

Synthesis and Characterization and of transition metal (II) Complexes of 1-(3, 5-bis(tri fluoromethyl) phenyl -4-4-4-trifluorobutane-1,3-dione

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Abstract

Cu(II); Mn(II), Ni(II) and Co(II) complexes of 1-(3,5-bis(tri fluoromethyl) phenyl -4-4-4-trifluorobutane-1,3-dione derived from 3,5-bis-trifluoromethyl acetophenone and trifluoroacetate have been synthesized and characterized by elemental analysis, FTIR, UV-Visible spectroscopy, and TG-DTA. The UV spectra showed that the ligand form square planar complex with Cu(II) while it forms octahedral complexes with Mn(II), Ni(II) and Co(II).

Keywords - square planar complex, octahedral complexes, trifluorobutane-1,3-diketone, Cu(II); Mn(II), Ni(II) and Co(II) complexes

I. INTRODUCTION

Several synthetic metal complexes which mimic the behavior of complicated biomolecules are known and at present the study of such compounds are receiving much attention. One such example is curcuminoids, the active chemical component present in traditional Indian plant *curcuma longa* (turmeric). They are 1, 3-diketones in which the diketo function is directly attached to olefinic groups. The importance of 1,3-diketones in synthetic organic chemistry is amazing due to their accessibility, stability, and often unique properties make them promising for use in various fields of human activity. High reactivity of 1,3-diketones opens wide prospects for the design of a variety of organic compounds, including those structurally related to natural ones. Continuously growing interest in β -dicarbonyl compounds is observed among researchers working in various fields of medicinal chemistry and chemistry of metal complexes. Sol-gel syntheses with β -diketones afforded organic-inorganic hybrid materials used in gas sensors and molecular thermometers, as well as in the manufacture of optical fiber and light-converting materials [1-5]. Several synthetic metal complexes which mimic the behavior of complicated biomolecules are known and at present the study of such compounds are receiving much attention. 1,3-Diketones turned out to be excellent versatile intermediates in multicomponent reactions, in particular regio and stereoselective, which is especially important in the

synthesis of potentially biologically active compounds [6-9].

The chemistry of transition metal complexes with multidentate ligands has attracted particular attention because these metal ions can exhibit several oxidation states 1 [10]. Such complexes with different oxidation states have a strong role in bio-inorganic chemistry and redox enzyme systems [11,12] and may provide the basis of models for active sites of biological systems [13,14] or act as catalysts [15-17].

Copper(II) complexes play an important role in the active sites of a large number of metalloproteins in biological systems and potential application for numerous catalytic processes in living organisms that involve electron transfer reactions or activation of some antitumor substances [18]. These processes are also involved in bioinorganic [19] and medicinal chemistry [20]. In fact copper(II) chelates have been found to interact with biological systems and to exhibit antineoplastic activity [21-23] and antibacterial, antifungal [24,25] and anticancer activity [26]. In present paper synthesis of 1-(3, 5-bis(tri fluoromethyl) phenyl -4-4-4-trifluorobutane-1,3-dione was done by known [27] method and was used to synthesize new coordination compounds and studied their physical and chemical properties using IR, CHN, UV, and elucidated the structure of the new complexes.

II. EXPERIMENTAL

A. MATERIAL AND METHODOLOGY

All reagents used were of analytical grade and were used without further purification. Analytical grade solvents were used without further purification. 1-3, 5-bis(tri fluoromethyl) phenyl -4-4-4- trifluorobutane-1,3-dione, Copper chloride, Nickel chloride, Cobalt chloride, Manganese chloride, Ethanol, KOH and Methanol were purchased from Spectrochem chemicals. Melting points were determined on a Gallenkamp melting point apparatus. Infrared spectra

were recorded as KBr pellets on a Shimadzu FTIR-408 spectrophotometer. EDS analysis was performed at CIF, SPPU, Pune-7. Elemental analyses were performed on Quest flash 1112 Series EA Analyzer at SAIF, Punjab University, Chandigarh. Reactions were monitored by thin layer chromatography (TLC), carried out on 0.2 mm silica gel 60 F₂₅₄ Merck plates using UV light (254 and 366 nm) for detection.

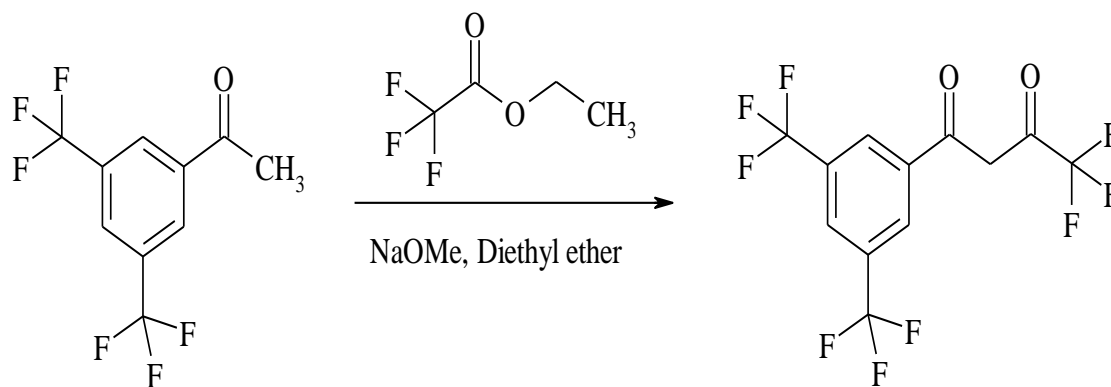
B. SYNTHESIS OF LIGAND AND COMPLEX

a) Synthesis of 1-(3,5-bis(tri fluoromethyl) phenyl)-4-4-trifluorobutane-1,3-dione (C₁₂H₅F₉O₂)

3,5 -Bistrifluoromethyl acetophenone was dissolved in diethyl ether and cooled to 0-5 oC. Sodium methoxide was then charged to it with stirring. Ethyl trifluoroacetate diluted in diethyl ether and added drop wise into the reaction mass over a period of 30 minutes at 0-5oC. The reaction mass was then stirred at 25-30oC for 12-14 hrs. Reaction was monitored by TLC (Chloroform: Methanol 9.5:0.5). After completion of the reaction 2N HCl was added to adjust pH to 4. Water was added and the organic layer separated was removed and dried over sodium sulfate and evaporated completely. Under reduce pressure to obtain the brown

oil. This oil was purified by column chromatography eluting with dichloromethane. The pure fraction were, collected and evaporated under reduce pressure to obtained a light yellow oil. Yield 8.0g(84%).

IR (KBr) 3527, 3469, 3282, 3131,1711, 1667,1556,1475,1396. ¹H NMR (300Hzs, DMSO-d₆): d-8.2(s, 1H, Ar-H), 3.71(s, 2H, CH₂), ¹³C, NMR(75MHz, DMSO-d₆): 206.10,203.1, 137.3, 131.2, 128.4, 127.5, 124.4 (2 Ar-CF₃), 117.2 (CF₃), 35.1(CH₂). MS(ESI:M/z352 [M+]) 123.95, 81.41; Anal. Cal. For C₁₂H₅F₉O₂ C, 40.93; H, 1.43; Found: C41.09; H, 1.82%



1-(3,5-bis(tri fluoromethyl) phenyl)-4-4-

4 trifluorobutane 1,3-dione

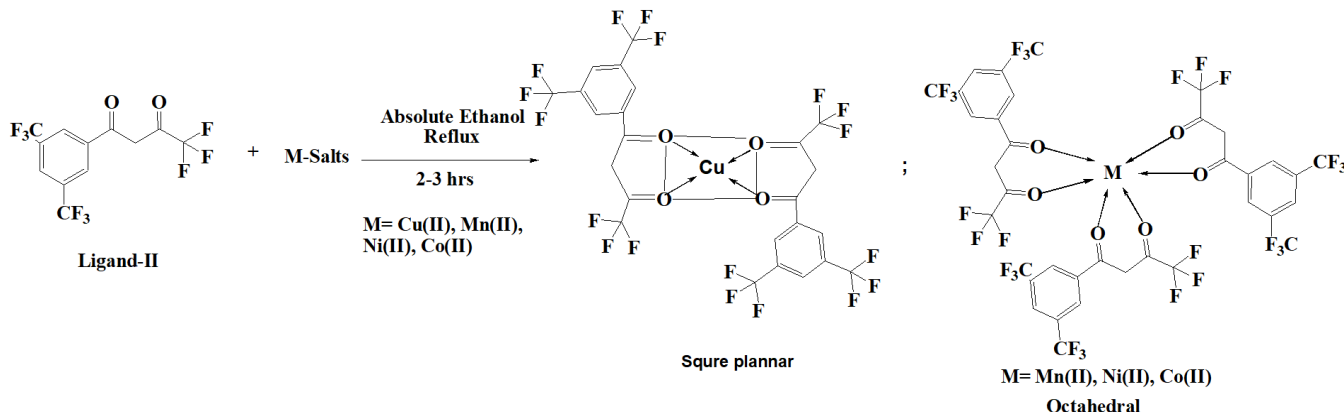
Scheme 1: Synthesis of ligand

b) Synthesis of metal Complexes of 1-(3,5-bis (trifluoromethyl) phenyl)-4-4-4 Trifluorobutane-1,3-dione

Trifluorobutane-1,3-dione

The metal complexes were prepared by mixing molar solution of ligand and metal solution (1:2, metal: ligand) in 10ml absolute alcohol. To the warm solution of ligand solution of metal salt (in alcohol) was added

drop wise. Then the mixture was refluxed for 2-3 hours, cooled and to this 10% alcoholic ammonia was added drop wise to increase pH changes to 7, product separated out with change in color. The product was digested in warm water for one hour and then kept it for overnight to separate all product, filter, wash with ethanol and dry it. The product purity was check by TLC.



Scheme II: Metal Complexes of 1-(3,5-bis (trifluoromethyl) phenyl)-4-4-4

Trifluorobutane-1,3-dione

III. RESULTS AND DISCUSSION

A. IR Spectroscopy of ligand and complexes

For β -diketone, the hydrogen bonded $-OH$ showed stretching $\nu_{(OH)}$ at 3527 and 3469 cm^{-1} for $\nu_{(C=O)}$ which are not observed in the IR spectrum of metal

complexes. This suggests participation of carbonyl groups in co-ordination through the both carbonyl group.

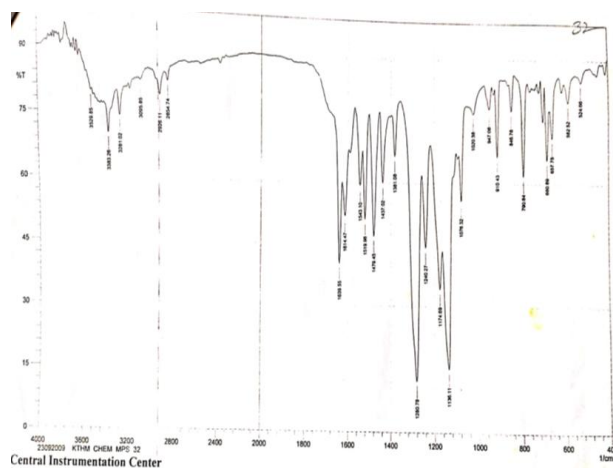


Fig. 1: Cu(II) complex of 1-(3,5-bis (trifluoromethyl) phenyl)-4-4-4-trifluorobutane 1,3-dione

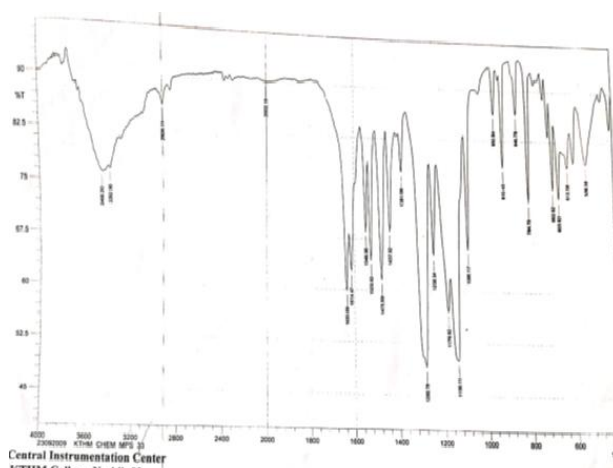


Fig. 2: Mn(II) complex of 1-(3,5-bis (trifluoro methyl) phenyl)-4-4-4-trifluorobutane 1,3-dione

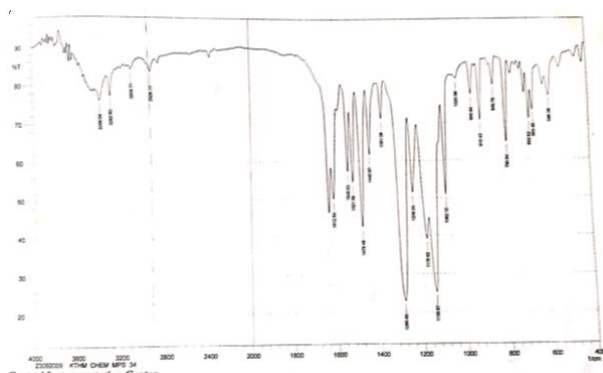


Fig. 3: Ni(II) complex of 1-(3,5-bis (trifluoromethyl) phenyl)-4-4-4-trifluorobutane 1,3-dione

IR of ligand showed peaks at 3527, 3469, 3282, 3131, 1711, 1667, 1556, 1475, 1396 cm^{-1} , whereas in Cu(II) complex the peaks at 1711 and 1667 cm^{-1} ; were shifted to 1639, 1614 cm^{-1} the O-Cu bond showed bending at 678 cm^{-1} (Fig. 1). The Mn(II) complex showed IR stretching at 1635 and 1614 cm^{-1} and O-Mn(II) bending at 613 cm^{-1} (Fig. 2). The Ni(II) complex showed IR stretching at 1640 and 1612 cm^{-1} and O-Ni(II) bending at 666 cm^{-1} (Fig. 3). The Co(II) complex showed IR stretching at 1633 and 1612 cm^{-1} and O-Co(II) bending at 667 cm^{-1} (Fig. 4).

B. THERMAL STUDIES:

The thermal decomposition behavior of metal complexes has been studied using TG & DTA techniques in an atmosphere of Nitrogen at a heating rate 10°C/min. The decomposition of the complexes takes place as shown in fig. 5-8.

a) TGA/DSC OF CU(II) COMPLEX:

The TGA/DSC curves of the synthesized Cu (II) complex, showed a weight loss occurring in two steps.

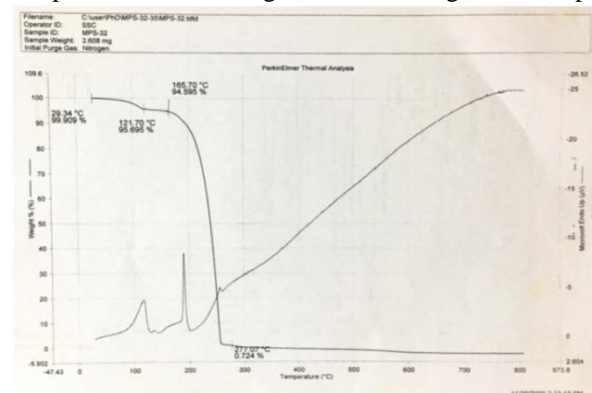


Fig. 5: Cu(II) complex 32

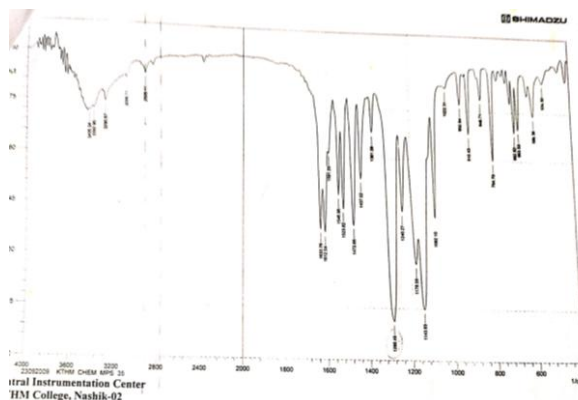


Fig. 4: Co(II) complex of 1-(3,5-bis (trifluoro methyl) phenyl)-4-4-4-trifluorobutane 1,3-dione

The first small weight loss (5.41%) is due to the occluded or adsorbed moisture near 121 °C and the second endothermic loss of 84.34 % is attributable to decomposition of Cu-complex and crystallization of CuO particles. The process accounts for one third of the total weight loss in the whole decomposition process from 165 to 277 °C according to the TGA result, with the major loss occurring between 200 to 350 °C. The theoretical weight loss calculated by conversion of the complex precursor to CuO is in good agreement with the measured value. (Fig. 5)

b) TGA/DSC OF MN(II) COMPLEX:

The TGA curve of Mn(II) complex shows a mass loss of 7.61 % (calcd. 6.82%) in the temperature range 100-150°C and endothermic DTA peak in the region 120 °C, indicates the loss of water molecule. The anhydrous complex first showed decomposition from 200°C to 335°C, with 81.32 % (calcd. 79.86 %) mass loss, which may be attributed to the removal of the coordinated part of the ligand. (Fig. 6)

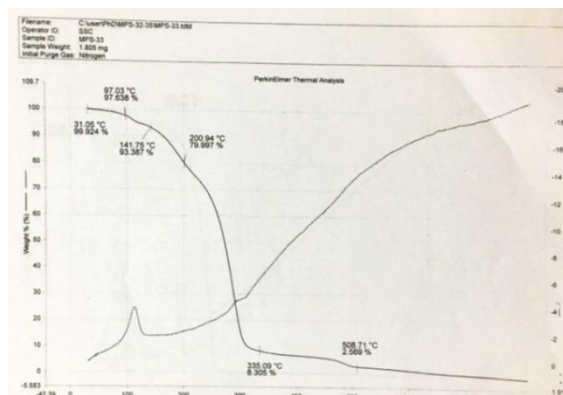


Fig. 6: Mn(II) complex 33

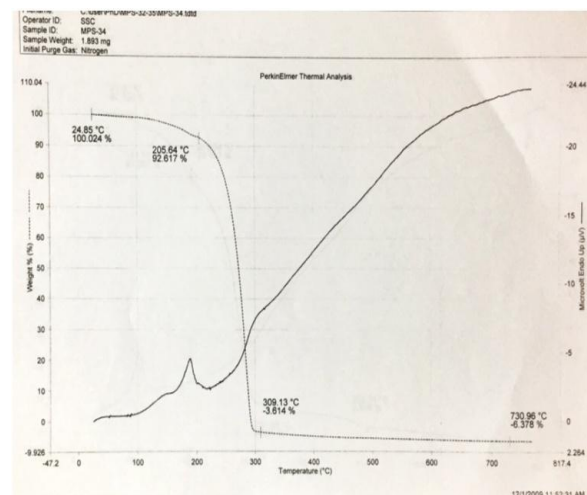


Fig. 7: Ni(II) complex 34

c) TGA/DSC OF NI(II) COMPLEX

The TGA curve of Ni(II) complex shows weight loss 7.390 % (calcd.8.21 %) in the temperature range 100-200°C and sharp endotherm at 170°C clearly indicate removal of water molecules. The anhydrous complex first showed decomposition from 210-310°C, with a 78.41 % (calcd. 75.41 %) mass loss due to the decomposition of the coordinated part of the ligand. and a exothermic peak with 315.32 °C in the DTA, which may be attributed to the removal of the non-coordinated part of the ligand. (Fig. 7)

d) TGA/DSC OF CO(II) COMPLEX

Figure 8 represents the TGA/DSC curves of the synthesized Co(II) complex. The TGA curve of Co(II) complex shows a weight loss occurring in two steps. The first small weight loss is due to the occluded or adsorbed moisture which at about 140 °C and the second exothermic loss of 77.448 % is attributable to decomposition of Mg complex and crystallization of CoO particles. The theoretical weight loss calculated by conversion of the complex precursor to CoO is in good agreement with the measured value. The process accounts for one third of the total weight loss in the

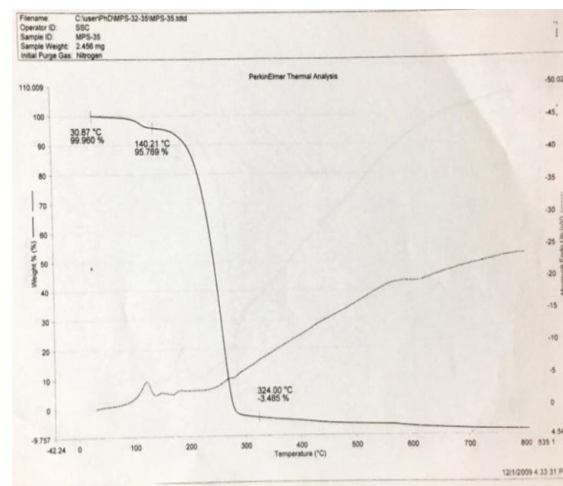


Fig. 8: Co(II) complex 35

whole decomposition process from 100 to 350 °C according to the TGA result, with the major loss occurring between 100 to 350 °C.

C. ELECTRONIC SPECTRA

The spectra of complex shows shifting in wavelength. The Cu(II) complex shows stretching at 213, 319, 377 and broad band at 685 nm. This indicates $\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ (LMCT) and d-d $2B_{1g} \rightarrow 2E_g$ and $2B_{1g} \rightarrow 2A_g$ transitions in metal complexes. The broadness of band may be due to Jahn Teller distribution, indicating square planar geometry of complex, (Fig. 9). The electronic spectra of the Mn(II) complex illustrates absorption bands at 208 nm, 374 nm and 459 nm which is a feature of octahedral geometry which corresponds to $6A_{1g} \rightarrow 4T_{2g}(G)$, $6A_{1g} \rightarrow 4E_{1g}$ transitions [20]. (Fig. 10)

The electronic spectra of the Ni(II) complex gave bands in the range of 207 nm to 611 nm. The bands were corresponds to $3 A_{1g}(F) \rightarrow 3T_{2g}(F)$, $A_{2g}(F) \rightarrow 3T_{1g}(F)$ and $3 A_{2g}(F) \rightarrow 3T_{1g}(F)$ transition, which are in good agreement with octahedral geometry [28]. Fig. 11

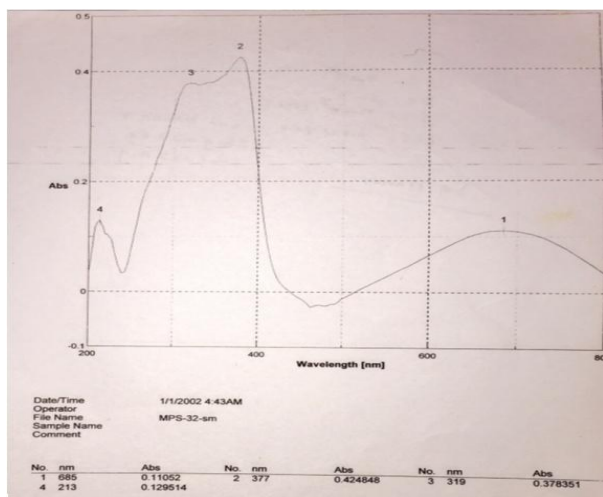


Fig. 9: Electronic Spectra of Cu(II) complex

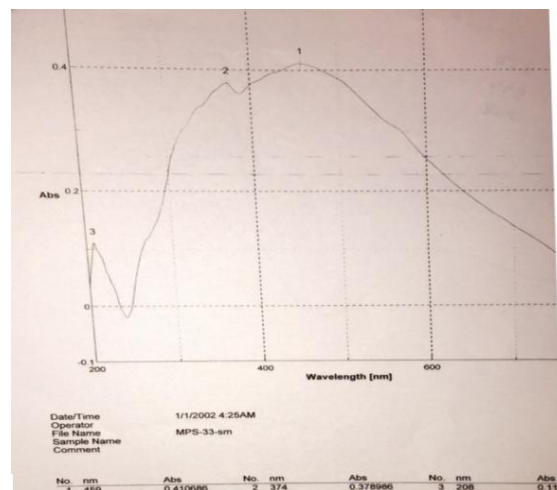


Fig.10: Electronic Spectra of Mn(II) complex

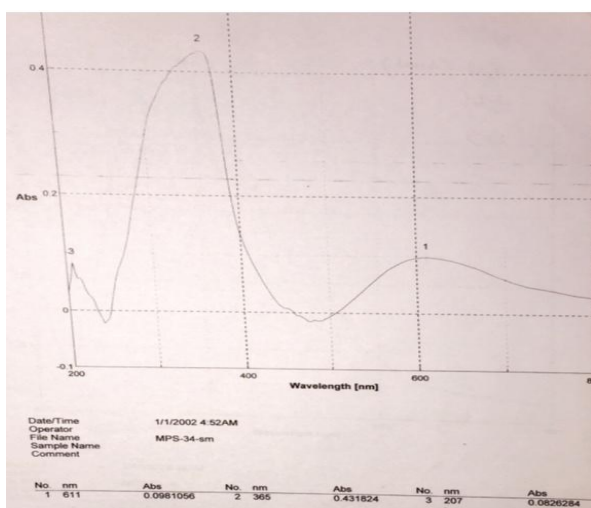


Fig. 11: Electronic Spectra of Ni(II) complex

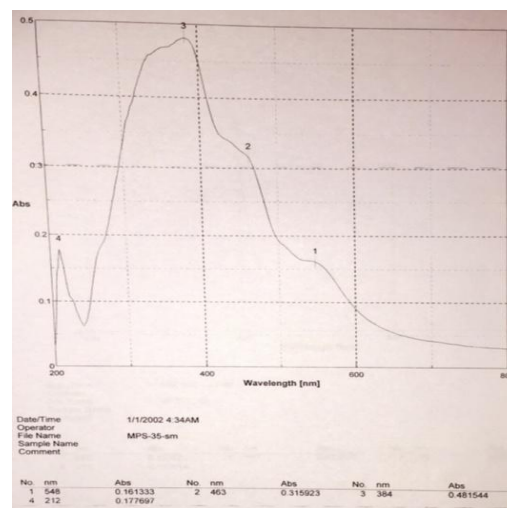


Fig. 12: Electronic Spectra of Co(II) complex

D. ELEMENTAL ANALYSIS OF METAL AND LIGAND

The elemental analysis of the ligand and the complexes are in agreement with the observed and

Table I: Metal Complexes of 1-(3,5bis (tri fluoromethyl) phenyl)-4-4-4 trifluorobutane 1,3-dione.

calculated for the expected structures of the complexes (Table 1).

M.F. of Complex	Color	%C	%H	%M
C ₂₄ H ₁₀ CuF ₁₈ O ₄	Green	37.54(cal),	1.31(cal)	8.28(cal)
		36.02(obs)	1.41(obs)	7.98(obs)
C ₃₆ H ₁₅ MnF ₂₇ O ₆	Brown	38.90(cal)	1.36(cal)	4.94(cal)

		38.96(obs)	1.06(obs)	-(obs)
C36H15NiF27O6	Green	38.77 (cal)	1.36(cal)	5.26 (cal)
		35.85(obs)	1.40(obs)	5.29(obs)
C36H15CoF27O6	Yellow	38.77(cal)	1.36(cal)	5.28(cal)
		35.99(obs)	1.24(obs)	7.98(obs)

CONCLUSION

New ligand (1-(3,5-bis(tri fluoromethyl) phenyl -4-4-4-trifluorobutane-1,3-dione) was used to form new complexes of transition metal complexes of Cu(II); Mn(II), Ni(II) and Co(II). FTIR, UV-Visible spectroscopy, and TG-DTA. The UV spectra showed that the ligand form square planar complex with Cu(II) while it forms octahedral complexes with Mn(II), Ni(II) and Co(II).

ACKNOWLEDGEMENT

Authors thanks toBCUD, SPPU Pune for financial assistant and KTHM College for facility.

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