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Synthesis and Spectroscopic Investigations of Coordination Compounds of Mo(VI) with Thiourea

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In continuation of our earlier work on Cr(III) and V(V) complexes with thiourea, Mo(VI) complexes of thiourea were synthesised at different pH. The complexes were soluble in water but insoluble in common organic solvents like ethanol, acetone and carbon disulphide. Their structural features have been investigated on the basis of elemental analysis, IR spectra, ^{1}H-NMR and ^{13}C NMR spectra, which confirm their octahedral structures.

INTRODUCTION

Thiourea and substituted thiourea compounds have been studied by various workers[1–3] for their donor properties, crystal structures[4] and biological activities. In case of thiourea, octahedral, square-planar and tetrahedral complexes are formed and their relative stabilities are determined by electronic rather than steric factors.

Several well characterised complexes of Cr(III), Mo(VI), W(VI), V(V) and Zr(IV) have been prepared but very few of them contain N- and S-containing ligands. Thus, the complexes of Mo(VI) with thiourea at different pH have been prepared and characterised by means of various physico-chemical techniques.

EXPERIMENTAL

Thiourea used was of E. Merck quality. Metal salt was of reagent grade. The complexes were prepared by mixing the solutions of metal salt and ligand prepared in hot distilled water. The pH of the resultant solution was then adjusted and refluxed on sand bath for about 4 h. The mixture was then filtered and crystallised. The crystals were then filtered, washed with acetone and dried in an electric oven at 110°C. The estimation of the metal was done by the method described by Salah Taleb[5].

RESULTS AND DISCUSSION

The complexes formed are stable in air and non-hygroscopic. They are soluble in distilled water and common organic solvents. The analytical data for the complexes are given in Table-1.

TABLE-1
ANALYTICAL DATA OF THE COMPLEXES OF MOLYBDENUM

No.	Complexes	pH	m.p. (°C)	% Analysis, Found (Calcd.)			
				M	C	H	N
I.	$[Mo(L)_3(OH)_3]H_2O$ (Yellowish green)	4	200	24.20 (24.40)	6.59 (9.16)	4.50 (4.30)	22.20 (21.40)
II.	$[Mo(L)(OH_5]OH$ (Green)	7	210	35.10 (35.02)	3.67 (4.38)	3.10 (3.60)	13.40 (10.20)
III.	$[Mo(L)(NH_3)(OH)_4]OH$ (Green)	9–10	190	35.00 (35.02)	4.90 (4.40)	3.70 (4.40)	14.80 (15.30)

L = NH_2CSNH_2

Infrared spectral data are presented in Tables 2 and 3. For a comparison, the spectral data of the ligand (thiourea) is also given.

TABLE-2
ASSIGNMENTS OF MID-RANGE INFRARED ABSORPTION BANDS (cm^{-1})

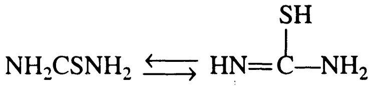
I	II	III	Thiourea	Assignments
	3500s (sh)	3500 (sh)	ν(OH)	ν(OH)
3400 m(sh)				ν(HOH)
3380s (br)				$\nu_{asym}(NH_2)$ + ν(HOH)
	3380m (br)	3380m (br)	3360m(br)	$\nu_{asym}(NH_2)$
3270s (br)	3270s (br)	3280m (v.br)	3260 m (sh)	$\nu_{asym}(NH_2)$
3180 (br)	3180s (br)	3170s (br)	3180m (br)	ν(NH)
3040m (sh)				ν(OH) (H-bonded)
1600 m (sh)	1585s-s(sh)	1610 m sh	1600 s (sh)	$\delta(NH_2)$
1470 m (sh)	1465 m (sh)	1465 m (sh)	1470s (sh)	Thioamide band I
1400m (sh)	1405s (br)	1400s (br)	1430 m (sh) and 1390 w (br)	Thioamide band II
1090 w (br)	1090 w (sh)	1080 w(sh)	1090 w (sh)	Thioamide band III
	690 m (br)	670 m (sh)	725 w (br)	Thioamide band IV Red shifted by 55 cm^{-1} in complex III
930 w (br)				
890 w (br)				$\pi(H_2O) + \pi(OH)$
850 w (br)				
	935 m (br)			π(OH) of coordinated groups
	885s (br)	920m (sh)		
	850 m (br)	870 s (br)		
		835 m (sh)		Coordinated NH_2
720 w (sh)				Coordinated through S-atom
670 w (sh)				
630 w (br)				

TABLE-3

ASSIGNMENTS OF THE FAR-INFRARED (cm^{-1}) ABSORPTION SPECTRA

I	II	III	Thiourea	signments
	630 m (sh)	630 m (br)	630 w	ν(C=N)+ν(C=S)
610 w (br)	560 (w)		620 w	ν(Mo—O)
590 w (br)		560 w (br)		ν(Mo—O)
470 w (br)	470 m (br)	470 m (br)	470 m (br)	δCNS +δCN_2 + πNH_2
210 m (sh)				ν(Mo—S)
	390 (w)**	390 m(br)		ν(Mo—N) (Compd. III)
	360 (w)**	*360m (br)		**ν(Mo←OH) (Compd. II)
	330 (vw)**	*360 m (br)		*ν(Mo←OH_2)(Compd. III)
	300 (vw)			
	280 (vw)	250 w (sh)		*ν(Mo—S)

There is a new shoulder band at 3400 cm^{-1} in the spectrum of complex $[Mo(L)_3(OH)_3]H_2O$ due to $\nu(H_2O)$ mode of vibration of lattice water[6, 7]. A broad and strong band at 3180 cm^{-1} is present in the spectrum of the ligand and complexes $[Mo(L)_3(OH)_3]H_2O$ and $[Mo(L)(OH)_5]OH$ which is associated with the ν(N—H) band[8, 9]. This band does not change its position on coordination indicating the absence of coordination through imino N-atom.



$$NH_2CSNH_2 \rightleftharpoons HN{=}\overset{\displaystyle SH \atop |}{C}{-}NH_2$$

The δNH_2 band of the ligand observed at 1600 cm^{-1} remains in the same position in complex I indicating the absence of coordination of metal ion through N-atom. This band gets red shifted to 1585 cm^{-1} in complex II and blue shifted to 1610 cm^{-1} in compound III. In complex I, there is a sharp and medium band at 210 cm^{-1} which is assigned to ν(Mo—S) mode of vibration[10, 11]. Two new bands at 610 and 590 cm^{-1} may be assigned to ν_{sym}(Mo—O) and ν_{asym}(Mo-O) modes of vibrations. Solubilities in water and low m.p. suggest its monomeric nature.

The spectrum of the ligand shows a doublet band at 630 and 620 cm^{-1} which have been assigned previously to ν(C—S)+ ν(C—N) and out-of-plane vibration by some workers[12]. The band at 630 cm^{-1} remains unaltered in compounds II and III in position and intensity of coordination but the band at 620 cm^{-1} disappeared supports the coordination of the ligand to metal ion through thiocarbonyl S-atom.

The 1H-NMR spectrum of the complex [Mo(L)3(OH)3]·H2O contains a broad signal at $\delta = 7.2$ ppm corresponding to 9 protons of three coordinated $H{-}N{=}\underset{| \atop S}{C}{-}NH_2$ ions. Equivalence of all these 9 protons indicates that the three coordinated groups are in the same magnetic environment. The presence of a very broad signal centred at $\delta = 5.05$ is due to the residual water molecule of D_2O

solvent. The signals at $\delta = 0.5$ to 3.8 ppm are due to 2 protons of lattice water molecule and 3 protons of coordinated hydroxyl groups. This confirms the different magnetic environments of the 3 coordinate —OH groups and protons of one molecule of lattice water.

The ^{1}H-NMR spectra of the complex $[Mo(L)(OH)_5]OH$ contains a very broad signal centred at $\delta = 7.2$ ppm corresponding to 3 protons of one molecule of coordinated thiourate ion. A very broad signal at 4.8 ppm corresponds to the residual H_2O molecules of the solvent D_2O. The 5 protons of the coordinated 5 —OH groups are most probably embedded in H_2O signal at $\delta = 4.8$ ppm. A rapid exchange between NH and NH_2 protons causes equivalent magnetic environment.

The ^{13}C-NMR spectrum of the above complex contains only one sharp signal at $\delta = 184.476$ ppm of intensity 6.598. It confirms that the single coordinated thiourea molecule contains only one type of C atom in the molecule of $[Mo(L(OH)_5]OH$.

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