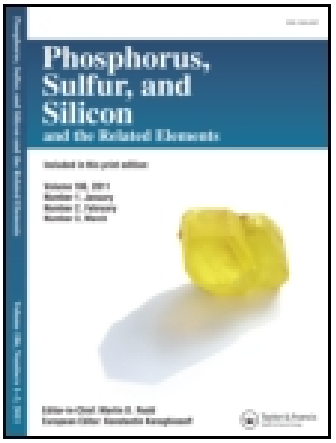

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis and Characterization of Diimine Adducts of BIS(N-Alkyl-N-Furfuryldithiocarbamato-S,S′)Cadmium(II): Crystal Structure of BIS(N-Furfuryl-N-Propyldithiocarbamato-S,S′)(1,10-Phenanthroline)Cadmium(II)

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SYNTHESIS AND CHARACTERIZATION OF DIIMINE ADDUCTS OF BIS(*N*-ALKYL-*N*-FURFURYLDITHIOCARBAMATO-S,S′)CADMIUM(II): CRYSTAL STRUCTURE OF BIS(*N*-FURFURYL-*N*-PROPYLDITHIOCARBAMATO-S,S′)(1,10-PHENANTHROLINE)CADMIUM(II)

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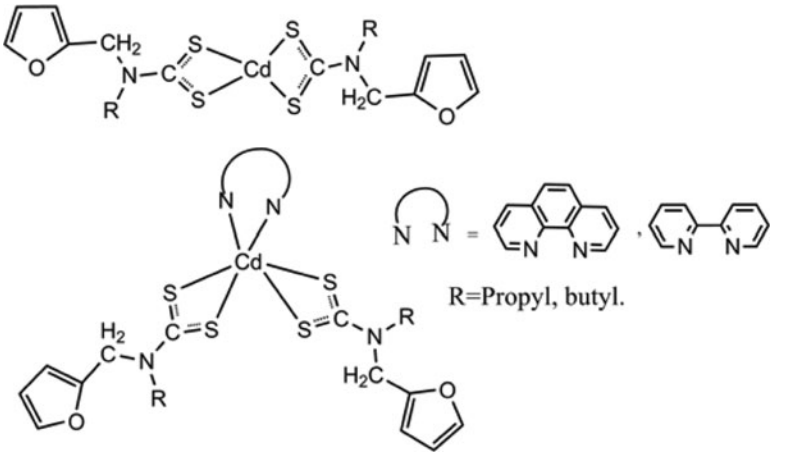
GRAPHICAL ABSTRACT



Abstract *A series of homoleptic and heteroleptic complexes: [Cd(fprdtc)$_2$] (**1**), [Cd(fprdtc)$_2$(1,10-phen)] (**2**), [Cd(fprdtc)$_2$(2,2′-bipy)] (**3**), [Cd(bufdtc)$_2$] (**4**), [Cd(bufdtc)$_2$(1,10-phen)] (**5**), and [Cd(bufdtc)$_2$(2,2′-bipy)] (**6**)(where fprdtc* = N-*furfuryl*-N-*propyldithiocarbamate; bufdtc* = N-*butyl*-N-*furfuryldithiocarbamate) have been prepared and characterized. A single crystal X-ray structural analysis was carried out for **2**. Reduction in ν_{C-N} (thioureide) for the heteroleptic complexes (**2**, **3**, **5**, and **6**) compared to that of homoleptic complexes (**1** and **4**) is attributed to the change in coordination number from four to six and steric effect exerted by 1,10-phenanthroline and 2,2′-bipyridine. The downfield shift of $N^{13}CS_2$ carbon signal for heteroleptic complexes from the chemical shift value of homoleptic complexes is also attributed to the increase in coordination number. Single crystal X-ray*

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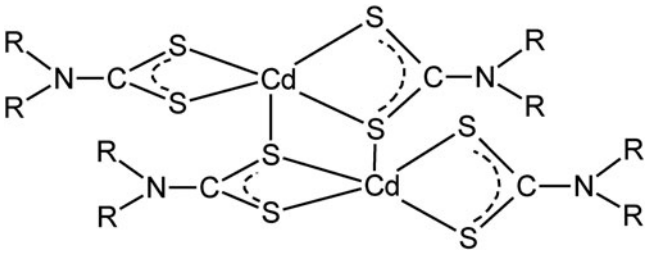
*structure of **2** indicates that the mononuclear structure of **2** shows symmetric coordination of the dithiocarbamate ligands and a distorted octahedral geometry for cadmium, defined by an N_2S_4 donor set, results. In this crystal structure, most significant π–π interaction is also observed.*

Keywords Dithiocarbamate; cadmium(II); spectroscopic characterization; single-crystal X-ray analysis; VBS analysis

INTRODUCTION

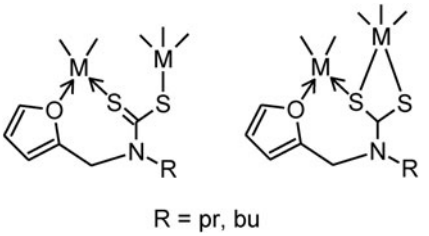
Dithiocarbamates and metal dithiocarbamate complexes are valuable compounds due to their interesting chemistry and wide utilities and applications such as nitrogen-oxygen trapping agents,[1] as antioxidants,[2] in organic synthesis[3], and medicine.[4] The affinity of 1,1-dithiolate ligands for metals such as zinc and cadmium was indicated by the fact that the ligands themselves can be employed as scavengers for these elements in biological media.[5] All cadmium dithiocarbamate complexes have binuclear molecular structures,[6,7] (Scheme 1) in which the mononuclear moieties $[Cd(S_2CNR_2)_2]$ are combined by two additional Cd–S bonds. Binuclear molecules involve two pairs of dithiocarbamate ligands with terminal chelating and tridentate bridging structure functions. The former dithiocarbamate ligands are S,S′-bidentately coordinated to cadmium and form planar four-membered chelate rings $[CdS_2C]$, where as the latter combine neighboring metal atoms into centrosymmetric dimers, forming an extended eight-membered tricyclic moiety $[Cd_2S_4C_2]$, which usually adopts a chair conformation. The only exception is the bis(dibutyldithiocarbamato-S,S′)cadmium(II), for which a boat conformation (with a twofold axis) has been established.[8]



Scheme 1 Structure of cadmium bis(dithiocarbamate) complex.

The treatment of cadmium dithiocarbamate complexes with nitrogen donor ligands generally results[9–11] in the monometallic compounds of general formula $[Cd(S_2CNR_2)_2(N\text{-donor})_x]$ ($x = 1$ or 2). The 1,10-phenanthroline and 2,2′-bipyridine are well known and frequently used ligands. The presence of added 1,10-phenanthroline and 2,2′-bipyridine in the coordination sphere increases the electron density on cadmium.[12] The heteroleptic complexes of metal dithiocarbamates with nitrogen heterocycles are of interest not only for expanding the scope of objects in coordination chemistry, but also in view of their potential applications. For example, the heteroleptic complexes of cadmium(II) dithiocarbamates with nitrogen donor ligands (pyridine, 1,10-phenanthroline, and 2,2′-bipyridine) are used as single source precursors for the preparation of CdS nanoparticles.[13–16] The dithiocarbamate complex core $M–S_2CNR_2$ could prove to be great synthetic utility, since a wide variety of organic substituents can be incorporated in this stable bidentate system. It gives rise to the

chemical "fine tuning" of the properties of the complex by variation of the substituent *R* in M–S_2CNR_2.[17] The furan has a very peculiar chemical behavior which is often not closely related to that of its homologous thiophene and pyrrole. The other reason for choosing the ligand containing a furyl ring is the presence of an extra oxygen atom which can possibly be utilized for coordination with another metal salt as shown in Scheme 2. The aim of the present work was to prepare Cd(II) complexes of two dithiocarbamate ligands and the reactivity of these complexes toward nitrogen donor ligands (1,10-phenanthroline, 2,2′-bipyridine). In this paper, we report the synthesis, spectral studies of complexes **1–6** along with the single crystal X-ray structure of **2**.



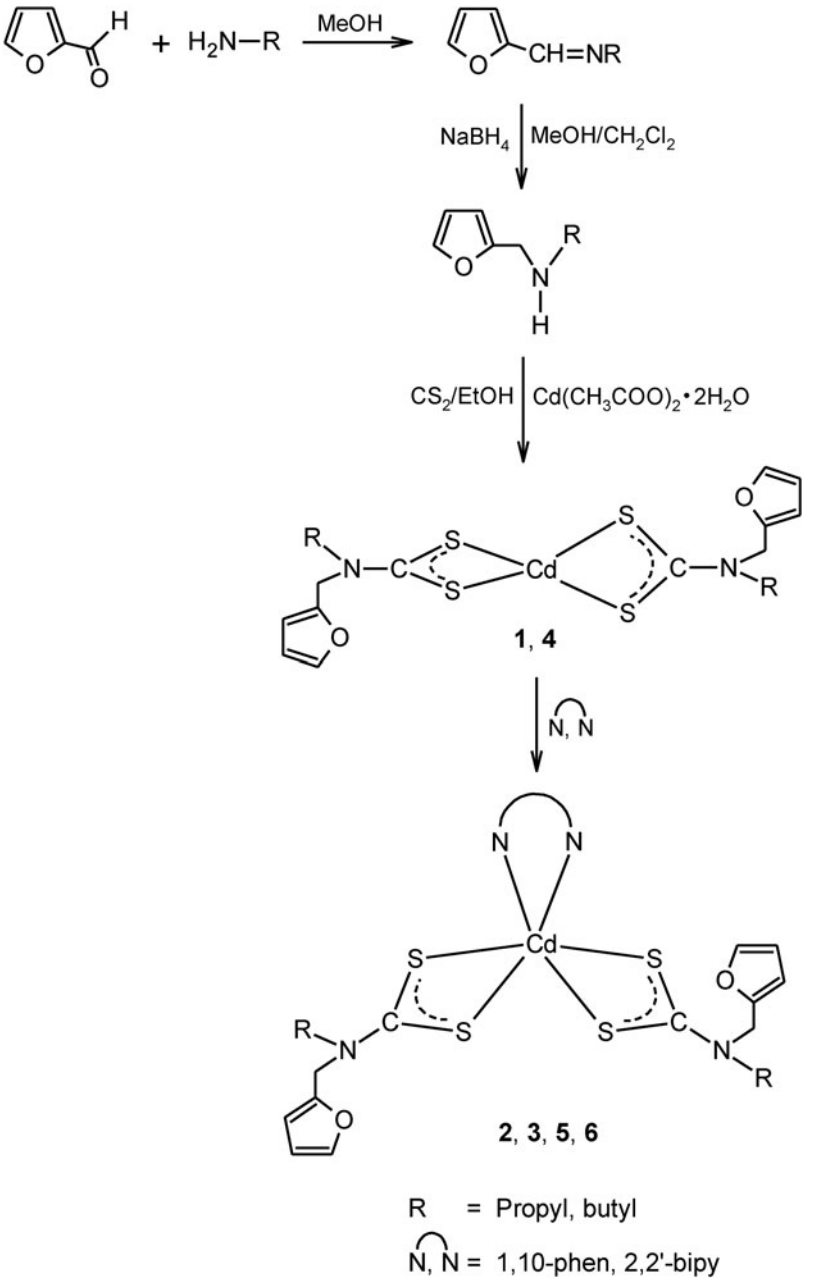
Scheme 2 Possible bonding modes of ligands involving the furyl ring.

RESULTS AND DISCUSSION

Homoleptic and heteroleptic complexes were prepared according to the synthetic procedure shown in Scheme 3. Furfuraldehyde was condensed with propylamine and butylamine to form the imine. Sodium borohydride reduction of imine in methanol-dichloromethane afforded secondary amine as yellow oil. Complexes **1** and **4** were prepared from *N*-furfuryl-*N*-propylamine and *N*-butyl-*N*-furfurylamine, respectively, in EtOH by reaction with carbon disulfide and $Cd(CH_3COO)_2$ in water. The reaction of complexes **1** and **4** with nitrogen donor ligands (1,10-phen, 2,2′-bipy) yielded heteroleptic complexes (**2**, **3**, **5**, and **6**). The complexes are quite stable at ambient conditions. They are soluble in water, methanol, dichloromethane, and insoluble in acetonitrile.

2.1. IR Spectra

Important absorptions in the dithiocarbamate complexes are due to $\nu_{C–N}$ and $\nu_{C–S}$ stretching modes.[18,19] The $\nu_{C–N}$ band has been used as a measure of the contribution of the thioureide form to the structure of the dithiocarbamate. For the complexes **1–6**, strong bands appeared around 1470 and 1010 cm^{-1} due to $\nu_{C–N}$ (thioureide) and $\nu_{C–S}$ vibrations, respectively. The shift in $\nu_{C–N}$ values to lower wave numbers for heteroleptic complexes compared to the parent complexes **1** and **4** is due to the change in geometry from tetrahedral to octahedral. The reduction in $\nu_{C–N}$ (thioureide) for similar adducts such as [Cd(2-mpipdtc)$_2$(1,10-phen)] (1420 cm^{-1}), [Cd(2-mpipdtc)$_2$(2,2′-bipy)] (1421 cm^1), [Cd(4-mpipdtc)$_2$(1,10-phen)] (1427 cm^{-1}), [Cd(4-mpipdtc)$_2$(2,2′-bipy)] (1420 cm^{-1}), and [Cd(S_2CN(Me)(Cy)$_2$(2,2′-bipy)] (1471 cm^{-1}) compared to [Cd(2-mpipdtc)$_2$](1429 cm^{-1}), [Cd(4-mpipdtc)$_2$](1445 cm^{-1}), and [(Cd(S_2CN(Me)(Cy))$_2$] (1482 cm^{-1}) are reported.[9,10] The $\nu_{C–S}$ band appear around 1010 cm^{-1} without any splitting supporting the bidentate



Scheme 3 Preparation of **1** and **4**.

coordination of the dithiocarbamate ligands.[18] The ring frequencies associated with 1,10-phenanthroline and 2,2′-bipyridine are observed in the range of 1600–1000 cm^{-1}. In the present study, **2** and **5** show bands around 1620, 1590, and 1508 cm^{-1} whereas **3** and **6** show bands at 1593 and 1567 cm^{-1}. Other bands are masked by those due to dithiocarbamate ligand.

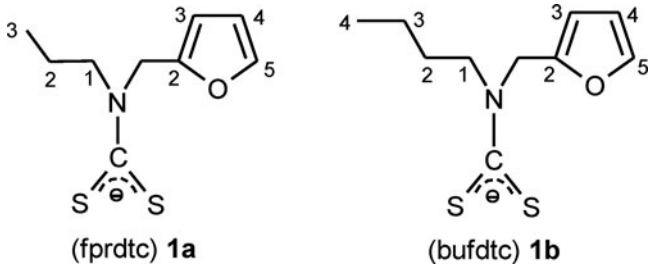


Figure 1 Structure and numbering of ligands: (fprdtc) **1a** and (bufdtc) **1b**.

2.2. ^{1}H NMR Spectra

Structure and numbering of ligands are given in Figure 1. NMR spectra were recorded at room temperature using TMS as internal reference. $CDCl_3$ was used as a solvent. ^{1}H and ^{13}C NMR spectra of **1** and **4** are shown in Figures S1–S4 (Supplemental Materials).

For complexes **1–3**, the signals due to methylene protons of propyl (NCH_2) and furfuryl groups appear around 3.80 and 5.15 ppm. In the case of complexes **4–6**, a singlet observed around 5.15 ppm is assigned to methylene protons of furfuryl group and NCH_2 (butyl) protons appear as a triplet around 3.85 ppm. The other aliphatic protons of propyl and butyl groups resonate in the region 0.84–3.89 ppm. The observed deshielding of the methylene protons in all the complexes is attributed to the release of electrons on the nitrogen of the dithiocarbamate toward the sulfur (or the metal) *via* the thioureide π-system. The signals observed around 6.45, 6.35, and 7.35 ppm are assigned to the protons present in the furfuryl ring. The signals observed in the higher frequency region 7.00–9.45 ppm for **2** and **5** and 7.80–9.04 ppm for **3** and **6** are assigned to the protons present in the 1,10-phenanthroline and 2,2′-bipyridine, respectively.

2.3. ^{13}C NMR Spectra

The δ ($N^{13}CS_2$) appeared in the expected region (above 202 ppm) for d^{10} metal dithiocarbamates.[21] In all the complexes **1–6**, these signals are observed in the region 204.9–208.4 ppm, which indicate the bidentate character of the dithiocarbamate ligands. The $N^{13}CS_2$ carbon sites of heteroleptic complexes are additionally deshielded compared to the homoleptic parent complexes **1** and **4**. Additional coordination of nitrogenous bases to cadmium dithiocarbamates yields a decrease of nitrogen-carbon partial double bond character and, as a result of that, the displacement of electron density from carbon and nitrogen of dithiocarbamate.[22] This explains the additional deshielding of carbon sites in the $N^{13}CS_2$ of heteroleptic complexes. This observation is supported by the lower ν_{C-N} value observed in the IR spectra of heteroleptic complexes.

2.4. Single Crystal X-ray Structural Analysis

The structure of **2** was confirmed by a single crystal X-ray analysis. Details of the crystal data and structure refinement parameters for **2** are summarized in Table 1. Selected bond distances and angles are listed in Table 2. The ORTEP diagram is shown Figure 2. Complex **2** is chelated by two symmetrically coordinating dithiocarbamate ligands [Cd–S2 = 2.6707(7), Cd–S3 = 2.6698(8), Cd–S4 = 2.6691(8), and Cd–S5 = 2.6631(8) Å] and also

Table 1 Crystal data, data collection, and refinement parameters for **2**

Empirical formula	$C_{30}H_{32}N_4O_2S_4Cd$
FW	721.24
Crystal dimensions (mm)	0.3 × 0.2 × 0.2
Crystal system	Triclinic
Space group	*P*–1
a/Å	9.6727(2)
b/Å	11.0445(3)
c/Å	15.3080(4)
α/°	84.829(2)
β/°	79.073(2)
γ/°	87.203(2)
V/Å^3	1598.33(7)
Z	2
Dc/g cm^{-3}	1.499
μ/cm^{-1}	0.978
F(000)	736
λ /Å	Mo*K*α (0.71073)
θ Range/°	3.49–26.00
Index ranges	$-11 \le h \le 11$, $-13 \le k \le 13$, $-18 \le l \le 18$
Reflections collected/unique	29885/6265
Observed reflections [$I > 2\sigma$(I)]	5143
Weighting scheme	Calc. $w = 1/(\sigma^2(F_o{}^2) + (0.0302P)^2 + 0.7152P)$, where $P = (F_o{}^2 + 2F_c{}^2)/3$
Number of parameters refined	372
$R[F^2 > 2\sigma(F^2)]$	0.0319
$wR(F^2)$	0.0665
GOOF	1.025

symmetrically by one 1,10-phenanthroline ligand. The symmetric mode of coordination of the dithiocarbamate ligands is reflected in the narrow range associated C·····S bond distances, i.e., 1.707(3) to 1.727(3) Å, which are in fact experimentally equivalent. The cadmium centre in **2** exists within an N_2S_4-donor set that defines a distorted octahedral geometry. The greatest distortion from ideal octahedral geometry is manifested in the

Table 2 Selected bond distances (Å) and bond angles (°) for **2**

Bond distance (Å)		Bond angle (°)	
Cd1–S2	2.6707(7)	S2–Cd1–S3	67.44(2)
Cd1–S3	2.6698(8)	S4–Cd1–S5	67.56(3)
Cd1–S4	2.6691(8)	S3–C1–S2	119.07(16)
Cd1–S5	2.6631(8)	S4–C26–S5	119.56(17)
N2–C1	1.340(3)	N2–C1–S2	120.9(2)
N27–C26	1.347(4)	N2–C1–S3	120.0(2)
Cd1–N23	2.402(2)	S5–C26–N27	119.8(2)
Cd1–N12	2.408(2)	S4–C26–N27	120.6(2)
C1–S2	1.727(3)	S2–Cd1–S5	111.77(3)
C1–S3	1.712(3)	S3–Cd1–S4	161.74(2)
C26–S5	1.707(3)		
C26–S4	1.724(3)		

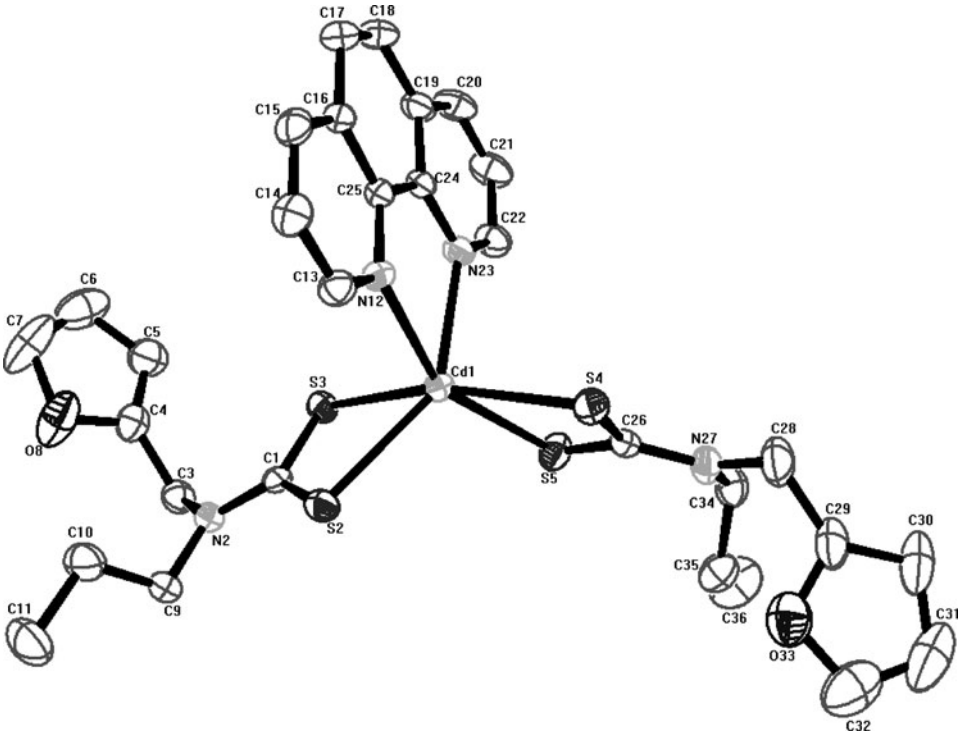


Figure 2 ORTEP diagram of the molecular structure of **2**.

N23–Cd–S2 angle of 145.60(6)°, probably reflecting the influence of three tight chelate angles in the structure [N23–Cd–N12 = 69.20(7)°, S5–Cd–S4 = 67.56(3)°, and S2–Cd–S3 = 67.44(2)°]. 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 dithiocarbamate complexes.[23–25] The ν_{C-N} thioureide distance [1.344(4) Å] observed in the present compound is similar to other dialkyldithiocarbamate complexes [23–25] which confirms a considerable double bond character in keeping with the infrared spectroscopic data. This reflects a significant contribution made by the thioureide canonical form as discussed earlier.[26] The 1,10-phenanthroline ligand is almost planar. Molecular parameters associated with 1,10-phenanthroline are normal.

The packing in **2** shows π-π stacking interactions involving the 1,10-phenanthroline ring system. The shortest π-π ring-centroid separation of 3.691(2) Å involves the centroid Cg^1 of the C16–C25 ring and its inversion – generated partner $Cg1^i$ (symmetry code: i = −x, 1−y,1−z (Figure S5, Table 3).

2.5. VBS Analysis

In the present study, the VBS method is applied to [Cd(fprdtc)$_2$(1,10-phen)] (**2**) to estimate the effective valence of the metal ion from the bond lengths reported from the crystal structure, calculated by two procedures.[27,28] The values are 2.00 (OK/B) and 2.04 (B/OK), confirming the valency to be 2.0 as expected.

Table 3 Geometry of $\pi-\pi$ interactions

CgI	CgJ	CgI···CgJ (Å)	CgI···P (Å)	α (°)	β (°)	Δ (Å)
1	$1^{(i)}$	3.691(2)	3.374	0.00	23.93	1.496
1	$2^{(i)}$	3.709(2)	3.356	2.06	25.58	1.568

Symmetry code: $i = -x, 1-y, 1-z$.

Cg represents the center of gravity of the rings N12–C25 and C16–C25, respectively, Cg1 ring A and Cg2 ring B. CgI···CgJ represents the distance between the ring centroids; CgI . . . P, the perpendicular distance of the centroid of one ring from the plane of the other. α is the dihedral angle between the planes of rings I and J; β is the angle between normal to the centroid of ring I and the line joining ring centroids; Δ is the displacement of the centroid of ring J relative to the intersection point of the normal to the centroid of ring I and the least-squares plane of ring J.

CONCLUSIONS

Six new complexes were prepared and characterized through elemental analysis and spectroscopic studies. The spectral studies on complexes indicate that the additional coordination of nitrogen donors decreases the nitrogen-carbon partial double bond character of dithiocarbamate ligands. A single crystal X-ray structure of **2** shows that the cadmium atom exists in a distorted octahedral geometry defined by an N_2S_4 donor set.

EXPERIMENTAL

All reagents and solvents were commercially available high-grade materials (Merck/Sd fine/Himedia) and used as received. Elemental analysis was performed by Perkin Elmer 2400 series (II) CHN analyzer. IR spectra were recorded on a THERMO NICOLET AVATAR 330 FT-IR spectrophotometer (range 4000–400 cm^{-1}) as KBr pellet. The NMR spectra were recorded on Bruker NMR spectrometer operating at 400 MHz for ^1H NMR and 100.63 MHz for ^{13}C NMR at room temperature in $CDCl_3$, using TMS as internal reference.

4.1. X-ray Crystallography

Diffraction data for **2** were recorded on an "Xcalibur, Sapphire 3" diffractometer using graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$) at ambient temperature. The structure was solved by SHELXS-97 [29] and refined by full matrix least-squares method in SHELXL-97.[29] All the nonhydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically.

4.2. Preparation of Amines

N-Furfuryl-*N*-propylamine and *N*-butyl-*N*-furfurylamine were prepared by general methods reported earlier.[30] ^1H and ^{13}C NMR spectral data are given in supplemental materials.

4.3. Preparation of [Cd(fprdtc)$_2$] (1)

N-Furfuryl-*N*-propylamine (4.0 mmol, 0.55 g) in ethanol was mixed with carbon disulfide (4.0 mmol, 0.3 mL) under ice cold conditions. To the resultant yellow

dithiocarbamic acid solution, an aqueous solution of $Cd(CH_3COO)_2{\cdot}2H_2O$ (2.0 mmol, 0.533 g) was added with constant stirring. The solid which precipitated was washed several times with cold water and then dried (Scheme 3).

Yield 74%, mp 213–215°C. IR (KBr, cm^{-1}): ν = 2927 ($\nu_{C-H(aliph.)}$), 1477 (ν_{C-N}), 1014 (ν_{C-S}). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.91 (t, 6H, J = 7.4 Hz, N−CH_2−CH_2−$C\underline{H}_3$), 1.73–1.79 (m, 4H, N−CH_2−$C\underline{H}_2$−CH_3), 3.84 (t, 4H, J = 8.0 Hz, N−$C\underline{H}_2$−CH_2−CH_3), 5.12 (s, 4H, NCH_2 (furfuryl)), 6.45 (d, 2H, J = 3.2 Hz, H–3 (furyl)), 6.37 (t, 2H, J = 1.6 Hz, H–4 (furyl)), 7.40 (b, 2H, H–5 (furyl)). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 11.3 (N−CH_2−CH_2−$\underline{C}H_3$), 20.0 (N−CH_2−$\underline{C}H_2$−CH_3), 52.4 (N−$\underline{C}H_2$−CH_2−CH_3), 57.7 (NCH_2 (furfuryl)), 110.0, 110.7, 142.5, 148.9 (furyl ring carbons), 205.2 (NCS_2). Anal. calcd. for $C_{18}H_{24}S_4N_2O_2Cd$ (%): C, 39.96; H, 4.47; N, 5.18. Found (%): C, 39.63; H, 4.36; N 5.09.

4.4. Preparation of [Cd(fprdtc)$_2$(1,10-phen)] (2)

A hot solution of 1,10-phenanthroline (2.0 mmol, 0.40 g) in ethanol was added to a hot solution of complex **1** (1.0 mmol, 0.541 g) in chloroform. The resulting solution was cooled and petroleum ether (boiling range: 40–60°C) was added (100 mL). An yellow precipitate of the heteroleptic complex separated out, which was filtered and dried. Single crystals suitable for X-ray structural analysis were obtained from dichloromethane-acetonitrile (2:1) solvent mixture (Scheme 3).

Yield 64%; mp 271–273°C. IR (KBr, cm^{-1}): ν = 3045 ($\nu_{C-H(arom.)}$), 2923 ($\nu_{C-H(aliph.)}$), 1620, 1592, 1508 (1,10-phen), 1459 (ν_{C-N}), 1010 (ν_{C-S}). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.84 (t, 6H, J = 7.4 Hz, N–CH_2−CH_2−$C\underline{H}_3$), 1.60–1.74 (m, 4H, N−$C\underline{H}_2$−CH_2−CH_3), 3.82 (t, 4H, J = 8.0 Hz, N−$C\underline{H}_2$−CH_2−CH_3), 5.17 (s, 4H, NCH_2 (furfuryl)), 6.37 (b, 2H, H–3 (furyl)), 6.29 (b, 2H, H–4 (furyl)), 7.31 (b, 2H, H–5 (furyl)), 9.43 (b, 2H, H–2 (1,10-phen)), 7.80 (dd, 2H, J = 4.4, 4.8 Hz, H–3 (1,10-phen)), 8.39 (d, 2H, J = 7.6 Hz, H–4 (1,10-phen)), 7.87 (s, 2H, H–5 (1,10-phen)). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 11.2 (N−CH_2−CH_2−$\underline{C}H_3$), 20.0 (N−CH_2−$\underline{C}H_2$−CH_3), 51.8 (N−$C\underline{H}_2$−CH_2−CH_3), 56.9 (NCH_2 (furfuryl)), 109.2, 110.5, 142.0, 149.8 (furyl ring carbons), 150.1 (C–2 (1,10-phen)), 124.6 (C–3 (1,10-phen)), 128.9 (C–4a (1,10-phen)), 137.8 (C–4 (1,10-phen)), 126.8 (C–5 (1,10-phen)), 208.4 (NCS_2). Anal. calcd. for $C_{30}H_{32}S_4N_4O_2Cd$ (%): C, 49.96; H, 4.47 ; N, 7.77. Found (%): C, 49.59; H, 4.39; N, 7.61.

4.5. Preparation of [Cd(fprdtc)$_2$(2,2′-bipy)] (3)

A hot solution of 2,2′-bipyridine (2.0 mmol, 0.31 g) in ethanol (20 mL) was added to a hot solution of complex **1** (1.0 mmol, 0.541 g) in chloroform (25 mL). The resulting solution was cooled and petroleum ether (boiling range: 40–60°C) was added (100 mL). The yellow precipitate of the heteroleptic complex separated out, which was filtered and then dried (Scheme 2).

Yield 64%, mp 265–267°C. IR (KBr, cm^{-1}): ν = 3053 ($\nu_{C-H(arom.)}$), 2929 ($\nu_{C-H(aliph.)}$), 1593, 1567 (2,2′-bipy), 1469 (ν_{C-N}), 1009 (ν_{C-S}). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.84 (t, 6H, J = 7.2 Hz, N−CH_2−CH_2−$C\underline{H}_3$), 1.64–1.76 (m, 4H, N−CH_2−$C\underline{H}_2$−CH_3), 3.82 (t, 4H, J = 8.0 Hz, N−$C\underline{H}_2$−CH_2−CH_3), 5.16 (s, 4H, NCH_2 (furfuryl)), 6.37 (b, 2H, H–3 (furyl)), 6.30 (b, 2H, H–4 (furyl)), 7.32 (b, 2H, H–5 (furyl)), 9.04 (d, 2H, J = 4.4 Hz, H–3 (2,2′-bipy)), 7.46 (t, 2H, J = 6.2 Hz, H–4 (2,2′-bipy)), 7.91 (t, 2H, J = 7.8 Hz, H–5 (2,2′-bipy)), 8.13 (d, 2H, J = 8.0 Hz, H–6

(2,2′-bipy)). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 11.2 (N−CH_2−CH_2−CH_3), 20.0 (N−CH_2−CH_2−CH_3), 51.9 (N−CH_2−CH_2−CH_3), 57.0 (NCH_2 (furfuryl)), 109.3, 110.5, 142.1, 149.7 (furyl ring carbons), 150.5 (C–1 (2,2′-bipy)), 150.0 (C–3 (2,2′-bipy)), 125.5 (C–4 (2,2′-bipy)), 138.8 (C–5 (2,2′-bipy)), 121.3 (C–6 (2,2′-bipy)), 207.9 (NCS_2). Anal. calcd. for $C_{28}H_{32}O_2S_4N_4Cd$ (%): C, 48.23; H, 4.63; N, 8.04. Found (%): C, 48.01; H, 4.51; N, 7.88.

4.6. Preparation of [Cd(bufdtc)$_2$] (4)

A method similar to that described for the synthesis of **1** was adopted; however *N*-furfuryl-*N*- butylamine was used instead of *N*-furfuryl-*N*-propylamine.

Yield 67%, mp 230–232 °C. IR (KBr, cm^{-1}): ν = 2955 ($\nu_{C-H(aliph.)}$), 1481 (ν_{C-N}), 1011 (ν_{C-S}). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.91 (t, 6H, J = 7.4 Hz, N−CH_2−CH_2−CH_2−CH_3), 1.28–1.34 (m, 4H, N−CH_2−CH_2−CH_2−CH_3), 1.69–1.73 (m, 4H, N−CH_2−CH_2−CH_2−CH_3), 3.89 (t, 4H, J = 8.0 Hz, N−CH_2−CH_2−CH_2−CH_3), 5.14 (s, 4H, NCH_2 (furfuryl)), 6.45 (d, 2H, J = 2.8 Hz, H–3 (furyl)), 6.35 (b, 2H, H–4 (furyl)), 7.39 (b, 2H, H–5 (furyl)). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 13.8 (N−CH_2−CH_2−CH_2−CH_3), 20.1 (N−CH_2−CH_2−CH_2−CH_3), 28.5 (N−CH_2−CH_2−CH_2−CH_3), 52.4 (N−CH_2−CH_2−CH_2−CH_3), 56.0 (NCH_2 (furfuryl)), 110.3, 110.7, 142.5, 149.0 (furyl ring carbons), 204.9 (NCS_2). Anal. calcd. for $C_{20}H_{26}S_4O_2N_2Cd$ (%): C, 42.21; H, 4.96; N, 4.92. Found (%): C, 41.97; H, 4.83; N, 4.80.

4.7. Preparation of [Cd(bufdtc)$_2$(1,10-phen)] (5)

A method similar to that described for the synthesis of **2** was adopted; however complex **4** was used instead of complex **1**.

Yield 61%, mp 243–245 °C. IR (KBr, cm^{-1}): ν = 3049 ($\nu_{C-H(arom.)}$), 2927 ($\nu_{C-H(aliph.)}$), 1619, 1590, 1507 (1,10-phen), 1468 (ν_{C-N}), 1013 (ν_{C-S}). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.87 (t, 6H, J = 7.4 Hz, N−CH_2−CH_2−CH_2−CH_3), 1.21–1.30 (m, 4H, N−CH_2−CH_2−CH_2−CH_3); 1.60–1.71 (m, 4H, N−CH_2−CH_2−CH_2−CH_3), 3.86 (t, 4H, J = 7.6 Hz, N−CH_2−CH_2−CH_2−CH_3), 5.17 (s, 4H, NCH_2 (furfuryl)), 6.37 (b, 2H, H–3 (furyl)), 6.30 (b, 2H, H–4 (furyl)), 7.31 (b, 2H, H–5 (furyl)), 9.45 (d, 2H, J = 3.2 Hz, H–2 (1,10-phen)), 7.81 (dd, J = 4.4, 4.8 Hz, H–3 (1,10-phen)), 8.40 (d, 2H, J = 8.0 Hz, H–4 (1,10-phen)), 7.88 (s, 2H, H–5 (1,10-phen)). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 13.8 (N−CH_2−CH_2−CH_2−CH_3), 20.1 (N−CH_2−CH_2−CH_2−CH_3), 28.5 (N−CH_2−CH_2−CH_2−CH_3), 51.7 (N−CH_2−CH_2−CH_2−CH_3), 55.1 (NCH_2 (furfuryl)), 109.2, 110.5, 141.7, 149.8 (furyl ring carbons), 150.1 (C–2 (1,10-phen)), 124.6 (C–3 (1,10-phen)), 137.8 (C–4 (1,10-phen)), 128.9 (C–4a (1,10-phen)), 126.8 (C–5 (1,10-phen)), 208.2 (NCS_2). Anal. calcd. for $C_{32}H_{34}N_4O_2S_4Cd$ (%): C, 51.29; H, 4.84; N, 7.48. Found (%): C, 50.86; H, 4.76; N, 7.32.

4.8. Preparation of [Cd(bufdtc)$_2$(2,2′-bipy)] (6)

A method similar to that described for the synthesis of **3** was adopted; however complex **4** was used instead of complex **1**.

Yield 60%, mp 216–218°C. IR (KBr, cm^{-1}): ν = 3047 ($\nu_{C-H(arom.)}$), 2927 ($\nu_{C-H(aliph.)}$), 1592, 1567 (2,2′-bipy), 1470 (ν_{C-N}), 1011 (ν_{C-S}). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.89 (t, 6H, J = 7.2 Hz, N−CH_2−CH_2−CH_2−CH_3), 1.24–1.30 (m,

4H, N−CH_2−CH_2−CH_2−CH_3), 1.63–1.71 (m, 4H, N−CH_2−CH_2−CH_2−CH_3), 3.86 (t, 4H, $J = 8.0$ Hz, N−CH_2−CH_2−CH_2−CH_3), 5.15 (s, 2H, NCH_2 (furfuryl)), 6.39 (d, 2H, $J = 2.8$ Hz, H–3 (furyl)), 6.32 (b, 2H, H–4 (furyl)), 7.34 (b, 2H, H–5 (furyl)), 9.05 (b, 2H, H–3 (2,2′-bipy)), 7.48 (t, 2H, $J = 5.8$ Hz, H–4 (2,2′-bipy)), 7.94 (t, 2H, $J = 7.6$ Hz, H–5 (2,2′-bipy)), 8.17 (d, 2H, $J = 8.0$ Hz, H–6 (2,2′-bipy)). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 13.8$ (N−CH_2−CH_2−CH_2−CH_3), 20.1 (N−CH_2−CH_2−CH_2−CH_3), 28.5 (N−CH_2−CH_2−CH_2−CH_3), 51.8 (N−CH_2−CH_2−CH_2−CH_3), 55.2 (NCH_2 (furfuryl)), 109.4, 110.5, 142.1, 149.7, 149.9 (furyl ring carbons), 160.0 (C–2 (2,2′-bipy)), 151.2 (C–3 (2,2′-bipy)), 125.3 (C–4 (2,2′-bipy)), 138.6 (C–5 (2,2′-bipy)), 121.2 (C–6 (2,2′-bipy)), 207.6 (NCS_2). Anal. calcd. for $C_{30}H_{34}O_2N_4S_4Cd$ (%): C, 49.68; H, 5.00; N, 7.72. Found (%): C, 49.45; H, 4.87; N, 7.33.

SUPPLEMENTAL MATERIAL

Supplementary data for this article can be accessed on the publisher's website, www.tandfonline.com/gpss

Crystallographic data have been deposited with the Cambridge Crystallographic Centre: Deposition number CCDC-955354 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CBZ, IEZ, UK.

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