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Synthesis and Spectral Studies of Manganese(II), Cobalt(II), Nickel(II), Copper(II), Chromium(III) and Iron(III) Complexes of Schiff Base Derived from Hydrazine Hydrate

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The Schiff base *p*-methoxy phenyl carbonyl hydrazone (PMPCH) and its complexes with Mn(II), Co(II), Ni(II) Cu(II), Cr(III) and Fe(III) have been prepared and characterized on the basis of analytical, magnetic measurements, IR and electronic spectral data. Various ligand fields and different parameters have been found to be consistent with octahedral structure. Schiff bases and some complexes have been tested against the fungi A. *niger* and A. *flavus*.

Key Words: *p*-Methoxy phenyl carbonyl hydrazone, Mn(II), Co(II), Ni(II), Cu(II), Cr(III), Fe(III) complexes.

INTRODUCTION

The preparation of heterocyclic ligands containing carbonyl and azomethine groups with potential binding ability has drawn a lot of attention because of their fungicidal[1], herbicidal[2], antibacterial and antiinflammatory[3] properties. Coordination behaviour of this ligand with several metal ions is found in biological systems[4, 5]. In the present work, the synthesis and characterization of *p*-methoxy phenyl carbonyl hydrazone and its complexes with various transition metal ions is described.

EXPERIMENTAL

All the chemicals were used of AR grade. The phenylglyoxal was prepared according to the known methods[6].

Schiff base *p*-methoxy phenyl carbonyl hydrazone (PMPCH) and its coordination behaviour with Mn(II), Co(II), Ni(II), Cu(II), Cr(III) and Fe(III) salts. On complexation, it has been observed that the Schiff base PMPCH acts as tridentate forming chelate ring imparting considerable stability for the resulting complexes.

Preparation of ligands:

***p*-Methoxy phenyl-carbonyl hydrazone (PMPCH):** Solution of phenyl glyoxal (10 mmol) in glacial acetic acid was mixed with hydrazine hydrate (10 mmol) in ethanol with vigorous shaking. The resulting product was poured in ice-cold water and kept overnight. The light brown coloured solid was recrystallized and dried in air (Fig. 1).

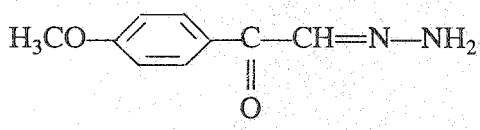

Fig. 1. *p*-Methoxy phenyl-carbonyl hydrazone (PMPCH)

Preparation of complexes

Metal complexes with ligand (PMPCH): The complexes of Mn(II), Co(II), Ni(II), Cu(II), Cr(III) and Fe(III) were prepared by mixing the ethanolic solution of metal chloride with the ethanolic solution of the ligand (1 : 2) and refluxed for 4–5 h. The solvent was distilled off under reduced pressure. The resulting product was washed with ethanol and filtered. All the complexes were dried in air at room temperature.

RESULTS AND DISCUSSION

All the complexes are soluble in DMF and dioxane but insoluble in common organic solvents such as methanol, ethanol, acetone and benzene. The analytical data indicate 1 : 2 metal to ligand stoichiometry.

Magnetic measurements

Magnetic moment of Mn(II) is 5.76 B.M. indicating the octahedral geometry[7] of the complex. The values are in close agreement with the spin-only value for Mn(II) complex due to high spin, non-degenerate orbitals. The magnetic moment value for the Co(II) complex is 4.80 B.M. expected for the octahedral geometry[8, 9]. The magnetic moment value for the Ni(II) complex is 2.88 B.M. which suggestsoctahedral geometry[10] but is slightly higher than the spin only value of 2.83 B.M. probably due to slight distortion from the pure octahedral to D_{4h} symmetry. Cu(II) complexes have magnetic moment value 1.90 B.M. indicating that it is magnetically normal six coordinated spin free octahedral complex[11, 12] having one unpaired electron. The Cr(III) complex has magnetic moment value 3.89 B.M. which is in agreement with the presence of three unpaired electrons and suggests octahedral stereochemistry[13]. The Fe(III) complex has magnetic moment value 5.91 B.M. indicating good agreement with that reported for octahedral Fe(III) complex[14].

Electronic spectra

The electronic spectra of Mn(II) complex with PMPCH exhibit four bands expected for octahedral geometry. It is observed that the bands representing corresponding transition and energy in terms of Racah parameter[15] are $^6A_{1g} \rightarrow {}^4T_{1g}(4G)$ (10B + 5C); $^6A_{1g} \rightarrow {}^4E_g\ {}^6A_{1g}(4G)$ (10B + 5C); $^6A_{1g} \rightarrow {}^4E_g(4D)$ (17B + 5C) and $^6A_{1g} \rightarrow {}^4T_{1g}(4P)$ (17B + 7C). The values of shown bands are 16852, 23526, 27870 and 28826 cm^{-1}, since the energies of $^6A_{1g} \rightarrow {}^4E_g\ {}^6A_{1g}(4G)$ and $^6A_{1g} \rightarrow {}^4E_g(4D)$ transitions are independent of Dq and depend[16] only on B and C. The values for the parameter Dq using the relation Dq/B = 1.1, Slater Condon-Shortly[17] parameters F_2 and F_4, nephelauxetic ratio (β) and nephelauxetic

function for coordinated ligands (hx) have been calculated. The observed transition energies and calculated parameters are given in Table-1. It has been observed that lower value of (β) and higher value of (hx) indicate the increase in covalent character of the complex.

The electronic spectra of the Co(II) complex exhibiting three bands are assigned to spin-allowed transitions $^4T_{1g} \rightarrow {}^4T_{2g}(F)(\nu_1)$, $^4T_{1g} \rightarrow {}^4A_{2g}(F)(\nu_2)$ and $^4T_{1g} \rightarrow {}^4t_{1g}(P)(\nu_3)$. The occurrence of these transitions suggests an octahedral geometry for the complex[18]. The bands in the region of these transitions are $\nu_1 = 11494$, $\nu_2 = 16393$ and $\nu_3 = 20408$. Its position was calculated using Konig's equation[19]. An attempt has been made to calculate 10 Dq and B using these ν_2 and ν_3 according to method (C). ν_1 was also calculated by using the value of 10 Dq and B. Method C is quite encouraging to calculate 10 Dq, B and ν_1 because:

(i) The ratio $(\nu_2)_{obs}/(\nu_1)_{calcd.}$ is found to be 2.20 as required for octahedral Co(II) complex[20].

(ii) 10 Dq calculated by method (C) and that determined by $(\nu_2)_{obs} - (\nu_1)_{calcd.}$ is found to be in good agreement with the experimental values.

Various crystal field parameters such as 10 Dq, B, C, β, F_2, F_4 and f for Co(II) complex have been calculated by the standard method[21]. The results are listed in Table-1.

TABLE-1
ELECTRONIC SPECTRA AND THEIR ASSIGNMENTS OF CRYSTAL FIELD PARAMETERS OF Mn(II), Co(II), Ni(II), Cu(II), Cr(III) AND Fe(III) SCHIFF BASE COMPLEXES

Complexes	B	10 Dq	C	β	f	h	λ	F_2	F_4	ν_2/ν_1
$[Mn(C_9H_{10}N_2O_2)_2Cl_2]$	702	7722	3144	81	90	2.71	1.72	1151	89.8	—
$[Co(C_9H_{10}N_2O_2)_2Cl_2]$	894	8596	4139	92	92	—	—	1485	118	1.77
$[Ni(C_9H_{10}N_2O_2)_2Cl_2]$	796	10380	3749	77	16	1.91	164.81	1331	107	1.60
$[Cu(C_9H_{10}N_2O_2)_2Cl_2]$	—	15490	—	—	29	—	—	—	—	—
$[Cr(C_9H_{10}N_2O_2)_2Cl_2]Cl$	829	16350	3730.5	90	96	0.47	113.48	1361	106	1.43
$[Fe(C_9H_{10}N_2O_2)_2Cl_2]Cl$	564	11844	2608	55	84	1.87	72.51	45891	32860	—

The electronic spectrum of Ni(II) complex exhibits three spin allowed transitions at 10380, 16580 and 26491 cm^{-1} which may be assignable to the transitions[22] $^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_1)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$, respectively, so it is expected for octahedral Ni(II) complex. These spectral data are utilized to complete the important ligand field parameters 10 Dq, B and using the ligand field theory of spin allowed transition in d^8 configuration. The values of B and 10 Dq were employed to calculate ν_2 or ν_3 and the results are given in Table-1.

(i) The ratio ν_2/ν_1 of the complex lies in the range required for octahedral Ni(II) complex.

(ii) Comparison of 10 Dq and B values of the complex indicates that the ligand gives rise to a strong ligand field and leads to a strong covalent bond.

(iii) The values of β indicate considerable covalent character of metal ligand bond in the complex.

(iv) Values of λ are found to be considerably lower than the values for the free ion (λ_0).

The Cr(III) complex of PMPCH exhibits three bands at 16350, 23440 and 36581 cm^{-1} which may be assigned to the transition $^4A_{2g} \rightarrow {}^4T_{2g}(F)$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$, respectively. The spectral parameters ν_2/ν_1, Dq/B, B, β have been found satisfactory and the values are in good agreement with the reported values for octahedral Cr(III) complex[23].

The electronic spectra of Fe(III) complex exhibited five bands in the region 13544, 16429, 18619, 25070 and 26346 cm^{-1} attributed to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$, $T_{2g} \rightarrow \pi^*$, $\pi \rightarrow e_g$ and $\pi \rightarrow \pi^*$ transitions, respectively. In these five transitions first two intense bands may be assigned to d-d transition[24] and other three charge transfer bands[25, 26] The values of various crystal field parameters, *viz.*, 10 Dq (11851 cm^{-1}), B (564 cm^{-1}), C (2610 cm^{-1}). C/B (*ca.* 4.62), F_2 (*ca.* 45.9kK), F_4 (*ca.* 32.8 kK) and F_2/F_4 (*ca.* 1.4 kK) support the octahedral geometry of Fe(III) complex. From the calculation of ligand field parameters we conclude that in complexation, the values of F_2 and F_4 are much reduced from the free ion value due to expanded radial function for the *d*-electrons. Similarly, the reduction of B values indicates considerable covalent character in the metal-ligand bond.

Infrared spectra

IR spectral data of Schiff base metal complexes are shown in Table-2. In the IR spectra of the Mn(II) complex a band *ca.* 1591 cm^{-1} having lower shifting than the Schiff base (*ca.* 1603 cm^{-1}) indicates that the azomethine nitrogen is participating in chelation[27]. Frequencies at *ca.* 1658 cm^{-1} belong to ν(C=O) band, respectively, indicative of the involvement of carbonyl oxygen[28] on chelation. The IR spectra showing three peaks at *ca.* 518, *ca.* 476 and *ca.* 270 belong to ν(M—N), ν(M—O) and ν(M—Cl) bands[29], respectively.

TABLE-2
KEY IR FREQUENCIES (cm^{-1}) OF SCHIFF BASE AND ITS Mn(II), Co(II), Ni(II), Cu(II), Cr(III) AND Fe(III) COMPLEXES

Complexes	ν(>C=O—)	ν(>C=N—)	ν(M—O)	ν(M—N)	ν(M—Cl)
$C_9H_{10}N_2O_2$	1658	1603	—	—	—
$[Mn(C_9H_{10}N_2O_2)_2Cl_2]$	1630	1591	463	518	270
$[Co(C_9H_{10}N_2O_2)_2Cl_2]$	1687	1597	462	568	285
$[Ni(C_9H_{10}N_2O_2)_2Cl_2]$	1688	1597	497	567	260
$[Cu(C_9H_{10}N_2O_2)_2Cl_2]$	1706	1601	478	525	290
$[Cr(C_9H_{10}N_2O_2)_2Cl_2]Cl$	1688	1597	484	568	275
$[Fe(C_9H_{10}N_2O_2)_2Cl_2]Cl$	1780	1597	465	518	310

The IR spectra of three Co(II), Ni(II), Cu(II) complexes bands at *ca.* 1597, 1597 and 1601 cm^{-1} were shifted to lower side thereby suggesting participation of azomethine group in the coordination. The spectra of the complexes show a considerable shift (*ca.* 19–48 cm^{-1}) of the carbonyl stretching of higher frequency[30, 31] indicating a decrease in the stretching force constant of C=O as a

consequence of coordination through its oxygen. These have been further confirmed by appearance of ν(M—O), ν(M—N) and ν(M—Cl) bands at 462, 497, 473, 568, 567, 525 cm^{-1} and 285, 260, 290 cm^{-1}, respectively[32].

The IR spectra of the Schiff base exhibit a weak band in the range of 1658 cm^{-1}. This band is assigned to the >C═O group. In the complexes except the complex of Schiff base, bands shift towards higher wavenumber, while in this complex the band is shifted towards lower wavenumber. This shifting of bands suggests the coordination through >C═O group. The Cr(III) and Fe(III) complexes display a negative shift[33] of the azomethine (>C═N—) group of Schiff bases in their corresponding complexes. This shifting suggests that in the complexes, the ligand is coordinated to the metal ion through nitrogen of azomethine group. Three new bands are observed in the chromium complex in the region 568, 484 and 275 cm^{-1}, which are assigned to ν(M—N), ν(M—O) and ν(M—Cl) bands, respectively, while in the iron complex bands are observed in the region 518, 465 and 310 cm^{-1}, espectively.

Biocidal activities

All the 7 compounds have been tested for their antifungal activities against the fungi such as *A. niger* and *A. flavus*. The antifungal activity of the compounds was checked by food-poison technique. Seven days old cultures of *A. niger* and *A. flavus* were used as test organisms which were grown on dextrose-agar medium. The temperature was maintained at 25°C during the growth of both fungi and the average of three replicates was recorded. The percentage inhibition[34] was calculated as

$$\frac{(C - T) \times 100}{C}$$

where C = diameter of fungus colony in control plate.

All the complexes were found to be active against all the fungicidal tests (Table-3).

TABLE-3
ANTIFUNGAL ACTIVITY OF Mn(II), Co(II), Ni(II), Cu(II), Cr(III) AND Fe(III) COMPLEXES

Compounds	% of inhibition zone					
	Aspergillus niger (Conc. in ppm)			*Aspergillus flavus* (Conc. in ppm)		
	250	500	1000	250	500	1000
$C_9H_{10}N_2O_2$	82.45	88.43	100	72	94.29	97.14
$[Mn(C_9H_{10}N_2O_2)_2Cl_2]$	56	74.12	87	50	100	100
$[Co(C_9H_{10}N_2O_2)_2Cl_2]$	45	61.90	100	55.5	95.43	100
$[Ni(C_9H_{10}N_2O_2)_2Cl_2]$	65.40	79.30	98.50	45.4	100	100
$[Cu(C_9H_{10}N_2O_2)_2Cl_2]$	54.50	68.70	100	82	88	100
$[Cr(C_9H_{10}N_2O_2)_2Cl_2]Cl$	58	88.10	100	54	71.43	91.31
$[Fe(C_9H_{10}N_2O_2)_2Cl_2]Cl$	59.50	87.40	99.44	64	82.40	100

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