

## NOTE

**Phenoxy Derivatives of Bis (pyridine) Tungsten(VI)  
Disulphidodichloride**

P. DABAS† and M.K. RASTOGI\*

*Department of Chemistry  
Hindu College, Delhi-110 007, India*

A number of phenoxy derivatives of tungsten(VI) disulphidodichloride in pyridine solution have been synthesized. Their physical characteristics, magnetic susceptibility, electronic and IR spectra are reported.

Tungsten(VI) disulphidodichloride has been reported<sup>1</sup>. When treated with monohydric phenols in 1 : 2 ratio in pyridine solution, both the chlorine atoms are substituted by respective phenoxy groups to give diphenoxy derivatives. But in di- and trihydric phenols having two hydroxyl groups in *ortho* position, both chlorine atoms are substituted by chelating phenoxy groups. Two molecules of pyridine crystallize with the product. Special precautions were taken to exclude moisture from apparatus and chemicals. Pure phenols (after recrystallization or distillation) were used in the synthesis. Tungsten was estimated as 8-hydroxyquinolate and weighed as  $WO_3$ .<sup>2</sup> Nitrogen, carbon and hydrogen were estimated by microanalytical method.

**Preparation of bis (pyridine) tungsten(VI) disulphidodiphenoxide**

To 0.80 g (0.0025 mol) tungsten(VI) disulphidodichloride in 50 mL pyridine was added 0.55 g (0.006 mol) of phenol and the mixture was refluxed at *ca.* 115°C for 45–48 h. The reaction mixture was cooled and filtered through G-4 sintered glass disc. The filtrate was evaporated under reduced pressure at 40–50°C. The black pasty residue was washed with benzene and then with hot petroleum ether (60°–80°C). The black crystalline solid obtained corresponded to the formula  $(PhO)_2WS_2 \cdot 2Py$ .

Other phenoxy derivatives were prepared by the same procedure.

The compounds are crystalline solids, brown to black in colour, stable in dry atmosphere except the cresoxy derivatives which are sensitive towards moisture. They are not soluble in common organic solvents, but completely soluble in Lewis bases like DMSO and acid amides. They decompose on heating and are hydrolysed by hot water, dilute acids and alkalis. The compounds are diamagnetic, the magnetic susceptibilities of the compounds range  $(-0.28 \times 10^{-6} \text{ emu/g})$  for catecholate, to  $(-8.16 \times 10^{-6} \text{ emu/g})$  for pyrogallolate. The electronic spectra

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†Department of Chemistry, Gargi College, New Delhi, India.

of the compounds have a sharp peak within the range 37500–35500  $\text{cm}^{-1}$ , which may be assigned to charge transfer from (O→W), (N→W) or (S→W)<sup>3</sup>.

TABLE-I  
CHARACTERISTICS AND ANALYTICAL DATA OF PHENOXY DERIVATIVES OF  
BIS(PYRIDINE) TUNGSTEN(VI) DISULPHIDODICHLORIDE

Compound	Colour	Analysis %, Found (Calcd.)			
		W	S	C	H
WS <sub>2</sub> (OC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> (Phenol)	Black	30.95 (31.05)	10.75 (10.83)	44.50 (44.62)	3.30 (3.38)
WS <sub>2</sub> (OC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ( <i>o</i> -Cresol)	Dark brown	29.50 (29.65)	10.25 (10.34)	46.40 (46.44)	3.75 (3.87)
WS <sub>2</sub> (OC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ( <i>m</i> -Cresol)	Brown black	29.60 (29.65)	10.28 (10.34)	46.35 (46.35)	3.80 (3.87)
WS <sub>2</sub> (OC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ( <i>p</i> -Cresol)	Dark brown	29.55 (29.65)	10.30 (10.34)	46.30 (46.44)	3.80 (3.87)
WS <sub>2</sub> (OC <sub>10</sub> H <sub>7</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ( $\alpha$ -Naphthol)	Brown	26.50 (26.56)	9.20 (9.26)	51.95 (51.05)	3.40 (3.46)
WS <sub>2</sub> (OC <sub>10</sub> H <sub>7</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ( $\beta$ -Naphthol)	Brown	26.50 (26.56)	9.20 (9.26)	52.00 (52.05)	3.38 (3.46)
WS <sub>2</sub> (OC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ( <i>o</i> -Nitrophenol)	Black	26.90 (26.95)	9.35 (9.40)	38.65 (38.73)	2.60 (2.64)
WS <sub>2</sub> (OC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ( <i>p</i> -Nitrophenol)	Black brown	26.85 (26.95)	9.32 (9.40)	38.60 (38.73)	2.54 (2.64)
WS <sub>2</sub> (O <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> (Catechol)	Black	35.70 (35.76)	12.35 (12.47)	37.30 (37.38)	2.65 (2.72)
WS <sub>2</sub> (O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> (Resorcinol)	Black	29.40 (29.45)	10.20 (10.27)	42.25 (42.33)	3.15 (3.20)
WS <sub>2</sub> (O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> (Quinol)	Dark brown	29.35 (29.45)	10.20 (10.27)	42.27 (42.33)	3.14 (3.20)
WS <sub>2</sub> (O <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> (Pyrogallol)	Brown	34.60 (34.68)	12.00 (12.09)	36.20 (36.24)	2.58 (2.64)
WS <sub>2</sub> (O <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> (Phloroglucinol)	Brown	27.95 (28.02)	9.70 (9.77)	40.20 (40.26)	3.00 (3.04)

In the IR spectra of the monohydric phenolic derivatives the absence of absorption band at 3600–3500  $\text{cm}^{-1}$  due to free phenolic hydroxyl group<sup>4</sup> indicates that phenolic group has participated in combination. In dihydroxy phenolic derivatives, the catechol derivative shows no absorption in the above mentioned range indicating the participation of both hydroxyl groups in bond formation with the metal giving chelate structure. But the resorcinol and quinol derivatives show a strong absorption *ca.* 3390  $\text{cm}^{-1}$  indicating the presence of hydroxyl group; the O—H stretching frequency is lowered probably due to intermolecular hydrogen bonding. A band *ca.* 1650  $\text{cm}^{-1}$  in the IR spectra of these compounds may be due to O—H deformation in-plane. In principle the

appearance of two O—H bands could also be admitted and explained by splitting of vibrational levels due to proton tunneling<sup>5</sup>.

In trihydric phenolic derivatives, the pyrogallolate was obtained by the reaction of the reactants in 1 : 1 molar ratio. Chelation is favourable in this case as pyrogallol contains two hydroxyl groups in the *ortho* position. But in case of phloroglucinol derivative the reaction takes place in molar ratio 1 : 2 as phloroglucinol does not have two hydroxyl groups in *ortho* position. The presence of free hydroxyl group in pyrogallol and phloroglucinol derivatives is indicated by presence of a band at *ca.* 3410  $\text{cm}^{-1}$ . A weak to medium intensity band *ca.* 1190  $\text{cm}^{-1}$  is due to the deformation mode of the hydroxyl group<sup>6</sup> probably somewhat restricted due to hydrogen bond formation. Absorption band of *ca.* 1430  $\text{cm}^{-1}$  is due to metal-phenoxide (M—O—C) stretching frequency<sup>7</sup>. A medium intensity band *ca.* 1150  $\text{cm}^{-1}$  is probably due to the C—O stretching frequency<sup>8</sup>. The nitro group in the two nitrophenol derivatives is indicated by the appearance of absorption peaks *ca.* 1530  $\text{cm}^{-1}$  (asymmetric stretching) and *ca.* 1320  $\text{cm}^{-1}$  (symmetric stretching)<sup>9</sup>. The band in the range 500–460  $\text{cm}^{-1}$  indicates that W=S terminal group is retained in all these complexes<sup>10</sup>. The W—N bands may overlap with W=S stretching frequency in this region. All these compounds showed the absorption bands due to pyridine ring. However due to overlapping of aromatic vibrations of phenoxy rings it is not easy to assign aromatic vibrations of pyridine.

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