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The Preparation of Novel Schiff Bases from *o*-Acetoacetylphenol and 1,2-Propanediamine

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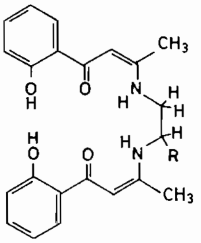
The application of β-ketophenols to the synthesis of compartmental ligands capable of forming homo- and heterobinuclear complexes has been established through the preparation and characterisation of the Schiff base $(H_2\text{-aap})_2$en, (I), and its metal complexes [1, 2].

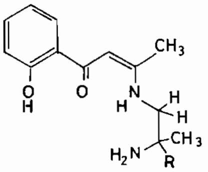


(I), R = H

(II), R = CH$_3$

The reaction of *o*-acetoacetylphenol (H_2aap) with 1,2-propanediamine (pn) in 2:1 stoichiometric ratio in ethanol yielded the corresponding compartmental ligand $(H_2aap)_2$pn, (II), the formulation of which is supported by analytical[†] and spectral data m.s., P^+ at m/e = 394; ^{1}H NMR ($CDCl_3$), 1.37 (3H,d,CH_3), 2.03(3H,s,CH_3), 2.05(3H,s,CH_3), 3.43(2H,t,CH_2), 3.87(1H,m,C*H*(CH_3)), 5.64(1H,s,–CH=), 5.66 (1H, s,–CH=), 6.76–7.58(8H,m,C_6H_4), 11.1(2H,bd,NH) and 13.36(2H,bd,OH) ppm; IR bands occur at 2980(w), 1600(s), 1575(s), 1555(m), 1480(m), 1250(s) and 740(m) cm^{-1}. Representative mononuclear complexes of (II) with Cu(II)$_{(N_2O_2)}$, Ni(II)$_{(N_2O_2)}$, and $UO_{2(O_2O_2)}$[††] have been synthesised together with the homobinuclear copper(II) complex and the heterobinuclear Cu(II)UO_2 complex establishing a similar ligand complexation pattern to that previously determined for (I) [1].

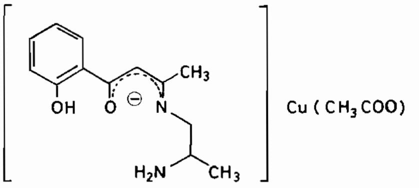
If, however, the reaction of H_2aap and pn was carried out in 1:1 ratio in ethanol using conditions of high dilution the 'half-unit' H_2aappn, (III), was obtained in good yield. That the acyclic species and not the corresponding diazepine has been formed is shown by the m.s. (P^+ at m/e = 234), IR (3380(m), 2800(w), 1600(s), 1575(m), 1540(s), 1515(m), 1480(s), 1255(s) and 760(m) cm^{-1}) and ^{1}H NMR spectra (1.13(3H,d,CH_3), 2.05(3H,s,CH_3), 3.13(3H, m,C*H*$_2$C*H*(CH_3)), 5.67 (1H,s,Ch), 6.75–7.60(4H,m, C_6H_4) and 11.12(1H,bd,OH) ppm). Diazepine formation has been found in the reaction of H_2aap with 1,2-diaminobenzene [3, 4] and it has been suggested that the potential steric interaction between the methyl groups on H_2aap and the 3,4 hydrogen atoms of the aromatic ring would inhibit formation of an acyclic compartmental Schiff base. If the more flexible *cis*-1,2-diaminocyclohexane is used in Schiff base formation from H_2aap then the acyclic compartmental ligand is isolated [5]. It is therefore plausible that in the reaction of H_2aap with pn a similar steric inhibition, due to methyl–methyl interaction, can to a certain extent govern the reaction pathway enabling formation of the 'half-unit'. The reaction of H_2aap with 1,2-diamino-2-methylpropane (dp) was carried out, as this diamine offers more steric crowding, and gave H_2aapdp, (IV), in good yield. (IV) was characterised by its m.s. (P^+ at m/e = 248), IR (2800(w), 1600(s), 1575(m), 1545(s), 1480(m), 1255(s) and 760(m) cm^{-1}) and ^{1}H NMR spectra ($CDCl_3$), (1.18(6H,s,CH_3), 2.07(3H,s,CH_3), 3.17(2H,d,CH_2), 5.69 (1H,s,CH), 6.77–7.61(4H,m,C_6H_4) and 11.27 (1H,bd,OH) ppm). In both III and IV very broad resonances are found at *ca.* 13.5 ppm.



(III), R = H

(IV), R = CH$_3$

Metal complexes of (III) have been prepared; the reaction of (III) with $M(CH_3COO)_2$, (M = Cu and Ni), in ethanol gave (III), Cu(CH_3COO) and (III), Ni(CH_3COO) respectively. The precise nature of these complexes is not certain but the copper complex



gave a blue colour with N,N,N′,N′-tetramethyl-1,4-diaminobenzene on aerobic interaction, as has been

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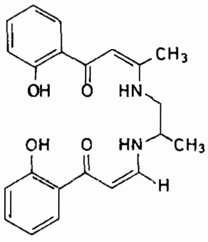
[†] Satisfactory microanalyses have been obtained for the reported compounds.

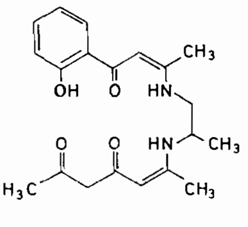
[††] The subscripts refer to the compartmental occupancy; N_2O_2 indicates the Schiff base donor set and O_2O_2 indicates the salicylaldehyde-like set. For the heterobinuclear complex the inner metal precedes the outer metal (see reference 2).

found for several binuclear Cu(II) complexes but not for mononuclear complexes [6].

H_2aap reacts with (III) to give (II) utilising the availability of a reactive amino group. The potential application of (III) to the synthesis of asymmetric compartmental ligands was therefore investigated. The reaction of (III) with the so-called ω-formyl-*o*-hydroxyacetophenone (H_2fap) [7] gave (V) as an oil (P^+ at m/e = 380) and a similar reaction with 2,4,6-heptanetrione gave (VI), also as an oil (P^+ at m/e = 358). Mononuclear $Cu(II)_{(N_2O_2)}$, $Ni(II)_{(N_2O_2)}$, and $UO_{2(O_2O_2)}$ complexes were prepared from (V) and (VI). These complexes have different IR spectra from those of the previously prepared symmetrical products [1, 2], and the copper and nickel complexes show the correct parent peaks in the m.s. (— the uranyl complexes were found to be involatile). The preparation of such complexes emphasises the usefulness of the 'half-units' in providing a facile extension to the available range of compartmental ligands.



(V)



(VI)

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