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Magnetic properties of binuclear manganese(II), cobalt(II), nickel(II) and copper(II) complexes of a macrocyclic ligand derived from pyridine-*N*-oxide, and crystal structure of the nickel complex ☆

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Abstract

The preparation of complexes $M_2L(NO_3)_4 \cdot 2CH_3OH \cdot nH_2O$ (**4a–d**) (M=Mn, Co, Ni, Cu; $L=C_{18}H_{22}N_6O_4$ (**3**); $n=0.5$ or 1) from pyridine-1-oxide-2,6-dialdehyde, 1,2-diaminoethane and the metal(II) nitrate is reported. The complex $[Ni_2L(H_2O)_4](NO_3)_4 \cdot 2H_2O$ (**5**) was also prepared and its crystal structure determined. **5** is monoclinic, space group $P2_1/n$, $a=11.831(8)$, $b=12.168(8)$, $c=12.329(7)$ Å, $\beta=114.26(5)°$, $Z=2$. In the cyclic ligand **3**, the pyridine-1-oxide rings are linked by CH(OH).NH.$(CH_2)_2$.N:CH groups, showing that partial hydrolysis of the expected Schiff-base ligand has occurred during synthesis of the complex. In the centrosymmetric complex **5**, the Ni^{2+} ions are bridged in a planar Ni_2O_2 unit by the N-oxide oxygen atoms, the ligand adopting a non-planar 'stepped' conformation with pyramidal stereochemistry at the bridging O atoms. Six-fold coordination of each Ni^{2+} ion is completed by two N atoms and two *cis* water molecules. The magnetic susceptibilities of **4a–d** were measured between 5 and 300 K and analysed to obtain values of the parameter J in the exchange Hamiltonian $-2J\mathbf{S}_1 \cdot \mathbf{S}_2$: $J=-1.15$, -5.0, -15.5 and $+3.3$ cm^{-1}, respectively. These values are discussed in terms of the contributing orbital pathways.

Keywords: Binuclear complexes; Manganese complexes; Cobalt complexes; Nickel complexes; Copper complexes; Macrocyclic ligand complexes; Magnetism

1. Introduction

Ligands that incorporate a bridging group holding two or more metal ions in a fixed molecular environment are becoming widely used as tools in such research areas as magnetism, catalysis, and enzyme modelling. One extremely useful bridging group is the phenolate ion, which can occur either alone [1] or as part of a chelating ligand or a macrocycle [2] such as the binucleating ligands **1** introduced by Robson [3]. Pyridine-*N*-oxide (pyno), which is isoelectronic with phenolate, can also act as a bridging group [4], and with the aim of extending the range of binucleating ligands we have investigated a number of chelating and macrocyclic ligands that incorporate pyno as the bridging unit.

We were particularly interested in ligands **2**, the *N*-oxide analogues of **1**, for the following reasons. First, a number of metal complexes of **1** have been studied magnetically [3,5], and we expected to be able to obtain a similar range of complexes of **2**. Studies in which different combinations of metal ions are placed in a fixed ligand environment and the magnetic coupling interactions are compared are especially useful in understanding the mechanism of superexchange [6]. Secondly, it would be of interest to examine the effect, on the structure and magnetic coupling in a complex of a ligand such as **1**, of replacing the bridging group $C–O^-$ by the isoelectronic $N^+–O^-$.

We report here the results of an attempt to prepare complexes of the ligand **2a**, which in fact yielded

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☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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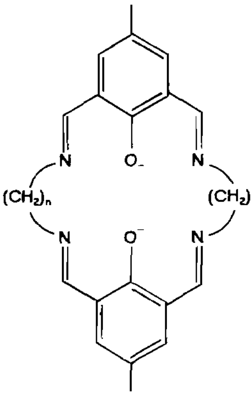
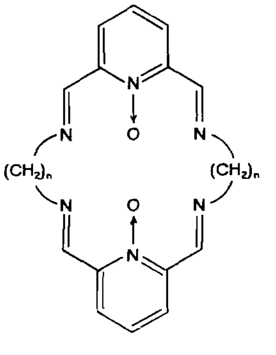
complexes of a novel macrocyclic ligand 3. The magnetic susceptibilities of binuclear complexes of 3 with manganese(II), cobalt(II), nickel(II) and copper(II) have been measured, and are analysed to obtain values of the exchange parameters. The crystal structure of a binuclear nickel complex of 3 has been determined, and is used as a basis for understanding these parameters.

Although many macrocyclic ligands incorporating pyridine are known [7], we believe this is the first report of one containing pyridine-*N*-oxide.



1
(a. n=2; b. n=3)



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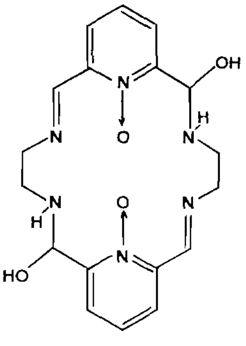
(a. n=2; b. n=3)



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2. Results and discussion

2.1. Synthesis and characterisation of complexes $M_2L(NO_3)_4 \cdot 2CH_3OH \cdot nH_2O$ (4a–d) ($L=3$; $M=$Mn, Co, Ni, Cu, respectively) and $[Ni_2L(H_2O)_4](NO_3)_4 \cdot 2H_2O$ (5)

The methanol solvates 4 were obtained by condensing pyridine-1-oxide-2,6-dialdehyde with 1,2-diaminoethane, and reacting the resulting Schiff base with the metal nitrate in methanol. Microanalysis confirmed the formulae with $n=0.5$ or 1. The four complexes **4a–d** all have slightly different IR spectra, and their X-ray powder photographs show that they are not isomorphous. However, the IR spectra and X-ray powder patterns of the Co and Ni compounds, although not identical, are sufficiently similar to suggest that these two must have very similar crystal and molecular structures.

Slow evaporation in air of a solution of **4c** in water/methanol (2:5) gave green crystals of a nickel complex 5 for which CHN analysis indicated complete loss of methanol and incorporation of additional water. As described below, this compound contains ligand 3 in which two of the four CH:N groups of the expected macrocycle **2a** have become partially hydrolysed to CH(OH)NH groups. We do not have crystal structures of any of the complexes 4, and we therefore cannot be certain that these too contain ligand 3 rather than **2a**. However, the similarity of the IR spectrum of 5 with the spectra of complexes 4 supports this assumption, and strong support also comes from the ferromagnetic coupling observed in the copper complex **4d**, which can readily be understood (as we discuss below) on the basis of the structure found for complex 5, but contrasts with the strongly antiferromagnetic coupling usually found in copper complexes of **1a**, **1b** and similar Schiff-base ligands [2b,5,8]. Microanalysis of the complexes 4 indicated the presence of only two CH_3OH molecules and 0.5 or one H_2O molecule in the formula, and since a total of four such molecules would be required to complete six-fold coordination of the metal ions, it is likely that the CH(OH) groups, or possibly the nitrate ions, are also involved in coordination, at least in the Ni and Co complexes.

2.2. Crystal structure of 5

Fig. 1 is a view of the binuclear cation, with the atom numbering, and Fig. 2 shows the arrangement of the cations and nitrate anions in the unit cell. The fractional coordinates of all non-hydrogen atoms are listed in Table 1, and selected bond lengths and angles in Table 2.

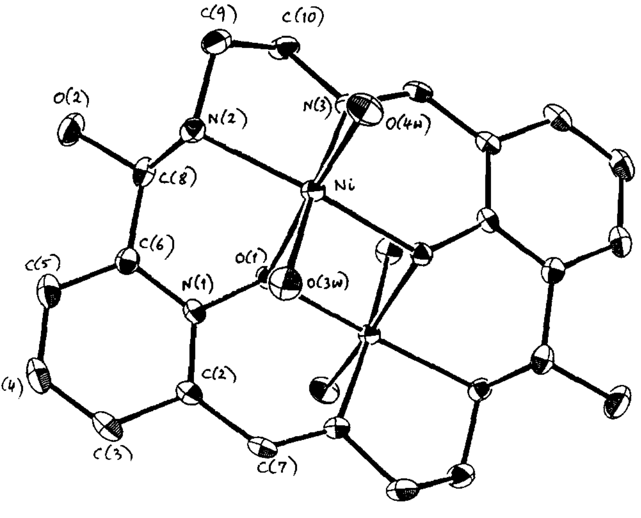

Fig. 1. View of the cation $[Ni_2L(H_2O)_4]^{4+}$ of complex 5 with hydrogen atoms omitted.

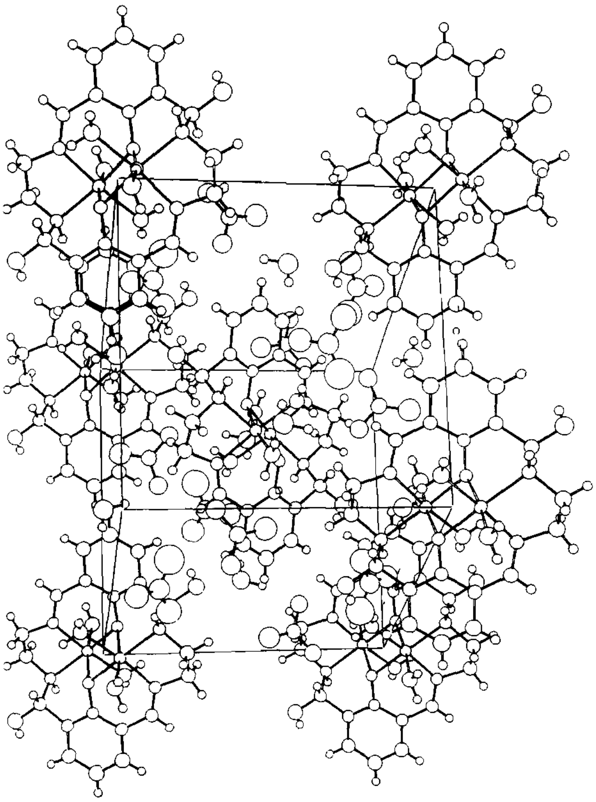

Fig. 2. Unit cell of complex 5. Seven cations are shown.

Each nickel atom is in approximately octahedral *cis*-N_2O_4 coordination, with the two water molecules *cis* to each other. The nickel atoms are bridged by the *N*-oxide oxygen atoms in a planar centrosymmetric Ni_2O_2 unit, with Ni–O bond lengths of 2.130 (*trans* to H_2O) and 2.078 (*trans* to NH) Å, Ni–O–Ni angle 100.7°, and Ni···Ni distance 3.242 Å. The macrocycle as a whole has a 'stepped' structure, in which two parallel, approximately planar segments, each consisting of a pyridine ring and an almost coplanar six-membered chelate ring, make angles of ~66° with the central Ni_2O_2 plane. The presence of two CH:N groups (C(7)–N(3) 1.264 Å, C(2)–C(7)–N(3) 126.9°) and two CH(OH)NH groups (C(8)–N(2) 1.476, C(8)–O(2) 1.394 Å, C(6)–C(8)–N(2) 107.7, C(6)–C(8)–O(2) 111.3, O(2)–C(8)–N(2) 109.6°) is clearly shown. The bond angles around O(1) of 109.0, 127.3 and 100.7° indicate the pyramidal stereochemistry at this atom.

Most of the hydrogen atoms were located in Fourier difference functions after anisotropic refinement of the non-H atoms. On the basis of their positions, and short interatomic contacts (O···O 2.74–2.93, O···N 2.86 Å), there is evidence of a hydrogen-bonding network in which the ligand NH groups are linked to NO_3^- ions, NO_3^- to both coordinated and non-coordinated water molecules, and non-coordinated H_2O to the ligand OH groups and coordinated H_2O molecules.

Table 1
Positional parameters and B_{eq} for $[Ni_2(O_4N_6C_{18}H_{22})(H_2O)_4](NO_3)_4 \cdot 2H_2O$

Atom	x	y	z	B_{eq}
Ni	0.13974(4)	0.04637(4)	0.07063(4)	1.81(2)
O(1)	−0.0108(2)	0.0506(2)	−0.1005(2)	1.89(9)
O(2)	0.1867(2)	0.3015(2)	−0.1441(3)	3.7(1)
O(3w)	0.1966(2)	−0.0839(2)	0.0065(2)	2.9(1)
O(4w)	0.2899(2)	0.0196(2)	0.2287(2)	3.2(1)
O(5w)	0.5332(3)	0.0215(3)	0.2659(3)	4.9(2)
O(41)	0.3421(3)	0.1656(3)	0.5915(3)	4.4(1)
O(42)	0.3278(3)	0.2064(3)	0.4162(3)	4.3(1)
O(43)	0.2809(4)	0.0461(3)	0.4529(3)	6.3(2)
O(51)	0.6205(3)	0.0677(4)	0.0798(3)	6.7(2)
O(52)	0.4746(3)	0.1809(4)	0.0633(4)	7.7(2)
O(53)	0.5565(5)	0.1777(4)	−0.0620(5)	10.8(3)
N(1)	0.0338(2)	0.0361(3)	−0.1845(2)	1.9(1)
N(2)	0.2156(3)	0.1750(3)	0.0085(3)	2.1(1)
N(3)	0.0877(3)	0.1675(2)	0.1495(3)	2.1(1)
N(4)	0.3167(3)	0.1391(3)	0.4872(3)	3.2(2)
N(5)	0.5470(4)	0.1443(4)	0.0247(4)	5.1(2)
C(2)	0.0163(3)	−0.0594(3)	−0.2474(3)	2.2(1)
C(3)	0.0656(4)	−0.0658(4)	−0.3327(3)	3.1(2)
C(4)	0.1313(4)	0.0189(4)	−0.3497(4)	3.4(2)
C(5)	0.1526(4)	0.1114(3)	−0.2808(4)	3.0(2)
C(6)	0.1048(3)	0.1191(3)	−0.1961(3)	2.3(2)
C(7)	−0.0407(3)	−0.1574(3)	−0.2243(3)	2.3(2)
C(8)	0.1313(3)	0.2146(3)	−0.1105(4)	2.4(2)
C(9)	0.2441(3)	0.2613(3)	0.1023(4)	2.8(2)
C(10)	0.1335(3)	0.2759(3)	0.1334(4)	2.8(2)
H(2n)	0.2898	0.1534	−0.0006	5.0
H(3)	0.0542	−0.1285	−0.3755	3.6
H(4)	0.1564	0.0135	−0.4060	4.3
H(4o)	0.1986	0.2846	−0.1837	5.5
H(5)	0.2040	0.1730	−0.2888	2.8
H(7)	0.0368	0.2174	0.2661	2.2
H(8)	0.0578	0.2388	−0.1070	2.4
H(3w1)	0.2602	−0.0910	0.0034	5.2
H(3w2)	0.1861	−0.1408	0.0389	5.3
H(4w1)	0.3787	0.0248	0.2448	6.5
H(4w2)	0.2861	0.0432	0.2922	5.9
H(5w1)	0.5766	−0.0472	0.3069	7.4
H(5w2)	0.5424	0.0250	0.2143	7.1
H(91)	0.3209	0.2390	0.1730	2.7
H(92)	0.2663	0.3305	0.0770	3.3
H(101)	0.0669	0.3134	0.0683	2.6
H(102)	0.1537	0.3171	0.2046	2.4

The structure of 5 is unusual in several respects. One is the presence of the $CH(OH).NH.(CH_2)_2.N{:}CH$ bridging chains. This partial hydrolysis of the Schiff-base ligand was unexpected, since it does not appear to have been observed in complexes of ligands **1**. However, somewhat similar partial solvolysis has been recorded during the metal template synthesis of certain Schiff-base ligands, where the stereochemical requirements of the metal template ion apparently induce conversion to a more flexible coordination site [7]. For example, when the complex $[Cu(bpe)]ClO_4$ (bpe = *N*,*N*′-bis-(2-pyridylmethylene)-1,2-diaminoethane) was treated with chloride in methanol solution,

Table 2
Selected interatomic distances (Å) and bond angles (°) in $[Ni_2L(H_2O)_4](NO_3)_4 \cdot 2H_2O$ (**5**)

Ni–Ni′	3.242(3)	O2–C8	1.394(4)
Ni–O1	2.130(4)	N2–C8	1.476(5)
Ni–O1′	2.078(3)	N2–C9	1.495(4)
Ni–O3w	2.008(3)	N3–C7	1.264(5)
Ni–O4w	2.053(4)	N3–C10	1.471(5)
Ni–N2	2.099(3)	C2–C7	1.455(5)
Ni–N3	1.997(3)	C6–C8	1.513(6)
O1–N1	1.354(4)	C9–C10	1.517(5)
O1–Ni–O1′	79.3(1)	Ni–O1–Ni′	100.7
O1–Ni–O3w	84.7(1)	Ni–O1–N1	109.0(2)
O1–Ni–O4w	171.6(1)	Ni′–O1–N1	127.3(2)
O1–Ni–N2	85.9(1)	Ni–N2–C8	113.0(2)
O1–Ni–N3	99.5(1)	Ni–N2–C9	103.7(2)
O1′–Ni–O3w	90.6(1)	C8–N2–C9	112.6(3)
O1′–Ni–O4w	98.9(1)	Ni–N3–C7	126.9(3)
O1′–Ni–N2	160.6(1)	Ni–N3–C10	113.1(2)
O1′–Ni–N3	86.4(1)	C7–N3–C10	118.9(3)
O3w–Ni–O4w	87.1(1)	N3–C7–C2	126.9(3)
O3w–Ni–N2	100.5(1)	O2–C8–N2	109.6(3)
O3w–Ni–N3	174.3(1)	O2–C8–C6	111.3(3)
O4w–Ni–N2	97.6(1)	N2–C8–C6	107.7(3)
O4w–Ni–N3	88.5(1)	N2–C9–C10	109.5(3)
N2–Ni–N3	83.8(1)	N3–C10–C9	109.4(3)

$[Cu(bpe,MeOH)Cl]ClO_4$ was obtained [9], for which crystal structure analysis showed the presence of $CH(OCH_3).NH.(CH_2)_2.N:CH$ linkages with geometry quite similar to that in **5** [10]. Analogous solvolysis reactions of other Schiff-base ligands had earlier been postulated on spectroscopic evidence [11]. In the case of **5**, the partial hydrolysis presumably occurred during the reaction of **2a** with Ni^{2+}, since no template ion was present in the initial ligand synthesis.

In contrast to the 'stepped' structure of **5**, with pyramidal bonding at O(1), all complexes of ligands similar to **1a** or **1b** have so far been found to have essentially flat structures with planar stereochemistry at the bridging phenolic O atoms [5b,c,f,g,12]. This is the case even in complexes of the ligand derived from **1b** by reduction of the CH:N groups to CH_2NH [13]. Planar stereochemistry is also found in the compounds $[M_2\text{-}\mu\text{-}(4\text{-}CH_3C_6H_4O)_2Cl_4]$ (M = Mn, Fe, Co, Zn, Cd) in which the phenolate ion is not part of a multidentate ligand [1] [1]. In complexes in which pyridine-*N*-oxide is a bridging ligand, however, both planar [16] and pyramidal [17] bonding at the bridging O atom have been observed. Thus, although the requirement for tetrahedral geometry at the saturated atoms C(8) and N(2) may have been the determining factor in formation of the 'stepped' structure of **5**, greater flexibility at the *N*-oxide O atom may have played a part. Another possible factor is the smaller size of the cavity available to the metal ions in ligands with the ethylene bridge of **1a** or **2a** compared with that in the propylene-linked **1b** or **2b**. To our knowledge only two crystal structures have been reported that involve ligands of the former type, both complexes of Cu^{2+}, with typical distances Cu–O ~1.90, Cu···Cu 2.87 Å [5f,12c], whereas in the many structures of complexes of **1b** and its relatives, typical distances Cu–O ~1.98, Cu···Cu 3.11 Å are found [5,12a,b].

2.3. Magnetic properties

The magnetic susceptibilities of the methanol solvates **4a–d** were measured on powdered samples between 5 and 300 K. Appropriate theoretical expressions were then fitted to the unweighted data by least-squares, minimising $\Sigma[\chi_{obs}-\chi_{calc}]^2$ by the Simplex method [18].

2.3.1. Manganese(II) complex *4a*

We assume the Heisenberg exchange Hamiltonian $-2J\mathbf{S}_1\cdot\mathbf{S}_2$, with $S=\frac{5}{2}$ and $g=2.0$ for each ion. Application of the Van Vleck equation [19] gives Eq. (1), where χ_M is the susceptibility per mole of binuclear complex and $x=J/kT$. Eq. (1) also allows for the presence

$$\chi_M=(2N_Ag^2\mu_B^2/kT)(e^{2x}+5e^{6x}+14e^{12x}+30e^{20x}+55e^{30x})$$
$$\times(1-\rho)/(1+3e^{2x}+5e^{6x}+7e^{12x}+9e^{20x}+11e^{30x})$$
$$+(2N_Ag^2\mu_B^2/3kT)(35\rho/4) \qquad (1)$$

of a fraction ρ of Mn^{2+} ions present as monomeric impurity. The best-fit values $J=-1.15$ cm^{-1} and $\rho=0.053$ were obtained, with the discrepancy index $R=0.0029$, where R is defined as $\{\Sigma[\chi_{obs}-\chi_{calc}]^2/\Sigma[\chi_{obs}]^2\}^{1/2}$. Fig. 3 shows the good agreement between the calculated and observed values of the magnetic

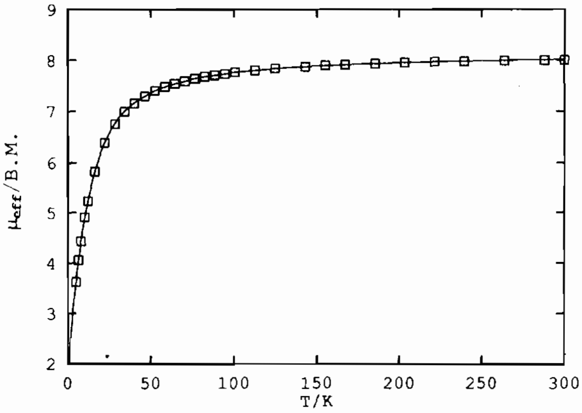

Fig. 3. Magnetic moment of $Mn_2L(NO_3)_4\cdot 2CH_3OH\cdot H_2O$ (**4a**) plotted against temperature. The calculated curve is for $g=2$, $J=-1.15$ cm^{-1}, $\rho=0.053$.

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[1] Pyramidal bridge geometry has been observed in certain phenolate-bridged complexes of other types, e.g. a binuclear copper complex containing piperazine side groups and a μ-hydroxo group [14], and a tetranuclear nickel complex of a macrocyclic ligand containing four μ-phenolato groups [15], but in these cases the pyramidal geometry is probably enforced by the ligand stereochemistry.

moment per dimer, $\mu_{\mathrm{eff}}=\sqrt{(3k/N_A\mu_0)}\sqrt{(\chi_M T)}$, in units of the Bohr magneton (BM)[2].

2.3.2. *Cobalt(II) complex **4b***

Based on the structure of **5**, we assume that the Co^{2+} ions are in approximately octahedral *cis*-N_2O_4 coordination, and consider the octahedral ground term $^4T_{1g}$ subject to the combined effects of spin–orbit coupling and the low-symmetry components of the ligand field, which we regard as roughly tetragonal. The two ions then suffer a simultaneous but weaker perturbation due to exchange.

The problem of calculating the effect of an exchange interaction between orbitally degenerate ions has been considered by several authors, and can become very complicated [6a,20]. Because our objective is to obtain an approximate measure of the strength of the interaction, for comparison with that in the Mn, Ni and Cu complexes, and because of experimental limitations (we have only powder data), we adopt the following simplified approach [6a,c,21]. Using the T–P analogy, we write the Hamiltonian in the form of Eq. (2), where

$$\begin{aligned}\mathscr{H} = &-2J\mathbf{S}_1\cdot\mathbf{S}_2-kA\lambda(\mathbf{L}_1\cdot\mathbf{S}_1+\mathbf{L}_2\cdot\mathbf{S}_2)\\ &+D(L_{z1}{}^2+L_{z2}{}^2-\tfrac{4}{3})-kA\mu_B(\mathbf{L}_1+\mathbf{L}_2)\cdot\mathbf{H}\\ &+2\mu_B(\mathbf{S}_1+\mathbf{S}_2)\cdot\mathbf{H} \qquad (2)\end{aligned}$$

the second term represents spin–orbit coupling, the third an axial distortion, and the fourth and fifth terms are the orbital and spin contributions to the magnetic energy. In this case $L_1=L_2=1$, $S_1=S_2=\frac{3}{2}$, D is the tetragonal splitting of the T_{1g} terms, k is an orbital reduction factor to allow for covalency, and A $(1\leqslant A\leqslant\frac{3}{2})$ takes account of spin–orbit mixing between the $^4T_{1g}(F)$ and $^4T_{1g}(P)$ terms. Strictly speaking, J is now not a single constant but an orbital operator, giving rise to anisotropic exchange. We regard it here as a constant, so as to derive an overall value which will make a fairer comparison possible than if orbital effects had been neglected altogether, but we recognise the restricted significance that can be attached to this single value.

The average susceptibility was calculated [22] at each temperature by diagonalisation of the matrix of Eq. (2)[3], and was fitted to the data with J, kA, λ, D, and a fraction ρ of paramagnetic impurity as fitting parameters. (The impurity was assumed to obey the Curie law with a moment of $5.0\mu_B$.) A correction for temperature-independent paramagnetism of 0.0002 cm^3 mol^{-1} Co^{2+} was included [6a]. Reasonable fits were obtained with J in the range -5.0 ± 0.3 cm^{-1}, $D\sim400\pm200$ cm^{-1}, $\lambda\sim130\pm50$ cm^{-1}, $kA\sim1.0$ and $\rho\sim0.02$, as illustrated in Fig. 4 with $R=0.034$. (This may be compared with the best fit obtained by treating Co^{2+} as a 'spin-only' ion, which gave $J=-6.4$ cm^{-1} and $g=2.44$, with $R=0.055$. The reduction in the apparent J value when orbital effects are included as above has been noted previously [6a]. The value of J is similar to that found in $[Co_2X(py)_4]^{2+}$ ($X^{2-}=$ **1b**), -4.1 cm^{-1} [5c].

2.3.3. *Nickel(II) complex **4c***

For two Ni^{2+} ions in axially distorted octahedral environments, the usual Hamiltonian is Eq. (3), where

$$\mathscr{H}=-2J\mathbf{S}_1\cdot\mathbf{S}_2+D(S_{z1}{}^2+S_{z2}{}^2-\tfrac{4}{3})+g\mu_B(\mathbf{S}_1+\mathbf{S}_2)\cdot\mathbf{H} \quad (3)$$

$S_1=S_2=1$ and D is the zero-field splitting of the $^3A_{2g}$ ground terms due to tetragonal distortion and second-order spin–orbit coupling. Fitting by the matrix method [22] indicated $|D|<1$ cm^{-1}, and this parameter was subsequently omitted. The best fit then gave $J=-15.5$ cm^{-1}, $g=2.16$, $\chi_{\mathrm{tip}}=0.00042$ cm^3 mol^{-1} and $\rho=0.022$, with $R=0.0072$, Fig. 5. The t.i.p. contribution is similar to that expected in nickel complexes [23]. The value of J may be compared with the values found in $[Ni_2X(py)_4]^{2+}$ ($X^{2-}=$ **1b**), -23 [5c]; $[Ni_2X'(H_2O)_4]^{2+}$, -17; $[Ni_2X'(H_2O)_2(NCS)_2]$, -21; and $[Ni_2X'(MeOH)_2(ClO_4)_2]$, -29.5 cm^{-1} [13b], where X'^{2-} is **1b** with the CH:N groups reduced to CH_2NH.

2.3.4. *Copper(II) complex **4d***

Calculation of the susceptibility by the matrix method from Hamiltonian (4) with $S_1=S_2=\frac{1}{2}$, and fitting to

$$\mathscr{H}=-2\mathbf{S}_1\cdot\mathbf{S}_2+g\mu_B S_z H \quad (4)$$

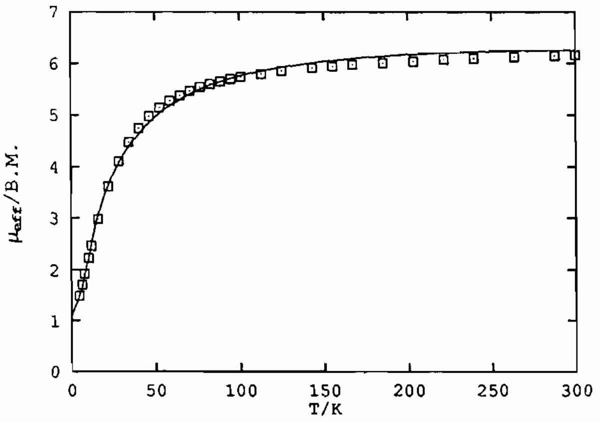

Fig. 4. Magnetic moment of $Co_2L(NO_3)_4\cdot2CH_3OH\cdot H_2O$ (**4b**) plotted against temperature. The calculated curve is for $J=-5.0$ cm^{-1}, $D=380$ cm^{-1}, $\lambda=-130$ cm^{-1}, $kA=1.0$, $\rho=0.023$.

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[2] The Bohr magneton $\mu_B=eh/4\pi m_e=9.274\times10^{-21}$ erg $gauss^{-1}$ (c.g.s. e.m.u.) $=9.274\times10^{-24}$ J T^{-1} ($\equiv$ A m^2) (SI). $\mu_{\mathrm{eff}}/\mu_B=2.828[(\chi_M/cm^3\ mol^{-1})(T/K)]^{1/2}$ (c.g.s.) $=797.6[(\chi_M/m^3\ mol^{-1})(T/K)]^{1/2}$ (SI).

[3] We use two programs: a specialised one to calculate the parameter-free matrices of the five terms in (2) in the 144-fold basis of uncoupled L, M_L, S, M_S states; and a general-purpose one to diagonalise the complete matrix with the field alternately parallel and perpendicular to the z axis, calculate the susceptibility at each temperature from the eigenvalues and eigenvectors, and perform Simplex optimisation of the parameters.

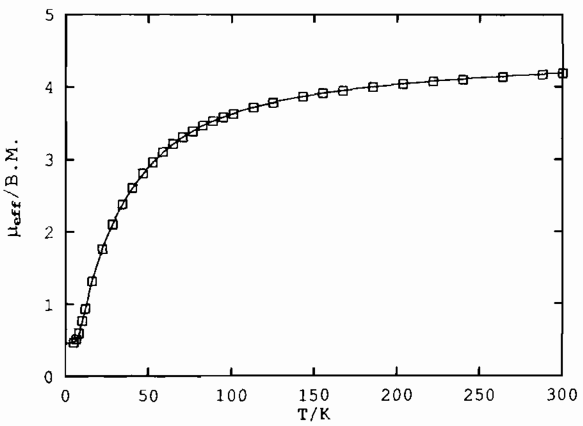

Fig. 5. Magnetic moment of $Ni_2L(NO_3)_4 \cdot 2CH_3OH \cdot \frac{1}{2}H_2O$ (**4c**) plotted against temperature. The calculated curve is for $g=2.16$, $J=-15.5$ cm^{-1}, $\rho=0.022$.

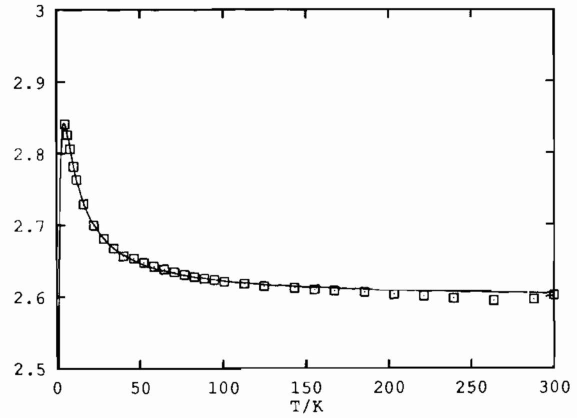

Fig. 6. Magnetic moment of $Cu_2L(NO_3)_4 \cdot 2CH_3OH \cdot H_2O$ (**4d**) plotted against temperature. The calculated curve is for $g=2.119$, $J=+3.3$ cm^{-1}, $\theta=-0.23°$.

the data with g, J and a Weiss constant θ as parameters, gave $J=+3.3$ cm^{-1}, $g=2.119$ and $\theta=-0.23°$, with $R=0.00043$, Fig. 6. (The use of a Weiss constant, whereby T is replaced by $T-\theta$, is an approximate device to allow for inter-dimer coupling. The occurrence of such coupling, here apparently antiferromagnetic, is consistent with the spin triplet ground state implied by the positive J value.) Calculation of the susceptibility by use of the Bleaney–Bowers equation [19] (which is less accurate at the lowest temperatures) gave a similar result ($J=+3.5$ cm^{-1} with $R=0.0005$). The positive J value observed is in marked contrast to the values (ranging from -294 to -816 cm^{-1}) found in the copper complexes of **1b** and its relatives [5].

2.4. Comparison of exchange in 4a–d

The values found for the exchange parameter J are collected in Table 3, where it can be seen that in the Mn, Co and Ni compounds the interaction is of antiferromagnetic sign and steadily increasing magnitude, whereas the Cu compound shows weakly ferromagnetic exchange. We now ask whether these observations can be explained on the basis of the structure found in **5**.

Table 3
Exchange parameters in the complexes $M_2L(NO_3)_4 \cdot 2CH_3OH \cdot xH_2O$ (**4a–d**)

M	n [a]	J (cm^{-1})	n^2J (cm^{-1})
Mn	5	−1.15(2)	−29(1)
Co	3	−5.0(3)	−45(3)
Ni	2	−15.5(1)	−62(1)
Cu	1	+3.3(3)	+3.3(3)

[a] n is number of unpaired electrons on M^{2+}.

To answer this question we assume that each spin-containing orbital ϕ_i on ion A interacts with a spin-containing orbital ϕ_j on ion B to give a contribution $-2J(\phi_i\phi_j)\mathbf{s}_i\cdot\mathbf{s}_j$. Provided that the ground electronic terms of both A and B are orbitally non-degenerate, the exchange Hamiltonian then has the form (5), where

$$\mathscr{H}_{ex}=-2J\mathbf{S}_A\cdot\mathbf{S}_B \qquad (5)$$

with

$$J=(1/n_An_B)\Sigma_{ij}J(\phi_i\phi_j) \qquad (6)$$

$\mathbf{S}_A=\Sigma\mathbf{s}_i$, $\mathbf{S}_B=\Sigma\mathbf{s}_j$, and n_A, n_B are the respective numbers of unpaired electrons on A and B. In our complexes $n_A=n_B=n$. Our experimental measurements provide the values of J, but the $J(\phi_i\phi_j)$ are the fundamental quantities of interest to us, and it is therefore the values of n^2J, also listed in Table 3, that we have to consider.

Theoretical justifications of Eqs. (5) and (6) have been given by several authors [6c,20,24]. We shall refer to the formalism developed by Kahn and co-workers [25], in which the orbitals ϕ_i, ϕ_j ('magnetic orbitals') are d orbitals of their respective ions modified by mixing with ligand orbitals up to and including the bridging ligand atoms. Each $J(\phi_i\phi_j)$, and hence also J, is the sum of two contributions: $J=J_{AF}+J_F$, where J_{AF} is negative (antiferromagnetic) and J_F positive (ferromagnetic). Both are determined largely by the overlap density $\phi_i\phi_j$ in the bridging region. J_{AF} is approximately proportional to the square of the overlap integral, and when present it is usually large compared with J_F, making $J(\phi_i\phi_j)$ negative. However, if ϕ_i, ϕ_j are orthogonal, J_{AF} (but not J_F) vanishes, and the resultant $J(\phi_i\phi_j)$ is then positive.

In Fig. 7 we show an idealised picture of the local metal environment, based on the structure of **5**. To simplify the model we 'average' the ligands along each O–M–N axis, giving overall idealised symmetry C_{2h}, each metal ion being in an approximately tetragonal ligand field, with its z axis directed towards one bridging O atom. Note that, because of the 'stepped' structure of the complex, the z axes of the ions are not coincident.

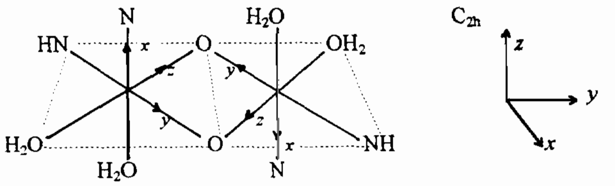

Fig. 7. The local metal ion environment in **5**, showing the coordinate axes of the two metal ions in idealised tetragonal geometry. By averaging the ligand fields along the O–M–N axes, the true symmetry C_i becomes C_{2h}, with the two-fold axis parallel to the z axis shown on the right.

The ligand field will be strongest in the xy plane, and the sequence of orbital energies is assumed to be $x^2-y^2>z^2>xy>xz,yz$. We shall designate the respective magnetic orbitals as θ, ϵ, ζ, η, ξ. In the C_{2h} symmetry of the binuclear system, θ, ϵ and ξ give rise to functions transforming as A_g and B_u, while η and ζ give functions belonging to the A_u and B_g irreducible representations. Functions in the first group are necessarily orthogonal to those in the second group.

Taking first the copper complex **4d**, we expect the single unpaired electron to be localised in the ϵ magnetic orbital of each ion. Hence we have

$$n^2J_{\mathrm{Cu}}=[J(\epsilon\epsilon)]_{\mathrm{Cu}}=[J_{\mathrm{AF}}(\epsilon\epsilon)+J_{\mathrm{F}}(\epsilon\epsilon)]_{\mathrm{Cu}}$$

with $n^2=1$. It is clear from Fig. 8 that the overlap density will give an overlap integral that is essentially zero. Hence $|J_{\mathrm{AF}}(\epsilon\epsilon)|<J_{\mathrm{F}}(\epsilon\epsilon)$, and the net interaction will be weakly ferromagnetic, as observed. Note that we have not invoked the Cu–O–Cu bond angle (which in any case we do not know). In hydroxo-bridged complexes of copper, where the bridging O atoms are in the same plane as the spin-containing orbitals of both Cu^{2+} ions, this angle is crucial in determining the sign and magnitude of J [26]. However, the 'stepped' structure of **5**, where each bridging O atom lies in the xy plane of one ion and on the z axis of the other, allows us to predict a small positive J in our copper complex regardless of the precise bridging angle.

It should be noted that in certain phenoxo-bridged binuclear copper complexes there is evidence that pyramidal geometry at the bridging oxygen atom leads to a reduction in the antiferromagnetic interaction or to weak ferromagnetism [14,27]. In the present case this feature does not play a part, so we are unable to confirm or refute the effect of bridge geometry on the copper–copper interaction. However, the J values for the Ni, Co and Mn complexes do not indicate a significant effect.

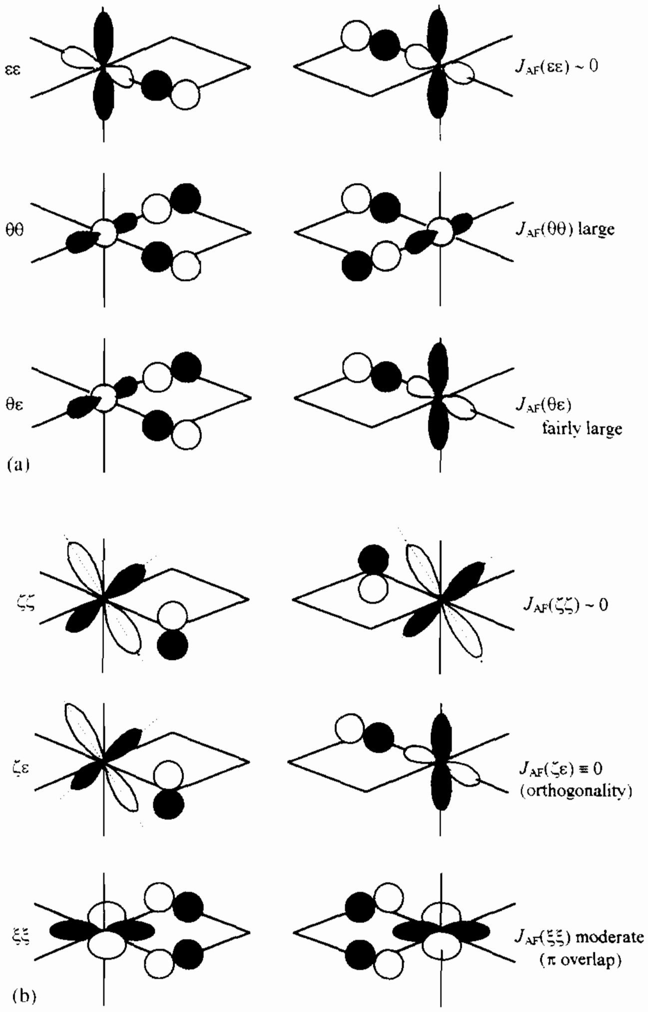

Fig. 8. The diagrams represent the magnetic orbitals associated with the left- and right-hand metal ions for some possible combinations of spin-containing orbitals. The integral of the overlap density in the bridging region is taken as an approximate measure of J_{AF} (cf. Ref. [25]).

In the nickel complex **4c**, the unpaired electrons will be in the θ and ϵ magnetic orbitals and we can write [6a,b]

$$n^2J_{\mathrm{Ni}}=[J(\theta\theta)+2J(\theta\epsilon)+J(\epsilon\epsilon)]_{\mathrm{Ni}}$$

with $n^2=4$. $J(\epsilon\epsilon)$ will again be weakly ferromagnetic, but $J(\theta\epsilon)$ and $J(\theta\theta)$ (see Fig. 8) should both be large and negative. Hence we expect a substantial negative value for n^2J_{Ni}, as observed. By expressing the $d(z^2)$ function in the form $2^{-1/2}[d(x^2-z^2)+d(y^2-z^2)]$ and examining the corresponding overlap diagrams, we estimate that the value of $J(\theta\theta)$ will be roughly similar to that of $2J(\theta\epsilon)$ and (since $n^2J_{\mathrm{Ni}}=-62\ \mathrm{cm}^{-1}$) probably in the region of $-33\ \mathrm{cm}^{-1}$.

In the case of the cobalt complex **4b**, we have an additional unpaired electron on each ion, located mainly in the ζ magnetic orbital. From the overlaps it is clear that $J_{\mathrm{AF}}(\zeta\zeta)\sim 0$, making $J(\zeta\zeta)$ weakly ferromagnetic, like $J(\epsilon\epsilon)$. Owing to the strict orthogonality in C_{2h} symmetry, $J_{\mathrm{AF}}(\zeta\epsilon)$ and $J_{\mathrm{AF}}(\zeta\theta)$ vanish, and hence the contributions from $J(\zeta\epsilon)$ and $J(\zeta\theta)$ will also be ferromagnetic. The net effect of the extra unpaired electron will thus be to make n^2J_{Co} less antiferromagnetic than n^2J_{Ni}, in agreement with observation. Because of the approximations inherent in our treatment of the effect of orbital angular momentum, a more quantitative analysis is not justified here.

Note that part of the reduction in the exchange parameter may be due to other factors, such as slightly longer M–μ-O bonds in the Co compared to the Ni complex. It is not possible to separate these from the effect of the additional ferromagnetic pathways.

In the Mn complex the single-ion ground state is an orbital singlet with five unpaired spins, and the twenty-five $J(\phi_i\phi_j)$ enter on an equal basis into the expression for n^2J_{Mn}. From overlap density considerations we expect significant AF contributions from $J(\xi\xi)$, $J(\xi\epsilon)$, $J(\xi\theta)$ and $J(\eta\zeta)$, but since these all involve π rather than σ overlaps, they are likely to be smaller in magnitude than those from $J(\theta\theta)$ and $J(\theta\epsilon)$ (a factor of $\sim\frac{1}{5}$ has been suggested [28]). $J(\eta\eta)$, like $J(\zeta\zeta)$, will be weakly ferromagnetic, and so will $J(\xi\zeta)$, $J(\xi\eta)$, $J(\eta\theta)$ and $J(\eta\epsilon)$, since their AF parts vanish by strict orthogonality. Thus, compared with the Co complex we have seven additional antiferromagnetic contributions of modest strength and nine ferromagnetic ones. The observed reduction of n^2J from -45 (Co) to -29 (Mn) cm^{-1} suggests that the latter dominate, although again some reduction is also to be expected from slightly increased bond lengths.

3. Experimental

The hydrated metal nitrates were AR, all other materials reagent grade.

3.1. *Preparation of ligand 2a*

2,6-Dimethylpyridine-1-oxide [29] was converted to pyridine-1-oxide-2,6-dialdehyde by selenium dioxide oxidation in pyridine solution [30]. Treatment of the dialdehyde (1 mol) with 1,2-diaminoethane (1 mol) in boiling methanol and concentration of the filtered solution gave the ligand as a light brown microcrystalline solid, which was used without further purification.

3.2. *Nickel complex 4c*

The ligand **2a** (0.26 g) was added to a solution of nickel nitrate tetrahydrate (0.6 g) in methanol (30 ml) and the mixture refluxed for 40 min. The green precipitate was filtered off, washed with methanol, and dried overnight in air. Yield 0.4 g (65%). *Anal.* Found: C, 29.1; H, 3.80; N, 17.2; Ni, 14.1. Calc. for $C_{18}H_{22}N_6O_4Ni_2(NO_3)_4 \cdot 2CH_3OH \cdot 0.5H_2O$: C, 29.4; H, 3.79; N, 17.0; Ni, 14.2%.

3.3. *Mn, Co and Cu complexes 4a,b,d*

These were obtained from the appropriate hydrated metal nitrates by the method used for the nickel complex.

4a: yellow powder. *Anal.* Found: C, 29.2; H, 3.90; N, 16.9. Calc. for $C_{18}H_{22}N_6O_4Mn_2(NO_3)_4 \cdot 2CH_3OH \cdot H_2O$: C, 29.1; H, 3.90; N, 17.0%.

4b: orange–red powder. *Anal.* Found: C, 28.5; H, 3.78; N, 16.8. Calc. for $C_{18}H_{22}N_6O_4Co_2(NO_3)_4 \cdot 2CH_3OH \cdot H_2O$: C, 28.8; H, 3.87; N, 16.8%.

4c: blue–green powder. *Anal.* Found: C, 28.6; H, 3.68; N, 16.8. Calc. for $C_{18}H_{22}N_6O_4Cu_2(NO_3)_4 \cdot 2CH_3OH \cdot H_2O$: C, 28.5; H, 3.82; N, 16.6%.

3.4. *Nickel complex 5*

A solution of **4b** (0.11 g) in water (2 ml) and methanol (5 ml) was allowed to evaporate slowly in air for 100 days. The dark green crystals were washed with a little methanol and dried in air. *Anal.* Found: C, 24.5; H, 3.99; N, 16.1. Calc. for $[C_{18}H_{22}N_6O_4Ni_2(H_2O)_4](NO_3)_4 \cdot 2H_2O$: C, 25.1; H, 3.99; N, 16.3%.

3.5. *Crystal structure analysis of 5*

$C_{18}H_{34}N_{10}O_{22}Ni_2$, $M_r = 860.0$. Dark green oblique prisms from methanol/water. Monoclinic, space group $P2_1/n$ (No. 14), $a = 11.831(8)$, $b = 12.168(8)$, $c = 12.329(7)$ Å, $V = 1618(4)$ Å^3, $Z = 2$, $\rho_{\mathrm{calc}} = 1.675$ g cm^{-3}, $F(000) = 888$, $\mu(\mathrm{Mo\ K}\alpha) = 12.7$ cm^{-1}. A crystal fragment $\sim 0.4 \times 0.3 \times 0.25$ mm was mounted on a Rigaku AFC6S diffractometer, and unit-cell determination and data collection were carried out with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Absorption corrections were not applied (max./min. absorption coefficients 1.446, 0.797). Of 3172 reflections, 3000 were unique and 2122 classified as observed ($I \geqslant 3\sigma(I)$). The structure was solved from the Patterson function and successive Fourier difference functions on all data, and refined by full-matrix least-squares, fitting 235 variables. Refinement converged to $R = 0.0355$, $R_w = 0.0350$ (maximum shift/error in last cycle 0.030). Most H atoms were found after anisotropic refinement of all non-H atoms, the remainder being inserted in calculated positions.

3.6. *Magnetic measurements*

Finely powdered specimens were sealed in gelatin capsules, and the susceptibility measured in a field of 1 T from 5 to 300 K with a SQUID magnetometer system (Quantum Design Inc., San Diego, CA, USA; model MPMS). The data were corrected for sample diamagnetism by use of Pascal constants and for diamagnetism of the capsule.

4. Conclusions

The binuclear nickel(II) complex **5**, prepared by condensing pyridine-1-oxide-2,6-dialdehyde with 1,2-

diaminoethane and treating the resulting Schiff base with the metal nitrate, contains a new macrocyclic ligand **3** in which the two *N*-oxide oxygen atoms act as bridging groups. The expected CH:N.$(CH_2)_2$.N:CH linking groups have been partially hydrolysed to CH(OH).NH.$(CH_2)_2$.N:CH, and in consequence the complex as a whole has a non-planar structure with pyramidal bonding at the bridging oxygen atoms and distorted octahedral coordination. The magnetic properties of binuclear manganese(II), cobalt(II), nickel(II) and copper(II) complexes of **3** have been investigated. Weak ferromagnetic coupling between the copper ions, and the trend in the antiferromagnetic coupling in the other complexes, are accounted for on the basis of the non-planar structure of **5** and the orbital pathways available.

5. Supplementary material

Full details of atomic fractional coordinates, thermal vibration parameters, interatomic distances and angles, least-squares planes and interplanar angles, and a list of observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Centre.

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