

LIGAND SUBSTITUTION EFFECTS IN URANYL *o*-HYDROXYARYL-CARBONYL COMPLEXES

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ABSTRACT

Twenty-two base adducts of uranyl *o*-hydroxyarylcarbonyl complexes [UO₂L₂B] (L = *o*-hydroxyarylcarbonyl compound, B = H₂O, pyridine, pyridine *N*-oxide) have been prepared. Pure field substituent parameters are used to derive a quantitative order of the electronic effects of the chelate ring substituents. Values of $\nu(\text{U}=\text{O})$ correlate well with these values. Evidence is cited suggesting almost complete non-aromaticity of the chelate ring, and the transmission of the electronic effects of the chelate ring substituent through the uranium atom in the pyridine and pyridine *N*-oxide base adducts.

INTRODUCTION

It has recently been shown [1] that pure field and resonance substituent parameters can be used to derive a quantitative order of the electronic effects ($\Sigma\sigma$) of the ligand substituents in a series of uranyl β -ketoenolates. Although there is some evidence [2] for electron delocalization in the chelate ring in β -ketoenolates, it has been suggested [3, 4] that the metal ion provides a barrier to complete freedom of movement of the π -electrons. In *o*-hydroxyarylcarbonyl chelate complexes it has been shown [5] that there is a certain amount of electron localization in the chelate ring, thus decreasing the possibility of resonance playing a part in the stabilization of these complexes. Here we discuss the application of field and resonance substituent parameters in uranyl *o*-hydroxyarylcarbonyl complexes.

Ligands used in this study were salicylaldehyde (SAL), ethyl salicylate (ESAL), *o*-hydroxyacetophenone (HAP), *o*-hydroxypropiophenone (HPP), methyl salicylate (MSAL) and phenyl salicylate (PSAL). Bases used in this study were H₂O, pyridine (py) and pyridine *N*-oxide (pyNO).

The electronic effects of the chelate ring substituent and the adducted base on characteristic group frequencies of the complexes will be discussed. These molecules are particularly suited to an IR investigation since they are all isostoechiometric and the U=O asymmetric stretching mode, $\nu(\text{U}=\text{O})$, can be unambiguously assigned.

EXPERIMENTAL

The majority of complexes described here are newly reported.

Aquo adducts

The *o*-hydroxyarylcarbonyl compound (0.0052 mole) in methanol (10 ml) is added to uranyl nitrate hexahydrate (1 g, 0.0026 mole) in methanol (40 ml). The mixture is vigorously stirred and 25 % aqueous NaOH is added dropwise. The complex precipitates. The amorphous orange solid is then filtered, washed with water and air dried.

Pyridine adducts

Uranyl nitrate hexahydrate (1g , 0.0026 mole) is dissolved in methanol (40 ml) and a mixture of the *o*-hydroxyarylcarbonyl compound (0.0052 mole) and pyridine (0.0026 mole) is added. The mixture is allowed to stand at room temperature. After 24 h the red crystalline product is filtered, washed with methanol and air dried.

An alternative method involves recrystallization of the aquo adduct from excess of pyridine. The complexes thus formed are filtered, washed with methanol and air dried.

The latter method is to be preferred where yields are of importance.

Pyridine N-oxide adducts

A procedure analogous to that used for the pyridine adducts yields the pure, red crystalline products. The addition of a little methanol is necessary to dissolve the pyridine *N*-oxide.

Infrared spectra

Infrared spectra were determined on Nujol mulls between caesium bromide plates on a Beckman IR-12 spectrophotometer calibrated against water vapour and carbon dioxide. For optimum reproducibility frequencies were read from the

wavenumber drum, not the chart paper. Duplicate spectra, determined with ordinate and abscissa scale expansion and again with a fresh sample of the compound, yielded a maximum discrepancy of 0.5 cm^{-1} in $\nu(\text{U-O})$.

Uranium analyses

Uranium analyses were performed as has been previously described [6] by ignition to $750\text{--}850^\circ\text{C}$ for several hours and weighing the residue as U_3O_8 .

RESULTS AND DISCUSSION

Raman, IR and theoretical evidence [7-9] unanimously supports the assignment of the intense band near 900 cm^{-1} in the spectra of all uranyl compounds to the asymmetric stretching frequency of the uranyl group. It has been shown [1] that in uranyl β -ketoenolates two bands occurring at around 528 and 403 cm^{-1} are probably metal sensitive modes. In uranyl *o*-hydroxyarylcarylcarbonyl complexes the complexity of the IR spectra is much greater than that of the corresponding β -ketoenolates, and for this reason no attempt is made here to interpret the far IR spectra and assign metal sensitive modes.

A very strong absorption centered at around 270 cm^{-1} has recently been assigned [10] as $\nu(\text{U-O})$ between the uranium atom and the oxygen atom of pyridine *N*-oxide in a series of compounds $\text{UO}_2\text{L}_2 \cdot \text{pyNO}$. This band is present in all the complexes discussed in this work, and is also present in uranyl β -ketoenolate complexes [11]. This band has previously been assigned [7], based on theoretical treatments, to the bending mode of the uranyl group, $\delta(\text{O-U-O})$. Our findings are consistent with the latter assignment.

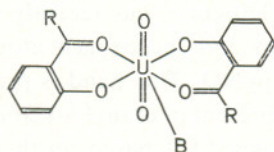
In metal acetylacetonates two bands are apparent in the $1500\text{--}1600 \text{ cm}^{-1}$ range. Earlier assignments of $\nu(\text{C-O})$ and $\nu(\text{C-C})$ by normal co-ordinate analyses [12, 13] have been reversed by a further analysis [14], and by ^{18}O -labelling of the carbonyl oxygen [15]. Thus the higher band is assigned to $\nu(\text{C=O})$ and the lower to $\nu(\text{C-C})$. These assignments are upheld in a recent paper [16] concerning first-row transition metal(III) β -ketoenolates where it was shown that $\nu(\text{C=O})$ exhibits a dependence on the CFSE that is generally similar to that exhibited by $\nu(\text{M-O})$ and the inverse of that shown by $\nu(\text{C-C})$ on the basis of the higher frequency band being assigned to $\nu(\text{C=O})$. In the spectra of the uranyl *o*-hydroxyarylcarylcarbonyl complexes studied here, two bands are also observed between 1500 and 1650 cm^{-1} . On the basis of the assignments of these two bands in spectra of the β -ketoenolates discussed above, the band of higher frequency is assigned to $\nu(\text{C=O})$ and the lower frequency band to $\nu(\text{C-C})$. That $\nu(\text{C=O})$ occurs at higher frequency in the *o*-hydroxyarylcarylcarbonyl complexes than in the β -ketoenolates is evidence for a greater degree of electron localization about the C=O bond in the

TABLE I

ANALYTICAL AND IR DATA FOR URANYL *o*-HYDROXYARYLCARBONYL BASE ADDUCT COMPLEXES [UO₂(L)₂B]

Complex	R in (I)	Calculated (%)				Found (%)				$\nu(U-O)$ (cm ⁻¹)	$\nu(C=O)$ (cm ⁻¹)
		C	H	N	U	C	H	N	U		
UO ₂ (HPP) ₂ · H ₂ O	Et	36.9	3.4	—	40.6	36.2	3.2	—	40.4	925	1611
UO ₂ (HPP) ₂ · py	Et	42.7	3.6	2.2	36.8	41.9	3.7	2.1	36.6	899	1607
UO ₂ (HPP) ₂ · pyNO	Et	41.6	3.5	2.1	35.9	41.3	3.6	2.2	36.2	890	1612
UO ₂ (HAP) ₂ · H ₂ O	Me	34.4	2.9	—	42.6	34.7	2.7	—	42.2	925	1613
UO ₂ (HAP) ₂ · py	Me	40.7	3.1	2.3	38.4	40.7	2.7	2.4	38.5	900	1609
UO ₂ (HAP) ₂ · pyNO	Me	39.7	3.0	2.2	37.5	39.3	2.7	2.4	37.6	891	1614
UO ₂ (SAL) ₂ · H ₂ O	H	31.7	2.3	—	44.9	31.4	2.1	—	44.3	925	1627
UO ₂ (SAL) ₂ · py	H	38.6	2.6	2.4	40.3	39.2	2.6	2.4	40.0	901	1614
UO ₂ (SAL) ₂ · pyNO	H	37.6	2.5	2.3	39.2	37.2	2.6	2.2	39.5	895	1627
UO ₂ (ESAL) ₂ · H ₂ O	OEt	35.0	3.3	—	38.5	35.3	3.2	—	38.2	925	1639
UO ₂ (ESAL) ₂ · py	OEt	40.7	3.4	2.1	35.0	40.6	3.4	2.1	34.9	907	1631
UO ₂ (ESAL) ₂ · pyNO	OEt	39.7	3.3	2.0	34.2	39.7	3.1	2.0	34.9	900	1639
UO ₂ (MSAL) ₂ · py	OMe	38.7	2.9	2.2	36.5	38.2	2.8	2.2	36.5	908	1630
UO ₂ (PSAL) ₂ · py	OPh	48.0	3.0	1.8	30.7	48.4	2.8	1.6	30.4	915	1652

former complexes. Evidently fusion of the benzene ring with the chelate ring leads to considerable localization of electrons in the chelate ring system which would appear to exist essentially in the form represented in formula I.



(II)

Support for the unsymmetrical structure of the chelate ring is provided by the X-ray crystallographic examination [17, 18] of bis(salicylaldehydato)copper(II) and diaquobis(salicylaldehydato)nickel(II) in which it was determined that the C=O bond (in formula I) is considerably shorter than the C—O bond.

Any attempt to correlate group frequencies with the electronic effects of a substituent requires some quantitative index of the mode of transmission of the electronic effect. Hammett substituent parameters [19] cannot be used for *o*-hydroxyarylcabonyl complexes as this would assume aromaticity of the chelate ring. It has been indicated above that since the oxygen atoms of the chelate ring are non-equivalent and the C=O bonds have different lengths, it is unlikely that the chelate ring should be aromatic. We therefore use the recently derived [20] pure field (\mathcal{F}) and resonance (\mathcal{R}) parameters which are independent of the site of substitution. The electronic effect (σ) of the *o*-hydroxyarylcabonyl chelate ring substituent (R in formula I) is given by eqn. (1)

$$\sigma = f\mathcal{F} + r\mathcal{R} \quad (1)$$

where f and r are the relative weightings of \mathcal{F} and \mathcal{R} respectively.

It has been shown [1] that, except for phenyl substituents, use of $f = 0.75$ and $r = 0.25$ yields values of σ which decrease monotonically with decrease in $\nu(\text{U}-\text{O})$ in a series of uranyl β -ketoenolates. Phenyl substituted β -ketoenolates require an increased contribution from \mathcal{R} to account for the contribution of the various resonance forms possible. In the case of the *o*-hydroxyarylcarbonyl complexes, the weighting of \mathcal{R} must be considerably decreased since, theoretically, resonance is highly unlikely in the chelate ring because of electron localization. Hence any transmission of electronic effects by the substituent must be considered

TABLE 2

SUBSTITUENT DATA FOR URANYL *o*-HYDROXYARYLCARBONYL COMPLEXES

Ligand	R	\mathcal{F}	\mathcal{R}	f	r	σ	$\nu(\text{U}-\text{O})$ py adduct (cm^{-1})
HPP	C_2H_5	-0.07	-0.11	0.75	0.25	-0.08	899
HAP	CH_3	-0.05	-0.14	0.75	0.25	-0.07	900
SAL	H	0.00	0.00	—	—	0.00	901
ESAL	OC_2H_5	+0.36	-0.44	0.75	0.25	+0.16	907
MSAL	OCH_3	+0.41	-0.50	0.75	0.25	+0.19	908
PSAL	OC_6H_5	+0.75	-0.74	0.75	0.25	+0.54	915

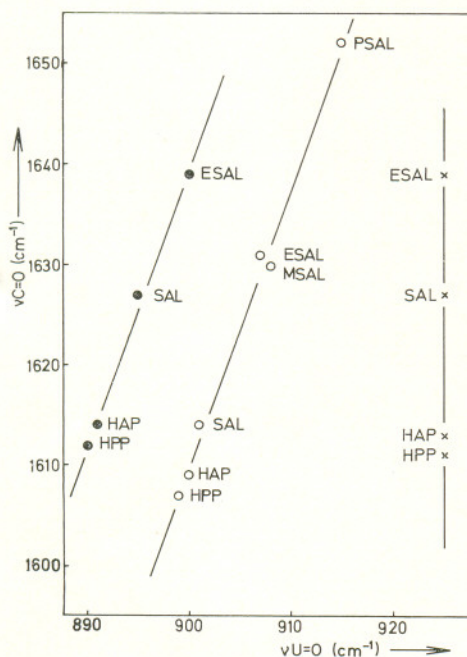


Fig. 1. Relationship between $\nu(\text{C}=\text{O})$ and $\nu(\text{U}=\text{O})$ for complexes $[\text{UO}_2(\text{L})_2\text{B}]$. (●), B = pyNO, (○), B = py; (×), B = H_2O .

to take place via an almost pure field mechanism. Substituent data are summarised in Table 2.

As can be seen from Fig. 1, $\nu(\text{U}=\text{O})$ and $\nu(\text{C}=\text{O})$ are simultaneously increased or decreased by substitution in the chelate ring for the pyridine and pyridine *N*-oxide base adducts. In the case of the aquo adducts however, substitution in the chelate ring causes a shift of $\nu(\text{C}=\text{O})$, but $\nu(\text{U}=\text{O})$ remains constant throughout the series. For any particular *o*-hydroxyarylcarbonyl complex, substitution of pyridine *N*-oxide for pyridine causes a shift of $\nu(\text{U}=\text{O})$ to lower frequencies, implying, on the basis of an earlier communication [21], that pyridine *N*-oxide has a higher ligand field strength than pyridine, assuming $\text{U} \rightarrow \text{pyridine}$ and $\text{U} \rightarrow \text{pyridine } N\text{-oxide}$ π -bonding to be of a similar magnitude. The more polar nature of the oxygen atom in the amine oxides compared to other oxo-donors such as water and the alcohols makes the bonding by its lone pair electrons stronger.

In the case of the aquo adducts it is of interest to note that whilst there is a substantial shift of $\nu(\text{C}=\text{O})$ on changing R (formula I), $\nu(\text{U}=\text{O})$ remains constant. A possible explanation is that since H_2O cannot enter into strong $\text{U} \rightarrow \text{H}_2\text{O}$ π -bonding, the electronic effect of the ring substituent may well be confined to the chelate ring. In the case of pyridine and pyridine *N*-oxide however, the aromatic heterocyclic ring could act as an electron sink, therefore the possibility of

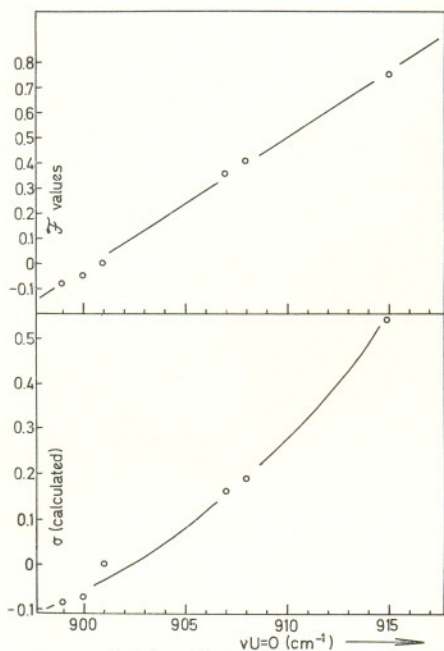


Fig. 2. Relationship between $\nu(\text{U}=\text{O})$ and σ (calculated) and \mathcal{F} values.

transmission of electronic effects through the uranium atom becomes apparent. If this is so, pyridine and pyridine *N*-oxide adducts would be expected to show changes in $\nu(\text{U-O})$ with change of R (formula I), whereas the aquo adducts would not.

Figure 2 shows a plot of the calculated σ values (assuming $f = 0.75$ and $r = 0.25$) against $\nu(\text{U-O})$ for the pyridine adducts of the *o*-hydroxyarylcarbonyl complexes. Whilst it is apparent that there is a general trend, i.e., electron withdrawing substituents cause an increase in the bond order of the U=O bond, it would appear that use of $f = 1.00$ and $r = 0.00$ (i.e., pure \mathcal{F} values, Fig. 2) gives better agreement in terms of relative electronic effect. It is interesting to note that plots of this nature utilizing the Hammett σ function or pure \mathcal{R} values show no trend.

In the light of this argument it would appear that the electronic effects of the substituent R (formula I) are transmitted by a pure field effect, electron localization reducing the aromaticity of the chelate ring to a minimum. On the same basis, it has been argued [1] that, in uranyl β -ketoenolates, the chelate ring does comprise a certain degree of aromaticity.

In an attempt to duplicate the results found for the uranyl β -ketoenolate system [1], the synthesis of a series of substituted pyridine adducts of the uranyl salicylaldehyde complex was attempted. The compounds were prepared in an analogous manner to the pyridine adduct. It was found that over the range from strongly electron withdrawing (4-CNC₅H₄N) to strongly electron releasing (4-NH₂C₅H₄N) substituents, $\nu(\text{U-O})$ and $\nu(\text{C-O})$ shifted over 2 and 4 cm⁻¹ respectively (Table 3). Substitution of the pyridine ring therefore has a negligible effect on the strength of U \rightarrow pyridine π -bonding in this series of complexes where the chelate ring is non-aromatic, indicating essentially no transmission of these effects through the uranium atom.

TABLE 3

R AND SUBSTITUENT DATA FOR COMPLEXES $[\text{UO}_2(\text{SAL})_2(\text{R-C}_5\text{H}_4\text{N})]^*$

R	Hammett σ	$\nu(\text{U-O})$	$\nu(\text{C-O})$
4-CN	+0.63	902	1612
4-COC ₆ H ₅	+0.46	901	1612
4-CO ₂ C ₂ H ₅	+0.40	902	1613
4-C ₆ H ₅	+0.01	902	1612
H	0.00	901	1614
4-C ₂ H ₅	-0.15	902	1614
4-CH ₃	-0.17	901	1616
4-NH ₂	-0.60	902	1614
4-N(CH ₃) ₂	-0.66	900	1616

* Pyridines with substituents such as -CN and -NH₂ are bound to uranium through the heterocyclic nitrogen, since the characteristic group frequencies of the substituent in the complexes are close to those of the free pyridines.

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