Wölfel (Technische Hochschule Darmstadt) provided access to the facilities (four-circle diffractometer and computer) of the Stoe + Cie. Application Laboratory, Darmstadt. The authors appreciate discussions on the manuscript with Dr. K. J. Wannowius. Propargylaldehyde was supplied by BASF, Ludwigshafen.

Registry No. II, 22119-38-6; IV, 88106-41-6; Cu(TMBC)$(ClO_4)_2$, 88106-43-8; Cu(TMBC)I(ClO_4), 88106-45-0; Cu(TMBC)$(N_3)(ClO_4)$, 88106-47-2; Cu(TMBC)Br(ClO_4), 88106-49-4; Cu(TMBC)$(NO_3)_2$, 88106-51-8; Ni(TMBC)$(ClO_4)_2$, 88106-53-0; Ni(TMBC)Br_2, 88106-54-1; Ni(TMBC)$(NO_3)_2$, 88106-56-3; Cu(TMBC)$(H_2O)^{2+}$, 88106-57-4; Cu(TMBC)N_3^+, 88106-46-1; Cu(TMBC)$^{2+}$, 88106-58-5.

Supplementary Material Available: Listings of observed and calculated structure factors and atomic parameters for TMBC, Cu(TMBC)$(N_3)(ClO_4)$, and Cu(TMBC)$(ClO_4)_2$ (105 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, Université de Paris Sud, 91405 Orsay, France, and Laboratoire de Chimie Structurale des Matériaux, Université Pierre et Marie Curie, 75232 Paris, France

Crystal Structure and Magnetic and EPR Properties of Bis(μ-azido)tetrakis(4-*tert*-butylpyridine)dicopper(II) Perchlorate: A New Copper(II) Dinuclear Complex with a Large Stabilization of the Ground Triplet State

SONIA SIKORAV,[1a] ITKA BKOUCHE-WAKSMAN,[1b] and OLIVIER KAHN*[1a]

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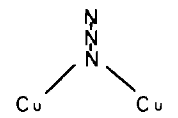
The title compound of formula $[Cu_2(t\text{-}Bupy)_4(N_3)_2](ClO_4)_2$, with *t*-Bupy = 4-*tert*-butylpyridine, has been synthesized, and its structure has been solved at room temperature. It crystallizes in the monoclinic system, of space group $P2_1/c$. Its lattice constants are a = 12.819 (3) Å, b = 13.76 (1) Å, c = 13.65 (1) Å, and β = 100.00 (2)° with Z = 2 dimeric units. The structure consists of $[Cu_2(t\text{-}Bupy)_4(N_3)_2]^{2+}$ dimeric cations and noncoordinated perchlorate anions. The copper(II) ions are fourfold coordinated with planar surroundings. They are bridged by azido groups in an end-on fashion. The Cu···Cu separation is 3.045 (3) Å, and the Cu–N–Cu bridging angle is 100.5 (6)°. The magnetic properties of the compound have been studied in the 2–300 K temperature range. They revealed that the ground state is the spin-triplet state, with a separation of 105 ± 20 cm^{-1} with regard to the low-lying spin-singlet state. The EPR powder spectrum confirms the nature of the ground state. On the assumption that the **D** and **g** tensor axes were coincident, this spectrum was interpreted with axial and rhombic zero-field splitting parameters, D = 0.42 (5) cm^{-1} and E = 0.02 (5) cm^{-1}. A new investigation of the magnetic properties of the copper azide $Cu(N_3)_2$ is also reported. This compound orders antiferromagnetically at T_N = 124 K. It is pointed out that this result is in no way a counterexample of the specific ability of the end-on azido bridges to stabilize the triplet state in copper(II) dinuclear complexes.

Introduction

Likely the most fascinating aspect of the chemistry of the μ-azido copper(II) dinuclear complexes is the versatility of their magnetic properties. In bibridged complexes with one or two end-on azido bridges like **1**, the interaction between the metal ions is strongly ferromagnetic and the energy gap between ground spin triplet and excited spin singlet may be so large that even at room temperature the S = 0 state is weakly populated.[2,3] In complexes with one or two end-to-end bridges like **2**, the interaction is strongly antiferromagnetic and the singlet state may be so stabilized with regard to the excited triplet state that the compound appears diamagnetic.[4,5] Finally, in complexes with asymmetric end-to-end azido bridges like **3**, with a short Cu–N$_\alpha$ bond and a long Cu–N$_\beta$ bond, the interaction is negligible when the geometry around the copper(II) ion is square pyramidal[2,6] or very weakly antiferromagnetic when this geometry tends to the trigonal bipyramid.[7] To rationalize these behaviors, two explanations have been proposed that correspond to two levels of sophistication of a same conceptual approach. The first theoretical approach only took into account the magnetic orbitals centered on each metal ion and the molecular orbitals constructed from them;[2] the second approach accounted for the role of the low-energy doubly occupied orbitals with a preponderant ligand character.[3] It has been shown that in the case of the azido bridges this could lead to a *spin-polarization effect*, due to the nature of the π_g HOMOs of N_3^-. Each π_g orbital[8] describes two paired electrons localized at the two extremities of N_3^-. At each instant, one of the two electrons has an α spin and the other one a β spin. When N_3^- bridges as in **1**, a π_g electron on the bridging nitrogen atom is partially delocalized toward the two d_{xy} metal orbitals; this favors the situation where the two metallic unpaired electrons are parallel, therefore the ferromagnetic interaction. In contrast, when N_3^- bridges as in **2**, an α-spin electron is partially delocalized toward a metal center and a β-spin electron is partially delocalized toward the other



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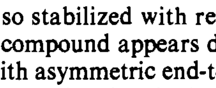

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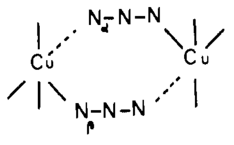

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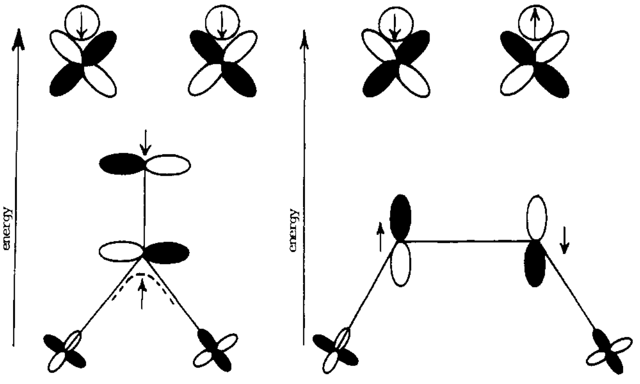
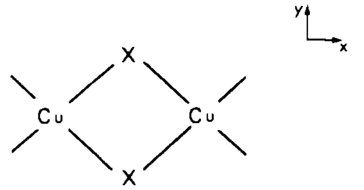
metal center, favoring the situation where the two metallic unpaired electrons are antiparallel, therefore the antiferromagnetic interaction. This spin-polarization effect is schematized in **4**, where the electrons in the bonding MOs with a preponderant ligand character are noted by ↑ and ↓ and the magnetic electrrons by circled ↑ and ↓.



4

Although we have not yet any definitive proof, our feeling is that this spin-polarization effect is the key factor with the end-on azido bridges. This would arise from the fact that the energy gap between the π_g level of N_3^- and the d metallic levels are close.[2] If this were true, the coupling would be ferromagnetic whatever the value of the Cu–N–Cu bridging angles or of the Cu···Cu separation may be. On the other hand, the accidental orthogonality of the *xy*-type magnetic orbitals, which may also explain the ferromagnetic interaction in networks like **5**, is destroyed by a small change of the structural parameters.[2,9] Therefore, it is important to check whether, as it has been found until now, all the end-on bis(μ-azido) copper(II) complexes exhibit a strong ferromagnetic interaction. In this paper, we describe a new complex of this kind. The investigation of its magnetic and EPR properties reveals that again the ground state is a spin triplet very separated in energy from the excited singlet state. We also present in the paper a new investigation of the magnetic properties of the polymeric copper(II) azide.



5

Experimental Section

Synthesis. A 185-mg sample (0.5×10^{-3} mol) of copper perchlorate dissolved in 5 mL of ethanol and 1 mL of an ethanolic molar solution (10^{-3} mol) of *t*-Bupy (4-*tert*-butylpyridine) were mixed together. To the limpid blue solution was added 32.5 mg (0.5×10^{-3} mol) of solid NaN_3. The solution was then filtered to separate a slight precipitate of the title compound. Dark blue single crystals of the same compound were obtained by slow evaporation. Anal. Calcd for $(C_{18}H_{26}N_5O_4ClCu)_2$: C, 45.47; H, 5.51; N, 14.73. Found: C, 45.36; H, 5.57; N, 14.62. $Cu(N_3)_2$ was prepared in the form of small crystals as described.[10] *Caution*! $Cu(N_3)_2$ is extremely explosive.

Crystallographic Data Collection and Refinement of the Structure. The X-ray structure study was carried out at room temperature on a prismatic 0.36 × 0.36 × 0.43 mm crystal sealed in a Lindemann glass capillary. The cell is monoclinic with space group $P2_1/c$ and $Z = 2$ dimeric units. The lattice parameters are $a = 12.819$ (3) Å, $b = 13.76$ (1) Å, $c = 13.65$ (1) Å, and $\beta = 100.00$ (2)°. The calculated and measured densities are respectively 1.30 and 1.30 (1) g cm^{-3} (flotation in $CCl_4 + CS_2$). Diffraction data were collected on a Nonius CAD-4 diffractometer using Mo Kα radiation and a graphite-crystal monochromator. The $\omega/2\omega$ scan technique was used to record 3322 independent reflections ($2\theta_{max} = 50°$), 2172 of them with $F > 2\sigma(F)$ were used in subsequent calculations. Three reflections were measured periodically to check crystal and electronic stabilities. The raw intensity data were corrected for the Lorentz–polarization effect, but no absorption ($\mu = 11.04$ cm^{-1}) or extinction corrections were applied.

On the basis of atomic positional parameters generated from the best electron density map produced by MULTAN,[11] all non-hydrogen atoms were located after a Fourier synthesis and a Fourier-difference synthesis. The structure was refined by the full-matrix least-squares method. The weighting scheme used was as follows: $F_o \leq 40$, $w = (F_o/40)^2$; $F_o > 40$, $w = (40/F_o)^2$. Scattering factors including real anomalous dispersion correction for Cu(II) were taken from the "International Tables of Crystallography". Refinement of hydrogen atoms positions found on a Fourier-difference synthesis did not show convergence to positions consistent with theoretical distances and angles. Introduction of all hydrogen atoms in theoretical positions without refinement increased the *R* factor. Finally, only the hydrogen atoms belonging to the *tert*-butylpyridine rings were introduced in theoretical positions (assuming C–H = 1 Å). Their thermal factors were set equal to those of the bound carbon atoms and were not allowed to vary. Anisotropic refinement of the thermal parameters of all non-hydrogen atoms resulted in final values of $R = 6.5\%$ and $R_w = 7.2\%$, with $R = \sum|F_o - |F_c||/\sum F_o$ and $R_w = (w(F_o - F_c)^2/wF_o^2)^{1/2}$. Accuracy of the structure is limited by the thermal instability of the compound; about one-third of the recorded intensities were weak and could not be used in refinement.

Magnetic Measurements. These were carried out with a Faraday type magnetometer equipped with a helium continuous-flow cryostat working in the 2–300 K temperature range. Independence of the magnetic susceptibility vs. the magnetic field was checked at both room temperature and 4.2 K. Mercury tetrakis(thiocyanato)cobaltate was used as a susceptibility standard. Diamagnetism correction was estimated at -340×10^{-6} cm^3 mol^{-1} for the title compound and -51×10^{-6} cm^3 mol^{-1} for $Cu(N_3)_2$.

EPR. The spectrum was recorded at X-band frequency with a Bruker ER 200 D spectrometer equipped with an Oxford Instruments continuous-flow cryostat. The magnetic field was determined with a Hall probe and the klystron frequency with a Hewlett-Packard frequency meter.

Description of the Structure

Atomic coordinates and thermal factors are given in Table I. The main distances and angles are listed in Tables II and III. The ORTEP view of the dimeric cation is represented in Figure 1, with the labeling scheme used.

The unit cell contains two dimeric cations $[Cu_2(t\text{-}Bupy)_4(N_3)_2]^{2+}$ and four noncoordinated perchlorate anions. A crystallographic inversion center relates the two parts of each dimeric unit. The copper(II) ion is bound to four nitrogen atoms; two of them belong to crystallographically independent *t*-Bupy molecules, and the other two belong to centrosymmetrically related azido bridges. The metal ion and its four nearest neighbors lie in the same mean plane. The angles and distances around copper(II) show a slightly distorted square-planar environment. The bridging network Cu–N_2–Cu is planar with a Cu···Cu separation of 3.045 (3) Å, which is significantly shorter than the Cu···Cu separation in the bis(end-on μ-azido) copper(II) complex of formula $[Cu_2(N_3)_4(C_{16}H_{34}N_2O_6)(H_2O)]$ (3.162 (1) Å).[2] The bridging angles Cu–N1–Cu($\bar{x},\bar{y},\bar{z}$) is equal to 100.5 (6)°, which is a value intermediate between those found in $[Cu_2(N_3)_4(C_{16}H_{34}N_2O_6)(H_2O)]$ (103.55°)[2] and in $[Cu_2(tmen)_2(N_3)(OH)](ClO_4)_2$ (close to 95.7°).[3] The end-on azido bridge is almost linear with N1–N2–N3 bond angle of 177 (6)°. The N1–N2 and N2–N3 bond lengths are equal to 1.18 (2) and 1.11 (3) Å,

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Table I. Positional and Anisotropic Thermal Parameters ($\times 10^4$) (with Esd's in Parentheses) and Isotropic B (Å^2) Parameters for Hydrogen Atoms[a]

	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	302 (1)	1010 (1)	405 (1)	49 (1)	32 (0)	75 (1)	2 (1)	−2 (0)	−2 (1)
Cl	379 (2)	428 (2)	−2111 (2)	84 (2)	48 (1)	58 (2)	0 (1)	16 (1)	6 (1)
O1	146 (5)	−353 (5)	−2020 (4)	111 (6)	52 (4)	54 (4)	−14 (4)	8 (4)	4 (3)
O2	678 (6)	1238 (5)	−1483 (5)	146 (7)	51 (5)	75 (5)	−8 (4)	33 (5)	−10 (4)
O3	741 (7)	771 (5)	−3121 (5)	157 (8)	72 (5)	61 (5)	−10 (5)	27 (5)	10 (4)
O4	1927 (6)	87 (7)	−1813 (7)	92 (6)	102 (6)	144 (8)	14 (5)	28 (6)	22 (6)
N1	937 (5)	−293 (5)	292 (5)	43 (5)	37 (4)	60 (5)	1 (4)	−4 (4)	0 (4)
N2	1705 (6)	−651 (6)	761 (7)	63 (6)	54 (5)	107 (7)	9 (4)	−19 (5)	−20 (5)
N3	2447 (10)	−976 (10)	1164 (12)	131 (10)	108 (9)	282 (17)	58 (9)	−125 (11)	−36 (12)
N5	1664 (5)	1620 (5)	1029 (6)	55 (5)	45 (4)	69 (6)	1 (4)	1 (5)	9 (4)
C10	1694 (7)	2140 (7)	1881 (8)	55 (6)	47 (6)	111 (9)	−9 (5)	0 (6)	−10 (6)
C11	2663 (8)	2521 (7)	2407 (8)	93 (8)	50 (6)	87 (9)	−15 (6)	−2 (7)	−9 (6)
C12	3612 (8)	2319 (7)	2075 (8)	78 (8)	56 (6)	75 (8)	−15 (6)	4 (6)	16 (6)
C13	3538 (7)	1794 (9)	1180 (9)	52 (6)	96 (8)	91 (9)	−15 (6)	19 (6)	6 (7)
C14	2551 (7)	1453 (8)	675 (8)	59 (7)	76 (7)	91 (9)	−12 (6)	12 (6)	8 (6)
C15	4686 (8)	2678 (10)	2653 (10)	76 (8)	106 (10)	111 (10)	−48 (7)	−33 (8)	31 (8)
C16	5601 (11)	2283 (19)	2228 (16)	74 (10)	333 (31)	223 (21)	−60 (15)	2 (12)	−74 (21)
C17	4741 (14)	3758 (12)	2582 (18)	184 (18)	119 (15)	338 (28)	−106 (14)	−118 (18)	74 (16)
C18	4795 (12)	2343 (15)	3730 (12)	156 (15)	220 (20)	133 (14)	−74 (14)	−80 (12)	75 (14)
N4	−544 (6)	2224 (5)	424 (6)	58 (5)	37 (4)	80 (6)	2 (4)	3 (5)	12 (4)
C1	−550 (7)	2877 (6)	−300 (7)	100 (9)	50 (6)	93 (9)	20 (6)	19 (8)	16 (6)
C2	−1165 (7)	3748 (6)	−300 (8)	60 (6)	50 (6)	80 (7)	6 (5)	1 (5)	3 (5)
C3	−1761 (6)	3924 (7)	442 (7)	55 (5)	41 (5)	87 (7)	6 (5)	15 (5)	0 (6)
C4	−1737 (8)	3212 (7)	1165 (9)	89 (8)	45 (6)	108 (9)	18 (6)	43 (7)	6 (6)
C5	−1137 (8)	2370 (7)	1147 (8)	100 (9)	47 (6)	92 (9)	17 (6)	45 (7)	14 (6)
C6	−2383 (8)	4858 (7)	457 (9)	80 (8)	41 (6)	127 (10)	19 (6)	23 (7)	6 (6)
C7	−2894 (18)	4927 (13)	1353 (22)	328 (30)	113 (13)	412 (35)	118 (17)	302 (29)	80 (17)
C8	−1646 (12)	5708 (8)	435 (11)	173 (14)	38 (6)	159 (14)	6 (7)	43 (11)	−5 (7)
C9	−3165 (17)	4973 (15)	−491 (19)	236 (22)	150 (16)	332 (30)	128 (16)	−170 (21)	−121 (18)
H1	0 (0)	2770 (0)	−830 (0)	4.0 (0)					
H2	−670 (0)	4000 (0)	0 (0)	3.8 (0)					
H4	−2170 (0)	3740 (0)	1640 (0)	4.0 (0)					
H5	−750 (0)	1390 (0)	1660 (0)	3.6 (0)					
H10	1040 (0)	2170 (0)	2130 (0)	5.0 (0)					
H11	2670 (0)	2750 (0)	3020 (0)	3.8 (0)					
H13	4000 (0)	1650 (0)	920 (0)	4.9 (0)					
H14	2540 (0)	1080 (0)	0 (0)	3.5 (0)					

[a] The form of the anisotropic thermal parameter is $\exp(-[(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)])$.

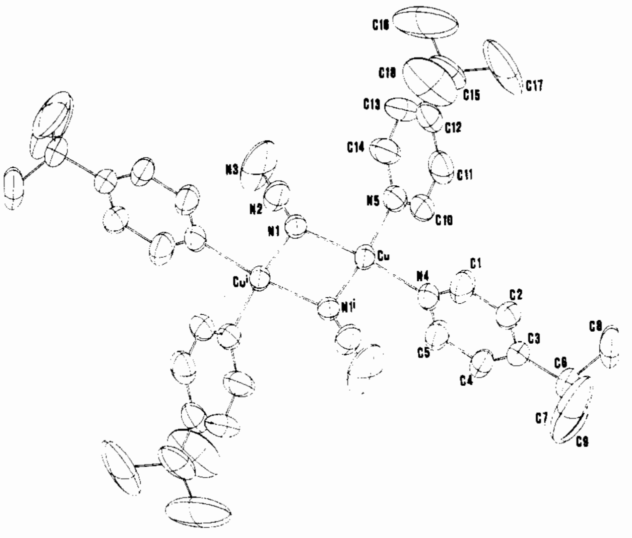

Figure 1. ORTEP view of the cation $[Cu_2(t\text{-Bupy})_4(N_3)_2]^{2+}$.

respectively, the longer bond involving the nitrogen atom linked to the metal. This is consistent with the structural results obtained with the other end-on-bridging azido ions[2,3,12,13] and also with the terminal azido ions.[4,14,15]

Table II. Distances (Å) and Angles (deg) (with Esd's in Parentheses)

	Around the Copper Atom		
Cu–Cu[a]	3.042 (3)	N1–Cu–N1[a]	79.5 (5)
N1–N1[a]	2.53 (2)	N1–Cu–N4	171 (2)
Cu–N1	1.99 (1)	N1–Cu–N5	94.0 (8)
Cu[a]–N1	1.97 (1)	N4–Cu–N5	94.6 (9)
Cu–N4	2.00 (1)	N4–Cu–N1[a]	91.8 (6)
Cu–N5	1.99 (1)	N5–Cu–N1[a]	173 (4)
Cu–N1–Cu[a]	100.5 (6)	Cu–N4–C1	119 (2)
Cu–N1–N2	130 (3)	Cu–N4–C5	121 (2)
Cu–N1[a]–N2[a]	123 (2)	Cu–N5–C10	119 (2)
		Cu–N5–C14	121 (2)
	In the Perchlorate Anion		
Cl–O1	1.45 (1)	O1–Cl–O2	110 (1)
Cl–O2	1.46 (1)	O1–Cl–O3	109 (1)
Cl–O3	1.42 (1)	O1–Cl–O4	109 (2)
Cl–O4	1.41 (2)	O2–Cl–O3	110 (2)
O1–O2	2.37 (2)	O2–Cl–O4	110 (2)
O1–O3	2.34 (2)	O3–Cl–O4	109 (2)
O1–O4	2.33 (2)		
O2–O3	2.36 (2)		
O2–O4	2.35 (2)		
O3–O4	2.31 (2)		
	Between the Perchlorate Ion and the Dimeric Cation		
Cl–N1	3.42 (1)	O2–N1[a]	3.13 (2)
Cl–C11	3.76 (2)	O3–C10[b]	3.17 (2)
O1–N1	3.07 (2)		

[a] $\bar{x}, \bar{y}, \bar{z}$. [b] $x, {}^1/_2 - y, {}^1/_2 + z$.

The bond lengths and angles within the *t*-Bupy molecules and the perchlorate anions do not warrant any particular comments. The angles between the mean planes of the *t*-Bupy

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Table III. Bond Distances (Å) and Angles (deg) (with Esd's in Parentheses) in the Azide Anion and in the *tert*-Butylpyridine Molecule

	Azide Anion		
N1-N2	1.18 (2)	N1-N2-N3	177 (6)
N2-N3	1.11 (3)		
	tert-Butylpyridine 1		
N4-C1	1.34 (2)	C5-N4-C1	120 (3)
N4-C5	1.36 (2)	N4-C1-C2	120 (3)
C1-C2	1.44 (2)	N4-C5-C4	121 (4)
C2-C3	1.39 (2)	C1-C2-C3	121 (3)
C3-C4	1.39 (2)	C2-C3-C4	117 (3)
C4-C5	1.39 (3)	C3-C4-C5	121 (4)
C3-C6	1.51 (2)	C2-C3-C6	121 (3)
C6-C7	1.49 (4)	C4-C3-C6	122 (3)
C6-C8	1.50 (3)	C3-C6-C7	112 (4)
C6-C9	1.50 (4)	C3-C6-C8	109 (3)
		C3-C6-C9	109 (4)
		C7-C6-C8	107 (4)
		C7-C6-C9	113 (5)
		C8-C6-C9	107 (4)
	tert-Butylpyridine 2		
N5-C10	1.36 (2)	C10-N5-C14	120 (3)
N5-C14	1.33 (2)	N5-C10-C11	121 (3)
C10-C11	1.42 (2)	N5-C14-C13	121 (3)
C11-C12	1.40 (2)	C10-C11-C12	120 (3)
C12-C13	1.41 (3)	C11-C12-C13	117 (3)
C13-C14	1.41 (3)	C12-C13-C14	121 (4)
C12-C15	1.54 (3)	C11-C12-C15	121 (3)
C15-C16	1.50 (4)	C13-C12-C15	122 (3)
C15-C17	1.49 (4)	C12-C15-C16	112 (4)
C15-C18	1.52 (4)	C12-C15-C17	109 (4)
		C12-C15-C18	109 (3)
		C16-C15-C17	108 (4)
		C16-C15-C18	108 (4)
		C17-C15-C18	112 (4)

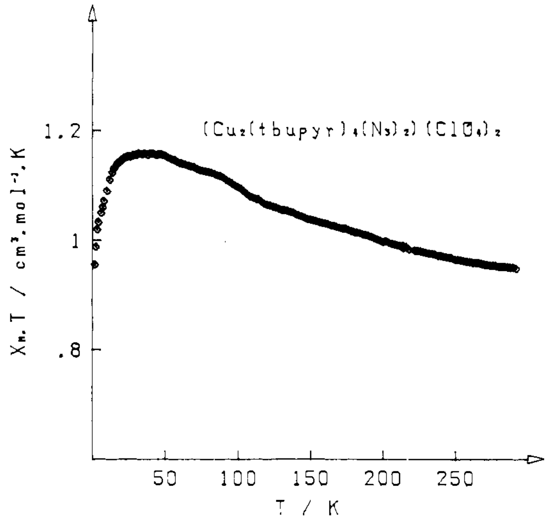

Figure 2. Temperature dependence of $\chi_M T$ for $[Cu_2(t\text{-}Bupy)_4(N_3)_2](ClO_4)_2$.

rings and the plane of the bridging network are 85° for *t*-Bupy 1 and 47° for *t*-Bupy 2 (see Figure 1).

Magnetic and EPR Properties

The magnetic behavior of the title compound is shown in Figure 2 in the form of the $\chi_M T$ vs. T plot, χ_M being the molar magnetic susceptibility and T the temperature. At room temperature $\chi_M T$ is equal to 0.95 cm^3 mol^{-1} K, which is a value already higher than what is expected for two noncoupled copper(II) ions, increases upon cooling, reaches a broad maximum in the range 60–18 K with $\chi_M T = 1.15 \pm 0.02$ cm^3 mol^{-1} K, and then decreases upon cooling to pumped liquid-helium temperature. This behavior is characteristic of a ferromagnetic interaction with a ground spin-triplet state very separated in energy from the excited spin-singlet state. In the low-temperature range, where $\chi_M T$ is almost constant, only the ground triplet state is significantly populated. In principle, it is possible to deduce from the magnetic data the energy gap J between the two low-lying states, the theoretical expression being

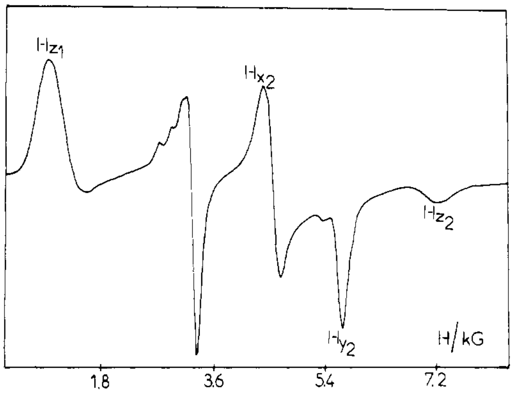

Figure 3. X-Band powder EPR spectrum of $[Cu_2(t\text{-}Bupy)_4(N_3)_2](ClO_4)_2$ at 4.2 K.

Table IV. Observed and Calculated Magnetic Fields for the Resonances of the EPR Spectrum of $[Cu_2(t\text{-}Bupy)_4(N_3)_2](ClO_4)_2$ (See Text)

	magnetic field, G			magnetic field, G	
resonance	obsd	calcd	resonance	obsd	calcd
H_{z_1}	1030	1057	H_{y_2}	5660	5665
H_{x_2}	4530	4532	H_{z_2}	7170	7173

$$\chi_M = \frac{2N\beta^2 g^2}{k(T-\theta)}[3 + \exp(-J/kT)]^{-1}$$

where the θ Weiss correction accounts here for both intermolecular effects and zero-field splitting (vide infra the EPR study). However, it has already been pointed out that the larger the stabilization of the triplet state, the less accurate the determination of J is.[2,3] Keeping in mind that the uncertainty on the result will be large, we determined J by a least-squares-fitting procedure and found $J = 105$ cm^{-1} with $g = 2.17$ and $\theta = -0.57$ K. The agreement factor defined as $\sum|(\chi_M T)_{\text{calcd}} - (\chi_M T)_{\text{obsd}}|^2/\sum|(\chi_M T)_{\text{obsd}}|^2$ is then equal to 2.25×10^{-4}. This minimum is extremely smooth so that the uncertainty may be estimated as ±20 cm^{-1}.

The powder EPR spectrum of the title complex at 4.2 K is shown in Figure 3. In contrast to the spectra of the previously described μ-azido copper(II) complexes with a ground triplet state,[2,3] this spectrum is nicely resolved. It exhibits four features at 1030, 4530, 5660, and 7170 G belonging to the actual compound and a sharp feature with a hyperfine structure around 3200 G, most likely due to a noncoupled dilute copper(II) impurity. We checked that no other feature was detectable up to 12 000 G. When the complex is heated the absolute intensities of the four features quickly diminish, but their relative intensities are unchanged. At room temperature, only the signal due to the impurity remains detectable. Both the form of the spectrum and its temperature dependence confirm that the ground state is a triplet state. The presence of only four features indicates that the axial zero-field splitting parameter D is larger than the value of the incident quantum (≃0.3 cm^{-1}). To interpret the spectrum quantitatively, we assumed that Wasseman's equations[16] were valid,

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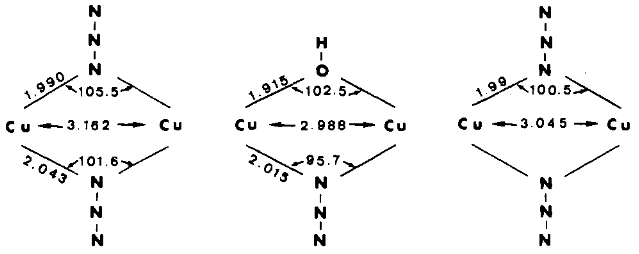
[16] Wasserman, E.; Synder, L. C.; Vager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

i.e. that the **D** and **g** tensors axes were coincident.[17] In this case, only one attribution leads to reasonable values for the principal values of the **g** tensor with $g_x = 2.06$ (4), $g_y = 2.00$ (3), $g_z = 2.21$ (5), $|D| = 0.42$ (5) cm^{-1}, and $E = 0.02$ (5) cm^{-1}. The agreement between observed and calculated fields is then excellent as shown in Table IV. The average value of g for the triplet state deduced from the EPR spectrum compares itself fairly well with the value deduced from the magnetic data (2.10 and 2.17, respectively). At this stage, it can be noted that this zero-field splitting cannot entirely account for the Weiss correction of −0.57 K. In absence of any other phenomenon, $|D| = 0.42$ (5) cm^{-1} would lead to $\theta = -0.12$ K. Therefore, we must admit that θ contains other effects like intermolecular interaction (the shortest Cu···Cu separation is ca. 12 Å) and experimental uncertainties.

Discussion and Conclusion

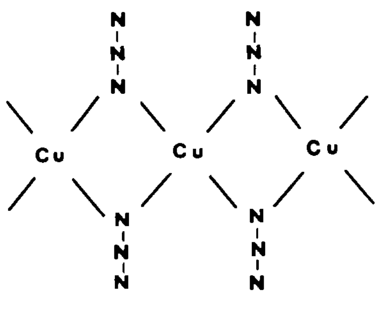
The magnetic and EPR properties of $[Cu_2(t\text{-}Bupy)_4(N_3)_2](ClO_4)_2$ confirm that the end-on azido bridges have a quite specific ability to stabilize the triplet state in copper(II) dinuclear species. Until now, three examples (and no counterexample) have been described. The bridging networks and the energy gaps J are compared in **6**.[2,3]



6

$[Cu_2(N_3)_4(C_{16}H_{34}N_2O_6)(H_2O)]$	$[Cu_2(tmen)_2(N_3)(OH)](ClO_4)_2$	$[Cu_2(t\text{-}Bupy)_4(N_3)_2](ClO_4)_2$
$J = 70 \pm 20\ cm^{-1}$	$J > 200\ cm^{-1}$	$J = 105 \pm 20\ cm^{-1}$

At this stage of our work, it does not seem possible to deduce a structure–magnetic properties correlation. However, we can notice that (i) the largest ferromagnetic interaction is obtained for the complex with only one end-on azido bridge and (ii) when the two bis(μ-azido) complexes are compared, the J energy gap is larger in the complex that has a smaller Cu–N–Cu bridging angle and a shorter Cu···Cu distance. There exists another compound in which copper(II) ions are bridged by two azido ligands in an end-on fashion, namely the copper(II) azide $Cu(N_3)_2$. However, the structure of this compound is very complicated.[12] At first sight, $Cu(N_3)_2$ is made of linear chains:



If these chains were magnetically isolated, the magnetic behavior of the compound should be that of a one-dimensional ferromagnet. Several systems of this kind have been recently

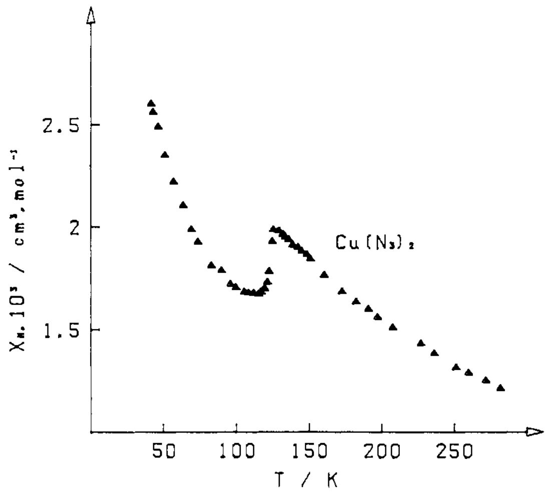
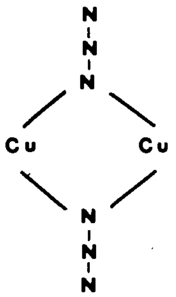
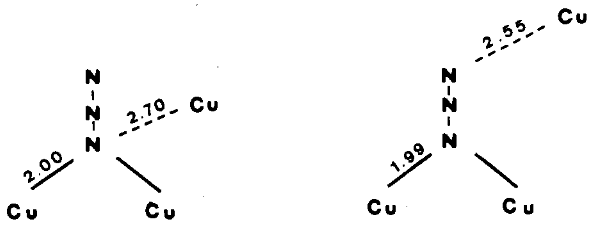


Figure 4. Temperature dependence of χ_M for $Cu(N_3)_2$.

described by Willett et al.[18] In fact, the chains are structurally coupled in two ways: (i) the chains are coupled two by two. In each network



one of the two nitrogen bridging atoms occupies the apical position around a copper(II) ion belonging to another chain; (ii) these double chains are coupled between them by the terminal atom of an azido bridge that occupies the second apical position around a copper(II) ion. So, there are two types of azido groups in $Cu(N_3)_2$, as shown in **7**.



7

We studied the magnetic properties of $Cu(N_3)_2$. The result is represented in Figure 4. The compound orders antiferromagnetically at 124 K. We did not detect any influence of the applied magnetic field in the range 0.5–1.2 T. This study had already been carried out by Singh,[19] who found a Neel temperature of 259 K. We do not see any explanation for this difference. The transition at 124 K was confirmed by differential thermal analysis. It is clear that the onset of an antiferromagnetic order is not related to the intrachain interaction through end-on azido bridges, since there is no magnetic order at one dimension.[18] The mechanism of the interaction between the metal ions in $Cu(N_3)_2$ is certainly very complicated, and only a neutron study could specify the magnetic structure of the antiferromagnetic phase. The im-

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portant point for our work is that $Cu(N_3)_2$ is in no way a counterexample of the ability of the end-on azido bridges to favor a ground triplet state in copper(II) dinuclear complexes.

Registry No. $[Cu_2(t\text{-Bupy})_4(N_3)_2](ClO_4)_2$, 88200-68-4; $Cu(N_3)_2$, 14215-30-6.

Supplementary Material Available: Listings of structure factor amplitudes and magnetic data (17 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Department, Manchester University, Manchester M13 9PL, England,
and Department of Chemistry, The University of Arizona, Tucson, Arizona 85721

Crystal Structure and Spectroscopic Studies of $[MoO_2(\text{L-cysOMe})_2]$

IAIN BUCHANAN,[1a] MARTIN MINELLI,[1b] MICHAEL T. ASHBY,[1b] TREVOR J. KING,[1c]
JOHN H. ENEMARK,*[1b] and C. DAVID GARNER*[1a]

Received April 22, 1983

$[MoO_2(\text{L-cysOMe})_2]$ crystallizes in the orthorhombic space group $P2_12_12$ with $a = 7.830$ (5), $b = 16.202$ (8), and $c = 5.861$ (3) Å, $V = 743.5$ Å^3, $Z = 2$. The structure was solved by direct methods followed by least-squares refinement using 1065 independent reflections to a final R value of 0.038 ($R_w = 0.054$). The molecules have crystallographic C_2 symmetry and possess the expected *cis*-dioxo (Mo–O = 1.714 (4) Å), *trans*-dithiolate (Mo–S = 2.414 (2) Å), and *cis*-diamino (Mo–N = 2.375 (5) Å) distorted octahedral configurations. The molecules crystallize with the Λ configuration at the metal, and the L-cysteine chelate rings have the λ conformation. $[MoO_2(\text{L-cysOMe})_2]$ exists as two isomers in solution, as observed by ^1H, ^{13}C, and ^{95}Mo NMR spectroscopy; these are assigned as the Λ and Δ diastereomers of the $MoO_2(S,N)_2$ complex and appear in relative amounts of ca. 5:1. Interconversion between these diastereomers has been observed by ^{95}Mo NMR spectroscopy. Coalescence of the two signals occurs at ca. 333 K and thus $\Delta G^\ddagger$ for the isomerization process is ca. 64 kJ mol^{-1}. The circular dichroism spectrum of $[MoO_2(\text{L-cysOMe})_2]$ resolves each of the two bands of the UV–visible spectrum (at ca. 352 aand 259 nm) into two components at 413/353 and 284/268 nm.

Introduction

The pursuit of chemical analogues of the molybdenum centers of the molybdoenzymes has led to significant developments in the synthesis and characterization of molybdenum complexes.[2] Measurement of the extended X-ray absorption fine structure (EXAFS) associated with the molybdenum K edge has provided direct evidence concerning the nature, number, and distance of the ligand donor atoms coordinated to molybdenum in several of these enzymes.[3-6] In the oxidized form of the molybdoenzymes which catalyze net oxygen-atom transfer reactions, the (presumed) molybdenum(VI) center is bound to one or more oxo groups and several sulfur ligands. In the specific instance of chicken liver sulfite oxidase, molybdenum(VI) appears to be coordinated to two oxo groups (Mo–O = ca. 1.68 Å) and two or three sulfur atoms (Mo–S = ca. 2.41 Å). Chemical systems that possess oxo and sulfur coordination of molybdenum(VI) include the cysteine ester complexes, $[MoO_2(\text{cysOR})_2]$, which have been known for some time, particularly for R = Me or Et.[7,8] However, a comprehensive characterization of these complexes has not been reported. Therefore, we have investigated the structure and spectroscopic properties of these systems. Herein we report the crystal structure of $[MoO_2(\text{L-cysOMe})_2]$ and some spectroscopic properties of this and the corresponding ethyl ester derivative. These studies were also stimulated by the chiral nature of the molybdenum center in complexes of this type, with reference to the circular dichroism (CD) properties of the molybdenum domain of sulfite oxidase,[9] and the desire to further demonstrate the sensitivity of ^{95}Mo NMR spectroscopy, for example, to distinguish between diastereomeric complexes.[10]

Experimental Section

Preparation of the Compounds. The ligands methyl and ethyl L-cysteinate were obtained as their hydrochlorides from Sigma. $[MoO_2(\text{L-cysOR})_2]$ (R = Me or Et) was prepared according to previously published procedures.[7,8] Anal. Calcd for $C_8H_{16}N_2MoO_6S_2$ (R = Me): C, 24.2; H, 4.1; N, 7.1; Mo, 24.2. Found: C, 24.1; H, 4.0; N, 7.0; Mo, 23.1. Calcd for $C_{10}H_{20}N_2MoO_6S_2$(R = Et): C, 28.3; H, 4.8; N, 6.6; Mo, 22.6. Found: C, 28.7; H, 5.0; N, 6.3; Mo, 22.4. Crystals of $[MoO_2(\text{L-cysOMe})_2]$ suitable for structure determination by X-ray crystallography were obtained by slow evaporation in air of a solution containing the compound dissolved in ethyl acetate. The crystals were obtained as yellow needles, which showed well-defined optical anisotropy to transmitted light when viewed through a polarizing microscope, being yellow when viewed in one orientation and green when viewed perpendicular to this.

X-ray Structure Determination. A well-formed crystal was mounted on a Syntex P2$_1$ autodiffractometer equipped with a scintillation counter and a graphite monochromator. The longest dimension of the crystal was approximately parallel to the ϕ axis. The results from the automatic centering, indexing, and least-squares routines and the axial photographs were consistent with a primitive orthorhombic lattice. Data were collected for the *hkl* octant and reduced to F_o^2 and $\sigma(F_o^2)$

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