Reactions Between Dinuclear Cu^{II}–Ni^{II} Complexes and the Nitrito Ligand: A New One-Dimensional Complex $[Cu(oxpn)Ni(\mu\text{-}NO_2)(trimen)]_n(ClO_4)_n$ with Nitrite Acting as a Tridentate Bridging Ligand and Ferro- and Antiferromagnetic Alternation

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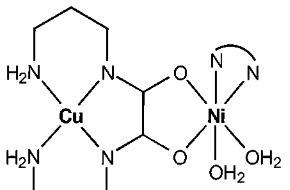
The reaction of $NiX_2 \cdot 6\,H_2O$ (X = NO_3^-, ClO_4^-), bidentate amine, [Cu(oxpn)] [oxpn = *N,N′*-bis(3-aminopropyl)oxamide] and sodium nitrite in ethanolic solution, leads to the formation of new Cu^{2+}–Ni^{2+} complexes of general formula $[Cu(oxpn)Ni(NO_2)(aa)]_n(X)_n$ [**1**, X = ClO_4^-, aa = *N,N,N′*-trimethylethylenediamine (trimen); **2**, X = ClO_4^-, aa = *N,N,N′N′*-tetramethylethylenediamine (tmen); **3**, X = ClO_4^-, aa = *N,N*-dimethyl-*N′*-ethylethylenediamine (dmeten); **4**, X = PF_6^-, aa = trimen; **5**, X = PF_6^-, aa = dmeten]. The structure of complex **1** consists of $[Cu(oxpn)Ni(trimen)]^{2+}$ units linked by a nitrite group acting as a tridentate ligand, giving a one-dimensional system separated by ClO_4^- anions. In contrast, the structure of complex **2** consists of isolated $[Cu(oxpn)Ni(NO_2)(tmen)]^+$ dinuclear units and uncoordinated ClO_4^- anions. The nitrite group acts as a bidentate ligand. Variable-temperature magnetic susceptibility studies were performed on **1–5**. The J value through the oxamidato bridge is close to –110 cm^{-1} in all five cases. For complex **1**, considered as a chain, a simulation of the $\chi_M T$ vs T was performed with the CLUMAG program. These calculations revealed the influence of the magnetic interactions between the dinuclear entities through the nitrito bridging ligand, on the susceptibility curves at low temperatures.

Introduction

In one-dimensional supramolecular self-assembly processes, we have found that very few complexes starting from polynuclear building blocks have been reported to date. McAuley et al.[1] reported the synthesis of a chloro-bridged polymeric copper(II) complex. Ribas et al., using (S,Se)CN⁻ bridging ligands, reported a one-dimensional system with Cu_3 entities,[2] and tetranuclear systems starting from Cu^{2+}–Ni^{2+} entities.[3] A one-dimensional structure has been reported from the self-assembly reaction between $[Fe(CN)_6]^{3-}$ and a Mn^{3+} Schiff-base derivative, in which the 1-D architecture is due to hydrogen bonds between trinuclear Mn^{3+}–Fe^{3+}–Mn^{3+} entities.[4] With [Cu(oxpn)], where oxpn is the dianion of *N,N′*-bis(3-aminopropyl)oxamide, the magnetic coupling in Cu–Cu, Cu–Ni or Cu–Mn dinuclear entities is strongly antiferromagnetic, owing to the broad overlap between the magnetic orbitals of the two metal ions through the corresponding molecular orbital of the oxamidato bridge.[5–10] Thus, we started with the dinuclear species $[Cu(oxpn)Ni(H_2O)_2(diamine)]^{2+}$ (Scheme 1) in an attempt to link these molecules ferro- or antiferromagnetically in order to study the spin topology of the final system.



Scheme 1. Structural formula of $[Cu(oxpn)Ni(H_2O)_2(aa)]^{2+}$

The ligand chosen for this was the nitrite group because of the number of different ways in which it can coordinate to a metal centre.[11] The factors influencing the type of nitrite coordination adopted are often delicately balanced. As a monodentate ligand it can bond through either nitrogen or oxygen, while as a bidentate ligand it can chelate or bridge either through nitrogen and oxygen or through oxygen only.[12] Very few examples of tridentate behaviour are known. This coordination mode may be accomplished in two ways. In the first case,[13] the NO_2^- ion is chelated to one metal through the two oxygens and bridged to a second metal ion through the nitrogen atom (Scheme 2a). In the second case,[14] the two metal ions are bridged through a

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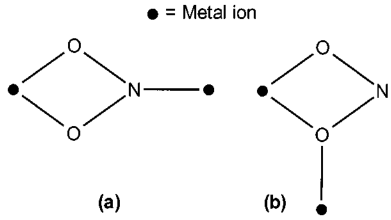
single oxygen atom while the second oxygen chelates to one of the metal ions (Scheme 2b).



Scheme 2. Trideutate coordination modes for the nitrite ion

Few studies have examined the magnetic exchange mediating properties of the bridging nitrite. Two polymeric Ni^{2+} complexes involving a two atom O,N-bridging mode show a moderate antiferromagnetic interaction ($J \approx -60$ cm^{-1}).[15] A Ni–Mn–Ni trinuclear complex involving the same coordination mode but also with azido bridging ligand has been reported.[12b] An interaction of the same sign and order of magnitude characterises a dinuclear Ni^{2+} complex with a combination of chelation and bridging through a single oxygen atom.[14] A weak ferromagnetic interaction ($J = 8$ cm^{-1}) is found in a dinuclear Cu^{2+} complex with a single O atom bridging mode[16] and a very weak one ($J = 1.33$ cm^{-1}) is found in a Mn–Ni bimetallic chain[13b] with nitro coordination at the Ni^{2+} centre and a bidentate nitrito coordination at Mn^{2+}. We report here five compounds of a new family of heterobimetallic polynuclear compounds obtained from Cu(oxpn)–Ni(diamine)–NO_2 with the counteranion ClO_4^- or PF_6^- (diamine = tmen, trimen, dmeten). The crystal structures of $[Cu(oxpn)Ni(\mu\text{-}NO_2)(trimen)]_n(ClO_4)_n$ (**1**), and $[Cu(oxpn)Ni(NO_2)(tmen)]ClO_4$ (**2**) are described. The crystal structure of complex **1** is found to be a chain of dimeric [Cu(oxpn)Ni(trimen)] units linked by the nitrite group acting as a tridentate ligand. The crystal structure of complex **2** is found to be dinuclear with isolated $[Cu(oxpn)Ni(NO_2)(tmen)]^+$ ions. We also report the magnetic properties of the five compounds. The magnetic behaviour of complexes **1** and **2** is markedly different at low temperatures; the other three complexes have an intermediate magnetic behaviour. For all complexes, the magnetic interactions were studied assuming only the strong antiferromagnetic coupling within the dinuclear Cu–Ni entity. Complex **1** was also studied using the ITO method, which reduces the size of the matrices.

Results and Discussion

Crystal Structures

The X-ray crystal structure of **1** consists of dimeric $[Cu(oxpn)Ni(trimen)]^{2+}$ units linked by the nitrite group acting as a tridentate ligand giving a one-dimensional system, separated by ClO_4^- anions. This tridentate nitrite coordination between Cu^{2+} and Ni^{2+}, which has not been reported previously, is a combination of chelation through the two oxygen atoms and bridging through a single oxygen atom (Scheme 2b). Selected bond lengths and angles are listed in Table 1 and the molecular structure and atom labelling is shown in Figure 1. The molecular structure of **2** consists of isolated $[Cu(oxpn)Ni(NO_2)(tmen)]^+$ dinuclear units and uncoordinated ClO_4^- anions. Selected bond lengths and angles are listed in Table 1 and the molecular structure and atom labelling is shown in Figure 2.

Table 1. Selected bond lengths [Å] and angles [deg] for $[Cu(oxpn)Ni(\mu\text{-}NO_2)(trimen)]_n(ClO_4)_n$ (**1**) and $[Cu(oxpn)Ni(NO_2)(tmen)]ClO_4$ (**2**)

Complex **1**			
Ni–O(1)	2.030(7)	Cu–N(3)	1.976(10)
Ni–O(2)	2.050(8)	Cu–N(2)	1.976(10)
Ni–N(6)	2.066(10)	Cu–N(1)	2.016(11)
Ni–O(4)	2.110(11)	Cu–N(4)	2.016(11)
Ni–N(5)	2.119(19)	O(4)–N(7)	1.250(2)
Ni–O(3)	2.152(8)	O(3)–N(7)	1.260(2)
Cu–O(3)	2.609(8)		
O(1)–Ni–O(2)	82.2(3)	N(6)–Ni–O(3)	91.3(4)
O(1)–Ni–N(6)	178.3(4)	O(4)–Ni–O(3)	57.8(4)
O(2)–Ni–N(6)	96.1(4)	N(5)–Ni–O(3)	160.9(4)
O(1)–Ni–O(4)	89.4(3)	N(3)–Cu–N(2)	82.4(4)
O(2)–Ni–O(4)	156.6(4)	N(3)–Cu–N(1)	176.6(5)
N(6)–Ni–O(4)	92.2(4)	N(2)–Cu–N(1)	94.3(4)
O(1)–Ni–N(5)	95.4(3)	N(3)–Cu–N(4)	94.0(5)
O(2)–Ni–N(5)	98.9(4)	N(2)–Cu. –N(4)	175.9(5)
N(6)–Ni–N(5)	84.7(4)	N(1)–Cu–N(4)	89.4(5)
O(4)–Ni–N(5)	103.6(4)	N(7)–O(3)–Ni	94.8(7)
O(1)–Ni–O(3)	89.1(4)	N(7)–O(4)–Ni	97.0(8)
O(2)–Ni–O(3)	100.1(4)	O(3)–N(7)–O(4)	110.4(4)
Cu–O(3)–Ni	58.67(6)		
Complex **2**			
Ni–O(1)	2.124(3)	Cu–N(6)	1.972(4)
Ni–O(2)	2.153(4)	Cu–N(7)	2.020(5)
Ni–O(3)	2.067(3)	Cu–N(8)	2.006(4)
Ni–O(4)	2.008(3)	Cu–N(9)	1.958(4)
Ni–N(1)	2.102(4)	O(1)–N(5)	1.260(6)
Ni–N(2)	2.119(4)	O(2)–N(5)	1.240(6)
O(4)–Ni–O(3)	82.36(11)	N(1)–Ni–O(2)	158.9(2)
O(4)–Ni–N(1)	99.7(2)	N(2)–Ni–O(2)	91.85(14)
O(3)–Ni–N(1)	92.71(14)	O(1)–Ni–O(2)	58.39(14)
O(4)–Ni–N(2)	89.59(12)	N(9)–Cu–N(6)	83.98(14)
O(3)–Ni–N(2)	171.32(12)	N(9)–Cu–N(8)	93.2(2)
N(1)–Ni–N(2)	85.4(2)	N(6)–Cu–N(8)	175.1(2)
O(4)–Ni–O(1)	158.91(14)	N(9)–Cu–N(7)	177.2(2)
O(3)–Ni–O(1)	92.50(12)	N(6)–Cu–N(7)	94.1(2)
N(1)–Ni–O(1)	101.0(2)	N(8)–Cu–N(7)	88.9(2)
N(2)–Ni–O(1)	96.18(13)	N(5)–O(1)–Ni	94.6(3)
O(4)–Ni–O(2)	101.28(14)	N(5)–O(2)–Ni	93.8(3)
O(3)–Ni–O(2)	92.93(14)	O(2)–N(5)–O(1)	113.2(4)

For both complexes, the Ni atoms are in a distorted octahedral environment. The four positions coplanar to the oxamidato bridge are occupied by the two oxygen atoms of this ligand [Ni–O = 2.030, 2.050 Å (**1**) and 2.008, 2.067 Å (**2**)], one nitrogen of the bidentate amine [Ni–N = 2.066 Å (**1**) and 2.119 Å (**2**)] and one oxygen of the nitrite ligand [Ni–O = 2.110 Å (**1**) and 2.124 Å (**2**)]. The other oxygen of the nitrite ligand occupies one of the two remaining positions [Ni–O = 2.152 Å (**1**) and 2.153 Å (**2**)] and the other nitrogen atom of the bidentate amine [Ni–N = 2.119 Å (**1**) and 2.102 Å (**2**)] occupies the other. The coordination polyhedron of Cu^{2+} is different for the two complexes. For complex **1** it can be considered as a square pyramid with apical elongation (4 + 1), the four nitrogen atoms of the oxpn organic ligand are placed in the basal position and the Cu–N

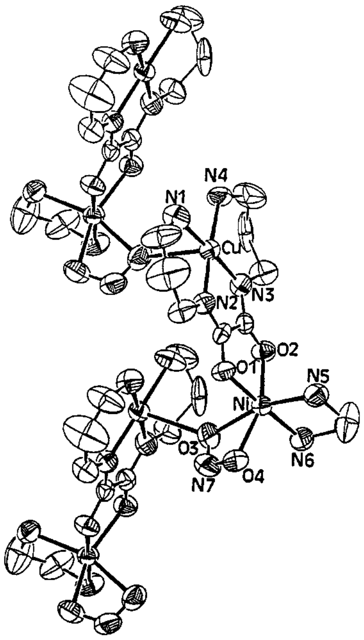


Figure 1. Drawing of the chain part of [Cu(oxpn)Ni(μ-NO_2)(trimen)]$_n$(ClO_4)$_n$ (**1**) with atom labelling scheme; methyl groups have been omitted for clarity

distances are close to 2.0 Å; the coordination is completed by one oxygen of the nitrite bridge (Cu–O = 2.609 Å). For complex **2** the copper atom is coordinated to the four nitrogen atoms of the oxpn organic ligand in a distorted square-planar geometry; the Cu–N distances are close to 2.0 Å. The Cu–Ni distances through the oxamidato bridge are 5.303 Å for complex **1** and 5.293 Å for **2**. The Cu–Ni separation within the dinuclear entities is 4.415 Å for **1** and 6.426 Å for **2**. Schematic representations of the packing for **1** and **2** are given in Figure 3 and Figure 4, respectively.

Magnetic Behaviour

Variable temperature (2–300 K) magnetic susceptibility data were collected for microcrystalline samples of compounds **1–5**. From room temperature down to ca. 25 K the $\chi_M T$ vs T plots correspond to the classical behaviour for an isolated Cu–Ni entity coupled antiferromagnetically. From ca. 25 K to 2 K we found two different behaviours: complex **1** shows a clear decrease in $\chi_M T$ from 20 K (0.46 cm^3 mol^{-1} K) to 2 K (0.40 cm^3 mol^{-1} K) and complex **2** shows the typical plateau for a dinuclear Cu–Ni complex, with no decrease in $\chi_M T$ in this zone (Figure 5), while complexes **3**, **4** and **5** show an intermediate behaviour.

The first fit was made from 300 K to ca. 20 K to study only the interaction within each Cu–Ni dinuclear moiety. The spin Hamiltonian that describes the isotropic magnetic exchange interaction in a Cu–Ni dinuclear complex is $H = -JS_{Cu}S_{Ni}$. There are two spin states, $S = 1/2$ and $3/2$. Assuming antiferromagnetic coupling, the ground state is $S = 1/2$ ($E = 0$) and the low-lying excited state is $S = 3/2$ ($E = -3J/2$). The g values for each state are related to those of the ions: $g_{3/2} = (1/3g_{Cu} + 2/3g_{Ni})$ and $g_{1/2} = (-1/3g_{Cu} + 4/3g_{Ni})$.[17] By substituting these values in the Van Vleck equation, a typical expression of the molar susceptibility can be deduced. The experimental and theoretical curves of χ_{MT} for complexes **1** and **2** are shown in Figure 5. The J and g values for the five new complexes are listed in Table 2. The J values for the five complexes (close to –110 cm^{-1}) agree with those reported in the literature for the Cu–Ni heterodinuclear complexes with the oxpn bridge.[7]

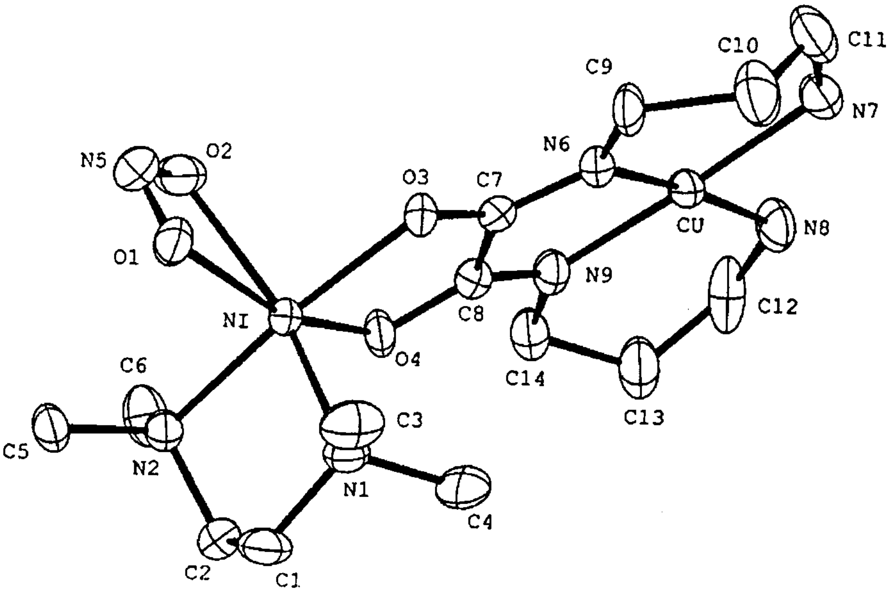


Figure 2. Drawing of the [Cu(oxpn)Ni(NO_2)(tmen)]ClO_4 (**2**) with atom labelling scheme; methyl groups have been omitted for clarity

Study of the Exchange of the Whole Chain for Complex 1

As can be seen from the crystal structure, the chain is formed by dinuclear entities linked by the bridging NO_2^- ligand (Figure 1). Such a ligand can transmit an additional interaction between the Ni–Cu entity causing two different

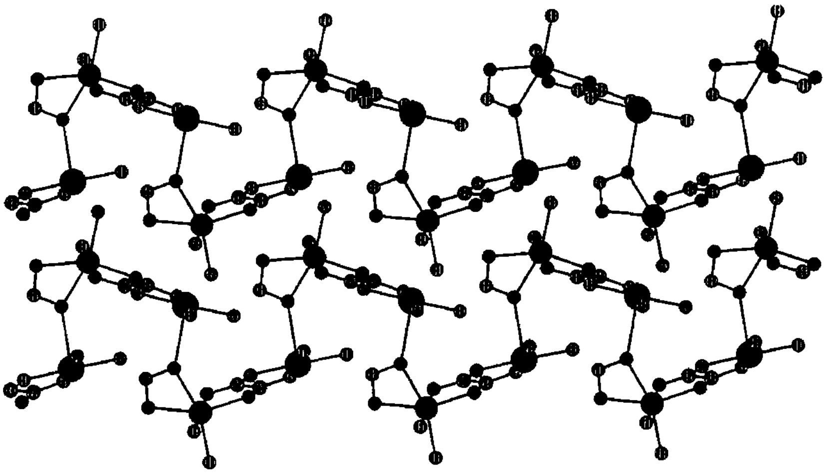


Figure 3. Schematic representation of the packing of $[Cu(oxpn)Ni(\mu\text{-}NO_2)(trimen)]_n(ClO_4)_n$ (**1**)

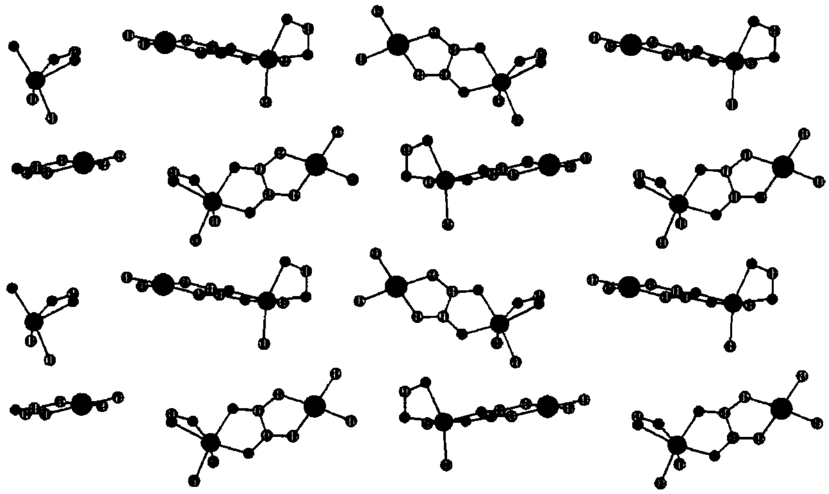


Figure 4. Schematic representation of the packing of $[Cu(oxpn)Ni(NO_2)(tmen)]ClO_4$ (**2**)

forms of the ground state at low temperature. These two forms are shown in Figure 6. If the magnetic interactions between these two entities are weakly ferromagnetic, the resulting total spin value will tend to zero at low temperatures, so the $\chi_M T$ curve would decrease and also tend to zero at these temperatures. In contrast, if the coupling were weakly antiferromagnetic $\chi_M T$ would tend to infinity at low temperatures.

In order to compare the theoretical magnetic behaviour for these extreme cases, a simulation of $\chi_M T$ vs. T for a ring of twelve atoms with alternate $S = 1$ and $S = 1/2$ spins was performed with the CLUMAG program.[18] The J_1 (coupling through the oxamidato bridge) value was fixed at –106 cm^{-1} and g was set at 2.25. The value of J_2 (coupling through the nitrite bridging ligand) was simulated between –20 and 20 cm^{-1}. As expected, with these small J_2 values the variation of $\chi_M T$ vs. T is observed only at low temperatures. The theoretical $\chi_M T$ vs. T curves are shown in Figure 7. When the J_2 coupling is antiferromagnetic $\chi_M T$ increases with decreasing temperature, tending to the six electrons value; when the J_2 coupling is ferromagnetic, $\chi_M T$ decreases with decreasing temperature, tending to zero.

From the magnetic point of view, all these aspects indicate that in this new 1-D complex the antiferromagnetic coupling through the oxamidato bridge is dominant. The coupling through the nitrito bridge is small but positive (J_2 = 1.1 cm^{-1} in complex **1** and is lower in the other complexes). A schematic representation of the orthogonality of the magnetic orbitals centred on the metal ions is shown in Figure 8.

The EPR spectra of the five complexes show a single band centred at $g = 2.24$. This band is sharp at low temperature (4 K) and becomes broader at higher temperature (77 and 298 K). This can be assigned to a transition between $|1/2,-1/2\rangle$, $|1/2,1/2\rangle$ of the $S = 1/2$ ground state of the dinuclear entity.

Experimental Section

Syntheses. – Starting Materials: Nickel(II) perchlorate, nickel(II) nitrate, sodium nitrite, ammonium hexafluorophosphate, *N,N,N',N'*-tetramethylethylenediamine (tmen), *N,N,N'*-trimethylethylenediamine (trimen), and *N,N*-dimethyl-*N'*-ethylethylenediam-

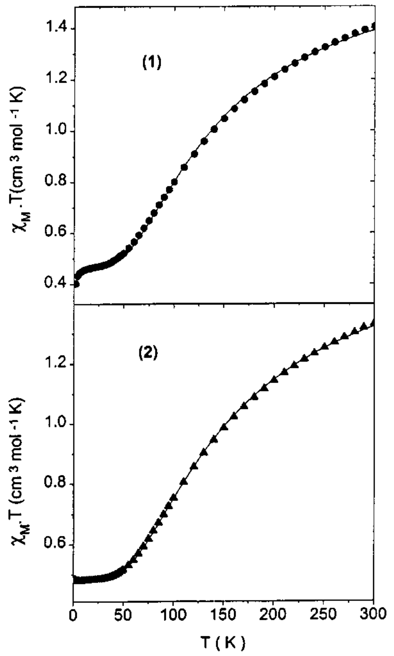


Figure 5. Plot of $\chi_M T$ vs temperature for $[Cu(oxpn)Ni(\mu\text{-}NO_2)(trimen)]_n(ClO_4)_n$ (**1**) and $[Cu(oxpn)Ni(NO_2)(tmen)]ClO_4$ (**2**); solid lines result from a fit of the data to the appropriate theoretical equation for a [Cu–Ni] complex

Table 2. Best-fit J and g parameters for **1–5** from 300–20 K of the $\chi_M T$ curves

Compound	J (cm^{-1})	g_{Cu}	g_{Ni}	R[a]
1	–106	2.25	2.25	$5\cdot10^{-5}$
2	–113	2.09	2.23	$2\cdot10^{-5}$
3	–108	2.04	2.26	$1\cdot10^{-5}$
4	–113	2.11	2.28	$1\cdot10^{-5}$
5	–111	2.14	2.31	$2\cdot10^{-5}$

[a] $R = \Sigma_i(\chi_{Mcal}T - \chi_{Mobs}T)^2/\Sigma_i(\chi_{Mobs}T)^2$.

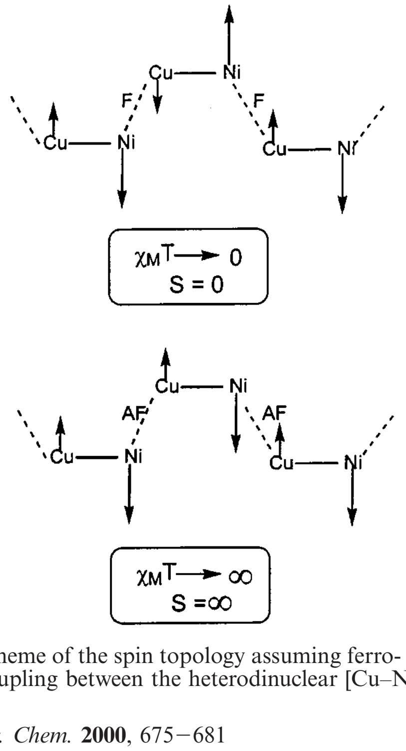


Figure 6. Scheme of the spin topology assuming ferro- or antiferromagnetic coupling between the heterodinuclear [Cu–Ni] entities

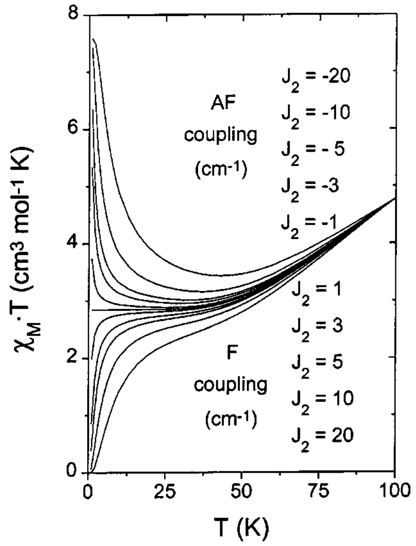


Figure 7. Theoretical curves obtained by the CLUMAG program for different J_2 values; in all cases J_1 and g were maintained constant and equal to the values obtained by fitting the complex **1** as a dinuclear entity: J_1 = –106 cm^{-1} and g = 2.25

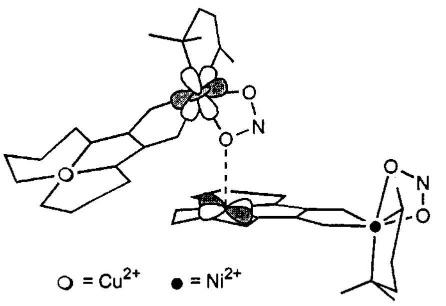


Figure 8. Schematic representation of the orthogonality of the magnetic orbitals centred on the metal ions

ine (dmeten) were purchased from Aldrich and used without further purification. [Cu(oxpn)], where oxpn is the dianion of *N,N'*-bis(3-aminopropyl)oxamide, was synthesised as previously described.[19] Ethanol was distilled before use.

Caution: *Although no incidents were recorded in this study, perchlorate salts containing organic ligands are potentially explosive. They should be prepared in small quantities and handled with extreme care.*

***catena*-$[Cu(oxpn)Ni(\mu\text{-}NO_2)(trimen)]ClO_4$ (1):** $NaNO_2$ (2.73 mmol) was added to an ethanolic solution (30 mL) of $[Cu(oxpn)Ni(H_2O)_2(trimen)](ClO_4)_2$ (2.73 mmol), prepared in situ by mixing [Cu(oxpn)] (2.73 mmol), $Ni(ClO_4)_2 \cdot x\,H_2O$ (2.73 mmol) and trimen (2.73 mmol), with constant stirring. The resulting blue solution was left to evaporate slowly at room temperature. Blue monocrystals suitable for an X-ray determination were collected after one week (yield ca. 70%). – $C_{13}H_{30}ClCuN_7NiO_8$ (570.14): calcd. C 27.38, H 5.30, N 17.20; found C 27.4, H 5.3, N 17.1.

$[Cu(oxpn)Ni(NO_2)(tmen)](ClO_4)$ (2): This complex was prepared in the same way as **1** but with *N,N,N',N'*-tetramethylethylenediamine (tmen) instead of *N,N,N'*-trimethylethylenediamine (trimen). Blue monocrystals suitable for X-ray determination were collected after 10 days (yield ca. 60%). – $C_{14}H_{32}ClCuN_7NiO_8$ (584.15): calcd. C 28.78, H 5.52, N 16.78; Cl, 6.07; found C 28.7, H 5.5, N 16.7; Cl, 6.2.

[Cu(oxpn)Ni(NO$_2$)(dmeten)](ClO$_4$) (3): This complex was prepared in the same way as **1** but with *N,N*-dimethyl-*N'*-ethylethylenediamine (dmeten) instead of *N,N,N'*- trimethylethylenediamine (trimen) (yield ca. 65%). – $C_{14}H_{32}ClCuN_7NiO_8$ (584.15): calcd. C 28.78, H 5.52, N 16.78; Cl, 6.07; found C 28.8, H 5.6, N 16.8; Cl, 6.1.

[Cu(oxpn)Ni(NO$_2$)(trimen)](PF$_6$) (4): NaNO$_2$ (2.73 mmol) and an ethanolic solution (7 mL) of $(NH_4)PF_6$ (1.36 mmol) were added to an ethanolic solution (30 mL) of [Cu(oxpn)Ni(H$_2$O)$_2$(trimen)](NO$_3$)$_2$ (2.73 mmol), prepared in situ by mixing [Cu(oxpn)] (2.73 mmol), $Ni(NO_3)_2 \cdot xH_2O$ (2.73 mmol) and trimen (2.73 mmol), with constant stirring. The resulting blue solution was left to evaporate slowly at room temperature (yield ca. 70%). – $C_{13}H_{30}CuF_6N_7NiO_4P$ (615.64): calcd. C 25.36, H 4.91, N 15.92; found C 25.2, H 5.1, N 15.8.

[Cu(oxpn)Ni(NO$_2$)(dmeten)](PF$_6$) (5): This complex was prepared in the same way as **4** but with *N,N*-dimethyl-*N'*-ethylethylenediamine (dmeten) instead of trimen (yield ca. 60%). – $C_{14}H_{32}CuF_6N_7NiO_4P$ (629.67): calcd. C 26.70, H 5.12, N 15.57; found C 26.8, H 5.2, N 15.4.

Despite all efforts no crystals suitable for X-ray determination were obtained for complexes **3**, **4**, or **5**.

X-ray Crystallography. - [Cu(oxpn)Ni(μ-NO$_2$)(trimen)]$_n$(ClO$_4$)$_n$ (1) and [Cu(oxpn)Ni(NO$_2$)(tmen)]ClO$_2$ (2): Prismatic crystals (0.1 × 0.2 × 0.2 mm) for **1** and (0.1 × 0.1 × 0.2 mm) for **2** were selected and mounted on an Enraf–Nonius CAD4 four-circle diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections ($12 < \theta < 21°$) and refined by least-squares methods. Intensities were collected with graphite monochromated Mo-K_α radiation, using ω/2θ scan-technique. For **1**, 3522 reflections were measured in the range $2.01 \leq \theta \leq 29.97°$, 3474 of which were nonequivalent by symmetry [R_{int} (on I) = 0.009]; 1763 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. For **2**, 4757 reflections were measured in the range $2.16 \leq \theta \leq 29.94°$, 4710 of which were nonequivalent by symmetry [R_{int} (on I) = 0.017]; 3896 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls; significant intensity decay was not observed. Lorentz-polarisation but not absorption corrections were made. The structure was solved by Direct Methods, using SHELXS[20] and refined by full-matrix least-squares method with SHELX93[21] using 3031 reflections for **1** and 4660 reflections for **2** (very negative intensities were not assumed). The function minimised was $\Sigma w \mid F_o \mid^2 - \mid F_c \mid^2 \mid^2$, where $w = [\sigma^2(I) + (0.0795P)^2]^{-1}$ for **1** and $w = [\sigma^2(I) + (0.0842\ P)^2]^{-1}$ for **2**, and $P = \mid F_o \mid^2 + 2 \mid F_c \mid^2)/3$, f, f' and f'' were taken from ref.[22] The extinction coefficient was 0.0002(2) for **1** and 0.0001(9) for **2**. The chirality of the structure was defined from the Flack coefficient,[23] which is equal to 0.01(3) for **1** for the results given. For complex **1** a carbon atom of the propanediamine moiety and the four O atoms of the perchlorate ion were located in disordered positions; an occupancy factor of 0.5 was assigned according to the height of the Fourier synthesis. 19 H atoms were located from a difference synthesis and refined with overall isotropic temperature factors, using a riding model. The final R (on F) factor was 0.057, wR (on $\mid F_o \mid^2$) = 0.122 and goodness of fit = 1.107 for all observed reflections. The number of parameters refined was 287. Maximum shift/esd = 0.06, mean shift/esd = 0.00. Maximum and minimum peaks in the final difference synthesis were 0.494 and –0.660 eÅ^{-3}, respectively. For complex **2** a carbon atom, C(13), of the oxpn ligand was located in a disordered position. 18 H atoms were located from a difference synthesis and refined with overall isotropic temperature factors and 12 H atoms were computed and refined with an overall isotropic temperature factor, using a riding model. Final R (on F) factor was 0.055, wR (on $\mid F_o \mid^2$) = 0.127 and goodness of fit = 1.115 for all observed reflections. The number of parameters refined was 372. Maximum shift/esd = 0.0, mean shift/esd = 0.00. The maximum and minimum peaks in the final difference synthesis were 0.629 and –0.589 eÅ^{-3}, respectively. Crystallographic data for **1** and **2** are shown in Table 3.

Table 3. Crystallographic data and experimental parameters for [Cu(oxpn)Ni(μ-NO$_2$)(trimen)]$_n$(ClO$_4$)$_n$ (**1**) and [Cu(oxpn)Ni(NO$_2$)(tmen)]ClO$_4$ (**2**)

	1	**2**
Empirical formula	$C_{13}H_{30}ClCuN_7NiO_8$	$C_{14}H_{32}ClCuN_7NiO_8$
Formula mass	570.14	584.15
Crystal system	monoclinic	orthorhombic
Space group	*Cc*	*Pcab*
T [K]	293(2)	293(2)
λ [Å]	0.71069	0.71069
a [Å]	17.018(2)	14.168(11)
b [Å]	14.706(6)	15.237(2)
c [Å]	11.132(4)	22.321(5)
α [°]	90	90
β [°]	125.06(2)	90
γ [°]	90	90
V [Å^3]	2280.5(13)	4819(4)
Z	4	8
d_{calcd} [g cm^{-3}]	1.661	1.616
μ [mm^{-1}]	1.928	1.827
R [a]	0.0573	0.0552
wR [b]	0.1217	0.1270

[a] R (on F) = $\Sigma \parallel F_o \mid - \mid F_c \parallel / \Sigma \mid F_o \mid$. – [b] wR (on F^2) = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2}$.

Atomic positional and thermal parameters, a complete list of bond lengths and angles, and F_o/F_c values are available as supplementary material from one of the authors. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-101760 **(1)** and CCDC-118817 **(2)**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44–1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Spectral and Magnetic Measurements: Magnetic measurements were carried out on polycrystalline samples with a Quantum Design MPMS SQUID susceptometer operating at a magnetic field of 0.5 T, between 2 and 300 K. EPR spectra were recorded on powder samples at X-band frequency with a Bruker 300E automatic spectrometer. EPR measurements were carried out in the "Servei de Magnetoquímica" (University of Barcelona).

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