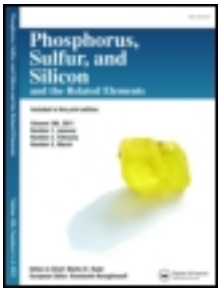

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HETEROCYCLO-SUBSTITUTED SULFA DRUGS: PART XI. NOVEL BIOLOGICALLY ACTIVE N-(PIPERIDINO-, MORPHOLINO-, PIPERAZINO-) DITHIOCARBAMYL-AZO DYES AND THEIR CHELATES

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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 synthesiezed via a reaction of 4-[(4′-heterocyclo-substituted) suflamoyl 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-mrpholino-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 metals[6]. Moreover, the azo compounds occupy a scientific position as excellent azo dyes, and as analytical reagents[10–12]. It is also reported that the replacement of hydrogen of the SO_2NH_2 group by heterocyclic amines enhances the fungicidal and bactericidal activity[13].

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 children[6].

In continuation of our interest in heterocyclo- substituted azo sulfonamide derivatives, we report the synthesis and charactersation of novel azo dye sulfa drugs based on N-piperidino-, N-morpholino-, N-piperazinodithiocarbamate 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. ^{1}H-NMR spectra were recorded on a Varian EM-390 MHz instrument in a suitable deuterated solvent (F_3CCO_2H) 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 diethylether 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′-(guanidinyl 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)

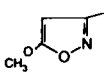
To ice cold solutions of N-piperidino-, N-morpholino., and/or N-piperazino- dithiocarbamate sodium salts (1, 83, 1.85, 1.84, 2.92g, 0.01 mol) in 25 ml of 50% sodium hydroxide solution, a cold hydrochloric acid solution of the diazonium salt was added dropwise with stirring. The reaction mixture was further 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).

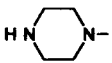
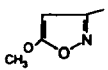
Synthesis of iron(III), copper(II) and mercury(II), azo (piperidin-, morpholin-, mono-, and bis- piperazine-)-N-yl dithiocarbamate chelates (I′a-h – IV′a-h) (I″a-h – IV″a-h) and (I‴a-h – IV‴a-h)

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 throughly with distilled water, dried and recrystallized from ethanol and dried over P_4O_{10} (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)*	*MicrocanalysisCalculated/(Found)*			
						% C	*% H*	*% N*	*% S*
Ia		H -	189	85	$C_{12}H16N_4O_2S_3$	41.80	4.70	16.26	21.90
					(344.64)	(42.08)	(4.65)	(16.30)	(28.10)
Ib			182	88	$C_{14}H18N_4O_3S_3$	43.50	4.69	14.50	24.89
					(386.50)	(44.00)	(5.08)	(14.38)	(24.81)
Ic			192	72	$C_{13}H18N_6O_2S_3$	40.39	4.69	21.75	24.89
					(386.51)	(40.12)	(4.72)	(21.70)	(24.80)
Id			195	70	$C_{16}H_{18}O_2N_6S_3$	45.48	4.29	19.89	22.76
					(422.54)	(45.53)	(4.32)	(19.82)	(22.70)
Ie			210	68	$C_{17}H_{20}N_6O_2S_3$	46.77	4.62	19.25	22.03
					(436.57)	(46.71)	(4.69)	(19.30)	(22.00)
If			215	69	$C_{18}H_{22}N_6O_2S_3$	27.98	4.90	18.65	21.30
					(450.60)	(48.02)	(4.82)	(18.60)	(21.26)
Ig			202	72	$C_{15}H_{17}N_5O_2S_4$	42.13	4.00	16.38	29.99
					(427.29)	(42.20)	(4.02)	(16.41)	(23.02)
Ih			220	70	$C_{16}H_{19}N_5O_4S_3$	43.52	4.34	15.86	21.79
					(441.54)	(43.50)	(4.40)	(15.80)	(21.82)

Compd.No	*Cyclic Amine*	*R*	*mp. °C*	*Yield (%)*	*Molecular.Formula (M W)*	*MicrocanalysisCalculated/(Found)*			
						% C	*% H*	*% N*	*% S*
IIa		H	175	89	C_{11} H14 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} H16 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} H16 N_6 O_3 S_3 (388.49)	37.09 (37.20)	4.15 (4.09)	21.64 (21.70)	24.76 (24.67)
IId			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)
IIf			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)*	*MicrocanalysisCalculated/(Found)*			
						% C	*% H*	*% N*	*% S*
IIIa		H	190	86	C_{11} H15 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} H17 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} H17 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)

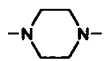
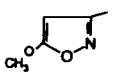
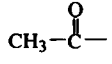
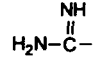
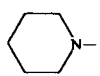
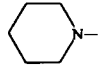
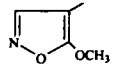
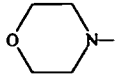
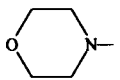
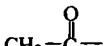
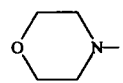
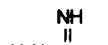
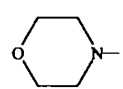
Compd.No	*Cyclic Amine*	*R*	*mp. °C*	*Yield (%)*	*Molecular.Formula (M W)*	*MicrocanalysisCalculated/(Found)*			
						% C	*% H*	*% N*	*% S*
IVa		H	218	90	$C_{18}H20N_8O_4S_6$ (604.78)	35.75 (35.80)	3.30 (3.38)	18.53 (18.60)	31.80 (13.72)
IVb			224	87	$C_{22}H24N_8O_6S_6$ (688.85)	38.36 (38.41)	3.50 (3.43)	16.27 (16.35)	27.93 (27.86)
IVc			230	82	$C_{20}H24N_{12}O_4S_3$ (688.87)	34.87 (34.90)	3.50 (3.53)	24.40 (24.41)	27.93 (27.90)
IVd			236	78	$C_{26}H_{24}N_{12}O_4S_6$ (760.39)	41.04 (41.10)	3.18 (3.20)	22.09 (22.05)	25.28 (25.22)
IVe			228	75	$C_{28}H_{28}N_{12}O_4S_6$ (788.98)	42.62 (42.60)	3.58 (3.60)	21.13 (21.27)	24.38 (24.40)
IVf			240	70	$C_{30}H_{32}N_{12}O_4S_6$ (817.04)	44.09 (44.12)	3.95 (4.05)	20.57 (20.61)	23.55 (23.50)
IVg			233	71	$C_{24}H_{22}N_{10}O_4S_8$ (771.02)	37.38 (37.40)	2.87 (2.95)	18.17 (18.10)	33.27 (33.20)
IVh			243	78	$C_{26}H_{26}N_{10}O_8S_6$ (798.93)	39.09 (39.10)	3.28 (3.22)	17.53 (17.51)	24.08 (24.10)

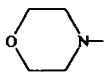
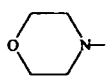
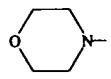
TABLE II Physical and Analytical Data of Dithiocarbamyl Heterocycloamine Azo Dye Iron(III), Copper(II), Mercury(II) Chelates

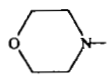
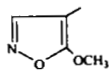
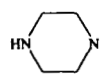
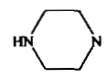
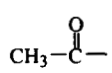
Compd. No	*Cyclic Amine*	*R*	*mp. °C*	*Yield (%)*	*Molecular Formula (M W)*	*Microanalysis Calculated / (Found)*					
						% C	*% H*	*% N*	*% S*	*% Cl*	*% M*
'Ia		H	292	85	C_{12} H16 N4 O_2 S_3Fe Cl_3	28.43	3.20	11.05	18.98	20.99	11.02
					(506.86)	(28.35)	(3.15)	(11.15)	(18.90)	(21.05)	(10.89)
"Ia			251	75	C_{12} H16 N4 O_2 S_3Cu Cl_2	30.08	3.40	11.69	20.08	14.80	13.26
					(479.09)	(30.00)	(3.32)	(11.70)	(20.00)	(14.72)	(13.88)
"'Ia			268	87	C_{12} H16 N4 O_2 S_3Hg Cl_2	23.40	2.60	9.09	15.60	11.51	32.56
					(616.14)	(23.35)	(2.55)	(9.00)	(15.68)	(11.57)	(33.26)
'Ib			295	80	C_{14} H_{18} N4 O_3 S_3 Fe Cl_3	30.60	3.30	10.20	17.53	19.39	10.18
					(548.72)	(30.55)	(3.38)	(10.18)	(17.62)	(19.42)	(11.21)
"Ib			285	85	C_{14} H_{18} N4 O_3 S_3 Cu Cl_2	32.28	3.48	10.76	18.46	13.61	12.20
					(520.95)	(32.32)	(3.52)	(10.70)	(18.52)	(13.55)	(12.67)
"'Ib			273	78	C_{14} H_{18} N4 O_3 S_3 Hg Cl_2	25.55	2.76	8.50	14.60	10.78	30.48
					(658.00)	(25.60)	(2.70)	(8.58)	(14.52)	(10.82)	(31.01)
'Ic			301	78	C_{13} H_{18} N6 O_2 S_3 Fe Cl_3	28.45	3.30	15.32	17.53	19.38	10.18
					(548.73)	(28.50)	(3.25)	(15.38)	(17.50)	(19.42)	(10.29)
"Ic			295	71	C_{13} H_{18} N6 O_2 S_3 Cu Cl_2	29.97	3.48	16.13	18.46	13.61	12.19
					(520.96)	(29.92)	(3.52)	(16.20)	(18.52)	(13.57)	(11.98)
"'Ic			287	66	C_{13} H_{18} N6 O_2 S_3 Hg Cl_2	23.73	2.76	12.77	14.62	10.78	30.48
					(658.01)	(23.67)	(2.80)	(12.70)	(14.68)	(10.82)	(31.21)

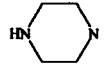
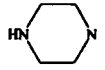
Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)					
						% C	% H	% N	% S	% Cl	% M
'Id			305	78	$C_{16}H_{18}N6O_2S_3FeCl_3$	34.49	3.10	14.37	16.45	18.19	9.55
					(584.75)	(35.00)	(3.00)	(14.41)	(16.58)	(18.09)	(10.00)
''Id			295	70	$C_{12}H_{16}N6O_2S_3CuCl_2$	34.49	3.26	15.09	17.27	12.73	11.41
					(557.08)	(34.87)	(3.46)	(15.12)	(17.19)	(12.93)	(11.67)
'''Id			280	73	$C_{16}H_{18}N6O_2S_3HgCl_2$	27.69	2.61	12.11	13.86	10.22	28.90
					(694.04)	(28.00)	(2.50)	(12.10)	(13.67)	(10.11)	(29.00)
'Ie			295	75	$C_{17}H_{20}N6O_6S_3FeCl_3$	34.10	3.37	14.04	16.06	17.76	9.33
					(598.78)	(34.00)	(3.87)	(14.00)	(16.00)	(18.02)	(9.56)
''Ie			287	68	$C_{17}H_{20}N6O_2S_3CuCl_2$	35.76	3.53	14.72	16.85	12.42	11.28
					(571.02)	(35.50)	(3.72)	(14.82)	(17.00)	(12.61)	(11.32)
'''Ie			280	65	$C_{17}H_{20}N6O_3S_3HgCl_2$	28.83	2.85	11.87	13.58	10.02	28.33
					(708.07)	(29.00)	(2.29)	(11.92)	(13.88)	(10.00)	(28.00)
'If			285	79	$C_{18}H_{22}N6O_2S_3FeCl_3$	35.28	3.62	13.72	15.70	17.36	9.10
					(612.82)	(35.32)	(3.60)	(13.68)	(15.74)	(13.29)	(9.00)
''If			279	82	$C_{18}H_{22}N6O_2S_3CuCl_2$	36.95	3.79	14.37	16.44	12.12	10.86
					(585.05)	(37.01)	(3.71)	(14.40)	(16.40)	(12.10)	(11.00)
'''If			270	70	$C_{18}H_{22}N6O_2S_3HgCl_2$	29.94	3.07	11.64	13.30	9.82	27.78
					(722.10)	(30.01)	(3.10)	(11.70)	(13.22)	(9.89)	(28.00)

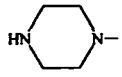
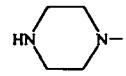
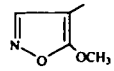
Compd. No	*Cyclic Amine*	*R*	*mp. °C*	*Yield (%)*	*Molecular Formula (M W)*	*Microanalysis Calculated / (Found)*					
						% C	*% H*	*% N*	*% S*	*% Cl*	*% M*
'Ig			301	77	$C_{15}H_{17}N5O_2S_4FeCl_3$	30.54	2.90	1188	21.75	18.02	9.47
					(589.81)	(30.50)	(2.82)	(11.92)	(21.82)	(17.28)	(9.58)
''Ig			290	73	$C_{15}H_{17}N5O_2S_4CuCl_2$	32.05	3.05	12.46	22.80	12.60	11.30
					(62.04)	(3.12)	(3.12)	(12.40)	(22.75)	(12.63)	(11.50)
'''Ig			282	65	$C_{15}H_{17}N5O_2S_4HgCl_2$	25.77	2.45	10.02	18.35	10.14	28.69
					(699.09)	(25.82)	(2.50)	(10.12)	(18.28)	(10.20)	(28.81
'Ih			298	78	$C_{16}H_{19}N5O_4S_3FeCl_3$	31.83	3.17	11.59	15.93	17.62	9.25
					(603.76)	(31.10)	(2.95)	(11.80)	(15.12)	(16.97)	(9.00)
''Ih			290	71	$C_{16}H_{19}N5O_4S_3UCl_2$	33.36	3.33	12.16	16.70	12.10	9.695
					(575.99)	(32.76)	(2.87)	(11.09)	(5.95)	(11.82)	(9.92)
'''Ih			282	65	$C_{16}H_{19}N5O_4S_3HgCl_2$	26.95	2.69	9.82	13.49	9.94	28.13
					(713.04)	(27.15)	(3.37)	(9.31)	(12.89)	(10.15)	(28.70)
'IIa			278	81	$C_{11}H_{14}N4O_3S_3FeCl_3$	25.97	2.77	11.02	18.90	20.90	10.98
					(508.66)	(26.01)	(2.08)	(11.10)	(18.96)	(20.99)	(11.12)
''IIa		H	283	76	$C_{11}H_{14}N4O_3S_3CuCl_2$	27.47	2.90	11.65	20.00	14.75	13.20
					(480.89)	(27.52)	(2.85)	(11.72)	(19.89)	(14.82)	(12.98)
'''IIa			268	70	$C_{11}H_{14}N4O_3S_3HgCl_2$	21.38	2.28	9.07	15.57	11.48	32.46
					(617.94)	(21.42)	(2.32)	(9.00)	(15.62)	(11.52)	(33.18)

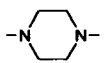
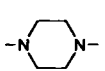
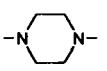
Compd. No	*Cyclic Amine*	*R*	*mp. °C*	*Yield (%)*	*Molecular Formula (M W)*	*Microanalysis Calculated / (Found)*					
						% C	*% H*	*% N*	*% S*	*% Cl*	*% M*
'IIb			287	83	$C_{13}H_{16}N4O_4S_3FeCl_3$	28.35	2.90	10.17	17.47	19.32	10.14
					(550.69)	(28.40)	(2.98)	(10.21)	(17.40)	(19.28)	(10.72)
''IIb			280	70	$C_{13}H_{16}N4O_4S_3CuCl_2$	29.86	3.08	10.71	18.39	13.56	12.15
					(522.93)	(29.91)	(3.12)	(10.69)	(18.42)	(13.50)	(12.29)
'''IIb			272	65	$C_{13}H_{16}N4O_4S_3HgCl_2$	23.66	2.44	8.49	14.57	10.74	30.39
					(559.98)	(23.60)	(2.50)	(8.52)	(14.50)	(10.66)	(30.98)
'IIc			269	71	$C_{12}H_{16}N6O_3S_3FeCl_3$	26.17	2.90	15.72	17.47	19.32	10.14
					(550.71)	(26.20	(2.85)	(15.65)	(17.53)	(19.28)	(9.98)
''IIc			275	78	$C_{12}H_{16}N6O_2S_3CuCl_2$	27.56	3.08	16.07	18.39	13.56	12.15
					(522.94)	(27.50)	(3.00)	(16.10)	(18.42)	(13.50)	(12.89)
'''IIc			260	70	$C_{12}H_{16}N6O_3S_3HgCl_2$	21.84	2.44	12.77	14.57	10.70	30.39
					(559.99)	(21.76)	(2.51)	(12.70)	(14.49)	(10.68)	(30.91)
'IId			301	75	$C_{15}H_{16}N6O_3S_3FeCl_3$	30.70	2.75	14.33	16.39	18.13	9.52
					(586.73)	(31.01)	(2.91)	(14.56)	(16.71)	(18.31)	(9.71)
''IId			285	70	$C_{15}H_{16}N6O_3S_3CuCl_2$	32.23	2.89	15.04	17.21	12.69	11.37
					(558.97)	(32.51)	(3.11)	(15.00)	(17.01)	(12.91)	(11.51)
'''IId			271	65	$C_{15}H_{16}N6O_3S_3HgCl_2$	25.88	2.32	12.08	13.82	10.19	28.80
					(696.02)	(26.11)	(2.52)	(12.00)	(14.00)	(10.30)	(29.00)

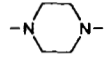
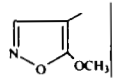
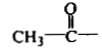
Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)					
						% C	% H	% N	% S	% Cl	% M
'IIe			305	80	$C_{16}H_{18}N6O_3S_3FeCl_3$	31.99	3.02	13.99	16.01	17.71	9.30
					(600.75)	(32.21)	(3.00)	(14.00)	(16.00)	(17.91)	(9.00)
''IIe			290	82	$C_{16}H_{18}N6O_3S_3CuCl_2$	33.54	3.17	14.67	16.78	12.38	11.09
					(572.99)	(33.75)	(3.10)	(14.73)	(17.00)	(12.42)	(11.11)
'''IIe			278	89	$C_{16}H_{18}N6O_3S_3HgCl_2$	27.06	2.55	11.84	13.55	9.99	28.50
					(710.04)	(27.11)	(3.00)	(11.84)	(13.83)	(10.00)	(29.00)
'IIf			295	82	$C_{17}H_{20}N6O_3S_3FeCl_3$	33.21	3.28	13.67	15.65	17.30	9.08
					(614.79)	(33.18)	(3.35)	(13.60)	(15.58)	(17.35)	(9.11)
''IIf			287	71	$C_{17}H_{20}N6O_3S_3CuCl_2$	34.78	3.40	14.30	16.39	12.08	10.80
					(587.02)	(34.70)	(3.48)	(14.29)	(16.42)	(12.00)	10.99
'''IIf			271	65	$C_{17}H_{20}N6O_3S_3HgCl_2$	28.20	2.80	11.60	13.28	9.79	27.70
					(724.07)	(28.25)	(2.82)	(11.56)	(13.38)	(9.80)	(27.99)
'IIg			307	72	$C_{14}H_{15}N5O_3S_4FeCl_3$	28.40	2.56	11.84	21.67	17.97	9.44
					(591.78)	(28.35)	(2.61)	(11.90)	(21.72)	(17.90)	(9.67)
''IIg			296	68	$C_{14}H_{15}N5O_3S_4CuCl_2$	29.80	2.68	12.42	22.74	12.44	11.27
					(564.01)	(29.75)	(2.73)	(12.38)	(22.68)	(12.51)	(11.50)
'''IIg			280	78	$C_{14}H_{15}N_5O_3S_4HgCl_2$	23.98	2.16	9.99	18.30	10.11	28.60
					(701.06)	(23.91)	(2.21)	(10.01)	(18.22)	(10.19)	(29.87)

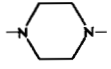
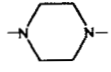
Compd. No	*Cyclic Amine*	*R*	*mp. °C*	*Yield (%)*	*Molecular Formula (M W)*	*Microanalysis Calculated / (Found)*					
						% C	*% H*	*% N*	*% S*	*% Cl*	*% M*
'IIh			305	80	$C_{15}H_{17}N5O_3S_3FeCl_3$	29.89	2.83	11.56	15.88	17.56	9.21
					(605.74)	(29.18)	(3.31)	(11.92)	(15.01)	(18.12)	(8.89)
''IIh			292	73	$C_{15}H_{17}N5O_5S_3CuCl_2$	31.17	2.94	12.14	16.69	12.28	10.99
					(577.97)	(32.01)	(3.11)	(13.01)	(15.75)	(11.98)	(10.28)
'''IIh			280	68	$C_{15}H_{17}N5O_5S_3HgCl_2$	25.20	2.40	9.81	12.45	9.92	28.05
					(715.02)	(26.00)	(3.25)	(8.89)	(12.87)	(10.35)	(27.91)
'IIIa		H	308	68	$C_{11}H_{15}N_5O_3S_3FeCl_3$	26.02	2.98	13.80	18.95	20.95	11.00
					(507.68)	(26.12)	3.00	(13.72)	(19.00)	(20.87)	(11.08)
''IIIa			301	62	$C_{11}H_{15}N_5O_2S_3CuCl_2$	27.53	3.15	14.60	20.00	14.78	13.20
					(479.91)	(27.49)	(3.21)	(14.57)	(19.93)	(14.81)	(13.87)
'''IIIa			295	70	$C_{11}H_{15}N_5O_2S_3HgCl_2$	21.40	2.45	11.35	15.59	11.90	32.50
					(616.96)	(21.36)	(2.52)	(11.40)	(15.60)	(11.81)	(23.08)
'IIIb			310	72	$C_{13}H_{17}N_5O_3S_3FeCl_3$	28.40	3.10	12.74	17.50	19.31	10.16
					(549.72)	(28.47)	(3.08)	(12.69)	(17.45)	(19.37)	(9.97)
''IIIb			300	78	$C_{13}H_{17}N_5O_3S_3CuCl_2$	29.90	3.28	13.42	18.43	13.58	12.17
					(521.95)	(30.01)	(3.31)	(13.35)	(18.40)	(13.61)	(12.71)
'''IIIb			290	68	$C_{13}H_{17}N_5O_3S_3HgCl_2$	23.69	2.60	10.63	14.60	10.76	30.44
					(659.00)	(23.80)	(2.53)	(10.70)	(14.55)	(10.82)	(31.01)

Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)					
						% C	% H	% N	% S	% Cl	% M
'IIIc			300	65	$C_{12}H_{17}N_7O_2S_3FeCl_3$	26.22	3.12	17.84	17.50	19.35	10.16
					(549.72)	(26.30)	(3.10)	(17.91)	(17.58)	(19.40)	(9.98)
"IIIc			292	69	$C_{12}H_{17}N_7O_2S_3CuCl_2$	27.60	3.28	18.79	18.43	13.58	12.16
					(521.96)	(27.55)	(3.37)	(18.81)	(18.40)	(13.62)	(12.56)
"'IIIc			287	73	$C_{12}H_{17}N_7O_2S_3HgCl_2$	21.87	2.60	14.88	14.60	10.76	30.44
					(659.01)	(21.90)	(2.53)	(14.80)	(14.58)	(10.82)	(31.01)
'IIId			315	70	$C_{15}H_{17}N_7O_2S_3FeCl_3$	30.76	2.93	16.74	16.42	18.16	9.50
					(585.75)	(31.21)	(3.22)	(17.12)	(15.98)	(18.62)	(10.32)
"IIId			305	63	$C_{15}H_{17}N_7O_2S_3CuCl_2$	32.29	3.07	17.57	17.24	12.71	11.39
					(557.98)	(33.12)	(2.91)	(17.89)	(16.89)	(13.11)	(11.95)
"'IIId			290	65	$C_{15}H_{17}N_7O_2S_3HgCl_2$	25.92	3.47	14.11	13.84	10.20	38.86
					(695.03)	(26.21)	(3.21)	(13.81)	(14.29)	(9.98)	(38.09)
'IIIe			320	78	$C_{16}H_{19}N_7O_2S_3FeCl_3$	32.04	3.19	16.35	16.04	17.73	9.30
					(599.77)	(32.77)	(2.99)	(16.89)	(15.88)	(18.12)	(10.08)
"IIIe			309	70	$C_{16}H_{19}N_7O_2CuCl_2$	33.59	3.35	17.14	16.82	12.40	11.11
					(572.00)	(34.12)	(3.89)	(17.00)	(17.22)	(11.98)	(12.01)
"'IIIe			295	72	$C_{16}H_{19}N_7O_2S_3HgCl_2$	27.10	2.70	13.83	13.57	10.00	28.28
					(709.05)	(26.98)	(3.30)	(14.21)	(14.21)	(10.82)	(27.99)

Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)					
						% C	% H	% N	% S	% Cl	% M
'IIIf			315	80	$C_{17}H_{21}N_7O_2S_3FeCl_3$	33.26	3.45	15.97	15.67	17.33	9.09
					(613.80)	(33.34)	(3.52)	(15.89)	(15.60)	(17.30)	(9.22)
''IIIf			300	76	$C_{17}H_{21}N_7O_2S_3CuCl_2$	34.84	3.60	16.71	16.41	12.09	10.84
					(586.04)	(34.90)	(3.52)	(16.68)	(16.38)	(12.12)	(11.00)
'''IIIf			289	70	$C_{17}H_{21}N_7O_2S_3HgCl_2$	28.23	2.93	13.56	13.30	9.80	27.70
					(723.09)	(28.30)	(2.89)	(13.62)	(13.35)	(9.75)	(28.20)
'IIIh			310	75	$C_{14}H_{16}N_6O_2S_4FeCl_3$	28.46	2.73	14.23	21.71	18.00	9.45
					(590.80)	(28.51)	(2.80)	(14.31)	(21.62)	(18.08)	(10.08)
''IIIh			302	68	$C_{14}H_{16}N_6O_2S_4CuCl_2$	29.88	2.86	14.93	22.78	15.59	11.28
					(536.02)	(29.92)	(2.27)	(14.97)	(22.83)	(15.50)	(10.98)
'''IIIh			290	64	$C_{14}H_{16}N_6O_2S_4HgCl_2$	24.02	2.30	12.01	18.32	10.13	28.65
					(700.08)	(24.10)	(2.25)	(12.00)	(18.28)	(10.10)	(29.08)
'IIIh			320	72	$C_{15}H_{18}N_6O_4S_3FeCl_3$	29.80	3.00	13.90	15.91	17.59	9.24
					(604.53)	(30.09)	(2.78)	(13.00)	(16.19)	(16.98)	(10.02)
''IIIh			312	64	$C_{15}H_{18}N_6O_4S_3CuCl_2$	31.23	3.14	14.59	16.76	12.29	10.01
					(576.98)	(32.00)	(2.98)	(14.00)	(16.02)	(11.98)	(11.20)
'''IIIh			301	61	$C_{15}H_{18}N_6O_4S_3HgCl_2$	25.23	2.54	11.77	13.47	9.93	28.09
					(714.03)	(26.03)	(3.01)	(11.01)	(12.98)	(10.19)	(27.99)

Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)					
						% C	% H	% N	% S	% Cl	% M
'IVe			295	81	$C_{28}H_{28}N_{12}O_4S_6Fe_2Cl_6$	30.20	2.54	15.10	17.28	19.11	10.03
					(1113.41)	(30.30)	(2.62)	(15.07)	(17.32)	(19.18)	(10.08)
''IVe			290	75	$C_{28}H_{20}N_{12}O_4S_6Cu_2Cl_4$	31.79	2.67	15.89	18.19	13.41	12.01
					(1057.88)	(31.81)	(2.72)	(15.92)	(18.21)	(13.58)	(12.10)
'''IVe			285	69	$C_{28}H_{28}N_{12}O_4S_6Hg_2Cl_4$	25.25	2.12	12.62	14.44	10.65	30.12
					(1331.98)	(25.21)	(2.02)	(12.70)	(14.51)	(10.77)	(30.20)
'IVf			208	77	$C_{30}H_{32}N_{12}O_4S_6Fe_2Cl_6$	31.56	2.83	14.73	16.85	18.64	9.78
					(1141.48)	(31.62)	(2.80)	(14.77)	(16.90)	(18.59)	(9.82)
''IVf			301	72	$C_{30}H_{32}N_{12}O_4S_6Cu_2Cl_4$	33.18	2.97	15.48	17.72	13.06	11.70
					(1085.94)	(33.20)	(2.91)	(15.39)	(17.77)	(13.00)	(11.79)
'''IVf			291	63	$C_{30}H_{32}N_{12}O_4S_6Hg_2Cl_4$	26.49	2.37	12.36	14.15	10.43	29.50
					(1360.04)	(26.52)	(2.40)	(12.22)	(14.20)	(10.38)	(30.00)
'IVg			309	72	$C_{24}H_{22}N_{10}O_4S_8Fe_2Cl_6$	26.30	2.03	12.79	23.42	19.42	10.19
					(1095.45)	(26.27)	(2.10)	(12.82)	(23.35)	(19.39)	(10.21)
''IVg			300	68	$C_{24}H_{22}N_{10}O_4S_8Cu_2Cl_4$	27.72	2.13	13.47	24.67	13.04	12.22
					(1039.92)	(27.69)	(2.21)	(13.52)	(24.71)	(13.00)	(12.30)
'''IVg			288	60	$C_{24}H_{22}N_{10}O_4S_8Hg_2Cl_4$	21.90	1.69	10.66	19.52	10.79	30.50
					(1314.02)	(21.95)	(1.60)	(10.72)	(19.50)	(10.81)	(30.65)

Compd. No	Cyclic Amine	R	mp. °C	Yield (%)	Molecular Formula (M W)	Microanalysis Calculated / (Found)					
						% C	% H	% N	% S	% Cl	% M
'IVh			330	83	$C_{26}H_{26}N_{10}O_8S_6FeCl_3$	32.48	2.73	14.57	20.02	11.06	5.81
					(961.15)	(33.00)	(2.59)	(15.09)	(19.87)	(11.19)	(6.01)
"IVh			322	76	$C_{26}H_{26}N_{10}O_8S_6CuCl_2$	33.46	2.81	2.81	20.61	7.59	6.81
					(933.38)	(32.71)	(3.21)	(2.21)	(20.01)	(8.23)	(7.01)
"'IVh			307	70	$C_{26}H_{26}N_{10}O_8S_6HgCl_2$	29.17	2.45	2.45	17.97	6.62	18.74
					(1070.43)	(31.00)	(2.30)	(12.98)	(17.09)	(7.28)	(19.08)
'IVa			308	82	$C_{18}H_{20}N_8O_4S_6Fe_2Cl_6$	23.26	2.17	12.06	20.70	22.89	12.02
					(929.21)	(23.30)	(2.21)	(11.92)	(20.68)	(22.91)	(12.08)
"IVa		H	300	75	$C_{18}H_{20}N_8O_4S_6Cu_2Cl_4$	24.74	2.31	12.83	22.02	16.23	14.55
					(873.68)	(24.69)	(2.29)	(12.91)	(22.00)	(16.31)	(14.78)
"IVa			292	71	$C_{18}H_{20}N_8O_4S_6Hg_2Cl_4$	18.83	1.76	9.76	16.76	12.36	34.95
					(1147.78)	(18.79)	(1.82)	(9.81)	(16.70)	(13.30)	(35.00)
'IVb			312	83	$C_{22}H_{24}N_8O_6S_6Fe_2Cl_6$	26.08	2.39	11.06	18.99	20.99	11.02
					(1013.28)	(26.12)	(2.40)	(11.00)	(19.00)	(20.90)	(11.10)
"IVb			305	76	$C_{22}H_{24}N_8O_6S_6Cu_2Cl_4$	27.58	2.53	11.70	20.09	14.80	13.27
					(957.75)	(27.60)	(2.60)	(11.65)	(20.10)	(14.73)	(13.30)
"'IVb			293	69	$C_{22}H_{24}N_8O_6S_6Hg_2Cl_4$	21.45	1.96	9.09	15.62	11.51	32.57
					(1231.87)	(21.50)	(1.90)	(9.12)	(15.58)	(11.48)	(32.61)

Compd. No	*Cyclic Amine*	*R*	*mp. °C*	*Yield (%)*	*Molecular Formula (M W)*	*Microanalysis Calculated / (Found)*					
						% C	*% H*	*% N*	*% S*	*% Cl*	*% M*
'IVc			315	75	$C_{20}H_{24}N_{12}O_4S_6Fe_2Cl_6$ (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)
''IVc			305	70	$C_{20}H_{24}N_{12}O_4S_6Cu_2Cl_4$ (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)
'''IVc			300	65	$C_{20}H_{24}N_{12}O_4S_6Hg_2Cl_4$ (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)
'IVd			320	80	$C_{26}H_{24}N_{12}O_4S_6Fe_2Cl_6$ (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)
''IVd			307	73	$C_{26}H_{24}N_{12}O_4S_6Cu_2Cl_4$ (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)
'''IVd			295	66	$C_{26}H_{24}N_{12}O_4S_6Hg_2Cl_4$ (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

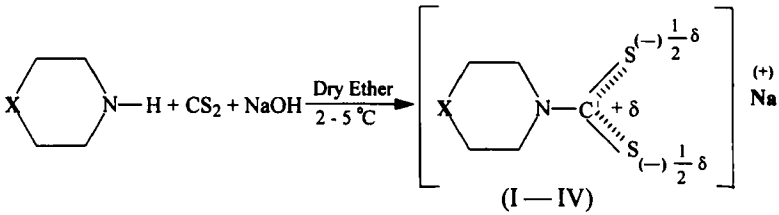
Antibacterial and Antifungal Activity

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 marcescems (DSM/608), Bacillus cereus (DSM 345), Pseudomonas aerginosa (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, ($NaNO_3$, 2g; KH_2 PO_4, 1g; Mg SO_4. $7H_2O$, 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 fangi. The inhibition zones of microbial growth produced by different compounds were measured[35].

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 chorides 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 — IV)

I	$\frac{X}{CH_2}$	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 ^{1}H-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-lengthes 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- Dithiocarbamyl Azo-Sulpha Drugs and Their Iron(III), Copper(II), Mercury(II) Chelates (Cm^{-1})

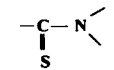
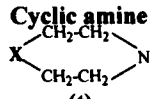
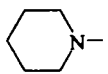
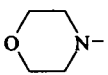
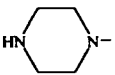
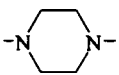
Compd. No	ν *N=N*	ν *SO_2 (asym.)*	ν *SO_2 (sym.)*	ν *SO_2 NH*	ν *CH_3- sulpha*	ν *C-H Ar*	ν 	ν *Me-S*	ν *C-H Cyclic Amine*		ν *N-H_2 sulphonamise*	*-O CH_3*
Ia	1595	1355	1165	1375	–	755	1325	–	2700	1295	3280	–
′Ia	1575	1345	1150	1362	–	750	1300	355	2775	1250	3200	–
″Ia	1570	1348	1145	1363	–	750	1300	350	2770	1240	3210	–
‴Ia	1568	1345	1147	1365	–	748	1305	350	2770	1240	3200	–
IIb	1600	1360	1160	1375	2990	755	1320	–	2705	1290	–	–
′IIb	1580	1355	1145	1365	2995	745	1300	355	2780	1250	–	–
′IIb	1575	1345	1140	1360	2995	745	1300	348	2775	1240	–	–
‴IIb	1570	1345	1145	1365	2995	450	1305	350	2770	1240	–	–
IVh	1605	1360	1155	1375	–	750	1325	–	2700	1295	–	2875
′IVh	1585	1350	1140	1370	–	745	1320	350	2780	1250	–	2865
″IVh	1570	1345	1140	1365	–	740	1310	345	2775	1245	–	2860
‴IVh	1530	1345	1145	1360	–	745	1305	345	2770	1245	–	1865

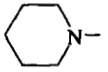
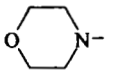
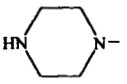
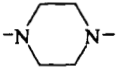
TABLE IV 1H-NMR Spectra of Some Piperidino-, Morpholino- and mono-, bis- Piperazino-Dithiocarbamyl Azo-Sulpha Drugs and Their Chelates in $CDCl_3$ (Chemical Shifts) in δ ppm

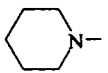
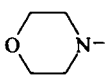
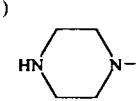
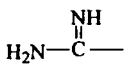
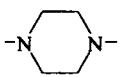
Compd. No	*Aromatic Prowtons (m)*	*SO_2NH (s)*	*CH_3. Sulpha (s)*	**Cyclic amine**  **(t)**	
Ib	7.20 – 7.82 (4H)	8.75 (1H)	2.35 (3H)	**X** = CH_2	-
'Ib	7.40 – 8.08 (4H)	8.70 (1H)	2.30 (3H)	2.70 – 2.85 (2t, 4H, 2α CH_2)	-
''Ib	7.35 – 8.08 (4H)	8.65 (1H)	2.32 (3H)	3.55 – 3.75 (2t, 4H, 2β CH_2)	-
'''Ib	4.70 – 8.08 (4H)	8.65 (1H)	2.30 (3H)	3.85 (t, 2H, γCH_2) piperidine	-
IIb	7.51 – 7.75 (4H)	8.72 (1H)	2.25 (3H)	**X** = O	-
'IIb	7.25 – 7.85 (4H)	8.70 (1H)	2.20 (3H)	2.70 – 2.80 (2t, 4H, 2α CH_2)	-
''IIb	7.30 – 7.80 (4H)	8.68 (1H)	2.20 (3H)	3.35–3.65 (2t, 4H, 2β CH_2)	-
'''IIb	7.30 – 7.80 (4H)	8.65 (1H)	2.22 (3H)	Morpholine	-
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)

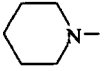
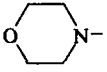
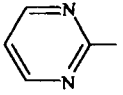
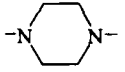
IR spectra of ligands and their chelates confirmed the structures by the presence of this azo group (-N = N-) band at 1565 Cm^{-1}, asym and sym (SO_2 NH) band at 1360 Cm^{-1}, and 1140 Cm^{-1}. In addition, the attachment of the ligands to the Fe^{+3}, Cu^{+2}, Hg^{+2}metal ions are manifested by the 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.

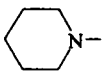
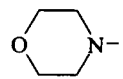
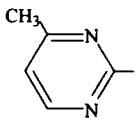
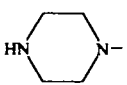
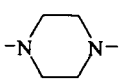
TABLE V Antimicrobial Screening of N-(piperidino-, morpholino-, piperazino-) Dithiocarbamyl Azo-Sulpha Drugs and Their Iron(III), Copper(II) and Mercury(II) Chelates

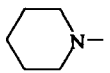
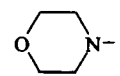
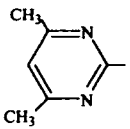
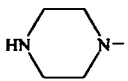
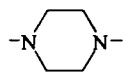
Compd. No.	*Cyclic Amine*	*R*	*Antibacterial activity*						*Antifungal activity*		
			Serratia marcescens DSM 1608[a]	*Bacillus cereus DSM 345*	*Pseudomonas aeruginosa DSM 1299*	*Micrococcus roseus DSM 348*	*Klebsiella pneumoniae DSM 581*	*Staphylococcus aureus DSM 581*	*Aspergillus flavus Link AUCC 164*[b]	*Penicillium chrysogenum Thom AUCC 530*	*Alternaria alternata (Fries) Keissler AUCC 1110*
Ia		H	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			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

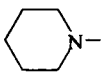
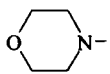
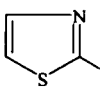
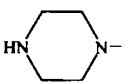
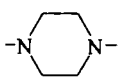
Compd. No.	Cyclic Amine	R	Antibacterial activity						Antifungal activity		
			Serratia marcescens DSM 1608[a]	*Bacillus cereus DSM 345*	*Pseudomonas aerugi-nosa DSM 1299*	*Micrococcus roseus DSM 348*	*Klebsiella pneumoniae DSM 581*	*Staphylococcus aureus DSM 581*	*Aspergillus flavus Link AUCC 164*[b]	*Penicillium chrysogenum Thom AUCC 530*	*Alternaria alternata (Fries) Keissler AUCC 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)
'Ib			4.2	3.5	7.5	6.2	8.2	8.7	4.1	7.9	3.9
''Ib			5.8	-ve	8.8	7.1	9.1	7.2	-ve	6.1	5.2
'''Ib			9.1	8.9	11.8	12.2	10.9	11.2	10.2	9.8	8.9
IIb			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)
'IIb			5.2	3.0	2.8	5.9	8.7	9.1	5.2	6.1	9.6
''IIb			-ve	4.2	5.6	6.9	8.2	8.7	6.3	-ve	8.9
'''IIb			9.9	10.3	9.85	11.2	12.8	13.9	9.9	10.1	12.8
IIIb			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)
'IIIb			8.5	2.0	11.0	11.2	1.0	0.9	6.5	9.5	6.1
''IIIb			9.6	4.9	12.5	12.9	-ve	13.0	-ve	10.8	-ve
'''IIIb			12.6	0.1	13.9	14.5	10.1	15.6	10.1	13.2	9.8
IVb			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)
'IVb			5.2	3.0	8.2	6.8	4.0	6.2	-ve	4.2	6.0
''IVb			7.0	4.0	7.5	9.5	5.5	7.0	3.8	3.0	4.0
'''IVb			9.1	10.1	11.8	12.7	9.8	8.9	9.0	10.0	9.9

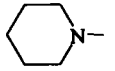
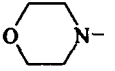
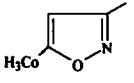
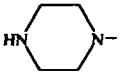
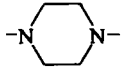
Compd. No.	Cyclic Amine	R	Antibacterial activity						Antifungal activity		
			Serratia marcescens DSM 1608[a]	*Bacillus cereus DSM 345*	*Pseudomonas aeruginosa DSM 1299*	*Micrococcus roseus DSM 348*	*Klebsiella pneumoniae DSM 581*	*Staphylococcus aureus DSM 581*	*Aspergillus flavus Link AUCC 164*[b]	*Penicillium chrysogenum Thom AUCC 530*	*Alternaria alternata (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
'''Ic			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
'''IIc			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		
			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 AUCC 164*[b]	*Penicillium chrysogenum Thom AUCC 530*	*Alternaria alternata (Fries) Keissler AUCC 1110*
Id			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)
'Id			3.5	5.0	8.5	7.0	7.5	6.5	6.0	8.5	7.0
''Id			-ve	4.0	6.5	6.0	6.5	5.0	-ve	7.0	6.5
'''Id			8.0	9.5	10.0	10.5	11.5	9.5	8.5	12.0	10.0
IId			-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)
'IId			2.5	-ve	5.5	7.5	7.0	7.5	5.5	8.0	5.0
''IId			-ve	1.5	2.5	2.5	5.5	4.5	-ve	2.8	-ve
'''IId			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		
			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 AUCC 164*[b]	*Penicillium chrysogenum Thom AUCC 530*	*Alternaria alternata (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
IIe			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)
'IIe			2.5	-ve	4.5	6.5	8.0	5.5	-ve	2.5	7.0
''IIe			-ve	-ve	2.5	3.5	6.0	-ve	-ve	-ve	5.5
'''IIe			7.0	6.5	9.0	10.5	11.5	10.0	6.5	5.5	12.5
IIIe			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)
'IIIe			5.5	3.0	4.5	8.5	8.0	6.0	-ve	1.5	6.5
''IIIe			2.5	-ve	2.0	7.0	6.5	3.0	-ve	-ve	3.5
'''IIIe			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		
			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 AUCC 164*[b]	*Penicillium chrysogenum Thom AUCC 530*	*Alternaria alternata (Fries) Keissler AUCC 1110*
If			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)
'If			4.0	2.5	7.0	6.5	5.0	4.5	8.5	4.5	7.5
''If			3.0	-ve	5.0	5.5	-ve	3.0	6.0	2.5	6.0
'''If			9.0	8.0	9.5	10.5	9.0	7.5	10.0	7.0	11.0
IIf			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)
'IIf			-ve	2.0	6.0	6.0	-ve	4.0	7.0	2.0	7.0
''IIf			-ve	-ve	4.0	5.0	-ve	2.0	4.5	-ve	5.5
'''IIf			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			
			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 AUCC 164*[b]	*Penicillium chrysogenum Thom AUCC 530*	*Alternaria alternata (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)
'Ig			2.0	5.5	5.0	10.0	5.5	6.5	9.5	8.5	11.0
''Ig			-ve	-ve	4.0	5.5	3.5	4.0	5.5	-ve	8.0
'''Ig			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)
'IIg			-ve	3.0	-ve	9.5	-ve	4.5	7.5	5.5	8.0
''IIg			-ve	-ve	1.0	6.5	-ve	-ve	3.5	-ve	5.5
'''IIg			6.0	7.5	8.5	11.0	7.5	8.0	9.5	8.5	10.5
IIIg			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)
'IIIg			2.5	5.0	6.5	9.0	5.8	6.0	9.0	7.0	10.0
''IIIg			-ve	-ve	3.0	6.0	2.5	-ve	4.5	-ve	6.5
'''IIIg			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)
'IVg			3.0	5.5	6.0	8.5	6.5	7.0	8.5	8.0	7.0
''IVg			1.5	1.5	8.5	5.5	3.0	1.5	6.0	1.5	7.5
'''IVg			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		
			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 AUCC 164*[b]	*Penicillium chrysogenum Thom AUCC 530*	*Alternaria alternata (Fries) Keissler AUCC 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)
'Ih			3.5	6.5	5.0	9.0	5.5	7.5	9.5	8.0	9.0
''Ih			-ve	-ve	2.0	5.0	2.0	4.0	5.5	2.0	3.0
'''Ih			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)
'IIh			-ve	4.0	4.5	6.0	-ve	5.5	7.5	7.5	8.0
''IIh			-ve	-ve	4.0	-ve	1.0	-ve	3.5	1.0	2.0
'''IIh			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)
'IIIh			5.5	8.5	6.5	8.5	5.5	10.0	7.5	8.5	9.5
'''IIIh			-ve	5.5	-ve	5.5	4.0	7.0	6.0	-ve	5.0
'''IIIh			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)
'IVh			5.5	8.5	8.0	9.0	65.5	9.5	7.0	-ve	8.5
''IVh			6.0	5.5	4.0	7.0	7.5	5.5	4.0	1.5	-ve
'''IVh			8.5	9.5	12.0	11.5	25.5	11.5	10.5	9.5	12.0

a. DSM = Deutsche Semmlungvos Microorgamifman (German Collection of microorganisms).
b. AUCC = Assiut University Culture Collection.
c. (-ve) = Compound not active biologically.
d. (Values) = Inhibition zones of the free p-aminobenzene sulphonamide derivatives (normal sulpha drugs).

^{1}HNMR spectra of some representative compounds using deutrated 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, SO_2NH_2), δ 2.70–2.85 (2t, 4H, 2α CH_2), δ 3.55–3.70 (2 t, 4H, β.CH_2), δ 3.85 (t, 2H, γ CH_2) 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).

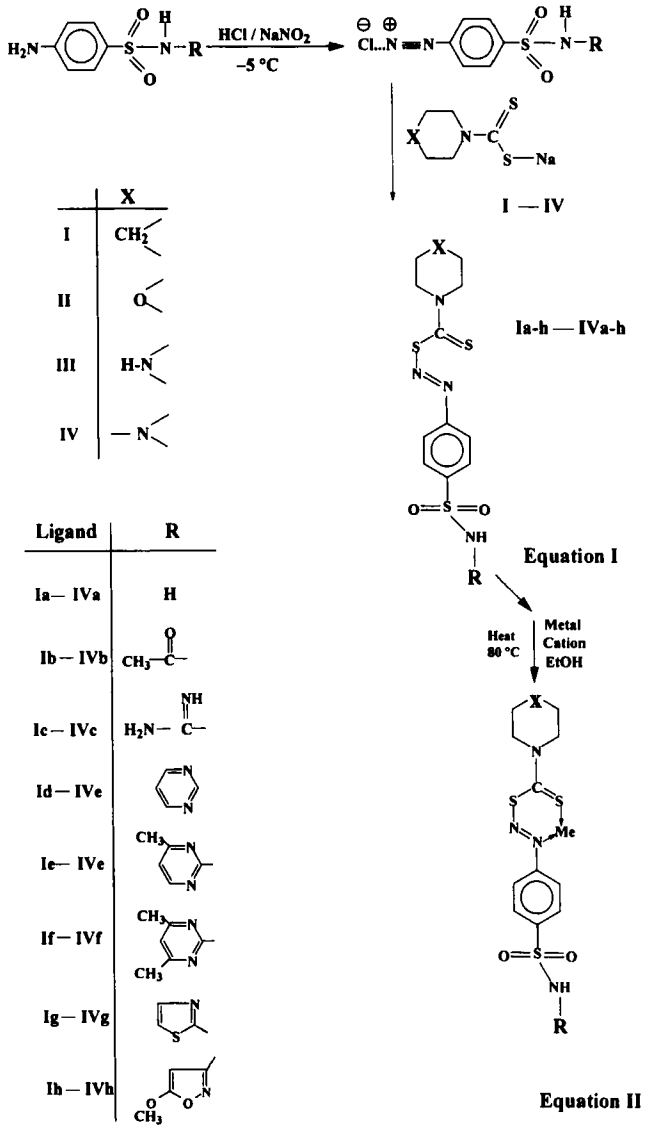
BIOLOGICAL EVALUATION

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 ware 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)] 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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