C6	120.1 (2)
N1 <sup>i</sup> —Cd1—Cl1 <sup>i</sup>	86.68 (4)	C4—C5—H5	120.0
N1—Cd1—Cl1 <sup>i</sup>	93.32 (4)	C6—C5—H5	120.0
O1 <sup>i</sup> —Cd1—Cl1 <sup>i</sup>	87.83 (4)	C1—C6—C5	119.51 (18)
O1—Cd1—Cl1 <sup>i</sup>	92.17 (4)	C1—C6—C7	118.98 (18)
Cl1—Cd1—Cl1 <sup>i</sup>	180.00 (2)	C5—C6—C7	121.51 (18)
C10—S1—C8	87.32 (9)	N1—C10—N3	110.67 (16)
C11—O1—Cd1	122.51 (14)	N1—C10—S1	139.33 (15)
C11—O1—H1A	118.8	N3—C10—S1	110.00 (14)
Cd1—O1—H1A	118.7	N4—C8—C9	122.19 (18)
C10—N1—N2	106.37 (15)	N4—C8—S1	117.17 (15)
C10—N1—Cd1	124.10 (12)	C9—C8—S1	120.63 (15)
N2—N1—Cd1	129.41 (12)	C8—C9—H9A	109.5
C7—N2—N1	108.57 (15)	C8—C9—H9B	109.5
N2—C7—N3	108.37 (16)	H9A—C9—H9B	109.5
N2—C7—C6	125.23 (17)	C8—C9—H9C	109.5
N3—C7—C6	126.40 (17)	H9A—C9—H9C	109.5
C10—N3—C7	106.01 (15)	H9B—C9—H9C	109.5
C10—N3—N4	117.68 (15)	O1—C11—H10A	109.5
C7—N3—N4	136.30 (15)	O1—C11—H10B	109.5
C8—N4—N3	107.80 (15)	H10A—C11—H10B	109.5
C6—C1—C2	119.8 (2)	O1—C11—H10C	109.5
C6—C1—H1	120.1	H10A—C11—H10C	109.5
C2—C1—H1	120.1	H10B—C11—H10C	109.5

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A $\cdots$ Cl1 <sup>ii</sup>	0.93	2.57	3.2005 (16)	126

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

Fig. 1

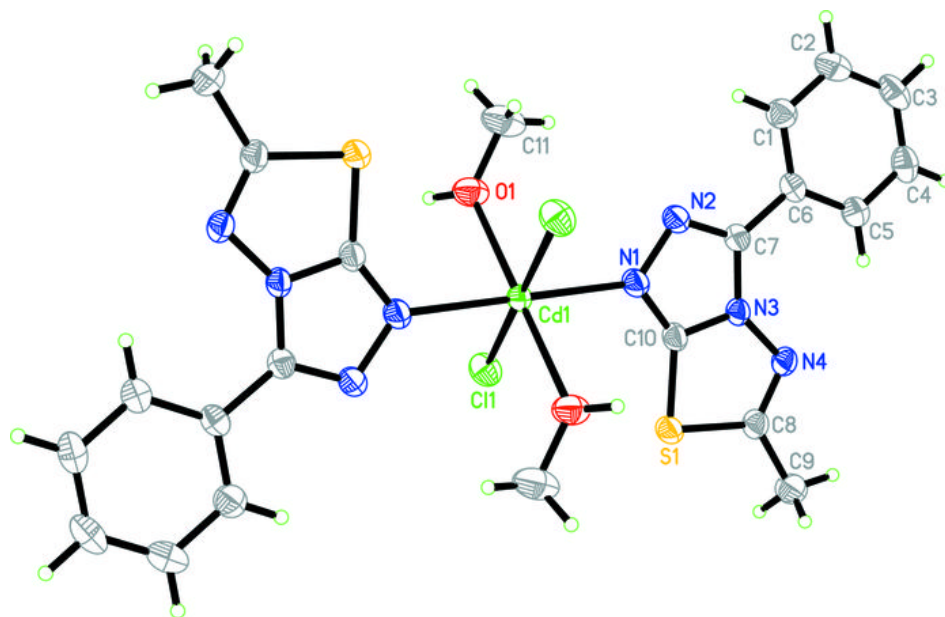




Fig. 2

