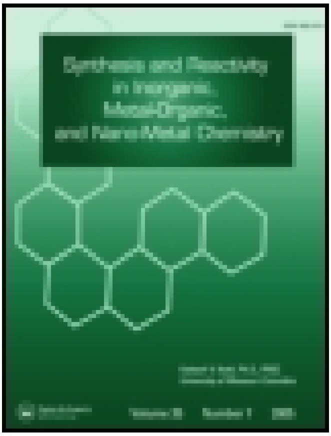

Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

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Synthesis, Characterization, X-Ray Diffraction Studies and Antifungal Activity of Cobalt(II) Complexes with Some aroylhydrazines

K. K. Narang [a] , Vinod P. Singh [a] , S. K. Singh [b] & G. D. Mishra [b]

[a] Department of Chemistry , Banaras Hindu University , Varanasi, 221005, India

[b] Department of Mycology and Plant Pathology , Institute of Agricultural Sciences, Banaras Hindu University , Varanasi, 221005, India

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SYNTHESIS, CHARACTERIZATION, X-RAY DIFFRACTION STUDIES AND ANTIFUNGAL ACTIVITY OF COBALT(II) COMPLEXES WITH SOME AROYLHYDRAZINES

K. K. Narang* and Vinod P. Singh
Department of Chemistry, Banaras Hindu University,
Varanasi-221005, India

and

S. K. Singh and G. D. Mishra
Department of Mycology and Plant Pathology, Institute
of Agricultural Sciences, Banaras Hindu University,
Varanasi-221005, India

ABSTRACT

Cobalt(II) complexes of the type $[Co(L)_2(H_2O)_2]X_2$, where L = benzoylhydrazine, $C_6H_5CONHNH_2$ (BH) or isonicotinoylhydrazine, $NC_5H_4CONHNH_2$ (INH); X = Cl^-, NO_3^- and $\frac{1}{2}SO_4^{2-}$ and $[Co(BH)_3]X_2.nH_2O$, where X = Cl^- and NO_3^- and n = 0 or 3, were synthesized and characterized by elemental analyses, molar conductance, magnetic moments and electronic and IR spectra. All the complexes are 1:3 electrolytes and soluble in water, ethanol, DMF and DMSO. The complexes are spin-free octahedral and the ligands bond to the metal ion via >C=O and NH_2 groups. Dehydration studies indicate the presence of coordinated water molecule in most of the complexes. X-ray powder diffraction parameters for some of the complexes correspond to a tetragonal crystal lattice. The complexes show a fair degree of antifungal activity against a number of pathogenic fungi viz. *Alternaria tenuissima*, *A. alternata*, *A. triticina*, *A. brassicae*,

A. sesami, Curvularia lunata, Pseudocercospora sp., Colletotrichum capsici, Fusarium oxysporum udam, F. oxysporum lini and Helminthosporum sativum.

INTRODUCTION

Cobalt(II) complexes, besides existing in several stereochemical dispositions, interact with molecular oxygen ultimately oxidising the complexed Co(II) to Co(III). The best studied examples are cobalt(II)- Schiff base complexes which take up O_2 in DMF or pyridine solution[1]. Since aroylhydrazines are basic ligands and coordinate with metal ions, there is little possibility of Co(II) being readily oxidized by atmospheric oxygen and stable Co(II) complexes are expected. Therefore, a number of cobalt(II) complexes with aroylhydrazines such as benzoylhydrazine ($C_6H_5CONHNH_2$) and isonicotinoylhydrazine ($NC_5H_4CONHNH_2$) were synthesized and their physico-chemical properties and antifungal properties are discussed in this paper.

EXPERIMENTAL

Materials

All the chemicals used were of BDH (AnalaR) or equivalent grade. INH was obtained from CDH Chemicals, New Delhi and used after recrystallization from ethanol.

Benzoylhydrazine, $C_6H_5CONHNH_2$ (BH) was prepared by refluxing methyl benzoate (13.6 mL, 100 mmol, neat) with hydrazine hydrate (5.0 mL, 100 mmol, neat) in 1:1 molar ratio for 6 hours. On cooling a solid product was obtained. The product was filtered by suction and washed with distilled water. BH (m.p. 112°) was recrystallized from hot benzene. Yield 10.2 g, 75 %. Found: C, 61.58; H, 5.67; N, 20.42. Calc. for $C_7H_8N_2O$: C, 61.76; H, 5.88; N, 20.59 %.

Synthesis of the Complexes

The cobalt(II) complexes of BH and INH were synthesized by reacting 50 mL aqueous solutions containing 10 mmol each of $CoCl_2.6H_2O$ (2.4 g), $Co(NO_3)_2.6H_2O$ (3.0 g) and $CoSO_4.xH_2O$ (2.5 g) with 10, 20 and 30 mmol each of BH (1.4, 2.7 and 4.2 g) and INH (1.4, 2.8 and 4.2 g) in 50 mL warm (50°C) aqueous ethanol (30 %, v/v) corresponding to 1:1, 1:2 and 1:3 metal:ligand molar ratios, respectively. On concentrating the reaction solutions to one third of the volume on a water bath the complexes formed in solution slowly crystallized at room temperature upon standing for 24-48 hours. The complexes were filtered, washed thoroughly with aqueous ethanol (30 %, v/v) and dried in a desiccator over anhydrous calcium chloride at room temperature.

Analysis of the Complexes

The complexes were analysed for their metal content gravimetrically by the literature procedures[2] after decomposing the organic matter with a mixture of concentrated nitric and hydrochloric acid and evaporating the residue to dryness with concentrated sulfuric acid. Cl^- and SO_4^{2-} were determined gravimetrically as AgCl and $BaSO_4$, respectively. C, H and N were analysed on a Perkin-Elmer 240C model microanalyzer. The analytical and physico-chemical data are given in Tables 1-3.

Physico-chemical Measurements

The molar conductance of 10^{-3} M solutions in water were measured at room temperature on a WTW conductivity meter. The room temperature magnetic susceptibilities of the complexes were determined on a Faraday type balance (Cahn, magnetic susceptibility apparatus) using $[CoHg(SCN)_4]$ as calibrant and the experimental magnetic susceptibilities were corrected for diamagnetism[3].

Table 1. Analytical and Physico-chemical Data of the Complexes

Complex Colour	Empirical formula (Yield %)	Melting point (°C)	Analysis Found (Calcd.) % Metal	Anion	C	H	N	Molar conductance in water ($ohm^{-1}mol^{-1}cm^{2}$)
$[Co(BH)_3]Cl_2.3H_2O$ Red	$C_{21}H_{30}N_6O_6Cl_2.Co$ (80)	172	9.66 (9.97)	12.21 (11.99)	42.25 (42.57)	4.91 (5.07)	14.02 (14.19)	221.0
$[Co(BH)_2(H_2O)_2]Cl_2$ Dark red	$C_{14}H_{20}N_8O_4Cl_2.Co$ (70)	180	13.56 (13.47)	15.90 (16.21)	38.56 (38.36)	4.42 (4.57)	12.80 (12.78)	224.4
$[Co(INH)_2(H_2O)_2]Cl_2$ Brown	$C_{12}H_{18}N_6O_4Cl_2.Co$ (75)	232	13.24 (13.41)	16.20 (16.14)	32.51 (32.73)	3.96 (4.09)	19.21 (19.09)	218.3
$[Co(BH)_3](NO_3)_2$ Light pink	$C_{21}H_{24}N_8O_9.Co$ (80)	231	10.00 (9.98)	-	42.41 (42.64)	3.89 (4.06)	19.10 (18.95)	232.3
$[Co(BH)_2(H_2O)_2](NO_3)_2$ Pink	$C_{14}H_{20}N_6O_{10}.Co$ (70)	218	11.89 (12.02)	-	34.47 (34.22)	3.97 (4.07)	17.16 (17.11)	243.6
$[Co(INH)_2(H_2O)_2](NO_3)_2$ Brick red	$C_{12}H_{18}N_8O_{10}Co$ (75)	260	12.00 (11.97)	-	29.42 (29.21)	3.76 (3.65)	22.48 (22.72)	226.2
$[Co(BH)_2(H_2O)_2]SO_4$ Red	$C_{14}H_{20}N_4O_8S.Co$ (70)	>300	12.52 (12.74)	20.55 (20.73)	36.36 (36.28)	4.27 (4.32)	11.90 (12.09)	209.1
$[Co(INH)_2(H_2O)_2]SO_4$ Brown	$C_{12}H_{18}N_6O_8S.Co$ (70)	>300	12.50 (12.69)	20.50 (20.64)	30.78 (30.97)	3.84 (3.87)	17.93 (18.06)	199.6

Table 2. Magnetic Moments, Electronic Spectral Data and Ligand Field Parameters of the Complexes

Complex	μ_{eff} (B.M.)	Band maxima (cm^{-1})		10 Dq (cm^{-1})	B (cm^{-1})	β	β' (%)	LFSE (K cal/mol)
		ν_1	ν_3					
$[Co(BH)_3]Cl_2.3H_2O$	5.12	9090	20120	10210	815	0.841	15.8	23.27
$[Co(BH)_2(H_2O)_2]Cl_2$	4.70	9145	19840	10290	790	0.815	18.5	23.45
$[Co(INH)_2(H_2O)_2]Cl_2$	4.85	8330	20830	9550	910	0.936	6.4	21.76
$[Co(BH)_3](NO_3)_2$	4.86	9260	20200	10470	805	0.830	17.0	23.86
$[Co(BH)_2(H_2O)_2](NO_3)_2$	4.98	9295	19890	10530	780	0.803	19.7	24.00
$[Co(INH)_2(H_2O)_2](NO_3)_2$	4.68	9260	20620	10460	835	0.862	13.8	23.84
$[Co(BH)_2(H_2O)_2]SO_4$	4.75	9260	20200	10470	805	0.830	17.0	23.86
$[Co(INH)_2(H_2O)_2]\ SO_4$	4.90	8330	20410	9620	875	0.901	9.9	21.93

Table 3. Important IR Spectral Bands and Their Assignments

Compound	νOH + νNH	Amide I ν(C=O)	Amide II	Amide III	ν(N–N)	ν(M–O)	ν(M–N)	Anion bands
BH	3290b	1665s	1570s	1370s	885w	-	-	-
INH	3220b	1670s	1560s	1370s	980w	-	-	-
$[Co(BH)_3]Cl_2.3H_2O$	3340b, 3240b	1640s	1555s	1375s	940w	510w	300w	260w
$[Co(BH)_2(H_2O)_2]Cl_2$	3360b, 3260b	1640s	1545s	1375s	935w	495w	325w	260w
$[Co(INH)_2(H_2O)_2]Cl_2$	3430b, 3170b	1650s	1545m	1372s	1015w	520w	325w	280w
$[Co(BH)_3](NO_3)_2$	3380b, 3220b	1640s	1560s	1375s	915w	495w	320w	1400m, 830w, 710w
$[Co(BH)_2(H_2O)_2](NO_3)_2$	3360b, 3240b	1645s	1545m	1375s	905w	520w	325w	1400m, 825w, 710w
$[Co(INH)_2(H_2O)_2](NO_3)_2$	3420b, 3200b	1655s	1540m	1370s	1010w	510w	325w	1390m, 825w, 710w
$[Co(BH)_2(H_2O)_2]SO_4$	3340b, 3260b	1640s	1545s	1375s	935w	495w	325w	1130s
$[Co(INH)_2(H_2O)_2]SO_4$	3360b, 3200b	1645s	1540s	1375s	915w	495w	320w	1135s

Electronic and infrared spectra of the ligands and the complexes were recorded in Nujol on a Cary-14 and Perkin-Elmer 783 spectrophotometers, respectively. Powder X-ray diffraction patterns were recorded on a Phillips PW 1130 apparatus using CuK$_\alpha$ radiation (Table 4).

Antifungal Screening

The ligands as well as their complexes were screened for their antifungal activity against several pathogenic fungal species (Table 5). These species were isolated from the infected organs of host plants on potato dextrose agar (potato 250 g + dextrose 20 g + agar 20 g) medium. The cultures of the fungi were purified by the single spore isolation technique.

The compounds were separately dissolved in water in different concentrations (100, 250, 500, 750 and 1000 ppm) for testing against spore germination. A drop of the solution of each compound from different concentrations was kept on a glass slide and conidia (approx 200), fungal reproducing spores, were mixed in each drop of solution separately with the help of an inoculating needle. Each treatment was replicated thrice and a parallel control set in water was run concurrently on separate glass slides. All the slides were incubated in humid chambers (humidity 95 %) at 25 ± 2°C for 24 hours. Each slide was observed under the microscope for spore germination and the percent inhibition of spore germination was finally calculated.

RESULTS AND DISCUSSION

The analytical data of the complexes (Table 1) indicate that although reactions between cobalt(II), BH or INH have been carried out in 1:1, 1:2 and 1:3 (M : L) ratio, only BH formed 1:3 (M : L) complexes with cobalt(II) chloride and nitrate. 1:2 (M : L) complexes were formed with all other metal salts and ligands, 1:1

Table 4. Observed and Calculated Q and hkl Values for $[Co(BH)_2(H_2O)_2](NO_3)_2$ and $[Co(BH)_2(H_2O)_2]SO_4$

Powder pattern line	2 θ	d	Relative intensity	$Q_{obs.}$	$Q_{cal.}$	hkl
			$[Co(BH)_2(H_2O)_2](NO_3)_2$			
1	6.018	14.6860	4569	0.0046	0.0046	100
2	7.466	11.8409	45	0.0071	0.0071	001
3	9.532	9.2781	88	0.0116	0.0117	101
4	10.729	8.2457	48	0.0147	0.0163	111
5	11.822	7.4857	5562	0.0178	0.0184	200
6	14.738	6.0104	138	0.0277	0.0284	002
7	16.933	5.2360	35	0.0365	0.0368	220
8	17.599	5.0893	95	0.0393	0.0376	112
9	18.699	4.7452	48	0.0444	0.0439	221
10	19.195	4.6237	82	0.0468	0.0468	202
11	20.086	4.4206	101	0.0512	0.0514	212
12	22.613	3.9320	46	0.0647	0.0652	222
13	23.546	3.7783	54	0.0700	0.0698	302
14	25.423	2.5034	51	0.0815	0.0823	203
15	28.229	3.1612	43	0.1001	0.1007	223
16	29.584	3.0195	44	0.1097	0.1099	313
17	31.060	2.8792	28	0.1206	0.1204	422
18	31.776	2.8160	31	0.1261	0.1267	511
19	32.560	2.7500	33	0.1317	0.1320	204
20	39.237	2.2931	35	0.1902	0.1911	621
21	39.878	2.2606	29	0.1957	0.1957	541
22	41.726	2.1646	43	0.2134	0.2141	631
23	44.311	2.0442	21	0.2393	0.2392	640
24	56.783	1.6213	20	0.3804	0.3804	734
25	60.792	1.5236	26	0.4308	0.4319	483
26	61.784	1.5015	26	0.4436	0.4442	546
27	63.687	1.4611	19	0.4684	0.4671	861
28	64.286	1.4490	28	0.4763	0.4765	745

Contd. ...

Table 4. (Contd. ...)

Powder pattern line	2 θ	d	Relative intensity	$Q_{obs.}$	$Q_{cal.}$	hkl
			$[Co(BH)_2(H_2O)_2]SO_4$			
1	6.078	14.5399	638	0.0047	0.0047	100
2	7.872	11.2302	40	0.0079	0.0079	001
3	10.273	8.6106	195	0.0134	0.0126	101
4	11.698	7.5649	43	0.0174	0.0174	111
5	12.145	7.2876	416	0.0188	0.0188	200
6	13.277	6.6684	29	0.0225	0.0235	210
7	14.771	5.9920	31	0.0278	0.0267	201
8	20.123	4.4127	117	0.0513	0.0504	202
9	20.790	4.2725	33	0.0548	0.0548	311
10	22.961	3.8731	22	0.0667	0.0690	321
11	24.460	3.6392	42	0.0755	0.0758	103
12	25.086	3.5497	66	0.0794	0.0799	410

complexes were not obtained under these conditions. The reactions leading to complex formation may have proceeded as follows:

$$CoX_2 \cdot 6H_2O \quad + \quad 2\,(L) \quad \longrightarrow \quad [Co(L)_2(H_2O)_2]X_2$$

where L = BH or INH; X = Cl^-, NO_3^- or $\frac{1}{2}SO_4^{2-}$

and $CoX_2.6H_2O \quad + \quad 3\,(BH) \quad \longrightarrow \quad [Co(BH)_3]X_2.nH_2O$

where X = Cl^- or NO_3^-; n = 0, 3.

All the complexes are intensely coloured and stable solids. The BH complexes are red or pink in colour and the INH complexes are brown. The cobalt(II) sulfate complexes are non-melting up to 300°C, whereas the remaining complexes melt between 170-260°C. All the complexes are fairly soluble in water, ethanol, DMF, DMSO and pyridine but insoluble in chloroform, acetone, ether and benzene. The complexes show molar conductance values of 10^{-3} M solution between 200-243 $ohm^{-1}\ mol^{-1}\ cm^2$ in water at room temperature, suggesting that all the complexes are 1:2 electrolytes[4].

Table 5A. Antifungal Activity of Cobalt(II) Complexes and Their Components

Compound	% Inhibition of spore germination											
	Alternaria tenuissima (ppm)				*A. alternata* (ppm)				*A. triticina* (ppm)			
	100	250	500	750	100	250	500	750	100	250	500	750
BH	8	20	56	91	11	27	53	81	8	21	48	84
INH	6	11	55	72	7	10	33	63	6	13	44	63
$CoCl_2.6H_2O$	30	67	85	96	31	68	77	96	30	58	82	92
$Co(NO_3)_2.6H_2O$	44	70	85	100	34	83	90	100	42	70	88	100
$CoSO_4.xH_2O$	11	41	51	70	17	39	54	68	13	31	45	65
$[Co(BH)_3]Cl_2.3H_2O$	42	85	100	100	42	73	100	100	35	70	100	100
$[Co(INH)_2(H_2O)_2]Cl_2$	36	71	100	100	37	71	94	100	32	67	88	100
$[Co(BH)_3](NO_3)_2$	54	76	100	100	45	60	100	100	48	87	100	100
$[Co(INH)_2(H_2O)_2](NO_3)_2$	46	67	89	100	35	85	100	100	44	80	97	100
$[Co(BH)_2(H_2O)_2]SO_4$	19	44	53	90	19	44	77	91	18	40	63	82
$[Co(INH)_2(H_2O)_2]SO_4$	17	42	49	81	18	42	73	90	17	35	60	80

Contd. ...

Table 5 A. (Contd. ...)

Compound	% Inhibition of spore germination							
	A. brassicae (ppm)				*A. sesami* (ppm)			
	100	250	500	750	100	250	500	750
BH	9	18	57	77	8	22	53	72
INH	6	13	44	74	4	8	23	31
$CoCl_2 \cdot 6H_2O$	24	56	81	94	32	58	76	93
$Co(NO_3)_2 \cdot 6H_2O$	44	75	90	100	45	75	86	100
$CoSO_4 \cdot xH_2O$	7	38	54	67	13	31	56	72
$[Co(BH)_3]Cl_2 \cdot 3H_2O$	37	93	100	100	35	85	100	100
$[Co(INH)_2(H_2O)_2]Cl_2$	28	60	82	100	33	67	80	100
$[Co(BH)_3](NO_3)_2$	53	86	100	100	59	81	100	100
$[Co(INH)_2(H_2O)_2](NO_3)_2$	47	81	96	100	46	80	93	100
$[Co(BH)_2(H_2O)_2]SO_4$	20	50	68	91	29	43	79	86
$[Co(INH)_2(H_2O)_2]SO_4$	16	30	68	85	17	33	76	84

Table 5B. Antifungal Activity of Cobalt(II) Complexes and Their Components

Compound	% Inhibition of spore germination											
	Curvularia lunata ppm				*Pseudocercospora* sp. ppm				*Collatotrichum capsici* ppm			
	100	250	500	750	100	250	500	750	100	250	500	750
BH	6	19	44	60	15	35	48	76	14	32	45	68
INH	4	18	25	44	13	28	38	67	11	28	45	62
$CoCl_2 \cdot 6H_2O$	10	46	68	84	20	61	80	100	25	63	81	100
$Co(NO_3)_2 \cdot 6H_2O$	36	63	81	100	48	61	87	100	42	77	88	100
$CoSO_4 \cdot xH_2O$	9	19	56	69	8	25	44	74	15	47	66	73
$[Co(BH)_3]Cl_2 \cdot 3H_2O$	17	72	100	100	59	94	100	100	49	89	100	100
$[Co(INH)_2(H_2O)_2]Cl_2$	11	39	62	92	36	55	83	100	31	65	85	100
$[Co(BH)_3](NO_3)_2$	40	66	96	100	55	71	100	100	56	80	100	100
$[Co(INH)_2(H_2O)_2](NO_3)_2$	38	64	90	100	48	63	93	100	48	78	91	100
$[Co(BH)_2(H_2O)_2]SO_4$	15	34	69	80	26	54	85	100	24	51	85	100
$[Co(INH)_2(H_2O)_2]SO_4$	12	21	51	72	21	52	80	100	22	48	76	100

Contd. ...

Table 5B. (Contd. ...)

Compound	% Inhibition of spore germination											
	Fusarium oxysporum udam (ppm)				*F. oxysporum lini* (ppm)				*Helminthosporum sativum* (ppm)			
	100	250	500	750	100	250	500	750	100	250	500	750
BH	21	36	64	80	33	43	65	87	21	40	70	84
INH	16	30	60	76	26	37	55	83	11	29	54	76
$CoCl_2.6H_2O$	26	76	90	100	33	70	86	100	23	63	82	100
$Co(NO_3)_2.6H_2O$	34	85	100	100	42	78	90	100	28	69	85	100
$CoSO_4.xH_2O$	17	36	55	81	19	43	68	79	15	46	65	77
$[Co(BH)_3]Cl_2.3H_2O$	40	83	100	100	44	86	100	100	30	74	100	100
$[Co(INH)_2(H_2O)_2]Cl_2$	37	81	100	100	40	82	100	100	24	68	86	100
$[Co(BH)_3](NO_3)_2$	46	85	100	100	48	80	100	100	34	76	90	100
$[Co(INH)_2(H_2O)_2](NO_3)_2$	41	87	100	100	45	80	100	100	31	56	87	100
$[Co(BH)_2(H_2O)_2]SO_4$	30	61	94	100	39	75	92	100	22	52	78	100
$[Co(INH)_2(H_2O)_2]SO_4$	26	56	87	100	36	68	80	100	18	48	73	89

Dehydration Studies

Dehydration studies have been carried out between 80-150°C. $[Co(BH)_3]Cl_2.3H_2O$, show an increasing weight loss only up to 110°C without any change in colour indicating the presence of approximately three water molecules in the lattice. The remaining complexes show weight loss between 130-150°C accompanied by a change in colour from pink to blue, suggesting that the water molecules are coordinated to the metal ion. The change in colour may be due to a change in the stereochemistry of the complexes from octahedral to tetrahedral upon removal of two water molecules.

Magnetic Moments and Electronic Spectra

Octahedral, tetrahedral and square planar cobalt(II) complexes show magnetic moments between 4.7 - 5.2, 4.2 - 4.8 and 2.2 - 2.9 B.M., respectively, because of the orbital contribution[5]. The μ_{eff} values observed between 4.68 - 5.12 B.M. for the present cobalt(II) complexes were fairly close to those reported for three unpaired electrons in an octahedral environment.

Cobalt(II) complexes gave rise to three absorption bands in the visible region under the influence of the octahedral field by the excitation of the electron from the ground state $^4T_{1g}(F)$ to the excited states $^4T_{2g}(F)$, $^4A_{2g}(F)$ and $^4T_{1g}(P)$. In case of $[Co(H_2O)_6]^{2+}$, three transitions were observed at 8130, 17540 and 21980 cm^{-1}[6], respectively. In the present case only two bands were observed between 8330 - 9295 cm^{-1} (ν_1) and 19840 - 20830 cm^{-1} (ν_3) suggesting octahedral geometry for the complexes. The ν_2 transition was not observed due to very weak intensity[6]. The various ligand field parameters (10 Dq, B, β, β^o and LFSE) were also calculated and indicate a considerable covalent character of the M-L bonds (Table 2).

Infrared Spectra

The bonding of the ligands BH and INH to cobalt(II) has been judged by a careful comparison of the infrared spectra of the complexes with those of the free ligands in Nujol mulls. A few significant bands have been selected to observe the effect on ligand vibration in the complexes.

In BH and INH complexes, the ν(N-H) bands are normally broad but the centre of the bands are shifted to lower frequencies (40-60 cm^{-1}) compared to those observed in the parent ligands at 3290 and 3220 cm^{-1}, respectively (Table 3). This signifies bonding of the terminal $-NH_2$ group to the metal. The amide I band, ν(C=O) is used for judging the coordination of the C=O group. In BH and INH ν(C=O) appears at 1665 and 1670 cm^{-1}, respectively. In all the complexes ν(C=O) is shifted to lower frequency by 20-30 cm^{-1}, indicating coordination of the C=O group to the metal[7]. The amide II band of BH and INH appearing at 1570 and 1560 cm^{-1}, respectively, appear to have shifted considerably to lower frequency upon complex formation. Compared to the ligands bands, a shift to higher frequency (5-10 cm^{-1}) is observed in the amide III bands in all the complexes supporting coordination through the C=O group[8].

A weak band, ν(N-N), appearing at 885 and 980 cm^{-1} in BH and INH, respectively, shifted to higher frequency by 40-60 cm^{-1} suggesting involvement of the $-NH_2$ group in bonding[9]. In the ligands, aromatic rings show absorptions around 1600, 1500 and 1410 cm^{-1}. These vibrations remain either unaltered or slightly shifted in position in the spectra of all the complexes indicating non-involvement of the phenyl or pyridyl ring in the coordination[7].

Lattice water absorbs in the region 3550-3200 cm^{-1} (antisymmetric and asymmetric O-H stretching) and at 1630-1610 cm^{-1} (H-O-H bending modes)[10]. These vibrations of water overlap with

N-H stretching and bending modes and the region 3550-3200 cm^{-1} is generally broad in the complexes containing water molecules. Besides showing the above vibrations, most of the present complexes, except $[Co(BH)_3]Cl_2 \cdot 3H_2O$, also show weak bands between 900-940, 750-770 and 640-660 cm^{-1} due to wagging, twisting and rocking modes of coordinated water molecules[12].

In all the cobalt(II) nitrate complexes the bands appearing near 1400, 825 and 710 cm^{-1} suggest ionically bonded NO_3^- groups. Similarly, in the cobalt(II) sulfate complexes a band observed at ~1130 cm^{-1} suggests an ionic sulfate group. The non-ligand bands occurring between 495-520 cm^{-1} have been assigned to ν(M-O). The new frequencies occurring in the 300-325 cm^{-1} and 260-280 cm^{-1} ranges have been tentatively assigned to ν(M-N) and ν(M-Cl), respectively[12].

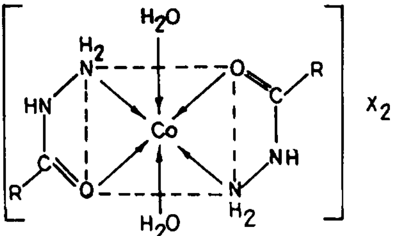
Based on the above discussion, two general structures for the metal complexes are proposed in Fig. 1.

X-Ray Diffraction Studies

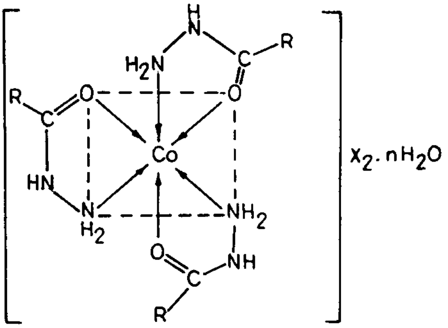
X-ray powder diffraction method provides a way of investigating, within limits, the crystallography of a crystal in powder form. The diffraction patterns for $[Co(BH)_2(H_2O)_2](NO_3)_2$ and $[Co(BH)_2(H_2O)_2]SO_4$ were recorded and successfully indexed by Ito's method[13] (Table 4). The following lattice constants were obtained:

	a	b	c (Å)
$[Co(BH)_2(H_2O)_2](NO_3)_2$	6.02	6.02	7.46
$[Co(BH)_2(H_2O)_2]SO_4$	6.08	6.08	7.87

These values ($a = b \neq c$) are consistent with a tetragonal crystal lattice[13].



Where $X = Cl^-$, NO_3^- or $\frac{1}{2} SO_4^{2-}$; $R = C_6H_5$ (BH), NC_5H_4 (INH)



Where $X = Cl^-$, NO_3^- ; $R = C_6H_5$ (BH); $n = 0$ and 3

Fig. 1. Representative Structures of the Cobalt(II) Complexes

Antifungal Activity

The experimental data (Table 5) indicate that the ligands, metal salts and their complexes show a varying degree of activity against fungi viz. *Alternaria tenuissima*, *A. alternata*, *A. triticina*, *A. brassicae*, *A. sesami*, *Curvularia lunata*, *Pseudocercospora* sp., *Colletotrichum capsici*, *Fusarium oxysporum udam*, *F. oxysporum lini* and *Helminthosporum sativum* at 100, 250, 500, 750 and 1000 ppm. The effect is susceptible to the concentration of the compound used for inhibition. Their activity is greatly enhanced at the higher concentration. All the complexes show 100 % activity at 1000 ppm, many of them even at 750 ppm and a few at 500 ppm. The metal complexes show greater activity than the ligands or the corresponding metal salts alone. BH and its complexes seem to be slightly more toxic than INH and its complexes. The complexes vary in their antifungal activity with respect to the anions in the order: $NO_3^- > Cl^- > SO_4^{2-}$.

The toxicity of the complexes can be related to the strength of the metal - ligand bond, besides other factors such as size of the cation[14], receptor sites[15], diffusion[16] and a combined effect of the metal and the ligand[17] for inactivation of the biomoieties.

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Referee I: W. R. Mason
Referee II: I. O. Kady