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SYNTHESIS AND SPECTRAL STUDIES OF Mn (II) COMPLEXES WITH 2-HEPTANONE SEMICARBAZONE AND THIOSEMICARBAZONE

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ABSTRACT: Complexes of Manganese(II) of general composition $Mn(L)_2X_2$ have been synthesized with ligand 2-heptanone semicarbazone and 2-heptanone thiosemicarbazone (where L = 2-heptanone semicarbazone or 2-hepatanone thiosemicarbazone and X=Cl^-, SO_4^{2}-, CH_3COO^-, NCS^-, ClO_4^-) The IR spectral data of ligands indicate the involvement of sulphur/oxygen and nitrogen in coordination to the central metal. The molar conductance of the complexes of the complexes in fresh solution of DMSO lies in the range of 10 -20 Ω^{-1} cm^2mol^{-1} indicating their non-electrolyte behaviour thus the complexes may be formulated as $[M(L_2)X_2]$. Ligands were characterized by Mass, NMR, and IR. All the complexes were characterized by elemental analysis, magnetic moments, IR, electronic and EPR spectral studies. All the manganese (II) complexes in present study show magnetic moment in the range of 5.90-6.05 B.M; corresponding to five unpaired electrons and hence these are high-spin complexes. The Schiff's base ligands forms hexacoordinated complexes having octahedral geometry for Mn(II).

INTRODUCTION: Schiff's base such as thiosemicarbazone and semicarbazone are important class of compounds which have long attracted attention, owing to their remarkable biological and pharmacological properties [1]. Complexes of thiosemicarbazone with transition metals have received attention because of their biological activities including antitumor, antibacterial, fungicidal and ant-carcinogenic properties [2-9]. The well documented biological activities of several thiosemicarbazone often have been attributed to their ability to form chelates with transition metal ions [10]. These metal complexes, especially those containing manganese (II), are more active than the uncoordinated thiosemicarbazones molecules.

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MATERIAL AND METHODS: All the chemicals used were of A R grade and produced from sigma Aldrich, Bangalore, India .Metal salts were purchase from E. Merck, India and were used as received

Synthesis of ligand L_1: Ethanolic solution of 0.01 mole semicarbazide hydrochloride (1.11g) and 0.01mole of sodium acetate (0.82g) were dissolved in 50 ml of distilled water and 0.01 mole of 2-heptanone (1.42ml) was added to it.50 ml of alcohol was added to this mixture, the reacting mix shaken thoroughly and refluxed for about an hour on a water bath. On cooling, white crystalline semicarbazone separated out. It was filtered washed with ethanol and dried over P_4O_{10}.

Synthesis of ligand L_2: An ethanolic solution of thiosemicarbazide (0.91g,0.01mol) and ethanolic solution of the 2-heptanone 1.42ml, 0.01 mol were mixed together in equimolar (1:1) ratio a small amount of glacial acetic acid was added and the contents were refluxed on a water bath for about one hour and then concentrated. On cooling in an ice bath yellowish coloured thiosemicarbazone separated out. Analytical data of the ligands L_1 and L_2 are given in **table 1**.

Table 1: The analytical data of the ligands

Elemental analysis found /(calculated)						
Ligand	**Colour**	**Yield%**	**M.P ^{0}C**	**C%**	**H%**	**N%**
L_1 = hsc ($C_8H_{17}N_3O$)	White	85	127^{0}C	56.14 (56.10)	9.94 (9.89)	24.56 24.53)
L_2 =htc ($C_8H_{17}N_3S$)	Yellow	80	77^{0}C	51.4 (50.9)	9.1 (9.0)	22.5 (23.0)

Synthesis of the Complexes: An ethanolic solution of the corresponding ligand (0.1 mol) was mixed with (0.05 mol) of aqueous solution of manganese salt (chloride, acetate, chlorate, thiocynate). The mixture was shaken thoroughly, refluxed for about 1 to 2 hour on a water bath and then cooled, when white crystals appeared. The separated crystals were filtered, washed with 50% ethanol, and finally dried at 60^{o}C in an electric oven. Analytical data for the complexes are given in **Table 2**.

Analysis: The Carbon and hydrogen were analysed on Carlo-Erba 1106 elemental analyzer .the nitrogen content of the complexes was determined using Kjeldahl's method. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibilities were measured at room temperature on a gouy balance. Electronic impact mass spectrum was recorded on JEOL, JMS-DX-303 Mass spectrometer. Proton (^{1}H) NMR spectra were recorded on Hitachi FT-NMR model R-600 spectrometer using DMSO as a solvent. Chemical shift are given in ppm relative to tetramethylsilane.IR spectra (CsI) were recorded on FTIR spectrum BX-II spectrometer. The electronic spectra were recorded in DMSO on Schimadzu U mini -1240 spectrophotometer.

RESULTS AND DISCUSSION: The complexes were synthesized by reacting ligands with the metal ions in 2:1 ratio in ethanolic medium .the ligands behaves as bidentate coordinate through sulphur/ oxygen and nitrogen donor atoms. The analytic data, magnetic susceptibility, and spectral analysis agree well with the proposed composition of formed complexes. All the complexes have shown good solubility in DMSO.

The molar conductance of the complexes in fresh solution of DMSO lies in the range of 10-20 Ω-1 cm^2 mol^{-1} indicating their non-electrolytic behaviour [11].

TABLE 2: ANALYTICAL DATA FOR THE FOR COMPLEXES

Elemental analysis found (calculated)							
	Colour	**Yield%**	**M.P.**	**Mn%**	**C%**	**H%**	**N%**
Mn(hsc)$_2$Cl$_2$	Yellowish	65	134	11.77 (11.70)	41.11 (41.15)	7.28 (7.10)	17.98 (17.95)
Mn(hsc)$_2$(CH$_3$COO)$_2$	Cream	80	142	10.67 (10.61)	46.60 (46.69)	7.76 (7.91)	16.31 (16.28)
Mn(hsc)$_2$(NCS)$_2$	White	70	133	10.72 (10.70)	42.10 (42.15)	6.62 (6.54)	21.83 (20.89)
Mn(hsc)$_2$(ClO$_4$)$_2$	Whitish Cream	55	136	9.24 (9.29)	32.26 (32.30)	5.71 (5.89)	14.11 (14.24)
Mn(htc)$_2$CI$_2$	Cream	65	80	11.02 (10.97)	38.47 (38.42)	6.81 (6.90)	16.83 (16.80)
Mn(htc)$_2$(CH$_3$COO)$_2$	White	80	89	10.05 (9.95)	43.87 (43.75)	7.31 (7.29)	15.35 (15.38)
Mn(htc)$_2$(NCS)2	Cream	75	85	10.99 (10.00)	39.63 (39.70)	6.23 (6.27)	20.55 (20.54)
Mn(htc)$_2$(CI04)2	Light Cream	50	83	8.77 (8.68)	30.62 (30.65)	5.42 (5.46)	13.39 (13.40)

Mass Spectra: The electronic impact mass spectrum of the ligand L_1 showed a molecular ion peak at m/z =171amu corresponding to species $[C_8H_{17}N_3O]^+$, which confirms the proposed formula of ligand L_1. The electronic impact mass spectrum of the ligand L_2 showed a molecular ion peak at m/z=187 amu corresponding to the species $[C_8H_{17}N_3S]^+$, which confirms the proposed formula of ligands L_2.

IR Spectra: The assignments of the significant IR spectral bands and its metal complexes are presented in **Table 3**.

L_1IR: The characteristic absorption of the carbonyl group in 2-heptanone semicarbazone is observed at 1900-1700 cm^{-1} [12]. In the complexes this band is shifted towards the lower side by ~45 cm^{-1}. This amide II band in semicarbazone has been observed at 1556-1588 cm^{-1}. In the complexes, this band is also shifted towards lower wave number by ~30 cm^{-1}. These observation suggested coordination through the ν C=O oxygen. The strong bond at 1650-1600 cm^{-1} in 2-heptanone semicarbazone apparently has large contribution from ν(C=N) [13].

Coordination through 'O ' increases double bond character of the ν(C=N) band in all complexes as compared to the ligand. The observation indicates that the 2-heptanone semicarbazone behaves as bidentate ligand.

L_2-IR –In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide –NH-C=S functional group. The ν(S-H) band at 2560 cm^{-1} is absent in the IR spectrum of ligand but ν(N-H) band at ca. 3214 cm^{-1} is present, indicating that in the solid state, the ligand remains as the thione tautomer. The position of ν(C=N) band of the thiosemicarbazone appeared at 1600 cm^{-1} is shifted towards lower wave number in the complexes indicating coordinated via the azomethine nitrogen [14, 15].

This also confirmed by the appearance of the bands in the range of 420-473cm^{-1}, this was been assigned to the ν(M-N). A medium band found at 1090 cm-1 is due to the ν(N-N) group of the thiosemicarbazone. The position of this band is shifted towards higher wave number in the spectra of complexes. It is due to the increase in the bond strength, which again confirms the coordination via the azomethine nitrogen.

The band appearing at ca.832 cm^{-1} corresponding to ν(C=S) in the IR spectrum of ligand is shifted towards lower wave number. It indicates that thione sulphur coordinates to the metal ion [16]. Thus it may be concluded that the ligand behaves as bidentate chelating agent coordinating through azomethine nitrogen and thiolate sulphur [17]. Important infrared spectral bands are given in Table 3.

TABLE 3: IMPORTANT INFRARED SPECTRAL (cm^{-1}) BANDS AND THEIR ASSIGNMENTS

	ν (C=N)	ν(C=S)	ν(C=O)	ν(Mn-N)	ν (Mn-S)	ν(Cl$^-$)	ν(CH$_3$COO$^-$)	ν(NCS$^-$)	ν(ClO$_4^-$)
L_1	1558	-	1655	-	-	-	-	-	-
L_2	1586	840	-	-	-	-	-	-	-
Mn(hsc)Cl$_2$	1590	-	1670	420	-	700	-	-	-
Mn(hsc)$_2$(CH$_3$COO)$_2$	1600	-	1663	430	-	-	2565	-	-
Mn(hsc)$_2$ (NCS)$_2$	1609	-	1662	435	-	-	-	2050	1065
Mn(hsc)$_2$(ClO$_4$)$_2$	1615	-	1660	443	-	-	-	-	-
Mn(htc)$_2$Cl$_2$	1591	836	-	460	320	710	-	-	-
Mn(htc)$_2$(CH$_3$COO)$_2$	1600	830	-	465	325	-	2570	-	-
Mn (htc)$_2$(NCS)$_2$	1610	828	-	468	330	-	-	2046	-
Mn (htc)$_2$(ClO$_4$)$_2$	1615	825	-	473	325	-	-	-	1110

Ligands Field Parameter: Stability of the half-filled d-shell, manganese (II) generally forms high-spin complexes which have an orbitally degenerate ^6S ground state term and the spin-only moment of 5.92 B.M. is expected, which is independent of temperature and of the stereochemistry [18].

All the manganese (II) complexes in the present study show magnetic moment in the range of 5.90-6.05 B.M. [**Table 4**], there by indicating the presence of five unpaired spins and hence these are high-spin complexes.

Electronic spectra of the complexes show weak absorption in the visible region. This suggests a near octahedral geometry around manganese (II) [19]. The intensities of octahedral manganese (II) complexes are externally low as a consequence of their doubly forbidden nature. Molar extinction coefficients in the region 10^{-2}-10^{-1} lcm^{-1} $mo1^{-1}$ are commonly observed.

The complexes under study exhibit four week absorption bands in the range 30303-32775, 27780-29800, 22180-24800, and 16000-18250 cm^{-1}. These bands may be assigned as $^6A_{1g} \rightarrow {}^4T_{1g}$ (^4G) (10B+5C), $^6A_{1g} \rightarrow {}^4E_{g,}$ $^4A_{1g}$ (^4G) (10B+5C), $^6A_{1g} \rightarrow {}^4E_{g,(}$$^4D$) (17B+5C) and $^6A_{1g} \rightarrow {}^4T_{1g}$ (^4P) Transitions respectively [20, 21, 22] [**Table 5**]. The experimentally observed transition energies and calculated value for parameters B, C, Dq, and β are shown [**Table 6**].

The value obtained for the parameters B and by using the transitions $^6A_{1g} \rightarrow {}^4T_{1g}$ (^4G) and $^6A_{1g} \rightarrow {}^4T_{1g}$ (^4P) are negative which has no physical significance, while transition $^6A_{1g} \rightarrow {}^4E_{g,}$, $^4A_{1g}$ (^4G) and $^6A_{1g} \rightarrow {}^4T_{1g}$ (^4P) yield absurd values for B and hence these values are not included in the table .the best values for the parameters B and C could be obtained using transition $^6A_{1g} \rightarrow {}^4E_{g,}$, $^4A_{1g}$ (^4G) and $^6A_{1g} \rightarrow {}^4E_{g}$,($^4D$). This is due to fact that energies of these two transitions are independent of crystal field splitting energy and depend [23] only on the parameters B and C. The value for the parameters Dq could be evaluated with the help of curve transition energies vs Dq given by Orgel [24, 25, 26]. The value for the parameters Dq could not be obtained using the transition $^6A_{1g} \rightarrow {}^4E_{g,}$, $^4A_{1g}$ (^4G) and $^6A_{1g} \rightarrow {}^4E_{g}$,($^4D$) because these transition are independent of Dq, with almost zero slope.

Parameters B and c are linear combination of certain coulomb and exchange integrals and are generally treated as empirical parameters, obtained from the spectra of free ion. Slater-Condon-shortly parameter F_2 and F_4 are related to the Racah interelectronic repulsion parameters B and C as follows [27] $B=F_2-5F_4$ and $c=35F_4$ by using values of the Racah parameters Band C values for the parameters B and C, values for the parameters F_2 and F_4 have been calculated [Table 6].

The electron-electron repulsion in the complex is less than in the free ion, resulting in an increased distance between electrons and thus in the free ion, resulting in an increased distance between electrons and thus an effective increase in the size of the orbitals .on increasing delocalisation the value of β decreases and is less than one in the complex.

An estimate of β has been obtained from the nephelauxetic parameter for the ligand (h_x) and nephelauxetic parameter of the metal ion K_m as $1-\beta=h_x K_m$ [28].

The value of parameter hx for the complexes have been calculated ,using the covalency contribution of manganese (II) ion (0.07), while the numerical value 786cm^{-1} for the parameter B of free Mn^{2+} ion has been used to calculate that the value for β. The value of β and h_x [Table 6] indicate that complexes under study have appreciable ionic character.

The ESR spectra of the complexes have been recorded as polycrystalline samples and in aqueous solutions (mentioned in **figure 1 and figure 2**). Polycrystalline complexes gie one broad isotropic signal centred around approximately free electron g-value [Table 4].

In polycrystalline samples, manganese(II) complexes usually give broad signals attributed to forbidden transitions where $\Delta M \pm 1$ (M =electron spin quantum number) and $\Delta m \neq 0$ (m =nuclear spin quantum number). The broadening of the spectrum in powder sample is analogous to that observed in the case of immobilised free radicals e.g., manganese (II) complex of concanavallin [29].

Broadening due to immobilisation of Mn(II) ion in the complex results because the rotational motion of Mn(II) is highly restricted. Another origin of line broadening is spin – relaxation [30], which is temperature dependent.

The intensity of forbidden transition [31] is inversely proportional to the square of the applied magnetic field, hence their intensities of the allowed signals. This aspect however is not covered in the present studies.

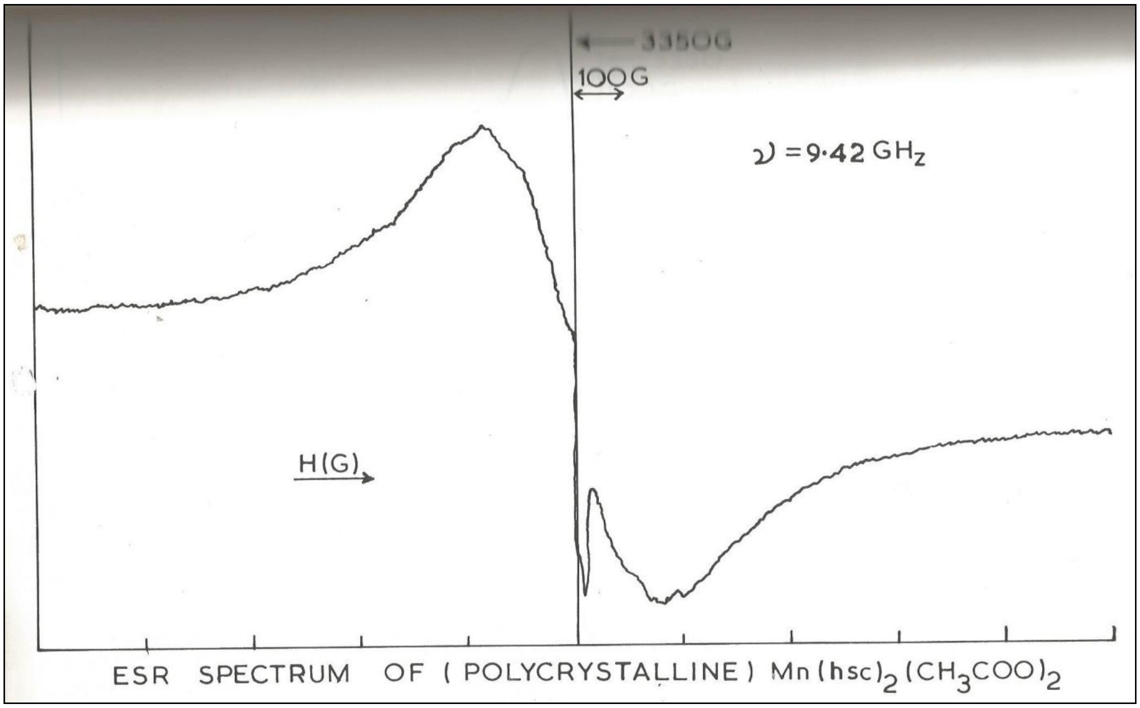

FIGURE 1: ESR SPECTRUM OF (POLYCRYTALLINE) $Mn(hsc)_2(CH_3COO)_2$

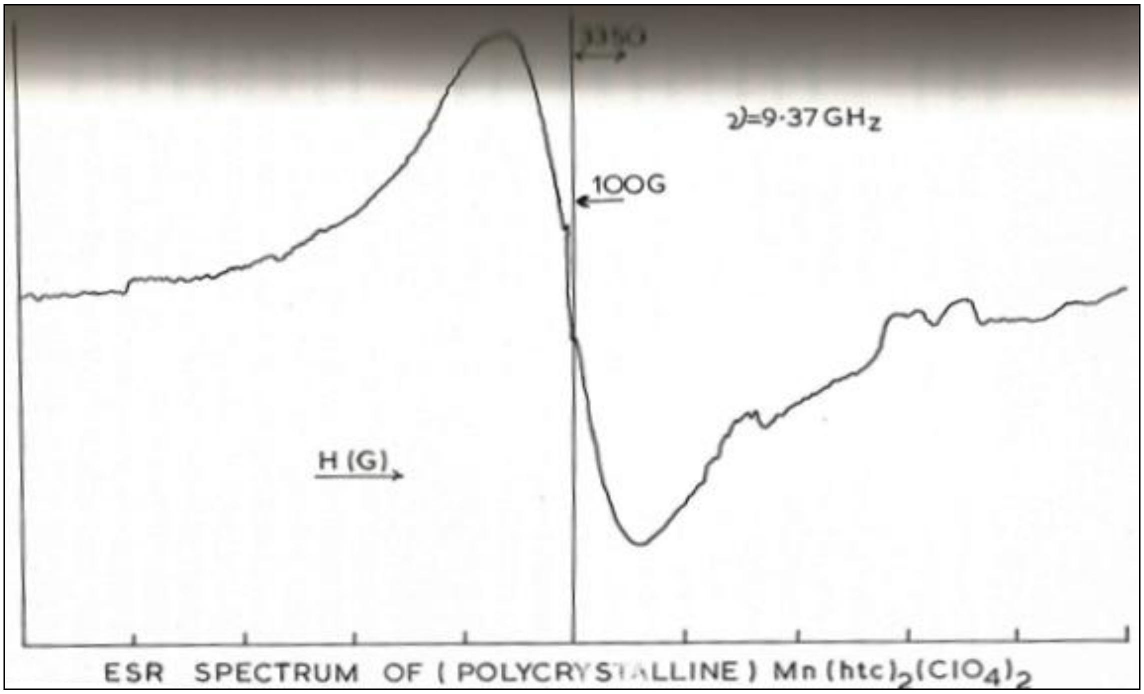

FIGURE 2: ESR SPECTRUM OF (POLYCRYSTALLINE) $Mn(htc)_2(CIO_4)_2$

TABLE 4: MAGNETIC MOMENTS (B.M) AND g – VALUE OF Mn (II) coMPLEXES OF 2-HEPTANONE SEMICARBAZONE AND 2-HEPTANONE THIOSEMICARBAZONE

Complex	μ_{eff} (B.M)	g-value
$Mn(hsc)Cl_2$	5.90	2.0172
$Mn(hsc)_2(CH_3COO)_2$	6.02	2.0030
$Mn\ (hsc)_2\ (NCS)_2$	5.97	2.6010
$Mn\ (hsc)_2(ClO4)_2$	6.05	2.0001
$Mn(htc)_2\ Cl_2$	5.93	1.9984
$Mn(htc)_2(CH_3COO)_2$	6.04	1.9984
$Mn(htc)_2(NCS)_2$	6.00	2.6950
$Mn(htc)_2\ (ClO4)_2$	6.02	2.0014

TABLE 5: ELECTRONIC SPECTRAL BANDS (cm^{-1}) AND THEIR TENTATIVE ASSIGNMENTS OF Mn(II) COMPLEXES OF 2-HEPTANONE SEMICARBAZONE AND 2-HEPTANONE THIOSEMICARBAZONE

Complex	$^6A_{1g} \rightarrow T_{1g}$ (^4G)	$^6A_{1g} \rightarrow$ ^4E_g $^4A_{1g}$ (^4G)	$^6A_{1g} \rightarrow$ E_g (^4D)	$^6A_{1g} \rightarrow$ $^4T_{1g}$ (^4P)
$Mn(hsc)Cl_{2\backslash}$	31125	28115	22180	18250
$Mn(hsc)_2(CH_3COO)_2$	31400	29300	24400	18190
$Mn(hsc)_2$ $(NCS)_2$	32775	29800	24500	17155
$Mn(hsc)_2(ClO4)_2$	32250	29400	24800	18225
$Mn(htc)_2$ Cl_2	31000	27780	24800	18225
$Mn(htc)_2(CH_3COO)_2$	30303	28100	22750	17240
$Mn(htc)_2(NCS)_{2\backslash}$	32766	29340	23100	16000
$Mn(htc)_2$ $(ClO4)_2$	30770	28170	24130	17240

TABLE 6: LIGAND FIELD PARAMETERS OF Mn(II) COMPLEXES OF 2-HEPTANONE SEMICARBAZONE AND 2-HEPTANONE THIOSEMICARBAZONE

Complex	Dq (cm^{-1})	B (cm^{-1})	C (cm^{-1})	B	F_4	F_2	h_x
$Mn(hsc)Cl_2$	927	852	3926	0.88	112	1412	1.72
$Mn(hsc)_2(CH_3COO)_2$	770	700	4460	0.72	127	1335	4.00
$Mn(hsc)_2$ $(NCS)_2$	785	714	4532	0.74	129	1359	3.71
$Mn(hsc)_2(ClO4)_2$	722	657	4506	0.68	128	1297	3.42
$Mn(htc)_2$ Cl_2	833	758	4040	0.78	115	1333	3.14
$Mn(htc)_2(CH_3COO)_2$	840	764	4092	0.79	116	11344	3.00
$Mn(htc)_2(NCS)_2$	634	577	4480	0.60	128	1217	5.17
$Mn(htc)_2$ (ClO_4^-)	980	891	4086	0.92	116	1474	1.14

CONCLUSION: The thiosemicarbazone and semicarbazone based Schiff's base have been synthesized and its coordination behaviour with Mn(II) has also been studied. On the basis of spectral studies Mn(II) complexes was found to have an octahedral geometry and indicate that complexes under study have appreciable ionic character. Manganese(II) complexes of 2-heptanone semicarbazone and 2-heptanone thiosemicarbazone give similar esr spectra in aqueous solution.

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