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Some Mixed Ligand Complexes of Tungsten Oxytetrachloride

P. DABAS† and M.K. RASTOGI*
Department of Chemistry
Hindu College, Delhi-110 007, India

Some mixed ligand derivatives of $WOCl_4$ have been synthesized and characterized by their elemental analysis, IR and electronic spectra. The amide ligands are attached to tungsten atom within coordination sphere providing an octahedral geometry to the complex molecule. The amide ligand is removable by simple heating. The tungsten atom-phenoxy linkage is slowly ruptured by boiling in alcohol. This particular property has been utilised for the synthesis of mixed phenoxy complexes without amide ligands but with cyclopentadienide and indenide groups—a new way of synthesis of mixed phenoxy complexes containing π-bonded cyclopentadienyl and indenyl groups.

INTRODUCTION

Tungsten oxytetrachloride is a scarlet red crystalline solid, highly unstable in air. A number of dicyclopentadienyl and bisindenyl derivatives of this compound have been reported in the literature.[1] In this communication some mixed ligand derivatives of this compound are reported. The ligands used are di- and trihydric phenols (catechol, resorcinol, quinol, pyrogallol and phloroglucinol), amides (urea and dimethyl formamide) and cyclopentadienyl and indenyl groups. It has been observed that the phenoxy linkages are ruptured on boiling the complexes in alcohol for a long time. The amide ligands are removed from the complexes by simple heating leaving behind mixed phenoxy complexes.

EXPERIMENTAL

Preparation of dimethyl formamide oxytungsten(VI) diphenolates

About 1.0 g of $WOCl_4$ was refluxed with various phenols in molar ratios 1:2 separately in dimethyl formamide for about 6–7 h in a fume cupboard. Hydrochloric acid fumes were evolved during the reaction and when they cease to come out the reaction mixtures were cooled and filtered. The coloured filtrate in each case was concentrated by evaporation under reduced pressure and then cooled. Crystalline solids separated out which were filtered out and washed with benzene. They were recrystallized from acetone. Their composition corresponded to the general formula $(CHONC_2H_6)WO(phenoxy)_2$-(I). The complexes are

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†Department of Chemistry, Gargi College, New Delhi-110 049, India..

brownish solids insoluble in benzene, chloroform, but soluble in alcohol and acetone. The crystals decompose on heating in the temperature range 75–100°C. They are not very much sensitive towards moisture.

The urea derivatives were obtained from the complexes-I by refluxing about 1.0 g of complexes-I and urea in molar ratios 1:1 in absolute alcohol till no more urea dissolves (3–4 h). The reaction mixture was filtered hot and kept for crystallization. The crystals were separated, washed with benzene and recrystallized from alcohol. Their analysis corresponded to the composition $(CON_2H_4)WO(phenoxy)_2$-(II). These are yellowish brown or greyish brown solids, more stable in air as compared to complexes-I. They decompose on heating around *ca.* 110°C. These complexes are soluble in alcohol and tetrahydrofuran, but are insoluble in benzene and chloroform.

Preparation of dimethyl formamide dicyclopentadienyl (or bis-indenyl) oxytungsten(VI) diphenolates

About 1.0 g of the complexes-I were refluxed with cyclopentadiene (or indene) in molar ratios 1 : 2 in a mixture of alcohol and tetrahydrofuran (1 : 1) for about 20 h. The reaction mixture was filtered and the solvent was removed by evaporation under reduced pressure. Waxy residues were obtained which on extraction with hot petroleum ether (60–80°C) gave dark brown coloured crystalline solids. They were recrystallized from tetrahydrofuran, well washed with ether and dried. Their analytical composition corresponded to the formula $(CHONC_2H_6)D_2WO(phenoxy)_2$-(III). These complexes are less stable and decompose at *ca.* 75°C. They are easily hydrolysed by dilute acids, alkalis and hot water. They are soluble in alcohol and tetrahydrofuran, but are insoluble in benzene and chloroform.

The cyclopentadienyl and indenyl derivatives of complexes-II were also prepared in a similar manner. Their analytical data corresponded to the formula $(CON_2H_4)D_2WO(phenoxy)_2$-(IV). They are dark brown in colour, but are somewhat more stable, decomposing at *ca.* 100°C. They are soluble in alcohol and tetrahydrofuran but are insoluble in benzene and chloroform.

RESULTS AND DISCUSSIONS

From the composition (Table-1), molecular weight determination and infrared spectra of the complexes the following inferences were made: All these complexes contain hexacoordinated tungsten(VI) with octahedral disposition of the ligands. The two polyhydric phenolic ligands form chelates. Dimethyl formamide ligand is substituted by urea in alcohol probably via the formation of unstable intermediate containing coordinated alcohol molecule in place of dimethyl formamide molecule. Thus replacement of the monodentate amide ligand takes place within the coordination sphere without the rupture of the phenoxy linkages. All these complexes decompose when their alcoholic solutions are kept for a long time (3–4 days) giving resinous products. The polyhydric phenolic chelate ring is slowly ruptured due to solvolysis. This fact has been utilized for preparing the cyclopentadienyl or indenyl derivatives.

TABLE-1
DATA ON SOME REPRESENTATIVE MIXED LIGAND COMPLEXES OF TUNGSTEN OXYTETRACHLORIDE

Compound (colour)	Analysis %, Found (Calcd.)				M.W. Found (Calcd.)
	W	C	H	N	
$(CHONC_2H_6)WO(C_6H_4O_2)_2$ (catecholate) (brown)	37.83 (37.62)	36.53 (36.80)	3.21 (3.06)	2.64 (2.86)	501.34 (489)
$(CHONC_2H_6)WO(C_6H_4O_3)_2$ (phloroglucinolate) (dark brown)	35.18 (35.31)	34.63 (34.54)	3.01 (2.87)	2.73 (2.68)	508.97 (521)
$(CON_2H_4)WO(C_6H_4O_2)_2$ (resorcinolâte) (grey brown)	38.27 (38.63)	32.88 (32.77)	2.48 (2.52)	5.70 (5.88)	487.83 (476)
$(CON_2H_4)WO(C_6H_4O_3)_2$ (Pyrogallate) (yellow brown)	35.97 (36.22)	30.45 (30.70)	2.18 (2.36)	5.42 (5.51)	513.67 (508)
$(CHONC_2H_6)(C_5H_5)_2WO(C_6H_5O_2)_2$ (quinolate) (dark brown)	30.07 (29.62)	48.18 (48.30)	4.42 (4.34)	2.34 (2.25)	632.35 (621)
$(CHONC_2H_6)(C_5H_5)_2WO(C_6H_5O_3)_2$ (phloroglucinolate) (brown)	28.19 (28.48)	45.63 (45.94)	4.08 (4.13)	2.34 (2.14)	671.3 (653)
$(CON_2H_4)(C_5H_5)_2WO(C_6H_5O_2)_2$ (Catecholate) (red brown)	30.32 (30.26)	45.61 (45.39)	4.03 (3.94)	4.72 (4.60)	617.25 (608)
$(CON_2H_4)(C_5H_5)_2WO(C_6H_5O_3)_2$ (pyrogallate) (dark brown)	29.10 (28.75)	43.46 (43.12)	3.62 (3.75)	4.22 (4.37)	629.65 (640)
$(CHONC_2H_6)(C_9H_7)_2WO(C_6H_5O_2)_2$ (resorcinolate) (dark brown)	25.39 (25.52)	54.63 (54.92)	4.32 (4.29)	2.07 (1.94)	739.71 (721)
$(CHONC_2H_6)(C_9H_7)_2WO(C_6H_5O_3)_2$ (phloroglucinolate) (brownish black)	24.13 (24.43)	52.80 (52.58)	4.30 (4.11)	3.91 (4.15)	742.82 (753)
$(CON_2H_4)(C_9H_7)_2WO(C_6H_5O_2)_2$ (quinolate) (brown)	25.68 (25.98)	54.38 (53.95)	3.81 (3.95)	4.18 (3.95)	723.72 (708)
$(CON_2H_4)(C_9H_7)_2WO(C_6H_5O_3)_2$ (pyrogallate) (dark brown)	24.72 (24.86)	50.30 (50.02)	3.75 (3.78)	3.92 (3.78)	756.34 (740)
$(C_5H_5)_2WO(C_6H_5O_2)_2$ (resorcinolate) (dark brown)	33.43 (33.57)	48.51 (48.17)	3.52 (3.65)	—	559.43 (548)
$(C_5H_5)_2WO(C_6H_5O_3)_2$ (pyrogallate) (brown)	31.93 (31.72)	45.62 (45.51)	3.39 (3.44)	—	583.24 (580)
$(C_9H_7)WO(C_6H_5O_2)_2$ (quinolate) (brown black)	28.57 (28.39)	55.31 (55.55)	3.84 (3.70)	—	635.69 (648)
$(C_9H_7)_2WO(C_6H_5O_3)_2$ (phloroglucinolate) (brown)	26.92 (27.06)	52.71 (52.94)	3.39 (3.43)	—	691.73 (680)

The dimethylformamide complexes lose dimethylformamide molecule on heating them at 70°C for about 24 h, leaving the phenoxy derivatives. On heating urea complexes to *ca.* 80°C, urea sublimes off slowly leaving the phenoxy derivatives. These phenoxy derivatives $D_2WO(phenoxy)_2$ are exactly identical with the one reported earlier.[1] Tungsten remains penta-coordinated in these phenoxy cyclopentadienyl or indenyl complexes. It is curious to note that the WO group in the compounds remains unaffected during all these chemical reactions.

Infrared spectra

The structures of the prepared complexes were identified from their infrared spectra. The trihydric phenoxy complexes show a sharp band *ca.* 3550 cm^{-1} and *ca.* 1310 cm^{-1}. These are evidently O—H stretching and out-of-plane bending frequencies due to free hydroxyl group.[2, 3] In this respect they differ from dihydric phenolic complexes. The N—H stretching frequency in these complexes (3490 cm^{-1}) overlaps with the O—H stretching frequency but there are other broad bands at *ca.* 3340 cm^{-1} and *ca.* 3170 cm^{-1} which may be due to N—H stretching. A band at *ca.* 1660 cm^{-1} is due to NH_2 deformation mode which is not observed in case of dimethyl formamide complexes.[4, 5] The monodentate amide ligands are attached to tungsten through oxygen is shown by the appearance of C═O stretching frequency at *ca.* 1290 cm^{-1} being lowered due to coordination through oxygen.[6]

Actually a group of vibrations occur within the range 1400–1100 cm^{-1} which may be due to O—H deformations[7], C—C skeletal mode, C—H in-plane deformation,[8] and metal phenoxide (W—O—C) stretching frequencies.[9] The 1, 2; 1, 3; 1, 4; 1, 2, 3 and 1, 3, 5 substituted phenyl rings in these complexes are differentiated from their C—H stretching, C—H out-of-plane deformations and absorption bands in the region at *ca.* 2000–1650 cm^{-1}. The observed C—H stretching frequencies for the respective phenyl rings are: at *ca.* 3000, 1590, 1555, 1480, 1180, 1100, 1020; *ca.* 3000, 1600, 1495, 1440, 1170, 1090, 1020; *ca.* 3000, 1600, 1500, 1470, 1160, 1110; *ca.* 3000, 1600, 1490, 1145, 1100, 1040, 1000; and *ca.* 3000, 1600, 1510, 1080 cm^{-1}.[10] The C—H out-of-plane deformation frequencies increase from 1, 2; 1, 3; to 1, 4 and 1, 3, 5, but for 1, 2, 3 it is nearly the same as in 1, 2 phenyl rings. The observed values are: *ca.* 750, *ca.* 800, *ca.* 825, *ca.* 775, and *ca.* 850 cm^{-1} respectively. The observed weak bands in the region 2000–1650 cm^{-1} for the various substitution patterns are: *ca.* 1890, 1780, 1690; *ca.* 1940, 1860, 1750; *ca.* 1880, 1770; *ca.* 1925, 1860, 1780; and *ca.* 1925, 1750 cm^{-1} respectively.[10]

The presence of cyclopentadienyl rings in complexes-III and IV is identified by their usual bands at *ca.* 2990 cm^{-1} due to symmetrical C—H stretching, *ca.* 1450 cm^{-1} due to C—C stretching, *ca.* 1140 cm^{-1} due to ring breathing, *ca.* 1030 cm^{-1} due to C—H in-plane bending, and a band at *ca.* 840 cm^{-1} due to C—H out-of-plane bending.[11] The additional bands for the indenyl group appear at *ca.* 1620 cm^{-1} due to C—C stretching, *ca.* 740 cm^{-1} due to C—H out-of-plane bending, and *ca.* 700 cm^{-1} due to methylene rocking vibrations.[12] The rings are probably parallel in these complexes as there is a single broad band of medium intensity at *ca.* 1040 cm^{-1}.[11] But they become canted in the compounds left after slow heating for a long time as a characteristic doublet of medium intensity appears *ca.* 1050 cm^{-1} and two medium intensity bands *ca.* 900–850 cm^{-1} due to ring deformations in the residues.[13–15] Complexes-III and IV also contain a free hydroxyl group in them as is indicated by the existence of a band at *ca.* 3530 cm^{-1} due to O—H stretching in their spectra.

The existence of a band at *ca.* 970 cm^{-1} indicates that terminal W═O group remains intact in all these complexes.[16] The electronic spectra of these complexes give peaks near visible range indicating that the delocalization of π-e^- in the cyclopentadienyl or indenyl ligands and in the phenoxy residues extends over the molecule through the metal atom.

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