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Effect of size of metal ion on MS_4N_2 chromophore: Synthesis, spectral and single crystal X-ray structural studies on (2,2′-bipyridine)bis(*N*-cyclohexyl-*N*-methyldithiocarbamato)M(II) (M = zinc, cadmium)

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ABSTRACT

Isomorphous complexes $[Zn(S_2CN(Me)Cy)_2(bipy)]$ (**1**) and $[Cd(S_2CN(Me)Cy)_2(bipy)]$ (**2**) (where Cy(Me)NCS_2^- = *N*-cyclohexyl-*N*-methyldithiocarbamate anion and bipy = 2,2′-bipyridine) have been synthesised. Their structures and spectroscopic properties have been studied by IR, ^1H and ^{13}C NMR spectroscopy and single crystal X-ray analysis. IR spectrum of the complexes show the contribution of thioureide form to the structures. ^1H NMR spectra of the complexes showed the desheilding of methyl protons and H-1 of cyclohexyl group on complexation. The downfield shift of $N^{13}CS_2$, methyl carbon and C-1 of cyclohexyl group carbon signals for **2** (205.5, 36.7 and 64.4 ppm) from the chemical shift value of **1** (204.2, 35.6 and 63.1 ppm) is attributed to the movement of more electron density from dithiocarbamate towards cadmium. Single crystal X-ray structures of **1** and **2** indicate that the central metal atom is in a distorted octahedral environment for both complexes. The presence of added 2,2′-bipyridine ligand in the coordination sphere of $M(S_2CN(Me)Cy)_2$ increases Zn–S distances and decreases S–Zn–S angles in **1** and slightly increases Cd–S distances in **2**. S–Cd–S angles are not affected. This is due to the relatively larger size of the cadmium ion compared to zinc ion which alleviates the strain involved in transformation from tetrahedral to octahedral.

1. Introduction

Group XII dithiocarbamates have found wide practical application as additives to pavement asphalt, as antioxidants and lubricants and vulcanizing agents and as potent pesticides [1,2]. A recent work has established that dithiocarbamates of zinc and cadmium are useful precursors for the synthesis of ZnS and CdS nano particles, respectively [3,4] and have application as non-linear optical materials [5]. The affinity of 1,1-dithiolate ligands for metals such as zinc and cadmium was indicated by the fact that the ligands can be employed as scavengers for these elements in biological media. Besides that, nitrogen donor adducts of dithiocarbamate complexes are also widely used in the preparation of thin semiconductor [6–8] and electroluminescent [9,10] films of transition metal sulfides, the basis of electronic and solar cell technology [11].

In our previous publications we reported synthesis, spectral and structural studies on bis(dialkyldithiocarbamato)M(II) complexes with different nitrogenous bases [12,13]. In the present work, in order to understand the influence of the size of metal ion on MS_4N_2 chromophore, we report the synthesis, spectral and structural characterization of two new complexes **1** and **2**.

2. Experimental

All reagents and solvents were commercially available high-grade materials (Merck/Sigma–Aldrich/Sd fine/spectrochem) and used as received.

2.1. Physical measurements

IR spectra were recorded on a Thermo NICOLET AVATAR 330 FT-IR Spectrophotometer (range: 400–4000 cm^{-1}) as KBr pellets. The NMR spectra were recorded on a BRUKER-NMR500MHzBRU-NMR Spectrometer operating at 500 MHz. CdS has been characterized by X-ray powder diffraction using X'Per PRO diffractometer with Cu Kα radiation ($\lambda = 1.54$ Å).

2.2. X-ray crystallography

Details of the crystal data and structure refinement for **1** and **2** are summarized in Table 1. The intensity data were collected at

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Table 1
Crystal data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{26}H_{36}N_4S_4Zn$	$C_{26}H_{36}CdN_4S_4$
Formula weight	598.20	645.23
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71073
Crystal system, space group	orthorhombic, Pbca	orthorhombic, Pcab
Unit cell dimensions		
a (Å)	17.87(5)	9.547(5)
b (Å)	9.50(5)	17.735(4)
c (Å)	33.64(5)	34.335(3)
α (°)	90°	90°
β (°)	90°	90°
γ (°)	90°	90°
Volume ($Å^3$)	5714(4)	5813(4)
Z, D_{calc} (mg/m^3)	8, 1.391	8, 1.474
Absorption coefficient (mm^{-1})	1.174	1.061
F (0 0 0)	2512	2656
Crystal size (mm)	0.22 × 0.20 × 0.16	0.20 × 0.16 × 0.16
θ Range for data collection	1.21–25.00°	1.19–25.00°
Limiting indices	$-21 \leqslant h \leqslant 21$, $-11 \leqslant k \leqslant 9$, $-40 \leqslant l \leqslant 35$	$-11 \leqslant h \leqslant 11$, $-18 \leqslant k \leqslant 21$, $-22 \leqslant l \leqslant 40$
Reflections collected/unique	24281/5029 [R(int) = 0.0236]	27289/5102 [R(int) = 0.0227]
Completeness to θ = 25.00	99.9%	99.8%
Maximum and minimum transmission	0.8465 and 0.7932	0.8475 and 0.8196
Data/restraints/parameters	5029/0/327	5102/0/326
Goodness-of-fit (GOF) on F^2	1.10	1.187
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0326, wR_2 = 0.0765	R_1 = 0.0322, wR_2 = 0.0602
R indices (all data)	R_1 = 0.0422, wR_2 = 0.0872	R_1 = 0.0429, wR_2 = 0.0689
Largest difference in peak and hole (e $Å^-3$)	0.318 and −0.235	0.314 and −0.809

ambient temperature on a Bruker axs Kappa apex II CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by SIR 92 [14] and refined by full matrix least squares with SHELXL-97 [15]. All non hydrogen atoms were refined anisotropically and all hydrogen atoms were fixed geometrically. Selected bond distances and angles are presented in Table 2.

2.3. Preparation of the complexes (1) and (2)

The bis(*N*-cyclohexyl-*N*-methyldithiocarbamato)M(II) (M = Zn, Cd) complexes were prepared using the established procedure [16]. Adducts were prepared by adding a hot solution of 2,2′-bipyridine (2 mmol) in ethanol to a hot solution of $[M(S_2CN(Me)Cy)_2]$ (1 mmol) in chloroform. The resulting solution was cooled and then added with petroleum ether (boiling range 40–60 °C). Yellow precipitate of the adducts were separated out.

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**.

Compound	**1**	**2**
C(7)–N(1)	1.343(4)	1.332(4)
C(14)–N(2)	1.329(3)	1.328(4)
C(7)–S(2)	1.707(3)	1.715(3)
C(7)–S(1)	1.714(3)	1.717(3)
C(14)–S(4)	1.717(3)	1.712(3)
C(14)–S(3)	1.718(3)	1.724(3)
N(6)–M(1)	2.211(2)	2.418(3)
N(8)–M(1)	2.219(2)	2.424(3)
S(1)–M(l)	2.5767(11)	2.6214(11)
S(2)–M(l)	2.4811(8)	2.6515(10)
S(3)–M(l)	2.4691(9)	2.6487(10
S(4)–M(l)	2.5199(8)	2.6621(12)
S(2)–C(7)–S(1)	117.19(15)	118.6(2)
S(4)–C(14)–S(3	116.42(15)	118.4(2)
N(6)–M(1)–N(8)	73.23(8)	66.84(9)
S{3)–M(1)–S(4)	71.62(3)	67.54(3)
S(2)–M(l)–S(1)	70.47(3)	68.07(3)
S(3)–M(l)–S(4)	71.62(3)	67.54(3)

2.4. Preparation of CdS from (2)

One gram of $[Cd(S_2CN(Me)Cy)_2(bipy)]$ was dissolved in 15 ml of ethylenediamine in a flask, and then heated to reflux (117 °C), and maintained at this temperature for 2 min. The yellowish CdS precipitate was filtered off and washed with ethanol.

Attempts to separate ZnS from $[Zn(S_2CN(Me)Cy)_2(bipy)]$ were not successful.

2.4.1. $[Zn(S_2CN(Me)Cy)_2(bipy)]$ (1)

IR(KBr)cm^{-1}: 1472 (ν_{C-N}(thioureide)), 971 (ν_{C-S}), 1594 (bipy (ring frequency)), 3055 (aromatic, ν_{C-H}). ^1H NMR δ (ppm); 1.05–1.08 (m, axial H-4), 1.29–1.39 (m, H-3), 1.64 (d, equatorial H-4), 1.77–1.85 (m, H-2), 3.27 (s, $-CH_3$), 4.92–4.99 (m, H-1),7.43 (t, H-4 (bipy)), 7.89 (t, H-5 (bipy)), 8.21 (d, H-6(bipy)), 9.09 (d, H-3(bipy)). ^{13}C NMR δ (ppm); 25.39 (C-4), 25.44 (C-3), 29.91 (C-2), 35.62 (CH_3), 63.14 (C-1), 120.82 (C-6(bipy)), 124.84 (C-4(bipy)), 138.16 (C-5(bipy)), 149.16 (C-3(bipy)), 151.94 (C-1′(bipy)), 204.23 (NCS_2).

2.4.2. $[Cd(S_2CN(Me)Cy)_2(bipy)]$ (2)

IR(KBr)cm^{-1}: 1471 (C–N), 968 (C–S), 1592 (bipy (ring frequency)), 3055 (aromatic, C–H). ^1H NMR δ (ppm); 1.04–1.08 (m, axial H-4), 1.25–1.37 (m, H-3), 1.62 (d, equatorial H-4), 1.74–1.85 (m, H-2), 3.29 (s, $-CH_3$), 5.06–5.11 (m, H-1), 7.44 (t, H-4 (bipy)), 7.90 (t, H-5(bipy)), 8.13 (d, H-6 (bipy)), 9.00 (d, H-3 (bipy)). ^{13}C NMR δ (ppm); 25.48 (C-4), 25.53 (C-3), 29.99 (C-2), 36.68 (CH_3), 64.35 (C-1), 121.21 (C-6′(bipy)), 125.39 (C-4′(bipy)), 138.70 (C-5′(bipy)), 149.62 (C-3′(bipy)), 150.61 (C-1′(bipy)), 205.51 (NCS_2).

3. Results and discussion

3.1. Infrared spectral studies

The ν_{C-N} has been used as a measure of the contribution of the thioureide form to the complexes [17]. In the present study, complexes **1** and **2** show thioureide ν_{C-N} band at 1472, 1471 cm^{-1},

Table 3
Band valence sums for zinc and cadmium complexes.

Compound	Coordination number	V_i (OK/B)	V_i (B/OK)	References[b]
$[Zn(S_2CN(Me)Cy)_2]$	4	1.96	2.02	[25]
$[Zn(S_2CN(Me)Cy)_2(bipy)]$	6	1.85	1.89	this work
$[Cd(deadtc)_2]_2$	4[a]	1.95	2.00	[26]
$[Cd(pipdfc)_2]_2$	4[a]	2.05	2.10	[27]
$[Cd(S_2CN(Me)Cy)_2(bipy)]$	6	2.06	2.10	this work

[a] Actual coordination number is five including a long M–S bond.

[b] The crystal structure data of the complexes were obtained from the corresponding literature.

respectively, indicating the partial double bond character. The shift in ν_{C-N} values to lower wave number compared to the parent $[Zn(S_2CN(Me)Cy)_2]$ (ν_{C-N} = 1488 cm^{-1}) and $[Cd(S_2CN(Me)Cy)_2]$ (ν_{C-N} = 1482 cm^{-1}) is due to the change in coordination geometry from tetrahedral to octahedral [18]. However, ring frequencies associated with 2,2′-bipyridine are observed in the 1600–1000 cm^{-1}. In the present study, complexes **1** and **2** show bands at 1594 and 1592 cm^{-1}, respectively. Other bands are masked by those due to dithiocarbamate ligand.

3.2. ^1H NMR spectral analysis

A singlet observed around 3.28 ppm and a multiplet observed in the region of 4.92–5.11 ppm for the complexes **1** and **2** are due to methyl protons and H-1 proton of cyclohexyl group, respectively. The observed deshielding of the methyl protons and H-1 proton of cyclohexyl group in both cases [19] is attributed to the release of electrons on the nitrogen of the NR_2 groups, forcing high electron density towards the sulfur (or the metal) via the thioureide π-system. Although the magnitude of the deshielding decreases with the increase in distance from the metal center or the thioureide bond, the other proton signals of cyclohexyl group are also slightly deshielded on complexation. The signals observed in the downfield region of 7.43–9.09 ppm are assigned to the proton present in the 2,2′-bipyridine.

3.3. ^{13}C NMR spectral studies

The signal for methyl and C-1 (cyclohexyl) carbon atoms adjacent to the nitrogen atom appear around 36 and 64 ppm. A downfield shift of the methyl and C-1 (cyclohexyl) carbon signals in both the complexes is an indication of the important consequence of the complexation process, viz., a significant thioureide $N^{\delta+}\cdots C^{\delta-}$ contribution to the stability of the complexes and a resultant reduction in the electron density. The other cyclohexyl group carbon signals in both the complexes are not greatly affected in complexation because of the relative distance from the thioureide π-system and the metal center. The ^{13}C NMR peaks of the group $N^{13}CS_2$ are found in both cases, at around 205 ppm, which indicates the bidentate character of the ligand [20]. The $N^{13}CS_2$, methyl carbon and C-1 carbon of cychlohexyl group carbon signals for **2** are observed at 205.5, 36.7 and 64.4 ppm, respectively, with small downfield shift of about 1 ppm compared to that of the corresponding signals in **1** (204.2, 35.6 and 63.1 ppm). The observed deshielding in **2** is attributed to the movement of more electron density from dithiocarbamate ligand towards the cadmium on complexation. This is due to large size of cadmium ion in **2** experiences less steric effect involved in transformation from tetrahedral to octahedral. Aromatic carbon signals are observed in the downfield region 120.8–152.0 ppm for the synthesized complexes. The observed small differences in **1** and **2** compared to the free 2,2′-bipyridine signals can be attributed to charge delocalization which prevents the movement of electron density from the adjacent carbons.

3.4. VBS analysis

Valence bond sum values were calculated by two procedures OK/B [21] and B/OK [22]. The VBS values for **1** and **2** are also compared with those whose structures have been reported in the literature. The valence bond sums of various complexes are given in Table 3. VBS values (1.96) OK/B; 2.02 (B/OK)) are almost 2.0 for parent $[Zn(S_2CN(Me)Cy)_2]$ and the values are greater than the sum of 1.85 (OK/B); 1.89 (B/OK) for **1**. The decrease in VBS values in the case of **1** can be ascribed to the increase in Zn–S distances (which are longer than those observed in $[Zn(S_2CN(Me)Cy)_2]$), due to the presence of an additional neutral ligand. In all the cadmium complexes, whether four coordinated or six coordinated, the VBS has been found to be close to 2.0. It has already been reported

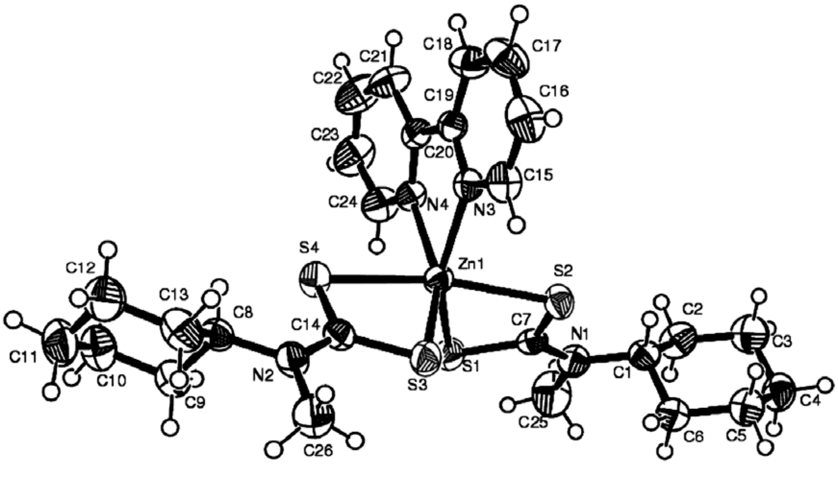

Fig. 1. ORTEP diagram of $[Zn(S_2CN(Me)Cy)_2(bipy)]$.

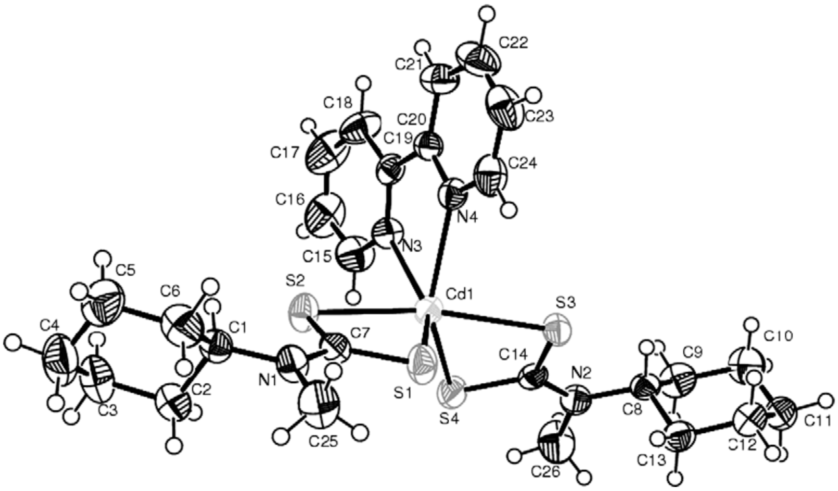

Fig. 2. ORTEP diagram of [Cd($S_2CN(Me)Cy)_2$(bipy)].

[23] that in the case of the cadmium dithiocarbamate complexes and their adducts, no observable changes are seen in VBS values. Due to larger size of cadmium ion compared to zinc ion, the Cd–S distances are not much affected by the change in coordination geometry from tetrahedral to octahedral.

3.5. Single crystal X-ray studies

The ORTEP of [Zn($S_2CN(Me)Cy)_2$(bipy)] and [Cd($S_2CN(Me)Cy)_2$ (bipy)] are shown in Figs. 1 and 2, respectively. The structures of **1** and **2** contain eight discrete monomeric units per unit cell. In both complexes the metal atom is situated at the center of the distorted octahedral arrangement of four sulfur atoms from the chelating dithiocarbamate groups and two nitrogen atoms from the chelating 2,2′-bipyridine ligand. The distinct asymmetry in M–S distances is due to the steric effect exerted by 2,2′-bipyridine, as observed for similar adducts [19]. The C–S distances are symmetric, indicating that the presence of an additional neutral ligand affects only the M–S distances. The C–S distances are to a considerable extent shorter than the typical C–S single bond distance 1.81 Å. Therefore, all the C–S bonds in the present structure are of partial double bond character as observed in most of the dithiocarbamates [24]. Average C–N distance of **1** and **2** are 1.336(3) Å and 1.330(4) Å, which clearly indicates that the π-electron density is delocalized over the S_2CN moiety and that this bond has a strong double bond character. Comparison of bond parameters (Table 2) of **1** and **2** shows that M–S and M–N bonds are longer and S–M–S angles are smaller in **2** than that found in **1** due to the larger size of cadmium compared to zinc. The 2,2′-bipyridine and cyclohexane rings show normal bond parameters. The cyclohexane ring is in the chair conformation.

Of particular interest with respect to the dithiocarbamate–metal bonding are the M–S, and C–S and C–N distances and the related angles. A comparison of the bond parameters associated with similar compounds is given in Table 4. No significant changes in C–N, C–S bond lengths and S–C–S angles are observed. In complex **1**, Zn–S distances are longer and S–Zn–S angles are less compared to those observed in parent [Zn($S_2CN(Me)Cy)_2$] complex due to the increased coordination around zinc. But in complex **2**, acceptance of an additional neutral ligand causes only slight increase in Cd–S distance. S–Cd–S angles are not affected. This is expected on the basis of a relatively larger size of cadmium ion compared to zinc ion, which alleviates the strain involved in the transformation from tetrahedral to octahedral geometry. However, comparison of the bond parameters of **2** is only possible with similar compounds and not with the parent [Cd($S_2CN(Me)Cy)_2$] because of the lack of data.

3.6. X-ray powder diffraction studies on CdS

Fig. 3 shows the XRD pattern of the prepared CdS. The presence of crystal planes of hexagonal CdS structure by this method is

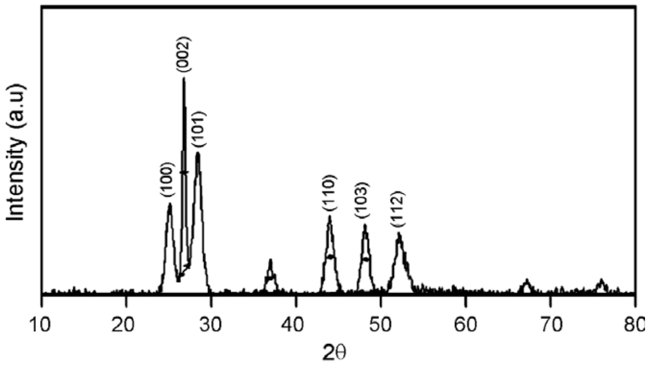

Fig. 3. X-ray powder diffraction pattern of CdS.

Table 4
Comparative structural parameters.

Compound	Coordination number	S–M–S	S–C–S	M–S	C–S	S_2C–N	References
[Zn($S_2CN(Me)Cy)_2$]	4	78.11(3)	116.97(20)	2.3445(10)	1.733(3)	1.319(4)	[25]
[Zn($S_2CN(Me)Cy)_2$(2,2′-bipy)]	6	71.05(3)	116.81(15)	2.5115(9)	1.718(3)	1.336(3)	this work
[Cd(deadtc)$_2$]	4[a]	68.36(2)	118.92(16)	2.5967 (9)	1.730(3)	1.334(2)	[26]
[Cd(pipdtc)$_2$]	4[a]	68.01(3)	118.7(3)	2.5610(9)	1.735(3)	1.326(4)	[27]
[Zn($S_2CN(Me)Cy)_2$(2,2′-bipy)]	6	67.80(4)	118.5(2)	2.6459(11)	1.717(3)	1.330(4)	this work

The bond distances and angles are mean values.

[a] It has been suggested thai the coordination number is essentially five.

consistent with the literature data of JCPDS card file No. 41-1049. The presence of diffraction peak $2\theta = 28.5^\circ$, 52.2° correspond to the crystal planes of wurtzite CdS structure. The absence of diffraction peak $2\theta = 31.5^\circ$ indicates the lack of zinc blend structure in the sample [28]. The broad peaks indicate that the particles are small in size. The size of CdS particles estimated from the Scherrer formula is 12 nm.

4. Conclusion

Two crystalline isomorphous compounds **1** and **2** were prepared and studied by means of IR, NMR spectroscopy, valence bond sum parameter and single crystal X-ray diffraction. ^{13}C NMR spectral data give an insight into the direction of displacement of the electron density which can be correlated with the size of the metal ion. Comparison of bond parameters of **1** and **2** with those observed in similar bisdithiocarbamates shows the following trends: M–S distances increase, S–Zn–S angles decrease and S–Cd–S angles are not affected on adduct formation. Comparison of bond parameters of **1** and **2** shows that M–S and M–N bonds are longer and S–M–S angle is smaller in **2** than that found in **1** due to the larger size of Cd^{2+} compared to Zn^{2+} (Cd^{2+}: 109 pm; Zn^{2+}: 88 pm). The observation is a manifestation of the size effects of the metal ions involved. All other parameters including the thioureide bond distances show very little differences for the **1** and **2**.

Supplementary data

CCDC 701407 and 701408 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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