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SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITIES OF NEW DITHIOCARBAMATE AND ITS COMPLEXES WITH Co(II), Ni(II), Cu(II) AND Zn(II) IONS

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ABSTRACT

The synthesis of new metal (II) dithiocarbamate complexes of general formula $[M(L)_2]$ where M = Co(II), Ni(II), Cu(II) and Zn(II). The dithiocarbamate complexes were characterized by elemental analysis UV-Vis, FTIR, magnetic susceptibility, molar conductivity, melting points mass spectra and ^{1}H NMR. The antibacterial activates of synthesized compound were studied against two Gram-negative species *Escherichia coli*, *Salmonella* and one gram positive species *Staphylococcus*. The conductivity data confirm the nonelectrolyte nature of the complexes.

Key words: Dithiocarbamate, 2-aminopyrimidin, Biological activate.

INTRODUCTION

Dithiocarbamate (dtc) is an interesting class of organic compounds and inorganic chemistry. These compounds have abilities to react and form a stable complexes with range of transition metals[1-3]. Dithiocarbamate can act as monodentate, bidentate ligands and are considered as soft donors showing excellent coordination ability[4]. In addition, their compounds are very useful material, which have shown different applications in several aspects including industry[5], agriculture[6,7] and analytical chemistry[8]. These compounds are being investigated in order to gain insight in to the nature of the sulfur-metal bond in many bimolecular[9] and also because of their potential role in cancer disease treatment[10,11]. Many works described the preparation and characterization the legends contained pyrimidine such

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as Schiff base[12]. Furthermore, dithiocarbamates derivatives are used as precursors for the production of metal sulfide nanoparticles[13], and in the preparation of pesticides[14].

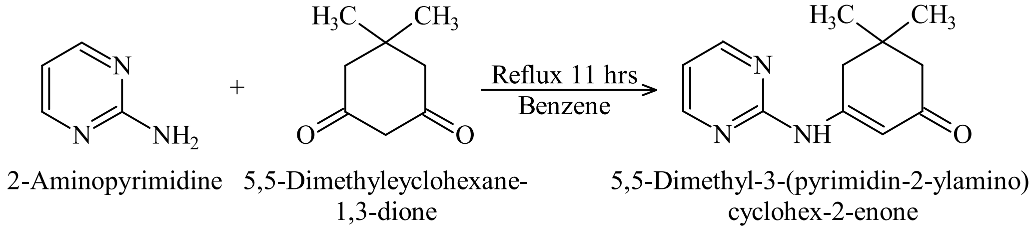
The aim of the present study was to synthesis, characterization and biologic activities of new (DMCHPYDTC) 5,5-dimethyl-3-oxocyclohex-1-enyl (pyrimidin-2-yl) dithiocarbamate with the Co(II), Ni(II), Cu(II) and Zn(II).

EXPERIMENTAL

All chemicals used were of highest purity (BDH, Fluka or Merck) and used out further purification. Elemental analysis (C.H.N and S) were carried out on a (EURO EA 3000 Single). IR spectra were recorded with FT-IR-8000 Shimadzu, in the range of (4000-400) cm^{-1}. Absorption spectra were recorded using Shimadzu UV-Vis 1700 spectrophotometer. Mass spectra were obtained by GC-Mass QP-2010. ^1H NMR spectra were acquired in DMSO using Brucker, Model: Ultra 300 MHz, Switzerland with tetramethylsilane (TMS). Electrical conductivity measured by Digital conductivity meter WTW, 720 with solute concentration of 10^{-3} M in DMSO at room temperature. Magnetic moments were measured with a magnetic susceptibility (Xg) were carried out at 20°C by Faraday and metal percentage were determined using atomic absorption technique by atomic absorption spectrophotometer-5000, Perkin-Elmer.

Preparation of 5,5-dimethyl-3-(pyrimidin-2-ylamino) cyclohex-2-enone(14)

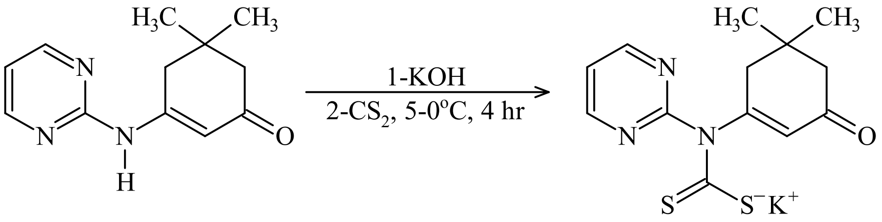
The compound [1] was prepared using the following of 5,5-dimethylcyclohexane-1,3-dione (7.13 mmol) was grinded together with 2-amino pyrimidine (7.10 mmol), then adding (25 mL) of dry benzene and a few drops of glacial acetic acid were added to reaction mixture with continuous stirring, then resulting was refluxed for 11 hrs. The product precipitate was obtained by filtration and recrystallized from. The preparation is shown in **Scheme 1**. Yield 1.29 (83%), M.P. (129°C).



Scheme 1

Preparation of potassium salt of dithiocarbamate ligand

The new dtc ligand was prepared by mixture compound (1) (0.05 mol) was dissolved in 10 mL absolute alcohol and potassium hydroxide (0.05 mol) were mixed stirred vigorously in ice bath. Carbon disulfide (0.05 mol) was added in drop wise. Stirring continued for one in ice bath and another three hours at (30°C), resulting in the formation of solid mass, which was filtered and washed with diethyl ether. The preparation is shown in **Scheme 2**. Yield: 12.43 g (75%) with m.p. (211°C). ^{1}H NMR data (ppm) Fig. 1: 0.86 (6H), 3.61 (2H), 5.38 (H), 9.64 (H), 7.13 (H), 6.63-6.53 (H). The mass spectrum Fig. 2 of the dithiocarbamate ligand showed the peak at m\z = 331.50 (25%) corresponding to $C_{13}H_{14}N_3OS_2$. Peaks detected at m\z = 224.36 (95%), 121 (15%) corresponding to $C_7H_7NOS_2^-K^+$, $C_7H_7NO^+$, respectively.



5,5-Dimethyl-3-(pyrimidin-2-ylamino) cyclohex-3-enone

Potassium 3,3-dimethyl-5-oxo cyclohex-1-enyl (pyrimidin-2-yl) carbom odithioate

Scheme 2

Preparation of metal complexes

The metal complexes were prepared by mixing of (30 mL) ethanol solution of the metal salt (0.005 mol) with (0.001 mol) potassium dithiocarbamate dissolved in (30) ethanol solution. The reaction mixture was refluxed for 1 hrs with constant stirring. The solution allowed to cool temperature and the precipitate was filtration and washed by methanol.

RESULTS AND DISCUSSION

The analytical data in Table 1 indicates that dtc and all complexes were found to be stable in air and insoluble in water but soluble in common organic solvent. The observed molar conductance value of the complexes in DMSO were non electrolytic nature. The mole ratio method was used to determine the ratio of metal and ligand. The study shows the ligand coordinated to metal in 1:2 ratio. Physical data and analysis of ligand and its complexes are listed in Table 1.

Table 1: Physical data and analysis of ligand and its complexes

S. No.	Complex, mol, Formula, mol. wt.	Color, Yield (%)	Decomposition temp. (^oC)	Analyses % Found (Cal.)		
				C	H	M
1	$C_{13}H_{14}N_3OS_2$ 331.50	Orange 75%	211	4.15 (4.26)	47.04 (47.10)	-
2	$Co(C_{26}H_{24}N_6O_2S_4)$ 643.73	Drakegreen 56.93	> 350	48.30 48.51	4.1 4.38	8.95 9.15
3	$Ni(C_{26}H_{24}N_6O_2S_4)$ 643.49	Drake green 50.99	> 350	48.20 48.53	4.3 4.39	8.90 9.12
4	$Cu(C_{26}H_{24}N_6O_2S_4)$ 648.35	Orange yellow 45	> 350	48 48.17	4 4.35	9.56 9.80
5	$Zn(C_{26}H_{24}N_6O_2S_4)$ 650.21	Orange 41.8	> 350	52.50 52.64	3.89 4.02	12.90 13.03

Infrared spectra

The data of the IR spectra of dtc ligand and its metal complexes were compared with the IR spectra of the free ligand in order to determine the involvement of coordination sites in chelation and to detect the changes that might have taken place. The obtained data are given in Table 2 and shown in Fig. 3-7.

Table 2: FTIR spectral data of complexes (cm^{-1})

Comp.	ν_{ar} (C-H)	V_{alp}(C-H)	ν (C = C)	ν ($N=CS_2$)	ν $(C\text{-}N)_{ring}$	ν(CS_2)
dtc	3089w	2974m	1537s	1462s	1629w	1001s 1043s
L_2Co	3051w	2974m	1548s	1460s	1645	997s 1031m
L_2Ni	3128w	2972m	1533s	1471s	1643	972w 1014s
L_2Cu	3132w	2976m	1571s	1462s	1649	1002s 1029m
L_2Zn	3110w	2954m	1565s	1460s	1635	997s 1013m

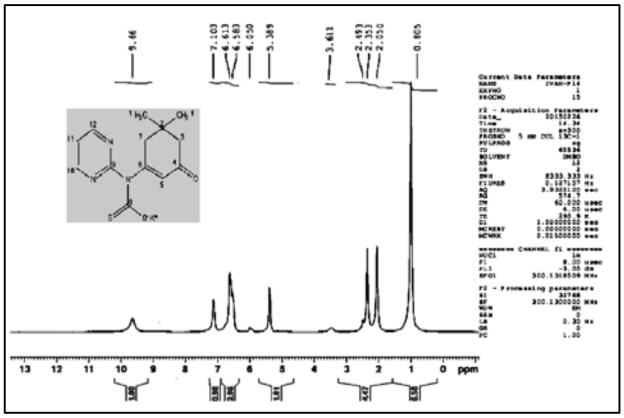


Fig. 1: ^{1}H NMR spectrum of dtc ligand in DMSO

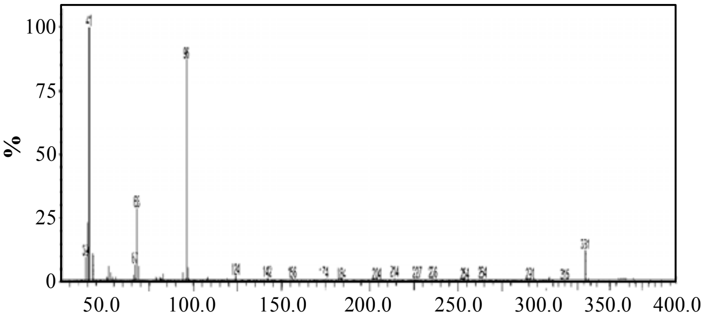


Fig. 2: Mass spectrum of dtc ligand

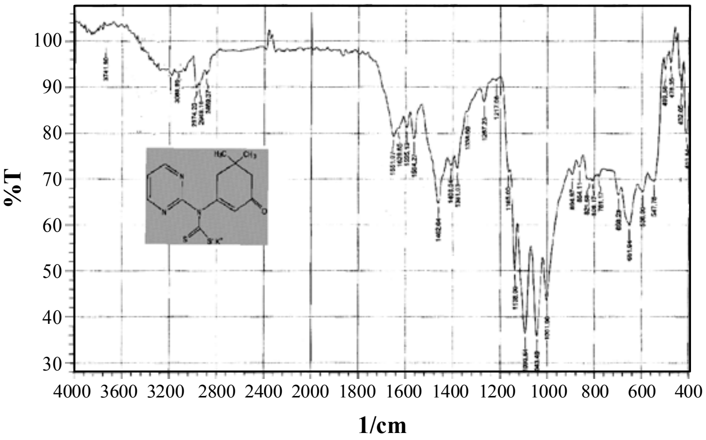


Fig. 3: IR Spectrum of ligand dithiocarbamate

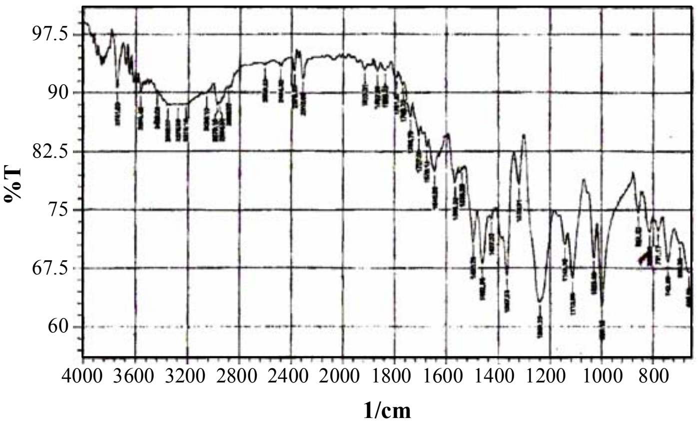


Fig. 4: IR Spectrum of CoII) complex

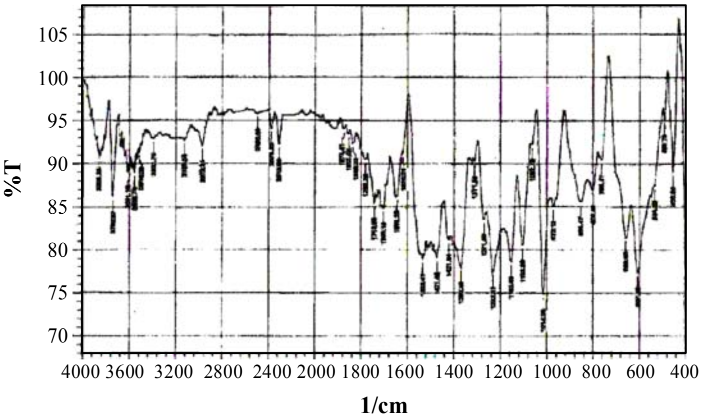


Fig. 5: IR Spectrum of Ni(II) complex

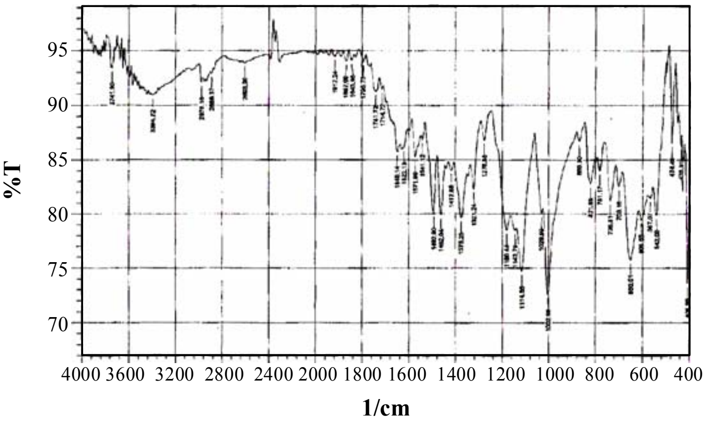


Fig. 6: IR Spectrum of Cu(II) complexes

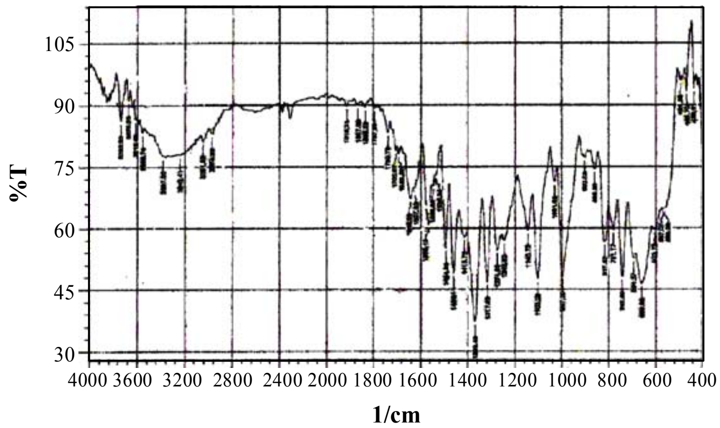


Fig. 7: IR Spectrum of Zn(II) complexes

Important absorption infrared spectrum of the free ligand exhibited strong high intensity bands due to C-Ssy, as, C-N at 1001, 1043, 1462 cm^{-1}, respectively. In these complexes a strong band observed in the region 1460-1471 cm^{-1} is attributed to (C-N) stretching vibration that are intermediate between single band (C-N) (1250-1350 cm^{-1}) and double bands (C=N) (1630-1690 cm^{-1}), suggesting partial delocalization of π-electron density within the dithiocarbamate functions[15]. For CS_2 bands of strong intensity was observed in the rang 1031-997 cm^{-1}, which due to (CSS) vibration. This has shifted of 17-25 cm^{-1}, in comparison to the corresponding band in the free ligand, which indicates that the dithiocarbamate ligand coordinating with metal through sulfur atoms[16]. At lower frequency the complexes exhibited band 400-300 cm^{-1}, which are assigned to the ν(M-S) stretching mode[17].

Electronic spectra and magnetic moment

The electronic spectrum of the ligand exhibits intense absorption bands at 299, 367 nm assigned to π-π^* and $n \rightarrow \pi^*$ transition. In complexes, this band was shifted to higher wavelength region. The Co(II) complex displays addition bands in the d-d region at 507 and 625 nm, related to ${}^4A_{2(F)} \rightarrow {}^4T_{2(F)}$ and ${}^4A_{2(F)} \rightarrow {}^4T_{1\,(P)}$ characteristic for tetrahedral geometry. The magntic moments value of μ_{eff} (4 B.M) attributed to tetrahedral geometry. The Ni(II) complex showed tow absorption bands at 420 and 508 nm typical of tetrahedral geometry and were assigned to ${}^3T_{1(F)} \rightarrow {}^3T_{2(F)}$ and ${}^3T_{1(F)} \rightarrow {}^3T_{1(P)}$ transition, respectively. The magntic moment value of μ_{eff} (3.70 B.M) attributed to tetrahedral geometry[18]. The Cu(II) complex band at 416 nm were assigned to ${}^2T_2 \rightarrow {}^2E$ transition. The magntic moment value of μ_{eff} (1.74) B.M attributed to tetrahedral geometry[19]. The Zn(II) complex had only charge transfer transition from metal to ligand at 280 and 372 nm since no d-d transition is expected. This complex was expectedly diamagnetic and tetrahedral[20]. It is shown in Fig. 8-12.

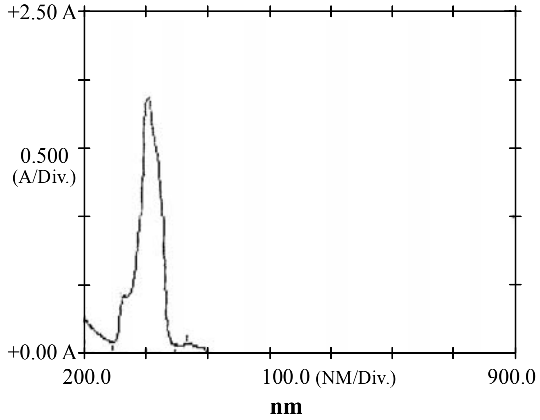


Fig. 8: Electronic spectrum of ligand dithiocarbamate

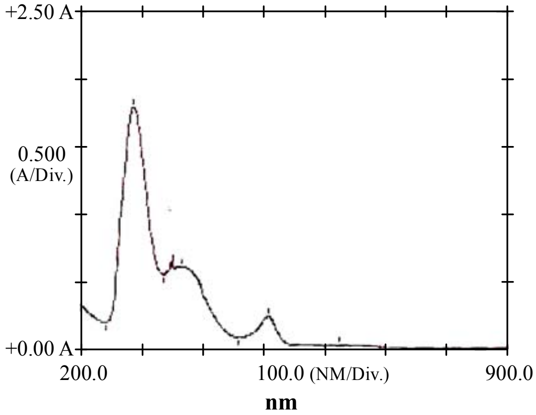


Fig. 9: Electronic spectrum of Co(II) complexes

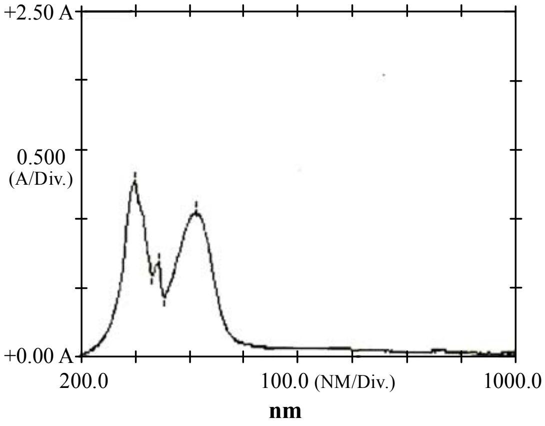


Fig. 10: Electronic spectrum of Cu(II) complexes

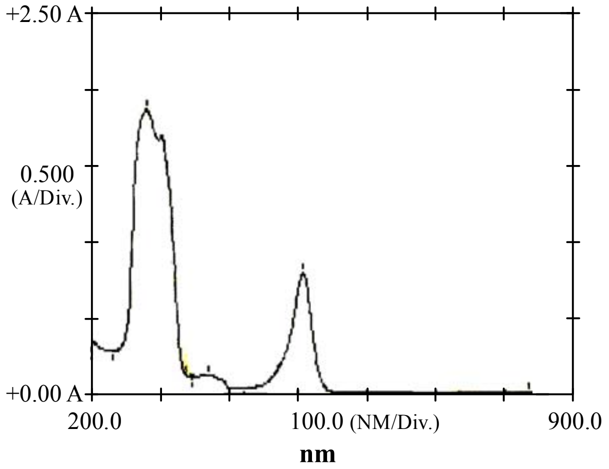


Fig. 11: Electronic spectrum of Zn(II) complexes

Biological activity

The author in this present investigation attempted to find out the antibacterial activity of ligand their metal complexes against *Salmonella tyoi*, *Staphylococcus* and *E. Coli* choosing serial paper disc method Table 3. The result of the biological activity of the metal complexes indicated the following facts. A comparative study of the ligand and their complexes indicates that the metal chelates exhibited higher antibacterial activity than that of the free ligand. The zones of inhibition of the ligand metal complexes were in the Table 3. The activity was compared with a zone of inhibition was measured in mm.

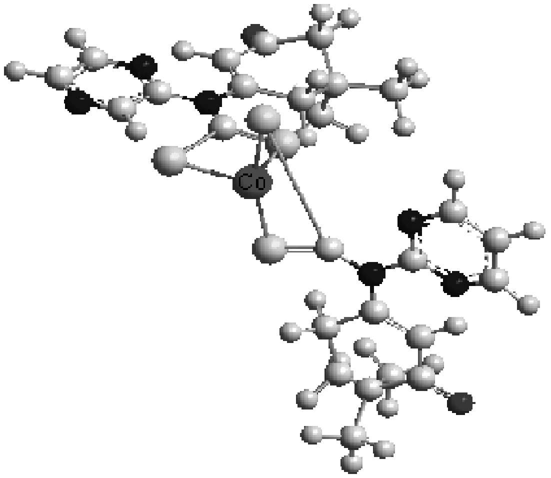


Fig. 12: Proposed structure of tetrahedral geometry [Co(L_2)]

Table 3: Antibacterial activity of the metal complexes total area of zone of clearance in mm

Compound	*Salmonella*	*Staphylococcus*	*E. coli*
Ligand	22	24	25
L_2 Co	26	27	27
L_2Ni	24	25	26
L_2Cu	23	25	25
L_2Zn	23	24	25

CONCLUSION

This paper report the preparation and identification of new dithiocarbamate ligand and its complexes with Co(II), Ni(II), Cu(II) and Zn(II) metal ions. The inaccessible products were characterization by accessible techniques. All the proposed geometry of the complexes are tetrahedral. According to these results, the structural formulas of these complexes is proposed in Fig. 12.

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