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Note

# Cd(II)–NCS/NCO complexes of 1-alkyl-2-(arylazo)imidazole: Single crystal X-ray structure of [Cd(HaaiMe)$_2$(SCN)$_2$]

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**Abstract**

The reaction of Cd(OAc)$_2 \cdot 4H_2O$ and 1-alkyl-2-(arylazo)imidazole [RaaiR′ where R = H (**a**), Me (**b**); R′ = Me (**1**/**3**/**5**), Et (**2**/**4**/**6**)] and NH$_4$NCS/NaNCO in methanol in 1:2:2 mole ratio has afforded [Cd(RaaiR′)$_2$(NCS)$_2$] (**3**,**4**) and [Cd(RaaiR′)$_2$(NCO)$_2$] (**5**,**6**) complexes. The complexes are characterized by different physicochemical methods and in one case, the structure was confirmed by single crystal X-ray diffraction study for title compounds.

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*Keywords:* Arylazoimidazoles; Cadmium(II) complexes; Octahedral; X-ray

## 1. Introduction

We are interested to design imidazole-containing ligands. There are two basic reasons to concentrate on imidazole type systems: biochemical ubiquity and an alternative to polypyridines. The metal complexes of polypyridines have received much attention because of rich electrochemistry, interesting optical properties, bioinorganic chemistry and catalyses [1–7]. This has led to the modification of the ligand system inserting different substituents, presence of other donor centers etc [7–13]. Ligand synthesis using imidazole as heterocyclic backbone is of much advantage because of the biochemical importance of this molecule [14,15]. Imidazole carries *meta*-related two N centers of different basicity and can bind strongly heavy metal ions [16,17]. We have designed a surface modified extractant by anchoring imidazole to polystyrene by azo group (–N=N–) and have been used for the separation of heavy metals from drinking water, environmental samples, medicinal samples and ores, minerals [18]. The fundamental property of interaction between metal ions and organic ligands has been utilized in the design of functional materials. Azoimidazoles is one such system. It has also been used to extract anions through protonation of imidazole motif and subsequent interaction with anions via hydrogen bonding [19]. The exo-bidentate behaviour of the ligand has been eliminated by N(1)-alkylation. The coordination chemistry of 1-alkyl-2-(arylazo)imidazoles (RaaiR′) has been studied by us [20–26] and others [27,28] using transition metals.

In RaaiR′, the active function is the azoimine group (–N=N–C=N–) which is isoelectronic with diimine function (–N=C–C=N–). The non-transition metal complexes of arylazoimidazole has been reported recently by us [29–32]. This ligand acts as a potential bidentate chelator with

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heavier transition metals [20–26]. It comprises with uni- or bidenticity when coordinated with 3d block [20–22] and non-transition metals [29–32]. The Group 12 (Zn, Cd, Hg) metal complexes do not have CFSE and the stereochemistry of the complexes has been controlled by steric effect and the M–N bond strength. As a part of our programme to explore the coordination chemistry of Group 12 metal complexes of arylazoimidazoles, we wish to report in this work the Cd(II)-thiocyanato/isocyanato complexes of 1-alkyl-2-(arylazo)imidaz- oles (RaaiR′). The X-ray structure of one of the complexes has been described.

## 2. Experimental

### 2.1. Materials

Published methods [20] were used to prepare 1-alkyl-2-(arylazo)imidazoles (RaaiR′ where R = H (**a**), Me (**b**); R′ = Me (**1**,**3**,**5**), Et (**2**,**4**,**6**)). All other chemicals and organic solvents used for preparation work were of reagent grade received from SRL, India.

### 2.2. Physical measurements

Microanalyses (C, H, N) were performed using a Perkin–Elmer 2400 CHNO/S elemental analyzer. Spectroscopic measurements were carried out using the following instruments: UV–Vis spectra, reflectance spectra, JASCO UV–Vis/NIR model V-570; IR spectra (KBr disk, 4000–200 cm$^{-1}$), JASCO FT-IR model 420.

### 2.3. Preparation of bis-thiocyanato bis-[1-methyl-2-(phenylazo)imidazole] cadmium(II)

#### 2.3.1. [Cd(HaaiMe)$_2$(NCS)$_2$] (**3a**)

Methanolic solution (15 ml) of 1-methyl-2-(phenylazo)imidazole (HaaiMe, 0.22 g, 1.18 mmol) was added dropwise to Cd(OAc)$_2$ · 4H$_2$O (0.15 g, 0.5 mmol) in the same solvent (20 ml) at room temperature (298 K). Then aqueous-methanolic solution of NH$_4$NCS (0.08 g, 1.05 mmol) was added dropwise. The mixture was stirred for 15 min and filtered. Filtrate was kept undisturbed for few days. Orange-red crystals were obtained and washed with cold water and methanol. Finally, they were dried in vacuo. Isolated yield was 0.185 g, (62%).

All other complexes were prepared by the same procedure and yield varied 60–70%. Microanalytical data of the complexes are as follows: [Cd(HaaiMe)$_2$(NCS)$_2$](**3a**): *Anal.* Calc. for $C_{22}H_{20}N_{10}S_2Cd$: C, 43.96; H, 3.33; N, 23.31. Found: C, 43.90; H, 3.27; N, 23.38%. [Cd(MeaaiMe)$_2$(NCS)$_2$] (**3b**): *Anal.* Calc. for $C_{24}H_{24}N_{10}S_2Cd$: C, 45.82; H, 3.81; N, 22.27. Found: C, 45.73; H, 3.74; N, 22.18%. [Cd(HaaiEt)$_2$(NCS)$_2$] (**4a**): *Anal.* Calc. for $C_{24}H_{24}N_{10}S_2Cd$: C, 45.82; H, 3.81; N, 22.27. Found: C, 45.76; H, 3.74; N, 22.18%. [Cd(MeaaiEt)$_2$(NCS)$_2$] (**4b**): *Anal.* Calc. for $C_{26}H_{28}N_{10}S_2Cd$: C, 47.53; H, 4.26; N, 21.32. Found: C, 47.44; H, 4.18; N, 21.24%.

### 2.4. Preparation of bis-isocyanato-bis-[1-methyl-2-(phenylazo)imidazole] cadmium(II)

#### 2.4.1. [Cd(HaaiMe)$_2$(NCO)$_2$] (**5a**)

Methanolic solution (15 ml) of 1-methyl-2-(phenylazo)imidazole (HaaiMe, 0.22 g, 1.18 mmol) was added dropwise to Cd(OAc)$_2$ · 4H$_2$O (0.15 g, 0.5 mmol) in the same solvent (20 ml) at room temperature (298 K). Then aqueous-methanolic solution of NaNCO (0.07 g, 1.08 mmol) was added dropwise. The mixture was stirred for 15 min and filtered. Filtrate was kept undisturbed for few days. Orange-red crystals were obtained and washed with cold water and methanol. Finally they were dried in vacuum. Isolated yield was 0.15 g, (53%).

All other complexes were prepared by the same procedure and yield varied 60–70%. Microanalytical data of the complexes are as follows: [Cd(HaaiMe)$_2$(NCO)$_2$] (**5a**): *Anal.* Calc. for $C_{22}H_{20}N_{10}O_2Cd$: C, 46.45; H, 3.52; N, 24.63. Found: C, 46.32; H, 3.60; N, 24.48%. [Cd(MeaaiMe)$_2$(NCO)$_2$] (**5b**): *Anal.* Calc. for $C_{24}H_{24}N_{10}O_2Cd$: C, 48.29; H, 4.02; N, 23.47. Found: C, 48.18; H, 3.94; N, 23.33%. [Cd(HaaiEt)$_2$(NCO)$_2$] (**6a**): *Anal.* Calc. for $C_{24}H_{24}N_{10}O_2Cd$: C, 48.29; H, 4.02; N, 23.47. Found: C, 48.20; H, 3.90; N, 23.35%. [Cd(MeaaiEt)$_2$(NCO)$_2$] (**6b**): *Anal.* Calc. for $C_{26}H_{28}N_{10}O_2Cd$: C, 49.97; H, 4.48; N, 22.42. Found: C, 49.81; H, 4.43; N, 22.35%.

### 2.5. X-ray crystal structure analysis of [Cd(HaaiMe)$_2$(NCS)$_2$] (**3a**)

Crystal is growing (orange block, 0.3 × 0.3 × 0.2 mm$^3$) by slow evaporation of methanolic solution of mixture containing Cd(OAc)$_2$, HaaiMe and NH$_4$CNS in 1:2:2 molar ratio. A summary of the crystallographic data and structure refinement parameters are given in Table 1. Data were collected with Siemens SMART CCD diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The intensity data were corrected for Lorentz and polarisation effects and an empirical absorption correction was employed using SAINT program. A total of 16633 reflections [range $3.4 \leqslant 2\theta \leqslant 56.74°$] were collected and 3600 were assumed observed applying the condition $I > 2\sigma(I)$. The structure was solved by direct methods and followed by successive Fourier and difference Fourier syntheses. Full matrix least squares refinements on $F^2$ were carried out for both cases using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were fixed geometrically and refined using the riding model. In the final difference Fourier map the residual minima and maxima were −0.554 and 0.939 e/Å$^3$. Complex neutral atom scattering factors were used throughout. All calculations were carried out using SHELXS-97, SHELXL-97, PLATON-99, ORTEP programs.

Table 1
Summarized crystallographic data for $[Cd(HaaiMe)_2(NCS)_2]$ (**3a**)

| | $[Cd(HaaiMe)_2(NCS)_2]$ (**3a**) |
|---|---|
| Empirical formula | $C_{22}H_{20}CdN_{10}S_2$ |
| Formula weight | 601.03 |
| Temperature (K) | 293 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ (No. 14) |
| *Unit cell dimensions* | |
| $a$ (Å) | 8.9960(9) |
| $b$ (Å) | 15.3217(15) |
| $c$ (Å) | 19.352(2) |
| $\beta$ (°) | 91.445(2) |
| $V$ (Å)$^3$ | 2666.5(5) |
| $Z$ | 4 |
| $\lambda$ (Å) | 0.71073 |
| $\mu$(Mo K$\alpha$) (mm$^{-1}$) | 1.006 |
| $D_{calc}$ (mg m$^{-3}$) | 1.497 |
| Refine parameters | 316 |
| Total collected data | 16633 |
| Unique data [$I > 2\sigma$(I)] | 3600 |
| $R_1$[a][$I > 2\sigma(I)$] | 0.0760 |
| $wR_2$[b] | 0.2644 |
| Goodness-of-fit | 1.03 |

[a] $R = \sum|F_o - F_c|/\sum F_o$.

[b] $wR = [\sum w(F_o^2 - F_c^2)/\sum wF_o^4]^{1/2}$ are general but $w = 1/[\sigma^2(F_o^2) + (0.1616P)^2 + (0.0000P)]$, where $P = (F_o^2 + 2F_c^2)/3$.

## 3. Result and discussion

### 3.1. Synthesis and formulation

The reaction of $Cd(OAc)_2 \cdot 4H_2O$, RaaiR′ and $NH_4CNS$ in the mole proportion of 1:1:2 has synthesized $\mu_{1,3}$-NCS bridged cadmium polymer [30]. The reaction of $Cd(ClO_4)_2$ or $Cd(NO_3)_2$ salt with excess of RaaiR′, however synthesized tetrahedral $Cd(RaaiR')_4{}^{2+}$ compounds [32]. In this work we are using different compositions of the metal:ligand:$NCS^-$. Methanolic solution of $Cd(OAc)_2 \cdot 4H_2O$ and RaaiR′ in the mole ratio of 1:2 followed by the addition of 2 equivalent of $NH_4NCS$ or NaNCO at later stage has isolated complexes of the composition $[Cd(RaaiR')_2(NCS)_2]$ (**3**,**4**) and $[Cd(RaaiR')_2(NCO)_2]$ (**5**,**6**), respectively. The microanalytical data support the composition of the complexes. They are non-electrolyte in nature.

### 3.2. Spectral studies

#### 3.2.1. IR spectra

In the infrared spectra, the point of interest is the band due to the thiocyanate (–NCS)/isocyanate (–NCO), azo (–N=N–) and imine (–C=N–) groups in the complexes. The spectra show very strong band at 2063–2067 cm$^{-1}$ for **3** and**4** which are assigned to $\nu$(NCS) (Table 2). The compounds **5**, **6** show very strong band at 2190–2208 cm$^{-1}$ and have been assigned to $\nu$(NCO). Moderately intense stretchings at ca. 1595 and ca. 1445 cm$^{-1}$ are due to $\nu$(C=N) and $\nu$(N=N), respectively. In free ligands [22,29] $\nu$(N=N) and $\nu$(C=N) appear at 1455–1460 and 1605–1615 cm$^{-1}$. In the complexes, these are shifted to lower frequency region which are in support of coordination of azo-N and imine-N to Cd(II) centre.

#### 3.2.2. Electronic spectra

The solution electronic spectra of the complexes **3** and **4** show intense transition <400 nm and are assigned to ligand centered transitions. Two weak ($\varepsilon \sim 10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$) transitions are observed at >440 nm (Table 2). The ligands are π-acidic and $Cd^{2+}$ is a $d^{10}$ system, thus the transition may be assigned to d(Cd) → π* (ligand) transition.

#### 3.2.3. $^1H$ NMR spectra

The $^1H$ NMR spectra of $[Cd(RaaiR')_2(NCS)_2]$ (**3**,**4**) and $[Cd(RaaiR')_2(NCO)_2]$ (**5**,**6**) were recorded in $CD_3CN$. The spectral data are collected in Table 3. The proton numbering pattern is shown in Scheme 1. The assignment has been made on the basis of spin–spin interaction and on comparing with reported data [30–32]. Imidazole protons (4- and 5-H) of $[Cd(RaaiR')_2(NCS)_2]$ (**3**,**4**) appear at ca. 7.5 and 7.3 ppm and are singlet in nature which may be due to rapid proton exchange with solvent proton ($CD_3CN$ is hydrolysed on exposure to air). In $Cd(RaaiR')_2(NCO)_2$ (**5**,**6**) 4-H appears at ~0.3 ppm (ca. 7.6 ppm) higher $\delta$ than 5-H (ca. 7.3 ppm). It is concluded that 4-H is closer to the metal centre. This is also supported from single crystal X-ray structure (Fig. 2) where RaaiR′ is bounded to Cd(II) through N(3) center only. Influence of anion ligand is also reflected from the NMR data; being a better electron withdrawing agent NCO than NCS, the chemical shift of the coordinated ligands in **5**, **6** are shifted to higher $\delta$ by about 0.1 ppm. N(1)–Me appears at ca. 4 ppm; N(1)–$CH_2$–$CH_3$ shows quartet and triplet splitting signals at ca. 4.4 ($J = 9.0$ Hz) and ca. 1.6 ($J = 7.5$ Hz) ppm, respectively, for –$CH_2$, and –$CH_3$ groups. The N(1)–$CH_2$–Ph gives a singlet response at ~5.35 ppm. Aryl protons (7-11-H) appear at usual position (7.4–7.8 ppm) and suffer shifting to downfield position with reference to free ligand value.

### 3.3. Molecular structure

The molecular structure of $[Cd(NCS)_2(HaaiMe)_2]$ (**3a**) is shown in Fig. 1. Bond distances and angles are set out in Table 4. The metric parameters (Table 2) and figure show distorted $CdN_6$ coordination sphere. The octahedral coordination is satisfied by four N centers from two HaaiMe ligands and other two N-centres from two NCS groups. HaaiMe acts as bidentate N(imidazole), N(azo) chelator. The chelating N–Cd–N bond angle is N(1)–Cd(1)–N(4), 67.2(2)° and lies in the limiting value of Group 12 complexes of azoheterocycles [29–32]. Other chelate angle N(5)–Cd(1)–N(8) is very low, 62.2(1)°. Very long Cd(1)–N(8) bond distance (2.919(2) Å) may be due to the low chelate angle. In pseudo-octahedral compounds of type $MX_2(N,N')_2$, five different isomers are possible: two compounds having *trans*-$MX_2$ configuration and three

Table 2
UV–Vis spectra[a], and IR[b]

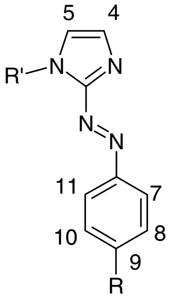
| Compound | UV–Vis spectral data ($\lambda_{max}$/nm) ($10^{-3}$ $\varepsilon$ $M^{-1}$ $cm^{-1}$) | IR spectra, $cm^{-1}$ | | |
|---|---|---|---|---|
| | | $\nu$(NCS/NCO) | $\nu$(C=N) | $\nu$(N=N) |
| [Cd(HaaiMe)$_2$(NCS)$_2$] (**3a**) | 432(0.99), 386(2.81), 372(2.77), 232(1.33) | 2060 | 1590 | 1440 |
| [Cd(MeaaiMe)$_2$(NCS)$_2$] (**3b**) | 442(1.69), 384(3.74), 372(2.83), 234(1.22) | 2060 | 1598 | 1444 |
| [Cd(HaaiEt)$_2$(NCS)$_2$] (**4a**) | 432(1.42), 390(3.45), 356(3.97), 236(1.67) | 2055 | 1585 | 1445 |
| [Cd(MeaaiEt)$_2$(NCS)$_2$] (**4b**) | 434(1.51), 386(3.29), 370(3.20), 244(1.09) | 2060 | 1595 | 1440 |
| [Cd(HaaiMe)$_2$(NCO)$_2$] (**5a**) | 445(0.73), 395(2.65), 370(2.67), 238(1.40) | 2190 | 1600 | 1448 |
| [Cd(MeaaiMe)$_2$(NCO)$_2$] (**5b**) | 452(0.69), 398(3.45), 370(2.73), 236(1.32) | 2202 | 1594 | 1450 |
| [Cd(HaaiEt)$_2$(NCO)$_2$] (**6a**) | 438(1.28), 396(3.55), 350(3.75), 240(1.74) | 2208 | 1605 | 1455 |
| [Cd(MeaaiEt)$_2$(NCO)$_2$] (**6b**) | 444(1.21), 392(3.16), 360(3.10), 244(1.26) | 2195 | 1600 | 1450 |

[a] In $CH_3OH$.
[b] In KBr disk.

Table 3
$^1H$ NMR spectral data in $CD_3CN$ at room temperature

| Compound | $\delta$, ppm (J, Hz) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 4-H[a] | 5-Ha | 7,11-Ha | 8-10-H | 9-Me | 1-Me | 1-CH$_2$[c] | (1-CH$_2$)CH$_3$[d] |
| **3a** | 7.48(7.0) | 7.27(7.0) | 7.90(7.5) | 7.44[b] | | 4.09 | | |
| **3b** | 7.50(7.0) | 7.27(7.0) | 7.92(7.5) | 7.34(7.5)[a] | 2.45 | 4.11 | | |
| **4a** | 7.53(7.5) | 7.28(7.5) | 7.91(7.8) | 7.46[b] | | | 4.42 (12.0) | 1.52 (7.5) |
| **4b** | 7.51(7.5) | 7.32(7.5) | 7.89(7.5) | 7.34(7.5)[a] | 2.45 | | 4.50 (12.0) | 1.57 (7.5) |
| **5a** | 7.61(7.0) | 7.30(7.0) | 7.92(7.5) | 7.55[b] | | 4.10 | | |
| **5b** | 7.64(7.5) | 7.32(7.5) | 7.95(7.8) | 7.37(7.0)[a] | 2.47 | 4.13 | | |
| **6a** | 7.62(7.0) | 7.30(7.0) | 7.95(7.0) | 7.51[b] | | | 4.04 (10.0) | 1.55 (7.0) |
| **6b** | 7.59(7.0) | 7.29(7.0) | 7.92(7.0) | 7.34(7.0)[a] | | | 4.52 (10.0) | 1.58 (7.0) |

[a] Doublet.
[b] Multiplet.
[c] Quartet.
[d] Triplet.



Scheme 1. RaaiR′: R = H (**1**,**3**,**5**); Me (**2**, **4**, **6**) R′ = Me (**a**), Et (**b**).

compounds having *cis*-MX$_2$ configuration [25]. Sequence of coordination of pairs of donor centers following pairs of X, N and N′ donor centers the isomers are assigned as *trans–cis–cis*, *trans–trans–trans*, *cis–trans–trans*, *cis–trans–cis*, and *cis–cis–cis*. The orientation of donor centers in the present complex about Cd(II) has constituted *cis–cis–cis* type geometrical isomer. The atomic arrangements Cd(1), N(1), C(1), N(3), N(4); Cd(1), N(5), C(12), N(7), N(8) constitute two chelate planes (deviation < 0.03 Å) and are inclined at dihedral ca. 70°. The pendant phenyl groups are also planar and make dihedral of ca. 7° with respective chelated azoimine fragment. Three atomic arrangements Cd(1), N(4), N(5), N(8), N(9) (plane-1); Cd(1), N(1), N(8), N(9), N(10) (plane-2); Cd(1), N(1), N(4), N(5), N(10) (plane-3) constitute three molecular

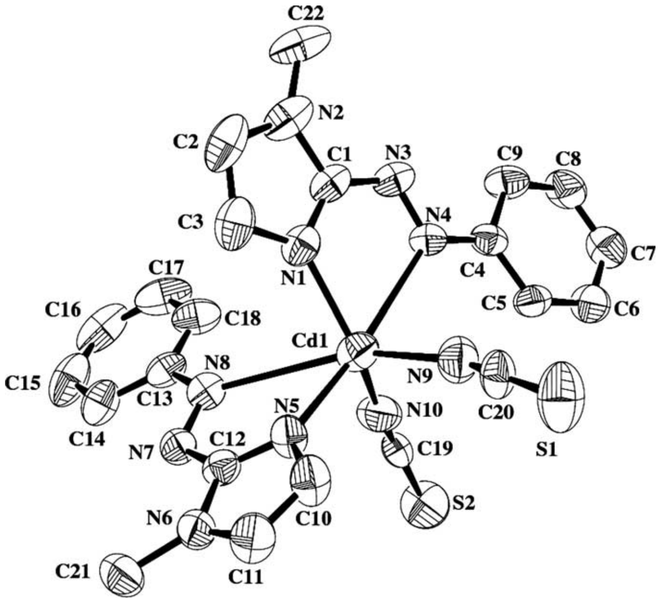


Fig. 1. ORTEP diagram of [Cd(HaaiMe)$_2$(NCS)$_2$] (with 50% probability ellipsoids).

Table 4
Selected bond distances and bond angles of **3a**

| Bond distance (Å) | | Bond angle (°) | |
|---|---|---|---|
| Cd(1)–N(1) | 2.086(6) | N(1)–Cd(1)–N(4) | 67.2(2) |
| Cd(1)–N(4) | 2.677(5) | N(1)–Cd(1)–N(5) | 105.4(2) |
| Cd(1)–N(5) | 2.202(5) | N(1)–Cd(1)–N(9) | 111.2(3) |
| Cd(1)–N(9) | 2.124(8) | N(1)–Cd(1)–N(10) | 130.9(3) |
| Cd(1)–N(10) | 2.044(6) | N(4)–Cd(1)–N(5) | 171.81(17) |
| S(1)–C(20) | 1.616(8) | N(4)–Cd(1)–N(9) | 87.8(2) |
| S(2) –C(19) | 1.608(7) | N(4)–Cd(1)–N(10) | 86.5(2) |
| N(9)–C(20) | 1.137(11) | N(5)–Cd(1)–N(9) | 92.0(2) |
| N(10)–C(19) | 1.120(9) | N(5)–Cd(1)–N(10) | 101.3(2) |
| N(3)-N(4) | 1.243(8) | N(9)–Cd(1)–N(10) | 108.2(3) |
| N(7) –N(8) | 1.253(7) | Cd(1)–N(4)–N(3) | 111.4(4) |
| Cd(1)-N(8) | 2.919(2) | N(8)–Cd(1)–N(5) | 62.2(1) |
| | | N(8)–Cd(1)–N(9) | 154.1(7) |
| | | N(8)–Cd(1)–N(10) | 78.0(2) |
| | | N(8)–Cd(1)–N(1) | 79.1(3) |
| | | N(8)–Cd(1)–N(4) | 117.9(3) |

planes and maximum deviation has been observed for N(azo) (N(4/8)) and they make dihedral 75–88°.

There are three types of N-centres: N(imidazole) (N(1)/N(5)), N(azo) (N(4)/N(8)) and N(thiocyanato) (N(9)/N(10)). The Cd–N(thiocyanato) and Cd–N(imidazole) distances do not differ widely. The Cd–N(azo) distances are the longest in the series and they are not equivalent: Cd(1)–N(4), 2.677(5) and Cd(1)–N(8), 2.919(2) Å. It is because the N(azo) requires considerably more room than the other two types of N-donors. There are at least two steric reasons for this. First, the N(azo) belongs to exocyclic N=N along with a pendant phenyl group; thus the van der Waals repulsion will be greater than N(imidazole). The lowering in overall symmetry is manifested by the elongation of two Cd–N(azo) distances. However, the Cd–N(azo) distances are less than the sum of the van der Waals radii of Cd(II) (1.58 Å) and N(azo) (1.55 Å) [33,34]. This implies covalent interaction of N(azo) and Cd(II).

Three different types of non-covalent interactions (C–H–S; C–H–π and π–π) are observed in the packing view of the molecule (Figs. 2–4). Hydrogen bonding with non-bonded S is scarce [35]. The coordinated M–NC*S* is hydrogen bonded with H of $N–CH_3$ group and 1-D chain has been generated along the $x$-direction [C(22)–H(22b)–S(1): C–H, 0.96 Å; H–S(1), 2.76 Å; C(22)–S(1), 3.602(10) Å; ∠C(22)–H(22B)–S(1), 164°; symmetry: $x$, $1/2 - y$, $1/2 + z$] (Fig. 2). It is proposed that S in M–NCS is more electronegative and less polarisable than sulfide-S and may exhibit an affinity to acidic-H. In fact, this proton abstracting affinity in dilute acid solution is

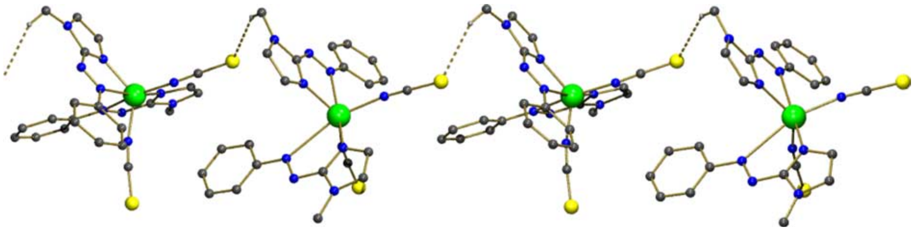


Fig. 2. 1-D chain constituted by hydrogen bonding along $x$-direction.

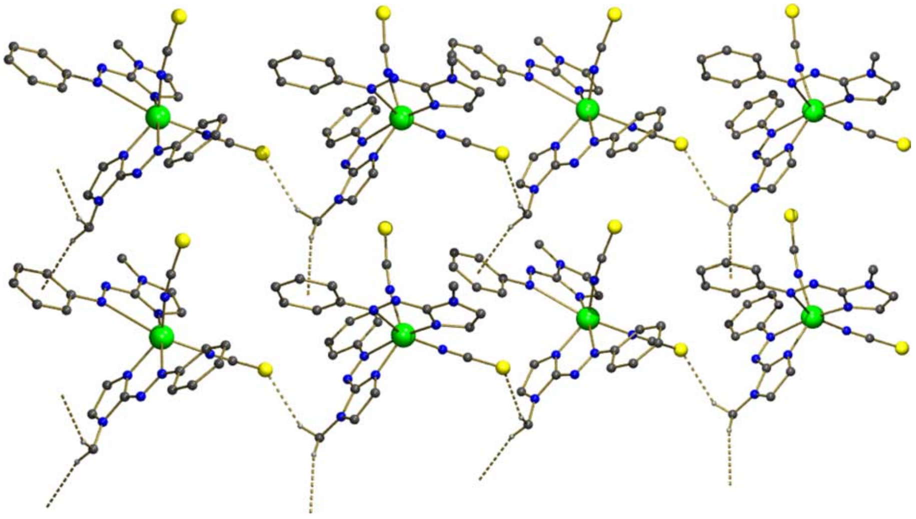


Fig. 3. Sheet formation of 1D chain by C–H–π interaction.

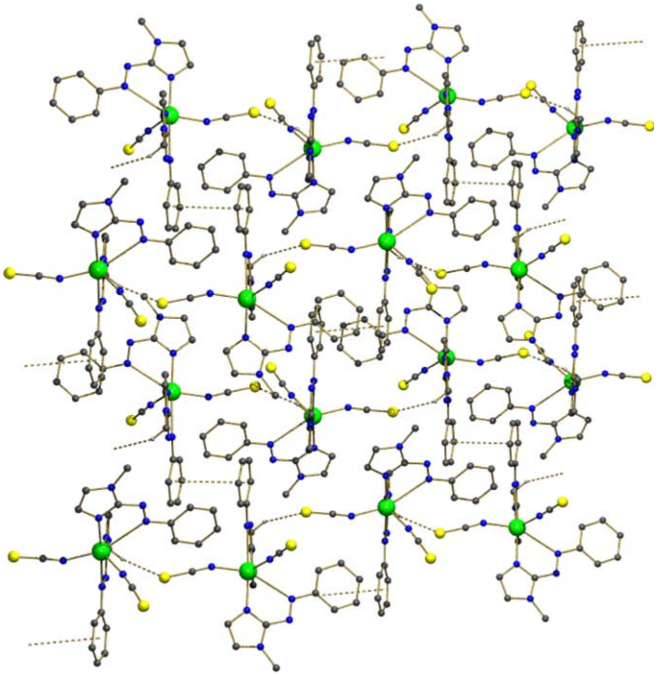


Fig. 4. Unit cell pack showing π–π interaction between inter-chain pendant phenyl groups.

responsible for liberation of $H_2S$ from thiourea, thiocarbamate [36] and serves as a very good supplement of $H_2S$ gas in analytical laboratory for environmental reasons. The C–H–π interaction is also observed in C(22)–H(22A)–Cg (5): H–Cg, 2.75 Å; ∠C(22)–H(22A)–Cg(5), 164°; where Cg(5) stands for pendant phenyl ring, C(13), C(14), C(15), C(16), C(17), C(18) (symmetry: $1+x$, $y$, $z$) (Fig. 3). An inter-chain π–π interaction is observed between pendant Ph rings, Cg(4)–Cg(9), 3.887(4) Å (Cg(4): C(4), C(5), C(6), C(7), C(8), C(9); Cg(9): C(4a), C(5a), C(6a), C(7a), C(8a), C(9a) where a stands for the neighboring molecule symmetry, $1-x$, $-y$, $1-z$) which constitutes a supramolecular structure (Fig. 4).

## 4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic data center, CCDC No. 274228 for $[Cd(HaaiMe)_2(NCS)_2]$ (**3a**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1FZ, UK.

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