SYNTHESIS OF METHYL, BENZYL AND PSEUDO-HALOGENO CO (III) COMPLEXES OF A DIOXIME CONTAINING A CROWN ETHER MOIETY

SangeetaSahu

Department of Applied Chemistry, Bhila iInstitute of Technology, Kendri, New Raipur-493661 (Chhattisgarh) INDIA sangeetasahu76@gmail.com

Abstract

In view of the importance of the macrocyclic chemistry, the Cobalt (II) complexes of several new categories of azamacrocycles were synthesized. Here we describes a new quadridentate ligand 5,6-Benzo(15-crown-5)4,7-diaza deca-2,9-ethanedial dioxime $(C_{18}H_{24}N_4O_7)$. This chelate coordinates with cobalt in the equatorial position as a monoanion leaving the axial sites vacant for coordination by a variety of monodentate ligands, thereby paving the way for the synthesis of pseudo halogeno and alkyl Co(III) complexes. The macrocyclic ligands and their complexes have been characterized by elemental analysis, molecular weight determination, conductance, IR and NMR spectral studies. The spectral data suggested tetra coordinated state for cobalt, its geometry is tetrahedral. Conductivity data suggests that they behave as electrolytes. The formulation of the complexes has been established on the basis of chemical composition. Further analysis for C, H, and N and may be required for complete description of the complexes. The ligand and their complexes have been used as catalyst in many industries.

Keywords: Cobalt, Macrocyclic complex, synthesis, spectroscopy

1. INTRODUCTION

Crown ether compounds, first synthesized by Pederson, who described ⁽¹⁾ their ion binding properties have been a focus of interest. This is because of their possible chemical and biological application and their unusual binding capacity, salvation and transport effect. ⁽²⁾

Vic –Dioximes containing mildly acidic hydroxyl groups and slightly basic nitrogen atoms are amphoteric and their transition metal complexes have widely studied as analytical reagents⁽³⁾. They have also been examined as compounds with columnar stacking which is thought to be the reason for their semiconducting properties⁽⁴⁾. Here we describes a new quadridentate ligand 5,6-Benzo(15-crown-5)4,7-diaza deca-2,9-ethanedial dioxime (C₁₈H₂₄N₄O₇). This chelate coordinates with cobalt in the equatorial position as a monoanion leaving the axial sites vacant for coordination by a variety of monodentate ligands, thereby paving the way for the synthesis of pseudo halogeno and alkyl Co(III) complexes.

2. EXPERIMENTAL

4,5-Diamino benzo (15-crown-5) was prepared according to a reported method(5).

2.1 Materials and methods

In view of the importance of macro cyclic chemistry, the Co(III) complexes of new categories of aza macro cyclic were synthesized. Template condensation of ethane dionemonoxime was dissolved in water at 60oC under nitrogen atmosphere. 4,5-diamino benzo 915-crown-5)was added in small portion to this solution and ethanol was then added to reaction mixture, which was stirred at 45oC for 18 hrs, then under reflex for one hour. After cooling to 5oC the mixture was filtered, washed with water coldethanol and ether and then dried in vacuo to yield the corresponding metal complex of the following yellow colored solid macro cyclic legend - 5,6-Benzo(15-crown-5)4,7-diaza deca-2,9-ethanedial dioxime (C18H24N4O7).



Macro cyclic legend – 5,6-Benzo(15-crown-5)4,7-diaza deca-2,9-ethanedial dioxime (C18H24N4O7). Or (H2L)

2.2 Materials

Solvents and reagents used in the synthesis of Co (III) complexes were reagent grade and were used without further purification.

2.3 Synthesis of [Co (C18H23N4O7)Br2]:

A solution of CoBr2.6H2O (3.27 g,10mmol) in dry acetone (30 ml) was added drop wise to a solution of the free ligand of air was then used to agitate the solution for vigorous stirring for two hours. The dark green solution was filtered to remove undisclosed particles and allow to stand overnight at room temperature. The dark green crystalline mass was filtered, washed with dry acetone followed by dry ether and collected under vacuum over dried anhydrous calcium chloride.

13C Η NMR 9DMSO-d6) δ-144.54, 143.19, 140.79, 127.38; 97.81, 62.35-60.15; 10.47; Yield (3.25 g, 79.65%)



Structure of [Co (C₁₈H₂₃N₄O₇)Br₂]

2.4 Synthesis of [Co (C18H23N4O7)(NCS)(Br):

A green solution of [Co (C18H23N4O7)Br2] (0.63g,1 mmol) in aqueous hot methyl alcohol (1:8) (20ml) with stirring at 600C for one hour. The volume of the reaction mixture was then allowed to stand overnight in the refrigerator at ooC. The resulting pale green crystalline product was filtered off, washed with cold water and cold ethanol and then dried in vacuo. The product was recrystallised from methanol,

13 { C } H NMR(DMSO-d6)- δ-142.88;142.22,140.93;128.40;100.44,62.17-60.01;16.93,10.75; Yield (0.460GM;66.23%).



Structure of [Co (C₁₈H₂₃N₄O₇)(NCS)(Br)

3. RESULT AND DISCUSSION:

3.1 Chemical analysis

Microanalysis for carbon, hydrogen and nitrogen were carried out at the regional sophisticated instrumentation centre, central drug research institute (CDRI) Lucknow.(Table-1.1)

Table 1.1: Analytical	and physical	data for the	dioxime	and its
	complexe	es		

Compou	Col	Yield	Μ		%	Foun	d (
nd	our	(%),	+	Calculated)			
		M.P. ⁰		С	н	N	М
		С		C		- 1	111
(C ₁₈ H ₂₄ N	Pal	162°C	4	(52	(5.	(13.	
₄ O ₇). Or	e		0	.94	88)	72)	-
(H_2L)	yell		9)	5.7	13.6	
	ow			52.	2	0	
				80			
	D	100	-	(0.1	(2)	(0.0	(0)
Co	Dar	100	6	(34	(3.	(8.9	(9.
$(C_{18}H_{23}N)$	k		2	.50	67)	4)	41)
$_{4}O_{7})Br_{2}$	gre		4)	3.5	8.80	9.3
	en			34.	2		0
				40			
Со	Pal	175	6	(37	(3.	(11.	(9.
$(C_{18}H_{23}N$	e		2	.75	80)	59)	75)
₄ O ₇)(NC	gre		2)	3.7	11.4	9.6
S)Br	en			37.	0	0	2
				60			

3.2Physical measurements

The structure of the ligand was determined by a combination of elemental analysis-NMR, IR and mass spectral data. Conductivity data of the complex was recorded using their 0.01 M aqueous solution, with the help of a DDR Conductivity meter type 304. A Jeol D-300 (El/Cl) spectrometer was used for obtaining the mass spectra of the ligand hydrochlorides of low molecular weight. Infrared spectra in the range 4000-250cm-1 were recorded by Perkin Elmer infrared spectrometer in KBr pellets. FTIR spectra of a number of compound were recorded by Shimadzu 8201 PC (4000-350 cm-1) infrared spectrophotometer. The pmr spectra were taken in D2O solution and recorded on bruker DRX300 (300 MHz. PT NMR) using tetra methylsilane as an internal standard.

3.3 Nuclear magnetic resonance spectra

In the 1 H-NMR-spectrum of H2L(C18H24N4O7) the(N-OH) proton appears as a singler at δ 12.09 ppm which disappears uppn deuterium exchange; aromatic protons are observed at (7.30 as a singlet.In the13C H NMR –spectrum of H2L((C18H24N4O7), the carbon resonance of the azomethine groups neighboringbenzo and hydroxylimino groups are found at δ 153.80 and 151.50 ppm respectively, at lower fields as given literature(6).

The 1 H-NMR-spectrum of [Co (C18H23N4O7)Br2]; shows significant chemical shift for the deuterium exchangeable hydrogen-bridging (OH) proton at δ (17.40ppm) in the lower field region, which can be assigned to the formation of desired complex. The 13C $\{H\}$ NMR spectrum of Co (C18H23N4O7)Br2 generally resemble that observed for the free ligand.

Table-1.2: 1H-NMR-Spectral data for the dioxime and some
of its complexes

S.N o.	COMPOUND	О-Н-О	- OCH ₂ C H ₂ O-	Ar-H
1.	(C ₁₈ H ₂₄ N ₄ O ₇). Or (H ₂ L)	-	4.10- 3.50(m,1 6H)	7.28(s, 2H)
2.	Co (C ₁₈ H ₂₃ N ₄ O ₇)B r ₂	17.40(s, 2H)	3.90- 3.36(m,1 6H)	7.04(s, 2H)
3.	Co (C ₁₈ H ₂₃ N ₄ O ₇)(NCS)Br	17.32(s, 1H)	4.02- 3.50(m,1 6H)	7.10(s, 2H)

3.4 Infrared spectra:

The IR-spectrum of (C18H24N4O7) H2L also provides additional data confirming the structure. The ligand shows no characteristic absorptions assignable to either NH2 or (C=O) function but it has a broad resonance at 3180 cm-1which can be attributed to v(O-H) of the oxime groups. The sharp and intence peak at 1650 cm-1 is attributed to the stretching vibration of (C=N) groups attached to the oximegroups (7). The FAB+ (Fast atom bombardment positive, m-nitro C6H5CH2OH as matrix) pattern observed for this compound shows both [M+1]+ and [M+H2O+2] ions at m/z-409and 428 respectively.

The broad vibrations at 3180 cm-1 in the free ligand are shifted to 2410 cm-1 in the complex [Co (C18H23N4O7)Br2] and can be attributed to the formation of an intramolecular hydrogen bond(8,9). The stretching vibrations of azomethine groups at complex. The mass spectrum of this dibromocobalt (III) complex showed apeak at m/z 624 [M] and confirmed the proposed structure.

Table1.3: Main IR Spectral data for the dioxime and its
complexes

S.NO	COMPOUND	Δ(Ο	N(C=N	N(N
•		-H)	-0)
		H)		
1.	$(C_{18}H_{24}N_4O_7)$. Or	-	1650	980
	(H ₂ L)		1610	
2.	Co (C ₁₈ H ₂₃ N ₄ O ₇)Br ₂	240	1616	945
		0	1595	
3.	Со	241	1610	940
	(C ₁₈ H ₂₃ N ₄ O ₇)(NCS)	0	1570	
	Br			

3180cm-1[v(O-H)(H2L)]; 2070cm-1[v(SCN-)];2175 and 2165cm-1

3.5 Mass Spectra:

Mass spectral data and chemical analysis confirm (1:1) (metal: ligand) ratio. The FAB mass spectra of [Co (C18H23N4O7)(NCS)(Br) showed the peaks as expected at m/z-622 [M+H2O+1].The IR spectra of the complexes are similar to that of dibromo cobalt(III) complex expect for the presence of the (SCN) stretching vibrations as expected. The thiocyano groups may coordinate with cobalt through nitrogen or the sulphurdonar(10).

3.6 Solubility, Conductivity and Other Data:

The compounds are highly soluble in water and generally in polar solvents like ethanol, methanol, DMF, DMSO etc. The colourof (C18H24N4O7). Or (H2L), Co (C18H23N4O7)Br2,

Co (C18H23N4O7)(CN)Br are Pale yellow ,Dark green and Pale green respectively. The complexes are thermally stable and decompose above 2000C (11,12).

CONCLUTIONS

The synthesis of macrocyclic complexes In view of the importance of the macrocyclic chemistry, cobalt (II) complexes of several new categories of new quadridentate ligand 5,6-Benzo(15-crown-5)4,7-diaza deca-2,9-ethanedial dioxime (C18H24N4O7) were synthesized. Template condensation of new quadridentate ligand 5.6-Benzo(15crown-5)4,7-diaza deca-2,9-ethanedial dioxime (C18H24N4O7) with CoBr2.6H2O in dry acetone vielded the corresponding complexes Co metal such as (C18H23N4O7)Br2] and then [Co (C18H23N4O7)Br2] in aqueous hot methyl alcohol (1:8) yield the macrocyclic complex [Co (C18H23N4O7)(NCS)(Br).The macrocyclic ligands and their complexes have been characterized by elemental analysis, molecular weight determination, conductance, IR and NMR spectral studies. The spectral data suggested tetra coordinated state for cobalt (III), its geometry is tetrahedral. Conductivity data suggests that they behave as electrolytes. The formulation of the complexes has been established on the basis of chemical composition. The ligand and their complexes have been used as catalyst in many industries.

REFERENCES

[1]. Pederrson, C.J., J.Am. Chem. Soc. 93 (1967)7017.

[2]. Bajaj A.V.and Poonia, N.S., Coord. Chem. Rev; 87 (1988) 55.
[3]. Gok, Y., New, J., Chem; 20(1996) 971, Welcher,
F. j., Org. Anal. Reagents 3(1947) 154; Serin S., Gok,
Y., Karabocek, S. and Gultekin, N.Analyst; 119(1994) 1629.

[4]. ThomasT.W.and Underhill,A.E.,Chem. Soc. Rev; 191972)99.

[5]. Gok, Y., Org. Prep. Proced. Int. 22 (1990)641.

[6]. Altin K.R., Klummp G.W., DekoningH.and Van Den Winkel, Y., Recl. Trav. Chem. Pays. Bas, 113 (1994) 329;
Van Arkel B., Vander Baan J.L.,Balt S.,Bickelhaupt, F.,de Bolster W.G. and Klumpp, G.W.,Tetrahedron 51 (1995) 4161.
[7]. Yamazaki N. and Hohokbe Y., Bull.Chem. Soc.Japan44 (1971) 63.

[8]. BlineR.andHadzi D.,J.Chem. Soc.(1958)4536.

[9]. Nakamoto K.,Infra red spectra of Inorganic and coordination compounds Wiley,Interscience, New York91970).

[10]. Sun L., Hammarstorm, L., Akermark, B. and Styring S., Chem. Soc. Rev; 30, 36 (2001).

[11]. McFarland S.A., Magde D., and Finney N.S., Inorg. Chem; 44, 4066 (2005).