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The Interaction of a New Acyclic Schiff Base with Dioxouranium(VI) and Nickel(II) Ions

D E FENTON and S E GAYDA

Department of Chemistry, The University, Sheffield S3 7HF, U K

U CASELLATO, M VIDALI and P A VIGATO

Laboratorio di Chimica e Tecnologia dei Radioelementi CNR, Area di Ricerca, Corso Stati Uniti 10, 35100 Padova, Italy

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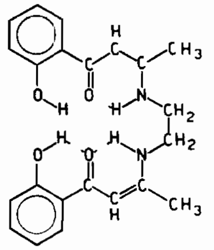
The synthesis of homo- and hetero-binuclear metal complexes of ligands containing dissimilar coordination sites has been reported [1–6] We report here the synthesis and characterisation of a new binucleating ligand in which the coordination sites have different donor atom sets and its interactions with dioxouranium(VI) and nickel(II) ions to yield mono- and binuclear complexes

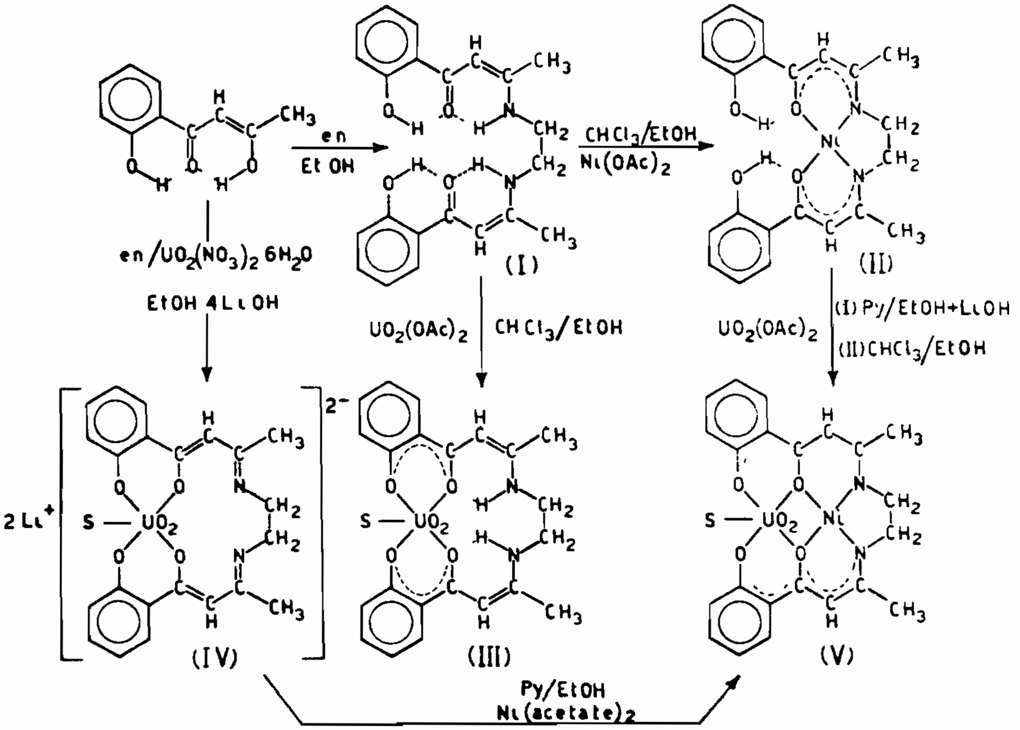


(1) H$_4$ aapen

The ligand (I) has been prepared by condensation of 1,2-diaminoethane (en) with *o*-acetoacetylphenol in ethanol Its formulation is supported by analytical and spectral data [^{1}H nmr (CDCl$_3$), 2 10 (6H, s, CH$_3$), 3.61 (4H, m, CH$_2$), 5 71 (2H, s, CH), 6 71–7 64 (8H, m, C$_6$H$_4$), 11 1 (2H, bd, N···H···O) and 13.33 ppm (2H, s, OH), i r bands are observed at 3400 (w), 3040 (w), 1600, 1575, 1550, 1515 and 760 cm^{-1}, m s , P$^+$ at m/e = 380] Mononuclear and binuclear complexes can be obtained according to the scheme

The reaction of a CHCl$_3$ solution of the ligand with an ethanolic solution of nickel(II) or dioxouranium(VI) acetate, in equimolar ratio, gave mononuclear complexes of the type H$_2$aapenM (II, III) Their formulations have been supported by analytical and physico-chemical data The magnetic moment of H$_2$aapenNi (0 85BM at 295 °K) indicates an almost square planar configuration with the N$_2$O$_2$ coordination site around the central atom in accordance with the drs and solution (py, dmso, CHCl$_3$) electronic spectra which show peaks at 575 nm and 568 nm respectively It may be noted that there is no change in the peak position on going from py to dmso to CHCl$_3$ solution indicating preservation of the square planar configuration in donor solvents The i r shows bands at 1615, 1592, 1513 and 1360 cm^{-1}

The dioxouranium(VI) complex shows a peak at 422 nm in the drs spectrum, and the i r showed bands at 1625, 1595, 1561, 1549, 1344, 910 and 891 cm^{-1} The latter may be ascribed to ν_3 (O=U=O)



The magnetic moment is 0.39 BM at 295 °K. We believe that the dioxouranium(VI) occupies the O_2O_2 coordination site in agreement with its 'harder' character, and because when a β-ketoamine reacts with dioxouranium(VI) salts it suffers a hydrolysis reaction and the corresponding dioxouranium(VI)–β-diketonate is obtained [7, 8]. Furthermore in the complex [[6,6′-(1,2-ethanediyldinitrilo)bis[2,4-heptanedionato]](2-)-O,O′,O″,O‴](methanol)dioxouranium(VI) where the dioxouranium(VI) is presented with a choice of N_2O_2 or O_2O_2 donor atom sets, the crystal structure confirms that the O_2O_2 set is used for metal coordination [5]. The dioxouranium(VI) complex was also prepared as $Li_2[aapenUO_2(S)]$ (IV; S = solvent) by a template synthesis. The coordinated solvent molecule may be substituted by a neutral monodentate ligand such as dmso. The i.r. of this complex shows bands at 1622, 1600, 1589 (bd) and 890 (ν_3 (O=U=O)) cm^{-1}.

The mononuclear complexes react with metal salts in EtOH/$CHCl_3$ or pyridine/EtOH in the presence of LiOH to give the binuclear species (V). In these complexes the i.r. spectra show bands at 1610(sh), 1592, 1515, 1345 and 898 (ν_3 (O=U=O)) cm^{-1}. The drs and solution electronc spectra show bands at 565 nm, 580 nm (py) and 570 nm (dmso) respectively. The magnetic moment at 295 °K is 0.85 BM, corresponding to the value obtained for H_2aapenNi, and confirming that nickel(II) occupies the N_2O_2 chamber. If it was in the O_2O_2 chamber the nickel (II) would be solvated and the species paramagnetic.

It is possible to prepare a series of hetero- and homobinuclear complexes of the ligand and a detailed investigation of this area is now in progress.

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