

Synthesis and characterization of iron(III) complexes of diacetyl-bis(4-methoxybenzoyl hydrazone)

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A few mono- and binuclear iron(III) complexes have been isolated by the reaction of diacetyl-bis(4-methoxybenzoyl hydrazone), H_2 dambhon with iron salts under varied reaction conditions. Some reactions of $[(dambhon)Fe(Cl)(H_2O)]_2 \cdot 4H_2O$, isolated in this study, with acetylacetone, pyridine, $SnCl_2$ and PPh_3 have been carried out which afforded new iron(III) complexes. The new complex $[(dambhon)Fe(PPh_3)Cl]$, thus prepared, smoothly reacts with thiomethanol, *N*-trimethylsilyldimethylamine, benzyltrimethylsilane, and *p*-bis(trimethylsilylmethyl)benzene leading to the isolation of several new iron(III) and organoiron(III) compounds. The complexes are characterized on the basis of elemental analyses, molar conductance, molecular weight, magnetic susceptibilities and spectroscopic (electronic, IR and Mössbauer) data. The ligand H_2 dambhon in these complexes functions as a NNOO donor either as a mono- or dianion or neutral ligand.

In view of the diverse properties of the hydrazones and their wide applications, we have witnessed an increased interest in the study of their complexing abilities toward different transition and non-transition metal ions¹. Recently we have synthesized several new hydrazone ligands starting from 4-methoxybenzoyl hydrazide and studied their metal complexes². The present paper describes the synthesis, characterisation and reactivity of some iron(III) complexes of diacetyl-bis(4-methoxybenzoyl hydrazone), H_2 dambhon (Structure I).

Materials and Methods

The elemental analyses, spectroscopic and conductance measurements were done as described previously³. Solvents were dried and purified by usual procedures.

The IR spectra (KBr discs) were recorded on a Perkin-Elmer 781 spectrophotometer; conductivity measurements in DMSO (10^{-3} M) were carried out using a conductivity bridge of Leeds and Northrup Co. Cat no 4959. Mössbauer spectra at room temperature were recorded by ECIL MBS-35 spectrometer connected with a 250 channel MCA in constant acceleration mode. Calibration of the drive system has been done using a high purity natural iron foil. A ~ 5 mC⁵⁷ Co (Rh matrix) source was used. The experimental points were fitted visually assuming Lorentzian line

shape. The programme developed by Von Meerwall was used⁴. Mössbauer data were recorded at IACS, Calcutta. The molecular weights of the complexes were determined by Rast's method.

Preparation of the ligand and complexes

4-Methoxybenzoyl hydrazide was prepared via the preparation of 4-methoxymethylbenzoate by a published method⁵ followed by treatment with 85% hydrazine hydrate.

Synthesis of H_2 dambhon

4-Methoxybenzoyl hydrazide (3.32 g, 0.02 mol) was dissolved in hot ethanol (40 cm³) and to this was added diacetyl (0.86 g, 0.01 mol) in ethanol (30 cm³) at room temperature and the mixture stirred for 4 h. A white powder separated out, which was filtered, washed with ethanol and dried *in vacuo*, yield 80%, m.pt. 250-254°C (dec.).

Synthesis of complexes

An equimolar (0.005 mol) methanolic (15 cm³) solution of $FeCl_3 \cdot 6H_2O$ or $Fe(NO_3)_3 \cdot 9H_2O$ was allowed to reflux for 3h with a methanolic (15 cm³) suspension of H_2 dambhon on a steam bath to get a clear solution. The solution on concentration and cooling afforded $[(dambhon)Fe(Cl)H_2O]_2 \cdot 4H_2O$, (1) or $[(dambhon)Fe(NO_3)]_2 \cdot 2H_2O$, (2). The complex $[(dambhon)Fe(Cl)]_2 \cdot 7H_2O$, (3) was isolated in a similar way when a methanolic (15 cm³)

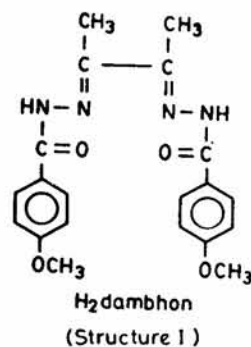
solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was treated with the methanolic (15 cm^3) solution of the sodium salt of the ligand $\text{H}_2\text{dambhon}$ [obtained by the treatment of sodium metal (0.23 g , 0.01 mol) with the methanolic suspension (15 cm^3) of $\text{H}_2\text{dambhon}$ (1.91 g , 0.005 mol)]. To the equimolar mixture (0.005 mol) of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{H}_2\text{dambhon}$ in methanol (30 cm^3) was added equimolar quantities of glycine, salicylaldehyde and acetylacetone and the mixture heated under reflux for 3h on a steam bath yielding thereby $[(\text{H}_2\text{dambhon})\text{Fe}(\text{gly})](\text{NO}_3)_2$, (4), $[(\text{Hdambhon})\text{Fe}(\text{sal})]\text{NO}_3$, (5) and $[(\text{Hdambhon})\text{Fe}(\text{acac})]\text{NO}_3$, (6) respectively. All the complexes mentioned above are soluble in coordinating solvents, while complexes (1), (3), (4), (5) and (6) are also soluble in methanol and water except (3) which is not soluble in water. Excepting (2), all other complexes were recrystallized from methanol or methanol-acetone mixture and the yields were in the range 60-80%.

Reactions of $[(\text{dambhon})\text{Fe}(\text{Cl})\text{H}_2\text{O}] \cdot 4\text{H}_2\text{O}$ (1) with Hacac, SnCl_2 , Py and Ph_3P

The compound (1) (2.81 g , 0.005 mol) was dissolved in methanol (30 cm^3) and to this solution was added acetylacetone (0.5 g , 0.005 mol) and Et_3N (0.51 g , 0.005 mol) and the mixture heated under reflux for 2-h. It was then filtered and the filtrate on concentration and treatment with ether afforded $[(\text{dambhon})\text{Fe}(\text{acac})] \cdot \text{H}_2\text{O}$, (7). Similarly, the reaction of (1) and anhydrous SnCl_2 in dry THF afforded $[(\text{dambhon})\text{Fe}(\text{SnCl}_3)(\text{H}_2\text{O})]$; (8). The compound $[(\text{dambhon})\text{Fe}(\text{Py})\text{Cl}]$, (9) was isolated on recrystallisation of the compound (1) from freshly distilled pyridine. The compound (1) and Ph_3P , taken in methanol, was heated under reflux for 30 min to isolate $[(\text{dambhon})\text{Fe}(\text{Ph}_3\text{P})\text{Cl}]$, (10).

Reactions of $[(\text{dambhon})\text{Fe}(\text{Ph}_3\text{P})\text{Cl}]$, (10) with MeSH, $\text{SiMe}_3(\text{NMe}_2)$, $\text{PhCH}_2\text{SiMe}_3$ and $p\text{-Me}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{SiMe}_3$

The compound (10) was added to MeSH (1:1 molar ratio) in nitromethane:toluene (50:50, v/v) mixture and the contents heated under gentle reflux in presence of a stoichiometric amount of Et_3N for 30 min. The mixture was then filtered which on concentration under vacuum yielded $[(\text{dambhon})\text{Fe}(\text{SMe})(\text{PPh}_3)]$, (11). Similar reaction of (10) with $\text{SiMe}_3(\text{NMe}_2)$, $\text{PhCH}_2\text{SiMe}_3$ and $p\text{-Me}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{SiMe}_3$ yielded $[(\text{dambhon})\text{Fe}(\text{PPh}_3)(\text{NMe}_2)]$, (12); $[(\text{dambhon})(\text{Ph}_3\text{P})\text{FeCH}_2\text{Ph}]$, (13) and $[(\text{dambhon})(\text{Ph}_3\text{P})\text{FeCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Fe}(\text{PPh}_3)(\text{dambhon})]$ (14) respectively in good yields (~70%). All the above complexes are solu-



ble in methanol, nitromethane and coordinating solvents. However, the complex (14) is soluble only in coordinating solvents. All the complexes except (14) were recrystallized from MeOH-MeNO₂ mixtures.

Results and Discussion

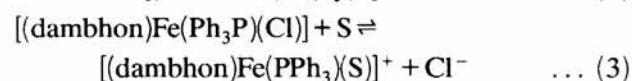
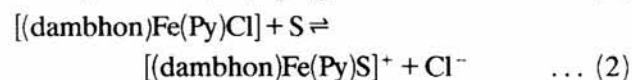
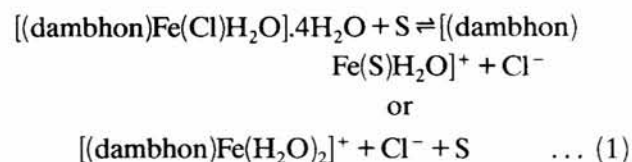
The reaction of 2 mols of diacetyl with 1 mol of 4-methoxybenzoylhydrazide in ethanol results in the formation of stable hydrazone, $\text{H}_2\text{dambhon}$. The reaction of $\text{H}_2\text{dambhon}$ with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ under different reaction conditions yielded coloured iron(III) hydrazone complexes (1) to (6). The complex (1) smoothly reacts with Hacac, SnCl_2 , Py and PPh_3 leading to the formation of many new iron(III) complexes involving dibasic quadridentate N_2O_2 donor ligand. The complex $[(\text{dambhon})\text{Fe}(\text{PPh}_3)\text{Cl}]$, (10) also reacted with MeSH and $\text{SiMe}_3(\text{NMe}_2)$, to yield thiolato-(11) and amido-(12) complexes of iron(III). In connection with the synthesis of (12), mention may be made that desilylation reaction has recently been demonstrated in different laboratories as the elegant route for the synthesis of new coordination and organometallic compounds⁶⁻⁸. Successful isolation of (12) by the desilylation route tempted us to investigate further in this direction and we allowed the compound (10) to react with $\text{C}_6\text{H}_5\text{CH}_2\text{SiMe}_3$ and $p\text{-Me}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{SiMe}_3$ leading thereby to the isolation of (13) and (14) respectively in good yields. Elimination of Me_3SiCl is possibly the driving force of these reactions.

Formation of different types of complexes is made possible by coordination of the ligand $\text{H}_2\text{dambhon}$ either as mono- or di-anion or as neutral ligand. The monoanion, Hdambhon-, results from deprotonation of one of the enolised carbonyl groups, leading to the formation of the cationic complexes $[(\text{Hdambhon})\text{Fe}(\text{L}-\text{L})]^+$, [where $\text{L}-\text{L} = \text{Sal}^-$, (5); acac^- , (6)]. Depending on the reaction conditions, the hydrazone ligands may be enolised to generate azine chromophore,

the -OH group thus formed may be deprotonated to give a dianionic ligand dambhon^{2-} . The formation of the complexes with dianion ligand is easily obtained when $\text{H}_2\text{dambhon}$ reacted with $\text{FeCl}_3 \cdot n\text{H}_2\text{O}$ in presence of sodium metal or better in presence of sodium acetate. The complexes (1)-(3) and (7)-(10) are thus formed. In complex (4), however, $\text{H}_2\text{dambhon}$ functions as a neutral tetradentate ligand.

The analytical data of the iron(III) complexes are presented in Table 1. The analytical results and molecular weights (determined by Rast's method) support the formulations shown in the Table 1. The molar conductance values showed that the compounds (2), (3), (7), (8) and (11)-(14) are non-electrolytic in their behaviour in DMSO. The compounds (1), (5), (6), (9) and (10) behave as 1:1 electrolytes though it appears from the formulations that the complexes (1), (9) and (10)

should be neutral. The complex (4) behaves as 1:2 electrolyte in DMSO. The observation of Λ_m values for the complexes (1), (9) and (10) may be rationalised by suggesting the following solvolytic reactions (Eqs. 1-3).



(where S = solvent)

The solid state magnetic moments determined at room temperature are typical of high-spin⁶ A

Table 1—Analytical data of the complexes

Complex	Mol. wt. Found (Calcd.)	M.P. (°C)	Found(Calcd.), %			μ_{eff}^b B.M.	Λ_m $\text{cm}^2 \text{ohm}^{-1}$ mol^{-1}
			C	H	N		
$[(\text{dambhon})\text{Fe}(\text{Cl})\text{H}_2\text{O}] \cdot 4\text{H}_2\text{O}$, (1) Pinkish brown	549 (561.3)	150 (dec.)	42.49 (42.75)	5.27 (5.34)	9.53 (9.97)	5.88	26.5
$[(\text{dambhon})\text{Fe}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}]$, (2) Deep green	—	130 (dec.)	46.2 (46.52)	4.26 (4.26)	13.85 (13.57)	5.37	12.2
$[(\text{dambhon})\text{Fe}(\text{Cl})]_2 \cdot 7\text{H}_2\text{O}$, (3) Black	—	255 (dec.)	45.20 (44.91)	5.42 (5.05)	10.20 (10.48)	5.14	8.9
$[(\text{H}_2\text{dambhon})\text{Fe}(\text{gly})](\text{NO}_3)_2$, (4) Green	621 (635.8)	300	41.02 (41.52)	3.93 (4.08)	15.20 (15.41)	5.86	135.5
$[(\text{Hdambhon})\text{Fe}(\text{Sal})]\text{NO}_3$, (5) Black	595 (619.8)	220 (dec.)	52.82 (52.27)	4.09 (4.19)	11.25 (11.29)	5.78	58.8
$[(\text{Hdambhon})\text{Fe}(\text{acac})]\text{NO}_3$, (6) Deep green	590 (597.8)	195-200 (dec.)	50.38 (50.18)	4.50 (4.68)	11.50 (11.70)	5.90	53.5
$[(\text{dambhon})\text{Fe}(\text{acac})]\text{H}_2\text{O}$, (7) Deep green	—	275	54.88 (54.26)	5.38 (5.24)	10.25 (10.13)	5.80	10.6
$[(\text{dambhon})\text{Fe}(\text{SnCl}_3)(\text{H}_2\text{O})]$, (8) Brown	662 (679)	170	35.49 (35.34)	3.27 (3.24)	8.27 (8.24)	5.96	11.2
$[(\text{dambhon})\text{Fe}(\text{Py})\text{Cl}]$, (9) Brown	542 (550.3)	280	54.11 (54.51)	4.70 (4.54)	12.10 (12.72)	5.90	25.8
$[(\text{dambhon})\text{Fe}(\text{PPh}_3)\text{Cl}]$, (10) Red Brown	724 (733.3)	300	62.33 (62.18)	4.58 (4.77)	7.28 (7.63)	5.90	25.5
$[(\text{dambhon})\text{Fe}(\text{SMe})(\text{PPh}_3)]$, (11) Yellow Brown	720 (744.8)	300	62.53 (62.83)	5.28 (5.10)	7.22 (7.51)	5.88	10.2
$[(\text{dambhon})\text{Fe}(\text{PPh}_3)(\text{NMe}_2)]$, (12) Brown	728 (741.8)	245	64.30 (64.70)	5.21 (5.52)	9.92 (9.43)	5.85	78.5
$[(\text{dambhon})(\text{PPh}_3)\text{Fe}-\text{CH}_2\text{Ph}]$, (13) Yellow Brown	—	190-195 (dec.)	68.70 (68.45)	5.81 (5.32)	7.28 (7.09)	5.89	9.4
$[(\text{dambhon})(\text{Ph}_3\text{P})\text{Fe}-\text{CH}_2-\text{C}_6\text{H}_4\text{CH}_2$ $\text{Fe}(\text{PPh}_3)(\text{dambhon})]$, (14) Light Brown	—	285 (dec.)	67.44 (67.21)	5.00 (5.20)	7.66 (7.47)	5.95	11.5

b - Solid state at room temperature

Fe(III) complexes, being in the spin-only range (Table 1) of 5.85-6.00 B.M. for the complexes (1), (4)-(14), while the complexes (2) and (3) have values 5.37 and 5.14 B.M. per iron atom respectively. Spin-free pseudo-octahedral structures may tentatively be assigned to the complexes (1) and (4)-(14). Therefore, it can be concluded that $H_2dambhon$ behaves towards iron(III) as a ligand with a relatively weak ligand field. On the other hand, iron(III) complexes (2) and (3) with moment values 5.37 and 5.14 B.M. respectively may attain the oxo-bridged dimeric structures in the solid state. (Chloro-bridged structure, however, cannot be ruled out from these data). In this pseudo-octahedral geometry, the antiferromagnetic exchange interaction may be present between the two iron centres thus reducing the room temperature magnetic moment values to 5.37 and 5.14 B.M. respectively. Similar spin-spin exchange is shown by the binuclear iron(III) complexes reported earlier¹⁰.

The Mössbauer spectra exhibit broad singlet at room temperature with very weak absorbance and with half-width at half-height ranging from 0.67 to 1.15 mm S^{-1} . As for example, the Mössbauer spectrum of $[Fe(dambhon)(acac)]NO_3$, (7) measured at room temperature shows a broad singlet at $\delta = 0.67$ mm S^{-1} relative to sodium nitroprusside spectrum at room temperature. This value of isomer shift is typical of those usually found for high-spin pseudo-octahedral iron(III) complexes¹¹. This extensively broadened singlet being attributed primarily to partial spin-spin relaxation of magnetic hyperfine interactions associated with electronic states available to the d^5 ion. On the other hand, the Mössbauer spectrum of the complex $[Fe(dambhon)Cl]_2 \cdot 7H_2O$, (3) (with μ_{eff} value of 5.14 B.M. at room temperature) measured at room temperature shows well resolved quadrupole splitting with $QS = 0.851$ mm S^{-1} and $IS = 0.629$ mm S^{-1} (relative to $Na_2[Fe(CN)_5NO] \cdot 2H_2O$) confirms the presence of high-spin iron(III). The intensity of the two lines are not equal, with the peak-height ratio $I^-/I^+ = 1.42$ and $\Gamma^- = 0.362$, and $\Gamma^+ = 0.511$ mm S^{-1} , while the integral intensities of both lines are the same.

The magnetic moment value of 5.19 B.M. of (3) at room temperature and stoichiometry of the compound indicate a dimeric structure possibly with chloro-bridges. Alternatively, another type of bridging possibility is that found in $[Fe(Salen)Cl]_2$ (ref. 12). In this compound, a dimer is formed by two square-pyramidal units where the two basal planes are parallel and are in close proximity. An

oxygen atom of the Salen bonded to one iron(III) ion also bonds to the second iron(III) ion.

The electronic spectra of the iron(III) complexes have been measured in DMSO and several bands are observed in the range 250-625 nm. Since the complexes are mainly high-spin type and have no spin allowed $d-d$ transitions, the absorptions are attributed to charge-transfer bands and intra-ligand bands^{13,14}. It is common for all complexes that only a few well developed absorption maxima ($\epsilon < 700$) are formed in the visible region, the other appearing as broad absorption bands or shoulders. The electronic spectra of (4) to (7) were dependent on concentrations and absorption ~ 455 nm slowly diminished its intensity upon dilution. This may be due to the dissociation of the complexes in solution on standing. This indirectly suggests cis- β -coordination of the ligand $dambhon^{2-}$ in these complexes¹⁵. The optical absorption spectra of antiferromagnetically coupled high-spin iron(III) complexes exhibit an enhancement of the intensity of the long wavelength (800-900 nm) $d-d$ bands. This can be explained at least in part by the removal of the 'spin-forbiddleness' of the transition¹⁶. Besides, observations of bands in the region of wavelengths from 600-700 nm (in hemerythrin species, a class of iron protein) which have been assigned to $d-d$ transitions. The extinction coefficients of these bands ($\epsilon \approx 20-50$ per Fe atom) are much larger than expected for 'spin-forbidden' $d-d$ transitions in monomeric high-spin iron(III) complexes. The intensification of the bands has been attributed to an exchange interaction coupling of the two iron atoms¹⁷. In the light of the discussion, the bands observed at 625 and 640 nm in the complexes (2) and (3) respectively suggest di-iron complex formation. This is in line with the above discussion of magnetic moments observed for the two compounds at room temperature and Mössbauer spectral data.

The infrared spectra of the iron complexes has been measured in KBr phase. The free ligand shows bands for $\nu NH \sim 3280-3310$ cm^{-1} , which disappeared in the complexes (1), (2), (3), (7) and (14) suggesting that the ligand acts in the enol form and binds with the metal ions after deprotonation as a dianionic ligand. The νNH band in the complexes (1), (5) and (6) remain almost unaffected, which lends support to the keto-form of the ligand $H_2dambhon$.

The free ligand exhibits amide-I, $\nu C=N$; amide-II and III bands at $\sim 1650, 1605, 1775, 1495, 1255$ cm^{-1} respectively. The negative shifts of amide-I ($\Delta\nu = 10-30$ cm^{-1}), $\nu C=N$ ($\Delta\nu = 5-30$ cm^{-1}) and

amide-II ($\Delta\nu = 5-30 \text{ cm}^{-1}$) and a positive shift ($\Delta\nu = 15-20 \text{ cm}^{-1}$) of amide-III in the spectra of the complexes (4), (5) and (6) indicate neutral quadridentate nature of the ligand in (4) and monobasic quadridentate nature in the complexes (5) and (6) and coordination occur through two imino nitrogens and two carbonyl oxygen atoms. These bands disappeared in the deprotonated complexes (1)-(3) and (7)-(14) suggesting enolisation of the keto groups followed by the formation of complexes through deprotonation.

The amide-I band $\nu\text{C}=\text{O}$ of the free ligand H_2 dambhon was also lowered by $\sim 20 \text{ cm}^{-1}$ in the complexes (5) and (6), containing the mono-deprotonated ligand. The features discussed above are in agreement with the analogous lowering of *ca* $20-30 \text{ cm}^{-1}$ observed in other transition metal aroyl-hydrazone complexes¹⁸. However, the presence of strong band(s) $\sim 1600-1615 \text{ cm}^{-1}$ is diagnostic of the azine chromophore ($>\text{C}=\text{N}-\text{N}=\text{C}<$)¹⁹. Further, in the mono-deprotonated compounds (5) and (6), an increase in the intensity of the band centred at $1600-1610 \text{ cm}^{-1}$, due to the $>\text{C}=\text{N}-\text{N}=\text{C}<$ residue¹⁸, can be observed together with the appearance of a strong band at 1050 cm^{-1} due to $\nu(\text{C}-\text{O}-)$ ^{20,21}, in addition to νNH band at 3185 cm^{-1} . On the other hand, all other complexes with deprotonated ligands showed neither absorption band due to νNH stretching nor the amide-I band $\nu\text{C}=\text{O}$ but instead showed same strong absorption at ~ 1610 and 1035 cm^{-1} . The vibrations observed $\sim 1550-1510$ and $1380-1330 \text{ cm}^{-1}$ are characteristic of νNCO ²². In the free ligand, $\nu\text{C}=\text{N}$ appears $\sim 1605 \text{ cm}^{-1}$, while this band shifted to $\sim 1585-1600 \text{ cm}^{-1}$ suggesting coordination of azomethine nitrogen²². The complexes (1)-(3), (7) and (8) show broad medium bands in the region $3600-3300 \text{ cm}^{-1}$, which are assignable to OH stretching vibrations due to the presence of water. The presence of a band $\sim 1630 \text{ cm}^{-1}$ in the complexes (1) and (8) indicates the presence of coordinated water, which is further substantiated by the appearance of wagging modes of H_2O at ~ 940 and 755 cm^{-1} respectively²³. Coordination of pyridine in the complex (9) is demonstrated by the infrared absorption band $\sim 760 \text{ cm}^{-1}$ (ref. 24). Appearance of bands $\sim 835-850 \text{ cm}^{-1}$ in the iron complexes (2) and (3) may be taken as Fe-O-Fe vibrations suggesting the presence of di-iron species in the said complexes²⁵.

The complexes (4)-(6) shows bands at ~ 1385 and 1370 cm^{-1} demonstrating thereby the presence of free NO_3^- ion in these complexes. The ab-

sorption bands at ~ 1455 and 1235 cm^{-1} in the complex (2) are assignable to the ν_1 (NO stretching) and ν_4 (NO_2 asymmetric stretching) vibrations, respectively²⁶. Thus it may be inferred that bonded NO_3^- (unidentate) group is present in this complex²⁷. For the complexes (6) and (7), the oxygen bonded chelating acetylacetonate anion has been inferred from the vibrational spectral data²⁸, which in the present complexes show $\nu\text{C}\equiv\text{O}$ in the range $1550-1590 \text{ cm}^{-1}$; while $\nu\text{C}=\text{O}$ is observed in the range $1520-1540 \text{ cm}^{-1}$. It may be mentioned here that the $\nu\text{C}=\text{O}$ for C-bonded acetylacetonate occurs above 1650 cm^{-1} . Despite the added complexities due to the presence of $\text{C}\equiv\text{N}$ and $\text{C}=\text{C}$ stretching modes of the ligands involved in these complexes, the spectral data clearly shows the presence of oxygen bonded chelating acetylacetonate anion in these mixed chelates of iron(III). Despite the extra difficulties in interpreting the $\nu_{\text{sym}} \text{CO}$ and $\nu_{\text{asym}} \text{COO}$ of glycinate anion in (4) due to the presence of NO_3^- and H_2 dambhon, the infrared bands at 1350 (s) and 1670 (sh) cm^{-1} can be assigned to $\nu_{\text{sym}} \text{COO}$ and $\nu_{\text{asym}} \text{COO}$ respectively or the coordinated glycinate anion²⁹.

A strong band at 335 cm^{-1} observed in the complex (8) suggests the presence of σ -bonded SnCl_3^- group in this complex³⁰.

It is quite clear that the aroyl hydrazone, H_2 dambhon present in the complex (1)-(3), (7)-(14) act as a dibasic tetradentate ligand. On the other hand, it functions as a neutral tetradentate ligand in the complex (4) and as a monobasic, tetradentate ligand in the complexes (5) and (6). It is now well known that the same hydrazone ligand can function as a neutral or anionic multidentate ligand in different complexes formed under different reaction conditions.

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