

Spectral studies on some transition metal complexes of 3-(4'-pyridyl)-4-phenyl-triazoline-5-thione

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(Received: August 25, 2009; Accepted: September 30, 2009)

ABSTRACT

3-(4' – Pyridyl)-4-phenyl-triazoline-5-thione(PPytTH) forms stable coloured solid and acts as monodentate with Mn(II) and bidentate (N, S) with Co(II), Ni(II), Cu(II), Fe(III) and Ti(III) ions. The nature of shifts and change in intensity of all four thioamide bands of the ligand are used as diagnostic for metal-ligand bonding. Crystal field parameters in electronic spectra and metal-ligand vibrations in far-ir spectra of complexes have been tentatively assigned.

Key words: Metal complexes, Triazole, Nature of bonding.

INTRODUCTION

In continuation of our work¹⁻² on the complexes of 3-(4'-Pyridyl)-4-phenyl-triazoline-5-thione (PPytTH) (I), we report here the synthesis, spectral characterization and reactivity study of Mn(II), Co(II), Ni(II), Cu(II), Fe (III) and Ti(III) complexes of (I).

EXPERIMENTAL

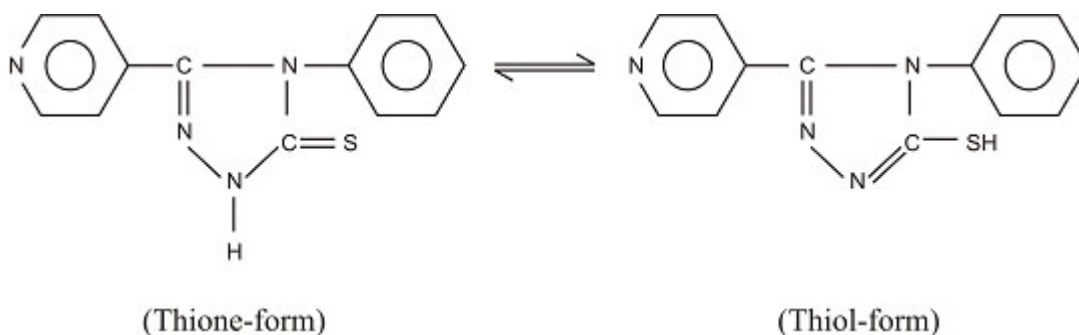
All reagents used were of AR or CP-grade. The ligand (PPytTH) was prepared slightly modified method reported in literature³. The complexes were prepared in aqueous ethanolic medium using a general method. Metal chloride and ligand solution were mixed in an appropriate molar ratio and refluxed on water bath for two hours. The pH of mixture was adjusted 6 or 8 using dil. HCl and Pyridine. The mixture was further stirred on magnetic stirrer for 1h and evaporated almost to dryness. The coloured complexes were washed with cold ethanol and ethyl methyl ketone and dried at

120°C in an electric oven. The analytical and physical data of complexes are given in Table 1.

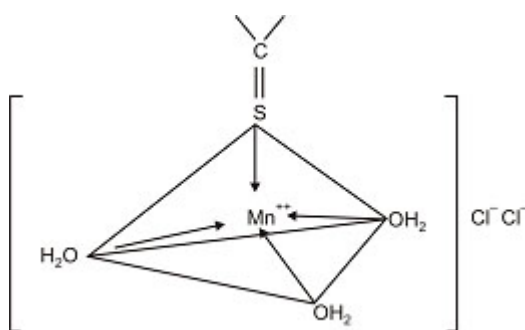
Carbon, hydrogen and nitrogen analyses were performed by microanalysis division RSIC, CDRI, Lucknow. Infrared spectra were recorded in KBr disc on a perkin-Elmer 621 spectrophotometer and reflectance spectra were recorded on a Beckman DU. Spectrophotometer attached with a standard reflectance attachment. MgO was used as a reference. Molar conductance (10^{-3} M) of complexes were measured in DMF using Wiss-Werkstätten weihen obb type LBR conductivity meter. Magnetic measurement were made on gouy balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant.

RESULTS AND DISCUSSION

3-(4'-Pyridyl)-4-phenyl-triazoline-5-thione(PPytTH) forms stable coloured solid and acts as monodentate with Mn(II) and bidentate (N,S) with Co(II), Ni(II), Cu(II), Fe (III) and Ti(III) ion. All complexes are thermally stable up to 250°C and



Scheme 1: (PPyTTH, or I)

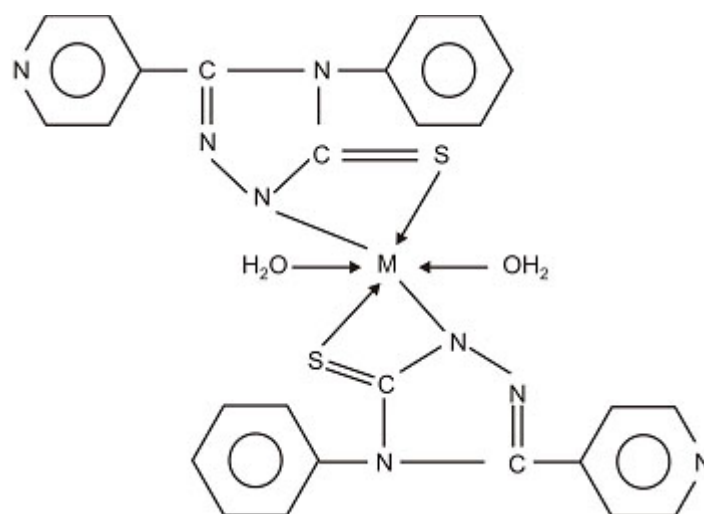


Scheme 2: Td. str of Mn (II) complex cation

they are partially soluble in MeOH, EtOH, CHCl_3 , CCl_4 and petroleum ether. However, fair solubility was attributed in DMF. The 10^{-3} M solution in DMF complexes display molar conductance equal to 160, 90.72 and 85.52 mhos for Mn(II), Fe(III) and Ti(III) complexes respectively indicating their electrolytic nature. However, very low value of molar conductance of Co(II), Ni(II) and Cu(II) complexes reveal their non-electrolytic nature. So, the complexes can be formulated as in Table 1.

Infrared spectra and Nature of Bonding

The ligand (PPyTTH) contains thioamide



Scheme 3: Oh. Str. of complexes Co(II), Ni(II), Cu (II)

group ($\text{H}-\overset{\text{I}}{\text{N}}-\overset{\text{I}}{\text{C}}=\text{S}$) and give rise to four characteristic thioamide bands at 1480 (s) cm^{-1} (Band I), 1290 (s) cm^{-1} and 1240 (m) cm^{-1} (Band II), 1090 (m) cm^{-1} (Band III) and 785 (m) cm^{-1} (Band IV) in the infrared spectra⁴⁻⁶. These bands are affected differently by different modes of coordination. A comparison of the IR spectra of ligand and complexes indicate that simultaneous Metal – N and Metal – S bonding results in a decrease in the frequency of thioamide band IV by 40-80 cm^{-1} . Band II experiences a blue shift of the order of 15 cm^{-1} . Band III is considerably lowered in intensity and thioamide band I is red shifted to the extent of 25 – 50 cm^{-1} . Thioamide band III and band IV have major contribution from $\nu_{\text{C}=\text{S}}$ ⁷. Bonding through only thiocarbonyl sulphur in Mn(II) complexes results red shifting of these bands due to increase in CN bond order and decrease in CS bond order⁸⁻¹⁰.

Far ir spectra of complexes contain some new bands. The new medium intensity bands at 510-520 cm^{-1} and 470-480 cm^{-1} tentatively assigned to $\nu_{\text{M}-\text{N}}$ and $\nu_{\text{M}-\text{O}}$ modes vibrations respectively¹¹. The presence of only one $\nu_{\text{M}-\text{O}}$ band in Co (II), Ni(II), Cu(II), Fe(III) and Ti(III) complexes indicates that their coordinated water molecules are at trans-positions. More than one $\nu_{\text{Mn}-\text{O}}$ bands are in

agreement with the tetrahedral structure of the Mn(II) complex. Metal sulphur stretching mode in all complexes was observed below 400 cm^{-1} .

Magnetic Moment and Electronic spectra

The room temperature (300 K) magnetic moment of Mn(II) complex was found to be 5.81 BM, which indicates five unpaired electrons and divalent oxidation state of manganese in typical tetrahedral structure.¹² All spectral bands in visible region of electronic spectra are above 20000 cm^{-1} which also supports tetrahedral structure. Rao et al¹³, Forster and co-workers¹⁴ and other workers¹⁵⁻¹⁶ have observed that tetrahedral Mn(II) complexes display absorption bands above 20000 cm^{-1} and octahedral Mn(II) complexes exhibit at least one band below 20000 cm^{-1} . The three d-d transition bands at Ca.23809 cm^{-1} , Ca.28100 cm^{-1} and Ca. 29200 cm^{-1} which are assigned to ${}^6\text{A}_1 \rightarrow {}^4\text{E}$ (${}^4\text{G}$ state), ${}^6\text{A}_1 \rightarrow {}^4\text{T}_1$ (${}^4\text{P}$ state), ${}^6\text{A}_1 \rightarrow {}^4\text{A}_2$ (${}^4\text{F}$ state) modes of transition respectively. A relatively higher intensity transition at 33000 cm^{-1} was attributed to CT transition. The spectral band positions suggests the existence of tetrahedral configuration for Mn(II) complex.¹⁷

The magnetic moment of Co(II) complex was observed 4.30 BM which indicated spin free octahedral structure¹⁸. Electronic spectrum of this

Table 1 : Analytical and physical data of complexes

S. No	Complex/(Colour,pH of isolation)	Ωm (DMF, 10^{-3} M) mhos $\text{cm}^2 \text{mol}^{-1}$	μ_{off} BM	% Found/(Calcd)			
				C	H	N	Metal
1.	[Mn(PPytTH) (H ₂ O) ₃] Cl ₂ (Yellow, 6)	160	5.81	36.1 (35.9)	3.8 (3.7)	13.3 (13.0)	13.2 (13.7)
2.	[Co(PPytT) ₂ (Py) ₂] (olive green, 8)	6.31	4.30	60.1 (59.8)	4.0 (3.8)	19.4 (19.3)	8.6 (8.2)
3.	[Ni (PPytT) ₂ (Py) ₂] (Green, 8)	5.21	3.72	60.2 (59.8)	4.1 (3.9)	19.8 (19.4)	8.6 (8.1)
4.	[Cu(PPytT) ₂ (H ₂ O) ₂] (yellow-green, 8)	4.31	1.67	50.8 (51.5)	3.7 (4.6)	18.2 (18.4)	11.2 (10.5)
5.	[Fe (PPytT) ₂ (H ₂ O) ₂] Cl (Yellow-brwon,8)	90.72	6.30	49.8 (49.3)	3.6 (3.4)	17.8 (17.6)	9.1 (8.8)
6.	[Ti (PPytT) ₂ (H ₂ O) ₂]Cl (Yellow, 8)	85.52	1.71	50.2 (49.7)	3.3 (3.5)	18.1 (17.9)	8.2 (8.0)

complex also supports octahedral symmetry around Co(II) and display three bands at 7800 cm^{-1} , 15600 cm^{-1} and 18500 cm^{-1} which are tentatively assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively¹⁸. The value of $Dq = 850\text{ cm}^{-1}$, $B^1 = 780\text{ cm}^{-1}$ and $B = 0.70$ suggest distorted octahedral structure. Besides this, a high energy band at Ca. 23364 cm^{-1} was observed which may be probably due to tetragonal distortion along Z-axis.¹⁹

The magnetic moment of Ni(II) complex was found 3.4 BM which indicate six co-ordinated octahedral geometry²⁰. The reflectance spectrum of this complex supports this observation and shows three major bands at 10400 cm^{-1} , 15900 cm^{-1} and 21300 cm^{-1} of weak intensity assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions respectively and characteristic of octahedral Ni(II) complexes.²¹ The crystal field parameters, $\nu_2 / \nu_1 = 1.52$, $Dq^{XY} = 1040\text{ cm}^{-1}$, $B^1 = 578\text{ cm}^{-1}$ and $B = 0.55$ are calculated putting $\nu_1 = 10400\text{ cm}^{-1}$ and $\nu_2 = 15900\text{ cm}^{-1}$ clearly indicate octahedral structure of the complex.

The low value of B^1 and B puts this ligand towards the strong end of the nephelauxetic series and coordination through sulphur.²²

The Cu(II) complex shows bands at 10700 cm^{-1} , 13200 cm^{-1} and 16000 cm^{-1} probably due to octahedral structure²³ and assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions respectively. The value of magnetic moment (1.67 BM) also supports distorted octahedral structure of complex.

The observed magnetic moment of Fe(III) complex was found to be 6.30 BM which indicate high spin trivalent iron ($s = 5/2$) with $3d^5$ configuration having ground term ${}^6A_{1g}$ and is temperature independent. The reflectance spectra of the Fe(III) complex is consistent with the octahedral nature of the complex. The bands obtained at 14728 cm^{-1} , 19600 cm^{-1} and 22935 cm^{-1} may be assigned to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4E_g$ respectively following Ballhausen²⁴ and Balt et al²⁵. Hence distorted octahedral geometry of this complex may be assigned. The magnetic moment (1.71 BM) of Ti(III) complex suggest d^1 configuration and only one very broad spectral bands centred at 22000 cm^{-1} corresponding to $t_{2g} \rightarrow e_g$ transition and octahedral structure may be assumed.

Thus, on the basis of aforesaid arguments the following tentative structure may be assigned to these complexes.

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