Journal of King Saud University – Science (2013) **25**, 157–166

King Saud University
Journal of King Saud University – Science
www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Synthesis, spectral, thermal and antibacterial studies of Cd(II), Mn(II) and Fe(III) complexes containing trithiocarbonate 1,3,4-thiadiazole moiety

Mahasin Alias, Huda Kassum, Carolin Shakir *

Department of Chemistry, College of Science for Women, University of Baghdad, Baghdad, Iraq

Received 12 September 2012; accepted 11 November 2012
Available online 1 December 2012

KEYWORDS
Trithiocarbonate;
Thiadiazole;
Techniques;
In vitro;
Microorganisms

Abstract A new metal complex of Cd(II), Mn(II) and Fe(III) derived from potassium 2-carbomethoxy amino-5-trithiocarbonate 1,3,4-thiadiazole (CATT) and potassium 2-*N*(4-*N*,*N*-dimethylaminobenzyliden)-4-trithiocarbonate1,3,4-thiadiazole (DBTT), has been synthesized. Structural features of these complexes were obtained in the solid state by several techniques using flame atomic absorption, elemental analyses C, H, N and S, FT-IR, UV–vis spectra, thermal analyses TGA, conductivity and magnetic susceptibility measurements. Spectral data suggest an octahedral structure around the metal ion except cadmium (II) complexes that have tetrahedral geometry. The antibacterial activity of ligands and their metal complexes *in vitro* against the microorganisms: *Pseudomonas aeruginosa* (as gram negative strain bacteria) and *Staphylococcus aureus* (as gram positive strain bacteria) was examined using two different concentrations (10 and 5 mM) in nutrient agar media and some complexes showed noticeable activity against the tested microorganisms comparaing them to ampicillin as the standard drug.

1. Introduction

The thiadiazole ring and its derivatives posses good coordination behavior, since they have a sulfur atom and two nitrogen atoms in addition to the substituent having a donating group in the structure (March and Smith, 2007), therefore the study of its metallic complexes is of structural importance in addition to many important applications such as fungicidal and leshmanicidal activities (Łukaszuk et al., 2007; Foroumadi et al., 2005). Trithiocarbonate complexes have received attention because of the dual nature of the metal-CS_3 moiety as an electrophilic and nucleophilic reagent, which makes them versatile intermediates for the synthesis of other thio species by their participation in (i) alkylation at the exocyclic sulfur atom,

---

* Corresponding author. Address: Department of Chemistry, College of Science for Women, University of Baghdad, Jadiriyah, P.O. Box 47162, Iraq. Tel.: +964 7902789368.
E-mail address: carolin.sh86@yahoo.com (C. Shakir).

Peer review under responsibility of King Saud University.
doi:10.1016/j.jksus.2012.11.002

Production and hosting by Elsevier

(ii) displacement of weakly bound ligands from metal complexes, (iii) reaction with unsaturated species to give binuclear complexes, (iv) cycloaddition of activated alkynes, (v) sulfur extraction to give CS_2 complexes, or (vi) sulfur addition to give CS_4^{2-} complexes (Vicente et al., 1995, 1997). Organic trithiocarbonates have received much attention due to their numerous industrial, synthetic and medicinal applications (Ishii and Nakayama, 2005). They have been used extensively as pharmaceuticals, agrochemicals (Dehmel et al., 2007), intermediates in organic synthesis, for the protection of the thiol functionality, in free radical polymerization reactions, as lubricating additives, in material science, in froth flotation for the recovery of minerals from their ores and for the absorption properties of the metals (Wuts and Greene, 2007; Choi et al., 1998; Srivastava et al., 1990; Chaturvedi et al., 2008).

In the present work, new derivatives of the trithiocarbonate with acetate and azomethine moieties in the structure of the thiadiazole ring were synthesized, and it Cd(II), Mn(II) and Fe(III) complexes were prepared to investigate the coordination behavior of these new compound and their antibacterial activity.

2. Experimental

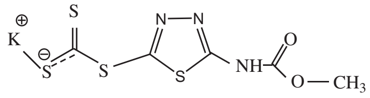
2.1. Instrumentation

All the chemicals were of analytical analar grade. Metal salts used in this study are cadmium chloride dihydrate $CdCl_2{\cdot}2H_2O$ from (BDH), magnesium acetate tetrahydrate $Mn(OAc)_2{\cdot}4H_2O$ from (Fluka) and ferric chloride tetrahydrate $FeCl_3{\cdot}4H_2O$ from (Fluka). The metal analyses were performed by a Perkin Elmer 5000 Atomic Absorption Spectrophotometer. Elemental analyses (C, H, N and S) of compounds were carried out with EM-034·mth. The electronic spectra were recorded on a Shimadzu (UV–vis 1600A) Ultra Violate Spectrophotometer using a quartz cell at a wave length range of 200–1100 nm. FT-IR spectra were recorded on a Shimadzo 8400 Fourier Transform Spectrophotometer by using a CsI disc in the wave number range of 4000–200 cm^{-1}. Thermal analysis TGA was performed with 4000 Perkin–Elmer. Magnetic susceptibility measurements were determined using the Magnetic Susceptibility Balance of the Johnson matting catalytic system division, England at room temperature. The molar conductance was measured in DMSO as a solvent at room temperature using Coring Conductivity Meter 220. Melting point apparatus of Gallencamp M.F.B-600.01 was used.

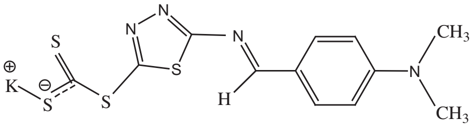
2.2. Synthesis of ligands (CATT & DBTT)

2.2.1. Synthesis of potassium 2-carbomethoxy amino-5-trithiocarbonate mercapato 1,3,4-thiadiazole (CATT)

This ligand was prepared by the reaction of methyl chloroformate with 2-amino-5-mercapto1,3,4-thiadiazole in the presence of pyridine, methyl chloroformate (1.16 ml) was added drop wise to a solution of (2 g, 1.5 mmol) 2-amino-5-mercapto-1,3,4-thiadiazole in (5.42 ml) pyridine with continuous stringing for 1 h, the mixture was diluted with (24.63 ml) cold distilled water and dilute HCl at pH 3. A pale precipitate was formed collected by filtration washed excessively with cold distilled water and dried in an oven at 70°C. 2 g, 0.01 mmol of the previous mixture was dissolved in 20 ml of absolute ethanol in the presence of 1.5 ml CS_2 and 0.58 g, 0.01 mol of KOH was



(CATT): $C_5H_4N_3O_2S_4K$



(DBTT): $C_{12}H_{11}N_4S_4K$

Scheme 1 Structures of the new ligands CATT & DBTT.

Table 1 Physical data of the new ligands CATT, DBTT and their metal complexes.

Comp.	Color	M.P. (°C)	Yield (%)	M.Wt (g mol^{-1})	Elemental analyses found (Calc.)				Metal percentage	
					C	H	N	S	Found	Calc.
(CATT)	Yellow	210	62.2	305.09	19.45 (19.66)	1.20 (1.31)	13.99 (13.76)	41.69 (41.95)	–	–
$Cd(CATT)_2$	Off white	240d	54.3	782.41	24.03 (24.54)	3.11 (3.32)	10.30 (10.73)	32.35 (32.72)	14.05	14.36
$Mn(CATT)_2$	Brown	190	71.9	668.93	21.27 (21.52)	2.48 (2.69)	12.45 (12.55)	38.05 (38.27)	7.90	8.21
$Fe_2(CATT)_4$	Brown	120d	55.7	1282.69	18.38 (18.71)	1.67 (1.56)	13.32 (13.09)	39.44 (39.91)	8.54	8.70
(DBTT)	Dark orange	150	70.0	378.09	38.25 (38.08)	2.98 (2.91)	14.55 (14.81)	33.53 (33.85)	–	–
Cd(DBTT)	Light orange	270d	66.5	670.91	35.25 (35.77)	5.75 (5.21)	8.18 (8.34)	19.47 (19.07)	16.32	16.75
Mn(DBTT)	Brown	235d	70.02	506.93	33.27 (33.14)	3.68 (3.94)	11.35 (11.04)	25.66 (25.25)	10.65	10.83
Fe(DBTT)	Dark brown	260d	68.8	575.84	33.92 (33.34)	3.77 (3.99)	9.92 (9.72)	21.95 (22.22)	9.60	9.70

d = decomposition degree.