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Dioxouranium(VI) Complexes with Polydentate Schiff Bases Containing Acetal Groups*

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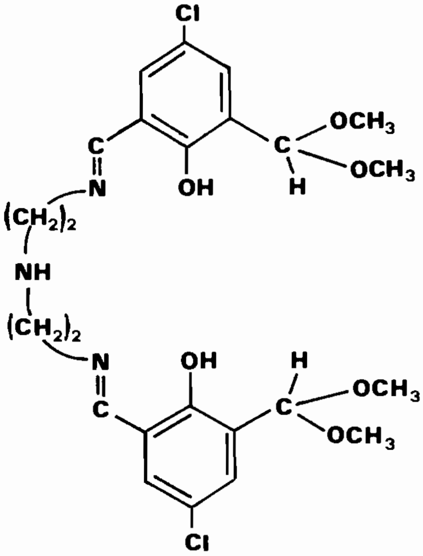
Diformylphenols are widely used as intermediates in the synthesis of multidentate ligands by condensation with polyamines. A general method of preparing metal complexes is to reflux methanolic solutions containing diformylphenol and the amine in stoichiometric ratios in the presence of the appropriate metal salt.

In this way we prepared and characterized mononuclear and binuclear complexes containing f-block elements [1–4]. Moreover, we observed that the reaction of 2,6-diformyl-4-chlorophenol [H(DIAL)] and 2,6-diformyl-4-methylphenol [H(MDA)] with the amines $(H_2N-CH_2-CH_2-)_2X$ (X = NH and S) in methanolic uranyl acetate solutions yielded solid products which seemed to contain acetal groups. We started then a detailed study on the behaviour of formylphenol precursors in alcoholic media.

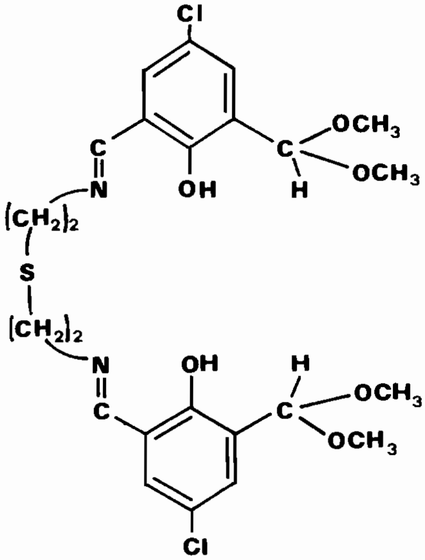
In anhydrous methanol both H(DIAL) and H(MDA) transform gradually into the corresponding dimethylacetal derivatives 2-dimethylacetal-4-chloro-6-formylphenol [H(ALAC)] and 2-dimethylacetal-4-methyl-6-formylphenol [H(MAC)], which have been isolated and characterized by electronic, infrared and ^1H and ^{13}C NMR measurements [5–7]. In aqueous methanol containing hydrochloric acid, the acetals change immediately into the parent dialdehydes.

When uranyl acetate is reacted with either H(DIAL) or H(MDA) in methanol, the nature of the products depends on temperature, time and water content. Under opportune conditions either the dialdehyde derivatives $[UO_2(DIAL)_2(L)]$ and $[UO_2(MDA)_2(L)]$, or the acetal derivatives $[UO_2(ALAC)_2(L)]$ and $[UO_2(MAC)_2(L)]$ can be isolated (L = H_2O or MeOH). The thermal degradation of these complexes yields $[UO_2(DIAL)_2]$ and $[UO_2(MDA)_2]$ as decomposition intermediates.

Owing to the versatility of dialdehydes, the template synthesis of Schiff base uranyl complexes by amine condensation in methanol can give in principle mixtures of aldehyde and acetal derivatives, easily identified by the proton NMR signals at about 10.7 ppm (aldehyde CH) and 6.5 ppm (acetal CH). In order to characterize fully the acetal derivatives, we prepared the ligands:



$H_2(NAC)$



$H_2(SAC)$

The crystal structures of the related complexes $[UO_2(NAC)]$ and $[UO_2(SAC)]$ show that the ligands act as pentadentate. In $[UO_2(NAC)]$ the five donor atoms lie in a plane perpendicular to the UO_2 moiety,

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whereas in $[UO_2(SAC)]$ the sulphur atom is appreciably out of the coordination plane, the U–S distance being 3.003 Å. The ^1H and ^{13}C NMR spectra indicate that ligands and complexes are stable in d_6-DMSO and $CDCl_3$. When the template synthesis is carried out in ethanol, the corresponding diethylacetal derivatives are isolated in a quantitative yield, whereas in isopropyl alcohol traces of water seem to cause the complete hydrolysis of the acetal groups to form the parent aldehyde complexes.

The results of this study point out the influence of the reaction medium on the synthesis of Schiff base complexes by using diformylphenols as starting products. Moreover, the hydrolysis of complexes containing alkylacetal groups yields complexes having aldehyde groups in the appropriate position to be used in further condensation to obtain binuclear complexes.

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