Cobalt (III) Complexes of Oxaazamacrocycles Derived from β-diketones and 1, 12-diamino-4, 9-dioxadodecane

Mamta[1], **Mithlesh Agrawal**[2]

Department of Chemistry, University of Rajasthan, Jaipur – 302 004, India

Abstract: ***Co (III) complexes of the type [Co (L)Cl_2]Cl (L –dioxodiazamacrocyclic with 17-membered ring) were synthesized by the template condensation of Cobalt (III) with a mixture of two different ligands i.e. β -diketones, such as 2, 4-pentanedione, 1-phenyl-1, 3-butanedione and 1, 3-diphenyl-1, 3-propanedioneand dioxadiamines such as 1, 12-diamino-4, 9-dioxadodecane in 1:1:1 molar ratio. Different techniques like elemental analysis, FT-IR, FAB massspectroscopy, and magnetic properties, were characterized to complexes.***

Keywords: cobalt complexes, macrocyclic complexes, magnetic moments, IR spectra, electronic spectra

1. Introduction

Transition metal complexes of multidentate Schiff base ligand especially tetradentate Schiff bases have great applicability's in catalysis and material chemistry [1–5]. Tetradentate Schiff bases withN_2O_2 donor set atoms provide suitable coordination environments for a wide variety of metal ions [6]. Recently, Mitra and coworkers have explored the chemistry of nickel (II) complex using a symmetric N_4 donor tetradentate Schiff base ligand. Apart from this, transition metal complexes with symmetric and asymmetric Schiff bases have also been explored by Mitra et al. [7]. Cobalt complexes of tetradentate Schiff base ligands have gained importance as they biomimic the metal-containing sites in cobalamine (B12) coenzymes, metalloproteins and metalloenzymes [8–12]. They also act as oxygen activators and as a model system for dioxygen carriers [13–17]. Cobalt Schiff base complexes are also used as potent antiviral, antibacterial and antitumor agents [18].

2. Experimental

Materials

$CoCl_2.6H_2O$ (Fluka), 1, 12-diamino-4, 9-dioxadodecane (Aldrich) 2, 4-pentanedione (Aldrich), 1-phenyl-1, 3-butanedione (Aldrich) and 1, 3-diphenyl-1, 3-propanedione (Aldrich) and 1-butanol (Merck) were distilled before use.

Analytical methods and measurements

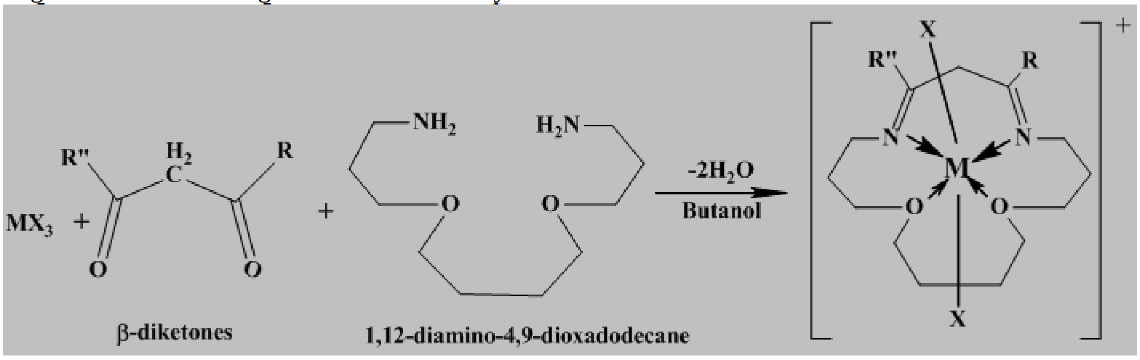
Cobalt was determined volumetrically by EDTA using Xylenol orange as indicator. Nitrogen was determined by the kjeldahl method. The FTIR spectra were recorded as KBr pellets in the region 4000–200 cm-1 on a SHIMADZU-JAPAN8400S. Conductances were determined on a Systronics Direct Reading conductivity meter-304. FAB-mass 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 nm-800 nm on a SYSTRONICS UV-VIS Spectrophotometer

Synthesis of Co (III) complexes of oxaazamacrocycles derived from β–diketones

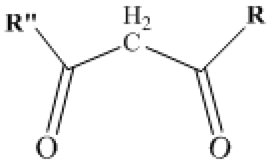
To $CoCl_2$.$6H_2O$ (.81gm) dissolved in 10 ml of *n*-butanol was added dropwise a butanolic solution of 1, 3-diphenyl-1, 3-propanedione (.763gm) under continuous stirring. Then a butanolicsoltuion of 1, 12-diamino-4, 9-dioxadodecane (.695gm in 10 ml) was added and the contents were stirred for 6 h. It was aerated to oxidize Co (II) to Co (III). The solid product was filtered, washed with *n*-butanol and dried under reduced pressure. A similar procedure was adopted for the synthesis of Co (III) complexes of macrocycles derived 2, 4-pentanedione, and 1-phenyl-1, 3-butanedione

3. Results and Discussion

Co (III) complexes of 17-membered oxaazamacro cycles were prepared by template condensation of *β*–diketones such as 2, 4-pentanedione, 1-phenyl-1, 3-butanedione with 1, 12-diamino-4, 9-dioxadodecane, in the presence of Co (III) chloride (Scheme 1)



β-Diketones



R'' R		
2, 4-pentanedione	$-CH_3$	$-CH_3$
1-phenylbutane-1, 3-dione	$-CH_3$	$-C_6H_5$
1, 3-diphenylpropane-1, 3-dione	$-C_6H_5$	$-C_6H_5$

IR Spectra

The IR spectra of the complexes are compared with those of free ligand in order to determine the coordination sites that may involve in complex formation. The important spectral features of the ligands involve a strong absorption band around 1610- 1630 cm^{-1} arises due to C=N stretching, conforming to the formation of the Schiff base. This band occurs at lower frequency in the complexes indicating participation of the azomethine nitrogen in coordination [19]. Two weak bands observed in all the complexes in the range of 500–580 cm^{-1} and 445–510 cm^{-1} are assigned to M– N and M–O (M = cobalt (III)) stretching, respectively. Schiff base in the complexes thus coordinate in a tetradentate fashion through two azomethine–N and two O (in ligand) which was confirmed by mass spectral studies. The bands around 2850-3000 cm^{-1} are assigned to υC-H of aromatic and aliphatic C-H of the coordinated Schiff base ligand. Characteristics ring mode of the aromatic component of the Schiff base ligands were also observed in these complexes. The bands present in the range 300-320 cm^{-1} may be assigned to ν (M–Cl) vibration.[20-23]. A medium intensity absorption band in the region 1400-1500 cm- may be assigned for phenyl ring absorption [24].

4. Magnetic Measurements and Electronic Spectral Studies

All the cobalt (III) complexes is diamagnetic nature, in accordance with an octahedral low spin (d^6) cobalt (III) indicating thereby the preferred octahedral geometry of the complexes. Band assignment for Co (III) is in the range of ≈17000-36000 cm^{-1}.

FAB Mass

FAB mass spectral data of the trivalent cobalt complexes derived from β-diketones with 1, 12-diamino-4, 9-dioxadodecane

Table: FAB mass spectral data of the of Co (III) macocyclic complexes

Sr. No.	*Complexes*	*Mol. Wt.*	*Molecular ion peak $[M]^+$ & $[M+2]^+$ at m/z*	*Important peaks due to complex fragmentation*
1	$[Co\ (C_{15}H_{28}N_2O_2)Cl_2]Cl$	433.51	$[M]^+$ = 431.1 (^{35}Cl), $[M+2]^+$ = 433.1 (^{37}Cl)	$[Co\ (C_{15}H_{28}N_2O_2)Cl_2]^+$ =396 $[Co\ (C_{15}H_{28}N_2O_2)Cl]^+$ =361 $[Co\ (C_{15}H_{28}N_2O_2)]^+$ =326 $[C_{15}H_{28}N_2O_2]^+$ =268
2	$[Co\ (C_{20}H_{30}N_2O_2)Cl_2]Cl$	495.59	$[M]^+$ = 494. 9 (^{35}Cl), $[M+2]^+$ = 496. 9 (^{37}Cl)	$[Co\ (C_{20}H_{30}N_2O_2)Cl_2]^+$ =459 $[Co\ (C_{20}H_{30}N_2O_2)Cl]^+$ =424 $[Co\ (C_{20}H_{30}N_2O_2)]^+$ =389 $[C_{20}H_{30}N_2O_2]^+$ =331
3	$[Co\ (C_{25}H_{32}N_2O_2)Cl_2]Cl$	557.65	$[M]^+$ = 557.3 (^{35}Cl), $[M+2]^+$ = 555.3 (^{37}Cl)	$[Co\ (C_{25}H_{32}N_2O_2)Cl_2]^+$ = 522 $[Co\ (C_{25}H_{32}N_2O_2)Cl]^+$ =487 $[Co\ (C_{25}H_{32}N_2O_2)]^+$ =452 $[C_{25}H_{32}N_2O_2]^+$ =394

Analyses and characterisation of Co (III) complexes.

S.NO	Complexes Molecular wt (gm)	Colour and Yield	Analysis % Found (calculated)						Molar conductance $\Omega^{-1}cm^2mol^{-1}$	Decom Temp. (C^0)
			M	C	H	O	N	Cl		
1	$[Co\ (C_{15}H_{28}N_2O_2)Cl_2]Cl$ 433.51	Blackish (40.8%)	13.0 (13.5)	41.53 (41.55)	6.2 (6.5)	6.9 (7.3)	6.1 (6.4)	24.0 (24.4)	23.6	345
2	$[Co\ (C_{20}H_{30}N_2O_2)Cl_2]Cl$ 495.59	Yellowish (44.6%)	11.3 (11.8)	47.9 (48.4)	5.8 (6.1)	5.4 (5.6)	6.0 (6.4)	21.1 (21.4)	18.9	333
3	$[Co\ (C_{25}H_{32}N_2O_2)Cl_2]Cl$ 557.65	Greenish (42.3%)	10.2 (10.5)	53.6 (53.8)	5.8 (5.7)	5.2 (5.7)	5.1 (5.0)	19.0 (19.04)	24	360

5. Acknowledgements

The authors express their sincere thank to the Head of the Department of Chemistry, University of Rajasthan, Jaipur, for their encouragement and providing the research facilities and to Head of the Department of Chemistry, Banasthali Vidyapith, Banasthali (Rajasthan) for providing the magnetic measurement and CDRI Lucknow for C, H, Analyses FAB mass spectral data.

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