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Adducts of $WOCl_4$ and WO_2Cl_2 with Some Lewis Bases

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Solutions of $WOCl_4$ in benzene react with some Lewis bases to form 1 : 1 or 1 : 2 adducts with the Lewis bases (pyridine, *o*-phenanthroline, 2,2′-bipyridyl, aniline, *o*-, *m*-, *p*-toluidines, thiourea and anthracene), while WO_2Cl_2 react with some Lewis bases (pyridine, 2,2′-bipyridyl, formamide, benzamide, urea, naphthalene, anthracene and phenanthrene) in solvents like MeCN, DMSO etc. to give 1 : 1 or 1 : 2 adducts. It appears that the Lewis base molecules enter into the coordination sphere of tungsten.

INTRODUCTION

$WOCl_4$ and WO_2Cl_2 have been reported in the literature[1]. A survey of the chemical literature revealed that only few adducts of $WOCl_4$ and WO_2Cl_2 have been reported. Dori[2] has given a good account of these adducts in his review. Adducts of $WOCl_4$ with alkylcyanides, tetrahydrofuran, dioxane, pyridine, azoxybenzene and diars have been reported[3]. These adducts are six- or seven-coordinate complexes exhibiting one strong infrared absorption band around 950 cm^{-1}. The adducts of WO_2Cl_2 with some monodentate and bidentate ligands have been synthesized[4]. These reported adducts of WO_2Cl_2 exhibit the characteristic *cis*-WO_2 infrared spectra with strong bands around 950 and 900 cm^{-1}. It was thought desirable to prepare some adducts of $WOCl_4$ and WO_2Cl_2 with some Lewis bases as the prepared adducts were found to be more stable than the parent compounds probably due to their being coordinatively saturated.

EXPERIMENTAL

All the reactions were carried out in non-aqueous solvents in dry atmosphere using pure and dry solvents and reactants. $WOCl_4$ and WO_2Cl_2 were prepared as mentioned in the literature[1]. Quickfit glassware of standard interchangeable glass joints was used in all the syntheses. Tungsten was determined gravimetrically[5] as WO_3, carbon and hydrogen by microanalytical methods and chlorine, nitrogen and sulphur were determined by semimicroanalytical methods[5]. The IR spectra of the adducts were recorded on a Perkin-Elmer IR spectrometer model-621 and a Shimadzu Spectrophotometer IR-435 in KBr pellets and in Nujol mulis in the ranges 4000–200 cm^{-1} and 4000–400 cm^{-1}, respectively. The electronic spectra

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were recorded on a Shimadzu UV-visible spectrophotometer UV-260. The magnetic susceptibilities of the compounds were measured by Gouy's method at room temperature using carefully degassed distilled water as the calibrant. The electrical conductance was measured on a Beckmann conductivity bridge model RC-18A in nitrobenzene. The molecular weights of the compounds were determined cryoscopically and ebullioscopically using nitrobenzene and acetone as solvents.

Preparation of tetrachlorooxo(thiourea) tungsten(VI)

A quantity of 1.1 g (0.003 mol) of $WOCl_4$ was dissolved in 50 mL of benzene and 0.3 g (0.003 mol) solid thiourea was added in small lots and the reactants were well shaken. A blue crystalline precipitate was obtained which was filtered, washed with benzene and dried. The analysis of the blue solid corresponds to the formula $WOCl_4(NH_2)_2CS$. The solid is unstable as the colour of the solid slowly changes to grey.

Adducts with aniline, pyridine, *o*-, *m*- and *p*-toluidine were obtained by a similar procedure.

Preparation of tetrachlorooxo(bipyridyl) tungsten(VI)

To a solution of 1.2 g (0.003 mol) of $WOCl_4$ in 60 mL of benzene, 0.8 g (0.005 mol) 2,2′-bipyridyl was slowly added with constant stirring. The reaction mixture was refluxed for 8 h and filtered. The brown coloured solution on evaporation to dryness under reduced pressure yielded a green solid. It was washed several times with petroleum ether and dried. The olive green solid was found to have the composition $WOCl_4 \cdot C_{10}H_8N_2$.

Adducts with 1,10-phenanthroline and anthracene were obtained by a similar procedure. All the products with $WOCl_4$ were recrystallized from THF/ether mixture (1:5).

Preparation of dichlorodioxobis(urea) tungsten(VI)

A quantity of 1.2 g (0.004 mol) of WO_2Cl_2 was added to a clear solution of 0.5 g (0.008 mol) of urea in 30 mL of benzene. The reaction mixture was kept at 70°C for about 6 h, cooled and filtered. The light green solid was washed with benzene till no trace of urea was obtained. Finally, it was washed with petroleum ether and dried. The analysis of the solid corresponded to the formula $WO_2Cl_2 \cdot 2N_2H_4CO$.

The adduct with naphthalene was obtained by a similar procedure. The adducts with pyridine and benzamide were obtained in acetonitrile as solvent.

Preparation of dichlorodioxo(bipyridyl) tungsten(VI)

1.2 g (0.004 mol) of WO_2Cl_2 was refluxed with a solution of 1.1 g (0.007 mol) of 2,2′-bipyridyl in 30 mL of DMSO for 4 h. The reaction mixture was filtered and the clear deep red filtrate was evaporated to dryness under reduced pressure. The light brown solid was washed well with petroleum ether and dried. On analysis it was found to correspond to the formula $WO_2Cl_2 \cdot C_{10}H_8N_2$.

Adducts with anthracene and phenanthrene were obtained by a similar

procedure. They were found to possess the formulae $WO_2Cl_2 \cdot 2C_{14}H_{10}$ and $WO_2Cl_2 \cdot 2C_{14}H_{10}$ respectively, as confirmed by the analyses.

Preparation of dichlorodioxidi(formamide) tungsten(VI)

1.2 g (0.004 mol) of WO_2Cl_2 was refluxed with 20 mL of formamide for about 48 h when a white residue was obtained. It was filtered, washed with petroleum ether repeatedly and dried. The analysis of the solid corresponded to the formula $WO_2Cl_2 \cdot 2HCONH_2$.

All the adducts of WO_2Cl_2 were recrystallized from acetonitrile.

RESULTS AND DISCUSSION

All the adducts of $WOCl_4$ and WO_2Cl_2 are coloured and start decomposing before melting. They are decomposed by hot aqueous solutions of acids and bases. Most of them are stable in air. Their analytical and physical data are given in Tables 1 and 2.

The IR spectra of the pyridine adducts showed the ν(ring) at *ca.* 1590, 1570, 1475 and 1440 cm^{-1}, the ring skeletal vibrations appeared at *ca.* 1040 and 990 cm^{-1}. The δ(ring) band appeared at *ca.* 650 cm^{-1} whereas the π(ring) band at *ca.* 470 cm^{-1}. The band at *ca.* 3300 cm^{-1} may be due to ν(C—H), the bands at *ca.* 1230, 1150 and 1070 cm^{-1} may be assigned to δ(C—H) while the bands at *ca.* 750 and 710 cm^{-1} may be assigned to π(C—H).[6] Upon complex formation, the pyridine vibration in the high frequency region are not shifted appreciably but there is a shift noted in the low frequency region. The in-plane ring deformations and out-of-plane ring deformations are shifted to higher frequencies at 645 and 465 cm^{-1} respectively. The ν(W—N) appeared at *ca.* 350 cm^{-1}. All these observations suggest coordination of pyridine to tungsten through N-atom.

In the IR spectra of the 1,10-phenanthroline adduct the bands at 3250 cm^{-1} may be assigned to ν(C—H), δ(C—H) bands appearing at 1250, 1180 and 1075 cm^{-1} while the bands at 780 and 710 cm^{-1} may be assigned to π(C—H). The ν(ring) appearing at 1590, 1530, 1490, 1440 cm^{-1}, the δ(ring) appearing at 610 cm^{-1} and the bands at 1010 and 980 cm^{-1} may be assigned to the ring skeletal vibrations[4].

The bands at *ca.* 3300 cm^{-1} in the IR spectra of 2,2′-bipyridyl adducts may be assigned to ν(C—H); the bands at *ca.* 1250, 1160 and 1080 cm^{-1} may be assigned to δ(C—H) while the bands at *ca.* 780 and 720 cm^{-1} may be due to π(C—H). The bands assigned to ν(ring) appeared at *ca.* 1600, 1530, 1480 and 1450 cm^{-1} and the bands due to δ(ring) and π(ring) appeared at *ca.* 630 cm^{-1} and 500 cm^{-1} respectively. The ring skeletal vibrations were seen[7] at *ca.* 1020 and 990 cm^{-1}. The high frequency region bands in the *o*-phenanthroline and 2,2′-bipyridyl adducts are not metal-sensitive. The ν(W—N) appeared at *ca.* 375 cm^{-1} indicating coordination through N.

The IR spectra of the aniline adduct showed bands at 3450 cm^{-1} due to $\nu_{asym}(NH)$, at 3400 cm^{-1} due to $\nu_{sym}(NH)$ and at 1615 cm^{-1} due to δ(NH). The $\rho_t(NH)$ and $\rho_w(NH)$ appeared at 1060 and 540 cm^{-1} respectively. The first overtone of the torsional vibrations appearing at 475 cm^{-1} overlaps with the

ν(W—N) and ν(W—Cl) within this region[8,9]. The ν(C—N) appeared at 1325 and 1200 cm^{-1}, somewhat lowered due to (N—W) bonding in the adduct[10]. The ν(C—H) appeared at 3070, 3030, 1870, 1730 cm^{-1}; weak bands at 1140, 1110 and 1030 cm^{-1} may be assigned to δ(C—H) while a band at 740 cm^{-1} may be due to π(C—H). The ring skeletal vibrations appeared at 1600, 1575 and 1490 cm^{-1} in the IR spectra[11]. The band at 400 cm^{-1} may be assigned to ν(W—N) indicating coordination through N.

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF ADDUCTS OF $WOCl_4$ WITH LEWIS BASES

Compound	Colour	Analysis % Found (Calcd.)			
		W	Cl	C	N
$WOCl_4 \cdot C_5H_5N$ (pyridine)	Creamish white	42.55 (42.49)	32.66 (32.79)	16.48 (16.62)	3.31 (3.23)
$WOCl_4 \cdot C_{12}H_8N_2$ (1,10-phenanthroline)	Pink	35.17 (35.24)	27.09 (27.20)	27.50 (27.58)	5.26 (5.36)
$WOCl_4 \cdot C_{10}H_8N_2$ (2,2'-bipyridyl)	Dark green	36.82 (36.94)	28.62 (28.51)	24.14 (24.09)	5.53 (5.62)
$WOCl_4 \cdot 2C_6H_5NH_2$ (Aniline)	Light brown	34.75 (34.84)	26.75 (26.89)	27.18 (27.27)	5.35 (5.30)
$WOCl_4 \cdot 2C_6H_4CH_3NH_2$ (*o*-toluidine)	Dirty violet	32.88 (33.09)	25.45 (25.53)	30.13 (30.21)	4.95 (5.03)
$WOCl_4 \cdot 2C_6H_4CH_3NH_2$ (*m*-toluidine)	Brownish black	33.18 (33.09)	25.32 (25.53)	30.27 (30.21)	4.92 (5.03)
$WOCl_4 \cdot 2C_6H_4CH_3NH_2$ (*p*-toluidine)	Light brown	32.95 (33.09)	25.68 (25.53)	30.11 (30.21)	5.10 (5.03)
$WOCl_4 \cdot N_2H_4CS$ (Thiourea)	Grey	43.89 (44.01)	33.85 (33.97)	2.91 (2.87)	6.61 (6.69)
$WOCl_4 \cdot 2C_{14}H_{10}$ (Anthracene)	Light brown	26.28 (26.36)	20.28 (20.34)	48.05 (48.13)	—

The IR spectra of *o*-, *m*- and *p*-toluidine adducts showed ν_{asym}(NH) at *ca.* 3400 cm^{-1}, ν_{sym}(NH) at 3350 cm^{-1} and δ(NH) at *ca.* 1580 cm^{-1}, ρ_t(NH) at *ca.* 1070 cm^{-1} and ρ_w(NH) at *ca.* 500 cm^{-1}. The ν(CN) appeared at *ca.* 1315 and 1240 cm^{-1} lowered due to N—W bonding. The 1,2; 1,3; and 1,4 substituted phenyl rings in the three toluidine adducts are differentiated by their ν(CH), π(CH) and bands in the region 2000–1600 cm^{-1}. The ν(CH) for the respective adducts are observed at *ca.* 2800, 1580, 1510, 1480, 1120 and 1030 cm^{-1}, *ca.* 2900, 1590, 1490, 1460, 1160, 1075 and 1030 cm^{-1} and *ca.* 2800, 1615, 1500, 1480, 1170, 1110 and 800 cm^{-1}, respectively. The observed bands assigned to π(CH) are at *ca.* 810, 800 and 745 cm^{-1} respectively. The weak bands in the region 2000–1600

cm^{-1} for the three toluidine adducts appeared at *ca.* 1880 and 1710; *ca.* 1960, 1900 and 1760; and at *ca.* 1900 and 1730 cm^{-1} respectively[12]. The bands at *ca.* 1370 cm^{-1} may be assigned to δ(CH) of the CH_3—C group and at *ca.* 930 cm^{-1} due to ρ_r of the CH_3—C group[13]. The band at *ca.* 410 cm^{-1} may be assigned to ν(W—N) indicating the coordination of the molecules through N-atom.

TABLE-2
PHYSICAL AND ANALYTICAL DATA OF ADDUCTS
OF WO_2Cl_2 WITH LEWIS BASES

Compound	Colour	Analysis %, Found (Calcd)			
		W	Cl	N	C
$WO_2Cl_2 \cdot C_5H_5N$ (Pyridine)	Bright yellow	48.55 (48.67)	18.69 (18.78)	3.80 (3.70)	18.93 (19.04)
$WO_2Cl_2 \cdot C_{10}H_8N_2$ (Bipyridyl)	Light brown	41.42 (41.53)	15.88 (16.02)	6.27 (6.32)	27.15 (27.08)
$WO_2Cl_2 \cdot 2HCONH_2$ (Formamide)	White	48.72 (48.80)	18.75 (18.83)	7.51 (7.42)	6.29 (6.36)
$WO_2Cl_2 \cdot C_6H_5CONH_2$ (Benzamide)	Yellow	44.95 (45.09)	17.47 (17.40)	3.36 (3.43)	20.48 (20.58)
$WO_2Cl_2 \cdot 2N_2H_4CO$ (Urea)	Light green	45.08 (45.20)	17.27 (17.44)	13.58 (13.75)	5.75 (5.89)
$WO_2Cl_2 \cdot 2C_{10}H_8$ (Naphthalene)	Yellow	33.71 (33.88)	12.95 (13.07)	—	44.25 (44.19)
$WO_2Cl_2 \cdot 2C_{14}H_{10}$ (Anthracene)	Brown	28.55 (28.61)	11.11 (11.04)	—	52.18 (52.25)
$WO_2Cl_2 \cdot 2C_{14}H_{10}$ (Phenanthrene)	Dirty brown	28.67 (28.61)	10.94 (11.04)	—	52.19 (52.25)

The IR spectra of the formamide, the benzamide and the urea adducts showed bands at *ca.* 3410, 3320 cm^{-1} and 3210 cm^{-1} which may be assigned to $\nu_{asym}(NH)$ and $\nu_{sym}(NH)$. The amide II band or the band due to $\delta(NH_2)$ appeared at *ca.* 1590 cm^{-1}.[11] The lowering of the ν(C=O) or the amide I band to *ca.* 1450 cm^{-1} as compared to the free ligands (1725 cm^{-1} for formamide, 1760 cm^{-1} for benzamide and 1685 cm^{-1} for urea) indicated that the amides are coordinated to the tungsten atom through the oxygen atom[14]. A group of vibrations are observed within the range 1500–1100 cm^{-1} which may be due to ν(C=O), ν(CN) and the origin of some of them is not clear. The formamide adduct showed a band at 2960 cm^{-1} which may be assigned to the aldehydic ν(CH)[15]. The benzamide adduct showed bands at 3010, 1600, 1570, 1530 and 1390 cm^{-1} which may be assigned to ν(CH); the π(CH) appeared at 720 cm^{-1} while the bands at 1250, 1090 and 1015 cm^{-1}

may be assigned to δ(CH). The ν(W—O) in these adducts appeared in the range 450–400 cm^{-1}.

The IR spectra of the thiourea adduct showed bands at 3440, 3320 and 3240 cm^{-1} which may be assigned to $\nu_{asym}(NH)$ and $\nu_{sym}(NH)$, respectively. The bands at 1630, 1460, 1425 and 1000 cm^{-1} may be considered as composite bands of $\delta(NH_2)$, ν(CN) and ν(C=S) respectively. The lowering of the last frequency from 1086 cm^{-1} in thiourea to 1000 cm^{-1} indicates that thiourea is bonded through the sulphur atom to the tungsten atom[16]. The dark blue colour of the complex also points to coordmation through sulphur. The bands at 720 cm^{-1} may be assigned to ν(C=S) and may have some contributions from the δ(NCS). The lowering of this frequency and rise in ν(CN) also points to coordination through sulphur[17].

In the IR spectra of the naphthalene, anthracene and phenanthrene adducts, the ν(CH) appeared in two distinct regions, 3050–3000 cm^{-1} and 2950–2900 cm^{-1}. This split in the ν(CH) indicated the difference in the hydrogen atoms of the hydrocarbon ligand rings. The decrease in C—C skeletal vibrations and appearance of new bands at *ca.* 1590, 1450 and 1380 cm^{-1} indicated that the formation of these adducts involve π-electrons[18]. The δ(CH) is observed in the form of many bands between 1200–950 cm^{-1} for the naphthalene adducts, in two groups at 1140 and 1040 cm^{-1} for the anthracene adduct, and bands in the range 1500–1000 cm^{-1} for the phenanthrene adduct. The π(CH) in naphthalene adduct appeared as 4 bands in the range 860–720 cm^{-1}, two strong bands at 870 and 720 cm^{-1} in the anthracene adduct and in the phenanthrene adduct as bands in the range 880–600 cm^{-1}.[12] Thus, it appears that the aromatic hydrocarbon molecules are considerably distorted.

All the adducts of $WOCl_4$ showed a band at *ca.* 950 cm^{-1} which may be assigned to the presence of a terminal W=O group. Absence of a strong band at *ca.* 750 cm^{-1} indicates the absence of oxygen bridge, whereas the adducts of WO_2Cl_2 showed two bands at *ca.* 970 cm^{-1} and *ca.* 920 cm^{-1} due to ν(W=O), indicating that they probably contain a discrete O=W=O group with oxygens at the *cis*-position[4]. Absence of a strong band at *ca.* 730 cm^{-1} indicate the absence of oxygen bridge[19]. The suggested structures of the adducts are given in Fig. 1.

Electronic spectra

The $WOCl_4$ adducts showed sharp and intense band at *ca.* 47000 cm^{-1} which may be assigned to charge transfer (O→W). There are other broad bands at *ca.* 29500 cm^{-1} and 24400 cm^{-1} which may also be assigned to charge transfer (Cl→W)[20]. The WO_2Cl_2 adducts showed sharp bands at *ca.* 48000 cm^{-1} which may be assigned to charge transfer (O→W) and other charge transfer at *ca.* 41500 cm^{-1} and 28500 cm^{-1} due to (Cl→W)[20].

Electrical conductivities and magnetic susceptibilities

The molar conductivities of the adducts are low (1–3 $ohm^{-1}\,cm^2\,mol^{-1}$) indicating that they are essentially nonelectrolytes. Their magnetic susceptibilities are low (0.025–0.035 B.M) indicating that they all are diamagnetic with no unpaired electrons. They are monomeric as indicated by their molecular weight.

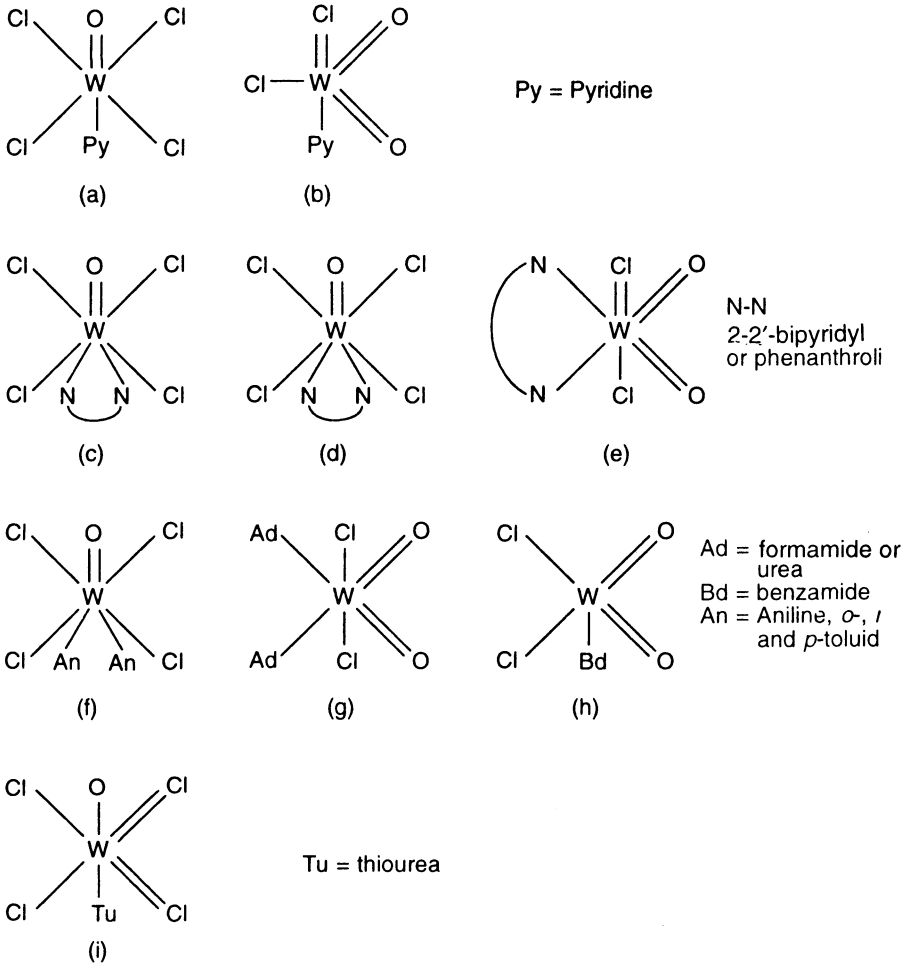

Fig. 1

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