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Homo- and Heterobinuclear Complexes of 2-Acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene

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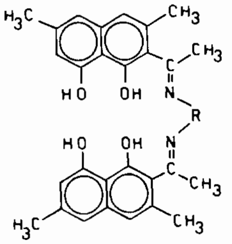
New Schiff bases derived from 2-acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene and diamines or triamines have been prepared and characterized. They are potentially hexadentate compartmental ligands with different donor sets for complex formation, one 'inside', with two nitrogen and two oxygen donor atoms (O_2N_2) and a second, 'outside', with four oxygen donor atoms (O_2O_2).

The interactions of these ligands with different metal ions have been investigated to study their coordination selectivity. Pure mononuclear complexes of the type M(H_2addn-diam) (diam = en or tn) have been prepared and characterized by chemical analysis and spectral measurements. Nickel(II) and copper(II) mononuclear complexes were used as ligands to prepare binuclear M'M(addn-diam)S_x complexes (M = Ni(II) or Cu(II); M' = Ni(II), Cu(II), UO_2(VI); S = H_2O or solvent x = 1, 2 or 0). Characterization of these compounds was achieved on the basis of analytical, infrared, visible spectra and magnetic susceptibility results. In all cases the results are consistent for pure compounds with M in the 'inside' N_2O_2 site and M' in 'outside' O_2O_2 site.

Introduction

Hetero-metal polynuclear complexes are of current interest in connection with spin exchange, electron-transfer between metal ions and their considerable significance for the area of bio-inorganic catalysis. One obvious reflection of this is the rapid development of heterobinuclear cluster chemistry [1–11]. In previous papers [2–4] we have reported the preparation of a new class of ligands which are potentially tetraanionic and hexadentate and can be expected to chelate two different metals giving a neutral binuclear molecule.

We now report the syntheses of new ligands of this class, prepared by the condensation of α,ω-alkyldiamines with 2-acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene. The ligands:



have two adjacent and dissimilar co-ordination compartments, the donor sets of which resemble either 1,8-dihydroxynaphthalene (O_2O_2) or Schiff bases of *o*-hydroxyacetophenone (N_2O_2). This study deals with the coordination selectivity of the two sites in the ligands, the synthesis of pure mononuclear complexes and the use of some of these compounds as ligands toward other metal ions.

Experimental

2-acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene (H_2addn) was prepared by the literature method [12] and its purity was checked by elemental analysis, ^{1}H nmr and ir data. The preparation involved the self-condensation of 2,4,6-heptanetrione under mildly basic conditions; the transformation requires three consecutive aldol condensations. All the solvents were used without purification.

Preparation of the Schiff Bases

H_2addn (0.002 mol) was dissolved in hot ethanol (10 ml). To this solution the appropriate diamine (0.001 mol) in ethanol (10 ml) was added all at once. The reaction was refluxed for 4–5 h during which time a bright yellow precipitate was formed. The yellow solid was filtered, washed twice with ethanol and dried *in vacuo.*

Preparation of Mononuclear Complexes M(H_2addn-diam) (M = Ni(II), Cu(II); diam = en, tn; M = VO(IV), diam = tn)

Two general methods have been used to prepare the mononuclear compounds: a) The appropriate ligand (0.001 mol) was suspended in approximately 200 ml of methanol. The suspension was brought to reflux under stirring, and the metal acetate was dissolved (Ni(II) or Cu(II)) or suspended (VO(IV)) in methanol (50 ml) and added in its entirety. The solution was refluxed for 3–6 h. During this time the color of the solution changed and a precipitate was formed. After allowing the flask to come to room temperature, the solid was filtered, washed with methanol and chloroform and dried *in vacuo*;

b) The ligand (0.001 mol) was dissolved (H_2addn-tn) or suspended (H_2addn-en) in 300 ml $CHCl_3$. The mixture was brought to reflux under stirring and the metal acetate in methanol was added all at once. The solution was kept at reflux for 10 h. The precipitate was filtered, washed with methanol, $CHCl_3$ and dried *in vacuo.*

Using the same methods the binuclear complex, $(VO)_2$(addn-en)(H_2O), was obtained.

Preparation of UO_2(H_2addn-diam)L (L = EtOH or H_2O, diam = en, tn, dien)

An ethanolic solution of uranyl nitrate hexahydrate (0.001 mol) was added, under stirring, to an ethanolic suspension of the appropriate ligand (0.001 mol). The color of the suspension immediately became dark red as the ligand reacted. The reaction mixture was refluxed for 12 h. The hot solution was filtered and the precipitate washed with ethanol and $CHCl_3$ and dried *in vacuo.*

Preparation of $Li_2[UO_2$(addn-diam)$H_2O]$ (diam = en, tn or dien)

The ligand (0.001 mol) was suspended in hot ethanol; the suspension was brought to reflux under stirring and LiOH (0.004 mol), dissolved in ethanol, was immediately added. The reaction mixture was kept under these conditions for 30 minutes and then uranyl nitrate hexahydrate (0.001 mol in 50 ml of ethanol) was added. The reaction mixture was refluxed for 6 h. The warm solution was filtered and the precipitate washed with ethanol and $CHCl_3$ and dried *in vacuo.*

Interaction of M(acetate)$_2\cdot H_2O_n$ with H_4addn-dien (M = Ni(II), Cu(II) and VO(IV)

We have tried many preparative routes for mononuclear complexes of this ligand, varying both the molar ratio of M/ligand and the solvent. In all cases we have obtained the homobinuclear species only.

Preparation of the Homo-binuclear Complexes

These compounds were prepared by two general methods:

a) A methanolic solution of LiOH (0.004 mol in 60 ml) was added to a suspension of the ligand (0.001 mol) in methanol (200 ml). The suspension was brought to reflux under stirring and after 30 minutes the appropriate metal acetate (0.002 mol), dissolved in methanol (50 ml), was added. The reaction mixture was refluxed for 6 h. The warm suspension was filtered and the solid washed with methanol and $CHCl_3$ and dried *in vacuo.*

b) The mononuclear complex (0.001 mol) was dissolved in the minimum amount of pyridine and the solution was brought to reflux. LiOH (0.002 mol) dissolved in methanol was added and after 30 minutes the appropriate metal acetate dissolved in 50 ml of methanol. The solution was refluxed for 6 h and then evaporated to dryness under vacuum. The residue was treated with methanol. The solid was filtered and washed with methanol and $CHCl_3$ and dried *in vacuo.*

The hetero-binuclear complexes were obtained using method (b) only.

Physical Measurements

Infrared spectra were obtained in the range 4000–400 cm^{-1} using a Perkin-Elmer 577 spectrometer. Solid state spectra were recorded as KBr pellets and also as nujol mulls. Ultraviolet–visible–near infrared spectra were obtained with a Cary 14 recording spectrometer in dmso or $CHCl_3$ solutions. Magnetic susceptibility measurements on solid samples were obtained by the Gouy method using a Brucker-Sartorius balance. The apparatus was calibrated with $Ni(en)_3SO_4$; diamagnetic corrections were made employing Pascal's constants [13]). The ^1H nmr spectra were recorded at 220 MHz using a Perkin-Elmer R34 spectrometer. The metal analyses were carried out with a Perkin-Elmer 403 atomic absorption spectrometer. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU 6 spectrometer.

Results and Discussion

Ligands

2-Acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene (H_2addn) was prepared by the literature method [12] as a precursor for the synthesis of the Schiff bases. Its mass spectrum shows a strong peak corresponding to the mass of the parent molecular ion (P^+) at 230

TABLE I. Analytical Data and Parent Peaks for the Ligands.

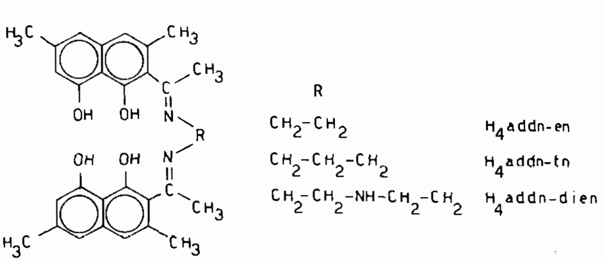
Compound	C%		H%		N%		MW	P^+ (m/e)
	Calc.	Found	Calc.	Found	Calc.	Found		
H_2addn	73.02	73.31	6.13	6.27			230.25	230
H_4addn-en	74.33	74.10	6.65	6.80	5.80	5.54	484.71	484
H_4addn-tn	74.80	75.01	6.88	6.72	5.65	5.43	498.73	498
H_4addn-dien	72.81	72.70	7.06	7.20	8.00	8.08	527.82	527

TABLE II. Physico-chemical Data of the Ligands.

Compound	I.R. (cm^{-1})			U.V.			^1H nmr (ppm)							
	$\nu_{C=O}$	$\nu_{C=N}$	ν_{C-O}	(nm)			CH_3			H naphthalene			CH_2	
H_2addn	1640		1270				2.40	2.60	2.70		6.85			
H_4addn-en		1601	1280	305	440	460								
H_4addn-tn		1625	1280	305	435	455	2.30	2.40	2.50	6.46	6.48	6.60	2.25	3.78
H_4addn-dien		1590	1280	305	435	445	2.22	2.30	2.41	6.30	6.45	6.57	3.05	3.61

m/e. The hydroxyl ir stretching band consists of a broad signal (400 cm^{-1} wide) centered at about 3050 cm^{-1}; this band could result from the overlapping of the individual OH absorptions. Both the position of the band(s) and the extreme width are compatible with strong intramolecular association. The ^1H nmr data indicate that there is a strong hydrogen bond; the single proton peak at 10.18 ppm is assigned to a 'phenolic' proton, no further signal was observed up to 16 ppm. Other peaks were found at 6.68 and 6.85 ppm due to the β and α naphthalene protons respectively, at 2.70 ppm due to the CH_3CO protons and at 2.60 and 2.40 ppm due to the 3- and 6-methyl group protons respectively.

Reactions of H_2addn with ethane-1,2-diamine (en), propane-1,3-diamine (tn) or diethylenetriamine (dien), in molar ratio 2:1 in refluxing ethanol gave yellow crystalline solids; these were found to be the acyclic Schiff bases:



Their mass spectra show base peaks at 484 m/e (H_4addn-en), 498 m/e (H_4addn-tn) and 527 m/e (H_4addn-dien), corresponding to the parent molecular ions (Table I). The high intensities of the peaks are in accord with the stabilization of the molecule by strong intramolecular hydrogen bonding. Additionally there is a small peak, in all the spectra, at 540, 554 and 583 m/e respectively.

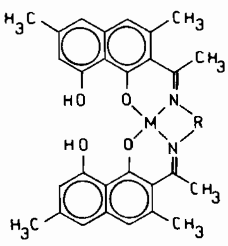
It is probable that the high molecular weight peak in the ligands arises as follows:

$$H_2\text{addn} + \text{diam} \longrightarrow H_4\text{addn-diam} \xrightarrow[\text{(base)}]{\text{EtOH}} Et_2H_2\text{addn-diam}$$

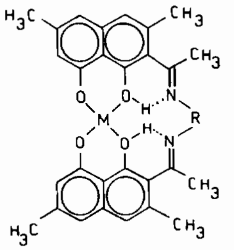
the last product is present in small traces and is not detectable in the elemental analyses. Only for H_4addn-dien were traces of the ethylate ligand detected in the ^1H nmr spectra. The ir spectra of the Schiff bases show a broad band in the hydroxyl stretching frequency region compatible with extensive intramolecular H-bonding in the solid state. The strong band at about 1600 cm^{-1} is assigned to the C=N stretch, the shift of this band to lower energies being in agreement with intramolecular H-bonding. The ^1H nmr were recorded for H_4addn-tn and H_4addn-dien, only, H_4addn-en was too insoluble in $CDCl_3$ or d_6-dmso to allow this measurement. In Table II we report the ^1H nmr data together with some other properties of these acyclic Schiff bases. The absence up to 16 ppm of any signals due to the OH protons indicates that the hydrogen bonds are strong. The pre-eminent resonances occur at about 2.40, 3.30 and 6.50 ppm. The three signals in the 2.20–2.50 ppm region are due to the inequivalent methyl group protons, the lower to the keto-imino methyl protons and the others to the 3- and 6-methyl protons. The methylene protons are present as triplets at 2.25 and 3.78 ppm (H_4addn-tn) and 3.05 and 3.61 ppm (H_4addn-dien). The three inequivalent naphthalenic protons are present at 6.46 and 6.60 ppm (H_4addn-tn) and at 6.30, 6.45 and 6.57 ppm (H_4addn-dien). In addition, in the H_4addn-dien spectrum there is the presence of signals assigned to $O-CH_2-CH_3$ protons at 1.40 ppm (triplet) and 3.70 ppm (quartet), these signals probably arise from the presence of Et_2H_2-addn-dien.

Mononuclear Complexes

The reactions of these acyclic compounds with Cu(II), Ni(II), VO(IV) and UO_2(VI) were investigated in order to study their coordination selectivity. In each case two isomers may be obtained from these reactions:



Isomer I (N_2O_2)



Isomer II (O_2O_2)

When copper(II) or nickel(II) acetate reacted with H_4-addn-diam (diam = en, tn) in hot methanol or methanol/$CHCl_3$ mixtures, microcrystalline precipitates were obtained which were shown, analytically, to be mononuclear complexes.

All of these complexes gave weak ir absorptions in the 3150–3300 cm^{-1} region, assigned to hydrogen bonded OH, and strong bands at 1630 cm^{-1} and 1340 cm^{-1} characteristic of $\nu_{C=N}$ (coordinated) and ν_{C-O} (phenolic). These bands are present in the free ligands also and are shifted by 20–30 cm^{-1} [14] suggesting that the metal ions are N_2O_2 coordinated. The electronic spectra of Ni(H_2addn-en) and Ni(H_2addn-tn) show single bands at 584 nm and 572 nm which are similar to those found for Ni(salen) and Ni(saltn) [15]. This provides further evidence for N_2O_2 coordination. Although the spectral data strongly suggest the presence of the N_2O_2 isomer they do not give any information concerning purity with respect to the O_2O_2 isomer. The magnetic susceptibility allows us to ascertain the isomer purity since when Ni(II) is N_2O_2 coordinated it must be in a square planar geometry and diamagnetic. The O_2O_2 isomer would be expected to produce a paramagnetic octahedral Ni(II) through addition of solvent molecules or by oligomerization as in $[Ni(acac)_2]_3$ [16]. The Ni(II) complexes are diamagnetic, and so it has been concluded that the isolated products are $-N_2O_2$ isomers in a pure form.

The electronic spectra of Cu(H_2addn-en) and Cu(H_2addn-tn) show bands at 555 nm and 528 nm respectively. These bands lie in the range for square planar (N_2O_2) copper(II) coordination [17]. The room temperature magnetic moments do not allow assessment of the isomeric purity (1.36 BM for Cu(H_2addn-en) and 1.60 BM for Cu(H_2addn-tn)). Both values are lower than the spin only value (1.78 BM) and this suggests that an intermolecular coupling between two copper(II) atoms takes place.

A dimeric situation involving copper–oxygen bonding interactions has been found for Cu(salen) [18, 19] although this does not exist for Cu(saltn) [19]. The reaction of H_4addn-dien with $M(OAc)_2$ (M = Cu(II) or Ni(II)) yields binuclear complexes only.

Uranyl nitrate reacts with the ligands to yield UO_2(H_2addn-diam)H_2O complexes; they are monomers and the uranyl(VI) occupies the O_2O_2 site. The ir spectra confirm this hypothesis as the $\nu_{C=N}$ stretching modes lie at 1600 cm^{-1}, the same frequencies as in the free ligands, suggesting that the N_2O_2 site is not affected by coordination of the uranyl ion. The bands due to the ν_{O-U-O} lie at 890 cm^{-1}. The electronic spectra show a single band at 450 nm due to the f- and charge transfer transitions.

When the reactions are carried out in presence of LiOH the $Li_2[UO_2$addn-diam)$H_2O]$ complexes have been prepared; their physico-chemical properties are similar to those of the UO_2(H_2addn-diam)H_2O complexes. The reaction of VO(acetate)$_2$ in methanol with the ligands H_4addn-en or H_4addn-dien in methanol yields the binuclear complexes $(VO)_2$-(addn-diam)$(H_2O)_2$ (diam = en or dien). The electronic spectra, recorded in dmso solution, exhibit a single band at about 550 nm and no other bands were observed up to 1000 nm. The frequency and the intensity of these bands are consistent with a d–d transition. The magnetic moments are lower than the spin only value expected for a d^1 system, 1.54 BM ($(VO)_2$(addn-en)$(H_2O)_2$) and 1.44 BM ($(VO)_2$(addn-dien)$(H_2O)_2$); this suggests an antiferromagnetic exchange interaction between pairs of oxovanadium(IV) ions in the complexes, although the presence of one VO(V) cannot be ruled out. The ir spectra are similar to those found for the uranyl ion complexes; the strong band at 940 cm^{-1} is due to the ν_{V-O} stretching mode.

VO(acetate)$_2$ reacts with the ligand H_4addn-tn to yield the mononuclear chelate VO(H_2addn-tn)-(H_2O). From spectroscopic properties it is not possible to tell with certainty where the oxovanadium is coordinated and whether the product is one pure isomer. However, in analogous compounds where VO(IV) is presented with a choice of N_2O_2 and O_2O_2 donor set structural data confirm that the O_2O_2 isomer is obtained [5]. The magnetic moment (0.76 BM) is very much lower than the spin only

TABLE III. Analytical Data for the Complexes.

Complex	C%		H%		N%		Others		
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
$Cu(H_2addn\text{-}en)$	65.97	65.54	5.53	5.42	5.13	5.05	11.64	11.25	(Cu)
$Ni(H_2addn\text{-}en)$	66.56	66.64	5.59	5.52	5.17	5.16	10.85	11.04	(Ni)
$Li_2[UO_2(addn\text{-}en)\cdot H_2O]$	46.04	45.65	3.86	4.04	3.58	3.48			
$UO_2(H_2addn\text{-}en)\cdot 2H_2O$	45.68	45.41	4.09	4.18	3.55	3.41			
$Cu(H_2addn\text{-}tn)\cdot H_2O$	64.59	64.31	5.92	5.90	4.84	4.71	11.00	10.76	(Cu)
$Ni(H_2addn\text{-}tn)$	67.04	67.05	5.80	5.85	5.04	5.00	10.58	10.69	(Ni)
$Li_2[UO_2(addn\text{-}tn)\cdot H_2O]$	46.74	45.91	4.04	3.95	3.52	3.43			
$UO_2(addn\text{-}tn)\cdot EtOH$	48.71	49.01	4.71	4.25	3.45	3.60			
$UO_2(addn\text{-}dien)\cdot H_2O$	47.22	47.01	4.58	4.37	5.16	5.10			
$VO(addn\text{-}tn)\cdot H_2O$	64.02	64.21	5.89	5.43	4.81	5.21			
$Ni_2(addn\text{-}en)\cdot 2H_2O$	56.65	56.28	5.07	5.06	4.40	4.18	18.48	18.70	(Ni)
$Ni_2(addn\text{-}tn)\cdot 2H_2O$	57.44	57.61	5.29	4.95	4.32	4.51	18.11	18.50	(Ni)
$Ni_2(addn\text{-}dien)$	59.95	60.21	5.18	5.19	6.55	6.69	18.37	18.40	(Ni)
$Ni(Cu(addn\text{-}en)$	59.57	59.83	4.66	5.01	4.63	4.65	9.70 10.50	9.80 10.20	(Ni) (Cu)
$NiCu(addn\text{-}tn)$	60.35	60.19	4.90	4.85	4.54	4.52	9.51 10.30	9.70 10.40	(Ni) (Cu)
$NiUO_2(addn\text{-}en)\cdot H_2O$	43.44	43.48	4.34	3.81	3.37	3.28	7.07	6.98	(Ni)
$NiUO_2(addn\text{-}tn)\cdot H_2O$	44.24	44.71	3.83	3.91	3.33	3.68	6.97	7.01	(Ni)
$Cu_2(addn\text{-}en)$	59.10	58.76	4.62	4.80	4.59	4.48	20.84	20.10	(Cu)
$Cu_2(addn\text{-}tn)$	59.69	60.12	4.84	5.08	4.49	4.46	20.37	19.80	(Cu)
$Cu_2(addn\text{-}dien)$	59.06	59.06	5.11	5.20	6.44	6.68	19.53	19.70	(Cu)
$(VO)_2(addn\text{-}en)\cdot 2H_2O$	58.06	57.80	5.19	5.03	4.51	4.73			
$(VO)_2(addn\text{-}dien)\cdot 2H_2O$	58.08	57.78	5.64	5.21	6.35	6.48			

value, suggesting an antiferromagnetic exchange in which the vanadyl oxygen acts as ligand in the solid state. This is also in accordance with the lowering of the $\nu_{V=O}$ stretching frequency to 854 cm^{-1} [22]. A structure similar to that proposed has been found, by X-ray data, for VOsaltn [21]. However such a low magnetic moment may be also indicative that oxovanadium(IV) is partially oxidized to VO(V) in the complex. This could agree with our results, in fact by reaction of $VOCl_2$ with H_4addn-tn we have obtained the diamagnetic mononuclear compound $VO(H_2$-addn-tn)$OH(H_2O)$ [28] (Tables III, IV).

Binuclear Complexes

The choice of the mononuclear $M(H_2addn\text{-}diam)$ chelates (M = Ni(II) or Cu = (II)) as ligands used to prepare homo- and hetero-binuclear complexes was made for the following reasons: 1) the Ni(II) and Cu(II) in the N_2O_2 site are expected to be relatively difficult to displace; 2) the compounds are easily prepared in good yields and high purity.

The ir spectra of binuclear complexes do not differ much from those of the mononuclear chelates; the only significant change has been found for $\nu_{C=N}$ stretch which is shifted towards higher frequencies by 5–20 cm^{-1}.

In binuclear complexes containing the uranyl ion a strong band due to the ν_{O-U-O}, is present at about 890 cm^{-1} as in the mononuclear complexes. The homobinuclear copper(II) complexes have reduced magnetic moments at room temperature; this is in accord with those observed for many homobinuclear copper(II) complexes in which antiferromagnetic behaviour predominates [9, 23]. The electronic spectrum of Cu_2addn-en shows two absorption bands in the visible region, the first at 550 nm is comparable with the band in mononuclear $Cu(H_2addn\text{-}en)$ chelate, therefore we suggest that this band may be assigned to the 'inside' copper(II) (CuN_2O_2 chromophore). The second band is at 675 nm and can be assigned to the 'outside' copper bound to four oxygen atoms. Cu_2(addn-tn) has only a very broad band at 590 nm and this suggests that both copper(II) ions

TABLE IV. Selected IR (cm^{-1}) and Absorption (nm) Bands and Effective Magnetic Moments (B.M.) of the Complexes.

Complex	IR			UV	μ_{eff}
	$\nu_{C=N}$	ν_{C-O}	Others		
$Cu(H_2addn\text{-}en)$	1640	1330		552	1.36
$Ni(H_2addn\text{-}en)$	1630	1335		582	diam.
$Li_2[UO_2(addn\text{-}en)\cdot H_2O]$	1601	1335	890 ($\nu_{3\ O-U-O}$)	450	diam.
$UO_2(H_2addn\text{-}en)\cdot 2H_2O$	1600	1335	885 ($\nu_{3\ O-U-O}$)	440	diam.
$Cu(H_2addn\text{-}tn)\cdot H_2O$	1635	1340		560	1.60
$Ni(H_2addn\text{-}tn)$	1635	1340		570	diam.
$Li_2[UO_2(addn\text{-}tn)\cdot H_2O]$	1625		890 ($\nu_{3\ O-U-O}$)	444	diam.
$UO_2(addn\text{-}tn)\cdot EtOH$	1625		890 ($\nu_{3\ O-U-O}$)	440	diam.
$UO_2(addn\text{-}dien)\cdot H_2O$	1600	1340	885 ($\nu_{3\ O-U-O}$)	440	diam.
$VO(addn\text{-}tn)\cdot H_2O$	1605	1345	840 ($\nu_{V=O}$)	550	0.76
$Ni_2(addn\text{-}en)\cdot 2H_2O$	1640	1335		580 880	3.48
$Ni_2(addn\text{-}tn)\cdot 2H_2O$	1635	1335		545	3.15
$Ni_2(addn\text{-}dien)$	1625	1330		538	2.53
$Ni(Cu(addn\text{-}en)$	1620	1335		530 625	2.28
$NiCu(addn\text{-}tn)$	1600	1340		525 625	1.70
$NiUO_2(addn\text{-}en)\cdot H_2O$	1605	1335	890 ($\nu_{3\ O-U-O}$)	540	1.23
$NiUO_2(addn\text{-}tn)\cdot H_2O$	1605	1335	895 ($\nu_{3\ O-U-O}$)	530	2.46
$Cu_2(addn\text{-}en)$	1620	1335		550 675	1.71
$Cu_2(addn\text{-}tn)$	1630	1330		590	1.59
$Cu_2(addn\text{-}dien)$	1601	1330		530	1.70
$(VO)_2(addn\text{-}en)\cdot 2H_2O$	1601	1330	955 ($\nu_{V=O}$)	554	1.52
$(VO)_2(addn\text{-}dien)\cdot 2H_2O$	1601	1330	954 ($\nu_{V=O}$)	555	1.44

have a nearly planar coordination. The electronic spectrum of the Cu_2(addn-dien) complex shows a single band at 530 nm and it was impossible under our experimental conditions to detect other bands up to 750 nm where the Cu_2O_2 chromophore could have an absorption.

The room temperature magnetic moments of the binuclear M'Ni(addn-diam)xH_2O (x = 0 or 2) can be used to help assign the compartmental occupancy of the ligand. All the values are explicable assuming that the 'inside' tetracoordinate Ni(II) is square planar and diamagnetic and so retains its N_2O_2 occupancy. On this basis the magnetic moments of the complexes are as expected for isolated d^9 and d^8 octahedral ions, the total contribution coming from the metal in the O_2O_2 compartment. The square planar coordination of 'inside' Ni(II) in the complexes $Ni_2(addn\text{-}en)(H_2O)_2$ and $Ni_2(addn\text{-}tn)(H_2O)_2$ is confirmed by the presence of d–d bands in the 545–580 nm region. Since square planar Ni(II) does not have an absorption band above 600 nm, other bands in this region are attributable to the second Ni(II); however only for $Ni_2(addn\text{-}tn)(H_2O)_2$ was a band, at 880 nm, found. From these spectroscopic data it is difficult to interprete the coordination around the second Ni(II) ion, but the magnetic moments 3.84 BM ($Ni_2(addn\text{-}en)(H_2O)_2$) and 3.15 BM ($Ni_2(addn\text{-}tn)(H_2O)_2$) suggest that the Ni(II) in the O_2O_2 environment would most likely be octahedral and achieves six-coordination by water coordination or oligomerization. These complexes are further examples of compounds in which two similar ions, having different states spin, are held together by a single ligand; the high and low spin metals are here bridged by phenolic oxygens [3, 27]. The low magnetic moment of Ni_2(addn-dien) (2.53 BM) is most difficult to interprete since it was impossible to prepare the mononuclear complex for comparison. It is likely that the 'inside' Ni(II) can be a four coordinated N_2O_2 pseudo-square planar complex, as suggested for Ni(saldien) which was a magnetic moment of 0.80 BM [24]. This coordination is indicated by the electronic spectrum of Ni_2(addn-dien) which shows an absorption band at 538 nm and with the lack, in its ir spectrum, of a sharp N–H stretching indicating that the secondary nitrogen is not coordinated to the nickel ion [25]. The second Ni(II), in the O_2O_2 site, would most likely be six-coordinated by oligomerization and so the low magnetic moment could arise from magnetic exchange interactions between the two paramagnetic Ni(II) ions.

The electronic spectra of the CuNi(addn-en) and CuNi(addn-tn) complexes possess two bands at about 630 and 525 nm. The first band is essentially similar to the band found for Cu_2(addn-diam) and is tentatively assigned to the 'outside' copper(II), the second band is due to a Ni(II) ion in a square planar geometry. The molar magnetic moments are 2.28 BM (CuNi(addn-en)) and 1.70 BM (CuNi(addn-tn)). Spectral and magnetic properties therefore indicate that these complexes are composed of one diamagnetic Ni(II) and one Cu(II) ions.

The mass spectrum of CuNi(addn-en) was recorded to see if it was a 1:1 mixture of Ni_2(addn-en) and Cu_2(addn-en). The mass spectra of the corresponding homobinuclear complexes show parent peaks due to the mononuclear compound and a very weak peak due to the binuclear species was found only for the homobinuclear Ni(II) chelate. CuNi(addn-en) shows the parent peak for monomeric Ni(H_2addn-en) but no CuNi(addn-en) or Cu(H_2addn-en) peaks. This behaviour is similar to the Cu_2(addn-en) complex and may be due to the lability of the second metal in the spectrometer.

The electronic spectra of UO_2Ni(addn-diam) (diam = en or tn) show a band at 525 nm suggesting that the Ni(II) would be in a square planar configuration in the N_2O_2 site; in addition a shoulder at 450 nm due to electronic transition of the UO_2 group has been found. However the magnetic moments of 2.61 BM (UO_2Ni(addn-en)(H_2O)) and 2.46 BM (UO_2Ni(addn-tn)(H_2O)), are too high to consider the Ni(II) as in a square planar geometry. On the other hand the moments are lower than expected for high spin Ni(II). These values can be explained by considering a tetrahedral distortion of the Ni(II) in O_2N_2 site due to the introduction of uranyl(VI) ion in the adjacent O_2O_2 compartment, as found in the single crystal X-ray structure of UO_2Ni(aapen)dmso complex [26].

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