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# Metal Complexes of some Tetraketones and their Schiff Bases

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*Metal complexes of the tetraketones N-(o-tolyl)-diacetoacetamide ($H_2L_a$) and 1,1'-(2,6-pyridyl)bis-1,3-butanedione ($H_2L_b$) are reported. The reaction of $H_2L_b$ with hydroxyalkyl- and hydroxyarylamines to yield Schiff bases ($H_4L$) is given and metal complexes of the type, $M_2L$, $M(H_4L)X_2$ and $M_2(H_2L)X_2$ have been prepared.*

*The properties of the metal complexes are discussed and suggested structures presented.*

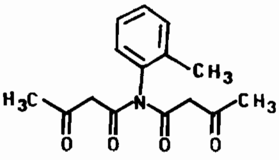
## Introduction

In studies of polynuclear complexes it would be of value to investigate a homologous series of complexes in which the members of the series contain successively one, two, three, *etc.*, metal ions. If the metal ions are in similar environments then the variation in the properties of the complexes on changing the number of the metal centres could be critically assessed. The polyketones represent a class of ligands capable of producing such a series.

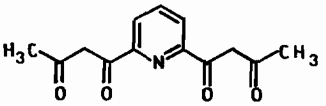
The first members of the series, the 1,3-diketones have been well studied and need no further comment at this point [1, 2]; the next members, the 1,3,5-triketones, have been less well studied but there are several papers concerning the binuclear derivatives of these ligands [3, 4]. Recently a linear trinuclear nickel(II) triketonate, hexaaqua-dihydroxobis(1,1,1-trifluoro-2,4,6-heptane-trionato)trinickel(II), has been reported [5].

Studies on 1,3,5,7-tetraketones have given bi- and tri-nuclear complexes [6]; 1,7-diphenyl-1,3,5,7-heptantetraone gave the homotrinuclear complexes, $Cu_3L_2(H_2O)_3$, $Ni_3L_2(H_2O)_6$ and $Co_3L_2(H_2O)_6$ and the x-ray structure of the heterodinuclear complex $(UO_2)_2NiL_2(pyridine)_4$ has been solved and shows that the dioxouranium(VI) moieties occupy terminal sites whilst the nickel(II) occupies the central site [7].

In a previous paper [8] we have reported the preparation and properties of the tetraketones 1,1'-(1,3-phenylene)-bis-1,3-butanedione, 1,1'(1,4-phenylene)-bis-1,3-butanedione and 1,4-bis(acetoacetyl)-piperazine. We report here the synthesis and properties of metal complexes of the tetraketones N-(*o*-tolyl)-diacetoacetamide ($H_2L_a$) and 1,1-(2,6-pyridyl)bis-1,3-butanedione ($H_2L_b$), and of the Schiff base derivatives of $H_2L_b$.



$H_2LA$



$H_2LB$

## Experimental

Microanalytical data were obtained via the Microanalytical Services at the Universities of Sheffield and Padua. Mass spectra were run on an MS12 mass spectrometer; i.r. spectra on a Perkin Elmer 297 infrared spectrophotometer as KBr discs; electronic spectra on a Cary 14 spectrometer and magnetic measurements carried out using the Gouy technique at room temperature with $CuSO_4 \cdot 5H_2O$ as a calibrant. $^1H$ nmr were recorded on a Perkin Elmer R34 spectrometer at 220 MHz. The ligand $H_2L_a$ was used as purchased from Aldrich.

Diethyl,2,6-pyridinedicarboxylate was prepared from 2,6-pyridine-dicarboxylic acid according to the method of Cram [9].

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*Preparation of Binuclear Complexes* $M_2(L_a)_2 \cdot nS$ ($M$ = *Zn*, $n = 0$; $M$ = *Cu*, $n = 2$, $S = H_2O$; $M$ = *Ni, Mn*, $n = 6$, $S = H_2O$; $M = UO_2$, $n = 1$, $S$ = *EtOH*)

To an ethanolic solution of the ligand (1 mmol) and NaOH (1 mmol) was slowly added metal acetate (1 mmol) in ethanol (100 ml). The coloured solution was kept at 25 °C for several hours. The mixture was then allowed to stand at room temperature for 2 h and the precipitate collected by filtration, washed with ethanol, and dried *in vacuo.*

*Preparation of Trinuclear Complexes from* $H_2L_a$

These complexes were prepared by two different routes:

1. The binuclear complex (1 mmol) was suspended in ethanol (100 ml), to this suspension an ethanolic solution of metal perchlorate (1 mmol) was added. The mixture was stirred for 2 h., after this time a clear solution was obtained. The solution was evaporated to dryness and the residue treated with water and stirred for two days. The solid was filtered, washed with water and dried *in vacuo*. The elemental analyses agree with the formulation $M_3(L_a)_2(ClO_4)OH \cdot 2H_2O$.

2. An ethanolic solution of the metal perchlorate (3 mmol) was slowly added to an ethanolic solution of ligand (2 mmol). The resulting solution was stirred at room temperature for 2 h., and then evaporated to dryness. The residue was treated with water and the precipitate was filtered, washed with water, and dried *in vacuo*. Again the elemental analyses agree with the formulation $M_3(L_a)_2(ClO_4)OH \cdot 2H_2O$.

*Preparation of 1,1'-(2,6-pyridyl)bis-1,3-butanedione* $H_2L_b$)

Sodium wire (2.6 g, 0.113 mol) and diethyl ether (50 ml) were placed in a three-necked, round bottomflask fitted with a condenser and dropping funnel. The contents of the flask were agitated with a magnetic stirrer, while dry ethanol (10 ml) was added dropwise (n.b. It may be necessary to add a little extra ethanol for complete dissolution of the sodium). To the freshly prepared sodium ethoxide, acetone (7 ml) in benzene (30 ml) was added, followed quickly by diethyl 2,6-pyridinedicarboxylate (9.2 g, 0.04 mol). Stirring at room temperature was continued until the yellow sodium salt had precipitated out of the solution. The reaction was heated gently for 2 h., then cooled. The sodium salt was collected by filtration and washed throughly with diethyl ether before drying. The dry solid was added to dilute aqueous acetic acid (15%, 60 ml) and the resulting solid collected by filtration.

The crude product was dissolved in diethyl ether (200 ml). The solution was filtered to remove any insoluble material, washed with aqueous sodium bicarbonate solution (5%, 2·50 ml) and distilled water (50 ml), then dried over anhydrous magnesium sulphate. The product was obtained by evaporation of the solution to dryness, as an ochre-yellow solid. Yield 3–5 g. (30–50%). Micro-analysis: $C_{13}H_{13}NO_4$ requires C 63.17%, H 5.31%, N 5.67%. Found: C 63.29%, H 5.13%, N 5.60%. M.S. $P^+$ at m/e 247 corresponding to $C_{13}H_{13}NO_4$.

$^1$H nmr ($CDCl_3$): The spectrum shows the presence of tautomers: ~90% bis(keto-enol); ~9% keto–(keto-enol); ~1% bis(keto). 2.24(s), 2.31(s) ($CH_3$); 4.24(s) ($CH_2$diketo), 4.28(s) (keto–(keto-enol)); 6.73(s) (CH, keto–(keto-enol)); 6.82(s) (CH bis (ketoenol); 7.91–8.26(m) (aromatic); 15.60 (broad) (OH).

*Preparation of the Metal Complexes of* $H_2L_b$

The micro-analytical data are given in Table II. Two general procedures were followed in preparing the metal complexes.

1. The metal ethanoate (0.002 mol) in hot ethanol (50 ml) was added to a solution of ligand (0.002 mol) in hot ethanol (50 ml). The fine suspension which resulted was heated for a while to reduce the volume of the solvent, then centrifuged. The supernatant liquor was decanted and the remaining solid soxhleted with methanol, then dried *in vacuo.*

2. The metal ethanoate (0.002 mol) in pyridine (50 ml) was added to ligand (0.002 mol) in pyridine (25 ml), and the resulting solution was refluxed for several hours. The precipitate which formed was isolated by filtration, washed with methanol, then dried *in vacuo.*

*Preparation of Vanadyl Complex* $(VO)_2(L_b)_2$

$VO(SO_4)_2$ (0.002 mol) in hot ethanol (50 ml) was added to ligand (0.002 mol) also in hot ethanol (50 ml). The resulting solid was filtered and soxhleted with water, then methanol. The product was dried *in vacuo* over silica.

*Preparation of 1,1'-(2,6-pyridyl)bis-(6-hydroxy-3-methyl-4-azahex-2-ene-1-one),* ($H_4L_1$)

1,1'-(2,6-pyridyl)bis-1.3-butanedione ($H_2L_b$) (1.0 g, 0.004 mol) and 2-aminoethanol (0.49 g, 0.008 mol) were gently refluxed in ethanol (100 ml) for 1–2 hours. The resulting red solution was concentrated to ~30 ml, then cooled in a refrigerator. The product, which precipitated out of solution as pale yellow microcrystals, was collected, washed with cold ethanol (25 ml), then dried *in vacuo* over silica. Yield 0.9 g (67%).

*Preparation of other Hydroxyalkylimines*

The same method can be used to prepare a series of analogous compounds.

1. $H_2L_b$ (1.0 g, 0.004 mol) and 3-aminpropanol (0.61 g, 0.008 mol), in ethanol, yields 1,1'-(2,6-pyridyl)bis-(7-hydroxy-3-methyl-4-azahept-2-ene-1-one), ($H_4L_2$), as a yellow solid. Yield 1.05 g (72%).

2. $H_2L_b$ (1.0 g, 0.004 mol) and 4-aminobutanol (0.73 g, 0.008 mol) in ethanol, yields 1,1′-(2,6-pyridyl)bis-(8-hydroxy-3-methyl-4-azaoct-2-ene 1-one), ($H_4L_3$), as a yellow solid. Yield 0.86 g (56%).

3. $H_2L_b$ (1.0 g, 0,004 mol) and 5-aminopentanol (0.84 g, 0.008 mol), in ethanol, yields 1,1′-(2,6-pyridyl)bis-(9-hydroxy-3-methyl-4-azanon-2-ene-1-one), ($H_4L_4$), as a yellow solid. Yield 0.82 g (50%).

### *Preparation of $H_4L_5$*

$H_2L_b$ (1.0 g, 004 mol) and 2-aminophenol (0.88 g, 0.008 mol) were refluxed in methanol (100 ml) for 4–6 hours. 1,1′-(2,6-pyridyl)bis-[4-(2-hydroxyphenyl)-3-methyl-4-azabut-2-ene-1-one], precipitated out of solution as a yellow solid. The product was collected, washed with methanol, and dried *in vacuo* over silica. Yield 1.17 g (69%).

Micro-analytical data for these hydroxyimines are given in Table 2, along with mass spectral data.

### *Preparation of Complexes of $H_4L_1$ derived from Metal(II) Halides*

A general method was used for the preparation of these complexes. Metal(II) halide (0.002 mol) in hot absolute ethanol (50 ml) was added to $H_4L_1$ (0.34 g, 0.001 mol) in hot ethanol (50 ml). The resultant solution was heated on a steambath until the volume was 50 ml. The solution was allowed to cool, and the product precipitated out as a microcrystalline solid, which was washed with cold ethanol, then dried *in vacuo* over silica.

### *Preparation of Complexes of $H_4L_1$, $H_4L_3$ and $H_4L_5$ derived from Copper(II) Tetrafluoroborate, and Copper(II) Perchlorate*

The same procedure as that described for the reaction of with metal halides was followed, resulting in green precipitates which were isolated, washed with ethanol, and dried *in vacuo* over silica.

### *Preparation of Copper Complexes of the Type $Cu_2(L)$. ($L = H_4L_1, H_4L_2, H_4L_5$)*

A general procedure was used for the preparation of these complexes.

Copper(II) ethanoate (0.8 g, 0.004 mol) in hot 95% ethanol (100 ml) was added to a stirred solution of ligand (0.002 mol) in hot ethanol (50 ml). A precipitate formed immediately. The volume of solution was reduced by heating, and the resulting suspension was cooled. The fine precipitate was isolated by centrifuging the suspension, and decanting off the supernatant liquor. The slurry thus obtained was dried *in vacuo* over silica. The complex was purified by grinding the dry solid into a powder and soxhleting with a suitable solvent.

### *Preparation of $Zn_2(H_4L_1)(OAc)_2$–EtOH*

Zinc(II) ethanoate (0.66 g, 0.003 mol) in hot absolute ehtanol (50 ml) was added to $H_4L_1$ (0.5 g, 0.0015 mol) in hot absolute ethanol (100 ml). The resulting deep yellow solution was concentrated to 20 ml by heating, then cooled. A yellow precipitate formed which was filtered, washed with cold ethanol and dried *in vacuo* over silica.

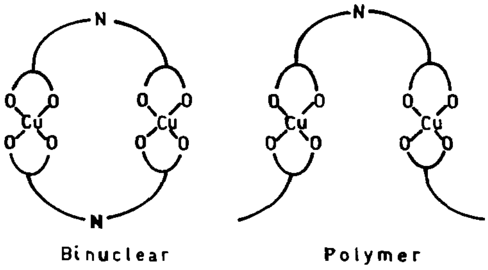
Microanalytical data for the metal complexes are given in Table II.

## Results and Discussion

### *Complexes of $H_2L_A$*

The reaction of $H_2L_A$ in ethanol with copper(II), nickel(II) manganese(II) zinc(II) acetates and with uranyl(VI) nitrate hexahydrate, in molar ratio 1:1 gave the compounds $Cu_2(L_A)_2 \cdot 2H_2O$, $Ni_2(L_A)_2 \cdot 6H_2O$, $Mn_2(L_A)_2 \cdot 6H_2O$, $Zn(L_A)_2$ and $UO_2(L_A)_2 \cdot 2EtOH$. The complexes are sparingly soluble in common organic solvents and more soluble in coordinating solvents such as dimethylsulphoxide or pyridine; for the uranyl(VI) complex, the compounds $UO_2(L_A)_2(py)_2$ and $UO_2(L_A)_2(dmso)_2$ can be obtained from these solvents.

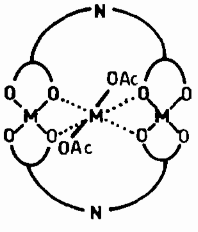
For all the binuclear complexes two structural forms can be proposed, (A) and (B)



(A) (B)

The infrared spectra of the complexes are characterized by the presence of two or three bands in the 1600–1500 cm$^{-1}$ region assigned to the C=O and C=C stretching modes. The first band at about 1590 cm$^{-1}$ is due to the stretching of the C=O group, and the second band at about 1525 cm$^{-1}$ is assigned to the C=C modes. A broad band ranging from 3400 –3200 cm$^{-1}$ is due to the stretching of the water. The uranyl(VI) complex shows an absorption peak at 900 cm$^{-1}$ due to the $\nu_3$ asymmetric O–U–O stretching mode. The electronic spectra of the copper(II) complexes in dimethylsulphoxide solution show a d–d band at about 680 nm probably due to pentacoordinated copper(II); the nickel(II) chelates show two bands at about 600 and 900 nm, typical of high-spin (not planar) nickel(II) species.

The uranyl binuclear complexes show a broad band at 450 nm attributed to the apical oxygen f transition of the uranyl moiety. The magnetic moment of the d-transition metal complexes are those for isolated metal ions and no magnetic coupling was detected. By reaction of the ligand $H_2L_A$ with the appropriate metal salt in a 2:3 molar ratio, trinuclear complexes can be obtained; trinuclear complexes can be also prepared by the reaction of the binuclear chelate with the appropriate metal perchlorate in a molar ratio 1:1. The structure (C)



Trinuclear

(C)

or a polimeric equivalent can be suggested for these trinuclear complexes. The infrared spectra are substantially similar to those of binuclear chelates; differences can be noted in the region of the stretching of the $ClO_4^-$ group. For $Ni(L_4)_2(OH)(ClO_4)\cdot 2H_2O$ and $Cu_3(L_A)_2(OH)(ClO_4)\cdot 2H_2O$, a broad band at 1100 $cm^{-1}$ due to the $\nu_3(F_2)$ and an intense band at about 630 $cm^{-1}$ due to $\nu_4(F_2)$ were found, indicating that the $ClO_4^-$ group is uncoordinated.

The electronic spectra have a shape similar to that of the binuclear chelates; the bands due to d–d transitions are shifted by about 30 nm towards lower energies, indicating that probably an interaction takes place among the metal ions. The magnetic moments, lower than the spin-only values, indicate a magnetic interaction between these ions.

*Complexes of $H_2L_b$*

The reaction of an alcoholic solution of the ligand with an equimolar amount of metal acetate ($Cu^{2+}$, $UO_2^{2+}$) results in the immediate precipitation of binuclear complexes of the type $M_2(L_b)_2(solvent)_n$ (n = 0,2). The compounds may be purified by soxhlet extraction with a suitable solvent, removing unreacted metal acetate and ligand. The oxovanadium(IV) complex is best prepared from oxovanadium(IV) sulphate as the acetate is difficult to remove from the product due to its low solubility. The $Co^{2+}$ and $Ni^{2+}$ complexes are conveniently prepared by refluxing equimolar quantities of the ligand and metal acetate in pyridine.

$M_2(L_b)_2(py)_4$ precipitates out of the solution and is readily isolated.

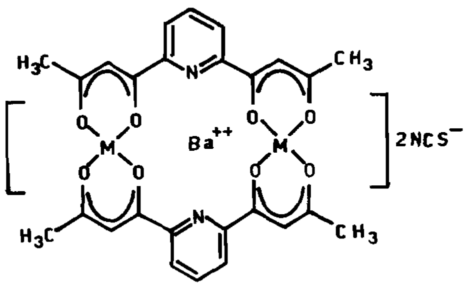
The complexes are insoluble in most common organic solvents, and sparingly soluble in coordinating solvents such as pyridine. Two structural forms may again be proposed for the products, (A) and (B). By analogy with metal complexes of 1,1′-(1,3-phenylene)bis-1,3-butanedione it is suggested that monomeric, binuclear complexes of the type (A) are formed [8]. This suggestion is also consistent with the proposal for binuclear complexes of the tetraketone, 1,7-diphenyl-1,3,5,7-heptane-tetraone [6].

The i.r. spectra of the metal complexes of $H_2L_b$ show three medium bands in the region 1500–1600 $cm^{-1}$. The band in the region 1500–1520 $cm^{-1}$ has been assigned to the C=C vibration while the two bands *ca.* 1545 and 1600 $cm^{-1}$ are associated with $C\overset{\cdots}{-}O$ and pyridine $C\overset{\cdots}{-}N$ vibrations. The dioxouranium(VI) complex has a peak at 910 $cm^{-1}$ ($\nu_3$ asymmetric O–U–O stretch).

The d.r.s. of the copper complex $Cu_2(L_b)_2$ gave two broad bands at 571 and 667 nm, comparable with those observed for bis(acetylacetonato)copper(II) and indicative of a square planar geometry [10]. The $Ni_2(L_b)_2$, 4py complex gave bands at 575 and 1031 nm, comparable with octahedral bis(acetylacetonato)nickel(II)dipyridine [11] and the cobalt complex also gave bands indicative of an octahedral environment, 520 and 1053 nm [12]. The spectrum of $(VO)_2(L_b)_2$, gave three bands at 459, 559 and 781 nm; similar bands are detected in the spectra of bis(diketonato)oxovanadium(IV) complexes [13].

The magnetic moments for the complexes were measured by the Gouy method at room temperature. The metal centres are quite far apart (*ca.* 6–7 Å) and so no direct interaction is anticipated in any exchange process occurring through the ligands. $Cu_2(L_b)_2$ has a moment of 1.39 BM and so some exchange is likely. A moment of 1.44 BM per Cu was recorded for the corresponding dinuclear copper complex of 1,1′-(1,1-phenylene)bis(1,3-butanedione) [8]. The nickel, cobalt and oxovanadium complexes gave reduced magnetic moment values of 2.29, 3.48 and 1.21 BM per metal atom respectively.

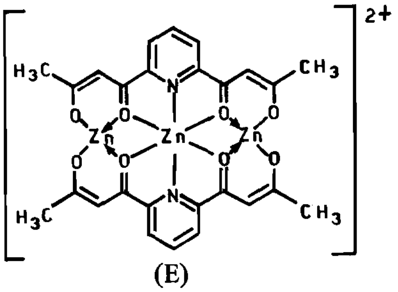
The reaction of $Cu_2(L_b)_2$, or $Ni_2(L_b)_2$,4py, with a slight molar excess of $Ba(SCN)_2$ in hot ethanol, gave in each case a light-green compound. These compounds analysed as $Cu_2Ba(L_b)_2(SCN)_2$ and $Ni_2Ba(L_b)_2(SCN)_2$ respectively. If KNCS was used then only the binuclear precursors were recovered. There are slight modifications in the spectra of the trinuclear species; the i.r. spectra display bands at 2050 $cm^{-1}$ (Cu) and 2080 $cm^{-1}$ (Ni) due to the thiocyanato anion, and there are minor displacements of the bands detected for the parent dinuclear species. Similarly in the d.r.s. modifications are noted. For the copper complex, bands are seen at 463 and 690 nm; and for the nickel complex bands are found at 460, 610 and 1087 nm. In both spectra a new band has occurred at *ca.* 460 nm: this may be due to charge transfer from the metal to the thiocyanate, or the barium ion may have perturbed the energy levels of the copper or nickel to produce another allowed transition. The magnetic moments are very close to those of the binuclear species, 2.39 BM for Ni(II) and 1.35 BM for Cu(II). The suggested struc-



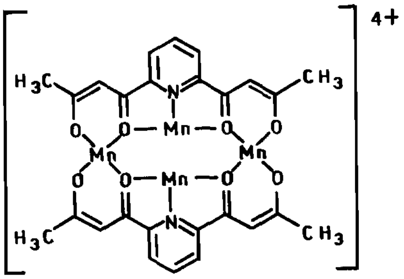
(D) M, = Cu++, Ni++

ture for these complexes is (D), and this is comparable with the heterotrinuclear $(UO_2)_2Ni$ complex of 1,7-diphenyl-1,3,5,7-heptanetetraone [7].

Two further compounds which could reproducibly be assigned multinuclear structures were obtained from the reaction of zinc(II) acetate, or manganese(II) acetate with $H_2L_b$. In the former a pale-yellow solid analysing consistently as $Zn_3(L_b)_2(OAc)_2$ was obtained, suggesting the trinuclear structure (E), and in the latter an orange solid analysing as $Mn_4(L_b)_2(OAc)_4$ was recovered for which the tetranuclear structure (F) is plausible. The central cavity could contain two metal ions, as binuclear transition metal complexes of related hexadentate Schiff base macrocycles are readily available [14].



(E)

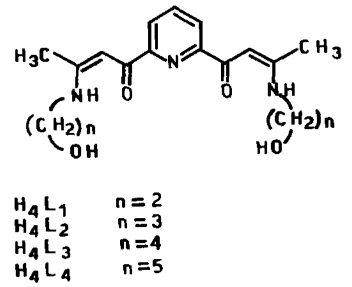


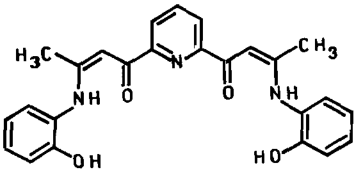
(F)

It is possible that the large central cavity, together with the general insolubility of the complexes, hinders trinuclear formation; the larger radius of barium would facilitate trinucleation but generally in order to build up an array of metals it would be required to reduce the central size in order to promote coordination.

*Schiff Bases derived from $H_2L_b$*

The tetraketone $H_2L_b$ was reacted with a series of hydroxyalkyl- and hydroxyaryl-amines in ethanol to give the Schiff bases $H_4L_1$–$H_4L_5$. The compounds were characterized by microanalysis (Table II) and the presence of the parent peak in the m.s., i.r. and $^1H$ nmr spectra. The $^1H$ nmr spectra are summarized in Table I and indicate that the bases are in the bis(enamine) form with no imine form detected.





$H_4L_5$

TABLE I. $^1H$ nmr Data for the Hydroxyalkyl- and Hydroxyarylimines (ppm: $d_6$-dmso).

| | $H_4L_1$ | $H_4L_2$ | $H_4L_3$ | $H_4L_4$ | $H_4L_5$ |
|---|---|---|---|---|---|
| $CH_3$ | 2.30(s) | 2.23(s) | 2.16(s) | 2.17(s) | 2.27(s) |
| CH(vinyl) | 6.57(s) | 6.56(s) | 6.44(s) | 6.41(s) | 6.72(s) |
| Aromatic(phenyl) | | | | | 6.84–7.24(n) |
| Aromatic(pyr.) | 8.01–8.82(m) | 8.08(m) | 7.90–8.05(m) | 8.02(m) | 8.05(m) |
| OH | 5.07(bd) | 4.70(bd) | | | 9.97(s) |
| NH | 11.77(t) | 11.50(t) | 11.45(t) | 11.42(t) | 13.28(s) |
| $CH_2)_n$ | 3.58(q) | 1.81(q) | 1.65(m) | 1.48(m) | |
| | 3.78(q) | 3.51(q) | 3.41(q) | 1.62(m) | |
| | | 3.57(q) | 3.63(t) | 3.42(q) | |

TABLE II. Microanalytical Data (Required Values in Parentheses).

| | %C | %H | %N | $P^+$ at m/e |
|---|---|---|---|---|
| (A) Schiff bases | | | | |
| $H_4L_1$ | 61.18(61.23) | 6.86(6.97) | 12.73(12.61) | 333 |
| $H_4L_2$ | 62.72(63.12) | 7.16(7.54) | 11.39(11.63) | 361 |
| $H_4L_3$ | 64.61(64.74) | 8.00(8.04) | 10.82(10.79) | 389 |
| $H_4L_4$ | 65.89(66.15) | 8.57(8.45) | 9.93(10.06) | 417 |
| $H_4L_5$ | 69.61(69.91) | 5.38(5.41) | 9.71(9.79) | 429 |
| (B) Complexes of $H_2L_b$ | | | | |
| $Cu_2(L_b)_2$, $O{\cdot}5H_2O$ | 49.80(49.83) | 3.78(3.71) | 4.29(4.47) | |
| $Ni_2(L_b)_2$, 4py | 58.97(59.77) | 4.40(4.59) | 9.42(9.09) | |
| $Co_2(L_b)_2$, 4py | 58.70(59.74) | 4.80(4.59) | 9.11(9.09) | |
| $(VO)_2(L_b)_2$ | 49.30(50.01) | 3.54(3.56) | 4.59(4.49) | |
| $(UO_2)_2(L_b)_2$2MeOH | 30.45(30.72) | 2.66(2.76) | 2.49(2.56) | |
| $Cu_2Ba(L_b)_2(NCS)_2$, 2MeOH | 39.04(39.28) | 2.91(3.08) | 5.71(6.11) | |
| $Nc_2Ba(L_b)_2(NCS)_2$ | 39.02(39.11) | 3.49(2.58) | 6.68(6.51) | |
| $Mn_4(L_b)_2(OAc)_4$ | 42.81(43.14) | 3.57(3.63) | 3.21(2.96) | |
| $Zn_3(L_b)_2(OAc)_2$ | 44.10(44.77) | 3.18(3.51) | 3.69(3.48) | |
| (C) Complexes of Schiff bases | | | | |
| $Cu_2(L_1)$, $O{\cdot}25H_2O$ | 44.28(44.28) | 4.34(4.27) | 9.05(9.12) | |
| $Cu_2(L_2)$ | 47.23(47.09) | 4.95(5.21) | 8.29(8.67) | |
| $Cu_2(L_5)$ | 54.23(53.94) | 3.93(4.17) | 7.33(7.55) | |
| $Zn_2(H_2L_1)(OAc)_2$, EtOH | 45.54(45.20) | 5.52(5.45) | 7.21(6.88) | |
| $Cu(H_4L_1)Cl_2$, $1/2H_2O$ | 42.79(42.81) | 4.97(5.08) | 8.61(8.81) | |
| $Mn(H_4L_1)Cl_2$ | 44.31(44.46) | 4.83(5.05 | 9.17(9.15) | |
| $Cu(H_4L_1)(BF_4)_2$ | 35.57(35.78) | 3.78(4.07) | 7.48(7.37) | |
| $Cu_2(H_2L_1)Br_2$, $2H_2O$ | 29.70(31.19) | 3.38(3.86) | 6.05(6.40) | |
| $Cu_2(H_2L_3)(BF_4)_2$, 2MeOH | 37.01(36.72) | 5.20(4.97) | 5.53(5.59) | |
| $Cu_2(H_2L_1)(ClO_4)_2$2EtOH | 32.39(32.44) | 3.74(3.88) | 6.06(5.97) | |

Although no structural data are available it is proposed that the condensation reaction occurs at the terminal ketone function in agreement with reports of similar reactions in which condensations take place at the least hindered sites [15]. The i.r. spectra of the alkane-derived species show a sharp peak at ~3400 $cm^{-1}$ due to the hydroxyl–OH stretching frequency, and bands at ~1600 $cm^{-1}$ and 1560 $cm^{-1}$ attributable to the $C\overset{\cdots}{-}O$ and $C\overset{\cdots}{-}C$ + $C\overset{\cdots}{-}N$ vibrations. For the aromatic species ($L_5$) the hydroxyl peak occurs at 3250 $cm^{-1}$ and several strong sharp bands are seen in the region 1500–1605 $cm^{-1}$ due to $C\overset{\cdots}{-}C$, $C\overset{\cdots}{-}O$ and $C\overset{\cdots}{-}N$ vibrations.

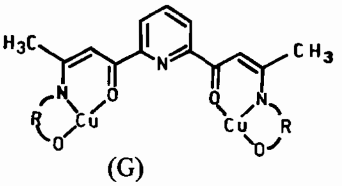
The hydroxylalkyl- and hydroxylarylimines are potentially heptadentate ligands with a maximum proton loss of four, to give tetraanionic species. The prospect of the ligands acting as binucleating ligands for different metals has been investigated.

### *Metal Complexes of the Schiff Bases*

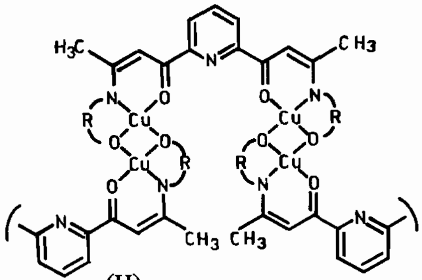
The reactions of the Schiff bases with metal salts gave in many instances intractable materials. However complexes of three distinct stoichiometries have been isolated, depending upon the ligand and on the metal salt used; $M_2L$; $M(H_4L)X_2$ and $M_2(H_2L)X_2$.

#### *(i)* $M_2L$

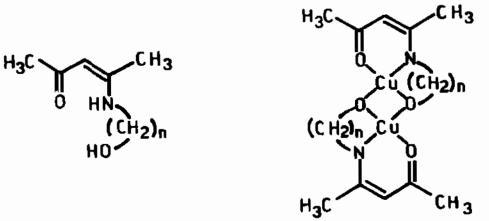
The reaction of $H_4L_1$, $H_4L_2$ and $H_4L_5$ with two molar equivalents of copper(II) ethanoate in ethanol or methanol yields complexes of the type $Cu_2(L)$. The complexes are insoluble in many common organic solvents and are too involatile to give a m.s.. Three strong bands are present between 1500 and 1600 $cm^{-1}$ in the i.r. spectra of $Cu_2(L_1)$ and $Cu_2(L_2)$; the band at 1600 $cm^{-1}$ is assigned to the pyridine C=N frequency, while the bands at 1560 and 1500 $cm^{-1}$ are attributed to $C\overset{\cdots}{-}O$ and $C\overset{\cdots}{-}C$ + $C\overset{\cdots}{-}N$ vibrations respectively. The i.r. spectrum of $Cu_2(L_5)$ also displays three bands in this region; the band for pyridine is at 1565 $cm^{-1}$ and the other two bands are at 1550 and 1485 $cm^{-1}$. No band attributable to the –OH was detected, implying that it has been deprotonated. The basic structural unit present in $Cu_2(L)$ is proposed as (G). However it is possible that an association will occur to replace the unfavorable three coordination of copper by four coordination. This would give the polymeric species (H) and would parallel the known behaviour of copper complexes of tridentate Schiff bases [1] derived from acetylacetone and hydroxyalkylamines which give binuclear, rather than 3-coordinate mononuclear, derivatives [1, 16].



(G)



(H)



(J)

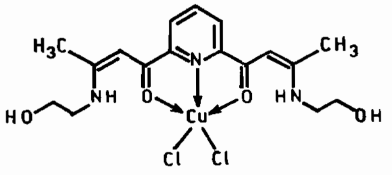
The magnetic moments for $Cu_2(L_1)$, $Cu_2(L_2)$ and $Cu_2(L_5)$ are reduced over the spin only value having $\mu_{eff}$ per Cu atom of 1.30, 0.60 and 0.93 BM respectively. This would be in accord with the associated structure, although none of these moments are as low as that for J(N = 3) which has a value of 0.41 BM per Cu atom [17]. The d.r.s. of $Cu_2(L_1)$ and $Cu_2(L_5)$ give single bands at 641 nm while $Cu_2(L_2)$ has a band at 570 nm; bands in the region of 620 nm are usually associated with square planar, or tetragonally distorted octahedral geometries [12].

The reaction of $H_4(L_5)$ with $Cu(BF_4)_2$ also gave $Cu_2(L_5)$.

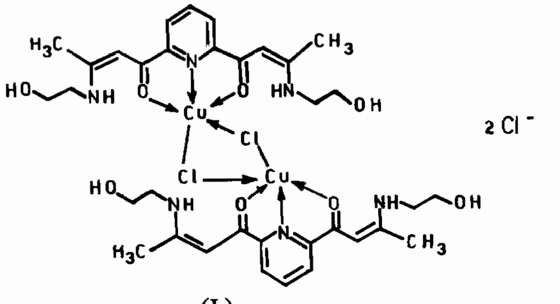
### *(ii) M(H$_4$L)X$_2$*

The reaction of $H_4(L_1)$ with copper(II) chloride, or manganese(II) chloride, gave $CuH_4(L_1)Cl_2$ and $MnH_4(L_1)Cl_2$ respectively. Both complexes gave three bands in the region of 1535–1600 cm$^{-1}$ in the i.r. spectra. The band at 1545 cm$^{-1}$ in $CuH_4(L_1)Cl_2$ is assigned to C$\overset{\cdots}{-}$N + C$\overset{\cdots}{-}$C, that at 1580 cm$^{-1}$ to C$\overset{\cdots}{-}$O and that at 1605 cm$^{-1}$ to the pyridine C$\overset{\cdots}{-}$N vibrations. The corresponding bands in the manganese complex are at 1535, 1570 and 1602 cm$^{-1}$. Both spectra show a sharp, strong band at 3450 cm$^{-1}$ indicative of –OH, and showing that no deprotonation has occurred.

The compounds are soluble in a number of solvents, tending to rule out polymers, and two alternatives (K and L) for which there are literature precedents are proposed for the structure.

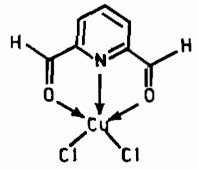


(K)

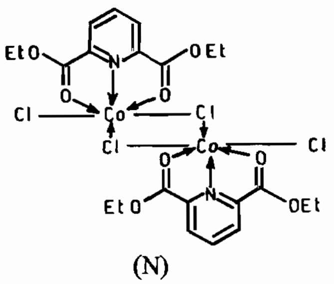


(L)

(K) is similar to the structure proposed for the copper(II) complex of 2,6-formylpyridine, $Cu(L)Cl_2$, (M) which has a magnetic moment of 1.84 BM as expected for isolated Cu(II) ions [18]. The dimeric structure (L) is similar to that determined for the cobalt complex, Co(diethyl-2,6-dicarboxylato)Cl, (N) which has Co–Cl–Co bridges [19]. The magnetic moment of $CuH_4(L_1)Cl_2$ is 1.94 BM and so suggests that the monomeric structure is likely; it is possible that the dimeric species (L) exchange processes would lead to a reduced magnetic moment.



(M)

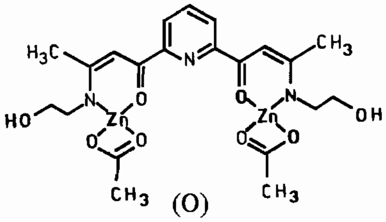


(N)

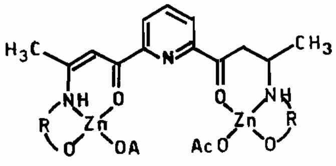
The reaction of $Cu(BF_4)_2$ with $H_4(L_1)$ gives the complex $CuH_4(L_1)(BF_4)_2$; the i.r. spectrum shows bands at 1615, 1580 and 1560 cm$^{-1}$ assigned as previously and the magnetic moment is 1.89 BM. This suggests that a similar monomeric structure to (K) exists, with the $BF_4$ anions probably non-coordinated.

### (iii) $M_2(H_2L)X_2$

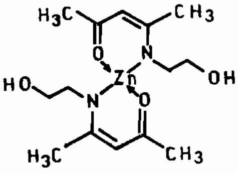
The reaction of zinc(II) ethanoate with $H_4(L_1)$ and $H_4(L_5)$ gave compounds of the type $Zn_2(H_2L)(OAc)_2$. The i.r. spectra again display three bands in the region 1540–1605 $cm^{-1}$ and these are assigned as previously. The bands appear at 1540, 1575 and 1605 $cm^{-1}$ for $Zn_2H_2(L_1)(OAc)_2$ and at 1555, 1575, 1605 $cm^{-1}$ for $Zn_2H_2(L_5)(OAc)_2$. The complexes are slightly soluble in polar solvents but, as throughout this work, it has not been possible to grow crystals suitable for X-ray structure determinations. Two structural possibilities, (O) and (P), are proposed, one of which, (O), has a literature analogy; the zinc complex of the Schiff base derived from acetylacetone and ethanolamine has been attributed the structure (Q) [20].



(O)

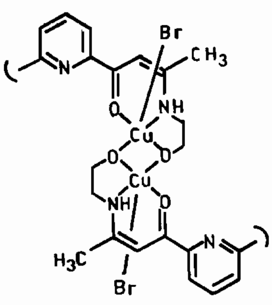


(P)

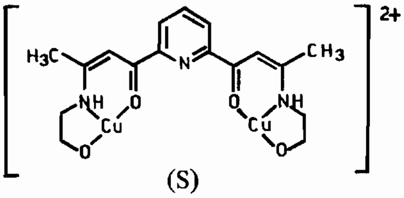


(Q)

The presence of a broad band at 3400 $cm^{-1}$ in the i.r. spectrum of $Zn_2H_2(L_1)(OAc)_2$ suggests that (O) is the likely structure. Other complexes of formula $M_2[(H_2L)X_2]$ have been prepared for $Cu_2H_2(L_1)Br_2$, $Cu_2H_2(L_3)(BF_4)_2$ and $Cu_2H_2(L_1)(ClO_4)_2$. The i.r. spectra of the $CuBr_2$ complex differs from that of $CuH_4(L_1)Cl_2$ in that only two bands are seen in the 1500–1600 $cm^{-1}$ region of the i.r. at 1510 and 1600 $cm^{-1}$; no bands are detected in the 3200–3500 $cm^{-1}$ region, indicating loss of the hydroxyl proton. The compound shows a reduced moment of 1.1 BM per copper atom which suggests that association occurs to give a polymeric array (R) rather than a discrete monomer (S).



(R)



(S)

The reaction of $Cu(BF_4)_2$ with $H_4(L_3)$ gave a complex of stoichiometry $Cu_2H_2(L_3)(BF_4)_2$ whose i.r. spectrum shows bands at 1610, 1580 and 1500 $cm^{-1}$ assigned as previously. No hydroxyl frequency was detected. The magnetic moment per copper atom is 1.06 BM and an associated species similar to (R) is therefore proposed, with non-coordinated $BF_4$ anions present.

$Cu_2H_2(L_1)(ClO_4)_2$ has bands at 1630, 1600 and 1545 $cm^{-1}$ and a multiplet at *ca.* 1100 $cm^{-1}$ due to the presence of monodentate perchlorate. The magnetic moment per copper atom is 1.18 BM, again suggesting an associated species.

## Acknowledgement

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## References

1 R. C. Mehrotra, R. Bohra and D. P. Gaur, 'Metal β-diketonates and Allied Derivates', Academic Press (London), 1978.

2 J. P. Fackler, jr., *Progress Inorg. Chem.*, *7*, 361 (1966).

3 U. Casellato, P. A. Vigato and M. Vidali, *Coord. Chem. Rev.*, *23*, 31 (1977).

4 M. D. Glick and R. L. Lintvedt, *Progress Inorg. Chem.*, *2*, 233 (1976).

5 G. J. Long, D. Lindner, R. L. Lintvedt and J. W. Guthrie, *Inorg. Chem.*, *21*, 1431 (1982).

6 P. Andrelczyk and R. L. Lintvedt, *J. Am. Chem. Soc.*, *94*, 8633 (1972).

7 R. L. Lintvedt, B. A. Schoenfelner, C. Ceccarelli and M. D. Glick, *Inorg. Chem.*, *21*, 2113 (1982).

8 D. E. Fenton, C. M. Regan, U. Casellato, P. A. Vigato

and M. Vidali, *Inorg. Chem. Acta, 58*, 83 (1982).
9 M. Newcomb, J. M. Tinko, D. M. Walba and D. J. Cram, *J. Am. Chem. Soc., 99*, 6392 (1977).
10 R. R. Belford and W. A. Yeranos, *Mol. Phys., 6*, 121 (1963).
11 A. W. Addison and D. P. Graddon, *Austral. J. Chem., 21*, 2003 (1968).
12 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, Amsterdam, (1968).
13 J. Selbin, *Chem. Revs, 65*, 153 (1965).
14 S. M. Nelson, *Pure Appl. Chem., 52*, 2461 (1980).
15 D. E. Fenton and S. E. Gayda, *J.C.S. Dalton*, 2101 (1977) and references therein.
16 J. A. Bertrand and P. G. Eller, *Progr. Inorg. Chem., 21*, 29 (1976).
17 J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta, 4*, 203 (1970).
18 A. Salameh, B. C. Uff, Y. Saykali and W. A. Tayim, *J. Inorg. Nucl. Chem., 42*, 43 (1980).
19 G. Singh and D. B. Sowerby, *J.C.S. Dalton*, 490 (1977).
20 R. K. Mehta, K. N. Kaul and R. K. Gupta, *J. Ind. Chem. Soc., 51*, 1028 (1974).