

A μ -hydroxy- μ -nitritodicopper(II) core embedded in a AgNO_2 matrix: synthesis, structure and magnetism

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Received 2nd July 1998, Accepted 29th September 1998

The copper complex $[\text{L}_2\text{Cu}_2(\mu\text{-NO}_2)(\mu\text{-OH})\text{Ag}_2(\text{NO}_2)_4]$ ($\text{L} = 1,4,7$ -trimethyl-1,4,7-triazacyclononane) has been synthesized and characterized by X-ray crystallography and from temperature-dependent susceptibility measurements which established a fairly strong, intramolecular, antiferromagnetic exchange coupling ($J = -193 \text{ cm}^{-1}$, $H = -2JS_1 \cdot S_2$, $S_1 = S_2 = 1/2$) and the 1,2-co-ordination mode of the nitrito bridge to be an extremely good mediator of spin coupling.

Introduction

The co-ordination mode of the nitrite ion is unusual, because of the number of different ways in which it can bind to a metal.¹⁻¹⁵ Towards Cu^{II} it behaves as a monodentate ligand *via* either nitrogen or oxygen; it can also act either in a symmetrical end-to-end μ -1,3 ONO-bridging mode, the unsymmetrical two-atom O,N mode or *via* a single oxygen atom. A few examples of tridentate behaviour are also known. Although there is a long history and a prolific literature on the subject of exchange coupling in binuclear copper(II) complexes,¹⁶ unsymmetrical dibridged systems, particularly those containing nitrite ions, are, however, not well documented.^{2,7} So it is of interest to learn how nitrite reacts with binuclear copper species particularly from the viewpoints of structure and exchange coupling.

Moreover, Cu-NO_x complexes are relevant in the study of copper-containing enzymes involved in the denitrification process,¹⁷ *i.e.* the bacterial dissimilatory reduction of nitrate and nitrite to NO , N_2O and N_2 . In particular, copper-nitrite complexes are potentially relevant to the nitrite reductases which convert NO_2^- into NO and/or N_2O , reactions presumed to proceed by nitrite binding to copper(II).

With the above points in mind we prepared the copper complex $[\text{L}_2\text{Cu}_2(\mu\text{-NO}_2)(\mu\text{-OH})\text{Ag}_2(\text{NO}_2)_4]$ **1** ($\text{L} = 1,4,7$ -trimethyl-1,4,7-triazacyclononane), which contains *one* two-atom O,N-bridging nitrite and *one* hydroxo group and can be considered as a binuclear copper(II) complex, magnetically diluted with Ag^+ and NO_2^- ions. Here we report the synthesis, crystal structure and the exchange coupling constant determined from the temperature-dependent magnetic susceptibility data of **1**. In this connection **1** will also be compared with another copper(II) complex,⁷ in which the metal ions are also unsymmetrically dibridged but *via* an alkoxide and a nitrito ligand.

Experimental

The ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (**L**) was prepared according to a published procedure.¹⁸ All other reagents were used as received. Microanalyses were performed by Mikroanalytisches Laboratorium Dornis and Kolbe, Mülheim an der Ruhr. Copper was determined gravimetrically by using *N*-benzoyl-*N*-phenylhydroxylamine. Fourier transform IR spectroscopy on KBr pellets was performed on a

Perkin-Elmer 2000 FT-IR instrument. Magnetic susceptibilities of powdered samples were recorded on a SQUID magnetometer (MPMS, Quantum Design) in the temperature range 2–290 K with an applied field of 1 T. Experimental susceptibility data were corrected for the underlying diamagnetism using Pascal's constants. Mass spectra were recorded in the electrospray-ionization (ESI) mode in acetonitrile using a V 8200 spectrometer.

Preparation of $[\text{L}_2\text{Cu}_2(\mu\text{-NO}_2)(\mu\text{-OH})\text{Ag}_2(\text{NO}_2)_4]$ **1**

1,4,7-Trimethyl-1,4,7-triazacyclononane (0.51 g, 3 mmol) was added to a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.40 g, 2.4 mmol) in distilled methanol (80 ml). The solution was stirred at room temperature for 15 min. To the resulting deep green solution AgNO_2 (1.85 g, 12 mmol) was added and the suspension stirred for 2 h. The precipitated AgCl and the residual AgNO_2 were filtered off and the deep green filtrate was concentrated to about 50 ml, when the crystallization started. The suspension was cooled to 4 °C for 2 h and the green crystals were collected by filtration and air-dried. Yield: 0.27 g (24%) (Found: C, 23.2; H, 4.7; Ag, 23.1; Cu, 23.4; N, 16.6. Calc. for $\text{C}_{18}\text{H}_{43}\text{Ag}_2\text{Cu}_2\text{N}_{11}\text{O}_{11}$: C, 23.19; H, 4.65; Ag, 23.14; Cu, 23.19; N, 16.52%). IR (KBr, cm^{-1}): 3500–3400(br)m, 1465s,m, 1270s and 1009s,m. UV-VIS in CH_3CN : λ/nm ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$) 635(154) and 1000(58.6). ESI-MS(CH_3CN): m/z (relative intensity, %) 934 (1), 914 (1), 606 (100), 560 (40), 514 (38) and 280 (65).

Crystal structure determination

The crystallographic data for complex **1** are summarized in Table 1. Graphite monochromated Mo-K α X-radiation was used. Intensity data collected at 293(2) K were corrected for Lorentz-polarization and absorption effects (ψ scans) in the usual manner. The structures were solved by direct methods by using the Siemens SHELXTL-V5 package.¹⁹ The function minimized during full-matrix least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. The hydrogen atoms were placed at calculated positions with isotropic thermal parameters and refined with a riding model. All non-hydrogen atoms were refined with anisotropic thermal parameters.

CCDC reference number 186/1181.

See <http://www.rsc.org/suppdata/dt/1998/3801/> for crystallographic files in .cif format.

Table 1 Crystallographic data for $[\text{L}_2\text{Cu}_2(\text{NO}_2)(\text{OH})\text{Ag}_2(\text{NO}_2)_4] \mathbf{1}$

Formula	$\text{C}_{18}\text{H}_{43}\text{Ag}_2\text{Cu}_2\text{N}_{11}\text{O}_{11}$
Formula weight	932.44
Crystal size/mm	$0.44 \times 0.15 \times 0.13$
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
$a/\text{\AA}$	8.726(2)
$b/\text{\AA}$	17.216(3)
$c/\text{\AA}$	21.631(4)
$V/\text{\AA}^3$	3249.6(11)
Z	4
$D_c/\text{g cm}^{-3}$	1.904
Diffractometer	Siemens R3m/V
$\lambda(\text{Mo-K}\alpha)/\text{\AA}$	0.71073
μ/mm^{-1}	2.546
$F(000)$	1868
θ Range/ $^\circ$	2.22–27.56
Index ranges	$-11 \leq h \leq 0, 0 \leq k \leq 22,$ $0 \leq l \leq 28$
Reflections collected	4215
Maximum, minimum transmission	0.903, 0.344
Data/restraints/parameters	4213/0/406
$R1, wR [I > 2\sigma(I)]$	0.0716, 0.1586
(all data)	0.1382, 0.2012

$$^a R1 = \sum(|F_o| - |F_c|) / \sum F_o$$

Results and discussion

That the reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with the macrocyclic amine ligand **L** in methanol affords the dichloride salt of the cation $[\text{Cu}_2(\mu\text{-Cl})_2\text{L}_2]^{2+}$ is known from our earlier work.²⁰ Treatment of the mentioned dication with AgNO_2 affords complex **1**, which is presumably formed by substitution of a bridging hydroxo group²¹ in $[\text{Cu}_2(\mu\text{-OH})_2\text{L}_2]^{2+}$ by a nitrite ion. Complex **1** can be considered as a cluster formed through the interaction of the ions $[\text{Cu}_2(\text{NO}_2)(\text{OH})\text{L}_2]^{2+}$ and $[\text{Ag}_2(\text{NO}_2)_4]^{2-}$. It is interesting in this connection that the azide analogue of the cation in **1** contains a symmetrical 1,1-azide bridging mode.²⁰

Besides the bands belonging to the macrocyclic amine **L** in the IR spectrum complex **1** exhibits a broad, medium-intense band in the region 3500 cm^{-1} , which can be assigned to $\nu(\text{OH})$. The sharp bands at 1465 and 1009 cm^{-1} are due to $\nu(\text{N}=\text{O})$ and $\nu(\text{N}-\text{O})$, respectively, indicating the $\mu(\text{NO})$ bridging mode of the nitrito ligand, whereas the strong band at 1270 cm^{-1} is assignable to the $\nu_{\text{sym}}(\text{NO}_2)$ mode showing a three-co-ordinate nitrite group. A sharp but weak band is also observed at 893 cm^{-1} , which may be due to the wagging mode $\delta(\text{ONO})$ vibration. Thus the IR spectrum clearly excludes the monodentate bonding *via* a single oxygen atom of the nitrite ion¹ in **1**.

The ESI mass spectrum of complex **1** was recorded in acetonitrile solution. The indication that **1** contains silver atoms was first obtained from the ESI-MS data. The isotope pattern of the signals characterizes the number of silver atoms in the masses. Selected signals (m/z) in the ESI-MS of **1**, including the assignments, are $934[\text{L}_2\text{Cu}_2(\text{OH})(\text{NO}_2)_5\text{Ag}_2]$, $914[\text{L}_2\text{Cu}_2(\text{NO}_2)_5\text{Ag}_2]$, $606[\text{L}_2\text{Cu}_2(\text{NO}_2)_3]$, 100 , $560[\text{L}_2\text{Cu}_2(\text{NO}_2)_2]$, 40 , $514[\text{L}_2\text{Cu}_2\text{NO}_2]$, 38 and $280[\text{LCuNO}]$, 65%. These data are in accord with the structure determination described below.

The electronic spectrum of complex **1** in acetonitrile is consistent with the square-pyramidal CuN_3O_2 and CuN_4O chromophores since it displays two weak d-d transitions in the visible region at 635 ($\epsilon = 154$) and at 1000 nm ($59 \text{ M}^{-1} \text{ cm}^{-1}$) in agreement with a $(d_{x^2-y^2})^1$ ground state of the copper(II) ions.

Molecular structure of complex 1

A view of the asymmetric unit together with the atom-numbering scheme is given in Fig. 1(a). The structure deter-

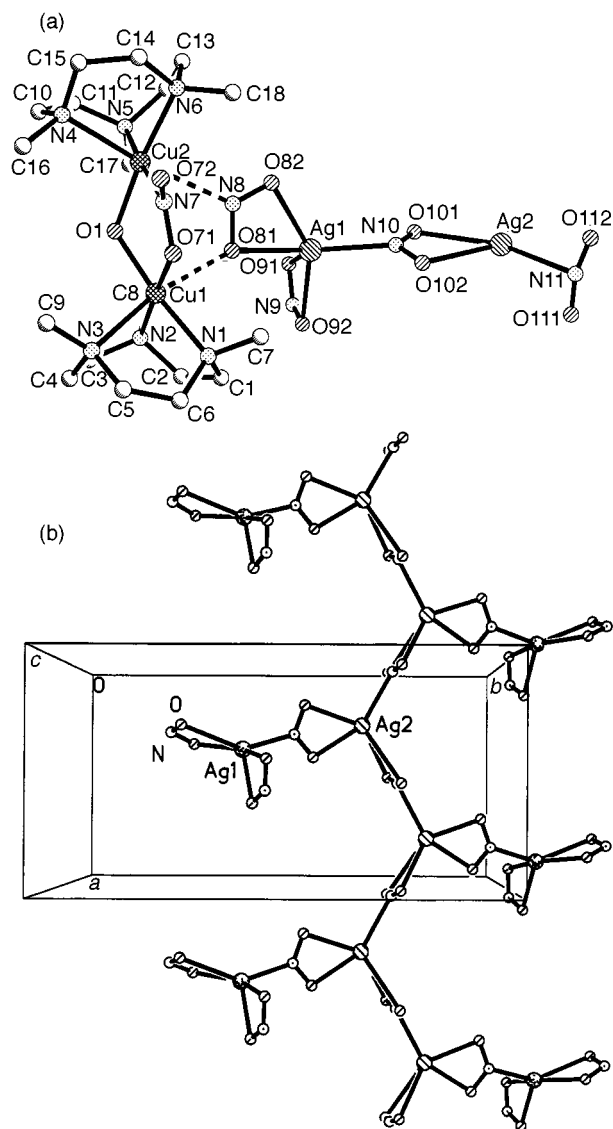


Fig. 1 Views of (a) the asymmetric unit in complex **1**, (b) the $\text{Ag}(\text{NO}_2)_x$ chains along $[100]$.

mination and hence the derived geometrical parameters suffer from rather bad crystal quality and disordered nitrito groups $\text{N}(7)\text{O}_2$ and $\text{N}(10)\text{O}_2$. The disorder is indicated by large and elongated anisotropic displacement parameters of the oxygen atoms $\text{O}(72)$ and $\text{O}(101)$. Refinement with a split model did not lead to any improvement. Selected bond lengths and angles for **1** are listed in Table 2.

The packing consists of dinuclear copper moieties $\text{Cu}_2\text{L}_2(\mu\text{-NO}_2)(\mu\text{-OH})$ and infinite zigzag chains of $[\text{Ag}(\text{NO}_2)]_x$ along $[100]$. The Cu atoms $\text{Cu}(1)$ and $\text{Cu}(2)$ are linked through a symmetric $\mu\text{-OH}$ bridging ligand with $\text{Cu}-\text{O}(1)$ bond lengths of $1.928(10) \text{ \AA}$ and an unsymmetric bridging O,N nitrito ligand with $\text{Cu}(1)-\text{O}(71)$ $2.062(10)$, $\text{O}(71)-\text{N}(7)$ $1.25(2)$ and $\text{Cu}(2)-\text{N}(7)$ $2.07(2) \text{ \AA}$. Similar geometries of the Cu_2 core with bridging $\mu\text{-OR}$ and $\mu\text{-NO}_2$ ligands are known for complexes $[\text{Cu}_2(\text{bipy})_2(\mu\text{-OCH}_3)(\mu\text{-NO}_2)][\text{NO}_2]_2$ **2** and $[\text{Cu}_2(\text{L-Et})(\mu\text{-NO}_2)][\text{ClO}_4]_2$ **3**, where “bipy” stands for 2,2'-bipyridine and “HL-Et” for a binucleating ligand *N,N,N',N'*-tetrakis(1-ethylbenzimidazol-2-yl)-2-hydroxy-1,3-diaminopropane. It is of interest that the $\text{Cu} \cdots \text{Cu}$ separation of $3.299(2) \text{ \AA}$ in **1** is shorter than that in **2**, $3.403(1) \text{ \AA}$, and **3**, $3.325(2) \text{ \AA}$.

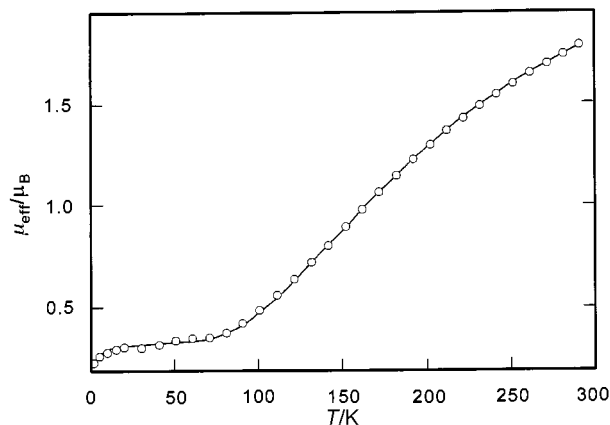
Two tridentate amine ligands **L** complete the distorted square-pyramidal co-ordination sphere of the two copper(II) centres. The basal planes, defined by $\text{Cu}(1)\text{O}(1)\text{O}(71)\text{N}(1)\text{N}(2)$ and $\text{Cu}(2)\text{O}(1)\text{N}(7)\text{N}(5)\text{N}(6)$, set up a dihedral angle of 40° . The average basal $\text{Cu}-\text{N}_{\text{amine}}$ bonds which are *trans* to the

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

Cu(1)–O(1)	1.928(10)	Cu(2)–O(1)	1.927(9)
Cu(1)–O(71)	2.062(10)	Cu(2)–N(5)	2.064(14)
Cu(1)–N(1)	2.078(13)	Cu(2)–N(7)	2.070(15)
Cu(1)–N(2)	2.108(13)	Cu(2)–N(6)	2.089(11)
Cu(1)–N(3)	2.257(12)	Cu(2)–N(4)	2.275(13)
Ag(1)–N(10)	2.32(2)	N(8)–O(81)	1.22(2)
Ag(1)–O(82)	2.392(13)	N(8)–O(82)	1.22(2)
Ag(1)–O(91)	2.40(2)	N(9)–O(92)	1.18(2)
Ag(1)–O(92)	2.43(2)	N(9)–O(91)	1.18(2)
Ag(1)–O(81)	2.520(12)	N(10)–O(101)	1.16(3)
Ag(2)–O(101)	2.43(2)	N(10)–O(102)	1.19(2)
Ag(2)–N(11)	2.49(3)	N(11)–O(112)	1.03(3)
Ag(2)–O(102)	2.56(2)	N(11)–O(111)	1.07(2)
		N(7)–O(71)	1.25(2)
		N(7)–O(72)	1.26(2)
O(1)–Cu(1)–O(71)	86.2(4)	O(1)–Cu(2)–N(5)	96.5(5)
O(1)–Cu(1)–N(1)	173.3(4)	O(1)–Cu(2)–N(7)	83.9(5)
O(71)–Cu(1)–N(1)	90.9(5)	N(5)–Cu(2)–N(7)	175.2(7)
O(1)–Cu(1)–N(2)	99.1(5)	O(1)–Cu(2)–N(6)	173.5(4)
O(71)–Cu(1)–N(2)	173.9(5)	N(5)–Cu(2)–N(6)	83.6(5)
N(1)–Cu(1)–N(2)	84.2(5)	N(7)–Cu(2)–N(6)	95.4(5)
O(1)–Cu(1)–N(3)	103.5(4)	O(1)–Cu(2)–N(4)	104.3(4)
O(71)–Cu(1)–N(3)	92.6(4)	N(5)–Cu(2)–N(4)	80.8(7)
N(1)–Cu(1)–N(3)	82.6(4)	N(7)–Cu(2)–N(4)	103.7(7)
N(2)–Cu(1)–N(3)	83.2(5)	N(6)–Cu(2)–N(4)	82.1(5)
N(10)–Ag(1)–O(82)	109.6(6)	O(82)–Ag(1)–O(81)	49.1(4)
N(10)–Ag(1)–O(91)	109.8(8)	O(91)–Ag(1)–O(81)	111.3(7)
O(82)–Ag(1)–O(91)	121.1(7)	O(92)–Ag(1)–O(81)	104.0(8)
N(10)–Ag(1)–O(92)	100.4(9)	O(101)–Ag(2)–N(11)	151.9(7)
O(82)–Ag(1)–O(92)	149.6(8)	O(101)–Ag(2)–O(102)	47.7(7)
O(91)–Ag(1)–O(92)	48.5(9)	N(11)–Ag(2)–O(102)	104.2(7)
N(10)–Ag(1)–O(81)	138.8(7)		

hydroxo and nitrito ligands are shorter (by 0.16 to 0.20 Å) than the apical Cu–N_{amine} bonds as is always observed in square-pyramidal copper(II) complexes containing the macrocyclic ligand L.²² Interestingly, the vacant sixth co-ordination site *trans* to the apical Cu–N_{amine} bond is occupied either by one oxygen atom, Cu(1)···O(81) 2.45 Å, or one nitrogen atom, Cu(2)···N(8) 2.71 Å, of a AgNO₂ group. These intermolecular contacts are rather long, indicating that they are very weak. Thus a square-pyramidal geometry rather than a distorted octahedral co-ordination for both copper centres is a rather appropriate description for **1**. Complex **1** can thus be envisaged as a dinuclear copper(II) complex embedded in a matrix of diamagnetic AgNO₂, as is described below and confirmed by the magnetic susceptibility study.

Silver atom Ag(1) is fivefold co-ordinated in an irregular arrangement by one nitrogen and four oxygen atoms. The nitrito anions act as bidentate ligands through their two oxygen atoms. The resulting Ag–O contact lengths for Ag(1) range from 2.392(13) to 2.520(12) Å for the oxygen atoms numbered 8 and 9 and those for Ag(2) from 2.43(2) to 2.73(2) for O atoms numbered 10 and 11. A nitrogen atom from a third NO₂ group then occupies the remaining co-ordination site with bond lengths of Ag(1)–N(10) 2.32(2) and Ag(2)–N(11) 2.49(3) Å. The infinite AgNO₂ zigzag chains [Fig. 1(b)] are solely formed by Ag(2) and the nitrito group 11, and the symmetry related equivalents to give the repetitive arrangement –Ag(O₂N)–Ag(O₂N)Ag– with a Ag–Ag–Ag angle of 115.6(5)°. Additionally, each Ag(2) atom is linked *via* the O₂N(10) anion to a terminal Ag(1)(O₂N)₂ unit including nitrito groups 8 and 9. Of these, group 8 takes part in the above described co-ordination pattern of the copper centres. There are few other reported structures²³ containing nitrito-co-ordinated silver atoms. Most of them comprise isolated Ag(NO₂) moieties. A more complex structure with NO₂-co-ordinated Ag and Co atoms has been described recently.²⁴ A somewhat related arrangement of infinite Pb–NO₂ chains, but with ninefold co-ordination of

**Fig. 2** Plot of μ_{eff} vs. T for complex **1**. The solid line represents the simulation with the spin Hamiltonian $H = -2JS_1 \cdot S_2$.

the metal nitrito and nitrate groups, was reported for $\text{K}_2\text{Pb}(\text{NO}_2)_3(\text{NO}_3) \cdot \text{H}_2\text{O}$.⁴

Magnetic susceptibility study

Magnetic susceptibility data for a polycrystalline sample of complex **1** were collected in the temperature range 2–290 K in order to characterize the nature and magnitude of the exchange interaction propagated by the bridging 1,2- μ -nitrito ligand. We use the Heisenberg spin Hamiltonian in the form $H = -2JS_1 \cdot S_2$ for an isotropic exchange coupling with $S_1 = S_2 = 1/2$. The cryomagnetic property of **1** is shown in Fig. 2 in the form of a μ_{eff} vs. T plot. The magnetic moment of 1.79 μ_{B} at 290 K decreases very rapidly with decreasing temperature, reaching a value of 0.35 μ_{B} at 70 K which remains nearly constant until 15 K with a value of 0.30 μ_{B} and then it starts to decrease reaching a value of 0.23 μ_{B} at 2 K. This magnetic behaviour is quite characteristic of an antiferromagnetic coupling between the paramagnetic copper(II) centres. The experimental magnetic data were simulated using a least-squares fitting computer program with a full-matrix diagonalization approach including exchange coupling, Zeeman splitting and the temperature independent paramagnetism (TIP) for the copper(II) ion. The least-squares fitting, shown as the solid line in Fig. 2, of the experimental data leads to $J = -193 \text{ cm}^{-1}$ and $g = 2.28$. A paramagnetic impurity (3.3%) with an $S = 1/2$, had also to be considered to account for the residual moment of $\approx 0.30 \mu_{\text{B}}$ at low temperatures. Thus the copper centres in **1** are antiferromagnetically exchange coupled with a singlet ground state, and the triplet state lying 386 cm^{-1} above the ground state.

Previously we reported in a short communication the structural and preliminary susceptibility (93–293 K) results of the dinuclear copper(II) complex $[\text{Cu}_2(\mu\text{-OH})_2\text{L}_2][\text{ClO}_4]_2$.²¹ For the purpose of comparison low-temperature (2–290 K) susceptibility data for the above bis(μ -hydroxo)dicopper(II) complex have been obtained. The exchange coupling constant $J = -50.2 \text{ cm}^{-1}$ and $g = 2.286$ have been evaluated from the new measurement, indicating that the antiferromagnetic coupling through the nitrito group is strong in **1**.

Since the observed J value is composed of ferromagnetic and antiferromagnetic contributions and these are in turn influenced by a variety of structural and electronic factors,²⁵ it is difficult to give a definite explanation for the relatively strong coupling in complex **1**, although some pertinent observations and partial rationalization will be attempted. Complex **1** can be viewed as a dinuclear square-pyramidal d^9 copper(II) species where the magnetic $d_{x^2-y^2}$ orbitals are intermolecularly bridged by one hydroxo and one 1,2- μ -nitrito group. The electronic spectrum of **1** in CH₃CN is also in complete agreement with the $(d_{x^2-y^2})^1$ ground state orbitals. It has been pointed out by several authors^{7,26,27} that the extent of

superexchange interaction through two different bridging ligands in dinuclear copper(II) complexes can be rationalized on the basis of the concept of ligand orbital complementarity. Inspection of the ligand HOMOs reveals complementarity; as a consequence hydroxide and nitrite ligands provide orbital interaction pathways that act in concert to make the anti-symmetric (ϕ_A) significantly different in energy from symmetric (ϕ_S) combinations of metal and ligand orbitals, thus resulting in strong antiferromagnetism. It is interesting that for a similar μ -alkoxo- μ -1,2-nitrito copper(II) complex $[\text{Cu}_2(\text{L-Et})(\text{NO}_2)]^{2+}$ **3**,⁷ having comparable large coupling ($J = -139 \text{ cm}^{-1}$) but *via* d_z magnetic orbitals, the Cu–O–Cu angle is larger (127.1°) than that in **1** (117.6°). Hence, we are prone to recognize that the present co-ordination mode of the nitrito bridge is an extremely good mediator of antiferromagnetic coupling. Similar strong antiferromagnetic coupling between copper(II) sites *via* N,O bridging has been documented before in oximate species.^{22b}

Acknowledgements

We acknowledge the support of this work by the Fonds der Chemischen Industrie. Our thanks are also due to the skilful technical assistance of Frau D. Kreft and Herr U. Pieper.

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Paper 8/05104F