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TRIS-(1, 10-PHENANTHROLINE) COBALT (III) BROMIDE CHLORIDE HEXAHYDRATE: SYNTHESIS, CHARACTERIZATION, ANTIMICROBIAL SCREENING AND XRD STUDIES

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ABSTRACT

A novel complex, tris-(1,10-phenanthroline)cobalt(III) bromide chloride, viz., [Co (phen)$_3$] Br_xCl_y has been prepared and characterized by UV-visible, FT-IR and ^{1}H NMR spectral analysis. The single crystal XRD- analysis of the complex reveals that composition of the complex corresponds to [Co (phen)$_3$]$Br_{1.5}Cl_{1.5}$. $6H_2O$ and hence, it may be named, as tris-(1,10-phenanthroline-k^2 N,N') cobalt (III) 1.5 bromide 1.5 chloride hexahydrate. The complex was subjected to antimicrobial screening and found to show good activity.

Key words: XRD Analysis, Cobalt (III) complex, 1,10–Phenanthroline, Antimicrobial activity.

INTRODUCTION

1,10-Phenanthroline is a versatile hetrocyclic chelating ligand leading to the formation of a rigid planar metal complexes[1,2]. Such complexes have potential applications in chemical, biochemical, photochemical and biological reactions. Tris (1,10-phenanthroline) lanthanum (III) trithiocyanate, has been reported to have anticancer activity[3]. A large number of cobalt complexes have been studied for their antimicrobial activity due to their ease of synthesis and aqueous stability[4]. Polyethyleneiminecobalt (III) phenanthroline complexes are used as indicator for electrochemical detection of DNA hybridization[5]. Crystals of mixed halogen complexes are rarely reported in literature[6]. We have synthesized one such complex, grown as single crystal and its crystal structure was analysed by XRD method. This complex was screened for *in vitro* antibacterial and antifungal activities against various microorganisms and found to exhibit good activity.

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EXPERIMENTAL

Preparation of $[Co(phen)_3]Br_{1.5}Cl_{1.5}.6H_2O$

Cobalt (II) chloride (0.005 mole) and cobalt (II) bromide (0.005 mole) were taken in 150 mL of acetone and stirred for 30 minutes to get homogeneous solution. Then 1,10-phenanthroline monohydrate (0.02 mol) was dissolved in 100 mL of acetone and it was slowly added, with constant stirring, to the solution of mixture of cobalt (II) chloride and cobalt (II) bromide in acetone. About 2 mL of hydrogen peroxide solution was added drop by drop and allowed to react for two hours. After completion of the reaction, a dark red coloured solution was formed. The reaction mixture was allowed to settle for two hours. The dark red coloured product was filtered and washed with excess acetone and dried in a dessicator (yield 78 %). The single crystal suitable for XRD analysis was grown from ethanol by slow evaporation method.

Spectral studies

The UV-Visible spectrum of the complex (1×10^{-4} M in methanol), was obtained from Lambda-25 spectrophotometer using 1 cm matched quartz cells. IR spectrum was obtained using Perkin-Elmer IR spectrophotometer in KBr disc. The ^1H NMR spectrum was recorded in CD_3OD using Joel-500 MHz NMR spectrophotometer.

XRD Studies

The single crystal X-ray diffraction studies were carried out using Bruker axs kappa Apex II single crystal X-ray diffractometer equipped with graphite monochromated Mo(Kα) (λ= 0.7107 Å) radiation and CCD detector.

Antimicrobial studies

The *in vitro* antimicrobial studies of the complex were carried out using different microorganisms by disc diffusion method. The bacterial inoculums were prepared by growing the cells in Mueller Hinton Broth, MHB, (Himedia) for 24 hrs at 37°C. These cell suspensions were diluted with sterile MHB to provide initial cell counts of about 104 CFU/mL. Yeast was grown on Sabouraud Dextrose Broth (SDB) at 28°C for 48 hrs. Antifungal activity was determined by antifungal susceptibility test by preparing potato dextrose broth and inoculating the cultures kept in shaker for 4 days at 28°C

RESULTS AND DISCUSSION

The electronic spectrum of the complex exhibits two intense absorption bands at 250

and 295 nm. The former can be assigned to the intra ligand $\pi \rightarrow \pi^*$ transition in 1,10-phenanthroline ligand and later can be assigned to ligand to metal charge transfer (LMCT) (Fig. 1).

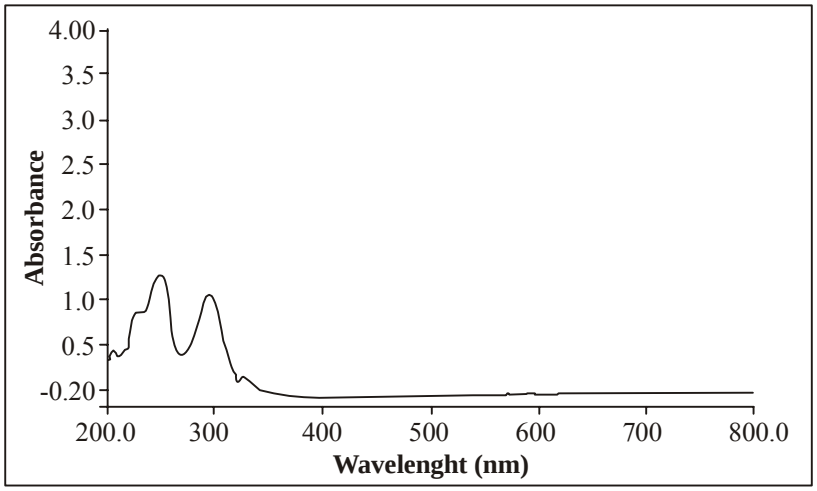

Fig. 1: Electronic spectrum of 1×10^{-4} M tris-(1,10-phenanthroline) cobalt (III) bromide chloride in methanol

The IR spectrum show characteristic stretching frequencies at 3394, 3052, 1624, 1139 and 423 cm^{-1} corresponding to $\gamma_{(O-H)}$ H_2O, $\gamma_{(C-H)}$, $\gamma_{(C=C)}$, $\gamma_{(C=C-H)}$, $\gamma_{(Co-N)}$ of 1,10-phenanthroline ligand, respectively[7] (Fig. 2).

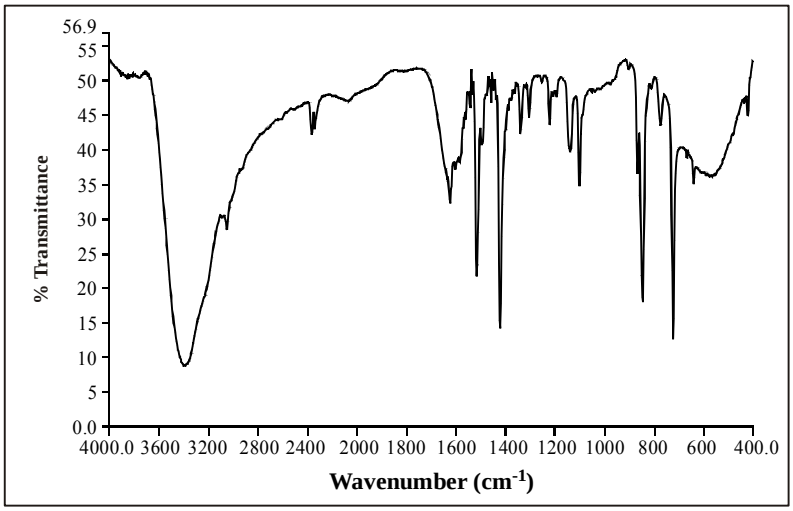

Fig. 2: FT-IR spectrum of tris-(1,10-phenanthroline) cobalt (III) bromide chloride hexahdrate in KBr disc

The ^{1}H NMR doublet at 9.17-9.20 ppm can be assigned to protons attached to C_2 and C_9 ; whereas, the singlet at 8.58 ppm may be due to protons at C_5 and C_6. Similarly, multiplet in the range 8.01-8.09 ppm may arise due to protons at C_3 and C_8 and doublet at 7.80-7.90 ppm may be assigned to protons attached to C_4 and C_7 of 1,10-phenanthroline ligand[7] (Fig. 3).

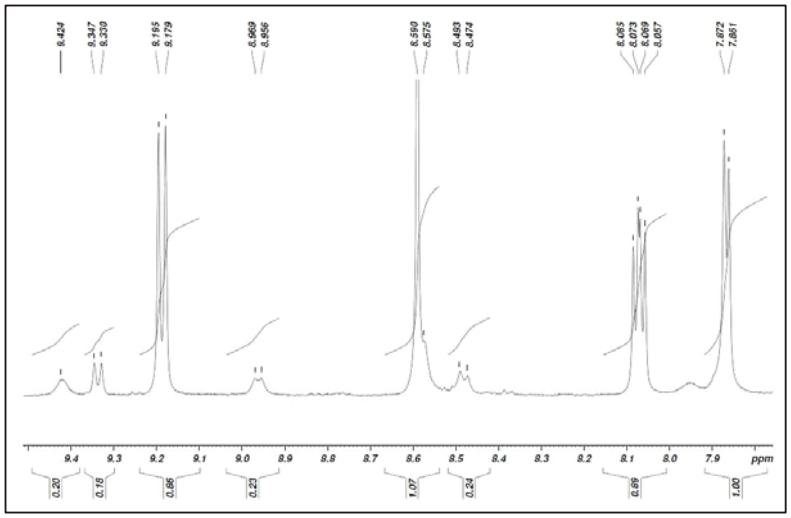

Fig. 3: ^{1}H NMR spectrum of tris-(1,10-phenanthroline) cobalt (III) bromide chloride in CD_3OD

The crystal data for the complex is given in Table 1. The crystal packing of the complex consists of eight molecules per unit cell and each complex molecule, i.e. $[Co(phen)_3]Br_{1.5}Cl_{1.5}$. $6H_2O$ contains a complex cation tris (1,10-phenanthroline) cobalt (III), 1.5 bromide and 1.5 chloride as counter anions and hydration by six molecules of water.

Table 1: Crystal data for $[Co(phen)_3]Br_{1.5}Cl_{1.5}.6\ H_2O$

CCDC No.	**752372**
Empirical formula	$C_{36}\,H_{24}\,N_6\,Co\ 6(H_2O)\ 1.5(Br\ Cl)$
Formula weight	880.68
Temperature	293 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/m

Cont…

CCDC No.	**752372**
Unit cell dimensions	a = 23.7694 (8) Å α = 90°. b = 21.5427 (7) Å β = 108.426 (1)° c = 15.7194 (5) Å γ = 90°.
Volume	7636.6(4) Å ^{3}
Z	8
Absorption coefficient	2.18 mm^{-1}
F(000)	3576
Crystal size	0.30 mm x 0.20 m x 0.20 mm

The cobalt (III) resides in distorted octahedral geometry, and it is cheated by six nitrogen atoms of the two 1,10-phenanthroline ligands. These complex molecules assemble hydrophobic layers via π - π interaction. The charge of the cationic complex molecule is balanced by an average of 1.5 bromide ion and 1.5 chloride ion. These anions and water molecules are linked to each other by O-H…Br, O-H…Cl, O-H…O hydrogen bondings to form hydrophilic layer. There is one more water molecule present in the cavities of the cationic complex molecule (Figs. 4 and 5).

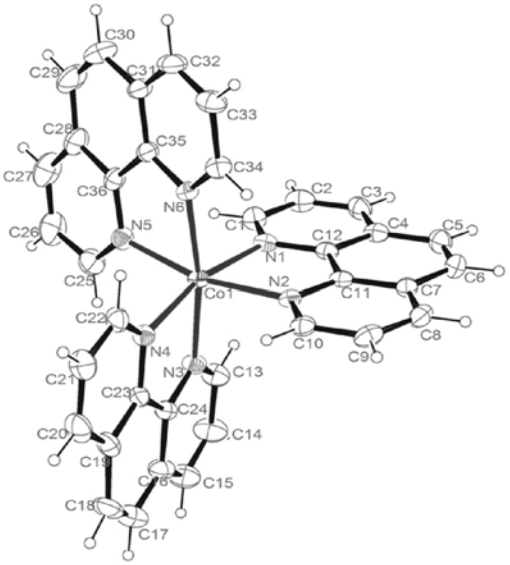

Fig. 4: Structure of the cationic complex molecule. Displacement ellipsoids drawn at 25% probability level

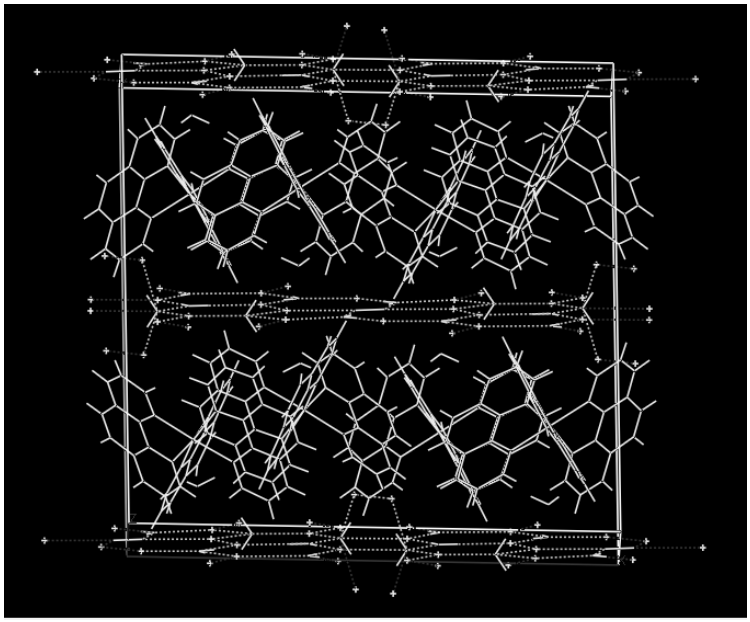

Fig-5: The molecular structure of the complex, viewed along the *c* axis. Hydrogen bonds are shown as dashed lines

The complex was screened *in vitro* for its antimicrobial activity against certain pathogenic bacterial and fungal species using disc diffusion method. The complex was found to exhibit considerable activity against various bacterial and fungal species. The results are given in Tables 2 and 3.

Table 2: Antibacterial activity of $[Co(C_{12}H_8N_2)_3]\ Br_{1.5}Cl_{1.5}.6H_2O$

Code No.	Name of the microbe	(µg/disc)			Standard
		250	500	1000	
25923	*S. aureus*	15	18	21	14
840	*Yersinia enterocolitica*	20	22	25	20
2760	*X. pvoryzae (Erwinia amylovora)*	20	25	25	20
15380	*P. aerugenosa*	17	22	24	13
451	*V. parahaemolyticus*	13	16	19	0
1738	*V. fischeri*	12	16	20	15

Cont…

Code No.	Name of the microbe	(µg/disc)			Standard
		250	500	1000	
111	*Enterobacter aerogens*	13	15	18	17
441	*B. subtilis*	16	18	22	23
25922	*E.coli*	-	-	-	14
1771	*Proteus vulgaris*	22	24	28	16

Standard used: *Streptomycin*

Table 3: Antifungal activity of $[Co(C_{12}H_8N_2)_3]$ $Br_{1.5}Cl_{1.5}.6H_2O$

Microorganisms	Zone of inhibition			
	Day-1	Day-2	Day-3	Day-4
C. albicans				
$[Co(C_{12}H_8N_2)_3]$ $Br_{1.5}Cl_{1.5}.6H_2O$	8	9	10	11
Control	8	10	12	12
Standard	-	-	-	3
A. flavus				
$[Co(C_{12}H_8N_2)_3]$ $Br_{1.5}Cl_{1.5}.6H_2O$	-	13	19	22
Control	10	27	34	39
Standard	-	5	15	20

Standard used : *Ampotericin-B*

The complex showed good activity against the microbes *S. aureus, P. aerugenosa, V. parahaemolyticus* and *Proteus vulgaris* at 250 (µg/disc) and no activity against *E. coli* when compared to the standard used. In case of antifungal activity, it shows good activity against *A. flavus*

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