

## Synthesis of some molybdenum(V) and tungsten(V) complexes of 1-aryl-2,5-dithiohydrazodicarbonamides

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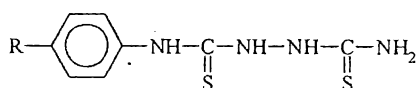
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Molybdenum and tungsten complexes of the type  $M_2O_4L_2(H_2O)_2$  [where  $M = Mo^V, W^V$ ,  $LH = 1\text{-phenyl-2,5-dithiohydrazodicarbonamide (PTHCH)}$ ,  $1\text{-}p\text{-methylphenyl-2,5-dithiohydrazodicarbonamide (MePTHCH)}$ ,  $1\text{-}p\text{-methoxyphenyl-2,5-dithiohydrazodicarbonamide (MeOPTHCH)}$ ,  $1\text{-}p\text{-chlorophenyl-2,5-dithiohydrazodicarbonamide (ClPTHCH)}$ ] have been synthesized. The complexes are non-ionic and diamagnetic in nature. Although the complexes are ESR inactive, +5 oxidation state of the metal ions in octahedral geometry has been suggested. IR and electronic spectral studies indicate dinuclear-type of complexes with  $M_2O_4^{2+}$  moiety. Monoanionic bidentate mode of bonding for all the ligands is suggested. X-Ray powder diffraction of the complexes exhibits amorphous nature of the complexes.

In continuation of a few molybdenum and tungsten complexes reported from this laboratory<sup>1</sup> and application of molybdenum and tungsten complexes of dithiohydrazodicarbonamides as effective extreme pressure lubrication additives<sup>2</sup>, the present communication reports synthesis and characterization of a series of molybdenum and tungsten complexes of various substituted dithiohydrazodicarbonamides (Fig. 1) and their characterization by various physicochemical techniques.



R = H, 1-phenyl-2,5-dithiohydrazodicarbonamide (PTHCH)

R =  $CH_3$ , 1-*p*-methylphenyl-2,5-dithiohydrazodicarbonamide (MePTHCH)

R =  $O-CH_3$ , 1-*p*-methoxyphenyl-2,5-dithiohydrazodicarbonamide (MeOPTHCH)

R = Cl, 1-*p*-chlorophenyl-2,5-dithiohydrazodicarbonamide (ClPTHCH)

Fig. 1

### Results and discussion

The analytical data are in accord with the compositions of the complexes. All the compounds decomposed above 200°. The amount of water in the hydrated complexes was determined. The weight loss by heating the complex up to 120° was found almost negligible. However, further heat-

ing in the range 120–160° resulted in weight loss corresponding to two water molecules. This has been confirmed by metal analysis of the resulting anhydrous complex. Removal of water molecules at relatively higher temperature indicates coordinated nature of the water molecules. This contention is further supported by identification of a band in IR spectra of hydrated complexes at  $\sim 850\text{ cm}^{-1}$ .

All the complexes are almost insoluble in common organic solvents but, comparatively, more soluble in coordinating solvents like DMF, DMSO. Molar conductance values in DMF indicate non-ionic nature of all the complexes. X-Ray powder diffraction of the complexes shows no d-lines but a diffused broad band, which indicates the amorphous nature of these complexes.

As indicated by the analytical data, the complexes of the types  $M_2O_4L_2(H_2O)_2$ , where  $M = Mo^V$  or  $W^V$  and  $LH = PTHCH, MePTHCH, MeOPTHCH, ClPTHCH$ , are most likely to be formed.

All the synthesized complexes exhibit diamagnetic behaviour instead of showing magnetic moment due to one electron expected for  $Mo^V$  and  $W^V$ . Diamagnetism shown by above complexes may be due to complete spin neutralization in a dimer. The two metal centers each with  $d^1$  configuration, have strong antiferromagnetic exchange within the molecule. Thus, these observations are indicative of dinuclear structure of the complexes<sup>3</sup>.

Electronic spectra of all the complexes in DMF show two bands around 14500 and  $18500\text{ cm}^{-1}$  assignable to  $^2B_2$

**Table 1.** Important IR spectral data (cm<sup>-1</sup>) and their assignments

Complex	$\nu(\text{OH})$	$\nu(\text{NH})$ $\nu(\text{NH}_2)$	Thioamide I ( $\beta\text{NH} + \nu\text{CN}$ )	Thioamide II ( $\nu\text{CN} + \beta\text{NH}$ )	Thioamide IV $\nu(\text{C}=\text{S})/\nu(\text{C}-\text{S})$	$\nu\text{NH}_2$	$\nu(\text{N}-\text{N})$	$\nu(\text{M}=\text{O}_1)$	$\nu(\text{M}-\text{O}_b-\text{M})$
PTHCH		3420–3390 3210–3150	1500	1300	840	1640	900		
$\text{Mo}_2\text{O}_4(\text{PTHCH})_2(\text{H}_2\text{O})_2$	3500	3400–3380 3250–3180	1560	1390	830, 700	1640	930	960	740 480
$\text{W}_2\text{O}_4(\text{PTHCH})_2(\text{H}_2\text{O})_2$	3500	3420–3390 3250–3190	1540	1400	820, 720	1645	920	940	700
MePTHCH		3400–3380 3220–3100	1510	1310	850	1650	910		
$\text{Mo}_2\text{O}_4(\text{MePTHCH})_2(\text{H}_2\text{O})_2$	3500	3400–3385 3250–3185	1570	1410	840, 710	1650	940	965	745 490
$\text{W}_2\text{O}_4(\text{MePTHCH})_2(\text{H}_2\text{O})_2$	3500	3410–3380 3250–3190	1580	1400	830, 740	1655	950	930	710
MeOPTHCH		3400–3350 3250–3150	1520	1290	840	1640	900		
$\text{Mo}_2\text{O}_4(\text{MeOPTHCH})_2(\text{H}_2\text{O})_2$	3500	3405–3355 3250–3195	1580	1395	830, 700	1635	940	970	750 490
$\text{W}_2\text{O}_4(\text{MeOPTHCH})_2(\text{H}_2\text{O})_2$	3600	3400–3360 3250–3200	1560	1410	835, 740	1630	920	940	720
CIPTHCH		3410–3380 3260–3150	1500	1320	860	1635	910		
$\text{Mo}_2\text{O}_4(\text{CIPTHCH})_2(\text{H}_2\text{O})_2$	3600	3400–3380 3250–3195	1580	1410	840, 720	1635	940	960	740 480
$\text{W}_2\text{O}_4(\text{CIPTHCH})_2(\text{H}_2\text{O})_2$	3600	3400–3390 3250–3200	1590	1400	840, 720	16.30	950	935	700

$\rightarrow {}^2E$  and  ${}^2B_2 \rightarrow {}^2B_1$  transitions, respectively, supporting six coordinated (+5) oxidation state of metal ion. The band around 22500 cm<sup>-1</sup> indicates the presence of  $\text{M}_2\text{O}_4^{2+}$  moiety<sup>4</sup> in all the complexes. Besides, an intense band at  $\sim 370$  nm is in spectra of all the complexes, is assigned as charge transfer band. The electronic spectra, therefore, support the dinuclear structure of the complexes.

All the complexes are ESR inactive, indicating dinuclear structure of the complexes as discussed on the basis of magnetic moment and electronic spectral studies<sup>5</sup>.

<sup>1</sup>H NMR spectrum of the ligand PTHCH<sup>6</sup> exhibits D<sub>2</sub>O exchangeable resonance signals at  $\delta$  9.7 (2H, s, -NH-NH-) and 2.6 (2H, s, -NH<sub>2</sub>). Aromatic protons together with NH protons are observed at  $\delta$  6.7–7.8 (m). However, spectrum of its molybdenum complex shows -NH-NH- proton signals at  $\delta$  9.5 ppm due to one proton only, supporting the view that one proton has undergone deprotonation after thioenolization to form the complex. Other proton signals of the ligand have undergone a little deshielding in the com-

plex as the electronic environment around them has changed to some extent after complexation.

<sup>13</sup>C NMR spectra of the ligand PTHCH and its Mo<sup>V</sup> complex show a group of peaks at 123.6–139.1 and 123.6–141.2 ppm, respectively assignable to aromatic carbon atoms<sup>7</sup>. The number of carbon atoms observed in the spectra agrees with number of carbon atoms present in the ligand and its complex. Besides, the spectrum of the ligand is characterized by a peak at 176.8 ppm which may be due to C=S groups<sup>7</sup>. However, in the spectrum of the complexes, C=S groups are observed at 162.7 and 161.2 ppm, indicating different electronic environment around both the C=S groups upon complexation.

The IR spectrum of the ligand phenyldithiohydrazodicarbonamide (PTHCH) exhibits four bands at 3420, 3390, 3210 and 3150 cm<sup>-1</sup> which are assigned to  $\nu\text{NH}(\text{NH}_2)$ ,  $\nu\text{NH}(\text{Ar}-\text{NH}_2)$  and  $\nu\text{NH}(-\text{NH}-\text{NH}-)$  respectively<sup>6</sup>. These bands appear respectively at 3400, 3380, 3220 and 3100 cm<sup>-1</sup> in case of MePTHCH, at 3400, 3350, 3250 and 3150

$\text{cm}^{-1}$ , in case of MeOPTHCH and at 3410, 3380, 3260 and  $3150\text{ cm}^{-1}$  in case of ClPTHCH ligands. The position of the first two bands remains almost unaffected in all the molybdenum and tungsten complexes, indicating that the primary amino nitrogen is not involved in the coordination. The third ligand band becomes broad and the fourth one is absent in the complexes, suggesting that at least one of the  $>\text{NH}$  groups is involved in the coordination and formation of the deprotonated complex. In all the ligands, thioamide IV bands appear around  $840\text{ cm}^{-1}$  which is mainly due to  $\nu\text{C}=\text{S}$  stretching. In the complexes of these ligands thioamide IV bands remain almost unchanged and a new band appears at  $700\text{--}720\text{ cm}^{-1}$  (C–S), suggesting that one of the (C=S) groups is not involved in the coordination. The appearance of a new band at  $700\text{--}720\text{ cm}^{-1}$  in the spectra of the complexes indicates the coordination of the metal through the 'thiolo' sulfur<sup>8</sup>.

The  $\beta\text{-NH}_2$  band observed around  $1640\text{ cm}^{-1}$  in all complexes indicates that the primary amino nitrogen is not involved in the bonding. The  $\nu\text{N-N}$  ligand band around  $1080\text{ cm}^{-1}$  undergoes a positive shift of  $20\text{--}40\text{ cm}^{-1}$  in all the complexes which is indicative of the involvement of one of the hydrazinic nitrogens in the coordination<sup>9</sup>.

Thioamide band-I [ $\beta\text{NH} + \nu\text{CN}$ ] and thioamide band II [ $\nu\text{CN} + \nu\text{NH}$ ]<sup>10</sup> occurring in the ligands at  $\sim 1500$  and  $\sim 1300\text{ cm}^{-1}$ , respectively, undergo higher energy shift of  $20\text{--}90\text{ cm}^{-1}$  in the complexes due to the reduction of C=S bond order from two to one and increase in C–N bond order from one to two as a result of thioenolization.

IR spectra of all the complexes contain a new band at  $\sim 3500$  and  $\sim 850\text{ cm}^{-1}$  which are assigned to the stretching and rocking modes of the coordinated water molecules. In case of all the molybdenum complexes, the bands around 960, 740 and  $480\text{ cm}^{-1}$  are due to  $\nu\text{Mo}=\text{O}_t$ ,  $\nu_{\text{as}}\text{Mo}-\text{O}_b-\text{Mo}$  and  $\nu_s\text{Mo}-\text{O}_b-\text{Mo}$  respectively (where  $\text{O}_t$  and  $\text{O}_b$  stand for terminal and bridged oxygens). The spectra of the tungsten complexes exhibit  $\nu\text{W}=\text{O}_t$ ,  $\nu_{\text{as}}\text{W}-\text{O}_b-\text{W}$  and  $\nu_s\text{W}-\text{O}_b-\text{W}$  at around 940, 700 and  $500\text{ cm}^{-1}$  respectively<sup>4</sup>.

Based on the results discussed above, it is suggested that the ligands used for synthesis of complexes act as monoanionic bidentate through one of the hydrazinic nitrogens and sulfur formed by thioenolization resulting into five membered chelate ring.

## Experimental

All the chemicals used in this study were of A.R. grade. The ligands 1-aryl-2,5-dithiohydrazocarbonamides were

prepared by refluxing thiosemicarbazide with appropriate arylisothiocyanates in 50% ethanol as described in literature<sup>11</sup>.

### Preparation of the complexes :

For preparation of the molybdenum complexes sodium molybdate (0.482 g, 20 mmol) was dissolved in water (50 ml) and pH of the solution was maintained at  $\sim 2$  by adding dil. HCl. To this solution ethanolic solution (50 ml) of the corresponding ligand ( $\sim 20$  mmol) was added with constant stirring. The reaction mixture was digested by heating on a water-bath for  $\sim 1$  h. The precipitate obtained was washed with hot water followed by diethyl ether and dried *in vacuo* for 20 min.

For the tungsten complexes, sodium tungstate (0.660 g, 20 mmol) was dissolved in water (50 ml) and pH of the solution was adjusted to  $\sim 2$  by adding dil. HCl. It was filtered and to the filtrate hot ethanolic solution (50 ml) of the corresponding ligand ( $\sim 20$  mmol) was added dropwise with constant stirring. The reaction mixture was digested by heating on a water bath for  $\sim 0.5$  h. The resulting brown precipitate was washed with hot water, ethanol followed by diethyl ether and finally dried *in vacuo* for 20 min.

The complexes were analyzed for metal and sulfur gravimetrically.

Room temperature magnetic susceptibility was measured on a Cahn Faraday electrobalance using cobalt mercury tetrathiocyanate as a calibrant. Electrical conductance of the complexes was measured at room temperature in  $10^{-3}\text{ M}$  DMF on a Pye conductivity meter. Electronic spectra (DMF) were recorded on a Cary-14 spectrophotometer, IR spectra (KBr) on a Perkin-Elmer 783 spectrophotometer and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra ( $\text{DMSO}-d_6$ ) on a JEOL FX 90 Q spectrometer using tetramethylsilane as an internal standard.

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## Note

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