

Synthesis, Characterization, Spectroscopic and Antimicrobial Activity Studies of Pyrimidine Dithiocarbamate Macrocyclic Complexes

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The ligands disodium salts of thiobarbituric acid (Na_2L^1) and 5,5-diethylbarbituric acid (Na_2L^2) and their transition metal complexes of the type $[\text{M}_2(\text{L}^1)_2]$ and $[\text{M}_2(\text{L}^2)_2]$, where $\text{M} = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$, have been synthesized. The transition metal(II) complexes have been characterized by a range of techniques including IR, ^1H NMR, UV-visible spectroscopy, magnetic moment measurements, elemental analyses and molar conductance measurements. The spectroscopic studies indicate, that the reaction of L^1 and L^2 with a divalent metal ions form binuclear dithiocarbamate macrocyclic complexes. The molar conductivity measurements suggest, that all of the complexes are non-electrolytes. The magnetic moment values and electronic spectra reveal that the Ni(II) and Cu(II) complexes are square-planar, while Mn(II), Co(II) and Zn(II) complexes are tetrahedral. All of the compounds have been screened for antimicrobial activity against *Staphylococcus aureus* (gram-positive bacteria) and *Escherichia coli* (gram-negative bacteria). The results show that all the compounds inhibit the growth of bacteria. All the complexes showed better activity as compared with the ligands.

Key words: dithiocarbamate ligands, transition metal(II) complexes, antimicrobial activity

The presence of pyrimidine groups in the macrocyclic framework offers the opportunity to obtain highly stable metal complexes, which have attracted considerable interest in recent years for its importance in nature [1–2]. Binuclear metal complexes remain a classical topic of coordination chemistry and, hence, have been used for studies of metal-metal interaction, and also have been considered as models for metalloproteins. The coordination chemistry of dithiocarbamates has been discussed in detail [3]. Thermal decomposition under nitrogen of Ni(II) complex with dithiocarbamate of α -aminoacids (glycine, DL-alanine, DL-valine and DL-leucine) has been studied [4]. Dithiocarbamate ligands readily coordinate with all transition metal ions through their two donor sulfur atoms, while in some cases, the bidentate anions also act as a bridge between two transition metal centers [5]. Some salts of dithiocarbamate derivatives show interesting biological effects, including anti-alkylation [6], anti-HIV properties [7] and anti-tumor activity. They have anti-thyroidal activity and frequently act as biocidal active. Barbiturates and derivatives also have been reported

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as sedatives hypnotics drugs [8]. Recently, the Cu(II) and Co(II) complexes with barbiturate ion have been synthesized [9] and the interaction of copper ion with barbiturate ion was studied by UV-visible spectra, cyclic voltammetry and X-ray crystal structure.

In this paper we report the synthesis of the disodium salt of 4-thio-2,6-pyrimidine-dione dithiocarbamate (Na_2L^1) and 6,6-diethyl-2,4,6-pyrimidinetrione dithiocarbamate (Na_2L^2), by the interaction of thiobarbituric acid, carbondisulfide, NaOH and 5,5-diethylbarbituric acid, carbondisulfide, NaOH in 1:2:2, molar ratio, respectively. The complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) ions with ligands L^1 and L^2 also have been prepared and their mode of bonding is explored.

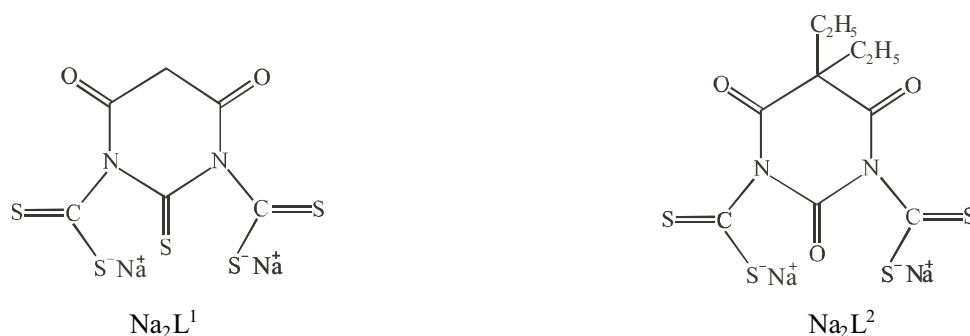


Figure 1. Suggested structures of disodium salts thiobarbituric acid and 5,5-diethylbarbituric acid.

EXPERIMENTAL

Thiobarbituric acid (E. Merck), 5,5-diethylbarbituric acid (Koch Light), carbon disulfide, sodium hydroxide and metal(II) chlorides (BDH) were used as received. Elemental analyses were carried out with a Carlo Erba 1106 Thomas and Coleman analyzer. Infrared spectra ($4000\text{--}200\text{ cm}^{-1}$) in KBr were recorded on a model 621 Perkin-Elmer spectrometer. The electronic spectra of the metal complexes in DMSO were recorded on a EZ201 Perkin-Elmer spectrometer. Magnetic susceptibility measurements were done with an Allied research model 155 vibrating sample magnetometer at room temperature. The metals were determined by complexometric titration with EDTA [10]. The molar conductances of the complexes were measured using a Systronics 321 conductivity bridge in DMSO.

Synthesis of disodium salt of thiobarbituric acid (L^1). Carbondisulfide (100 mmol, 6 mL) was added to an ethanolic solution (100 mL) of thiobarbituric acid (50 mmol, 7.2 g) in ice-bath ($5\text{--}10^\circ\text{C}$). In this mixture, sodium hydroxide (100 mmol, 4 g) dissolved in the minimum quantity of water was added. This solution was stirred for 8 h. The white precipitate obtained was filtered, washed with dry ether and dried *in vacuo*. Yield 58%.

Synthesis of disodium salt of 5,5-diethylbarbituric acid (L^2). In the synthesis of ligand L^2 , carbondisulfide (100 mmol, 6 mL) was added dropwise to the solution of 5,5-diethylbarbituric acid (50 mmol, 9.2 g) in ethanol (100 mL) with constant stirring in ice bath ($5\text{--}10^\circ\text{C}$). An aqueous solution of sodium hydroxide (100 mmol, 4 g) dissolved in minimum quantity of water was added dropwise to it. The reaction mixture was stirred for 4 h, until a precipitate appeared. A cream product thus obtained, was filtered, washed with methanol and hexane and dried *in vacuo*. Yield 42%.

Synthesis of the complexes of ligand (L^1). The ligand L^1 (20 mmol, 6.8 g) was dissolved in ethanol (50 mL) and a solution of nickel(II) chloride (20 mmol, 4.8 g) in 25 mL ethanol was added dropwise with continuous stirring to it. The mixture was refluxed for 10 h; a light yellowish brown product appeared.

The precipitate was filtered, washed with methanol and dry ether and dried *in vacuo*. Yield 48%. The Mn(II) and Zn(II) complexes were synthesized by the same method. The precipitates that formed were filtered, washed with methanol and hexane and dried *in vacuo*. Yields 45–61%. Preparation of copper(II) complex was done by taking ligand L¹ (20 mmol, 6.8 g) in ethanol (50 mL) and treated it with Cu(II) chloride (20 mmol, 3.4 g) in ethanol (25 mL) and the mixture stirred for 12 h. The product, obtained as a brown solid, was filtered and washed with methanol and hexane and dried *in vacuo*. Yield 46%.

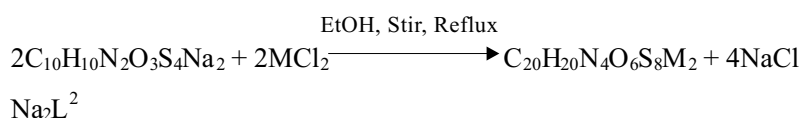
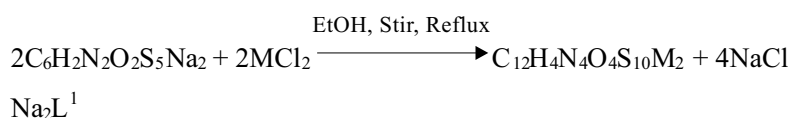
The Co₂(L¹)₂ complex was synthesized using ligand L¹ (20 mmol, 6.8 g) in 50 mL ethanol and the solution of cobalt(II) chloride (20 mmol, 2.4 g) in ethanol (25 mL). The mixture was stirred for 10 h. The precipitate that formed was filtered, washed with methanol and hexane and dried *in vacuo* to give the product as a dark blue solid. Yield 48%.

Synthesis of the complexes of ligand (L²). Ni₂(L²)₂ complex was prepared by the addition of ligand L² (20 mmol, 7.6 g) in ethanol (100 mL) to nickel(II) chloride (20 mmol, 4.8 g) in 25 mL ethanol. The reaction mixture was continuously stirred for 7 h. A yellow product was obtained then filtered and washed with methanol, hexane and dried *in vacuo*. Yield 46%. The Mn(II), Co(II), Cu(II), Zn(II) complexes were synthesized by the same procedure. The precipitates were filtered, washed with methanol and hexane and dried *in vacuo*. Yields 38–45%.

Antibacterial activity test. As a preliminary screening for antibacterial activity, the compounds were tested against the strains of gram (+) *Staphylococcus aureus* and gram (–) bacteria *Escherichia coli* in DMSO *in vitro* by agar diffusion method [11]. The stock solutions of the compounds were prepared by dissolving 0.5–1.0 mg/mL of each compound in dimethylsulfoxide (DMSO). The bacteria were grown in nutrient broth at 37°C for 48 h. The test compounds (DMSO solutions) were added dropwise to a 6 mm diameter filter paper (Whatman No. 4) discs placed at the center of each agar plate and dried under sterile condition. The width of the growth inhibition zone around the discs was measured in millimeter after 24 h incubation. DMSO was used as control and gentamicin as standard drug. All tests were repeated three times and average data were taken as the final results.

RESULTS AND DISCUSSION

The synthesis of binuclear macrocycles L¹ and L², which are based on metal-dithiocarbamates interactions is illustrated by the reactions. The metal-dithiocarbamate can be prepared by the insertion method or by replacement reaction method, but we have synthesized the macrocyclic complexes by the replacement reaction method.



The complexes were found to have M₂(L¹)₂ and M₂(L²)₂ composition, where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), the molecular formulae of these complexes were supported by elemental analysis. The colour, melting points and molar conductances of all the compounds are given in Table 1. The complexes are soluble in

DMSO, DMF and CH₃CN. The conductivity measurements of these macrocyclic complexes in DMSO 10⁻³ M (12–32 Ω⁻¹ cm² mol⁻¹) show that all these complexes are non-electrolytic in nature [12].

Table 1. Colour, m.p., yield and molar conductances of ligands and their complexes.

Compounds	Colour	M.p. (°C)	Yield (%)	Λ _M (Ω ⁻¹ cm ² mole ⁻¹)
C ₆ H ₂ N ₂ O ₂ S ₅ Na ₂ , (L ¹)	White	140	58	–
[Mn ₂ (L ¹) ₂] [C ₁₂ H ₄ N ₄ O ₄ S ₁₀ Mn ₂]	Light yellow	289 d	45	14
[Co ₂ (L ¹) ₂] [C ₆ H ₂ N ₂ O ₂ S ₅ Co ₂]	Dark blue	310 d	48	18
[Ni ₂ (L ¹) ₂] [C ₆ H ₂ N ₂ O ₂ S ₅ Ni ₂]	Light yellowish brown	340 d	48	24
[Cu ₂ (L ¹) ₂] [C ₆ H ₂ N ₂ O ₂ S ₅ Cu ₂]	Brown	360 d	46	32
[Zn ₂ (L ¹) ₂] [C ₆ H ₂ N ₂ O ₂ S ₅ Zn ₂]	White	342 d	61	26
C ₁₀ H ₁₀ N ₂ O ₃ S ₄ Na ₂ , (L ²)	Cream	148	42	–
[Mn ₂ (L ²) ₂] [C ₂₀ H ₂₀ N ₄ O ₆ S ₈ Mn ₂]	Light brown	275 d	38	12
[Co ₂ (L ²) ₂] [C ₂₀ H ₂₀ N ₄ O ₆ S ₈ Co ₂]	Bluish green	290 d	45	16
[Ni ₂ (L ²) ₂] [C ₂₀ H ₂₀ N ₄ O ₆ S ₈ Ni ₂]	Yellow	320 d	46	20
[Cu ₂ (L ²) ₂] [C ₂₀ H ₂₀ N ₄ O ₆ S ₈ Cu ₂]	Dark blue	352 d	40	30
[Zn ₂ (L ²) ₂] [C ₂₀ H ₂₀ N ₄ O ₆ S ₈ Zn ₂]	White	330 d	43	27

IR spectra. The infrared spectra of the ligand L¹ and L² and their complexes are given in Table 2. One medium intensity band at 1630 cm⁻¹ assigned to ν(C=O) has been observed in macrocycle L¹, and its metal(II) complexes which are nearly similarly to that of parent molecule, thiobarbituric acid. But in the case of ligand L² two medium intensity bands in the 1630–1720 cm⁻¹ range assigned to ν(C=O) have been observed. In the complexes of binuclear thiobarbituric acid and 5,5-diethylbarbituric acid (L¹ and L²), the two ν(N–H) bands are absent indicating the replacement of all ν(N–H) bands by ν(C–N) bands. In the binuclear macrocyclic complexes, the dithiocarbamate moiety is symmetrically bound to the metal(II) ion, because they exhibit a single C–S absorption band at about 1000 cm⁻¹. Therefore, it is clear that they are symmetrically bound with the metal(II) ion. In the metal(II) complexes of ligands L¹ and L², the low energy bands are observed at 1585 cm⁻¹, due to the ring stretching mode of pyrimidine. The C–N stretching frequency is also diagnostic of the chelation of dithiocarbamate

groups. The thioureide band appeared at 1440–1482 cm^{-1} [13], which is intermediate between C=N (1640–1690 cm^{-1}) and C–N band (1250–1360 cm^{-1}) indicating partial double bond character between carbon and nitrogen. The bands observed between 1130–1290 cm^{-1} are due to coupled vibration of the NCS_2 group [14]. The medium intensity bands in 345–420 cm^{-1} region correspond to the $\nu(\text{M–S})$. In the metal(II) complexes of the ligands L^1 and L^2 the absence of other band and presence of new absorption bands appeared in 365–425 cm^{-1} region are indicative of metal-sulphur stretching frequencies.

Table 2. Characteristic IR bands of the ligands and their complexes.

Compounds	$\nu(\text{C=O})$	$\nu(\text{C}\cdots\text{S})$	$\nu(\text{C}\cdots\text{N})$	$\nu(\text{NCS}_2)$	Ring vibrations	$\nu(\text{M–S})$
Na_2L^1	1630 m	1000 s	1482 m	1155 s, 1250 m, 1282 s	1580 s	–
$\text{Mn}_2(\text{L}^1)_2$	1624 m	1005 s	1442 m	1150 s, 1250 m, 1290 s	1590 s	390 w
$\text{Co}_2(\text{L}^1)_2$	1632 m	997 s	1465 m	1160 s, 1240 m, 1275 s	1580 s	425 w
$\text{Ni}_2(\text{L}^1)_2$	1627 m	1000 s	1474 m	1142 s, 1275 m, 1270 s	1592 s	375 w
$\text{Cu}_2(\text{L}^1)_2$	1634 m	995 s	1452 m	1130 s, 1260 m, 1275 s	1586 s	365 w
$\text{Zn}_2(\text{L}^1)_2$	1622 m	1000 s	1460 m	1150 s, 1250 m, 1280 s	1585 s	375 w
Na_2L^2	1630 m 1654 m	998 s	1455 m	1158 s, 1265 m, 1288 s	1580 s	–
$\text{Mn}_2(\text{L}^2)_2$	1635 m 1710 m	1005 s	1446 m	1153 s, 1256 m, 1275 s	1588 s	392 w
$\text{Co}_2(\text{L}^2)_2$	1667 m 1720 m	1002 s	1476 m	1155 s, 1238 m, 1290 s	1590 s	402 w
$\text{Ni}_2(\text{L}^2)_2$	1642 m 1698 m	1000 s	1440 m	1144 s, 1275 m, 1270 s	1582 s	365 w
$\text{Cu}_2(\text{L}^2)_2$	1642 m 1705 m	995 s	1448 m	1145 s, 1256 m, 1276 s	1595 s	390 w
$\text{Zn}_2(\text{L}^2)_2$	1710 m 1647 m	1000 s	1467 m	1130 s, 1250 m, 1280 s	1588 s	376 w

Electronic spectra and magnetic moments. The electronic spectra of Mn(II) complexes of ligands L^1 and L^2 exhibit two bands in addition to a charge transfer band at 29540 cm^{-1} , 24220 cm^{-1} , 20250 cm^{-1} and 29850 cm^{-1} , 24390 cm^{-1} , 20410 cm^{-1} which correspond to $^4\text{A}_1(\text{G}) \leftarrow ^6\text{A}_1$ and $^4\text{T}_1(\text{G}) \leftarrow ^6\text{A}_1$ transitions, respectively. The magnetic moment value is lower than that calculated for Mn(II) ion with tetrahedral geometry, which is due to the coupling interaction between two metal ions. In addition to charge transfer bands at 20590 cm^{-1} and 20480 cm^{-1} , for both $\text{Co}_2(\text{L}^1)_2$ and $\text{Co}_2(\text{L}^2)_2$ complexes, one band at 11820 cm^{-1} and 11930 cm^{-1} have also been observed, which is assigned to $^4\text{T}_1(\text{P}) \leftarrow ^4\text{A}_2(\text{F})$ transition. The observed μ_{eff} value is 2.71

B.M. for Co(II) complex of L^1 and 2.67 B.M. for ligand L^2 . The magnetic moment values are significantly lower than the theoretical value for three unpaired electrons (3.88 B.M.). The low value of μ_{eff} suggests the formation of low spin tetrahedral cobalt(II) complex and it is due to coupled interaction of two metal ions. The spectra of Ni(II) complexes of dithiocarbamates L^1 and L^2 show two bands at 22290 cm^{-1} , 22470 cm^{-1} and respectively at 19240 cm^{-1} , 19045 cm^{-1} which are assigned to ${}^1B_{1g} \leftarrow {}^1A_{1g}$ and ${}^1A_{2g} \leftarrow {}^1A_{1g}$ transitions. These two bands are very close to observed position (19000 cm^{-1}), which is the characteristic of a square planar [15] nickel(II) ion. Low intensity, long wavelength $d-d$ bands have been reported [16] in the literature for Ni(II) dithiocarbamate system. It is known that for square planar Cu(II) complexes the magnetic moment value falls in 1.82–1.86 B.M range while for tetrahedral copper(II) ion, the μ_{eff} value is slightly larger 1.92–2.00 B.M. But in the present work for $\text{Cu}_2(L^1)_2$ and $\text{Cu}_2(L^2)_2$ complexes, the magnetic moment values 1.22 B.M and 1.24 B.M. have been observed. The electronic absorption spectra of both the tetrahedral and square planar Cu(II) ions are nearly identical. It is difficult to assign their geometry. However, the magnetic moment and electronic spectra (Table 3) suggest square planar geometry for Cu(II) ion [17]. No transitions were observed in the visible region for Zn(II) complexes of L^1 and L^2 consistent with the d^{10} configuration of the Zn(II) ion. From the above studies, the structures of the dithiocarbamate complexes of ligands L^1 and L^2 are suggested.

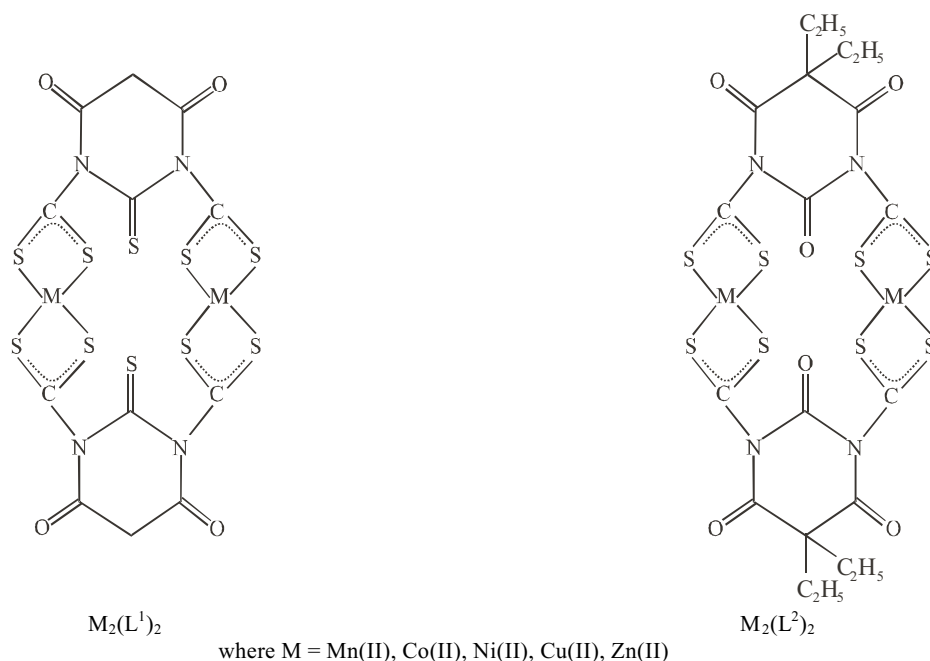


Figure 2. Suggested structures of dithiocarbamate complexes of ligands L^1 and L^2 .

Table 3. Electronic spectral band, magnetic moment and ligand field parameters of the macrocyclic complexes.

Compound	Magnetic moment (B.M.)	Electronic bands (cm ⁻¹)	Possible assignment	ϵ^a	10 Dq (cm ⁻¹)	(B) (cm ⁻¹)	β
Mn ₂ (L ¹) ₂	4.75	29540 24220 20250	Charge Transfer ⁴ A ₁ (G) ← ⁶ A ₁ ⁴ T ₁ (G) ← ⁶ A ₁	12 14 10	8925	750	0.78
Co ₂ (L ¹) ₂	2.71	20590 11870	Charge Transfer ⁴ T ₁ (P) ← ⁴ A ₂ (F)	14 11	—	—	—
Ni ₂ (L ¹) ₂	Diamagnetic	22290 19240	¹ B _{1g} ← ¹ A _{1g} ¹ A _{2g} ← ¹ A _{1g}	13 16	—	—	—
Cu ₂ (L ¹) ₂	1.22	18220 12190	¹ A _{1g} ← ² B _{1g} ² E _g ← ² B _{1g}	20 18	—	—	—
Zn ₂ (L ¹) ₂	Diamagnetic	—	—	—	—	—	—
Mn ₂ (L ²) ₂	4.68	29850 24390 20410	Charge Transfer ⁴ A ₁ (G) ← ⁶ A ₁ ⁴ T ₁ (G) ← ⁶ A ₁	15 12 14	8748	729	0.76
Co ₂ (L ²) ₂	2.67	20480 11930	Charge Transfer ⁴ T ₁ (P) ← ⁴ A ₂ (F)	17 12	—	—	—
Ni ₂ (L ²) ₂	Diamagnetic	22470 19045	¹ B _{1g} ← ¹ A _{1g} ¹ A _{2g} ← ¹ A _{1g}	12 14	—	—	—
Cu ₂ (L ²) ₂	1.24	18350 12120	² A _{1g} ← ² B _{1g} ² E _g ← ² B _{1g}	18 20	—	—	—
Zn ₂ (L ²) ₂	Diamagnetic	—	—	—	—	—	—

^a $\epsilon = \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$.**Table 4.** Antibacterial activity of ligands and complexes (Zone formation in mm).

Compounds	<i>S. aureus</i>		<i>E. coli</i>	
	0.5 mg cm ⁻¹	1.0 mg cm ⁻¹	0.5 mg cm ⁻¹	1.0 mg cm ⁻¹
*Gentamicin	7	10	7	9
Ligand Na ₂ L ¹	12	13	10	13
Ligand Na ₂ L ²	13	14	11	15
Mn ₂ (L ¹) ₂	24	32	20	34
Co ₂ (L ¹) ₂	26	38	24	31
Ni ₂ (L ¹) ₂	28	32	20	34
Cu ₂ (L ¹) ₂	18	33	23	29
Zn ₂ (L ¹) ₂	21	30	24	32

Table 4 (continuation)

Mn ₂ (L ³) ₂	26	34	20	30
Co ₂ (L ²) ₂	29	42	26	38
Ni ₂ (L ²) ₂	22	30	18	28
Cu ₂ (L ²) ₂	27	32	21	34
Zn ₂ (L ²) ₂	25	38	17	30

*Bactericides

Antimicrobial activity. The results of antibacterial activity of all the test compounds are shown in Table 4. The susceptibility of certain strains of bacterium towards dithiocarbamate ligands and their complexes was judged by measuring the size of inhibition diameter. These compounds showed antimicrobial activity against *S. aureus* (gram (+) bacteria) and *E. coli* (gram (–) bacteria). The results showed that the metal complexes were found to have higher activity than that of the free ligands and standard drug gentamicin (bactericides).

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