Accepted Manuscript

Influence of functionalities over polymer, trimer, dimer formation and optical properties of cadmium dithiocarbamates

Krishna K. Manar, Manoj K. Yadav, Anamika, Michael G.B. Drew, Nanhai Singh

PII:	\$0277-5387(16)30281-9
DOI:	http://dx.doi.org/10.1016/j.poly.2016.06.047
Reference:	POLY 12088
To appear in:	Polyhedron
Received Date:	5 May 2016
Accepted Date:	17 June 2016



Please cite this article as: K.K. Manar, M.K. Yadav, Anamika, M.G.B. Drew, N. Singh, Influence of functionalities over polymer, trimer, dimer formation and optical properties of cadmium dithiocarbamates, *Polyhedron* (2016), doi: http://dx.doi.org/10.1016/j.poly.2016.06.047

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Influence of functionalities over polymer, trimer, dimer formation and optical properties of cadmium dithiocarbamates

Krishna K. Manar,^a Manoj K. Yadav,^a Anamika,^a Michael G. B. Drew^b and Nanhai Singh^{*a}

^{*a*}Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi 221005, India Fax: +91-542-2386127, E-mail: <u>nsingh@bhu.ac.in</u>, <u>nsinghbhu@gmail.com</u> ^{*b*}Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD (U.K.)

Abstract

Homoleptic cadmium(II) bis(dithiocarbamate) complexes having polymeric $[Cd(L)_2]_{\infty}$ (L = C7H5O2CH2NCS2CH2C6H5 (L1), 1; C₆H₄NO₂CH₂NCS₂CH₂C₄H₃O (L2), 2; C₆H₄FCH₂NCS₂CH₂C₄H₃O (L3), 3). trinuclear $[Cd(L4)_2]_3$ (L4)4-= (L5 ClC₆H₄CH₂NCS₂CH₂C₄H₃O, **4**) and dinuclear $[Cd(L5)_2]_2$, _ $ClC_6H_4CH_2NCS_2CH_2C_6H_5$, 5) structures have been synthesized and characterized by elemental analyses, spectroscopy (IR, ¹H and ¹³C {¹H} NMR and UV-Vis.) and their structures have been revealed by X-ray crystallography. In 1-3 the dithiocarbamate ligands are uniquely bonded to the Cd atoms in a μ_2,κ^2 S,S-chelating-bridging fashion, portraying 1D coordination polymeric structures in which the cadmium(II) ions adopt six coordinate distorted octahedral structures. In 4 the six dithiocarbamate ligands are spectacularly arranged about the Cd atoms resulting in a centrosymmetric trinuclear complex in which the central metal adopts an octahedral geometry and the terminal Cd atoms are in square pyramidal environments. Complex 5 has the well-established centrosymmetric dimeric structure in which the metal atoms have a five-coordinate trigonal bipyramidal geometry. Complexes 1-4 are rare examples of polymeric and trinuclear cadmium dithiocarbamate complexes. 1-5 show luminescent characteristics in solution and in the solid state arising from the metal perturbed intra-ligand charge transfer (ILCT) states. Their TG analyses show a single step decomposition with the formation of CdS nanoparticles, which have been examined by PXRD and HRTEM.

1. Introduction

Growing interest in dithiocarbamate ligand chemistry is due to the functionalization of the substituents on the N atom of the dithiocarbamate unit, which allows more complex architectures via secondary interactions and the modification of their physical properties [1-7]. Metal 1,1-dithiolates, including those of group 12 (Zn, Cd, Hg) metal dithiocarbamates, are becoming increasingly important due to their rich variety of structures, optical properties and molecular precursors for the formation of metal sulfide materials [4-6]. In contrast to a plethora of examples of Zn(II) dithiocarbamates [2,3b] showing structural diversity, the number and structural types of cadmium dithiocarbamate complexes reported to date are extremely limited [1c,4,5]. Indeed the majority of known structures are centrosymmetric dimers. In recent years some group 12 metal complexes with pyridyl functionalized dithiocarbamate ligands involving distant hetero Py(N) and S,S-donor atoms displaying

polymeric structures have been described [3b,7]. However, recently the time and solvent dependent crystallization of cadmium bis(dithiocarbamate) produced the coordination polymer [$\{Cd[S_2CN(iPr)-CH_2CH_2OH]_2\}_3$ ·MeCN]_∞[5a].

The geometric constraints imposed by the substituents on the coordination spheres are crucial in the stabilization of their overall structures. It is therefore critical to make changes to the dithiocarbamate ligand environment in order to map out their fascinating structural features and properties. Accordingly, on the 3- or 4- position of the benzene rings, substituents with varying electronegativities, such as F, Cl, O and NO₂, were incorporated in the dithiocarbamate unit. The synthesis, crystal structures, photoluminescent characteristics and thermal decomposition of the cadmium complexes 1-5 with new functionalized dithiocarbamate ligands (Figure 1) have been undertaken. The polymeric (1-3), trimeric (4) and dimeric (5) complexes thus formed and the supramolecular arrays sustained via secondary interactions in these complexes are described in this contribution.

----- Figure 1 ----

2. Experimental

2.1. Materials and general methods

The reagent grade chemicals $Cd(OOCCH_3)_2 \cdot 2H_2O$ and 1,3-benzodioxole-5-carbaldehyde (Aldrich), 4-fluorobenzaldehyde, 4-chlorobenzaldehyde, 3-chlorobenzaldehyde and 4-nitrobenzaldehyde, (Avra), benzylamine, furfurylamine and carbon disulfide (S D Fine-Chem) were used as received. The solvents were purified by standard procedures. All reactions were carried out under ambient conditions.

The melting points were determined in open capillaries on a Gallenkamp's apparatus and are uncorrected. Elemental analysis (C, H, N) were performed on an Exeter CE-440 element analyzer and sulfur was determined gravimetrically as BaSO₄ [8]. IR (KBr discs) in the range 4000-400 cm⁻¹ and ¹H and ¹³C {¹H} NMR spectra were recorded in CDCl₃ solution on Perkin Elmer IR and JEOL AL300 FT NMR spectrophotometers respectively. Chemical shifts are quoted in parts per million (δ , ppm) with (CH₃)₄Si (TMS) as internal standard for ¹H and ¹³C {¹H} NMR. The UV-Vis. absorption (200-800 nm) and photoluminescence spectral measurements were carried out on Shimadzu UV-1800 and Horiba JobinYvon and Fluorolog-3 spectrophotometers respectively. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer STA 6000 TG/DTA Thermogravimetric Analyzer with a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere. Powder X-ray diffraction (PXRD) measurements were made

on a Brüker D8 diffractometer with Cu K α radiation ($\lambda = 1.541836$ Å) in the 2 θ range 10-60°, with a scan speed and a step size of 1° and 0.02° min⁻¹ respectively. The transmission electron microscopy measurements were conducted on a JEOL JEM-2100F field emission transmission electron microscope operating at 200 kV. The samples were prepared by placing 1-3 μ L of ethanol solutions of the complexes on copper grids and drying under a lamp.

2.2. Synthesis of the dithiocarbamate ligands (KL1-KL5) and complexes $[Cd(L)_2]$ (L = L1 (1), L2 (2), L3 (3), L4 (4), L5 (5)

The secondary amines required for the synthesis of dithiocarbamate ligands were synthesized by the reaction of 1,3-benzodioxole-5-carbaldehyde (0.150 g, 1 mmol), 4-nitrobenzaldehyde (0.151 g, 1 mmol), 4-fluorobenzaldehyde (0.124 g, 1 mmol), 3-chlorobenzaldehyde (0.140 g, 1 mmol) or 4-chlorobenzaldehyde (0.140 g, 1 mmol) and benzylamine (0.107 g, 1 mmol) or furfurylamine (0.097g, 1 mmol) dissolved in 15 mL ethanol and refluxed for 8 h. The resulting reaction mixture was kept in an ice bath, stirred and then NaBH₄ and methanol were added to reduce the Schiff base to a secondary amine. The product was extracted with dichloromethane (50 mL) and washed with distilled water (3 x 20 mL). The oily yellow to light pink product was collected on solvent removal. The potassium salts of the dithiocarbamate ligands (KL1-KL6) were prepared by the reaction of the secondary amines thus obtained. KL1-KL6 were dissolved in 10 mL THF, and KOH (0.056 g, 1 mmol) was added followed by addition of carbon disulfide (0.076 g, 1 mmol) under ice-cold conditions. The reaction mixture was stirred for 2-3 h and the solvent was removed on a rotary evaporator. The product obtained was washed 2-3 times with diethyl ether to yield a pale yellow solid product.

The complexes 1-5 were prepared according to the following general procedure. To a 20 mL stirred methanol solution of the ligand KL1 (0.35 g, 1 mmol), KL2 (0.34 g, 1 mmol), KL3 (0.31 g, 1 mmol), KL4 (0.33 g, 1 mmol) or KL5 (0.34 g, 1 mmol)), was added gradually a 20 mL methanol:water (80:20) solution of Cd(OOCCH₃)₂·2H₂O (0.13 g, 0.5 mmol). In each case the reaction mixture was stirred for 6 h, resulting in the formation of a light yellow product. The precipitate thus formed was filtered off, washed with methanol followed by diethylether. Light yellow crystals of 1-5 were obtained within three to four weeks by dissolving the compounds in dichloromethane and layering with acetonitrile.

2.3. Characterisation data

2.3.1. Ligands (KL1-KL5)

KL1, Yield: 0.26 g, 75%. IR (KBr, cm⁻¹): 1330 v(C=N), 1076 v(C-S). ¹H NMR (300.40 MHz, CDCl₃, δ , ppm): 7.18-7.10 (m, 5H, -C₆H₅), 6.91-6.60 (s, 3H, -C₆H₃CH₂O₂), 5.84 (s, 2H, -CH₂C₆H₃O₂), 5.29-5.20 (s, 4H, -CH₂C₆H₃CH₂O₂, -CH₂C₆H₅), ¹³C {¹H} NMR (75.45 MHz, CDCl₃, δ , ppm): 215.95 (CS₂), 147.00, 146.27, 138.47, 132.44 (-C₆H₅), 128.42, 127.62, 126.91, 121.01 (-C₆H₃CH₂O₂), 108.30 (-CH₂C₆H₃CH₂O₂), 53.94 (-CH₂C₆H₅, -CH₂C₇H₅O₂).

KL2, Yield: 0.24 g, 73%. IR (KBr, cm⁻¹): 1304 v(C=N), 1016 v(C–S). ¹H NMR (300.40 MHz, CDCl₃, δ , ppm): 8.10-7.39 (m, 4H, -C₆H₄), 6.28-6.22 (m, 3H, C₄H₃O), 5.55 (s, 2H, -CH₂C₄H₃O), 5.37 (s, 2H -CH₂C₆H₅NO₂). ¹³C {¹H} NMR (75.45 MHz, CDCl₃, δ , ppm): 216.69 (CS₂), 152.12, 147.39, 146.08, 141.80, 128.10, 123.09 (-C₆H₅), 110.41-107.73 (-C₄H₃O), 54.08 (-CH₂C₆H₄NO₂), 47.74 (-CH₂C₄H₃O).

KL3, Yield: 0.21 g, 68%. IR (KBr, cm⁻¹): 1271 v(C=N), 1065 v(C-S). ¹H NMR (300.40 MHz, CDCl₃, δ , ppm): 7.48-7.07 (m, 4H, C₆H₄), 6.33-6.22 (m, 3H, -C₄H₃O), 5.38 (s, 2H, -CH₂C₄H₃O), 5.30 (s, 2H -CH₂C₆H₄F). ¹³C {¹H} NMR (75.45 MHz, CDCl₃, δ , ppm): 216.20 (CS₂), 152.08, 141.73, 134.73, 129.35, 129.26, 114.88 (C₆H₅), 110.44-107.93 (-C₄H₃O), 53.03 (-CH₂C₆H₅F), 46.83 (-CH₂C₄H₃O).

KL4, Yield: 0.23 g, 70%. IR (KBr, cm⁻¹): 1285 v(C=N), 1070 v(C-S). ¹H NMR (300.40 MHz, CDCl₃, δ , ppm): 7.48-7.23 (m, 4H, -C₆H₄), 6.33-6.22 (m, 3H, -C₄H₃O), 5.39 (s, 2H, -CH₂C₄H₃O), 5.29 (s, 2H -CH₂C₆H₄Cl). ¹³C {¹H} NMR (75.45 MHz, CDCl₃, δ , ppm): 216.44 (CS₂), 152.11, 141.65, 137.75, 130.82, 129.13, 127.89 (-C₆H₄), 110.35–110.83 (-C₄H₃O), 53.04 (-CH₂C₆H₅Cl), 46.83 (-CH₂C₄H₃O).

KL5, Yield: 0.34 g, 72%. IR (KBr, cm⁻¹): 1300 v(C=N), 1084 v(C–S). ¹H NMR (300.40 MHz, CDCl₃, δ , ppm): 7.29-7.10 (m, 5H, -C₆H₅), 7.06-7.03 (m, 4H, -C₆H₄), 5.24 (s, 2H, -CH₂C₆H₅), 5.24 (s, 2H -CH₂C₆H₄). ¹³C {¹H} NMR (77.00 MHz, CDCl₃, δ , ppm): 216.20 (CS₂), 141.27, 138.32, 138.19, 130.71 (-C₆H₅),130.15, 129.90, 128.63, 127.15, 126.71, 122.20 (-C₆H₄), 54.65 (-CH₂C₆H₅), 53.95 (-CH₂C₆H₄Cl).

2.3.2. Complexes 1-5

1, Yield: 0.31 g, 83%. M.p.: 196-200 °C. Anal. calcd. for $C_{32}H_{28}O_4N_2S_4Cd$: C 51.57, H 3.79, N 3.76, S 17.17. Found: C 51.35, H 3.66, N 3.55, S 17.02. IR (KBr, cm⁻¹): 1494 v(C=N), 1040 v(C-S). ¹H NMR (300.40 MHz, CDCl₃, δ , ppm): 7.33-7.25 (m, 10H, -C₆H₅), 6.92-6.74 (s, 6H, -C₆H₃CH₂O₂), 5.91 (s, 4H, -CH₂C₆H₃O₂), 5.16-5.05 (s, 4H, -CH₂C₆H₃CH₂O₂, -

CH₂C₆H₅), ¹³C {¹H} NMR (75.45 MHz, CDCl₃, δ , ppm): 206.53 (CS₂), 148.00, 147.43 (-C₆H₅), 134.84, 128.82, 128.59, 127.96, 121.76 (-C₆H₃CH₂O₂), 108.73 (-CH₂C₆H₃CH₂O₂), 57.43 (-CH₂C₆H₅, -CH₂C₇H₅O₂), UV-Vis. (nujol/CH₂Cl₂, λ_{max} , nm, ϵ (M⁻¹ cm⁻¹)): 320, 370, 425/270 (1.38 x 10⁴), 290 (8.76 x 10³).

2, Yield: 0.29 g, 81%. M.p. 179-183 °C. Anal. calcd. for $C_{26}H_{22}O_6N_4S_4Cd$: C 42.95, H 3.05, N 7.71, S 17.60. Found: C 42.75, H 2.98, N 7.60, S 17.41. IR (KBr, cm⁻¹): 1516 v(C=N), 1014 v(C–S). ¹H NMR (300.40 MHz, CDCl₃, δ , ppm): 8.14-7.25 (m, 4H, -C₆H₄), 6.39-6.31 (m, 3H, C₄H₃O), 5.29 (s, 4H, -CH₂C₄H₃O), 5.15 (s, 4H -CH₂C₆H₅NO₂). ¹³C {¹H} NMR (75.45 MHz, CDCl₃, δ , ppm): 206.69 (CS₂), 148.26, 142.67, 133.76, 128.86 (-C₆H₅), 110.68-110.46 (-C₄H₃O), 58.05 (-CH₂C₆H₅), 50.84 (-CH₂C₄H₃O), UV-Vis. (nujol/CH₂Cl₂, λ_{max} , nm, ϵ (M⁻¹ cm⁻¹): 320, 370, 425/270 (1.50 x 10⁴), 290 (8.42 x 10³).

3, Yield: 0.27 g, 80%. M.p. 125-130 °C. Anal. calcd. for $C_{26}H_{22}F_2O_2N_2S_4Cd$: C 46.39, H 3.29, N 4.16, S 19.01. Found: C 46.22, H 3.35, N3.95, S 18.83. IR (KBr, cm⁻¹): 1508 v(C=N), 1015 v(C-S). ¹H NMR (300.40 MHz, CDCl₃, δ , ppm): 7.59-7.13 (m, 4H, C₆H₄), 6.39 (m, 3H, -C₄H₃O), 5.13 (s, 4H, -CH₂C₄H₃O), 5.06 (s, 4H -CH₂C₆H₄F). ¹³C {¹H} NMR (75.45 MHz, CDCl₃, δ , ppm): 208.74 (CS₂), 163.06, 159.84, 149.16, 142.84, 129.41, 129.30 (C₆H₅), 110.62-109.56 (-C₄H₃O), 56.75 (-CH₂C₆H₅F), 50.55 (-CH₂C₄H₃O), UV-Vis. (nujol/CH₂Cl₂, λ_{max} , nm, ϵ (M⁻¹ cm⁻¹)): 320, 370, 425/ 270 (1.92 x 10⁴), 290 (8.29 x 10³).

4, Yield: 0.29 g, 83%, M.p. 140-145 °C. Anal. calcd. For $C_{78}H_{66}Cl_6O_6N_6S_{12}Cd_3$: C 44.23, H 3.14, N 3.97, S 18.13. Found: C 44.05, H 3.20, N 3.79, S 17.76. IR (KBr, cm⁻¹): 1465 v(C=N), 1012 v(C-S). ¹H NMR (300.40 MHz, CDCl₃, δ , ppm): 7.35-7.25 (m, 4H, -C₆H₄), 6.39-6.32 (m, 3H, -C₄H₃O), 5.17 (s, 4H, -CH₂C₄H₃O), 5.04 (s, 4H -CH₂C₆H₄Cl). ¹³C {¹H} NMR (75.45 MHz, CDCl₃, δ , ppm): 206.70 (CS₂), 148.26, 142.67, 133.76, 128.86 (-C₆H₅), 110.68-110.46 (-C₄H₃O), 58.05 (-CH₂C₆H₅Cl), 50.84 (-CH₂C₄H₃O), UV-Vis. (nujol/CH₂Cl₂, λ_{max} , nm, ϵ (M⁻¹ cm⁻¹)): 320, 370, 425/270 (1.40 x 10⁴), 290 (5.15 x 10³).

5, Yield: 0.27 g, 76%. M.p. 148-152 °C. Anal. calcd. For $C_{60}H_{52}Cl_4N_4S_8Cd_2$: C 49.62, H 3.61, N 3.86, S 17.62. Found: C 49.45, H 3.71, N 3.65, S 17.43. IR (KBr, cm⁻¹): 1475 v(C=N), 988 v(C–S). ¹H NMR (300.40 MHz, CDCl₃, δ , ppm): 7.28-7.16 (m, 5H, -C₆H₅), 7.02-7.16 (m, 4H, -C₆H₄), 5.02 (s, 4H, -CH₂C₆H₅), 5.07 (s, 4H -CH₂C₆H₄). ¹³C {¹H} NMR (77.00 MHz, CDCl₃, δ , ppm): 207.31 (CS₂), 137.13, 134.75, 134.55, 131.04, 130.81, 130.32

 $(-C_6H_5)$, 128.75-122.74 $(-C_6H_4)$, 58.28 $(-CH_2C_6H_5)$, 57.90 $(-CH_2C_6H_4Cl)$, UV-Vis. (nujol/CH₂Cl₂, λ_{max} , nm, ϵ (M⁻¹ cm⁻¹)): 320, 370, 425/270 (2.31 x 10⁴), 290 (7.81 x 10³).

2.4. X-ray structure determinations

Single crystal X-ray diffraction data for the samples were measured on an Oxford Diffraction X-calibur CCD diffractometer using Mo K α radiation at 293 K for all samples, except for **4** where the temperature was 150 K. Data reductions were carried out using the CrysAlis program [9]. The structures were solved by direct methods using SHELXS-97 [10] and refined on F² by a full matrix least squares technique using SHELXL-97 [11]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically fixed with thermal parameters equivalent to 1.2 times the Ueq value of the appropriate carrier atom. In **2** the five-membered rings are disordered with the oxygen atoms at two positions given occupation factors of x and 1-x, with x refining to 0.55(2). In **4**, a similar disorder was found in the furan rings with the oxygen atoms at two positions. The disorder was treated similarly with x refining to 0.613(9). Diagrams for all the complexes were drawn using the ORTEP, Diamond and Mercury softwares [12].

2.5. Theoretical calculations

Single point calculations were carried out using the Gaussian 03 program [13]. Structures were optimized using the B3LYP density functional together with basis sets LANL2DZ for Cd, 6-31+G* for S and 6-31G for the remaining atoms. Input models were taken from the crystal structures, but with hydrogen atoms given theoretical positions.

3. Results and discussion

The homoleptic complexes 1-5 were obtained in good yields by facile metathetical reactions between Cd(OOCCH₃)₂·2H₂O and the potassium salt of the ligands (KL1-KL6) in a 1:2 molar ratio, in 80:20 v/v methanol:water solution. The complexes are air-stable and melt in the 125-200 °C temperature range. All the complexes have been characterised by spectroscopy (IR, ¹H and ¹³C NMR and UV-Vis.) and their solid phase luminescent behaviors have been studied. Solid state structural determinations by X-ray crystallography revealed polymeric (1-3), trinuclear (4) and dinuclear (5) structures. The justification for the formation of rare polymeric (1-3) and trinuclear (4) structures and the involvement of remarkable C-H...F, C-H...O and H...H interactions observed in some complexes, sustaining the

supramolecular structures, have been assessed by theoretical calculations. Their solution and solid phase luminescence have been studied. The TGA decomposition products, yielding CdS particles, have been examined by PXRD and HRTEM.

In the solid phase, when excited at 290-300 nm (Figure 2) complexes **1-5** show an emission band near 400 nm with a Stokes shift of 80-100 nm, originating from the metal perturbed ILCT states of the dithiocarbamate ligands. It is to be noted that despite conformational rigidity upon coordination of the ligands to the metals and the extended structures, the luminescent intensity of the polymeric complexes **1-3** are somewhat weaker due to the presence of more the electronegative substituents F, N and O in the benzene ring of the dithiocarbamate group acting as quencher than the tri- and dinuclear analogs (**4** and **5**) which contain the relatively less electronegative chlorine atom. Upon excitation at 280 nm (Figure S1) in CH₂Cl₂ solution, complex **5** show an emission band near 330 nm, whereas the polymer **2** and trimer **4** show emissions near 440 nm. This significant difference in emission spectra between solid and solution may be attributed to the changes of the structures in solution.

-----Figure 2 -

3.1. Crystal Structures

Single crystals of complexes **1-5** were obtained within 3-4 weeks from a dichloromethane solution layered by acetonitrile. Their molecular structures have been determined by X-ray crystallography and are depicted in Figures S2-S4. Crystal data and refinement details are listed (Table 1) and selected bond lengths and bond angles are given in Tables S1-S3.

-----Table 1-----

The Cd²⁺ ion, with a d¹⁰ configuration, shows no stereochemical preferences arising from ligand field stabilization effects and therefore in principle it can display a variety of coordination numbers, viz. 4, 5 and 6, and geometries. The crystallographic asymmetric unit of **1-3** consists of one formula unit of the complexes $[Cd(L)_2]_{\infty}$ (L = L1 **1**, L2 **2**, L3 **3**). These complexes adopt similar structures in which the cadmium atom has a six coordinate distorted octahedral environment and forms 1D coordination polymeric structures (Figure 3) based on sequential edge-shared octahedra (Figure S5). In **1**, **2** and **3** each dithiocarbamate group is bonded to the cadmium atom in a μ_2 , κ^2 -S,S chelating-bridging fashion. In all three structures, the metal atom occupies a 2-fold axis, being bonded to the ligand in a asymmetric bidentate fashion with the Cd(1)-S(11) bond distance (range 2.541(1)-2.578(1) Å) being shorter than the Cd(1)-S(13) bond distance (range 2.791(2)-2.822(1) Å). In addition, the Cd(1)-S(13ⁱ)

bond distances are in the range 2.749(1)-2.760(2) Å. These distances to S(13) and $S(13^i)$ are somewhat longer than those observed for dimeric Cd(II) dithiocarbamate complexes (Table 2) [4a,5a] because of the higher coordination number of 6 about the metal center in the polymeric structures. The justification for this polymeric structure has been investigated by DFT calculations. First the energy of the monomeric 4-coordinate fragment was calculated and compared to the structure containing a central 6-coordinate metal with 2 outer 5coordinate metals. The energy difference E(trimer)-3*E(monomer) is -42.55 kcal mol⁻¹, thus validating the formation of the trimer. However, it is clear that the structure of the 4coordinate fragment from the polymer, with a very distorted equatorial plane, is not what would be found in such a moiety and therefore the structure was geometry optimized and refined as expected to a tetrahedral structure in which the two chelate planes are perpendicular. This trimeric fragment, taken from complex **1**, was also geometry optimised and the resulting energy difference of E(trimer)-3*E(monomer) reduced to -17.25 kcal mol⁻¹.

-----Table 2-----

The complexes 1-3 are rare examples of Cd(II) bis(dithiocarbamate) coordination polymers, reported to date for the Py(N) [4a] or the S,S- donor [5a] atoms of the dithiocarbamate ligands. They can be described as clathrates that contain channels in which the second component can be trapped [14] (Figure S6).

-----Figure 3 -----

A noteworthy feature of **1** is the formation of an unusual closed-shell hydrogen-hydrogen (H-H = 2.34 Å) interaction (Figure 4) between the piperonyl hydrogen atoms of the dithiocarbamate groups on neighboring molecules in the polymeric structure, which is smaller than the sum of the van der Waals radii for the hydrogen atoms. This may be attributed to the hydrogen atoms attached to the carbon atom bonded to oxygen atoms under consideration that may induce partial positive and negative charges on the hydrogen atoms involved in bonding [15]. Such a type of H-H interaction is rare and distinctly different from the hydrogen, agostic and anagostic bonding in the compounds [15a].

To test the significance of this interaction, we constructed a dimer containing two such interactions (Figure 4) However single-point calculations show that the energy difference E(dimer)-2*E(monomer) is +0.59 kcal mol⁻¹ and therefore in this case these H...H interactions are slightly repulsive.

------Figure 4 -----

The structures of complexes **2** and **3** are stabilized by non-covalent (C(37)-H...O(1/2-x,-1/2+y, 3/2-z), 2.373, $\pi \cdots \pi$, 4.352, 5.200; 2.654; C-H...S, 2.925 Å) and (C(31)-H...(F-C)(1x,1/2+y,3/2-z), 2.516,9 C(34)-H...(F-C)(3/2-x, -1/2+y, 3/2-z2.777 Å; C-H... π , 3.575 Å) [16] interactions (Figures 5, 6, S7 and S8). The C-H...O interactions have been investigated by DFT calculations. As shown in Figure 5, two molecules are connected across a centre of symmetry by two C-H...O interactions. Single point energy calculations show E(dimer)-2*E(monomer) to be -1.46 kcal mol⁻¹, indicating a weak attractive interaction. There are two C-H...F interactions of interest. One C-H...F interaction, shown in Figure 6, gave a value of -1.74 kcal mol⁻¹ for E(dimer)-2*E(monomer). In addition there are two C-H...F interactions across a centre of symmetry, and here the E(dimer)-2*E(monomer) difference was calculated as -2.49 kcal mol⁻¹. In the crystal packing of **1-3**, the central CdC₂S₄ core formed by the surrounding molecules organize a 'flower-like' pattern along the 'c' axis (Figure S9).



Unlike the polymeric structures established for 1-3, complex 4 is a rare centrosymmetric trinuclear molecule [4a] where six dithiocarbamate ligands are uniquely bonded to three cadmium atoms in a κ^2 S,S-chelating-bridging as well as S,S-chelating fashion. As shown in Figures 7 and S3, the inner Cd(1) atom is situated on a centre of symmetry in a six-coordinate octahedral environment, while the outer Cd(2) atoms occupy square pyramidal environments. These terminal Cd(2) atoms are asymmetrically S,S-chelated by two dithiocarbamate ligands with distances to the S(11) and S(13) atoms of 2.550(2) and 2.652(2) Å and to the S(41) and S(43) atoms of 2.554(2) and 2.709(2) Å respectively. The longer bond formed to the S(43) atom is no doubt due to the fact that it forms a bridge to the Cd(1) atom. The geometry around the Cd(2) atom is best considered as a highly distorted square pyramid as the τ value is 0.30 compared to 0.0 for an ideal square pyramid and 1.0 for a trigonal bipyramid. The two chelating ligands around the Cd(2) atom intersect at an angle of $35.11(5)^{\circ}$ and form a distorted equatorial plane with an r.m.s. deviation of 0.186 Å. Thus the environment of the Cd(2) atom is very different from that of the Cd(1) atom where the equatorial plane is perforce planar. The metal atom Cd(2) is displaced by 0.577(1) Å from the equatorial plane in the direction of the S(71) atom, bonded at a distance of 2.638(2) Å and which occupies an

axial position and also forms a bridge to the Cd(1) atom. Thus the dithiocarbamate groups are bonded to the central Cd(1) and terminal Cd(2) atoms in a μ_2,κ^2 S,S-chelating-bridging manner, thereby spectacularly forming a trinuclear structure. In this complex the central Cd(1) atom lies at the center of symmetry and is bonded to two chelating dithiocarbamate groups via the atoms S(71) and S(73) at distances of 2.707(2) and 2.585(2) Å, the longer bond being found to the bridging sulfur atom S(71). Additionally, two S(43) atoms, which are already bonded to the Cd(2) atom, occupy axial positions at the Cd(1) atom at 2.889(2) Å, completing the distorted octahedral geometry about Cd(1) centre.

-----Figure 7------Figure 7------

The Cd(1)···Cd(2) distance of 3.851(1) Å within the molecule may indicate weak metalmetal interactions. The supramolecular structure of this complex is stabilized by C-H··· π , C-H···S (Figure S10) and C-H···Cl interactions, as shown in Figure S11a. Notably the oxygen atom on the furfuryl ring and sulfur atom in the dithiocarbamate unit form a seven-membered ring tropolium-like structure, thereby stabilizing the supramolecular network in the crystal structure of **4** (Figure S11b).

Single point DFT calculations were carried out on the trimer and the individual fourcoordinate monomers around the Cd(1) and Cd(2) atoms. The energy of the symmetric square planar monomer around the Cd(1) atom was found to be more stable by -9.82 kcal mol⁻¹ than the distorted geometry around the Cd(2) atom. The trimer was found to be more stable by -26.98 kcal mol⁻¹ compared to the three distinct monomers, showing that the trimer is more stable in the gas phase and that its formation in the crystal structure is not due to packing effects.

Complex **5** forms a centrosymmetric dimeric structure (Figure S4), which is similar to the few structurally characterized cadmium(II) dithiocarbamate complexes reported so far [5,17,18]. The cadmium atom is bonded to two bidentate ligands at 2.545(3)-2.607(3) Å and an additional sulfur atom S(41ⁱ) at a distance of 2.610(2) Å, which bridges to the other metal atom. The two four-membered bidentate rings intersect at an angle of 49.4(1)^o in **5**. In the dimeric structure the cadmium atoms are five-coordinate with a τ value of 0.618, thus indicating that **5** has a distorted trigonal bipyramid geometry.

A comparison of the geometrical details of complexes **1-5** are given in Table 2. The closest S···S contacts in the range 3.903-4.118 Å in complexes **1-5** do not account for the substantial

S···S intermolecular interactions in the solid state. Concomitant with the distances at 1.33(1)-1.34(1) Å, the C-N bonds are intermediate between C-N single and double bond lengths in **1**-**5**, due to the dominant contribution of the canonical form. The C-S bond lengths in the range 1.695(5)-1.750(5) Å are shorter than the C-S single bond distance of 1.82 Å due to partial conjugation over the N-C-S unit.

4. Thermal decomposition

The TGA plots are displayed (Figure S12) and the results are summarized in Table 3. The TGA curves show a single step decomposition with the loss of organic fragments between 226 and 379 °C, leaving residues consistent with the values calculated for the mass percentage of bulk CdS. TG analyses reveal that complexes 1-5 may serve as potential single source precursors for the formation of CdS materials.

-----Table 3------

The powder X-ray diffraction patterns (PXRD) for the TGA residues of 1-5 (Figure S13) show broadened peaks indicating that the particles of CdS are of nanosize. The d-spacing observed at $(2\theta) \ 26.5^{\circ}$ corresponds to the [002] plane of hexagonal CdS [19a]. All compounds show peaks at (110), (103) and (112) characteristic of wurtzite CdS [19b] in the XRD patterns. A comparison of the diffraction peak positions of the TG decomposition products with those of the standard (ICDD card no. 41-1049, 65-3414) reveals the hexagonal phase of CdS.

The HRTEM images of CdS particles produced by the TGA decomposition of representative complexes **1**, **4** and **5** are displayed (Figure S14, a-f). The HRTEM results show that the CdS nanoparticles [19] are approximately spherical in shape with a particle size of 50 nm, shown in Figure S14 (a), (c) and (e). Further resolution at 5 nm shows rod-shaped particles of for the decomposition product of **1**, **4** and **5**, Figure S14 (b, d and f).

4. Conclusions

New functionalized cadmium bis(dithiocarbamate) complexes having rare polymeric (1-3), trinuclear (4) and dinuclear (5) structures have been synthesized and fully characterized. In these complexes the supramolecular structures are shown to be sustained by attractive H···H, C-H···F, C-H···O, C-H···Cl, C-H···S, C-H··· π and π ··· π , interactions. The unusual structures of 1-4 and the H···H, C-H···O, C-H···F-C interactions have been supported by theoretical calculations. Complexes 1-5 show luminescent characteristics in solution and in

the solid phase. A study of their TG decomposition products reveals that they could serve as single source molecular precursors for the preparation of CdS nanoparticles.

Acknowledgements

We gratefully acknowledge the Science and Engineering Research Board (SERB) for financial support through Project: SB/SI/IC-15/2014 (NS), the University Grants Commission (UGC), New Delhi for SRF (KKM) and the Department of Chemistry, CAS-UGC-I, Banaras Hindu University for the X-ray and infrastructural facilities. We also thank the University of Reading and EPSRC for funds for the diffractometer used for determination of the structure of **4**.

Appendix A. Supplementary data

CCDC 1400102-1400105 and 1400107 contains the supplementary crystallographic data for 1-4 and 5. These data be obtained free of charge via can 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 email: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org.

References

[1] (a) D. Coucouvanis, Prog. Inorg. Chem. 11 (1970) 233; (b) D. Coucouvanis, Prog. Inorg. Chem. 26 (1979) 301; (c) G. Hogarth, Prog. Inorg. Chem. 53 (2005) 71; (d) G. Hogarth, Med. Chem. 12(12) (2007) 1202; (e) E. R. T. Tiekink, I. Haiduc, Prog. Inorg., Chem. 54, (2005) 127; (f) P. J. Heard, Prog. Inorg. Chem. 53 (2005) 268; (g) J. Cookson, P. D. Beer, Dalton Trans. (2007) 1459; (h) E. J. Mensforth, M. R. Hill, S. R. Batten, Inorg. Chim. Acta 403 (2013) 9.

[2] (a) E. R. T. Tiekink, CrystEngComm. 5 (2003) 101; (b) R. E. Benson, C.A. Ellis, C. E. Lewis, E. R. T. Tiekink, CrystEngComm. 9 (2007) 930.

[3] (a) V. Kumar, V. Singh, A. N. Gupta, M. G. B. Drew, N. Singh, Dalton Trans. 44 (2015)
1716; (b) V. Singh, V. Kumar, A. N. Gupta, M. G. B. Drew, N. Singh, New J. Chem. 38
(2014) 3737; (c) A. Kumar, R. Chauhan, K. C. Molloy, G. K. Köhn, L. Bahadur, N. Singh,
Chem. Eur. J. 16 (2010) 4307; (d) N. Singh, A. Kumar, K. C. Molloy, M. F. Mahon, Dalton
Trans. (2008) 4999; (e) G. Rajput, M. K. Yadav, M. G. B. Drew, N. Singh, Inorg. Chem. 54

(2015) 2572; (f) G. Rajput, M. K. Yadav, M. G. B. Drew, N. Singh Dalton Trans. 44 (2015) 5909.

[4] (a) V. Kumar, V. Singh, A. N. Gupta, K. K. Manar, M. G. B. Drew, N. Singh, CrystEngComm. 16 (2014) 6765; (b) T. Trindade, P. O'Brien, J. Mater. Chem. 6 (1996) 343;
(c) P. O'Brien, J. R. Walsh, I. M. Watson, M. Motevalli, L. Henriksen, J. Chem. Soc., Dalton Trans. (1996) 2491; (d) M. A. Malik, N. Revaprasadu, P. O'Brien, Chem. Mater. 13 (2001) 913; (e) P. S. Nair, T. Radhakrishnan, N. Revaprasadu, G. A. Kolawole, P. O'Brien, Chem. Commun. (2002) 564.

[5] (a) Y. S. Tan, A. L. Sudlow, K. C. Molloy, Y. Morishima, K. Fujisawa, W. J. Jackson, W. Henderson, S. N. B. A. Halim, S. W. Ng, E. R. T. Tiekink, Cryst. Growth Des. 13 (2013) 3046; (b) C. M. Dee, E. R. T. Tiekink, Z. Kristallogr. 217 (2002) 85; (c) J. S. Casas, A. Sanchez, J. Bravo, S. Garcia-Fontan, E. E. Castellano, M. M. Jones, Inorg. Chim. Acta 158 (1989) 119. (d) K. Ramasamy, V. L. Kuznetsov, K. Gopal, M. A. Malik, J. Raftery, P. P. Edwards, P. O'Brien, Chem. Mater. 25 (2013) 266.

[6] (a) N. Hollingsworth, A. Roffey, H.-U. Islam, M. Mercy, A. Roldan, W. Bras, M. Wolthers, C. R. A. Catlow, G. Sankar, G. Hogarth, N. H. de Leeuw, Chem. Mater. 26 (2014) 6281; (b) D. Fan, M. Afzaal, M. A. Mallik, C. Q. Nguyen, P. O'Brien, P. J. Thomas, Coord. Chem. Rev. 251 (2007) 1878; (c) N. Alam, M. S. Hill, G. K. Kohn, M. Zeller, M. Mazhar, K. C. Molloy, Chem. Mater. 20 (2008) 6157; (d) H. C. Levintis, S. P. King, A. Sudlow, M. S. Hill, K. C. Molloy, S. A. Haque, Nanolett. 10 (2010) 1253.

[7] (a) V. Singh, A. Kumar, R. Prasad, G. Rajput, M. G. B. Drew, N. Singh, CrystEngComm.13 (2011) 6817; (b) A. N. Gupta, V. Kumar, V. Singh, K. K. Manar, M. G. B. Drew, N. Singh, CrystEngComm. 16 (2014) 9299.

[8] A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, ELBS and Longman, London, (1961) E8.

[9] Oxford Diffraction, CrysAlis CCD, RED, version 1.711.13, copyright (1995–2003), Oxford Diffraction Poland Sp.

[10] G. M. Sheldrick, SHELXS97, Program for Crystal Structure Solution, University of Gottingen, Gottingen (1997).

[11] G. M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Gottingen, Gottingen (1997).

[12] M. N. Burnett and C. K. Johnson, ORTEP-III, Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, USA (1996).

[13] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, revision C.02; Gaussian, Inc.: Wallingford . CT, U.S.A.

[14] (a) J. Kim, D. Whang, J. I. Lee, K. Kim, J. Chem. Soc., Chem. Commun. (1993) 1400;
(b) S. Nishikiori, C. I. Ratcliffe, J. A, Ripmeesters, J. Am. Chem. Soc. 114 (1992) 8590; (c) Takafumi Kitazawa, J. Mater. Chem. 8 (1998) 671.

[15] (a) C. F. Matta, J. Hernandez-Trujillo, T. Tang, R. F. W. Bader, Chem. Eur. J. 9 (2003)
1940; (b) J. Cioslowski, S. T. Mixon, Can. J. Chem. 70 (1992) 443; (c) P. L. A. Popelier, G. Logothetis, J. Organomet. Chem. 555 (1998) 101; (d) W. Scherer, W. Hieringer, M. Spiegler,
P. Sirsch, G. S. McGrady, A. J. Downs, A. Haaland, B. Pedersen, Chem. Commun. (1998)
2471.

[16] (a) T. S. Thakur, M. T. Kirchner, D. Bläser, R. Boese, G. R. Desiraju, CrystEngComm. 12 (2010) 2079; (b) V. R. Thalladi, H. Weiss, D. Bla1ser, R. Boese, A. Nangia, G. R. Desiraju, J. Am. Chem. Soc. 120 (1998) 8702.

[17] (a) M. J. Cox, E. R. T. Tiekink, Z. Kristallogr. 214 (1999) 670; (b) Y. Zhong, W. Zhang,J. Fan, M. Tan, C. S. Lai, E. R. T. Tiekink, Acta Crystallogr. E60 (2004) m1633.

[18] V. I. Alexander, V. G. Andrey, A. K. Alexey, A. I. Maxim, N. A. Oleg, W. Forsling, Inorg. Chim. Acta 359 (2006) 3855.

[19] (a) N. Molato, N. Revaprasadu, M.J. Moloto, P. O'Brien, M. Helliwell, Polyhedron 26 (2007) 3947; (b) Y. Li, X. Li, C. Yang, Y. Li, J. Mater. Chem. 13 (2003) 2641.

Compound	1	2	3	4	5
Chemical formula	$C_{32}H_{28}Cd_1N_2O_4S_4$	$C_{26}H_{22}Cd_1N_4O_6S_4$	$C_{26}H_{22}Cd_1F_2N_2O_2S_4\\$	C ₇₈ H ₆₆ Cd ₃ Cl ₆ N ₆ O ₆ S ₁₂	$C_{60}H_{52}Cd_{2}Cl_{4}N_{4}S_{8}$
Formula weight	745.20	727.12	673.10	2118.00	1452.14
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	C2/c	C2/c	I2/a	P 1	ΡĪ
a(Å)	29.600(11)	32.563(3)	8.1055(4)	12.480(5)	10.9841(18)
b (Å)	12.999(5)	11.0399(9)	11.0157(5)	13.775(5)	12.627(2)
c (Å)	8.137(4)	8.0979(6)	29.7296(15)	14.028(5)	12.6482(17)
α (°)	90	9990	90	109.396(5)	110.124(14)
β (°)	94.250(5)	99.808(7)	92.814(5)	103.317(5)	107.153(13)
γ (°)	90	90	90	97.946(5)	95.680(14)
$V(\mathring{A}^3)$	3122(2)	2868.6(4)	2651.3(2)	2152.1(14)	1534.1(4)
Ζ	4	4	4	1	1
$\rho calc (g cm^{-3})$	1.585	1.684	1.686	1.634	1.572
$T\left(K ight)$	293(2)	293(2)	150(2)	293(2)	293(2)
μ (Mo Ka) (mm ⁻¹)	1.007	1.101	1.181	1.266	1.182
F(000)	1512	1464	1352	1062	732
Reflections collected	12147	6280	9124	17581	11579
Independent reflections	3514	3179	3852	9480	6752
Reflections with I $> 2\sigma(I)$	2555	2379	3354	5269	3005
Final indices [I > $2\sigma(I)$] R_1^a , w R_2^b	0.0601,0.1578	0.0500, 0.1297,	0.0295, 0.0653	0.0630, 0.1486	0.0952, 0.2551
$R_{1[a]}, wR_{2[b]}$ [all data]	0.0838, 0.1816	0.0715, 0.1437	0.0368, 0.0682	0.1259, 0.1805	0.1865, 0.3086
GOF ^c	0.979	1.088	1.054	0.959	0.925
Residual electronDensity, e/Å ³	1.855, -1.597	0.845, -0.648	0.430, -0.739	1.289,0.742	1.888, -0.737

Table 1. Crystallographic data and refinement parameters for complexes 1-5

 ${}^{a}R_{1} = \Sigma \|Fo| - Fc\|/\Sigma |Fo|, {}^{b}wR_{2} = \{[\Sigma w (Fo^{2} - Fc^{2})/\Sigma w (Fo^{2})^{2}]\}^{1/2}, {}^{c}GOF = S = \{\Sigma [w(Fo^{2} - Fc^{2})^{2}]/(n-p)\}^{1/2},$

where n is the number of reflections, and p is the number of the refined parameters.

Complex	Cd-S (Å)	Geometry	Structure	Ref
$[Cd(CS_2C_7H_5O_2CH_2NCH_2C_6H_5)_2]_{\infty} (1)$	2.5781(14)-2.7914(17)	OCT	1-D polymer	a
$[Cd(CS_{2}C_{6}H_{4}NO_{2}CH_{2}NCH_{2}C_{4}H_{3})_{2}]_{\infty} (2)$	2.5744(11-2.7719(11)	OCT	1-D polymer	a
$[Cd(CS_2C_6H_4FCH_2NCH_2C_4H_3O)_2]_{\infty}(3)$	2.5413(5)-2.8219(5)	OCT	1-D polymer	a
$[\{Cd[S_2CN(iPr)CH_2CH_2OH]_2\}_3 \cdot MeCN]_{\infty}$	2.580-2.774	OCT	1-D polymer	5a
$[Cd(S_2CC_5H_4NCH_2NCH_2C_6H_5)_2]_{\infty}$	2.6521(10)-2.6874(9)	OCT	2-D polymer	4a
$[Cd((S_2CC_5H_4NCH_2)_2N)_2]_{\infty}$	2.6629(9)-2.6800(9)	OCT	2-D polymer	4a
$[Cd(S_2CC_5H_4NCH_2NCH_2C_4H_3O)_2]_{\infty}$	2.6251(9)-2.6773(9)	OCT	2-D polymer	4a
$[Cd_{3}(S_{2}CCIC_{6}H_{4}CH_{2}NCH_{2}C_{4}H_{3}O)_{6}] (4)$	2.5499(18)-2.8885(17)	SP, OCT	Trinuclear	а
$[Cd_3(S_2CCH_3C_6H_4CH_2NCH_2C_4H_3O)_6]$	2.5384(17)-2.9143(13)	SP, OCT	Trinuclear	4a
$[Cd_2[S_2C 3-ClC_6H_4CH_2NCS_2CH_2C_6H_5]$ (5)	2.540(3)- 2.842(3)	ТВР	Dinuclear	а
[Cd ₂ [S ₂ CN(iPr)CH ₂ CH ₂ OH] ₄ ·2H ₂ O·2MeCN]	2.579-2.742	SP	Dinuclear	5a
[Cd ₂ (S ₂ CC ₈ H ₆ NCH ₂ NCH ₂ NC ₅ H ₄) ₄]	2.5701(14)-2.6895(14)	SP	Dinuclear	4a
$[Cd(S_2CNC_4H_{10})_2]_2$	2.5359(5)-2.8123(5)	SP	Dinuclear	5b
Cd[S ₂ CN(n-C ₄ H ₉) ₂] ₂	2.513(5)- 2.888(5)	TBP	Dinuclear	5c

 Table 2. A comparison of selected geometrical details of complexes 1-5 with previously reported analogous dithio complexes

^aThis work. OCT = octahedral, SP = square pyramid, TBP = trigonal bipyramidal.

	T in TGA (°C)	Residue wt. observed (calcd.) %	Expected product of decomposition	
1	260-332	38.9(35.39)	CdS	
2	240-379	59.5(61.64)	CdS	
3	238-307	64.1(64.66)	CdS	
4	226-308	40.9(40.25)	CdS	
5	260-355	39.8(40.76)	CdS	

 Table 3. TGA results for complexes 1-5

Figures with captions



Figure 1. Potassium salts (KL1-KL5) of the dithiocarbamate ligands used in this work.





Figure 4. The C–H···H-C interactions in complex 1 involved in the supramolecular network organization (hydrogen atoms, except those involved in the interactions, are omitted for clarity).



SCRIPT EPI ٥D

Figure 5. Supramolecular structure of 2 stabilized by C-H···O interactions (hydrogen atoms, except those involved



interactions, are omitted for clarity).





Justification

- Five Cd(II) complexes of new functionalized dithiocarbamate ligands have been • synthesized and characterized.
- X-ray crystallography has revealed rare polymeric and trimeric structures. •
- The supramolecular structures have been sustained by C-H....F-C, C-H...O and H...H • non-covalent interactions, which have been corroborated by theoretical calculations.
- All the complexes showed luminescent characteristics. •
- TG analysis and decomposition products have been examined. •

Graphical Abstract

Homoleptic cadmium(II) bis(dithiocarbamate) complexes displaying 1D coordination polymeric (1-3), trimeric (4) and dimeric (5) structures have been synthesized and fully characterized. Their luminescent properties have been studied.

