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Synthesis of 2,4-Dinitrophenylhydrazone Derivatives of Co(II), Cu(II) and Ni(II) Complexes of β-Diketones/ β-Ketoesters and Their Antimicrobial Activities

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2,4-Dinitrophenylhydrazone derivatives of Co(II), Ni(II) and Cu(II) complexes have been synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility and spectral data. The antimicrobial activities of the complexes have been studied..

Key Words: Synthesis, 2,4-Dinitrophenyl hydrazone, Cu^{2+}, Co^{2+}, Ni^{2+} complexes, Antimicrobial activity.

INTRODUCTION

Most of the studies reported on hydrazones have centred around those derived from simple aldehydes and ketones[1, 2] and much less work had been reported on β-diketo derivatives[3]. Among the reactions studied, phenylhydrazones derived from metal β-diketones/β-ketoesters have not received considerable attention. In continuation of our research interest in the antimicrobial study, we herein report the synthesis of 2,4-dinitrophenyl hydrazone derivatives of Co(II), Ni(II) and Cu(II) complexes of β-diketones/β-ketoesters and their antimicrobial activities.

RESULTS AND DISCUSSION

All the compounds are stable at room temperature. An examination of the elemental analysis of the products listed in Table-1 reveals the formation of 1 : 2 (metal : ligand) complexes. Molar conductance values of these complexes (10^{-3} M in DMSO) at room temperature are found in the range of 3.3 to 6.9 mho cm^{-2} mol^{-1} indicating their non-electrolytic nature[4]. The magnetic susceptibility measurements reveal square-planar geometry for copper and cobalt complexes and tetrahedral for nickel complex.

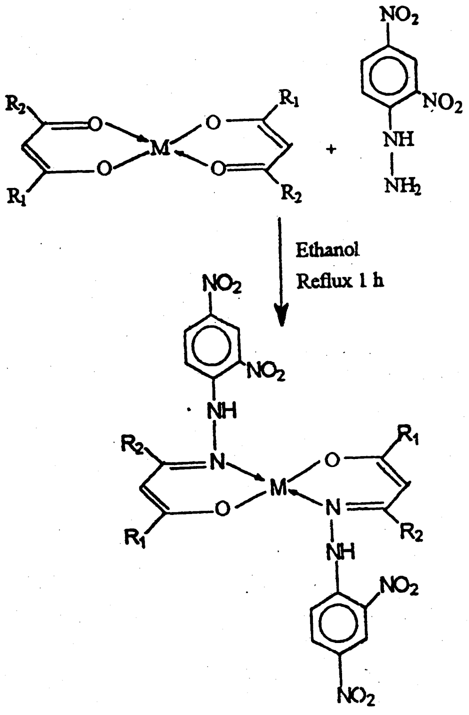
The IR spectrum of the complexes shows specific IR bands for azomethine linkage ν(C═N) at 1600–1560 cm^{-1} region and ν(N—N) stretching at 1000–900 cm^{-1} diagnostic of hydrazone formation[5]. New bands in metal complexes are observed at 1560–1520 cm^{-1}, characteristic of ν(C—N—N═C), thus confirming that azomethine nitrogen takes part in coordination[6]. The sharp band at 3300–3240 cm^{-1} region shows the presence of N—H group. The band due to ketonic ν(C═O) at 1660 cm^{-1} was found to be absent in the product complexes, indicating the metal coordination with nitrogen of 2,4-dinitrophenylhydrazine.

TABLE-1
ANALYTICAL DATA OF THE METAL COMPLEXES

No.	Complex (colour)	%Analysis, Found (Calcd.)				Yield (%)	μ_{eff} (B.M)	λm (mho $cm^{-2}mol^{-1}$)
		M	C	H	N			
1.	$Cu(acacP)_2$ (green)	9.9 (10.2)	42.1 (42.5)	3.2 (3.5)	17.5 (18.1)	56	2.6	3.3
2.	$Co(acacP)_2$ (yellow)	9.3 (9.6)	42.5 (42.8)	3.1 (3.5)	17.9 (18.1)	59	3.5	6.1
3.	$Ni(acacP)_2$ (orange)	9.4 (9.5)	42.1 (42.8)	3.4 (3.5)	17.8 (18.1)	53	4.4	6.5
4.	$Cu(EAAP)_2$ (pale green)	9.1 (9.3)	42.5 (42.8)	3.1 (3.5)	18.5 (18.1)	46	2.4	4.2
5.	$Ni(EAAP)_2$ (orange)	8.1 (8.7)	42.0 (42.8)	3.2 (3.5)	18.2 (18.1)	54	4.1	6.9

Probable mechanistic pathways for the reaction

Formation of phenylhydrazone is characteristic reaction of carbonyl group with phenylhydrazine. It is well known that pyrazole derivatives are formed when β-diketone/β-ketoester reacts with phenylhydrazine[7]. But, in this case metal 2,4-dinitrophenylhydrazone derivatives are formed which is due to central metal atom of the metal β-diketone/β-ketoester. Presence of metal prohibits the possibility of pyrazole ring derivatives. Therefore, the probable reaction could be written as:



where M = Co(II), Ni(II), Cu(II); $R_1 = R_2 = CH_3$ in β-diketone; $R_1 = OC_2H_5$; $R_2 = CH_3$ in β-ketoester.

Antimicrobial study

All the product complexes were tested for antimicrobial activity. Mueller-Hinton agar was used for testing the susceptibility of microorganisms to antibacterial agents by well diffusion method[8] using pyridine as solvent, at a concentration of 100 μg/10 μL against gram positive (*Staphylococcus aureus*) and gram negative (*Escherichia coli*) bacteria. The minimum inhibitory concentrations (MIC) values were determined at the end of an incubation period of 24 h at 37°C. The results are presented in Table-2. The results show that all the compounds are antimicrobially active. The order of activity of the complexes towards *Staphylococcus aureus* and *Escherichia coli* is Ni(II) > Co(II) > Cu(II). It is obvious that the product complexes are more active than the parent complexes. It is worth mentioning that the antimicrobial activity gets enhanced with the introduction of nitro group in phenylhydrazine in comparison to our earlier report[9]. The present study proves that the newly synthesized compounds may find application for therapeutic purposes in human diseases provided they are nontoxic to human body.

TABLE-2
ANTIBACTERIAL ACTIVITY DATA OF THE COMPLEXES

No.	Complex	Inhibition zone (mm) at concentration (100 μg/10 μL)	
		S. aureus	*E. coli*
Product complex			
1.	$Cu(acacP)_2$	11	12
2.	$Co(acacP)_2$	15	17
3.	$Ni(acacP)_2$	19	21
4.	$Cu(EAAP)_2$	10	8
5.	$Ni(EAAP)_2$	16	18
Parent complex			
6.	$Cu(acac)_2$	6	5
7.	$Co(acac)_2$	4	5
8.	$Ni(acac)_2$	5	6
9.	$Cu(EAA)_2$	5	4
10.	$Ni(EAA)_2$	6	6

EXPERIMENTAL

All the chemicals were of AR grade. IR spectra were recorded on a Perkin-Elmer-783 spectrophotometer. KBr disc method was used for recording the IR spectra. UV spectra were recorded on Shimadzu-160 spectrophotometer. Magnetic susceptibility measurements were carried out using the Gouy method. Mercury(II) tetrathiocyanatocobaltate(II) was used as calibrant. The molar conductivity of the complexes was measured using dimethyl sulphoxide as a solvent.

Muller-Hinton agar was used for testing the susceptibility of microorganisms to antibacterial agents using the well-diffusion technique.

Synthesis of parent complexes: The parent complexes were prepared according to the literature procedure[10]. An ethanolic solution of acetylacetone/ethylacetoacetate was added to a known amount of metal salt dissolved in water in 2 : 1 (ligand : metal) ratio. Precipitation of chelate product takes place upon addition of aqueous ammonia with stirring at pH 7–8. The precipitated chelate was filtered off, washed with ethanol and dried.

Synthesis of product complexes: A solution of 2,4-dinitrophenylhydrazine in ethanol was added to metal β-diketonate/β-ketoester dissolved in ethanol in stoichiometric amount. The reaction mixture was refluxed for about 1 h with occasional stirring. Then the contents were cooled for 2 h. The solid 2,4-dinitrophenylhydrazone product was filtered off and dried.

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