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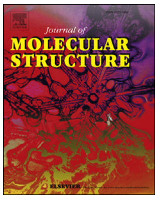

Synthesis, structural characterization, and thermal stability studies of heteroleptic cadmium(II) dithiocarbamate with different pyridyl groups

Damian C. Onwudiwe [a], [b], *, Eric C. Hosten [c]

[a] Material Science Innovation and Modelling (MaSIM) Research Focus Area, Faculty of Natural Science and Agriculture, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho, South Africa
[b] Department of Chemistry, Faculty of Natural Science and Agriculture, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa
[c] Department of Chemistry, Nelson Mandela University, P.O Box 77000, Port Elizabeth 6031, South Africa

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ABSTRACT

The synthesis, characterization and crystal structures of three chloroform solvated adducts of cadmium with mixed ligands of *N*-alkyl-*N*-phenyldithiocarbamate and pyridine, 2,2-bipyridine and 1, 10 phenanthroline represented as [CdL^{1}L^2 (py)$_2$]·CHCl$_3$ **(1)**, [CdL^{1}L^{2}bpy]·CHCl$_3$ **(2)**, and [CdL^{1}L^{2}phen]·CHCl$_3$ **(3)** (L^1 = *N*-methyl-*N*-phenyldithiocarbamate, L^2 = *N*-ethyl-*N*-phenyldithiocarbamate, py = pyridine, bpy = 2,2-bipyridine and phen = 1,10-phenanthroline) respectively are reported. Complex 1, which crystallized in the monoclinic space group P-1, is a centrosymmetric dimeric structure where each Cd center is bonded to two monodentate pyridine, a bidentate terminal dithiocarbamate, and another bidentate bridging dithiocarbamate to form a four-membered ring. Complex 2 crystallized in the monoclinic space group $P2_1/c$, with four discrete monomeric molecules in the asymmetric unit. The structure presents a cadmium atom coordinated by two sulphur atoms of a dithiocarbamate ligand and two nitrogen atoms of the 2,2′-bipyridine to form a CdS_4N_2 fragment, thus giving the structure around the Cd atom a distorted trigonal prism geometry. Complex 3 contains two discrete monomeric molecules of (phenanthroline) (*N*, *N*—methyl phenyl—*N*, *N*—ethyl phenyl dithiocarbamato)cadmium (II) per unit cell, and the complex crystallized in the triclinic space group P-1. The structure showed that the Cd atom is bonded to two bidentate dithiocarbamate ligands and to one bidentate phenanthroline ligand in a distorted trigonal prism geometry. All the compounds resulted in CdS as residue upon thermal decomposition process conducted under inert atmosphere.

1. Introduction

As a ligand of the dithiolate group, dithiocarbamate have demonstrated great benefits in the construction of new supramolecular structural motifs [1]. Their complexes with transition metals have been greatly studied due to their rich and diverse structural varieties and applications in various fields such as agriculture, medicine, biological processes and analytical chemistry. In recent years, the complexes have been explored in materials chemistry as molecular precursors for the preparation of metal sulphide nanoparticles and thin films [2–6]. One of the striking features of the chemistry of dithiocarbamate is the ability to substantially modify the bonding behaviour and electronic properties of the dithiocarbamate ligands by incorporating some functionalities into the nitrogen of the dithiocarbamate moiety. This gives rise to various interesting architectures and modified properties [7].

Among the transition elements, the group 12 triad has drawn specific attention. Although various structural motifs has been reported for Zn and Hg complexes, which could differ from monomeric to tetrameric, including different linear polymeric architectures, to some three-dimensional network structures, the chemistry of cadmium was earlier reported to lack structural

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* Corresponding author. Material Science Innovation and Modelling (MaSIM) Research Focus Area, Faculty of Natural Science and Agriculture, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho, South Africa.
E-mail address: Damian.Onwudiwe@nwu.ac.za (D.C. Onwudiwe).

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variety [8]. Consequently, cadmium complexes attracted less attention compared to the other two metals of the zinc triad. However, more structural varieties for cadmium dithiocarbamates have been revealed in recent studies (than earlier on considered) and the number of structural motifs has been on the increase [9–11]; thus, facilitating different research interests on cadmium dithiocarbamate.

Cadmium dithiocarbamate complexes, with the cadmium atom in a partially coordinatively unsaturated environment, are able to bond to molecules with S–, N–, P-donor bases reversibly. The results of these additional reactions are intermolecular heteroleptic complexes of higher coordination number generally referred to as adducts [12].

In the past few years, our group have been exploring the chemistry, properties, structures and applications of complexes obtained using *N*-alkyl-*N*-phenyl dithiocarbamate ligands with the zinc triads [13–15]. Among the triads, different N-donor lewis base adducts of zinc and cadmium has been reported [16–19]. We have continued to study this class of compounds, and in this report we present the spectroscopic and structural characterization of cadmium complexes with mixed ligands dithiocarbamate which have been "adducted" using pyridine, bipyridine and 1,10-phenanthroline. In addition, the thermal decomposition studies of the complexes were also studied.

2. Experimental

2.1. Starting materials

The chemicals used in this study were products of Sigma–Aldrich Co., and the solvents were from Merck Co. The reagents were used as received. The ligands: ammonium *N*-methyl-*N*-phenyl dithiocarbamate and *N*-ethyl-*N*-phenyl dithiocarbamate were synthesized following previously described method [13]. The precursor complex, *N*, *N*–methyl phenyl–*N*, *N*–ethyl phenyl dithiocarbamato) cadmium(II) [CdL^{1}L^2, was prepared following a literature procedure [15].

2.2. Physical measurements

The elemental (C, H, N, S) analyses were performed using Elementar, Vario EL Cube, set up for CHNS analysis. ^{1}H and ^{13}C-NMR spectra analyses were carried out on a 600 MHz Bruker Avance III NMR spectrometers using deuterated CDCl$_3$. Infra-red spectra were recorded using a Bruker alpha-P FTIR spectrophotometer. Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were performed simultaneous using SDTQ 600 Thermal instrument under nitrogen atmosphere.

2.3. Synthesis of (pyridyl) (N,N–methylphenyl–N,N–ethylphenyl dithiocarbamato)cadmium(II) (**1**)

The compound was prepared by refluxing 0.4 g of [CdL^{1}L^2] in 40 mL pyridine at a temperature between 80 and 85 °C. After 3 h, the solution was filtered to remove any unreacted substance and left in a fume cupboard to dry out. The crude product was rinsed with ethanol and recrystallized from hot chloroform. Single crystals suitable for X-ray analysis were obtained in chloroform-ethanol mixture.

Yield: 0.75 g, 81%; Anal. Calc. for $Cd_2C_{44}H_{46}N_6S_8$,CHCl$_3$ (1259.59 g/mol): C, 42.91; H, 3.76; N, 6.67; S, 20.37 Found: C, 43.29; H, 3.31; N, 7.19; S, 21.96%.

2.4. Synthesis of (2,2′ bipyridyl) (N,N–methylphenyl–N,N–ethylphenyl dithiocarbamato) cadmium(II) (**2**)

To a 20 mL hot chloroform suspension of [CdL^{1}L^2] (0.49 g, 0.001 mol) in round-bottom flask, was added 20 mL hot ethanol solution of 2, 2′-bipyridine (0.156 g, 0.001 mol). The resulting bright yellow solution was refluxed for 45 min, cooled and filtered. The solution was left in a quiet environment to give single crystals suitable for X-ray analysis after 4 days.

Yield: 0.47 g, 77%; Anal. Calc. for $CdC_{27}H_{26}N_4S_4$,CHCl$_3$ (766.57 g/mol): C, 43.87; H, 3.55; N, 7.31; S, 16.73; Found: C, 44.08; H, 3.31; N, 7.44; S, 17.02%.

2.5. Synthesis of (phenanthroline) (N, N–methyl phenyl–N, N–ethyl phenyl dithiocarbamato) cadmium(II) (**3**)

The compound was prepared by introducing 20 mL hot chloroform solution of 1,10′ phenanthroline (0.2 g, 0.001 mol) into a hot 20 mL chloroform suspension of [CdL^{1}L^2] (0.49 g, 0.001 mol). The resulting bright yellow solution was refluxed for 45 min, then reduced to about 30 mL, and filtered. The faint yellow solids which separated out from the solution after 48 h were filtered. Single crystals suitable for X-ray crystallographic analysis were gotten from slow evaporation of a mixture of dichloromethane–ethanol.

Yield: 0.52 g, 66%; Anal. Calc. for $CdC_{29}H_{26}N_4S_4$,CHCl$_3$ (790.59 g/mol): C, 45.57; H, 3.44; N, 7.09; S, 16.22; Found: C, 45.98; H, 3.24; N, 7.13; S, 15.92%. The synthesis route for complexes 1–3 is presented in Scheme 1.

2.6. X-ray crystallography

The single crystal X-ray diffraction studies of compounds 1, 2, and 3 were performed at 200 K using a Bruker Kappa Apex II diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). APEXII was used for data collection and SAINT for cell refinement and data reduction [20]. The structures were solved by direct methods using SHELXT-2014 [21], and refined by least-squares procedures using SHELXL-2014 [22] with SHELXLE [23] as a graphical interface. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were calculated in idealized geometrical positions. The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [22]), with Uiso(H) set to 1.5Ueq(C). Data were corrected for absorption effects by the numerical methods using SADABS [20].

3. Results and discussion

3.1. Spectroscopic studies

The relevant infrared bands of the complexes are presented in Table 1. The vibrational frequencies in the 1470–1490 cm^{-1} region in the three complexes is ascribed to the thiureide vibrations υ(CN). The positions of this vibration in relation to the CN stretching frequency band, which is observed in single (1350–1250 cm^{-1}) and double bonded (1690–1640 cm^{-1}) carbon-nitrogen, suggest an intermediate bond order [24,25]. The peak due to the C=S stretching vibration are observed between 960 and 1000 cm^{-1}. The peak observed in this region is a diagnostic criterion for monodentate and bidentate bonding fashion in dithiocarbamate [26]. A single