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Synthesis and spectroscopic characterization of some transition metal complexes of a new hexadentate $N_2S_2O_2$ Schiff base ligand

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Abstract

A novel interesting hexadentate dibasic $N_2S_2O_2$ donor Schiff base ligand, H_4dcsalpte, was synthesized by the condensation of 3-formylsalicylic acid and 1,2-di(*o*-aminophenylthio)ethane and characterized. The reactions of the ligand with different metal(II/III)salts under varied reaction conditions afforded a series of metal complexes. The ligand, H_4dcsalpte, behaves either as a dibasic or neutral hexadentate one, depending on the reaction conditions. Structural investigations on the ligand and their complexes have been made based on elemental analyses, molar conductance values, magnetic moment values, cryomagnetic and spectral (UV–vis, IR, ^{1}H NMR, and Mössbauer) data. Based on magnetic susceptibility, Mössbauer and electronic spectral data the iron(III) complex [Fe^{III}(H_2dcsalpte)]ClO$_4$ (**8**), isolated in the present investigation, it is inferred that the spin states 5/2 and 1/2 are in equilibrium. Similarly a tri-iron(III) complex [Fe$^{III}_3$(H_2dcsalpte)(H_3dcsalpte)Cl$_3$]Cl$_3$ (**7**), isolated in this study, has been inferred to contain two iron(III) sites in tetrahedral environment and one in the octahedral environment. The aerial oxidation of an equimolar mixture of H_4dcsalpte and Co(CH$_3$COO)$_2$·4H$_2$O in ethanol under reflux gave two products, [Co(H_2dcsalpte)]CH$_3$COO (**10**) and [(*H*btcsaldm)Co(*H*bvcsaldm)] (**11**), a cobalt(III) complex bound to two dissimilar tridentate NSO donor ligands formed as a result of the oxidative cleavage of the C−S bond. In the complex **11**, *H*btcsaldm stands for the dianion of the tridentate Schiff base ligand *N*-(2′-benzenethiol)-3-carboxysalicylaldimine and *H*bvcsaldm stands for the mono anion of the tridentate Schiff base ligand *N*-(benzene-2′-S-vinyl)-3-carboxysalicylaldimine, both being formed as a result of the oxidative cleavage of H_4dcsalpte.

1. Introduction

There is currently considerable interest in the coordination chemistry of polydentate ligands of multifaceted importance and their metal complexes; analytical applications, synthetic utility and biological activity are of special interest to chemists. Recently we have synthesized many multidentate ligands derived from 3-fromylsalicylic acid, characterized them and studied their metal complexes and biological activity [1–11].

The reactivity of some of these newly synthesized complexes have also been studied leading to newer syntheses of many new coordination, organometallic and organic compounds [12,13]. Of late, we have synthesized a new hexadentate $N_2S_2O_2$ donor Schiff base ligand, 1,2-di{(3-carboxyl)*o*-salicylaldiminophenylthio}ethane (abbreviated as H_4dcsalpte), by the condensation of 3-formylsalicylic acid and 1,2-di(*o*-aminophenylthio)ethane (abbreviated as dapte) (Scheme 1).

The present paper records the results of synthesis and characterization of the metal complexes of H_4dcsalpte with nickel(II), cobalt(II), cobalt(III), copper(II), palladium(II), iron(III) and manganese(III) ions. Reports on these types of hexadentate $N_2S_2O_2$ donor ligands are not much available in literature, excepting our own work [14,15] and a brief report on the complex of cobalt(III) by Dwyer et al. [16] with 1,2-di(*o*-salicylaldiminophenylthio)ethane. Metal complexes of

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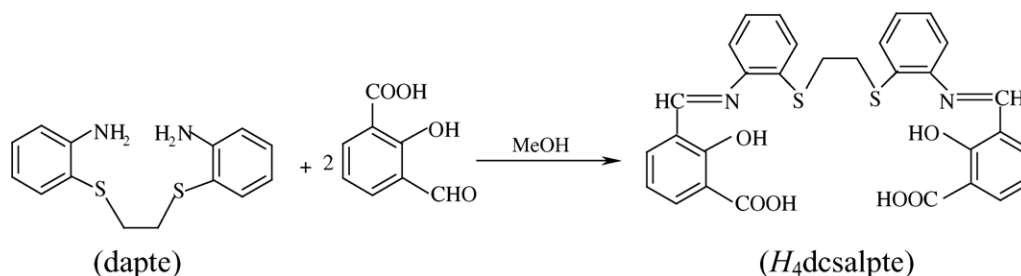
Scheme 1. Formation of the Schiff base ligand H_4dcsalpte.

ligands containing NSO donor sequence were reviewed [17] in 1974. A recent report [18] on the complexation behaviour of hexadentate ligands possessing N_2O_4 and $N_2S_2O_2$ cores towards cobalt(II), nickel(II) and zinc(II) salts promoted us to report our results on the reactions of H_4dcsalpte with nickel(II), cobalt(II), cobalt(III), copper(II), palladium(II), iron(III) and manganese(III) salts.

In this study iron(III) salts were particularly taken up in view of its importance in biological systems. The sulphur–nitrogen donor ligands are also of particular interest in this respect. Moreover, the polynuclear iron(III) complexes are of special interest due to their presence as "clusters" in several enzymes and also in oxygen carrying proteins [19]. Besides, iron(III) complexes show unusual magnetic properties [20,21]. The iron(III) complex formed with $FeCl_3$ is very interesting in the sense that a trinuclear complex is formed with metal:ligand ratio 3:2 even when the reactants are taken in a 1:1 molar ratio. The manganese(III) and cobalt(III) complexes of the ligand (H_4dcsalpte) under investigation are studied for the sake of comparison with the corresponding iron(III) complex. The complexation reaction of $Fe(ClO_4)_3$ with H_4dcsalpte was studied with a view to see whether a weakly coordinating anion (i.e. ClO_4^-) can act as a bridging anion to generate a trinuclear complex as seen in the case of $[Fe_2(dapte–H_2)_2(ClO_4)_2]$, where dapte–$H_2$ stands for dianion for 1,2-di(o-aminophenylthio)ethane [22].

2. Experimental

2.1. Materials

All solvents and chemicals were purified and dried before use according to standard procedures [23,24]. Metal salts used were all of AR grade. $Fe(ClO_4)_3$ was prepared by reacting ferric hydroxide with stoichiometric quantity of $HClO_4$ and concentrating the solution by evaporation. $Mn(CH_3COO)_3 \cdot 4H_2O$ was prepared as described in [25]. The palladium(II) complex, Na_2PdCl_4 was prepared from $PdCl_2$ by the standard method [26].

2.2. Physical measurements

The elemental analyses for carbon, hydrogen and nitrogen were carried out at the Regional Sophisticated Instrumenta-

tion Centre, the Central Drug Research Institute, Lucknow. The electronic spectra (MeOH, CH_2Cl_2, CH_3NO_2, DMSO or Nujol) were recorded on Hitachi 200-20 and Shimadzu UV-2401PC spectrophotometers and infrared spectra (KBr or Nujol or hexachlorobutadiene; more than one media were used for some compounds) on a Perkin-Elmer 1330 and L120-000A spectrophotometers. The molar conductance was measured in DMSO (10^{-3} M solution) using an Elico conductivity bridge. The magnetic susceptibility was determined by the Guoy method. Molecular weights were determined by Rast's method [27] or by vapour pressure Osmometry. Mössbauer spectra and cryomagnetic data were recorded at the USIC, Roorkee.

2.3. Synthesis of ligand, 1,2-di{(3-carboxyl)o-salicylaldiminophenylthio}ethane (H_4dcsalpte)

This ligand was prepared by reacting 1,2-di(o-aminophenylthio)ethane [28] (2.45 g, 9 mmol) with 3-formylsalicylic acid (2.988 g, 18 mmol) in ethanol (100 mL) under reflux (4 h). The yellow solid compound was recovered by filtration, washed with ethanol and dried over fused $CaCl_2$. The ligand is slightly soluble in MeOH, EtOH, highly soluble in DMSO and CH_3NO_2.

2.4. Preparation of the complexes

2.4.1. $[Ni(H_2dcsalpte)]$ (**1**), $[Co(H_2dcsalpte)]$ (**2**), $[Cu(H_2dcsalpte)]$ (**3**), $[Pd(H_4dcsalpte)]Cl_2$ (**4**)

All the above complexes were prepared by the following general procedure in an atmosphere of dinitrogen: to a solution of H_4dcsalpte (0.572 g, 0.001 mol) in methanol–nitromethane mixture (50:50, v/v) was added with stirring a solution of metal acetate hydrate (0.001 mol) (in the case of Ni, Co, Cu) and of Na_2PdCl_4 (in the case of Pd) in ethanol and heated under reflux for 4–5 h on a water bath. The metal complexes that precipitated out during reflux were filtered off, washed thoroughly with ethanol and dried in a vacuum desiccator over fused $CaCl_2$.

All the compounds are soluble in coordinating solvents and partly soluble in polar organic solvents. Appreciably soluble in methanol and ethanol. They are insoluble in non-polar organic solvents.

2.4.2. [Mn(H$_2$dcsalpte)]CH$_3$COO (5)

Manganese(III) acetate dihydrate, Mn(CH$_3$COO)$_3$·2H$_2$O (1.34 g, 5 mmol) was dissolved in ethanol (50 mL) and then added to the boiling solution of the ligand (H$_4$dcsalpte) (2.86 g, 5 mmol) in dry ethanol–nitromethane mixture (50:50, v/v) (80 mL) and mixture was heated under gentle reflux over water bath for 1 h. The pH of the solution was then adjusted to about 7 by adding methanolic NH$_4$OH solution and re-fluxed for another 3 h and filtered while hot. The volume of the filtrate was reduced to half and cooled to ∼5 °C when yellowish brown solid compound separated out. The compound was collected by filtration and washed with dry ethanol and dried in vacuo over fused CaCl$_2$. The compound is highly soluble in coordinating solvents, appreciably so in methanol, ethanol and nitromethane. It is insoluble in non-polar organic solvents.

2.4.3. [Mn(H$_2$dcsalpte)]Cl (6)

This brown compound was prepared by the addition of lithium chloride (1.05 g, 25 mmol) to a refluxing (1 h) mixture of Mn(CH$_3$COO)$_2$·2H$_2$O (6.7 g, 25 mmol) and the Schiff base H$_4$dcsalpte (14.32 g, 25 mmol) in methanol (70 mL). The solid compound that was separated out on slow evaporation was washed with a mixture benzene–petroleum ether (50:50, v/v) and dried in vacuum desiccator. The compound is soluble in coordinating solvents, and also in polar organic solvents. It is also soluble in warm water but the compound is not stable in aqueous medium. It is insoluble in non-polar organic solvents.

2.4.4. [Fe$_3$(H$_2$dcsalpte)(H$_3$dcsalpte)Cl$_3$]Cl$_3$ (7)

To the boiling suspension of the ligand, H$_4$dcsalpte (0.572 g, 1 mmol) in dry ethanol (40 mL) an ethanol (20 mL) solution of anhydrous FeCl$_3$ (0.163 g, 1 mmol) was added and the mixture was gently heated on water bath for 6 h. The dark green crystals separated were filtered, washed with ethanol and dried in vacuo. The compound is soluble in coordinating solvents, warm water and nitromethane. It is moderately soluble in ethanol and methanol. It is insoluble in benzene, ether.

2.4.5. [Fe(H$_2$dcsalpte)]ClO$_4$ (8)

This greenish yellow compound was prepared by the same procedure as adopted for the compound **7** described above excepting that Fe(ClO$_4$)$_3$ (0.264 g, 1 mmol) was taken as the starting metal salt. It is soluble in coordinating solvents, water, methanol and nitromethane. It is insoluble in non-polar organic solvents.

2.4.6. [Co(H$_2$dcsalpte)]Cl (9)

This reddish brown compound was prepared by the aerial oxidation (10 h) of a refluxed equimolar mixture of CoCl$_2$·4H$_2$O and the ligand H$_4$dcsalpte in ethanol. The dark mother liquor produced reddish brown compound on concentration and cooling. Solubility as recorded for the compound **8** above.

2.4.7. [Co(H$_2$dcsalpte)]CH$_3$COO (10)

The acetato complex was prepared by the same procedure as described for the compound **9** above excepting that Co(CH$_3$COO)$_2$·4H$_2$O was taken as the starting metal salt.

2.4.8. [(Hbtcsaldm)Co(Hbvcsaldm)] (11)

The filtrate of compound **10**, on concentration and cooling gave this dark brown compound. It is soluble in coordinating solvents.

3. Results and discussion

3.1. Syntheses

The reaction of 3-formylsalicylic acid with 1,2-di(*o*-aminophenylthio)ethane in ethanol under reflux afforded yellow Schiff base, 1,2–di{(3-carboxyl)*o*-salicylaldiminophenylthio}ethane (H$_4$dcsalpte) (Scheme 1) in good yield. The Schiff base, H$_4$dcsalpte, reacts smoothly with Ni(CH$_3$COO)$_2$·4H$_2$O, Co(CH$_3$COO)$_2$·4H$_2$O, Cu(CH$_3$COO)$_2$·H$_2$O, Na$_2$PdCl$_4$, Mn(CH$_3$COO)$_3$·2H$_2$O, FeCl$_3$, Fe(ClO$_4$)$_3$, CoCl$_2$·4H$_2$O in ethanol or methanol–nitromethane mixture under varied reaction conditions afforded a series of new coloured complexes [Ni(H$_2$dcsalpte)] (**1**), [Co(H$_2$dcsalpte)] (**2**), [Cu(H$_2$dcsalpte)] (**3**), [Pd(H$_4$dcsalpte)]Cl$_2$ (**4**), [Mn(H$_2$dcsalpte)]CH$_3$COO (**5**), [Mn(H$_2$dcsalpte)]Cl (**6**), [Co(H$_2$dcsalpte)]Cl (**9**) and [Co(H$_2$dcsalpte)]CH$_3$COO (**10**) in which the Schiff base H$_4$dcsalpte involves mainly its dianionic form as N$_2$S$_2$O$_2$ donor hexadentate ligand (Table 1).

The ligand H$_4$dcsalpte, however, yielded a green tri-iron(III) complex [Fe$_3$(H$_2$dcsalpte)(H$_3$dcsalpte)Cl$_3$]Cl$_3$ (**7**) when reacted with anhydrous FeCl$_3$. The analogous reaction of H$_4$dcsalpte with Fe(ClO$_4$)$_3$, however, yielded the mononuclear six-coordinated iron(III) complex [Fe(H$_2$dcsalpte)]ClO$_4$ (**8**). The anions of the metal salts used have no appreciable effect on the composition of the complexes. Even in the presence or absence of a base, the same products are obtained. This indicates that the deprotonation of the ligand takes place quite easily, except on reaction with Na$_2$PdCl$_4$ where the ligand functions as a neutral one. The complexes are microcrystalline in nature and attempts to grow single crystals have been unsuccessful. The results also show (see later discussion) that in the tri-iron(III) complex (**7**) one ligand functions as a dibasic hexadentate ligand (combining with two iron(III) centres), while the second ligand unit functions as a monobasic pentadentate ligand (combining with two iron(III) centres with hydroxyl group being remained uncomplexed). The COOH groups of each ligand do not involve in complex formation. The corresponding reaction of H$_4$dcsalpte with Mn(CH$_3$COO)$_3$·2H$_2$O and CoCl$_2$·6H$_2$O also afforded six coordinated mononuclear complexes [Mn(H$_2$dscalpte)]CH$_3$COO (**5**) and [Co(H$_2$dcsalpte)]Cl (**9**), respectively. On the other hand, aerial oxidation of a mixture
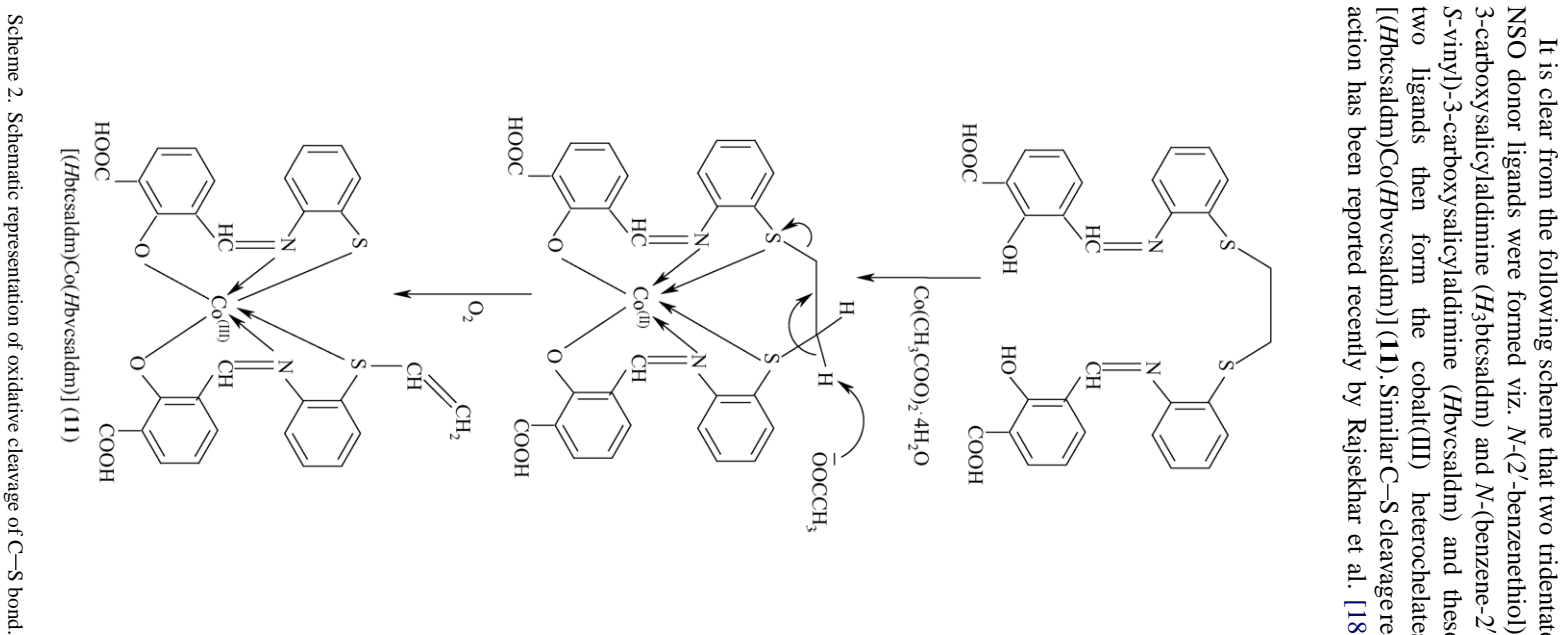
Table 1
Some characterization data of the complexes[a,b]

Compound	Colour	Molecular weight found (calculated)	mp (°C)	Yield (%)	Analyses found (calculated) (%)				
					C	H	N	M	C1
H_4dcsalpte	Yellow	558.00 (572.66)	220–222 (dec.)	80	62.73 (62.92)	4.26 (4.22)	4.93 (4.89)	–	–
[Ni(H_2dcsalpte)] (**1**)	Purple	610.00 (629.33)	>280 (dec.)	65	57.40 (57.26)	3.80 (3.52)	4.65 (4.45)	9.48 (9.33)	–
[Co(H_2dcsalpte)] (**2**)	Brown	598.00 (629.57)	>295 (dec.)	60	57.68 (57.23)	3.29 (3.52)	4.28 (4.45)	9.08 (9.36)	–
[Cu(H_2dcsalpte)] (**3**)	Green	622.00 (634.19)	>290 (dec.)	65	56.24 (56.82)	3.75 (3.50)	4.00 (4.42)	10.21 (10.02)	–
[Pd(H_4dcsalpte)Cl$_2$] (**4**)	Orange red	758.00 (749.97)	>300 (dec.)	60	48.29 (48.04)	3.42 (3.22)	3.88 (3.73)	14.80 (14.19)	9.65 (9.45)
[Mn(H_2dcsalpte)]CH$_3$COO (**5**)	Yellow brown	670.00 (684.62)	190–194 (dec.)	60	56.80 (56.14)	3.50 (3.68)	4.29 (4.09)	8.28 (8.02)	–
[Mn(H_2dcsalpte)]Cl (**6**)	Reddish brown	652.00 (661.03)	292–295 (dec.)	70	54.33 (54.51)	3.18 (3.35)	4.82 (4.24)	8.27 (8.31)	5.44 (5.36)
[Fe$_3$(H_2dcsalpte)(H_3dcsalpte)Cl$_3$]Cl$_3$ (**7**)	Green	1480.00 (1522.55)	260–264 (dec.)	65	47.49 (47.33)	2.70 (2.98)	3.97 (3.68)	11.52 (11.00)	13.72 (13.97)
[Fe(H_2dcsalpte)]ClO$_4$ (**8**)	Greenish Yellow	750.00 (725.93)	280–283 (dec.)	70	49.50 (49.63)	3.44 (3.05)	3.66 (3.86)	7.38 (7.69)	4.75 (4.88)
[Co(H_2dcsalpte)]Cl (**9**)	Reddish brown	652.00 (665.03)	284–287 (dec.)	60	54.48 (54.14)	3.78 (3.33)	4.02 (4.21)	8.98 (8.86)	5.66 (5.33)
[Co(H_2dcsalpte)]CH$_3$COO (**10**)	Brown	672.00 (688.62)	280–285 (dec.)	55	55.66 (55.81)	3.68 (3.66)	4.27 (4.07)	8.66 (8.56)	–
[(Hbtcsaldm)Co(Hbvcsaldm)] (**11**)	Brown	631.00 (616.00)	222–224 (dec.)	25	56.32 (56.49)	3.50 (3.41)	4.62 (4.54)	9.42 (9.58)	–

[a] Solid state at room temperature.
[b] diamagnetic.

of H_4dcsalpte and Co(CH$_3$COO)$_2$·4H$_2$O yielded two six coordinate complexes [Co(H_3dcsalpte)]CH$_3$COO (**10**) and [(Hbtcsaldm)Co(Hbvcsaldm)] (**11**), where H_3btcsaldm and H_2bvcsaldm are two dissimilar tridentate NSO donor ligands and formed as a result of oxidative cleavage of C–S bond of H_4dcsalpte, the schematic representation of which are given below (Scheme 2).
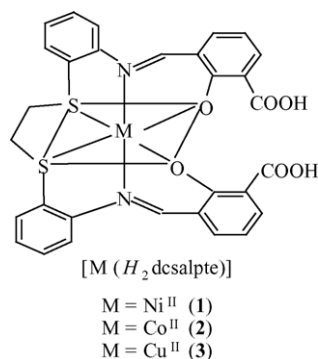
It is clear from the following scheme that two tridentate NSO donor ligands were formed viz. N-(2′-benzenethiol)-3-carboxysalicylaldimine (H_3btcsaldm) and N-(benzene-2′-S-vinyl)-3-carboxysalicylaldimine (Hbvcsaldm) and these two ligands then form the cobalt(III) heterochelates [(Hbtcsaldm)Co(Hbvcsaldm)] (**11**). Similar C–S cleavage reaction has been reported recently by Rajsekhar et al. [18]

Scheme 2. Schematic representation of oxidative cleavage of C–S bond.

Fig. 1. Proposed structure for the complexes **1–3**.

Fig. 2. Proposed structure for the complexes **5**, **6**, **8–10**.

when 1,2-di(salicylaldiminophenylthio)ethane was allowed to react with $Co(CH_3COO)_2 \cdot 4H_2O$ under argon atmosphere and then oxidized with dioxygen.

The newly synthesized complexes have been characterized by elemental analyses, molecular weights, molar conductances, magnetic moment values, cryomagnetic data and spectroscopic (UV–vis, IR, ^{1}HNMR and Mössbauer) data. The characterization data are depicted in Table 1, which support their formulations. So the proposed structures of the complexes are shown in Figs. 1–3.

3.2. Magnetic moments and molar conductances

The room temperature magnetic moment and molar conductance data of the complexes set out in Table 2. The observed magnetic moments support the structures proposed, i.e. all except the palladium(II) complex (**4**) and tri-iron(III) complex (**7**) are octahedral. The observed moment of 3.06 BM for the complex [Co^{II}(H$_2$dcsalpte)] (**2**) is slightly lower than that expected value for an octahedral cobalt(II) complex. Though it may seen anomalous, but the normal magnetic moments of six-coordinate cobalt(II) complex should fall near the extremes of the range from ca. 1.8 to 5.2 BM [29]. One survey of cobalt(II) chemistry [30] shows that there are moments falling through out this entire range. Stoufer et al. showed [31] an equilibrium between a doublet and a quartet state does indeed exist for the complex bis-
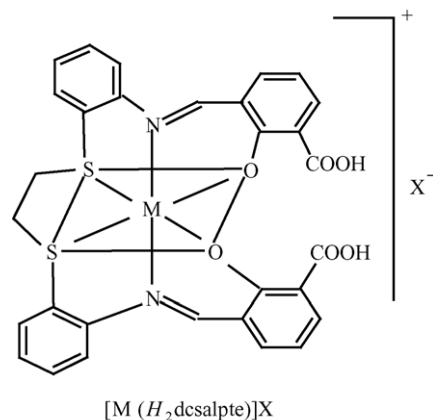
(2,6-pyridinedialdehydrazone)cobalt(II) iodide which has a moment of 3.04 BM at 300 K. A study of the temperature dependence of the magnetic susceptibility by the workers showed that the magnetic moment of the complex varies from 1.9 BM at 80 K to 3.7 BM at 337 K.

The observed magnetic moment of 5.89 BM per iron atom for the complex [Fe$_3$(H$_2$dcsalpte)(H$_3$dcsalpte)Cl$_3$]Cl$_3$ (**7**) at room temperature is suggestive of a polynuclear structure [32] for the complex since the ground state for high-spin iron(III) is $^6A_1$ term and there is virtually no orbital contribution to the spin value. The observed moment value, therefore, rarely varies from the spin-only moment. The susceptibility curve over a temperature range 80–300 K (see Fig. 4) for the complex **7** is observed to follow a normal Curie–Weiss behaviour and therefore rules out any possibility of μ-oxo bridges in which case, the complex should have shown anti-ferromagnetic behaviour. The phenolic oxygen might bridge weakly but would not contribute a μ-oxo bridge.
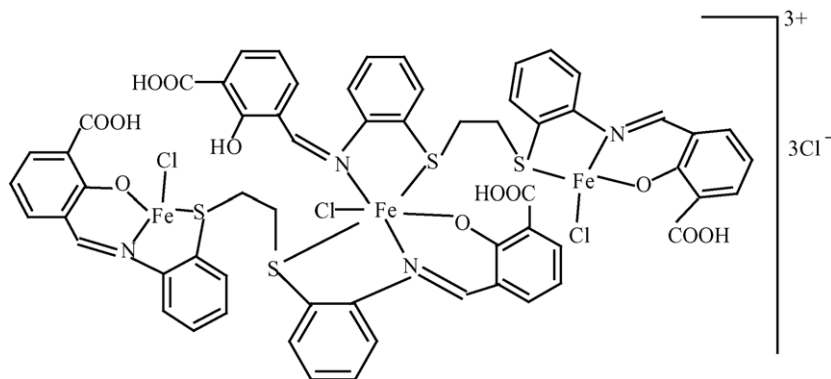

Fig. 3. Proposed structure for the complex [Fe$_3$(H$_2$dcsalpte)(H$_3$dcsalpte)Cl$_3$]Cl$_3$ (**7**).

Table 2
The room temperature magnetic moments and molar conductivity data of the complexes

Complex	μ_{eff} (BM)[a]	Λ_M[b] ($\Omega\,cm^2\,mol^{-1}$)
[Ni(H_2dcsalpte)] (**1**)	3.42	8.7
[Co(H_2dcsalpte)] (**2**)	3.06	10.2
[Cu(H_2dcsalpte)] (**3**)	1.93	6.8
[Pd(H_4dcsalpte)Cl_2] (**4**)	Dia[c]	80.2
[Mn(H_2dcsalpte)]CH_3COO (**5**)	4.91	48.5
[Mn(H_2dcsalpte)]Cl (**6**)	4.88	47.0
[Fe$_3$(H_2dcsalpte)(H_3dcsalpte)Cl_3]Cl_3 (**7**)	5.89 per iron atom	112.5
[Fe(H_2dcsalpte)]ClO_4 (**8**)	3.50	48.5
[Co(H_2dcsalpte)]Cl (**9**)	Dia[c]	47.8
[Co(H_2dcsalpte)]CH_3COO (**10**)	Dia[c]	49.8
[(Hbtcsaldm)Co(Hbvcsaldm)] (**11**)	Dia[c]	11.2

[a] At room temperature.
[b] 10^{-3} M solution in DMSO at room temperature.
[c] Diamagnetic.

The magnetic moment of the complex [Fe(H_2dcsalpte)]ClO_4 (**8**) has been found to be 3.50 BM which may seem quite anomalous. The μ_{eff} value is too small for high-spin ($S = 5/2$) ($\mu_{eff} = 5.9$ BM) and too large for low-spin ($S = 1/2$) ($\mu_{eff} = 2.0$ BM) iron(III) complexes. For iron(III) compounds of intermediate spin ($S = 3/2$), the expected μ_{eff} value is ca. 4.0 BM. The present observed value (may be considered as intermediate value) can result from (i) anti-ferromagnetic type interaction assuming a trimeric structure, (ii) a spin-equilibrium between low- and high-spin sates, or (iii) quantum mechanical mixing of spin sates [33]. A trimeric structure does not fit with the analytical data and hence discarded. There is a possibility of the second and third alternatives. But, for the third alternative, the spin-admixed system usually occurs between quartet and sextet states. The moment 3.50 BM is low for such a system. The second alternative that a spin-equilibrium exists between low-spin

and high-spin states is more appropriate. Equilibria of the type ($S = 1/2$) $\rightleftarrows$ ($S = 5/2$) are well characterized for several iron(III) compounds. Tris(dithiocarbamato)iron(III) compounds [34], tris(monothiocarbamato)iron(III) compounds [35,36], tris(mono-thio-β-diketonato)iron(III) compounds [37,38], [Fe(X-sal)$_2$trien]$^+$ and [Fe(acac-X)$_2$trien]$^+$ [39,40], [Fe(X-Salmeen)$_2$]$^+$ [41], [Fe(SalAPA)$_2$]ClO_4 [42] and [Fe(3-X-Salbenz)$_2$]$^+$ [43] complexes are some of the complexes that have been studied.

Of these, study on a complex [Fe(acac)$_2$trien][BPh$_4$] with a magnetic moment of 3.04 BM is worth mentioning [39]. The Mössbauer spectrum of the said complex possesses a broad signal at $\delta = 0.78$ mm/s which can be assigned to a ^{6}A spin-state. In addition, however, on the extreme wings of this broad singlet, there are two well-defined signals, which appear to be the components of a large quadruple-split doublet ($\delta = 0.46$ and $\Delta E = 2.17$ mm/s). The same Mössbauer pattern has been reported for the ^{2}T = ^{6}A spin-equilibrium for [Fe(Sal$_2$trien)][PF$_6$], where the quadruple-spin doublet ($\Delta E = 2.97$ mm/s) has been assigned to a ^{2}T ($S = 1/2$) spin-state [40]. The Mössbauer spectrum of the present iron(III) complex [Fe(H_2dcsalpte)]ClO_4 (**8**) is recorded in Table 3 along with Mössbauer spectral data obtained for the tri-iron(III) complex [Fe$_3$(H_2dcsalpte)(H_3dcsalpte)Cl_3]Cl_3 (**7**). The relevant Mössbauer spectra of the iron(III) and tri-iron(III) complexes are shown in Figs. 5 and 6. The complex **8** has a broad singlet at $\delta = 0.34$ mm/s and two well-defined signals ($\delta = 0.47$ mm/s, $\Delta E = 2.48$ mm/s). Thus, by analogy, the quadruple-split doublet of [Fe(H_2dcsalpte)]ClO_4 (**8**) is tentatively assigned to ^{2}T state which should be ca. 83% populated.

Such anomalous magnetic moments have also been observed for [Fe(X-Salmeen)$_2$trien][PF$_6$] complex [41]. The X = 3-OCH_3 and 3-NO_2 compounds have room temperature magnetic moments of 3.2 and 3.4 BM, respectively. More about these will be discussed while discussing the Mössbauer spectra of the present complex **8**.

Furthermore, it should also be noted that most of the ($S = 1/2$) $\rightleftarrows$ ($S = 5/2$) systems contain Fe—S (as in our case)
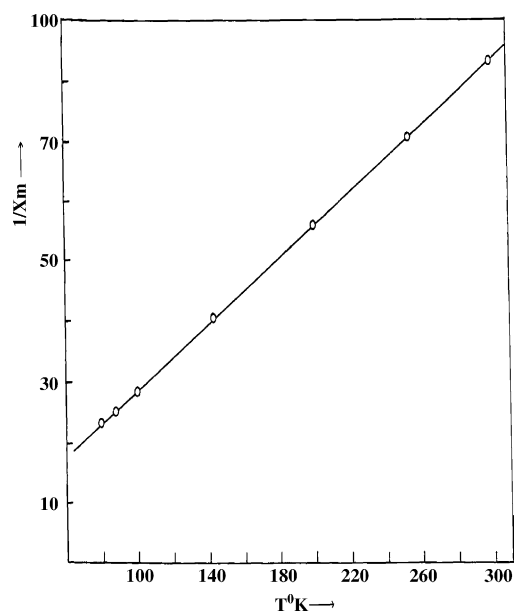

Fig. 4. Susceptibility curve of [Fe$_3$(H_2dcsalpte)(H_3dcsalpte)Cl_3]Cl_3 (**7**) over a temperature range 80–300 K.
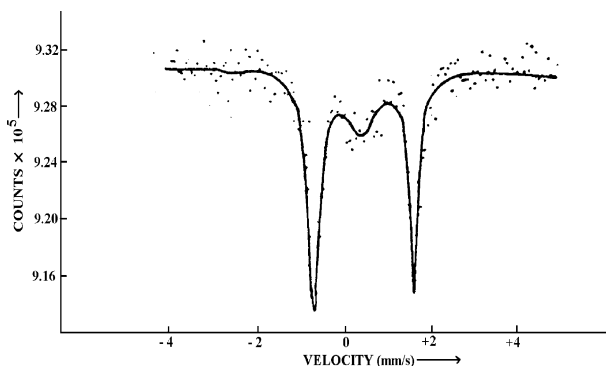
Table 3
Some important infrared bands of the ligand and the complexes with their tentative assignments

Complex	Frequencies (cm^{-1})					
	OH	C=O	C=N	−S−CH$_2$	M−N + M−O	M−S
H_4dcsalpte	3440	1680	1620	690, 650	–	–
[Ni(H_2dcsalpte)] (**1**)	3455 (br)	1710	160	660, 640	510, 505, 490, 450, 415	325–305
[Co(H_2dcsalpte)] (**2**)	3400 (br)	1690	1615	650, 610	560, 550, 505, 530, 460, 420	365–240
[Cu(H_2dcsalpte)] (**3**)	3500 (br)	1700	1610	645, 615	570, 555, 545, 530	470–370
[Pd(H_4dcsalpte)Cl$_2$] (**4**)	3500 (br)	1705	1615	650, 610	485, 460, 430, 420	385–295
[Fe$_3$(H_2dcsalpte)(H_3dcsalpte)Cl$_3$]Cl$_3$ (**7**)	3480 (br), 3410 (br)	1700	1610	640, 610	340	315
[Fe(H_2dcsalpte)]ClO$_4$ (**8**)[a]	3500 (br)	1700	1610	640, 625	560, 510, 490, 455	420–280

[a] ν(ClO$_4$) observed at 1090 cm^{-1} as a strong broad band.
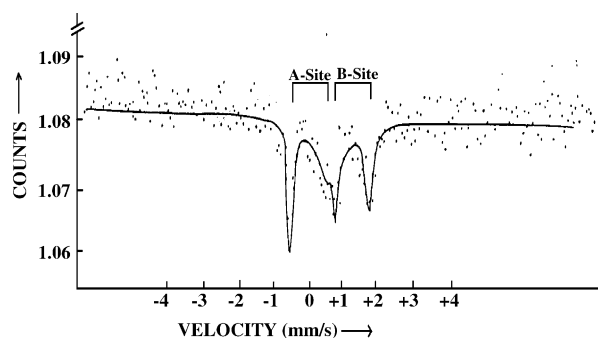
Fig. 5. Mössbauer spectra of [Fe$_3$(H_2dcsalpte)(H_3dcsalpte)Cl$_3$]Cl$_3$ (**7**) using sodium nitroprusside as standard.

or Fe−Se bonds where large reduction in the Racah inter-electronic repulsion parameters apparently produce strong enough fields to induce spin-crossover for iron(III) [44]. The other hexadentate analogues have only Fe−N and Fe−O bonds and for these compounds it is probably the large tetragonal distortion from octahedral symmetry that is mainly responsible for inducing spin-crossover.

So, considering all the above aspects, it is probable that [Fe(H_2dcsalpte)]ClO$_4$ (**8**) is a complex in which the spin states 5/2 and 1/2 are in equilibrium. Low temperature magnetic susceptibility measurements could have thrown more light on this phenomenon, but unfortunately due to our limited resources, low-temperature

Fig. 6. Mössbauer spectra of [Fe(H_2dcsalpte)]ClO$_4$ (**8**) using sodium nitroprusside as standard.

measurements could made on only one sample, namely, [Fe$_3$(H_2dcsalpte)(H_3dcsalpte)Cl$_3$]Cl$_3$ (**7**).

Molar conductance values of these compounds (Table 2) suggest that the complexes **1–3** and **11** are non-electrolytes, while complexes **5**, **6** and **8–10** are 1:1 electrolytes in DMSO. The palladium(II) complex (**4**) is 1:2 electrolyte and tri-iron(III) complex (**7**) is a 1:3 electrolyte in the same solvent [45]. These data supports the formulations of the complexes.

3.3. IR, ^{1}H NMR and electronic spectral data of the ligand (H_4dcsalpte)

The ligand exhibits absorptions due to carboxyl (1680 cm^{-1}), hydroxyl (3440 cm^{-1}) and imino (1620 cm^{-1}) groups. It is well established that the position of the absorptions due to carboxyl, hydroxyl and imino group depend on the physical state of the compound, nature of the neighbouring groups and the possibility of the hydrogen bonding [46]. Since in the ligand the imino, hydroxyl and carboxyl groups are *ortho* to each other, the possibility of intramolecular hydrogen bonding between the above-mentioned groups is very high.

The usual absorption bands for the free carboxyl group lies around 1700 cm^{-1}. The observed lower value in the ligand is in keeping with the values observed in compounds in which intramolecular hydrogen bonds are present. The carboxyl group in salicylic acid absorbs at 1655 cm^{-1} and maleic acid shows absorption at 1705 cm^{-1}, while fumaric acid absorbs at 1680 cm^{-1}. The shift to a lower frequency in salicylic acid and fumaric acids has been ascribed to internal hydrogen bonding [47]. This is further substantiated by the fact that carboxyl bands shift towards higher energies (1690–1720 cm^{-1}) in the mono-nuclear metal complexes **1–3**, **4–6** and **8–10** (see later discussion) where the hydrogen bond is removed by the metal occupying the inner compartment, having the outer compartment vacant (some important IR bands of the ligand and the complexes along with their tentative assignments are shown in Table 3).

Structure of the ligand H_4dcsalpte is also ascertained with the ^{1}H NMR spectral study. The spectrum has been recorded in solution of the compound in trifluoroacetic acid (TFA), in which the ligand exhibits doublet in the region δ 8.7–9.0 ppm due to imino proton (H−C=N−). The split in the absorption

is possibly due to internal hydrogen bonding between the azomethine nitrogen and the adjacent phenolic group. The possibility of protonation of azomethine group in TFA may be another factor responsible for the observed split in the azomethine proton. The observed doublet can also be due to the presence of *syn* and *anti* isomers of the ligand, and this can not be ruled out. Signals for aromatic protons observed at δ 6.8–8.5 ppm (m) (14H) and $-S-CH_2-CH_2-S-$ protons at δ 2.75 ppm (s) (4H).

It may be mentioned here that the signals for the bridging protons of $-S-CH_2-CH_2-S-$ moiety of the ligand slightly shifted to δ 2.88 ppm in the complex **10**. On the other hand, it completely disappears in the complex **11**, instead two new multiplets appeared centred at δ 5.6–6.0 ppm, which may be due to the vinyl protons ($-S-CH=CH_2$). This supports oxidative cleavage of C–S bond in the H_4dcsalpte producing compound **11**.

Electronic spectral data also support the structural formulation of the ligand. The band observed at 285 nm ($\varepsilon = 20,000$) is assigned to $\pi \rightarrow \pi^*$ transition. A band around 370 nm ($\varepsilon = 19,800$) (ε in $1\,cm^{-1}\,mol^{-1}$) appears as shoulder and may be assigned to $n \rightarrow \pi^*$ transition of phenolic moiety. A prominent band appeared at around 400 nm assignable to the quinonoid form of the ligand present in equilibrium with the phenolimine moiety. A prominent band appeared at around 400 nm assignable to the quinonoid form of the ligand present in equilibrium with the phenol-imine tautomer. The observed doublets for the azomethine proton in the ^{1}H NMR spectrum (see above) of the ligand support the formulation of the ligand as the quinonoid form being in equilibrium with phenol-imine tautomer. This is a tentative suggestion.

3.4. Infrared spectra of the metal complexes

The spectral characteristics are summarized in Table 3 along with their tentative assignments. All the complexes isolated in the present study exhibit free carboxyl band in the region 1680–1720 cm^{-1} indicating that the O_2O_2 compartment (outer compartment) is left unoccupied in the complexes. There is a band in the region 1610–1615 cm^{-1} assignable to coordinated imino group, which is lower than the band found in the ligand. A broad band in the region 3400–3500 cm^{-1} is assignable to O–H stretching. However, a band at 3410 cm^{-1} in the complex **7** indicates that $-OH$ remains free for this particular complex (Fig. 3). The ν(C–O) (aromatic carbon and phenolic oxygen) of the free ligand at 1370 cm^{-1} is shifted ($\Delta\nu = 10-15\,cm^{-1}$) in all the complexes suggesting M–O linkage. However, in the palladium(II) complex (**4**) no lowering of the ν(C–O) mode is observed, suggesting that Pd–O bonding is absent. It is interesting to note that this band is split in the complex **7** giving rise of the two bands at 1380 and 1400 cm^{-1}, respectively. These facts suggest formulation of **7** as a trinuclear complex with free phenolic group (Fig. 3). The ν($-S-CH_2$) mode of the free ligand appeared as a split band at 690 and 650 cm^{-1}. However, this mode is shifted

in the spectra of the complexes and appears at 660–650 and 640–610 cm^{-1} suggesting the bonding of the metal ion through sulphur atom of the ligand. This is further supported by the presence of bands at 325 cm^{-1} (Ni–S), 360 cm^{-1} (Co–S), 470 cm^{-1} (Cu–S) and 385 cm^{-1} (Pd–S), 315 cm^{-1} (Fe–S) in the far IR spectra of the complexes [15,48]. The ν(C–S) mode of the ligand at 785 cm^{-1} is also shifted by about 35 cm^{-1} in the complexes indicating formation of M–S linkages. With regard to the nature of perchlorate ion in the complex **8**, the complex shows a strong band centred at 1090 cm^{-1}, a weak one at 960 cm^{-1} and a sharp one at 630 cm^{-1}, features typical of ionic perchlorates [49]. The presence of linkages through N and O donor atoms in the present metal complexes is supported by the appearance of bands at 510–415 ($\nu_{Ni-N} + \nu_{Ni-O}$), 560–420 cm^{-1} ($\nu_{Co-N} + \nu_{Co-O}$), 570–530 cm^{-1} ($\nu_{Cu-N} + \nu_{Cu-O}$) and 340 cm^{-1} ($\nu_{Fe-N} + \nu_{Fe-O}$). Bands at 485–429 cm^{-1} for palladium(II) complex (**4**) can be assigned to ν(Pd–N) [15,48].

It is pertinent to mention here that the complex **11** exhibited a strong vibration at 1535 cm^{-1} assignable to ν(C=C) arising from the S-vinyl moiety ($-S-CH=CH_2$) formed as a result of the C–S bond cleavage in H_4dcsalpte (see above).

3.5. Electronic spectra of the metal complexes

The electronic spectral data of the ligand and the complexes are depicted in Table 4. The electronic spectra in solution agree well with the pseudo-octahedral geometry for the complexes of nickel(II) (**1**), cobalt(II) (**2**), copper(II) (**3**), manganese(III) (**5** and **6**), iron(III) (**8**), cobalt(III) (**9** and **10**). The complex [Ni(H_2dcsalpte)] (**1**) shows three bands at 21,978, 32,573 and 36,764 cm^{-1} (sh) assignable to $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$(P) and charge transfer transition respectively [50]. The band observed at 11,111 cm^{-1} may be due to $^3A_{2g} \rightarrow {}^3T_{2g}$(Oh). This along with the magnetic moment suggest pseudo-octahedral structure for the complex under discussion in which the nickel(II) ion is in the inner compartment with all the six donor sites $N_2S_2O_2$ coordinating to the metal ion, leaving the O_2O_2 compartment vacant. Similarly based on the same geometry, the bands observed at 17,667 and 24,630 cm^{-1} for the complex [Co(H_2dcsalpte)] (**2**) may tentatively be assigned to $^4T_{1g}$(F) $\rightarrow {}^4T_{2g}$ and $^4T_{1g}$(F) $\rightarrow {}^4T_{1g}$(P) transitions, respectively [48]. The green copper(II) complex, [Cu(H_2dcsalpte)] (**3**) shows only one band at 25,252 cm^{-1}, which is consistent with a distorted octahedral geometry. It is also reported that the green or blue copper(II) complexes are usually tetragonally distorted [51]. It is, therefore, plausible that the present copper(II) complex (**3**) has a distorted octahedral geometry. The palladium(II) complex, [Pd(H_4dcsalpte)]Cl$_2$ (**4**), on the other hand, shows strong bands in the UV region with a shoulder at 21,739 cm^{-1} which may be tentatively assigned to $^1A_{1g} \rightarrow {}^1E_g$ transition in a square planar geometry [51]. However, completely satisfactory interpretation is still lacking for such type of complexes. The relative energies of the d-orbitals in square planar palladium(II)

Table 4
Electronic spectral data of the ligand and metal complexes

Complex	Solvent	λ_{max} (cm^{-1})
H_4dcsalpte	Dichloromethane	27027, 35087
[Ni(H_2dcsalpte)] (**1**)	Methanol	21978, 32573, 36764 (sh)
[Co(H_2dcsalpte)] (**2**)	Methanol	17667, 24630, 38461
[Cu(H_2dcsalpte)] (**3**)	DMF	25252, 36496
[Pd(H_4dcsalpte)]Cl$_2$ (**4**)	Nitrobenzene	21739 (sh), 22988, 30864, 34722
[Mn(H_2dcsalpte)]CH$_3$COO (**5**)	Dichloromethane	13793, 21985, 37735, 43103
[Fe$_3$(H_2dcsalpte)(H_3dcsalpte)Cl$_3$]Cl$_3$ (**7**)	Dichloromethane	16129, 27027, 28571, 32258, 43478
[Fe$_3$(H_2dcsalpte)(H_3dcsalpte)Cl$_3$]Cl$_3$ (**7**)	Nujol	16260, 25641
[Fe(H_2dcsalpte)]ClO$_4$ (**8**)	Dichloromethane	16806, 25641 (sh), 30769 (sh), 33112, 40322
[Co(H_2dcsalpte)]Cl (**9**)	Methanol	16760, 25860, 38390
[Co(H_2dcsalpte)]CH$_3$COO (**10**)	Methanol	13855, 17540, 27875, 37538

complexes are $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz}, d_{yz}$. From circular dichroism studies of propylenediamine complexes of palladium(II), however, the ordering of the d-orbitals has been suggested [52] to be $d_{x^2-y^2} > d_{xy} > d_{xz}, d_{yz} > d_{z^2}$ which is identical to that found in the tetrachloro complex [53]. The electronic spectra of the palladium(II) complexes are extremely difficult to assign with certainty, because of the strong ligand field splitting of most of the d–d bands are observed at high energy ranges and the split component overlap with the bands due to charge-transfer(s) and ligand-based transitions. The band at 21,739 cm^{-1} of the present complex has been assigned to $^1A_{1g} \rightarrow {}^1E_g$ transitions and the other high-energy bands are probably due to charge-transfer and inter-ligand transitions.

The electronic spectra of the iron(III) complexes were measured both in the solid phase and in the solution. In general, the electronic transitions for iron(III) systems are spin-forbidden and hence weak, and are often marked by charge-transfer bands. However, in several spin equilibrium systems, the high spin ($S = 5/2$) form has been characterized by transition at 18,000–20,000 cm^{-1} and the low-spin ($S = 1/2$) form by transition at ~14,000–16,000 cm^{-1} [38,39,54]. In nujol mull the complex [Fe(H_2dcsalpte)]ClO$_4$ (**8**) shows a band at 15,151 cm^{-1} which can be assigned to high spin. In solution, a band appears at 16,806 cm^{-1} which is due to low-spin, but a shoulder at 25,641 cm^{-1} cannot definitely be assigned to high-spin. But solid-state spectrum is definitely in accordance with spin equilibrium systems.

The complex [Fe$_3$(H_2dcsalpte)(H_3dcsalpte)Cl$_3$]Cl$_3$ (**7**) has both octahedral and tetrahedral iron sites (Fig. 3) as evidenced from its electronic spectra (see also discussion of magnetic moments and Mössbauer spectra). Appearance of a band around ~16,000 cm^{-1} may tentatively be assigned to $^6A_1 \rightarrow {}^4T_{1g}$(G) in tetrahedral geometry of iron(III),

while the band around 25,000 cm^{-1} (in nujol mull) may be due to transitions $^6A_1 \rightarrow {}^4A_1$(G) in an octahedral geometry of iron(III) [50]. Other bands in solution may be due to charge transfer transitions. The bands at 13,793 cm^{-1} in the complex [Mn(H_2dcsalpte)]CH$_3$COO (**5**) may be due to $^5E_g \rightarrow {}^5T_{2g}$ transition [50]. Band at 28,985 cm^{-1} for the complex may be a spin-allowed transition as compared to Mn(CN)$_6^{3-}$ which has a band in solution [55] at 31,000 cm^{-1}.

A pseudo-octahedral structure may be proposed for the complex [Co(H_2dcsalpte)]Cl (**9**) based on the appearance of absorption bands at about 16,760 and 25,860 cm^{-1} which tentatively assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively [50]. The other transition, $^1A_{1g} \rightarrow {}^3T_{1g}$ for the same geometry of a cobalt(III) complex should appear at lower wave number, which could not be detected in the present case due to the limitations in scanning range of the instrument used. For the complex [Co(H_2dcsalpte)]CH$_3$COO (**10**), however, the $^1A_{1g} \rightarrow {}^3T_{2g}$ transition observed around 13,855 cm^{-1}, while the transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ were observed at about 17,540 and 27,875 cm^{-1}, respectively suggesting thereby the pseudo-octahedral structure for the said complex [50]. The other strong bands observed may be due to charge-transfer transition in origin.

3.6. Mössbauer spectra of iron(III) complexes

The Mössbauer spectra of the iron(III) complexes [Fe$_3$(H_2dcsalpte)(H_3dcsalpte)Cl$_3$]Cl$_3$ (**7**) and [Fe(H_2dcsalpte)]ClO$_4$ (**8**) are shown in Figs. 5 and 6 and relevant Mössbauer spectral data are set out in Table 5.

The spectra were analyzed by least square fit programme developed by E. von Meerwal [56]. The Mössbauer

Table 5
Mössbauer spectral data of the iron(III) complexes

Complex	Quadruple -splitting, ΔE (mm/s)	Isomer shift, δ (mm/s)
[Fe$_3$(H_2dcsalpte)(H_3dcsalpte)Cl$_3$]Cl$_3$ (**7**)	1.18 (A site)	0 (A site)
	0.98 (B site)	1.18 (B site)
[Fe(H_2dcsalpte)]ClO$_4$ (**8**)	2.48	0.47
	–	0.34

parameters were measured with respect to sodium nitroprusside as standard. From the measured isomer shift and quadruple splitting values, it is seen that the iron atoms are in the +3 oxidation state [57,58]. These values are corrected to a few percent (Table 5).

From the spectrum and Mössbauer data of $[Fe_3(H_2dcsalpte)(H_3dcsalpte)Cl_3]Cl_3$ (**7**), it is obvious that there are three iron sites, all of them in the +3 oxidation state. The intensities of the two lines for the spectrum are also not equal; there is also evidence of relaxation effects [31]. All the three iron sites are high-spin. The quadruple splitting shows that there is no cubic symmetry at the iron(III) sites. The ratio of resonance area of A and B sites is approximately 2:1 (see Fig. 5) suggesting thereby the presence of two high-spin iron(III) centres at A site and one high-spin centre at B site. It may be assumed from the Mössbauer data that A site is a distorted tetrahedral and B site is distorted octahedral site.

The Mössbauer spectra of $[Fe(H_2dcsalpte)]ClO_4$ (**8**) at 298 K shows a broad singlet at $\delta = 0.34$ mm/s and two well defined signals ($\delta = 0.47$, $\Delta E = 2.48$). Thus, as has already been discussed under the section of magnetic moment, the quadruple-split doublet of the complex is tentatively assigned to ^2T state, which should be ca 83%, populated. The broad singlet, which is assigned to high-spin state, does not totally disappear at 80 K and so there is some population of high-spin even at that temperature. Probably at further lower temperatures (which we could not attain), this singlet would disappear and a spectrum solely due to low-spin states would remain. The spectrum is mainly due to the low-spin iron(III) and an absence of the excessive spectral broadening to low-temperature indicates that anti-ferromagnetism does not contribute to the anomalous magnetic behaviour [57,58]. Therefore, the spectrum of this particular complex consists of a superimposition of both the low- and high-spin signals. The isomer shift and quadruple splitting values are consistent with similar complexes with anomalous magnetic moments [39–41].

Acknowledgements

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