SYNTHESIS AND CHARACTERIZATION OF MALONIC ACID DIHYDRAZIDE AND ITS METAL COMPLEXES

SÍNTESE E CARACTERIZAÇÃO DE DIHIRAZIDA MELÓNICA E SEUS COMPLEXOS DE METAIS

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RESUMO

Uma nova série de complexos foi sintetizado através da reação entre malonil dihidrazida (MAH) e manganês, cobre, níquel, zinco, cádmio, cobalto e sais férricos em meio metanólico. Os complexos obtidos foram caracterizados por análise elementar, medidas de condutância molares, eletrônica, de IV e estudos espectrais de RMN de ^{1}H. Com base nos resultados obtidos, a estequiometria do Fe (III)-MAH e do Co(III)-MAH foi proposta para ser de 1:3 e que para o Cu(II)-MAH, Cd(II)-MAH, Zn(II) -MAH, Mn(II)-MAH, Ni(II)-MAH foi proposta para ser 1:2 (M:L). Foi sugerido que o nitrogênio presente na azometina (>C=N-), grupo com a forma enólica do ligante estava envolvido na formação de complexos. Uma representação clara indicando os sítios ligantes de cada complexo foi descrita. Os complexos metálicos apresentam diferentes arranjos geométricos, tais como tetraédricos, quadrados planos e octaédricos.

Palavras chaves: Ácido malônico dihidrazida, complexos metálicos, análise elementar, caracterização espectral, geometria molecular.

ABSTRACT

A new series of complexes was synthesized by the reaction between malonyl dihydrazide (MAH) and manganese, copper, nickel, zinc, cadmium, cobalt and ferric salts in methanolic medium. The complexes were characterized by elemental analysis, molar conductance measurements, electronic, IR and ^{1}H NMR spectral studies. Based on the results obtained, the stoichiometry of Fe(III)-MAH and Co(III)-MAH was proposed to be 1:3 and that for Cu(II)-MAH, Cd(II)-MAH, Zn(II)-MAH, Mn(II)-MAH, Ni(II)-MAH was proposed to be 1:2 (M:L). It was suggested that the nitrogen present in the azomethine (>C=N-) group of the enolic form present in the ligand was involved in the formation of complexes. A clear picturisation indicating the bonding sites were depicted for each complex. The metal complexes exhibit different geometries such as tetrahedral, square planar and octahedral arrangements.

Keywords: *Malonic acid dihydrazide, metal complexes, elemental analysis, spectral characterization, molecular geometry.*

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1) INTRODUCTION

Malonic acid dihydrazide has been extensively utilized for the synthesis of macrocyclic metal complexes. Macrocyclic metal complexes are of great interest due to their resemblance to naturally occurring macrocycles, analytical, industrial and medical applications (Singh *et al.,* 2007; Lindoy, 1989; Ma *et al.,* 2006; Gloe, 2005; Constable, 1999; Singh *et al.,* 2007). Macrocyclic metal chelating agents are useful for detecting tumor lesions (Kosmas *et al.,* 1992). Malonic acid dihydrazide has been utilized for the synthesis of mixed ligand complexes having excellent industrial and medicinal applications (Halli *et al.,* 2012; Chandra and Kapoor, 1982; Dharam *et al.,* 20102; Miroslava *et al,* 2011; Mishra *et al.,* 2007. Dobosz *et al.,* 2007; Sonawane *et al.,* 2008). However, structural, spectral, and chemical characteristics of complexes are often strongly dependent on the nature of the ligand and its structure (Nejo *et al.,* 2010; Vafazadeh and Kashfi, 2007; Raman *et al.,* 2007; Nathan *et al.,* 2003). Literature survey reveals that not much work has been carried out using acid hydrazides as ligands in recent times. Keeping in view the paucity of information and the significance of malonic acid dihydrazide in different fields, the authors have synthesized and characterized Mn(II), Zn(II), Ni(II), Cu(II), Cd(II), Fe(III), Co(III) complexes of MAH.

2) MATERIALS AND METHODS

The chemicals employed in the studies were analytical grade procured from Merck India Limited. The ligand (MAH) and its metal complexes were analyzed for C, H and N by micro analytical techniques. Analysis report for C, H and N was obtained from Central Drug Research Institute (CDRI), Lucknow, India. pH measurements were made using pH meter Model L1-10, ELICO Private Limited, Hyderabad, India. Conductivity measurements were made using conductivity meter 303 manufactured by Systronics India Limited. The electronic spectra were recorded on Schimadzu UV-160 spectrophotometer. The IR spectra were recorded on Perkin-Elmer-283 spectrometer. Vibrating sample magnetometer at RSIC, IIT, Chennai was employed for the determination of the magnetic susceptibilities of metal complexes in solid state at room temperature. ^{1}H NMR spectra were obtained from Regional Science Instrumentation Center, Indian Institute of Science, Mumbai, India.

2.1. Synthesis of malonic acid dihydrazide

A mixture of dimethylmalonate (23.0 mL), 99-100% hydrazine hydrate (19.4 mL) was taken on a watch glass and scratched with a glass rod for few minutes to get white crystals. The crystals were dried and recrystallized from 1:1 methanol.

2.2. Synthesis of M-MAH complexes

M-MAH complex was prepared by refluxing a mixture of 50 mL of methanolic solution containing metal salt (2.5 mmol) and malonic acid dihydrazide (5.0 mmol in case of Mn(II) and Zn(II), 2.5 mmol in case of Ni(II), Cu(II) and Cd(II) and 7.5 mmol in case of Fe(III) and Co(III)) for about 1 hour. The reaction mixture was cooled, crystalline mass obtained was filtered, washed with distilled water and dried in vacuo.

2.3. Estimation of metal content in complexes

Known amount (0.200 g) of the metal complex was decomposed with concentrated nitric acid. The excess nitric acid was expelled by evaporating with concentrated sulphuric acid. The process was repeated till the organic part of the complex was completely lost. The residue was cooled, dissolved in water and the metal ions were determined by standard procedures. Iron after reduction with $SnCl_2$ was determined by dichrometry (Vogel, 1961), copper by iodometry (Vogel, 1961), nickel by gravimetry (Vogel, 1961), manganese, cobalt, zinc and cadmium by complexometry (Vogel, 1961).

3) RESULTS AND DISCUSSION:

The elemental analysis data was in good agreement with the theoretically calculated values shown in the parenthesis (Table 1). This was supported by the structures assigned for the complexes by different physico-chemical techniques. The stoichiometric ratio of metal to ligand for the complexes have been deduced to be 1:2 for the complexes 2, 5, 6, 7, 8 and 1:3 for the complexes 3 and 4. The molar conductivity values of the metal complexes determined in DMF solutions of concentration 1×10^{-3} M are shown in Table 1. The values were in the range 11.2 – 26.2 mho cm^2 mole^{-1}. Hence it was concluded that the complexes were nonelectrolytic in nature (Geary, 1971).

I. Mn(II)-MAH complex

Large number of manganese(II) complexes with octahedral coordination are known. The ground state of manganese(II) (d^5) in high spin octahedral coordination is $^6A_{1g}$. The alteration of the electron distribution in the octahedral coordination results in the pairing of electrons. However because of weak spin orbit interactions, very weak absorption bands that might correspond to $^6A_{1g} \rightarrow {}^4T_{1g(G)}$, $^6A_{1g} \rightarrow {}^4T_{2g(G)}$ and $^6A_{1g} \rightarrow {}^4E_{g(G)}$ transitions (Sengupta *et al.,* 1981; Preti and Tosi, 1976; Sharada and Ganorkar, 1978; Pappalardo, 1959; Hemendra *et al.,* 1988) may occur. The complex under investigation gave three bands at around 15602, 17805 and 22800 cm^{-1}. These bands arise due to above mentioned transitions for Mn(II)-MAH complex having octahedral geometry. The magnetic moment value of 5.30 BM also lends support to the octahedral geometry.

II. Fe(III)-MAH complex

Fe^{+3} ion is isoelectronic with Mn^{+2} ion. The electronic spectrum of the Fe(III)-MAH complex is almost similar to that of manganese(II)-MAH complex except that the numerical values of spectral frequencies observed i.e. 9756, 11442 and 18308 cm^{-1} were less than that of Mn(II)-MAH complex. Fe(III) is high spin in most of its octahedral complexes. The ground state of Fe(III) is $^6A_{1g}$ and four weak transitions are expected (Bertrand and Eller, 1974) in this state. However low spin complexes with t_{2g}^{5} configuration possess $^2T_{2g}$ ground state and even in this case also four transitions are expected (Lever, 1984). The magnetic moment value is 2.09 BM. The greatest loss of exchange energy occurs when the d^5 configuration is forced to pair up resulting in the apparent stability of half-filled d-subshell and such a pairing leads to the formation of low spin complexes. It is well known that, because of the presence of empty e_g orbitals, ligands are allowed to come closer to the central metal ion in low spin complexes. This fact was further confirmed by the magnetic moment value of 2.09 BM. Based on the electronic spectral data and magnetic moment values, an octahedral geometry is suggested for Fe(III)-MAH complex.

III. Co(III)-MAH complex

In general all cobalt(III) complexes are octahedral. The free cobalt ion (d^6), has qualitatively the same energy level diagram as that of iron(II). In case of cobalt(III), the $^1A_{1g}$ state originating in one of the high energy singlet states of the free ion drops rapidly and crosses $^5T_{2g}$ state at a very low value of Δ. Thus in general all Co(III) complexes are expected to consist of transition from the $^1A_{1g}$ ground state to other singlet states. The two absorption bands found in the visible region at 19898 and 27786 cm^{-1} represent transitions to the upper states $^1T_{1g}$ and $^1T_{2g}$ respectively. The electronic spectral data and diamagnetic nature suggest an octahedral structure for the complex.

IV. Ni(II)-MAH complex

The ground state of Ni(II) ion in octahedral coordination is $^3A_{2g}$ ($t_{2g}^6 e_g^2$). Three absorption bands are possible corresponding to transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g(F)}$ and $^3A_{2g} \rightarrow {}^3T_{1g(P)}$. These three spin allowed transitions normally occur in the range 7000-13000, 11000-20000 and 19000-27000 cm^{-1} respectively. In the present investigations, Ni(II)-MAH complex in DMF solution gave three peaks at 11218, 18982 and 28435 cm^{-1}. The ν_2/ν_1 value observed was 1.692 which the lower than the ν_2/ν_1 value of 1.800 observed for the regular octahedral nickel-aqua complex. The lower value of ν_2/ν_1 was attributed to the asymmetric environment around Ni(II). The Racah parameter value (B) and nephelauxetic factor (β) suggest the delocalization of d-orbitals and covalence of the metal-ligand bond in metal complexes. The ground state of regular octahedral complex is $^3A_{2g}$ which arbitrarily is not degenerate and hence orbital angular momentum contribution to the magnetic phenomenon is absent. The μ_{eff} value should be equivalent to a spin only value of 2.8 BM. The slightly greater value of 3.3 BM observed for Ni(II) complex may be due to the spin orbit coupling between the ground state $^3A_{2g}$ and the first excited state $^3T_{2g}$. Based on the above arguments, an octahedral structure was proposed for the Ni(II)-MAH complex.

V. Cu(II)-MAH complex

Cu(II) forms complexes which are either distorted octahedral with a limiting structure of square planar or tetrahedral. The ground term in square planar geometry is $^3B_{1g}$ and the excited terms are $^2A_{1g}$, $^2B_{2g}$ and ^2E_g and hence three transitions are to be expected. Square planar Cu(II) complexes are expected to give three peaks which usually overlap to give one or two broad peaks (Lever, 1984; Sutton, 1968). The d-d bands of square planar complexes (Fackler *et al.,* 1963; Werden *et al.,* 1966) are usually observed at around 14000 and 22000 cm^{-1}. In the present investigation, two bands one at 17905 cm^{-1} and the other at 27520 cm^{-1} were observed. The latter band may be attributed to the ligand to metal charge transfer transition. The band at 17905 cm^{-1} may be attributed either to $^2B_{1g} \rightarrow {}^2B_{2g}$ or $^2B_{1g} \rightarrow {}^2E_g$ transition. Irrespective of stereochemistry, Cu(II) complexes possess one unpaired electron. The higher magnetic moment value i.e. 2.09 BM (Figgis and Lewis, 1965) for the complex under investigation (greater than 1.90 BM) could be due to spin orbit coupling. Based on the elemental analysis data, spectral data and the magnetic moment value, a square planar structure is proposed for the complex.

VI. Zn(II) and Cd(II) complexes of MAH

Zn(II) and Cd(II) complexes possess d^{10} configuration and hence do not show spectral absorptions due to d-d transitions. The complexes were diamagnetic in nature. Based on the elemental analysis, conductance and infrared spectral data, a tetrahedral geometry is suggested for Zn(II) and Cd(II)-MAH complexes.

b. IR spectral details

The IR spectral data of the ligand MAH and its Mn(II), Fe(III), Co(III), Ni(II), Cu(II), Zn(II), Cd(II) complexes are presented Table 3.

3.2.1 Infrared spectrum of the ligand

A doublet noticed at around 3545 cm^{-1} and 3460 cm^{-1} was due to the presence of -NH$_2$ group. A band at 3217 cm^{-1} was ascribed to the –NH group attached to the carbonyl group. A doublet at 2950 cm^{-1} and 2840 cm^{-1} is attributed to the –CH$_2$ group. Another band at 1630 cm^{-1} may be ascribed to the >C=O group.

3.2.2 IR spectra of Mn(II) and Ni(II)-MAH complexes

The important IR frequencies exhibited by Mn(II)-MAH and Ni(II)-MAH complexes together with their assignments are given in Table 3. Some of the bands in the IR spectrum of the ligand undergo appreciable shift towards lower frequencies. The band at 2855 cm^{-1} in the spectrum of Mn(II)-MAH and at 2845 cm^{-1} in that of Ni(II)-MAH complexes was not present in the spectrum of ligand and was due to the enolic –OH group. This suggests that the reagent in these complexes was in the enolic form and not in the keto form as was present in the free ligand. The bands at 3545 and 3460 cm^{-1} corresponding to –NH$_2$ group were shifted to lower values by about 50 cm^{-1} in the spectra of Mn(II) and Ni(II)-MAH complexes. This shift was ascribed to the strong intramolecular hydrogen bonding between nitrogen of –NH$_2$ and hydrogen of enolic –OH. The appearance of a new band at 1595 cm^{-1} in both the complexes may be attributed to amide II-NH$_2$ group. A band at 1630 cm^{-1} due to the amide carbonyl group was absent in the spectra of complexes. This further suggests that the reagent in the complexes was in the enolic form. Similarly a band at 3217 cm^{-1} due to –NH stretching has also disappeared in the spectra of complexes suggesting that not only the reagent was present in the enolic form, but the nitrogen of the –NH group was involved in coordination with the metal ion. New band which was not observed in the spectrum of free ligand was found at 1610 cm^{-1} and 1615 cm^{-1} in the spectra of Mn(II) and Ni(II)-MAH complexes. This may be due to the presence of azomethine (>C=N-) group in the complexes. Further, the spectra of complexes contain new bands at 365, 463 and 614, 638 cm^{-1} due to νM-Cl (Ferraro, 1971) and νM-N (Beecroft *et al.,*1974; Ferraro and Walkers, 1965) vibrations respectively. A shift in νN-N to higher wave numbers was observed in the spectra of complexes and this was due to the coordination of ligand via azomethine nitrogen in a bidentate manner.

Elemental analysis data predicts the ratio of metal to ligand to be 1:2. Taking into consideration the elemental analysis and IR spectral data, an octahedral structure was proposed for the complexes. The four coordinate positions were occupied by four nitrogen atoms and the remaining two by chloride ions. The fact that no precipitate was obtained when a solution of the complex in DMF was treated with silver nitrate solution indicated the presence of the chloride ions inside the coordinate sphere. The structural formulae and bonding sites are depicted in Fig. 1.

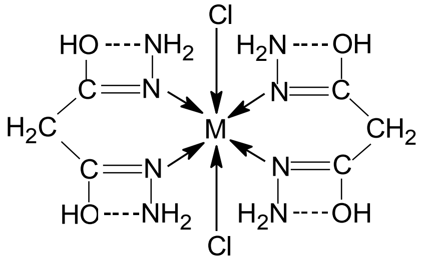

Figure 1. Structural formula of M-MAH complex. M = Mn(II), Ni(II).

3.2.3 IR spectra of Fe(III) and Co(III)-MAH complexes

The spectral data of Fe(III) and Co(III)-MAH complexes are presented in Table 3. The IR spectra was almost similar to that of Mn(II) and Ni(II) complexes except that the band due to νM-Cl was not observed.

The elemental analysis data predicts the composition of the metal complex to be 1:3 (metal:ligand). Based on the IR spectral data and the analytical data, an octahedral geometry was proposed for Fe(III) and Co(III)-MAH complexes. The absence of νM-Cl indicates that all the six coordination sites were satisfied by azomethine nitrogen atoms. The structural formulae and bonding sites are shown in Fig. 2.

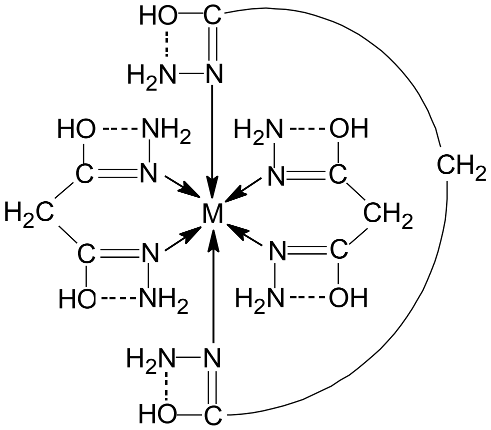

Figure 2. Structural formula of M-MAH complex. M = Fe(III), Co(III)

3.2.4. IR spectra of Cu(II), Zn(II) and Cd(II)-MAH complexes

The spectral data of these complexes is presented in Table 3. The composition of the complexes determined from the elemental analysis data was 1:2 (metal:ligand). The most preferred geometry for d^{10} systems is tetrahedral geometry. Hence tetrahedral configuration was suggested for Zn(II) and Cd(II) complexes. However Cu(II) being a d^9 ion, electronic spectral data was also important in deciding the geometry of the complex. The suggested structure for Cu(II) complex is square planar. The structural formulae and bonding sites are depicted in Fig. 3.

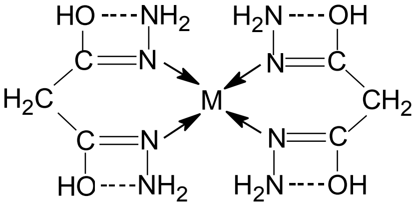

Figure 3. Structural formula of M-MAH complex. M = Cu(II), Zn(II), Cd(II).

3.3. NMR spectral details

The ^1H NMR spectral data of the ligand MAH and its Mn(II), Fe(III), Co(III), Ni(II), Cu(II), Zn(II) and Cd(II) complexes recorded in DMSO d^6 using TMS as an internal standard are shown in the Table 4.

The signals of ^1H NMR spectra for the reagent (1) and the complexes (2-8) appeared at 4.75 (1), 4.70 (2), 4.80 (3), 4.81 (4), 4.82 (5), 4.78 (6), 4.70 (7), 4.72 (8) ppm were assigned to methylene protons. Two distorted NMR signals at around 6.30 ppm and 10.50 ppm in the spectrum of the reagent were due to amino and imino protons respectively. NMR signal which was not observed in the spectrum of the free ligand and noticed in the range 5.10-5.25 ppm in the spectra of the complexes were attributed to the presence of –OH proton. This suggests that enolic form of the ligand was interacting with the metal ion during the formation of the complexes. The signals observed for the amino protons in the reagent were not affected in the spectra of complexes. This indicates that the $-NH_2$ group was not involved in coordination. The signal corresponding to the imino proton observed in free ligand was absent in spectra of complexes. This fact further confirms presence of enolic form of the ligand.

4) CONCLUSIONS

Malonic acid dihydrazide complexes of Mn(II) Cu(II) nickel, Zn(II), Cd(II), Co(III) and Fe(III) were synthesized and characterized by elemental analysis, molar conductance measurements, electronic spectral, IR spectral and ^{1}H NMR spectral studies. The stoichiometric of Fe(III)-MAH and Co(III)-MAH was found to be 1:3 where as that for Cu(II)-MAH, Cd(II)-MAH, Zn(II)-MAH, Mn(II)-MAH, Ni(II)-MAH was reported to be 1:2 (M:L). The geometry of the complex was proposed in each case.

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Table 1. Characterization details of M-MAH

M-MAH	Colour	Melting point (°C)	Molecular weight	Found (cal) %				μ_{eff} BM	molar conductivity mho cm^2 mole^{-1}
				C	H	N	M		
M=Mn(II)	Pale yellow	123	388	18.57 (18.61)	3.64 (3.67)	28.87 (28.92)	14.15 (14.26)	5.40	11.2
M=Fe(III)	Dark brown	158	451	23.97 (24.05)	5.24 (5.34)	36.99 (37.09)	12.15 (12.33)	2.09	12.8
M=Co(III)	Light pink	165	454	23.81 (23.89)	5.21 (5.30)	36.77 (36.85)	12.74 (12.92)	Dia-magnetic	-
M=Ni(II)	Pale green	178	321	22.24 (22.32)	4.90 (4.99)	34.63 (34.70)	18.00 (18.18)	3.42	26.2
M=Cu(II)	Deep blue	203	326	21.89 (21.99)	4.83 (4.92)	34.10 (34.20)	19.20 (19.38)	2.19	20.6
M=Zn(II)	Pale yellow	215	328	21.78 (21.86)	4.80 (4.89)	33.90 (33.99)	19.66 (19.84)	Dia-magnetic	-
M=Cd(II)	Pale yellow	236	375	19.06 (19.13)	4.20 (4.28)	29.68 (29.75)	29.70 (29.84)	Dia-magnetic	-

Table 2. Electronic spectral data of M-MAH

M-MAH	Frequency			ν_2/ν_1	B	β
	ν_1	ν_2	ν_3			
M=Mn(II)	15602	17805	22800	1.141	860	0.4807
M=Fe(III)	9756	11442	18308	1.173	1015	2.2147
M=Co(III)	-	19898	27786	-	1065	-
M=Ni(II)	11218	18982	28435	1.692	1030	0.8908
M=Cu(II)	17905	27520	-	1.537	-	-
M=Zn(II)	-	-	-	-	-	-
M=Cd(II)	-	-	-	-	-	-

Table 3. IR absorption frequencies (cm^{-1}) and their assignments for MAH and M-MAH

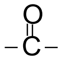
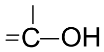
Group	**MAH**	**M-MAH**						
		Mn(II)	**Fe(III)**	**Co(III)**	**Ni(II)**	**Cu(II)**	**Zn(II)**	**Cd(II)**
-CH$_2$	2950 2840	2950 2840	2950 2840	2950 2840	2950 2840	2950 2840	2950 2840	2950 2840
 $-\overset{\overset{O}{\|\|}}{C}-$ (Amide I)	1630	-	-	-	-	-	-	-
-NH	3217	-	-	-	-	-	-	-
-NH$_2$	3545 3460	3495 3410	3490 3405	3490 3410	3495 3415	3490 3415	3500 3415	3505 3415
-NH$_2$ (Amide II)	-	1595	1595	1595	1595	1595	1595	1595
 $=\overset{\|}{C}-OH$	-	2855	2850	2865	2845	2875	2865	2850
>C=N	-	1610	1605	1610	1615	1610	1615	1617
M-Cl	-	463	-	-	365	-	-	-
M-N	-	613	615	616	638	618	618	616
N-N	1045	1078	1071	1073	1075	1080	1076	1072

Table 4. ^{1}H NMR spectral data (δ ppm) and their assignments for MAH and M-MAH

MAH/ M-MAH	**-CH$_2$ (singlet)**	**-OH (singlet)**	**-NH- distorted peak**	**-NH$_2$ distorted triplet**
MAH	4.75	-	10.50	6.30
M=Mn(II)	4.70	5.25	-	6.10
M=Fe(III)	4.80	5.10	-	6.12
M=Co(III)	4.81	5.15	-	6.13
M=Ni(II)	4.82	5.20	-	6.15
M=Cu(II)	4.78	5.22	-	6.14
M=Zn(II)	4.70	5.24	-	6.00
M=Cd(II)	4.72	5.24	-	6.18