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Heterodinuclear Copper(II)–Nickel(II) Complexes with Unusual Asymmetrical Bridges from a New and Versatile Dioxime Multidentate Ligand. Magneto–Structural Study

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When H_2L (α,ω-bis((1,3-dimethyl-5-nitrosouracil-6-yl)amino)propane) in hydroethanolic basic medium is reacted with a copper(II) salt, the complex $[Cu(L)(H_2O)]\cdot 3H_2O$ (**1**) is obtained. This complex can be used as ligand for the preparation of heterodinuclear complexes. Thus, reaction of **1** with either $[Ni(CTH)](ClO_4)_2$ or a neutral aqueous solution of $[Ni(OH)(Me_3[12]N_3)]_2(ClO_4)_2$ gives rise to the complexes $[Cu(ClO_4)(\mu\text{-}L)Ni(CTH)](ClO_4)\cdot H_2O$ (**2**) and $[Cu(ClO_4)(\mu\text{-}L^1)Ni(Me_3[12]N_3)](ClO_4)\cdot H_2O$ (**3**) (H_2L^1 is obtained from H_2L by elimination of a CO molecule from one of the pyrimidine rings, leading to an imidazole ring in **3**; $Me_3[12]N_3$ = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene and CTH = *d,l*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane). The structures of these complexes have been solved by X-ray crystallographic methods. Complex **1** crystallizes in the triclinic system, space group $P\bar{1}$, with cell constants a = 8.208(1) Å, b = 10.468(1) Å, c = 13.335(2) Å, α = 81.74(1)°, β = 81.42(1)°, γ = 76.61(1)° and Z = 2. The structure consists of neutral $[Cu(L)(H_2O)]$ molecules and three lattice water molecules, which are involved in an extended network of hydrogen bonds. The CuN_4O coordination polyhedron exhibits a distorted square-pyramidal geometry, in which two amino and two oximato nitrogen atoms at about 2 Å form the basal plane whereas the oxygen atom from a water molecule occupies the apical position at a longer distance of 2.284(2) Å. Crystals of **2** are monoclinic, space group $P2_1/c$, with cell constants a = 18.046(3) Å, b = 12.541(1) Å, c = 19.471(4) Å, β = 101.08(1)°, and Z = 4. The structure of **2** consists of one $[Cu(ClO_4)(\mu\text{-}L)Ni(CTH)]^+$ cation, one perchlorate anion, and one nonbonded lattice water molecule. In the dinuclear cation, the coordination of the precursor **1** to the $[Ni(CTH)]^{2+}$ moiety takes place through an exocyclic oxygen atom of the uracil ring and a *syn–anti* nitroso–oximato group disordered on two sets of crystallographic positions, one with a 78% occupancy and the other with a 22% occupancy. The intramolecular Cu···Ni distance is 4.972(1) Å. The Cu(II) ion occupying the inside site of the L^{2-} ligand exhibits a distorted square-pyramidal coordination environment. The basal plane comprises of two amino and one oximate nitrogen atoms and either an oxygen (occupancy 0.78) or a nitrogen atom (occupancy 0.22) from the other oximato group. The fifth position is occupied by a disordered oxygen atom, from a perchlorate anion with occupancy factors of 0.56 and 0.44, respectively. The nickel(II) ion is in a distorted octahedral geometry. Crystals of **3** are orthorombic, space group $Pna2_1$, with cell constants a = 20.046(5) Å, b = 10.462(2) Å, c = 35.397(7) Å and Z = 8. The asymmetric unit of **3** contains two crystallographic independent heterodinuclear cations $[Cu(ClO_4)(\mu\text{-}L^1)Ni(Me_3[12]N_3)]^+$, two nonbonded perchlorate anions, and two lattice water molecules. Within each heterodinuclear cation copper(II) and nickel(II) are bibridged by one diatomic *syn–syn* group and one *O*-monatomic nitroso–oximato group from the pyrimidine and imidazole rings, respectively. The angle at the bridging oxygen are 120.1(8) and 119.3(7)° for each one of the molecules whereas the intramolecular copper–nickel distances are 3.440(4) and 3.452(4) Å. The coordination geometry around each copper(II) is distorted square-pyramidal CuN_3O_2. The basal plane comprises of two amino and one oximato nitrogens and one oximato oxygen, whereas an oxygen atom of a disordered perchlorate anion occupies the apical position. The Ni(II) ion is in a distorted square pyramidal NiN_3O_2 environment. The basal plane is defined by two oximato oxygens and two nitrogens from the $Me_3[12]N_3$ ligand, the remaining nitrogen atom occupying the apical position. Magnetic susceptibility measurements in the temperature range 4.2–298 K revealed the occurrence of a weak intermolecular magnetic exchange interaction between copper(II) ions in **1** ($2J = -2.3\ cm^{-1}$), whereas **2** and **3** were found to exhibit a strong antiferromagnetic interaction between copper(II) and nickel(II) ions with J values of 123.6 cm^{-1} and larger than 500 cm^{-1}, respectively. For **2**, below 50 K only the $S = {}^1/_2$ state is thermally populated, whereas for **3**, the spin exchange interaction causes a complete or nearly complete spin coupling even at room temperature. The room temperature powder EPR spectrum of **2** exhibits a very large and intense signal independent of the temperature at approximately g = 2.2 and a broad signal at approximate g = 4.0, which vanishes when the temperature decreases. This is interpreted as being due to an axial ZFS in the excited quartet state. The powder EPR spectrum of **3** does not exhibit any signal at about g = 4, which may indicate that only the $S = {}^1/_2$ state is thermally populated at room temperature, this is in good agreement with the magnetic data. The difference between the exchange coupling observed for **2** and **3** is discussed in terms of structural differences in the bridging network.

Introduction

Heterobimetallic complexes are of current interest in connection with spin exchange and charge transfer between metal ions,[1] in the domain of metalloproteins for their potential use as models for the active sites of many enzyme systems,[2] and in designing new magnetic materials, such as new molecular-based magnets.[3]

In order to synthesize heteronuclear complexes, a good starting

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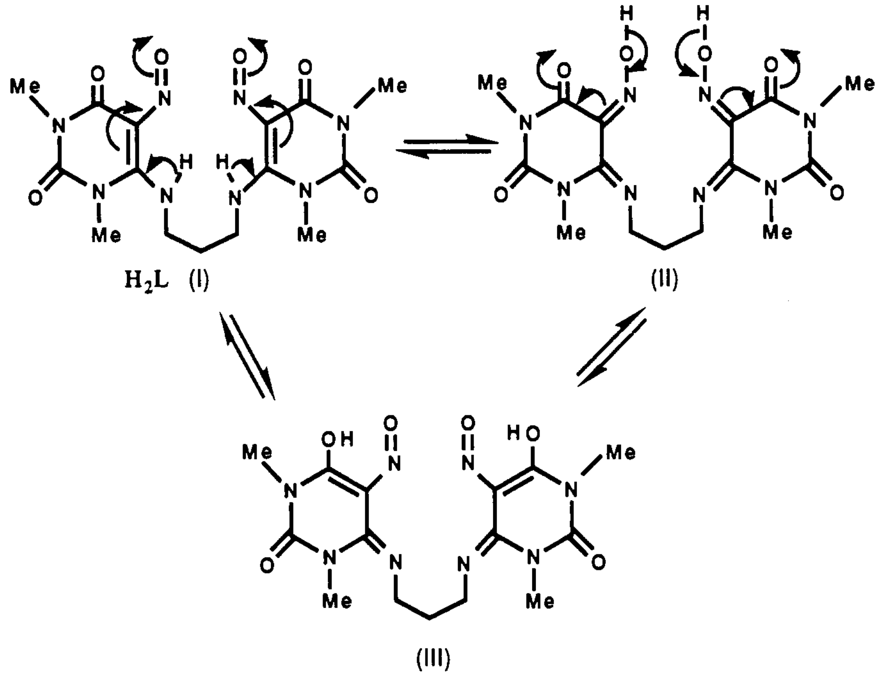
Scheme 1



point is to use metal complexes as ligands; it means metal complexes containing potential donor groups for another metal ion or metal complex with empty coordination sites. Copper(II) complexes with several ligands derived from oxalates and oxamidates are clear and typical examples of paramagnetic ligands that act as chelate agents toward a second metal ion, giving rise to dinuclear, trinuclear, and chain metal complexes. In the last few years, they have been widely investigated for their use in the design of molecular-based magnets.[3,4] New bridging systems that can mediate stronger magnetic interactions than oxalate and oxamidate derivatives would be suitable candidates for designing new ferro- and ferrimagnetic materials which could order magnetically at low temperature.

It is known that the oximate group can function as a bridge between two metal ions, generally mediating a strong antiferromagnetic spin exchange which causes, in some cases, complete or nearly complete spin coupling even at room temperature.[5] However, it is only quite recently that bis(oximato)metal(II) complexes (where oximato represents dimethylglyoximato, diphenylglyoximato, 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioximato, and phenylarylazo oximato) have been used as precursors for homo- and heteropolynuclear complexes.[5a,6] It should be noted that all these complexes contain double symmetrical oximato bridges in the *syn–syn* conformation. Moreover, to our knowledge, no crystal structures of heterodinuclear complexes with oximato bridging ligands have been so far reported.

In this study we aimed to synthesize heterodinuclear complexes with double asymmetrical bridges, in which the nitroso–oximato group (hereafter NO) might adopt a *syn–anti* conformation, in order to gain information concerning the effectiveness of such bridging systems in propagating exchange interaction. For this, we have used the polydentate ligand α,ω-bis((1,3-dimethyl-5-nitrosouracil-6-yl)amino)propane (hereafter H_2L, see Scheme 1), in which the competition between the ability of the NO groups and their nearest-neighboring oxygen atoms as bridging ligands may afford diverse structures.

This paper deals with the synthesis, structure and magnetic properties of three new complexes: the mononuclear precursor $[Cu(L)(H_2O)]\cdot 3H_2O$ (**1**) and the oximate-bridged binuclear copper(II)–nickel(II) complexes $[Cu(ClO_4)(\mu\text{-}L)Ni(CTH)](ClO_4)\cdot H_2O$ (**2**) (CTH = *d,l*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane) and $[Cu(ClO_4)(\mu\text{-}L^1)Ni(Me_3[12]N_3)](ClO_4)\cdot H_2O$ (**3**) (H_2L^1 is obtained from H_2L by elimination of a CO molecule in one of the pyrimidine rings, $Me_3[12]N_3$ = 2,4,4-trimethyl-1,5,9-triazacyclo-dodec-1-ene). As far we are aware, they are the first examples of copper(II)–nickel(II) complexes containing oximato and/or double asymmetrical bridges.

Experimental Section

α,ω-Bis((1,3-dimethyl-5-nitrosouracil-6-yl)amine)propane (H_2L) was prepared by literature methods.[7] Synthesis and characterization of $[Ni(CTH)](ClO_4)_2$ and $[Ni(OH)(Me_3[12]N_3)]_2(ClO_4)_2$ complexes were prepared as previously described.[8,9]

Synthesis of the Complexes. *Caution*! Perchlorate salts of metal complexes are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

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$[Cu(L)(H_2O)]\cdot 3H_2O$ (1). The ligand H_2L (1.2 mmol, 0.5 g) was dissolved in 50 mL of a methanol/water mixture (2:1) containing potassium hydroxide (2.5 mmol, 1.40 g). After a few minutes, an orange solution was obtained, and any amount of insoluble material present was filtered off. To this filtrate was added, with continuous stirring, copper(II) acetate monohydrate (0.25 g), resulting in a black homogeneous solution. After 1 day at room temperature, black crystals were obtained, which were filtered off, washed with methanol, and air-dried; yield 61%.

Anal. Calcd for $C_{15}H_{26}N_8O_{10}Cu$: C, 33.2; H, 4.8; N, 20.7; Cu, 11.7. Found: C, 33.1; H, 4.9; N, 20.6; Cu, 11.9.

$[Cu(ClO_4)(\mu\text{-}L)Ni(CTH)](ClO_4)\cdot H_2O$ (2). A solution of $[Ni(CTH)](ClO_4)_2$ (1 mmol, 0.54 g) in 50 mL of water was added to a stirred solution of **1** (1 mmol, 0.54 g) in 50 mL of water. The heterodinuclear complex immediately precipitates as brown-reddish powder with a yield of 71%. Suitable crystals for X-ray analysis were obtained by evaporation of an acetone solution of the complex at room temperature.

Anal. Calcd for $C_{31}H_{56}N_{12}O_{15}Cl_2CuNi$: C, 36.1; H, 5.4; N, 16.3; Cu, 6.2; Ni, 5.7. Found: C, 35.9; H, 6.2; N, 16.2; Cu, 6.0; Ni, 5.5.

$[Cu(ClO_4)(\mu\text{-}L^1)Ni(Me_3[12]N_3)](ClO_4)\cdot H_2O$ (3). To a suspension of $[Ni(OH)(Me_3[12]N_3)]_2(ClO_4)_2$ (0.5 mmol, 0.39 g) in 50 mL of water, perchloric acid (10%) was added dropwise with constant stirring to obtain a neutral and clear blue solution. This solution was added to one of **1** (1 mmol, 0.54 g) in 50 mL of water. The resulting dark-red solution kept at room temperature provided crysals of $[Cu(ClO_4)(\mu\text{-}L^1)Ni(Me_3[12]N_3)](ClO_4)\cdot H_2O$, which were filtered off and air-dried; yield 31%.

Anal. Calcd for $C_{26}H_{47}N_{11}O_{14}Cl_2CuNi$: C, 33.5; H, 5.1; N, 16.6; Cu, 6.8; Ni, 6.3. Found: C, 33.6; H, 5.5; N, 16.2; Cu, 6.1; Ni, 5.9.

Physical Measurements. Microanalyses and infrared and EPR spectra as well as the magnetic susceptibility data were obtained as already described.[10] ^1H-NMR spectrum of the ligand H_2L was recorded on a Bruker AM-300 spectrometer using DMSO-d_6 as solvent.

X-ray Data Collection and Structure Determination of the Compounds. Single-crystal collections for **1**–**3** were performed at 295 K with a Nicolet P3F diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). The unit cell parameters were calculated by least-squares refinement of 25 well-centered reflections in the ranges of $18 < 2\theta < 27$, $20 < 2\theta < 28$ and $20 < 2\theta < 26$, for **1**–**3**, respectively. The data were collected by ω scan mode ($3 < 2\theta < 53$). Intensities of three reflections monitored periodically exhibited no significant variation. Data were corrected for Lorentz and polarization effects, and in the case of **2**, an empirical absorption correction was performed (ψ scans). The structures were solved using the SHELXS 86 program[11] and subsequent Fourier syntheses and least-squares refinements using the XTAL program.[12] Neutral-atomic scattering and dispersion factors were those included in the program packages. The function minimized was $\sum w(\Delta F)^2$ $[1/w = \sigma^2(F_o)]$. Crystal data and details of data collection are listed in Table 1.

For **1**, the structure was solved by direct methods. ΔF map calculated after anisotropic refinement of non-hydrogen atoms revealed approximate positions of all hydrogen atoms. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms with isotropic thermal parameters.

For **2**, the structure was solved by the Patterson method and subsequent Fourier map. The structure is partly disordered. Both perchlorate ions exhibit rotational disorder. In the weakly coordinated ClO_4^- ion all oxygen atoms occupy two positions having population parameters 0.44(1) and 0.56(1). The two forms of the noncoordinated ClO_4^- ion have the oxygen O(42) in common and they differ by rotation around Cl(2)–O(42) bond. The rest of the three oxygen atoms each occupies two positions with population parameters 0.62(1) and 0.38(1). Also the noncoordinated lattice water molecule is disordered occupying two positions with population parameters 0.49 and 0.51. After refinement of this atomic arrangement subsequent Fourier synthesis revealed two maxima of 1.5 and 1.8 e Å^{-3} in the vicinity of the nitroso group N(15)–O(15) indicating disorder and two bridging modes of the group. Refinement of the two orientations resulted in the population parameters 0.78(2) and 0.22(2) for N(15)–O(15) and N(15A)–O(15A), respectively. The disordered non-H atoms were refined isotropically and the rest of the non-H atoms anisotropically. All the H atoms except those of methyl groups and those of the water molecules were included in the calculations in fixed positions (d = 1.0 Å and U = 0.06 Å^2). The H-atoms were not refined. Maximum and minimum heights in the final difference Fourier map are 0.8 and –0.7 e Å^{-3}.

Table 1. Crystallographic Data for the Complexes **1**–**3**

	1	**2**	**3**
formula	$C_{15}H_{26}N_8O_{10}Cu$	$C_{31}H_{56}N_{12}O_{15}Cl_2CuNi$	$C_{26}H_{47}N_{11}O_{14}Cl_2CuNi$
fw	542.0	1030.0	930.9
cryst syst	triclinic	monoclinic	orthorombic
space group	$P\bar{1}$	$P2_1/c$	$Pna2_1$
a, Å	8.208(1)	18.046(3)	20.046(5)
b, Å	10.468(1)	12.541(1)	10.462(2)
c, Å	13.335(2)	19.471(4)	35.397(7)
α, deg	81.74(1)	90	90
β, deg	81.42(1)	101.08(1)	90
γ, deg	76.61(1)	90	90
V, Å^3	1095.0(5)	4324(1)	7424(3)
Z	2	4	8
ρ_{calcd}, gcm^{-3}	1.644	1.582	1.665
μ, mm^{-1}	1.07	1.13	1.33
T, °C	22	22	22
λ, Å	0.71069	0.71069	0.71069
R^a	0.044	0.073	0.083
$R_w{}^a$	0.031	0.073	0.060

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

For **3**, the structure was also solved by Patterson method and successive Fourier map. Space group $Pna2_1$ was confirmed through absent reflections and structure analysis. Cu, Ni, and Cl atoms were refined anisotropically, and O, N, and C atoms, isotropically. The H atoms, except those of the methyl groups and those of the lattice water molecules, were included in the calculations in fixed positions (X–H = 1.00 Å and U = 0.06 Å^2) and were not refined. Refinement of the enantiomeric model did not decrease the R factor.

Atomic coordinates and isotropic thermal displacements parameters for the non-hydrogen atoms are listed in Tables 2–4 for complexes **1**–**3**, respectively.

Results and Discussion

The H_2L ligand contains two ionizable protons that are involved in the amino–nitroso–ketone (**I**) $\rightleftharpoons$ imino–oxime–ketone (**II**) $\rightleftharpoons$ imino–nitroso–enol (**III**) tautomeric equilibrium (see Scheme 1). IR and ^1H-NMR results seem to indicate that form **II** is dominant in both the solid state and solution. Thus, the IR spectrum exhibits strong ν(OH) bands in the 3550–3424 cm^{-1} region, weak ν(NH) bands in the 3335-3300 cm^{-1} region and strong C(4)=O bands at 1659 and 1625 cm^{-1}. The ^1H-NMR spectrum is not very informative because of the low solubility of H_2L in DMSO, but clearly exhibits a wide signal centered at 15.7 ppm which may be assignable to OH protons rather than NH ones. Even though form **II** is dominant in solution, just prior to complexation the tautomeric equilibrium may be modified by several factors, such as the nature of the solvent, the presence of base, or the nature of the metal cation, and therefore, a potentially rich coordination chemistry is available. Nevertheless, the tetradentate coordination modes of the ligand, in which the metal ion occupies the inside site, are expected to be favored over the outside bidentate ones. Our results (see below) are in accord with this consideration, since when H_2L was allowed to react in basic medium with a copper(II) salt, the neutral 1:1 mononuclear complex $[Cu(L)(H_2O)]\cdot 3H_2O$ (**1**) was obtained in good yield. As can be seen in Scheme 2, this complex contains potential donor groups, such as oximato and carbonyl oxygen atoms, for another metal, and therefore it may be used as ligand to afford binuclear complexes with either double symmetrical oximate bridges (see Scheme 2, reaction I) or double asymmetrical oximate/carbonyl bridges (reaction II). The NO groups would adopt a *syn–syn* conformation in the former and *syn–anti* in the latter.

In this study we have used $[Ni(CTH)]^{2+}$ and $[Ni(Me_3[12]N_3(H_2O)_2]^{2+}$ as counterparts. The former, a square planar complex with empty coordination sites, has been shown to react

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Table 2. Fractional Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of **1**

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*,[a] Å^2
Cu(1)	0.24109(6)	0.35291(4)	0.05703(3)	0.0371(2)
N(1)	0.2297(4)	0.1668(3)	0.3526(2)	0.047(1)
C(1)	0.1083(5)	0.0788(4)	0.3771(3)	0.067(2)
O(2)	0.3066(4)	0.0994(2)	0.5104(2)	0.068(1)
C(2)	0.3106(5)	0.1767(3)	0.4343(3)	0.051(2)
N(3)	0.3928(4)	0.2798(3)	0.4250(2)	0.050(1)
C(3)	0.4790(6)	0.2849(4)	0.5133(3)	0.072(2)
O(4)	0.4411(3)	0.4790(2)	0.3515(2)	0.061(1)
C(4)	0.3863(5)	0.3822(3)	0.3456(3)	0.046(1)
O(5)	0.3793(3)	0.5310(2)	0.1517(2)	0.062(1)
N(5)	0.3193(4)	0.4314(3)	0.1663(2)	0.047(1)
C(5)	0.3156(4)	0.3590(3)	0.2580(2)	0.039(1)
N(6)	0.2213(3)	0.2131(2)	0.1722(2)	0.040(1)
C(6)	0.2515(4)	0.2401(3)	0.2578(2)	0.041(1)
C(7)	0.1908(5)	0.0849(3)	0.1572(3)	0.050(2)
C(8)	0.2509(5)	0.0575(3)	0.0474(3)	0.049(2)
N(11)	0.0473(4)	0.3281(3)	−0.2061(2)	0.043(1)
C(11)	−0.0610(5)	0.2315(4)	−0.1977(3)	0.062(2)
O(12)	0.0246(4)	0.3625(3)	−0.3758(2)	0.079(1)
C(12)	0.0619(5)	0.3990(4)	−0.3020(3)	0.051(2)
N(13)	0.1213(4)	0.5143(3)	−0.3108(2)	0.046(1)
C(13)	0.1326(6)	0.5870(4)	−0.4149(3)	0.067(2)
O(14)	0.1863(3)	0.6796(2)	−0.2433(2)	0.058(1)
C(14)	0.1547(4)	0.5696(3)	−0.2300(3)	0.042(1)
O(15)	0.2334(3)	0.6192(2)	−0.0416(2)	0.054(1)
N(15)	0.2044(3)	0.5090(2)	−0.0480(2)	0.041(1)
C(15)	0.1542(4)	0.4842(3)	−0.1335(2)	0.035(1)
N(16)	0.1469(3)	0.2757(2)	−0.0425(2)	0.036(1)
C(16)	0.1155(4)	0.3536(3)	−0.1241(2)	0.037(1)
C(17)	0.1368(5)	0.1355(3)	−0.0282(3)	0.047(2)
O(20)	0.5119(3)	0.2765(2)	−0.0126(2)	0.044(1)
O(21)	0.6912(4)	0.1413(2)	0.1423(2)	0.074(1)
O(22)	0.5019(4)	0.2597(3)	−0.2285(2)	0.075(1)
O(23)	0.5971(5)	−0.0465(3)	0.2884(2)	0.106(2)

[a] U has been defined as $U = {}^1/_3 \sum_i\sum_j U_{ij} (a_i\&\cdot a_j^*)(a_i\cdot a_j)$.

Table 3. Fractional Atomic Coordinates and Isotropic Displacement and Site Occupation Parameters for the Non-Hydrogen Atoms of **2**

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*,[a] Å^2	PP
Cu(1)	0.32179(5)	0.19171(7)	0.23853(5)	0.0468(3)	
Ni(1)	0.19542(5)	−0.11077(7)	0.33450(4)	0.0332(3)	
N(1)	0.4704(3)	0.4441(5)	0.2479(3)	0.046(2)	
C(1)	0.4759(5)	0.4876(7)	0.1768(4)	0.070(4)	
O(2)	0.5600(3)	0.5638(5)	0.2934(3)	0.075(3)	
C(2)	0.5236(4)	0.4848(7)	0.3023(5)	0.056(3)	
N(3)	0.5317(4)	0.4376(6)	0.3675(4)	0.065(3)	
C(3)	0.5847(6)	0.4869(9)	0.4280(5)	0.104(5)	
O(4)	0.5063(4)	0.3085(5)	0.4394(3)	0.097(3)	
C(4)	0.4938(4)	0.3438(7)	0.3815(4)	0.059(3)	
O(5)	0.4073(3)	0.1564(4)	0.3772(3)	0.065(2)	
N(5)	0.3985(3)	0.2152(5)	0.3248(3)	0.048(2)	
C(5)	0.4422(4)	0.3024(6)	0.3219(4)	0.045(3)	
N(6)	0.3650(3)	0.3265(4)	0.2111(3)	0.045(2)	
C(6)	0.4239(4)	0.3579(5)	0.2559(4)	0.042(3)	
C(7)	0.3262(5)	0.3920(6)	0.1524(4)	0.055(3)	
C(8)	0.2454(5)	0.3577(6)	0.1306(4)	0.053(3)	
N(11)	0.1751(3)	0.0439(5)	0.0744(3)	0.046(2)	
C(11)	0.2103(5)	0.0586(7)	0.0101(4)	0.071(4)	
O(12)	0.0820(3)	−0.0500(5)	0.0076(2)	0.072(2)	
C(12)	0.1145(4)	−0.0242(6)	0.0640(4)	0.048(3)	
N(13)	0.0920(3)	−0.0634(5)	0.1246(3)	0.051(2)	
C(13)	0.0217(5)	−0.1302(7)	0.1142(4)	0.078(4)	
O(14)	0.1250(3)	−0.1202(4)	0.2360(2)	0.050(2)	
C(14)	0.1391(4)	−0.0637(6)	0.1885(3)	0.042(3)	
O(15)	0.2960(4)	0.0624(5)	0.2863(3)	0.047(2)	0.7800
O(15A)	0.271(1)	−0.000(2)	0.308(1)	0.042(5)	0.2200
N(15)	0.2393(4)	0.0032(6)	0.2665(4)	0.035(2)	0.7800
N(15A)	0.261(2)	0.048(2)	0.247(1)	0.042(7)	0.2200
C(15)	0.2029(4)	0.0078(5)	0.1980(3)	0.042(3)	
N(16)	0.2511(3)	0.1651(5)	0.1503(3)	0.047(2)	
C(16)	0.2133(4)	0.0782(6)	0.1400(4)	0.042(3)	
C(17)	0.2384(4)	0.2506(6)	0.0969(4)	0.059(3)	
N(18)	0.2780(3)	−0.0891(4)	0.4236(3)	0.037(2)	
C(19)	0.3580(4)	−0.1107(6)	0.4169(4)	0.049(3)	
C(20)	0.3678(4)	−0.2256(6)	0.3981(4)	0.055(3)	
C(21)	0.3357(4)	−0.2640(6)	0.3250(4)	0.057(3)	
N(22)	0.2505(3)	−0.2536(4)	0.3090(3)	0.040(2)	
C(23)	0.2134(4)	−0.3403(6)	0.3411(4)	0.058(3)	
C(24)	0.1308(4)	−0.3203(6)	0.3367(4)	0.051(3)	
N(25)	0.1196(3)	−0.2183(4)	0.3708(3)	0.035(2)	
C(26)	0.0392(4)	−0.1871(6)	0.3591(3)	0.048(3)	
C(27)	0.0305(4)	−0.0840(7)	0.3975(4)	0.056(3)	
C(28)	0.0551(5)	0.0222(7)	0.3723(4)	0.063(3)	
N(29)	0.1404(3)	0.0216(4)	0.3750(3)	0.045(2)	
C(30)	0.1857(4)	0.0383(6)	0.4454(4)	0.050(3)	
C(31)	0.2673(4)	0.0205(5)	0.4474(4)	0.050(3)	
C(32)	0.4140(4)	−0.0819(7)	0.4874(4)	0.077(4)	
C(33)	0.3596(5)	−0.3821(7)	0.3182(5)	0.082(4)	
C(34)	0.3656(4)	−0.1965(7)	0.2691(4)	0.068(3)	
C(35)	−0.0115(4)	−0.2778(7)	0.3802(4)	0.069(4)	
C(36)	0.0348(5)	0.1137(7)	0.4205(5)	0.086(4)	
C(37)	0.0154(5)	0.0445(7)	0.2971(4)	0.078(4)	
Cl(1)	0.1821(2)	0.3179(2)	0.3190(1)	0.077(1)	
O(38)	0.250(1)	0.338(2)	0.302(1)	0.106(6)	0.4400
O(39)	0.1432(9)	0.232(1)	0.2658(7)	0.077(4)	0.4400
O(40)	0.1345(9)	0.396(1)	0.3323(9)	0.104(5)	0.4400
O(41)	0.205(1)	0.264(1)	0.3920(9)	0.114(6)	0.4400
O(38A)	0.255(1)	0.369(2)	0.336(1)	0.160(8)	0.5600
O(39A)	0.1917(8)	0.236(1)	0.2760(7)	0.106(5)	0.5600
O(40A)	0.1357(8)	0.401(1)	0.2793(8)	0.128(5)	0.5600
O(41A)	0.1501(8)	0.288(1)	0.3761(7)	0.100(4)	0.5600
Cl(2)	0.2233(2)	−0.2872(2)	0.0901(1)	0.082(1)	
O(42)	0.2830(5)	−0.3572(7)	0.0952(4)	0.131(3)	
O(43)	0.1910(7)	−0.316(1)	0.1493(7)	0.123(4)	0.6200
O(44)	0.1640(7)	−0.295(1)	0.0332(6)	0.099(4)	0.6200
O(45)	0.2493(7)	−0.178(1)	0.1046(7)	0.115(4)	0.6200
O(43A)	0.156(2)	−0.363(3)	0.074(2)	0.22(1)	0.3800
O(44A)	0.222(1)	−0.241(1)	0.022(1)	0.101(6)	0.3800
O(45A)	0.218(1)	−0.215(2)	0.1367(9)	0.089(5)	0.3800
O(46)	0.3974(9)	0.240(1)	0.5201(8)	0.121(5)	0.4900
O(46A)	0.3525(8)	0.291(1)	0.4796(7)	0.110(5)	0.5100

[a] U has been defined as $U = {}^1/_3\sum_i\sum_j U_{ij} (a_i^*\cdot a_j^*)(a_i\cdot a_j)$.

with bidentate ligand complexes, such as the tetrachlorozincate(II) anion[13a] and (oxamato)copper(II)[13b] and (dithiooxalate)-Cr(III) complexes,[13c] to form always cis-octahedral heterodinuclear adducts. The $[Ni(Me_3[12]N_3)(H_2O)_2]^{2+}$ contains two water molecules that can be easily replaced by a bidentate ligand complex leading to heterodinuclear complexes with pentacoordinated nickel(II) ions.

The reactions of **1** with $[Ni(CTH)](ClO_4)_2$ in water and with a neutral aqueous solution of $[Ni(OH)(Me_3[12]N_3)]_2(ClO_4)_2$ give rise to the complexes $[Cu(ClO_4)(\mu\text{-}L)Ni(CTH)](ClO_4)\cdot H_2O$ (**2**) and $[Cu(ClO_4)(\mu\text{-}L^1)Ni(Me_3[12]N_3)](ClO_4)\cdot H_2O$ (**3**), respectively.

Crystal Structure of 1. The structure of **1** consists of neutral $[Cu(L)(H_2O)]$ molecules and three lattice water molecules, which are involved in an extended network of hydrogen bonds. A perspective view of the molecular structure with the atomic numbering scheme is shown in Figure 1. Selected intramolecular bond distances and angles are listed in Table 5.

The copper(II) ion is in a (4 + 1) surrounding. The four nearest neighbors, at about 2 Å, are the four nitrogen atoms N(5), N(15), N(6), and N(16) from the double-deprotonated L^{2-} ligand, while the oxygen atom O(20) belonging to a water molecule is coordinated at a longer distance of 2.284(2) Å. The (4 + 1) coordination environment is compatible with two idealized geometries: square pyramidal and trigonal bipyramidal. According to the procedure described by Addison et al.,[14] the magnitude of the square-based pyramid distortion can be measured by τ value (τ is 1.0 for the regular trigonal bipyramid and 0.0 for the square-based pyramid). The calculated τ value is 0.14 so that the copper(II) coordination polyhedron, CuN_4O, is not far removed from

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Table 4. Fractional Atomic Coordinates and Isotropic Displacement Parameters for the Non-Hydrogen Atoms of **3**

atom	*x/a*	*y/b*	*z/c*	U,[a] Å^2
Cu(1)[b]	0.1091(1)	0.0365(3)	0	0.041(2)
Ni(1)	0.0077(1)	–0.1878(3)	–0.0418(1)	0.038(2)
N(1)	0.2522(9)	–0.084(2)	0.0737(5)	0.033(5)
C(1)	0.302(1)	0.011(2)	0.0828(7)	0.051(7)
O(2)	0.317(1)	–0.227(2)	0.1053(6)	0.071(7)
C(2)	0.270(2)	–0.197(3)	0.0856(9)	0.071(9)
N(3)	0.233(1)	–0.320(2)	0.0732(7)	0.073(8)
C(3)	0.256(1)	–0.450(3)	0.0880(8)	0.08(1)
O(4)	0.1528(9)	–0.406(2)	0.0370(6)	0.075(7)
C(4)	0.184(1)	–0.306(3)	0.0481(8)	0.046(7)
O(5)	0.0836(8)	–0.236(1)	–0.0072(5)	0.039(5)
N(5)	0.1163(9)	–0.149(2)	0.0115(6)	0.040(6)
C(5)	0.167(1)	–0.177(2)	0.0346(7)	0.038(7)
N(6)	0.1705(9)	0.042(2)	0.0433(6)	0.049(6)
C(6)	0.197(1)	–0.065(2)	0.0521(6)	0.029(6)
C(7)	0.187(1)	0.164(2)	0.0624(7)	0.062(8)
C(8)	0.131(1)	0.262(2)	0.0579(8)	0.042(8)
C(9)	0.132(1)	0.314(2)	0.0187(7)	0.044(6)
N(10)	0.1099(9)	0.220(2)	–0.0109(6)	0.032(6)
C(10)	0.098(1)	0.255(2)	–0.0506(8)	0.036(8)
N(11)	0.1147(9)	0.369(2)	–0.0622(6)	0.040(6)
C(11)	0.157(1)	0.484(3)	–0.0550(9)	0.065(9)
O(12)	0.0989(8)	0.444(2)	–0.1239(5)	0.068(6)
C(12)	0.094(1)	0.361(2)	–0.0995(7)	0.046(7)
N(13)	0.063(1)	0.244(2)	–0.1057(6)	0.033(6)
C(13)	0.034(1)	0.199(2)	–0.1428(7)	0.049(7)
O(14)	0.0501(7)	–0.007(1)	–0.0396(5)	0.044(4)
N(14)	0.0425(9)	0.059(2)	–0.0723(5)	0.042(5)
C(14)	0.069(1)	0.172(2)	–0.0735(7)	0.039(7)
C(15)	–0.016(2)	–0.245(2)	–0.117(1)	0.06(1)
C(16)	–0.035(1)	–0.207(3)	–0.1598(8)	0.066(9)
C(17)	0.059(1)	–0.248(2)	–0.1114(7)	0.038(8)
C(18)	–0.045(1)	–0.377(3)	–0.1108(8)	0.057(8)
C(19)	–0.043(1)	–0.433(2)	–0.0737(7)	0.036(6)
C(20)	–0.068(1)	–0.573(2)	–0.0696(7)	0.048(7)
N(21)	–0.0199(9)	–0.373(2)	–0.0450(7)	0.043(6)
C(22)	–0.021(1)	–0.430(3)	–0.0057(8)	0.068(8)
C(23)	–0.068(1)	–0.376(3)	0.0179(9)	0.08(1)
C(24)	–0.058(1)	–0.234(3)	0.029(1)	0.07(1)
N(25)	–0.061(1)	–0.138(2)	–0.0012(7)	0.054(6)
C(26)	–0.129(1)	–0.121(3)	–0.0157(8)	0.070(9)
C(27)	–0.135(1)	–0.059(2)	–0.0548(7)	0.062(8)
C(28)	–0.113(1)	–0.137(3)	–0.0873(8)	0.072(9)
N(29)	–0.0415(9)	–0.148(2)	–0.0890(6)	0.039(5)
Cu(101)	0.3502(1)	0.0462(3)	0.20818(9)	0.040(2)
Ni(101)	0.2469(2)	–0.1790(3)	0.02489(1)	0.036(2)
N(101)	0.494(1)	–0.083(2)	0.1324(6)	0.050(7)
C(101)	0.543(1)	0.014(2)	0.1223(7)	0.049(7)
O(102)	0.556(1)	–0.222(2)	0.1028(7)	0.078(7)
C(102)	0.509(1)	–0.213(2)	0.1245(7)	0.030(6)
N(103)	0.476(1)	–0.313(2)	0.1374(6)	0.052(6)
C(103)	0.492(1)	–0.441(3)	0.1225(8)	0.066(9)
O(104)	0.3960(8)	–0.394(2)	0.1729(5)	0.062(6)
C(104)	0.425(1)	–0.301(3)	0.1627(7)	0.042(7)
O(105)	0.3207(8)	–0.228(1)	0.2126(6)	0.047(5)
N(105)	0.3560(9)	–0.139(2)	0.1974(6)	0.043(6)
C(105)	0.405(1)	–0.170(2)	0.1736(7)	0.039(7)
N(106)	0.4119(8)	0.055(2)	0.1656(5)	0.036(5)
C(106)	0.441(1)	–0.054(2)	0.1555(7)	0.049(7)
C(107)	0.426(1)	0.175(2)	0.1446(6)	0.038(6)
C(108)	0.370(2)	0.267(2)	0.1546(9)	0.06(1)
C(109)	0.370(1)	0.328(2)	0.1942(7)	0.046(7)
N(110)	0.352(1)	0.225(2)	0.2209(7)	0.045(7)
C(110)	0.346(1)	0.260(2)	0.2512(8)	0.024(6)
N(111)	0.354(1)	0.377(2)	0.2744(6)	0.050(6)
C(111)	0.394(1)	0.483(2)	0.2597(7)	0.047(7)
O(112)	0.3384(7)	0.452(2)	0.3345(5)	0.055(5)
C(112)	0.334(1)	0.362(2)	0.3120(7)	0.039(7)
N(113)	0.309(1)	0.249(2)	0.3206(7)	0.055(8)
C(113)	0.270(1)	0.211(2)	0.3505(7)	0.046(7)
O(114)	0.2892(7)	0.002(1)	0.2480(4)	0.036(4)
N(114)	0.2809(9)	0.070(2)	0.2826(6)	0.044(6)
C(114)	0.309(1)	0.175(2)	0.2840(6)	0.031(6)
C(115)	0.226(1)	–0.240(2)	0.3281(9)	0.037(8)
C(116)	0.202(1)	–0.206(3)	0.3669(9)	0.071(9)
C(117)	0.300(1)	–0.243(2)	0.3278(8)	0.040(8)
C(118)	0.195(1)	–0.369(2)	0.3185(7)	0.044(7)
C(119)	0.202(1)	–0.431(2)	0.2782(7)	0.047(7)
C(120)	0.173(1)	–0.568(2)	0.2788(7)	0.054(7)
N(121)	0.2214(8)	–0.364(2)	0.2492(6)	0.035(5)
C(122)	0.217(1)	–0.421(2)	0.2132(7)	0.049(7)
C(123)	0.168(1)	–0.360(2)	0.1858(7)	0.057(8)
C(124)	0.176(1)	–0.217(2)	0.1767(9)	0.055(8)
N(125)	0.177(1)	–0.131(2)	0.2109(7)	0.068(7)
C(126)	0.107(1)	–0.123(3)	0.2253(8)	0.070(9)
C(127)	0.105(1)	–0.045(2)	0.2614(7)	0.059(7)
C(128)	0.127(1)	–0.130(2)	0.2961(7)	0.062(8)
N(129)	0.200(1)	–0.142(2)	0.3005(6)	0.044(6)
Cl(1)	0.1677(5)	0.2043(9)	0.1716(3)	0.077(6)
O(30)	0.107(2)	0.169(3)	0.1547(8)	0.16(1)
O(31)	0.191(1)	0.322(2)	0.1494(7)	0.121(9)
O(32)	0.214(1)	0.094(2)	0.1626(7)	0.129(9)
O(33)	0.170(1)	0.224(2)	0.2100(9)	0.108(8)
Cl(2)	0.4322(5)	0.3069(8)	0.0368(3)	0.071(6)
O(34)	0.428(1)	0.300(3)	–0.0017(9)	0.128(9)
O(35)	0.4548(9)	0.189(2)	0.0496(6)	0.084(6)
O(36)	0.369(2)	0.338(3)	0.051(1)	0.20(1)
O(37)	0.478(1)	0.405(2)	0.0430(7)	0.127(9)
Cl(3)	0.2534(4)	0.4303(9)	0.4423(3)	0.083(6)
O(38)	0.216(1)	0.452(3)	0.4764(8)	0.15(1)
O(39)	0.301(1)	0.529(2)	0.4395(6)	0.118(8)
O(40)	0.209(1)	0.440(2)	0.4110(6)	0.095(7)
O(41)	0.279(1)	0.295(3)	0.4456(7)	0.131(9)
Cl(4)	–0.0140(4)	0.5755(8)	0.2668(3)	0.069(6)
O(42)	0.028(1)	0.563(2)	0.3001(6)	0.085(7)
O(43)	–0.051(1)	0.688(3)	0.2704(7)	0.135(9)
O(44)	–0.063(1)	0.481(2)	0.2606(7)	0.109(8)
O(45)	0.022(1)	0.561(2)	0.2317(7)	0.119(8)
O(46)	0.271(2)	0.264(2)	–0.0233(9)	0.16(1)
O(47)	0.022(2)	0.236(2)	0.2403(9)	0.14(1)

[a] U has been defined as $U = {}^1/_3\sum_i\sum_j U_{ij}(a_i^*\cdot a_j^*)(a_i\cdot a_j)$. [b] The z-coordinate has been fixed for fixing the origin.

a square pyramidal geometry. The four nitrogen atoms of the basal plane are almost coplanar; the deviation of the copper(II) from the mean basal plane toward the axial donor is 0.152(1) Å. The dihedral angles between the mean basal plane and the aromatic uracil rings are 11.7(1) and 8.27(9)°, indicating that the entire molecule is essentially planar.

The tetradentate behaviour of the ligand results in the formation of two nearly equivalent five-membered chelate rings including nitroso and amino nitrogen atoms and one six-membered chelate ring including the $-N-(CH_2)_3-N-$ fragment. The latter ring exhibits a boat conformation.

Because the ligand acts in a double-deprotonated fashion there are neither amino nor oxime protons in **1**. In good accord with this, the average N–O, C–N (nitroso) bond lengths and C–N–O bond angle of 1.240 and 1.345 Å and 120.6°, respectively, agree quite well with the values 1.26 ± 0.02 and 1.36 ± 0.02 Å and 121 ± 2° found for several oximato complexes only containing dissociated oxime groups.[15] Likewise, bond lengths and angles in the $C(NR)—C(N{=}O)—C{=}O$ fragments compare quite well with those observed for complexes of the related ligand 6-amino-3-methyl-5-nitrosouracil,[16] in which, like H_2L in **1**, the ligand is coordinated through the nitrogen atoms of the nitroso group and the deprotonated amino group. Indeed, the ligand is found to be in the keto–nitroso form since, in both halves of **1**, C–O and N–O bond distances are close to those expected for double bonds, whereas C–N(amine) and C–N(nitroso) bond lengths are intermediates between those corresponding to a single and a double bond. The remaining bond lengths and angles of the ligand molecule in the structure do not differ significantly from those reported for other complexes of related ligands.[10,16]

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(15) Korvenranta, J.; Saarinen, H.; Nasakkala, M. *Inorg. Chem.* **1982**, *21*, 4296.

(16) Romero, M. A.; Moreno, M. N.; Ruiz, J.; Sanchez, P.; Nieto, F. *Inorg. Chem.* **1986**, *25*, 1498.

Scheme 2

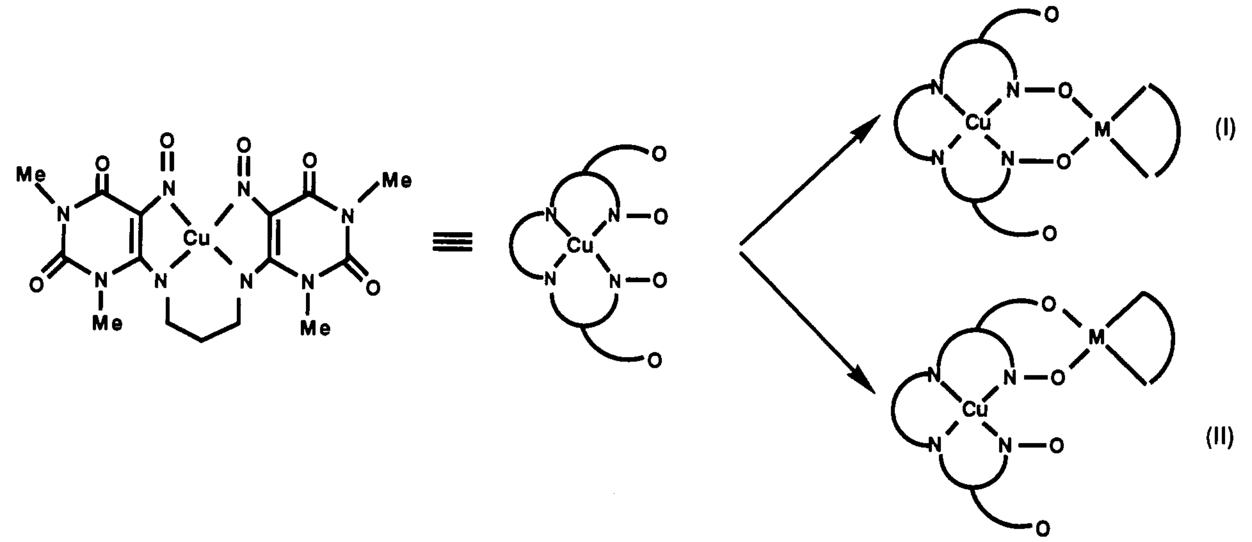

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **1**

Cu–N(5)	2.019(3)	N(5)–O(5)	1.232(4)
Cu–N(15)	1.990(3)	N(15)–O(15)	1.248(4)
Cu–N(6)	1.979(3)	C(4)–O(4)	1.216(5)
Cu–N(16)	1.979(3)	C(14)–O(14)	1.221(4)
Cu–O(20)	2.284(2)	C(5)–N(5)	1.343(4)
C(15)–C(16)	1.458(5)	C(15)–N(15)	1.346(5)
C(5)–C(6)	1.460(5)	C(7)–C(8)	1.519(5)
C(6)–N(6)	1.287(5)	C(17)–C(8)	1.500(5)
C(16)–N(16)	1.283(4)		
N(5)–Cu–N(6)	80.4(1)	Cu–N(5)–O(5)	124.8(2)
N(5)–Cu–N(15)	100.4(1)	Cu–N(15)–O(15)	125.4(2)
N(5)–Cu–N(16)	175.3(1)	Cu–N(5)–C(5)	114.3(3)
N(5)–Cu–O(20)	92.0(1)	Cu–N(15)–C(15)	113.8(2)
N(6)–Cu–N(15)	166.6(1)	O(5)–N(5)–C(5)	120.6(3)
N(6)–Cu–N(16)	97.0(1)	O(15)–N(15)–C(15)	120.6(3)
N(6)–Cu–O(20)	100.0(1)	C(7)–C(8)–C(17)	114.2(3)
N(15)–Cu–N(16)	81.1(1)	Cu–N(6)–C(7)	121.7(2)
N(15)–Cu–O(20)	93.3(1)	Cu–N(16)–C(17)	121.6(2)
N(16)–Cu–O(20)	92.4(1)		
Relevant Hydrogen Bond Distances (Å)[a]			
$O(5)–O(20)^{I}$	2.750(3)	$O(15)–O(20)^{I}$	2.796(4)
$O(5)–O(22)^{I}$	2.955(4)	$O(15)–O(21)^{I}$	2.823(3)
$O(22)–O(23)^{II}$	2.797(5)	O(21)–O(23)	2.723(4)
O(20)–O(21)	2.745(4)	O(20)–O(22)	2.924(4)
$O(23)–O(2)^{III}$	2.852(4)		

[a] Key: (I) $1 - x, 1 - y, -z$; (II) $1 - x, -y, -z$; (III) $1 - x, -y, 1 - z$.

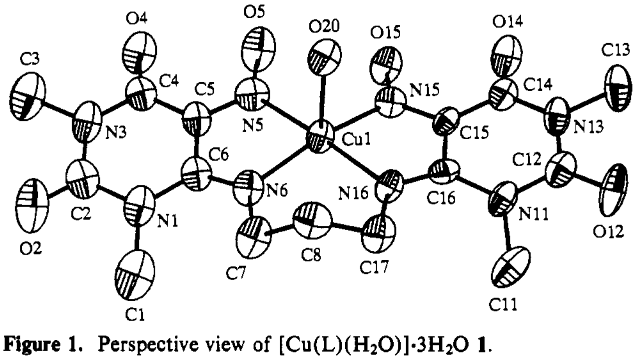

Figure 1. Perspective view of $[Cu(L)(H_2O)]\cdot 3H_2O$ **1**.

Each two $[Cu(L)(H_2O)]$ molecules are bridged by hydrogen bonds, including the oxygen atom O(20) of the coordinated water molecule belonging to a $[Cu(L)(H_2O)]$ molecule and the oxygen atoms $O(15)^{I}$ and $O(5)^{I}$ belonging to a neighboring symmetry-related (I: $1 - x$, $1 - y$, $-z$) molecule giving rise to a centrosymmetrical dinuclear unit with a $Cu\cdots Cu^{I}$ distance of 5.7139(2) Å.

These dinuclear units are connected by hydrogen bonds involving the nitroso oxygens O(5) and O(15) and the coordinated and noncoordinated water molecules leading to a centrosymmetrical ring consisting of eight molecules of water with a $Cu-Cu^{II}$ (II: $1 - x, -y, -z$) distance of 7.8565(8) Å. Owing to these hydrogen bond interactions, the compound may be considered as a zigzag chain of Cu(II) ions along the *b* axis. A simplified view of the hydrogen-bonded zigzag chain for **1** is given in Figure 2. Finally, the chains are interconnected by a hydrogen bond formed between the lattice water molecule O(23) and $O(2)^{III}$ (III: $1 - x, -y, 1 - z$) of a neighboring chain. Relevant hydrogen-bonding distances are also given in Table 5.

Crystal Structure of 2. The asymmetric unit cell of **2** contains one $[Cu(ClO_4)(\mu\text{-}L)Ni(CTH)]^+$ cation, one perchlorate anion and one non-bonded molecule of water. A perspective view of $[Cu(\mu\text{-}L)Ni(CTH)]$ cation together with the atom-labeling scheme is given in Figure 3. Selected bond lengths and angles are listed in Table 6.

As can be seen in Figure 3, the coordination of the precursor **1** to the $[Ni(CTH)]^{2+}$ moiety does not take place through the expected positions, O(15) and O(5), but through the exocyclic oxygen atom O(14) of one uracil ring and the N(15)–O(15) nitroso–oximato group disordered one two sets of crystallographic positions, one with a 78% occupancy (N(15)–O(15)) and the other with a 22% occupancy (N(15A)–O(15A)). This disorder leads to two different bridging conformations of the NO group, namely Cu–O(15)–N(15)–Ni and Cu–N(15A)–O(15A)–Ni. The first one gives rise to six- and five-membered rings including Cu(II) and Ni(II) ions, respectively, in the bridging region of the molecule, whereas in the second one those rings include Ni(II) and Cu(II) ions, respectively. Interestingly enough, the double bridge between Cu(II) and Ni(II) ions is of an asymmetrical nature. To the best of our knowledge, all Cu(II)–Ni(II) dinuclear complexes so far reported exhibited symmetrical double bridges.

Another noticeable feature of the structure is the *syn–anti* conformation that the N–O bridging group is forced to adopt, as a consequence of the existence of coordinating atoms (N(16) and O(14)) in the nearest-neighboring positions to the NO bridging group (see Chart 1, structure **IV**). It is well-known that oxime ligands can adopt many types of bridging conformations such as O-monoatomic (**V**), monoatomic and bidentate, (**VI**) and *syn–syn* (**VII**). It must be noted that even though numerous examples exist of well structurally characterized metal complexes containing types **VI** and **VII** of oxime bridging conformations,[5,6,17] to the best of our knowledge, no metal complexes with *syn–anti* oxime bridges (**IV**), as occurs in **2**, so far have been reported. Moreover,

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(17) Kurzak, B. Farkas, E.; Glowiak, T. Kozlowski, H. *J. Chem. Soc. Dalton Trans.* **1991**, 163.

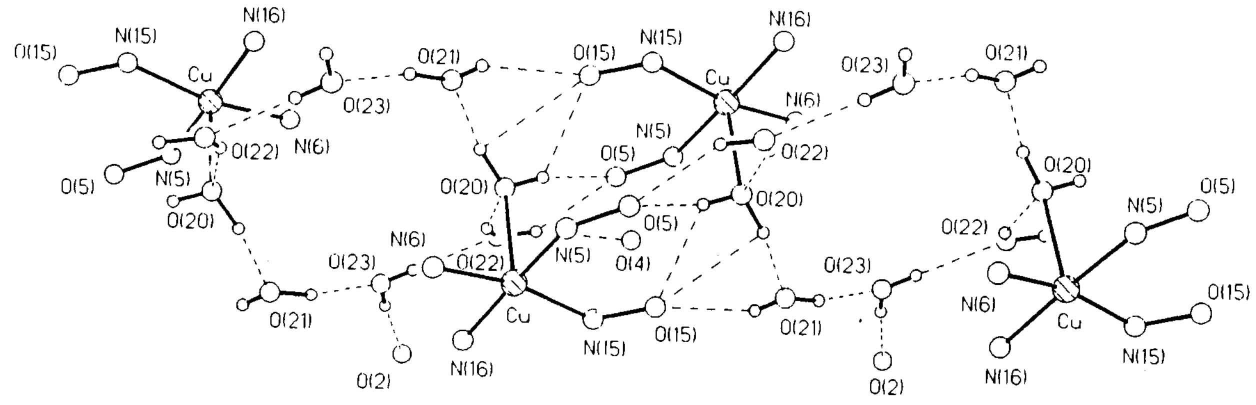


Figure 2. Simplified view of the hydrogen bonded zigzag chain of $[Cu(L)(H_2O)]\cdot 3H_2O$ **1**.

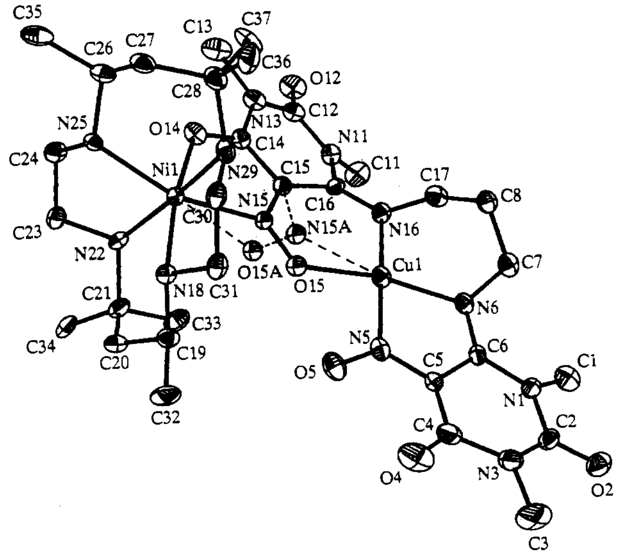
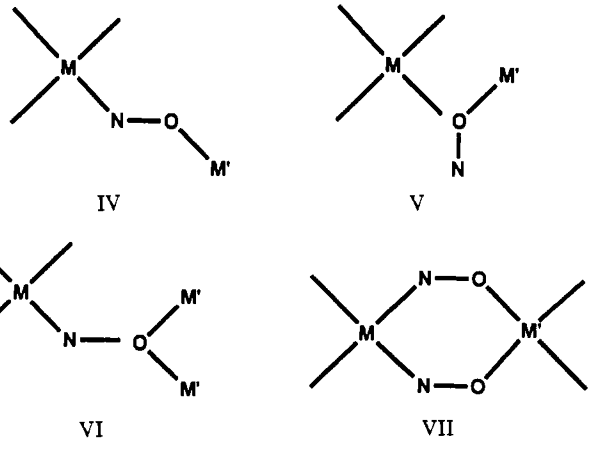


Figure 3. Perspective view of the cation $[Cu(ClO_4)(\mu\text{-}L)Ni(CTH)]^+$. Perchlorate anions and the molecule of water are omitted for clearity.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **2**

Cu–N(5)	1.983(5)	Cu–N(16)	1.963(5)
Cu–N(6)	1.978(6)	Cu–O(38)	2.69(2)
Cu–O(15)	1.969(7)	Cu–O(39A)	2.65(2)
Cu–N(15A)	2.13(3)	N(5)–O(5)	1.243(8)
N(15)–O(15)	1.26(1)	N(15A)–O(15A)	1.31(4)
N(5)–C(5)	1.357(9)	N(15)–C(15)	1.37(1)
N(15A)–C(15)	1.38(3)	C(5)–C(6)	1.44(1)
C(15)–C(16)	1.47(1)	C(6)–N(6)	1.301(9)
C(16)–N(16)	1.280(9)	C(4)–O(4)	1.19(1)
C(14)–O(14)	1.229(1)	Ni–N(15)	2.196(8)
Ni–O(15A)	2.08(2)	Ni–O(14)	2.091(4)
Ni–N(18)	2.077(5)	Ni–N(29)	2.169(6)
Ni–N(25)	2.136(6)	Ni–N(22)	2.152(6)
N(5)–Cu–N(6)	81.7(2)	N(5)–Cu–N(15A)	110.0(7)
N(5)–Cu–O(15)	84.9(3)	O(15)–Cu–N(15A)	25.1(7)
N(5)–Cu–N(16)	176.3(3)	O(15)–Cu–O(39A)	75.0(4)
N(5)–Cu–O(38)	80.2(4)	O(15)–Cu–N(16)	95.8(2)
N(5)–Cu–O(39A)	104.3(3)	O(15)–Cu–O(38)	99.5(5)
N(6)–Cu–O(15)	166.6(2)	N(15A)–Cu–N(16)	70.7(7)
N(6)–Cu–N(15A)	168.3(7)	N(15A)–Cu–O(38)	104.0(1)
N(6)–Cu–N(16)	97.6(2)	N(15A)–Cu–O(39A)	70.2(9)
N(6)–Cu–O(38)	78.0(5)	N(16)–Cu–O(38)	103.2(4)
N(6)–Cu–O(39A)	108.1(4)	N(16)–Cu–O(39A)	79.4(3)
O(38)–Cu–O(39A)	36.4(5)	O(14)–Ni–O(15A)	97.2(6)
O(14)–Ni–N(15)	73.1(2)	O(14)–Ni–N(15)	170.4(2)
O(14)–Ni–N(18)	97.9(2)	O(14)–Ni–N(25)	87.3(2)
O(14)–Ni–N(28)	88.1(2)	O(15A)–Ni–N(15)	24.2(6)
O(15A)–Ni–N(15)	73.6(6)	O(15A)–Ni–N(18)	87.0(7)
O(15A)–Ni–N(25)	174.8(6)	O(15A)–Ni–N(28)	98.2(6)
N(15)–Ni–N(15)	97.7(2)	N(15)–Ni–N(18)	88.0(3)
N(15)–Ni–N(25)	159.8(2)	N(15)–Ni–N(28)	99.6(3)
N(15)–Ni–N(18)	84.3(2)	N(15)–Ni–N(25)	102.0(2)
N(15)–Ni–N(28)	90.7(2)	N(18)–Ni–N(25)	89.7(2)
N(18)–Ni–N(28)	171.5(2)	N(25)–Ni–N(28)	84.5(2)

Chart 1



it is only recently that the first structurally characterized compound containing type–V bridging conformation has been reported.[6i]

The Cu(II) ion occupying the inside site of the double deprotonated ligand L^{2-} exhibits a 4 + 1 coordination environment. Four short bonds of *ca.* 2 Å are formed with N(5), N(6), and N(16) and with either O(15) (occupancy factor of 0.78) or N(15A) (occupancy factor of 0.22). The fifth position is occupied by a disordered oxygen atom, O(38) and O(39A), from a perchlorate anion with occupancy factors of 0.44 and 0.56, respectively. The disordered perchlorate anion is semicoordinated with Cu–O(38) and Cu–O(39A) bond distances of 2.69(2) and 2.65(2) Å, respectively. Both N_4O and N_3O_2 coordination polyhedra display a geometry very close to square pyramidal with τ values of 0.16 and 0.14, respectively. The four equatorial atoms N(5), N(6), N(16), and O(15) are coplanar with deviations from the least-square plane lower than 0.04 Å. However, the N(15A) atom deviates by 0.11(3) Å from the mean plane [N(5), N(6), N(16)k, N(15A)]. The copper ion is lifted less than 0.034(1) Å from the mean basal planes to the apical position.

A comparison of the structural results for **2** with those of **1** clearly points out that many important structural modifications occur in **1** after its coordination to the $[Ni(CTH)]^{2+}$ moiety: (i) The conformation of the nitroso–oximato bridging group with a 78% occupancy gives rise to a six-membered ring including copper(II) ion instead of the five-membered ring found in **1**. (ii) The conformation with 22% occupancy gives rise to, as in **1**, a five-membered ring, but in which the N(15A)–Cu (2.13(3) Å) and N(15A)–O(15A) (1.31(4) Å) bond distances are about 0.1 Å longer than the respective average values found in **1**. Moreover, the N(15A)–Cu–N(16) internal angle closes to 70.7(7)°, while the external angle is 110.0(7)°. (iii) The LCu part of the molecule is not coplanar, since the uracil ring containing the disordered

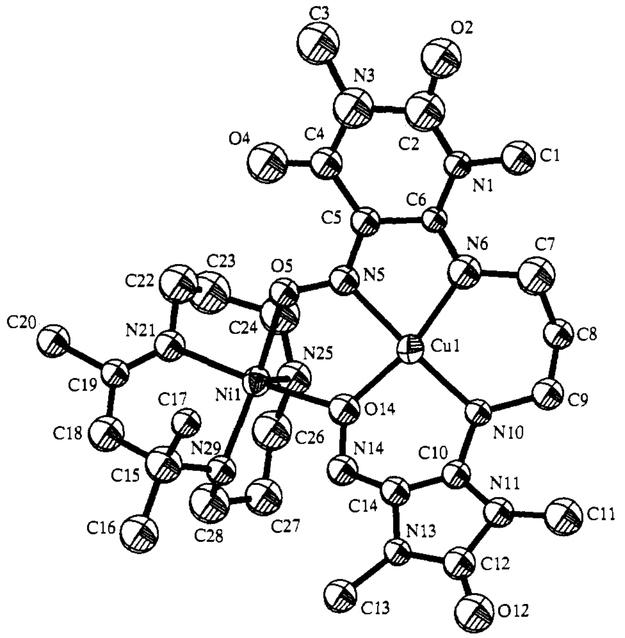


Figure 4. Perspective view of the cation $[Cu(ClO_4)(\mu\text{-}L^1)Ni(Me_3[12]N_3)]^+$. Perchlorate anions and the molecule of water are omitted for clearity.

NO and O(14) bridging groups is bent at the N(16) and O(15) positions. The dihedral angle between the mean plane defined by N(5), N(6), N(16), and O(15) and that of the pyrimidine ring N(11) to C(16) is 20.5(2)°. In addition, this ring shows significant deviations from planarity. Thus, the atoms C(16) and N(13) deviate by 0.163(8) and 0.120(7) Å, respectively, from the mean plane.

On the other hand, the remaining bond lengths and angles in the ligand molecule do not significantly differ from those found in **1**.

The nickel(II) ion is pseudooctahedrically coordinated by the four nitrogen atoms of the CTH ligand and O(14) and by either N(15) (occupancy factor of 78%) or O(15A) (occupancy factor of 22%) from the L^{2-} ligand. O(14), N(15) (or O(15A)), N(25), and N(18) define the equatorial plane whereas N(22) and N(29) are in apical positions. The N_4O_2 coordination polyhedron is somewhat less distorted than the N_5O one, since the N(25)–Ni–O(15A) trans angle is 174.8(6)° whereas the N(25)–Ni–N(15) is 159.8(2)°. It must be pointed out that the chelate coordination involving the O(4) exocyclic atom of the uracil moiety is quite unusual. This has been previously observed only in the complexes $[Cd(AMNU)_2]$[16] (where AMNU is the 6-amino-3-methyl-5-nitrosouracilato anion) and $[L^3\{Ni(CTH)\}_2](ClO_4)_2$[18] (where L^3 is α,ω-bis((1,3-dimethyl-5-nitrosouracil-6-yl)amino)butane). Bond lengths and angles in the CTH ligand itself have normal values.[8]

Intramolecular separation between metal ions is Cu···Ni = 4.972(1) Å. In the crystal, the copper atom of each dinuclear unit is weakly coordinated by the exocyclic oxygen atom O(2) $(1 - x, -^1/_2 + y, ^1/_2 - z)$ of the symmetrically related adjacent molecule, with a Cu–O(2) distance of 2.831(6) Å. Thus, the interaction between adjacent cations gives rise to an infinite zigzag chain running along *b* axis.

Crystal structure of 3. The asymmetric unit of **3** contains two crystallographically independent heterodinuclear cations $[Cu(ClO_4)(\mu\text{-}L^1)Ni(Me_3[12]N_3)]^+$, two nonbonded perchlorate anions and two lattice water molecules. A perspective view of the heterodinuclear cation for molecule I with the atom-numbering scheme is given in Figure 4. Selected bond distances and bond angles are given in Table 7.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **3**

Cu(1)–N(5)	1.99(2)	Cu(101)–N(105)	1.98(2)
Cu(1)–N(6)	1.97(2)	Cu(101)–N(106)	1.95(2)
Cu(1)–N(10)	1.95(2)	Cu(101)–N(110)	1.92(2)
Cu(1)–O(14)	1.89(2)	Cu(101)–O(114)	1.92(2)
Cu(1)–O(39)	2.79(2)	Cu(101)–O(44)	2.56(2)
Ni(1)–O(5)	2.02(2)	Ni(101)–O(105)	2.03(2)
Ni(1)–O(14)	2.08(1)	Ni(101)–O(114)	2.08(1)
Ni(1)–N(21)	2.01(2)	Ni(101)–N(121)	2.00(2)
Ni(1)–N(25)	2.06(2)	Ni(101)–N(125)	2.00(2)
Ni(1)–N(29)	1.98(2)	Ni(101)–N(129)	2.09(2)
N(5)–O(5)	1.30(2)	N(105)–O(105)	2.03(2)
N(14)–O(14)	1.35(3)	N(114)–O(114)	2.08(1)
N(5)–Cu(1)–N(6)	79.8(8)	N(105)–Cu(101)–N(106)	82.1(8)
N(5)–Cu(1)–N(10)	175.3(8)	N(105)–Cu(101)–N(110)	175.0(9)
N(5)–Cu(1)–O(14)	88.0(7)	N(105)–Cu(101)–O(114)	86.8(7)
N(5)–Cu(1)–O(39)	94.8(7)	N(105)–Cu(101)–O(44)	89.5(8)
N(6)–Cu(1)–N(10)	96.9(8)	N(106)–Cu(101)–N(110)	97.0(8)
N(6)–Cu(1)–O(14)	167.8(7)	N(106)–Cu(101)–O(114)	168.9(7)
N(6)–Cu(1)–O(39)	101.3(7)	N(106)–Cu(101)–O(44)	97.8(7)
N(10)–Cu(1)–O(14)	95.3(7)	N(110)–Cu(101)–O(114)	94.1(8)
N(10)–Cu(1)–O(39)	82.5(8)	N(110)–Cu(101)–O(44)	85.8(8)
O(14)–Cu(1)–O(39)	80.0(7)	O(114)–Cu(101)–O(44)	82.7(7)
O(5)–Ni(1)–O(14)	83.9(6)	O(105)–Ni(101)–O(114)	85.5(6)
O(5)–Ni(1)–N(21)	90.2(7)	O(105)–Ni(101)–N(121)	86.9(7)
O(5)–Ni(1)–N(25)	98.3(8)	O(105)–Ni(101)–N(125)	98.4(9)
O(5)–Ni(1)–N(29)	159.8(3)	O(105)–Ni(101)–N(129)	158.4(8)
O(14)–Ni(1)–N(21)	171.7(7)	O(114)–Ni(101)–N(121)	170.7(6)
O(14)–Ni(1)–N(25)	91.0(7)	O(114)–Ni(101)–N(125)	92.4(7)
O(14)–Ni(1)–N(29)	92.6(7)	O(114)–Ni(101)–N(129)	91.5(7)
N(21)–Ni(1)–N(25)	95.6(8)	N(121)–Ni(101)–N(125)	94.0(8)
N(21)–Ni(1)–N(29)	91.0(8)	N(121)–Ni(101)–N(129)	93.5(8)
N(25)–Ni(1)–N(29)	101.7(8)	N(125)–Ni(101)–N(129)	103.1(9)
Cu(1)–O(14)–Ni(1)	120.1(8)	Cu(101)–O(114)–Ni(101)	119.3(7)

A noticeable feature of the structure is the elimination of one CO molecule from a pyrimidine ring of the L^{2-} ligand in **1**, leading to an imidazole ring in **3**. It should be noted that a similar process has been shown to occur in other uracil derivatives such as 1,3-dimethyl-5,6-diaminouracil. When this compound is dissolved in water containing an iron(III) salt, it gives rise to 1,3-dimethyl-2,4,5-imidazoleinetrione in good yield. It seems to be that the elimination of CO and the simultaneous ring size reduction takes place through a nonaromatic intermediate.[19]

Within each heterodinuclear cation $[Cu(ClO_4)(\mu\text{-}L^1)Ni(Me_3[12]N_3)]^+$, copper(II) and nickel(II) are bibridged by two nitroso–oximate groups, one diatomic *syn–syn* and one O-monoatomic, from the pyrimidine and imidazole rings, respectively. This results in intramolecular copper–nickel distances of 3.440(4) and 3.452(4) Å for molecules I and II, respectively, which are much smaller than those found in **2**. The angles at the bridging oxygen Cu(1)–O(14)–Ni(1) and Cu(101)–O(114)–Ni(101) are 120.1(8) and 119.3(7)°, respectively. It should be noted that the coordination mode, in which an oxime group acts as a bridging ligand only through the oxygen atom, has recently been observed for the first time in the complex $\{[Cu_2(dmg)(Hdmg)(H_2dmg)]_2(SO_4)\}\cdot2.5H_2O$ (where H_2dmg is dimethylglyoxime).[6i]

The coordination geometry around each copper(II) ion is best described as a distorted square pyramidal CuN_4O (τ is 0.12 for molecule I and 0.10 for molecule II). The basal plane is defined by the N(6) and N(10) amine nitrogen atoms and the N(5) and O(14) atoms of the diatomic and monoatomic bringing groups, respectively, whereas an oxygen atom of a disordered perchlorate anion occupies the axial position. The four equatorial bonds around copper(II) ion for both molecules are similar, with values ranging from 1.92 to 1.97 Å, whereas the axial bonds are 2.80(2) (Cu–O(39)) and 2.60(2) Å (Cu–O(44)) for molecules I and II, respectively. The four equatorial atoms at each copper are practically coplanar with deviations from the least square plane lower than 0.09 Å. The copper atoms are lifted by 0.024(3) and

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[18] Colacio, E.; Escuer, A.; Kivekas, R.; Klinga, M.; Romerosa, A. Unpublished results.

[19] Okamoto, Y.; Ogura, K.; Kurasawa, Y.; Kinoshita, T. *Heterocycles* **1984**, *22*, 1231.

–0.038(4) Å from the corresponding mean planes. The coordination of the ligand to copper(II) results in the formation of two six-membered chelate rings and one five-membered chelate ring, like those observed in **2**.

The Ni(II) ion is in a distorted square pyramidal NiN_3O_2 environment (τ = 0.20 for molecule I and 0.21 for molecule II). The O(5) and O(14) atoms of the bridging nitroso-oximate groups and two nitrogen atoms of the ($Me_3[12]N_3$) ligand comprise the basal plane whereas the nitrogen atom N(25) occupies the axial position. The dihedral angle between the basal coordination planes of the CuN_4O and NiN_3O_2 square-pyramidal coordination polyhedra for molecules I and II are 7.8(6) and 6.9(4)°, respectively. The Ni–O and Ni–N bond lengths for molecules I and II are quite similar, with values ranging from 1.98(2) to 2.08(1) Å (average value 2.03 Å) and from 2.00(2) to 2.09(2) Å (average value 2.04 Å), respectively. These values are in agreement with those previously observed for other nickel(II) complexes containing the ($Me_3[12]N_3$) ligand.[9]

Magnetic Data. Although the main interest in **1** consists in its capability to behave as precursor for homo- and heteropolynuclear compounds, the existence of an extended network of hydrogen bonds connecting copper(II) atoms in this complex has driven us to perform a detailed study, including ESR spectroscopy and cryomagnetic susceptibility, in order to investigate the possible magnetic exchange coupling between copper(II) ions.

The *X*-band EPR spectrum of **1** at 290 and 90 K looks like that of an axial doublet ($g_\perp$ = 2.02, $g_\parallel$ = 2.11) with a $d_{x^2-y^2}$ ground state. However, a weak half-field forbidden transition, $\Delta M = \pm 2$, is observed at 90 K, clearly pointing out the presence of exchange coupling between copper(II) ions.

Magnetic susceptibility data were collected on a powdered sample in the range 5–280 K. The temperature dependence of the product $\chi_M T$, which is shown in Figure 5, reveals that the complex displays an overall antiferromagnetic behavior. Thus, from 280 to *ca.* 40 K, $\chi_M T$ remains practically constant and equal to 0.48 emu, in good accord with the value expected for isolated copper(II) ions. Lowering the temperature, $\chi_M T$ decreases, yielding a value of 0.25 emu at 5 K.

From the magnetic point of view, the complex **1** can be better viewed as $[Cu(L)(H_2O)]$ units held together in pairs by hydrogen bonds so that the experimental susceptibilities corrected for the diamagnetism of the ligands (L and H_2O) were fitted to the Bleaney–Bowers equation to yield $2J$ = –2.3 cm^{-1} and g = 2.11 with $R = 1.2 \times 10^{-3}$. It must be pointed out that the fit of the data to polynuclear chain model of interaction did not yield any improvement of the fit.

The $2J$ value is much smaller than those observed for the majority of the copper(II) complexes of amino- or imino-alcohols containing triatomic OH···O bridges[20] ($2J$ varying up to *ca.* 100 cm^{-1}), but higher than those for the complexes $[Cu_2(tren)_2X_2]^{2+}$ (where X = NCS or NCO and tren, 2,2′,2″-triaminotriethylamine) with extended bridges of the type Cu–X···H–N–Cu[21] ($2J < -0.16$ cm^{-1}). Assuming that in **1** the exchange interaction is supported by the bridging networks Cu–N(5)–O(5)···H–O(20)^I–Cu^I (and Cu–N(15)–O(15)···H–O(20)^I–Cu^I) a better comparison can be made with hydrogen-bonded dinuclear complexes having exchange pathways of similar extended nature and involving a position on the copper(II) ion where the unpaired spin density is very weak. This is the case of the complex $[Cu_2(tren)_2(CN)_2](BPPh_4)$,[22] for which a $2J$ value of –3.6 cm^{-1} has been reported. In view of this the observed value for **1** is not unexpected.

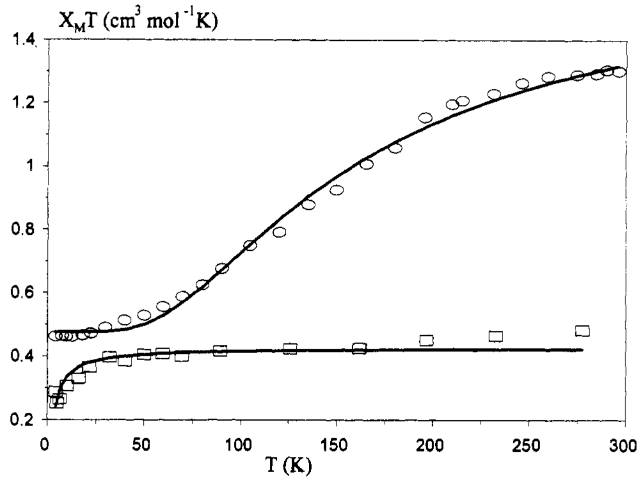

Figure 5. Temperature dependence of $\chi_M T$ for **1** (□) and **2** (○). Solid lines were generated from the best-fit magnetic parameters.

Magnetic susceptibility data for **2** and **3** were collected on powdered samples in the range 4.2–298 K. While for **2**, the $\chi_M T$ values decrease continuously upon cooling reaching a plateau below *ca.* 50 K with $\chi_M T$ = 0.50 emu, for **3**, $\chi_M T$ remains practically constant and equal to 0.5 cm^3 K mol^{-1}, in all the temperature range. The two low-lying states for a copper(II)–nickel(II) pair are a spin doublet and a spin quartet, which are separated by an energy of $3J/2$. The magnetic behavior of both complexes clearly shows that the spin doublet is the lowest, which is evidence of an antiferromagnetically coupled Cu(II)–Ni(II) pair. For **2**, below 50 K only the $S = {}^1/_2$ state is thermally populated, whereas for **3**, the spin exchange interaction is so strong as to attain a complete or nearly complete spin coupling even at room temperature.

The analysis of the magnetic data was carried out by using the theoretical expression of $\chi_M T$ for such a compound, in which the zero field splitting within the quartet state is neglected (the spin Hamiltonian was taken in the form $H = -J{\cdot}S_1{\cdot}S_2$):

$$\chi_M T = \left(\frac{N\beta^2}{4k}\right)\frac{\left[g_{1/2}{}^2 + 10g_{3/2}{}^2\exp\left(\frac{3J}{2kT}\right)\right]}{1 + 2\exp\left(\frac{3J}{2kT}\right)}$$

Here χ_M denotes the susceptibility per heterobinuclear molecule, $g_{1/2}$ and $g_{3/2}$ are the g factors associated with the doublet and quartet states, respectively, and the remaining symbols have their usual meanings. $g_{1/2}$ and $g_{3/2}$ may be related to the local factors g_{Cu} and g_{Ni} according to[23]

$$g_{1/2} = -{}^1/_3 g_{Cu} + {}^4/_3 g_{Ni}$$

$$g_{3/2} = {}^1/_3 g_{Cu} + {}^2/_3 g_{Ni}$$

Least-squares fitting of the experimental data for **2** (Figure 5) leads to J = –123.6 cm^{-1}, g_{Cu} = 2.30 and g_{Ni} = 2.24 and $R = 5 \times 10^{-4}$. For complex **3** a complete spin coupling at room temperature means a J value larger than –500 cm^{-1}. The energy gap between doublet and quartet states is *ca.* 184 and >750 cm^{-1} for complexes **2** and **3**, respectively.

Complexes **2** and **3** have rather different powder EPR spectra (Figure 6). Thus, at room temperature the spectrum of **2** exhibits a very large and intense signal centered at g = 2.20 and a smaller and broad one at t = 4.40. The intensity of the first signal is independent of the temperature but becomes narrower and sharper upon cooling down. The intensity of the second signal progressively decrease as does the temperature and disappears at N_2 liquid temperature. Similar EPR spectra have been recently

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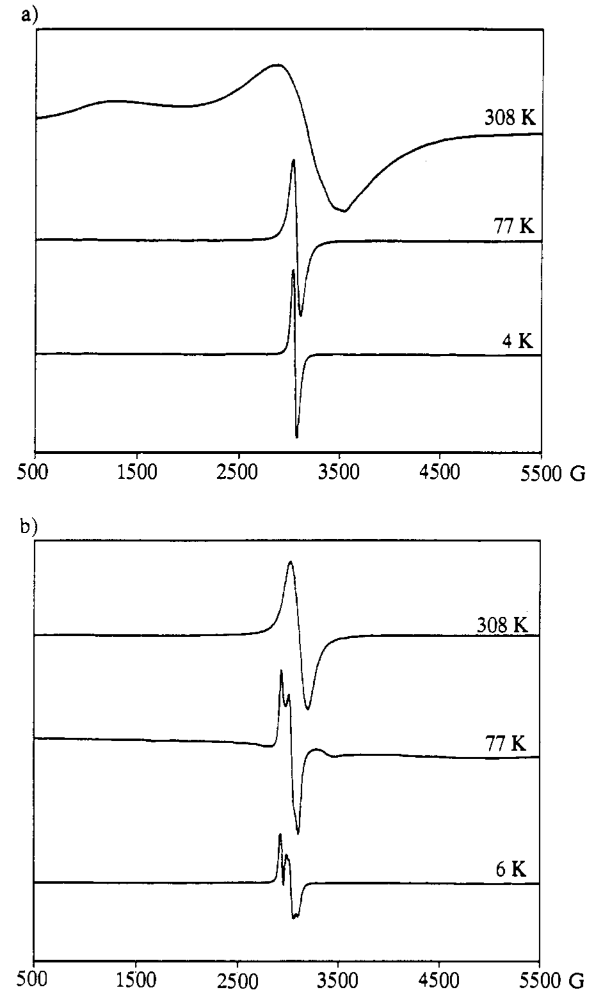

Figure 6. X-band powder EPR spectra at different temperature for **2** (a) and **3** (b).

reported for copper(II)–nickel(II) complexes with oxamidate derivatives bridging ligands.[13b,24] Obviously, the temperature dependence of the EPR spectra does not correspond to that expected for a single doublet ground state. This fact can be explained in a satisfactory way by assuming the existence of a moderately strong zero-field splitting (ZFS) within the quartet state, which leads to two Kramers doublets, $|^3/_2,\pm^1/_2\rangle$ and $|^3/_2,\pm^3/_2\rangle$. If an axial symmetry is assumed in the ZFS, the allowed $|^3/_2,\pm^1/_2\rangle \rightarrow |^3/_2,\pm^3/_2\rangle$ transition may produce two anisotropic signals, one near to the g_e value ($g = 2.25$) and other one about half-field ($g = 4.40$).[25] When the temperature is lowered to about 77 K, the quartet is depopulated, as revealed by the magnetic study, then both signals disappear and only the isotropic signal corresponding to the allowed transition within the $S = {}^1/_2$ ground state remains in the spectrum.

Magnetic data of complex **3** clearly showed that only the $S = {}^1/_2$ state is thermally populated at room temperature. In good accord with this, the powder EPR spectrum of **3** does not exhibit any signal at about $g = 4$ and furthermore, the signal at $g = 2.25$ is narrower and sharper than that observed for **2**. On the other hand, as the sample is cooling down from room temperature, the signal at $g = 2.25$ becomes anisotropic, and at 4.12 K, four signals are clearly resolved in the range $g = 2.18$–2.30. This agrees with the fact that the calculated g tensors of pentacoordinated nickel(II) centers are much more anisotropic than those of octahedral nickel(II) centers in CuNi complexes.[26] However, it must be pointed out that the number of observed signals does not correspond to that expected for a simple ground doublet state. Probably, the observed spectrum is the result of the superimposition of two doublet spectra, one for each crystallographically independent CuNi molecule in the asymmetric unit.

Analysis of the magnetic data has shown that compounds **2** and **3** exhibit a very different exchange coupling. This fact must be primarily due to the structural differences in the bridging networks, since, in both complexes, the metal orbits involved in the exchange interaction, $d_{x^2-y^2}$ for copper(II) and $d_{x^2-y^2}$ and d_{z^2} for nickel(II), are favorably oriented to interact with orbitals of the bridging groups.

As indicated above, in complex **2**, copper(II) and nickel(II) ions are bibridged by one nitroso–oximate group and the O(14) exocyclic atom from an uracil ring. The exchange interaction must be mainly supported by the former group since the exchange pathway involving O(14) is rather extended. The poorer support of the exchange provided by this pathway is evidenced by the weak exchange interactions observed for the complexes [{Cu(L′)(py)}·3H_2O][27] and [Cu(L′)(Him)]$_2$[28] (L′ = 5-(2′-carboxyphenyl)azo)-1,3-dimethylbarbituric acid and Him = imidazole), which have an exchange pathway very similar to that involving O(14) in **2**.

Indeed, bridging oximate groups are known to be very efficient in mediating very strong antiferromagnetic interaction, which are provided by an orbital exchange pathway essentially of σ nature. Thus, for instance, bi- and trinuclear copper(II) complexes with double oximate bridges generally exhibit complete or nearly complete spin coupling even at room temperature.[5] In connection with this, it may be noted that the dinuclear complex [Cu(μ-L)Cu(bipy)]$(ClO_4)_2$,[29] (where bipy is 2,2′-bipyridyl) with the same ligand as **2** and double oximato bridges in cis arrangement, is diamagnetic at room temperature. In view of this, the magnitude of J for **2** (−126.3 cm^{-1}) is not unexpected. This value is very close to those previously reported for copper(II)–nickel(II) complexes with oxamido bridging ligands[13b,30] but lower than those for copper(II)–nickel(II) containing bis(phenolate).[31]

The dramatic increase in antiferromagnetic coupling of **3** with respect to **2** may be related with the existence in the former of an O-monoatomic NO bridging group with an average Cu–O–Ni bond angle of 119.7°. In this way, extended-Hückel calculations by means of the CACAO[32] program show that the gap existing in the HOMO–LUMO region is poorly sensitive to the coordination of the NO group, either in the *syn–syn* conformation or in the *syn–anti* one, to those observed for **3** and **2**, respectively, and to the M–N–O or M–O–N bond angles.

On the other hand, it is well-known that, in planar bis(μ-hydroxo)copper(II) dimers, the antiferromagnetic coupling increases as does the Cu–O–Cu bridging angle for values larger than 97.5°.[33] Thus, for Cu–O–Cu bridging angles of 104.4° a $2J$ value of −509 cm^{-1} has been reported.[34] Other systems also

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containing Cu–O–Cu bridges seems to follow a similar trend. Bis(μ-phenoxide)[35] and bis(μ-pyridine *N*-oxide)[36] complexes with Cu–O–Cu angles of 101.8 and 110.0° and $2J$ values of −857 and −935 cm^{-1}, respectively, are good examples of this. Relevant to this discussion is the complex $[Cu(HB(3,5\text{-}iPr_2pz)_3)]_2(OH)(N_3)$[37] (where $HB(3,5\text{-}iPr_2pz)$ is tris(3,5-diisopropylpyrazolyl)borate), which contains one hydroxo bridge with a Cu–O–Cu angle of 148.4° and one end-to-end azide bridge and exhibits diamagnetic behavior at room temperature.

Specially interesting for comparative purposes is the magnetic behavior observed for the dinuclear complex $[\{Cu_2(dmg)(HDmg)(H_2dmg)\}_2(SO_4)]\cdot 2.5H_2O$.[6i] This complex, which contains a bridging network analogous to that found in **3**, with a Cu–O–Cu angle of 114.2°, exhibits a very strong antiferromagnetic interaction with $J = -950$ cm^{-1}. It is must be pointed out that this J value is similar to that reported for the analogous complex containing double oximate bridges in cis arrangement with $J > 1000$ cm^{-1}.[6e]

From above considerations, one may qualitatively understand the magnitude of the interaction in **3**, since both the diatomic NO bridging group and the O-monoatomic one, with a relatively large Cu–O–Ni briding angle of 119.7°, favor a very strong antiferromagnetic exchange interaction, which leads to a nearly complete spin coupling at room temperature.

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Supplementary Material Available: Tables S1–S7, listing crystallographic data, fractional hydrogen atom coordinates, and isotropic and anisotropic thermal parameters for complexes **1**–**3** (8 pages). Ordering information is given on any current masthead page.

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