in spite of the distortion, the bridging network $CuC_2S_2N_2Cu$ remains planar with short Cu–N and Cu–S bond lengths. An extended Hückel calculation on the fivefold-coordinated chromophore confirmed that the spin density around each metal center is strongly delocalized toward the nitrogen and sulfur bridging atoms.

The powder EPR spectrum of **11** was recorded. At room temperature, it exhibits an almost symmetrical feature centered at $g = 2.10$ (8), the intensity of which decreases when the sample is cooled as expected for a triplet excited state situated at 730 cm^{-1} above the diamagnetic ground state. Around 120 K, the signal vanishes and the spectrum only shows the signal corresponding to the monomeric impurity detected in magnetism.

Conclusion

We synthesized three novel binucleating dithiooxamide derivatives and from them several copper(II) binuclear complexes.

The magnetic properties of these complexes are quite similar. All exhibit a strong antiferromagnetic interaction with singlet–triplet energy gaps around 600 cm^{-1}. This result confirms the specific ability of the dithiooxamide bridge to propagate the electronic effects between copper(II) ions far away from each other. It is noteworthy that the magnitude of the interaction remains unchanged in $Cu_2DT(metOMe)_2X_2$ (**10** and **11**), where the environments of the metal centers are trigonal bipyramidal instead of coplanar. In other words, the modification of the geometry of the chromophores does not lead to a reversal of the magnetic orbitals, in contrast with what happens in the μ-oxalato copper(II) binuclear complexes.[28]

As opposed to the magnetic properties, the redox properties present great differences. They are strongly influenced by the nature of the amino acid amides of dithiooxalic acid. While $[Cu_2DT(glyglyEtOH)_2]^{2-}(NBu_4)_2 \cdot 2H_2O$ (**6**) does not show any reduction step between 0 and −1.7 V (vs. SCE), $Cu_2DT(metOMe)_2X_2$ (**10** and **11**) is very easily reduced. On the other hand, **6** can be reversibly oxidized to the $Cu^{II}Cu^{III}$ species, which unfortunately is chemically unstable. These differences are essentially due to the presence of donating nitrogen atoms in the peptide derivative and to that of a withdrawing sulfur atom in the methionine methyl ester derivatives.

Finally, we wish to emphasize that the compound $Cu_2DT(metOMe)_2Br_2$ (**11**) is the first one in which the coordination of the sulfur atom of the methionine has been structurally characterized.

Acknowledgment. This work was supported by the SNEA (P), to which we want to express our gratitude.

Registry No. **1**, 92957-64-7; **2**, 3916-40-3; **3**, 2641-02-3; **4**, 92957-65-8; **5**, 92957-68-1; **6**, 92984-11-7; **7**, 92957-66-9; **8**, 92957-69-2; **9**, 92957-67-0; **10**, 92957-70-5; **11**, 92984-12-8; **12**, 92984-13-9; phthalic anhydride, 85-44-9; glycylglycine, 556-50-3; dithiooxamide, 79-40-3; methionine, 63-68-3; ethanolamine, 141-43-5.

Supplementary Material Available: Listings of structure factor amplitudes and anisotropic thermal parameters for **11** (7 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, ERA No. 672,
Université de Paris-Sud, 91405 Orsay, France, and Laboratoire de Chimie Structurale des Matériaux,
Université Pierre et Marie Curie, 75230 Paris, France

Crystal Structure and Magnetic Properties of $[Cu_2(tmen)_2(N_3)_3](PF_6)$ (tmen = *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine): A Copper(II) Chain Compound with both Single Symmetrical and Double Dissymmetrical End-to-End Azido Bridges

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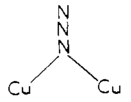
Received April 2, 1984

The title compound has been synthesized, and its crystal structure has been solved at room temperature. It crystallizes in the monoclinic system, space group $P2_1/c$. Its lattice constants are $a = 12.713$ (1) Å, $b = 31.240$ (4) Å, $c = 13.259$ (6) Å, and $\beta = 102.17$ (2)° with $Z = 8$ binuclear units. The structure consists of zigzag chains of binuclear cations $[Cu_2(tmen)_2(N_3)_3]^+$ parallel to the *c* direction and noncoordinated PF_6^- anions. Within the binuclear unit, the copper atoms are bridged by a single azido group in a symmetrical end-to-end fashion with a Cu···Cu mean separation of 4.439 Å. The binuclear units are linked to each other by a double dissymmetrical end-to-end azido bridge with a Cu···Cu mean separation of 5.131 Å. Each copper atom is surrounded by five nitrogen atoms, two from tmen (=*N*,*N*,*N'*,*N'*-tetramethylethylenediamine) and three from the azido groups, occupying the vertices of a slightly distorted square-based pyramid. The two basal planes within a binuclear unit make a mean dihedral angle of 46°. The magnetic properties of the title compound have been investigated in the 30–300 K temperature range. The molar magnetic susceptibility very closely follows the behavior expected for an antiferromagnetically coupled copper(II) binuclear complex with a singlet–triplet energy gap $J = -308.6$ cm^{-1}. The X-band powder EPR spectrum is poorly resolved. It exhibits a resonance in the triplet excited state that vanishes at low temperature. It is shown that the interaction occurs through the symmetrical azido bridge. Its mechanism is discussed, and the concept of spin polarization effect is recalled.

Introduction

The variety of molecular architecture of (μ-azido)copper(II) binuclear complexes leads to a large range of magnetic properties.[2]

When N_3^- bridges in the end-on fashion, as in **1**, the ferromagnetic interaction is favored. Two complexes with two end-on azido bridges have already been described. Both exhibit a spin triplet ground state with a relatively large triplet–singlet



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[1] (a) Université Pierre et Marie Curie. (b) Université de Paris-Sud.

[2] Magnetostructural correlations in exchange-coupled systems: Gatteschi, D., Kahn, O., Willett, R. D., Eds. *NATO Adv. Study Inst. Ser. C*, in press.

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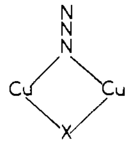
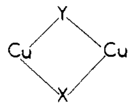
separation.[3,4] When two copper(II) ions are bridged by an end-on azido and another ligand X, the sign and the magnitude of the interaction, of course, depend also on the nature of X. However, preliminary results suggest that in the network

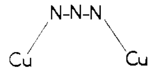


the interaction is less antiferromagnetic (or more ferromagnetic) than in any other



network.[5] With X = OH^-, an exceptionally large stabilization of the triplet state has been found.[6]

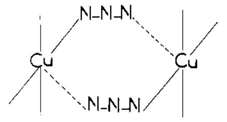
When N_3^- bridges in a symmetrical end-to-end fashion as in **2**, the interaction is strongly antiferromagnetic. In most



2

of the reported cases, the stabilization of the singlet ground state is so large that the excited triplet state is totally depopulated, even at room temperature, and the compound appears diamagnetic.[3,7-9]

Finally, N_3^- can also bridge in a dissymetrical end-to-end fashion as shown in **3**. In such a case, the interaction is either



3

negligible when the geometry around the metal is square pyramidal,[3,10] or very weakly antiferromagnetic when this geometry tends toward the trigonal bipyramid.[11]

In the system $Cu(II)/N_3^-/tmen$ with tmen = *N,N,N′,N′*-tetramethylenediamine, the situations **1** and **3** have already been reported. An end-on azido bridge has been found in $[Cu_2(tmen)_2(N_3)(OH)](ClO_4)_2$, the second bridge being an hydroxo group.[6] As already mentioned, the interaction in this complex is ferromagnetic. Two dissymmetrical end-to-end azido bridges have been found in $[Cu(tmen)(N_3)_2]_2$ where the interaction between the metal centers is negligible.[10] In this paper, we describe a new compound, namely $[Cu_2(tmen)_2(N_3)_3](PF_6)$ where one of the azido groups bridges in a symmetrical end-to-end fashion, as in **2**, and the two other ones bridge in a dissymmetrical end-to-end fashion, as in **3**. The investigation of the magnetic properties of this compound will show that the interaction through the former azido is antiferromagnetic and through the latter are negligible, leading to spin singlet pair ground states.

Table I. Crystallographic Data Collection and Refinement Conditions

space group	$P2_1/c$
unit cell parameters	$a = 12.713$ (1) Å $b = 31.240$ (4) Å $c = 13.259$ (6) Å $\beta = 102.17$ (2)° $V = 5148$ Å^3 $Z = 8$ dimeric units
mol wt	630.52
D_{expt1}	1.63 g cm^{-3}
D_{measd}	1.60 (5) g cm^{-3} (flotation in $CCl_4 + C_2H_5I$)
cryst shape	prismatic
cryst size	0.286 × 0.286 × 0.858 mm
radiation	Cu Kα
monochromator	graphite
abs coeff (μ)	32.82 cm^{-1}
$2\theta_{max}$	99.93°
no. of collcd reflcns	7936
no. of indep reflcns	6401
no. of reflcns for refinement	3309 [$F > 2\sigma(F)$]
no. of variable parameters	614
final agreement factors	$R = 0.075$; $R_w = 0.079$

Experimental Section

Synthesis. To a solution of 368 mg (10^{-3} mol) of copper(II) perchlorate in 5 mL of water was added successively a solution of 116 mg (10^{-3} mol) of tmen in 5 mL of water, then a solution of 130 mg (2×10^{-3} mol) of NaN_3 in 20 mL of water, and finally a solution of 168 mg (10^{-3} mol) of $NaPF_6$ in 5 mL of water. By slow evaporation, first appear dark green single crystals of $[Cu(tmen)(N_3)_2]_2$ and then well-shaped dark blue single crystals of the title compound. Anal. Calcd for $C_{12}H_{32}N_{13}F_6PCu_2$: C, 22.85; H, 5.19; N, 28.88; Cu, 20.17. Found: C, 23.06; H, 5.13; N, 28.85; Cu, 20.6.

Crystallographic Data Collection and Refinement of the Structure. The X-ray structure study was carried out at room temperature on a crystal sealed in a Lindemann glass capillary. Diffraction data were collected on a Phillips four-circle diffractometer, with the $\omega/2\theta$ scan technique. Information concerning the crystallographic data collection is given in Table I. Two different speeds of data collection were used: fast from θ_{max} through 25° and slow from 25° through 50°. Three reflections were measured periodically to check crystal and electronic stabilities. The raw intensity data were corrected for Lorentz-polarization effects, but no absorption or extinction corrections were applied.

Starting with atomic positional parameters generated from the best electronic density map produced by MULTAN, all non-hydrogen atoms were located after a Fourier synthesis and two Fourier-difference syntheses. The structure was refined by the full-matrix least-squares method. The weighting scheme used was $F_o < 80$, $w = (F_o/80)^2$; $F_o > 80$, $w = (40/F_o)^2$. Scattering factors including real anomalous dispersion correction for copper and P atoms were taken from the International Tables of Crystallography.

The convergence of thermal parameters of the light atoms was unusually slow. Both the instability of the compound and the thermal diffuse scattering may explain these difficulties. A first experiment had to be interrupted because the crystal decomposed in the X-ray beam. The data used in this work were collected on a second crystal. Although the number of collected reflections was high, many could not be used in calculations owing to their weak accuracy. For some strong reflections, F_o is greater than F_c. This is due to thermal diffuse scattering observed on Weissenberg photographs of reciprocal planes either perpendicular to the *c* direction or making an angle of 40° with *c*. There are strong streaks in the whole range of θ, but especially at low angles, along the reciprocal rows of spots collinear with the origin. In the refinement process, when *R* reached the value of 0.08, F_o values were replaced by corresponding F_c values for 18 low-order reflections very affected by the streaks (with background variations between 15% and 65%). The convergence was then reached in few cycles of refinement, with the *R* value of 0.076. The F_o values of the

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Table II. Positional Parameters ($\times 10^4$)

	x	y	z
Cu1	3520 (1)	3464 (1)	753 (2)
Cu2	3545 (1)	4076 (1)	−4256 (2)
Cu3	6117 (1)	3479 (1)	3569 (2)
Cu4	6139 (1)	3980 (1)	−1435 (2)
P1	9812 (3)	4870 (1)	2261 (3)
P2	9842 (3)	2325 (1)	2171 (3)
F11	9830 (13)	4974 (7)	1143 (11)
F12	10088 (13)	5312 (6)	2574 (15)
F13	9443 (15)	4451 (5)	1761 (16)
F14	8583 (9)	4977 (5)	2070 (11)
F15	11046 (8)	4783 (5)	2460 (10)
F16	9708 (11)	4746 (5)	3345 (11)
F21	8601 (8)	2336 (5)	1973 (10)
F22	11098 (9)	2332 (6)	2398 (11)
F23	9866 (16)	1883 (5)	2345 (18)
F24	9738 (11)	2369 (6)	3287 (10)
F25	9868 (13)	2806 (5)	2027 (18)
F26	9925 (10)	2278 (5)	1050 (10)
$N1_c$	3455 (10)	3846 (5)	4098 (11)
$N2_b$	4021 (9)	3597 (4)	3783 (10)
$N3_a$	4577 (9)	3339 (4)	3490 (10)
$N4_a$	5081 (9)	4271 (3)	−4103 (10)
$N5_b$	5638 (9)	4075 (3)	−4528 (9)
$N6_c$	6241 (10)	3884 (4)	−4924 (11)
$N7_{\alpha}$	4052 (10)	3499 (3)	−3589 (13)
$N8_{\beta}$	4881 (9)	3490 (3)	−3002 (11)
$N9_{\gamma}$	5699 (9)	3476 (3)	−2429 (10)
$N10_{\gamma}$	5744 (10)	4006 (3)	2625 (11)
$N11_{\beta}$	4930 (10)	4003 (3)	2049 (12)
$N12_{\alpha}$	4113 (10)	4017 (3)	1436 (12)
$N13_a$	4608 (9)	4152 (4)	−1567 (11)
$N14_b$	4030 (10)	3916 (5)	−1215 (11)
$N15_c$	3463 (11)	3669 (5)	−915 (13)
$N16_a$	5005 (9)	3224 (4)	915 (11)
$N17_b$	5587 (9)	3386 (4)	465 (9)
$N18_c$	6217 (11)	3559 (5)	41 (12)
$N1_A$	2900 (9)	2864 (3)	452 (11)
$C1_{A_1}$	3398 (15)	2566 (5)	1341 (18)
$C1_{A_2}$	3054 (18)	2708 (7)	−556 (18)
C11	1737 (14)	2892 (5)	408 (18)
C12	1306 (12)	3325 (5)	88 (15)
$N1_B$	1978 (8)	3655 (3)	727 (9)
$C1_{B_1}$	1709 (14)	4080 (6)	174 (22)
$C1_{B_2}$	1801 (16)	3671 (7)	1818 (17)
$N2_A$	3034 (8)	4703 (3)	−4564 (10)
$C2_{A_1}$	3183 (15)	4822 (5)	−5619 (15)
$C2_{A_2}$	3635 (16)	4986 (4)	−3754 (17)
C21	1876 (13)	4709 (5)	−4529 (16)
C22	1360 (11)	4287 (4)	−4861 (15)
$N2_B$	2001 (8)	3937 (3)	−4241 (10)
$C2_{B_1}$	1605 (13)	3527 (5)	−4809 (19)
$C2_{B_2}$	1805 (14)	3926 (6)	−3215 (16)
$N3_A$	7678 (8)	3537 (3)	3518 (10)
$C3_{A_1}$	8160 (13)	3976 (4)	3848 (17)
$C3_{A_2}$	7842 (13)	3442 (6)	2462 (14)
C31	8262 (12)	3226 (4)	4317 (14)
C32	7684 (12)	2804 (5)	4140 (14)
$N3_B$	6515 (9)	2877 (3)	4165 (10)
$C3_{B_1}$	6328 (15)	2851 (5)	5217 (13)
$C3_{B_2}$	5861 (14)	2543 (5)	3486 (14)
$N4_A$	7705 (8)	3874 (3)	−1439 (9)
$C4_{A_1}$	8062 (12)	3428 (5)	−1166 (17)
$C4_{A_2}$	7903 (15)	3959 (6)	−2490 (16)
C41	8309 (11)	4182 (5)	−673 (14)
C42	7822 (11)	4608 (5)	−801 (16)
$N4_B$	6625 (10)	4572 (3)	−819 (11)
$C4_{B_1}$	6020 (14)	4912 (5)	−1510 (13)
$C4_{B_2}$	6434 (17)	4589 (6)	261 (17)

18 reflections were then put back in refinement. The atomic coordinates converged very fast; the values obtained do not differ notably from those obtained before introduction of F_c. The thermal parameters of all atoms converged in few cycles, except those of the *F* atoms for which several cycles were again necessary to reach convergence. The final value of *R* is 0.075. A last Fourier-difference synthesis showed broad maxima at possible positions for hydrogen atoms; therefore, they were not introduced in calculations. Positional parameters are given in Table II and anisotropic thermal parameters in Table VIII.[12]

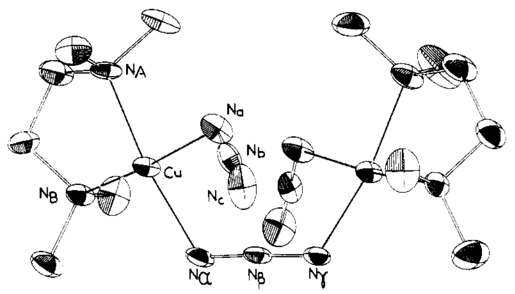

Figure 1. Perspective view of the binuclear cation $[Cu_2(tmen)_2(N_3)_3]^+$ in which the strong exchange interaction occurs.

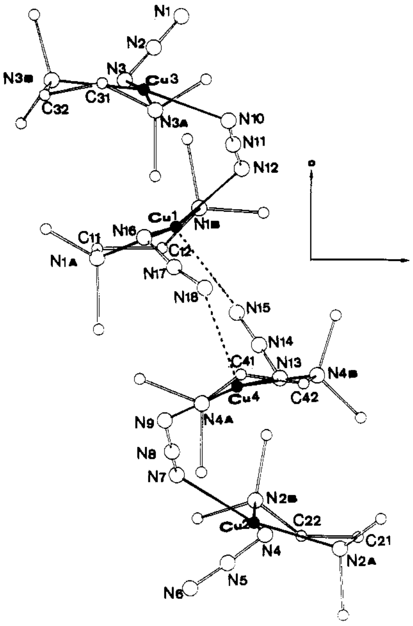

Figure 2. Perspective view of the asymmetric unit showing the association of two binuclear cations.

Magnetic Measurements. They were carried out with a Faraday type magnetometer equipped with a He continuous-flow cryostat. The polycrystalline sample weighed about 10 mg. Independence of the magnetic susceptibility vs. the magnetic field was checked at room temperature. Mercury tetrakis(thiocyanato)cobaltate was used as a susceptibility standard. Diamagnetic correction was estimated at -350×10^{-6} cm^3 mol^{-1} and TIP at 120×10^{-6} cm^3 mol^{-1}. The EPR spectrum was recorded with a Bruker ER 200 D spectrometer equipped with a He continuous-flow cryostat, a Hall probe, and a frequency meter.

Description of the Structure

The structure consists of extended chains of binuclear cations $[Cu_2(tmen)_2(N_3)_3]^+$ with short Cu···Cu separations through a single symmetrical azido bridge and long Cu···Cu separations through a double dissymmetrical azido bridge, the PF_6^- anions being located between the chains. The unit cell contains eight binuclear cations and eight noncoordinated hexafluorophosphate anions. The asymmetric unit contains two crystallographically independent but very similar binuclear cations. The surroundings of the four independent copper atoms are also very similar. The perspective view of one of the binuclear cations is represented in Figure 1, and the view of the chain is represented in Figure 2. Selected distances and angles are listed in Tables III–VII.[12]

Each copper atom is surrounded by five nitrogen atoms occupying the vertices of a slightly distorted square-based pyramid. The basal plane is made of the two nitrogen atoms

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(12) Supplmentary material.

Table III. Bond Distances (Å) and Angles (deg), with Esd's in Parentheses, around the Copper Atoms

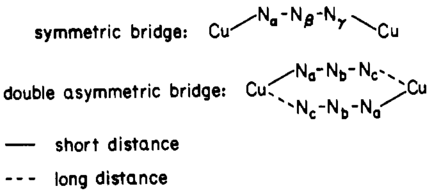
Binuclear Cation 1

around Cu1		around Cu3	
Cu1-N1$_A$	2.04 (1)	Cu3-N3$_A$	2.01 (1)
-N1$_B$	2.04 (1)	-N3$_B$	2.06 (1)
-N16$_a$	2.00 (1)	-N3$_a$	1.99 (1)
-N12$_\alpha$	2.02 (1)	-N10$_\gamma$	2.06 (1)
-N15$_c$	2.29 (2)	-N6$_c$	2.34 (1)
N1$_A$-Cu1-N1$_B$	86.3 (4)	N3$_A$-Cu3-N3$_B$	86.0 (5)
-N16$_a$	89.7 (5)	-N3$_a$	171.1 (5)
-N12$_\alpha$	164.9 (4)	-N10$_\gamma$	90.5 (5)
-N15$_c$	97.8 (5)	-N6$_c$	95.2 (5)
N1$_B$-Cu1-N16$_a$	172.9 (5)	N3$_B$-Cu3-N3$_a$	88.8 (5)
-N12$_\alpha$	91.3 (4)	-N10$_\gamma$	165.4 (5)
-N15$_c$	93.8 (5)	-N6$_c$	101.5 (5)
N16$_a$-Cu1-N12$_\alpha$	91.0 (5)	N3$_a$-Cu3-N10$_\gamma$	92.6 (5)
-N15$_c$	92.6 (5)	-N6$_c$	93.0 (5)
N12$_\alpha$-Cu1-N15$_c$	97.2 (6)	N10$_\gamma$-Cu3-N6$_c$	92.9 (5)

Binuclear Cation 2

around Cu2		around Cu4	
Cu2-N2$_A$	2.08 (1)	Cu4-N4$_A$	2.02 (1)
-N2$_B$	2.02 (1)	-N4$_B$	2.06 (1)
-N4$_a$	2.01 (1)	-N13$_a$	1.99 (1)
-N7$_\alpha$	2.05 (1)	-N9$_\gamma$	2.05 (1)
-N1$_c$	2.28 (1)	-N18$_c$	2.34 (2)
N2$_A$-Cu2-N2$_B$	86.6 (4)	N4$_A$-Cu4-N4$_B$	86.3 (4)
-N4$_a$	89.5 (4)	-N13$_a$	172.0 (5)
-N7$_\alpha$	166.0 (6)	-N9$_\gamma$	90.4 (4)
-N1$_c$	99.1 (5)	-N18$_c$	92.4 (5)
N2$_B$-Cu2-N4$_a$	171.9 (5)	N4$_B$-Cu4-N13$_a$	90.0 (5)
-N7$_\alpha$	91.4 (5)	-N9$_\gamma$	163.6 (6)
-N1$_c$	95.1 (5)	-N18$_c$	102.5 (5)
N4$_a$-Cu2-N7$_\alpha$	90.7 (5)	N13$_a$-Cu4-N9$_\gamma$	91.2 (5)
-N1$_c$	92.5 (5)	-N18$_c$	95.4 (6)
N7$_\alpha$-Cu2-N1$_c$	94.8 (6)	N9$_\gamma$-Cu4-N18$_c$	93.6 (5)

Table IV. Bond Distances (Å) and Angles (deg), with Esd's in Parentheses, in the Azide Anions



In Binuclear Cations: One Symmetric Bridge

binuclear cation 1		binuclear cation 2	
Cu1···Cu3	4.433 (2)	Cu2···Cu4	4.444 (2)
N12$_\alpha$-N11$_\beta$	1.18 (2)	N7$_\alpha$-N8$_\beta$	1.17 (2)
N11$_\beta$-N10$_\gamma$	1.15 (2)	N8$_\beta$-N9$_\gamma$	1.15 (2)
N12$_\alpha$-N11$_\beta$-N10$_\gamma$	177 (1)	N7$_\alpha$-N8$_\beta$-N9$_\gamma$	179 (1)
Cu1-N12$_\alpha$-N11$_\beta$	118 (1)	Cu2-N7$_\alpha$-N8$_\beta$	118 (1)
Cu3-N10$_\gamma$-N11$_\beta$	117 (1)	Cu4-N9$_\gamma$-N8$_\beta$	119 (1)
Between Binuclear Cations: Two Asymmetric Bridges			
Cu1···Cu4	5.117 (2)	Cu2···Cu3	5.144 (2)
N16$_a$-N17$_b$	1.16 (2)	N4$_a$-N5$_b$	1.17 (2)
N17$_b$-N18$_c$	1.20 (2)	N5$_b$-N6$_c$	1.18 (2)
N16$_a$-N17$_b$-N18$_c$	177 (1)	N4$_a$-N5$_b$-N6$_c$	177 (1)
N13$_a$-N14$_b$	1.20 (2)	N3$_a$-N2$_b$	1.19 (2)
N14$_b$-N15$_c$	1.18 (2)	N2$_b$-N1$_c$	1.19 (2)
N13$_a$-N14$_b$-N15$_c$	176 (2)	N3$_a$-N2$_b$-N1$_c$	178 (1)
Cu1-N16$_a$-N17$_b$	118 (1)	Cu2-N4$_a$-N5$_b$	118 (1)
Cu4-N13a-N14$_b$	118 (1)	Cu3-N3$_a$-N2$_b$	119 (1)
Cu1-N15$_c$-N14$_b$	128 (2)	Cu2-N1$_c$-N2$_b$	129 (1)
Cu4-N18$_c$-N17$_b$	137 (1)	Cu3-N6$_c$-N5$_b$	136 (1)

Table V. Bond Distances (Å) and Angles (deg), with Esd's in Parentheses[a]

In Chain			
Cu2^a-Cu3-Cu1	91.58 (4)	Cu1-Cu4-Cu2	92.45 (5)
Cu3-Cu1-Cu4	90.93 (4)	Cu4-Cu2-Cu3^b	90.07 (5)
Between Chains			
Cu2-Cu2^i	7.346 (5)	Cu4-Cu3^c	7.682 (4)
Cu2-Cu3^j	7.694 (4)		
Of P-Cu Nearest Distances			
Cu1-P2^d	6.413 (4)	Cu2-P1^g	6.386 (4)
Cu1-P2^e	6.462 (5)	Cu2-P1^b	6.389 (5)
Cu4-P1^f	6.555 (4)	Cu3-P2^h	6.480 (4)
Cu4-P1	6.626 (4)	Cu3-P2	6.525 (5)

[a] Key: (a) $x, y, 1 + x$; (b) $x, y, -1 + x$; (c) $x, \frac{1}{2} - y, -\frac{1}{2} + z$; (d) $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (e) $-1 + x, y, z$; (f) $2 - x, 1 - y, -z$; (g) $-1 + x, y, -1 + z$; (h) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (i) $1 - x, 1 - y, -1 - z$; (j) $1 - x, 1 - y, -z$.

N_A and N_B of tmen, an atom N_α (or N_γ) of the symmetrical azido bridge, and an atom N_a of one of the dissymmetrical azido bridges, the apical position being occupied by the N_c atom of the other dissymmetrical azido bridge. In the basal plane, the bond lengths vary from 1.99 (1) to 2.08 (1) Å and the bond angles from 86.0 (5) to 92.6 (5)°. The Cu–N_c apical bond lengths are 2.29 and 2.34 Å, alternatively. The basal nitrogen atoms deviate from the corresponding least-squares plane by ca. 0.07 Å, and the metal atom is pulled out of this plane toward the apical site by 0.20 Å. The two basal planes of $[Cu_2(tmen)_2(N_3)_3]^+$ make a mean dihedral angle of 46°. The copper atoms in the binuclear cation are bridged by an azido group in a symmetrical end-to-end fashion with a Cu–N_α (or Cu–N_γ) mean distance of 2.05 Å. The copper atoms and the azido bridge do not lie in the same plane. The two terminal nitrogen atoms (N_α, N_γ) are an average ±0.29 Å apart from the plane containing the copper atoms and the central nitrogen atom. The N_α–N_β–N_γ mean angle is 178°, and the Cu–N_α–N_β (or Cu–N_γ–N_β) mean angle is 118°. The Cu–N_α (or Cu–N_γ) mean bond length is 2.04 Å. The Cu···Cu mean separation is 4.439 Å, which is intermediate between the value found in the copper(II) cryptate $Cu_2(N_3)_4(C_{18}H_{38}N_2S_4)$ containing a double symmetrical end-to-end azido bridge[7] [Cu···Cu = 5.145 (0) Å] and that found in a (μ-azido,μ-alkoxide)copper(II) complex presented as a model of the azido derivative of the methemocyanine[8] [Cu···Cu = 3.615 (3) Å].

The binuclear cations $[Cu_2(tmen)_2(N_3)_3]^+$ are linked to each other by a double dissymmetrical azido bridge and form zigzag alternating chains parallel to the *c* direction. The mean value of the short Cu–N bond length is 2.00 Å; the long Cu–N mean bond lengths are 2.29 Å in one bridge and 2.34 Å in the other bridge. The dissymmetry is less pronounced than in $[Cu(tmen)(N_3)_2]_2$[10] [1.979 (5), 2.456 (6) Å] but more pronounced than in $[Cu_2(Me_5dien)(N_3)_2](BPh_4)_2$[11] [1.985 (4), 2.252 (5) Å]. The network $Cu_2(N_3)_2$ is not planar as found in $[Cu_2(Me_5dien)(N_3)_2](BPh_4)_2$. The mean deviation of the terminal nitrogen atoms (N_a, N_c) with regard to the plane containing the copper atom and the central nitrogen atom in a network Cu–N_a–N_b–N_c···Cu is ±0.14 Å when Cu–N_c is 2.34 Å and ±0.35 Å when Cu–N_c is 2.29 Å. The N_a–N_b–N_c mean angle is 177°. The Cu–N_a–N_b mean angle is 118°, and the Cu–N_c–N_b mean angle is 129° when Cu–N_c is 2.29 Å and 137° when Cu–N_c is 2.34 Å. The bond lengths N_a–N_b and N_b–N_c are equal within the experimental uncertainties with a mean value of 1.18 Å. The Cu···Cu mean separation through the double dissymmetrical azido bridge is 5.131 Å, which is intermediate between the value found in $[Cu(tmen)(N_3)_2]_2$[10] [Cu···Cu = 5.004 (2) Å] and that found in $[Cu_2(Me_5dien)_2(N_3)_2](BPh_4)_2$[11] [Cu···Cu = 5.227 (7) Å], both with a dissymmetrical end-to-end azido bridge.

The bond lengths and angles and the intraligand torsion angles in tmen agree with already observed values.[6,10,13-15] In

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(13) Mitchell, T. P.; Bernard, W. H.; Wasson, J. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 2096–2101.

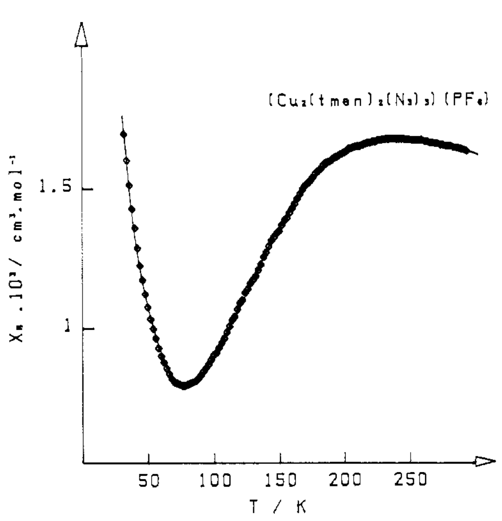


Figure 3. Experimental (◇) and theoretical (—) temperature dependences of the molar magnetic susceptibility of $[Cu_2(tmen)_2(N_3)_3](PF_6)$.

the same way, the geometry of the PF_6^- anions does not warrant any additional comments.[12] These anions are located between the chains with the nearest distance between P and Cu atoms of 6.386 (4) Å. The shortest Cu···Cu separation between metal atoms belonging to two different chains is 7.346 (5) Å.

To conclude this section, we point out that the peculiar structure of the binuclear cation $[Cu_2(tmen)_2(N_3)_3]^+$ with a single azido bridge and noncoplanar basal planes results from a competition between the influences of the two kinds of azido bridges linked to the same copper atom.

Magnetic Properties

The magnetic behavior of $[Cu_2(tmen)_2(N_3)_3](PF_6)$ is shown in Figure 3 in the form of the temperature dependence of the molar magnetic susceptibility χ_M in the range $30 < T/K < 300$. Upon cooling down, χ_M first increases, reaches a rounded maximum around 230 K, then decreases down to a minimum around 75 K, and finally increases again. This behavior is typical of a large antiferromagnetic interaction, the Curie-like tail at low temperature being due to a very small proportion, ρ, of noncoupled copper(II) impurity. If we assume that the observed magnetic curve is intrinsic to the binuclear entity $[Cu_2(tmen)_2(N_3)_3]^+$, then χ_M may be expressed as

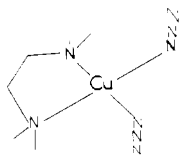
$$\chi_M = \frac{2N\beta^2g^2}{kT}[3 + \exp(-J/kT)]^{-1}(1 - \rho) + \frac{N\beta^2g^2}{2kT}\rho$$

where the symbols have their usual meaning. J is the singlet–triplet energy gap, and the molecular weight of the impurity is assumed to be equal to that of the actual complex. The J, g, and ρ parameters were determined by looking for the minimum of $R = \Sigma(\chi_M^{obsd} - \chi_M^{calcd})^2/\Sigma(\chi_M^{obsd})^2$. These parameters were found as $J = -308.6$ cm^{-1}, $g = 2.11$ (2), and $\rho = 0.0592$. R is then equal to 8.9×10^{-5}, which corresponds to an excellent agreement between observed and calculated magnetic data. Owing to the quality of this agreement, we did not look for estimating the magnitude of the interdimer interaction through the dissymmetrical azido bridges. The ratio J_{inter}/J_{intra} is too small to be determined by the magnetic technique. It can be recalled here that in $[Cu(tmen)(N_3)_2]_2$ where the two metal centers are also bridged by two dissymmetrical end-to-end azido groups, the interaction was found negligible.[10]

The X-band powder EPR spectrum of $[Cu_2(tmen)_2(N_3)_3](PF_6)$ is poorly resolved. It exhibits only a very large resonance centered at $g = 2.09$, of which the intensity varies as expected for an excited triplet state at 308 cm^{-1} above the diamagnetic ground state. At very low temperature, this feature vanishes and the spectrum only shows the signal corresponding to the monomeric impurity with a well-resolved hyperfine structure. This aspect of the spectrum likely arises from exchange broadening due to the interdimer interactions. In some way, we can say that the compound $[Cu_2(tmen)_2(N_3)_3](PF_6)$ behaves as a binuclear complex in magnetism but that its polymeric structure is apparent in EPR.

Discussion

We begin this section with a few words concerning the relation between synthesis and structure of the title compound. It is likely clear for the reader that the obtained structure was completely unexpected for us. At the initial stage of this work, we wanted to prepare the binuclear cation $[Cu_2(tmen)_2(N_3)_2]^{2+}$ with two end-on azido bridges. In fact, using copper(II) perchlorate, we obtained the mixed bridged complex $[Cu_2(tmen)_2(N_3)(OH)](ClO_4)_2$.[6] Therefore, we tried to modify the counteranion with the hope of synthesizing the bis(μ-azido) species, and using PF_6^-, we obtained this surprising chain structure with both symmetrical and dissymmetrical end-to-end azido bridges. One can notice that, in this structure, we have the same fragment **4** as in $[Cu(tmen)(N_3)_2]_2$,[10] with the azido groups oriented up and down, respectively, with regard to the mean basal plane CuN_4. In $[Cu(tmen)(N_3)_2]_2$, the terminal nitrogen atom of one of the azido groups occupies the apical position with regard to the copper atom of another fragment, giving rise to a very weak interaction between the two fragments. In $[Cu_2(tmen)_2(N_3)_3](PF_6)$, in addition to this weak interaction, the second azido group is equally shared by two fragments **4**, giving rise to a strong interaction. The double dissymmetrical bridge does not occur when ClO_4^- is present, likely because ClO_4^- itself occupies the apical positions. On the other hand, the reasons why ClO_4^- and PF_6^- lead to end-on and end-to-end bridges, respectively, remain completely unclear for us.



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Let us approach now the exchange interaction phenomenon in $[Cu_2(tmen)_2(N_3)_3](PF_6)$. The quasi-absence of interaction through the double dissymmetrical bridge has already been explained.[3,6,10] It is due to the fact that the spin density around a copper(II) ion in a square-pyramidal environment is essentially localized in the basal plane, with a very weak, if not negligible, contribution on the apical site. As for the large antiferromagnetic interaction within the $[Cu_2(tmen)_2(N_3)_3]^+$ binuclear unit, it confirms the ability of the symmetrical end-to-end azido bridges to give a strong stabilization of the singlet state between copper(II) ions relatively far away from each other. The magnitude of the interaction is however less pronounced than in the other reported compounds with the same type of bridge. This is certainly due to the structural differences between $[Cu_2(tmen)_2(N_3)_3](PF_6)$ and the already described complexes with one or two end-to-end bridges.[7-9] In the former compound, there is a single bridge within the binuclear unit whereas the other compounds were doubly bridged, either with two azido or with one azido and the oxygen atom of a phenolato or an alkoxide group. Moreover, in the title compound, the two basal planes in which the metal orbitals involved in the exchange interaction phenomenon are

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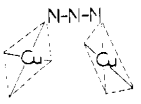
(14) Arcus, C.; Fivizzani, K. P.; Pavkovic, S. F. *J. Inorg. Nucl. Chem.* **1977**, *39*, 285–287.

(15) Julve, M.; Verdaguer, M.; Gleizes, A.; Philoche-Levisalles, M.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 3808–3818.

localized[15] make a dihedral angle of 46° as schematized in **5**; in the other complexes, these basal planes are coplanar as shown in **6**.



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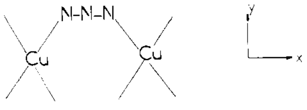

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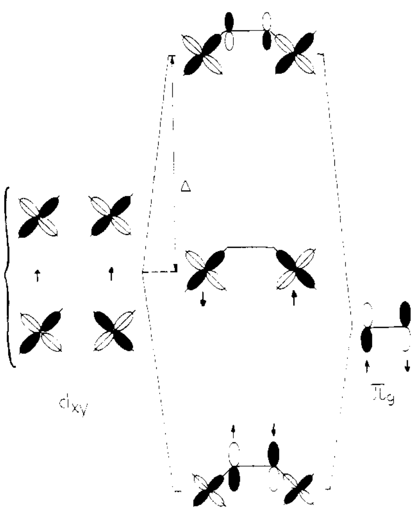
The key role in the strong stabilization of the singlet state observed with end-to-end azido bridges is played by the π_g HOMO's of N_3^- (see **7**).[4,6] The interaction between these π_g's and the d_{xy} metal orbitals give rise to the following: (i) An antibonding MO, antisymmetric regarding the mirror plane perpendicular to the azido bridge, appears. This MO is destabilized by an energy, Δ, with regard to the *xy*-type MO, symmetric regarding the mirror plane. The larger Δ is, the more stabilized the singlet state. More precisely, in absence of any other effect, the magnitude of the antiferromagnetic interaction varies as Δ^2. This is an *active electron effect.* (ii) A bonding MO appears in which an electron of π_g with an α spin is delocalized toward one of the copper(II) ions (e.g. A) and the other electron with the β spin is delocalized toward the other copper(II) ion (B). Hence, the unpaired electron around A will have a probability of spin β larger than $^1/_2$ and the unpaired electron around B a probability of a spin α larger than $^1/_2$, which favors the singlet state as ground state. This is the so-called *spin polarization effect*. Both, the active electron effect and the spin polarization effect favor the singlet state as ground state. As usual in copper(II) binuclear complexes, the phenomenon is enhanced when the two *xy*-type metal orbitals are localized in the same plane.[15] That is why the in-plane situation **6** is more favorable than the out-of-plane situation **5**.



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Registry No. $[Cu_2(tmen)_2(N_3)_3](PF_6)$, 93255-78-8.

Supplementary Material Available: Listings of structure factor amplitudes, bond distances and angles (Tables VI and VII), and anisotropic thermal parameters (Table VIII) (26 pages). Ordering information is given on any current masthead page.

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Luminescence and NMR Studies of the Conformational Isomers of Lanthanide Complexes with an Optically Active Polyaza Polycarboxylic Macrocycle

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A variety of luminescence techniques were used to study the nature of the complexes formed between [1*R*-(1*R**,4*R**,7*R**,10*R**)]-$\alpha,\alpha',\alpha'',\alpha'''$-tetramethyl-1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (abbreviated as DOTMA) and several lanthanide ions. High-resolution luminescence spectra of EuDOTMA as a microcrystalline powder and in the aqueous phase clearly demonstrated that while a single Eu(III) species exists in the solid state, two nonequivalent species exist in solution. The circularly polarized luminescence spectrum of EuDOTMA showed only small degrees of observable optical activity in the species thought to be axially symmetric and large amounts of chirality in the species not possessing such symmetry. Comparison of the ground- and excited-state optical activities of TbDOTMA revealed that essentially no geometrical changes accompany the promotion of the Tb(III) ion into an excited f state. The exchange between the two complex isomers was found to be slow on the NMR time scale, and thus it was possible to deduce the structures of the two isomers. The relative concentrations of all the solution species were found to depend on the size of the lanthanide ion and on the functional groups present on the macrocycle. Finally, the DOTMA compounds were shown to be very rigid, with the conformation of the ethylenediamine groups of the macrocyclic ring undergoing a very slow inversion between 0 and 100 °C.

Introduction

The complexing abilities of macrocyclic ligands have led to numerous investigations in the coordination properties of these molecules. Generally, a wide variety of cations are capable of being bound by a macrocycle, but most of these studies have been restricted to the alkali-metal and alkaline-earth ions. Since the report by King and Heckley[1] that lanthanide compounds of macrocyclic polyethers could be formed, the efforts of many investigators have led to the synthesis of new compounds with intriguing properties. These investigations have

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(1) King, R. B.; Heckley, P. R. *J. Am. Chem. Soc.* **1974**, *96*, 3118.

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