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Synthesis and Structural Elucidation of Mixed Ligand Complexes of Mn(II), Zn(II) and Cd(II) with 2,5–Dihydroxybutyrophenone thiosemicarbazone as Primary Ligand and 2–Pyridine ethanol as Secondary Ligand

Chemistry

KEYWORDS: 2,5–Dihydroxybutyrophenone thiosemicarbazone, 2–pyridine ethanol, Mn(II), Zn(II) and Cd(II) complexes

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ABSTRACT

Mixed ligand complexes of Mn(II), Zn(II) and Cd(II) with 2,5–dihydroxybutyrophen-one thiosemicarbazone and 2–pyridine ethanol have been isolated and characterized by analytical data, molar conductance, magnetic measurements, electronic spectra, IR spectra and thermogravimetric analysis. Mn(II) complexes were found to have octahedral structure while Zn(II) and Cd(II) complexes possess distorted tetrahedral structure.

Introduction

Interest in thiosemicarbazones has aroused from past few decades largely as a result of its wide range of applications as antibacterial, antifungal, chemotherapeutic, and bioanalytical agents[1-3]. Mixed ligand complexes play a vital role in the activation of enzymes, storage and transport of active substances. A good deal of work has been reported on the preparation and structural investigation of thiosemicarbazones and their complexes due to their capability of acting as multidentate NS, NNS, SNNS donor with the formation of either mono- or bi- or polynuclear complexes[4-5]. In addition to their interesting ligational properties, thiosemicarbazones and their complexes had important biological applications. As the coordination of the metal ions to thiosemicarbazones improves their efficacy and improve their bioactivity[6-7]. Present paper deals with the study of synthesis and structural elucidation of mixed ligand complexes of Mn(II), Zn(II) and Cd(II).

Experimental

All chemicals used were of A.R grade. Melting points of the complexes were determined in open capillaries. The conductivity measurements were made on Systronic Conductometer model 303 using DMF. Magnetic moments were measured by Guoy method using $Hg[Co(CNS)_4]$ as a calibrant. The metal contents were determined using standard methods. The analytical data, colour, conductivity measurements and magnetic moments have been recorded. IR spectra (KBr) were recorded on a Perkin Elmer 577 grating IR spectrophotometer.

Synthesis of 2,5–dihydroxybutyrophen-one thiosemicarbazone ligand

2,5–Dihyroxybutyrophenone was prepared by the literature method[8]. Its thiosemicarbazone was obtained by refluxing ethanolic solution with thiosemicarbazide in concentrated HCl for 2 hours on water bath. On cooling, a light yellow compound separated out. It was filtered, washed with ethanol, dry ether and dried well under anhydrous conditions.

Preparation of Mn(II), Zn(II) and Cd(II) complexes

An ethanolic solution (25ml) of metal salts of Mn(II), Zn(II) and Cd(II) was added gradually to a stirred ethanolic solution(25ml) of 2,5–dihydroxybutyro-phenone thiosemicarbazone and secondary ligand 2–pyridine ethanol to get (1:1:1) molar ratio. The resulting solution was refluxed for 3-4 hours on water bath. The complex was precipitated, cooled and then filtered. The product obtained was washed with small amounts of ethanol and then dried in vacuum.

Results and Discussion

The physical and elemental analysis data for the complexes are listed in Table-1. All the analytical data are in good agreement with the empirical formulae of the synthesized complexes. All the complexes are stable in air. They have varied colours and are soluble in common coordinated solvents such as dimethylsulfoxide, acetone, dimethylform-amide. All the complexes have been decomposed with concentrated nitric acid for analytical purposes. Metal contents have been determined gravimetrically. Relative molecular weights of the ligands and their complexes have been determined cryoscopically. Conductivity data of 10^{-3} M solution of Mn(II) complex in DMSO suggested their non-electrolytic naturewhile that of Zn(II) and Cd(II) complexes correspond to 1:1 electrolytic nature. The electrolytic nature of Zn(II) and Cd(II) complexes is further confirmed by formation of white curdy precipitates on addition of alcoholic $AgNO_3$ to the solution of complexes in DMSO[9].

Magnetic Measurements

Mn(II) ion, in weak octahedral field with ground state $(t_{2g})^3(e_g)^2$, has magnetic moment 5.70-6.00 B.M. corresponding to five unpaired electrons whereas in the strong field it assumes $(t_{2g})^5$ configuration with only one unpaired spin. Mn(II) complex show magnetic moment value 5.95 B.M. indicating high spin octahedral geometry[10].

Zn(II) and Cd(II) ions have d^{10} configuration and usually attain tetrahedral geometry using sp^3 hybridization. Due to fully filled d-orbitals, Zn(II) and Cd(II) complexes are diamagnetic since d-d transitions in such complexes are not possible. The magnetic moment value of Zn(II) and Cd(II) complexes is in the range of 0.18 to 0.24 B.M which shows their diamagnetic nature[11].

Electronic Spectra

The electronic spectra of Mn(II) complex in DMF shows bands in the range 18300-18750, 22500-23400, 24650-25700, 28400-29000 and 34200-35550 cm^{-1} corresponding to the spin-forbidden transitions from the ground state to ^4G, ^4P and ^4D excited state of the ion. These bands may be assigned to following transitions:

$^6A_{1g}(G)$ $^4T_{1g}(^4G)$;

$^6A_{1g}(G)$® $^4T_{2g}(^4G)$;

$^6A_{1g}(G)$® $^4E_g(^4G)$, $^4A_{1g}(^4G)$;

$^6A_1g(G)$® $^4T_{2g}(^4D)$ and

$^6A_{1g}(G)$® $^4T_{1g}(^4P)$

These transitions suggest octahedral geometry for Mn(II) complex. The calculated values of ligand field parameters viz. 10 Dq, B , F2 and F4 are also in good accordance with the octahedral stereochemistry of Mn(II) complex. The value of is less than unity indicating the considerable amount of covalency in the bond formed between the metal atom and the donor atom of the ligand. Zn(II) and Cd(II) complexes are found to be diamagnetic as expected for d^{10} system because d-d transitions are not possible hence electronic spectra did not give any fruitful information[12-13].

IR Spectra

On comparing the IR absorption spectra of free ligands and their complexes, probable active coordination sites of ligands bonding with the metal ions have been located. The N-N stretching band at 1040-1030 cm^{-1} in the spectra of thiosemicarbazones shows a positive shift of 15-20 cm^{-1} in the spectra of the complexes. This indicates the bonding of metal ion with azomethine N of the ligand. A band corresponding to (CH=N) around 1660-1640 cm^{-1} shifts to lower frequency region in spectra of all the complexes which confirms the bonding of azomethine N with metal ions. The IR spectra of thiosemicarbazone ligand shows (NH) ~3220 cm^{-1} and (C=S) ~925 cm^{-1}. These bands disappear in the spectra of their complexes. In spectra of complexes, appearance of new band near 750 cm^{-1} is assigned to (C-S). The spectra of the complexes shows change in frequency of (N-C-N), (C=S) and (NH-C=S). The disappearance of (–NH-C=S) absorption frequency with the formation of new band for azine (C=N-N=C) at 1560-1580 cm^{-1} suggests coordination of the metal ion through the azine nitrogen and thiol sulphur of the enolic form of thiosemicarbazone. A band observed at 3210cm^{-1} assigned to NH_2 in the thiosemicarbazones, which remain unchanged, indicating the non-participation of the $–NH_2$ group during complexation. A broad frequency band, due to phenolic –OH at 3490 cm^{-1} in the spectra of ligand is observed almost at the same position in spectra of all the complexes but the intensity is found to be low in Mn(II) complex, indicating that only a single –OH group takes part in the reaction with Mn(II). The (C-O) phenolic stretch shifts to higher energy by 10 cm^{-1} in Mn(II) complex indicating coordination of phenolic –O with Mn(II) ion while in Zn(II) and Cd(II) complexes, the phenolic –OH frequency remains unchanged indicating the non- participation of phenolic –OH group of thiosemicarbazone ligand[14].

A medium band existing in the spectrum of 2–pyridine ethanol at 3250 cm^{-1} shows a positive shift of 20-30 cm^{-1} in all the complexes. This suggests the weakening of hydrogen bond and coordination of metal ion through oxygen of 'OH' group. A strong band at 1600-1625 cm^{-1} which is assigned to the (C=N) mode shifts to lower energy side by 15-20 cm^{-1} in complexes indicating coordination of nitrogen to the metal ion. An additional band at ~280 cm^{-1} in the spectra of all the complexes also confirms the coordination of pyridine - nitrogen with the metal ion. Some new non-ligand bands appeared in the far IR region around 500-300 cm^{-1} have been noticed in spectra of all the complexes. These bands are assigned to (M–N), (M–O) and (M–S), respectively. Zn(II) and Cd(II) complexes exhibit an additional band around 260 cm^{-1} which may be assigned to (M–Cl) vibrations[15].

The IR-spectra of Mn(II) complex exhibit bands in region 3400-3390 cm^{-1} and 880-890 cm^{-1} assignable to stretching and rocking modes of coordinated water molecule while a broad band at ~3420 cm^{-1} in the spectra of Zn(II) and Cd(II) complexes indicates the presence of lattice held water molecule[16].

Thermogravimetric analysis

The weight loss observed by TG analysis of Mn(II) complex at temperature 130°C corresponds to the elimination of one molecule of water and supports further the presence of one coordinated water molecule while Zn(II) and Cd(II) complexes show the weight loss equivalent to one water molecule at about 85-90°C which indicates the presence of only one lattice held water molecule[17].

Conclusion

IR spectral data indicates that 2,5–dihydroxy butyrophenone thiosemicarbazone ligand acts as tridentate in Mn(II) complex and bidentate in Zn(II) and Cd(II) complexes while secondary ligand 2–pyridine ethanol serve as bidentate ligand in all the complexes under study. TG data reveals coordination of one water molecule in Mn(II) complex while the study confirms the presence of one lattice held water molecule in Zn(II) and Cd(II) complexes. On the basis of elemental analysis, magnetic moment data, conductivity measurements, electronic spectra, IR spectra and thermogravimetric analysis, the geometry of Mn(II) complex is suggested as octahedral while that of Zn(II) and Cd(II) complexes as distorted tetrahedral as shown in Fig.1 and Fig.2.

Table – 1

Analytical data of Mn(II), Zn(II) and Cd(II) mixed ligand complexes

S. No	Complexes	% chemical analysis; found (calculated)						μeff (B.M.)	Dm in DMSO (ohm^{-1} cm^{2}mol^{-1})	Colour M.P. (°C)	Mol. Wt. Found (Calcd.)
		C	H	N	S	Cl	Metal				
1	[Mn($C_{13}H_{17}O_2N_3S$)(C-H_2ON)H_2O]	48.40 (48.32)	5.32 (5.30)	12.12 (12.12)	7.30 (7.13)	—	12.33 (12.29)	5.95	68.72	Brown 202	440.80 (446.94)
2	[Zn($C_{13}H_{17}O_2N_3S$)(C-H_2ON)]Cl•H_2O	43.65 (43.82)	4.34 (4.86)	11.28 (11.36)	6.45 (6.49)	7.15 (7.20)	13.63 (13.26)	Diamagnetic	81.45	Light yellow 143	489.64 (492.88)
3	[Cd($C_{13}H_{17}O_2N_3S$)(C-H_2ON)]Cl•H_2O	40.45 (40.06)	4.65 (4.44)	10.25 (10.37)	6.00 (5.92)	6.45 (6.57)	21.05 (20.82)	Diamagnetic	83.25	Cream 140	555.6 (539.9)

Table - 2

Main IR Bands (cm^{-1}) observed in the Spectra of Mn(II), Zn(II) and Cd(II) mixed ligand complexes

S. No.	Complexes	ν(C=N)	ν(C=N–N=C)	ν(C-S)	ν(N-N)	ν(OH) (2-pyridine ethanol)	ν(M–N)	ν (M–O)	ν (M–S)	ν (M–Cl)
1	[Mn($C_{13}H_{17}O_2N_3S$)(C-H_2ON)H_2O]	1630	1570	740	1050	3380	470	390	320	—
2	[Zn($C_{13}H_{17}O_2N_3S$)(C-H_2ON)]Cl•H_2O	1650	1580	750	1060	3270	470	330	310	250
3	[Cd($C_{13}H_{17}O_2N_3S$)(C-H_2ON)]Cl•H_2O	1640	1560	740	1060	3290	460	390	300	260

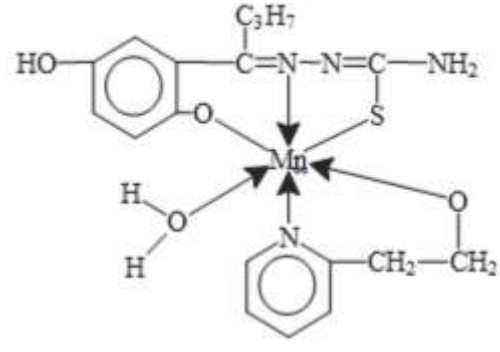

Fig.1

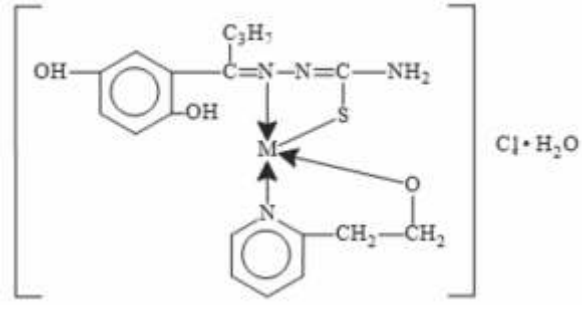

Fig. 2 (where M = Z_n(II)/Cd(II))

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