

## Structural systematics of some metal complexes with 4,5-diazafluoren-9-one

ABHIJIT PAL<sup>a</sup>, BHASKAR BISWAS<sup>a,b</sup>, MERRY MITRA<sup>a</sup>, CHANDRA SHEKHAR PUROHIT<sup>c</sup>, CHIA-HER LIN<sup>d</sup> and RAJARSHI GHOSH<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, The University of Burdwan, Burdwan 713 104, India

<sup>b</sup>Department of Chemistry, Raghunathpur College, Purulia 723 133, India

<sup>c</sup>Department of Chemical Sciences, National Institute of Science Education and Research, Bhubaneswar 751 005, India

<sup>d</sup>Department of Chemistry, Chung Yuan Christian University, Chung Li 32023, Taiwan, Republic of China  
e-mail: rajarshi\_chem@yahoo.co.in

MS received 25 September 2013; revised 20 January 2014; accepted 27 January 2014

**Abstract.** Synthesis and X-ray structural characterization of three complexes of type *cis*-[M(dafone)<sub>2</sub>(NCS)<sub>2</sub>] (M = Co(II), **1**; Ni(II), **2**; Zn(II), **3**; dafone = 4,5-diazafluoren-9-one) and a polymer *cis*-[Cd(dafone)(NCS)<sub>2</sub>]<sub>n</sub> (**4**) have been reported. Each of the four complexes is crystallized in orthorhombic crystal system. Structural study reveals that each metal(II) centre in the four complexes adopts distorted octahedral geometry with MN<sub>6</sub> chromophore in **1-3** and MN<sub>4</sub>S<sub>2</sub> chromophore in **4**. The room temperature steady-state fluorescence intensity of dafone in dimethyl formamide at 402 nm is found to be quenched in these reported dafone complexes (**1-4**).

**Keywords.** Transition metal ions; imine ligand; crystal structure; fluorescence.

### 1. Introduction

Design and synthesis of coordination compounds of different nuclearity are being continued<sup>1,2</sup> because of their various synthetic, structural and physicochemical features. Different diimine ligands are being used<sup>3,4</sup> in this direction because of synthetic accessibilities and spectroscopic properties of their own and the complexes synthesized there from. Common bipyridyls with diimine functions such as 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), etc. and their derivatives are often used<sup>3,4</sup> to synthesize variety of complexes with different nuclearity and interesting properties. The ambidentate thiocyanates, having soft sulphur and hard nitrogen donor centres, show a number of coordination motifs<sup>5</sup> towards metal ions exhibiting different molecular structures with different dimensionalities.<sup>5</sup> In recent times a number of transition and innertransition metal complexes from diimine donors as a part of Schiff base ligand had been reported by our group.<sup>6</sup> In this study, we have used 4,5-diazafluoren-9-one

(dafone),<sup>7</sup> the diimine with larger chelate bite than the bpy and phen (free dafone: 3.05 Å, bpy: 2.62 Å, phen: 2.64 Å),<sup>8</sup> oxidized from 1,10-phenanthroline to synthesize a series of complexes with Co(NCS)<sub>2</sub> (**1**), Ni(NCS)<sub>2</sub> (**2**),<sup>8a,8b</sup> Zn(NCS)<sub>2</sub> (**3**) and Cd(NCS)<sub>2</sub> (**4**). Interestingly, the X-ray structural analyses in each case reveal that all these are *cis* complexes and the mononuclear *cis* moiety of Cd(NCS)<sub>2</sub> forms polymer because of the soft-hard nature of the thiocyanate. The complexes also show room temperature steady-state fluorescence behaviour. Though a few of the Cu(II),<sup>8a,8b,9</sup> Ni(II),<sup>8a,8b</sup> Zn(II),<sup>8c</sup> Ru(II)<sup>10</sup> and Pt(II)<sup>8c</sup> complexes of dafone are reported in literature, here we have tried to establish the structural systematics and photophysical behaviour of a group of new complexes including a reported one.<sup>8a,8b</sup>

### 2. Experimental

#### 2.1 Preparation of the complexes **1-4**

2.1a *Chemicals, solvents and starting materials:* High purity 1,10 phenanthroline (E Merck, India), potassium permanganate (E Merck, India), potassium

\*For correspondence

hydroxide (E Merck, India), cobalt(II) perchlorate hexahydrate (E Merck, India), nickel(II) nitrate hexahydrate (E Merck, India), zinc(II) acetate dihydrate (E Merck, India) and cadmium(II) acetate dihydrate (E Merck, India) and all other solvents were purchased from the respective companies and used as received. Solvents were dried according to standard procedure and distilled prior to use.

(*Caution!* Perchlorate salts of metal ions are potentially explosive, especially in the presence of organic ligands. Only a small amount of material should be prepared and it should be handled with care.)

**2.1b Preparation of *L* and **1-4**:** The ligand dafone was prepared using a reported method.<sup>10</sup> The ligand was characterized by X-ray crystallography (figure 1, table 1).

Dafone (0.364 g, 2 mmol) in methanol was added slowly to the methanolic solution of  $\text{Co}(\text{ClO}_4)_2$  (0.361 g, 1 mmol) resulting in a light brown coloured solution which was intensified on gradual addition of  $\text{NH}_4\text{NCS}$  (0.152 g, 2 mmol). The final reaction solution was kept in open air for slow evaporation. Light brown crystals appeared after about a week. Yield: (based on metal salt) 0.388 g (72.00%). Anal. Calc. for  $\text{C}_{24}\text{H}_{12}\text{N}_6\text{O}_2\text{S}_2\text{Co}$  (**1**): C, 53.43; H, 2.24; N, 15.58; Found: C, 52.96; H, 2.58; N, 16.01. Selected IR bands (KBr pellet,  $\text{cm}^{-1}$ ): 1586, 1737, 2070, 2083. UV-Vis ( $\lambda$ , nm; dimethylformamide): 269, 304, 316, 528, 623.

The aqueous solution of  $\text{Ni}(\text{NO}_3)_2$  (0.290 g, 1 mmol) in a beaker was mixed with dafone (0.364 g, 2 mmol) in methanol slowly. The solid  $\text{NH}_4\text{NCS}$  (0.152 g, 2 mmol) was added in portion with continuous

stirring. The resultant solution was kept in open air for slow evaporation to obtain green crystals after 7 days. Yield: (based on metal salt) 0.380 g (75.00%). Anal. Calc. for  $\text{C}_{24}\text{H}_{12}\text{N}_6\text{O}_2\text{S}_2\text{Ni}$  (**2**): C, 56.85; H, 2.39; N, 16.58; Found: C, 56.24; H, 2.56; N, 17.15. Selected IR bands (KBr pellet,  $\text{cm}^{-1}$ ): 1584, 1638, 1737, 2083, 2097. UV-Vis ( $\lambda$ , nm; dimethylformamide): 268, 304, 316, 592, 660.

Solid  $\text{Zn}(\text{OAc})_2$  (0.219 g, 1 mmol) and aqueous  $\text{NH}_4\text{NCS}$  (0.152 g, 2 mmol) were consecutively added to methanolic solution of dafone (0.364 g, 2 mmol) to get a yellow solution. Light yellow crystals appeared from this solution after a week or so in open air at room temperature. Yield: (based on metal salt) 0.415 g (76.00%). Anal. Calc. for  $\text{C}_{24}\text{H}_{12}\text{N}_6\text{O}_2\text{S}_2\text{Zn}$  (**3**): C, 52.80; H, 2.22; N, 15.39; Found: C, 52.50; H, 2.13; N, 15.82. Selected IR bands (KBr pellet,  $\text{cm}^{-1}$ ): 1588, 1618, 1737, 2069, 2089. UV-Vis ( $\lambda$ , nm; dimethylformamide): 271, 303, 316.

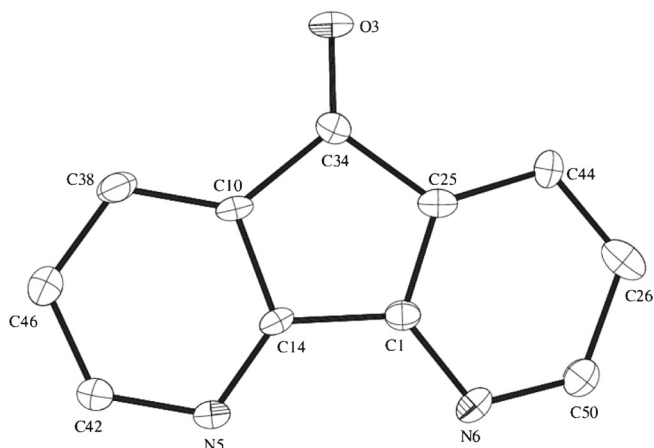
Complex **4** was prepared following the same procedure as for **3**. Only  $\text{Cd}(\text{OAc})_2$  (0.266 g, 1 mmol) was used in place of  $\text{Zn}(\text{OAc})_2$ . The proportion of dafone (0.182 g, 1 mmol) and  $\text{NH}_4\text{NCS}$  (0.152 g, 2 mmol) was also different. Yield: (based on metal salt) 0.575 g (70.00%). Anal. Calc. for  $\text{C}_{26}\text{H}_{12}\text{N}_8\text{O}_2\text{S}_4\text{Cd}_2$  (**4**): C, 38.01; H, 1.47; N, 13.64; Found: C, 38.95; H, 1.36; N, 14.05. Selected IR bands (KBr pellet,  $\text{cm}^{-1}$ ): 1586, 1638, 1729, 2069, 2096. UV-Vis ( $\lambda$ , nm; dimethylformamide): 269, 304, 316.

## 2.2 Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin–Elmer 2400 CHNS/O elemental analyser. UV-Vis, IR and fluorescence spectra (KBr discs, 4000–300  $\text{cm}^{-1}$ ) were recorded using a Shimadzu UV-Vis 2450 spectrophotometer, Perkin–Elmer FT-IR Omodel RX1 spectrometer and Perkin–Elmer LS55 fluorimeter, respectively.

## 2.3 X-ray diffraction

Single crystals of dafone and **1-4** suitable for X-ray crystallographic analysis were selected following examination under a microscope. Diffraction data at room temperature for dafone and **2**, respectively and for **1**, **3** and **4** were collected on a Bruker SMART APEX II CCD and Bruker-Kappa APEX II CCD diffractometers, respectively using  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Crystal data and refinement details are listed in table 1. Dafone was identified as  $\text{P2}_1/\text{c}$ , **1-3** were identified as  $\text{Pbcn}$  and **4** was identified as  $\text{Pbca}$



**Figure 1.** ORTEP of dafone with 20% ellipsoid probability for all non-hydrogen atoms.

**Table 1.** Crystal data and structure refinement parameters for dafone and 1–4.

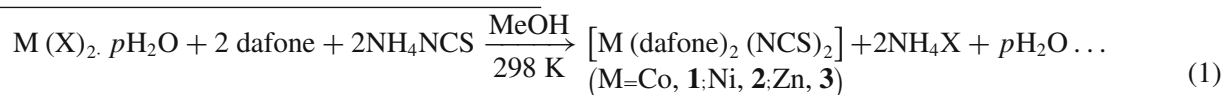
Parameters	Dafone	1	2	3	4
Empirical formula	$C_{11}H_6N_2O$	$C_{24}H_{12}N_6O_2S_2Co$	$C_{24}H_{12}N_6O_2S_2Ni$	$C_{24}H_{12}N_6O_2S_2Zn$	$C_{26}H_{12}N_8O_2S_4Cd_2$
Formula weight	182.18	539.47	507.00	545.89	821.48
Temperature (K)	293(2)	296(2)	295(2)	293.2	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	Pbcn	Pbcn	Pbcn	Pbca
<i>a</i> (Å)	20.0124(12)	13.2698(8)	13.234(4)	13.245 (5)	17.1019(5)
<i>b</i> (Å)	12.4068(7)	10.4060(6)	10.430(3)	10.334 (5)	13.0350(4)
<i>c</i> (Å)	6.8156(4)	16.5831(10)	16.504(5)	17.004 (5)	25.8627(7)
<i>V</i> (Å <sup>3</sup> )	1668.90(17)	2289.9(2)	2278.1(12)	2327.4 (16)	5765.4(3)
<i>Z</i>	8	8	4	4	8
$D_{calc}$ (Mgcm <sup>-3</sup> )	1.402	1.565	1.572	1.558	1.893
$\mu$ (mm <sup>-1</sup> )	0.095	0.968	1.071	1.270	1.806
<i>F</i> (000)	704	1092	1096	1104	3200
$\theta$ ranges (°)	1.03–28.30	2.77–23.94	2.47–29.01	2.77–26.18	2.86–24.59
<i>h</i> / <i>k</i> / <i>l</i>	–26/26, –16/16, –8/9	–16/15, –12/12, –18/20	–17/17, –13/14, –22/22	–16/16, –12/12, –16/21	–23/23, –17/16, –34/34
Reflections collected	15990	2239	20872	23187	76927
Independent reflections [ $R_{int}$ ]	2005	1578	2977	0.0594	7457
Completeness to $\theta$ (%)	99.6	99.2	98.1	99.4	99.5
Goodness-of-fit on $F^2$	0.817	1.027	0.982	1.056	1.051
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	0.1018	0.037	0.0502	0.0712	0.0411
<i>R</i> indices (all data)	0.4191	0.1027	0.1468	0.1025	0.0630
Largest peak and hole (eÅ <sup>-3</sup> )	0.367 and –0.419	0.046 and –0.274	0.401 and –0.921	0.616 and –0.595	1.219 and –0.656

space groups. The structures were solved by direct methods, and the structure solution and refinement were based on  $|F|^2$ . The final differences Fourier map showed the maximum and minimum peak heights at 0.367 and  $-0.419$  for dafone, 0.046 and  $-0.274$  for **1**, 0.401 and  $-0.921$  for **2**, 0.616 and  $-0.595$  for **3** and 1.219 and  $-0.656$  for **4** with no chemical significance. All calculations were carried out using SHELXL-97<sup>11</sup> and ORTEP-32.<sup>12</sup>

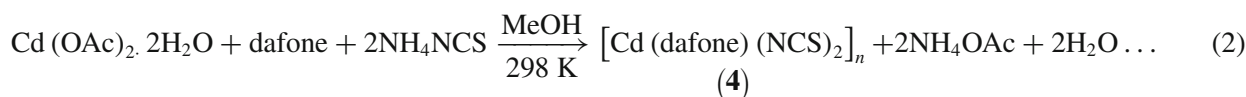
### 3. Results and discussion

#### 3.1 Synthesis and formulation

Reactions at room temperature with required molar ratio among metal(II) salts, dafone and ammonium thiocyanate in aqueous methanol produce the complexes **1–4** in good yield. The reactions can be generalized in the following way:



[M = Co (II), Ni (II), Zn (II); X = ClO<sub>4</sub>NO<sub>3</sub>, OAc, respectively; p = wholenumber]

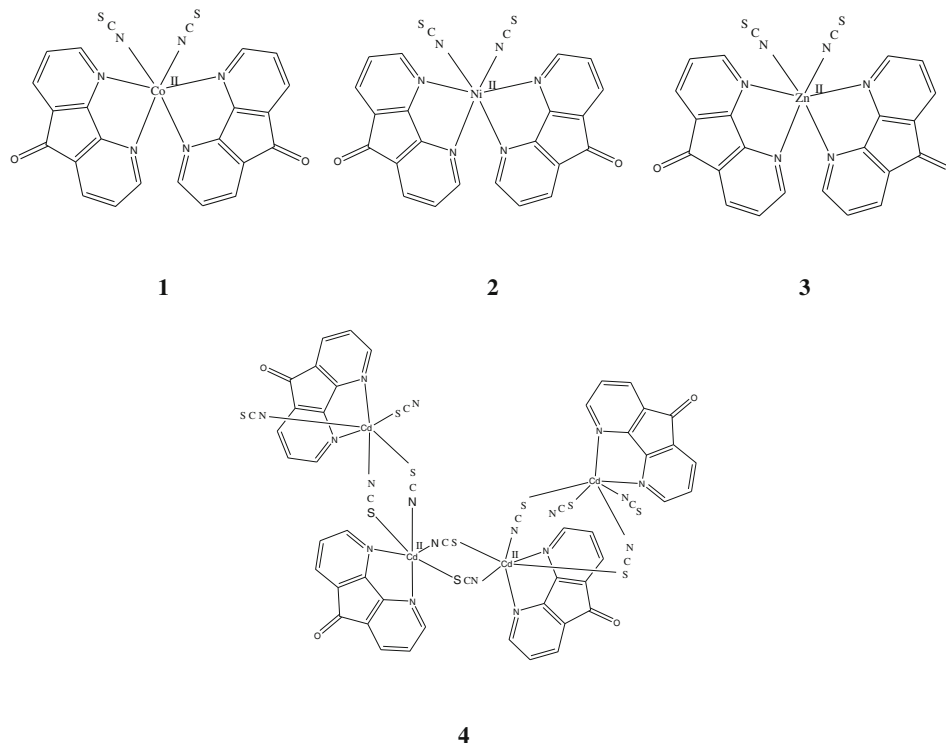


The complexes were characterized by microanalytical (C, H and N), spectroscopic and other physico-chemical results. The microanalytical data are in good conformity with the formulations of **1–4** (scheme 1). The moisture insensitive complexes are stable over long periods of time in powdery and crystalline states, and are soluble in dimethyl formamide only, but are insoluble in water, methanol, acetonitrile, etc. In the IR spectra, relatively intense peaks around 1580–1620 cm<sup>-1</sup> due to the C=N stretching frequency and weak bands

in the range of 2980–2900 cm<sup>-1</sup> due to the aliphatic C-H stretching frequency appear in both the complexes. Characteristic bands for carbonyl in dafone and thiocyanate in complexes appear at ~1720 and ~2100 cm<sup>-1</sup>.

#### 3.2 Description of crystal structure

3.2a X-ray structures: X-ray crystallographic characterization in each compound results in a distorted



Scheme 1. Line drawing structure of complexes **1–4**.

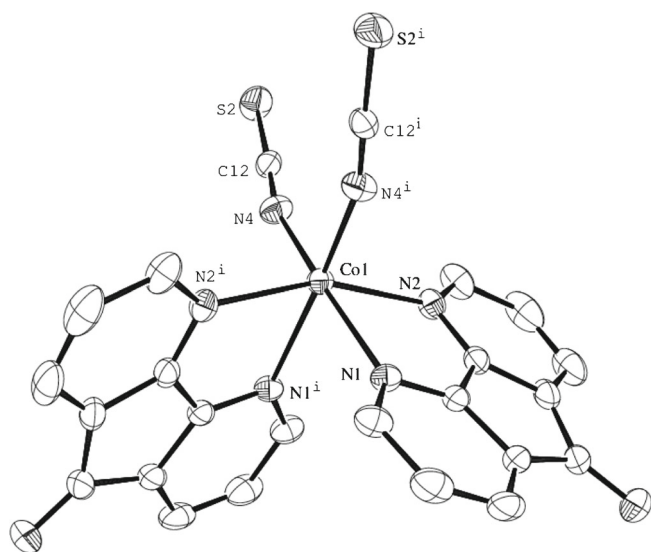
**Table 2.** Bond angle–bond distance parameters for **1**.

Bond distances			
Co(1)–N(1)	2.164(2)	Co(1)–N(1*)	2.264(3)
Co(1)–N(2)	1.973(2)	Co(1)–N(2*)	2.028(2)
Co(1)–N(4)	2.131(3)	Co(1)–N(4*)	2.227(2)
N(4)–C(12)	1.154(3)	C(12)–S(2)	1.606(3)
Bond angles			
N(1)–Co(1)–N(2)	79.75(8)	N(2)–Co(1)–N(4*)	101.28(9)
N(1)–Co(1)–N(4)	170.67(9)	N(1*)–Co(1)–N(4)	89.28(8)
N(1)–Co(1)–N(1*)	86.19(8)	N(2*)–Co(1)–N(4)	101.28(9)
N(1)–Co(1)–N(2*)	85.93(8)	N(4)–Co(1)–N(4*)	96.33(9)
N(1)–Co(1)–N(4*)	89.28(8)	N(1*)–Co(1)–N(2*)	79.75(8)
N(2)–Co(1)–N(4)	91.82(9)	N(1*)–Co(1)–N(4*)	170.67(9)
N(1*)–Co(1)–N(2)	85.93(8)	N(2*)–Co(1)–N(4*)	91.82(9)
N(2)–Co(1)–N(2*)	160.37(8)		

octahedral geometry with two thiocyanates in *cis* orientation. Owing to the larger chelate bite in dafone than in bpy and phen (free dafone: 3.05 Å, bpy: 2.62 Å, phen: 2.64 Å),<sup>8</sup> the complexes form one normal and one larger metal-imine bonds. Each of the crystal structures are described here.

#### [Co(dafone)<sub>2</sub>(NCS)<sub>2</sub>] (**1**)

Bond angle–bond distance data (table 2) describes the coordination geometry around Co(II) in **1** as a distorted *cis*-octahedron (figure 2) with two thiocyanates, where one imine nitrogen (N1\*) and one thiocyanato nitrogen (N4\*) occupy the axial position. The rest of the imine nitrogens (N1, N2 and N2\*) from two organic ligand units and another thiocyanato nitrogen (N4) occupy equatorial positions. The bond distance ranges in axial and equatorial positions are 0.037 Å and 0.191 Å, respectively. Interatomic bond distance data in



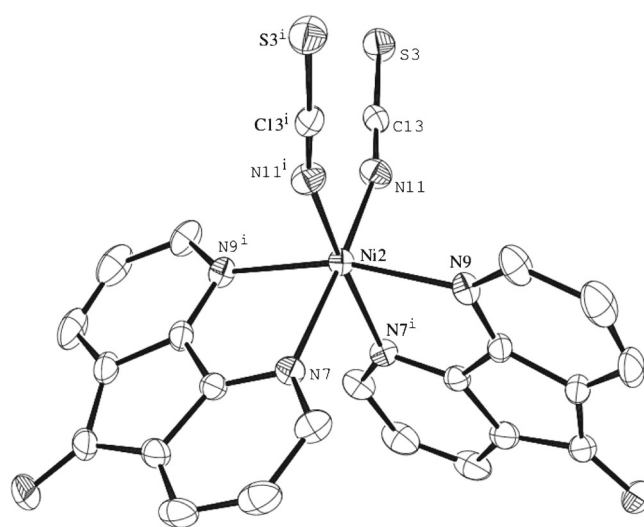
**Figure 2.** ORTEP of **1** with 20% ellipsoid probability for all non-hydrogen atoms.

linear thiocyanate is in good conformity (table 2; N(4)–C(12), 1.154(3) Å < C(12)–S(2), 1.606(3) Å) with its N coordination towards Co(II).

#### [Ni(dafone)<sub>2</sub>(NCS)<sub>2</sub>] (**2**)

Structural analysis reveals a distorted *cis*-octahedral geometry of **2** with Ni(II) at the metal centre (figure 3). According to bond angle–bond distance data (table 3), N7 (imine nitrogen) and N11 (thiocyanato nitrogen) are at axial position. The rest of the coordinating atoms N7\*, N9, N9\* (imine nitrogens) and N11\* (thiocyanato nitrogen) are at the equatorial position. The bond distance ranges in axial and equatorial positions are same (0.196 Å). N coordination of thiocyanate towards Ni(II) is confirmed by the shorter N–C bond (table 3, 1.152(5) Å) than the C–S bond (table 3, 1.618(4) Å).

#### [Zn(dafone)<sub>2</sub>(NCS)<sub>2</sub>] (**3**)



**Figure 3.** ORTEP of **2** with 20% ellipsoid probability for all non-hydrogen atoms.



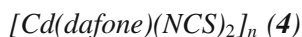
**Table 3.** Bond angle–bond distance parameters for **2**.

Bond distances			
Ni(2)-N(11*)	1.997(4)	Ni(2)-N(9)	2.172(3)
Ni(2)-N(11)	1.997(4)	Ni(2)-N(7*)	2.193(3)
Ni(2)-N(9*)	2.172(3)	Ni(2)-N(7)	2.193(3)
N(11)-C(13)	1.152(5)	C(13)-S(3)	1.618(4)
N(11)-C(13)	1.152(5)	C(13)-S(3)	1.618(4)
Bond angles			
N(11*)-Ni(2)-N(11)	93.8(2)	N(9*)-Ni(2)-N(7*)	86.79(11)
N(11*)-Ni(2)-N(9*)	98.65(13)	N(9)-Ni(2)-N(7*)	82.08(12)
N(11)-Ni(2)-N(9*)	91.85(14)	N(11*)-Ni(2)-N(7)	89.78(13)
N(11*)-Ni(2)-N(9)	91.85(14)	N(11)-Ni(2)-N(7)	173.35(13)
N(11)-Ni(2)-N(9)	98.65(13)	N(9*)-Ni(2)-N(7)	82.08(12)
N(9*)-Ni(2)-N(9)	164.63(18)	N(9)-Ni(2)-N(7)	86.79(11)
N(11*)-Ni(2)-N(7*)	173.35(13)	N(7*)-Ni(2)-N(7)	87.16(15)
N(11)-Ni(2)-N(7*)	89.78(13)		

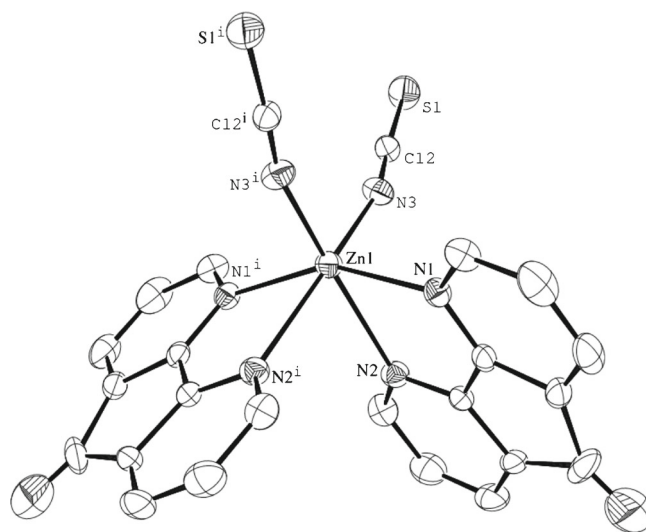
**Table 4.** Bond angle–bond distance parameters for **3**.

Bond distances			
Zn(1)-N(1)	2.193(5)	Zn(1)-N(1*)	2.193(5)
Zn(1)-N(2)	2.353(5)	Zn(1)-N(2*)	2.353(5)
Zn(1)-N(3)	2.007(6)	Zn(1)-N(3*)	2.007(6)
N(3)-C(12)	1.154(8)	C(12)-S(1)	1.604(8)
Bond angles			
N(1)-Zn(1)-N(2)	76.47(18)	N(3)-Zn(1)-N(3*)	98.9(3)
N(1)-Zn(1)-N(3)	103.1(2)	N(1*)-Zn(1)-N(2)	85.21(18)
N(1)-Zn(1)-N(1*)	155.1(3)	N(1*)-Zn(1)-N(3)	93.1(2)
N(1)-Zn(1)-N(2*)	85.21(18)	N(1*)-Zn(1)-N(2*)	76.47(18)
N(1)-Zn(1)-N(3*)	93.1(2)	N(1*)-Zn(1)-N(3*)	103.1(2)
N(2)-Zn(1)-N(3)	88.7(2)	N(2*)-Zn(1)-N(3)	168.3(2)
N(2)-Zn(1)-N(2*)	85.3(2)	N(2*)-Zn(1)-N(3*)	88.7(2)
N(2)-Zn(1)-N(3*)	168.3(2)		

Considering bond angle–bond distance parameters (table 4), the distorted octahedral geometry of **3** (figure 4) consists of two imine nitrogens (N1, N1\*), each from two different dafone units in the axial position. The other two imine nitrogens N2 and N2\* from two different dafone ligands and the two thiocyanato nitrogens N3 and N3\* are in equatorial position. The bond distance ranges in the axial and equatorial positions are zero and 0.346 Å, respectively. The shorter N-C bond ([table 4, 1.154(8) Å] than the C-S bond [table 4, 1.604(8) Å]) in the coordinated thiocyanate confirms N coordination in the complex.



From bond angle–bond distance data (table 5), the molecular structure of a mononuclear unit in **4** is described as distorted octahedron (figure 5) with two thiocyanato sulphurs (S1 and S2) at axial position, and two imine nitrogens (N1 and N2) from the ligand moiety, two nitrogens (N5 and N7) from two different

**Figure 4.** ORTEP of **3** with 20% ellipsoid probability for all non-hydrogen atoms.

thiocyanates occupy the equatorial position. Ambidentate thiocyanates are end-end bridged with the next

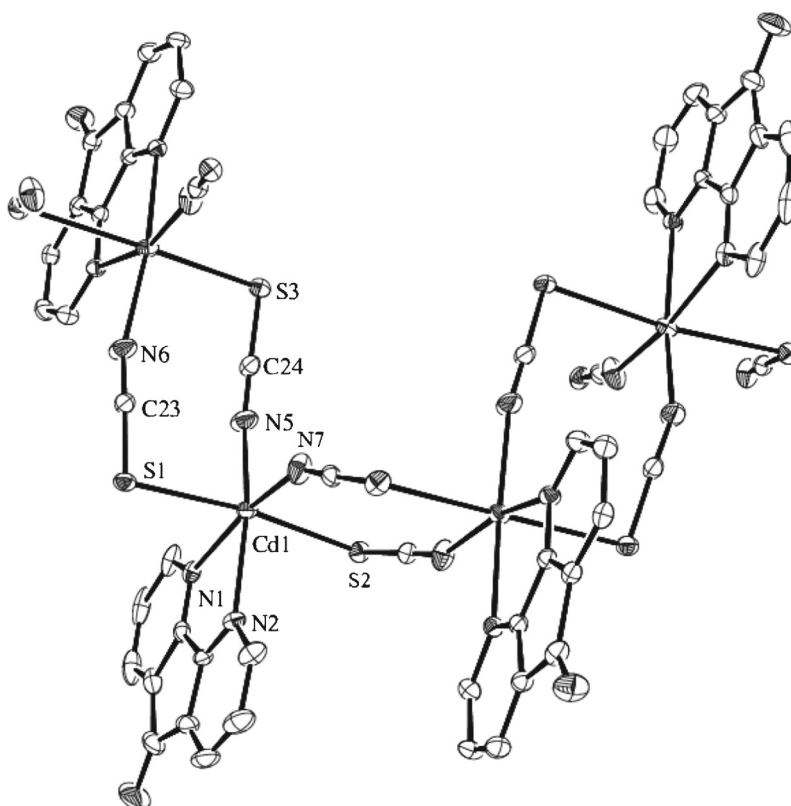
**Table 5.** Bond angle–bond distance parameters for **4**.

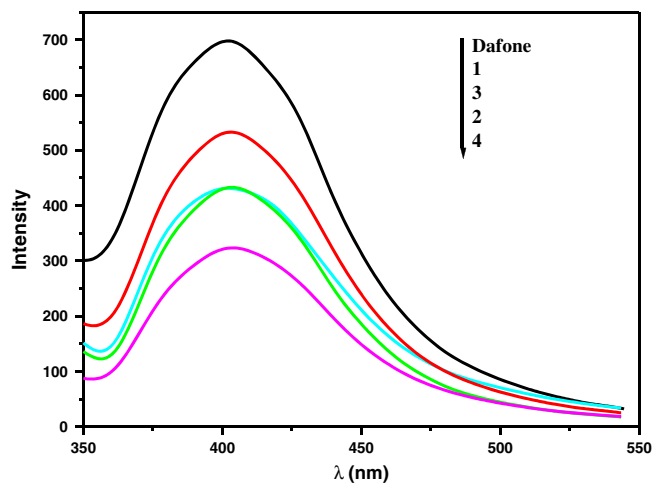
Bond distances			
Cd(1)–N(1)	2.447(3)	Cd(1)–S(1)	2.7587(10)
Cd(1)–N(2)	2.417(3)	Cd(1)–S(2)	2.7421(10)
Cd(1)–N(5)	2.250(3)		
Cd(1)–N(7)	2.241(3)		
Bond angles			
N(1)–Cd(1)–N(2)	74.48(10)	N(2)–Cd(1)–S(2)	87.67(7)
N(1)–Cd(1)–N(5)	90.71(13)	N(5)–Cd(1)–N(7)	100.73(16)
N(1)–Cd(1)–N(7)	168.55(14)	N(5)–Cd(1)–S(1)	93.30(9)
N(1)–Cd(1)–S(1)	89.74(7)	N(5)–Cd(1)–S(2)	92.08(9)
N(1)–Cd(1)–S(2)	85.84(7)	N(7)–Cd(1)–S(1)	89.21(10)
N(2)–Cd(1)–N(5)	165.17(13)	N(7)–Cd(1)–S(2)	94.06(10)
N(2)–Cd(1)–N(7)	94.07(14)	S(1)–Cd(1)–S(2)	173.07(3)
N(2)–Cd(1)–S(1)	86.01(7)		

Cd(II) centre. Bond distance ranges in the axial and equatorial positions are 0.0163 Å and 0.197 Å, respectively.

Owing to the larger chelate bite, as stated earlier, it will be found from tables 2–5 that one of the metal–imine distances for a single bidentate dafone Co(1)–N(1), Ni(2)–N(7), Zn(1)–N(2), Cd(2)–N(1) is larger than the other Co(1)–N(2), Ni(2)–N(9\*), Zn(1)–N(1), Cd(1)–N(2), respectively.

In case of **3**, hard N donors from dafone (the organic ligand backbone) make the borderline Zn(II) hard. Hence, N ends of NCS coordinate to Zn(II) making it a mononuclear complex with no S coordination. But for **4**, hard N donors from dafone do not increase hardness of the soft Cd(II) centre to that extent so that coordination with further N donor site(s) is possible. Rather, the soft S centre from another NCS unit binds to the Cd(II) centre. The N end of one NCS and S end of

**Figure 5.** ORTEP of **4** with 20% ellipsoid probability for all non-hydrogen atoms.



**Figure 6.** Room temperature steady-state emission of free ligand (dafone) and metal complexes.

the another NCS unit coordinate to other Cd(dafone)<sub>2</sub> moieties forming a coordination polymer.

### 3.3 Emission properties

A few reports on photophysical properties of metal bound dafone are available.<sup>8b,10,13</sup> Free dafone in dimethyl formamide shows emission band at 402 nm (figure 6) at room temperature when excited at 332 nm. Absorption bands of compounds **1** and **2** are assigned as spin allowed and that of **3** and **4** are intraligand transitions<sup>14</sup> (figures S1–S4, Supplementary file). All its complexes (**1–4**) show broad emission band (excitations at 332, 335, 336 and 334, respectively) in dimethyl formamide at about same wavelength as in dafone indicating charge transfer nature of transition.<sup>15</sup> Quenching of fluorescence of an organic moiety (ligand) by its complexation with transition metal ions is a common phenomenon,<sup>16</sup> which is explained by the process of magnetic perturbation, redox activity, electronic energy transfer, etc. Moreover, increasing spin–orbit coupling with heavier atoms relaxes the spin selection rule for radiative and radiationless transitions of the metal complexes resulting in quenching the emission intensity of lowest excited state.<sup>17</sup> All these physical phenomena are responsible for fluorescence intensity quenching in our complexes.

## 4. Conclusion

We have synthesized and crystallographically characterized four metal complexes of Co(II), Ni(II), Zn(II) and Cd(II) in combination with dafone and thiocyanate. In each case, the complexes form *cis* isomer which is in good agreement with the previously

reported compounds.<sup>8,9</sup> The room temperature steady-state emission of dafone is quenched in its complexes which are also in good conformity with the standard theories of spin-orbit coupling, magnetic perturbation, redox activity, electronic energy transfer, etc.

## Supplementary information

CCDC Nos. 941025, 941023 and 941024 contain supplementary crystallographic data for **1**, **3** and **4**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary figures S1–S4 can be seen in [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

## Acknowledgements

RG gratefully acknowledges the Department of Science and Technology (DST), New Delhi, India (F. No. SR/FT/CS-83/2010 dt. 11-02-2011) for financial assistance. MM is thankful to the University of Burdwan for her research fellowship.

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