



Impact of ferrocenyl and pyridyl groups attached to dithiocarbamate moieties on crystal structures and luminescent characteristics of group 12 metal complexes[☆]

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ABSTRACT

Metal-directed self assembly of ferrocenyl based pyridyl functionalized dithiocarbamates afforded the novel macrocyclic metal-organic coordination polymers, $[M(L)_2]_{\infty}$ ($M = \text{Zn(II)}$, $L = L2$ (*N*-ferrocenylmethyl-*N*-pyridin-4-ylmethyl) dithiocarbamate **2**, $M = \text{Cd(II)}$, $L = L1$ (*N*-ferrocenylmethyl-*N*-pyridin-3-ylmethyl) dithiocarbamate **3**); dimers $[M(L1)_2]_2$ ($M = \text{Zn(II)}$ **1**, Hg(II) **4**) and a mononuclear $[\text{Cd}(L2)(\text{phen})]$, ($\text{phen} = 1,10\text{-phenanthroline}$) complex **5**. These complexes have been characterised by elemental analysis, IR, UV–Vis., ¹H and ¹³C NMR spectroscopy and their structures have been investigated by X-ray crystallography. In **2** and **3** the metal ions are six-coordinate with two bidentate dithiocarbamate ligands L1 and L2 in an equatorial plane and axially bonded by two Py(N) of the dithiocarbamate ligands on neighbouring molecules thus establishing distorted octahedral geometry (MS_4N_2) in 2-D polymeric structures. In L1 where the Py(N) is in the 3-position, a centrosymmetric dinuclear complex **1** is formed in which the metal ions adopt square pyramidal geometry. In **1–4**, the dithiocarbamate ligands are uniquely bonded to the metal centres in a $\mu_2, \kappa^3\text{-N, S, S}$ bridging-chelating manner. In all the complexes the supramolecular structures are sustained via C–H ... π (MS_2C , chelate) interactions. These unusual interactions have been supported by theoretical calculations. All the complexes show luminescent emissions in the solid phase.

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1. Introduction

The discovery of ferrocene in 1951 by Pauson and Kealy [1] revolutionized the design and synthesis of new organometallic compounds, including those of the ferrocene based pyridyl and thio functionalized complexes, which are important because of their diverse applications as electrochemical sensors, NLO materials, catalysis, removal of toxic metal ions, antitumor agents and units for self-assembly of metal-organic coordination frameworks [2–7] and functional polymeric materials [8]. More recently we have focused our attention on pyridyl and/or ferrocene functionalized dithiocarbamate complexes with the goal of developing fascinating

structural features and sensitizers in TiO₂ dye sensitized solar cells for the conversion of light energy into electrical energy [9].

Within the domain of metal 1,1-dithiolate chemistry, the dithiocarbamate complexes have been heavily investigated due to their rich structural varieties and importance in diverse fields such as materials and analytical chemistry, molecular precursors for the preparation of thin film metal sulfides, rubber industry, agriculture, medicine and biological processes [10–13]. In recent years metal dithiocarbamates have been explored for their potential uses as single source precursors for the preparation of metal sulfides in the form of thin films which are important nanomaterials [12] because of easy modulation of substituents on the N atom of the dithio backbone that may potentially modify their decomposition behaviour. The bonding behaviour and steric and electronic properties of the dithiocarbamate ligands can be substantially modified by incorporation of the ferrocene and pyridyl functionalities that may potentially give rise to more intriguing architectures and physical properties.

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We hypothesized that the complementary approach for the synthesis of heterometallic dithiocarbamate complexes utilizing the ferrocene fragment attached to the pyridyl functionalized dithiocarbamate and group 12 metals (Zn, Cd, Hg) may be advantageous over binary metal complexes formed with the classical alkyl/aryl dithiocarbamates for several reasons, namely (i) it may provide a suitable scaffold for the preparation of the desired polynuclear complexes (ii) the pyridyl functionality may enhance electron delocalization and conformational rigidity in the polynuclear complexes and thus may tune their luminescent characteristics and (iii) despite some obvious group similarities, the Zn, Cd and Hg metals differ significantly in their bonding preferences with different donor atoms, Lewis acid activation properties, coordination numbers and geometries. The Zn(II) ion is on the borderline between hard and soft Lewis acids whereas the Hg(II) ion is distinctly soft as is the Cd(II) ion. Accordingly the Zn(II) ion has higher affinities for the borderline nitrogen donors whereas Hg(II) and Cd(II) ions show preferences for the soft sulfur donors in accordance with the HSAB principle. These attributes may make huge differences in their structures and properties. DFT calculations have been performed on some representative complexes to support the structures and less common interactions observed in these complexes. It is therefore critical to make changes to the ligand environments of dithiocarbamates by incorporation of pyridyl and ferrocene functionalities (Fig. 1) in order to map out the role of these ligands on the structural features and luminescent properties of their Zn (II), Cd(II) and Hg(II) complexes.

2. Experimental

2.1. Material and general methods

All reactions were carried out in the open at ambient temperature and pressure. The solvents were purified by standard procedures. All the reagent grade chemicals were received from the commercial sources and used without further purification. The secondary amines required for the synthesis of dithiocarbamate ligands were obtained by the condensation of 3-picolylamine/4-picolylamine and ferrocene aldehyde to give the corresponding imines, followed by their subsequent reduction with NaBH₄. The potassium salts of the ligands (Fig. 1), *N*-ferrocenyl-*N*-pyridin-3-ylmethyl dithiocarbamate (KL1) and *N*-ferrocenyl-*N*-pyridin-4-ylmethyl dithiocarbamate (KL2) were synthesized according to literature methods [9c,13] by the reaction of appropriate secondary amines, CS₂ and KOH. The experimental details pertaining to the elemental (C, H, N) analyses, IR, ¹H and ¹³C {¹H} NMR and UV–Vis. spectra. The photoluminescent spectra of the ligands and complexes **1–5** were recorded in the solid phase on a Perkin-Elmer LS 55 Fluorescence Spectrometer (U.K.) at 335 nm.

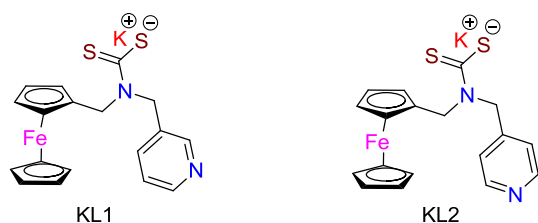


Fig. 1. The dithiocarbamate ligands used in this work.

2.2. Synthesis of complexes

2.2.1. [M(L)₂] (M = Zn, L = L1 **1**, L = L2 **2**; M = Cd, L = L1 **3**; M = Hg, L = L1 **4**)

The homoleptic complexes **1–4** were prepared by following this general procedure. To a 15 mL stirred methanol:dichloromethane (80:20, v/v) solution of the ligand KL1 (0.434 g, 1 mmol) or KL2 (0.434 g, 1 mmol), was added gradually a 5 mL methanol solution of Zn(COOCH₃)₂·2H₂O (0.110 g, 0.5 mmol), Cd(COOCH₃)₂·2H₂O (0.133 g, 0.5 mmol) or Hg(COOCH₃)₂ (0.159 g, 0.5 mmol) separately. In each case the reaction mixture was stirred for 3 h. Except for **4** which was precipitated after a short time, light yellow crystals of **1–3** were obtained by slow diffusion of the *in situ* formed complexes within 2–3 weeks. The light yellow crystals of **4** were obtained within two weeks after dissolving the compound in dichloromethane/DMF.

2.2.2. [Cd(phen)(L2)] **5**

The heteroleptic complex **5** was prepared by reaction of a 10 mL DMF solution of the precursor complex Cd(phen)(NO₃)₂·H₂O (0.452 g, 1.0 mmol) with a 5 mL solution of KL2 (0.217 g, 0.5 mmol) in the same solvent. The reaction mixture was stirred for 2 h at room. Slow diffusion afforded the light yellow crystals within 2–3 weeks.

2.3. Characterization data

1. Yield: (1.34 g, 81%). m.p. 216–218 °C. Anal. Calc. for C₇₂H₆₈Fe₄N₈S₈Zn₂: C 52.22, H 4.14, N 6.77. found: C 51.88, H 4.08, N 6.52. IR (KBr, cm⁻¹): 1452 ν(C=N), 1030 ν(C–S). UV–Vis.(nujol, λ_{max}/nm): 240, 300, 338, 432.

2. Yield: (0.72 g, 83%). m.p. 221–224 °C. Anal. Calc. for C₄₂H₅₀Fe₂N₆O₂S₄Zn: C 51.67, H 5.16, N 8.61. found: C 51.32, H 5.05, N 8.45. IR (KBr, cm⁻¹): 1468 ν(C=N), 992 ν(C–S). UV–Vis. (nujol, λ_{max}/nm): 260, 280, 310, 337, 383, 421.

3. Yield: (0.79 g, 86%). m.p. 223–225 °C. Anal. Calc. for C₃₈H₃₇Fe₂N₅S₄Cd: C 49.82, H 4.07, N 7.64. found: C 49.65, H 4.15, N 7.36. IR (KBr, cm⁻¹): 1469 ν(C=N), 999 ν(C–S). UV–Vis. (nujol, λ_{max}/nm): 247, 257, 292, 325, 347, 427.

4. Yield: (1.63 g, 85%). m.p. 186–188 °C. Anal. Calc. for C₇₂H₆₈Fe₄N₈S₈Hg₂: C 44.89, H 3.56, N 5.82. found: C 44.65, H 3.60, N 5.70. IR (KBr, cm⁻¹): 1458 ν(C=N), 992 ν(C–S). ¹H NMR (300.40 MHz, CDCl₃, δppm): 8.53–8.49 (2H, m, –C₅H₅N), 7.64–7.62 (3H, m, –C₅H₅N), 5.24 (2H, m, –CH₂C₆H₅N), 4.97 (2H, m, –CH₂Fc), 4.34 (4H, m, C₅H₅), 4.13 (s, 5H, Fc). ¹³C NMR (75.45 MHz, CDCl₃, δppm) 205.0 (CS₂), 149.0–132.1 (–C₅H₅N), 123.3 (C₅H₅), 51.6 (–CH₂NC₅H₅), 49.5 (–CH₂Fc). UV–Vis. (nujol, λ_{max}/nm): 240, 300, 330, 425.

5. Yield: (0.85 g, 79%). m.p. 210–213 °C. Anal. Calc. for C₅₀H₄₅Fe₂N₇S₄Cd: C 54.78, H 4.14, N 8.94. found: C 54.62, H 4.10, N 8.76. IR(KBr, cm⁻¹): 1470 ν(C=N), 1023 ν(C–S). UV–Vis.(nujol, λ_{max}/nm): 338, 378, 425.

2.4. X-ray crystal structure determinations

Intensity data for **1–3** were collected at 293 K and for **4** and **5** at 150 K on an Oxford Diffraction X-calibur CCD diffractometer. Data reductions for **1–5** were carried out by the CrysAlis program [14]. The structures were solved by direct methods using SHELXS-97 and refined on F² by full-matrix least-squares technique using SHELXL-97 [15]. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were geometrically fixed with thermal parameters equivalent to 1.2 times that of the atom to which they were bonded. In **1**, both rings in one ferrocenyl moiety were disordered over two sets of positions with occupancies x and 1–x, x refining to 0.53(2).

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