

Synthesis and Characterisation of Thioamide Bands in Cr(III) and V(V) Complexes with O- and N-Donor Ligands

VISHAL PATHAK, D.C. YADAV, M.P. GUPTA† and B.K. SRIVASTAVA*
Department of Chemistry, Narain (P.G.) College, Shikohabad (Firozabd), India

Complexes of chromium(III) and vanadium(V) with thiourea have been synthesised in acidic, neutral and alkaline media and characterised by elemental analysis, magnetic measurement, electronic, IR, ¹H NMR, UV-visible studies. The ν(NH) band and thioamide bands I, II, III and IV of the free ligand and their complexes have been analysed and the nature of metal-ligand bonding has been determined in the present paper.

INTRODUCTION

Thiourea is an interesting monodentate ligand coordinating only through sulphur or nitrogen or both. In most of earlier works^{1,2}, only thioamide band IV has been used for the diagnosis of metal-sulphur and metal-nitrogen bonding and changes in positions and intensities of all the four thioamide bands have not been investigated properly. In the present work, elemental analysis, different spectroscopic techniques, magnetic measurements have been used to elucidate the nature of metal-ligand bonding in the complexes of ligand containing a thioamide group.

EXPERIMENTAL

The ligand thiourea used was of E. Merck quality. Metal salts and the solvents were of reagent grade. Ethanolic solutions of chromium salt CrCl₃·6H₂O were mixed with ethanolic solution of the ligand in a desired molar ratio. Vanadium complexes were prepared by using ammonium metavanadate. The solution of the V-salt and the ligand was prepared in hot distilled water. The pH of the mixture was adjusted by using NH₄OH and dil. HCl. The mixture was refluxed on sand bath for about 4 h. The different coloured complexes obtained were filtered, washed with distilled water and with ethanol. The crystals were then dried in an electric oven at 110°C.

Microanalysis of the elements was carried out in microanalytical section of Central Drug Research Institute, Lucknow, India. Metal contents of the complexes were determined by standard methods³. Infrared spectra were recorded on a Perkin-Elmer 577 infrared spectrophotometer in the 4000–200 cm⁻¹ region as nujol or as KBr pellets. Calibration was done by using a polystyrene film. Ultraviolet and visible spectra were recorded in DMF solution on Carry-14 spectrophotometer; magnetic measurements were made at room temperature on the Gouy balance.

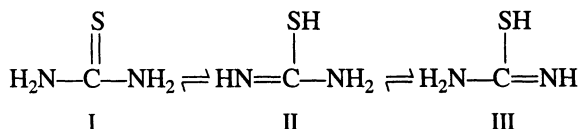
†Department of Chemistry, S. (P.G.) College, Hathras, India.

RESULTS AND DISCUSSION

The complexes were analysed for metal and halogens by standard methods and carbon, hydrogen and nitrogen by microanalytical methods. All complexes were coloured and nonhygroscopic. The complexes were generally insoluble in water and common organic solvents. Hence, its conductivity measurements could not be made. Its molecular weight could not be determined by cryoscopic methods. The analytical data for the complexes are given in Table-1.

The infrared spectra of thiourea have been studied by several workers⁴⁻⁶. On the basis of these works, the thioamide band I appears at 1470 cm^{-1} in the spectrum due to $\nu_{\text{asym}}(\text{CN}_2) + \delta(\text{NH}_2)$ mode of vibrations. The thioamide band II appears in the range of 1430–1390 cm^{-1} due to contribution from $\nu(\text{CN}_2) + \pi(\text{NH}_2) + \nu(\text{C}=\text{S})$. A band appears at 1090 cm^{-1} in the spectrum due to the $\nu(\text{CN}_2) + \pi(\text{NH}_2) + \nu(\text{C}=\text{S})$, modes of vibrations called thioamide III. The thioamide band (IV) appears at 725 cm^{-1} due to the contribution of $\nu(\text{C}=\text{S}) + \nu(\text{CN}_2) + \delta(\text{NH}_2) + \pi(\text{NH}_2)$. These assignments of thioamide bands are in agreement with Suzuki.⁷

The presence of $\nu(\text{SH})$ band at 2660 cm^{-1} in the infrared spectrum of thiourea indicates that it is present in the thione and thiol tautomeric form as shown below:



These thioamide bands undergo different types of changes on complexation of the ligand with metals Cr(III) and V(V) as shown in Table-2.

These observations are in accordance with the works of several earlier workers⁸⁻¹⁰, who investigated the complexes of similar ligand with different metal ions. However, only thioamide band IV has been used in earlier works for the diagnosis of metal-sulphur and metal-nitrogen bondings.

The structure and positions of metal-ligand vibrations have been located and presented in Table-3.

UV-visible spectra of the complexes showed practically no $d \rightarrow d$ transitions due to the use of very dilute solution. Only $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ transition in electronic spectra of the ligand and complexes have been observed. Here, nothing could be interpreted regarding the structure of the complexes on the basis of UV-visible spectra.

The ^1H NMR spectrum of the ligand thiourea indicates the presence of a broad signal centred at $\delta = 6.75$ ppm corresponding to 4 protons and a weak signal at $\delta = 2.05$ ppm corresponding to less than one proton. A sharp signal at 3.0 ppm is due to CH_3COCH_3 protons indicating that thiourea is mainly in thione form and thiol form is in very small percentage.

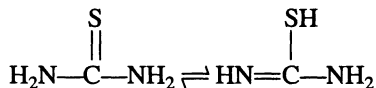


TABLE-I
ANALYTICAL AND MAGNETIC DATA OF THE COMPLEXES

Complexes (Colour)	pH	m.p. (°C)	% found (calcd.)				μ_{eff} (B.M.)
			M	C	H	N	
$[\text{Cr}_2(\text{L})\text{Cl}(\text{H}_2\text{O})_8]\text{Cl}_5 \cdot 3\text{H}_2\text{O}$ (Blue)	10	170-175	17.20 (17.60)	1.98 (2.03)	4.60 (4.40)	2.13 (4.74)	3.9 (36.04)
$\text{H}_4[\text{Cr}(\text{L})_6]\text{Cl} \cdot 3\text{H}_2\text{O}$ (Light green)	4-5	145	8.90 (8.91)	12.50 (12.33)	5.20 (5.50)	35.20 (28.79)	3.9 (6.08)
$[\text{Cr}(\text{L})\text{Cl}_3 \cdot (\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (Bluish green)	7	< 305	18.00 (18.02)	4.49 (4.16)	3.20 (3.40)	10.66 (9.72)	3.9 (36.55 (36.91))
$\text{H}^+[\text{V}(\text{L})_6]\text{H}_2\text{O}$ (Yellowish green)	3-4	42	9.10 (9.68)	13.90 (13.68)	4.50 (5.10)	33.40 (31.94)	Diamagnetic -
$\text{NH}_4^+[\text{V}(\text{L})_6]$ (Yellow)	10	65	9.50 (9.70)	14.90 (13.71)	4.50 (5.30)	33.40 (34.66)	Diamagnetic -
$\text{H}^+[\text{V}(\text{L})_6]\text{H}_2\text{O}$ (Yellow)	7	70	9.50 (9.30)	13.90 (13.70)	4.30 (4.90)	31.11 (32.20)	Diamagnetic -

L = $(\text{NH}_2\text{CSNH}_2)$

TABLE-2
CHANGE IN THIOAMIDE BANDS ALONG WITH THE NATURE OF BONDING

	Thioamide bonds				Inferences
	I	II	III	IV	
Ligand (L) (NH ₂ CSNH ₂)=back5	1470s, sh	1430m, sh 1390w, br	1090w, sh	725w, br	—
[Cr ₂ (L)Cl(H ₂ O)]Cl ₅ · 3H ₂ O	—	—	—	—	Bonding through N as well as S atom
H ₄ [Cr(L) ₆]Cl·2H ₂ O	1470m, sh	1420m, sh	1080w, sh	725w, sh	Absence of bonding through N atom
[Cr(L)Cl ₃ (H ₂ O) ₂]· H ₂ O	1460–1500m v.br	1385w, br	—	—	Bonding through S atom
H ⁺ [V(L) ₆]·H ₂ O	1470s, sh	1435s, sh	1090m, br	720w, br	Bonding through S atom
NH ₄ ⁺ [V(L) ₆]	1470s, sh	1440s, br 1390s, br	1100m, br	725w, sh	Bonding through S atom
H ⁺ [V(L) ₆]·H ₂ O	1470s, br	1410s, br	1080m, br	720m, sh	Bonding through S atom

TABLE-3
STRUCTURE AND POSITIONS OF METAL-LIGAND VIBRATIONS IN COMPLEXES

Complexes	Structure	Metal-ligand band (cm ⁻¹)
[Cr ₂ (L)Cl(H ₂ O) ₈]Cl ₅ ·3H ₂ O	Octahedral	v(Cr—O) (610)
		v(Cr ← OH ₂) (500)
		v(Cr—S) (250)
		v(Cr—Cl—Cr) (230) (bridging)
H ₄ [Cr(L) ₆]Cl·2H ₂ O	Octahedral	v(Cr—S) (240)
		[Cr(L)Cl ₃ (H ₂ O) ₂]·H ₂ O
[Cr(L)Cl ₃ (H ₂ O) ₂]·H ₂ O	Octahedral	v(Cr ← O) (610)
		v(Cr—OH ₂) (500)
		v(Cr—S) (240)
		v(Cr—Cl) (230)
H ⁺ [V(L) ₆]·H ₂ O	Octahedral	π H ₂ O of lattice water (980)
		v(V—S) (360)
NH ₄ ⁺ [V(L) ₆]	Octahedral	v(V—S) (360)
H ⁺ [V(L) ₆]·H ₂ O	Octahedral	v(V—S) (370)

The ¹H NMR spectrum of the complex H₄[Cr(L)₆]Cl·2H₂O contains three broad signals at 7.05 ppm corresponding to 18 protons, at δ = 3.5 ppm corresponding to 8 protons and at δ = 2.05 ppm corresponding to less than 1 proton confirming the presence of six HN=C⁻S—NH₂ ions coordinated to Cr(III) ion. Broadness of the signal at δ = 7.05 ppm is due to quadrupole effect of N atoms

of thiourea and further indicates the equivalence of all the protons of coordinated ligand ions.

The four H^+ ions and 4 protons of two molecules of lattice water gives rise to the broad signal at 3.5 ppm corresponding to 8 protons. A weak signal at $\delta = 2.05$ ppm is due to (NH + SH) protons which are in small percentage of thiol form of coordinated thiourea.

The 1H NMR spectra of the two complexes of vanadium(V), *i.e.*, $H^+ [V(L)_6]H_2O$ (pH = 4) and $H^+[V(L)_6]H_2O$ (pH = 7) are quite similar and show three unresolved multiplet broad signals in the region of $\delta = 5.8$ to 8.0 ppm corresponding to 18 protons of the six coordinated $HN=C\bar{S}-NH_2$ ions. The multiplet broad signal in this region also indicates different magnetic environments of the protons of coordinated ligand ions. The large broadness of these signals is because of quadrupole coupling with N atoms.

There is another very broad and strong signal at $\delta = 4.8$ ppm. It is due to residual protons of D_2O solvent. The two proton signal of one molecule of lattice water is most probably embeded in the broad signal at $\delta = 4.8$ ppm.

The 1H NMR spectrum of the complex $NH_4^+[V(L)_6]$ recorded in D_2O solvent using TMS indicator shows a sharp signal at $\delta = 3.8$ ppm and another multiplet signal at $\delta = 4.9$ ppm. As shown by the integration curve, the number of protons in this complex are one and a half times more than the other V(V) complexes. Other signals are very weak and correspond to much less than one proton. The 1H NMR spectra also confirm the octahedral structures of these complexes.

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