Asian Journal of Chemistry Vol. 9, No. 2 (1997), 183–186

Synthesis, Structural and Antimicrobial Activities of some Phenylhydrazone Derivatives of Metal β-diketonates/β-ketoesters

N. RAMAN*, A. SELVAN and A. SHUNMUGASUNDARAM
Department of Chemistry
VHNSN College, Virudhunagar-626 001, India

Phenylhydrazone derivatives of Cu(II), Ni(II), Co(II) and Co(III) complexes of β-diketones/β-ketoesters have been prepared. These complexes are characterised by elemental analyses, IR, UV spectral data, molar conductance and magnetic susceptibility. They are found to show the antimicrobial activities. The presence of azomethine moiety and chelation effect of the ligand with central metal atom enhance the antimicrobial activities.

INTRODUCTION

A search through literature reveals that 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-keto esters have not received considerable attention. It is therefore thought worthwhile to synthesise phenylhydrazones by the condensation of phenylhydrazine with β-diketones/β-keto esters of Cu(II), Ni(II), Co(II) and Co(III) complexes and to study their antimicrobial activities.

RESULTS AND DISCUSSION

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^{-4} M in DMSO) at room temperature are too small (Λ_m = 3.3–13.1 $ohm^{-1}cm^2\ mol^{-1}$) indicating their non-ionic nature[4]. The magnetic susceptibility measurements reveal square-planar geometry for copper and nickel complexes, tetrahedral for Co(II) complex and octahedral for Co(III) complex.

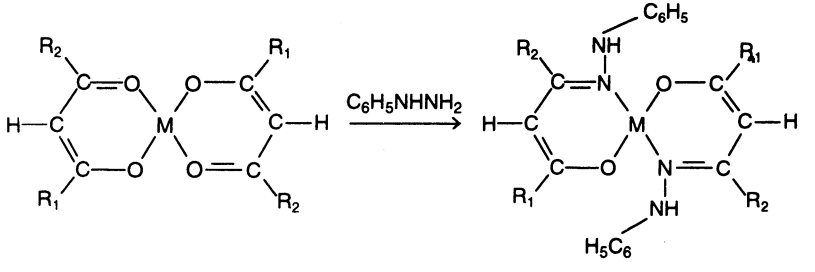
The IR spectrum of product complexes shows specific IR bands for azomethine linkage (C=N stretch) at 1600–1560 cm^{-1} region and N—N stretching at 1000–900 cm^{-1} diagnostic of hydrazone formation[5]. New bands are observed at 1570–1530 cm^{-1} characteristic of ν(C—N—N=C) thus confirming that azomethine nitrogen activity takes part in coordination[6]. The sharp band at 3380–3260 cm^{-1} region shows the presence of N—H group[7]. Band due to ketonic ν(C=O) at 1660 cm^{-1} is found to be absent in the product complexes.

TABLE-1
ANALYTICAL DATA OF THE COMPLEXES

No.	Complex (Colour)	% Analysis, Found (Calcd)				μ_{eff} (B.M.)	m.p. (°C)
		M	C	H	N		
1.	$Cu(EAAP)_2$ (Brownish yellow)	12.5 (12.6)	56.6 (56.4)	5.8 (5.9)	11.1 (11.2)	2.3	> 345
2.	$Cu(acacP)_2$ (Violet)	14.6 (14.3)	59.4 (59.5)	5.6 (5.8)	12.4 (12..6)	2.1	> 345
3.	$Co(acacP)_2$ (Pink)	13.1 (13.4)	60.3 (60.4)	5.6 (5.9)	12.6 (12.8)	3.8	113
4.	$Co(acacP)_3$ (Pale pink)	9.6 (9.4)	62.9 (63.2)	6.2 (6.2)	13.1 (13.4)	diamag	190
5.	$Ni(EAAP)_2$ (Pale green)	12.0 (11.8)	56.9 (56.8)	6.1 (6.0)	11.4 (11.3)	4.4	> 330

Probable mechanistic pathways for the reaction

Formation of phenylhydrazones 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[8]. But, in this case metal phenylhydrazone derivatives are formed which is due to central metal atom of the metal β-diketone/β-ketoester. Presence of metal prohibits the possibility of the formation of pyrazole ring derivatives. This fact is supported by IR, UV and magnetic susceptibility data. In several similar systems, the formation of metal phenylhydrazone derivatives has been established[6, 9, 10]. Therefore the probable reaction could be written as



where, M = Cu(II), Co(II), Ni(II)

$R_1 = R_2 = CH_3$ in β-diketone

$R_1 = OC_2H_5$; $R_2 = CH_3$ in β-ketoester

Antibacterial and antifungal activities

All the product complexes were screened *in vitro* for their antibacterial activity against the gram-positive bacteria *Escherichia coli* by well-diffusion technique. All the product complexes showed better inhibitory zone (Table-2) at a concentration of 1000 μg/10μL. Decreasing the concentration by about ten times the

activity of the complexes is also decreased about half the value of inhibition. All the product complexes were screened *in vitro* for their antifungal activity against *Candida albicans*. In all the complexes the MIC (minimal inhibitory concentration) values were found to be less than 10 μg/10 μL which showed the better inhibitory effect.

TABLE-2
ANTIBACTERIAL ACTIVITY DATA OF THE COMPLEXES

No	Complex	Inhibition zone (mm) of *Escherichia Coli* at concentration (μg/10 μL)	
		1000	100
Product complex			
1.	$Cu(EAAP)_2$	10	5
2.	$Cu(acacP)_2$	16	10
3.	$Co(acacP)_2$	18	10
4.	$Co(acacP)_3$	26	14
5.	$Ni(EAAP)_2$	30	16
Parent complex			
6.	$Cu(EAA)_2$	—	4
7.	$Cu(acac)_2$	—	5
8.	$Co(acac)_2$	—	5
9.	$Co(acac)_3$	—	5
10.	$Ni(EAA)_2$	—	6
Standard drug			
11.	Ampicillin (0.5 μg/10 μl in water)	14	

EXPERIMENTAL

All the chemicals were of AnlaR 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 UV-Visible Spectrophotometer. Magnetic susceptibility measurements were carried out employing the Gouy method. Mercury(II) tetrathiocyanatocobaltate(II) was used as calibrant. The molar conductivity of the complexes was measured on a Systronics 304 Digital Direct Reading Conductivity Meter using dimethyl sulphoxide as a solvent. Mueller-Hinton agar was used for testing the susceptibility of microorganisms to antibacterial agents using the well diffussion technique and Sabouraud Dextrose agar was used for testing the susceptibility of microorganisms to antifungal agents using the serial broth dilution technique[11].

The parent complexes were prepared according to the literature[12–14]. A solution of phenylhydrazine in ethanol was added to metal β-diketonate/β-ketoester dissolved in ethanol in stoichiometric amount. The reaction mixture was refluxed

for about 2 h with occassional stirring. Then the contents were cooled for 3h. The solid phenylhydrazone product was filtered and dried *in vacuo*.

ACKNOWLEDGEMENT

One of the authors (NR) thanks University Grants Commission, New Delhi for financial support.

REFERENCES

1. M. Katyal and Y. Dutt, *Talanta*, **22**, 151 (1975).
2. R.L. Dutta and M. Hossain, *J. Scient. Ind. Res.*, **44**, 635 (1985).
3. S. Jeyasree and K.K. Aravindakshan, *Trans. Met. Chem.*, **18**, 85 (1993).
4. H. Kaur and S.K. Sangal, *J. Indian Chem. Soc.*, **71**, 621 (1994).
5. S. Chandra and K.K. Sharma, *Trans. Met. Chem.*, **8**, 1 (1983).
6. S. Hingorani, K. Singh and B.V. Agarwala, *J. Indian Chem. Soc.*, **71**, 183 (1994).
7. D.B. Reddy, T. Seshamma, B. Seenaiah and M.V.R. Reddy, *Indian J. Chem.*, **30B**, 46 (1991).
8. I.L. Finar, Organic Chemistry, Vol. I: The Fundamental Principles, ELBS with Longman (England), 6th Edn. (1973).
9. P.V. Ananthalakshmi, D. Sandhyarani and V. Jayatyagaraju, *Asian J. Chem.*, **7**, 296 (1995).
10. J.M. Desai, S.I. Marjadi and C.M. Desai, *J. Indian Chem. Soc.*, **70**, 65 (1993).
11. R.F. Boyd, General Microbiology, International Edition, Virginia, 2nd Edn. (1988).
12. H.F. Holtzclaw Jr., A.H. Carlson and J.P. Collman, *J. Am. Chem. Soc.*, **78**, 1838 (1956).
13. H.F. Holtzclaw Jr., K.W.R. Johnson and F.W. Hengereldc, *J. Chem. Soc.*, **74**, 3776 (1952).
14. Therald Moller (Ed.), *Inorganic Syntheses*, **5**, 188 (1957).

(*Received:* 8 July 1996; *Accepted*: 25 October 1996) AJC-1177