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HETEROCYCLO-SUBSTITUTED SULFA DRUGS: PART XI. NOVEL BIOLOGICALLY ACTIVE N-(PIPERIDINO-, MORPHOLINO-, PIPERAZINO-) DITHIOCARBAMYL-AZO DYES AND THEIR CHELATES

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A Series of novel azo-sulfa drugs of piperidino-, morpholino-, mono-, and bis-piperazino-N-dithiocarbamyl-azo dyes (Ia-h – IV a-h) are synthesized via a reaction of 4-[(4'-heterocyclo-substituted) sulfonyl and/or sulfonyl] benzenediazonium salts with N-piperidino-, N-morpholino-, mono-, and bis- N-piperazino- dithiocarbamate sodium salts in acid medium to afford the corresponding azo dye legands. Interaction of these ligands with metal salts: iron(III), copper(II) and mercuric(II) chlorides in ethanolic solution afforded the corresponding metal chelates (I'a-h – 'IVa-h), (I''a-h – ''IVa-h) and (I'''a-h – '''IVa-h). Ligands and their metal chelates are characterized by microanalysis, IR, UV-Vis H-NMR spectroscopy and are screened *in vitro* for their antimicrobial activities. Chelation of ligands induces a remarkable increase in their antimicrobial activity.

Keywords: N-(piperidino-morpholino-piperazino-) dithiocarbamate azo dyes; chelation; biological activity

INTRODUCTION

Heterocyclo-substituted sulfa drug compounds containing azo group are of great value due to their usefulness as models for therapeutic effects and biological systems (antifungal, antibacterial)¹ having anticancer, antimalarial, antitubercular, anti-inflammatory properties,²⁻⁵ strong chelating agents for occupational poisoning by metals^{6,7} and are used as antidotes

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for chronic metal intoxication arising from therapy or household contamination^{8,9}. Optimum dosages of these antidotes circulate in the blood-stream without much depletion of the body's essential heavy metals⁶. Moreover, the azo compounds occupy a scientific position as excellent azo dyes, and as analytical reagents¹⁰⁻¹². It is also reported that the replacement of hydrogen of the SO_2NH_2 group by heterocyclic amines enhances the fungicidal and bactericidal activity¹³.

Deferoxamine mesylate is selective for iron with little or no effect for other metals. It is nontoxic and has been used in the treatment of hemochromatosis and as an effective antidote for the treatment of acute iron poisoning in children⁶.

In continuation of our interest in heterocyclo- substituted azo sulfonamide derivatives, we report the synthesis and characterisation of novel azo dye sulfa drugs based on N-piperidino-, N-morpholino-, N-piperazino-dithiocarbamate sodium salt moieties^{14,15} to give N-piperidino-, N-morpholino-, N-piperazino- dithiocarbamyl azo dye ligands and their complexes with some transition metals ions: Fe^{+3} , Cu^{+2} , Hg^{+2} . Our aim is also to test the change in the antimicrobial activity of azo dye ligands on chelation with these metals.

EXPERIMENTAL

All chemicals and solvents were reagent grade. The infrared spectra were obtained in KBr pellets by a Shimadzu IR 470 spectrophotometer. ^1H -NMR spectra were recorded on a Varian EM-390 MHz instrument in a suitable deuterated solvent ($\text{F}_3\text{CCO}_2\text{H}$) using TMS as internal reference.

Synthesis of piperidino-, morpholino-, and mono-, bis-, piperazino-N- dithiocarbamate sodium Salts (I – IV)

The sodium salts of these compounds were prepared by treating piperidine, morpholine and/or piperazine (reagent grades) in cold and dry diethyl-ether with carbon disulfide and adding sodium hydroxide solution with vigorous stirring over a 5h period. molar ratio: (cyclic amine): (CS_2): (NaOH) = (1) : (1) : (1). The crude products were recrystallized from isopropyl alcohol.

Preparation of p-[(p'-Heterocyclo-Substituted) Sulfamoyl and/or sulfonyl] benzenediozonium chlorides

The diazonium salts were prepared by diazotization of p'-(aminosulfonyl)-aniline, p'-(acetyl aminosulfonyl) aniline, p'-(guanidinyll sulfonyl) aniline, p'-(2''-pyridyl aminosulfonyl) aniline, p'-(2''-pyrimidyl aminosulfonyl) aniline, p'-(2''-(4- methyl) pyrimidyl aminosulfonyl) aniline, p'-(2''-(4,6- dimethyl) pyrimidyl- aminosulfonyl) aniline, p'-(2''-thiazolyl aminosulfonyl) aniline, p'-(2''-methoxazolylaminosulfonyl) aniline, (0.01 mol) dissolved in a mixture of acetone (20 ml) and 80 ml of 60% pure hydrochloric acid with sodium nitrite (0.7g, 0.01 mol) at 0 – 5°C with vigorous stirring over an 8 h period.

Synthesis of p'-[(p'-heterocyclo- substituted)-N-(piperidino-, morpholino-, (mono) – and (bis) – piperazino-)] phenylazo dithiocarbamate dyes (Ia-h – IV a-h)

To ice cold solutions of N-piperidino-, N-morpholino., and/or N-piperazino- dithiocarbamate sodium salts (1, 83, 1.85, 1.84, 2.92g, 0.01 mol) in 25 ml of 50% sodium hydroxide solution, a cold hydrochloric acid solution of the diazonium salt was added dropwise with stirring. The reaction mixture was further stirred and kept at 0 – 5°C for 7h followed by addition of 5% aqueous sodium hydroxide to pH 7, when a yellowish brown precipitate separated, excess of cold water was added. The product was collected, washed well with water, and recrystallized from ethanol (Table I).

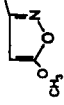
Synthesis of iron(III), copper(II) and mercury(II), azo (piperidin-, morpholin-, mono-, and bis- piperazine-)-N-yl dithiocarbamate chelates (I'a-h – IV'a-h) (I''a-h – IV''a-h) and (I'''a-h – IV'''a-h)

A boiling solution of the appropriate azo [(heterocyclo-substituted)-piperidino-, morpholino-, momo- and bis- piperazino- N-yl dithiocarbamate-azo dye ligand (0.01 mol) in a mixture of ethanol and dilute acetic acid 5% (5:1) was added dropwise with stirring to a solution of the given metal salt (0.01 mol): ferric chloride, copper chloride and mercuric chloride in ethanol (40 ml). Stirring was continued for 30 min at 80 °C. The reaction mixture was cooled and the precipitate was filtered, washed thoroughly with distilled water, dried and recrystallized from ethanol and dried over P₄O₁₀ (Table II).

TABLE I Physical and Analytical data of Dithiocarbamyl Heterocycloamine Azo Dye Sulpha Drugs (Ligands)

Compd.No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	MicroanalysisCalculated/(Found)			
						% C	% H	% N	% S
Ia		H -	189	85	C ₁₂ H ₁₆ N ₄ O ₂ S ₃ (344.64)	41.80 (42.08)	4.70 (4.65)	16.26 (16.30)	21.90 (28.10)
Ib			182	88	C ₁₄ H ₁₈ N ₄ O ₃ S ₃ (386.50)	43.50 (44.00)	4.69 (5.08)	14.50 (14.38)	24.89 (24.81)
Ic			192	72	C ₁₃ H ₁₈ N ₆ O ₂ S ₃ (386.51)	40.39 (40.12)	4.69 (4.72)	21.75 (21.70)	24.89 (24.80)
Id			195	70	C ₁₆ H ₁₈ O ₂ N ₆ S ₃ (422.54)	45.48 (45.53)	4.29 (4.32)	19.89 (19.82)	22.76 (22.70)
Ie			210	68	C ₁₇ H ₂₀ N ₆ O ₂ S ₃ (436.57)	46.77 (46.71)	4.62 (4.69)	19.25 (19.30)	22.03 (22.00)
If			215	69	C ₁₈ H ₂₂ N ₆ O ₂ S ₃ (450.60)	27.98 (48.02)	4.90 (4.82)	18.65 (18.60)	21.30 (21.26)
Ig			202	72	C ₁₅ H ₁₇ N ₅ O ₂ S ₄ (427.29)	42.13 (42.20)	4.00 (4.02)	16.38 (16.41)	29.99 (23.02)
Ih			220	70	C ₁₆ H ₁₉ N ₅ O ₄ S ₃ (441.54)	43.52 (43.50)	4.34 (4.40)	15.86 (15.80)	21.79 (21.82)

Compd.No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated/(Found)			
						% C	% H	% N	% S
IIa		H	175	89	C ₁₁ H ₁₄ N ₄ O ₃ S ₃ (346.44)	38.10 (37.88)	4.07 (4.12)	16.17 (16.20)	27.76 (27.81)
IIb			180	83	C ₁₃ H ₁₆ N ₄ O ₄ S ₃ (388.48)	40.19 (40.21)	4.15 (4.21)	14.42 (14.38)	24.76 (24.72)
IIc			202	75	C ₁₂ H ₁₆ N ₆ O ₃ S ₃ (388.49)	37.09 (37.20)	4.15 (4.09)	21.64 (21.70)	24.76 (24.67)
IIId			215	70	C ₁₅ H ₁₆ N ₆ O ₆ S ₃ (424.52)	42.44 (42.40)	3.80 (3.81)	19.80 (19.87)	22.66 (22.60)
IIe			220	72	C ₁₆ H ₁₈ N ₆ O ₃ S ₃ (438.54)	43.82 (43.80)	4.14 (4.17)	19.17 (19.12)	21.93 (21.91)
IIIf			198	69	C ₁₇ H ₂₀ N ₆ O ₃ S ₃ (452.57)	45.11 (45.08)	4.45 (4.50)	18.57 (18.61)	21.25 (21.20)
IIg			205	65	C ₁₄ H ₁₅ N ₅ O ₃ S ₄ (429.56)	39.14 (39.21)	3.52 (3.58)	16.31 (16.28)	29.86 (29.81)
IIh			218	74	C ₁₅ H ₁₇ N ₅ O ₅ S ₃ (443.52)	40.62 (40.60)	3.88 (3.82)	15.79 (15.81)	21.69 (21.72)

Compd.No	Cyclic Amine	R	mp, °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated/(Found)			
						% C	% H	% N	% S
IIIa		H	190	86	C ₁₁ H ₁₅ N ₅ O ₂ S ₃ (345.46)	38.24 (38.30)	4.38 (4.30)	20.27 (20.20)	27.80 (27.88)
IIIb			201	80	C ₁₃ H ₁₇ N ₅ O ₃ S ₃ (387.50)	40.29 (40.31)	4.40 (4.35)	18.07 (18.00)	24.82 (24.90)
IIIc			187	74	C ₁₂ H ₁₇ N ₇ O ₂ S ₃ (387.51)	37.19 (37.22)	4.40 (4.36)	25.30 (25.35)	24.82 (24.79)
IIId			205	78	C ₁₅ H ₁₇ N ₇ O ₂ S ₃ (423.53)	42.53 (42.57)	4.05 (4.10)	23.15 (23.10)	22.71 (22.66)
IIIe			220	69	C ₁₆ H ₁₉ N ₇ O ₂ S ₃ (437.55)	43.92 (43.90)	4.38 (4.40)	22.41 (22.37)	21.98 (21.95)
IIIf			215	72	C ₁₇ H ₂₁ N ₇ O ₂ S ₃ (451.59)	45.22 (45.17)	4.68 (4.59)	21.71 (21.78)	21.30 (21.25)
IIIg			212	78	C ₁₄ H ₁₆ N ₆ O ₂ S ₄ (428.58)	39.23 (39.30)	3.76 (3.72)	19.60 (19.55)	29.93 (30.00)
IIIh			225	79	C ₁₅ H ₁₈ N ₆ O ₄ S ₃ (442.53)	40.71 (40.70)	4.10 (4.13)	18.99 (18.91)	21.74 (21.76)

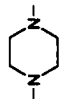
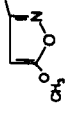
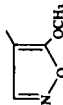
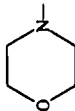
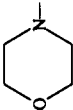
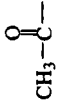
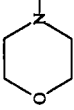
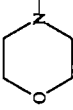
Compd.No	Cyclic Amine	R	mp, °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated/(Found)			
						% C	% H	% N	% S
IVa		H	218	90	C ₁₈ H ₂₀ N ₈ O ₄ S ₆ (604.78)	35.75 (35.80)	3.30 (3.38)	18.53 (18.60)	31.80 (13.72)
IVb			224	87	C ₂₂ H ₂₄ N ₈ O ₆ S ₆ (688.85)	38.36 (38.41)	3.50 (3.43)	16.27 (16.35)	27.93 (27.86)
IVc			230	82	C ₂₀ H ₂₄ N ₁₂ O ₄ S ₃ (688.87)	34.87 (34.90)	3.50 (3.53)	24.40 (24.41)	27.93 (27.90)
IVd			236	78	C ₂₆ H ₂₄ N ₁₂ O ₄ S ₆ (760.39)	41.04 (41.10)	3.18 (3.20)	22.09 (22.05)	25.28 (25.22)
IVe			228	75	C ₂₈ H ₂₈ N ₁₂ O ₄ S ₆ (788.98)	42.62 (42.60)	3.58 (3.60)	21.13 (21.27)	24.38 (24.40)
IVf			240	70	C ₃₀ H ₃₂ N ₁₂ O ₄ S ₆ (817.04)	44.09 (44.12)	3.95 (4.05)	20.57 (20.61)	23.55 (23.50)
IVg			233	71	C ₂₄ H ₂₂ N ₁₀ O ₄ S ₈ (771.02)	37.38 (37.40)	2.87 (2.95)	18.17 (18.10)	33.27 (33.20)
IVh			243	78	C ₂₆ H ₂₆ N ₁₀ O ₈ S ₆ (798.93)	39.09 (39.10)	3.28 (3.22)	17.53 (17.51)	24.08 (24.10)

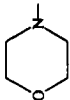
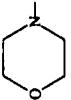
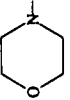
TABLE II Physical and Analytical Data of Dithiocarbamyl Heterocycloamine Azo Dye Iron(III), Copper(II), Mercury(II) Chelates

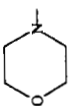
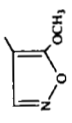
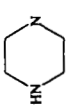
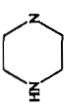
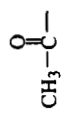
Compd. No	Cyclic Amine	R	mp, °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)					
						% C	% H	% N	% S	% Cl	% M
Ia		H	292	85	C ₁₂ H ₁₆ N ₄ O ₂ S ₃ FeCl ₃ (506.86)	28.43 (28.35)	3.20 (3.15)	11.05 (11.15)	18.98 (18.90)	20.99 (21.05)	11.02 (10.89)
IIa			251	75	C ₁₂ H ₁₆ N ₄ O ₂ S ₃ CuCl ₂ (479.09)	30.08 (30.00)	3.40 (3.32)	11.69 (11.70)	20.08 (20.00)	14.80 (14.72)	13.26 (13.88)
IIIa			268	87	C ₁₂ H ₁₆ N ₄ O ₂ S ₃ HgCl ₂ (616.14)	23.40 (23.35)	2.60 (2.55)	9.09 (9.00)	15.60 (15.68)	11.51 (11.57)	32.56 (33.26)
Ib			295	80	C ₁₄ H ₁₈ N ₄ O ₃ S ₃ FeCl ₃ (548.72)	30.60 (30.55)	3.30 (3.38)	10.20 (10.18)	17.53 (17.62)	19.39 (19.42)	10.18 (11.21)
IIb			285	85	C ₁₄ H ₁₈ N ₄ O ₃ S ₃ CuCl ₂ (520.95)	32.28 (32.32)	3.48 (3.52)	10.76 (10.70)	18.46 (18.52)	13.61 (13.55)	12.20 (12.67)
IIIb			273	78	C ₁₄ H ₁₈ N ₄ O ₃ S ₃ HgCl ₂ (658.00)	25.55 (25.60)	2.76 (2.70)	8.50 (8.58)	14.60 (14.52)	10.78 (10.82)	30.48 (31.01)
Ic			301	78	C ₁₃ H ₁₈ N ₆ O ₂ S ₃ FeCl ₃ (548.73)	28.45 (28.50)	3.30 (3.25)	15.32 (15.38)	17.53 (17.50)	19.38 (19.42)	10.18 (10.29)
IIc			295	71	C ₁₃ H ₁₈ N ₆ O ₂ S ₃ CuCl ₂ (520.96)	29.97 (29.92)	3.48 (3.52)	16.13 (16.20)	18.46 (18.52)	13.61 (13.57)	12.19 (11.98)
IIIc			287	66	C ₁₃ H ₁₈ N ₆ O ₂ S ₃ HgCl ₂ (658.01)	23.73 (23.67)	2.76 (2.80)	12.77 (12.70)	14.62 (14.68)	10.78 (10.82)	30.48 (31.21)

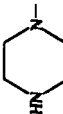
Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)						
						% C	% H	% N	% S	% Cl	% M	
'Id			305	78	C ₁₆ H ₁₈ N ₆ O ₂ S ₃ FeCl ₃ (584.75)	34.49 (35.00)	3.10 (3.00)	14.37 (14.41)	16.45 (16.58)	18.19 (18.09)	9.55 (10.00)	
"Id			295	70	C ₁₂ H ₁₆ N ₆ O ₂ S ₃ CuCl ₂ (557.08)	34.49 (34.87)	3.26 (3.46)	15.09 (15.12)	17.27 (17.19)	12.73 (12.93)	11.41 (11.67)	
""Id			280	73	C ₁₆ H ₁₈ N ₆ O ₂ S ₃ HgCl ₂ (694.04)	27.69 (28.00)	2.61 (2.50)	12.11 (12.10)	13.86 (13.67)	10.22 (10.11)	28.90 (29.00)	
'Ie			295	75	C ₁₇ H ₂₀ N ₆ O ₆ S ₃ FeCl ₃ (598.78)	34.10 (34.00)	3.37 (3.87)	14.04 (14.00)	16.06 (16.00)	17.76 (18.02)	9.33 (9.56)	
"Ie			287	68	C ₁₇ H ₂₀ N ₆ O ₂ S ₃ CuCl ₂ (571.02)	35.76 (35.50)	3.53 (3.72)	14.72 (14.82)	16.85 (17.00)	12.42 (12.61)	11.28 (11.32)	
""Ie			280	65	C ₁₇ H ₂₀ N ₆ O ₃ S ₃ HgCl ₂ (708.07)	28.83 (29.00)	2.85 (2.29)	11.87 (11.92)	13.58 (13.88)	10.02 (10.00)	28.33 (28.00)	
'If			285	79	C ₁₈ H ₂₂ N ₆ O ₂ S ₃ FeCl ₃ (612.82)	35.28 (35.32)	3.62 (3.60)	13.72 (13.68)	15.70 (15.74)	17.36 (13.29)	9.10 (9.00)	
""If			279	82	C ₁₈ H ₂₂ N ₆ O ₂ S ₃ CuCl ₂ (585.05)	36.95 (37.01)	3.79 (3.71)	14.37 (14.40)	16.44 (16.40)	12.12 (12.10)	10.86 (11.00)	
""If			270	70	C ₁₈ H ₂₂ N ₆ O ₂ S ₃ HgCl ₂ (722.10)	29.94 (30.01)	3.07 (3.10)	11.64 (11.70)	13.30 (13.22)	9.82 (9.89)	27.78 (28.00)	

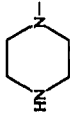
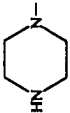
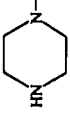
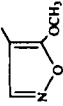
Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)					
						% C	% H	% N	% S	% Cl	% M
Ig			301	77	C ₁₅ H ₁₇ N ₅ O ₂ S ₄ FeCl ₃ (589.81)	30.54 (30.50)	2.90 (2.82)	11.88 (11.92)	21.75 (21.82)	18.02 (17.28)	9.47 (9.58)
IIg			290	73	C ₁₅ H ₁₇ N ₅ O ₂ S ₄ CuCl ₂ (62.04)	32.05 (3.12)	3.05 (3.12)	12.46 (12.40)	22.80 (22.75)	12.60 (12.63)	11.30 (11.50)
IIIg			282	65	C ₁₅ H ₁₇ N ₅ O ₂ S ₄ HgCl ₂ (699.09)	25.77 (25.82)	2.45 (2.50)	10.02 (10.12)	18.35 (18.28)	10.14 (10.20)	28.69 (28.81)
Ih			298	78	C ₁₆ H ₁₉ N ₅ O ₄ S ₃ FeCl ₃ (603.76)	31.83 (31.10)	3.17 (2.95)	11.59 (11.80)	15.93 (15.12)	17.62 (16.97)	9.25 (9.00)
IIh			290	71	C ₁₆ H ₁₉ N ₅ O ₄ S ₃ UCl ₂ (575.99)	33.36 (32.76)	3.33 (2.87)	12.16 (11.09)	16.70 (5.95)	12.10 (11.82)	9.695 (9.92)
IIIh			282	65	C ₁₆ H ₁₉ N ₅ O ₄ S ₃ HgCl ₂ (713.04)	26.95 (27.15)	2.69 (3.37)	9.82 (9.31)	13.49 (12.89)	9.94 (10.15)	28.13 (28.70)
IIa			278	81	C ₁₁ H ₁₄ N ₄ O ₃ S ₃ FeCl ₃ (508.66)	25.97 (26.01)	2.77 (2.08)	11.02 (11.10)	18.90 (18.96)	20.90 (20.99)	10.98 (11.12)
IIa		H	283	76	C ₁₁ H ₁₄ N ₄ O ₃ S ₃ CuCl ₂ (480.89)	27.47 (27.52)	2.90 (2.85)	11.65 (11.72)	20.00 (19.89)	14.75 (14.82)	13.20 (12.98)
IIa			268	70	C ₁₁ H ₁₄ N ₄ O ₃ S ₃ HgCl ₂ (617.94)	21.38 (21.42)	2.28 (2.32)	9.07 (9.00)	15.57 (15.62)	11.48 (11.52)	32.46 (33.18)

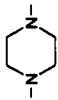
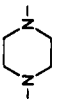
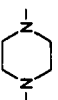
Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)						
						% C	% H	% N	% S	% Cl	% M	
"IIb			287	83	C ₁₃ H ₁₆ N ₄ O ₄ S ₃ Fe Cl ₃ (550.69)	28.35 (28.40)	2.90 (2.98)	10.17 (10.21)	17.47 (17.40)	19.32 (19.28)	10.14 (10.72)	
"IIb			280	70	C ₁₃ H ₁₆ N ₄ O ₄ S ₃ Cu Cl ₂ (522.93)	29.86 (29.91)	3.08 (3.12)	10.71 (10.69)	18.39 (18.42)	13.56 (13.50)	12.15 (12.29)	
"IIb			272	65	C ₁₃ H ₁₆ N ₄ O ₄ S ₃ Hg Cl ₂ (559.98)	23.66 (23.60)	2.44 (2.50)	8.49 (8.52)	14.57 (14.50)	10.74 (10.66)	30.39 (30.98)	
"IIc			269	71	C ₁₂ H ₁₆ N ₆ O ₃ S ₃ Fe Cl ₃ (550.71)	26.17 (26.20)	2.90 (2.85)	15.72 (15.65)	17.47 (17.53)	19.32 (19.28)	10.14 (9.98)	
"IIc			275	78	C ₁₂ H ₁₆ N ₆ O ₂ S ₃ Cu Cl ₂ (522.94)	27.56 (27.50)	3.08 (3.00)	16.07 (16.10)	18.39 (18.42)	13.56 (13.50)	12.15 (12.89)	
"IIc			260	70	C ₁₂ H ₁₆ N ₆ O ₃ S ₃ Hg Cl ₂ (559.99)	21.84 (21.76)	2.44 (2.51)	12.77 (12.70)	14.57 (14.49)	10.70 (10.68)	30.39 (30.91)	
"IIId			301	75	C ₁₅ H ₁₆ N ₆ O ₃ S ₃ Fe Cl ₃ (586.73)	30.70 (31.01)	2.75 (2.91)	14.33 (14.56)	16.39 (16.71)	18.13 (18.31)	9.52 (9.71)	
"IIId			285	70	C ₁₅ H ₁₆ N ₆ O ₃ S ₃ Cu Cl ₂ (558.97)	32.23 (32.51)	2.89 (3.11)	15.04 (15.00)	17.21 (17.01)	12.69 (12.91)	11.37 (11.51)	
"IIId			271	65	C ₁₅ H ₁₆ N ₆ O ₃ S ₃ Hg Cl ₂ (696.02)	25.88 (26.11)	2.32 (2.52)	12.08 (12.00)	13.82 (14.00)	10.19 (10.30)	28.80 (29.00)	

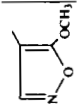
Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)						
						% C	% H	% N	% S	% Cl	% M	
'Ile			305	80	C ₁₆ H ₁₈ N ₆ O ₃ S ₃ Fe Cl ₃ (600.75)	31.99 (32.21)	3.02 (3.00)	13.99 (14.00)	16.01 (16.00)	17.71 (17.91)	9.30 (9.00)	
"Ile			290	82	C ₁₆ H ₁₈ N ₆ O ₃ S ₃ Cu Cl ₂ (572.99)	33.54 (33.75)	3.17 (3.10)	14.67 (14.73)	16.78 (17.00)	12.38 (12.42)	11.09 (11.11)	
""Ile			278	89	C ₁₆ H ₁₈ N ₆ O ₃ S ₃ Hg Cl ₂ (710.04)	27.06 (27.11)	2.55 (3.00)	11.84 (11.84)	13.55 (13.83)	9.99 (10.00)	28.50 (29.00)	
'IIf			295	82	C ₁₇ H ₂₀ N ₆ O ₃ S ₃ Fe Cl ₃ (614.79)	33.21 (33.18)	3.28 (3.35)	13.67 (13.60)	15.65 (15.58)	17.30 (17.35)	9.08 (9.11)	
"IIf			287	71	C ₁₇ H ₂₀ N ₆ O ₃ S ₃ Cu Cl ₂ (587.02)	34.78 (34.70)	3.40 (3.48)	14.30 (14.29)	16.39 (16.42)	12.08 (12.00)	10.80 (10.99)	
""IIf			271	65	C ₁₇ H ₂₀ N ₆ O ₃ S ₃ Hg Cl ₂ (724.07)	28.20 (28.25)	2.80 (2.82)	11.60 (11.56)	13.28 (13.38)	9.79 (9.80)	27.70 (27.99)	
'IIg			307	72	C ₁₄ H ₁₅ N ₅ O ₃ S ₄ Fe Cl ₃ (591.78)	28.40 (28.35)	2.56 (2.61)	11.84 (11.90)	21.67 (21.72)	17.97 (17.90)	9.44 (9.67)	
"IIg			296	68	C ₁₄ H ₁₅ N ₅ O ₃ S ₄ Cu Cl ₂ (564.01)	29.80 (29.75)	2.68 (2.73)	12.42 (12.38)	22.74 (22.68)	12.44 (12.51)	11.27 (11.50)	
""IIg			280	78	C ₁₄ H ₁₅ N ₅ O ₃ S ₄ Hg Cl ₂ (701.06)	23.98 (23.91)	2.16 (2.21)	9.99 (10.01)	18.30 (18.22)	10.11 (10.19)	28.60 (29.87)	

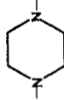
Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)						
						% C	% H	% N	% S	% Cl	% M	
'IIh			305	80	C ₁₅ H ₁₇ N ₅ O ₃ S ₃ FeCl ₃ (605.74)	29.89 (29.18)	2.83 (3.31)	11.56 (11.92)	15.88 (15.01)	17.56 (18.12)	9.21 (8.89)	
"IIh			292	73	C ₁₅ H ₁₇ N ₅ O ₃ S ₃ CuCl ₂ (577.97)	31.17 (32.01)	2.94 (3.11)	12.14 (13.01)	16.69 (15.75)	12.28 (11.98)	10.99 (10.28)	
'''IIh			280	68	C ₁₅ H ₁₇ N ₅ O ₃ S ₃ HgCl ₂ (715.02)	25.20 (26.00)	2.40 (3.25)	9.81 (8.89)	12.45 (12.87)	9.92 (10.35)	28.05 (27.91)	
'IIIa		H	308	68	C ₁₁ H ₁₅ N ₅ O ₃ S ₃ FeCl ₃ (507.68)	26.02 (26.12)	2.98 (3.00)	13.80 (13.72)	18.95 (19.00)	20.95 (20.87)	11.00 (11.08)	
"IIIa			301	62	C ₁₁ H ₁₅ N ₅ O ₂ S ₃ CuCl ₂ (479.91)	27.53 (27.49)	3.15 (3.21)	14.60 (14.57)	20.00 (19.93)	14.78 (14.81)	13.20 (13.87)	
'''IIIa			295	70	C ₁₁ H ₁₅ N ₅ O ₂ S ₃ HgCl ₂ (616.96)	21.40 (21.36)	2.45 (2.52)	11.35 (11.40)	15.59 (15.60)	11.90 (11.81)	32.50 (23.08)	
'IIlb			310	72	C ₁₃ H ₁₇ N ₅ O ₃ S ₃ FeCl ₃ (549.72)	28.40 (28.47)	3.10 (3.08)	12.74 (12.69)	17.50 (17.45)	19.31 (19.37)	10.16 (9.97)	
"IIlb			300	78	C ₁₃ H ₁₇ N ₅ O ₃ S ₃ CuCl ₂ (521.95)	29.90 (30.01)	3.28 (3.31)	13.42 (13.35)	18.43 (18.40)	13.58 (13.61)	12.17 (12.71)	
'''IIlb			290	68	C ₁₃ H ₁₇ N ₅ O ₃ S ₃ HgCl ₂ (659.00)	23.69 (23.80)	2.60 (2.53)	10.63 (10.70)	14.60 (14.55)	10.76 (10.82)	30.44 (31.01)	

Compd. No	Cyclic Amine	R	mp, °C	Yield (%)	Molecular Formula (MW)	Microanalysis Calculated / (Found)					
						% C	% H	% N	% S	% Cl	% M
'IIIc			300	65	C ₁₂ H ₁₇ N ₇ O ₂ S ₃ FeCl ₃ (549.72)	26.22 (26.30)	3.12 (3.10)	17.84 (17.91)	17.50 (17.58)	19.35 (19.40)	10.16 (9.98)
"IIIc			292	69	C ₁₂ H ₁₇ N ₇ O ₂ S ₃ CuCl ₂ (521.96)	27.60 (27.55)	3.28 (3.37)	18.79 (18.81)	18.43 (18.40)	13.58 (13.62)	12.16 (12.56)
'''IIIc			287	73	C ₁₂ H ₁₇ N ₇ O ₂ S ₃ HgCl ₂ (659.01)	21.87 (21.90)	2.60 (2.53)	14.88 (14.80)	14.60 (14.58)	10.76 (10.82)	30.44 (31.01)
'IIIId			315	70	C ₁₅ H ₁₇ N ₇ O ₂ S ₃ FeCl ₃ (585.75)	30.76 (31.21)	2.93 (3.22)	16.74 (17.12)	16.42 (15.98)	18.16 (18.62)	9.50 (10.32)
"IIIId			305	63	C ₁₅ H ₁₇ N ₇ O ₂ S ₃ CuCl ₂ (557.98)	32.29 (33.12)	3.07 (2.91)	17.57 (17.89)	17.24 (16.89)	12.71 (13.11)	11.39 (11.95)
'''IIIId			290	65	C ₁₅ H ₁₇ N ₇ O ₂ S ₃ HgCl ₂ (695.03)	25.92 (26.21)	3.47 (3.21)	14.11 (13.81)	13.84 (14.29)	10.20 (9.98)	38.86 (38.09)
'IIIe			320	78	C ₁₆ H ₁₉ N ₇ O ₂ S ₃ FeCl ₃ (599.77)	32.04 (32.77)	3.19 (2.99)	16.35 (16.89)	16.04 (15.88)	17.73 (18.12)	9.30 (10.08)
"IIIe			309	70	C ₁₆ H ₁₉ N ₇ O ₂ S ₃ CuCl ₂ (572.00)	33.59 (34.12)	3.35 (3.89)	17.14 (17.00)	16.82 (17.22)	12.40 (11.98)	11.11 (12.01)
'''IIIe			295	72	C ₁₆ H ₁₉ N ₇ O ₂ S ₃ HgCl ₂ (709.05)	27.10 (26.98)	2.70 (3.30)	13.83 (14.21)	13.57 (14.21)	10.00 (10.82)	28.28 (27.99)

Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)					
						% C	% H	% N	% S	% Cl	% M
"IIIh			315	80	C ₁₇ H ₂₁ N ₇ O ₂ S ₃ FeCl ₃ (613.80)	33.26 (33.34)	3.45 (3.52)	15.97 (15.89)	15.67 (15.60)	17.33 (17.30)	9.09 (9.22)
"IIIh			300	76	C ₁₇ H ₂₁ N ₇ O ₂ S ₃ CuCl ₂ (586.04)	34.84 (34.90)	3.60 (3.52)	16.71 (16.68)	16.41 (16.38)	12.09 (12.12)	10.84 (11.00)
"IIIh			289	70	C ₁₇ H ₂₁ N ₇ O ₂ S ₃ HgCl ₂ (723.09)	28.23 (28.30)	2.93 (2.89)	13.56 (13.62)	13.30 (13.35)	9.80 (9.75)	27.70 (28.20)
"IIIh			310	75	C ₁₄ H ₁₆ N ₆ O ₂ S ₄ FeCl ₃ (590.80)	28.46 (28.51)	2.73 (2.80)	14.23 (14.31)	21.71 (21.62)	18.00 (18.08)	9.45 (10.08)
"IIIh			302	68	C ₁₄ H ₁₆ N ₆ O ₂ S ₄ CuCl ₂ (536.02)	29.88 (29.92)	2.86 (2.27)	14.93 (14.97)	22.78 (22.83)	15.59 (15.50)	11.28 (10.98)
"IIIh			290	64	C ₁₄ H ₁₆ N ₆ O ₂ S ₄ HgCl ₂ (700.08)	24.02 (24.10)	2.30 (2.25)	12.01 (12.00)	18.32 (18.28)	10.13 (10.10)	28.65 (29.08)
"IIIh			320	72	C ₁₅ H ₁₈ N ₆ O ₄ S ₃ FeCl ₃ (604.53)	29.80 (30.09)	3.00 (2.78)	13.90 (13.00)	15.91 (16.19)	17.59 (16.98)	9.24 (10.02)
"IIIh			312	64	C ₁₅ H ₁₈ N ₆ O ₄ S ₃ CuCl ₂ (576.98)	31.23 (32.00)	3.14 (2.98)	14.59 (14.00)	16.76 (16.02)	12.29 (11.98)	10.01 (11.20)
"IIIh			301	61	C ₁₅ H ₁₈ N ₆ O ₄ S ₃ HgCl ₂ (714.03)	25.23 (26.03)	2.54 (3.01)	11.77 (11.01)	13.47 (12.98)	9.93 (10.19)	28.09 (27.99)

Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)					
						% C	% H	% N	% S	% Cl	% M
'Tve			295	81	C ₂₈ H ₂₈ N ₁₂ O ₄ S ₆ Fe ₂ Cl ₆ (1113.41)	30.20 (30.30)	2.54 (2.62)	15.10 (15.07)	17.28 (17.32)	19.11 (19.18)	10.03 (10.08)
"TVe			290	75	C ₂₈ H ₂₀ N ₁₂ O ₄ S ₆ Cu ₂ Cl ₄ (1057.88)	31.79 (31.81)	2.67 (2.72)	15.89 (15.92)	18.19 (18.21)	13.41 (13.58)	12.01 (12.10)
""TVe			285	69	C ₂₈ H ₂₈ N ₁₂ O ₄ S ₆ Hg ₂ Cl ₄ (1331.98)	25.25 (25.21)	2.12 (2.02)	12.62 (12.70)	14.44 (14.51)	10.65 (10.77)	30.12 (30.20)
'TVf			208	77	C ₃₀ H ₃₂ N ₁₂ O ₄ S ₆ Fe ₂ Cl ₆ (1141.48)	31.56 (31.62)	2.83 (2.80)	14.73 (14.77)	16.85 (16.90)	18.64 (18.59)	9.78 (9.82)
"TVf			301	72	C ₃₀ H ₃₂ N ₁₂ O ₄ S ₆ Cu ₂ Cl ₄ (1085.94)	33.18 (33.20)	2.97 (2.91)	15.48 (15.39)	17.72 (17.77)	13.06 (13.00)	11.70 (11.79)
""TVf			291	63	C ₃₀ H ₃₂ N ₁₂ O ₄ S ₆ Hg ₂ Cl ₄ (1360.04)	26.49 (26.52)	2.37 (2.40)	12.36 (12.22)	14.15 (14.20)	10.43 (10.38)	29.50 (30.00)
'TVg			309	72	C ₂₄ H ₂₂ N ₁₀ O ₄ S ₈ Fe ₂ Cl ₆ (1095.45)	26.30 (26.27)	2.03 (2.10)	12.79 (12.82)	23.42 (23.35)	19.42 (19.39)	10.19 (10.21)
"TVg			300	68	C ₂₄ H ₂₂ N ₁₀ O ₄ S ₈ Cu ₂ Cl ₄ (1039.92)	27.72 (27.69)	2.13 (2.21)	13.47 (13.52)	24.67 (24.71)	13.04 (13.00)	12.22 (12.30)
""TVg			288	60	C ₂₄ H ₂₂ N ₁₀ O ₄ S ₈ Hg ₂ Cl ₄ (1314.02)	21.90 (21.95)	1.69 (1.60)	10.66 (10.72)	19.52 (19.50)	10.79 (10.81)	30.50 (30.65)

Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)						
						% C	% H	% N	% S	% Cl	% M	
TVh			330	83	C ₂₆ H ₂₆ N ₁₀ O ₈ FeCl ₃ (961.15)	32.48 (33.00)	2.73 (2.59)	14.57 (15.09)	20.02 (19.87)	11.06 (11.19)	5.81 (6.01)	
"TVh			322	76	C ₂₆ H ₂₆ N ₁₀ O ₈ S ₆ CuCl ₂ (933.38)	33.46 (32.71)	2.81 (3.21)	2.81 (2.21)	20.61 (20.01)	7.59 (8.23)	6.81 (7.01)	
"TVh			307	70	C ₂₆ H ₂₆ N ₁₀ O ₈ S ₆ HgCl ₂ (1070.43)	29.17 (31.00)	2.45 (2.30)	2.45 (12.98)	17.97 (17.09)	6.62 (7.28)	18.74 (19.08)	
TVa			308	82	C ₁₈ H ₂₀ N ₈ O ₄ S ₆ Fe ₂ Cl ₆ (929.21)	23.26 (23.30)	2.17 (2.21)	12.06 (11.92)	20.70 (20.68)	22.89 (22.91)	12.02 (12.08)	
"TVa		H	300	75	C ₁₈ H ₂₀ N ₈ O ₄ S ₆ Cu ₂ Cl ₄ (873.68)	24.74 (24.69)	2.31 (2.29)	12.83 (12.91)	22.02 (22.00)	16.23 (16.31)	14.55 (14.78)	
"TVa			292	71	C ₁₈ H ₂₀ N ₈ O ₄ S ₆ Hg ₂ Cl ₄ (1147.78)	18.83 (18.79)	1.76 (1.82)	9.76 (9.81)	16.76 (16.70)	12.36 (13.30)	34.95 (35.00)	
TVb			312	83	C ₂₂ H ₂₄ N ₈ O ₆ S ₆ Fe ₂ Cl ₆ (1013.28)	26.08 (26.12)	2.39 (2.40)	11.06 (11.00)	18.99 (19.00)	20.99 (20.90)	11.02 (11.10)	
"TVb			305	76	C ₂₂ H ₂₄ N ₈ O ₆ S ₆ Cu ₂ Cl ₄ (957.75)	27.58 (27.60)	2.53 (2.60)	11.70 (11.65)	20.09 (20.10)	14.80 (14.73)	13.27 (13.30)	
"TVb			293	69	C ₂₂ H ₂₄ N ₈ O ₆ S ₆ Hg ₂ Cl ₄ (1231.87)	21.45 (21.50)	1.96 (1.90)	9.09 (9.12)	15.62 (15.58)	11.51 (11.48)	32.57 (32.61)	

Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)					
						% C	% H	% N	% S	% Cl	% M
TVc			315	75	C ₂₀ H ₂₄ N ₁₂ O ₄ S ₆ Fe ₂ Cl ₆ (1013.30)	23.70 (23.78)	2.40 (2.35)	16.59 (16.60)	18.98 (18.90)	20.99 (21.00)	11.02 (11.10)
TVc			305	70	C ₂₀ H ₂₄ N ₁₂ O ₄ S ₆ Cu ₂ Cl ₄ (957.77)	25.08 (25.12)	2.50 (2.46)	17.55 (17.50)	20.09 (20.12)	14.80 (14.73)	13.69 (13.72)
TVc			300	65	C ₂₀ H ₂₄ N ₁₂ O ₄ S ₆ Hg ₂ Cl ₄ (1231.78)	19.50 (19.46)	1.96 (1.90)	15.11 (15.20)	15.62 (15.56)	11.50 (11.55)	32.57 (32.62)
TVd			320	80	C ₂₆ H ₂₄ N ₁₂ O ₄ S ₆ Fe ₂ Cl ₆ (1085.36)	28.77 (28.85)	2.23 (2.15)	15.49 (15.67)	17.73 (17.29)	19.60 (19.81)	10.29 (10.31)
TVd			307	73	C ₂₆ H ₂₄ N ₁₂ O ₄ S ₆ Cu ₂ Cl ₄ (1029.83)	30.32 (30.00)	2.35 (2.51)	16.23 (16.40)	18.68 (18.52)	13.77 (13.50)	12.34 (12.46)
TVd			295	66	C ₂₆ H ₂₄ N ₁₂ O ₄ S ₆ Hg ₂ Cl ₄ (1303.93)	23.95 (24.00)	1.86 (1.95)	12.89 (13.00)	14.75 (14.83)	10.88 (11.00)	30.77 (30.81)

PHYSIOLOGICAL ACTIVITY

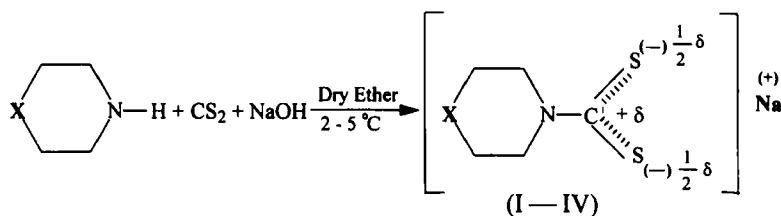
Antibacterial and Antifungal Activity

All the newly synthesized legands and their chelates were tested *in vitro* for antibacterial and antifungal activities which were measured by using the disc-diffusion method^(33,34). The tested compounds were dissolved in sterile N, N-dimethyl formamide (reagent grade) and added at a concentration of 0.5 mg/ disc. (Whatman No. 3 filter paper, 0.5 Cm diameter). The antibacterial spectrum was tested with six strains of bacteria, namely: *Serratia marcescens* (DSM/608), *Bacillus cereus* (DSM 345), *Pseudomonas aeruginosa* (DSM 1299), *Micrococcus roseus* (DSM 348), *Klebsiella pneumoniae* (DSM 581) and *Staphylococcus aureus* (DSM 346). Also, the antifungal effect was tested with three species of fungi, namely: *Aspergillus flavus* (Link Aucc 164), *Penicillium chrysogenum* (thom Aucc 530) and *Alternaria alternata* (Fries Keissler Aucc 1110). The culture medium for bacteria was normal nutrient agar (NA) (composed of beef extract, 3g peptone, 5g agar, 15g/L and adjusted to pH 7 before sterilization at 121 °C for 30 min). Glucose-Czapek's agar medium, (NaNO₃, 2g; KH₂ PO₄, 1g; Mg SO₄. 7H₂O, 0.5g; KCl/ 0.5g. glucose. 10g; agar, 15g/L of distilled water) was used for fungi. The inoculated plates were incubated at 37±1°C for 24–48 h in the case of bacteria and at 28 °C for 7–8 days in the case of fungi. The inhibition zones of microbial growth produced by different compounds were measured³⁵.

RESULTS AND DISCUSSION

On the basis of our previous studies of heterocyclo-substituted azo dye sulfonamide derivatives^{16–32} with observations on their antimicrobial importance prompted us to synthesize a novel series of azo-sulfa drugs derived from N-(piperidino-, morpholino-, mono- and bis piperaziono-) dithiocarbamic acid moieties.^{16,26} The compounds were synthesized via the reaction of 4-[4-heterocyclo-substituted) sulfamoyl and/or sulfonyl] benzene diazonium chlorides with N-(piperidino, morpholino-, piperazino-) dithiocarbamate sodium salts (I – IV) in acid medium to afford 4-[4-heterocyclo-substituted) sulfamoyl and/or sulfonyl] phenyl azo-S-dithiocarbamyl-N-piperidine, N-morpholine, mono-, and bis- N-

piperazine dyes (Ia-h – IV a-h). Heterocyclo-N-dithiocarbamate sodium salt can be represented as:



I	$\frac{\text{X}}{\text{CH}_2}$	Piperidine
II	O	Morpholine
III	NH	Piperazine (mono)
IV	N	Piperazine (bis)

The metal chelates are prepared via the reaction of ligands (Ia-h – IVa-h) with metal chlorides in ethanolic boiling solution (equal-molar ratio) to give iron chelates ('Ia-h – 'IVa-h), copper chelates ("Ia-h – "Va-h) and mercury chelates ("Ia-h – "IVa-h) as new chelated compounds containing heterocyclo-N-dithiocarbamyl-S-azo moieties and heterocyclo-substituted sulfamoyl and/or sulfonyl moieties. The aim was to study their biological activities and to ensure a wide variation in their electronegativity, solubility, antitubercular activity and their chemical properties.

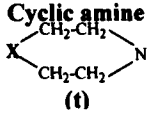
Ligands are reddish to yellowish brown, while their metal chlates are reddish yellow to pale greenish brown crystalline powders, which were confirmed by some representative IR spectra (Table III) and ^1H -NMR spectra (Table IV) along with microanalysis data (Table I,II).

Generally, the synthesized azo compounds displayed a prominent maximum UV absorption at 510–520 nm, in addition to other maxima at different wave-lengths depending upon the structure type of (R) substituents. Comparatively, the UV absorption characteristics are in good agreement with the recently reported data.³¹ However, this absorption maximum has been shifted to slightly lower wave-lengths 455–485 nm for iron, copper and mercury chelates. This hypsochromic shift may be attributed to the contribution of electrons of the chromophore (-N=N-) azo group and chromophore (C=S) thio group of dithiocarbamates in chelate formation.

TABLE III IR Spectra of Some Piperidino-, Morpholino- and mono-, bis- Piperazino- Dithiocarbonyl Azo-Sulpha Drugs and Their Iron(III), Copper(II), Mercury(II) Chelates (Cm^{-1})

Compd. No	$\nu \text{ N=N}$	$\nu \text{ SO}_2$ (<i>asym.</i>)	$\nu \text{ SO}_2$ (<i>sym.</i>)	$\nu \text{ SO}_2$ <i>NH</i>	$\nu \text{ CH}_3$ <i>sulpha</i>	$\nu \text{ C-H}$ <i>Ar</i>	$\nu \text{ C-S}$ $\text{V}-\text{C}-\text{S}$	$\nu \text{ Me-S}$	$\nu \text{ C-H}$ <i>Cyclic Amine</i>	$-\text{C}-\text{N}-\text{S}$	$\nu \text{ N-H}_2$ <i>sulphonamide</i>	$-\text{O CH}_3$
Ia	1595	1355	1165	1375	—	755	1325	—	2700	1295	3280	—
IIa	1575	1345	1150	1362	—	750	1300	355	2775	1250	3200	—
IIIa	1570	1348	1145	1363	—	750	1300	350	2770	1240	3210	—
IVa	1568	1345	1147	1365	—	748	1305	350	2770	1240	3200	—
IVb	1600	1360	1160	1375	2990	755	1320	—	2705	1290	—	—
VIIb	1580	1355	1145	1365	2995	745	1300	355	2780	1250	—	—
VIIIb	1575	1345	1140	1360	2995	745	1300	348	2775	1240	—	—
IXb	1570	1345	1145	1365	2995	450	1305	350	2770	1240	—	—
IVh	1605	1360	1155	1375	—	750	1325	—	2700	1295	—	2875
TVh	1585	1350	1140	1370	—	745	1320	350	2780	1250	—	2865
TVh	1570	1345	1140	1365	—	740	1310	345	2775	1245	—	2860
TVh	1530	1345	1145	1360	—	745	1305	345	2770	1245	—	1865

TABLE IV ¹H-NMR Spectra of Some Piperidino-, Morpholino- and mono-, bis- Piperazino-Dithiocarbamyl Azo-Sulpha Drugs and Their Chelates in CDCl₃ (Chemical Shifts) in δ ppm

Compd. No	Aromatic Protons (m)	SO ₂ NH (s)	CH ₃ . Sulpha (s)	Cyclic amine  (t)	
Ib	7.20 – 7.82 (4H)	8.75 (1H)	2.35 (3H)	X = CH₂ 2.70 – 2.85 (2t, 4H, 2α CH ₂)	-
'Ib	7.40 – 8.08 (4H)	8.70 (1H)	2.30 (3H)	3.55 – 3.75 (2t, 4H, 2β CH ₂)	-
''Ib	7.35 – 8.08 (4H)	8.65 (1H)	2.32 (3H)	3.85 (t, 2H, γCH ₂) piperidine	-
'''Ib	4.70 – 8.08 (4H)	8.65 (1H)	2.30 (3H)		-
IIb	7.51 – 7.75 (4H)	8.72 (1H)	2.25 (3H)	X = O 2.70 – 2.80 (2t, 4H, 2α CH ₂)	-
'IIb	7.25 – 7.85 (4H)	8.70 (1H)	2.20 (3H)	3.35–3.65 (2t, 4H, 2β CH ₂)	-
''IIb	7.30 – 7.80 (4H)	8.68 (1H)	2.20 (3H)	Morpholine	-
'''IIb	7.30 – 7.80 (4H)	8.65 (1H)	2.22 (3H)		-
IIId	6.80–7.00 (3H) 7.50–8.30 (4H)	8.85 (1H)	-		9.95 (1H)
'IIId	6.75–7.15 (3H) 7.60–8.40 (4H)	8.82 (1H)	-	X = NH 2.65–2.78 (2t, 4H, 2α CH ₂)	9.90 (1H)
''IIId	6.70 – 7.20 (3H) 7.85 – 8.50 (4H)	8.75 (1H)	-	3.30 – 3.75 (2t, 4H, 2β CH ₂) Piperazine (mono-)	9.80 (1H)
'''IIId	6.65 – 7.25 (3H) 7.75 – 8.85 (3H)	8.75 (1H)	-		9.85 (1H)

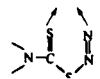
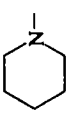
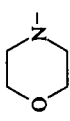
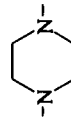
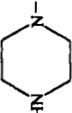
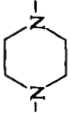
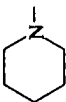
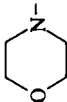
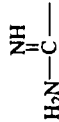
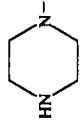
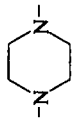
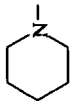
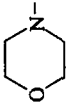
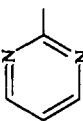
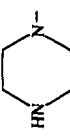
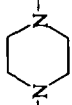
IR spectra of ligands and their chelates confirmed the structures by the presence of this azo group (-N=N-) band at 1565 Cm⁻¹, asym and sym (SO₂ NH) band at 1360 Cm⁻¹, and 1140 Cm⁻¹. In addition, the attachment of the ligands to the Fe⁺³, Cu⁺², Hg⁺² metal ions are manifested by the appearance of two coordinate bands ν (M←S) at 355 Cm⁻¹, and ν (M←N) at 360 Cm⁻¹ through the  dithiocarbamyl group and azo group-N=N- forming more stable six-membered rings than five-membered rings.

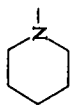
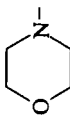
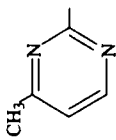
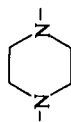
TABLE V Antimicrobial Screening of N-(piperidino-, morpholino-, piperazino-) Dithiocarbamyl Azo-Sulpha Drugs and Their Iron(III), Copper(II) and Mercury(II) Chelates

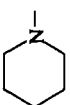
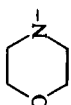
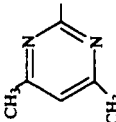
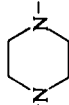
Compd. No.	Cyclic Amine	R	Antibacterial activity						Antifungal activity			
			<i>Serratia marcescens</i> DSM 1608 ^a	<i>Bacillus cereus</i> DSM 345	<i>Pseudo- monas aerugi- nosa</i> DSM 1299	<i>Micro- coccus roseus</i> DSM 348	<i>Klebsiella pneumo- niae</i> DSM 581	<i>Staphyl- lococcus aureus</i> DSM 581	<i>Asper- gillus Link flavus</i> AUGC 164 ^b	<i>Penicillium chrysogenum</i> Thom AUGC 530	<i>Alternaria alternata</i> (Fries) Keissler AUGC 1110	
Ia			7.0 (30)	6.0 (2.0)	5.0 (2.0)	8.0 (3.0)	10.0 (4.0)	9.0 (-ve)	5.8 (-ve)	12.0 (40)	9.5 (2.0)	
'Ia			-ve	5.8	4.1	7.2	8.1	8.5	9.0	11.1	9.0	
"Ia			6.8	-ve	5.0	-ve	5.2	2.8	4.8	9.5	8.5	
'''Ia			10.2	9.2	11.0	9.5	12.2	11.5	10.5	15.5	12.5	
IIa			3.0 (30)	5.6 (2.0)	6.6 (2.0)	7.0 (3.0)	8.0 (4.0)	9.5 (-ve)	9.0 (-ve)	7.5 (4.0)	3.8 (2.0)	
'IIa			8.2	6.0	7.5	6.5	7.8	8.5	10.1	-ve	4.2	
"IIa			7.8	-ve	9.0	-ve	6.6	7.2	9.8	8.2	-ve	
'''IIa			10.2	9.5	12.8	10.0	12.2	14.0	12.8	9.5	10.2	
IIIa		H	4.0 (3.0)	3.0 (2.0)	2.8 (2.0)	7.0 (3.0)	9.0 (4.0)	4.8 (-ve)	5.5 (-ve)	6.0 (4.0)	8.0 (2.0)	
'IIIa			-ve	4.2	3.2	8.2	-ve	5.5	-ve	5.5	7.3	
"IIIa			5.2	-ve	4.3	6.5	7.8	-ve	2.8	-ve	9.5	
'''IIIa			8.8	9.2	8.5	12.5	13.0	10.2	9.5	8.5	13.5	
IVa			7.0 (3.0)	6.0 (2.0)	5.0 (2.0)	8.5 (3.0)	11.0 (4.0)	9.0 (-ve)	8.5 (-ve)	6.0 (4.0)	5.5 (2.0)	
'IVa			6.0	4.0	4.8	7.2	8.6	7.1	6.5	4.6	6.1	
"IVa			-ve	6.5	6.3	8.1	-ve	8.2	7.7	-ve	5.8	
'''IVa			10.0	9.5	8.5	11.2	19.5	10.3	10.1	9.8	10.1	

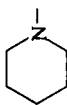
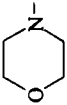
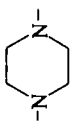
Compd. No.	Cyclic Amine	R	Antibacterial activity					Antifungal activity			
			Serratia marcescens DSM 1608 ^a	Bacillus cereus DSM 345	Pseudomonas aeruginosa DSM 1299	Micrococcus roseus DSM 348	Klebsiella pneumoniae DSM 581	Staphylococcus aureus DSM 581	Aspergillus flavus Link AUC ^b 164 ^b	Penicillium chrysogenum Thom AUC ^c 530	Alternaria alternata (Fries) Keissler AUC ^c 1110
Ib			5.5 (2.0)	4.0 (-ve)	8.0 (0.4)	6.0 (5.0)	7.0 (8.0)	8.5 (8.0)	-ve (-ve)	7.0 (5.0)	-ve (-ve)
IIb			4.2	3.5	7.5	6.2	8.2	8.7	4.1	7.9	3.9
IIIb			5.8	-ve	8.8	7.1	9.1	7.2	-ve	6.1	5.2
IVb			9.1	8.9	11.8	12.2	10.9	11.2	10.2	9.8	8.9
Vb			6.0 (2.0)	2.8 (-ve)	3.0 (0.4)	7.8 (5.0)	9.9 (8.0)	10.2 (8.0)	4.0 (-ve)	5.5 (5.0)	2.0 (-ve)
VIb			5.2	3.0	2.8	5.9	8.7	9.1	5.2	6.1	9.6
VIIb			-ve	4.2	5.6	6.9	8.2	8.7	6.3	-ve	8.9
VIIIb			9.9	10.3	9.85	11.2	12.8	13.9	9.9	10.1	12.8
IXb			10.0 (-ve)	10.0 (-ve)	9.0 (0.4)	10.8 (5.0)	11.2 (8.0)	12.8 (8.0)	-ve (-ve)	6.5 (5.0)	5.5 (-ve)
Xb			8.5	2.0	11.0	11.2	1.0	0.9	6.5	9.5	6.1
XIb			9.6	4.9	12.5	12.9	-ve	13.0	-ve	10.8	-ve
XIIb			12.6	0.1	13.9	14.5	10.1	15.6	10.1	13.2	9.8
XIIIb			6.1 (2.0)	3.8 (-ve)	9.1 (0.4)	7.5 (5.0)	6.0 (8.0)	5.0 (8.0)	4.9 (-ve)	3.0 (5.0)	5.5 (-ve)
XIVb			5.2	3.0	8.2	6.8	4.0	6.2	-ve	4.2	6.0
XVb			7.0	4.0	7.5	9.5	5.5	7.0	3.8	3.0	4.0
XVIb			9.1	10.1	11.8	12.7	9.8	8.9	9.0	10.0	9.9

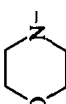
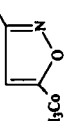
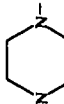
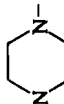
Compd. No.	Cyclic Amine	R	Antibacterial activity						Antifungal activity			
			<i>Serratia marcescens</i> DSM 1608 ^a	<i>Bacillus cereus</i> DSM 345	<i>Pseudo- monas aerugi- nosa</i> DSM 1299	<i>Micro- coccus roseus</i> DSM 348	<i>Klebsiella pneumo- niae</i> DSM 581	<i>Staphyl- lococcus aureus</i> DSM 581	<i>Asper- gillus flavus</i> Link AUCC 164 ^b	<i>Penicillium chrysogenum</i> Thom AUCC 530	<i>Alternaria alternata</i> (Fries) Keissler AUCC 1110	
Ic			5.0 (2.0)	10.5 (-ve)	6.0 (-ve)	11.0 (5.0)	9.0 (7.0)	8.5 (2.0)	12.0 (-ve)	4.0 (-ve)	3.0 (0.4)	
Ic			6.0	7.5	7.5	9.5	8.5	7.0	6.5	5.5	3.5	
Ic			4.0	-ve	5.0	10.0	8.0	8.5	-ve	3.5	-ve	
IIc			8.5	13.5	9.5	13.0	12.0	11.5	13.5	8.5	9.0	
IIc			6.0 (2.0)	9.5 (-ve)	8.5 (-ve)	9.5 (5.0)	9.0 (7.0)	9.5 (2.0)	11.0 (-ve)	5.0 (-ve)	6.0 (0.4)	
IIc			7.0	8.0	9.5	7.5	-ve	8.5	7.5	7.0	7.5	
IIc			4.5	-ve	-ve	5.5	8.0	7.5	-ve	6.5	7.0	
IIIc			8.0	11.0	10.0	12.0	11.5	10.5	12.5	9.5	10.5	
IIIc			7.0 (2.0)	7.0 (-ve)	6.5 (-ve)	8.0 (5.0)	7.5 (7.0)	8.5 (2.0)	7.5 (-ve)	4.0 (-ve)	5.0 (0.4)	
IIIc			5.0	6.0	6.0	7.5	8.5	8.0	8.0	5.5	6.5	
IIIc			3.5	5.0	-ve	6.0	7.0	7.5	7.0	4.5	-ve	
IIIc			8.5	9.0	8.5	10.5	11.0	11.5	9.5	8.5	10.5	
IVc			8.8 (2.0)	6.5 (-ve)	5.5 (-ve)	9.0 (5.0)	9.5 (7.0)	8.0 (2.0)	6.5 (-ve)	5.0 (-ve)	6.0 (0.4)	
IVc			9.0	7.0	2.5	8.0	10.0	8.5	6.0	6.0	8.5	
IVc			1.5	6.5	3.5	7.5	8.5	8.0	-ve	4.0	7.5	
IVc			10.0	9.5	8.5	10.0	12.0	11.0	8.5	9.0	10.5	

Compd. No.	Cyclic Amine	R	Antibacterial activity					Antifungal activity			
			<i>Serratia marcescens</i> DSM 1608 ^a	<i>Bacillus cereus</i> DSM 345	<i>Pseudo-monas aeruginosa</i> DSM 1299	<i>Micro-coccus roseus</i> DSM 348	<i>Klebsiella pneumo-niae</i> DSM 581	<i>Staphyl-lococcus aureus</i> DSM 581	<i>Asper-gillus flavus</i> Link 164 ^b	<i>Penicillium chrysogenum</i> Thom AUCC 530	<i>Alternaria alternata</i> (Fries) Keissler AUCC 1110
IId			4.0 (20)	6.0 (-ve)	9.5 (4.0)	8.0 (5.0)	7.0 (8.0)	6.0 (8.0)	5.5 (-ve)	9.5 (5.0)	8.0 (-ve)
IIId			3.5	5.0	8.5	7.0	7.5	6.5	6.0	8.5	7.0
IIId			-ve	4.0	6.5	6.0	6.5	5.0	-ve	7.0	6.5
IIId			8.0	9.5	10.0	10.5	11.5	9.5	8.5	12.0	10.0
IIId			-ve (20)	4.0 (-ve)	7.5 (4.0)	7.0 (5.0)	8.0 (8.0)	8.0	-ve (-ve)	7.5 (5.0)	5.0 (-ve)
IIId			2.5	-ve	5.5	7.5	7.0	7.5	5.5	8.0	5.0
IIId			-ve	1.5	2.5	2.5	5.5	4.5	-ve	2.8	-ve
IIId			7.5	8.5	0.5	9.5	11.5	12.0	9.5	12.5	9.0
IIId			3.5 (20)	5.0 (-ve)	5.5 (4.0)	6.5 (5.0)	7.0 (8.0)	9.0	2.5 (-ve)	8.5 (5.0)	6.0 (-ve)
IIId			2.5	3.5	-ve	6.0	5.5	8.5	2.0	6.5	-ve
IIId			-ve	2.0	2.5	3.0	-ve	6.5	-ve	5.5	1.5
IIId			7.5	9.5	8.5	9.5	10.5	11.5	7.5	10.5	7.5
IVd			5.0 (20)	8.0 (-ve)	9.5 (4.0)	7.5 (5.0)	9.5 (8.0)	8.0	3.5 (-ve)	0.5 (5.0)	6.0 (-ve)
IVd			4.5	6.5	8.0	7.0	8.5	7.0	-ve	7.0	5.5
IVd			3.5	7.5	5.5	4.5	5.5	4.8	-ve	3.5	-ve
IVd			9.0	10.5	11.5	12.5	11.0	9.0	7.5	0.0	8.5

Compd. No.	Cyclic Amine	R	Antibacterial activity						Antifungal activity			
			<i>Serratia marcescens</i> DSM 1608 ^a	<i>Bacillus cereus</i> DSM 345	<i>Pseudo- monas aerugi- nosa</i> DSM 1299	<i>Micro- coccus roseus</i> DSM 348	<i>Klebsiella pneumo- niae</i> DSM 581	<i>Staphyl- lococcus aureus</i> DSM 581	<i>Asper- gillus Link flavus</i> AUCC 164 ^b	<i>Penicillium chrysogenum</i> Thom AUCC 530	<i>Alternaria alternata</i> (Fries) Keissler AUCC 1110	
Ie			5.0 (2.0)	2.5 (1.0)	3.0 (2.0)	7.3 (6.0)	8.0 (9.0)	5.0 (9.0)	3.0 (-ve)	-ve (-ve)	7.0 (5.0)	
'Ie			5.5	-ve	4.0	8.0	9.0	6.5	2.5	3.0	8.5	
"Ie			-ve	-ve	2.0	5.5	6.5	5.5	-ve	1.5	7.0	
'''Ie			8.5	6.5	8.5	9.5	10.5	9.5	7.0	6.0	10.5	
Ile			9.0 (2.0)	1.5 (1.0)	4.0 (2.0)	6.0 (6.0)	7.0 (9.0)	6.0 (9.0)	2.5 (-ve)	-ve (-ve)	8.5 (5.0)	
'Ile			2.5	-ve	4.5	6.5	8.0	5.5	-ve	2.5	7.0	
"Ile			-ve	-ve	2.5	3.5	6.0	-ve	-ve	-ve	5.5	
'''Ile			7.0	6.5	9.0	10.5	11.5	10.0	6.5	5.5	12.5	
IIle			6.0 (2.0)	3.5 (1.0)	5.0 (2.0)	8.5 (6.0)	9.5 (9.0)	7.0 (9.0)	4.0 (-ve)	2.0 (-ve)	9.0 (5.0)	
'IIle			5.5	3.0	4.5	8.5	8.0	6.0	-ve	1.5	6.5	
"IIle			2.5	-ve	2.0	7.0	6.5	3.0	-ve	-ve	3.5	
'''IIle			8.5	7.0	8.0	10.0	11.5	10.0	6.5	2.5	1.5	
IVe			8.5 (2.0)	4.5 (1.0)	5.5 (2.0)	9.5 (6.0)	10.0 (9.0)	8.5 (9.0)	4.0 (-ve)	3.5 (-ve)	9.0 (5.0)	
'IVe			7.0	2.5	5.0	8.0	9.5	8.0	2.0	1.5	8.5	
"IVe			5.5	3.5	2.0	6.5	7.0	4.0	-ve	0.5	6.0	
'''IVe			11.5	8.5	7.0	12.0	13.0	10.5	7.0	8.5	12.0	

Compd. No.	Cyclic Amine	R	Antibacterial activity					Antifungal activity			
			<i>Serratia marcescens</i> DSM 1608 ^a	<i>Bacillus cereus</i> DSM 345	<i>Pseudo-monas aeruginosa</i> DSM 1299	<i>Micrococcus roseus</i> DSM 348	<i>Klebsiella pneumoniae</i> DSM 581	<i>Staphylococcus aureus</i> DSM 581	<i>Aspergillus flavus</i> Link AUCC 164 ^b	<i>Penicillium chrysogenum</i> Thom AUCC 530	<i>Alternaria alternata</i> (Fries) Keissler AUCC 1110
IIf			5.0 (3.0)	3.0 (2.0)	8.0 (7.0)	6.0 (7.0)	4.0 (7.0)	5.0 (4.0)	8.0 (2.0)	4.0 (-ve)	8.0 (3.0)
IIIf			4.0	2.5	7.0	6.5	5.0	4.5	8.5	4.5	7.5
IIIf			3.0	-ve	5.0	5.5	-ve	3.0	6.0	2.5	6.0
IIIf			9.0	8.0	9.5	10.5	9.0	7.5	10.0	7.0	11.0
IIIf			9.5 (3.0)	2.5 (2.0)	6.5 (7.0)	7.0 (7.0)	6.0 (7.0)	4.5 (4.0)	6.5 (2.0)	3.5 (-ve)	8.0 (3.0)
IIIf			-ve	2.0	6.0	6.0	-ve	4.0	7.0	2.0	7.0
IIIf			-ve	-ve	4.0	5.0	-ve	2.0	4.5	-ve	5.5
IIIf			8.0	7.0	9.0	10.0	8.0	7.5	9.5	7.0	10.0
IIIf			6.0 (3.0)	4.0 (2.0)	8.5 (7.0)	9.0 (7.0)	8.0 (7.0)	6.0 (4.0)	5.0 (2.0)	4.0 (-ve)	9.5 (3.0)
IIIf			5.5	3.0	6.5	8.0	8.5	6.5	-ve	2.0	8.5
IIIf			3.5	-ve	5.5	5.0	7.0	-ve	-ve	-ve	6.0
IIIf			9.5	7.5	10.0	11.5	12.5	9.5	10.0	8.0	12.0
IVf			7.0 (3.0)	5.0 (2.0)	9.0 (7.0)	9.5 (7.0)	8.5 (7.0)	7.5 (4.0)	-ve (2.0)	5.5 (-ve)	9.0 (3.0)
IVf			7.5	3.0	7.5	6.5	5.5	7.0	2.5	4.0	7.5
IVf			3.0	4.5	6.5	8.0	3.5	6.5	-ve	2.0	3.5
IVf			9.5	8.5	10.0	11.5	10.0	12.0	7.5	10.0	12.0

Compd. No.	Cyclic Amine	R	Antibacterial activity					Antifungal activity				
			<i>Serratia marcescens</i> 1608 ^a	<i>Bacillus cereus</i> DSM 345	<i>Pseudo-monas aeruginosa</i> DSM 1299	<i>Micrococcus roseus</i> DSM 348	<i>Klebsiella pneumoniae</i> DSM 581	<i>Staphylococcus aureus</i> DSM 581	<i>Aspergillus flavus</i> Link AUCC 164 ^b	<i>Penicillium chrysogenum</i> Thom AUCC 530	<i>Alternaria alternata</i> (Fries) Keissler AUCC 1110	
Ig			2.0 (-ve)	5.0 (1.0)	4.0 (8.0)	9.5 (8.0)	4.5 (5.0)	6.0 (3.0)	9.0 (3.0)	10.5 (-ve)	12.0 (-ve)	
I'g			2.0	5.5	5.0	10.0	5.5	6.5	9.5	8.5	11.0	
II'g			-ve	-ve	4.0	5.5	3.5	4.0	5.5	-ve	8.0	
III'g			6.5	8.0	9.0	11.0	8.5	7.5	11.5	12.5	13.0	
IIg			1.5 (-ve)	4.0 (1.0)	3.0 (8.0)	10.0 (8.0)	3.5 (5.0)	5.0 (3.0)	8.0 (3.0)	7.0 (-ve)	9.0 (-ve)	
IV'g			-ve	3.0	-ve	9.5	-ve	4.5	7.5	5.5	8.0	
V'g			-ve	-ve	1.0	6.5	-ve	-ve	3.5	-ve	5.5	
VI'g			6.0	7.5	8.5	11.0	7.5	8.0	9.5	8.5	10.5	
VIIg			3.5 (-ve)	6.0 (1.0)	7.0 (8.0)	10.0 (8.0)	7.0 (5.0)	8.0 (3.0)	9.5 (3.0)	11.0 (-ve)	11.5 (-ve)	
VIIG			2.5	5.0	6.5	9.0	5.8	6.0	9.0	7.0	10.0	
VII'g			-ve	-ve	3.0	6.0	2.5	-ve	4.5	-ve	6.5	
VIII'g			7.5	8.5	9.0	11.5	9.0	9.5	10.5	12.5	14.0	
IVg			4.0 (-ve)	6.5 (1.0)	7.5 (8.0)	10.5 (8.0)	7.5 (5.0)	9.0 (3.0)	10.0 (3.0)	10.0 (-ve)	9.5 (-ve)	
IV'g			3.0	5.5	6.0	8.5	6.5	7.0	8.5	8.0	7.0	
VIV'g			1.5	1.5	8.5	5.5	3.0	1.5	6.0	1.5	7.5	
VIV'g			8.0	9.5	10.0	11.0	9.5	10.0	12.0	11.5	10.5	

Compd. No.	Cyclic Amine	R	Antibacterial activity						Antifungal activity			
			<i>Serratia marcescens</i> DSM 1608 ^a	<i>Bacillus cereus</i> DSM 345	<i>Pseudo-monas aeruginosa</i> DSM 1299	<i>Micrococcus roseus</i> DSM 348	<i>Klebsiella pneumoniae</i> DSM 581	<i>Staphylococcus aureus</i> DSM 581	<i>Aspergillus flavus</i> Link AUC ^b 164 ^b	<i>Penicillium chrysogenum</i> Thom AUC ^b 530	<i>Alternaria alternata</i> (Fries) Keissler AUC ^b 1110	
Ih			3.0 (-ve) ^c	8.0 (1.0) ^d	4.0 (8.0)	9.5 (8.0)	6.0 (5.0)	7.0 (3.0)	9.0 (3.0)	9.0 (-ve)	11.0 (-ve)	
Th			3.5	6.5	5.0	9.0	5.5	7.5	9.5	8.0	9.0	
Th			-ve	-ve	2.0	5.0	2.0	4.0	5.5	2.0	3.0	
Th			7.8	9.5	8.0	10.0	9.0	9.5	10.0	12.0	13.5	
IIh			2.0(-ve)	6.5(1.0)	5.0(8.0)	7.0(8.0)	3.5(5.0)	6.5 (3.0)	8.0 (3.0)	8.0 (-ve)	9.0 (-ve)	
Th			-ve	4.0	4.5	6.0	-ve	5.5	7.5	7.5	8.0	
Th			-ve	-ve	4.0	-ve	1.0	-ve	3.5	1.0	2.0	
Th			6.5	8.5	9.0	9.5	7.0	9.0	11.5	10.0	10.5	
IIIh			5.0 (-ve)	9.0 (1.0)	6.0 (8.0)	10.0 (8.0)	7.0 (5.0)	9.5 (3.0)	10.0 (3.0)	8.0 (-ve)	10.0 (-ve)	
Th			5.5	8.5	6.5	8.5	5.5	10.0	7.5	8.5	9.5	
Th			-ve	5.5	-ve	5.5	4.0	7.0	6.0	-ve	5.0	
Th			7.5	10.0	8.5	12.0	9.5	10.0	12.0	10.0	11.5	
IVh			6.5 (-ve)	10.0 (1.0)	9.0 (8.0)	10.0 (8.0)	8.5 (5.0)	10.0 (3.0)	9.5 (3.0)	8.0 (-ve)	10.0 (-ve)	
TVh			5.5	8.5	8.0	9.0	65.5	9.5	7.0	-ve	8.5	
TVh			6.0	5.5	4.0	7.0	7.5	5.5	4.0	1.5	-ve	
TVh			8.5	9.5	12.0	11.5	25.5	11.5	10.5	9.5	12.0	

a. DSM = Deutsche Sammlung von Mikroorganismen (German Collection of microorganisms).

b. AUC = Assiat University Culture Collection.

c. (-ve) = Compound not active biologically.

d. (Values) = Inhibition zones of the free p-aminobenzene sulphonamide derivatives (normal sulpha drugs).

¹HNMR spectra of some representative compounds using deuterated solvent (CDL3) are in good accordance with the proposed structures, and the following signals were assigned for compounds (Ia – '''Ia) as: δ 7.20–7.82 (m, 4H, aromatic protons), δ 8.75 (s, 2H, SO₂NH₂), δ 2.70–2.85 (2t, 4H, 2 α CH₂), δ 3.55–3.70 (2 t, 4H, β .CH₂), δ 3.85 (t, 2H, γ CH₂) for piperidine ring (Table IV). The metal to ligand ratio in both iron, copper, mercury was found to be 1 : 1 as indicated by elementary analysis for nitrogen and sulfur (Table I, 2).

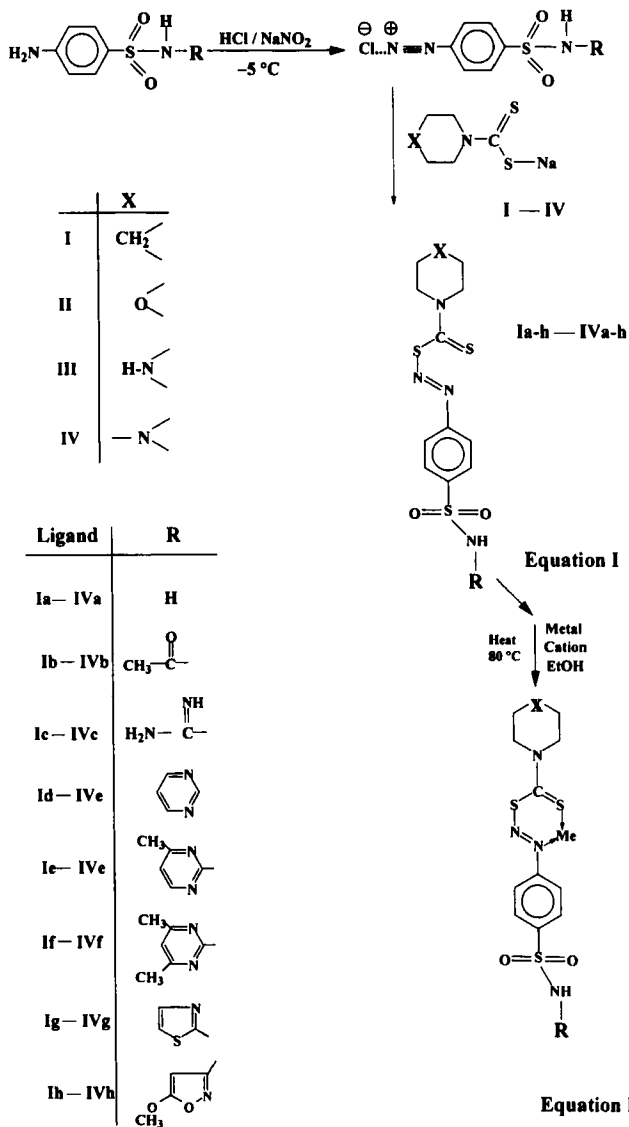
BIOLOGICAL EVALUATION

Antibacterial Activity

The results obtained from antibacterial effects indicated that all synthesized compounds [(Ia – IVa) – (Ih – IVh)] ligands and their chelates [(‘Ia – '''IVa) – (‘Ih – '''IVh)], exhibited pronounced activities against all bacteria used (inhibition zones ranged from 2.0–25.5 mm). On the other hand, ligands of heterocyclo amine dithiocarbamyl azo dye derivatives are comparatively more active and have more remarkable effects than the free p-amino-benzene sulphonamide derivatives (normal sulpha drugs) against *Micrococcus roseus*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*. Furthermore, 1,4-bis-piperazino- dithiocarbamyl ligands and their iron and copper chelates exhibited clear activities against bacteria used. Interestingly, mercury chelates of all ligands [('''Ia – '''IVa) – ('''Ih – '''IVh)] exhibited particularly strong effects against all bacteria used (inhibition zones ranged from 8.5 – 25.5 mm.)

Antifungal Activity

The synthesized compounds (ligands and their chelates) also possessed excellent antifungal activities (inhibition zones ranged from 4.0 – 14.0 mm). Ligands (Ic – IVc), (Id – IVd) and (Ih – IVh), and their chelates [(‘Ic – ‘IVc) – ('''Ic – '''IVc)], [(‘Id – ‘IVd) – ('''Id – '''IVd)] and [(‘Ih – ‘IVh) – ('''Ih – '''IVh)] indicated high activity against *Penicillium chrysogenum*. Furthermore, ligands (Ie – IVe), (If – IVf), (Ig – IVg) and their chelates [(Ie – ‘IVe), ('''Ie – '''IVe)], [(‘If – ‘IVf) – ('''If – '''IVf)] and [(‘Ig – ‘IVg) – ('''Ig – '''IVg)]



('''Ig — '''IVg)) have more potent effects against *Alternaria alternata*. On the other hand, all mercury chelates have potent effects (inhibition zones ranged from 9.0 – 14.0 mm) against all fungi tested (Table V).

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