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An Unprecedented Asymmetric End-On Azido-Bridged Copper(II) Imino Nitroxide Complex: Structure, Magnetic Properties, and Density Functional Theory Analysis

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The dinuclear copper(II) complex $[Cu_2(\mu_{1,1}\text{-}N_3)_2(\text{im-2py})_2(N_3)_2]$ [im-2py = 2-(2-pyridyl)-4,4,5,5-tetramethylimidazolinyl-1-oxy] has been prepared and structurally characterized. The crystal structure consists of a dinuclear unit in which the Cu^{II} ions are bridged by two azido ions in a end-on asymmetric fashion and the imino nitroxide radicals are chelating by the two imino N atoms. Accordingly, the magnetic susceptibility data were analyzed considering a linear spin-coupling scheme rad(1)–Cu(2)–Cu(3)–rad(4) (with $S_i = {}^1/_2$, $i = 1–4$), where the Heisenberg spin Hamiltonian assumes the general form $-2\sum_{i<j}\hat{S}_i\hat{S}_j$. Considering only first-neighbor spin-coupling constants ($J_{13} = J_{24} = J_{14} = 0$), magnetic susceptibility measurements show that the copper(II) imino nitroxide **rad**–**Cu**–(Cu–rad)≡(rad–Cu)–**Cu**–**rad** exchange coupling is ferromagnetic and large ($J_{12} = J_{34} = J_1 > +190$ cm^{-1}), as is expected for copper imino nitroxide species, and the copper–copper (rad)–**Cu**–**Cu**–(rad) coupling through the asymmetric double end-on azide bridges appeared antiferromagnetic and rather large [$J_{23} = J_2 = -43(2)$ cm^{-1}]. By contrast, a density functional theory analysis of the system through the computation of broken-symmetry-state energies resulted in $J_2 \approx 0$ cm^{-1}. This apparent paradox is resolved by introducing a second-neighbor **rad**–(Cu)–**Cu**–(rad)≡(rad)–**Cu**–(Cu)–**rad** spin-coupling constant $J_{13} = J_{24} = J_3$, which turns out to be antiferromagnetic both experimentally (when J_2 is set equal to zero) and computationally.

Introduction

Metal−nitroxide magnetic interactions are generally antiferromagnetic except in a few cases when the geometry of the coordination sphere results in an orthogonal arrangement of the magnetic orbitals.[1] This happens in copper(II) nitronyl nitroxide complexes; when the radical ligand is axially bound by the O atom to a square-pyramidal or octahedral Cu ion, the metal−radical magnetic coupling is weakly ferromagnetic, in contrast to the equatorial situation, which results in strong spin pairing.[2] More interestingly, strong ferromagnetic couplings ($J \approx +200$ cm^{-1}; $H = -2\sum_{i<j}\hat{S}_i\hat{S}_j$) have been observed in copper(II) and nickel(II) imino nitroxide complexes, where the free radical is coordinated to the metal ion by the imino N atom.[3,4] Recently, this feature has been used for designing high-spin (HS) $M^{III}−Ni^{II}$ (M = Cr, Fe) clusters ($[(M_2(CN_{12})Ni_3(\text{im-2py})_6]$, im-2py = 2-(2-pyridyl)-

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4,4,5,5-tetramethylimidazolyl-1-oxy) having a ground spin state of high multiplicity in which six terminal imino nitroxides coordinated to the three nickel(II) ions are included.[5] In this complex, the free radicals are ferromagnetically coupled to the polynuclear core, increasing the spin from $S = 4$ to 7 in the case of M = Fe.

Considering that this strategy may have wide application to increasing the spin of other polynuclear metal fragments, we investigated the behavior of azido-bridged species incorporating imino nitroxides. The azido anion has versatile coordination properties leading to variable nuclearities—binuclear[6] and tetranuclear[7]—and variable dimensionalities—one-,[8] two-,[9] and three-dimensional[10]—depending on the metal ion. It is a versatile magnetic coupler that, in Cu^{II} derivatives, can mediate antiferromagnetic interactions in an end-to-end ($\mu_{1,3}$) bridging mode and ferromagnetic couplings in an end-on ($\mu_{1,1}$) bridging mode.[11]

The properties of these two ligands are attracting much attention, and it appears promising to combine the two strategies in order to design polynuclear structures built up with the azido anion and Cu ions coordinated by an imino nitroxide radical ligand because extended exchange-coupled structures and/or HS species were expected to result. In a first attempt, we report herein the synthesis, X-ray structure, magnetic properties, and subsequent preliminary density functional theory (DFT) analysis of such an azido-bridged binuclear Cu^{II} complex $[Cu_2(\mu_{1,1}\text{-}N_3)_2(\text{im-2py})_2(N_3)_2]$, where the binuclear core has a rare asymmetric structure.[12] Although in this complex the binuclear fragment has a metal−azido double-bridged end-on structure and the metal−radical interaction is strongly ferromagnetic, the ground spin state is a singlet. The origin of the antiferromagnetic coupling between the two Cu−NO $S = 1$ subunits was therefore further investigated.

Experimental Section

Materials. All reagents and chemicals were purchased from commercial sources and used as received. 2-(2-Pyridyl)-4,4,5,5-tetramethylimidazolinyl-1-oxy (im-2py) was prepared as previously reported.[13]

Synthesis of $[Cu_2(\mu_{1,1}\text{-}N_3)_2(\text{im-2py})_2(N_3)_2]$ (1). $Cu(NO_3)_2 \cdot 3H_2O$ (0.241 g, 1 mmol) and im-2py (0.218 g, 1 mmol) were mixed in 30 mL of methanol. An aqueous solution (10 mL) of NaN_3 (0.130 g, 2 mmol) was added to this solution. The mixture was stirred for 1 h and filtered off. The filtrate was kept at room temperature for 1 week, and well-formed brown crystals of $[Cu_2(\mu_{1,1}\text{-}N_3)_2(\text{im-2py})_2(N_3)_2]$ were obtained (228 mg, 62%). Anal. Calcd for $C_{24}H_{32}Cu_2N_{18}O_2$: C, 39.40; H, 4.41; N, 34.04. Found: C, 39.14; H, 4.34; N, 33.84. IR (KBr): $\nu_{as}(N_3^-)$ 2050vs, 2025s cm^{-1}; ν(NO) 1354s cm^{-1}. ***Caution!*** *Explosion occurred in the 50−100 °C range before melting.*

Physical Measurements. Elemental analyses for C, H, and N were carried out on a Perkin-Elmer elemental analyzer model 240. The IR spectrum was taken on a Shimadzu IR spectrophotometer model 408, using KBr pellets. Variable-temperature magnetic susceptibilities were measured on a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

Crystal data: $C_{24}H_{32}Cu_2N_{18}O_2$, $M = 731.76$, monoclinic, space group $P2_1/c$, $a = 10.9638(15)$ Å, $b = 19.811(3)$ Å, $c = 7.2993(10)$ Å, $\beta = 103.571(3)°$, $U = 1541.2(4)$ Å^3, $Z = 2$, $F(000) = 752$, $\mu = 14.37$ cm^{-1}.

The X-ray crystal data were collected at room temperature on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) using a brown crystal of approximate dimensions 0.15 × 0.15 × 0.15 mm. A total of 6339 reflections were collected in the $1.91 < \theta < 25.03°$ range including 2720 independent reflections ($R_{int} = 0.0458$). The structure was solved by direct methods using the *SHELXS-97* program.[14] The H atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using *SHELXL 97*,[15] and the goodness of fit on F^2 was 0.952. The final agreement factor values are R1 = 0.0421, wR2 = 0.0965 [$I > 2\sigma(I)$] and R1 = $\sum(||F_o| - |F_c||)/\sum|F_0|$, wR2 = $(\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2)^2$, $w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.0102P]$ where $P = (F_o^2 + 2F_c^2)/3$. Maximum and minimum peaks in the final difference Fourier synthesis were 0.313 and −0.367 e Å^{-3}.

Results and Discussion

Crystal Structure. An ORTEP drawing of the molecular structure with the atom-labeling scheme is shown in Figure 1. Selected bond distances and bond angles are summarized in Table 1.

The crystal structure consists of centrosymmetric dinuclear units $[Cu_2(\mu_{1,1}\text{-}N_3)_2(\text{im-2py})_2(N_3)_2]$ in which the Cu^{II} ions are bridged by two azido ligands in an end-on fashion. Each metal ion has a 4 + 1 distorted square-pyramidal environment (Figure 1) whose basal plane [N(1), N(2), N(4A), and N(7)] comprises two N atoms [N(1) and N(2)] belonging to the chelating imino nitroxide ligand and two N atoms from a bridging azido [N(4A)] and a terminal azido [N(7)] anions.

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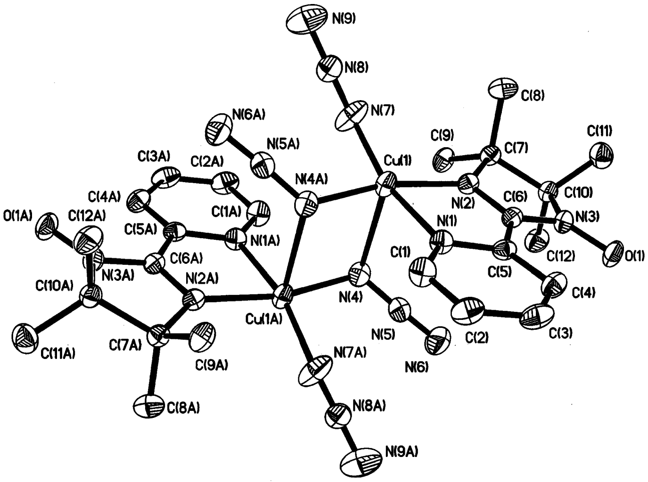

Figure 1. ORTEP drawing with 30% thermal ellipsoid probability showing the atom labeling of $[Cu_2(\mu_{1,1}\text{-}N_3)_2(\text{im-2py})_2(N_3)_2]$.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[Cu_2(\mu_{1,1}\text{-}N_3)_2(\text{im-2py})_2(N_3)_2]^a$

Cu(1)−N(2)	2.016(3)	Cu(1)−N(1)	2.059(3)
Cu(1)−N(7)	1.935(4)	Cu(1)−N(4A)	1.948(4)
Cu(1)−N(4)	2.434(4)	O(1)−N(3)	1.268(4)
N(7)−Cu(1)−N(2)	95.02(16)	N(7)−Cu(1)−N(4A)	96.26(17)
N(4A)−Cu(1)−N(2)	167.69(15)	N(7)−Cu(1)−N(1)	164.36(19)
N(4A)−Cu(1)−N(1)	90.95(15)	N(2)−Cu(1)−N(1)	79.34(13)
C(5)−N(1)−Cu(1)	115.4(3)	C(6)−N(2)−Cu(1)	114.0(3)
O(1)−N(3)−C(6)	126.1(3)	O(1)−N(3)−C(10)	123.5(3)
Cu(1A)−N(4)−Cu(1)	95.15(15)	N(6)−N(5)−N(4)	176.8(5)
N(7)−N(8)−N(9)	174.6(5)		

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1, -y, -z + 2$.

The Cu(1)−N(1), Cu(1)−N(2), Cu(1)−N(7), and Cu−N(4A) in-plane distances are 2.059(3), 2.016(3), 1.935(4), and 1.948(4) Å, respectively. One N atom [N(4)] from the second azido bridge occupies the axial position at a distance of 2.434(4) Å, with the Cu atom being displaced toward this apical site by 0.0695 Å from the basal plane. The bridging azido anion is quasi-linear [176.8(5)° for N(4)−N(5)−N(6)], the bond angle Cu(1)−N(4)−Cu(1A) is 95.1(1)°, and the Cu−Cu separation is 3.252 Å.

In the radical ligand, the oxyl bond length, N(3)−O(1) = 1.268(4) Å, is similar to N−O distances already reported in analogous complexes,[3−5,16] and the O(1)−N(3)−C(6)−N(2) plane of the free-radical ligand makes angles of 12.4° and 8.9° with the metal basal plane and the pyridyl ring, respectively.

A stacking diagram is shown in Figure 2. The dinuclear units are linked by fairly weak bonds [Cu(1)−N(6A) = 3.441 Å] to form one-dimensional chains along the *z* axis and completing the metal coordination sphere to *pseudo*-octahedral.

Therefore, the complex may be viewed as chains of binuclear units in which the end-on bridging azido ligands of a molecule are also end-to-end bridging for another unit along the chain. Other intermolecular contacts (3.656 Å) are observed between uncoordinated N−O groups of neighboring molecules belonging to adjacent chains.

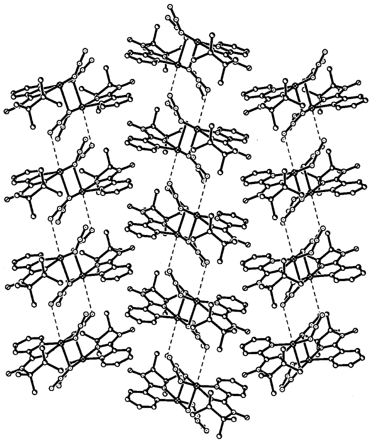

Figure 2. View of the packing of dinuclear units $[Cu_2(\mu_{1,1}\text{-}N_3)_2(\text{im-2py})_2(N_3)_2]$.

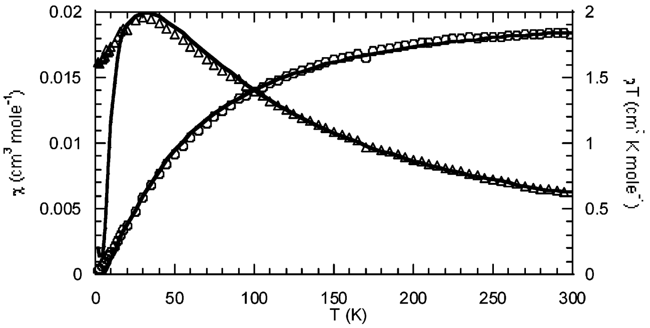

Figure 3. Plots of χ_M (△) and $\chi_M T$ (○) vs T for $[Cu_2(\mu_{1,1}\text{-}N_3)_2(\text{im-2py})_2(N_3)_2]$. The solid lines correspond to the best theoretical fit.

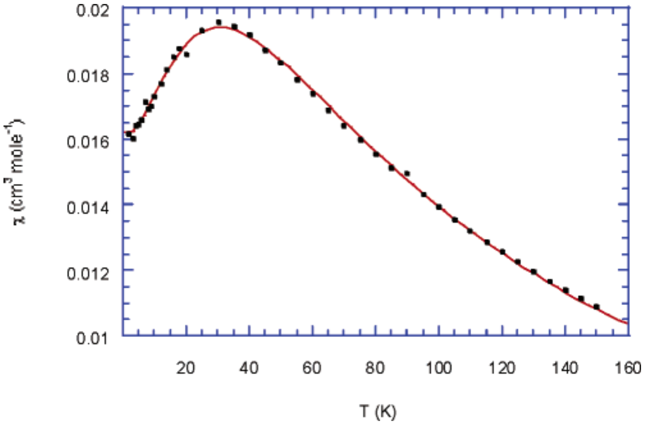

Figure 4. Low-temperature magnetic data (<150 K) in the form of χ_M vs T. The solid line was drawn with the parameters reported in the text and according to ref 19.

Magnetic Properties

The magnetic susceptibility data are shown in Figures 3 and 4 in the form of χ_M and $\chi_M T$ vs T plots. The value of $\chi_M T$ at room temperature (1.85 cm^3 K mol^{-1}) is larger than expected for four isolated $S = {}^1/_2$ spins (1.5 cm^3 K mol^{-1}) if $g = 2$; however, it might hold for $g = 2.22$. As the temperature is lowered, the $\chi_M T$ value continuously decreases and reaches a value of 0.03 cm^3 K mol^{-1} at 2 K, a variation that suggests a singlet ground spin state for the complex.

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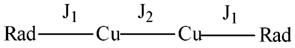
Chart 1



$$\mathrm{Rad}\overset{J_1}{\text{———}}\mathrm{Cu}\overset{J_2}{\text{———}}\mathrm{Cu}\overset{J_1}{\text{———}}\mathrm{Rad}$$

Confirmation that antiferromagnetic interactions are operative comes from the variation of χ_M, which exhibits a maximum at 28 K, a rather high temperature value. In addition, the variation of $1/\chi_M$ vs T exhibits a Curie−Weiss behavior with a large negative value of $\theta = -61$ K.

Although close intermolecular contacts have been mentioned when discussing the crystal structure, in a first attempt, the binuclear clusters were assumed to be really isolated at high temperature (>20 K). Accordingly, the system was first modeled as a linear array of spins $S = {}^1/_2$ (Chart 1). Only first-neighbor interactions were considered, and the corresponding Heisenberg spin Hamiltonian ($\hat{H} = 1J\hat{S}_1\hat{S}_2 - 2J_2\hat{S}_2\hat{S}_3 - 2J_1\hat{S}_3\hat{S}_4$, $S_1 = S_2 = S_3 = S_4 = {}^1/_2$) was diagonalized numerically using a homemade program including the Minuit subroutine for fitting of the data.[17]

It soon appeared that g was strongly correlated with the J's, and to minimize problems, the g value ($g = 2.065$) was determined by electron paramagnetic resonance and entered in the fitting process as a fixed parameter. The best-fit values were as follows: $g = 2.065$ (fixed), $J_1 = +190(51)$ cm^{-1}, $J_2 = -43(2)$ cm^{-1}, $R = 6 \times 10^{-4}$ ($R = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\sum[(\chi_M)_{obs}]^2$). It is worth noting that the experimental high-temperature data could not be reproduced by considering negative values of both interactions or by reversing the sign of the coupling constants. These values reproduced fairly well the high-temperature data including the maximum observed in the temperature dependence of χ_M, but attempts to fit the low-temperature data were unsuccessful. In particular, modeling of the intercluster interaction in the frame of the mean-field approximation did slightly improve the fit, but a large zJ value ($zJ = -13$ cm^{-1}) was obtained. Moreover, the slower than expected decrease of χ below 15 K was never reproduced. As usual for ferromagnetic interactions, J_1 is not accurately determined;[18] fitting the data as χ or χT afforded different J_1 values, +170 and +210 cm^{-1}, respectively (mean value 190 cm^{-1}), without a significant change of the R factor value.

Note that $g = 2.065$ at room temperature is consistent with $J_1 > +200$ cm^{-1} because for a quartet state one expects $g_Q = (g_{NO} + g_{Cu})/2$. Taking $g_{NO} = 2$, one obtained $g_{Cu} = 2.13$, a value close to that reported in related complexes involving diamagnetic ligands.[12] Accordingly, the smaller (1.85 cm^3 K mol^{-1}) than 2 (for two independent spins $S = 1$) of χT at room temperature is the signature of rather large antiferromagnetic interactions showing up even at high temperature, in agreement with the fairly large value of J_2 (−43 cm^{-1}).

Upon examination of the structural data, close contacts have been mentioned, which suggest that the magnetic data should be analyzed as chains of four-spin systems rather than isolated clusters. Indeed, along the z axis, the Cu^{II} ions might be viewed as linked alternatively by end-on and end-to-end azido bridges, while along the y axis, owing to contacts between uncoordinated NO groups of adjacent molecules, one should consider chains of antiferromagnetically coupled four-spin systems. Calculations of χ_M for such chains including three different ferro- and antiferromagnetic coupling constants are an intractable problem that we solved approximatively considering the following features. Along the z axis, the end-to-end pattern occurs with a very long Cu−N(6A) bond of 3.441 Å, a situation which, according to a recent study, should result in a very weak antiferromagnetic interaction.[12] In contrast, along the y axis, uncoordinated oxyl groups are arranged at the corners of a distorted parallelogram [O(1)−N(3) = 1.268 Å, N(3)−O(1B) = 4.24 Å, O(1B)−N(3B) = 1.268 Å, N(3B)−O(1) = 4.21 Å, O(1)−O(1B) = 3.67 Å; O(1)−N(3)−O(1B) = 113°] and the π^* magnetic orbitals make an angle of 41°. In this situation, the inter-N−oxyl interaction is expected to be antiferromagnetic with a magnitude as large as −30 cm^{-1}.[2]

Therefore, considering the large J_1 ferromagnetic metal−radical coupling, the low-temperature data (<150 K) were modeled as an alternating antiferromagnetic chain of spins $S = 1$ for which a numerical expression is available.[19] The following best-fit values were obtained: $g = 2.065$ (fixed), $J_2/k = -27$ K, and $\alpha = 0.69$. Taking into account that the real spins are $S = {}^1/_2$, the coupling constant is $J_2 = -38$ cm^{-1}, which compares fairly well to that figured out in the modeling of the high-temperature data (−43 cm^{-1}). This model brings $J'_{NO-NO} = -26$ cm^{-1}.

Therefore, this study seemed to bring a safe qualitative picture of the coupling scheme within the cluster and particularly a fairly large antiferromagnetic J_{Cu-Cu} interaction. However, this analysis had to be reconsidered in light of a subsequent DFT analysis of the magnetic coupling in this asymmetric complex.

DFT Calculations. DFT calculations were performed in order to provide a semiquantitative analysis of the exchange-coupling scheme in the system. They relied on the LCAO-ADF (Amsterdam Density Functional 2004.01 code developed by Te Velde and Baerends[20]) including the "VBP" exchange−correlation potential (Vosko, Wilk, and Nusair exchange and correlation energy,[21] completed by nonlocal gradient corrections to the exchange by Becke[22] and to the correlation by Perdew[23]) and triple-ζ (plus polarization) basis sets for all atoms.[24] The molecular structure was that obtained by X-ray crystallography.

The broken-symmetry states $|BS\rangle$ were computed as outer products of monomer (NO or Cu) spin functions of the form $\Pi_{k=1-4}|S_k Ms_k\rangle$. These are not pure spin states but monodeterminant states where the projection of the local NO radical (1 and 4) and Cu (2 and 3) spins are monitored to be up (↑) or down (↓). Pure spin states are then linear combinations of

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these BS states via Clebsch–Jordan coefficients.[25] For a four-spin system, this yielded up to six possible combinations of "ups" and "downs" (see model IV in the Appendix). The procedure is very similar to that published by Bencini and Totti.[26]

First- and second-neighbor spin-exchange interactions have been considered, resulting in the following spin Hamiltonian $\hat{H} = -2J_1\hat{S}_1\hat{S}_2 - 2J_2\hat{S}_2\hat{S}_3 - 2J_1\hat{S}_3\hat{S}_4 - 2J_3(\hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_4)$. The energies of the corresponding BS states are given in the Appendix, based on the fact that $\langle Ms_i|\langle Ms_j|\hat{S}_i\hat{S}_j|Ms_i\rangle|Ms_j\rangle = Ms_iMs_j$ (only the term $S_{iz}S_{jz}$ contributes[25]).

To gain insight into the spin-coupling scheme, a series of three preliminary calculations aiming at computing J values for "isolated" spin pairs (models I–III in the Appendix) were performed. Thus, when both oxyl NO groups were replaced by NOH (model I: HON–**Cu**–**Cu**–NOH), J_2 was found to be nearly 0 cm^{-1} within a few reciprocal centimeters accuracy. For comparison, the **Cu**–**Cu** exchange-coupling constant was also computed for another recently reported asymmetric end-on double-azido-bridged Cu^{II} complex whose structure, involving diamagnetic ligands, is similar to that of **1** and for which a weak antiferromagnetic Cu–Cu interaction ($J = -4.2$ cm^{-1}) was reported.[12a] Koner et al. linked this antiferromagnetic behavior with the fact that this complex presents a long Cu–N distance (≈2.5 Å) within the binuclear core.[27] Computationally, it was found to be $J_2 \approx 0$ (±4) cm^{-1}. For complex **1**, the axial Cu–N distance (2.434 Å) is similarly larger than the cutoff distance (2.05 Å) determined theoretically for the ferromagnetic/antiferromagnetic transition.[27]

The NO(1)–Cu(2) pair was then isolated by replacing Cu(3) by a Zn atom and NO(4) by NOH (model II: **ON**–**Cu**–Zn–NOH) to afford $J_1 = +226$ cm^{-1}, which agrees well with the experimental value of +190 cm^{-1}. Guessing that an exchange coupling J_3 might be operative between NO(1) and Cu(3) (in order to enforce antiferromagnetism between the two $S = 1$ Cu–NO^0 subunits because $J_2 \approx 0$), J_3 was computed by again neutralizing the middle Cu spin (model III: **ON**–Zn–**Cu**–NOH), leading to $J_3 = -261$ cm^{-1}. Finally, the whole complex was considered (model IV: **ON**–**Cu**–**Cu**–**NO**). The ferromagnetic exchange coupling J_1 does not vary significantly in magnitude (in the range 210–226 cm^{-1}). The same is true for J_2 (Cu–Cu), always computed close to zero (within a few reciprocal centimeters). The antiferromagnetic J_3 constant, however, decreased from −261 cm^{-1} (model III) to −126 cm^{-1} (model IV). This theoretical analysis may illustrate that spin-exchange constants are not directly transferable from dimers to tetramers because of the appearance of many-body terms.[28] A further DFT investigation devoted to this problem would go beyond the scope of the present work.

Finally, the four-spin system was considered as two $S = 1$ (Cu–NO) subunits, with the Heisenberg spin Hamiltonian $\hat{H} = -2J\hat{S}_A\hat{S}_B$ and $S_A = S_B = 1$, and from the states "a" (of energy $-2J$) and "b" (of energy $+2J$) of model IV (see the Appendix), an exchange-coupling constant of −61 cm^{-1} was computed. Considering that the broken-symmetry formalism that we relied on overestimates antiferromagnetic interactions,[25] this computed coupling constant is in fairly good agreement with that determined experimentally.

These results are further substantiated by a qualitative spin population analysis[24] because its distribution over the complex allows one to visualize the spread of the magnetic orbitals involved and the zones where overlap occurs.

In the "Cu monomer" (HON–**Cu**–Zn–NOH), significant spin populations are found on the Cu(1) site (0.478) as well as on the four N atoms N(4A), N(7), N(1), and N(2) defining the basal plane. More precisely, the nearest bridging azido group, N(4A)–N(5A)–N(6A) = **0.080**, −0.007, 0.105, and the terminal azido anion N(7)–N(8)–N(9) = **0.092**, −0.016, 0.130, are involved. We found as well spin population on N(1) (**0.055**) and N(2) (**0.071**), the imino N atoms of the ligand.

In the "NO monomer" (**rad**–Zn–Zn–NOH), large spin populations are found on N(3)–O(1), 0.25 and 0.41, respectively, as well as on N(2) (0.26) as expected. However, nonnegligible spin populations are also found quite far from the NO oxyl group; three of the four azido groups are involved [except N(4–6)], especially N(4A)–N(5A)–N(6A) (0.025, −0.003, 0.015, respectively), which is also part of the Cu(1) magnetic orbital. By symmetry, these considerations apply to the other Cu and NO sites.

As can be seen, the two first-neighbor Cu(1) and O(1)–N(3)–N(2) magnetic orbitals are mutually orthogonal at the level of the N(2) atomic site: the last three nitroxide atoms are part of a delocalized π system whose orbitals are orthogonal to the Cu basal plane. As N(2) receives spin population contributions from both magnetic orbitals, this explains at once the large J_1 ferromagnetic value. Let us still note that there is a secondary overlap region [N(7–9)], which should yield an antiferromagnetic contribution to J_1. However, both experiments and DFT computations result in the ferromagnetic term dominating the antiferromagnetic one in J_1.

Turning now to the HON–**Cu**–**Cu**–NOH "dimer", the Cu spin populations are nearly identical in magnitude (±0.47) for both the HS ($S = 1$) and BS ($Ms = 0$) states, resulting in an expected very small exchange coupling constant ($J_2 \approx 0$ cm^{-1}), as found.

In the second-neighbor "dimer" (**rad**–Zn–**Cu**–NOH), from the HS to BS case, there are two significant changes in the spin populations: that of Cu(1) drops from 0.480 (HS) to 0.437 (BS), and those of O(1A)–N(3A)–N(2A) decrease from (0.413, 0.256, 0.268) to (0.391, 0.241, 0.249). This indicates that the two magnetic orbitals exchange spin populations (i.e., communicate). As found above, that overlap occurs mainly at the level of the bridging N(4A)–N(5A)–N(6A) group (see above), varying from (0.090, −0.009, 0.108) in the HS state to (0.058, −0.005, −0.084) in the BS

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state, respectively. A resulting antiferromagnetic interaction between the two second-neighbor magnetic orbitals is thus expected.

Both experimental and theoretical findings (especially that of a second-neighbor antiferromagnetic Cu−nitroxide coupling) are therefore fully vindicated by this qualitative spin population analysis.

Conclusion

An azido end-on bi-bridged binuclear Cu^{II} complex including two chelating imino nitroxide ligands was characterized and exhibits a rare asymmetric structure where each bridging anion is coordinated axially to one Cu ion and equatorially to the second metal center. As expected, a large metal−nitroxide ferromagnetic exchange coupling was observed whose magnitude compares well with that reported for closely related complexes.[3] Indeed, very similar binding features ensuring the orthogonality of the magnetic orbitals and resulting in large ferromagnetic metal−radical interactions ($+200$ cm^{-1}) are observed in all copper(II) imino nitroxide complexes.

Nevertheless, this four-spin system has a singlet ground spin state as observed for other asymmetric double-bridged azido binuclear Cu^{II} complexes for which weak antiferromagnetic Cu−Cu interaction have been reported.[12] Surprisingly, however, in $[Cu_2(\mu_{1,1}\text{-}N_3)_2(\text{im-2py})_2(N_3)_2]$, a spin state of low multiplicity is much more stabilized by 1 order of magnitude.

DFT calculations performed on this complex (and related models) point to a strong ON−Cu ferromagnetic coupling, a weak (nearly zero) exchange coupling between the Cu spins, but a consequent strong antiferromagnetic coupling between the two $S = 1$ subunits through an indirect second-neighbor Cu−(Cu)−NO path.

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Appendix

For DFT results, see Table A1. J values are given in cm^{-1} (1 eV ≈ 8066 cm^{-1}).

Table A1

model		BS states	E_k (eV), E_k' (cm^{-1})[b]	H_k	$J_1 = J_{Cu-NO}$	$J_2 = J_{Cu-Cu}$	$J_3 = J_{Cu-NO'}$
I[a]	a	o↑↑o	−475.471 (+4)	$-J_2/2$		≈0	
	b	o↑↓o	−475.472 (−4)	$+J_2/2$			
II[a]	a	↑↑o o	−470.262 (−113)	$-J_1/2$	226		
	b	↑↓o o	−470.234 (+113)	$+J_1/2$			
III[a]	a	↑o↑o	−470.172 (+129)	$-J_3/2$			−261
	b	↑o↓o	−470.204 (−129)	$+J_3/2$			
IV[b]	a	↑↑↑↑	−469.471 (−90)	$-J_2/2 - J_1 - J_3$	210	≈0	−126
	b	↓↓↑↑	−469.502 (−340)	$+J_2/2 - J_1 + J_3$			
	c	↓↑↑↓	−469.450 (+80)	$-J_2/2 + J_1 + J_3$			
	d	↓↑↑↑	−469.459 (+7)	$-J_2/2$			
	e	↑↓↑↑	−469.460 (−1)	$+J_2/2$			
	f	↑↓↑↓	−469.418 (+338)	$+J_2/2 + J_1 - J_3$			

[a] The spins of these models are extinguished by protonation of the NO^0 radical and/or replacement of the Cu atom by a Zn atom (see the main text). [b] Optimized J values have been obtained by a mean least-squares procedure. There are $2^4 = 16$ different ways of combining the spins. Taking first into account the double degeneracy due to spin reversal (↑ ↔ ↓), there are eight broken-symmetry states left. Moreover, spin configurations (d: ↓↑↑↑ ≡ ↑↓↓↓) and (e: ↑↓↑↑ ≡ ↓↑↓↓) are degenerate and are therefore counted twice to ensure that $\sum_{k=1-8} H_k = 0$ as it should be, where H_k is the Heisenberg spin Hamiltonian energy of the corresponding (broken-symmetry) spin state. DFT bonding energies E_k are consequently replaced by $E_k' = E_k - E_{av}$ with $E_{av} = (\sum_k E_k)/8$, so that $\sum_k E_k' = 0$. The error function is then defined as $\text{err} = \sum_k (E_k' - H_k)^2$. The optimized set of J values yields a standard deviation of $(\text{err}/8)^{1/2} = 4$ cm^{-1} (5×10^{-4} eV; i.e., the fit is very good when compared to the E_k' energy range [±340 cm^{-1}], and a Heisenberg spin Hamiltonian is thus adequate to describe the computed DFT energy differences).

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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