





Dr. Mamta http:// <u>www.sasjournals.com</u> http:// <u>www.jbcr.co.in</u> jbiolchemres@gmail.com

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Synthesis and Characterization of Macrocyclic Complexes Co(III) with Oxa-amine and a-diketone Mithlesh Agrawal and Mamta

Department of Chemistry, University of Rajasthan, Jaipur – 302004, India

ABSTRACT

A unique macrocyclicCo(III) compounds have been synthesized by treating oxa-azamacrocycles with cobalt chloride in butanol. These complexes were characterized with the help of elemental analyses, electronic, infrared, and mass spectral studies. On the basis of these studies, a six coordinate octahedral geometry for these complexes have been proposed. The biological activities of these complexes have been tested in vitro to evaluate their activity against Gram +ve and Gram –ve bacteria. Keywords: Synthesis; Co(III) complexes; oxa-azamacrocyclic Schiff bases and Antibacterial studies.

INTRODUCTION

The design and study of metal containing macrocycles is an interesting field of chemistry (Chandra et al. 2007). Over the last few years, very active research in macrocyclic chemistry has attracted the interest of inorganic chemists(Singh et al 2007). The chemistry of macrocyclic complexes is of considerable interest because of their applications for modeling bioinorganic systems, catalysis and analytical practice (Gloe et al. 2005). Spontaneous self-assembly reactions have been considered as vehicles for reliable and economical preparation of macrocyclic complexes. Hence these reactions hold a fascination for chemists to mimic anabolic reaction without enzymes. Nature prefers macrocyclic derivatives for many fundamental biological functions such as photosynthesis and transport of oxygen in mammalian and other respiratory systems (Guerriero et al 1995). Macrocyclic ligands form more stable complexes as compared to analogous open chain ligands (Shakir et al 2007). In-situ one pot template synthesis is the most widely adopted method for preparation of macrocyclic complexes(Salvati-Niasariet al 2007). A number of nitrogen and oxygen donor macrocyclic derivatives have been used for a long time in analytical, industrial and medical applications (Tian et al 2006). Macrocyclic metal complexes are of great importance due to their resemblances with many natural systems such as porphyrins and cobalamines(Chandra et al 2007). Some macrocyclic complexes have been found to exhibit potential antibacterial activities (Singh et al 2006, Singh et al 2007).

Experimental

All the chemicalsi.e 1,12-diamino-4,9-dioxadodecane, 2,3-butanedione, 4,4'-dimethylbenzil, 3,4-hexanedione, 1-phenyl-1,2-propanedione, and 2,3-pentanedione, benzyl used were procured from Aldrich and Merck respectively. Metal salt were purchased from Fluka and were used as received. Solvent used were of standard grade.

Synthesis of complexes

A template reaction was carried out for the formation of the complexes. A butanolic solution (10ml) of the metal salt (.81gm) was mixed with a butanolic solution (10 ml) of 1,12-diamino-4,9-dioxadodecane (0.695gm)and with anbutanolic solution (10ml)of α -diketonesi.e 2,3-butanedione (0.293gm), 2,3pentanedione (.340gm), 3,4-hexanedione (.38gm), 1-phenyl-1,2-propanedione (.504gm), Benzil (.71 gm), 4,4-dimethylbenzil (.811gm)in the presence of a few drops of concentrated HCl. The solution was stirred for about 5 to 6 h in each case which resulted in the formation of precipitate. The mixture was cooled and filtered. The precipitate was washed with the butanol and dried in vacuo in a desiccator over anhydrous calcium chloride at room temperature. Yield: 40–55%.

Physical measurements

Cobalt was determined volumetrically by EDTA using Xylenol orange as indicator. Nitrogen was determined by the kjeldahl method. The FTIR spectra were recorded as KBr pellets in the region 4000–200 cm⁻¹ on a SHIMADZU-JAPAN8400S. FABmass spectra were recorded on Jeol SX102/DA-600 mass spectrometer/Data System using Argon/Xenon (6kV, 10mA) as the FAB gas. Electronic spectra were recorded in DMSO in the range of 200-800 nm on a SYSTRONICS UV-VIS Spectrophotometer.

Results and discussion

A series of oxa-azamacrocyclic complexes [MLX₂]X were synthesized by the template condensation of α -diketones, and 1,12-diamino-4,9-dioxadodecane with metal ions in a 1:1:1 molar ratio, which may be represented by the following reactions:



Where $M = Co; X = Cl^{-}$,

Scheme: Template synthesis of 16-membered metal complexes.

	R"	R
2,3-butanedione	-CH ₃	-CH ₃
2,3-pentanedione	-CH ₃	-CH ₂ CH ₃
3,4-hexanedione	-CH ₂ CH ₃	-CH ₂ CH ₃
1-phenylpropane-1,2-dione	-CH ₃	-C ₆ H ₅
1,2-diphenylethane-1,2-dione or Benzil	$-C_6H_5$	-C ₆ H ₅
4,4'-dimethylbenzil	-(CH ₃)C ₆ H ₄	-(CH ₃)C ₆ H ₄

IR Spectra

A study and comparison of infrared spectra of free ligand and its metal complexes infers that the ligand behaves as neutral tetradentate and its metals are coordinated through N and O. The absorption at 1620 cm⁻¹ in free ligand can be attributed to (C=N) stretching vibration of imine nitrogen, which is in a good agreement with previous observations. On complexation this frequency was observed to be shifted to a lower wave number .These observations suggest the involvement of unsaturated nitrogen atoms of the azomethine groups in bonding with the metal ions. The IR spectral bands in the ligand are practically unchanged in the complexes but show some new bands with medium to weak intensity in the 520-450 cm⁻¹ region tentatively assigned to (M–N) and (M–O). (M–Cl) is tentatively assigned in the 300–320 cm⁻¹ region (Agarwal et al 2005, Chandra et al 2004).

Electronic spectra

The electronic absorption spectra of the ligands and their complexes were recorded in DMSO solution. Electronic absorption spectral studies combined with magnetic studies give an insight into thestereochemistry of the complexes. The Π - Π * transition of the ligands is observed around 270 nm. The diamagnetism exhibited by the complexes suggests them to be cobalt (III) complexes. The coordination number being six, an octahedral geometry is suggested for these complexes, which is further substantiated by the electronic absorption spectra (Lever et al 1968). The electronic absorption spectrum of the diamagnetic cobalt (III) complexes shows intense bands around 400 nm which may be due to the overlap of the charge-transfer band over the d-d transition. The intra-ligand Π - Π *transition is observed around 375 to 395 nm.

S. No	Concentration 10 µg/ disk		<i>Bacillus subtilis</i> Test zone of inhibition (mm)	Streptococcus pneumonia, Test zone of inhibition (mm)	Pseudomona s aeruginosa Test zone of inhibition (mm)	<i>Klebsiellapneumon iae</i> Test zone of inhibition (mm)	
1.	[Co(C ₁₄ H ₂₆ N ₂ O ₂)Cl ₂]Cl	20 µl	No zone of	No zone of	No zone of	No zone of inhibition	
		40 µl	7	No zone of inhibition	No zone of inhibition	10	
		60 µl	No zone of inhibition	No zone of inhibition	No zone of inhibition	No zone of inhibition	
		80 µl	No zone of inhibition	5	No zone of inhibition	No zone of inhibition	
	[Co(C ₁₅ H ₂₈ N ₂ O ₂)Cl ₂]Cl	20 µl	No zone of inhibition	No zone of inhibition	No zone of inhibition	No zone of inhibition	
2.		40 µl	9	No zone of inhibition	No zone of inhibition	No zone of inhibition	
		60 µl	No zone of inhibition	No zone of inhibition	No zone of inhibition	No zone of inhibition	
		80 µl	No zone of inhibition	No zone of inhibition	No zone of inhibition	No zone of inhibition	
3.	[Co(C ₁₆ H ₃₀ N ₂ O ₂)Cl ₂]Cl	20 µl	No zone of inhibition	10	No zone of inhibition	No zone of inhibition	
		40 µl	No zone of inhibition	No zone of inhibition	No zone of inhibition	6	
		60 µl	No zone of inhibition	No zone of inhibition	No zone of inhibition	No zone of inhibition	
		80 µl	No zone of inhibition	No zone of inhibition	11	No zone of inhibition	
4.	[Co(C ₁₉ H ₂₈ N ₂ O ₂)Cl ₂]Cl	20 µl	No zone of inhibition	No zone of inhibition	No zone of inhibition	No zone of inhibition	
		40 µl	No zone of inhibition	No zone of inhibition	No zone of inhibition	8	
		60 µl	No zone of inhibition	No zone of inhibition	No zone of inhibition	No zone of inhibition	
		80 µl	No zone of inhibition	No zone of inhibition	6	No zone of inhibition	

Table 1. Antimicrobial activit	v of the Cobalt () complexes.
	y of the cosult (, complexes.

Biological Activity

It is known that chelation tends to make the ligand act as more powerful and potent bactericidal agents, thus killing more of the bacteria than the ligand. It is observed that, in a complex, the positive charge of the metal is partially shared with the donor atoms present in the ligands, and there may be π -electron delocalization over the whole chelate (Wissner et al 2000).

This increases the lipophilic character of the metal chelate and favours its permeation through the lipoid layer of the bacterial membranes. The increased lipophilic character of these complexes seems to be the reason of their enhanced potent antibacterial activity. There are other factors which also increase the activity, which are solubility, conductivity, and bond length between the metal and the ligand.

Mass Spectra

The FAB mass spectra of Co(III) macrocyclic complexes have been recorded. All the spectra exhibit parent peaks due to molecular ions (M^+). The proposed molecular formula of these complexes was confirmed by comparing their molecular formula weights with m/z values. This data is in good agreement with the respective molecular formulae.The molecular ion [M]⁺ and [M+2]⁺ peak for cobalt (III) complexes derived from 1,12-diamino-4,9-dioxadodecane and α -diketones were as follows:m/z= [M]⁺ = 418.7 (³⁵Cl), [M+2]⁺ = 420.7 (³⁷Cl) [Mol.Wt.-419], m/z=[M]⁺ = 433.2 (³⁵Cl), [M+2]⁺ = 435.2 (³⁷Cl)[Mol.Wt.-433], m/z = [M]⁺ = 446.1 (³⁵Cl), [M+2]⁺ = 448.1 (³⁷Cl) [Mol.Wt.- 447], m/z=[M]⁺ = 554.4 (³⁵Cl), [M+2]⁺ = 552.4 (³⁷Cl) [Mol.Wt.- 554], m/z= [M]⁺ = 543.63 (³⁵Cl), [M+2]⁺ = 541.63 (³⁷Cl) [Mol.Wt.- 543], m/z= [M]⁺ = 571 (³⁵Cl), [M+2]⁺ = 573(³⁷Cl) [Mol.Wt.- 571]

		Colour	Analysis % Found (calculated)					Deco	
S. No.	Complexes Molecular wt (gm)	and Yield	м	С	н	0	Z	Cl	m Temp. (C ⁰)
1.	[Co(C ₁₄ H ₂₆ N ₂ O ₂)Cl ₂]Cl 419.36	Brown (53.5%)	13.96 (14.04)	39.57 (40.00)	6.15 (6.25)	7.2 (7.5)	6.4 (6.6)	25.1 (25.3)	315
2.	[Co(C ₁₅ H ₂₈ N ₂ O ₂)Cl ₂]Cl 433.59	Orange (40.8%)	13.1 (13.5)	41.40 (41.55)	6.3 (6.5)	7.0 (7.3)	6.6 (6.4)	24.2 (24.4)	265
3.	[Co(C ₁₆ H ₃₀ N ₂ O ₂)Cl ₂]Cl 447.54	Dark Green (55%)	12. 94 (13.1)	42.6 (42.9)	6.3 (6.7)	6.8 (7.1)	6.0 (6.2)	23.6 (23.7)	290
4.	[Co(C ₁₉ H ₂₈ N ₂ O ₂)Cl ₂]Cl 554.48	Bluish (48.4%)	11.9 (12.2)	47.17 (47.3)	5.9 (5.8)	6.5 (6.6)	5.5 (5.8)	22.01 (22.05)	283
5.	[Co(C ₂₄ H ₃₀ N ₂ O ₂ Cl ₂]Cl 543.63	Red (48.6%)	10.7 (10.8)	52.9 (53.0)	5.6 (5.5)	5.6 (5.8)	5.0 (5.1)	19.2 (19.5)	277
6.	[Co(C ₂₆ H ₃₄ N ₂ O ₂)Cl ₂]Cl 571.59	Orange (50.5%)	10.2 (10.3)	54.1 (54.6)	5.9 (6.0)	5.3 (5.5)	4.5 (4.9)	18.4 (18.5)	320

ANALYSIS AND CHARACTERIZATION OF MACROCYCLIC COMPLEXES

CONCLUSIONS

The present investigation deals with the synthesis and characterization of macrocyclic complexes of transition metal such as Co(III). On the basis of various physicochemical studies performed the complexes are found to be diamagnetic in nature and are having octahedral geometry.

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Corresponding author: Mithlesh Agrawal and Mamta, Department of Chemistry, University of Rajasthan, Jaipur – 302004, India Email: <u>mamta.gpc@gmail.com</u>