

Preparation and Crystal and Molecular Structure of [*NN'*-*o*-Phenylenebis(salicylideneiminato)UO₂(EtOH)]

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Summary The synthesis and the molecular structure of [*NN'*-*o*-phenylenebis(salicylideneiminato)UO₂(EtOH)] are reported together with i.r. and relative stability data for similar complexes.

THE molecular structure, characterisation, and reactivity of the complex [*NN'*-*o*-phenylenebis(salicylideneiminato)UO₂(EtOH)] have been studied as part of a search for ligands selective for large cations of the actinide (MO₂²⁺) type.

The complex was obtained from the reaction of UO₂Cl₂·3H₂O or UO₂(NO₃)₂·6H₂O with stoichiometric amounts of the Schiff base ligand (sal-*o*-phdH₂),¹ or by condensation of salicylaldehyde with *o*-phenylenediamine in the presence of uranyl salts. Both methods employ EtOH as solvent at room temperature. The molecular weight in CHCl₃ solution is consistent with a monomeric formula. The ν (C=N) (1602 and 1598 sh cm⁻¹) and ν_{as} (O-U-O) (910 cm⁻¹) stretching bands are consistent with the formation of the complex. The absence of a ν (OH) stretching peak in the range 3600—3200 cm⁻¹ could be attributed to the presence of hydrogen bonds.

In order to elucidate the mode of sal-*o*-phdH₂ bonding, a X-ray structural determination of the complex was carried out. Crystals of moderate quality were obtained from an absolute ethanol solution and they were found to be monoclinic with $a = 10.382$, $b = 9.564$, $c = 23.026$ Å; $\beta = 107.78^\circ$; space group $P2_1/c$; $Z = 4$. Intensity measurements were carried out using a Siemens-AED four-circle automatic diffractometer (Cu- $K\alpha$ radiation; $\theta \leq 65^\circ$). The intensity of 543 reflexions out of the 3708 possible was less than $2\sigma(I)$ and these were considered as unobserved. Patterson, Fourier, and least-squares methods have been used to determine and refine atomic parameters, the present unweighted discrepancy index being 0.064 (all atoms, with the exception of uranium, have been given isotopic thermal

parameters). At this stage the following anomalies were observed near the ethanolic carbon atoms: (a) the refined thermal parameters were *ca.* 12 Å²; (b) the electron densities at these sites were relatively low with considerable elongation. These anomalies could be explained if the ethyl group is disordered, taking two possible orientations with relative occupancies not yet refined.

No correction for absorption or extinction has yet been applied, nor has allowance been made for the imaginary part of the uranium scattering factor. The uranyl group is surrounded equatorially by an irregular pentagon determined by two oxygen and two nitrogen atoms of sal-*o*-phd and by the oxygen atom of ethanol (Figure).

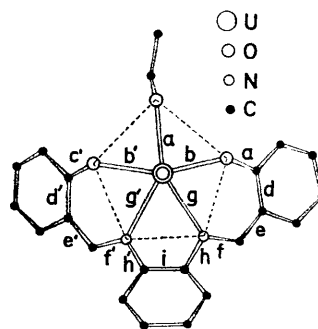


FIGURE. Projection of the molecule on to the mean plane of the co-ordination pentagon.

This pentagon is slightly puckered around the uranium level as seems to be normal for compounds of this type² with the ethanol oxygen having significant deviation (0.22 Å). The bond lengths (Å) and angles ($^\circ$), standard deviation *ca.* 2°, for the "inner core" of the compound are listed in the Table; e.s.d.'s of bond lengths average 0.02 Å (U-O and

Intertomic distances (Å) and angles (degrees); letters refer to those of the Figure.

a	2.46	e'	1.45	a b	80.8	c'd'	119.9	g'h'	115.5
b	2.24	f	1.31	a b'	78.0	d e	124.4	h f	118.7
b'	2.28	f'	1.30	b g	70.1	d'e'	124.8	h'f'	118.6
c	1.33	g	2.55	b'g'	69.3	e f	124.7	h i	115.3
c'	1.36	g'	2.54	g g'	62.4	e'f'	123.3	h'i	115.9
d	1.41	h	1.42	b c	132.1	f g	126.7		
d'	1.38	h'	1.40	b'c'	125.1	f'g'	125.8		
e	1.44	i	1.42	c d	119.5	g h	114.5		

U-N) and 0.03 Å (other distances). The uranyl U-O distances, both 1.77 Å, are consistent with those reported in the literature, as is the uranyl angle (179°).³

The only short intermolecular distance is EtOH...O-(sal-o-phd) (2.63 Å). Considering that the angle OH...O-C is 113.8°, it is likely that a hydrogen bond is present.⁴

The ethanol co-ordinated to the uranium atom undergoes substitution reaction with monodentate ligands such as pyridine, aniline, dimethyl sulphoxide, and triphenyl-

phosphine oxide under mild conditions. Substitution reactions of the type:

$$[\text{UO}_2(\text{sal-o-phd})\text{L}] + \text{L}' \rightarrow [\text{UO}_2(\text{sal-o-phd})\text{L}'] + \text{L}$$

carried out in CH₂Cl-CH₂Cl at 30°, give the relative stability sequence Ph₃PO > Me₃SO > py ≥ PhNH₂ > EtOH.

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