Polyhedron 29 (2010) 3147–3156

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Copper(II) complexes of thioarylazo-pentanedione: Structures, magnetism, redox properties and correlation with DFT calculations

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ARTICLE INFO

Article history:
Received 16 November 2009
Accepted 7 August 2010
Available online 24 August 2010

Keywords:
Azoacetylacetonate
Copper(II) complex
Bridged dimer
Antiferromagetic coupling
Spin density

ABSTRACT

Copper(II) complexes of 3-((2-(alkylthio)phenylazo)-2,4-pentanedione, tridentate O, N, S donor ligands, are described in this work. Chloride bridged copper(II) polymers (**1**) and thiocyanato bridged copper(II) dimmers (**2**) are characterized by a single crystal X-ray diffraction study. The complexes show antiferromagnetic interactions, with $J = -0.5 \pm 0.1$ cm^{-1} (**1a**) and -25.8 ± 0.5 cm^{-1} (**2b**), which implies stronger coupling in the –SCN-bridging compound. The spectra, redox and magnetism are explained by DFT studies.

1. Introduction

Copper is second to iron in its usefulness in life and society. The metal and its compounds are used in every sphere of life. The potential role played by copper ions, present in the active sites of many metalloproteins having the CuN_2S_2 chromophore [1–7], has stimulated the design of new ligand frames having N, S donor sets and their copper complexes as models for providing a better understanding of biological systems [8–11]. The copper(II)-N,S chelates have antineoplastic activities [12–20] and act as efficient photosensitizers to cleave DNA [21,22]. The magnetic properties of copper complexes, as discrete complexes and bridging dimers, trimers, etc., are of great importance because of their potential applications [23–25]. As a consequence, there has been continued interest in the investigation of copper(II) complexes with the $[Cu^{II}_2(\mu\text{-}X)_2]$ (X = Cl^-, Br^-, N_3^-, SCN^-, etc.) core which display different structures with a variety of Cu–X bond distances and Cu–X–Cu bridge angles, depending on the type of terminal donor atoms and other structure varying parameters [26,27].

The metal complexes of O, N and S donor ligands has expanded enormously [28–33] and embraces very wide and diversified subjects comprising vast areas of organometallic compounds and catalysts, various aspects of bioinorganic chemistry, metal clusters, supramolecular complexes, etc. In the development of the coordination chemistry of N-donor centers, imine, –N=C– and azo groups, –N=N– have assumed leading roles. The coordination chemistry of transition metals with azo ligands is of interest due to the observation of several interesting properties [34–38]. Azo compounds are used as dyes and pigments. They exhibit antifungal and antibacterial properties. The metal complexes of azo dyes show more efficient activity than the organic molecules alone, due to charge sharing and the availability of a binding site about the metal ion, and have been put forward as photo-stable, weather stable pigments [34–36]. Recently, some metal complexes of dyes have found applications in photoelectronic devices, optical recording media, light emitting diodes, field effect transistors, photovoltaic cells (PVCs) [37,38,39–42], etc. The azo function is photochromatic, induces easy charge transfer and exhibits intense colour in the visible region. Compounds containing the azo group are also pH-responsive and redox active [43–49,50]. In analytical chemistry, azo compounds have been used as acid–base and metallochromic indicators [51–55]. Some of them play a role as efficient and selective spectrophotometric reagents, colorants in textile industry and have been used in solid phase extraction processes [56–59]. The π-acidity and metal binding ability of the azo nitrogen have drawn interest to the exploration of the chemistry of metal complexes incorporating azo ligands. Thus, the synthesis of ligands incorporating the azo function in different backbones is an inspiring field of research. We have been engaged for last decade in the design of azo-conjugated ligands and characterization of their metal complexes [50,56–59,60,61,62–65,66]. Acetylacetone has an active $-CH_2-$ group and undergoes electrophilic substitution by the diazonium ion, Ar-N=N–, to synthesise azo

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doi:10.1016/j.poly.2010.08.024

compounds. Because of the potential application of acetylacetonato metal chelates, chemists are trying to synthesize newer derivatives and their complexes. Arylazo appended acetylacetone has been known in the literature since 1925 [67–69]. However, thioarylazo (R–S–C_6H_4–N=N–) functionalized acetylacetone is hitherto unknown. We have undertaken a programme to synthesise, 3-((2-(alkylthio)phenylazo)-2,4-pentanedione, and then to synthesise copper(II) complexes with this compound as a ligand. In some cases the structures were confirmed by a X-ray diffraction study. Variable temperature magnetic measurements were carried out to explain the magnetic interactions present in the complexes. The electronic, redox and magnetic properties are explained by DFT computation using an optimized geometry for the complexes.

2. Experimental

2.1. Materials and measurements

Acetylacetone (Hacac), 2-aminothiophenol, iodomethane (MeI), iodoethane (EtI), $CuCl_2$, $2H_2O$ and NH_4SCN were purchased from E. Merck, India. All other chemicals used were of A.R. quality and were used as received. The organic solvents were purified and dried by standard methods [70]. The 2-(alkylthio)anilines were prepared by a reported procedure [71].

UV–Vis spectra were recorded using a Perkin–Elmer Lambda 25 UV–Vis spectrophotometer and infrared spectra were obtained from a Perkin–Elmer Spectrum RX1 instrument. Microanalyses were collected on a Perkin–Elmer 2400 CHN elemental analyser. ^{1}H NMR spectra were recorded on a Brucker 300 MHz FT-NMR. The room temperature magnetic moments were measured using a Magnetic Susceptibility Balance, Sherwood Scientific Cambridge, UK. Molar conductances (Λ_M) were measured in a Systronics conductivity meter 304 model using ca. 10^{-3} M solutions in acetonitrile. Electrochemical measurements were performed using computer-controlled PAR model 250 VersaStat electrochemical instruments with Pt-disk electrodes. All measurements were carried out under a nitrogen environment at 298 K with reference to SCE in acetonitrile using [nBu$_4$N][ClO_4] as the supporting electrolyte. The reported potentials are uncorrected for the junction potential. EPR spectra were measured in MeCN–CH_2Cl_2 solution at room temperature (298 K) and at liquid nitrogen temperature (77 K) using a Bruker EPR spectrometer model EMX 10/12, X-band ER 4119 HS cylindrical resonator.

2.1.1. Preparation of the ligands

2.1.1.1. 3-(2-(Methylthio)phenylazo)-2,4-pentanedione, HL^1. Into a 50 ml ethanol solution of 2-(amino)thiophenol (2.9 g, 0.023 mol), metallic sodium (0.534 g, 0.023 mol) was slowly added under cold conditions, stirring with a magnetic stirrer. Stirring was continued for 1 h, maintaining the cold conditions, whereupon the colour changed from yellow to orange. Then 1.45 ml (0.023 mol) of MeI was added under the same conditions, and the stirring was continued for 30 min. The mixture was then refluxed for 2 h at 65–70 °C in a water bath, and the colour of the solution changed to red. The whole mixture was then poured into a large excess of water, a gummy mass separated out, and it was extracted in benzene and washed with water. The benzene was then removed by a rotary evaporator. The gummy mass was then dissolved 1:1 in HCl, and $NaNO_2$ solution was added dropwise to it at 0–5 °C. This solution was then added to a Na_2CO_3 solution of acetylacetone (2.34 ml, 0.023 mol) dropwise. A yellowish orange precipitate was obtained; it was filtered and washed with cold water, dried over $CaCl_2$ desiccators. Yield 4.80 g (82.6%), m.p. 121 °C. Microanalytical data: *Anal.* Calc. for $C_{12}H_{14}N_2O_2S$: C, 57.58; H, 5.64; N, 11.19. Found: C, 57.44; H, 5.67; N, 11.06%. IR data (KBr disc) (ν, cm^{-1}): 1671(s), 1626(m), 1506, 1357, 1319. ^{1}H NMR data in $CDCl_3$ (δ, ppm): 15.05 (OH, s), 7.78 (11-H, d, J = 8.1 Hz), 7.49 (8-H, d, J = 7.2 Hz), 7.35 (9-H, t, J = 7.7 Hz), 7.16 (10-H, t, J = 7.2 Hz), 2.63 (1-CH_3, s), 2.51 (5-CH_3, s), 2.47 (12-CH_3, s). ^{13}C NMR data in $CDCl_3$ (δ, ppm): 197.1 (2-C), 196.9 (4-C), 122.1–142.7 (ArC, 6C), 115.1 (3-C), 30.2 (1-C), 26.3 (5-C), 24.3 (12-C). λ_{max} ($\varepsilon \times 10^{-3}$, M^{-1} cm^{-1}): 397 (18.3); 380 (21.3); 275 (8.82); 253 (15.0) in $CHCl_3$.

2.1.1.2. 3-(2-(Ethylthio)phenylazo)-2,4-pentanedione, HL^2. 2-(Amino)-thioethylphenol was first synthesized following the above mentioned method using 3.0 g (0.024 mol) 2-(amino)thiophenol and 1.92 ml (0.024 mol) of EtI followed by coupling with 2.44 ml (0.024 mol) acetylacetone. A yellowish orange precipitate was obtained; it was filtered and washed with cold water, dried over $CaCl_2$ desiccators. Yield 4.95 g (78.1%), m.p. 101 °C. Microanalytical data: *Anal.* Calc. for $C_{13}H_{16}N_2O_2S$: C, 59.05; H, 6.10; N, 10.59. Found: C, 59.20; H, 6.08; N, 10.43%. IR data (KBr disc) (ν, cm^{-1}): 1673(s), 1627(m), 1507, 1358, 1321. ^{1}H NMR data in $CDCl_3$ (δ, ppm): 15.07 (OH, s), 7.80 (11-H, d, J = 8.2 Hz), 7.53 (8-H, d, J = 7.6 Hz), 7.40 (9-H, t, J = 7.7 Hz), 7.15 (10-H, t, J = 7.5 Hz), 2.80 (12-CH_2, q, J = 14.6 Hz), 2.64 (1-CH_3, s), 2.52 (5-H, s), 1.25 (13-CH_3, t, J = 7.3 Hz). ^{13}C NMR data in $CDCl_3$ (δ, ppm): 197.3(2-C), 197.1 (4-C), 122.7–143.0 (ArC, 6C), 115.3 (3-C), 31.5 (12-C), 30.0 (1-C), 26.6 (5-C), 14.7 (13-C). λ_{max} ($\varepsilon \times 10^{-3}$, M^{-1} cm^{-1}): 396 (14.3); 374 (17.6); 277 (5.63); 253 (12.6) in $CHCl_3$.

2.1.2. Preparation of 1/n[Cu(L^1)Cl]$_n$ (**1a**)

HL^1 (92.6 mg, 0.37 mmol) was dissolved in methanol (20 ml) and was added to a methanolic solution of $CuCl_2{\cdot}2H_2O$ (65.2 mg, 0.38 mmol) with stirring at room temperature and the stirring was continued for 1 h. The colour of the solution changed from orange yellow to blue green. The solution was then filtered and kept for crystallization after the addition of a few drops of DMF. Block shape crystals appeared on the inner wall of the beaker and were collected by filtration, washed with MeOH–water (1:1, v/v) and dried over $CaCl_2$ in a desiccator. Yield, 98 mg (76%). Microanalytical data: *Anal.* Calc. for $C_{12}H_{13}N_2O_2SClCu$: C, 41.38; H, 3.76; N, 8.04. Found: C, 41.29; H, 3.85; N, 8.00%. IR data (KBr disc) (ν, cm^{-1}): 1657, 1364, 305. λ_{max} ($\varepsilon \times 10^{-3}$, M^{-1} cm^{-1}): 608 (0.420); 405 (10.418); 290 (8.039); 268 (10.981) in $CHCl_3$.

2.1.3. Preparation of 1/n[Cu(L^2)Cl]$_n$ (**1b**)

The complex **1b** was prepared following the same procedure as **1a** using 100.3 mg (0.38 mmol) of HL^2 and 65.2 mg (0.38 mmol) of $CuCl_2{\cdot}2H_2O$. Yield, 101 mg (73%). Microanalytical data: *Anal.* Calc. for $C_{13}H_{15}N_2O_2SClCu$: C, 43.09; H, 4.17; N, 7.73. Found: C, 43.00; H, 4.20; N, 7.80%. IR data (KBr disc) (ν, cm^{-1}): 1652, 1355, 308. λ_{max} ($\varepsilon \times 10^{-3}$, M^{-1} cm^{-1}): 607 (0.529); 406 (14.493); 289 (11.024); 267 (15.109) in $CHCl_3$.

2.1.4. Preparation of [Cu(L^1)(SCN)]$_2$ (2a)

To a $CuCl_2{\cdot}2H_2O$ solution (85.3 mg, 0.50 mmol) in methanol (15 ml), HL^1 (121.3 mg, 0.49 mmol) was added in same solvent (15 ml MeOH) and the mixture was stirred for 30 min. Then NH_4SCN (938.3 mg, 0.50 mmol) in MeOH solution was added and the stirring was continued for another 2.5 h, whereupon the colour of the solution changed to greenish yellow. The solution was filtered and kept for crystallization, after the addition of few drops of DMF, by slow evaporation in air. A crystalline product was obtained within 3 days. The crystals were collected and washed with MeOH–water (1:1, v/v) and dried over $CaCl_2$ in a desiccator. Yield 127 mg (71%). Microanalytical data: *Anal.* Calc. for $C_{26}H_{26}N_6O_4S_4Cu_2$: C, 42.09; H, 3.53; N, 11.33. Found: C, 42.00; H, 3.50; N, 11.28%. IR data (KBr disc) (ν, cm^{-1}): 2110, 1659, 1356. λ_{max} ($\varepsilon \times 10^{-3}$, M^{-1} cm^{-1}): 599 (0.337); 420 (15.40), 374 (16.816); 327 (5.711); 278 (6.380) in $CHCl_3$.