Asian Journal of Chemistry Vol. 19, No. 1, (2007), 641–646

Synthesis and Characterization of Transition Metal Complexes with 1,5-Diamino 2,4-dimethyl 1,5-diaza 1,4-pentadiene

R.R. JHA* and P. MUKHARJEE
Department of Chemistry, Ranchi University, Ranchi-834 008, India
E-mail: rajranjanjha@yahoo.co.in

Metal complexes of the type $[M_3(DDDP)_2X_6(H_2O)_4]$ [where M = Mn^{2+}, Co^{2+} and Ni^{2+}, DDDP = 1,5-diamino 2,4-dimethyl 1,5-diaza 1,4-pentadiene, X = Cl^-, NO_3^- and ClO_4^-] have been synthesized in neutral medium. The ligand is coordinated to metal ion through azomethine nitrogen as indicated from IR spectra. Octahedral geometry has been proposed for the complexes on the basis of magnetic susceptibility and electronic spectral study. Thermal analysis of all the complexes shows similar pattern of decomposition. Weight loss takes place in one step, 175°C with exothermal peak in D.T.A. curve which corresponds to loss of four water molecules which shows that water molecuels are coordinated to metal ions. Fungicidal screening of the complexes shows them active against *Aspergillus niger*, *Fusarium orysporium* and *Helminthosporium oryzae*. These complexes are less active than the thio complexes.

Key Words: Mn^{2+}, Co^{2+}, Ni^{2+}, Complexes, 1,5-Diamino 2,4-dimethyl 1,5-diaza 1,4-pentadiene.

INTRODUCTION

Polydentate ligands having different geometry can coordinate to two or more metal ion[1]. Compounds containing vicinal dihydrazones are such systems which have received considerable attention in recent years[2, 3]. A few hydrazones are used as colorimetric reagents for the detection and determination of metal ions[4, 5]. The bactericidal[6], herbicidal[7], insecticidal[8] and fungicidal[9] properties of various hydrazones are also reported. Dihydrazone complexes have been used as intermediates in the synthesis of a series of novel complexes involving macrocyclic ring[10]. The dihydrazone complexes exhibit interesting chemical and structural properties due to the presence of conjugated π-electron system, $—N{=}\overset{|}{C}—N{=}\overset{|}{C}—N—$ in the ligand framework. The free amino groups of the coordinated dihydrazones are ideally oriented for further reaction with carbonyl groups in presence of metal ions resulting in five or six-membered annulated homo/hetero metal complexes. In the present work, we prepare complexes derived from different dihydrazones and elucidate their probable structures.

EXPERIMENTAL

All the chemicals and solvents were analytical grade reagents and solvents were used without further purification.

Preparation of the complexes: Acetyl acetone (2 mmol) in ethanol was treated dropwise with an ethanolic solution of the appropriate metal salt (3 mmol). The resulting mixture was refluxed for ½ h and hydrazine hydrate (4 mmol) was added dropwise with stirring. It was further refluxed for another 2 h. The precipitate obtained was cooled, filtered, washed with ethanol and ether and dried at room temprature and analysed[11]. The colour and analytical data of the metal complexes are recorded in Table-1.

TABLE-1
COLOUR AND ANALYTICAL DATA OF $[M_3(DDDP)_2X_6(H_2O)_4]$

Complex	Colour	Found (Calcd.) %				
		C	H	N	M	Cl
$[Ni_3(DDDP)_2Cl_6(H_2O)_4]$	Sky blue	16.60	4.30	15.70	24.40	29.60
		(16.74)	(4.46)	(15.62)	(24.55)	(29.71)
$[Ni_3(DDDP)_2(NO_3)_6(H_2O)_4]$	Dawn pink	13.50	3.40	22.20	20.10	–
		(13.70)	(3.65)	(22.37)	(20.09)	
$[Co_3(DDDP)_2Cl_6(H_2O)_4]$	Blue	16.50	4.50	15.40	24.40	29.90
		(16.71)	(4.46)	(24.65)	(29.67)	(29.67)
$[Co_3(DDDP)_2(NO_3)_6(H_2O)_4]$	Coral	13.40	3.70	22.10	20.20	–
		(13.68)	(3.65)	(22.35)	(20.18)	
$[Mn_3(DDDP)_2Cl_6(H_2O)_4]$	Off-white	17.10	4.60	15.90	23.20	30.20
		(17.00)	(4.53)	(15.86)	(23.37)	(30.17)

Infrared spectra in KBr pellets were recorded on a Perkin-Elmer 398 spectrophotometer. Reflectance spectra were recorded on a Cary-2390 spectrophotometer. Room temperature magnetic susceptibilities were measured by Gouy method. Thermogravimetric analyses were carried out by a Netzch-429. Simultaneous recording of TGA and DTA was done in a thermoanalyzer at a heating rate of 10°C min^{-1} in air.

RESULTS AND DISCUSSION

All the complexes are amorphous, high melting point and insoluble in water and common organic solvents. Freshly prepared samples are moderately soluble in DMF, dioxane and DMSO. Low conductance values observed in DMF for all the complexes indicate that they are non-electrolytes. All the complexes undergo decomposition without melting.

The infrared spectra of all the metal complexes under study exhibited an identical pattern suggesting that all the metal complexes are isostructural. As the Schiff base ligand could not be isolated, the spectra of the complexes were compared with the spectra of similar type of complexes with an identical ligand moiety[12, 13]. A number of changes are observed with respect to the spectrum of biacetyl hydrazone[14]. The broad band of medium intensity centred at *ca.* 3300 cm^{-1} may be assigned to the combination of symmetric and asymmetric mode of stretching vibration of NH_2 and H_2O respectively. This band position is comparatively lower than the normal ν(NH_2). The ν_{asym} and ν_{sym} vibrations of NH_2 group are shifted towards the lower frequency region in the metal complexes and observed to be *ca.* 3150 and 3080 cm^{-1} which has been reported[12] for the metal complexes by bihydrazones. These bands occupy intermediate positions observed for 1,2-diphenyl-1,2-dione dihydrazone and biacetyl dihydrazone[2, 3]. This sequence of the vibrational energy of ν(NH_2) may account for the high degree of conjugation in the present ligand moiety. The N—H bond strength is further reduced due to participation of the lone pair of electrons on nitrogen atoms of NH_2 group with the π-electron system of the conjugated $\text{—N=}\overset{|}{\text{C}}\text{—N=}\overset{|}{\text{C}}\text{—N—}$.

A more intense and sharp band observed at *ca.* 1610 cm^{-1} may be assigned to ν(C—N) stretching vibrations. The ν(C—N) generally observed at *ca.* 1580 cm^{-1} is shifted to higher frequency region in the present study. The shifting of this band to higher frequency region indicates the increase in bond order of the C—N bond which can be explained in terms of increase in π-electron density around nitrogen through conjugation[15]. The *d* electrons of the metal ions seem to have transferred to the orbitals of the ligand participating in conjugation. This M → L π-electron interaction is exhibited by the shifting of ν(C=N) band to higher frequency region. All the complexes exhibit weak bands in the region 460–440 cm^{-1} which may be attributed to ν(M—N) supporting our earlier observation[16].

A series of bands in the region 3000–2600 cm^{-1} which are structurally important may be assigned to ν(C—H) vibrations[17, 18]. A relatively strong band in the region 1465–1440 cm^{-1} may be attributed to the asymmetric C—CH_3 deformination, whereas a weak band at *ca.* 1380 cm^{-1} may be due to symmetric C—CH_3 deformation. The positions of these bands have been slightly shifted to the lower frequency region as compared to the free C—CH_3 vibration.

In the high frequency region a broad band centred at *ca.* 3350 cm^{-1} may be assigned to the presence of coordinated water molecules. This has been further supported by the appearance of a band[19] at *ca.* 850 cm^{-1}. This broadness of the band at *ca.* 3350 cm^{-1} may be due to intramolecular hydrogen bonding.

In addition to these vibrational bands, a few additional bands have been observed in the spectra of the nitrato complex. A band of strong intensity observed at *ca.* 1030 cm^{-1} and another at *ca.* 1270 cm^{-1} may be assigned to the ν(N—O) of the NO_3 group. No third band, expected to appear at *ca.* 1530 cm^{-1} for the ν(N—O), is observed which may be due to the overlapping of the ν(N—O) with the deformation vibration of C—CH_3 group. On comparison with the spectra of known uni and bidentate nitrato complexes[17], it is concluded that the nitrate group is coordinated in a unidentate manner.

The foregoing observations lead us to suggest a tentative structure (Fig. 1) for the complexes in which the azomethine nitrogen atoms of the dihydrazone satisfy four coordination numbers of the central metal ion whereas the amino groups satisfy two coordination positions of the terminal metal centres. The fifth and sixth coordination number of the central metal ion is satisfied by the amines while the third, fourth, fifth and sixth coordination numbers of the terminal metal centres are satisfied by anions and water molecules.

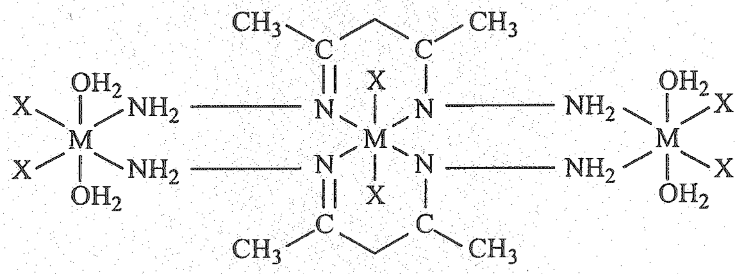

Fig. 1

The electronic spectral data and magnetic moment values of the complexes are recorded in Table-2.

TABLE-2
ELECTRON SPECTRAL DATA IN cm^{-1} (nm) AND MAGNETIC MOMENT VALUES OF [$M_3(DDDP)_2 \cdot 6(H_2O)_4$]

Complex	μ_{eff} (BM)	$3T_{1g}(F)$ ↑ $3A_{2g}$	$3T_{1g}$ ↑ $3A_{2g}$	$3T_{2g}$ ↑ $3A_{2g}$	$4A_{2g}(P)$ ↑ $4T_{1g}(F)$	CT	$4T_{1g}(S)$ ↑ $6A_{1g}(S)$	$4E_g$+$4A_{1g}$ ↑ $6A_{1g}(S)$	$4T_{2g}(D)$ ↑ $6A_{1g}(S)$
[$Ni_3(DDDP)_2Cl_6$ $(H_2O)_4$]	2.82	20,800 (500)	27,800 (359)	8,000 (1250)	–	–	–	–	–
[$Ni_3(DDDP)_2(NO_3)_6$ $(H_2O)_4$]	2.90	20,100 (497)	27,650 (361)	8,500 (1176)	–	–	–	–	–
[$Co_3(DDDP)_2Cl_6$ $(H_2O)_4$]	4.12	–	–	–	16,500 (625)	25,000 (400)	–	–	–
[$Co_3(DDDP)_2(NO_3)_6$ $(H_2O)_4$]	4.60	–	–	–	18,500 (540)	25,100 (389)	–	–	–
[$Mn_3(DDDP)_2Cl_6$ $(H_2O)_4$]	5.32	–	–	–	–	–	18,000 (555)	25,000 (400)	28,500 (350)

The electronic spectra of Ni(II) complexes show the characteristic features of complex with octahedral geometry around the metal ion and some degree of tetragonal distortion. Two intense bands observed at *ca.* 20,000 cm^{-1} (500 nm) and 27,800 cm^{-1} (359 nm) may be assigned to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions respectively. The higher intensity of the latter band may be due to the charge transfer phenomenon. Apart from these, another broad band between 10500–8000 cm^{-1} (1250–952 nm) may be assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$. The width of this band accounts for the distortion of the complex. The magnetic moment values of the Ni(II) complexes at room temperature are found to be lower than the normal magnetic moment value which may be due to the quenching of the orbitals. These values are in good agreement with nearly octahedral coordination of the ligand atoms about the Ni(II) ion[20, 21].

In case of Co(II) complexes, the ground state 4F splits into $^4T_{1g}$, $^4T_{2g}$ and $^4A_{1g}$ terms whose energy levels increase successively and the 4P term transforms as $^4T_{1g}$ under octahedral symmetry. The present Co(II) complexes exhibit a multiplet bank structure lying in the range of 18,500–16,500 cm^{-1} (625–540 nm) which may be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ transition and the structure of the complex can be assigned to an approximately octahedral one. Another band of strong intensity around 25,000 cm^{-1} (400 nm) may be assigned to charge transfer. The magnetic moments of the Co(II) complexes lie in the range of 4.1–4.6 BM which is lower than the normal magnetic moment values originating from the quenching of the metal ion orbitals.

The electronic spectra of Mn(II) complex show three distinct bands *ca.* 18,000 cm^{-1} (555 nm), 25000 cm^{-1} (400 nm) and 28,500 cm^{-1} (350 nm) which may be assigned to $^6A_{1g}(S) \rightarrow {}^4T_{1g}(S)$, $^6A_{1g}(S) \rightarrow {}^4E_g + {}^4A_{1g}(G)$ and $^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$ transitions, respectively. The magnetic moment value of Mn(II) complex is found to be 5.32 BM.

Basing on this discussion an octahedral arrangement[16, 17] may be proposed around the metal centre.

Thermal analysis: The temperature range of thermal analysis was room temperature to 840°C. All the complexes exhibited an identical pattern of decomposition. Hence, as an example, the decomposition pattern of the nickel chloro complex has been discussed below.

There was no weight loss up to 145°C suggesting the absence of lattice water[22, 23]. The weight loss started slowly after this temperature. The first weight loss was encountered at about 175°C with an exothermic peak at the same temperature. The presence of the exothermic peak suggests bond breaking. The weight loss corresponds to the loss of four water molecules, which suggests the presence of the water molecules in the same chemical environment[24, 25]. These observations further confirm the nature of water molecules to be coordinated. A stable product continues up to 345°C after which the organic constituents of the complexes start decomposing, finally leaving behind the metal oxide at 835°C. The thermal stability of the complexes is in the order of Mn > Ni > Co.

On the basis of these observations and infrared spectral data, the authors suggest that the water molecules are coordinated to the metal ions from the apical position whereas the central metal ion satisfies its fifth and sixth coordination number by anions (Fig. 1).

Fungicidal screening: The antifungal activity of the ligand and its metal complexes were tested against *Helminthosporium oryzae, Fusarium exosporium* and *Aspergillus niger* by the method of Horsfall[26]. The evaluation was carried out at 1000 ppm in dioxane. The amount of germination or growth inhibition was determined after inoculation of the fungal spores on to Czapexdox agar-agar medium containing the test sample. The whole system was kept in an incubator for five days at 30 ± 1°C. The percentage inhibition was calculated as follows:

$$\text{\% of inhibition} = \frac{100(P - Q)}{P}$$

where P = area of colony growth without test sample and Q = area of colony growth with test sample. When metal salts such as copper chloride, cobalt chloride are used as fungicides they cause damage to the level[27]. However, the coordination compounds do little damage. Among the complexes being reported here, the copper(II) complexes possess the highest fungitoxicity. However, this ligand and these complexes are less active than sulphur containing ligands.

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(*Received*: 13 January 2006; *Accepted*: 30 June 2006) AJC-4990