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Synthesis, Characterization and Antimicrobial Activity of V(IV) and Mo(VI) Complexes of Hydrazones

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Some new biologically active hydrazone complexes of V(IV) and Mo(VI) have been synthesized and characterized by IR and elemental analyses. The biological screening was done against two pathogenic bacteria, *i.e.*, *Klebsiella* and *Pseudomonas* and two non-pathogenic bacteria, *i.e.*, *Escherichia coli* and *Staphylococcus aureus* in order to explore their potential antimicrobial activities.

INTRODUCTION

Hydrazones and their metal complexes have been extensively used in many biological processes[1–5], *e.g.*, antitubercular[6, 7], antiinflammatory[8], anticancerous[9] and pharmacological agents[10–13]. The biological activities of these compounds depend mainly on the nature of acid and aldehyde or ketonic groups present along with metals associated with them. Many important vital enzymatic reactions are catalyzed by transition metals present in the cell[14]. Therefore, in the present work, we report the synthesis and characterization of V(IV) and Mo(VI) complexes of biologically active acid hydrazones.

EXPERIMENTAL

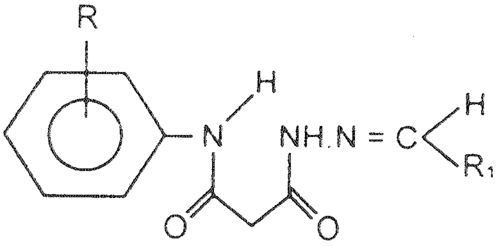
All the chemicals used were of AR grade. Melting points were taken in open capillary and are uncorrected. IR spectra in KBr were recorded on FTIR spectrophotometer (Jasco-410). All the hydrazides were prepared by the reaction of hydrazine hydrate with different esters.

2-(*p*-toluidine anilido) hydrazide, 2-[(N-acetyl)-*p*-toluidine anilido] acetohydrazide and 2-methyl-4-N-cyanoethyl-N-benzenesulphonyl benzaldehyde were prepared by reported methods[15, 16].

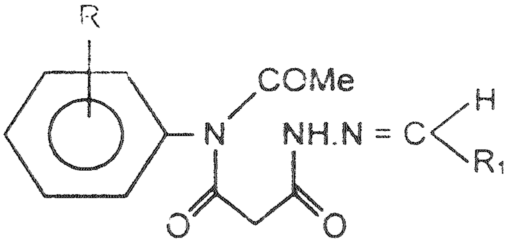
Preparation of Hydrazones

(I) 2-Methyl-(4-N-cyanoethyl)-N-benezenesulphonyl benzylidene-2′-(*p*-toluidine anilido) hydrazone (BTH) (Ia): 2-(*p*-toluidine anilido) hydrazide (0.207 g, 0.001 mol) and 2-methyl-(4-N-cyanoethyl)-N-benezenesulphonyl benzaldehyde (0.328 g, 0.001 mol) were dissolved in ethanol and a drop of concentrated H_2SO_4 was added.The mixture was stirred for 5 min. The resulting solid was recrystallized from ethanol as violet crystals (74%).

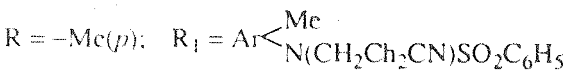
(II) 2-Methyl-(4-N-cyanoethyl)-N-benezene sulphonyl benzylidene-2'-[(N-acetyl)-*p*-toluidine anilido) acetohydrazone (BTAH) (Ib): 2-[(N-acetyl)-*p*-toluidine anilido) acetohydrazide (0.225 g, 0.001 mol) and 2-methyl-(4-N-cyanoethyl)-N-benezenesulphonyl benzaldehyde (0.328 g, 0.001 mol) were dissolved in ethanol and a drop of concentrated H_2SO_4 was added. Mixture was stirred for 5 min. The resulting solid was recrystallized from ethanol as grey crystals (72%).



I (a)



I (b)



$$R = -Me(p);\quad R_1 = Ar\!<\!\begin{matrix} Me \\ N(CH_2Ch_2CN)SO_2C_6H_5 \end{matrix}$$

(B) Preparation of Metal Complexes

(I) V(IV)-BTH Complex: Methanolic 0.485 g of ligand BTH was mixed with a methanolic solution of vanadyl chloride (0.173 g) with continuous stirring and refluxed for 4 h on a waterbath. On concentrating and cooling the resulting coloured crystalline compounds were obtained which were filtered, washed and dried in vacuum.

(II) V(IV)-BTAH Complex: Methanolic 0.527 g of ligand BTAH was mixed with a methanolic solution of vanadyl chloride (0.173 g) with continuous stirring and refluxed for 3 h on a waterbath. On concentrating and cooling the resulting coloured crystalline compounds were obtained which were filtered, washed and dried in vacuum.

(III) Mo(VI)-BTH Complex: Methanolic 0.485 g of ligand BTH was mixed with a methanolic solution of phosphomolybdic acid (0.225 g) with continuous stirring and refluxed for 3 h on a waterbath. On concentrating and cooling the resulting coloured crystalline compounds were obtained which were filtered, washed and dried in vacuum.

(IV) Mo(VI)-BTAH Complex: Methanolic 0.527 g of ligand BTAH was mixed with a methanolic solution of phosphomolybdic acid (0.225 g) with continuous stirring and refluxed for 2 h on a waterbath. On concentrating and cooling the resulting coloured crystalline compounds were obtained which were filtered, washed and dried in vacuum.

The biological experiments for determining the antimicrobial activity of new hydrazones and their metal complexes were done by serial dilution method[17]. In this method, graded dilution of the test compounds in a suitable nutrient medium are inoculated with the organism under examination using aseptic techniques and incubated under suitable conditions in an incubator at 37°C. The minimum inhibitory concentration (MIC) of the compound preventing detectable growth is taken as a measure of biocidal activity. The antimicrobial actions of all the hydrazones and their metal complexes have been screened, *in vitro*, against four bacterial species, *viz.*, *Klebsiella*, *Pseudomonas* (pathogenic), *Escherichia coli* and *Staphylococcus aureus* (non-pathogenic).

RESULTS AND DISCUSSION

All compounds gave satisfactory results for elemental analysis and IR spectra. The physical and analytical data of synthesized new hydrazones and their metal complexes are presented in Table-1.

TABLE-1
ANALYTICAL DATA OF SYNTHESIZED HYDRAZONES AND THEIR METAL COMPLEXES

Compounds	Colour	m.f. (m.w.)	m.p. (°C)	Elemental analysis (%), Calcd. (Found)			
				C	H	N	M
BTH	Violet	$C_{27}H_{27}N_50_4S$ (517)	201	62.66 62.63	05.22 05.20	13.53 13.52	—
BTAH	Grey	$C_{29}H_{29}N_55_4S$ (559)	208	62.25 62.23	05.18 05.15	12.52 12.50	—
V(IV) BTH	Dark brown	V-($C_{54}H_{54}N_{10}O_9S_2$) (1100.94)	218	58.85 58.80	04.90 04.88	12.71 12.68	04.62 04.60
V(IV)-BTAH	Greenish blue	V-($C_{58}H_{58}N_{10}O_{11}S_2$) (1184.94)	220	58.73 58.70	04.89 04.87	11.81 11.78	04.29 04.28
Mo(VI)-BTH	Light blue	Mo-($C_{54}H_{54}N_{10}O_{10}S_2$) (1161.94)	223	55.76 55.74	04.64 04.62	12.04 12.01	08.25 08.23
Mo(VI)-BTAH	Dark green	Mo-($C_{58}H_{58}N_{10}O_{12}S_2$) (1245.94)	228	55.86 55.82	04.65 04.63	11.23 11.20	07.70 07.69

A comparative study of the IR of hydrazones and metal complexes is helpful in evaluating the results.

Spectral interpretation of new hydrazones shows characteristic bands, *i.e.*, ν(N—H) stretching: 3320–3060 cm^{-1}, ν(C═O): 1750–1650 cm^{-1} and ν(C═N): 1640–1610 cm^{-1}.

A strong band around 1630 cm^{-1} indicates the formation of new acid hydrazone because this band appears due to condensation of hydrazide with aldehyde, when these hydrazones chelate with metals, the normal frequency of ν(C═O) stretching band is shifted towards lower frequency region. The lowering by 10–30 cm^{-1} in ν(C═N) azomethine nitrogen band frequency around 1700–1600 cm^{-1} suggests the coordination of acidhydrazone ligand to the metal ion through imino nitrogen of the amido group and azomethine nitrogen. Some new bands present confirm the formation of several new bands in the spectra of complexes at *ca.* 650, *ca.* 930, *ca.* 680 and *ca.* 950 cm^{-1} are due to ν(Mo←N), ν(O═Mo═O), V(V←N) and ν(V—O) vibrations, respectively.

Dioxo molybdenum complexes at *ca.* 930 cm^{-1} are assigned toν_{sym}(O=Mo=O) and ν_{asym}(O=Mo=O) vibrations indicating the presenc of *cis*-MoO_2 moiety and vanadyl complexes, together with high VO stretching wave numbers *ca.* 950 cm^{-1}, provide strong evidence for VO multiple bonding. The $d_\pi - p_\pi$ orbital overlap is involved in a multiple bond. This strong multiple bonding with the oxygen appears to be responsible for the *trans* influence of the oxo ligand, which disfavours attachment of a ligand *trans* to O[18].

Antimicrobial Action

On coordination of a potentially active organic ligand with a metal ion, the antimicrobial activity of the ligand is altered appreciably.

A close study of Table-2 reveals that all the hydrazones are physiologically active. However, their biostatic action is specific and selective against the nature of bacteria used. Further, a comparative study on the biocidal character of the synthesized ligands and their metal complexes shows an increase in the activity of metal complexes on being coordinated with the acid hydrazone molecule. Among the two metal ions used, *viz.*, V and Mo, the biological activity of molybdenum complexes has been noted much which maybe due to the unacceptable nature of Mo^{6+} by the cell of microorganisms.

TABLE-2
MINIMUM INHIBITORY CONCENTRATION (MIC) IN μg/mL OF METAL SALTS, ORGANIC LIGANDS AND THEIR METAL COMPLEXES

S.No.	Compounds	Bacteria			
		Klebsiella	*Pseudomonas*	*E. coli*	*S. aureus*
1.	BTH	50.00	> 100	75.00	25.00
2.	BTAH	25.00	50.00	100.00	75.00
3.	V(IV) BTH	12.50	50.00	6.25	3.12
4.	V(IV) BTaH	6.25	25.00	12.50	6.25
5.	Mo(VI) BTH	12.50	6.25	6.25	3.12
6.	Mo(VI) BTaH	12.50	3.12	6.25	12.50
7.	$VOCl_2 \cdot 2H_2O$	75.00	25.00	75.00	> 100
8.	$H_3PO_4 \cdot 12MoO_3 \cdot 24H_2O$	50.00	75.00	50.00	75

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