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Synthesis and structural characterization of a flexible tetradentate ligand and its copper(I) coordination polymers

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ABSTRACT

A tetradendate Schiff-base ligand, *N,N'*-bis-(4-chlorobenzylidene)-1,2-bis(2-aminophenylthio)ethane, L, and its copper(I) coordination polymers, $[Cu_2(\mu\text{-}I)_2\text{-}\mu\text{-}L]_n\cdot 2n(CH_3CN)$, LCuIS, and $[Cu_2(\mu\text{-}Cl)_2\text{-}\mu\text{-}L]_n$, were prepared. The products were characterized via their analytical and spectral properties. The crystal structures of the ligand molecule, L, and the complex, LCuIS, were determined by single-crystal X-ray diffraction methods. In both the free molecule and the complex, L adopts an anti, staggered, extended conformation. In LCuIS, prepared from L and CuI in acetonitrile, each Cu atom has a distorted tetrahedral coordination sphere composed of a nitrogen atom and a sulfur atom from L and two iodine ligands. LCuIS is a sheet polymer, formed from coordination polymer chains containing the dimetal clusters $Cu_2(\mu\text{-}I)_2$; the chains are cross-linked through $\pi\cdots\pi$ interactions of phenyl rings.

1. Introduction

The design and construction of metal–organic coordination polymers are of current interest in the fields of supramolecular chemistry and crystal engineering [1–3]. This interest arises from their intriguing variety of architectures and topologies [3–6]. Furthermore, research on the synthesis and characterization of metal–organic coordination polymers is greatly motivated by their potential applications ranging from catalysis [3–10], gas storage [3,5,6,8–10], magnetism [3–7,9,10], molecular sensing [3,6,9,10], non-linear optics [4,5,7,10], ion-exchange [3,4,6], electric conductivity [4,7,9], molecular separation [8,9], host–guest chemistry [4,9], and medicine [5]. Therefore, rational design and synthesis of materials with specific networks has become an important research concern [3].

A large number of coordination polymers with a wide variety of structural motifs has been prepared through the variation of reagents and reaction conditions [6,10]. The structure and the properties of such materials depend on several factors, such as the oxidation state and coordination geometry of central metals, structural chemistry of organic spacers, nature of solvents, pH value, temperature, the counter-anion and molar ratio of central metal to organic ligand [3,4,6,8–12]. In addition to these factors, weak interactions (H-bonding, π–π stacking, van der Waals) may also play a major role in ultimately controlling the network [11,13].

Among these factors, the selection of appropriate organic spacers has the greatest influence on determining the structural outcome of target polymers [4,12,14]. The organic spacers serve to link metal sites and to propagate structural information throughout the extended structure. Properties of the organic spacers, such as solubility, coordination preference, length, geometry and relative orientation of the donor groups, play a very important role in dictating polymer framework topology [12,15]. With conformationally flexible spacers, the competition between bridging and chelating coordination modes is an important factor in controlling the self-assembly process [16,17]. So, structural control of metal–organic reactions involving flexible ligands is a great challenge and unexpected topologies often result [6].

Cyanacure (1,2-bis(2-aminophenylthio)ethane) is a flexible dithio-arylether with two *ortho*–amino substituents, enabling it to form various Schiff-base ligands. Cyanacure itself is capable of forming metal complexes via chelation to metal ions from both nitrogen and sulfur atoms [1,18–21]. Cyanacure-derived Schiff-bases can adopt various binding modes such as tetradentate [1,17] or hexadentate [22,23] chelation to one metal center, tridentate chelation to one metal center [24], bridging in bis-bidentate [17,21] or bis-tridentate [23] mode between two metal centers to form bimetallic species, and bridging in bis-bidentate mode

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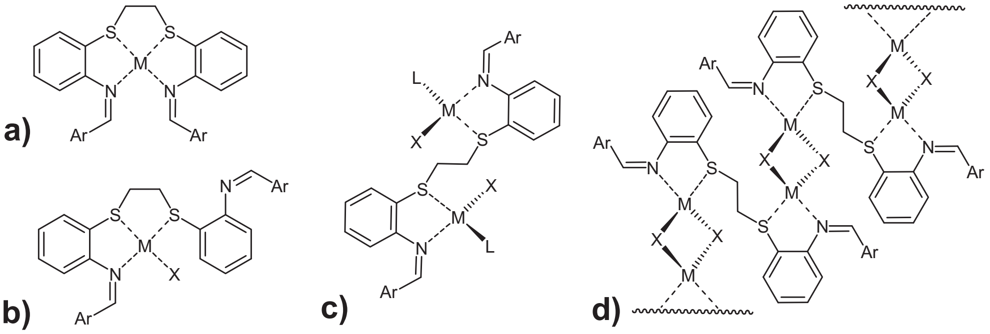

Scheme 1. Usual binding modes of cyanacure-derived Schiff-bases; (a) tetradentate chelating mode; (b) tridentate chelating mode; (c) monomeric bis-bidentate chelating mode; (d) polymeric bis-bidentate chelating mode.

between two metal halide clusters to form polymeric networks [2] (Scheme 1).

The formation of metal complexes by combination of Cu(I) halides and bidentate bridging ligands has been studied extensively and shown to results in 1D chain or 2D sheet networks through the linking of Cu_2X_2 moieties by bidentate bridging ligands [25]. A 1D coordination polymer composed of CuI and a cyanacure-derived Schiff-base, *N,N′*-bis-(2-thenylidene)-1,2-bis(2-aminophenylthio)ethane [2] has been reported previously. We report herein the preparation and structural characterization of *N,N′*-bis-(4-chlorobenzylidene)-1,2-bis(2-aminophenylthio)ethane, L, and its copper(I) halide coordination polymers.

2. Experimental

2.1. Material and physical measurements

1,2-Bis(2-aminophenylthio)ethane (Cyanacure) was prepared using a reported procedure [26]. Other reagents were commercially available and used as received. Elemental analyses (CHN) were performed using a Perkin-Elmer 2400 series (II) CHN elemental analyzer. ^{13}C NMR and ^{1}H NMR spectra were recorded on a Bruker Avance-300 MHz spectrometer employing tetramethylsilane as an internal reference. FTIR spectra were measured on a Perkin-Elmer 843 spectrometer. UV–Vis spectra were recorded on a Perkin-Elmer Lambda 25 instrument. Molar conductance measurements were carried out on a Metrohm Herisau E 382 conductometer.

2.2. Synthesis of the ligand, N,N′-bis-(4-chlorobenzylidene)-1,2-bis(2-aminophenylthio)ethane, L

4-Chlorobenzaldehyde (0.53 g, 2 mmol) was added to a solution of 1,2-bis(2-aminophenylthio)ethane (0.276 g, 1 mmol) in EtOH (25 cm^3). The mixture was stirred for 45 min to form a yellow precipitate which was then filtered, washed with cold ethanol and dried *in vaccuo*. Yield: 0.41 g (78%), mp 147 °C. *Anal.* Calc. for $C_{28}H_{22}Cl_2N_2S_2$: C, 64.48; H, 4.25; N, 5.37. Found: C, 64.59; H, 4.07; N, 5.36%. IR (KBr pellet, ν/cm^{-1}): 1621 (C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) in CH_3CN: 351(10775), 267(65915). ^{1}H NMR (DMSO-d_6, ppm): δ 3.17 (s, 4H), 7.13–7.29 (m, 8H), 7.58 (d, *J* = 8.4, 4H), 7.93 (d, *J* = 8.4, 4H), 8.53 (s, 2H). ^{13}C NMR (DMSO-d_6, ppm): δ 30.1, 118.2, 126.3, 126.7, 126.8, 129.0, 130.4, 131.1, 134.8, 136.3, 149.1, 159.3. Pale yellow crystals suitable for X-ray diffraction were obtained from slow diffusion of n-hexane in a solution of L in ethylacetate.

2.3. Syntheses of the complexes

To a boiling suspension of L (0.61 g, 1 mmol) in CH_3CN (15 cm^3), a solution of CuX (X = I or Cl) (2 mmol) in CH_3CN (15 cm^3) was added and the mixture was refluxed for 30 min. An orange precipitate was formed on cooling, which was filtered, washed with hot ethyl acetate and dried *in vaccuo*.

2.3.1. $[Cu_2(\mu\text{-}Cl)_2\text{-}\mu\text{-}L]_n$

Yield: 82%, mp 233 °C. *Anal.* Calc. for $C_{28}H_{22}Cl_4Cu_2N_2S_2$: C, 46.74; H, 3.08; N, 3.89. Found: C, 46.60; H, 2.80; N, 3.93%. FTIR (KBr pellet, ν/cm^{-1}): 1621 (C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) in CH_3CN: 350(9020), 268(51870). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in acetonitrile, 25 °C) 102.7. ^{1}H NMR (DMSO-d_6, ppm): δ 3.10 (s, 4H), 7.31–7.44 (m, 6H), 7.46 (d, *J* = 8.3, 4H), 7.67 (br s, 2H), 8.01 (d, *J* = 8.3, 4H), 8.85 (s, 2H). ^{13}C NMR (DMSO-d_6, ppm): δ 32.4, 120.0, 127.9, 128.2, 128.7, 130.5, 132.1, 133.6, 137.0, 138.8, 150.1, 161.9.

2.3.2. $[Cu_2(\mu\text{-}I)_2\text{-}\mu\text{-}L]_n$ and $[Cu_2(\mu\text{-}I)_2\text{-}\mu\text{-}L]_n\cdot 2n(CH_3CN)$, LCuIS

Yield: 76%, mp 230–231 °C. *Anal.* Calc. for $C_{28}H_{22}Cl_2Cu_2I_2N_2S_2$: C, 37.27; H, 2.46; N, 3.10. Found: C, 36.98; H, 2.21; N, 3.10%. IR (KBr pellet, ν/cm^{-1}): 1623 (C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) in CH_3CN: 360 (9750), 266 (71065), 252 (70895). Λ_M/Ω^{-1} cm^2 mol^{-1} (10^{-3} mol dm^{-3} in acetonitrile, 25 °C) 106.2. ^{1}H NMR (DMSO-d_6, ppm): δ 3.13 (s, 4H), 7.26–7.38 (m, 6H), 7.47 (d, *J* = 8.5, 4H), 7.51 (d, *J* = 7.6, 2H), 8.01 (d, *J* = 8.5, 4H), 8.69 (s, 2H). ^{13}C NMR (DMSO-d_6, ppm): δ 31.8, 119.3, 127.5, 128.0, 128.8, 130.7, 131.7, 134.1, 136.1, 136.7, 149.8, 161.4.

Salmon-pink crystals of $[Cu_2(\mu\text{-}I)_2\text{-}\mu\text{-}L]_n\cdot 2n(CH_3CN)$, LCuIS, suitable for X-ray diffraction were obtained by slow evaporation of solvent from a solution of $[Cu_2(\mu\text{-}I)_2\text{-}\mu\text{-}L]_n$ in acetonitrile.

2.4. X-ray crystallography

Crystals of L and LCuIS were mounted in oil on glass fibers and fixed in the cold nitrogen stream on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. Intensity data were measured at 140 K by thin-slice ω- and φ-scans. Data were processed using the CrysAlisPro-CCD and -RED [27] programs. The structures were determined by the direct methods routines in the SHELXS program [28] and refined by full-matrix least-squares methods, on F^2's, in SHELXL [28]. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. Scattering factors for neutral atoms were taken from reference [29]. Computer programs used in this analysis have been noted above, and were run through WinGX [30] on a Dell Precision 370 PC at the University of East Anglia. A summary of crystal and refinement data for L and LCuIS is given in Table 1.