Preparation, Properties, and Molecular Structure of Aquoglyoxalbis-(2-hydroxyanil)dioxouranium

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Summary The synthesis and the *X*-ray molecular structure of aquoglyoxalbis-(2-hydroxyanil)dioxouranium are reported.

Following previous investigations[1] we have determined the molecular structure and studied the reactivity of the complex obtained from uranyl salts [$UO_2Cl_2 \cdot 3H_2O$ or $UO_2(NO_3)_2 \cdot 6H_2O$] with stoicheiometric amounts of 2,2′-bisbenzoxazoline at room temperature in absolute ethanol.[2]†

Blue monoclinic crystals were obtained from an absolute ethanol solution, space group $P2_1/c$, $a = 7{\cdot}834$, $b = 15{\cdot}483$, $c = 11{\cdot}824$ Å, $\beta = 92{\cdot}65°$, $Z = 4$. The blue colour is consistent with mesomerism (conferred by planarity) of the co-ordinated organic ligand.

Cell dimensions and intensity data were measured at room temperature (Siemens four-circle diffractometer). Lattice and orientation parameters were derived using the Busing and Levy procedure.[3] In the reciprocal space corresponding to Θ 60° there are 2130 nonequivalent lattice sites excluding those prohibited by the space group, and of these, 1836 (86%) were observed above threshold. The $|F_0|$ data were the best least-squares values from two tube-current settings.[4]

Patterson, Fourier, and least-squares methods have been used to determine and refine atomic parameters, the present unweighted discrepancy index being 0·069 (all atoms, with the exception of uranium, have been given isotropic thermal parameters). 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 stereochemistry of the complex is shown in the Figure.

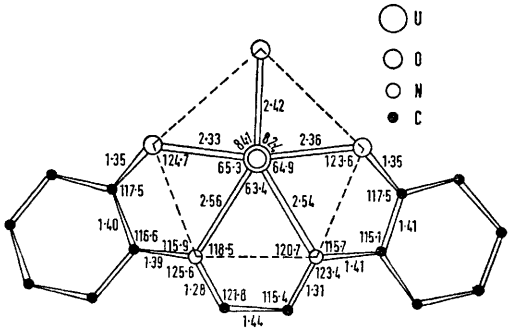

Figure. *Projection of the molecule on to the mean plane of the co-ordination pentagon. Bond lengths in* Å (*e.s.d.* 0·03, U–O *and* U–N 0·02 Å) *and angles in degrees* (*e.s.d.* ca. 2°). *Uranyl* U–O *distances are both* 1·77 Å *and the uranyl angle is* 179°.

The ^1H n.m.r. spectra show that a molecule of water is present and not a molecule of alcohol as in *NN′*-*o*-phenylenebis(salicylideneiminato)UO_2(EtOH) or in *NN′*-ethylenebis(salicylideneiminato)UO_2(MeOH). The pentagon of donor atoms is slightly puckered around the uranium, the oxygen of the water having a significant deviation (0·12 Å).

The U–O and U–N distances and the uranyl angle are consistent with those reported in the literature.[1,5]

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† A satisfactory analysis has been obtained.

The ligand within the equatorial plane is nearly planar (*cf.* ref. 1). Packing is mainly determined by the water molecule co-ordinated equatorially with two oxygen atoms of the Schiff's base of two adjacent molecules. Since the O–O distances are both 2·66 Å and the angle O–HOH–O is 102°, the presence of hydrogen bonds can be tentatively postulated.[6]

The co-ordinated water undergoes substitution with monodentate ligands such as py, $PhNH_2$, Me_2SO, and Ph_3PO under mild conditions.

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