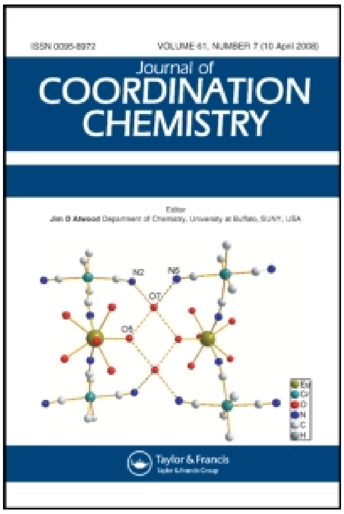


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Manganese(III) Schiff-base complexes involving heterocyclic β-diketone and diethylene triamine

C. K. Modi[a]; I. A. Patel[b]; B. T. Thaker[b]
[a] Department of Chemistry, Sardar Patel University, Gujarat, India [b] Department of Chemistry, Veer Narmad South Gujarat University, Gujarat, India

To cite this Article Modi, C. K. , Patel, I. A. and Thaker, B. T.(2008) 'Manganese(III) Schiff-base complexes involving heterocyclic β-diketone and diethylene triamine', Journal of Coordination Chemistry, 61: 19, 3110 — 3121
To link to this Article: DOI: 10.1080/00958970802007688
URL: http://dx.doi.org/10.1080/00958970802007688

Journal of Coordination Chemistry
Vol. 61, No. 19, 10 October 2008, 3110–3121

Taylor & Francis
Taylor & Francis Group

Manganese(III) Schiff-base complexes involving heterocyclic β-diketone and diethylene triamine

C. K. MODI*†, I. A. PATEL‡ and B. T. THAKER‡

†Department of Chemistry, Sardar Patel University,
Vallabh Vidyanagar – 388 120, Gujarat, India
‡Department of Chemistry, Veer Narmad South Gujarat University,
Surat – 395 007, Gujarat, India

(*Received 6 July 2007; in final form 10 December 2007*)

Synthesis, spectral, thermal and coordination aspects of pentadentate Schiff-base complexes of the type $[Mn(L)(X)] \cdot H_2O$ [where $H_2L = N,N'$–diethylamine *bis*(1-phenyl-3-methyl-4-acetylimino-2-pyrazoline-5-ol) and X=NCS, NO_3, ClO_4, CN or N_3] are reported. The Schiff-base ligand (H_2L) and metal complexes have been characterized by elemental analysis, FT-IR, ^{1}H-NMR, magnetic measurements, molar conductivity measurements, electronic spectra, cyclic voltammetric and thermal studies. Magnetic moment values are close to 4.9 B.M. indicating high spin complexes lacking exchange interaction. Infrared spectral data suggest coordination of the secondary amino group making the ligand pentadentate. All complexes are electrochemically inactive, indicating high stability. Thermal decomposition of the Schiff-base complexes indicates loss of water of hydration and decomposition of the ligand. Kinetic parameters such as order of reaction (n) and the energy of activation (E_a) are reported using the Horowitz–Metzger method, indicating first order kinetics and giving the activation entropy (ΔS^*), the activation enthalpy (ΔH^*) and the free energy of activation (ΔG^*).

Keywords: Pentadentate Schiff-base ligand (H_2L); Mn(III) complexes; Spectroscopic studies; Cyclic voltammetric studies; TG/DTG and DTA studies

1. Introduction

Manganese in various oxidation states is important in superoxide dismutase and azide insensitive catalase [1], manganese ribonucleotide reductase [2], manganese peroxidase [3] and the oxygen evolving complex in photosystem II of green plants [4]. Mn(III) ions are believed to play a role in at least three of the above enzymes: manganese superoxide dismutase, manganese catalase and oxygen evolving complex in photosystem (II) [5]. A family of Mn(III) Schiff-base complexes catalyzes reactions such as oxidative decarboxylation of carboxylic acids to the corresponding carbonyl compounds, oxidation of primary amines, 1,4-dicarboxypyridines and sulfides [6], C–H bond activation, olefin epoxidation, hydroxylation etc. [7].

---

*Corresponding author. Email: chetank.modi1@gmail.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802007688

Compounds containing pyrazole have been shown to exhibit antihyperglycemic, analgesic, anti-inflammatory, antipyretic, antibacterial and sedative-hypnotic activity [8–10]. Extensive studies have been devoted to pyrazole derivatives such as Celecoxib, a well-known cyclooxygenase-2 inhibitor [11–13]. Similarly, a few 1,5-diarylpyrazole derivatives exhibit non-nucleoside HIV-1 reverse transcriptase inhibitory activity [14]. Corresponding arylpyrazole derivatives have been recently identified as high affinity and selective A2B adenosine receptor antagonists [15].

Thermal analyses are widely applied in studying of thermal behavior of metal complexes [16–18]. The thermal behavior of complexes involving pyrazolone derivatives were studied by Xu *et al.* [19]. Pyrazolone-based Schiff bases are less extensive. Our laboratory has been exploring the chemistry of this class of ligand [20–24]. During the course of our research, we have synthesized tetradentate and hexadentate Schiff-base complexes of Mn(III) with heterocyclic β-diketones and various polyamines [25, 26]. Continuing our study, in this article we describe synthesis, spectral, thermal and coordination aspects of pentadentate Schiff-base complexes of Mn(III) involving heterocyclic β-diketone and diethylene triamine.

2. Experimental

All chemicals were of analytical grade. Organic solvents were purified by standard methods [27]. 1-Phenyl-3-methyl-2-pyrazoline-5-ol was purchased from E. Merck Ltd (India). Diethylenetriamine was purchased from Qualigens Fine Chemicals, India, and used without further purification. Manganese(III) complexes were synthesized using manganese(III) acetate prepared by using the Gündüz method [28]. 1-Phenyl-3-methyl-4-acetyl-2-pyrazoline-5-ol (PMAcP) was prepared as reported earlier [29].

2.1. *Synthesis of N,N′–diethylamine* bis*(1-phenyl-3-methyl-4-acetylimino-2-pyrazoline-5-ol) (H_2L)*

An ethanolic solution (50 mL) of PMAcP (2.16 g, 10 mmol) and an ethanolic solution (25 mL) of diethylenetriamine (0.54 mL, 5 mmol) in 2 : 1 molar ratio were mixed with constant stirring. Refluxing was carried out on a water bath for 4 h. The resulting mixture was allowed to stand overnight at room temperature. The formed pink crystals were collected by filtration, washed with diethyl ether and dried in air. Yield 75%, m.p. 86°C.

2.2. *Synthesis of Schiff-base complexes*

H_2L (2 mmol, 1.0 g) was dissolved in 25 mL of ethanol. To this solution, powdered $Mn(OAc)_3 \cdot 2H_2O$ (2 mmol, 0.54 g) was added with constant stirring over 30 min, followed by slow addition of 2 mmol of the inorganic salt containing the desired anion, $NaClO_4 \cdot 6H_2O$ (0.46 g), NH_4NCS (0.16 g), NH_4NO_3 (0.19 g), KCN (0.13 g) or NaN_3 (0.11 g) dissolved in (25 mL) ethanol. The reaction mixture was refluxed on a water bath for 3 h. The resulting solution was filtered, the solvent removed by slow evaporation, and the solid material thus obtained washed with water and diethyl ether, recrystallized from chloroform and dried over fused $CaCl_2$.

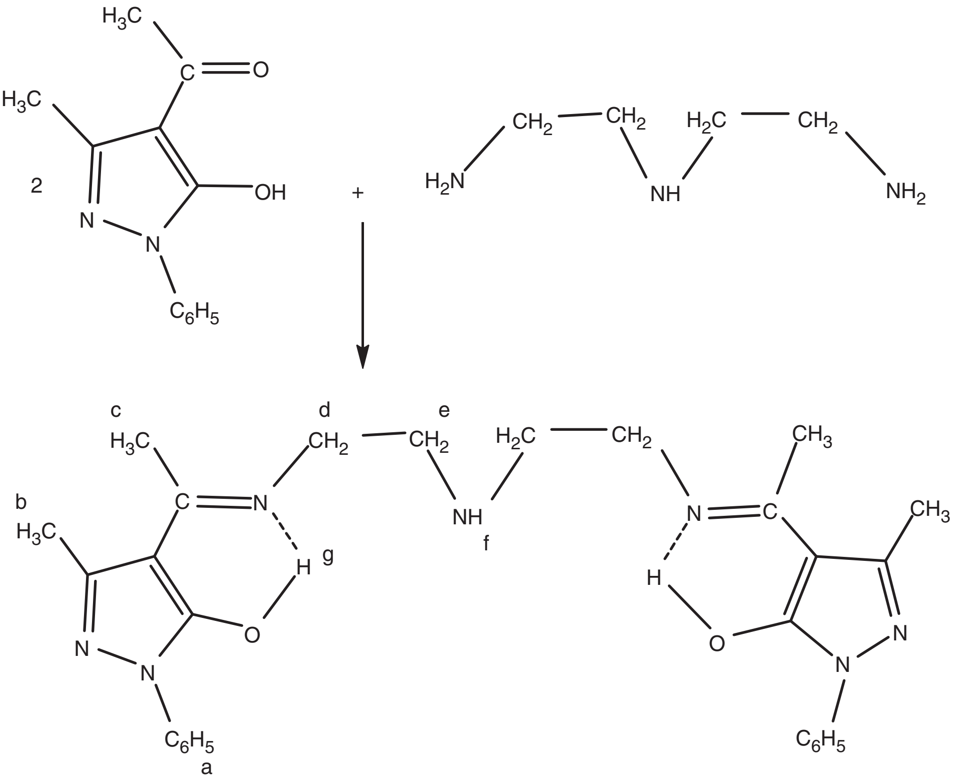
2.3. *Physical measurements*

Elemental analyses (C, H, N) were performed using a Carlo Ebra 1108 analyzer at the Central Drug Research Institute, Lucknow. Manganese was determined by EDTA [30] after decomposing the complex with a mixture of $HClO_4$, H_2SO_4 and HNO_3 (1 : 1.5 : 2.5). ^1H NMR spectra were recorded with JEOL-GSX-400 using $CDCl_3$ as solvent and TMS as an internal reference at SAIF, IIT, Mumbai. Infrared spectra were recorded with a 1310 Perkin-Elmer IR spectrophotometer (4000–400 cm^{-1}) using KBr pellets. The molar conductances of the complexes were recorded in 10^{-3} M MeOH solution on an ELICO conductivity bridge type CM 82T. Electronic spectra were recorded on a Shimadzu 160A UV–visible spectrophotometer using MeOH as the solvent blank. The magnetic moments were obtained by Gouy's method using mercury tetrathiocyanato cobaltate(II) as calibrant ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. units at 20°C). Diamagnetic corrections were made using Pascal's constants. Cyclic voltammetric studies were performed at the Department of Chemistry, IIT, Mumbai with a platinum disc (working), saturated calomel (reference) and platinum foil (counter) electrodes. Solutions ($\sim 10^{-3}$ M) were prepared in degassed acetonitrile, with 0.1 M tetrabutyl ammonium perchlorate as supporting electrolyte. The TGA/DTA studies were performed at the Regional Sophisticated Instrumentation Centre, IIT, Mumbai. The TG/DTG curves were obtained under non-isothermal conditions in N_2 at a heating rate of 10°C min^{-1} in the temperature range 50–800°C using a Al_2O_3 crucible with sample sizes from 3–7 mg.

3. Results and discussion

The Schiff-base is a condensation product of 1-phenyl-3-methyl-4-acetyl-2-pyrazoline-5-one and diethylenetriamine in 2 : 1 molar ratio (scheme 1). It has been established, from our work [25, 26] and the work of others [31], that the heterocyclic β-diketone Schiff bases exist in the enolic form, as shown in scheme 1.

The analytical and physical data of H_2L and its complexes are presented in table 1. The isolated solid complexes are stable at room temperature, non-hygroscopic and almost insoluble in water and diethyl ether but readily soluble in methanol, ethanol, chloroform, DMF and DMSO. Treatment of the complexes with potassium iodide liberated iodine indicating manganese in the +3 oxidation state, further supported by room temperature solid state magnetic moment values (table 1) which are close to 4.9 B.M., suggesting spin-free manganese(III) with four unpaired electrons. The molar conductances of 10^{-3} M MeOH [32, 33] solutions of the compounds lie in the range 0.03–0.86 $Ohm^{-1} cm^2 mol^{-1}$ showing non-electrolytes with coordinated anions. A slight increase in the molar conductances was observed after 2–4 h due to partial



Scheme 1. Suggested structure of the Schiff-base (H_2L).

dissociation of the complexes. The complexes are given in balanced chemical equations (1) and (2).

$$Mn(OOCCH_3)_3 \cdot 2H_2O + H_2L \rightarrow [Mn(L)(OOCCH_3)] \cdot H_2O + H_2O + 2CH_3COOH \quad (1)$$

$$Mn(L)(OOCCH_3)] \cdot H_2O + MX \rightarrow [Mn(L)X] \cdot H_2O + CH_3COOM \quad (2)$$

(where X = NCS, NO_3, ClO_4, CN or N_3 and M = NH_4, Na, K).

3.1. *IR spectral studies*

Infrared spectral bands and their tentative assignments are summarized in table 2. The infrared spectra of H_2L and $[Mn(L)CN] \cdot H_2O$ are shown in Supplemental Data. For H_2L, a broad band at $3390\,cm^{-1}$ assigned to $\nu(OH)$ of the enolic group suggests the enolic form in the solid state. In solution an NMR signal at $\delta\,11.25$ ppm corresponding to OH protons also is consistent with the enol form. The observed low frequency of $\nu(OH)$ with respect to the free hydroxyl group is due to

Table 1. Analytical and physical data for H_2L and its complexes.

				Found (Calcd) %						
Compound	Empirical formula	M.W./Color	m.p. (°C)	C	H	N	M	μ_{eff} (B.M.)	$^a\Lambda_M$	Yield (%)
H_2L	$C_{28}H_{33}N_7O_2$	499/Pink	86	67.36 (67.33)	6.62 (6.61)	19.68 (19.64)	–	–	–	75
$[Mn(L)NCS]\cdot H_2O$	$C_{29}H_{33}MnN_8O_3S$	628.63/Red	92	55.48 (55.41)	5.31 (5.29)	17.92 (17.83)	8.77 (8.74)	4.93	0.03	68
$[Mn(L)NO_3]\cdot H_2O$	$C_{28}H_{33}MnN_8O_6$	632.55/Red	98	53.18 (53.17)	5.24 (5.26)	17.78 (17.71)	8.70 (8.69)	4.88	0.09	66
$[Mn(L)ClO_4]\cdot H_2O$	$C_{28}H_{33}ClMnN_7O_7$	670.00/Brown	102	50.24 (50.19)	4.89 (4.96)	14.67 (14.63)	8.29 (8.20)	4.91	0.11	72
$[Mn(L)CN]\cdot H_2O$	$C_{29}H_{33}MnN_8O_3$	596.56/Red	96	58.44 (58.39)	5.56 (5.58)	18.83 (18.78)	9.26 (9.21)	4.90	0.25	70
$[Mn(L)N_3]\cdot H_2O$	$C_{28}H_{33}MnN_{10}O_3$	612.56/Red	94	54.99 (54.90)	5.46 (5.43)	22.91 (22.87)	8.92 (8.97)	5.12	0.86	68

Note: ^{a}Ohm^{-1} cm^2 mol^{-1}.

Table 2. IR spectral data (cm^{-1}) and electronic absorption data of H_2L and its metal complexes.

						Electronic absorption data in cm^{-1} (ε, $M^{-1}cm^{-1}$)	
Compounds	ν(–OH)	ν(C=N)	ν(C–O)	ν(M–N)	ν(M–O)	Charge transfer transition	d–d transition
H_2L	3390br	1636s	1353s	–	–	–	–
$[Mn(L)NCS]\cdot H_2O$	3400w	1629s	1367s	512w	472w	31,500 (5.32×10^3), 28,500 (4.26×10^3)	22,222 (2.10×10^3), 18,590 (1.98×10^3)
$[Mn(L)NO_3]\cdot H_2O$	3434w	1628s	1363s	515w	476w	31,590 (5.03×10^3), 26,800 (4.20×10^3)	18,500 (1.87×10^3)
$[Mn(L)ClO_4]\cdot H_2O$	3400m	1628s	1362s	520w	472w	31,500 (4.89×10^3), 28,985 (4.60×10^3)	19,011 (1.86×10^3)
$[Mn(L)CN]\cdot H_2O$	3420m	1629m	1365s	515w	476w	31,948 (5.00×10^3), 28,500 (4.60×10^3)	18,590 (1.83×10^3)
$[Mn(L)N_3]\cdot H_2O$	3400w	1628s	1363s	516w	480w	31,948 (5.13×10^3), 28,500 (4.32×10^3)	18,560 (1.96×10^3)

intramolecular H-bonding between H of OH and the azomethine nitrogen (scheme 1). A very sharp singlet at 3304 cm^{-1} is assigned to stretching of the secondary amino group. The strong band at ~1636 cm^{-1} is from the azomethine C=N stretch of the Schiff-base, while pyrazoline ring C=N frequency is observed at 1590 cm^{-1} [34, 35]. The ν(C–O) frequency is assigned to the peak observed at 1353 cm^{-1}. The aromatic C=C stretching vibrations is at 1540 cm^{-1}, while aromatic C–H stretching vibrations are at 3060 cm^{-1}. Bands at 1200, 1150, 1090, 1040 cm^{-1} and 845, 800, 760 cm^{-1} are assigned to in-plane and out-of-plane deformation bands of the aromatic C–H. The alkyl groups CH_2, CH_3 show stretching absorptions at 2990, 2965, 2880 and 2810 cm^{-1}, deformation bands at 1470 and 1390 cm^{-1} and rocking modes at 700 and 655 cm^{-1}, in good agreement with our previous findings [25, 26].

Infrared spectra of all the complexes (table 2) show a 6 cm^{-1} decrease in the C=N (azomethine) stretching frequency, indicating coordination via this nitrogen. The pyrazoline ring C=N stretching frequency remained at 1590 cm^{-1}, suggesting that the ring nitrogen does not take part in coordination. The thiocyanato complex shows a strong and sharp absorption band at 2079 cm^{-1} corresponding to ν(C=N). The stretching absorption due to ν(C–S) is useful in distinguishing N or S coordination of the thiocyanate group; ν(C–S) in the present complex lies in the range 780–860 cm^{-1} suggesting N coordination [36]. In the nitrato complex bands at 1480, 1385 and 1011 cm^{-1} may be assigned to ν_5, ν_1 and ν_2 for C_{2V} symmetry of the unidentate NO_3^-. The difference between ν_5 and ν_1 is 95 cm^{-1}, in agreement with reported values for coordinated NO_3^- [33, 37, 38]. For the perchlorate complex, bands centered at 1125 and 1100 cm^{-1} and a band at 935 cm^{-1} are observed. Free ClO_4^- exhibits bands near 1100 and 620 cm^{-1} corresponding to the two IR active modes (ν_3 and ν_4) of free ClO_4^- having *Td* symmetry [39]. Splitting of the first band into a doublet and the appearance of the new band near 950 cm^{-1} in the present complex suggest unidentate coordination. The cyano complex exhibited ν(C≡N) at 2100 cm^{-1}, higher by 20 cm^{-1} than the ν(C≡N) for free CN (i.e. 2080 cm^{-1} in aqueous solution), suggesting the coordination [40, 41]. The azido complex shows ν_{as}(NNN) at 2090 cm^{-1}, ν_s(NNN) at 1333 cm^{-1} and δ(NNN) at 550 cm^{-1}. Common in all the spectra is the absence of any band near 1580 cm^{-1}, assigned as a ν(COO) of coordinated acetate [42]. A broad band observed between 3400–3500 cm^{-1} is indicative of lattice water. Since the complexes begin to melt below 100°C, no attempt was made to record the IR spectra after dehydration. In two of the complexes, $[Mn(L)NO_3]\cdot H_2O$ and $[Mn(L)NCS]\cdot H_2O$, a weak band is observed adjacent to ν(C=N) (azomethine), probably the HOH bending mode of lattice water. Since the complexes are hydrated, ν(N–H) could not be observed due to overlap with ν(O–H). In the far–IR region, new bands at 512–520 and 472–480 cm^{-1} in the complexes are assigned to ν(M–N) [43] and $\nu(\mathrm{M–O})_{\mathrm{pyrazolone}}$, respectively. All of these data confirm H_2L as a dinegative pentadentate ligand forming a conjugated chelate ring, in the enolized form.

3.2. *^{1}H NMR spectral studies*

The ^{1}H NMR spectrum of the Schiff-base shows the phenyl protons as a group of multiplets between δ 7.10–8.10 ppm, including a sharp singlet at δ 7.26 ppm, due to the residual protons of $CDCl_3$. The resonance due to methyl protons b (see scheme 1) of the pyrazolone ring appears at δ 2.28 ppm. The sharp singlet observed at δ 2.24 ppm is attributed to protons c. The d protons, i.e. protons adjacent to the azomethine nitrogen, appear as a triplet at δ 3.01 ppm. The e protons, i.e. CH_2 protons adjacent to the –NH group are a complex multiplet at δ 2.36 ppm due to coupling with neighboring CH_2 protons. The f proton, i.e. –NH group proton is observed at δ 2.12 ppm. The hydroxyl proton g is present as a broad band at δ 11.25 ppm. The high δ value of the latter suggests intramolecular H-bonding (scheme 1), complementing the IR data.

The proton NMR spectra of the complexes are complicated and broad, an indication of the presence of Mn(III). In the complexes, the unpaired spin is delocalized to the methylene protons, but delocalization does not extend to 1-phenyl and 3-methyl protons as their peak positions remain unchanged.

3.3. *Electronic spectral studies*

Vol. 61, No. 19, 10 October 2008, Electronic absorption spectra of H_2L and its $[Mn(L)NO_3]\cdot H_2O$ complex are shown in Supplemental Data. The Schiff-base complexes (table 2) show a couple of bands in the ultraviolet portion of the spectrum which are of charge transfer origin at ~31,500 and ~28,500 cm^{-1}. The high energy of the first band suggests an intraligand charge transfer corresponding to the $\pi \rightarrow \pi^*$ transition of the azomethine group. Since Mn(III) is easily reduced, the second band in this region is suggested as a L → M charge transfer transition [25, 26]. $[Mn(L)NO_3]\cdot H_2O$ shows two d–d transitions near 22,222 and 18,500 cm^{-1}, whereas all other complexes showed only a single broad shoulder at ~18,500 cm^{-1}. From the electronic spectral data, a six coordinated distorted octahedral stereochemistry is proposed for all the complexes, supported by the low intensity of the d–d transitions. Accordingly, the band at ~18,500 cm^{-1} is assigned to the $^5B_{1g} \rightarrow {}^5A_{1g}$ transition and the band at ~22,222 cm^{-1} in $[Mn(L)NO_3]\cdot H_2O$ is assigned to the $^5B_{1g} \rightarrow {}^5E_{1g}$ transition. The absence of this band in the remaining complexes is due to the greater absorption in the ultraviolet portion of the spectrum. Similarly, the band corresponding to the $^5B_{1g} \rightarrow {}^5B_{2g}$ transition is not observed because of its low energy [44].

3.4. *Cyclic voltammetric studies*

The electrochemistry of the complexes is devoid of any redox potential over the entire range of the experiment. Attempts to carry out cyclic voltammetric studies at varied scan rates, i.e. 5, 10, 50 and 100 mV Sec^{-1} gave no redox activity. The observed inactivity points to high stability of the complexes, due to the presence of (1) phenyl groups (and perhaps CH_3) in the parent heterocyclic β-diketone which are good electron donors, (2) the Schiff-base is N-rich and N is a better σ donor and (3) the complexes have four chelate rings which may stabilize the complexes.

3.5. *Thermal studies*

Each decomposition follows the trend

$$\text{Solid-1} \xrightarrow{\text{heat}} \text{Solid-2} + \text{Gas}$$

This process comprises several stages. The method reported by Horowitz and Metzger [45] has been adopted. Plots of log [log w_∞/w_r] *versus* θ were linear for all of the decomposition steps, showing first order reaction over the entire range of decomposition for all of the complexes. The energy of activation Ea was calculated from the slopes of these plots for a particular stage. A typical Horowitz–Metzger plot for the thermal degradation of $[Mn(L)NCS] \cdot H_2O$ is shown in figure 1.

3.6. *Thermal behavior of the prepared complexes*

The TG thermogram of $[Mn(L)NCS] \cdot H_2O$ is taken as representative for the decomposition of these complexes. Thermoanalytical data of the complexes are given in table 3. The TG/DTG and DTA curves of $[Mn(L)NCS] \cdot H_2O$ are shown in figure 2. The decomposition undergoes three stages. The first mass loss (obs. 2.94%; calcd. 2.86%) in the temperature range 50–140°C corresponds to the loss of one water of hydration with an endothermic peak near 100°C in the DTA curve. The broad nature of this peak is due to melting. The water of hydration has also been substantiated by IR spectral data and the low activation energy (Ea) value (table 4) in their thermogravimetry. The second step of decomposition between 140 and 440°C, with a DTG peak at 329°C, corresponds to decomposition of thiocyanate anion, diethylenetriamine and one molecule of 1-phenyl-3-methyl-4-acetyl-2-pyrazoline-5-ol (PMAcP). The observed mass loss for this stage is 56.46%, consistent with the theoretical value of 56.69%. The DTA curve shows an exothermic peak at 364°C. The third stage occurs between 440 and 660°C, corresponding to decomposition of another molecule of 1-phenyl-3-methyl-4-acetyl-2-pyrazoline-5-ol (PMAcP), with mass loss of 29.26% (theoretical 29.15%). The maximum rate of mass loss is indicated by the DTG peak at 579°C and an exothermic peak at 562°C in DTA. The total mass loss (88.66%) coincides with the theoretical value of 88.70% (table 3).

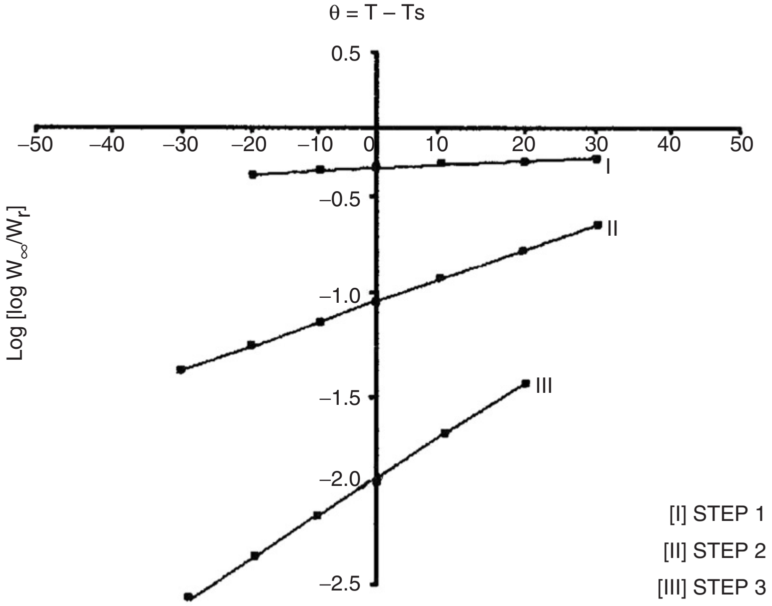


Figure 1. Horowitz–Metzger plot for the thermal degradation steps of $[Mn(L)NCS] \cdot H_2O$.

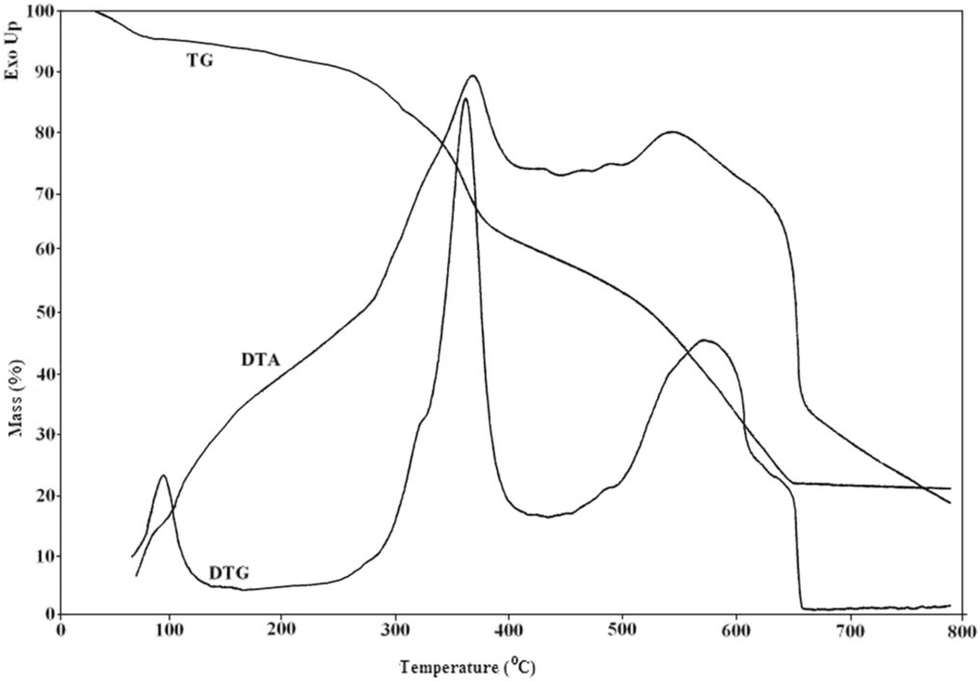


Figure 2. TG, DTG and DTA curves of $[Mn(L)NCS] \cdot H_2O$.

Table 3. Thermoanalytical results (TG, DTG and DTA) of the metal complexes.

Complex	TG range (°C)	DTA range (°C)	DTG max (°C)	Mass loss/% obs. (Calcd)	Assignment
$[Mn(L)NCS] \cdot H_2O$	50–140	60–120 (+)	98	2.94 (2.86)	Loss of one water of hydration
	140–440	270–420(−)	329	56.46 (56.69)	Removal of NCS ion + one moles of diethylenetriamine + PMAcP
	440–660	480–660(−)	579	29.26 (29.15)	Removal of remaining one mole of PMAcP
				88.66* (88.70)	leaving MnO residue
$[Mn(L)NO_3] \cdot H_2O$	50–140	40–130(+)	72	2.78 (2.85)	Loss of one water of hydration
	140–360	180–330(−)	256	56.79 (56.97)	Removal of NO_3 ion + one moles of diethylenetriamine + PMAcP
	360–580	460–590(−)	505	29.07 (28.97)	Removal of remaining one mole of PMAcP
				88.64* (88.79)	leaving MnO residue
$[Mn(L)ClO_4] \cdot H_2O$	50–140	–	94	2.86 (2.69)	Loss of one water of hydration
	140–430	160–330(−)	296	59.10 (59.38)	Removal of ClO_4 ion + one moles of diethylenetriamine + PMAcP
	430–650	480–640(−)	530	27.32 (27.34)	Removal of remaining one mole of PMAcP
				89.28* (89.42)	leaving MnO residue
$[Mn(L)CN] \cdot H_2O$	50–130	40–110(+)	90	3.07 (3.02)	Loss of one water of hydration
	130–380	220–310(−)	266	54.44 (54.38)	Removal of CN ion + one moles of diethylenetriamine + PMAcP
	380–630	460–610(−)	524	30.51 (30.72)	Removal of remaining one mole of PMAcP
				88.02* (88.11)	leaving MnO residue
$[Mn(L)N_3] \cdot H_2O$	50–130	40–100(+)	80	2.87 (2.94)	Loss of one water of hydration
	130–420	205–300(−)	259	55.68 (55.57)	Removal of N_3 ion + one moles of diethylenetriamine + PMAcP
	420–630	440–590(−)	511	29.67 (29.91)	Removal of remaining one mole of PMAcP
				88.22* (88.42)	leaving MnO residue

Note: (+): endothermic; (−): exothermic; *Total weight loss.

Table 4. Thermodynamic data for decomposition of metal complexes.

Complex	TG range (°C)	E_a(KJ mol^{-1})	ΔS^* (JK^{-1} mol^{-1})	ΔH^* (KJ mol^{-1})	ΔG^* (KJ mol^{-1})
$[Mn(L)NCS] \cdot H_2O$	50–140	4.96	−101.37	1.88	39.48
	140–440	36.23	−95.77	31.45	86.52
	440–660	98.58	−93.58	91.5	171.22
$[Mn(L)NO_3] \cdot H_2O$	50–140	3.89	−101.98	1.02	36.21
	140–360	31.17	−96.01	26.77	77.56
	360–580	77.35	−94.12	70.88	144.11
$[Mn(L)ClO_4] \cdot H_2O$	50–140	4.76	−101.48	1.71	38.95
	140–430	36.02	−95.75	31.29	85.77
	430–650	97.06	−93.42	90.38	165.4
$[Mn(L)CN] \cdot H_2O$	50–130	4.54	−101.61	1.52	38.41
	130–380	33.32	−95.84	28.84	80.5
	380–630	96.12	−93.42	89.5	163.95
$[Mn(L)N_3] \cdot H_2O$	50–130	4.28	−101.72	1.35	37.25
	130–420	32.01	−95.94	27.59	78.63
	420–630	82.28	−93.93	75.76	149.4

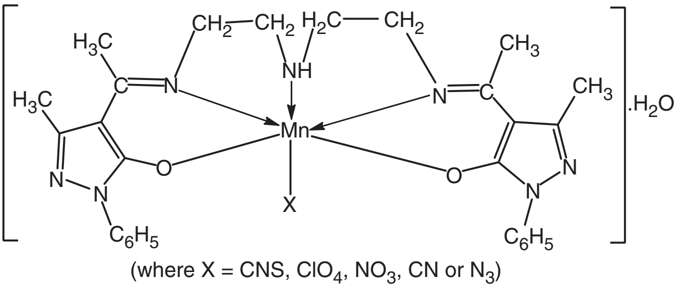


Figure 3. The proposed structure of the complexes.

3.7. *Calculation of activation thermodynamic parameters of the decomposed complexes*

The activation parameters of the decomposition process of dehydrated complexes were calculated [46–48] (table 4). The parameters show a slight variation due to the anions coordinated, despite the similar symmetry of the complexes. All complexes have negative entropy, indicating more ordered systems than reactants [49]. The energies of activation (E_a) suggest thermal stability order as: $[Mn(L)NCS] \cdot H_2O >$ $[Mn(L)ClO_4] \cdot H_2O > [Mn(L)CN] \cdot H_2O > [Mn(L)N_3] \cdot H_2O > [Mn(L)NO_3] \cdot H_2O$.

4. Conclusion

IR and ^{1}H NMR spectral studies reveal that H_2L exists in the tautomeric enol form. Magnetic moment values indicate that all the Mn(III) complexes are high spin, lacking exchange interactions. The IR spectra and thermal studies support the presence of one water of hydration in all the complexes. All complexes have negative entropy indicating that activated complexes have more order than reactants. Tentative structures of the complexes are shown in figure 3.

References

[1] G.W. Brudvig, R.H. Crabtree. *Prog. Inorg. Chem.*, **38**, 99 (1990).
[2] A. Willing, H. Fommay, G. Auling. *Eur. J. Biochem.*, **170**, 60 (1988).
[3] H. Warish, L. Akhileshwaran, M.H. Gold. *Biochemistry*, **27**, 5386 (1988); J.K. Flenn, L. Akhileshwaran, M.H. Gold. *Arch. Biochem. Biophys.*, **251**, 688 (1986).
[4] R. Debus. *Biochim. Biophys. Acta*, **1102**, 269 (1992).
[5] M.L. Kirk, M.S. Lab, S. Hatfield, V.L. Pecararo. *Inorg. Chem.*, **28**, 2037 (1989).
[6] V. Mirkhani, S. Tangestaninejad, M. Moghadam, M. Moghbel. *J. Bioorg. Med. Chem.*, **12**, 903 (2004).
[7] K.A. Jorgensen. *Chem. Rev.*, **89**, 431 (1989).
[8] K.L. Kees, J.J. Fitzgerald, K.E. Steiner, J.F. Mattes, B. Mihan, T. Tosi, D. Mondoro, M.L. McCaleb. *J. Med. Chem.*, **39**, 3920 (1996).
[9] S. Manfredini, R. Bazzanini, P.G. Baraldi, M. Guarneri, D. Simoni, M.E. Marongiu, A. Pani, E. Tramontano, P.L. Colla. *J. Med. Chem.*, **35**, 917 (1992).
[10] L.N. Jungheim. *Tetrahedron Lett.*, **30**, 1889 (1989).
[11] A.G. Habeeb, P.N.P. Rao, E.E. Knaus. *J. Med. Chem.*, **44**, 3039 (2001).
[12] R.R. Ranatunge, R.A. Earl, D.S. Garvey, D.R. Janero, L.G. Letts, A.M. Martino, M.G. Murty, S.K. Richardson, D.J. Schwalb, D.V. Young, I.S. Zemtseva. *Bioorg. Med. Chem. Lett.*, **14**, 6049 (2004).
[13] S.M. Sakya, K.M.L. DeMello, M.L. Minich, B. Rast, A. Shavnya, R.J. Rafka, D.A. Koss, H. Cheng, J. Li, B.H. Jaynes, C.B. Ziegler, D.W. Mann, C.F. Petras, S.B. Seibel, A.M. Silvia, D.M. George, L.A. Lund, S.St. Denis, A. Hickman, L. Michelle, M.L. Havwn, M.P. Lynch. *Bioorg. Med. Chem. Lett.*, **16**, 288 (2006).
[14] M.J. Genin, C. Biles, B.J. Keiser, S.M. Poppe, S.M. Swaney, W.G. Tarpley, Y. Yagi, D.L. Romero. *J. Med. Chem.*, **43**, 1034 (2000).
[15] E. Elzein, R. Kalla, X. Li, T. Perry, E. Parkhill, V. Palle, V. Varkhedkar, A. Gimbel, D. Zeng, D. Lustig, D. Leung, J. Zablocki. *Bioorg. Med. Chem. Lett.*, **16**, 302 (2006).
[16] M.A. Zayed, F.A. Nour El-Dien. *Thermochim. Acta*, **114**, 359 (1987).
[17] A.F. Petrovic, D.M. Petrovic, V.M. Leovac, M. Budimir. *J. Therm. Anal. Cal.*, **58**, 589 (1999).
[18] A.A. Soliman. *J. Therm. Anal. Cal.*, **63**, 221 (2001).
[19] G.-C. Xu, L. Zhang, L. Liu, G.-F. Liu, D.-Z. Jia. *Thermochim. Acta*, **429**, 31 (2005).
[20] B.T. Thaker, J. Lekhadia, A. Patel, P. Thaker. *Trans. Met. Chem.*, **19**, 623 (1994).
[21] C.K. Modi, B.T. Thaker. *Indian J. Chem.*, **41A**, 2544 (2002).
[22] I.A. Patel, P. Patel, S. Goldsmith, B.T. Thaker. *Indian J. Chem.*, **42**, 2487 (2003).
[23] K.R. Surati, B.T. Thaker. *J. Coord. Chem.*, **59**, 1191 (2006).
[24] B.T. Thaker, K.R. Surati, S. Oswal, R.N. Jadeja, V.K. Gupta. *Struct. Chem.*, **18**, 295 (2007).
[25] I.A. Patel, B.T. Thaker, P.B. Thaker. *Indian J. Chem.*, **37**, 429 (1998).
[26] I.A. Patel, B.T. Thaker. *Indian J. Chem.*, **38**, 427 (1999).
[27] A.I. Vogel. Edn. *Textbook of Practical Organic Chemistry*, 5th Edn, Longmans, London (1989).
[28] T. Gündüz, N. Gündüz, İ. Sakiyan. *Synth. React. Inorg. Met.-Org. Chem.*, **24**, 519 (1994).
[29] B.V. Patel, B.T. Thaker. *Synth. React. Inorg. Met.-Org. Chem.*, **16**, 1389 (1986).
[30] A.I. Vogel. *A Textbook of Quantitative Inorganic Analysis*, 3rd Edn, p. 434, Longmans, London (1978).
[31] A.K. Rana, J.R. Shah. *J. Indian Chem. Soc.*, **58**, 1100 (1981).
[32] W.J. Geary. *J. Coord. Chem.*, **7**, 81 (1971).
[33] N.T. Madhu, P.K. Radhakrishanan. *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 1663 (2001).
[34] P.M. Parikh, J.R. Shah. *Bull. De la Soc. Chemique De France*, **4**, 617 (1985).
[35] P.R. Patel, B.T. Thaker, S. Zele. *Indian J. Chem.*, **38A**, 563 (1999).
[36] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Edn, p. 270, Wiley, New York (1978).
[37] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Edn, p. 246, Wiley, New York (1978).
[38] S.M.E. Khalil, S.L. Stefan, K.A. Bashir. *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 927 (2001).
[39] K. Dey, K.C. Ray. *J. Inorg. Nucl. Chem.*, **37**, 695 (1975).
[40] L.J. Boucher. *J. Inorg. Nucl. Chem.*, **36**, 531 (1974).
[41] L.J. Boucher, V.W. Day. *Inorg. Chem.*, **6**, 1360 (1977).
[42] B.C. Sharma, C.C. Patel. *Indian J. Chem.*, **11**, 941 (1973).
[43] M. Mohapatta, V. Chakravortty, K.C. Das. *Polyhedron*, **8**, 1509 (1989).
[44] A.B. Joseph, J.M. Michael, V.L. Pecararo. *Inorg. Chem.*, **28**, 2044 (1988).
[45] H.H. Horowitz, G. Metzger. *Anal. Chem.*, **35**, 1464 (1963).
[46] M. Sekerci, F. Yakuphanoglu. *J. Therm. Anal. Cal.*, **75**, 189 (2004).
[47] C.K. Modi, S.H. Patel, M.N. Patel. *J. Therm. Anal. Cal.*, **87**, 441 (2007).
[48] A.A. Abou-Hussen, N.M. El-Metwally, E.M. Saad, A.A. El-Asmy. *J. Coord. Chem.*, **58**, 1735 (2005).
[49] G.G. Mohamed, Z.H. Abd El-Wahab. *J. Therm. Anal. Cal.*, **73**, 347 (2003).