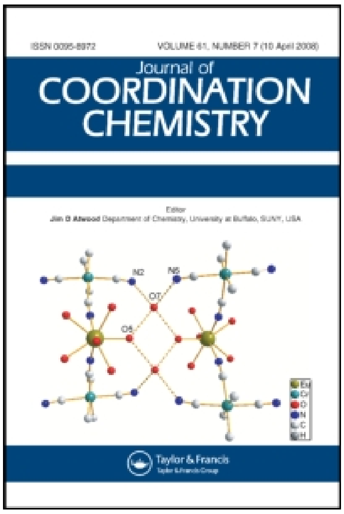

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Mixed ligand complexes of tungsten(VI) containing aroyl hydrazones and isothiocyanate

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Mixed ligand complexes of tungsten(VI) containing aroyl hydrazones and isothiocyanate

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Five complexes [$WO(NCS)_4L–L$] (where L–L = benzoic acid[1-(Furan-2-yl)methylene] hydrazide(BFMH), benzoic acid[(thiophen-2-yl)methylene]hydrazide(BTMH), benzoic acid [1-(thiophen-2-yl)ethylidene]hydrazide(BTEH), benzoic acid(phenylmethylene)hydrazide (BPMH) and benzoic acid[1-(anisol-3-yl) methylene]hydrazide(BAMH)) have been prepared by reaction of ammonium tetraisothiocyanatodioxotungstate(VI) with the corresponding ligand in aqueous medium in the presence of hydrochloric acid. The complexes have been characterized by elemental analysis, molar conductivity, magnetic moment measurements, IR, electronic spectra, thermogravimetric analysis TGA/DTA and ^{1}H NMR.

Keywords: Tungsten; Hydrazones; Isothiocyanate; Oxo

1. Introduction

Transition metal oxo-compounds hold an important place in the field of oxygen atom transfer processes in a wide range of catalytic reactions. Several molybdenum oxo, dioxo or μ-oxo complexes bearing various ligands which exhibit exceptional oxygen atom transfer capability either under stoichiometric or catalytic condition have been reported [1–4]. Several tungsten enzymes are known [5–7] and many models have been synthesized and studied [8, 9]. Moreover, tungsten-oxo and peroxo are also known to be active in oxidation reactions especially in aqueous medium [10]. However, oxo-tungsten(VI) complexes are few, probably because of non availability of suitable starting materials. In the present study, we use $(NH_4)_2[WO_2(NCS)_4]$ (obtained by interaction of $Na_2WO_4 \cdot H_2O$ and NH_4NCS in aqueous medium in presence of HCl by the reported method [11]) as starting material. The SCN^- ion is a good ligand and numerous thiocyanate complexes which may be either S- or N-bonded are usually analogues of halide complexes. The presence of large ligands in the coordination sphere tends to strain M–SCN and promote M–NCS bonding [12, 13]. In the present work we use aroyl hydrazones as ligands due to the broad applications of metal complexes of aroyl hydrazones in biological processes, such as in treatment of tumors, tuberculosis, leprosy, and mental disorder [14–17]. They are also known to act as herbicides, insecticides and

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acaricides [18, 19]. The biological activity of complexes has been attributed to complex-forming abilities of ligands with the metal ions present in cells [20].

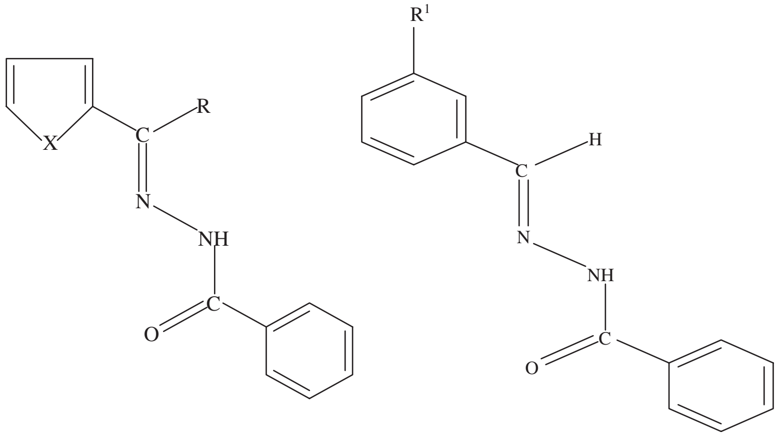
The present article describes the synthesis and characterization of some isothiocyanato complexes of oxotungten(VI) with aroyl hydrazone ligands *viz.*, benzoic acid [1-(Furan-2-yl)methylene]hydrazide(BFMH), benzoic acid[(thiophen-2-yl)methylene] hydrazide (BTMH), benzoic acid[1-(thiophen-2-yl)ethylidene]hydrazide(BTEH), benzoic acid(phenyl methylene)hydrazide(BPMH) and benzoic acid[1-(anisol-3-yl) methylene]hydrazide(BAMH), using $(NH_4)_2[WO_2(NCS)_4]$ as precursor [11].

The structures of ligands are given in scheme 1.

2. Experimental

2.1. *Reagents and reaction conditions*

Reagent grade furfuraldehyde (Himedia), thiophen-2-carboxaldehyde (Himedia), 2-acetyl thiophene (Himedia), benzaldehyde (Ranbaxy), anisaldehyde (Himedia) and benzhydrazide (Fluka) were used as received. The solvents used for the synthesis of ligands were distilled before use. Sodium tungstate and other chemicals were of reagent grade and used without further purification. The ligands were prepared by the reported method [21]. Carbon, hydrogen, nitrogen and sulfur were analyzed microanalytically using CHNS analyzer Leco model-932. Tungsten analysis was done by gravimetric method [22]. Molar conductivity was measured in DMF (10^{-3} M) at room temperature using an Elico conductivity bridge, type CM82T and a conductivity cell with cell constant of 0.74. Magnetic susceptibility of the complexes was recorded at room temperature using Guoy's balance and $Hg[Co(NCS)_4]$ as a standard. IR spectra of the complexes were recorded over the region 4000–500 cm^{-1} on a Perkin Elmer spectrophotometer using KBr discs. The electronic spectra of the complexes were recorded using a double beam UV-spectrophotometer type SL-164.



Scheme 1. (1) BFMH where X = O; R = H (2) BTMH where X = S; R = H (3) BTEH where X = S; R = CH_3 (4) BPMH where R^1 = H (5) BAMH where R^1 = OCH_3.

Thermogravimetric analyses (DTA-DTG-TG) were recorded on a Perkin-Elmer (Pyris Diamond) thermoanalyzer at heating rate of 10°C min.$^{-1}$ under nitrogen.

2.2. *Preparation of complexes*

In a typical preparation of complex, sodium tungstate dihydrate (0.00363 mol) and ammonium thiocyanate (0.038 mol) were dissolved in water (30 mL) at room temperature and 7.5 mL of 11 M HCl was added to the reaction mixture. The resulting yellow solution was cooled in an ice bath and ethanolic solution (10 mL) of the corresponding ligand (L–L) (0.00363 mol), where L–L = BFMH, BTMH, BTEH, BPMH and BAMH, was added to the solution. The reaction mixture was left undisturbed for one hour in an ice bath. The precipitates formed were filtered under suction, washed three to four times with water containing a few drops of HCl and dried *in vacuo*.

$$\mathrm{Na_2WO_4 \cdot 2H_2O + 4NH_4SCN \xrightarrow{H^+} (NH_4)_2[WO_2(NCS)_4] + 2NH_4OH + 2Na^+}$$

$$\mathrm{(NH_4)_2[WO_2(NCS)_4] + L - L \xrightarrow{H^+} [WO(SCN)_4L - L] + 2NH_4OH}$$

3. Results and discussion

The analytical and physico-chemical results (table 1) showed that all complexes are mononuclear with general formula [WO(NCS)$_4$L–L] (where L–L = BFMH, BTMH, BTEH, BPMH, BAMH). All complexes are colored, stable in air and soluble in DMSO and DMF. Moreover, magnetic susceptibility measurements at 30°C indicate the diamagnetic nature of the complexes.

3.1. *Conductance measurement*

The molar conductivity of these complexes measured in 10^{-3} M DMF is in the range 15–21 mho cm^2 mol^{-1}, much less than the value 70–160 mho cm^2 mol^{-1} for 1 : 1 electrolytes in DMF. Thus, these complexes are non-electrolytic in nature.

3.2. *Infrared spectra*

The IR spectra of all the complexes exhibit a band in the region 938–971 cm^{-1} due to ν(W=O). The bands for ν(CN), ν(CS) and ν(NCS) were observed in the spectra of the complexes at 2054–2075, 761–789 and 480–498 cm^{-1}, respectively, suggesting that the thiocyanate is N–bonded [23]. In the spectra of free ligand ν(N–H) at ca 3250 and ν(C=N) ca 1640 cm^{-1} indicate that ligands exist in keto form. The bands appearing in the spectra of the ligands ca 1660 and 1640 cm^{-1} are attributed to amide ν(C=O) and ν(C=N) modes, respectively [24]. The presence of ν(N–H) bands in the spectra of the complexes suggest that all ligands remain protonated in chelation. The amide bands ν(C=O) and ν(C=N) shift to lower frequencies (table 2) in the spectra of complexes suggesting involvement of

Table 1. Analytical data and physical properties of the complexes $WO(NCS)_4L–L$.

					% Found (Calcd)					
S. No.	Complex	Mol. wt. ($g\,mol^{-1}$)	Color	Decomp. temp. (°C)	C	H	N	S	W	Molar conductivity $mho\,cm^2\,mol^{-1}$
1	$WO(NCS)_4BFMH$	646.63	Brown	190	30.09 (29.71)	1.56 (1.55)	13.16 (12.99)	20.06 (19.83)	28.04 (28.43)	
2	$WO(NCS)_4BTMH$	662.70	Black	210	29.35 (28.99)	1.52 (1.52)	12.84 (12.68)	24.19 (24.46)	27.52 (27.74)	20
3	$WO(NCS)_4BTEH$	676.72	Brown	195	30.53 (30.17)	1.79 (1.78)	12.57 (12.41)	23.95 (23.69)	26.98 (27.16)	18
4	$WO(NCS)_4BPMH$	656.67	Light yellow	215	33.33 (32.92)	1.85 (1.84)	12.96 (12.79)	19.75 (19.53)	27.84 (27.99)	21
5	$WO(NCS)_4BAMH$	686.69	Yellow	210	33.62 (33.23)	2.06 (2.05)	12.38 (12.23)	18.87 (18.67)	26.54 (26.77)	15

carbonyl oxygen and azomethine nitrogen in coordination [25]. These observations suggest that the ligands are bidentate chelating, coordinating metal through carbonyl oxygen and azomethine nitrogen.

3.3. *Electronic spectra*

The electronic spectra (table 3) of the complexes dissolved in DMF exhibit two peaks in the region 480–495 and 620–650 nm. The first intense peak is due to the ligand to metal charge transfer transitions of oxo-tungsten [26]. The second peak of low intensity and low energy is unexpected in W(VI) complexes but has been found in some dioxomolybdenum complexes [27].

3.4. *TGA/DTA studies*

The TGA curve of [$WO(NCS)_4$(BTEH)] shows an initial weight loss of 17.83% up to 350°C corresponding to loss of C_6H_5CONH (calculated weight loss = 17.73%). The intermediate formed is thermally stable to 800°C. Further heating results in loss of 7.25% which corresponds to loss of one SCN at 850°C (calculated weight loss = 8.00%). After this no weight loss is observed to 1000°C, indicating a stable complex of composition [$WO(NCS)_3C_6H_6SN$] is formed.

3.5. *^{1}H NMR spectra*

The ^{1}H NMR spectra of ligands in DMSO show low field signals at 11.8–11.4 ppm for the imino proton confirming existence of the ligands in keto form. The CH=N is

Table 2. Important IR spectral bands (cm^{-1}) and their assignments.

S. No.	Complex	ν(W = O)	ν(C–N)	ν(C–S)	ν(NCS)	ν(C = O) (Ligand)	ν(C = N) (Ligand)	ν(N–H)
1	$WO(NCS)_4$BFMH	942	2062	789	488	1636 (1660)	1610 (1640)	3260
2	$WO(NCS)_4$BTMH	958	2062	782	480	1647 (1665)	1630 (1645)	3251
3	$WO(NCS)_4$BTEH	944	2054	775	489	1648 (1666)	1604 (1638)	3258
4	$WO(NCS)_4$BPMH	971	2075	761	498	1640 (1662)	1601 (1635)	3265
5	$WO(NCS)_4$BAMH	938	2075	780	495	1628 (1657)	1605 (1639)	3268

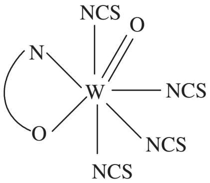
Table 3. Electronic spectra of complexes.

S. No.	Complex	L → M CT (nm) (ε, Litre $mol^{-1} cm^{-1}$)
1	$WO(NCS)_4$BFMH	490(4860)
2	$WO(NCS)_4$BTMH	481(4850)
3	$WO(NCS)_4$BTEH	482(5200)
4	$WO(NCS)_4$BPMH	495(5150)
5	$WO(NCS)_4$BAMH	484(5250)

observed at 8.40–8.60 ppm; aromatic protons occur as multiplets between δ 6.4–7.8 ppm. The resonance due to CH_3 in BTEH occurs at 2.43 ppm. The spectra of all complexes show low field signals for imino proton at nearly the same δ value as that of corresponding free ligand. The CH = N peak in complexes is shifted towards higher delta (8.70–8.85) due to deshielding because of bonding of azomethine nitrogen with tungsten.

4. Conclusion

All complexes are monomeric with composition, $WO(NCS)_4L–L$ (where L–L = BFMH, BTMH, BTEH, BPMH and BAMH) with + 6 oxidation state for W. The proposed structure is given below:



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