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ANTIMICROBIAL ACTIVITY OF NICKEL(II), COPPER(II) AND ZINC(II) CHELATES WITH 2,2'-BIPYRIDYLAMINE AND AROMATIC PHENOLS

A. D. Patel^a; V. M. Patel^a; J. D. Joshi^a

^a Department of Chemistry, Sardar Patel University, Gujarat, India

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NOTE

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A.D. PATEL, V.M. PATEL and J.D. JOSHI*

Department of Chemistry, Sardar Patel University, Vallabh Vidyanager 388 120, Gujarat, India

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The present paper reports the isolation of mixed ligand complexes of the type MAL, where M = Ni(II), Cu(II), Zn(II), A = 2,2'-bipyridylamine and L = aromatic phenols such as catechol (catecholato -2), pyrogallol (pyrogallolato -3), 2,3-dihydroxynaphthalene (2,3-dihydroxynaphthalato-2) or protocatechuic acid (protocatechuato-3). The antimicrobial activity of 2,2'-bipyridylamine and its Ni(II), Cu(II) and Zn(II) complexes is described.

KEYWORDS: Nickel(II), Copper(II), Zinc(II), 2,2'-bipyridylamine, phenols, complexes, antimicrobials, biological activity.

INTRODUCTION

Studies of formation constants of the mixed ligand systems (MAL), where A = 2,2'-bipyridyl or 2,2'-bipyridylamine and L = amino acids or polyhydroxy phenols have been carried out by earlier workers.¹⁻⁵ Schilt and Fritsch⁶ prepared a series of neutral complexes of the type $[M(\text{phen})_2(\text{NCS})_2]$, where M = Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and phen is 1,10-phenanthroline. Dutta and De⁷ isolated solid, mixed ligand complexes of Cu(II) containing 2,2'-bipyridyl or phenanthroline as primary ligand and glycine or alanine as secondary ligands. The study of formation constants⁸ and isolation⁹ of some of the mixed ligand systems (MAL), where M = Cu(II), Ni(II), Zn(II) or Cd(II) and L = catechol, pyrogallol or protocatechuic acid has been reported.

In the present communication, the isolation of heterochelates of Ni(II), Cu(II) or Zn(II) with 2,2'-bipyridylamine (A) and aromatic phenols such as catecholato(-2), pyrogallolato(-3), 2,3-dihydroxynaphthalato(-2) or protocatechuato(-3) is reported. The primary ligand 2,2'-bipyridylamine and the metal chelates have been tested for antimicrobial activity.

* Author for correspondence.

EXPERIMENTAL

Materials

Catechol, pyrogallol, 2,3-dihydroxynaphthalene and protocatechuic acid were of BDH Analar grade. 2,2'-Bipyridylamine was obtained from Fluka and sodium hydroxide from E. Merck. Stock solutions of Ni(II), Cu(II) and Zn(II) perchlorates were prepared and standardised by complexometric methods.¹⁰ Conductivity water was used in the synthesis of the complexes.

Isolation of Complexes

The complexes were prepared by adding 0.5 M (10 cm³) aqueous solutions of Ni(II), Cu(II) or Zn(II) perchlorates to 0.5 M (8 cm³) 2,2'-bipyridylamine solution in ethanol. After stirring well, 0.5 M (10 cm³) catechol, pyrogallol, 2,3-dihydroxynaphthalene or protocatechuic acid solution was added slowly with constant stirring. There was no immediate precipitation. The pH of the solution was raised to 7.0 using 0.5 M sodium hydroxide. This resulted in the precipitation of the solid. The complex thus obtained was washed well with a 1:1 mixture of ethanol and water to remove unreacted metal and ligand. All complexes were dried and stored in a vacuum desiccator.

Elemental analysis were performed with a Coleman CHN analyzer. The metal content was determined¹⁰ by titrations with EDTA.

RESULTS AND DISCUSSION

Analytical data for the complexes indicated 1:1:1 stoichiometry. All the chelates possess high melting points and are stable in air; they are partially soluble in ethanol but insoluble in water and other organic solvents; hence, it was not possible to characterize them by conventional spectroscopic methods.

Antimicrobial activity

In the present investigation, the ligands and their metal chelates have been tested for their effects on the growth of various microbial cultures and studied for their interactive role with *Pseudomonas fluorescens* (bacteria), *R. minuta* (yeast) and *Aspergillus niger* (fungi).

Effects of metal chelates and ligands on the growth of various microorganisms are presented in Table 1. Experiments were designed so as to measure increase or decrease in growth of microorganisms. In order to obtain information on interaction, metal ions were separately tested at concentrations equivalent to 500 ppm metal chelate. Ni(II), Cu(II) and Zn(II) showed significant inhibition of growth of all test organisms. 2,2'-Bipyridylamine showed very high inhibitory activity with only 10–20% growth as compared with the control. Ni(II) and Zn(II) chelates showed about 20 to 40% growth and the Cu(II) chelate showed about 50 to 80% growth of *P. fluorescens* and *A. niger*, (compared to control), but in case of *R. minuta* the metal chelates (Ni, Cu and Zn) did not show much activity. Patterns of activity are complex and no clear trend can be ascertained.

Table 1 Effect of Primary Ligand 2,2'-Bipyridylamine* and its Metal Chelates on the Growth of Microorganisms.

Compound	Bacteria		Yeast		Fungi	
	<i>P.fluorescens</i>		<i>R.minuta</i>		<i>A.niger</i>	
	O.D. (660 nm)	% Growth	O.D. (660 nm)	% Growth	Weight (gm)	% Growth
A	0.150	16	0.094	17	0.072	17
[Ni.A.catechol]H ₂ O	0.201	22	1.493	99	0.135	31
[Ni.A.2,3-dihydroxynaphthalene]H ₂ O	0.283	34	1.354	97	0.152	35
[Ni.A.protocatechuic acid]H ₂ O	0.410	44	1.370	98	0.125	29
[Cu.A.catechol]H ₂ O	0.467	50	1.115	80	0.235	54
[Cu.A.pyrogallo]H ₂ O	0.469	50	1.332	96	0.225	51
[Cu.A.2,3-dihydroxynaphthalene]H ₂ O	0.610	65	1.114	80	0.355	81
[Cu.A.protocatechuic acid]H ₂ O	0.688	74	1.097	79	0.320	73
[Zn.A.catechol]H ₂ O	0.277	18	1.382	98	0.097	41
[Zn.A.pyrogallo]H ₂ O	0.267	17	1.385	98	0.089	37
[Zn.A.2,3-dihydroxynaphthalene]H ₂ O	0.622	40	1.401	99	0.086	36
[Zn.A.protocatechuic acid]H ₂ O	0.620	40	1.496	109	0.076	32

*A = 2,2'-bipyridylamine; *Growth was compared with control and is expressed as %.

The results suggest that changes in structure due to coordination in mixed ligand complexes cause the growth of some microorganisms increase. Alternatively inhibitory effects may result. Thus for the synthesis of pharmacologically active derivatives of metal chelates, it is very important to know the role of metal ions.

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