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Binuclear Complexes of Tetraketones

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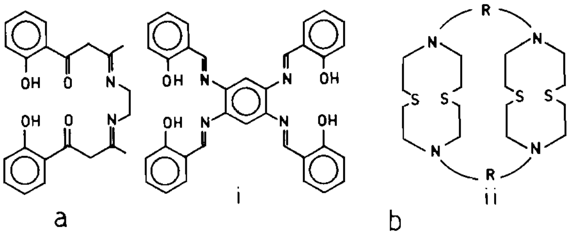
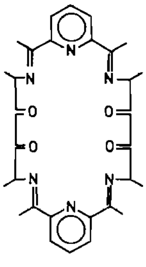
The tetraketones 1,1′-(1,3-phenylene)-bis-1,3-butanedione (H_2L_a) and 1,1′-(1,4-phenylene)-bis-1,3-butanedione (H_2L_b) have been isolated and characterised. They are potentially tetradentate ligands and H_2L_a could act as binucleating agent. The reaction of the tetraketones with different metal ions has been investigated. Homobinuclear complexes of the type $(ML)_2nS$ ($S = H_2O$, MeOH or pyridine; $n = 0, 1, 2, 4$) have been prepared and characterised on the basis of analytical, i.r. and visible spectra, and magnetic susceptibility data. Metal complexes of 1,4-bis(acetoacetyl)-piperazine (H_2L_c) have also been prepared.

Introduction

The area of binuclear complexes has grown extensively, stimulated by interest in their application to physico-chemical studies, catalysis and bio-inorganic chemistry, and has recently been comprehensively reviewed [1–3]. In general these complexes fall into two categories: (a), those in which two metal ions share two donor atoms [1–3] in complexes with ligands containing two adjacent coordination sites, in which the two central donor atoms bridge the metal ions and (b), those in which the donor atoms are not shared (*i.e.*, the use of isolated donor sets) [2, 4–7]. The last category comprises a wide range of complexes and may be further divided into two general sub-classes: (i) ligands in which the ligand compartments are separated by aromatic rings [5, 22, 23], (ii) ligands in which two planar macrocycles are constrained in a 'stacked' conformation [8]:



There are also macrocycles of the type:



which pick up two metal ions [9].

Members of the first sub-class have been designed to investigate the transmission of magnetic exchange interactions through conjugated systems, and those of the second sub-class represent a new approach to the binding and activation of small molecules such as Co, O_2 and N_2.

As a part of our program concerning the synthesis of potentially binucleating ligands and their interactions with metal ions we have prepared the tetraketones (H_2L_a) and (H_2L_b) as representatives of the first sub-class and investigated their properties together with those of (H_2L_c),

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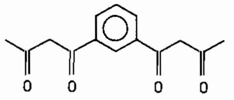
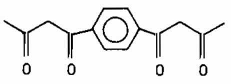
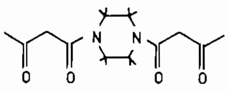
TABLE I. Elemental Analyses and Physico-chemical Properties of the Compounds.

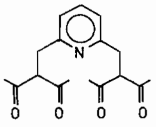
Compound	C%		H%		N%		P^+ m/e	Color
	calc.	found	calc.	found	calc.	found		
H_2L_a	68.28	68.20	5.73	5.47			246	yellow
H_2L_b	68.28	67.90	5.73	6.05			246	white
$(CuL_a)_2$	54.63	55.11	3.92	4.05			614	green
$(NiL_a)_2(H_2O)_4$	49.60	50.23	4.75	3.96			604	green
$(NiL_a)_2(py)_4$	62.50	62.13	4.80	5.33	6.07	6.29	604	green
$(CoL_a)_2(MeOH)_4$	52.32	53.01	5.49	5.94			–	red
$(VOL_a)_2H_2O$	52.51	52.70	4.09	3.46			–	green
$VO(HL_a)_2H_2O$	58.45	58.27	5.23	4.91			–	red
$CuVO(L_a)_2$	54.33	54.94	3.91	3.33			–	tan
$(ZnL_a)_2$	54.31	53.68	3.91	4.52			618	white
$(MnL_a)_2(H_2O)_4$	50.16	49.83	4.81	3.95			–	yellow
$(MgL_a)_2(H_2O)_4$	55.26	54.88	5.26	4.41			–	white
Tl_2L_a	25.75	26.23	1.85	2.10			–	yellow
$(UO_2L_a)_2(H_2O)_2$	31.59	32.00	2.65	2.70			–	red
$(UO_2L_a)_2(py)_2$	38.46	38.13	2.89	2.61	2.96	2.81	–	orange red
$(UO_2L_a)_2(MeOH)_2$	32.98	33.15	2.95	3.81			–	orange red
$TH(L_a)_2$	46.67	46.87	3.36	3.62			–	white
$(CuL_b)_2$	54.63	53.80	3.92	3.27			–	green
$(NiL_b)_2(H_2O)_4$	49.60	48.92	4.75	4.09			–	green
$(UO_2L_b)_2(H_2O)_2$	31.59	31.41	2.65	2.37			–	red
$(CuL_c)_2$	45.64	45.41	5.11	5.00	8.87	8.89	–	green
$(NiL_c)_2(H_2O)_4$	41.53	41.39	5.81	5.70	8.07	8.23	–	green
$(UO_2L_c)_2(H_2O)_2$	26.67	26.41	3.36	3.69	5.18	4.92	–	orange


H_2L_a


H_2L_b


H_2L_c

Studies on metal complexes of tetraketones are restricted to an account of the synthesis and properties of the Co(II), Ni(II) and Cu(II) complexes of 1,7-diphenyl-1,3,5,7-heptanetetraone [10]; the tetraketone:



has also been synthesised but only mononuclear complexes of it have been reported to date [11].

Experimental

Commercial reagent grade chemicals were used without further purification; analyses were performed by the Microanalytical Laboratories of the University of Padua and Sheffield; analytical results are shown in Tables I and II. Infrared spectra were recorded as KBr pellets and as nujol mulls in the range 4000–400 cm^{-1} using a Perkin Elmer 577 spectrometer. Ultraviolet, visible and near infrared spectra were obtained with a Cary 17 recording spectrometer. Magnetic susceptibility measurements on solid samples were obtained by the Gouy method using a Brucker Sartorius balance. The apparatus

TABLE II. ^1H and ^{13}C N.m.r. Spectra of the Ligands in $CDCl_3$ (ppm).

H_2L_a			
^1H	2.22	broad singlet	$-CH_3$
	6.23	singlet	$-CH-$
	7.53	triplet	aromatic protons
	8.03	doublet	
	8.35	singlet	
	10.83	broad singlet	$-OH$ groups
^{13}C	25.78		CH_3
	96.88		C–H
	125.40		aromatic C
	128.92		
	130.37		
	135.22		
	182.18		enol C from 'carbonyls'
	194.07		
H_2L_b			
^1H	7.92	singlet	aromatic protons
	6.20	singlet	$-CH-$
	2.21	singlet	$-CH_3$
^{13}C	26.20		$-CH_3$
	97.31		C=C
	127.04		aromatic C
	137.38		
	195.05		enol C from 'carbonyls'
H_2L_c			
^1H	14.50	singlet	enol –OH
	5.13	singlet	$-CH-$
	3.63	singlets	CH_2 from bridge and keto form
	3.58		
	3.44		
	2.26	singlet	$-CH_3$ keto
	1.95	singlet	$-CH_3$ enol
^{13}C	21.96		CH_3 enol
	30.39		CH_3 keto
	41.56		CH_2
	45.99		
	46.29		
	49.68		
	165.26		CO amido
	170.84		CO enol
	175.81		
	201.97		CO keto

was calibrated wtih $Ni(en)_3SO_4$; diamagnetic corrections were made employing Pascal's constants [12]. The ^1H and ^{13}C nmr spectra were recorded at 220 MHz using a Perkin-Elmer R34 spectrometer. Mass spectra were recorded using an MS12 spectrometer.

*Preparation of the Ligands H_2L_a and H_2L_b**

8 g Na wire were placed in a litre round bottomed flask containing 60 ml ethyl acetate, 11 g of the appropriate diacetylbenzene were added slowly. The reaction starts on gentle heating using a steam bath and becomes quite vigorous. It is refluxed for 4 hours or until the Na is used up. The flask was then allowed to cool and diethyl ether added to give a yellow solid. This was filtered, washed with ether and the yellow solid collected, dissolved in dilute acetic acid and extracted three times with diethyl ether. The extracts were combined and concentrated to give H_2L_a and H_2L_b as yellow solids.

Preparation of Homobinuclear Complexes

The complexes were prepared by two different routes:

(A) to the ligands (0.001 mol) dissolved in ethanol (100 ml) was slowly added metal acetate (0.002 mol) in ethanol (100 ml). The coloured solution was kept at reflux for several hours. The mixture was then allowed to cool and the solid was filtered and extracted (with ethanol), using a soxhlet extractor, for four hours. The solid residue was dried *in vacuo.*

(B) The ligand (0.01 mol) was dissolved in pyridine and metal acetate (0.002 mol) also dissolved in pyridine, was added. After several hours at reflux the solution was allowed to cool. The solid was filtered, washed with a small amount of pyridine and dried *in vacuo.* These compounds have the formula $(ML)_2npy$, n = 2 or 4.

The same pyridine solvated complexes have been obtained dissolving in hot pyridine the complexes prepared using method (A).

Preparation of the $(UO_2L)_2S_2$ (S = MeOH or py)

1.065 g of $(UO_2L)_2(H_2O)_2$ (0.01 mol) were dissolved in 100 ml of hot pyridine (or methanol). The solution was refluxed for three hours. The solid was filtered, washed with the appropriate solvent and dried *in vacuo.*

Reaction of $VO(acetate)_2$ with H_2L_a

0.246 g of the ligand (0.001 mol) were dissolved in ethanol and then 0.185 g of $VO(acetate)_2$, suspended in ethanol (100 ml), were added, and the reaction was stirred for 4 hr. The solution was then filtered and the solid residue was washed with ethanol. The dry green precipitate gave an elemental analysis corresponding to the binuclear compound $(VOL_a)_2H_2O$. The mother liquor was concentrated until a red precipitate was formed. The solid was filtered, washed with ethanol and dried under vacuum. The elemental analysis agrees with the formulation $VO(HL_a)_2$.

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*The H_2L_c ligand is an Aldrich product.

TABLE III. Spectral Data of Obtained Complexes.[a]

Complex	I.r. bands in the 1600–1500 cm^{-1} region	Other bands	U.V. (nm)
$(CuL_a)_2$	1595 1563 1516		560 670
$(NiL_a)_2(H_2O)_4$	1600 1563 1408 1480	3370 broad	625 1100
$(NiL_a)_2(py)_4$	1600 1563 1504 1480		585 990
$(CoL_a)_2(MeOH)_4$	1594 1560 1505	3380 broad	563 855 1209
$(VOL_a)H_2O$	1592 1560 1538 1518	3420 broad, 990 $\nu_{V=O}$	570
$VO(L_a)_2$	1600 1560 1503	960 $\nu_{V=O}$	560
$CuVO(L_a)_2$	1593 1563 1518	960 $\nu_{V=O}$	560 670
$(ZnL_a)_2$	1600 1570 1510		
$(MnL_a)_2(H_2O)_4$	1600 1562 1520 1516	3410	
$(MgL_a)_2(H_2O)_3$	1603 1570 1507	3400	
Tl_2L_a	1600 1565 1510 1500		
$(UO_2L_a)_2(H_2O)_2$	1595 1553 1503	3412 broad, 910 ν_{O-U-O}	475 385
$(UO_2L_a)_2(py)_2$	1612 1570 1522	928 ν_{O-U-O}	470 383
$(UO_2L_a)_2(MeOH)_2$	1605 1562 1523	907 ν_{O-U-O}	475 390
$Th(L_a)_2$	1612 1572 1527		
$(CuL_b)_2$	1580 1548 1513 1505		585
$(NiL_a)_2(H_2O)_4$	1573 1545 1520 1505		568 672
$(UO_2L_b)_2(H_2O)_2$	1588 1550 1512	3350 broad, 912 ν_{O-U-O}	470
$(CuL_c)_2$	1588 1565 1512		600
$(NiL_c)_2(H_2O)_4$	1600 1555 1500		560 805 965
$(UO_2L_c)_2(H_2O)_2$	1580 1562 1515	907 ν_{O-U-O}	463

[a] The ligands H_2L_a and H_2L_b show a broad ν_{OH} band at 3050 and at 3070 cm^{-1} respectively and a $\nu_{C=O}$ band at 1600 cm^{-1}; H_2L_c shows $\nu_{C=O}$ bands at 1710 and 1622 cm^{-1}.

Preparation of Heterobinuclear Complex $VOCu(L_a)_2$

An ethanol solution of copper(II) acetate tetrahydrate was slowly added to a solution containing a stoichiometric amount of $VO(HL_a)_2$. The reaction mixture was maintained at reflux for 4 hr and then the precipitate was filtered, washed with ethanol and dried under vacuum.

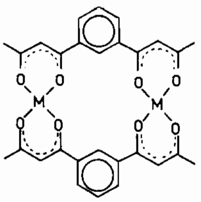
Discussion

The ligands H_2L_a and H_2L_b were prepared by adaptation of the method of Wittig [13, 14]. This involved the condensation of the required diacetylbenzene with ethylacetate in the presence of sodium wire, and gave good recovery of the ligands. H_2L_a and H_2L_b were characterised by i.r., m.s. (P^+ m/e = 246) and n.m.r. data.

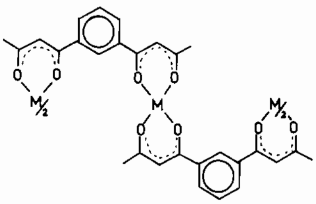
The i.r. spectra (KBr discs) show a broad band centered at 3050 cm^{-1}, and this combined with a broad absorption at *ca.* 1600 cm^{-1} indicates the presence of strong intramolecular hydrogen bonding. Table III summarises the ^1H and ^{13}C n.m.r. spectra in $CDCl_3$ solution. The data suggest that the ligands exist in virtually 100% enol form; signals due to methine protons are present at 6.23 (H_2L_a) and 6.20 (H_2L_b) p.p.m. with no peaks due to methylene protons. In the ^{13}C n.m.r. again no peaks ascribable to $-CH_2$ are seen, but those corresponding to $-CH$ are present. The values for C–O are suggestive of a delocalised carbonyl as seen in compounds such as pentane-2,4-dione, and dibenzoylmethane [15].

The reactions of the ligands with metal acetates in hot ethanol lead to the precipitation of complexes of the type $(ML)_2nEtOH$, n = 0,1,2,4. When pyridine was used as a solvent then complexes of the type $(ML)_2npy$, n = 1, 2, 4 were obtained; these complexes readily lost pyridine and so the reproduction of chemical analyses, especially for copper, proved difficult. Attempts to produce mononuclear complexes of the type (ML_2) have so far proved unsuccessful with the exception of $VO(HL_a)_2 \cdot H_2O$. This complex was recovered from the mother liquor after precipitation of $(VOL_a)_2 \cdot 2H_2O$ in the reaction of vanadyl(IV) acetate and H_2L_a. The cobalt(II) binuclear complexes were prepared in degassed methanol under dinitrogen. If the reaction was attempted in ethanol there were problems due to the poor solubility of cobalt(II) acetate and to the contamination of any product with basic cobalt(II) acetate, $Co_4O(OAc)_6$. The synthesis of this compound has not been recorded in the literature although the m.s. has [16], and the fragmentation pattern of our contaminant (P^+, m/e = 606) corresponds completely with the recorded spectrum. We were unable to isolate $Co_4O(OAc)_6$ in pure form, and did not observe its formation using MeOH as a solvent.

All the prepared complexes are insoluble in the common organic solvents, but soluble in coordinating solvents such as pyridine or DMSO. For complexes of H_2L_a, two structural forms may be proposed:



A



B

Although insolubility in organic solvents would suggest the polymeric (B) form, this is quite common for binuclear species [1], as is the solubility in coordinating solvents. The m.s. of the complexes $(CuL_a)_2$, $(NiL_a)_2 4H_2O$ and $(ZnL_a)_2$ however show P^+ at 614, 604 and 618 m/e respectively which correspond to the parent peaks for $(ML_a)_2$, and no peaks are found at higher mass number, indicating structure (A). Although for M = Co, VO, Mg, Mn and UO_2 the samples were too involatile for m.s. measurements, it is proposed that they are also homobinuclear by analogy with the Cu, Ni and Zn complexes.

The reaction of $VO(L_a)_2$ with copper acetate gave a buff-coloured solid analysing as $CuVO(L_a)_2$. The m.s. showed P^+ at m/e = 622, indicating a heterobinuclear complex.

The nickel(II) and copper(II) complexes with H_2L_b are involatile, in contrast to the above, and this indicates their existence as coordination polymers [17]. The uranyl(VI) complexes $(UO_2L_a)_2(H_2O)_2$ and $(UO_2L_b)_2(H_2O)_2$ show different solubilities in organic solvents; the first is soluble in the common coordinating solvents whereas the latter is not, again indicating the polymeric nature of species derived from H_2L_b. Models show that the steric constraints imposed by the 1,4-substitution would lead to such coordination polymers rather than monomeric species.

The reaction of $Th(NO_3)_4$ with the ligands in hot ethanol yielded the complexes $Th(L)_2$. The i.r. spectra show three bands in the 1600–1500 cm^{-1} region, and by comparison with reported spectra [18] we suggest that the coordination geometry of the metal ion may either be binuclear of type Th_2L_4 or polymeric of type $Th(L)_{2n}$. The complexes are insoluble and involatile and give no indication of structure type.

Solid electronic spectra of the copper(II) chelates show a broad absorption in the visible region with two maxima at 560 and 670 nm suggesting square coplanar copper(II). The spectra in pyridine are more intense and located at lower energy, indicating the presence of pyridine adducts. In the solid state the pyridine is lost slowly. The electronic spectra of the nickel(II) complexes are typical of octahedral nickel(II) species, *e.g.*, $Ni(acac)_2 2H_2O$ [19, 20]. The main features are two bands near 1200 and 685 nm; when water is substituted by pyridine the bands are found near 990 and 585 nm, typical of weakly tetragonal high spin nickel(II) species [20, 21]. An octahedral environment is also indicated in the electronic spectrum of $(CoL_a)_2 4H_2O$ where bands are detected at 1209, 853 and 563 nm.

The magnetic moments for the homobinuclear Cu(II) complexes ($\simeq$1.44 B.M.) are lower than the spin only value, but higher than the binuclear chelates in which two metal ions share two donor atoms. This is indicative that an exchange coupling is operative through the benzene ring, but the extent of this interaction is small. Ni(II) and Co(II) complexes show magnetic moments comparable with those expected for octahedral magnetically diluted ions ($\simeq$3.19 and 4.12 B.M. respectively).

To include the presence of intermolecular interactions the copper(II) and nickel(II) complexes of ligand H_2L_c have been prepared. The ligand exists prevalently in the keto-form, bands being detected at 1710 cm^{-1} (C=O) and 1622 cm^{-1} (amidic C=O) in the i.r. (KBr). The ^1H n.m.r. ($CDCl_3$) shows the presence of a keto–enol distribution (*ca.* 73%: 27% based on CH_3 signal peak height); this is also discerned in the ^{13}C ^1H n.m.r.

The complexes show different i.r. spectra from the free ligand and there is a shift of the C=O frequency to low energy indicating coordination. The physico-chemical properties do not allow unambiguous structural assignment. The electronic spectra suggest similar metal environment to the L_a and L_b derivatives, and the magnetic moments of 1.87 B.M. per copper and 3.15 B.M. per nickel atom are those expected for isolated ions. The uranyl(VI) complex is slightly soluble in common organic solvents, and more soluble in DMSO and pyridine, suggesting a monomeric structure of type A.

Acknowledgements

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