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Analysis of transition metal complexes of Rhodium(iii) containing trans–(14)–diene

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Abstract

Present Paper, to stretch out our examination to Ru(III) containing tetraazacyclic ligand with dicarbatylate anions. Keeping these realities in see, we report her in the union and charaterization of some new blended ligand edifices of Ru(III) containing dibasic acida as essential and 14 membered macrocyclic tetramine.

Keywords: transition metal complexes, Rhodium(iii) containing trans–(14)–diene

Introduction

The legating property of nitrogen givers in a macrocycles, the more noteworthy strength of the macrocycle have become a likely piece of general field of coordination science during the most recent couple of many years. A far reaching study of writing of the buildings of methyl subbed 14-membered macrocycles with a tetraaza contributor framework shows that a lot of work has been done on their combination and responses [1-4]. Some metal edifices of 5, 7, 7, 12, 14-hexamethyl-1, 4, 8, 11-tetraazacyclo-tetradeca 4, 11- diene have been accounted for by certain laborers [5-7]. Nair *et al.* [8] have arranged some new Cr(III) buildings of 5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradeca 4, 11- diene. Carboxylic corrosive composed with metal particle show germ-free properties on movies, strands and textures.

Synthesis of the salt of the macrocyclic ligands 5, 7, 7, 12, 14, 14-hexa methyl-1, 4, 8, 11-tetraazacyclotetradeca 4, 11,-diene dihydro bromide dihydrate, [$L.2HBr.2H_2O$]:

A solution of ethylenediamine (0.15 mol, 10 ml.) in methanol (100 ml) was cooled in an ice-bath and concentrated (48%) hydrobromic acid (0.32 mol, 35 ml) was added drop-wise. The white precipitate of ethylenediamine dihydrobromide was filtered off, washed with n-butanol, then ether and dried in vacuo. Acetone (100 ml) and ethylenediamine (30.0 g, 0.05 mol) were added to ethylenediamine dihydrobromide (11.1 g, 0.05 mol). The mixture was stirred and heated at 45°C for about 1 h. A copious precipitate (white) of the macrocyclic dihydrobromide was formed.

The solution was cooled and filtered off the product, washed with ice-cold acetone, then, ether and dried in vacuo, yield 14.08 g; m.p. 106-107 [decomp. lit. [2, 3] m.p. 107-108°C]. Found C, 8.12; N, 11.84, calc : for $C_{16}H_{32}N_4$, $2HBr.2H_2O$; C, 40.17, H, 8.00, and N,'11.71%.

General method for the precursor complexes of the type trans-[M(X) L] Cl where, M = Rh(III), X = Anion of dibasic acid; L = 5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradeca 4, 11,-diene:

A solution of metal salt (0.005 mol) in distilled ethanol (20 ml) was mixed homogeneously with the ethanolic solution of X (0.01 mol). To this mixture another ethanolic solution of L. $2HBr.2H_2O$ (0.05 ml) was added drop-wise with constant stirring. Then the mxiture was refluxed for about 3 hours on steam bath and a solid form of product appeared. The resulting product was then filtered off and washed with ethanol, ether and finally dried in vacua over silica gel.

Result and Discussion

The complexes have been prepared by the following general reaction:

$$M + DB + L \rightarrow [M(DB).L]$$

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where, M = Rh(III)DB = Anion 'of dicarboxylic acid and L = Trans-diene.

Elemental analysis and Conductivity

The analytical data and some physical properties of the complexes are given in tables 1 and 2 respectively.

Table 1: Analytical data and yields of the complexes

No.	Complex	Y%	M%	C%	H%	N%
1.	[Rh(dpa) L]	69	1652	57.78	6.42	8.96
			(16.22)	(57.52)	(6.16)	(8.64)
2.	[Rh(hpa) L]	65	18.34	53.45	6.77	9.96
			(18.42)	(53.22)	(6.44)	(6.62)
3.	[Rh(adp) L]	62	19.52	50.07	7.53	10.62
			(19.32)	(49.76)	(7.22)	(10.34)
4.	[Rh(glu) L]	60	20.05	49.12	7.40	10.91
			(19.88)	(48.86)	(7.16)	(10.70)

*Figures in the parenthesis are experimental values.

M = Metal, dpa^{2-} = $C_{14}H_8O_4$, hpa^{2-} = $C_9H_6O_4$, gdp^{2-} = $C_6H_{10}O_4$, glu^{2-} =$C_5H_6O_4$ and L = $C_{16}H_{32}H_4$.

All the complexes are soluble in dimethyl formamide and dimethylsulphoxide. The molar conductance values (as shown in table 2) indicate all the complexes are 1:1 electrolytes in DMSO.

Table 2: Physical properties of the complexes

Complex No.*	Decomp. point ($\pm 0.5^0$)**	Molar conductance ohm^{-1} cm^2 $mole^{-1}$	Effective magnetic moment (B.M)	Colour
1	264	114	1.68	Black
2	266	130	1.70	Black
3	235	124	3.68	Black
4.	220	136	3.70	Black

IR studies: Infrared spectral data of the complexes are shown in table-3.

Table 3: IR spectral data of the complexes

No.*	v (NH)	v (CN)	v (CO)	v (MN)	v (MO)
1	2928 s	1655 s	1420 w	450 s	340 s
2	2930 s	1640 s	1334 s	420 s	320 s
3	2920 m	1660 s	1342 s	438 s	345 s
4	2910 s	1463 s	1350 m	420 s	310 s

The observed v(C = O) bands at 1340-1420 cm^{-1} in the IR spectra of the complexes indicate that the dibasic acids are coordinated to the metal. This is further supported by the appearance of v(MO) stretching band at 310-345 cm^{-1}, in the IR region of the spectra of the complexes.

The appearance of v(N-H) and v(C=N) stretching modes for free trans--diene that appeared at ~ 3040 cm^{-1} and ~ 1670 cm^{-1} were found to be shifted to -2910 cm^{-1} and ~1640 cm^{-1} respectively in the complexes. This reveals the coordination of the macrocyclic ligand through nitrogen with the metals. Metal-nitrogen coordination was further supported by the appearance of v(M-N) modes at 420-450 cm^{-1} in the far IR region of the spectra of the complexes.

Magnetic and Electronic spectral studies

The observed values of effective magnetic moments of the complexes at room temperature are shown in table 2. Complexes have magnetic moment μ_{eff}, = 1.70-3.70 B.M corresponding to d^3 ion, thereby suggesting octahedral stereochemistry for these complexes. Complexes of Rh(III), display four d-d bands at 20202-20408, 29069-30187, 30110-304080 and 34013-34482 cm^{-1}. These bands corresponds to the transitions, $^2T_{2g} \rightarrow {}^4T_{lg}$, $^2T_{2g} \rightarrow {}^4T_{2g}$, $^2T_{2g} \rightarrow {}^2A_{2g}$ and $^2T_{2g} \rightarrow {}^4E_{lg}$ respectively, clearly suggesting the octahedral geometry of the complexes.

Table 4: Electronic spectral data of the complexes

Complexes*	Spectral band maxima (cm^{-1})		
	Band I	Band II	Band III
1	20202	29068	34011
2	20328	29760	34244
3	20364	29410	34362
4	220406	30485	34480

Conclusion

In the light of the above conversation, the likely broad structure of the edifices can be pictorized as follows :

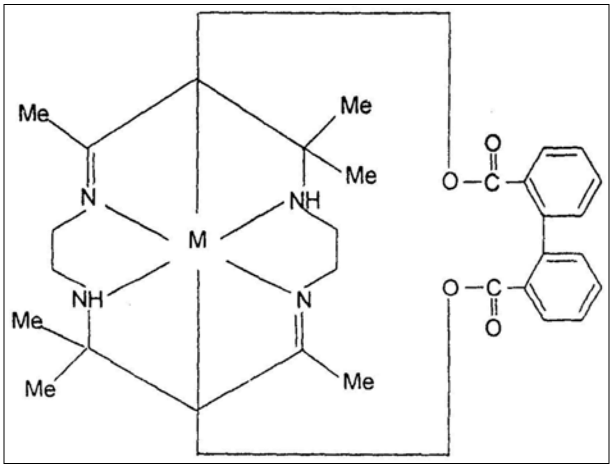

Fig. 1: Possible structure of the complexes

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