

Physico-chemical investigation on mixed-ligand manganese (II) and iron (II) complexes of 4-methylpiperazine-1-carbodithioate ligand and 1,10-phenanthroline or 2,2'-bipyridyl

Shashi B. Kalia · Geetanjali Kaushal ·
Rojila · Dharvinder Kumar

Received: 14 May 2011 / Accepted: 16 September 2011 / Published online: 21 October 2011
© Akadémiai Kiadó, Budapest, Hungary 2011

Abstract Some new mixed-ligand complexes of 4-methylpiperazine-1-carbodithioate (4-MPipzcdt) of the general formula $[M(4\text{-MPipzcdt})_a(L)_b]X$ ($L = 1,10\text{-phenanthroline (phen) or } 2,2'\text{-bipyridyl (bipy)}$; $A = H, a = 2, b = 1$ where $M = Mn(II), X = Cl_2$, and $M = Fe(II), X = SO_4$; $A = \text{nil}$ where $X = Cl$ when $M = Mn(II), a = 1, b = 2$ and $X = \text{nil}$ when $M = Mn(II), Fe(II), a = 2, b = 1$) have been prepared and characterized by elemental analyses, molar conductance, infrared and electronic absorption and variable temperature Mössbauer spectral and room temperature as well as variable temperature magnetic susceptibility measurements. Manganese(II) complexes have high spin cis-distorted octahedral structures and all the iron(II) mixed-ligand complexes exhibit spin free–spin paired (${}^5T_{2g} \rightleftharpoons {}^1A_{1g}$) equilibrium in distorted octahedral structure.

Keywords Manganese(II) · Iron(II) · Phenanthroline/bipyridyl · Magnetic · Thermal · 4-methylpiperazine-1-carbodithioate

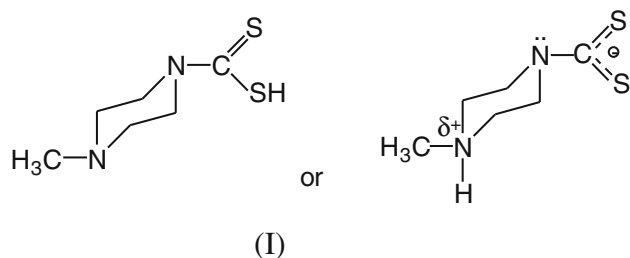
Introduction

Number of studies as well as reports on antifungal [1, 2], antibacterial [3–7], anti-alkylation [8, 9], anticancer and

apoptosis inducing activities [10] of the mixed-ligand metal dithiocarbamates derived from dialkyl secondary amines, in conjunction with primary and tertiary amines have been currently seen in literature. The problem of antibiotic resistance has now reached a crises point [11] and there is a need to redouble efforts towards the design of new synthetic compounds, so as to combat the rising menace of drug resistance. In addition to the importance of the mixed-ligand dithiocarbamate complexes for the enhanced biological activity, stabilization of low oxidation state of metal, i.e. Mn(II) and Fe(II) with dithiocarbamate ligands (which otherwise have the tendency to stabilize the higher oxidation states) has also been reported using π -acceptor auxiliary ligands. Iron(II) is known to exist in three different forms with dithiocarbamates as $Fe(R_2dtc)_2, A^+[Fe(R_2dtc)_3]^-$ ($A^+ = R_4N^+, Ph_4P^+$) and $Fe(R_2dtc)_2L$ ($L = o\text{-phen and bipy}$) [12–15]. Keeping in view the basic problem of easy oxidation of Mn(II) and Fe(II) to Mn(III) and Fe(III) and to avoid the precaution of removing all sources of oxygen, the stabilization of Mn(II) and Fe(II) with dithiocarbamate ligands has been tried in conjunction with the π -acceptor auxiliary ligands. The present study aims at isolating and investigating some manganese(II) and iron(II) complexes of 4-methylpiperazine-1-carbodithioic acid (I) and sodium 4-methylpiperazine-1-carbodithioate ligands (derivatives of saturated heterocyclic secondary amine) in conjunction with the nitrogenous bases 1,10-phenanthroline and 2,2'-bipyridyl. These bases can help in stabilizing metal atom in very low formal oxidation state, wherein extensive occupation of the ligand π^* orbitals takes place so that compounds can often be best formulated as having radical anion \bar{L} [16]. Use of mixed-ligand dithiocarbamate complexes has also been reported to result in augmentation of the biological activity [17].

S. B. Kalia (✉) · Rojila · D. Kumar
Department of Chemistry, Himachal Pradesh University,
Shimla 171005, India
e-mail: shashibalakalia@rediffmail.com

G. Kaushal
Department of Chemistry, Lyallpur Khalsa College,
Jalandhar, 144001, India



Experimental

All the chemicals used were of analytical reagent grade and used as such. The ligands 4-methyl-piperazine-1-carbodithioic acid (4-MPipzcdtH) and sodium-4-methylpiperazine-1-carbodithioate monohydrate (4-MPipzcdtNa·H₂O) were prepared by the method as reported earlier [18, 19].

Preparation of the complexes

$[M(4\text{-MPipzcdtH})_2(L)]X_2$ ($M = \text{Mn(II)}$ when $X = \text{Cl}$ and $M = \text{Fe(II)}$ when $X_2 = \text{SO}_4$, $L = \text{phen}$ or bipy)

To 5 mL methanolic solution of $\text{MX}_2 \cdot x\text{H}_2\text{O}$ (0.566 mmol) (0.112 g for $M = \text{Mn(II)}$ when $X = \text{Cl}$, $x = 4$ and 0.157 g for $M = \text{Fe(II)}$ when $X_2 = \text{SO}_4$, $x = 7$) was added with stirring 1.698 mmol methanolic solution (5 mL) of nitrogenous base phen (0.336 g) or bipy (0.265 g). Yellow coloured solution of the complex $[\text{Mn(L)}_3]\text{Cl}_2$ and dark red solution of the complex $[\text{Fe(L)}_3]\text{SO}_4$ was obtained [20]. To this solution was added with stirring slightly less than the stoichiometric amount of 4-MPipzcdtH (0.191 g; 1.09 mmol) in small portions (~10 mg) after successive intervals of 15 min in a total period of ~5 hours. The temperature of the reaction mixture was kept at about 30 °C. The coloured solid complexes were separated out, were filtered, washed with methanol and dried in air. Final drying was done by keeping the complexes overnight in a calcium chloride desiccator.

$[\text{Mn}(4\text{-MPipzcdtH})_2(\text{phen})]\text{Cl}_2$: Decomposition temperature: 245 °C; yield: 91%; IR(KBr) cm^{-1} : 1,615, 1,502, 988 (C = C and C = N); 1,216, 1,090, 810 (C–H deformations); Anal. ($\text{C}_{24}\text{H}_{32}\text{N}_6\text{S}_4\text{Cl}_2\text{Mn}$) Found: C 43.54; H 4.70; N 12.41; S 19.25; Mn 8.36; Cl 10.68; Calculated: C 43.77; H 4.86; N 12.76; S 19.45; Mn 8.34; Cl 10.79. $[\text{Mn}(4\text{-MPipzcdtH})_2(\text{bipy})]\text{Cl}_2$: Decomposition temperature: 190 °C; yield: 92%; IR(KBr) cm^{-1} : 1,594, 1,576, 1,483, 1,029 (C = C and C = N); 1,288, 1,141, 763, 739 (C–H deformations); Anal. ($\text{C}_{22}\text{H}_{32}\text{N}_6\text{S}_4\text{Cl}_2\text{Mn}$) Found: C 41.32; H 5.28; N 13.04; S 20.66; Mn 8.86; Cl 11.02; Calculated: C 41.64; H 5.04; N 13.25; S 20.19; Mn 8.66; Cl 11.19. $[\text{Fe}(4\text{-MPipzcdtH})_2(\text{phen})]\text{SO}_4$: Decomposition temperature: 250 °C; yield: 92%; IR(KBr) cm^{-1} : 1,623, 1,510, 1,028 (C = C and

C = N); 1,237, 1,143, 842 (C–H deformations); Anal. ($\text{C}_{24}\text{H}_{32}\text{N}_6\text{S}_5\text{O}_4\text{Fe}$) Found: C 42.10; H 4.60; N 12.36; S 23.55; Fe 8.04; Calculated: C 42.11; H 4.67; N 12.28; S 23.40; Fe 8.16. $[\text{Fe}(4\text{-MPipzcdtH})_2(\text{bipy})]\text{SO}_4$: Decomposition temperature: 250 °C; yield: 93%; IR(KBr) cm^{-1} : 1,593, 1,576, 1,486, 1,030 (C = C and C = N); 1,287, 1,144, 779, 739 (C–H deformations); Anal. ($\text{C}_{22}\text{H}_{32}\text{N}_6\text{S}_5\text{O}_4\text{Fe}$) Found: C 40.19; H 4.78; N 12.34; S 24.26; Fe 8.36; Calculated: C 40.00; H 4.84; N 12.73; S 24.24; Fe 8.46.

$[\text{Mn}(4\text{-MPipzcdt})(\text{L})_2]\text{Cl}$ ($L = \text{phen}$ and bipy)

Aqueous solution (5 mL) of 0.112 g, 0.566 mmol of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was added with stirring an aqueous solution (5 mL) of 1.698 mmol of nitrogenous base phen (0.336 g) or bipy (0.265 g). To the resulting yellow coloured solution of the $[\text{Mn(L)}_3]\text{Cl}_2$ complex was added with stirring an aqueous solution (5 mL) of 4-MPipzcdtNa·H₂O (0.122 g; 0.565 mmol). The reaction mixture was kept at 30 °C and was further stirred for another 2 hours till the froth formation ceased and precipitation took place. Orange coloured precipitates for mixed-ligand manganese complexes were obtained. The precipitates were filtered, washed with water and dried in air. Final drying of the product was done in a calcium chloride desiccator.

$[\text{Mn}(4\text{-MPipzcdt})(\text{phen})_2]\text{Cl}$: Decomposition temperature: 270 °C; yield: 91%; IR(KBr) cm^{-1} : 1,622, 1,515, 1,026 (C = C and C = N); 1,232, 1,145, 846 (C–H deformations); Anal. ($\text{C}_{24}\text{H}_{32}\text{N}_6\text{S}_4\text{Cl}_2\text{Mn}$) Found: C 57.54; H 4.30; N 13.41; S 10.25; Mn 8.76; Cl 5.68; Calculated: C 57.56; H 4.31; N 13.43; S 10.23; Mn 8.78; Cl 5.67.

$[\text{Mn}(4\text{-MPipzcdt})(\text{bipy})_2]\text{Cl}$: Decomposition temperature: 190 °C; yield: 92%; IR(KBr) cm^{-1} : 1,593, 1,576, 1,488, 1,035 (C = C and C = N); 1,286, 1,142, 762, 739 (C–H deformations); Anal. ($\text{C}_{22}\text{H}_{32}\text{N}_6\text{S}_4\text{Cl}_2\text{Mn}$) Found: C 54.04; H 4.30; N 14.41; S 11.25; Mn 9.76; Cl 6.08; Calculated: C 54.03; H 4.67; N 14.54; S 11.08; Mn 9.51; Cl 6.14.

$[\text{M}(4\text{-MPipzcdt})_2(\text{L})]$ ($M = \text{Mn(II)}$, Fe(II));
 $L = \text{phen}$ and bipy)

To an aqueous solution (5 mL) of 1.698 mmol of nitrogenous base, phen (0.336 g) or bipy (0.265 g) was added with stirring an aqueous solution (5 mL) of 0.566 mmol of $\text{MX}_2 \cdot x\text{H}_2\text{O}$ (0.112 g for $M = \text{Mn(II)}$ when $X = \text{Cl}$, $x = 4$ and 0.157 g for $M = \text{Fe(II)}$ when $X_2 = \text{SO}_4$, $x = 7$). The resulting coloured solution of the $[\text{M(L)}_3]X_2$ complex formed was yellow in case of manganese and dark red in case of iron. To these coloured solutions was added with stirring an aqueous solution (5 mL) of 4-MPipzcdtNa·H₂O (0.244 g; 1.13 mmol). The reaction mixture kept at 30 °C was further stirred for another 2 hours till the froth formation ceased (especially in case of manganese complex)

and precipitation took place. Orange coloured precipitates for manganese mixed-ligand complexes were obtained. The precipitates were filtered, washed with water and dried in air. Final drying of the product was done in a calcium chloride desiccator. In case of iron mixed-ligand complexes, the dark brown solid complexes were obtained in solution state along with the byproducts (phen or bipy and Na_2SO_4) of the reaction. To obtain the complexes in the pure state, the dark brown coloured complexes were extracted with benzene. The complex got extracted in upper layer of benzene, while the byproducts remained in the lower water layer. Pure state of the complex was obtained on evaporating the benzene solution.

[Mn(4-MPipzcdt)₂(phen)]: Decomposition temperature: 210 °C; yield: 93%; IR(KBr) cm^{-1} : 1,631, 1,516, 1,027 (C = C and C = N); 1,233, 1,146, 847 (C–H deformations); Anal. ($\text{C}_{24}\text{H}_{30}\text{N}_6\text{S}_4\text{Mn}$) Found: C 49.19; H 4.28; N 14.34; S 21.46; Mn 9.36; Calculated: C 49.23; H 5.12; N 14.36; S 21.88; Mn 9.39. [Mn(4-MPipzcdt)₂(bipy)]: Decomposition temperature: 190 °C; yield: 92%; IR(KBr) cm^{-1} : 1,593, 1,578, 1,488, 1,036 (C = C and C = N); 1,286, 1,142, 762, 739 (C–H deformations); Anal. ($\text{C}_{22}\text{H}_{32}\text{N}_6\text{S}_4\text{Mn}$) Found: C 47.09; H 4.98; N 14.59; S 22.36; Mn 9.66; Calculated: C 47.06; H 5.34; N 14.97; S 22.81; Mn 9.79. [Fe(4-MPipzcdt)₂(phen)]: Decomposition temperature: 210 °C; yield: 69%; IR(KBr) cm^{-1} : 1,631, 1,515, 1,034 (C = C and C = N); 1,245, 1,143, 848 (C–H deformations); Anal. ($\text{C}_{24}\text{H}_{30}\text{N}_6\text{S}_4\text{Fe}$) Found: C 49.11; H 5.28; N 14.34; S 21.35; Fe 9.36; Calculated: C 49.16; H 5.12; N 14.33; S 21.84; Fe 9.53. [Fe(4-MPipzcdt)₂(bipy)]: Decomposition temperature: 260 °C; yield: 95%; IR(KBr) cm^{-1} : 1,594, 1,577, 1,488, 1,031 (C = C and C = N); 1,288, 1,145, 764, 736 (C–H deformations); Anal. ($\text{C}_{22}\text{H}_{30}\text{N}_6\text{S}_4\text{Fe}$) Found: C 46.59; H 5.28; N 14.74; S 22.29; Fe 9.76; Calculated: C 46.98; H 5.33; N 14.95; S 22.78; Fe 9.93.

Elemental analyses

Carbon and hydrogen analyses were performed on an automatic Coleman-33 analyzer, while nitrogen was determined by Kjeldahl's method. Manganese in the complexes was determined by EDTA titration using Eriochrome Black T (EBT) indicator, while iron content was estimated by titration using ammonium thiocyanate as indicator. Chloride content was estimated volumetrically by mercuric nitrate titration using diphenylcarbazone indicator and sulphur was determined gravimetrically as barium sulphate.

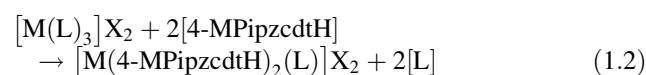
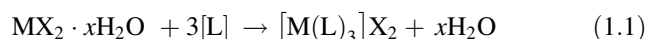
Physical measurements

Infrared spectra of mixed-ligand carbodithioate complexes were recorded as KBr pellets on Nicolet 5700 FT Infrared Spectrophotometer in the 4,000–600 cm^{-1} region. Infrared

spectra of all the complexes were recorded as Nujol mull with caesium chloride plates as windows in the 4,000–200 cm^{-1} region. Solution electronic absorption spectra of the complexes, with the solvent as the reference, in quartz glass cells were recorded on Cary 100 Bio UV–Visible recording Spectrophotometer (range 200–900 nm) and Analytikjena Specord 200 UV–Visible recording spectrophotometer. Molar conductances (10^{-3} M solutions in DMSO/methanol) were obtained at 25 ± 0.1 °C using a type Elico Conductivity Bridge CM-82T. The cell constant of the conductivity cell was 0.4530 cm^{-1} . Magnetic susceptibility measurements for the complexes were made on finally powdered samples using Gouy method. Magnetic susceptibilities of the samples were also measured on a Vibrating Sample Magnetometer PAR-155 with variable temperature cryostat (model-152). Mössbauer spectral measurements of the complexes were made on a cryophysics microprocessor-controlled Mössbauer spectrometer using a 25 m Ci $^{57}\text{Co/Rh}$ source.

Results and discussion

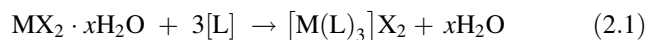
Two types of manganese and iron carbodithioate complexes, viz. (i) mixed-ligand complexes of zwitterionic 4-methylpiperazine-1-carbodithioic acid and 1,10-phenanthroline or 2,2'-bipyridyl and (ii) mixed-ligand complexes of normal 4-methylpiperazine-1-carbodithioate and 1,10-phenanthroline or 2,2'-bipyridyl have been reported in the present investigation. The preparation of the first type of mixed-ligand complexes can be described by the reactions 1.1 and 1.2.



L = phen or bipy

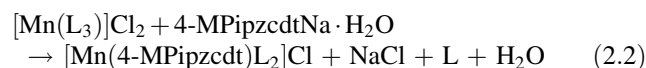
M = Mn(II) and X = Cl when $x = 4$; M = Fe(II) and $\text{X}_2 = \text{SO}_4$ when $x = 7$.

Mixed-ligand complexes of normal 4-methylpiperazine-1-carbodithioate and 1,10-phenanthroline or 2,2'-bipyridyl have further been divided into two types. The preparation of both types can be described by the reactions 2.1–2.3

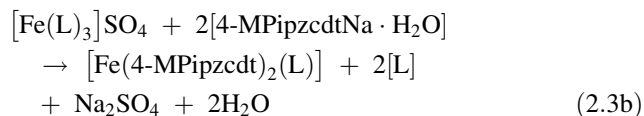
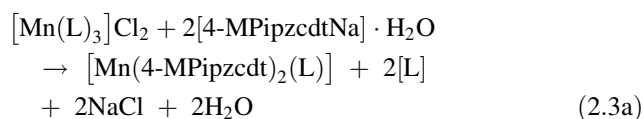


L = phen or bipy

M = Mn(II) and X = Cl when $x = 4$; M = Fe(II) and $\text{X}_2 = \text{SO}_4$ when $x = 7$.



Complexes of second type follow the reactions as:



All the complexes are stable in air, though were stored in a calcium chloride desiccator. The complexes do not melt but decompose between 150 and 270 °C. The mixed-ligand complexes of the type $[\text{M}(4\text{-MPipzcdtH})_2(\text{L})]\text{X}_2$ have fairly good solubility in DMSO only, while $[\text{M}(4\text{-MPipzcdt})_2(\text{L})]\text{Cl}$ and $[\text{M}(4\text{-MPipzcdt})_2(\text{L})]$ types of complexes exhibit good solubility in methanol and their solutions are quite stable. All the complexes have been investigated by infrared, solution electronic absorption spectra and room temperature and variable temperature magnetic susceptibility measurements. The $[\text{Mn}(4\text{-MPipzcdt})_2(\text{phen})]$ complex has also been characterized by thermogravimetric analysis study.

Infrared spectral studies

Mixed-ligand metal carbodithioates, viz. $[\text{M}(4\text{-MPipzcdtH})_2(\text{L})]\text{X}_2$, $[\text{M}(4\text{-MPipzcdt})_2(\text{L})]\text{Cl}$ and $[\text{M}(4\text{-MPipzcdt})_2(\text{L})]$ exhibit a strong band due to ($\text{C}=\text{N}$) stretching absorption in the range 1,440–1,417 cm^{-1} . The reduction in band frequency (4-MPipzcdtH = 1,442 cm^{-1} , 4-MPipzcdtNa·H₂O = 1,455 cm^{-1} and metal carbodithioic acid complexes = 1,493–1,461 cm^{-1}) [18, 19, 21, 22] is a clear indication of the reduced electron flow of the NCS_2^- moiety towards the central metal ion [23] consequent upon rearrangement of the in-plane ligand as a result of *cis*-octahedral formation [24, 25]. Decrease in electron flow is in consonance with the increase in electron charge donated by the nitrogenous bases, i.e. phen or bipy. The $\nu_a(\text{SCS})$ vibrations (999–972 cm^{-1}) exhibit a doublet (<20 cm^{-1}) and $\nu_s(\text{SCS})$ band (680–644 cm^{-1}) remains unsplit indicating unsymmetrical chelation of 4-MPipzcdt ligand [26]. For complexes of type 1, $[\text{M}(4\text{-MPipzcdtH})_2(\text{L})]\text{X}_2$, appearance of a broad band in the region 3,570–3,122 cm^{-1} assignable to the N–H stretching vibration points to the presence of the 4-MPipzcdtH ligand as Zwitterion. This band occurs at wave numbers higher than usual $\nu(\text{N-H})$ values of 3,400–3,200 cm^{-1} due to stronger interactions of lone electron pair on nitrogen with positively charged hydrogen.

The bands at 1,615 and 1,502 cm^{-1} due to C = C and C = N symmetric ring stretching and in-plane antisymmetric ring vibrations; in-plane ring C–H deformation vibrations at 1,216 and 1,090 cm^{-1} and due to C–H out-of-plane deformation vibrations at 810 and 739 cm^{-1} in free phen have been found to be shifted to higher frequency

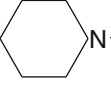
values at 1,631–1,621; 1,516–1,510; 1,034–1,025; 1,245–1,232; 1,146–1,143 and 848–842 cm^{-1} , respectively. Kinds of shifts are suggestive of binding of phen to the central metal ion. The C = C, C = N stretching modes and C–H in-plane deformation mode of free 2,2'-bipyridyl have been found at 1,583, 1,560, 1,457 and 992 cm^{-1} and 1,251, 1,090 cm^{-1} have been observed to be shifted to higher wave numbers in the regions 1,594–1,593, 1,578–1,576, 1,488–1,483 and 1,036–1,029 cm^{-1} and 1,288–1,286 and 1,145–1,141 cm^{-1} in bipy mixed-ligand complexes. This positive shift occurs due to maintenance of a ring current arising out of electron delocalization upon chelate formation [27]. The C–H out-of-plane deformation (756 cm^{-1} with a satellite band at 741 cm^{-1} in free bipy) in the complexes splits into two bands appearing at higher wave numbers 779–762 and 739–736 cm^{-1} is a diagnostic feature of coordination of bipy [28, 29]. The appearance of additional bands in the 361–310 cm^{-1} region as compared with free ligands reveals the formation of metal-sulphur bonds and hence to their stretching M–S vibrational modes. The M–N stretching mode appears at about 315–285 cm^{-1} . In mixed-ligand complexes of iron(II), simultaneous appearance of two M–S stretching frequencies points to the thermal population in two spin states.

Molar conductance studies

The DMSO solutions of mixed-ligand complexes $[\text{M}(4\text{-MPipzcdtH})_2(\text{L})]\text{X}_2$ exhibit molar conductance values between 135 and 145 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$, which is indicative of 1:2 electrolytic nature of the complexes while molar conductance values of methanolic solutions of $[\text{M}(4\text{-MPipzcdt})_2(\text{L}_2)]\text{Cl}$ (75–95 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$) and $[\text{M}(4\text{-MPipzcdt})_2(\text{L})]$ (20–40 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$) fall in the range of 1:1 and non-electrolytic behaviour, respectively [30].

Thermal studies

Curve of a single complex, $[\text{Mn}(4\text{-MPipzcdt})_2(\text{phen})]$ recorded in air indicated it to be stable up to 171 °C. Then, the complex revealed a continuous one step decomposition pattern up to 346 °C. The absence of any plateau in the TG curve (Fig. 1) suggested the non-formation of any stable intermediate. However, medium to weak intensity exotherms appeared at 262.10, 280.26 and 322 °C in DTA curve (Fig. 1) which are indicative of the probable decomposition of the complex occurring in more than one step. But the mass loss in TG curve did not correspond with the formation of any stable intermediate. The total weight loss of 48.50% against theoretical mass loss of 48.89% in the temperature range 171–346 °C inferred degradation through two cyclic

isothiocyanate $\text{H}_3\text{C}-\text{N}$  $\text{N}-\text{C}=\text{S}$ moieties (volatile in nature). While the remaining mass equivalent to 51.49% in the form of residue at 346 °C suggests the formation of MnS , molten sulphur and 1,10-phenanthroline as residue [31].

Magnetic susceptibility studies

The room temperature magnetic moment values for all the six mixed-ligand manganese(II) carbodithioate complexes with chromophores $[\text{MnS}_4\text{N}_2]$ and $[\text{MnS}_2\text{N}_4]$, viz. $[\text{Mn}(4\text{-MPipzcdtH})_2(\text{L})]\text{Cl}_2$, $[\text{Mn}(4\text{-MPipzcdt})(\text{L})_2]\text{Cl}$ and $[\text{Mn}(4\text{-MPipzcdt})_2(\text{L})]$ ($\text{L} = \text{phen, bipy}$) lie in the range 5.78–5.90 B.M., indicative of five unpaired electrons in a manganese(II), d^5 case [32]. The values are slightly lower than the spin-only value. These have been found to decrease with decrease in temperature (5.71–5.74 B.M. at 80 K). Similar observations have also been made by other authors on such type of manganese(II) mixed-ligand complexes [33, 34]. $1/\chi$ versus T plots (Fig. 2) are nearly linear in all the six complexes of present study and the magnetic moments show a continuous decrease with decrease in temperature. The possible explanation for decrease in magnetic moments with decrease of temperature for $[\text{Mn}(4\text{-MPipzcdtH})_2(\text{L})]\text{Cl}_2$ complex ($\mu_{\text{eff}} = 5.71$ B.M. at 80 K) (Fig. 2) could be attributed to spin-exchange coupled antiferromagnetic interactions. However, in the absence of X-ray diffraction study proposed chromophore $[\text{MnS}_4\text{N}_2]$ rules out this possibility due to least probability of having polymeric or dimeric structures.

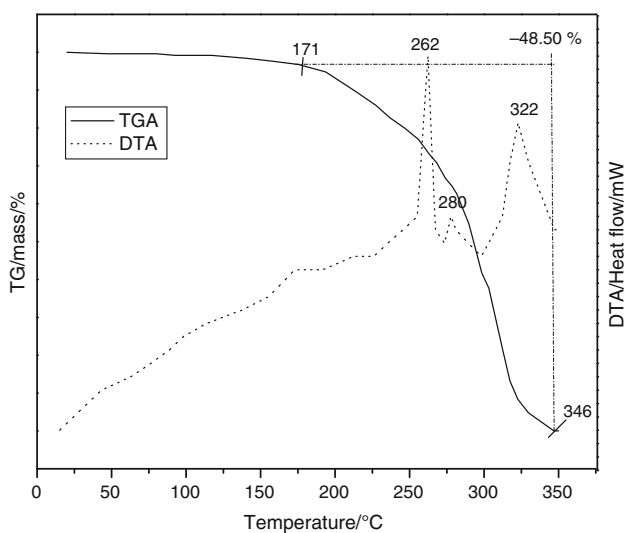


Fig. 1 TG/DTA curves of $[\text{Mn}(4\text{-MPipzcdt})_2(\text{phen})]$ complex

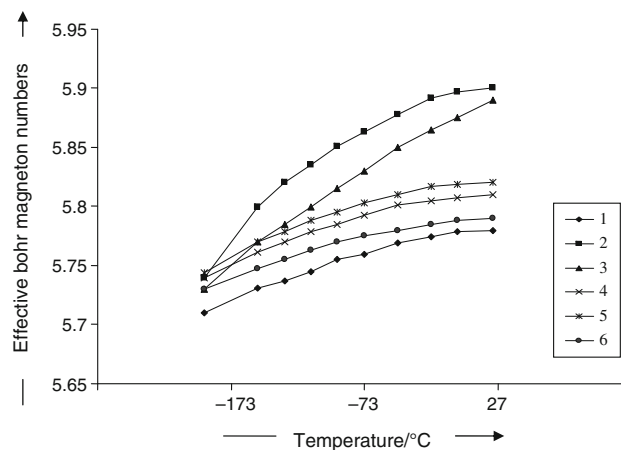


Fig. 2 Variation of effective Bohr magneton numbers with temperature of 1 $[\text{Mn}(4\text{-MPipzcdtH})_2(\text{phen})]\text{Cl}_2$, 2 $[\text{Mn}(4\text{-MPipzcdt})_2(\text{phen})]\text{Cl}$, 3 $[\text{Mn}(4\text{-MPipzcdt})_2(\text{phen})]$, 4 $[\text{Mn}(4\text{-MPipzcdtH})_2(\text{bipy})]\text{Cl}_2$, 5 $[\text{Mn}(4\text{-MPipzcdt})(\text{bipy})_2]\text{Cl}$, 6 $[\text{Mn}(4\text{-MPipzcdt})_2(\text{bipy})]$

The iron(II) complexes under study have room temperature μ_{eff} values in the range 4.10–4.23 B.M.. On decrease of temperature the μ_{eff} values decrease to 2.08–2.13 at 40 K (Fig. 3). For octahedral high-spin complexes of iron(II) with ${}^5T_{2g}$ ground term, the spin-orbit coupling constant is $\lambda = -100 \text{ cm}^{-1}$; the magnetic moment is expected to be about 5.5 B.M. at room temperature [35]. The moment is not expected to vary much with temperature. In complexes whose symmetry deviates from pure octahedral or due to electron delocalization, a reduction in this moment towards the spin-only value for four unpaired electrons (4.8 B.M.) is expected. For tetrahedral complexes, the moment will be given by $4.90(1 - 2\lambda/10Dq)$ when $\lambda = -100 \text{ cm}^{-1}$, and moments will thus be of the order of 5.1 B.M.

With strong field ligands, spin-pairing occurs and low-spin octahedral iron(II) complexes have the electron configuration ${}^6t_{2g}$; this configuration gives rise to the ${}^1A_{1g}$

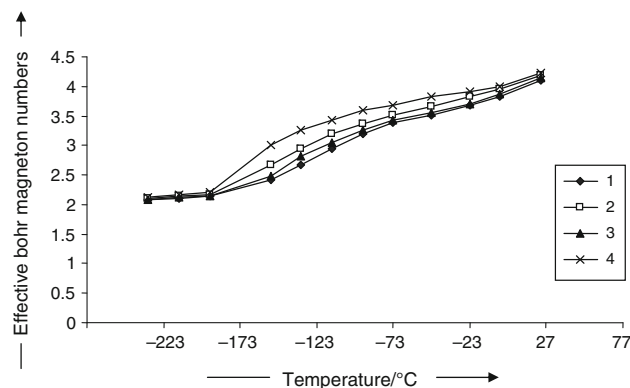


Fig. 3 Variation of effective Bohr magneton numbers with temperature of 1 $[\text{Fe}(4\text{-MPipzcdtH})_2(\text{phen})]\text{SO}_4$, 2 $[\text{Fe}(4\text{-MPipzcdt})_2(\text{phen})]$, 3 $[\text{Fe}(4\text{-MPipzcdtH})_2(\text{bipy})]\text{SO}_4$, 4 $[\text{Fe}(4\text{-MPipzcdt})_2(\text{bipy})]$

ground state having no first order Zeeman effect ($J = S = 0$). The positive susceptibilities observed for such complexes are due to the second-order Zeeman effect with higher ligand field terms. The susceptibilities are independent of temperature (T.I.P.). The low-spin octahedral iron(II) complex $[\text{K}_4\text{Fe}(\text{CN})_6]$ exhibits diamagnetic behaviour [36]. While the octahedral iron(II) complexes, viz. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Fe}(\text{MeCN})_6]^{2+}$, $[\text{Fe}(\text{NCSe})_6]^{4-}$ and $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ exhibit high-spin magnetic behaviour.

Since all the four iron(II) mixed-ligand complexes under study show large paramagnetism which does not correspond even to the value required for spin-free d^6 complexes indicating anomalous magnetic behaviour; however, the values lie between those for the high-spin and low-spin iron(II) complexes. The only explanation that could be offered for the large amount of paramagnetism is that there is a spin crossover phenomenon involving low-spin ($^1A_{1g}$) and high-spin ($^5T_{2g}$) states. It may be noted, however, that spin crossover system has been noticed in many complexes of iron(II), a d^6 system, e.g. $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$ [37] and mixed nitrogen- and oxygen-containing system, e.g. hemoprotein [38], and also in oxide systems of cobalt(III), another d^6 system [37]. For the iron(II) mixed-ligand complexes under investigation, it is possible that in the presence of strong nitrogenous bases the metal–ligand bond distances are decreased and a little increase in Δ is achieved and this increase may result in the two states $^5T_{2g}$ and $^1A_{1g}$, having almost the same energy [39, 40] resulting in a spin crossover equilibrium between them. The magnetic moment between 80 and 40 K for these complexes (Fig. 3) do not decrease appreciably thus indicating that pure low-spin iron(II) has not been achieved even up to 40 K.

With the μ_{HS} and μ_{LS} values of 5.5 and 0.0 B.M. at room temperature for high- and low-spin octahedral iron(II) complexes, respectively, the room temperature percentages of high-spin isomer in the four complexes, viz. $[\text{Fe}(4\text{-MPipzcdtH})_2(\text{phen})]\text{SO}_4$, $[\text{Fe}(4\text{-MPipzcdtH})_2(\text{bipy})]\text{SO}_4$, $[\text{Fe}(4\text{-MPipzcdt})_2(\text{phen})]$ and $[\text{Fe}(4\text{-MPipzcdt})_2(\text{bipy})]$ have been found to be 55.57, 56.65, 57.76 and 59.15, respectively.

Electronic absorption spectral studies

In methanol or DMSO solution (10^{-4} M) electronic absorption spectra, the yellow-orange coloured solutions for all the mixed-ligand complexes, viz. $[\text{Mn}(4\text{-MPipzcdtH})_2(\text{L})]\text{Cl}_2$, $[\text{Mn}(4\text{-MPipzcdt})(\text{L})_2]\text{Cl}$ and $[\text{Mn}(4\text{-MPipzcdt})_2(\text{L})]$ (L = phen, bipy) exhibit three well-defined bands in the ultra-violet and visible regions. The two bands around 11,487–13,568 cm^{-1} ($\epsilon = 10 \text{ L mol}^{-1}\text{cm}^{-1}$) and 19,576–20,501 cm^{-1} ($\epsilon = 3.0 \times 10^1 \text{ L mol}^{-1}\text{cm}^{-1}$) are weak bands. The absorption around 11,000 cm^{-1} in the present complexes can

be attributed to the transition $^4T_{1g} \leftarrow ^6A_{1g}$. The second band around 20,000 cm^{-1} may arise due to the transition $^4T_{2g} \leftarrow ^6A_{1g}$. The third band around 27,398–28,571 cm^{-1} ($\epsilon = 2.5 \times 10^3 \text{ L mol}^{-1}\text{cm}^{-1}$), an intense band is assigned to the transitions $^4A_{1g}$, $(G)^4E_g \leftarrow ^6A_{1g}$ [32, 41].

The positions of the visible spectral bands of the complexes under discussion are consistent with those reported for other manganese(II) mixed-ligand complexes [33]. It is further proposed that due to small bite of the 4-methylpiperazine-1-carbodithioate ligand, all the manganese complexes having $[\text{MnS}_4\text{N}_2]$ or $[\text{MnS}_2\text{N}_4]$ chromophore most plausibly prefer *cis*-distorted octahedral structure since, it will be quite strenuous for them to span *trans*-octahedral positions (Fig. 4). This is in consonance with MnL_4X_2 or MnL_2X_4 species exhibiting similar electronic absorption spectrum [41].

All the mixed-ligand iron(II) complexes under present discussion exhibit two doublets of medium intensity falling in the regions 16,216–19,723 cm^{-1} ($\epsilon = 1.0 \times 10^2 \text{ L mol}^{-1}\text{cm}^{-1}$) and 25,125–28,902 cm^{-1} ($\epsilon = 1.5 \times 10^2 \text{ L mol}^{-1}\text{cm}^{-1}$), and a weak intensity band in the range 9,308–11,350 cm^{-1} ($\epsilon = 3.0 \times 10^1 \text{ L mol}^{-1}\text{cm}^{-1}$), in their DMSO/methanol solution (10^{-4} M) electronic absorption spectra. The two high energy bands of medium intensity can be assigned to the spin-allowed $^1T_{1g} \leftarrow ^1A_{1g}$ and $^1T_{2g} \leftarrow ^1A_{1g}$ electronic transitions of octahedral low-spin iron(II) complexes, respectively. The third band may be assigned to the spin-forbidden $^3T_{2g}$, $^3T_{1g} \leftarrow ^1A_{1g}$ transitions [35]. As already discussed, the magnetic susceptibility studies reveal that these complexes observe spin crossover equilibrium between $^5T_{2g}$ and $^1A_{1g}$ spin states. Keeping this in view, the lowest energy band of medium intensity may also consist of absorption due to $^5E_g \leftarrow ^5T_{2g}$ transition [35]. Unsymmetrical shape of this band supports the contention of this band resulting from the overlapping of absorptions due to $^3T_{1g} \leftarrow ^1A_{1g}$ and $^5E_g \leftarrow ^5T_{2g}$ electronic transitions. The electronic spectral band assignments have been made in the distorted *cis*-octahedral geometry of the complexes. The appearance of two high-energy doublets further support the distorted octahedral geometry as is being expected for the iron(II) mixed-ligand complexes.

Mössbauer spectra

The complexes, viz. $[\text{Fe}(4\text{-MPipzcdtH})_2(\text{Phen})]\text{SO}_4$ and $[\text{Fe}(4\text{-MPipzcdt})_2(\text{Phen})]$ display only one signal (one Mössbauer doublet) at room temperature as well as at liquid nitrogen temperature in their computerized Mössbauer spectra. The Mössbauer spectrum of the complex $[\text{Fe}(4\text{-MPipzcdt})_2(\text{Phen})]$ is shown in Fig. 5. Though the Mössbauer spectra offer no direct support for the existence of the $^5T_{2g} \rightleftharpoons ^1A_{1g}$ spin equilibrium in iron(II)

Fig. 4 Proposed structures for the $[\text{MnS}_4\text{N}_2]$ or $[\text{MnS}_2\text{N}_4]$ chromophores

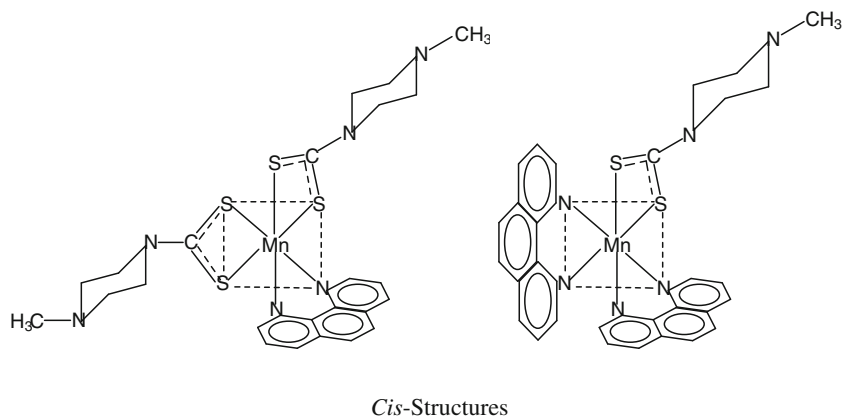


Fig. 5 Mössbauer spectra of $[\text{Fe}(4\text{-MPipzcdt})_2(\text{Phen})]$ at **a** 22 °C and **b** −196 °C

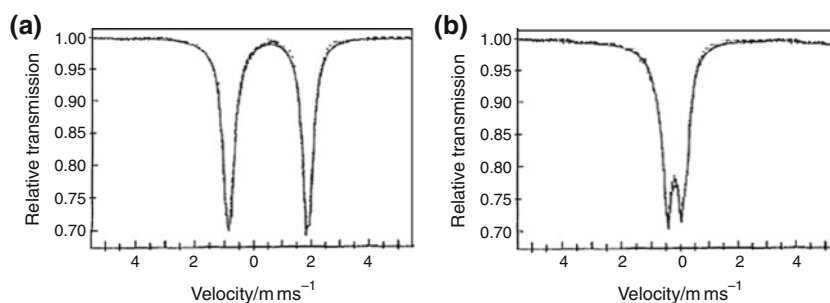


Table 1 Isomer shifts δ (mms^{-1}) and quadrupole splitting ΔE_Q (mms^{-1}) for ^{57}Fe iron(II) complexes

Sr. No.	Compound	δ	ΔE_Q
1	$[\text{Fe}(4\text{-MPipzcdt})_2(\text{Phen})]$	0.99 ± 0.05 (295 K)	2.91 ± 0.02 (295 K)
		0.39 ± 0.05 (77 K)	0.41 ± 0.02 (77 K)
2	$[\text{Fe}(4\text{-MPipzcdt})_2(\text{Phen})]\text{SO}_4$	0.99 ± 0.05 (295 K)	3.11 ± 0.02 (295 K)
		0.41 ± 0.05 (77 K)	0.85 ± 0.05 (77 K)

δ values are measured relative to the iron metal as the standard

carbodithioates which is invoked to explain the anomalous temperature dependence of the magnetic moments, yet the appearance of only one doublet and not a doublet of doublets has been explained on the basis of the existence of a rapid dynamic spin interconversion between $^5T_{2g}$ and $^1A_{1g}$ states [42]. The Mössbauer parameters, isomer shift δ and quadrupole splitting ΔE_Q are listed in Table 1. The magnitudes of the room temperature (295 K) chemical shifts (δ) values (0.99 mm/s) are close to those found for high-spin iron(II) compounds (1.00 mm/s) [37], while these values (0.41 and 0.39 mm/s) at 77 K are near to those for low-spin iron(II) compounds (0.3 mm/s). [43] Observation of decreasing trend in chemical shift values with decrease of temperature is consistent with previous studies on $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ complexes [42].

The quadrupole splitting values (ΔE_Q) for the iron(II) carbodithioate complexes under study lie in the range

3.11–2.91 mm/s (Table 1). When ligand arrangement in a strong field iron(II) complex does not consist of six equivalent ligands, quadrupole splitting will result for $^1A_{1g}$ spin state because electric field gradient is non zero for the $[\text{Fe}(4\text{-MPipzcdtH})_2(\text{Phen})]\text{SO}_4$ and $[\text{Fe}(4\text{-MPipzcdt})_2(\text{Phen})]$ complexes. However, large splittings for $^5T_{2g}$ state in the complexes of non zero electric field gradient because of asymmetry of electron distribution in d orbitals have been observed [43] for iron(II) complex, $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. At liquid nitrogen temperature, the observed decrease in the quadrupole splitting values (Table 1) for the two iron(II) carbodithioates is consistent with the increasing low-spin state population (inferred from the decrease in μ_{eff} value). This is in agreement with the values reported in the literature for iron(II) complex, i.e. $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, observing spin equilibrium between almost equienergetic $^5T_{2g}$ and $^1A_{1g}$ states.

Conclusions

Magnetic and spectral studies on some mixed-ligand manganese(II) and iron(II) complexes of 4-MPipzcdt ligand and 1,10-phen or 2,2-bipy reveal that manganese(II) complexes having cis-distorted octahedral structures with the chromophore $[\text{MnS}_4\text{N}_2]$ or $[\text{MnS}_2\text{N}_4]$ are all high-spin in nature irrespective of the nature of the central core. The paramagnetism decreases with decrease of temperature. All iron(II) mixed-ligand complexes having chromophore $[\text{FeS}_4\text{N}_2]$ or $[\text{FeS}_2\text{N}_4]$ exhibit high-spin–low-spin (${}^5T_{2g} \rightleftharpoons {}^1A_{1g}$) crossover phenomenon in distorted octahedral structure.

References

- Chauhan HPS, Shaik NM. Synthetic, spectral, thermal and antimicrobial studies on some mixed 1, 3-dithia-2-stannacyclopentane derivatives with dialkyldithiocarbamates. *J Inorg Biochem.* 2005;99:538–45.
- Sharma RN, Kumar A, Kumari A. Synthesis, characterization and antifungal studies of some As (III), Sb(III) and Bi(III) complexes with *o*-tolyl ammonium dithiocarbamate. *Asian J Chem.* 2003;15:57–61.
- Baikonova GG, Abdulina GA, Gazaliev AM. Synthesis and antimicrobial activity of the dithiocarbamates of anabasine, piperidine and morpholine dithiocarbamates. *Pharma Chem J.* 2004;38:19–20.
- Sharma R, Kaushik NK. Studies on organomercury(II) complexes with piperidine and 2-aminopyridine dithiocarbamates. *Indian J Chem.* 2004;43:769–72.
- Sovilz SP, Avramović N, Katsaros N. Infrared spectral, variable temperature magnetic susceptibility and Mössbauer spectral investigations on tris(carbodithioato) iron(III) complexes. *Transit Met Chem.* 2004;29:737–42.
- Yilmaz VT, Yazicilar TK, Cesur H. *Synth React Inorg Met-Org Chem.* 2003;33:589–605.
- Zeng MH, Liang H, Hu RX. *She-Qun Ying Jong Huaxue.* 2001;18:839.
- Gringeri A, Keng PC, Borch RF. Diethyldithiocarbamate inhibition of murine bone marrow toxicity caused by cis-diamminedichloroplatinum(II) or diammine-(1,1-cyclobutanedicarboxylato) platinum(II). *Cancer Res.* 1988;48:5708–12.
- Pannacciulli IM, Lerza RA, Bogliolo GU, Mencoboni MP. Effect of diethyldithiocarbamate on toxicity of doxorubicin, cyclophosphamide and cis-diammine chloroplatinum(II). *Braz J Cancer.* 1989;59:371.
- Borch RF, Bodenner DL, Katz JC. *Platinum coordination complexes in cancer chemotherapy.* Boston: Martinus Nijhoff; 1984. p. 154–64.
- Bentley PH, O'Hanlon PJ, editors. *Anti-infectives—recent advances in chemistry and structure-activity relationships.* Cambridge: The Royal Society of Chemistry; 1997. p. 338.
- Pignolet LH, Lewis RA, Holm RH. Synthesis and stereochemical rearrangements of complexes containing the Fe-S6 core. *J Am Chem Soc.* 1971;93:360–71.
- Illeperuma OA, Feltham RD. Crystal and molecular structure of iron(II) bis(diethyldithiocarbamate). *Inorg Chem.* 1975;14:3042.
- De Vries JLFK, Trooster JM, de Bo E. Iron(II) complexes with two and three dialkyldithiocarbamate ligands. Mossbauer and electronic spectra. *Inorg Chem.* 1973;12:2730–1.
- Holah DG, Murphy CN. Reactions of sodium *N,N*-diethyldithiocarbamate and potassium ethyl xanthate with some 3*d* transition metal halides in the presence of 2,2'-bipyridyl and 1,10-phenanthroline. *Can J Chem.* 1971;49:2726.
- Cotton FA, Wilkinson G. *Adv Inorg Chem.* 5th ed. New York: John Wiley; 1988.
- Kalia SB, Kaushal G, Kumar M, Singh S, Sharma A, Verma ML, Kanwar S. Antimicrobial and toxicological studies of some metal complexes of 4-methylpiperazine-1-carbodithioate and phenanthroline mixed ligands. *Braz J Microbiol.* 2009;40:916–22.
- Kalia SB, Kaushal G, Sharma DK, Verma BC. Studies on some new type of transition metal 4-methylpiperazine-1-carbodithioate complexes. *Synth React Inorg Met-Org Nano-Met Chem.* 2005;35:181–8.
- Manhas BS, Bala S. Infrared spectral, variable temperature magnetic susceptibility and Mössbauer spectral investigations on tris(carbodithioato) iron(III) complexes. *Polyhedron.* 1988;7:2465.
- Vogel AI. *A textbook of quantitative inorganic analysis.* 4th edition. Longmans Green: London; 1978. p. 742.
- Kalia SB, Kaushal G, Lumba K, Priyanka. Thermoanalytical investigations of 4-methylpiperazine-1-carbodithioic acid ligand and its iron(III), cobalt(II), copper(II) and zinc(II) complexes. *J Therm Anal Calorim.* 2008;91:609–13.
- Kalia SB, Kaushal G, Kumar M, Kumar S, Khanduja KL. Physicochemical studies on some 4-methyl piperazine-1-carbodithioate complexes of zinc(II), cadmium(II) and mercury(II). *Indian J Chem.* 2008;47:1323–32.
- Saravanan M, Ramalingam K, Bocelli G, Cantoni A. Crystallographic report: (2, 2'-bipyridyl)bis(ethanoldithiocarbamate) zinc(II). *Appl Organomet Chem.* 2004;18:86.
- Thirumaran S, Ramalingam K, Bocelli G, Cantoni A. Electron density distribution studies on ZnS4N2 chromophore in solution and solid phases: XPS and cyclic voltammetric studies on 1, 10-phenanthroline and 2, 2'-bipyridine adducts of bis(piperidinecarbodithioato-S, S')zinc(II). Single crystal X-ray structure of (2, 2'-bipyridine)bis-(piperidinecarbodithioato-S, S')zinc(II). *Polyhedron.* 1999;18:925–30.
- Hassan AMA, Soliman EM, Roudi A. Adduct formation by nickel(II) complexes of S-methyl hydrazine carbodithioate Schiff bases with 2, 2'-bipyridyl and 1, 10-phenanthroline. *Polyhedron.* 1989;8:925.
- Bonati F, Ugo R. *J Organomet Chem.* 1967;10:257.
- Reddy KH, Reddy PS. *Indian J Chem.* 2001;40:1118.
- Martin B, McWhinnie WR, Waing GM. 2:2'-dipyridyl complexes of cobalt, rhodium and iridium—II⁺: low-valent rhodium complexes. *J Inorg Nucl Chem.* 1961;23:207–23.
- Sinha SP. *Spectrochim Acta.* 1964;20:879.
- Geary WJ. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coord Chem Rev.* 1971;7:81–122.
- Ocakoglu Kasim, Emen FM. Thermal analysis of cis-(dithiocyanato)(1,10-phenanthroline-5,6-dione)(4,4'-dicarboxy-2,2'-bipyridyl)ruthenium(II) photosensitizer. *J Therm Anal Calorim.* 2011;104:1017–22.
- Abd El-Halim HF, Nour El-Dien FA, Mohamed GG, Mohamed NA. Synthesis, spectroscopic, thermal characterization, and antimicrobial activity of miconazole drug and its metal complexes. *J Therm Anal Calorim.* doi:10.1007/s10973-011-1784-2.
- Singh AK, Puri BK, Rawley RK. *Indian J Chem.* 1988;27:430–3.
- Pandeya KB, Singh R, Mathur PK, Singh RP. ESR spectra of mixed ligand manganese(II) dithiocarbamates. *Trans Met Chem.* 1986;11:347.
- Nicholls D. *Comprehensive inorganic chemistry.* vol 3. Oxford: Pergamon Press; 1973.
- Figgis BN. *Introduction to ligand fields.* New York: Interscience; 1966.

37. Carlin RL. Transition metal chemistry a series of advances. vol 4. New York: Marcel Dekker Inc; 1968.
38. Martin RL, White AH. *Trans Met Chem*. 1968;4:113.
39. Madeja K, König E. Zur frage der bindungsverhältnisse in komplexverbindungen des eisen(II) mit 1, 10-phenanthrolin. *J Inorg Nucl Chem*. 1963;25:377.
40. König E, Madeja K. *Chem Commun*. 1966;3:61.
41. Lever ABP. *Inorganic electronic spectroscopy*. Amsterdam: Elsevier; 1973.
42. Gutlich P, Goodwin HA. Spin crossover in transition metal compounds II topics in current chemistry. 2004;234:240.
43. Carlin RL. *Transition metal chemistry*. vol 4. New York: Marcel Dekker Inc; 1968. p. 170.