

Preparation and Physico Chemical Investigation of Manganese (II) Complexes with Hydrazone Ligands

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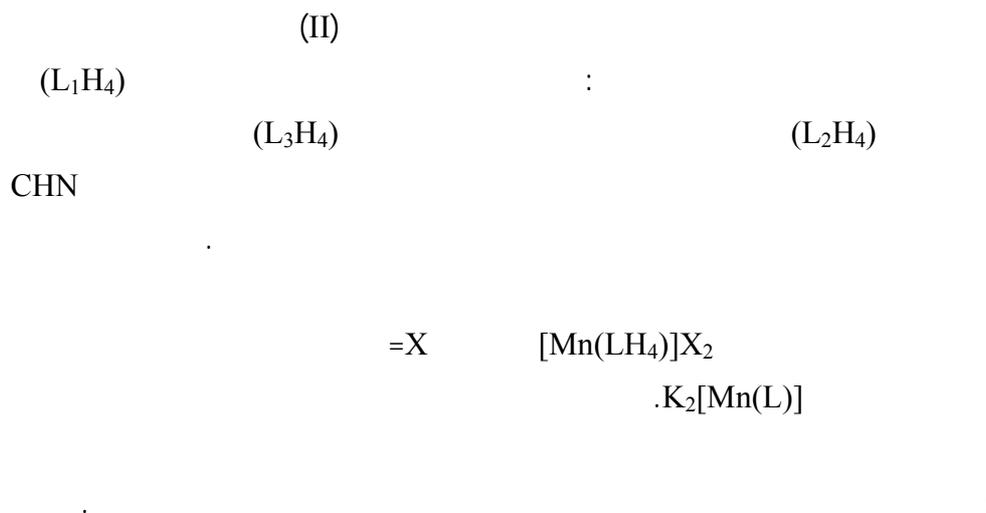
(Received 25/9/2018 ; Accepted 25/10/2018)

ABSTRACT

The work reported deals with the preparation and characterization of a number of new complexes of manganese (II). The complexes are formed by the reaction of the mentioned metal salts with three ligands of Schiff base type; the ligands are: dibenzoinlidenemalonoyldihydrazide (L_1H_4), dibenzoinlidenesuccinyldihydrazide (L_2H_4) and dibenzoinlidenephthalolyldihydrazide (L_3H_4). The prepared complexes have been characterized by molar conductance, CHN analysis, metal contents, electronic spectra, infrared spectra, and magnetic susceptibility measurements. The different studies suggest that all the complexes are hexacoordinated with octahedral geometry in the neutral medium; the ligands formed cationic complexes of the type $[Mn(LH_4)]X_2$ where $X=Cl^{-1}$ and NO_3^{-1} , while in a basic medium anionic complexes of the general formula $K_2[Mn(L)]$.

Keywords: Acid hydrazide, Hydrazone ligands, Schiff base complexes, Manganese (II) complexes.

(II)



INTRODUCTION

The coordination chemistry of hydrazones and their metal complexes have gained importance because of their use as a model for biological system. In addition, they are known to exhibit a wide variety of pharmacological properties such as analgesic, anti-inflammatory, antimalarial,

antithelmentic activity, antitubercular, hypotensive actions, xantitumor, anticonvulsant, and carcinostatic activity (Singh and Singh, 2013; Jang *et al.*, 2005; Sallomi *et al.*, 2011; Al-Shaheen *et al.*, 2012; Al-Shaheen *et al.*, 2013; Al-Shaheen *et al.*, 2017). Biological activities of hydrazone metal complexes are also reported for several transitional metals (Bernhardt *et al.*, 2008; Alagesan *et al.*, 2013; Sathyadevi *et al.*, 2012). Recently, considerable attention has been paid to chemistry of the metal complexes of Schiff bases containing oxygen, nitrogen and other donors because they offer many attractive properties such as displaying a double role of electron transport and light emission, higher thermal stability and easy sublimation (Saydam and Alkan, 2001; Ciobanu *et al.*, 2006; Sone and Fukuda, 1987). Schiff bases derived from the reaction of the aldehydes or ketones with hydrazides are very interesting since they are present in keto-enol forms and can form different types of complexes (Suresh and Prakash, 2011; Feng *et al.*, 2009; Wageih and Moawaad, 2001). In present work, new manganese complexes are formed with ligands derived from benzoin and malonyl dihydrazide (L_1H_4), succinyldihydrazide (L_2H_4) and phthaloyldihydrazide (L_3H_4), (Scheme 1) have been synthesized and are characterized by different chemical, physical and spectral methods.

EXPERIMENTAL

Material and Measurement

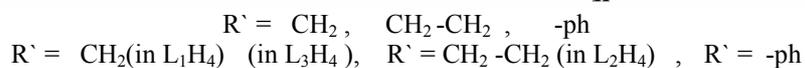
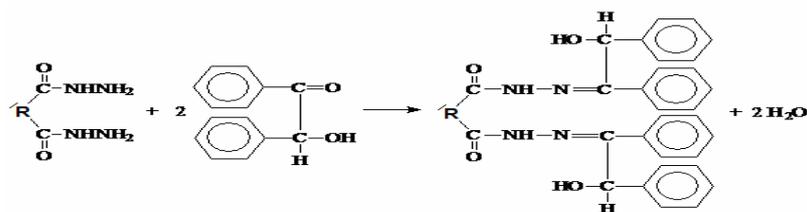
All the chemicals used were supplied from Fluka, BDH, Aldrich, Merck, Acid hydrazides, malonyl, succinyl and phthaloyl dihydrazides were prepared by the condensation of the corresponding esters and hydrazine hydrate in 1: 2 molar ratio according to the reported procedure (Baker *et al.*, 1950). Manganese contents were determined by atomic absorption method, CHN analyzer type vector, mode 1 E.A 3000 v.3.0 single Euro.in College of Pure Science/ University of Baghdad. Electronic spectra were recorded on Shimadzu UV-160 spectrophotometer for 10^{-3} M for complexes in DMF at 25°C using 1 cm quartz cell. Infrared absorption was recorded on a Perkin-Elmer 580 spectrophotometer as KBr Pelletes in the range 400-4000 cm^{-1} . Molar conductance of the complexes was measured at room temperature for 10^{-3} M in DMF solution using conductivity bridge type LF-42. Magnetic susceptibility of the complexes was measured by Bruker-BM6.

Preparation of Hydrazone

These were prepared according to the literature method (Baker *et al.*, 1950) by reacting to a solution of acid dihydrazide (0.01mole, 1.43g) malonyldihydrazide (MDH₂) or (0.01mole, 1.50g) succinyldihydrazide (SDH₂) or (0.01 mole, 2.15g) phthaloyldihydrazide (PDH₂) in ethanol 20 ml was add to the solution of benzoin (0.02mole, 4.70g) in ethanol. The reaction mixture was heated under reflux for 3-9 hrs. After cooling, fine precipitate was formed which was filtered off, washed with cold ethanol and dried in oven at 70-80 °C .

Preparation of the Metal Complexes

In order to the metal complexes (1:1 molar ratio, manganese salts: ligand), a general procedure has been used for the preparation of the complexes in neutral and basic medium. In neutral medium a solution of (0.001 mole, 0.125g) of manganese chloride or (0.001 mole, 0.178g) manganese nitrate in 10 ml of ethanol has been added to the solution of one of acid dihydrazides [L_1H_4 (0.001 mole, 0.520g) or L_2H_4 (0.001 mole, 0.534g) or L_3H_4 (0.001 mole, 0.582g)]. An ethanolic mixture containing manganese (II) salt and the ligand has been refluxed for about three hours. After cooling, the separated complexes were filtered off, recrystallized from hot water and dried. The alkaline medium complexes have been prepared by applying the same above amounts except that the ligands were treated with 1M KOH solution. Complete precipitation of the complexes were achieved at pH 9-10. The mixtures were left to stand for 30 minutes, then filtered off, recrystallized from hot water and dried in oven at 70-80 °C.



(Scheme 1)

Preparation of ligand, (L_1H_4), (L_2H_4), (L_3H_4)

RESULTS AND DISCUSSION

The reaction of benzoin and acid dihydrazide in ethanol gave the desired hydrazone ligand (L_1H_4), (L_2H_4), (L_3H_4) (Scheme 1) in excellent yield and purity. The analytical data and some of the physical properties of the prepared ligand and its complexes are shown in (Table 1) which indicates that metal chlorides and metal nitrate form 1:1 (M:L) complexes with general formula, $[M(LH_4)]X_2$ and $K_2[M(L)]$. For all the complexes, the metal contents and the molar conductance values are in a good agreement with the given formulations as shown (Table 1). The solid complexes are colored, and conductance in DMF (Sallomi and Al-Shaheen, 1994; Despaigne *et al.*, 2009; Chohan *et al.*, 2000). Most of the complexes melted in the temperature range 207-307°C. The molar conductivities of the complexes in DMF indicated the presence of two types of complexes, a molar conductance data of 10^{-3} M solutions of the complexes (Table 1) at room temperature which show values (110-188) $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ indicating that they are 1:2 electrolytes in the neutral medium, while in the basic medium as 2:1 electrolytes. (Geary, 1971).

Table 1: Some physical and analysis data of the ligand and their complexes

No. of Complexes	Formula	Color	M.P. (C°)	Λ_M DMF $\text{Ohm}^{-1} \cdot \text{Cm}^2 \cdot \text{mol}^{-1}$	% Mn analysis Calc. (obser)	% anal ysis, Calc. (obser)		
						C	H	N
	L_1H_4	Yellow	150			71.53 70.41	5.38 5.22	10.7 9.56
1	$[\text{Mn}(L_1H_4)]\text{Cl}_2$	Yellow	207	147	8.51 8.85	57.58 57.63	4.33 2.60	8.668. 91
2	$\text{K}_2[\text{Mn}(L_1)]$	Dark Yellow	232	110	8.47 8.67	57.31 50.04	3.69 3.72	8.627. 55
3	$[\text{Mn}(L_1H_4)](\text{NO}_3)_2$	Yellow	307	164	7.86 8.05	53.21 62.89	4.00 4.00	12.0 9.66
	L_2H_4	Yellow	190			71.91 69.58	5.61 5.39	10.4 10.3
4	$[\text{Mn}(L_2H_4)]\text{Cl}_2$	cream	255	187	8.33 8.61	58.18 58.34	4.54 4.64	8.488. 57
5	$\text{K}_2[\text{Mn}(L_2)]$	Dark Yellow	220	152	8.29 8.45	57.91 49.87	3.92 4.01	8.447. 46
6	$[\text{Mn}(L_2H_4)](\text{NO}_3)_2$	Light Yellow	242	135	7.71 7.96	53.85 65.03	4.20 4.07	11.78. 54
	L_3H_4	Yellow	144			74.22 73.13	5.15 5.09	9.62 8.75
7	$[\text{Mn}(L_3H_4)]\text{Cl}_2$	Light Yellow	261	178	7.76 8.32	61.01 61.12	4.23 4.49	7.908. 00
8	$\text{K}_2[\text{Mn}(L_3)]$	Dark Yellow	273	188	7.73 8.09	60.75 52.47	3.65 3.85	7.876. 80
9	$[\text{Mn}(L_3H_4)](\text{NO}_3)_2$	Yellow	288	147	7.22 7.44	56.76 60.96	3.94 3.81	11.07. 92

The electronic spectra of the metal complexes were carried out in DMF. The electronic spectra of Mn(II) complexes (Table 2) showed only one broad band centered at 13333-15060 cm^{-1} due to the transition ${}^2T_{2g} \rightarrow {}^2T_{1g}$. This band is due to the excitation states in system d^5 reported octahedral complexes (Nicholls, 1973; El-Tabl *et al.*, 2012; Singh *et al.*, 2013; Al-Shaheen and Al-Dabagh, 2009) octahedral geometry. In addition, high intensity bands were observed in the ultraviolet region of the spectra and assigned to C-T transitions which due to the partial electron density migration from the filled ligands π -orbital to the empty metal π -orbitals. The observed CT bands suggested the presence of some π -character in coordination bonds between the metal ions and the ligand. The magnetic moment of the prepared complexes at room temperature is presented in (Table 2). The results show that Mn(II) complexes (1.51-2.09) B.M. are all paramagnetic and in good agreement with the low spin octahedral structure (Sadhukhan *et al.*, 2011; Al-Shaheen, 2011).

Table 2: Electronic spectrum cm^{-1} and magnetic moment data of the complexes

No. of Complexes	Formula	μ^{eff} B.M.	ν_1	C.T
1	[Mn (L ₁ H ₄)]Cl ₂	1.95	13333	35087
2	K ₂ [Mn (L ₁)]	1.51	13386	40485
3	[Mn (L ₁ H ₄)](NO ₃) ₂	1.76	14598	33222
4	[Mn (L ₂ H ₄)]Cl ₂	1.51	13513	33222
5	K ₂ [Mn (L ₂)]	1.95	13477	36362
6	[Mn (L ₂ H ₄)](NO ₃) ₂	1.76	14598	20333
7	[Mn (L ₃ H ₄)]Cl ₂	2.09	14992	32051
8	K ₂ [Mn (L ₃)]	1.97	15060	36496
9	[Mn (L ₃ H ₄)](NO ₃) ₂	2.08	13513	33222

The coordination sites of the ligands were inferred by infrared spectroscopy, which is considered a useful technique for the IR spectra of the structure of complexes. The infrared data of the main absorption bands of the ligands and the complexes are given in (Table 3).

The important infrared spectral of the ligand showed a band at (3400-3500) cm^{-1} assigned to νOH . For the complexes, the stretching and deformation vibrations of OH groups were shifted to lower frequency in the (1,3,4,6,7,9) complexes while in the (2,5,8) complexes frequencies did not appear. (Nakamoto, 1997). In the infrared spectra of complexes, the absence of the bands due to OH-stretching and deformation vibrations was attributed to the coordination of the ligand through deprotonation of the alcoholic hydroxyl groups, compared to their positions in the free ligands spectrum indicating coordination of alcoholic hydroxyl groups through their oxygen atoms. The IR spectrum of the ligand showed a band at (3200-3300) cm^{-1} assigned to νNH . This band has been shifted to a lower frequency in (1,3,4,6,7,9) complexes formation (NH). This band however did not appear in the (2,5,8) complexes (Taylor *et al.*, 1974). The infrared spectral of the ligand showed a band at (1615-1630) cm^{-1} assigned to $\nu\text{C}=\text{N}$. In the complexes, the $\text{C}=\text{N}$ stretching band shows negative shift of about 15 - 45 cm^{-1} , indicating the involvement of azomethine nitrogen atom in complexes formulation (Taylor *et al.*, 1974; Abd-Elzaher, 2002). The stretching band of the azomethine group was also shifted, suggesting coordination through azomethine nitrogen. The $\nu\text{C}=\text{O}$ in the ligand appeared at (1675-1695) cm^{-1} ; this band shifted to lower frequency in the (1,3,4,6,7,9) complexes while in the (2,5,8) complexes frequencies did not appear.

In addition, the stretching vibration of C-O single bond split into two peaks due to (C-O) which supports the above suggested coordination of the hydroxyl groups without deprotonation (Sallomi and Al-Shaheen, 1998; Sallomi *et al.*, 2011) (Table 3). The negative shift of about 10 - 35 cm^{-1} in the stretching frequency of carbonyl group suggests coordination through the carbonyl oxygen atom as observed in similar acid hyrazide and hydrazine complexes (Holm *et al.*, 1966; Sallomi, 1998). On the other hand, the absence of the stretching band was due to NH and C=O moiety was attributed, as reported for similar cases (Stratton, 1969) to the presence of the

enol tautomer. The presence of these bands is strong evidence for the enolization deprotonation in alkaline solution. In all complexes of both types, positive shift was observed in the stretching vibration of N-N band. Since the shift is less than 50 cm^{-1} only one nitrogen atom is involved in bonding (Zhang *et al.*, 2005). In addition to the above mentioned perturbation in infrared spectra, new bands around $470 - 480\text{ cm}^{-1}$ and $430 - 440\text{ cm}^{-1}$ were observed and tentatively assigned to M-N and M-O stretching modes, respectively (Wilkinson *et al.*, 1987; Nakamoto, 1997).

Table 3: Important IR spectral bands (cm^{-1}) of the free ligands and their complexes

No. of Complexes	ν O-H	ν N-H	ν C=N	ν C=O	ν N-N	ν C-O	ν M-N	ν M-O
L_1H_4	3400	3250	1630	1685	1035	1200	-	-
1	3300	3245	1610	1675	1050	1180	480	440
2	-	-	1595	-	1055	1175	470	430
3	3250	3240	1600	1680	1050	1180	480	440
L_2H_4	3410	3300	1615	1695	1030	1220	-	-
4	3295	3280	1600	1685	1045	1200	475	430
5	-	-	1590	-	1040	1200	480	440
6	3300	3290	1585	1680	1040	1190	480	435
L_3H_4	3500	3200	1625	1675	1020	1020	-	-
7	3400	3195	1600	1660	1040	1180	480	440
8	-	-	1585	-	1050	1185	480	440
9	3400	3180	1580	1640	1050	1185	470	435

CONCLUSION

According to the above studies, it was concluded that all the ligands act as neutral hexadentate in neutral solution giving cationic complexes and coordinating through alcoholic oxygen, carbonyl oxygen and azomethine nitrogen atoms. Basic medium neutral complexes were obtained Fig. (1).

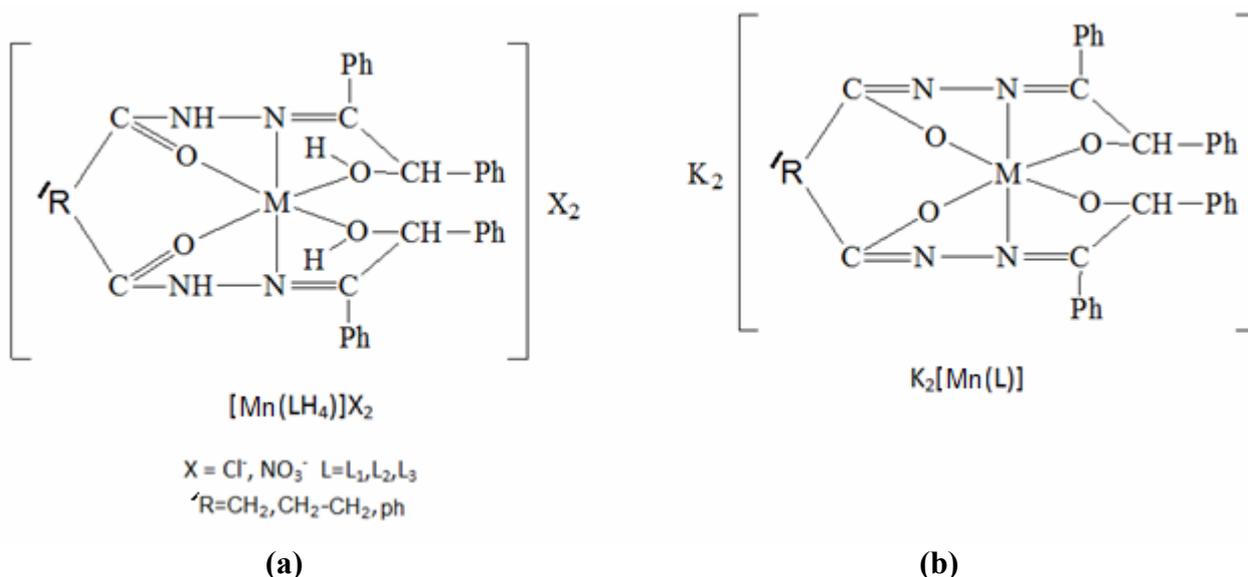


Fig. 1: The proposed structures of complexes

(a) : neutral medium

(b): basic medium

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