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# Metal Complexes of Binucleating Ligands Derived from 2,6-Diformyl- and 2,6-Diacetyl-4-methylphenol

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## Abstract

The preparation and complexing properties towards Cu(II), Ni(II) and $UO_2(VI)$ of acyclic and macrocyclic Schiff base ligands derived from the reaction of 2,6-diformyl- and 2,6-diacetyl-4-methylphenol with the facultative diamine 1,5-diamino-3-oxapentane and the functionalised diamine 1,3-diamino-2-hydroxy-propane are discussed.

## Introduction

The use of 2,6-diformyl-4-methylphenol as a precursor for the formation of acyclic and macrocyclic compartmental ligands has been well exploited, in particular by the groups of Robson, Kida and Gagné [1–4]. In contrast the analogous role of 2,6-diacetyl-4-methylphenol has been little studied [3–8]. The utilisation of facultative and functionalized diamines in the Schiff base reaction leading to compartmental ligands has also been limited to a few examples. Recently we have reported the synthesis of the acyclic and macrocyclic ligands derived from the condensation reactions of 2,6-diformyl-4-chlorophenol with 1,5-diamino-3-azapentane [9] and 1,5-diamino-3-thiapentane [10] and their metal-complexing properties. Herein we report the ligands derived from the condensation of 2,6-diformyl-4-methylphenol (dfmp-H) and 2,6-diacetyl-4-methylphenol (damp-H) with the facultative diamine 1,5-diamino-3-oxapentane (dop) and the functionalized diamine, 1,3-diamino-2-hydroxypropane (dhp).

## Experimental

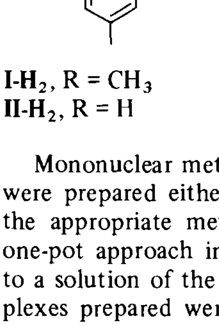
The procedures used for the preparation of the Schiff bases, and of the metal complexes are the standard ones used previously by ourselves and by Kida *et al.* [4]. The only modification has been in the employment of standard diamine solutions throughout.

Satisfactory microanalytical data were obtained.

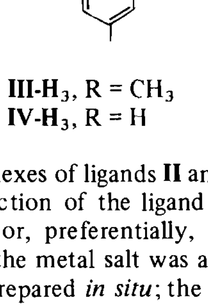
## Results and Discussion

### *Acyclic Ligands and Complexes*

The potentially binucleating ligands (**I**–**IV**) were prepared by a modification of the method of Kida and Okawa [4] in that a standard solution of the appropriate diamine in ethanol was titrated into a solution of the dicarbonylphenol in alcohol. After one hour reflux the solution was cooled; the precipitate was removed by filtration and washed with diethylether. The acyclic ligands were characterized by IR, $^1H$ NMR and MS (Table I).



**I-H$_2$**, R = $CH_3$
**II-H$_2$**, R = H



**III-H$_3$**, R = $CH_3$
**IV-H$_3$**, R = H

Mononuclear metal complexes of ligands **II** and **IV** were prepared either by reaction of the ligand with the appropriate metal salt, or, preferentially, by a one-pot approach in which the metal salt was added to a solution of the ligand prepared *in situ*; the complexes prepared were Cu(II), Ni(II)·$2H_2O$, $UO_2(II)$·

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TABLE I. Spectroscopic Data for the Acyclic Schiff Bases

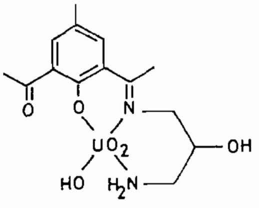
| Ligand | MS<br>($P^+$ $m/z$) | IR bands (C=O, C=N and C=C)<br>$cm^{-1}$ | $^1H$ NMR ($\delta$)<br>($CDCl_3$, TMS) |
|---|---|---|---|
| I-$H_2$ | 452 | 1660, 1650, 1620, 1530 | 2.23(6H, s, $CH_3$-arom)<br>2.67(6H, s, $CH_3$–C=O)<br>2.34(6H, s, $CH_3$–C=N)<br>7.34(2H, s, H-arom)<br>7.67(2H, s, H-arom)<br>3.91(4H, t, $CH_2$–N)<br>3.81(4H, t, $CH_2O$) |
| II-$H_2$ | 396 | 1660, 1642[a] | 2.23(6H, s, $CH_3$-arom)<br>7.25(2H, s, H-arom)<br>7.58(2H, s, H-arom)<br>3.75(8H, s, $CH_2$)<br>8.25(2H, s, CH=N)<br>10.42(2H, s, CH=O) |
| III-$H_3$ | 438 | 1660, 1620, 1530 | 2.28(6H, s, $CH_3$-arom)<br>2.65(6H, s, $CH_3$–C=O)<br>2.40(6H, s, $CH_3$–C=N)<br>7.45(2H, s, H-arom)<br>7.65(2H, s, H-arom)<br>3.78(4H, d, $CH_2$)<br>3.55(1H, n, CH) |
| IV-$H_3$ | 382 | 1670, 1635[a] | 2.28(6H, s, $CH_3$-arom)<br>7.30(2H, s, H-arom)<br>7.52(2H, s, H-arom)<br>3.55(5H, broad m, $CH_2$–CH)<br>8.40(2H, s, CH=N)<br>10.40(2H, s, CH=O) |

[a] No skeletal vibration detected, see ref. 4.

$2H_2O$, Cu(IV-H)·$H_2O$, Ni(IV-H)·$2H_2O$ and $UO_2$(IV-H)·$H_2O$.

Ligands **I** and **II** provide the adjacent dissimilar donor sets $-O_4-$ and $O_3N_2-$, and ligands **II** and **IV** provide the donor sets $-O_4-$ and $-O_2N_2(OH)-$. From the IR data it is proposed that for the complexes of **IV** the retention of $\nu$C=O at 1670 $cm^{-1}$ for the copper complex is indicative of an inner compartment occupancy [11], whereas for the nickel and uranyl complexes the shift to 1660 $cm^{-1}$ is indicative of outer compartment occupancy. Furthermore in the latter complexes the degree of hydration indicates that the metals are six- and seven-coordinated respectively. For the complex of **II** there is no shift in the carbonyl frequency and so it is proposed that the metal in each complex is coordinated in the inner compartment.

Attempts to systematically synthesize metal(II) complexes of **I** and **III** were not successful under the conditions used in the case of copper and nickel. The complex $UO_2$(I) was prepared and from the unshifted position of the $\nu$C=O at 1660 $cm^{-1}$ is assigned an inner compartment occupancy. This would give a seven-coordinated metal ion. An unusual half-unit complex is prepared from the reaction of damp-H and dhp is the presence of $UO_2(NO_3)_2 \cdot 6H_2O$ and LiOH. The bright orange product was identified as **V** from microanalytical and IR data.

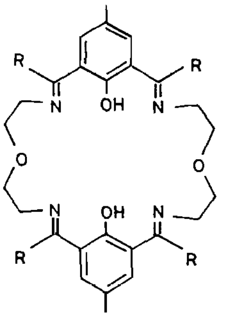


**V**

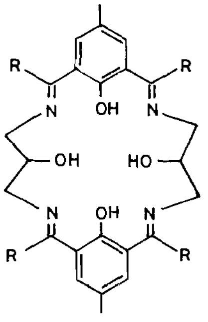
The IR shows bands at 3450 ($\nu$OH), and 3335 and 3275 ($\nu NH_2$), 1680 ($\nu$C=O) and 1610 ($\nu$C=N) $cm^{-1}$. It is plausible to consider that seven coordination of the uranium could be achieved through interaction with the carbonyl or aminoalcohol units; this could be intramolecular or more probably, on steric grounds, intermolecularly to give an aggregated structure. It was not found possible to add a second molecule of damp-H to give an acyclic Schiff base of type **III**.

### *Macrocyclic Ligands and Complexes*

Attempts to synthesize the free Schiff base macrocycles **VI**–**IX** were not successful. The reaction gave gums or oils, which, judged by their MS, appeared to be oligomeric in nature.

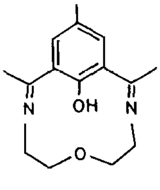


**VI**-$H_2$, R = $CH_3$
**VII**-$H_2$, R = H

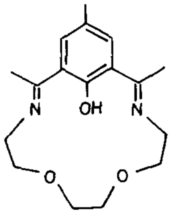


**VIII**-$H_4$, R = $CH_3$
**IX**-$H_4$, R = H

In the reaction of damp-H with dop, and also with the related diamine, 1,8-diamino-3,6-dioxaoctane, in methanol, viscous orange-yellow oils were recovered on work up. The MS gave parent peaks at *m/z* of 260 and 360 respectively corresponding to the formation of the [1 + 1] macrocycles **X** and **XI**. These products, however, were not analytically 'clean' and did not respond well to attempts to purify them using column chromatography.



**X**



**XI**

Employment of metal template procedures led to the preparation of dinuclear complexes of the required macrocycles, but not consistently or in good yield. In the diformyl case homodinuclear complexes of **VII** and **IX** were prepared for copper(II), nickel(II) and uranyl(VI) ions. The technique of using standard diamine solutions was employed and gave consistently good results. Only in the case of $(UO_2)_2$(**VII**)$(OAc)_2$ was an anhydrous complex recovered; for the remaining complexes high degrees of hydration were noted and these were dependent upon the nature of the drying procedure. The complexes prepared were $Cu_2$(**VII**)$(OAc)_2 \cdot nH_2O$ ($n = 4, 5$); $Ni_2$(**VII**)$(OAc)_2 \cdot 5H_2O$; $(UO_2)_2$(**VII**)$(OAc)_2$; $Cu_2$(**IX**)$(OAc)_2 \cdot nH_2O$ ($n = 4, 6$); $Ni_2$(**IX**)$(OAc)_2 \cdot 5H_2O$ and $(UO_2)_2$(**IX**)$(OAc)_2 \cdot 4H_2O$. It was not possible to grow crystals suitable for X-ray analysis and so the precise nature of the dinuclear sites is not certain.

With damp-H a limited number of macrocyclic species were obtained, being restricted to the dicopper(II) derivatives of **VI** and **VIII**, $Cu_2$(**VI**)$(ClO_4)_2$; $Cu$(**VI**)$(BF_4)_2 \cdot 2H_2O$ and $Cu_2$(**VIII**-$H_2$)$(ClO_4)_2$. In the latter complex two bands attributable to the imine stretching frequency were noted at 1625 and 1620 $cm^{-1}$ which suggest that there may be an asymmetry to the dinuclear environment. Again it was not possible to grow crystals suitable for study. The discrete nature of the macrocycle **VIII** however has been established in the structure of the mononuclear barium complex $Ba$(**VIII**-$H_4$)$(ClO_4)_2$ [12].

It is noteworthy that whilst mono- and dinuclear complexes of macrocycles derived from dfmp-H are reproducibly obtained [4] use of damp-H gave inconsistent results. This is probably due to the methyl groups present in the acetyl complex inhibiting the reaction of the carbonyl groups (positive inductive effect) and having greater steric requirements than the formyl group. Relatively few macrocycles have been obtained from damp-H, even when using diamines such as 1,2-diaminoethane and 1,2-diaminopropane [13].

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