

## Uranyl Phenoxides

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Uranyl phenoxides of the composition  $\text{UO}_2(\text{OR})_2$  ( $\text{R} = \text{Ph}$ ,  $o\text{-C}_6\text{H}_4\text{NO}_2$  and  $o\text{-C}_6\text{H}_4\text{Cl}$ ) have been prepared by refluxing uranyl chloride or acetate with excess of phenol in xylene. Molar conductances and IR data indicate a possible polymeric structure for these phenoxides. Acceptor properties of  $\text{UO}_2(\text{OC}_6\text{H}_5)_2$  have been established by isolating and characterising the adducts with bases.  $\text{UO}_2(\text{OC}_6\text{H}_5)_2$  reacts with alkali metal phenoxides to give double phenoxides of the type  $\text{M}_2[\text{UO}_2(\text{OC}_6\text{H}_5)_4]$ . Reactions of  $\text{UO}_2(\text{OC}_6\text{H}_5)_2$  with titanium and aluminium phenoxides afford the double phenoxides of composition  $\text{UO}_2[\text{Ti}(\text{OC}_6\text{H}_5)_6]$  and  $\text{UO}_2[\text{Al}(\text{OC}_6\text{H}_5)_4]_2$  respectively. These double phenoxides have also been characterised.

Funk and Andrae<sup>1,2</sup> reported the preparation of intensely coloured monomeric uranium(IV) phenoxides of composition  $\text{U}(\text{OR})_4$ , ( $\text{R} = \text{Ph}$ ,  $o\text{-C}_6\text{H}_4\text{Cl}$  or  $o\text{-C}_6\text{H}_4\text{NO}_2$ ). Preparation of pyridine adduct of  $\text{U}(\text{OPh})_4$  was also attempted by Andrae<sup>3</sup>. Except for a few sporadic reports, not much work seems to have been done on uranium(VI) phenoxides. We report herein the preparation and characterisation of uranyl phenoxides  $\text{UO}_2(\text{OR})_2$  ( $\text{R} = \text{C}_6\text{H}_5$ ,  $o\text{-C}_6\text{H}_4\text{NO}_2$  or  $o\text{-C}_6\text{H}_4\text{Cl}$ ). An attempt has also been made to establish their acceptor properties.

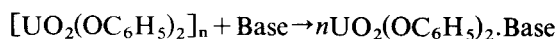
The uranyl phenoxides  $\text{UO}_2(\text{OR})_2$  ( $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4\text{Cl}$  or  $\text{C}_6\text{H}_4\text{NO}_2$ ) were prepared by refluxing uranyl chloride or uranyl acetate with excess of the corresponding phenol in xylene for 12 hr. Completion of the reaction was ascertained when hydrogen chloride ceased to evolve from the reaction mixture. The contents were filtered in a dry atmosphere and washed repeatedly with hot benzene to remove excess of phenol and finally dried *in vacuo*.

The stoichiometric composition of these compounds was established by elemental analyses (Table I). All these compounds are moisture-sensitive but are sufficiently stable in dry atmosphere. They are insoluble in most of the polar organic solvents. Molar conductance values of  $10^{-3}M$  solutions of these phenoxides in nitrobenzene indicate their non-electrolytic nature. Apparently on analogy with uranyl carboxylates<sup>4</sup> and sulphates<sup>5</sup>, these phenoxides are polymeric though the extent of association is less.

The infrared spectra of these phenoxides recorded in KBr matrix do not exhibit broad bands in the region

3400-3300  $\text{cm}^{-1}$ , unlike the phenols which display H-bonded  $\nu(\text{OH})$  in this region<sup>6</sup>. The  $\nu\text{C}-\text{O}$  (phenolic) modes of phenol,  $o\text{-ClC}_6\text{H}_4\text{OH}$  and  $o\text{-NO}_2\text{C}_6\text{H}_4\text{OH}$  which appear<sup>7</sup> at 1228, 1258 and 1264  $\text{cm}^{-1}$  respectively undergo shifts to lower wavenumbers. In addition to these, new bands are also observed in the range 520-530  $\text{cm}^{-1}$  in these phenoxides which may be attributed to bridging  $\nu\text{U}-\text{O}\rightarrow\text{U}$  modes, which is in agreement with earlier observations<sup>8</sup> that if polymerisation occurs through chlorine or oxygen then the corresponding modes are observed at lower regions as compared to terminal ones. No band that could be assigned to  $\nu\text{U}-\text{Cl}$  in the region 320-330  $\text{cm}^{-1}$  has been observed in these phenoxides<sup>9</sup>. Elemental analyses, conductance and infrared spectral data and insolubility in various solvents show that these phenoxides are polymeric in nature.

Attempts have also been made to establish the Lewis acid character of  $\text{UO}_2(\text{OC}_6\text{H}_5)_2$  by isolating some adducts with bases such as pyridine, piperidine, 2,2'-bipyridyl and 1,10-phenanthroline. In the presence of the base, the polymeric structure of the phenoxide breaks down to give monomeric form.



This is supported by the shift of  $\nu\text{U}-\text{O}\rightarrow\text{U}$  in the original phenoxide to higher wavenumbers on adduct formation. Further the  $\nu\text{C}=\text{N}$  of free pyridine at 1578  $\text{cm}^{-1}$  shifts to 1591  $\text{cm}^{-1}$  in the adduct<sup>10,11</sup>.

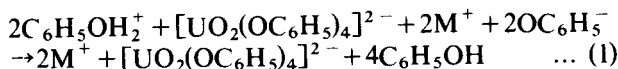
In the case of piperidine adduct the band at 3291  $\text{cm}^{-1}$  assigned<sup>12</sup> to  $\nu\text{N}-\text{H}$  of free piperidine is shifted to lower wavenumbers, whereas a band at 822  $\text{cm}^{-1}$  due to  $\delta\text{H}-\text{N}-\text{C}$  deformation of free piperidine moves to higher regions by  $\sim 30\text{-}40\text{ cm}^{-1}$  on adduct formation. In the case of  $\text{UO}_2(\text{OC}_6\text{H}_5)_2$ , 2,2'-bipyridyl, adduct formation has been ascertained from the shifts in  $\nu\text{C}=\text{C}$  and  $\nu\text{C}=\text{N}$  and the  $\text{C}-\text{H}$  out-of-plane deformation bands to the higher spectral regions. Coordination of 1,10-phenanthroline is established from the fact that a strong band at 1585  $\text{cm}^{-1}$  possibly due to a combination of  $\nu\text{C}=\text{C}$  and  $\nu\text{C}=\text{N}$  is shifted to higher wavenumbers on complexation<sup>13</sup>.

Malhotra and coworkers<sup>14</sup> have shown that organic tertiary bases and alkali metal phenoxides behave as solvo bases in fused phenol while transition metal phenoxides behave as solvo acids in fused phenol<sup>15</sup>. It was therefore, considered of interest to explore the behaviour of uranyl phenoxide in fused phenol. Acid behaviour of  $\text{UO}_2(\text{OC}_6\text{H}_5)_2$  has been demonstrated by carrying our titrations against alkali metal phenoxides

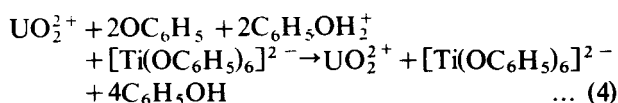
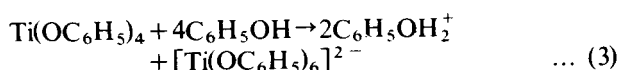
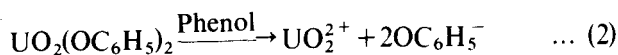
Table 1—Analytical Data

Compound	Colour (m.p. °C)	Found (Calc.) %		$\Lambda_m$	Mol. wt. found (Calc)
		Uranium	Ti, Al, Na, K		
$\text{UO}_2(\text{OC}_6\text{H}_5)_2$	Yellow (152)	52.34 (52.19)	—	—	—
$\text{UO}_2(\text{OC}_6\text{H}_4\text{Cl})_2$	Red (118)	46.14 (45.33)	—	—	—
$\text{UO}_2(\text{OC}_6\text{H}_4\text{NO}_2)_2$	Red (146)	42.82 (43.95)	—	—	—
$\text{UO}_2(\text{OC}_6\text{H}_5)_2\cdot\text{py}$	Yellow (>225)	44.12 (44.48)	—	1.2	518 (535)
$\text{UO}_2(\text{OC}_6\text{H}_5)_2\cdot\text{pip}$	Yellow (250d)	43.76 (43.99)	—	1.8	578 (541)
$\text{UO}_2(\text{OC}_6\text{H}_5)_2\cdot\text{bipy}$	Red (214d)	39.16 (38.88)	—	2.6	596 (612)
$\text{UO}_2(\text{OC}_6\text{H}_5)_2\cdot\text{phen}$	Brown (>250)	38.16 (37.42)	—	0.8	574 (636)
$\text{UO}_2\cdot\text{Ti}(\text{OC}_6\text{H}_5)_6$	Yellowish (131d)	27.12 (27.39)	5.48 (5.6)	22.6	896 (876)
$\text{UO}_2\cdot 2\text{Al}(\text{OC}_6\text{H}_5)_4$	Light Brown (201d)	22.84 (22.32)	4.98 (5.05)	28.4	1054 (1068)
$\text{Na}_2[\text{UO}_2(\text{OC}_6\text{H}_5)_4]$	Reddish Brown (110d)	34.86 (34.59)	6.27 (6.68)	18.2	694 (688)
$\text{K}_2[\text{UO}_2(\text{OC}_6\text{H}_5)_4]$	Brown (138d)	32.74 (33.05)	10.96 (10.83)	17.6	712 (720)

in fused phenol. Double phenoxides of composition  $\text{M}_2[\text{UO}_2(\text{OC}_6\text{H}_5)_4]$  where M is sodium and potassium have been isolated by refluxing uranyl phenoxide with alkali metal phenoxides in 1:2 molar ratio in xylene. The formation of the double phenoxides can be rationalised as follows. The alkali metal phenoxides dissociate to give phenoxide ion while uranyl phenoxide in the presence of phenol gives protonated phenol and  $[\text{UO}_2(\text{OC}_6\text{H}_5)_4]^{2-}$ . The overall neutralisation reaction occurs as shown in Eq. (1).



solvo base character of uranyl phenoxide in fused phenol has been established by carrying out conductometric titrations against titanium(IV) phenoxide and aluminium phenoxide. Evidently in the presence of strong phenoxide ion acceptors, uranyl phenoxide behaves as a base. Decrease in the conductance of the solution on the addition of titanium phenoxide establishes the basic character of uranyl phenoxide (see Eqs 2-4).



Double phenoxides of composition  $\text{UO}_2\cdot\text{Ti}(\text{OC}_6\text{H}_5)_6$  and  $\text{UO}_2\cdot 2\text{Al}(\text{OC}_6\text{H}_5)_4$  have been isolated and their stoichiometries have been established by elemental analyses. All these phenoxides are stable solids though slightly moisture-sensitive. Molar conductance values of these phenoxides in nitrobenzene ( $10^{-3}M$ ) show them to be fairly ionic.

In the infrared spectrum of the compound  $\text{UO}_2^{2+}\cdot\text{Ti}(\text{OC}_6\text{H}_5)_6^{2-}$ , apart from the band attributed to  $\text{UO}_2^{2+}$  species observed at  $878\text{cm}^{-1}$  the other important bands observed in the regions 560-580 and  $340\text{-}360\text{cm}^{-1}$  may be attributed<sup>16</sup> to  $\nu\text{Ti}-\text{O}$ . In the IR spectrum of  $\text{UO}_2^{2+}[\text{Al}(\text{OC}_6\text{H}_5)_4]_2$ , the band at  $860\text{cm}^{-1}$  may be assigned to  $\nu\text{U}=\text{O}$  while bands at 540, 578, 618 and 480 and  $492\text{cm}^{-1}$  may be assigned to  $\nu\text{Al}-\text{O}$  in a tetrahedral environment<sup>17</sup> which thus supports the ionic behaviour of these compounds.

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