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# The Preparation and Characterisation of Metal Complexes of a New Binucleating Ligand Having Two Different Coordination Sites

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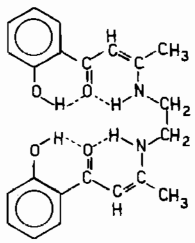
*A new ligand, referred to as $H_4$aapen, has been prepared; it is the ethylenediamine Schiff base derivative of o-acetoacetylphenol and has one site with two nitrogen and two oxygen atoms ($N_2O_2$) and a second site with four oxygen atoms ($O_2O_2$), two central oxygens being common to both sites. A series of mononuclear complexes have been prepared from this ligand in order to investigate the coordination selectivity of the two compartments. In Ni($H_2$aapen) the nickel(II) is in the $N_2O_2$ site, while in $UO_2$($H_2$aapen)-($H_2O$) and $Li_2[UO_2$(aapen)($H_2O$)]$H_2O$ the uranyl ions are in the $O_2O_2$ site. Positional isomers can be prepared with copper(II): one having the copper in the $O_2O_2$ site and the other with copper in the $N_2O_2$ one. The mononuclear complexes were used as ligands to prepare the binuclear complexes MM'-(aapen) (M = $Ni^{2+}$, $Cu^{2+}$, $UO_2^{2+}$; M' = $Ni^{2+}$, $Cu^{2+}$). These complexes were characterized on the basis of the analytical data, mass, ir, uv spectra and magnetic moments at room temperature.*

## Introduction

A number of studies have been carried out on the preparation and characterization of binuclear complexes of *d* and *f* metal ions with Schiff bases [1–4] and ligands with different types of coordination sites [5–9]. It is established that the number and type of donor atoms bonded to a metal ion have a profound effect on the chemical and physical properties associated with the metal ions. Moreover, under competitive conditions certain metals have a clear thermodynamic and/or kinetic preference for bonding to a specific donor atom. Therefore it was interesting to study ligands in which the coordinating sites contain different types of donor atoms. Further reason for interest in these systems stems from the strong magnetic superexchange between the metal ions, which are connected by bridging oxygens.

The ligand:



$H_4$ aapen

was prepared by condensation of 1,2-diaminoethane with *o*-acetoacetylphenol; it is a potentially tetra-anionic ligand with two nitrogen and four oxygen donor atoms and therefore is a good one with which to study the above problems. An advantage of this ligand is that the resulting complexes can be compared to well-known chelates of salicylaldehyde and the Schiff base of 2,4-pentanedione, since the binuclear complexes can be thought of as a fusion of the mononuclear parent compounds. The spectral, magnetic and chemical properties of the complexes in $N_2O_2$ or in $O_2O_2$ sites would be similar to the M(acacen) and M($o$-$OC_6H_4$-CHO)$_2$ respectively. The availability of information concerning the properties of Schiff bases of 2,4-pentanedione [10] and salicylaldehydates [11] allows one to study the binuclear complexes in a straightforward manner.

This study deals with the coordinative selectivity of the two sites in the ligand and the synthesis of pure binuclear complexes.

## Experimental

*o*-Acetoacetylphenol ($H_2$aap) was prepared by the method of Wittig [12] and its purity was checked by elemental analysis and $^1H$ nmr and ir data. The preparation involved the condensation of *o*-hydroxyacetophenone with ethylacetate in the presence of

TABLE I. Elemental Analyses and Physical Properties of the Ligand $H_2$aapen and the Complexes Prepared.

| Compound | C% |  | H% |  | N% |  | Other% |  | Color |
|---|---|---|---|---|---|---|---|---|---|
|  | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |  |
| $H_2$aapen | 69.45 | 69.55 | 6.36 | 6.48 | 7.36 | 7.23 |  |  | Yellow |
| Cu($H_2$aapen)·$CHCl_3$ | 49.20 | 49.60 | 4.13 | 4.36 | 4.99 | 5.11 | 12.28 | 11.60 (Cl) | Green |
| Cu($H_2$aapen) | 59.78 | 60.10 | 5.01 | 5.15 | 6.33 | 6.22 |  |  | Brown |
| Ni($H_2$aapen) | 60.45 | 61.01 | 5.09 | 5.35 | 6.41 | 6.69 |  |  | Brown–Green |
| $UO_2$($H_2$aapen)·($H_2O$) | 39.64 | 39.21 | 3.63 | 3.69 | 4.20 | 4.18 | 2.70 | 2.90 ($H_2O$ | Orange–Red |
| $Li_2$[$UO_2$(aapen)($H_2O$)]$H_2O$ | 37.93 | 38.19 | 3.44 | 3.31 | 4.02 | 3.92 | 5.16 | 5.65 ($H_2O$) | Orange–Red |
| $Li_2UO_2$(aapen)·(dmso) | 40.01 | 39.73 | 3.05 | 3.34 | 3.57 | 3.86 |  |  | Orange–Red |
| $UO_2$Ni(aapen)·(EtOH) | 38.37 | 38.76 | 3.49 | 3.76 | 3.73 | 3.54 |  |  | Brick–Red |
| $UO_2$Ni(aapen)·($H_2O$) | 36.53 | 36.72 | 3.06 | 3.28 | 3.87 | 3.91 | 2.48 | 2.93 ($H_2O$) | Brick–Red |
| $UO_2$Ni(aapen)·(dmso) | 36.80 | 36.92 | 3.34 | 3.51 | 4.24 | 4.15 |  |  | Brick–Red |
| $UO_2$Cu(aapen)·($H_2O$) | 36.29 | 36.54 | 3.04 | 3.37 | 3.84 | 3.73 | 2.47 | 2.85 ($H_2O$) | Brown–Red |
| $Ni_2$(aapen) | 53.50 | 53.25 | 4.08 | 4.31 | 5.67 | 5.54 |  |  | Yellow–Green |
| $Cu_2$(aapen) | 52.48 | 52.67 | 4.00 | 4.22 | 5.56 | 5.73 |  |  | Green |
| CuNi(aapen) | 52.99 | 53.13 | 4.04 | 4.17 | 5.61 | 5.84 |  |  | Green |

Na under reflux. The preparation of the Schiff base was achieved by condensation of $H_2$aap and ethylenediamine in methanol.

*Preparation of Mononuclear Complexes*

Mononuclear complexes were prepared by the following two general methods:

A) The Schiff base ligand (0.001 mol) dissolved in hot chloroform (150 ml) was added to the metal acetate (0.001 mol) dissolved in hot 95% ethanol (100 ml). The resulting mixture either precipitated the product immediately, or on reducing to a smaller volume by heating on a steam bath. The mixture was allowed to cool and the solid precipitate was collected by filtration and dried over silica gel under vacuum. Yields averaged 70%.

$H_4$aapen and nickel(II) acetate tetrahydrate yielded 3,3′-(1,2-ethanediyldinitrilo)bis-(1-*o*-hydroxyphenyl-1-butaneonato)(2-)$N^3$, $N^{3\prime}$, O, O′)nickel(II), Ni($H_2$aapen-$N_2O_2$) as a brown microcrystalline solid.

$H_4$aapen and copper(II) acetate dihydrate yielded chloroform (3, 3′, (1,2-ethanediyldinitrilo)bis-(1-*o*-hydroxyphenyl-1-butaneonato)(2-)O, O′, O″, O‴)-copper(II), Cu($H_2$aapen-$O_2O_2$)·$CHCl_3$ as a green solid.

$H_4$aapen and dioxouranium(VI) acetate dihydrate yielded aqua (3, 3′-(1,2-ethanediyldinitrilo)bis(1-*o*-hydroxyphenyl-1-butaneonato(2-)O,O′,O″,O‴)dioxouranium(VI), $UO_2$($H_2$aapen-$O_2O_2$)·$H_2O$ as a bright orange solid.

B) Metal acetate (0.001 mol) dissolved in hot 95% methanol was added to $H_4$aapen (0.001 mol) suspended in methanol. The resulting suspension was heated on a steam bath, under stirring, for 6 hr. The mixture was allowed to cool and the solid precipitate was collected by filtration and dried over silica gel under vacuum. Yields averaged 75%.

The $UO_2^{2+}$ and $Ni^{2+}$ $O_2O_2$ compounds can be obtained using this method, while for copper(II) the complex Cu($H_2$aapen-$N_2O_2$) was obtained.

*Preparation of $Li_2$[$UO_2$(aapen)($H_2O$)]$H_2O$*

To a methanolic solution (100 ml) of *o*-hydroxyacetylacetophenol (0.001 mol), ethylenediamine (0.0005 mol) in methanol and LiOH (0.002 mol) in water were added. After 20 min 25 ml of a methanolic solution containing dioxouranium(VI) nitrate (0.0005 mol) was added. The mixture was refluxed for 4 h. It was allowed to cool and the precipitated solid was collected by filtration and dried over silica gel under vacuum.

*Preparation of the Binuclear Complexes*

Two preparative routes have been used:

A) Two solutions were prepared: one containing the mononuclear complex (0.001 mol) dissolved in hot chloroform and the other containing the appropriate metal acetate (0.001 mol) in methanol. The metal acetate solution was added slowly to the ligand solution; the solution changed colour and on heating on a steam bath for *ca.* 5 minutes, a microcrystalline solid was precipitated. The precipitate was collected by filtration and dried over silica gel under vacuum.

B) The mononuclear complex (0.001 mol) was dissolved in pyridine (50 ml) and a methanol solution containing LiOH (0.002 mol) was added. After 10 minutes the appropriate metal acetate (0.001 mol) in methanol was added. The solution changed colour; the heating and stirring was continued for about 4 hr. The pyridine was removed under reduced pressure and the residue treated with hot methanol. The hot suspension was filtered and the precipitate washed with methanol and dried over silica gel under vacuum. Elemental analyses are shown in Table I.

### *Physical Measurements*

Ir spectra were recorded on a Perkin–Elmer 621 spectrometer using KBr discs. The spectra were calibrated in the 1600–1000 $cm^{-1}$ and 500 $cm^{-1}$ regions with polystyrene. Electronic spectra were recorded in dimethylsulphoxide, pyridine or $CHCl_3$ solutions or Nujol mulls, using a Cary 14 spectrometer. $^1H$ nmr spectra were recorded with a Varian T 60 spectrometer with $Si(CH_3)_4$ as an internal standard. Magnetic susceptibilities were measured by the Gouy method using a Brucker–Sartorius instrument. The apparatus was calibrated with $Ni(en)_3(ClO_4)_2$. The diamagnetic corrections were calculated from Pascal's constants.

Mass spectra were recorded with a Hitachi Perkin–Elmer RMU 6 spectrometer.

## Results and Discussion

The ligand $H_4$aapen was prepared by condensation of *o*-acetoacetylphenol with 1,2-diaminoethane in refluxing ethanol. Its $^1H$ nmr spectrum in $CDCl_3$ shows a signal at 2.1$\delta$ due to two equivalent methyl groups and a two proton peak at 5.7$\delta$ for –HC=C proton. The broad signals at 11.1 and 13.3$\delta$ are assigned to the N···H···O and OH protons respectively, since they disappear upon deuteration. The four methylene protons are present at 3.6$\delta$. In the KBr ir spectrum the absence of a free carbonyl stretching frequency strongly suggests the presence of hydrogen bonding. The mass spectrum exhibits a strong parent ion peak at m/e 380. This ligand reacts with metal acetates to give metal complexes which show clearly the coordination selectivity patterns available.

With uranyl(VI) acetate, in $CHCl_3$/EtOH or MeOH, the complex $UO_2(H_2aapen\text{-}O_2O_2)\cdot(H_2O)$ is obtained. The ir spectrum shows bands at 3040 $cm^{-1}$ due to $\nu$N–H, and three medium bands at 1620, 1598 and 1562 $cm^{-1}$ which were assigned to $\nu_{C=N}$ and $\nu_{C=O}$ + $\nu_{C=C}$ respectively; the phenolic $\nu_{C-O}$ lies at 1344 $cm^{-1}$. The visible spectrum presents a single band at about 420 nm which is very similar to that expected for electronic transitions mainly localized on the moiety bonded to the uranyl group. From these spectroscopic data it is not possible to tell with certainty which coordination site the $UO_2^{2+}$ occupies; however we believe that it is the $O_2O_2$ isomer, since in the complex (6,6′-(1,2ethanedienyldinitrilo)bis-(2,4-heptanetrione)(2-)O, O′, O″, O‴)MeOH-dioxouranium(VI), where the uranyl(VI) ion is presented with a choice of $N_2O_2$ or $O_2O_2$ donor atom set, the structural data confirm that the $O_2O_2$ isomer is obtained [13]. It is also more likely, on steric grounds, that the uranyl(VI) ion will occupy the $O_2$-$O_2$ chamber in which it has a greater opportunity to achieve its favored seven coordination.

By template synthesis in the presence of LiOH the complex $Li_2[UO_2(aapen\text{-}O_2O_2)(H_2O)]\cdot(H_2O)$ was obtained. Its physico-chemical data are quite similar to those of $UO_2(H_2aapen\text{-}O_2O_2)(H_2O)$, the only difference being in the ir spectrum, where the bands due to $\nu$ N–H and $\nu$C=N are absent and a new band at 1540 $cm^{-1}$ due to $\nu C\underline{\cdots}N$ appears. The $\nu_3$O–U–O band is shifted to lower frequencies in this complex.

Positional isomers of the mononuclear complex of copper(II) have been prepared. When $CHCl_3$/EtOH was used the green $O_2O_2$ isomer can be obtained, while in refluxing MeOH the light brown $N_2O_2$ one was obtained. There are large differences in the ir and uv spectra of these complexes. The electronic spectrum of the $N_2O_2$ isomer in $CHCl_3$ solution shows an absorption peak at 545 nm which presents close similarity to that of Cu(acacen) [14], and strongly suggests a $N_2O_2$ tetracoordinate planar structure for this complex. The magnetic moment (1.63 BM) and the great solubility in the common organic solvents agree with this configuration. The drs spectrum of the $O_2O_2$ green isomer shows a peak at 617 nm, assigned to the ligand field d–d transition band, and it is closely similar to that of bis(*o*-hydroxyacetophenonato)copper(II) [15]; its magnetic moment is 1.77 BM. The ir spectra are very different: $Cu(H_2aapen\text{-}N_2O_2)$ does not show the $\nu$C=N, which is present in the $O_2O_2$ isomer at 1640 $cm^{-1}$, but gives a band at 1515 $cm^{-1}$ assigned to a metal coordinated C=N bond and a phenolic O–H band at 3040 $cm^{-1}$ which is absent in the $O_2O_2$ isomer. Moreover the phenolic C–O stretching frequency lies at 1280 $cm^{-1}$, shifted about 35 $cm^{-1}$ to lower frequencies with respect to the $O_2O_2$ isomer, as expected for an uncoordinated phenol [20].

The analytical data for the mononuclear $Cu(H_2aapen\text{-}O_2O_2)$ complex suggest that a molecule of chloroform is present for every molecule of complex. The ir spectrum gave two medium bands at 1207 and 760 $cm^{-1}$ which are absent in the other complex and compare well with the bands at 1218 and 765 $cm^{-1}$ reported for chloroform [16]. $^1H$ nmr and ir studies of metal $\beta$-diketonates in solution with quantities of deuterochloroform added give evidence in support of hydrogen-bonding of deuterium of $CDCl_3$ to the oxygen atoms of the chelated ligands [17]. The X-ray crystal structure of Cu(salen)$\cdot CHCl_3$ shows that the complex exists as a dimer and that chloroform molecules are hydrogen-bonded to the oxygen atoms not involved in intramolecular bonding between the two molecular units of the dimer [18]. It is therefore suggested that the chloroform present in $Cu(H_2aapen)\cdot CHCl_3$ ($O_2O_2$) is hydrogenbonded to oxygen atoms of the ligand.

For $Ni(H_2aapen\text{-}N_2O_2)$ the spectral and magnetic data are consistent with the nickel ion coordinated to two nitrogen and two oxygen atoms in a square planar configuration. Its ir spectrum is similar to that

TABLE II. Infrared Data of the Prepared Complexes.

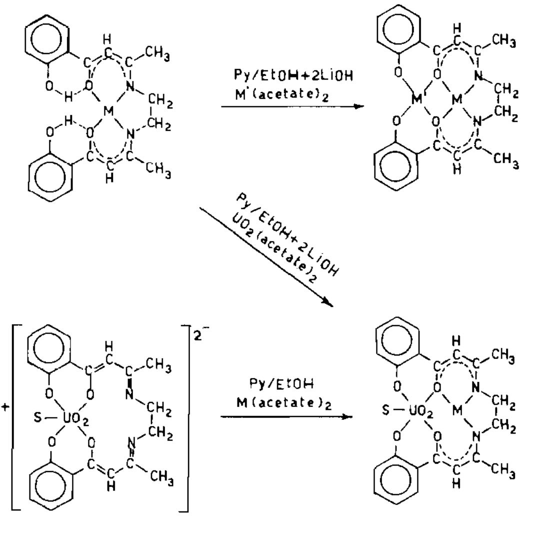
| Complex | $\nu$C=N | $\nu$C=O + C=C | $\nu C\underline{\cdots}N$ | Phenolic $\nu$C–O | Other Bands |
|---|---|---|---|---|---|
| $Cu(H_2aapen\text{-}O_2O_2)\cdot CHCl_3$ | 1640 | 1600, 1554 | | 1315 | 1207, 760 $(CHCl_3)$ |
| $Cu(H_2aapen\text{-}N_2O_2)$ | | 1590 | 1515 | 1280 | 3040 phenolic $\nu$OH |
| $Ni(H_2aapen\text{-}N_2O_2)$ | | 1615, 1591 | 1510 | 1280 | 3040 phenolic $\nu$OH |
| $UO_2(H_2aapen\text{-}O_2O_2)\cdot(H_2O)$ | 1620 | 1598, 1562 | | 1344 | 3430 $\nu$OH, 910 $\nu_3$O–U–O |
| $Li_2[UO_2(aapen\text{-}O_2O_2)(H_2O)]\cdot(H_2O)$ | | 1600, 1560 | 1540 | 1340 | 3440 $\nu$OH, 889 $\nu_3$O–U–O |
| $UO_2Ni(aapen)\cdot EtOH)$ | | 1605, 1591 | 1517 | 1345 | 3440 $\nu$OH, 905 $\nu_3$O–U–O |
| $UO_2Ni(aapen)\cdot(H_2O)$ | | 1610, 1592 | 1515 | 1350 | 3430 $\nu$OH, 898 $\nu_3$O–U–O |
| $UO_2Cu(aapen)\cdot(H_2O)$ | | 1613, 1598 | 1525 | 1345 | 3420 $\nu$OH, 899 $\nu_3$O–U–O |
| $Ni_2(aapen)$ | | 1595, 1570 | 1515 | 1310 | |
| $Cu_2(aapen)$ | | 1600 (broad) | 1515 | 1320 | |
| CuNi(aapen) | | 1600 (broad) | 1518 | 1315 | |

of $Cu(H_2aapen\text{-}N_2O_2)$ (Table II). The electronic spectrum in $CHCl_3$ contains a single band at 568 nm, which is completely comparable with that found for Ni(acacen) [14]. The same absorption peak is found when the spectrum is recorded in the solid state or in py or dmso solutions; the last indicates the preservation of the square planar configuration in donor solvents. Although the spectra strongly suggest the $N_2O_2$ isomer, they do not furnish useful information about purity with respect to the $O_2O_2$ isomer. The experimental value of the magnetic moment, however, shows that the complex is diamagnetic. The $O_2O_2$ isomer would be expected to produce a paramagnetic octahedral nickel(II) complex through the adduction of solvent molecules or by means of polymerization [19].

Reaction of the ligand with an equimolecular quantity of oxovanadium(IV) acetate gave a green crystalline product. The mass spectrum showed the presence of two different complexes. The lower temperature spectrum gave a parent peak at m/e 445 a.m.u. corresponding to $VO(H_2aapen)$, but the higher temperature spectrum gave two peaks at equal intensity at m/e 445 and 510 a.m.u., the latter peak corresponding to the di-oxovanadium(IV) complex $(VO)_2(aapen)$. The analysis of the mixture gave values which fit well with the analysis for a mixture of $(VO)_2(aapen)$:$VO(H_2aapen)$ 2:1. It was not possible to separate the two complexes from the mixture.

### *Binuclear Complexes*

Once it was established that the two sites in the Schiff base may specifically coordinate different metal ions, it became feasible to prepare pure mixed metal complexes in which the position of the two metal ions is known. We chose to use the $Ni(H_2aapen\text{-}N_2O_2)$, $Cu(H_2aapen\text{-}N_2O_2)$ and $Li_2[UO_2(aapen\text{-}O_2\text{-}O_2)(H_2O)]\cdot(H_2O)$ as ligands to bind a different or similar metal ion. The only binuclear species that could be isolated with method A was $UO_2Ni(aapen)$-$(C_2H_5OH)$. However, binuclear complexes were easily prepared by method B or by reaction of dilithium salt of the mononuclear dioxouranium(VI) complex according to the scheme:



M = Cu$^{II}$ or Ni$^{II}$ and M' = Cu$^{II}$ or Ni$^{II}$

The analytical data agree with the formulations proposed above. The ir spectra differ from those of the mononuclear parent compounds. The broad band at about 3430 cm$^{-1}$ is assigned to the OH stretching frequency of the solvent, the broadness of these bands being a good indication that the group is involved in hydrogen-bond formation. All these binuclear complexes have a strong band in the frequency range 1620–1600 cm$^{-1}$ which can be assigned to a C–O stretching mode. Other bands in the 1600–1560 cm$^{-1}$ region may be assigned to a $C\underline{\cdots}C$ stretch or $C\underline{\cdots}C$ plus $C\underline{\cdots}O$ modes. The band appearing at about 1520 cm$^{-1}$ is assigned to $C\underline{\cdots}N$

TABLE III. Electronic (nm) and Magnetic (BM) Data of the Prepared Complexes.

| Complex | Solid | $CHCl_3$ | dmso | Pyridine | $\mu_{eff}$ |
|---|---|---|---|---|---|
| Cu($H_2$aapen-$O_2O_2$) | 617[a] | | | | 1.77 |
| Cu($H_2$aapen-$N_2O_2$) | 520, 595 | 545 | 558 | 528 | 1.63 |
| Ni($H_2$aapen-$N_2O_2$) | 560; 575[a] | 568 | 568 | 568 | diam |
| $UO_2$($H_2$aapen-$O_2O_2$)($H_2O$) | 422 | | | | diam |
| $Li_2$[$UO_2$(aapen-$O_2O_2$)($H_2O$)]•($H_2O$) | 415 | | | | diam |
| $UO_2$Ni(aapen)($H_2O$)[b] | 555; 565[a] | | 568 | 568 | diam |
| $UO_2$Cu(aapen)($H_2O$) | 622sh | | 630sh | 628sh | 1.71 |
| $Cu_2$(aapen) | 570sh | 566, 530 | | | 1.84 |
| $Ni_2$(aapen) | 575br; 1080 | 582 | 575 | | 2.99 |
| CuNi(aapen) | 570 | | 570sh | | 2.08 |

[a] Drs spectra. [b] For the complex $UO_2$Ni(aapen)(EtOH) a magnetic moment of 0.85 BM has been found.

stretching vibrations displaced from their usual position as the result of metal ion coordination. The phenolic C–O stretching frequencies lie in the 1350–1310 $cm^{-1}$ range. In addition, for binuclear complexes containing the uranyl group the $\nu_3$ appears at about 900 $cm^{-1}$. The electronic spectrum of $UO_2$-Ni(aapen)($H_2O$) shows a single band at 568 nm (py, dmso) and 565 nm (drs) suggesting that the nickel(II) ion is in a nearly square planar configuration. The complex is diamagnetic, as found for the mononuclear nickel(II) complex, and it further suggests that nickel(II) has a nearly planar configuration in the $N_2O_2$ donor site. Again it is more likely on steric grounds that the uranyl ion would occupy the $O_2O_2$ site.

The electronic spectrum, in nujol mull or solution (py, dmso), for $UO_2$Cu(aapen)($H_2O$) shows a single peak at 622 nm and 628, 630 nm respectively. This band presents close similarity to the band for Cu(acacen) [14]; the red shift of this band can be affected by the presence of the uranyl(VI) ion in the adjacent $O_2O_2$ compartment. The magnetic moment (1.71 BM) agrees with the copper(II) in a square planar structure.

The CuNi(aapen) complex has in the electronic spectrum a single broad band centered at 570 nm and a magnetic moment of 2.08 BM. This value is explained by assuming that the nickel(II) ion is coordinated in a square-planar manner and is diamagnetic with the entire paramagnetism arising from the second metal.

Homobinuclear complexes $M_2$(aapen) (M = $Cu^{2+}$, $Ni^{2+}$) have been also obtained and their physicochemical properties are given in Tables II and III. The $CHCl_3$ solution spectrum of $Cu_2$(aapen) shows two bands at 566 nm and 530 nm. The 530 nm band, comparable to that for Cu(acacen) [14], is tentatively assigned to the copper(II) ion in the $N_2$-$O_2$ chamber. The 566 nm band, comparable with the band at 560 nm in the spectrum of Cu(salicylaldehydate)$_2$ [21], is tentatively assigned to the copper(II) in the $O_2O_2$ site. The magnetic moment of the dimer (1.84 BM) suggests that an antiferromagnetic spin-exchange interaction is operating. The binuclear $Ni_2$(aapen) complex has one band at about 575 nm (dmso) which seems to correspond to the band for mononuclear nickel(II) complex. The magnetic moment for the dimer is 2.99 BM, much lower than the expected spin only value. This may be explained by a) antiferromagnetic spin pairing between paramagnetic nickel ions, or b) formation of a binuclear species containing one paramagnetic (six-coordinate, $O_2O_2$) and one diamagnetic (four-coordinate, $N_2O_2$) nickel(II) ion. The latter possibility seems to be supported by the visible spectrum, which shows two bands at 575 nm (broad) and 1080 nm. This behaviour agrees with a nickel(II) ion in a square planar configuration and a nickel(II) in an octahedral environment.

There is no evidence for the achievement of the six-coordination by solvation by the nickel(II) ion in the $O_2O_2$ compartment, and it is possible that oligomerisation has occurred and the $Ni_2$(aapen) is not monomeric in the solid state.

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