Inorg. Chem. **1990**, *29*, 771–774 **771**

Contribution from the Laboratoires de Chimie (UA 1194), Département de Recherche Fondamentale, Centre d'Etudes Nucléaires, 38041 Grenoble Cedex, France, and EHICS, 1 rue Blaise Pascal, BP 269 67008 Strasbourg Cedex, France

Structural and Magnetic Properties of a Bis(nitroxyl) Binuclear Copper(II) Complex

Marc Drillon,[‡] André Grand,[†] and Paul Rey*[,†]

Received January 11, 1989

Bis(μ-ethoxo)bis[(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)pivaloylacetato]dicopper(II), a bis(nitroxyl)dicopper complex, has been prepared. Its crystal and molecular structures have been determined by a single-crystal X-ray analysis. The crystals are monoclinic, space group $P2_1/n$ with two molecules in a unit cell of dimensions a = 12.073 (3) Å, b = 11.510 (2) Å, c = 14.781 (2) Å, and β = 101.47 (2)°. The Cu_2O_2 core is planar, and the Cu–Cu separation is 2.974 (2) Å. The coordination geometry around each copper ion is roughly square pyramidal with axially bound nitroxyl ligands. Significant parameters of the coordinated nitroxide include Cu–O = 3.036 (4) Å. On the basis of metal–metal and metal–nitroxyl distances, the magnetic data are discussed in terms of four $S = {}^1/_2$ spin units involving two copper(II) ions of one molecule and two nitroxyl groups of neighboring molecules. It is found that the two copper ions are strongly antiferromagnetically coupled, $J = -538$ K, while the copper–nitroxyl interaction is ferromagnetic, $j = +12$ K. These results are of use in rationalizing magnetostructural correlations in metal–nitroxyl adducts and show that binuclear complexes might be used in the design of high-spin molecular species.

During the past decade, the coordination chemistry of the nitroxyl free radicals has grown steadily.[1-26] This development is mainly associated with studies aimed at understanding the coupling between nonequivalent spins and at designing molecular ferromagnets. Thus, ferro-[17] as well as ferrimagnetic[24] chains of alternating metal ions and organic free radicals have been reported. Using the same strategy but starting with metal complexes of higher nuclearity (nuclearity refers to the metal), one can expect to obtain molecular species with "subtle spin order",[27] i.e. species in which the spins are arranged in a more complicated way. In this paper, we present the structural and magnetic properties of such an oligomeric system: a bis(nitroxyl)dicopper(II) complex.

Although complexes of nitroxides with many transition-metal ions have been reported, much of the data available are devoted to copper(II) derivatives.[3-19] The magnitude of the metal–nitroxyl exchange interaction in these copper complexes ranges over several hundred wavenumbers depending on the structural features. Thus, those containing short-bonded nitroxyl ligands exhibit strong antiferromagnetism,[3-11] while those with long-bonded axial nitroxides exhibit a ferromagnetic behavior.[12-19] These magnetostructural correlations have been established from the study of oligonuclear species, and their understanding allowed the synthesis of ferromagnetic chains[17] to be carried out. It was therefore worthwhile to verify if the same correlations could apply to the dicopper(II) derivatives and eventually if one could use them as building blocks in the design of high spin molecular species.

Another aspect of the coordination chemistry of the nitroxides, which refers to complexes of higher nuclearity, is the redox properties of the copper derivatives. Although this field has not attracted much attention, it has been shown that solutions of copper halides and nitroxides are able to oxidize primary alcohols into aldehydes.[28] Moreover, it has been suggested that the active intermediate in this reaction might be the copper(II)–nitroxyl complex.[11] This redox behavior—the transfer of two electrons—leads one to expect that more than two electrons could be transfered by using a complex containing more than one copper ion and more than one radical ligand.

For both these reasons, we decided to investigate the properties of copper(II)-nitroxyl systems having a higher nuclearity than that of the derivatives yet reported. We described recently the synthesis and the properties of a series of nitroxyl β-diketonates[14] in which the copper ions are octahedrally coordinated to the equatorial β-diketones and two axial nitroxyl groups. This three-spin system has a $S = {}^3/_2$ ground state.[13] Since the formation of alkoxy-bridged binuclear species from mononuclear β-diketonates is well documented, we tried to react one of our complexes with alkoxides. It was anticipated that the binuclear derivative would retain the solid-state organization of the mononuclear complex, giving the opportunity of studying a bis(nitroxyl) dicopper(II) system (Figure 1).

Table I. Crystallographic Data

chem formula: $C_{36}H_{64}N_2O_{10}Cu_2$	fw = 811.96
a = 12.073 (3) Å	space group: $P2_1/n$
b = 11.510 (2) Å	T = 20 °C
c = 14.781 (2) Å	ρ_{calcd} = 1.34 g cm^{-3}
β = 101.47 (2)°	μ = 11.55 cm^{-1}
V = 2012.9 Å^{-3}	R = 0.045
Z = 2	R_w = 0.039

[†] Centre d'Etudes Nucléaires.

[‡] EHICS.

(1) For reviews, see: (a) Hendrickson, D. N. In *Magneto-structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D.; Kahn, O.; Eds., Reidel: Boston, 1984. (b) Milaeva, E. R.; Rubezhov, A. Z.; Prokof'ev, A. I.; Okhlobystin, O. Yu. *Usp. Khim.* **1982**, *51*, 1638; *Russ. Chem. Rev.* (*Engl. Transl.*) **1982**, *51*, 942. (c) Larionov, S. V. *Zh. Strukt. Khim.* **1982**, *23*, 125. (d) Eaton, G. R.; Eaton, S. S. *Coord. Chem. Rev.* **1978**, *26*, 207.

(2) Brown, D. G.; Maier, T.; Drago, R. S. *Inorg. Chem.* **1971**, *10*, 2804–2806.

(3) Lim, Y. Y.; Drago, R. S. *Inorg. Chem.* **1972**, *11*, 1334–1338.

(4) Richardson, P. F.; Kreilick, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 8183–8187.

(5) Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1981**, *20*, 2677–2681.

(6) Porter, L. C.; Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1983**, *22*, 1962–1964.

(7) Porter, L. C.; Doedens, R. J. *Inorg. Chem.* **1985**, *24*, 1006–1010.

(8) Porter, L. C.; Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1986**, *25*, 678–681.

(9) Laugier, J.; Rey, P.; Benelli, C.; Gatteschi, D.; Zanchini, C. *J. Am. Chem. Soc.* **1986**, *108*, 6931–6937.

(10) Gatteschi, D.; Laugier, J.; Rey, P.; Zanchini, C. *Inorg. Chem.* **1987**, *26*, 938–943.

(11) Caneschi, A.; Grand, A.; Laugier, J.; Rey, P.; Subra, R. *J. Am. Chem. Soc.* **1988**, *110*, 2307–2309.

(12) Anderson, O. P.; Kuechler, T. C. *Inorg. Chem.* **1980**, *19*, 1417–1423.

(13) Grand, A.; Rey, P.; Subra, R. *Inorg. Chem.* **1983**, *22*, 391–394.

(14) Laugier, J.; Ramasseul, R.; Rey, P.; Espie, J.-C.; Rassat, A. *Nouv. J. Chem.* **1983**, *7*, 11–14.

(15) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *J. Am. Chem. Soc.* **1984**, *106*, 5813–5818.

(16) Benelli, C.; Gatteschi, D.; Zanchini, C.; Latour, J.-M.; Rey, P. *Inorg. Chem.* **1986**, *25*, 4242–4244.

(17) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. *J. Am. Chem. Soc.* **1987**, *109*, 2191–2192.

(18) Caneschi, A.; Gatteschi, D.; Grand, A.; Laugier, J.; Pardi, L.; Rey, P. *Inorg. Chem.* **1988**, *27*, 1031–1035.

(19) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Hoffman, S. K.; Laugier, J.; Rey, P. *Inorg. Chem.* **1988**, *27*, 2392–2393.

(20) Dickman, M. H.; Porter, C. L.; Doedens, R. J. *Inorg. Chem.* **1986**, *25*, 2595–2599.

(21) Benelli, C.; Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 913–915.

(22) Cogne, A.; Grand, A.; Rey, P.; Subra, R. *J. Am. Chem. Soc.* **1987**, *109*, 7927–7929.

(23) Caneschi, A.; Gatteschi, D.; Laugier, J.; Pardi, L.; Rey, P. *Inorg. Chem.* **1988**, *27*, 2027–2032.

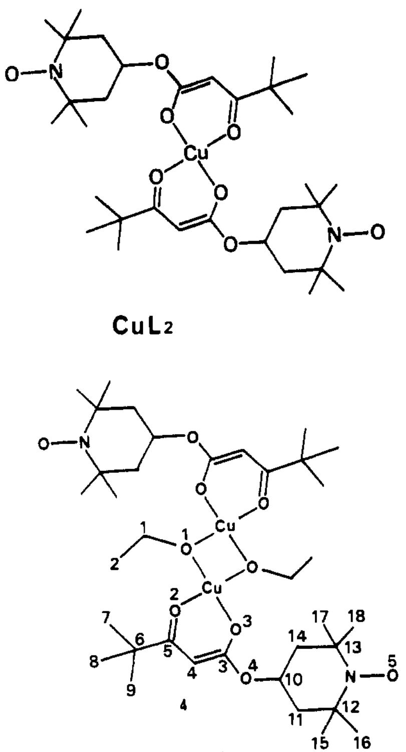

Figure 1. Chemical structures of CuL_2 and $(CuOEtL)_2$ showing the numbering of the atoms used in the tables of the structural parameters.

Table II. Atomic Coordinates ($\times 10^4$)

atom	x	y	z
Cu	4822 (1)	9441 (1)	9075 (1)
O(1)	5463 (3)	10786 (3)	9718 (2)
O(2)	3894 (3)	8184 (3)	8553 (2)
O(3)	5253 (3)	9813 (3)	7911 (2)
O(4)	5347 (3)	9534 (3)	6435 (2)
O(5)	7938 (3)	13158 (3)	5648 (3)
N	7301 (4)	12230 (4)	5768 (3)
C(1)	7301 (5)	11387 (6)	9566 (4)
C(2)	6117 (5)	11683 (5)	9422 (3)
C(3)	4929 (4)	9260 (4)	7186 (3)
C(4)	4162 (4)	8327 (4)	7027 (3)
C(5)	3680 (4)	7860 (4)	7720 (3)
C(6)	2806 (4)	6881 (5)	7508 (3)
C(7)	2888 (5)	6111 (5)	8335 (4)
C(8)	2945 (5)	6152 (5)	6693 (4)
C(9)	1658 (5)	7461 (6)	7303 (4)
C(10)	6134 (4)	10514 (5)	6502 (3)
C(11)	7007 (4)	10202 (4)	5940 (3)
C(12)	7875 (4)	11163 (5)	5973 (4)
C(13)	6266 (5)	12637 (5)	6105 (4)
C(14)	5514 (4)	11564 (5)	6095 (4)
C(15)	8561 (5)	10963 (5)	5234 (4)
C(16)	8678 (5)	11217 (5)	6917 (4)
C(17)	6590 (6)	13155 (5)	7072 (4)
C(18)	5648 (5)	13535 (5)	5459 (5)

Table III. Selected Bond Lengths (Å) and Angles (deg)

CuCu′	2.974 (1)	CuO(2)	1.897 (3)
CuO(1)	1.899 (3)	CuO(3)	1.942 (3)
CuO′(1)	1.902 (3)	CuO′(5)	3.036 (4)
NO(5)	1.287 (5)		
O(1)CuO′(1)	77.0 (2)	O′(1)CuO(3)	172.9 (3)
O(1)CuO(2)	166.9 (1)	O′(1)CuO′(5)	97.4 (1)
O(1)CuO(3)	96.3 (1)	O(2)CuO(3)	92.8 (1)
O(1)CuO′(5)	93.8 (1)	O(2)CuO′(5)	97.0 (1)
O′(1)CuO(2)	94.2 (1)	O(3)CuO′(5)	80.7 (1)
CuO(1)Cu′	103.0 (2)	NO′(5)Cu	156.8 (3)

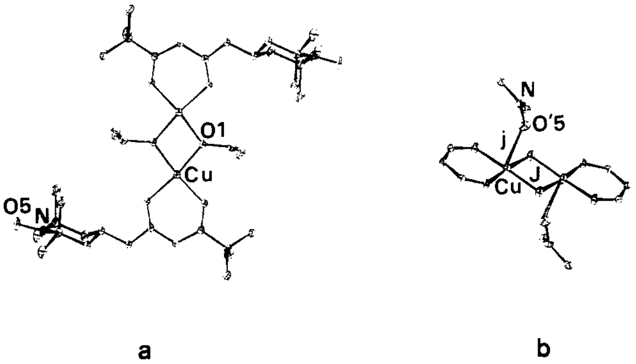

Figure 2. (a) View of the molecular structure of $(CuOEtL)_2$ with thermal ellipsoids drown at a 30% probability level. (b) Environment of the copper ions and definition of the magnetic interactions.

Experimental Section

Synthesis. Bis(μ-ethoxo)bis[(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)pivaloylacetato]dicopper(II), $(CuOEtL)_2$. Method A. A solution of sodium ethanolate was prepared by adding 50 mg of sodium to 50 mL of anhydrous ethanol. To this solution warmed to 60 °C under argon was added by portions 330 mg (0.5×10^{-3} mol) of CuL_2[13] (see Figure 1). The solution was stirred at 60 °C for $^1/_2$ h and allowed to cool down to room temperature. The purple precipitate was removed by filtration and dried under vacuum (157 mg, 77%); mp 238–240 °C dec. Anal. Calcd for $C_{36}H_{64}N_2O_{10}Cu_2$: C, 53.26; H, 7.95; N 3.45; O, 19.71; Cu, 15.65. Found: C, 53.31; H, 8.20; N, 3.47; O, 19.44; Cu, 15.53.

Method B. CuL_2 (0.5 g, 0.75×10^{-3} mol) was disolved by portions in 500 mL of refluxing ethanol under an argon atmosphere. The green solution gradually turned purple as it was refluxed for $^1/_2$ h. After the solution was allowed to stand at room temperature overnight, the purple crystals that formed were identical with those obtained by using method A.

X-ray Data Collection and Structure Determination. Attempts to recrystallize the compound from heptane, benzene, methylene choride, and chloroform were unsuccessful; the starting mononuclear complex CuL_2 was recovered in all cases. We ran several preparations starting from 100 mg of CuL_2 using method B, and in one of them were found crystals suitable for an X-ray diffraction study.

Preliminary Weissenberg photographs revealed the monoclinic system and exhibited systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) only compatible with the space group $P2_1/n$. The same crystal was mounted on an Enraf-Nonius CAD-4 four-circle diffractometer with monochromatized Mo Kα radiation. Accurate cell constants were derived from least-squares refinement of the setting angles of 25 reflections and are reported in Table I with other experimental parameters. The intensities of 3742 independent reflections ($2° < \theta < 25°$) were collected. Three standard reflections were periodically checked and showed no significant change during the course of data collection. The data were corrected for Lorentz and polarization factors and anomalous dispersion of copper atoms but not for absorption. Among the independent reflections collected, 2255 had $F_o > 3\sigma(F_o)$ and were used to refine the structural parameters.

The position of the copper atom was assigned from the double-intensity nonorigin peak appearing in the Harker sections of the Patterson map. Two successive Fourier synthesis allowed the localization of all the remaining non-hydrogen atoms. The structural parameters were refined by using XFLSN[29] with Cu, N, C, and O atoms anisotropic. At this stage of the refinement, a Fourier difference map showed significant electron density in positions that could be expected for most of the hydrogen atoms. They were introduced in the refinement model but not refined. Finally, the R values, $R_1 = (\sum w(F_o - F_c)^2/\sum wF_o^2)^{1/2}$ and $R_2 = (\sum|F_o - F_c|/\sum F_o)$, were respectively 0.039 and 0.045. The positional parameters are reported in Table II; relevant bond lengths and angles are given in Table III. Tables S1–S4 included as supplementary material in the

---

(24) Caneschi, A.; Gatteschi, D.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1988**, *27*, 1756–1761.

(25) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P.; Sessoli, R. *J. Am. Chem. Soc.* **1988**, *110*, 2795–2799.

(26) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1988**, *27*, 1553–1557.

(27) Pei, Y.; Kahn, O.; Sletten, J. *J. Am. Chem. Soc.* **1986**, *108*, 3143–3145.

(28) Semmelhack, M. F.; Schmid, C. R.; Cortes, D. A.; Chou, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 3374–3376.

(29) Busing, W. R.; Martin, K. O.; Levy, H. A. *Oak Ridge Natl. Lab* [*Rep.*], *ORNL* (*U.S.*) **1971**, *ORNL-594-37*.

microfilm edition of this journal, contain respectively all the crystallographic data, the bond lengths and angles, the anisotropic thermal parameters and a listing of the F_o and F_c values.

Magnetic Susceptibility Measurements. Magnetic susceptibility measurements were performed in the temperature range 1.3–300 K by using two different techniques. The low-temperature data (1.3–4 K) were obtained with a differential susceptibility setup operating at 80 Hz. At higher temperature, a SHE 905 superconducting SQUID susceptometer operating at 0.5 T was used. The linearity of the magnetization curve in a low applied field was checked down to 4 K. The data, corrected for the diamagnetic contribution of the constituent atoms (estimated from Pascal constants), were obtained with an accuracy better than 10^{-5} emu mol^{-1} for the susceptibility and a temperature uncertainty of 0.01–0.1 K, depending on the temperature region.

Results and Discussion

In Figure 2 is shown the molecular structure of $(CuOEtL)_2$ and a view of the intermolecular interactions. In this binuclear compound, the five oxygen atoms bound to the copper ion are located at the apices of a distorted square pyramid. The basal coordination sites are occupied by four oxygen atoms of one β-diketonate ligand and the two bridging μ-ethoxo groups, while the axial position is occupied by the oxygen atom of a nitroxyl group belonging to a neighboring molecule. The copper–oxygen (nitroxyl) distance is 3.036 (4) Å. There are some significant deviations from this idealized bonding pattern. The Cu(II) ion is coplanar with three of the oxygens (O(1), O′(1), O(3)), and these atoms can be taken to define the basal plane of the pyramid. One of the principal distortions from the local C_{4v} symmetry is then a displacement of O(2) by 0.37 Å below the basal plane, with a resultant deviation of the O(2)–Cu–O(1) = 166.7° and O(2)–Cu–O′(5) = 97.0° angles from the 180 and 90° values. At the same time, the Cu–O′(5) bond is bent toward the O(3) atom. All other O–Cu–O angles are within a few degrees of 90 and 180° except the O(1)–Cu–O′(1) angle (77.0°), the low value of which is due to the strain of the four-membered ring containing the copper atoms. This ring is perfectly planar by symmetry and perpendicular to the plane defined by the three atoms of the μ-ethoxo groups (O(1), C(1), C(2)). The piperidinyl-*N*-oxy fragment has the usual chair form and a pyramidal nitroxyl group;[30] the angle of the NO bond with the C(12)–N–C(13) plane is 26.1°. This fragment is attached to the β-diketonate ring through an ester linkage, the four atoms of which (C(10), O(4), C(3), O(3)), are nearly coplanar; in addition they are arranged in such a way that the N and O atoms of the nitroxyl group are close to the β-diketonate mean plane. Owing to the binding of the O(nitroxyl) atom to a copper ion of a neighboring molecule, the solid-state structure of the compound is organized as a three-dimensional network.

The five-coordinate bonding pattern of the copper ion in this complex is not unexpected, since this metal environment has been observed for most of the structurally characterized alkoxy-bridged β-diketonate derivatives so far reported.[31-33] The propensity of the copper ion to increase its coordination number in the β-diketonates is well established as well as the tendency of the alkoxy groups to bridge more than two metal ions. Therefore, the previously reported alkoxy-bridged copper derivatives exist as tetranuclear units, as a consequence of intermolecular interactions between the copper ion of a molecule and the alkoxy oxygen of another molecule. However, in the present case, it is very likely that steric crowding does not allow the binding of more than two metal ions to an alkoxy oxygen; thus, intermolecular metal–oxygen interactions involve a less hindered remote part of the complex, the nitroxyl group (see Figure 2b).

Due to this *intermolecular* axial ligation of the nitroxyl oxygen atom to the metal in the solid state, *intra-* as well as *intermolecular* metal–nitroxyl magnetic interactions are expected to occur in the complex. However, a study of closely related species in solution[34] has shown that the intramolecular copper–nitroxyl couplings are weak; they are not expected to affect the solid-state magnetic susceptibilities. Therefore, it is safe, as far as the solid-state magnetic properties are concerned, to consider this compound as isolated four $S = {}^1/_2$ spin systems formed by two copper(II) ions of one molecule and two nitroxyl groups of neighboring molecules as depicted in Figure 2b.

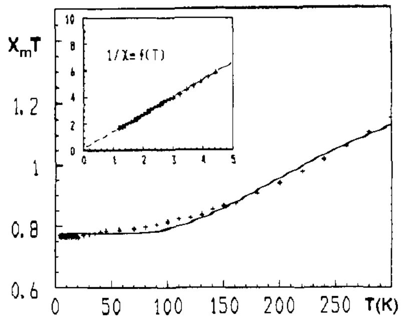

Figure 3. Experimental (+++) and theoretical (---) temperature dependence of $\chi_M T$.

The temperature dependence of the zero-field susceptibility is displayed in Figure 3 in the range 1.3–300 K. Clearly, the plot of $\chi_M T$ vs T is more revealing than χ_M to describe the high-temperature magnetic behavior of this copper–nitroxyl system. When the system is cooled down from room temperature to 4 K, $\chi_M T$ decreases, reaching an almost constant value below 50 K, which is very close to the theoretical value (0.75 emu K mol^{-1}) calculated for two noninteracting ${}^1/_2$ spins. On the other hand, the $\chi_M T$ value observed at high temperature is significantly lower than the sum of the Curie constants of the four isolated spins, pointing to a strong antiferromagnetic exchange interaction between the magnetic sites. This behavior strongly suggests that the copper–nitroxyl couplings, if they exist, are weak compared to the copper–copper interaction; indeed, it has been shown that such similar copper pairs are strongly coupled while axially bound nitroxides are weakly interacting. Therefore, in a first step, the assumption was made that at high temperature the organic free radicals behave as isolated ${}^1/_2$ spins. Accordingly, the variation of the $\chi_M T$ product was attributed, to a large extent, to the pair of exchange-coupled copper(II) ions, described by the isotropic Hamiltonian

$$H = -J\vec{S}_1 \cdot \vec{S}_2$$

where $\vec{S}_1$ and $\vec{S}_2$ refer to the spin operators for the Cu(II) sites ($S_1 = S_2 = {}^1/_2$) and J is the exchange constant. One readily notices that, due to a large antiferromagnetic coupling between the copper ions, the low-lying spin-state $S = 0$ ($S = S_1 + S_2$) is strongly stabilized with respect to the spin triplet $S = 1$. The superimposed magnetic susceptibility of the two "uncoupled" nitroxyl radicals gives rise to an additional offset on the $\chi_M T$ axis, so that, in the 4–50 K temperature range, an almost constant value of the $\chi_M T$ product is observed. The theoretical curve[35] obtained by least-squares fitting of the data is compared to the experiment in Figure 3; the best parameter values are $g_{Cu} = 2.04$ and $J = -530$ K.

However, on close examination of the low-temperature (1.3–4 K) dependence of χ^{-1} (see the inset in Figure 3), it appears that the actual susceptibility follows a Curie–Weiss law $\chi_M = 0.775/(T - 0.008)$ where the uncertainty on the Θ value is ±0.001. This result shows that a small molecular field related to a Cu–NO coupling is operating and that the assumption of two rigorously isolated nitroxyl groups is not consistent with the low temperature magnetic data. This leads to a conflicting situation since the negative value of Θ would suggest that the Cu–NO interaction is antiferromagnetic, at variance with the well-established mag-

---

(30) Lajzerowicz-Bonneteau, J. *Spin Labeling. Theory and Applications*; Berliner, L. J., Ed.; Academic Press: New York, 1976; p 239.

(31) Andrew, J. E.; Blake, A. B. *J. Chem. Soc., Dalton Trans.* **1973**, 1102–1107.

(32) Jezowska-Trzebiatowska, B.; Olejnik, Z.; Lis, T. *J. Chem. Soc., Dalton Trans.* **1981**, 251–254.

(33) Nashida, Y.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1986**, 2633–2640.

(34) Eaton, S. S.; Eaton, G. R. *Coord. Chem. Rev.* **1988**, *83*, 29–72.

(35) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London* **1952**, *A214*, 451–455.

Table IV. Analytical Expressions for the Energy Levels of the Four-Spin System

S	$E(S)$	$E(S)$ for $\lvert J\rvert \gg \lvert j\rvert$
0	$J/4 + j/2 - {}^1/_2(J^2 + 4j^2 - 2Jj)^{1/2}$	$-J/4 + j - j^2/J$
1	$-J/4 + j/2$	$-J/4 + j/2$
1	$J/4 - {}^1/_2(J^2 + j^2)^{1/2}$	$-J/4 - j^2/4J$
2	$-J/4 - j/2$	$-J/4 - j/2$
1	$J/4 + {}^1/_2(J^2 + j^2)^{1/2}$	$3J/4 + j^2/4J$
0	$J/4 + j/2 + {}^1/_2(J^2 + 4j^2 - 2jJ)^{1/2}$	$3J/4 + j^2/J$

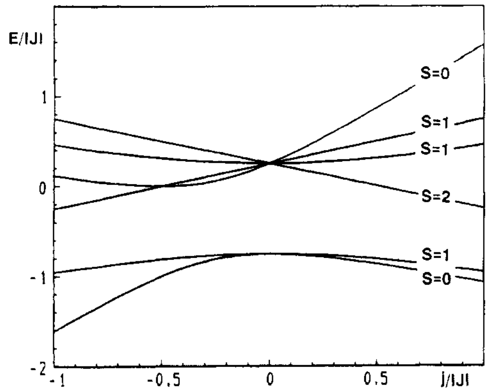

Figure 4. Energy diagram for the four-spin system for $|j/J| < 1$.

netostructural correlations in axially bound copper-nitroxyl complexes.

Therefore, in a second step, we have considered the centrosymmetric unit (NO-Cu-Cu-NO), involving two kinds of coupling constants between nearest neighbors. The exchange Hamiltonian is

$$H = -j(\vec{S}_1{\cdot}\vec{S}_2 + \vec{S}_3{\cdot}\vec{S}_4) - J\vec{S}_2{\cdot}\vec{S}_3$$

where $\vec{S}_1$ and $\vec{S}_4$ refer to the nitroxide sites and $\vec{S}_2$ and $\vec{S}_3$ refer to the copper ones; J is the coupling constant within the copper pair, and j is the copper-nitroxyl exchange parameter (see Figure 2b). Using the geometrical and spin space symmetries of the system, we have derived analytical expressions for the energy levels. They are listed in Table IV with the related spin multiplicities. Depending on the sign of J, two well distinct situations are encountered. Since, in the system under consideration, it is well established that the two metal atoms must be antiferromagnetically coupled,[36,37] we focus hereafter on the case corresponding to $J < 0$. The energy diagram is given in Figure 4 for $|j/J| < 1$. It reduces to a two sublevel scheme for $j = 0$, the multiplicities of which are in the ratio of 3:1. When the copper-nitroxyl interaction (j) increases, the most striking result is the stabilization of the $S = 0$ state whatever the sign of j. For $j > 0$, we notice that, as the energy increases, the spin configuration raises from $S = 0$ to $S = 2$ and then decreases to $S = 0$. Conversely, for $j < 0$, the upper level is always the $S = 2$ state.

Copper-nitroxyl interactions in axially bound mononuclear complexes have been rationalized through MO calculations[13,18]. Owing to the near orthogonality of the $d_{x^2-y^2}$ copper orbital and the π^* nitroxyl orbital, the coupling is ferromagnetic. Moreover, in examples with similar Cu-O(nitroxyl) distances[13] ($\approx$3 Å), this coupling is weak ($\approx$10-20 K). Therefore, since the $|J|$ value is large (500 K), it can be assumed that $|j| < |J|$ and that the first excited state $S = 1$ lies $E = -3j^2/4J$ above the ground singlet state $S = 0$. Thus, in the temperature range where only these two levels are thermally populated, the magnetic system may be viewed as a pair of ${}^1/_2$ spins exhibiting an antiferromagnetic coupling. Accordingly, the magnetic susceptibility does show a Curie-Weiss variation with a negative Θ value as illustrated in Figure 3. It is then straightforward, using the relationship $\Theta = E/4$ and the J value determined previously, to deduce the copper-nitroxyl interaction as $j = +15$ K ($\pm$3 K). Note that this interaction results in a second-order perturbation on the energy of the low-lying levels and, contrastingly, in a first-order effect on the upper levels. Hence, the sign of j might be deduced from the high-temperature susceptibility variation, but there is a large uncertainty on its magnitude due to the large copper-copper interaction.

The theoretical expression for the magnetic susceptibility of the system was derived from the eigenvalues of the four-spin system. If $|j| \ll |J|$, then

$$\chi = (2Ng^2\mu\beta^2/kT)(N/D)$$

$$N = 2 + 10e^{(J+j/2)/kT} + 2e^{J/kT} + 2e^{(J-j/2)/kT}$$

$$D = 4 + 5e^{(J+j/2)/kT} + 3e^{J/kT} + 3e^{(J-j/2)/kT} + e^{(J-j)/kT}$$

Least-squares fitting of the experimental values using this expression leads to the following parameters: $g = (g_{\mathrm{NO}} + g_{\mathrm{Cu}})/2 = 2.04$, $J = -538$ K and $j = +12$ K ($\pm$3 K). These are in fairly good agreement with those reported for related dicopper(II) systems[31-33] and axially bonded copper(II)-nitroxyl species.[13-18] Note that no assumption was made regarding the sign of j.

In summary, we report the synthesis, the structural and magnetic properties of a binuclear bis(nitroxyl)copper(II) complex. A complete analysis of the magnetic data is reported for this system of four $S = {}^1/_2$ spins, which allows for the determination of the copper-nitroxyl and the copper-copper coupling constants. This analysis shows that the same magnetostructural correlations as those found for mononuclear species apply to the dicopper-nitroxyl adducts. Therefore, since in some binuclear complexes the two metal atoms are ferromagnetically coupled, they can be used in the design of high spin metal-nitroxyl molecular species.

Supplementary Material Available: Table S1 (crystallographic data and experimental parameters), Table S2 (bond lengths and angles), and Table S3 (anisotropic thermal parameters) (4 pages); Table S4 (calculated and observed structure factors) (13 pages). Ordering information is given on any current masthead page.

---

(36) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173-241.
(37) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884-4899.