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Preparation and Antimicrobial Screening of Cu (II), Ni (II), Zn (II) Cd (II) Complexes

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Abstract: The metal complexes of Ni(II), Cu(II), Zn(II) Cd (II) with organic ligands *viz* Hydrazine hydrate, 1,2-N,N′-Bisammonium thiocarbamoyl ethane and 1,4-N,N′-Bisammonium thiocarbamoyl benzene have been prepared. These ligands and metal complexes of dithiocarbamates were screened for their antimicrobial activity against various microbs.

Keywords: Dithiocarbamates, Anti microbial Activity, Magnetic Moment

Introduction

Dithiocarbamates form a large number of complexes with transition metals and give rise to neutral complexes of the type $M(DTC)_X$, where X is the number of ligands attached to metal. As a chelating ligands, the dithiocarbamate co-ordinates with transition metal through both the sulfur atoms. In order to get potent biocidal agents we synthesized following type of dithiocarbamate ligands 1,2-N,N′-Bisammonium thiocarbamoyl ethane and 1,4-N,N′-Bisammonium thiocarbamoyl benzene and their metal complexes with Ni(II),Cu(II),Zn(II) and Cd(II).

Application

Organo Dithiocarbamates finds its application as qualitative analytical reagents for the determination of concentration of metal ion by gravimetric method. Number of biological profiles are reported in the literature for Dithiocarbamates. Over and above this, certain diamine derivatives find application in dyes industry and as antileprosy agents. The present research article reports the synthesis of dithiocarbamate ligands 1,2-N,N′ Bis ammonium dithiocarbamoyl Ethane , 1,4- N,N′ Bis ammonium dithiocarbamoyl Benzene and their metal complexes with Ni (II), Cu (II), Zn (II), Cd (II). The products are characterized by elemental analyses, room-temperature magnetic moment measurements and IR studies. The metal complexes were screened for antimicrobial activity and their structure were supported by spectral data. It was observed that the biological activity of certain organic compounds is enhanced by complex formation with metal ions.[1-3]

Experimental

The melting points of all the synthesized compounds were recorded in open glass capillaries and are uncorrected. IR absorption (ν cm^{-1}) spectra were scanned on Shimadzu 435-IR spectrophotometer using KBr pellet method ^1H NMR spectra were recorded on 90 MHz PMR spectrometer Jeol, using TMS as internal standard and DMSO-d_6 as solvent. Analytical grade metal chloride dihydrate of Merck were utilized and oven dried overnight at of 115^{0}C and store in a desiccator over phosphorous pentoxide.

Preparation of ligands[4]

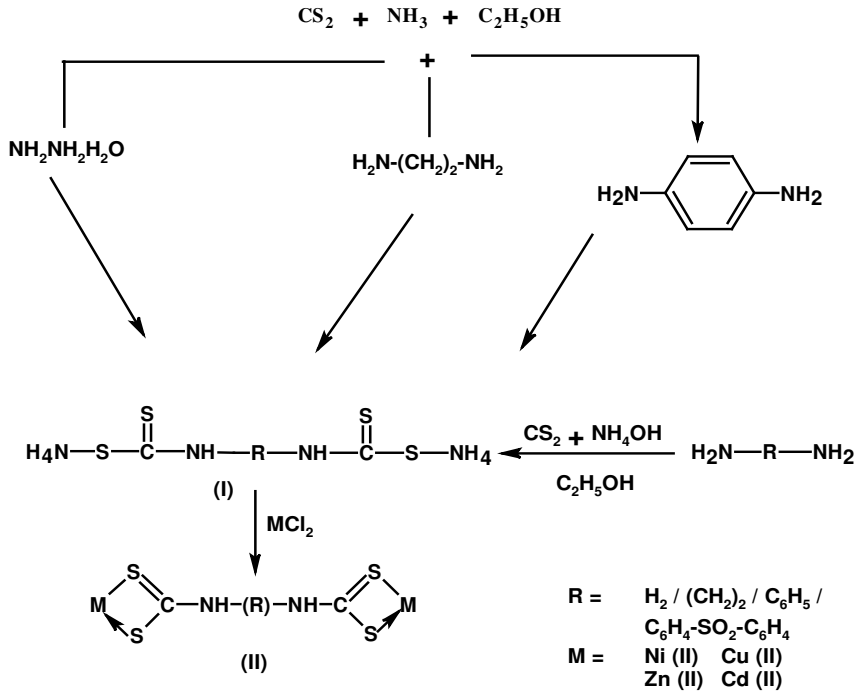
Ethylene diamine(0.1 M) was added drop wise to a mixture of carbon disulfide (0.2 M) in ethanol and liquor ammonia and were stirred vigorously, keeping the temperature at 0^{o}C for 2 hrs. The solid product so obtained was filtered and isolated. Yield 90 %, m.p.185^{o}C. The physical constants are recorded in the Table 1. Similarly 1, 4-N, N′-Bisammonium thiocarbamoyl benzene was synthesized.

Table 1. Physical Constant (Ligands)

R	Molecular Formula	M.P.	% of Sulfur		% of Nitrogen	
			Cal.	Found	Cal.	Found
-Nil-	$C_2H_{10}N_4S_4$	222°C	58.71	58.65	25.68	25.65
Ethyl	$C_4H_{14}N_4S_4$	200°C	43.53	43.50	90.04	90.00
Benzene	$C_8H_{14}N_4S_4$	280°C	43.59	34.57	15.13	15.02

Preparation of Metal Complexes

Analytical Reagent grade metal chloride dihydrate (Merck) were oven-dried overnight at 115^{o}C and stored in a desiccator over phosphorus pentoxide. Metal complexes of Cu (II), Ni (II), Cd (II), Zn (II) were prepared by refluxing the mixture of metallic chloride solution in water (0.2 M) with the ligands solution in ethanol for half an hour. The product was washed with water followed by ethanol and dried in vacuum. The elemental analysis were done by standard methods[5]. The I.R. spectra , visible spectra, magnetic moments, conductivity were measured and are discussed. The yield varied from 69 to 79 percentages. Percentage of Nitrogen and Sulfur are found to be similar to that of calculated given in the Table 2



Scheme

Table 2. Physical Constant (Metal Complexes)

R	M	Molecular Formula	Yield %	% of Nitrogen		% of Sulfur		% of Metal	
				Cal.	Found	Cal.	Found	Cal.	Found
-Nil-	Ni	$C_2H_2N_2S_4Ni_2$	70	9.33	9.30	42.66	42.64	39.33	39.28
-Nil-	Cu	$C_2H_2N_2S_4Cu_2$	73	9.06	9.00	41.42	41.40	41.10	41.06
-Nil-	Zn	$C_2H_2N_2S_4Zn_2$	75	8.94	8.92	40.89	40.87	41.85	41.81
-Nil-	Cd	$C_2H_2N_2S_4Cd_2$	74	6.87	6.85	31.44	31.42	55.28	55.24
Ethyl	Ni	$C_4H_6N_2S_4Ni_2$	70	8.53	8.57	39.02	38.99	35.97	35.94
Ethyl	Cu	$C_4H_6N_2S_4Cu_2$	77	8.30	8.29	37.98	37.96	38.41	38.38
Ethyl	Zn	$C_4H_6N_2S_4Zn_2$	75	8.21	8.20	37.53	37.52	33.67	33.63
Ethyl	Cd	$C_4H_6N_2S_4Cd$	78	6.43	6.42	29.42	29.40	46.58	46.53
Phenyl	Ni	$C_8H_6N_2S_4Ni_2$	79	7.44	7.42	34.04	33.99	31.38	31.34
Phenyl	Cu	$C_8H_6N_2S_4Cu_2$	76	7.27	7.25	33.24	33.22	32.98	32.93
Phenyl	Zn	$C_8H_6N_2S_4Zn_2$	78	7.19	7.17	32.90	32.89	33.67	33.63
Phenyl	Cd	$C_8H_6N_2S_4Cd_2$	76	5.79	5.78	26.50	26.46	46.58	46.53

Results and Discussion

Stoichiometry

Analytical study of the metal complexes shows that they are of type ML_2**.** Their electrical conductance measurements in DMF (2 to7 hm^{-1} mol^{-1}) show that they are non ionic.

Magnetic moments

The room temperature magnetic study shows that the Ni (II) complexes are diamagnetic showing square planar geometry. The Cu (II) complexes are paramagnetic and give higher magnetic moment of 2.06 to 2.11 BM as compared to spin only values is presumably due to spin-orbit coupling. The Zn (II) and Cd (II) complexes are diamagnetic due to non availability of unpaired electrons.

Spectral study

Ni (II) complexes show two absorption bands at 14260 – 14700 cm^{-1} and 17240-17850 cm^{-1} due to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$ d-d transition respectively supporting the square planar structure of Nickel complexes. For the square planner complexes of Copper (II) three absorption bands are expected corresponding to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$, and $^2B_{1g} \rightarrow {}^2E_g$. The absorption spectra of Zn(II) and Cd (II) complexes shows no bands due to d-d-transition. This phenomenon is natural as there is no possibility of transition due to non availability of empty d-orbital.

^1H NMR (DMSO-∂6)

δ ppm: 3.51 (t CH_2-CH_2) propane.

IR Spectra

Ligands shows bands around 1505 cm^{-1} C=N & 1510 cm^{-1} C=S . These bands are shifting in the complexes indicating the breaking of sulfur bonding. The band at C=N 1505 cm^{-1} of the ligands undergoes negative shift indicating the co-ordination linkage of sulfur.

IR (KBr)

Hydrazine hydrate : 3100 cm^{-1} (N-Hstr.),1395 cm^{-1} (C=S str.), 700 cm^{-1} (C-S str.),1460 cm^{-1} (C-Nstr.) ;1,2-N,N′-Bisammonium: 2920 cm^{-1} (C-H str. Asym.), 2865 cm^{-1} (C-H str. sym.) ; thiocarbamoyl ethane 3300 cm^{-1} (N-H str.Asym.), 1300 cm^{-1} (C-H str. sym.), 1300 cm^{-1} (C-N str.), 1510 cm^{-1} (C=S), 670 cm^{-1} (C-S) ; 1,4-N,N′-Bisammonium : 3200 cm^{-1} (C-H str.), 3500 cm^{-1} (N-H str.), 1580 cm^{-1} thiocarbamoyl benzene (C=S), 670 cm^{-1} (C-S)

Antimicrobial Activity

Antimicrobial Activity was carried out using the cup-plate method.

Antibacterial Activity [6]

The purified products were screened for their antibacterial activity. The nutrient agar broth prepared by the usual method was inoculated especially with 0.5ml for 24 hrs. old subculture of Gram positive bacteria Bacillus Subtilis(B.Subtilis) and Staphylococcus Pyogens (S.Pyogens) , Gram positive bacteria Escherichia coli(E.Coli) and Klebsiella Pneumoniae(K. Pneumoniae).

Antifungal Activity [7]

Aspergillus niger (S. niger) and Saccharomyces cerevisiae(S. cerevisiae) were employed for testing the fungicidal activity of 50 leg/ml using cup-plate method. The cultures were maintained on Sabouraud's agar alants. Purified compounds were used for testing the fungicidal activity.

The zones of inhibition of purified ligands and metal complexes are recorded in Table 3 and 4. From the experimental data of antimicrobial activity, it is evident that metal complexes are more active than their counter part ligands using DMF as solvent.

The antimicrobial activity was compared with four standard drugs viz. Ampicillin, Chloramphenicol, Norfloxacin, Griseofulvin.

Table 3. Antimicrobial Activity of Ligands

R	Zones Of Inhibition in mm					
	Antibacterial Activity			Antifungal Activity		
	B.subtilis	S.pyrogens	E.coli	K.pneumoniae	A.niger	S.cerevisiae
-Nil-	12	13	13	14	16	17
Ethanyl	14	13	12	12	13	17
Phenyl	15	14	13	15	15	16

Table 4. Antimicrobial Activity of Metal Complexes

R	R	Zones Of Inhibition in mm					
		Antibacterial Activity			Antifungal Activity		
		B.subtilis	S.pyogens	E.coli	K.pneumoniae	A.niger	S.cerevisiae
-Nil-	Ni	14	15	15	14	18	19
-Nil-	Cu	13	15	11	11	14	18
-Nil-	Zn	18	17	15	13	12	17
-Nil-	Cd	15	15	12	13	18	19
Ethanyl	Ni	16	16	13	15	17	17
Ethanyl	Cu	12	14	16	17	15	15
Ethanyl	Zn	15	16	17	18	18	18
Ethanyl	Cd	13	15	18	17	18	19
Phenyl	Ni	15	13	14	15	12	16
Phenyl	Cu	14	14	12	15	14	17
Phenyl	Zn	12	12	11	11	13	13
Phenyl	Cd	13	14	14	15	12	15

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