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Thioamide Bands and Nature of Bonding in the Metal Complexes of 3-(4-Pyridyl)-4-Phenyl Triazoline-5-Thione

R.N. PANDEY*, R.S.P. SINGH, (MRS.) RANI KUMARI, S.K. SINHA
and A.N. SAHAY
P.G. Centre of Chemistry (M.U.), College of Commerce,
Patna-800 020, India

3-(4-Pyridyl)-4-phenyl-triazoline-5-thione forms very stable complexes with Ag(I), Co(II), Cu(II), Pd(II) and Hg(II) ions at pH 6 or 7. The ligand coordinates through its thione tautomeric form. The nature of shifts and change in intensity of four thioamide bands of the ligand and complexes are thoroughly analysed. The increase in intensity of thioamide band IV in Hg(II)-complexes (pH $\sim$ 7) probably due to polymeric nature of complexes. The crystal field parameters Dq, B′ and β value were found to be 983 cm^{-1}, 702 cm^{-1} and 0.63 respectively in Co(II)-complexes suggesting the ligand towards strong end of the nephelauxetic series. Tentative structure and metal-ligand vibrations are resasonaly assigned.

INTRODUCTION

Organic molecules having thioamide (H–$\overset{|}{N}$–$\overset{|}{C}$=S) group give rise to four thioamide bands in their infrared spectra[1-3]. These bands are affected differently by different modes of coordination. It has been reported by several workers that the thioamide band IV can be used as diagnostic for M–L bonding [4-7]. However, several other groups of workers[8-11] have indicated that band IV alone cannot be used as a criterion for indicating whether coordination has taken place through S or through N or through both simultaneously. This aspect of coordination is very important and hence this work is concerned with investigation of this aspect of study using 3-(4-pyridyl)-4-phenyl-triazoline-5-thione (PPytTH) and Ag(I), Co(II), Pd(II), Cu(II) and Hg(II) metal ions.

EXPERIMENTAL

All chemicals used were of AnalaR grade or of chemically pure quality.

The ligand was prepared following the method reported in literature[13]. The complexes were prepared in ethanolic medium using a general method. Ethanolic metal salt and ligand solution were refluxed on water bath using M : L = 1 : 2 for 2 hrs. and cooled at room temperature. The pH of the mixture was adjusted 6 or 7 as desired using dil. mineral acid of corresponding salt and NaOH (2N) solution.

Coloured precipitate in every case was obtained which was further washed with ethanol and ether and dried over anhydrous $CaCl_2$ in a vacuum desiccator. The analytical data of complexes are given in Table 1.

RESULTS ADN DISCUSSION

3-(4-Pyridyl)-4-phenyl-triazoline-5-thione forms very stable complexes and it acts as a monodentate ligand with Ag(I), Pd(II), Co(II), Hg(II) ions. However, at pH 7 it forms inert type complex with Hg(II) ion. All are partially soluble in common organic solvents, such as methanol, ethanol, CCl_4, C_6H_6, $CHCl_3$ and petroleum ether. But Co(II) and Pd(II) complexes were fairly soluble in DMF. Magnetic moment of $[Co(PPytTH)_2(H_2O)_2Cl_2]$, $[Cu(PPytTH)(H_2O)_5]SO_4$ and $[Cu(PPytTH)(H_2O)_3Cl_2]$ were found to be 1.5, 1.16, and 0.98 BM respectively. the sub-normal value of magnetic moment of copper complexes is most probably due to polymeric nature of complexes or some degree of metal-metal interaction[13-15]. The polymeric natures of these copper complexes are also supported by their high m.pt. (> 300°C) and their insolubility in organic solvents. The value of magnetic moment lower than spin value of Co(II) complexes may be assumed as ligand is attached to the Co(II) ion by "lower level covalent bonds"[16,17].

In the light of previous observations[18], the value of magnetic moment are possible due to the equilibrium between the thermally accessible $^4T_{2g}$ and ^2E_g states. Moreover, partial oxidation of Co(II) to Co(III) may not be ruled out. Thus, octahedral structure of $[Co(PPytTH)_2(H_2O)_2Cl_2]$ is tentatively assigned on the basis of magnetic moment value and well supported by visible spectral data. Two bands at 17544 and 14286 cm^{-1} are observed due to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition respectively suggesting octahedral geometry[19]. The third expected transition band could not be observed due to instrumental limitation. Thus, putting $\nu_2 = 14286\ cm^{-1}$ and $\nu_3 = 17544\ cm^{-1}$, the value of $Dq = 983\ cm^{-1}$, $B' = 702\ cm^{-1}$ and $\beta = 0.62$. The value of β (0.69) puts the ligand towards the strong end of the nephelauxetic series[20].

Pd(II)-complexes contains one band at 24390 cm^{-1} followed by Iremendous absorption in UV region at 30769 and 37735 cm^{-1}. The band at 24390 cm^{-1} is assigned due to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition[21] and other two bands due to charge transfer having square planar structure. Diamagnetic nature of this complex also supports dsp^2-hybridisation for d^8-electronic configuration of Pd(II) ion. All Hg(II) complexes display charge transfer band between 250–260 nm as expected for d^{10} complexes. The electronic spectra of Cu(II) complexes in Nujol mull weak broad band observed between 560–570 nm are tentatively assigned to $^2T_{2g} \leftarrow {}^2E_g$ transition. The broadness of this band is assumed due to Jahn Teller distortion as expected for d^9 system and distorted octahedral configuration is most probable structure of all Cu(II) complexes.

The infrared spectral data of the ligand and complexes are given in Table 2.

TABLE 1
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Complexes	Colour	pH of Isolation	μ_{eff} (BM)	% Metal		% N		% C		% H	
				Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$[Ag(PPytTH)(H_2O)_3]NO_3 \cdot 3H_2O$	Light Brown	6	Dia.	21.43	20.75	12.96	13.46	28.01	27.69	4.61	4.64
$[Pd(PPytTH)(H_2O)Cl_2]$	Reddish yellow	8	Dia.	25.61	25.48	13.31	13.45	34.56	34.61	3.35	3.36
$[Co(PPytTH)_2(H_2O)_2Cl_2]$	Blue	7	1.5	9.50	9.13	17.68	17.37	45.01	44.58	4.32	4.33
$[Hg(PPytTH)(H_2O)Cl_2]$	Yellow	6	Dia.	37.51	37.72	11.50	11.02	27.34	27.64	2.50	2.51
$[Hg(PPytTH)(H_2O)Br_2]$	Deep brown	6	Dia.	32.98	32.32	9.41	9.03	23.63	23.20	1.95	1.94
$[Hg(PPytTH)(H_2O)I_2]$	Light brown	6	Dia.	28.34	28.07	8.01	7.84	20.53	20.16	1.60	1.68
$[Cu(PPytTH)(H_2O)_5]SO_4$	Yellowish green	7	0.98	13.01	12.90	11.90	11.47	29.34	29.50	4.44	4.54
$[Cu(PPytTH)(H_2O)_3Cl_2]$	Light green	6	1.16	15.01	14.75	13.21	13.11	36.80	36.53	3.99	3.98
$[Hg(PPytT)(H_2O)Cl]$	Light yellow	7	Dia.	41.32	40.50	11.50	11.31	29.62	29.09	2.22	2.10

TABLE 2

IMPORTANT INFRARED BANDS (cm^{-1}) OF THE LIGAND AND COMPLEXES

Compounds	ν_{H_2O}	ν_{SH}	ν_{NH}	Thioamide Bands				NO_3^-/SO_4^{2-}	ν_{M-X}	ν_{M-S}
				I	II	III	IV			
Ligand (PPytTH)	—	2550 mb	3060 mb	1480 s	1290 s 1240 m 1210 m	1090 m	785 m	—	—	—
$[Ag(PPytTH)(H_2O)_3NO_3\cdot3H_2O$	3400 sbr	—	3050 mb	1485 s	1290 m 1270 m 1240 m 1210 m	1070 w	760 s	1340 sb 855 m	—	300 w
$[Hg(PPytTH)(H_2O)Cl_2]$	3400 mb	—	3050 mb	1480 s	1280 w 1240 m 1210 m	1060 m	770 s	—	370 w	310 w 280 w
$[Hg(PPytTH)(H_2O)Br_2]$	3480 mb	—	3065 mb	1480 s	1290 vw 1240 mb 1200 w	1060 m 1050 m	770 s	—	390 w	300 w 290 w
$[Hg(PPytTH)(H_2O)I_2]$	3500 mb	—	3050 wb	1480 m	1255 m 1250 m 1240 m 1210 w	1070 w	775 s	—	380 w	310 w 295 w

TABLE 2 (*Contd.*)

Compounds	ν_{H_2O}	ν_{SH}	ν_{NH}	Thioamide Bands I	II	III	IV	NO_3^-/SO_4^{2-}	ν_{M-X}	ν_{M-S}
$[Hg(PPytT)(H_2O)Cl]$	3360 mb	—	—	1470 m	1280 w 1240 m 1210 m	1080 w	770 s	—	370 w	300 w 290 w
$[Pd(PPytTH)(H_2O)Cl_2]$	3400 mb	—	3100 mb	1480 s	1250 m 1230 m 1220 m 1210 m	1060 m 1040	770 m	—	415 w	370 w
$[Co(PPytTH)_2(H_2O)_2Cl_2]$	3500 mb	—	3060 w	1490 m	1300 w 1290 w 1280 w 1250 w 1210 w	1070 w 1060 w	760 m	—	410 w	380 w
$[Cu(PPytTH)(H_2O)_3Cl_2]$	3400 mb 1590 m	—	3100 m 3080 m 3060 m	1500 m 1490 s	1300 m 1280 w 1250 m 1215 m	1060 m	760 m	—	400 w	380 w
$[Cu(PPytTH)(H_2O)_5]SO_4$	3400 mb 1600 m	—	3050 w	1490 s	1280 w 1250 m 1220 m 1190 w	1070 m	770 m	1125 sb 630 m	—	370 w

M = metal
X = Cl, Br or I

Spectrum of the ligand shows weak bands in the 3000 cm region and above. The complexes also show bands in this region characteristic of aromatic ν_{C-H} and ν_{NH}. Beside this, there are broad bands in the spectra of complexes in the region of 3100–3500 cm^{-1} which may be assigned to coordinated or crystal water. The medium to strong bands in the 1600–1610 cm^{-1} region may be due to $\delta_{NH} + \delta_{OH}$. ν_{N-H} band of the ligand are red shifted (10 cm^{-1}) in almost all complexes most probably due to intermolecular hydrogen in the crystal lattice of all solid complexes. The weak broad band at 2550 cm^{-1} assigned to ν_{SH} of ligand is absent in all complexes indicating the thione form of the ligand in the complexes and metal-sulphur bonding may be assumed. Metal-sulphur bond in all complexes is supported by systematic shift in all thioamide bands[22,23] of the ligand. Thioamide band I ($\delta_{CH} + \delta_{NH} + \nu_{C-N}$) remains almost unchanged or is blue shifted (few cases) band II ($\nu_{C-N} + \nu_{C-S} + \delta_{CH} + \delta_{NH}$) splits and is red shifted. Band III ($\nu_{C-N} + \nu_{C-S}$) and band IV ($\nu_{C\underline{\cdots}S}$) are red shifted. Moreover, in [Hg(PPytT)(H_2O)Cl] simultaneous metal-sulphur and metal-nitrogen bonding results in slight red shift (10 cm^{-1}) of band III seems reasonable with a lowering in intensity. The blue shifting of thioamide band III and band IV due to formation of M–N bonding are probably compensated by red shifting of these bands (III and IV) due to formation of M–S bonding. However, in this complex M–N bonding is stronger than M–S bonding which results slight red shift specially in thioamide band IV. Increase in intensity of band IV may be due to polymeric nature of the complexes.

The very strong broad band at 1340 cm^{-1} and medium band at 855 cm^{-1} in [Ag(PPytTH)$(H_2O)_3$]$\cdot NO_3 \cdot 3H_2O$ indicate the presence of ionic nitrate and in [Cu(PPytTH)$(H_2O)_5$]SO_4 bands at 1125 (sh) and 630 (m) cm^{-1} are consistent with the presence of ionic sulphate[24]. Far infrared spectra of complexes contain some new bands. The weak bands at 510 and 460 cm^{-1} of Ag(I) complex are assigned to ν_{Ag-O} and at 300 cm^{-1} due to ν_{Ag-S} mode of vibrations. The presence of two ν_{Ag-O} modes indicate the presence of two types of coordinated water.

In Cu(II) complexes, ν_{Cu-Cl} (400 cm^{-1}), ν_{Cu-S} (375 ± 5 cm^{-1}), ν_{Cu-O} (480 ± 5 cm^{-1}) and in Co(II) complexes, ν_{Co-Cl} (410 cm^{-1}) and ν_{Co-S}(380 cm^{-1}) are in good agreement with previous literature.

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