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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

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KEYWORDS

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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,

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* 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).

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(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

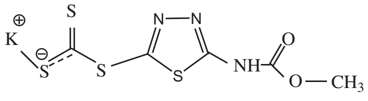
2.1. Instrumentation

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.

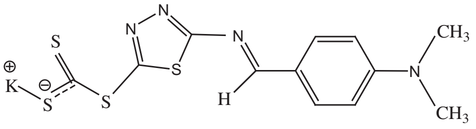
2.2. Synthesis of ligands (CATT & DBTT)

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.

added as alkali media. The mixture was refluxed for 3 h, then the solvent was evaporated and the precipitate (Scheme 1) was filtrated, then recrystallized from ethanol and distilled water. The physical properties are shown in (Table 1).

2.2.2. Synthesis of potassium 2-N(4-N,N-dimethylaminobenzyliden)-4-trithiocarbonate 1,3,4-thiadiazole (DBTT)

A mixture of (2 g, 0.015 mmol) 2-amino-5-mercapto1,3,4-thiadiazole and (3.07 g, 0.015 mmol) of 4,-*N*,*N*-dimethylaminobenzyliden in 10 ml of absolute ethanol and one drop of glacial acetic acid with continuous stringing was heated in a water bath at 60–70°C and reflexed for 1 h, then left to cool in an ice-water bath were an orange precipitate was obtained. 2 g, 0.0075 mol of the previous mixture, that is, 2-*N*(4,4-dimethylamin benzyliden)-5-mercapto1,3,4-thiadiazole in (20 ml) of absolute ethanol was added to 1.5 ml of CS_2 and 0.42 g, 0.0075 mol of KOH as alkali media. The mixture was refluxed for 3 h then the solvent was distilled off and the precipitated crystal was filtered and recrystallized from ethanol and distilled water to obtain an orange precipitate (Scheme 1). The physical properties can be shown in (Table 1).

2.3. Synthesis of complexes

New (CATT) (0.610 g, 2 mmol) in all complexes which contain a 1:2 ratio of M:L was dissolved in 10 ml of absolute ethanol, while 0.378 g, 1 mmol of complexes of the (DBTT) ligand which contains a 1:1 ratio of M:L also was dissolved in 10 ml of absolute ethanol followed by the addition (5 ml) of the metal salt drop by drop in ethanol and mixed together. The reaction mixture was allowed to stir magnetically for 1 h at room temperature. The resulting precipitate was filtered and washed with water and recrystallized from hot ethanol, then dried at 50°C for 1 h (Table 1).

2.4. Biological activity

The *in vitro* biological activity of the investigated ligands and their metal complexes was tested against the bacteria *Pseudomonas aeruginosa* and *Staphylococcus aureus* by disc diffusion method using nutrient agar as the medium. Each of the compounds was dissolved in DMSO and solutions of the concentrations (5 and 10 mM) were prepared separately. In a typical procedure, a well was made on an agar medium inoculated with the microorganism. The well was filled with the test solution using a micropipette and the plate was incubated for 24 h at 37°C. During this period, the test solution diffused and the growth of the inoculated microorganism was affected. The inhibition zone was developed, at which the concentration was noted.

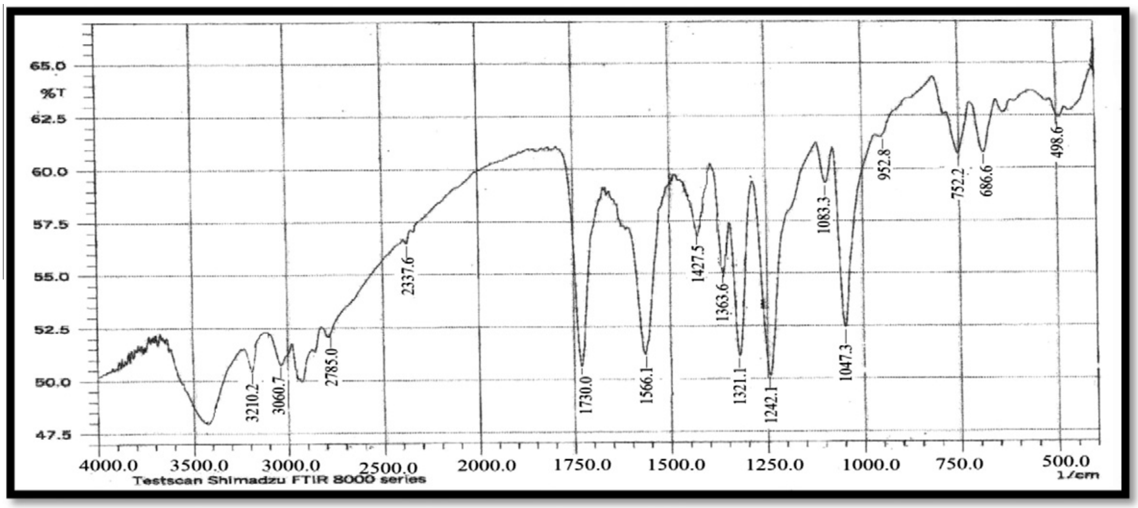
3. Results and discussion

3.1. Infrared spectra

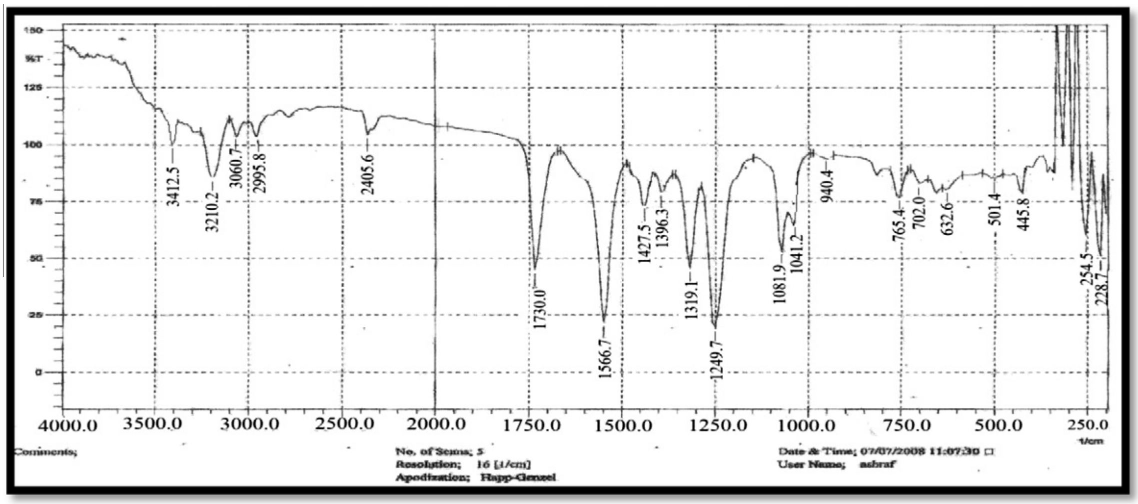
The FT-IR spectra analyses gave good information about the mode of coordination of the CATT and DBTT ligands to the metallic ions. The characteristic bands are presented in (Table 2). In the CATT ligand spectrum νNH vibration from the imide group is located at 3210 cm^{-1} which remained unchanged in all complexes also the band exhibited at 1566 cm^{-1} indicates the presence of the azomethine group νC=N which also remained without change in all the complexes (Bakkar et al., 2010; Maradiya and Patel, 2001), νNCS shows a band at a 1427 cm^{-1} that does not undergo any shifting in all the complexes (Nakomato, 2009). The frequencies appeared at 1730 and 1083 cm^{-1} which is attributed to νC=O and νCOC groups which remained unchanged in all the complexes for νC=O group while they show neglectable change for νCOC (Singh et al., 2012; Nakomato, 2009), another three bands appeared which attributed to the trithiocarbonate SCS_2 group located at 1047, 752 and 952 cm^{-1} which are assigned to the νC=S, νC–S and νC—S bands respectively, the νC=S and νC—S which undergo shift to lower frequencies in all the complexes except in the Mn(II) complex which exhibits shift to higher frequency in the νC=S group only, while the νC–S group undergos shift to higher frequencies in all the complexes and this supports the coordination of metal ions with the ligand (CATT) by these groups, that is, νC–S and νC—S (Vicente et al., 1997, 1995). The coordination of the trithiocarbonate of the (CATT) ligand to the Cd(II), Mn(II) and Fe(III) ions was also proved by the νM–S vibrations appearing in the range of 401–470 cm^{-1} which was absent in the spectrum of the ligand (Jain and Mishra, 2012). In the DBTT ligand exhibit νC=N band of the ring at 1527 cm^{-1} remained unchanged in all complexes, the νC=N band at 1591 cm^{-1} was observed due to the azomethine group which shows a shift to lower frequencies in all complexes almost between 10 and 31 cm^{-1} which may be refered to as the coordination of the ligand with metal ions by this group (Mitu et al., 2012), the νNCS band at the 1440–1450 cm^{-1} region was observed. The frequencies that appeared at 1031, 777 and 943 cm^{-1} are assigned to νC=S, νC–S and νC—S bands respectively, which undergo shift to higher frequencies in all complexes for νC–S, while they un-

Table 2 Diagnostic FT-IR bands of the ligands and their metal complexes (cm^{-1}).

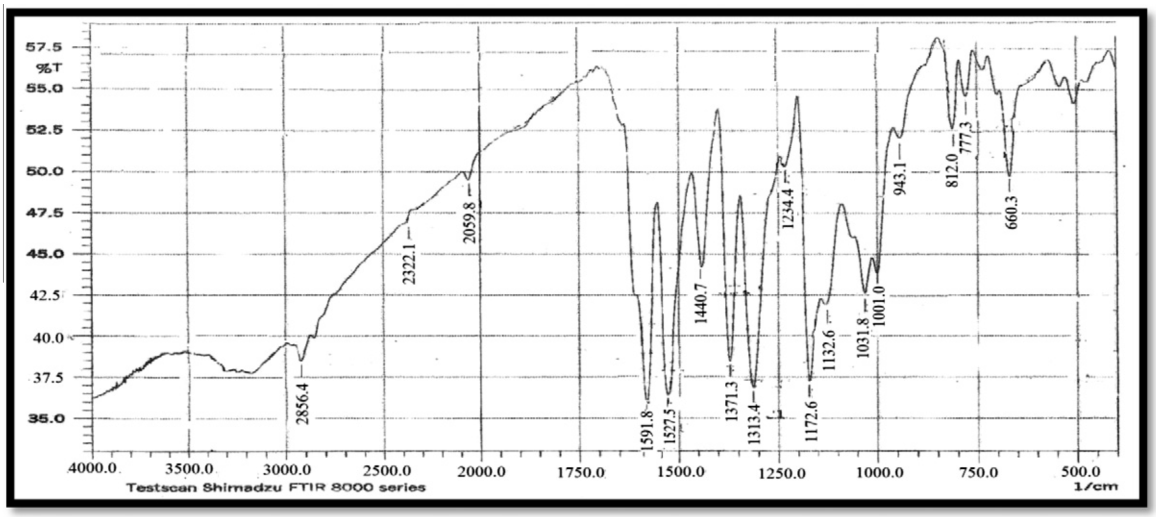
Comp.	νN–H	νC=N ring	νC=N	νNCS	νC=O	νCOC	νAr–N	νC=S	νC–S	νC···S	νM–N	νM–S	νM–X
(CATT)	3210	1566	–	1427	1730	1083	–	1047	752	952	–	–	–
Cd(CATT)$_2$	3210	1566	–	1427	1730	1081	–	1041	765	940	–	445	–
Mn(CATT)$_2$	3210	1566	–	1427	1730	1082	–	1056	786	941	–	401	M–O 478
Fe$_2$(CATT)$_4$	3210	1566	–	1427	1730	1082	–	1040	763	942	–	470	M–Cl 378
(DBTT)	–	1527	1591	1440	–	–	1371	1031	777	943	–	–	–
Cd(DBTT)	–	1527	1576	1450	–	–	1373	1026	792	933	538	420	M–Cl 385
Mn(DBTT)	–	1527	1560	1448	–	–	1373	1022	789	932	540	416	M–O 478
Fe(DBTT)	–	1527	1581	1448	–	–	1371	1026	786	930	535	424	M–Cl 392 M–O 488



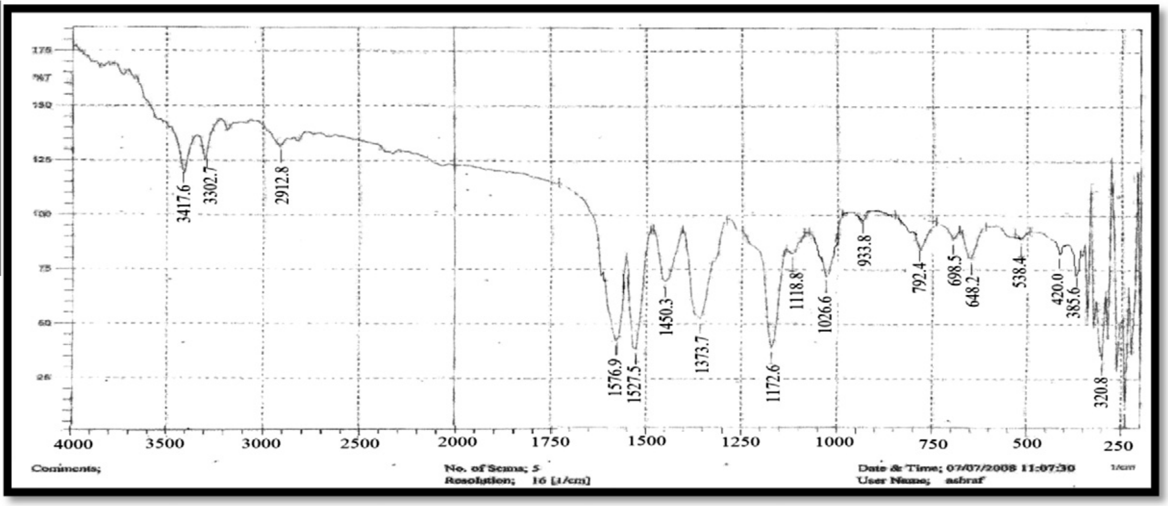
FTIR Spectra of (CATT)



FTIR Spectra of Cd(CATT)



FTIR Spectra of (DBTT)



FTIR Spectra of Cd(DBTT)

dergo shift to lower frequencies in all complexes for νC═S and νC—S (Vicente et al., 1997, 1995) and this refers to the coordination of metal ions with (DBTT) by both νC–S and νC—S bonds in addition to the νC═N group, another band exhibited at 1371 cm^{-1} refers to the νAr–N mode which undergoes a slight shift about 2 cm^{-1} in Cd(II) and Mn(II) complexes. Other new bands appeared which were supported by the appearance of frequencies of ν(M–S), ν(M–N), ν(M–Cl) and ν(M–O) bonds. A band observed around 3360–3417 cm^{-1} in the spectra of metal complexes, assigned to the νOH which refers to the presence of uncoordinated EtOH or H_2O (Nakomato, 2009; Soleimani, 2010).

3.2. Electronic spectra and magnetic moment

The nature of the ligand field around the metal ion has been deduced from the electronic spectra. The electronic spectra of these compounds were recorded as solution in the DMSO solvent.

3.2.1. Cd(II) complexes

The electronic spectra of the Cd(II) complex of the CATT ligand exhibit two transition bands at 23.786 and 28.571 cm^{-1}, while those of the DBTT ligand of the Cd(II) complex show three bands at 22.347, 27.027 and 32.894 cm^{-1} assigned to charge transfer transition (Solomon and Lever, 2006) (Table 3). Thus, the tetrahedral geometry has been suggested for these complexes. The conductivity measurements in DMSO at room temperature showed both complexes to be non-electrolytic in nature.

3.2.2. Mn(II) complexes

In the present work, the brown color of the Mn(II) complexes shows three bands at 11.688–12.658, 18.348–18.765 and

Table 3 Electronic spectra, conductance in DMSO solvent and magnetic moment (B.M.) for the prepared ligands and their metal complexes.

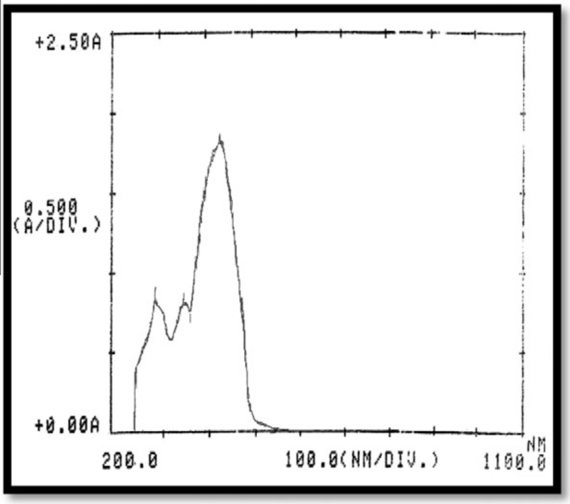
Comp.	Absorption bands (cm^{-1})	Assignment	B°	B$^{/}$	β	Dq/B$^{/}$	10Dq	15B$^{/}$	μ_{eff} B.M.	Nature of bond	μscm^{-1}	Suggested geometry
Cd (CATT)$_2$	23.786 28.571	ILCT	–	–	–	–	–	–	–	–	26	Td
Mn (CATT)$_2$	11.688 18.348 26.505	$^{6}A_{1}g\rightarrow{}^{4}T_{1}g_{(G)}$ $^{6}A_{1}g\rightarrow{}^{4}T_{2}g_{(G)}$ $^{6}A_{1}g\rightarrow{}^{6}A_{1}g + {}^{4}Eg$	860	550.5	0.64	1.9	10.459	9.789	4.88	Covalent	18	Oh
Fe$_2$ (CATT)$_4$	11.695 18.518 26.315	$^{6}A_{1}g\rightarrow{}^{4}T_{1}g$ $^{6}A_{1}g\rightarrow{}^{4}T_{2}g$ $^{6}A_{1}g\rightarrow{}^{6}A_{1}g + {}^{4}Eg$	1015	771.4	0.76	1.3	10.028	9.748	5.16	Ionic	15	Oh
Cd (DBTT)	22.347 27.027 32.894	ILCT	–	–	–	–	–	–	–	–	18	Td
Mn (DBTT)	12.658 18.765 27.766	$^{6}A_{1}g\rightarrow{}^{4}T_{1}g_{(G)}$ $^{6}A_{1}g\rightarrow{}^{4}T_{2}g_{(G)}$ $^{6}A_{1}g\rightarrow{}^{6}A_{1}g + {}^{4}Eg$	860	452.6	0.52	2.5	11.315	8.557	4.90	Covalent	26	Oh
Fe (DBTT)	11.960 19.615 26.950	$^{6}A_{1}g\rightarrow{}^{4}T_{1}g$ $^{6}A_{1}g\rightarrow{}^{4}T_{2}g$ $^{6}A_{1}g\rightarrow{}^{6}A_{1}g + {}^{4}Eg$	1015	829.2	0.81	1.35	11.194	10.685	4.91	Ionic	27	Oh

ILCT: Internal ligand charge transfer.

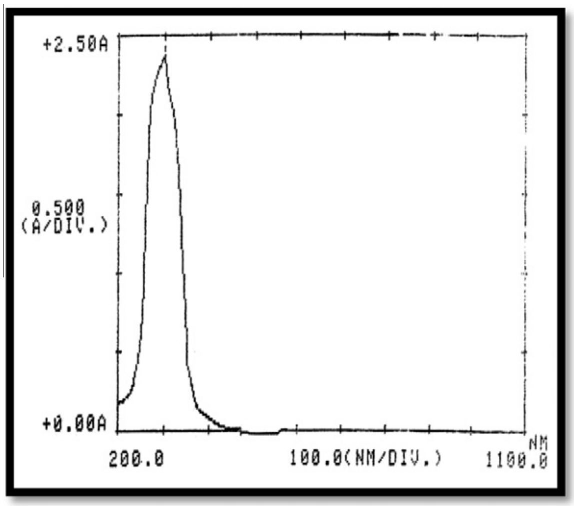
26.505–27.766 cm^{-1} assigned to $^6A_1g\rightarrow{}^4T_1g_{(G)}$, $^6A_1g\rightarrow{}^4T_2g_{(G)}$ and $^6A_1g\rightarrow{}^6A_1g$ + ^4Eg transitions which refer to octahedral geometry (Ghanim, 2012; Solomon and Lever, 2006) (Table 3). The μ_{eff} value ranged between 4.88 and 4.90 B.M. and this supports the suggested geometry of this complex (Singh et al., 2012), respectively and the conductivity measurement shows that the complexes is non-electrolytic in nature.

3.2.3. Fe(III) complexes

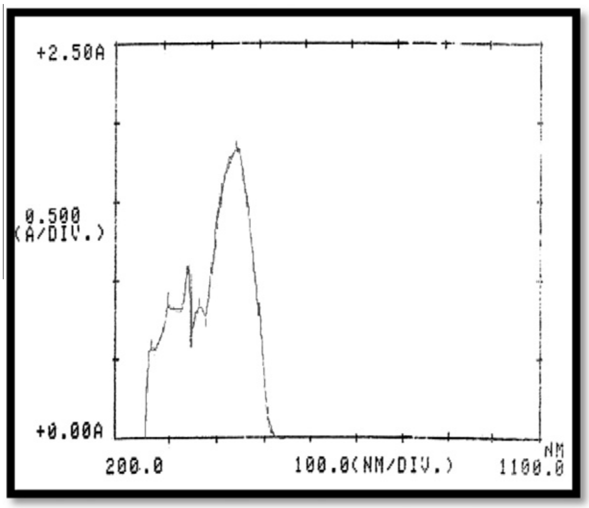
The absorption spectrum of the Fe(III) complexes of CATT and DBTT shows bands in the range of 11.695–11.960, 18.518–19.615 and 26.315–26.950 cm^{-1}, which may be assigned to $^6A_1g\rightarrow{}^4T_1g$ (ν_1), $^6A_1g\rightarrow{}^4T_2g$ (ν_2) and $^6A_1g\rightarrow{}^6A_1g$ + ^4Eg (ν_3) transitions, respectively (Solomon and Lever, 2006; Deshmukh et al., 2010). The magnetic moment is 4.91–5.16 B.M., thus octahedral geometry has been suggested for these complexes (Kumar et al., 2012). The value of various ligand field parameters, that is, 10Dq, B', β and 15B' were calculated using Tanabe-Sugano diagram for the d^3 system (Table 3). The conductance measurements indicate the non-conducting behaviors of these complexes.



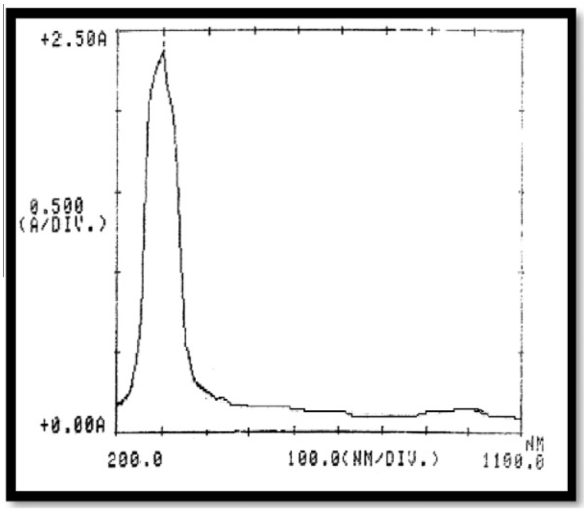
Electronic spectra of DBTT



Electronic spectra of CATT



Electronic Spectra of Cd(DBTT)



Electronic Spectra of Cd(CATT)

3.3. Thermal analyses

Thermal analyses by the TGA technique has proved to be very useful in determining the crystal water or ethanol content in complexes and their thermal stability and decomposition mode under a controlled heating rate. The weight loss was measured from 35 to 900°C at 20.00°C/min. In the Cd(CATT)$_2$ complex the decomposition started at 75°C and was completed at 795°C. A mass loss occurred within the temperature range 75–220°C, corresponding to three uncoordinated ethanols. Another two steps observed in the temperature range of 220–650

Table 4 Thermal analyses data for metal complexes of (CATT) & (DBTT).

Comp.	Dissociation stages	Temp range in TG (°C)	Weight loss found (Calcd.) (%)	Decomposition assignment
Cd(CATT)$_2$ (782.41)	Stage I	75–220	17.21 (17.63)	$3C_2H_5OH$
	Stage II	220–650	43.61 (43.45)	$2C_5H_4N_3O_2S$ of ligand
	Stage III	650–795	38.98 (38.90)	CdS_6
Mn(CATT)$_2$ (668.93)	Stage I	70–130	6.98 (6.87)	C_2H_5OH
	Stage II	130–250	5.65 (5.38)	Coordination water molecules
	Stage III	250–675	50.88 (50.82)	$2C_5H_4N_3O_2S$ of ligand
	Stage IV	675–845	36.66 (36.91)	MnS_6
Fe$_2$(CATT)$_4$ (1282.69)	Stage I	40–90	2.54 (2.80)	$2H_2O$
	Stage II	90–740	58.87 (58.54)	$4C_5H_4N_3O_2S$, Cl_2 of ligand
	Stage III	740–890	38.43 (38.64)	$2FeS_6$
Cd(DBTT) (670.91)	Stage I	50–230	27.35 (27.42)	$4C_2H_5OH$
	Stage II	230–320	4.57 (4.47)	$2CH_3$
	Stage III	320–760	37.31 (37.03)	$C_{10}H_5N_4S$, Cl of ligand
	Stage IV	760–880	31.20 (31.06)	CdS_3
Mn(DBTT) (506.93)	Stage I	40–90	7.05 (7.10)	H_2O
	Stage II	90–200	3.50 (3.55)	Coordination water molecules
	Stage III	200–270	11.68 (11.36)	OAc
	Stage IV	270–355	5.71 (5.91)	$2CH_3$
	Stage V	355–790	42.29 (42.01)	$C_{10}H_5N_4S$ of ligand
	Stage VI	790–900	29.88 (29.77)	MnS_3
Fe(DBTT) (575.84)	Stage I	80–210	15.88 (15.97)	$2C_2H_5OH$
	Stage II	210–260	3.32 (3.12)	Coordination water molecules
	Stage III	260–365	5.29 (5.20)	$2CH_3$
	Stage IV	365–810	49.88 (49.31)	$C_{10}H_5N_4S$, Cl_2 of ligand
	Stage V	810–900	26.67 (26.36)	FeS_3

and 650–795°C refer to the decomposition of $2C_5H_4N_3O_2S$ and CdS_6, respectively.

The Mn(CATT)$_2$ complex was stable up to 70°C and its decomposition started at this temperature and was completed at 845°C. A mass loss occurred within the temperature range of 70–130°C corresponding to the loss of EtOH molecules, 130–250°C refer to aqua H_2O molecules as well as two steps at 250–675 and 675–845°C corresponding to the decomposition of $2C_5H_4N_3O_2S$ of the ligand and MnS_6, respectively.

The TGA of Fe$_2$(CATT)$_4$ started from 40°C and was completed at 890°C. A mass loss occurred within the temperature range of 40–90°C corresponding to the loss of the outer sphere of water molecules, 90–740°C and 740–890°C refer to the decomposition of $4C_5H_4N_3O_2S$, Cl_2 and $2FeS_6$, respectively.

Cd(DBTT) shows four steps of weight loss in the temperature range of 50–230, 230–320, 320–760 and 760–880°C. These mass losses are attributed to ethanol molecules, the methyl group of the ligand, $C_{10}H_5N_4S$, the Cl of the ligand and CdS_3 respectively.

In Mn(DBTT) the first step of mass loss occurred within the temperature range of 40–90°C, corresponding to hydrate molecules, the second step that exhibits in the temperature range of 90–200°C refers to two aqua molecules, as well as the four steps that refer to OAc, $2CH_3$, the $C_{10}H_5N_4S$ of the ligand and MnS_3 were observed in the temperature range of 200–270, 270–335, 335–790 and 790–900°C respectively (Table 4).

The Fe(DBTT) complex was stable up to 80°C and its decomposition started at this temperature and was completed at 900°C. A mass loss occurred within the temperature range 80–210°C corresponding to the loss of 2EtOH molecules, 210–260°C refer to the coordinated water molecule as well as at 260–365, 365–810 and 810–900°C corresponding to the decomposition of $2CH_3$, $C_{10}H_5N_4S$ and MnS_6, respectively.

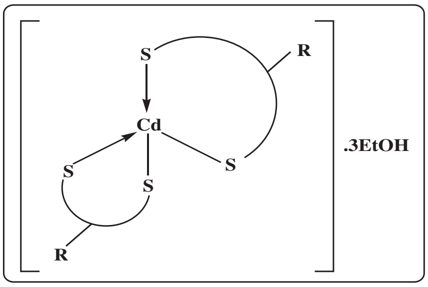
The determined temperature ranges, corresponding percent mass losses and decomposition assignment are given in (Table 4). Data from the thermal analyses sustain the molecular formulas assigned for these complexes. The structural formulas assigned to the complexes are presented in Fig. 1.

3.4. Suggested structure of complexes

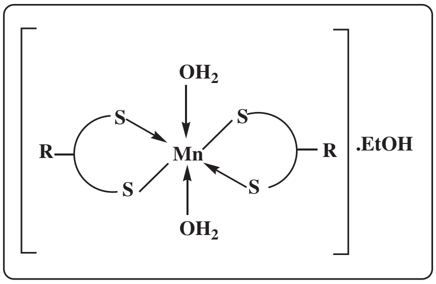
See Fig. 1.

3.5. Antibacterial activities

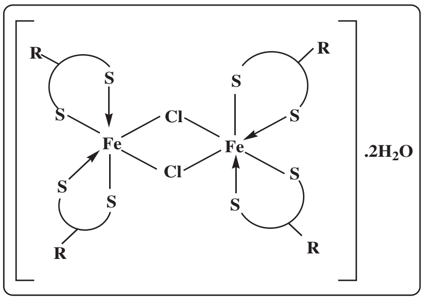
The *in vitro* antibacterial activity of the synthesized ligands and their corresponding metal complexes on selected bacteria *P. aeruginosa* and *S. aureus* was carried out and compared with the standard drug (Ampicillin). On comparing the biological activity of the ligands and their metal complexes with the standard drug, the values indicate that some complexes have higher antibacterial activity than the free ligands. In the Cd(II) complexes at 5 mM concentration the results recorded a higher inhibition zone of Cd(DBTT) and Cd(CATT)$_2$ respectively against *P. aeruginosa* comparable with the standard drug, the same effect was noticed against *S. aureus* but with a low inhibition zone comparable with the standard drug, while in



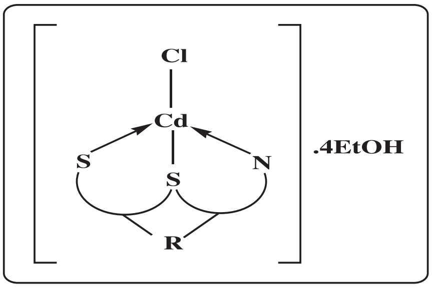
[Cd(CATT)$_2$].3EtOH



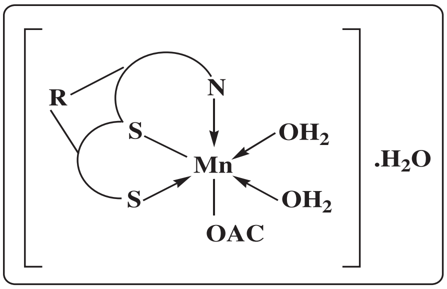
[Mn(CATT)$_2$(H$_2$O)$_2$].EtOH



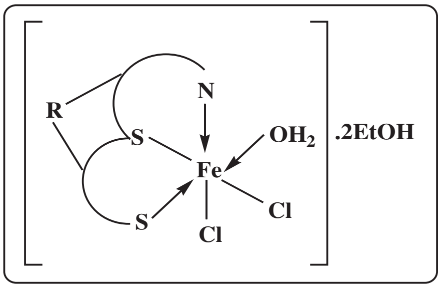
[Fe$_2$(CATT)$_4$Cl$_2$].2H$_2$O



[Cd(DBTT)Cl].4EtOH



[Mn(DBTT)OAc(H$_2$O)$_2$].H$_2$O



[Fe(DBTT)Cl$_2$(H$_2$O)].2EtOH

Figure 1 The suggested structures of prepared new complexes.

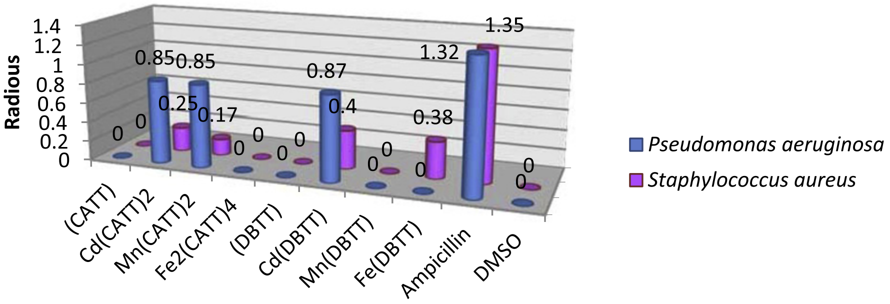


Figure 2 The effect of ligands and their metal complexes toward *Pseudomonas aeruginosa* and *Staphylococcus aureus* at concentration 5 mM.

10 mM concentration the results exhibit high biological activity of Cd(CATT)$_2$ against *P. aeruginosa*, while we noticed that in contrast Cd(DBTT) recorded high biological activity against *S. aureus* comparable with the standard drug. Figs. 2 and 3 shows that the Mn(CATT)$_2$ complex has better antibacterial activity in (5 mM) concentration against gram negative strain bacteria (*P. aeruginosa)* and negligible effect against gram positive strain bacteria (*S. aureus),* while the Mn(DBTT)

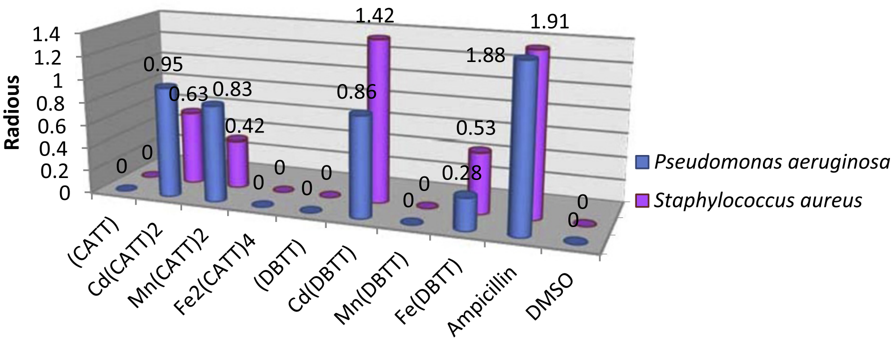


Figure 3 The effect of ligands and their metal complexes toward *Pseudomonas aeruginosa* and *Staphylococcus aureus* at concentration 10 mM.

Table 5 Antibacterial screening data for the ligands and their complexes.

Comp.	Diameter of inhibition zone (mm); concentration in mM			
	Pseudomonas aeruginosa		*Staphylococcus aureus*	
	5 mM	10 mM	5 mM	10 mM
(CATT)	–	–	–	–
Cd(CATT)$_2$	+ +	+ +	+	+ +
Mn(CATT)$_2$	+ +	+ +	–	+
Fe$_2$(CATT)$_4$	–	–	–	–
(DBTT)	–	–	–	–
Cd(DBTT)	+ +	+ +	+	+ + +
Mn(DBTT)	–	–	–	–
Fe(DBTT)	–	+	+	+
DMSO	–	–	–	–
Ampicillin	+ +	+ + +	+ +	+ + +

(–) No inhibition; (+) inhibition in diameter (0.25–0.82) mm; (+ +) inhibition in diameter (0.83–1.37) mm; (+ + +) inhibition in diameter (1.38–1.93) mm.

complex did not record any significant effect toward the two kinds of bacteria in this concentration. In 10 mM concentration the results exhibit a higher inhibition zone of Mn(CATT)$_2$ against *P. aeruginosa* and a moderate effect against *S. aureus,* while the Mn(DBTT) complex exhibits the same effect which was noticed in (5 mM) concentration. For Fe(III) complexes only the Fe(DBTT) complex recorded significant activity in high concentration, that is, 10 mM against two selected bacteria and the Fe(DBTT) complex in low concentration against the gram positive strain bacteria (*S. aureus*) only, whereas the Fe(DBTT) complex did not exhibit any significant effect in this concentration against another type of tested microorganism, that is, *P. aeruginosa*, and this effect was also observed in Fe$_2$(CATT)$_4$ in both concentrations and both kinds of tested bacteria comparable with the standard drug.

The higher inhibition zone of the metal complexes than those of the ligands can be explained on the basis of Overtone's concept and the Chelation theory. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with the donor groups. Further, it increases the delocalization of π-electrons over the whole chelating ring and enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms. There are other factors which also increase the activity such as solubility, conductivity and bond length between the metal and ligand (Mohamed et al., 2009; Chohan et al., 2004; Singh et al., 2008), the antibacterial data listed in (Table 5). The investigation of the antibacterial data revealed that the Mn(II) and Cd(II) complexes of the CATT ligand exhibited better antibacterial activity against *P. aeruginosa* compared to the other compounds as well as the standard drug ampicillin, while the results show that the Cd(II) of the DBTT ligand display high activity against *P. aeruginosa* and *S. aureus* in comparison to other compounds and ampicillin Figs. 2 and 3.

4. Conclusion

In the present research study, efforts were made to synthesize some new ligands of trithiocarbonate from 2-amino-5-mercapto1,3,4-thiadiazole. These synthesized compounds were used to prepare some new complexes, and these complexes are characterized by various physicochemical and spectral analyses. The results exhibit that the synthesized ligand CATT binds with metal ions in a bidentate manner, with S,S donor sites of trithiocarbonate, while the DBTT ligand binds with metal ions in tridentate by S,S donor sites of trithiocarbonate as well as the N atom of azomethine. Thermo gravimetric studies of the complexes also helped to characterize the complexes. The antibacterial data show the metal complexes to be more biologically active compared to those of the parent ligands against both microorganism species.

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