Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 118 (2014) 380–388

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Self assembled homodinuclear dithiocarbamates: One pot synthesis and spectral characterization

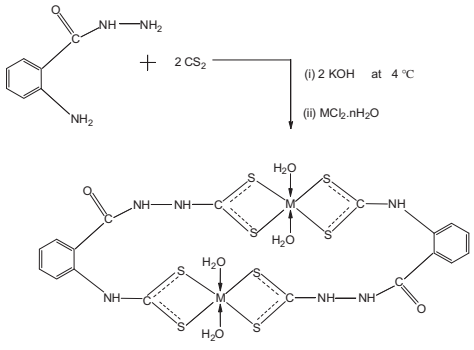
Shahab A.A. Nami [a,*], Ahmad Husain [b,1], Irfan Ullah [a]

[a] Department of Kulliyat, Faculty of Unani Medicine, Aligarh Muslim University, Aligarh 202002, India
[b] Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India

HIGHLIGHTS

- Self assembled homodinuclear complexes of the type $[M_2(Ldtc)_2{\cdot}4H_2O]$ derived from quadridentate ligand.
- All the transition metal complexes are found to have an octahedral arrangement of atoms.
- A symmetrical bidentate coordination of the dithiocarbamato moiety has been observed in all the complexes.
- The complexes exhibit a three-step thermolytic pattern and are non-electrolyte in nature.
- The energy-minimized structure of the molecule also showed that each metal atom acquires a distorted octahedral geometry.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 November 2012
Received in revised form 3 August 2013
Accepted 15 August 2013
Available online 28 August 2013

Keywords:
Self assembled dithiocarbamate
Homodinuclear
Transition metal complexes
2-Aminobenzohydrazide
Quadridentate ligand

ABSTRACT

Several self assembled homodinuclear complexes of the type $[M_2(Ldtc)_2{\cdot}4H_2O]$ derived from quadridentate ligand (Ldtc), where Ldtc = 2-aminobenzoylhydrazidebis(dithiocarbamate) and M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) have been reported. The *in situ* procedure gives high yield with the formation of single product as evident by TLC and various other physicochemical techniques. Elemental analysis, TGA, ^{1}H NMR, ^{13}C NMR, ESI mass spectrometry, EPR, UV–vis. and IR spectroscopy were used to characterize the homodinuclear complexes. The spectroscopic evidences and room temperature magnetic moment values suggest that all the complexes have octahedral geometry around the transition metal atom. A symmetrical bidentate coordination of the dithiocarbamato moiety has been observed in all the complexes. The energy-minimized structure of the molecule also showed that each metal atom acquires a distorted octahedral geometry. The complexes exhibit a three-step thermolytic pattern and are non-electrolyte in nature.

Introduction

Dithiocarbamates (DTC) form complexes with almost all the metals of periodic table, leading to the stabilization of a wide range of oxidation states of transition metal ions, for instance, Fe(IV), Cu(III), Ni(IV) and Au(III) [1,2] because of the delocalization of electrons on NCS_2 group [3]. Novelty is derived from their well-defined architecture and the bountiful metal-centred electrochemistry shown by these complexes [4]. A large number of mono- and bimetallic coordination compounds which exhibited interesting structural motifs and properties have been widely studied. DTC gained substantial attention due to the ease with which they can be synthesized and the fact that small interatomic distance between two sulfur atoms of the ligand confer stronger affinity between ligands

* Corresponding author. Tel.: +91 8439097792.
E-mail addresses: saanami.tc@amu.ac.in, saanchem@yahoo.co.in (S.A.A. Nami).
[1] Present address: Centre for Supramolecular Chemistry Research, Department of Chemistry, University of Cape Town, South Africa.

1386-1425/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2013.08.064

and the metal surface. Since their complexes are easily prepared, a wide range of applications have been made in diverse areas. Their strong affinity for the metal ions accounts for enzyme inhibition and thus, makes them biologically significant entities.

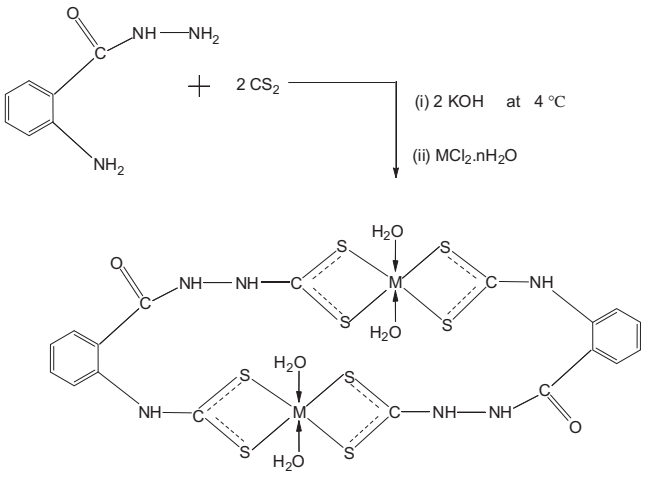
The dithiocarbamate can coordinate with metal ions in different bonding modes as a unidentate, bidentate, chelating or bridging ligand [5]. They can be useful tectons for the generation of assemblies capable to encapsulate guest molecules in a selective manner, since complex supramolecular architectures such as macrocycles, cages, catenanes and nanodimensional assemblies can be generated from a variety of combination with metal ions [6]. All dithiocarbamates exhibit the characteristic disulfur motif that binds to the metal in a bidentate fashion. The nitrogen may be functionalized in various ways to modify the physico-chemical properties of the ensuing metal complex, particularly its solubility and lipophilicity [7]. It is worth mentioning that macrocycles derived from dtc ligands can have unique redox, magnetic and photochemical properties [8]. They have been used as catalyst in the rubber industry and as pesticides [9]. The release of carbon disulfide is the mechanism behind the fungicidal and disinfectant properties observed in many dithiocarbamates (e.g. thiram). Diethyldithiocarbamate salts have been investigated for possible application in chronic alcoholic therapy i.e., tetraethyl thiuram disulfide (disulfiram, teruram) induces alcohol intolerance by inhibition of the acetaldehyde dehydrogenase enzyme [10] and treatment of HIV-patients [11], detection and analysis of biological produced NO, endogenously from NO synthesis [12] since adducts of NO with iron–dithiocarbamate have good stability in biological tissues [13,14]. They show cooperative binding where two ligands keep the metal ion in a planar position with approximate C_2v symmetry. The dithiocarbamate core, $M-S_2CNR_2$, could prove to be of great synthetic utility since a wide variety of organic substituent can be incorporated in the stable bidentate ligand. This allows the chemical 'fine-tuning' of the biological properties of the complex by variation of the substituent R in $M-S_2CNR_2$ [15].

Macrocyclic molecules have proved seminal in the field of supramolecular chemistry. The dithiocarbamate ligand has ability to synthesize a range of macrocyclic complexes. The coordination of transition metal ions together with an appropriate bis-dithiocarbamate salt results in the formation of dinuclear macrocyclic complexes. The choice of transition metal centre also provides useful characteristics to the molecules assisting in both structural elucidation and the monitoring of guest binding. Dithiocarbamate-stabilized macrocyclic structures have significant potential for the binding of charged guest species [16]. The synthesis of two- and three-dimensional macrocyclic and cage-like host molecules using metal directed self-assembly is a current area of intensive research activity.

Recently, we reported the synthesis of some dinuclear tin macrocycles [17] based on piperazine derived dtc ligands. In continuation of this work we are reporting a series of dinuclear transition metal complexes derived from dinucleating 2-aminobenzoylhydrazidebis(dithiocarbamate) ligand (Scheme 1).

Experimental

Hydrated metal (II) dichloride, potassium hydroxide (Merck India), methyl anthranilate (Acros), hydrazine hydrate and carbon disulfide (S. D. finechem India) were used as received. Acetone was distilled prior to use. Elemental analyses (C, H, N and S) were carried out with Elementar Vario EL III (Carlo Erba 1108) analyzer. The metal contents were estimated by complexometric titration [18]. IR spectra (4000–400 cm^{-1}) were recorded with a Perkin Elmer RXI FT-IR spectrometer as KBr disc while the 600–200 cm^{-1} range was scanned with CsI on a Nexus FT-IR Thermo Nicolet, Wisconsin. The Electronic spectra were recorded on a Cintra 5GBC spectrophotometer in DMSO. The NMR spectra were recorded with a BRUKER AV-500 in DMSO. The conductivity measurements were done with a CM-82T Elico conductivity bridge in DMSO. TGA was recorded with a Mettler Toledo thermal analyzer under nitrogen atmosphere. The weight of the sample was kept between 5 and 12 mg and the heating rate was maintained at 20 °C/min. The ESI mass spectra were recorded with a Micromass Quattro II using 1–2 mg of the sample. EPR spectra were recorded with a VARIAN, E-112 ESR Spectrometer (USA) using tetracyanoethylene (TCNE) as '*g*' (*g* = 2.0027) marker at room temperature. Room temperature magnetic susceptibility measurements were done with a 155 Allied Research vibrating sample magnetometer.



Scheme 1. One pot synthesis of metal dithiocarbamates $[M_2(Ldtc)_2{\cdot}4H_2O]$.

Synthesis of the complexes

2-Aminobenzoylhydrazide was prepared by the reaction of hydrazine hydrate with methyl anthranilate by known method [19,20]. To an acetone solution (20.0 mL) of 2-aminobenzoylhydrazide (5 mmol, 0.756 mg) carbon disulfide (10.0 mmol, 0.62 mL) was added dropwise with continuous stirring in an icebath followed by the addition of KOH (10 mmol, 0.56 g) dissolved in minimum amount of double distilled water. Reaction mixture was then stirred for three hours at 4 °C which turned yellow. Finally, an aqueous solution of the metal (II) chloride (5 mmol) was added to obtain an immediate precipitation (Scheme 1) which was further stirred for three hours at room temperature. It was filtered, washed thrice with acetone in order to remove trace quantities of unreacted 2-Aminobenzoylhydrazide and dried over P_2O_5 *in vacuo*. The purity of the complexes was checked by thin layer chromatography in Chloroform–methanol (55:5) system. All the complexes gave single spot when exposed to an iodine atmosphere.

Results and discussion

Elemental analysis, TGA, ^1H NMR, ^{13}C NMR, ESI mass spectrometry, EPR, UV–vis. and IR spectroscopy were used to characterize the complexes. The metal dithiocarbamates $[M_2(Ldtc)_2{\cdot}4H_2O]$ were obtained by one pot synthesis (Scheme 1). They are stable in air and are soluble in DMSO and DMF. Any attempt to crystallize the complexes was unsuccessful. The elemental analysis and other physical parameters are listed in Table 1. Their molar conductivity (10^{-3} M) in DMSO (Table 1) indicated them to be non-electrolyte [21].