Bis(didentate) open-chain and tetradentate pseudo-macrocyclic bridging co-ordination modes of *N*,*N′*-bis(1,3-dimethyl-5-nitroso-2,4-dioxopyrimidin-6-yl)butane-1,4-diamine

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The reaction of *N*,*N′*-bis(1,3-dimethyl-5-nitroso-2,4-dioxopyrimidin-6-yl)butane-1,4-diamine (H_2L^2) with copper(II) salts in ethanol yielded mononuclear complexes of formula [Cu(HL^2)X] (X is the anion of the corresponding copper salt). These mononuclear precursors reacted with either Cu^{II} and 2,2′-bipyridine (bipy) or [NiL][ClO_4]$_2$ (L = *d*,*l*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) to afford the homodinuclear complexes [Cu(μ-Cl)(μ-L^2)Cu(bipy)]ClO_4·$2H_2O$ **1** and [LNi(μ-H_2L^2)NiL][ClO_4]$_4$ **2**, respectively. Within the dinuclear cation of **1** the copper(II) ions exhibit a 4 + 1 co-ordination environment. The dioxime ligand bridges the basal planes of the metal ions through the oximate groups in a symmetrical *syn-syn* fashion, Cu(1)···Cu(2) being 3.364(3) Å, whereas their apical positions are occupied by a bridging Cl anion, with a Cu(1)–Cl(1)–Cu(2) angle of 80.42(7)°. A magnetic study of **1** revealed that the antiferromagnetic exchange is so strong as to cause complete spin pairing at room temperature. Complex **2** consists of a homodinuclear [LNi(μ-H_2L^2)NiL]$^{4+}$ cation and four non-co-ordinated perchlorate anions. The ligand adopts an unusual bis(didentate) open-chain co-ordination mode by elimination of the Cu atom occupying the inner site of the pseudo-macrocyclic ligand in the mononuclear precursor. This results in a Ni···Ni distance of 13.370(3) Å. The nickel(II) ions are octahedrally co-ordinated by four nitrogen atoms belonging to the macrocyclic ligand L and the N and O atoms from the nitroso and the neighbouring exocyclic group. The co-ordination modes of H_2L^2 are compared to those of the related *N*,*N′*-bis(1,3-dimethyl-5-nitroso-2,4-dioxopyrimidin-6-yl)propane-1,3-diamine (H_2L^1).

Homo- and hetero-bimetallic complexes are of current interest for inorganic chemists in connection with spin exchange between metal ions, in the domain of metalloproteins for their potential use as models for the active sites of many enzyme systems and in designing new molecular materials exhibiting unusual magnetic, optical and electrical properties.[1-3] One of the best and common strategies to design and synthesize polynuclear metal complexes is the use of mononuclear complexes as ligands. These complexes must contain donor groups for another metal ion or metal complex with empty co-ordination sites (Scheme 1). It is well known that oximato groups can bridge metal ions to afford polynuclear complexes,[4-7] in which the oximate generally mediates a very strong antiferromagnetic interaction, so that, in some cases,[4,6,7c] a nearly complete spin pairing is observed at room temperature. We recently reported[7] examples of structurally and magnetically characterized oximate-bridged homo- Cu^{II}–Cu^{II} and hetero-dinuclear Cu^{II}–Ni^{II} complexes with the ligand *N*,*N′*-bis(1,3-dimethyl-5-nitroso-2,4-dioxopyrimidin-6-yl)propane-1,3-diamine (H_2L^1). In these complexes the H_2L^1 ligand has shown different bridging-co-ordination modes depending upon the nature of the external fragment. Thus, when the mononuclear copper(II) precursors co-ordinate to a [Cu(bipy)]$^{2+}$ (bipy = 2,2′-bipyridine) fragment the ligand acts as a double symmetric oximate bridge [Scheme 1, reaction (a)], whereas when the external fragment is a nickel(II) N_3- or N_4-macrocyclic complex the ligand bridges in an asymmetric fashion.[6,7]

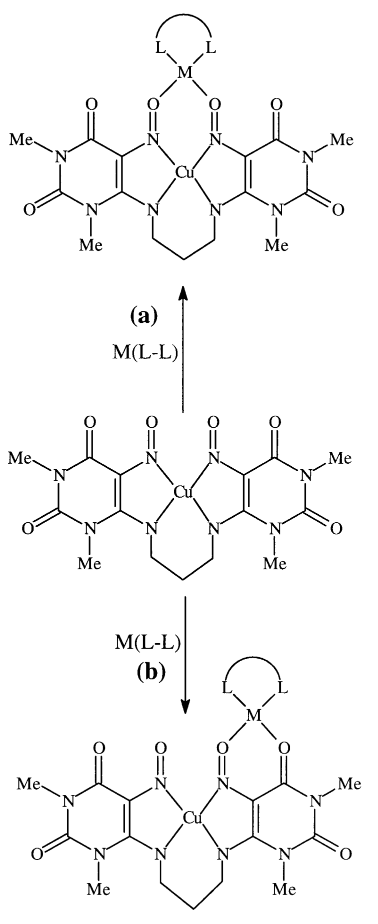
The present paper is devoted to the synthesis and characterization of two homodinuclear complexes of Cu^{II} and Ni^{II} of *N*,*N′*-bis(1,3-dimethyl-5-nitroso-2,4-dioxopyrimidin-6-yl)-butane-1,4-diamine (H_2L^2). The crystal structures and the magnetic properties are reported and the co-ordination modes of the H_2L^2 ligand compared to those exhibited by the related H_2L^1.

Experimental

Preparations

The compound H_2L^2 and [NiL][ClO_4]$_2$ (L = *d*,*l*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) were prepared by literature methods.[8,9]

[Cu(μ-Cl)(μ-L^2)Cu(bipy)]ClO_4·$2H_2O$ 1. This complex was prepared in two consecutive reactions. First, the precursor complex with formula [Cu(HL^2)Cl] was obtained by adding solid copper(II) chloride dihydrate (2.37 mmol, 0.32 g) to a stirred suspension of H_2L^2 (2.37 mmol, 1 g) in ethanol (50 cm^3) and then the mixture was refluxed for 1 h. A green powder formed, which was filtered off, washed with ethanol and air dried; yield 85% (Found: C, 45.1; H, 5.1; Cu, 15.2; N, 25.9. Calc. for $C_{16}H_{21}ClCuN_8O_6$: C, 45.3; H, 5.0; Cu, 14.95; N, 26.4%). Complex **1** was prepared by adding consecutively solid copper(II) perchlorate hexahydrate (0.181 mmol, 0.068 g) and 2,2′-bipyridine (0.181 mmol, 0.023 g) to an ethanolic suspension (50 cm^3) of [Cu(HL^2)Cl] (0.181 mmol, 0.1 g) heated at 60 °C. After a few min a black solution was obtained. After several days at room temperature black crystals appeared, which were collected, washed with ethanol and air dried; yield



Scheme 1

48% (Found: C, 36.0; H, 3.7; Cu, 14.9; N, 16.1. Calc. for $C_{26}H_{32}Cl_2Cu_2N_{10}O_{12}$: C, 35.7; H, 3.7; Cu, 14.55; N, 16.0%).

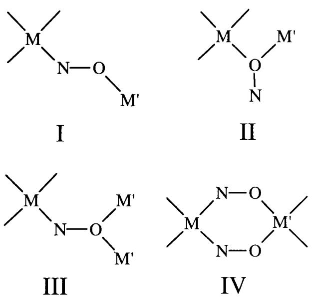
[LNi(μ-H$_2$L^2)NiL][ClO$_4$]$_4$ 2. This complex was also prepared in two consecutive reactions. First, [Cu(HL^2)(ClO$_4$)] was obtained by adding solid copper(II) perchlorate hexahydrate (2.37 mmol, 0.64 g) to a stirred suspension of H_2L^2 (2.37 mmol, 1 g) in ethanol (50 cm^3). The mixture was stirred overnight whereupon a green powder precipitated from the dark green homogeneous solution. This complex was filtered off, washed with ethanol and air dried, yield 60% (Found: C, 33.1; H, 3.7; Cu, 11.3; N, 18.9. Calc. for $C_{16}H_{21}ClCuN_8O_{10}$: C, 32.9; H, 3.6; Cu 10.85; N, 19.15%). Complex **2** was prepared by adding a solution of [NiL][ClO$_4$]$_2$ (0.122 mmol, 0.066 g) in acetonitrile–water (5 : 1, 10 cm^3) to a suspension of [Cu(HL^2)(ClO$_4$)] (0.122 mmol, 0.1 g) in ethanol (20 cm^3) and refluxing the resulting black solution for 1 h. After 1 d at room temperature dark brown crystals were collected, washed with methanol and air dried, yield 54% (Found: C, 37.9; H, 6.4; N, 14.5; Ni, 7.5. Calc. for $C_{48}H_{94}Cl_4N_{16}Ni_2O_{22}$: C, 38.25; H, 6.3; N, 14.9; Ni, 7.8%).

Physical measurements

Microanalyses, IR spectra and magnetic susceptibility data were obtained as described previously.[7a]

Crystallography

The unit-cell parameters were determined and the data collected on a Rigaku AFC7S diffractometer at −80 °C for complex **1** and on a Nicolet P3F diffractometer at 22 °C for **2**. Totals of 8130 and 7789 reflections were collected ($2\theta_{max} = 54$ and 53°) of which 3890 and 2964 unique reflections with $|F| > 4\sigma(F_o)$ were considered as observed for **1** and **2**, respectively. Crystallographic data are listed in Table 1. The data were corrected for Lorentz-polarization effects and for dispersion[10] and absorption (empirical correction). In the case of **1** a decay correction (−1.9%, linear) was also applied.



Scheme 2

The structures were solved by the heavy-atom method using the SHELXS 86 program[11] and subsequent Fourier synthesis. Least-squares refinements were performed by using the XTAL 3.2 package,[12] which minimized the function $\Sigma w(\Delta F)^2$ [$1/w = \sigma^2(F_o)$]. In the final refinement cycles all the non-hydrogen atoms of **1** and **2**, except those of the crystal water molecule O(36) of **1**, were refined with anisotropic displacement parameters. Atom O(36), which is disordered over two close positions [atomic populations 0.48(2) and 0.52(2), for O(36A) and O(36B), respectively], was refined with an isotropic displacement parameter. Approximate positions of the hydrogen atoms bonded to the water molecule O(35) of **1** were obtained from a Fourier-difference map and not refined, while those of the disordered crystal water molecule could not be positioned. Remaining hydrogen atoms of **1** and all hydrogen atoms of **2** were included in the calculations in fixed positions (C−H 0.96 and N−H 0.90 Å) with fixed displacement parameters.

Atomic co-ordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/451.

Results and Discussion

It is well known that oxime ligands may exhibit different bridging co-ordination modes (Scheme 2).[4–7] In previous studies[7] with the related compound H_2L^1 we succeeded in obtaining binuclear Cu^{II}–Cu^{II} and Cu^{II}–Ni^{II} complexes exhibiting bridging oxime conformations **I**, **II** and **IV**. While **I** and **II** were obtained for the Cu^{II}–Ni^{II} complexes,[7a,b] **IV** was only found for homopolynuclear copper(II) complexes.[6,7a] When H_2L^2 is used instead of H_2L^1, under similar reaction conditions, an analogous reaction pattern is expected, since the length of the $(CH_2)_n$ backbone chain is the only difference between the compounds ($n = 3$ and 4 for H_2L^1 and H_2L^2, respectively). In accordance, H_2L^2 readily reacts with copper(II) salts to yield mononuclear complexes in which the ligand adopts a tetradentate pseudo-macrocyclic co-ordination mode (Scheme 1). These mononuclear precursors contain potential donor groups, such as oximato and carbonyl oxygen atoms, for a second metal, and therefore may be used as ligands to afford binuclear complexes with either double symmetric oximate bridges [Scheme 1, reaction(a)] or double asymmetric oximate/carbonyl bridges [reaction(b)]. Thus, when the mononuclear precursor [Cu(HL^2)Cl] is treated with $Cu(ClO_4)_2\cdot6H_2O$ and 2,2′-bipyridine the dinuclear complex **1** is obtained, in which the oxime groups adopt the expected *syn-syn* conformation (Scheme 2, **IV**). It should be noted at this point that a second complex was isolated from the reaction solution. X-Ray results for this product showed that it corresponds to a mononuclear complex of formula [CuL^3-(bipy)]ClO$_4$ [HL^3 = violuric acid (pyrimidine-2,4,5,6-tetrone 5-oxime)], where HL^3 is formed by hydrolysis of the H_2L^2

Table 1 Crystal data and structure refinement for complexes **1** and **2***

	1	**2**
Formula	$C_{26}H_{32}Cl_2Cu_2N_{10}O_{12}$	$C_{48}H_{94}Cl_4N_{16}Ni_2O_{22}$
M	874.6	1506.6
Colour, shape	Blue, plate	Yellow, plate
Crystal size/mm	0.30 × 0.30 × 0.09	0.40 × 0.35 × 0.10
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$
a/Å	13.123(3)	18.083(6)
b/Å	14.949(4)	12.225(3)
c/Å	8.577(2)	15.775(5)
α/°	100.57(2)	
β/°	95.89(2)	98.50(3)
γ/°	91.71(2)	
U/Å^3	1643.2(7)	3449(2)
D_c/g cm^{-3}	1.769	1.452
Maximum, minimum transmission	0.906, 1.000	0.920, 1.000
μ(Mo-Kα)/mm^{-1}	1.54	0.78
T/K	193	295
Observed reflections	3890	2964
Parameters	470	416
Maximum, minimum electron density/e Å	0.8, −0.6	0.6, −0.4
R	0.071	0.063
R'	0.070	0.041
S	1.426	1.567

* Details in common: $Z = 2$; Mo-Kα radiation (λ 0.710 73 Å); $2\theta_{max}$ 53°: $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)/\Sigma|F_o|^2]^{\frac{1}{2}}$.

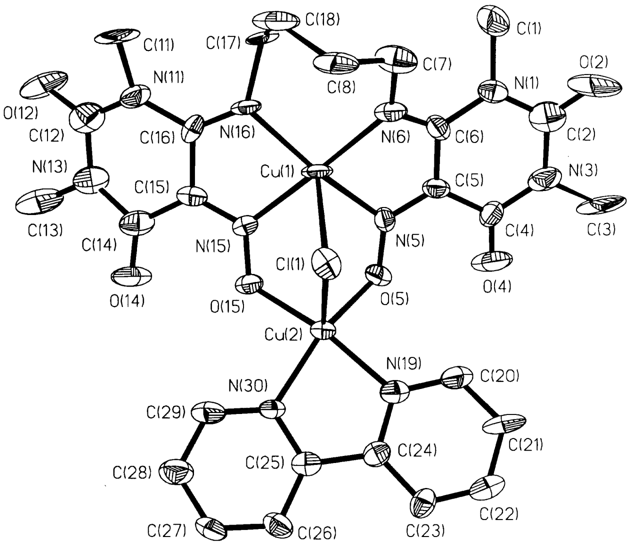


Fig. 1 Perspective view of the $[Cu(\mu\text{-}Cl)(\mu\text{-}L^2)Cu(bipy)]^+$ cation of complex **1**. Ellipsoids represent 40% probability

ligand.[13] This is not totally unexpected since it has been previously found for related ligands containing secondary amine groups.[13]

On the other hand, when the mononuclear precursor $[Cu(HL^2)(ClO_4)]$ reacts with $[NiL][ClO_4]_2$ the complex **2** is obtained. Surprisingly, and in contrast to the heterodinuclear Cu^{II}–Ni^{II} complexes reported for H_2L^1,[7a,b] **2** is a homodinuclear nickel(II) complex with no metal cation occupying the inner site of the ligand, so that this reaction takes place with the elimination of the copper(II) ion, giving rise to the bridging open-chain conformation of the ligand.

$[Cu(\mu\text{-}Cl)(\mu\text{-}L^2)Cu(bipy)]ClO_4\cdot 2H_2O$ 1

The structure of complex **1** consists of a $[Cu(\mu\text{-}Cl)(\mu\text{-}L^2)Cu(bipy)]^+$ cation, a perchlorate anion and two lattice water molecules. A view of the cation is shown in Fig. 1 and selected bond lengths and angles are listed in Table 2.

Table 2 Selected bond distances (Å) and angles (°) for complex **1**

Cu(1)–Cl(1)	2.602(2)	Cu(2)–Cl(1)	2.608(2)
Cu(1)–N(5)	1.996(6)	Cu(2)–O(5)	1.953(5)
Cu(1)–N(6)	1.993(8)	Cu(2)–O(15)	1.949(6)
Cu(1)–N(15)	2.007(7)	Cu(2)–N(19)	2.009(7)
Cu(1)–N(16)	1.990(7)	Cu(2)–N(30)	2.003(7)
Cl(1)–Cu(1)–N(5)	84.5(2)	Cl(1)–Cu(2)–O(5)	95.5(2)
Cl(1)–Cu(1)–N(6)	104.0(2)	Cl(1)–Cu(2)–O(15)	89.3(2)
Cl(1)–Cu(1)–N(15)	82.0(2)	Cl(1)–Cu(2)–N(19)	100.9(2)
Cl(1)–Cu(1)–N(16)	118.1(2)	Cl(1)–Cu(2)–N(30)	106.6(2)
N(5)–Cu(1)–N(6)	80.7(3)	O(5)–Cu(2)–O(15)	93.8(2)
N(5)–Cu(1)–N(15)	97.7(3)	O(5)–Cu(2)–N(19)	90.0(3)
N(5)–Cu(1)–N(16)	156.6(3)	O(5)–Cu(2)–N(30)	157.2(2)
N(6)–Cu(1)–N(15)	173.6(3)	O(15)–Cu(2)–N(19)	168.7(3)
N(6)–Cu(1)–N(16)	98.5(3)	O(15)–Cu(2)–N(30)	91.6(3)
N(15)–Cu(1)–N(16)	80.4(3)	N(19)–Cu(2)–N(30)	80.9(3)

Within the dinuclear unit the copper(II) ions are dibridged by two oximate groups in a *syn-syn* conformation and a chloride ion, resulting in a Cu · · · Cu distance of 3.364(3) Å. The Cu(1) ion occupies the inner site of the doubly deprotonated L^{2-} ligand, exhibiting a 4 + 1 co-ordination environment. The L^{2-} ligand co-ordinates to Cu(1) in a tetradentate fashion through atoms N(5), N(6), N(15) and N(16) to form the basal plane with bond distances of *ca.* 2 Å (see Table 2), while the fifth position is occupied by the bridging Cl(1) ion at a longer distance of 2.602(2) Å. According to Addison *et al.*[14] the τ value is 0.28, the Cu(1) co-ordination polyhedron being closer to a square-pyramidal geometry ($\tau = 1$ for a regular trigonal pyramid and 0 for a square-based pyramid). The four nitrogen atoms of the basal plane are almost coplanar with maximum deviation from the mean plane of 0.16(9) Å and the Cu(1) ion raised 0.263(1) Å toward the axial donor atom. Dihedral angles between the mean basal plane and the aromatic uracil rings are 10.1(2) and 20.9(3)°. Co-ordination of the ligand to the Cu(1) atom results in the formation of two five-membered rings [N(5), C(5),C(6),N(6),Cu(1) and N(15),C(15),C(16),N(16),Cu(1)] and a seven-membered chelate ring [N(6),C(7),C(8),C(18),C(17), N(16),Cu(1)]. Several studies[15,16] revealed that the geometrical distortions in copper(II) co-ordination environments, as a consequence of steric constraints produced by seven-membered chelate rings, are larger for a macrocyclic ligand than for a pseudo-macrocyclic one due to the greater flexibility of this latter.[15a] Our results are in accord with this since the geometrical features of the Cu(1) fragment are very similar to those exhibited by the related complexes of H_2L^1.[6,7] However, steric crowding, largely due to the presence of the tetramethylene linkage between the uracil rings, remains in the system as revealed by the non-planarity of the uracil rings which are inclined at 30.7(3)° with respect to each other in order to keep a nearly ideal square-pyramidal geometry around the Cu(1) ion.

The Cu(2) atom also exhibits a 4 + 1 co-ordination environment. Four short bonds, of *ca.* 2 Å, are formed by O(5) and O(15) from the nitroso bridging groups and N(19) and N(30) atoms belonging to the bipy ligand. The fifth position is occupied by the bridging Cl(1) ion at a longer distance of 2.608(2) Å. The geometry around the Cu(2) atom is closer to square pyramidal ($\tau = 0.19$), with a maximum deviation from the basal plane of 0.127(9) Å and the Cu(2) ion raised 0.265(1) Å toward the Cl(1) ion. Dihedral angles between the mean basal plane and the pyridine rings are 13.1(3) and 14.0(2)°, and between both pyridine rings 3.5(3)°. The dihedral angle between the Cu(1) and Cu(2) basal planes is 51.0(3)°, whereas the bridging Cu(1)–Cl(1)–Cu(2) angle is 80.42(7)°.

At room temperature complex **1** exhibits complete spin pairing, thus indicating that the strong antiferromagnetic exchange interaction has an exchange parameter J (with $H = JS_1S_2$) larger than 1000 cm^{-1}. The strong antiferromagnetic interaction could be interpreted on the basis of the nature of the

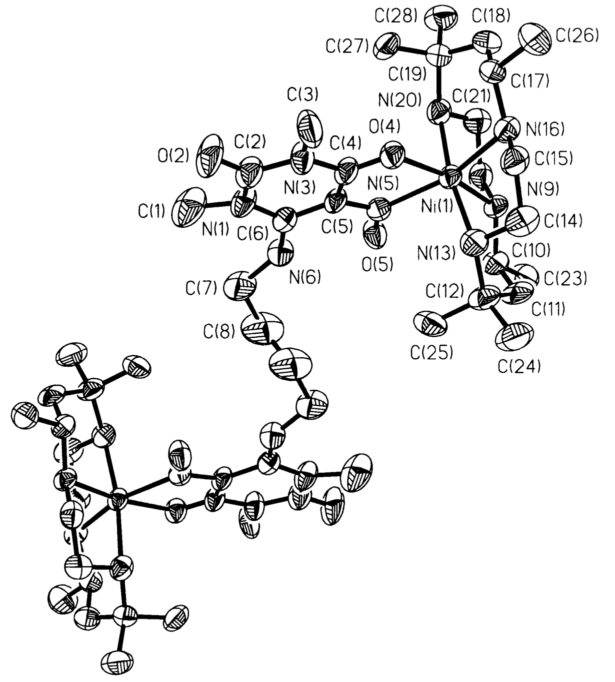


Fig. 2 Perspective view of the $[LNi(\mu\text{-}H_2L^2)NiL]^{4+}$ cation of complex **2**. Ellipsoids represent 40% probability

magnetic orbitals on Cu(1) and Cu(2) and the bridging oximato groups. Atoms Cu(1) and Cu(2) have square-pyramidal environments, in which the unpaired electron is adequately described by a $d_{x^2-y^2}$ type orbital. In the former the magnetic orbital points along the Cu–N directions in the basal plane, whereas in the latter it points from the metal toward the oxygen atoms of the two NO bridging groups. Since the lobes of the oximato molecular orbital involved in the superexchange pathway are pseudo-spherical,[7c] it is expected that both magnetic orbitals on Cu(1) and Cu(2), delocalized toward the 2p oxygen and nitrogen orbitals of the NO bridges, are favourably oriented to give a strong overlap and hence a strong antiferromagnetic interaction. In addition, there is another possibility of a Cu(1)–Cu(2) exchange interaction through Cu(1)–Cl(1)–Cu(2); this may yield either ferro- or antiferro-magnetic interactions depending on the structural parameter Φ/R_0, where Φ is the Cu–Cl–Cu angle (in °) and R_0 the out-of-plane Cu–Cl bond length (in Å).[1,17] Although recently criticized from a physical standpoint,[18] the empirical correlation Φ/R_0 leads to the conclusion that a weak antiferromagnetic coupling ($J' < 10$ cm^{-1}) is expected for a Φ/R_0 value of 30.9° Å^{-1} ($\Phi = 80.42°$ and $R_0 = 2.602$ Å). In addition, since the chloride bridges the copper ions in axial positions, where the spin density of the unpaired electron is very low, there may only be a very weak exchange interaction *via* the chloride. Thus, we suggest that J is largely determined by the exchange pathway involving the oximato groups.

It is well known that the oximato group generally mediates a strong antiferromagnetic interaction, which gives rise to a complete spin pairing at room temperature in some polynuclear oximato-bridged copper(II) complexes.[4,6,7c] The vast majority of the complexes having a very strong antiferromagnetic coupling at room temperature, as observed in **1**, exhibit a coplanar structure, which could suggest that a planar structure is essential for attaining a complete spin pairing at ambient temperature. However, this assumption should be used with caution, since complex **1**, as well as several other examples,[6,16] exhibit essentially complete spin pairing at room temperature with non-planar structures. In fact, extended-Hückel calculations on bridging oximate systems have shown that the gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO) is only moderately affected by either the displacement of the copper atom out of the co-ordination basal plane or the dihedral angle between the basal and oximate planes.[7c] We feel that other factors, such as the nature of the oximate ligand itself and of the 'end-cap' ligands, may be, at least, as important in determining the exchange interaction as the structural parameters of the bridging fragment.

Table 3 Selected bond distances (Å) and angles (°) for complex **2**

Ni(1)–O(4)	2.133(4)	Ni(1)–N(13)	2.150(5)
Ni(1)–N(5)	2.128(5)	Ni(1)–N(16)	2.123(5)
Ni(1)–N(9)	2.081(5)	Ni(1)–N(20)	2.155(4)
O(4)–Ni(1)–N(5)	76.5(2)	N(5)–Ni(1)–N(20)	88.5(2)
O(4)–Ni(1)–N(9)	171.1(2)	N(9)–Ni(1)–N(13)	90.4(2)
O(4)–Ni(1)–N(13)	87.3(2)	N(9)–Ni(1)–N(16)	103.0(2)
O(4)–Ni(1)–N(16)	85.4(2)	N(9)–Ni(1)–N(20)	84.9(2)
O(4)–Ni(1)–N(20)	98.3(2)	N(13)–Ni(1)–N(16)	84.8(2)
N(5)–Ni(1)–N(9)	95.3(2)	N(13)–Ni(1)–N(20)	171.7(2)
N(5)–Ni(1)–N(13)	98.7(2)	N(16)–Ni(1)–N(20)	89.6(2)
N(5)–Ni(1)–N(16)	161.4(2)		

$[LNi(\mu\text{-}H_2L^2)NiL][ClO_4]_4$ 2

The molecular structure of complex **2** is depicted in Fig. 2. Selected bond distances and angles are listed in Table 3. The structure consists of a discrete homodimetallic cation $[LNi(\mu\text{-}H_2L^2)NiL]^{4+}$ and four non-co-ordinated perchlorate anions. The dinuclear cation has C_i symmetry, with the inversion centre located at the middle of the $N(CH_2)_4N$ chain. The open-chain bridging co-ordination mode of the H_2L^2 ligand results in a Ni · · · Ni distance of 13.370(3) Å. The nickel(II) ions are roughly octahedrally co-ordinated by four nitrogen atoms belonging to the macrocyclic ligand L at *ca.* 2.1 Å (see Table 3) and the N(5) and O(4) atoms from the nitroso and the carbonyl groups of the H_2L^2 ligand, with Ni-N(5) and Ni-O(4) bond lengths of 2.128(5) and 2.133(4) Å, respectively. In this octahedral description the basal plane is defined by the O(4), N(5), N(9) and N(16) atoms while N(20) and N(13) occupy the apical positions. The co-ordination mode of the H_2L^2 ligand gives rise to a five-membered chelate ring, which forms a dihedral angle with the uracil ring of 3.5(2)°. It should be pointed out that this co-ordination mode, involving the exocyclic carbonyl group and the nitroso nitrogen atom, is quite usual for *o*-nitroso-oxo groups in pyrimidine derivatives.[19] Remaining bond lengths and angles are well within their usual values and do not deserve further comment.

The magnetic data for complex **2** correspond to those expected for two isolated nickel(II) ions with no zero-field-splitting effects in the temperature range 8.5–250 K ($\chi_m T$ remains constant at 2.4 cm^3 K mol^{-1}). This behaviour is consistent with the large $Ni^{II} \cdots Ni^{II}$ distance observed for this complex and the absence of a suitable pathway for the exchange magnetic interaction.

Conclusion

The reactivity and co-ordination modes of H_2L^2 are, as expected, similar to those exhibited by H_2L^1 when it is treated either with copper(II) salts or $[Cu(bipy)]^{2+}$ to obtain mono- or di-nuclear copper(II) complexes with *syn-syn* oximato bridging groups.[6,7a] However, when the mononuclear precursor is treated with a nickel(II) macrocyclic complex double asymmetric bridges are found (Scheme 1).[7b,c] This co-ordination pattern seems to be due to the steric requirements of the external fragment rather than the nature of the metal ion, *i.e.* copper(II) or nickel(II). Nevertheless, the lengthening of the aliphatic chain from propane to butane decreases the stability of the mononuclear precursors of H_2L^2 toward the dissociation equilibrium $[CuL^2] = Cu^{2+} + (L^2)^{2-}$. This latter fact is supported by the preparation of complex **2**, which is obtained by elimination of the Cu^{II} from the inner site as a consequence of the distortion induced in the system by the bulky $[NiL]^{2+}$ cation. Once the exit of the copper ion takes place the H_2L^2 ligand adopts an open-chain conformation to co-ordinate to a second $[NiL]^{2+}$ cation to yield **2**. In the case of **1**, both the smaller size of the $[Cu(bipy)]^{2+}$ cation and the existence of the bridging Cl(1) ion stabilize the system precluding the exit of the Cu(1) atom from the inner site of the pseudo-macrocyclic ligand.

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