

reaction coordinate. The rate of the spin-change reaction has in all cases which have been investigated found to be of the order of magnitude of 10^6 – 10^7 s⁻¹, so the rate of the racemization reaction will not be restricted by any spin-change bottleneck.

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Supplementary Material Available: Listings of thermal parameters, hydrogen atom positions, and bond distances and angles for [Fe(tpcn)](ClO₄)₂ and Figure 4, a stereoview of the unit cell (4 pages). Ordering information is given on any current masthead page.

Contribution from the Lehrstuhl für Anorganische Chemie I, Ruhr-Universität, D-4630 Bochum, FRG, and Anorganisch Chemisches Institut der Universität, D-6900 Heidelberg, FRG

Magnetic Exchange Interactions in Some Novel μ -Azido-Bridged Copper(II) Dimers. Crystal Structures of [L₂Cu₂(μ -N₃)(N₃)₂](ClO₄)·H₂O, LCu(N₃)₂, [L₂Cu₂(μ -N₃)₂(ClO₄)₂], and L'Cu(N₃)₂ (L = N,N',N''-Trimethyl-1,4,7-triazacyclononane and L' = 1,4,7-Triazacyclononane)

Phalguni Chaudhuri,*^{1a} Karen Oder,^{1a} Karl Wiegardt,^{1a} Bernhard Nuber,^{1b} and Johannes Weiss*^{1b}

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The reaction of Cu(ClO₄)₂·6H₂O in aqueous solution with N,N',N''-trimethyl-1,4,7-triazacyclononane (L = C₉H₂₁N₃) and sodium azide yields black crystals of [L₂Cu₂(μ -N₃)(N₃)₂](ClO₄)·H₂O (1) and [L₂Cu₂(μ -N₃)₂(ClO₄)₂] (3). If Cu(CH₃COO)₂ is used as starting material, neutral complexes LCu(N₃)₂ (2) and L'Cu(N₃)₂ (4) could be isolated as crystalline solids, where L' represents 1,4,7-triazacyclononane (C₉H₁₃N₃). The crystal structures of 1–4 have been determined by X-ray crystallography. 1 crystallizes in the monoclinic system, space group C2/c, with $a = 29.64$ (1) Å, $b = 14.756$ (5) Å, $c = 15.700$ (4) Å, $\beta = 117.42$ (2)°, and $Z = 8$. The structure was refined to a final R value of 0.053 for 5193 unique reflections. The structure consists of binuclear [L₂Cu₂(μ -N₃)(N₃)₂]⁺ cations and uncoordinated ClO₄⁻ anions and water of crystallization. The geometry around the Cu centers is square-pyramidal; they are linked together by a symmetrical end-to-end-coordinated azido ligand. The spins of the two Cu(II) centers are strongly antiferromagnetically coupled ($J = -331$ (10) cm⁻¹). 2 crystallizes in the monoclinic system, space group P2₁/n, with $a = 7.972$ (2) Å, $b = 11.663$ (5) Å, $c = 12.053$ (4) Å, $\beta = 91.96$ (3)°, and $Z = 4$. The structure was refined to a final R value of 0.036 for 2857 unique reflections. The structure consists of monomeric LCu(N₃)₂ molecules, which are packed in pairs in the solid state. The geometry around the Cu center is square-pyramidal. No magnetic exchange interactions between the Cu centers have been observed at temperatures between 100 and 300 K. 3 crystallizes in the monoclinic system, space group C2/c, with $a = 23.63$ (1) Å, $b = 7.852$ (3) Å, $c = 16.384$ (5) Å, $\beta = 93.68$ (3)°, and $Z = 4$. The structure was refined to a final R value of 0.061 for 1724 reflections. The structure consists of binuclear [L₂Cu₂(μ -N₃)₂(ClO₄)₂] where the two Cu centers are connected via two symmetrical end-to-end-coordinated azido bridges. One perchlorate anion is weakly bonded to each copper ion via one oxygen atom. The geometry around the Cu centers is tetragonally elongated octahedral. 3 is strongly antiferromagnetically coupled ($J < -400$ cm⁻¹). 4 crystallizes in the monoclinic system, space group P2₁/n, with $a = 13.626$ (3) Å, $b = 7.875$ (2) Å, $c = 14.415$ (5) Å, $\beta = 113.11$ (2)°, and $Z = 4$. The structure was refined to a final R value of 0.056 for 2447 unique reflections. The structure consists of neutral molecules L'Cu(N₃)₂, which are packed in pairs in the crystal. The geometry around the Cu center is square-pyramidal. No magnetic exchange interaction between 100 and 300 K has been detected.

Introduction

In the elucidation of the structures of binuclear copper active sites (type III) in hemocyanins, the azide metabolized forms of the oxidized metalloproteins play an important role.^{2–6} The electronic spectra, ESR spectra, resonance Raman spectra, and, most importantly, the magnetic spin exchange interactions of these metazido forms differ in many instances significantly from the respective properties of the oxidized copper-containing protein. Thus, useful information concerning the structure of the active sites may be deduced. A necessary prerequisite of such studies is the detailed knowledge and understanding on a molecular basis of magnetic and spectroscopic properties of well-characterized (X-ray structure) low-molecular-weight binuclear and mononuclear azide-containing copper(II) model compounds. In recent years a large number of azide-bridged copper(II) complexes have been prepared and their magnetic properties have been discussed on various levels of sophistication.^{7–16} It is the enormous variation

of magnetic exchange interactions leading to diamagnetic, antiferromagnetic (weakly and very strongly coupled), and ferromagnetic azide-bridged copper(II) dimers that lends these materials as ideal probes for the elucidation of magneto-structural correlations in these exchange-coupled systems.¹⁷

Here we report the syntheses, crystal structures, and magnetic properties of four closely related copper(II) azide complexes. The geometry around the Cu(II) centers is in all four complexes slightly distorted square-based pyramidal; the complexes contain the

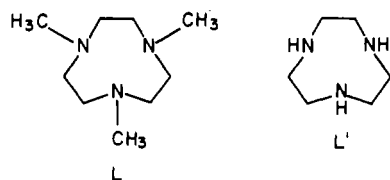
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Table I. Experimental Details of the X-ray Diffraction Studies of Complexes 1-4

	1	2	3	4
(A) Crystal Parameters at 22 °C				
<i>a</i> , Å	29.64 (1)	7.972 (2)	23.63 (1)	13.626 (3)
<i>b</i> , Å	14.756 (5)	11.663 (5)	7.852 (3)	7.875 (2)
<i>c</i> , Å	15.700 (4)	12.053 (4)	16.384 (5)	14.415 (5)
β , deg	117.42 (2)	91.96 (3)	93.68 (3)	113.11 (2)
<i>V</i> , Å ³	6094.8	1120	3034.2	1422.7
<i>Z</i>	8	4	4	4
mol wt	713.1	318.8	752.6	276.8
space group	<i>C2/c</i> (<i>C</i> _{2h} ²)	<i>P2₁/n</i> (<i>C</i> _{2h} ²)	<i>C2/c</i> (<i>C</i> _{2h} ²)	<i>P2₁/n</i> (<i>C</i> _{2h} ²)
<i>D</i> _{calcd} , g cm ⁻³	1.52	1.64	1.65	1.49
cryst dimens, mm ³	0.3 × 0.53 × 0.75	0.15 × 0.20 × 0.70	0.11 × 0.19 × 0.65	0.25 × 0.25 × 0.30
(B) Measurement of Intensity Data (22 °C)				
instrument	AED II (Siemens)	Syntex R3	AED II (Siemens)	AED II (Siemens)
radiation		Mo K α (graphite monochromatized)		
2 θ limits, deg	2.5-60	2.5-65	2.5-57	2.5-60
scan type	ω	θ -2 θ	ω	ω
octant	$\pm h, k, l$	$\pm h, k, l$	$\pm h, k, l$	$\pm h, k, l$
(C) Treatment of Intensity Data				
reduction to preliminary <i>F</i> _o and $\sigma(F_o)$		cor for bkgd, attenuators, and Lorentz-polarization effects of monochromatized X-radiation in the usual manner		
abs cor	empirical	empirical	empirical	empirical
μ , cm ⁻¹	14.7	18.7	15.6	14.7
max and min transmission coeff	0.43-0.32	1.0-0.79	0.63-0.53	0.123-0.087
obsd data	5256	2886	2011	2974
unique data (<i>I</i> > 2 $\sigma(I)$)	5193	2857	1724	2447
no. of refined parameters	366	145	190	172
<i>R</i>	0.053	0.036	0.061	0.056
<i>R</i> _w	0.047	0.033	0.053	0.050

macrocycles *N,N',N''*-trimethyl-1,4,7-triazacyclononane (L) or 1,4,7-triazacyclononane (L'), which are facially coordinated with



one ligand nitrogen in the apical position. Two such moieties are linked together via one end-to-end azido bridge in [L₂Cu₂(μ -N₃)(N₃)₂](ClO₄)₂·H₂O (1) and two symmetrical end-to-end μ -N₃ bridges in [L₂Cu₂(μ -N₃)₂(ClO₄)₂] (3). In LCu(N₃)₂ (2) and L'Cu(N₃)₂ (4), two molecules are packed in pairs in the crystals and very weak asymmetric (μ -N₃)₂ bridging may be envisaged in both cases. From variable-temperature susceptibility measurements strong intramolecular antiferromagnetic exchange coupling is deduced for (1) and (3), whereas in 2 and 4 the coupling between the copper(II) centers is negligible.

Experimental Section

The ligands *N,N',N''*-trimethyl-1,4,7-triazacyclononane (L)¹⁸ and 1,4,7-triazacyclononane (L')¹⁹ were prepared as described in the literature.

Caution! Perchlorates may explode, especially when heated!

[L₂Cu₂(μ -N₃)(N₃)₂](ClO₄)₂·H₂O (1). To an aqueous solution (50 mL) of Cu(ClO₄)₂·6H₂O (0.74 g) was added 1 M methanolic solution (2 mL) of *N,N',N''*-trimethyl-1,4,7-triazacyclononane at room temperature with stirring. Then an aqueous solution (50 mL) of sodium azide (0.15 g) was added. This solution was allowed to stand at 0 °C for 12 h, during which time black crystals precipitated, which were filtered off and air-dried (yield 0.74 g, 53%). Anal. Calcd for C₁₈H₄₂N₁₅Cu₂ClO₄: C, 31.1; H, 6.1; N, 30.2; Cu, 18.3; ClO₄, 14.3. Found: C, 30.9; H, 6.3; N, 30.4; Cu, 18.8; ClO₄, 14.5.

LCu(N₃)₂ (2). To an aqueous solution (40 mL) of Cu(CH₃CO₂)₂ (0.45 g) were added at room temperature with stirring a 1 M methanolic solution (2 mL) of *N,N',N''*-trimethyl-1,4,7-triazacyclononane and NaN₃ (0.15 g) dissolved in water (20 mL). After 12 h at 0 °C green-black crystals precipitated, which were filtered off and air-dried (yield 0.6 g,

47%). Anal. Calcd for C₉H₂₁N₉Cu: C, 33.90; H, 6.64; N, 39.53; Cu, 19.93. Found: C, 33.8; H, 6.6; N, 39.7; Cu, 19.7.

[L₂Cu₂(μ -N₃)₂(ClO₄)₂] (3). **Method A.** To an aqueous solution (50 mL) of Cu(ClO₄)₂·6H₂O (0.74 g) and 2 mL of a 1 M methanolic solution of *N,N',N''*-trimethyl-1,4,7-triazacyclononane was added with stirring at room temperature sodium azide (0.15 g) dissolved in 50 mL of water. Then sodium perchlorate hydrate (0.24 g) was added. After 3-4 h at 0 °C black, needle-shaped crystals precipitated, which were filtered off and air-dried (yield 0.3 g, 42%).

Method B. Recrystallization of 2 from a 1 M aqueous solution of NaClO₄ yielded 3 after 12 h at 0 °C. Anal. Calcd for C₁₈H₄₂N₁₂Cl₂Cu₂O₈: C, 28.7; H, 5.6; N, 22.3; Cu, 16.3; ClO₄, 26.4. Found: C, 28.8; H, 5.6; N, 22.2; Cu, 17.1; ClO₄, 26.5.

L'Cu(N₃)₂ (4). To Cu(CH₃CO₂)₂ (0.45 g) dissolved in water (50 mL) was added a 1 M methanolic solution of 1,4,7-triazacyclononane (2 mL) at room temperature with stirring. A solution of NaN₃ (0.15 g) in water (40 mL) was added. After 2-3 days in an open vessel at 20 °C green crystals precipitated, which were filtered off and air-dried (yield 0.3 g, 55%). Anal. Calcd for C₆H₁₅N₉Cu: C, 26.0; H, 5.5; N, 45.5; Cu, 23.0. Found: C, 26.4; H, 5.6; N, 46.0; Cu, 22.5.

X-ray Structure Determinations. Well-formed crystals of 1-4 were obtained from aqueous solutions left standing at 0 °C. Precise lattice constants and diffracted intensities were obtained from measurements carried out on an AED II (Siemens) diffractometer for 1, 3, and 4 and on a Syntex R3 diffractometer for 2. The setting angles of 32 reflections were determined with use of the automatic centering program supplied with the computer-controlled diffractometers. Least-squares refinements of these reflections led to the lattice constants summarized in Table I. Intensity data were measured at 22 °C by θ -2 θ scans for 2 and ω scans for all other crystals. They were corrected for Lorentz and polarization effects in the usual manner. Empirical absorption corrections have been carried out in all cases.²⁰

The structures were readily solved via conventional Patterson and Fourier syntheses. In all structure-factor calculations the atomic scattering factors used were taken from ref 21. The effect of anomalous dispersion was included for all non-hydrogen atoms. The values of $\Delta f'$ and $\Delta f''$ used were those given in ref 22. The structures were refined by full-matrix least-squares methods. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where the weights *w* were taken as 1/ $\sigma(F)^2$. All non-

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(22) Reference 21, Table 2.3.2.

Table II. Atomic Coordinates ($\times 10^4$) of **1**

atom	x	y	z
Cu1	4390.7 (2)	1989.5 (4)	4032.1 (4)
Cu2	2933.8 (2)	510.9 (4)	1553.9 (4)
N11	2985 (2)	836 (3)	2815 (3)
N12	3153 (2)	1538 (3)	3212 (3)
N13	3322 (2)	2202 (3)	3622 (4)
N21	4272 (2)	659 (3)	3946 (3)
N22	4081 (2)	274 (3)	3190 (3)
N23	3898 (2)	-126 (3)	2478 (3)
N31	3272 (2)	1726 (3)	1478 (3)
N32	3688 (2)	1905 (3)	2037 (3)
N33	4112 (2)	2095 (3)	2581 (3)
N1	5220 (1)	2011 (3)	4459 (3)
N2	4646 (1)	1951 (3)	5505 (3)
N3	4483 (2)	3375 (3)	4225 (3)
C1	5486 (2)	1900 (4)	5513 (4)
C2	5140 (2)	1483 (4)	5875 (3)
C3	4695 (2)	2905 (4)	5868 (4)
C4	4383 (2)	3537 (4)	5052 (4)
C5	5019 (2)	3628 (4)	4458 (4)
C6	5268 (2)	2920 (4)	4131 (4)
C7	5364 (2)	1309 (4)	3977 (4)
C8	4304 (2)	1434 (4)	5772 (4)
C9	4119 (2)	3914 (4)	3388 (4)
N4	2890 (1)	37 (3)	289 (3)
N5	2599 (2)	-730 (3)	1563 (3)
N6	2130 (2)	943 (3)	633 (3)
C11	2928 (2)	-971 (4)	424 (4)
C12	2562 (2)	-1300 (4)	762 (4)
C13	2094 (2)	-460 (4)	1463 (4)
C14	1815 (2)	175 (4)	645 (4)
C15	2144 (2)	1068 (4)	-287 (4)
C16	2393 (2)	304 (4)	-573 (3)
C17	3317 (2)	352 (4)	109 (4)
C18	2878 (2)	-1227 (4)	2478 (4)
C19	2002 (2)	1774 (4)	957 (4)
O11	1242.2 (6)	1440 (1)	2838 (1)
O1	1068 (3)	2335 (5)	2778 (5)
O2	1157 (3)	889 (6)	3414 (6)
O3	1023 (4)	1194 (4)	1925 (5)
O4	1731 (3)	1425 (7)	3106 (7)

Table III. Atomic Coordinates ($\times 10^4$) of **2**

atom	x	y	z
Cu	3237.0 (5)	1620.3 (9)	283.2 (5)
N4	2581 (4)	3880 (7)	861 (4)
N5	3067 (4)	3271 (7)	-908 (3)
N6	1590 (4)	1177 (6)	-558 (3)
C1	2977 (7)	5260 (10)	403 (6)
C2	2777 (6)	5013 (10)	-681 (6)
C3	2179 (5)	2463 (11)	-1784 (5)
C4	1269 (5)	2036 (9)	-1524 (5)
C5	1060 (6)	1971 (10)	60 (6)
C6	1423 (6)	3723 (11)	411 (6)
C7	3052 (6)	4012 (12)	1990 (5)
C8	4035 (5)	3340 (11)	-1171 (5)
C9	1330 (5)	-666 (8)	-701 (5)
N1	3249 (5)	-122 (8)	1278 (4)
N2	4018 (5)	-526 (7)	1986 (4)
N3	4741 (6)	-959 (9)	2690 (5)
N7	4789 (4)	2177 (7)	1005 (4)
N8	5473 (4)	1460 (7)	875 (3)
N9	6191 (4)	810 (8)	783 (4)

hydrogen atoms were refined with the assumption of anisotropic thermal motion. The contribution of hydrogen bound to carbon was introduced in calculated positions ($C-H = 0.96 \text{ \AA}$ and sp^3 -hybridized carbon atoms). These hydrogens were assumed to have isotropic thermal motion. The final values of $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ are given in Table I. Final difference Fourier syntheses of all structures were essentially featureless. The final atomic positional parameters are given in Tables II-V for **1**, **2**, **3**, and **4**, respectively. Listings of observed and calculated structure factors, anisotropic thermal parameters, and calculated positional parameters of hydrogen atoms are available as supplementary material.

Physical Measurements. Infrared spectra were taken as KBr pellets on a Beckman Aculab 10 infrared spectrophotometer. Electronic ab-

Table IV. Atomic Coordinates ($\times 10^4$) of **3**

atom	x	y	z
Cu1	1632.5 (4)	980 (1)	-625.1 (6)
C11	4154 (1)	1412 (3)	-1198 (2)
O11	4555 (4)	535 (12)	-709 (6)
O12	3751 (5)	2052 (15)	-682 (7)
O13	3870 (4)	392 (13)	-1761 (5)
O14	4412 (4)	2754 (12)	-1584 (6)
N11	2245 (3)	369 (9)	233 (5)
N12	2612 (3)	1170 (9)	549 (4)
N13	2984 (3)	1834 (9)	907 (4)
N1	1198 (3)	-1193 (9)	-358 (4)
N2	942 (3)	1536 (9)	-1419 (4)
N3	1938 (3)	-572 (9)	-1660 (4)
C1	617 (4)	-1001 (18)	-734 (7)
C2	489 (4)	510 (14)	-1093 (10)
C3	1055 (5)	929 (16)	-2224 (6)
C4	1609 (4)	216 (15)	-2354 (5)
C5	1756 (6)	2246 (14)	-1480 (8)
C6	1514 (6)	7415 (12)	-727 (8)
C7	1172 (4)	-1538 (13)	550 (5)
C8	768 (4)	3362 (11)	-1458 (6)
C9	2554 (4)	-395 (15)	-1748 (7)

Table V. Atomic Coordinates ($\times 10^4$) of **4**

atom	x	y	z
Cu1	2442.6 (4)	1291.7 (2)	193.1 (2)
N1	1922 (3)	2999 (2)	205 (2)
N2	366 (3)	1291 (2)	-1104 (2)
N3	3891 (3)	1692 (2)	-1149 (2)
C1	97 (4)	3079 (2)	-77 (2)
C2	-372 (4)	2442 (2)	-1139 (2)
C3	1250 (4)	971 (3)	-2116 (2)
C4	2919 (4)	1584 (3)	-2209 (2)
C5	4446 (4)	2889 (3)	-903 (3)
C6	2973 (4)	3618 (2)	-584 (3)
N11	1722 (3)	1182 (2)	1755 (2)
N12	2362 (3)	505 (2)	2379 (2)
N13	2944 (4)	-132 (2)	3012 (2)
N21	7032 (3)	370 (2)	-180 (2)
N22	6528 (3)	844 (2)	629 (2)
N23	5994 (4)	1334 (2)	1374 (2)

sorption spectra were measured on a Perkin-Elmer Lambda 9 spectrophotometer. Spectra were measured in solution, and the positions of absorption maxima were checked by measuring the reflectance spectrum (KBr pellets) of the respective solid in order to ensure the identity of species in solution and in the solid state. Variable-temperature susceptibility measurements were recorded between 100 and 298 K by using the Faraday method (Sartorius microbalance, Bruker B-E 100088 research magnet, and Bruker B-VT automatic temperature control). Diamagnetic corrections were applied with use of Pascal's constants.²³ χ_D values were estimated as $-344 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for **1**, $-317 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for **2**, $-370 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for **3**, and $-236 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for **4**.

Results

Syntheses of Complexes. The macrocycle *N,N',N''*-tri-methyl-1,4,7-triazacyclononane (L) forms a very stable 1:1 complex with copper(II) ions in aqueous solution, which forms a series of azido complexes upon addition of sodium azide. In the presence of perchlorate anions, i.e. with use of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ as starting material, black crystals of X-ray quality of $[\text{L}_2\text{Cu}_2(\mu\text{-N}_3)(\text{N}_3)_2](\text{ClO}_4) \cdot \text{H}_2\text{O}$ (**1**) formed at 0°C within 12 h. At higher perchlorate concentrations a different product was obtained as black, needle-shaped crystals from the above solution, $[\text{L}_2\text{Cu}_2(\mu\text{-N}_3)_2](\text{ClO}_4)_2$ (**3**), which in the light of its crystal structure determination (see below) may also be formulated as the neutral complex $[\text{L}_2\text{Cu}_2(\mu\text{-N}_3)_2(\text{ClO}_4)_2]$, since in the solid state each ClO_4^- anion is coordinated via one oxygen atom to one Cu(II).

With use of $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ as starting material in the absence of ClO_4^- anions under otherwise identical conditions, black crystals of $\text{LCu}(\text{N}_3)_2$ (**2**) were obtained, which may be considered a dimer,

(23) Selwood, P. *Magnetochemistry*, 2nd ed.; Interscience: Wiley: New York, 1956.

Table VI. Spectroscopic Properties of Complexes 1-4

complex	electronic spectrum ^a	$\nu_{as}(N_3)$, cm^{-1}
1	633 (516), 1002 (59)	2040, 2000
2	638 (519), 1000 (32)	2025, 1980
3	634 (515), 1010 (52)	2030, 2000
4	631 (210), 964 (26) ^b	2040

^a λ_{max} in nm (ϵ in $\text{L mol}^{-1} \text{cm}^{-1}$ per dimer); measured in methanol.
^b ϵ values are per Cu(II) atom.

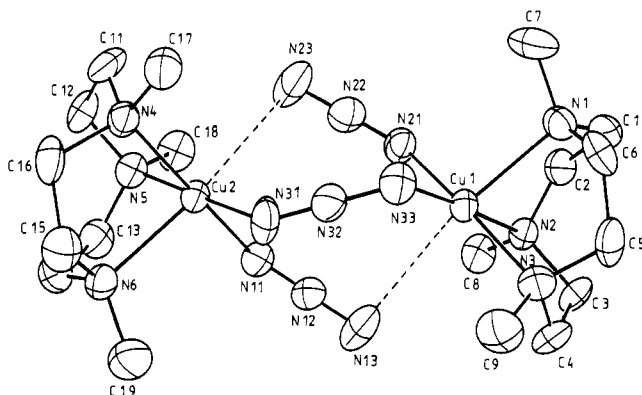


Figure 1. Molecular geometry and atomic labeling scheme of the monocation $[\text{L}_2\text{Cu}_2(\mu\text{-N}_3)(\text{N}_3)_2]^+$ in **1**. The dotted lines indicate very weak $\text{Cu}\cdots\text{N}$ interactions.

$[\text{L}_2\text{Cu}_2(\mu\text{-N}_3)_2(\text{N}_3)_2]$, in the solid state. The same reaction afforded green-black crystals of $\text{L}'\text{Cu}(\text{N}_3)_2$ (**4**) with use of the simple macrocycle 1,4,7-triazacyclononane (L').

The azido ligands present in **1**, **2**, and **3** give two stretching frequencies: a split sharp peak between 1980 and 2040 cm^{-1} , which is assigned to the antisymmetric $\nu(\text{N-N})$ stretching frequency, and a weak peak at $\sim 1300 \text{ cm}^{-1}$ ($\nu_s(\text{N-N})$), which has not been identified unambiguously due to overlapping bands in this region of the coordinated macrocycle. The data are summarized in Table VI. In **4** only one sharp band at 2040 cm^{-1} has been observed.

The electronic spectra of **1-4** are very similar (Table VI) due to the fact that the geometry of the Cu(II) centers in all complexes is square-based pyramidal.

Description of the Structure of 1. Crystals of **1** consist of dimeric cations $[\text{L}_2\text{Cu}_2(\mu\text{-N}_3)(\text{N}_3)_2]^+$ and well-separated perchlorate anions and molecules of water of crystallization. Figure 1 shows a perspective view of the complex cation. In Table VII bond distances and angles of the Cu_2N_{15} core are summarized. The geometries around the two Cu(II) ions are identical within experimental error and are best considered square-base pyramidal with each metal ion bonded to three nitrogen atoms of a macrocyclic ligand and to a terminal and a bridging azide in the basal plane. The two Cu(II) atoms are linked via one end-to-end-bridging azide. The Cu-N bond distances are 2.040 (4) Å (Cu1-N33) and 2.084 (4) Å (Cu2-N33); the Cu-N-N bond angles are 122.6 (3) and 121.4 (4)°. The Cu...Cu distance is 4.803 (2) Å. The perchlorate anions and H_2O molecules are not coordinated to the metal ions.

It is noted that the two terminal azide groups interact weakly through their N_γ atoms with one Cu(II), respectively. The corresponding Cu...N interactions are at distances of 2.944 (6) Å (Cu1-N13) and 2.709 (6) Å (Cu2-N23) and are directed toward the axis of the respective square-based pyramidal polyhedron of the Cu(II) ions. Therefore, the geometry of the Cu(II) ions may also be considered to be tetragonally elongated octahedral. The axial Cu-N bond distances of the amine nitrogen atoms are also longer (2.230 (4) and 2.236 (4) Å) than those in the basal plane.

Interestingly, the nickel(II) analogue of (**1**) has recently been prepared and characterized by X-ray crystallography.²⁴ In this

Table VII. Bond Distances (Å) and Angles (deg) in **1**

Cu1-N21	1.989 (4)	Cu2-N11	1.973 (4)
Cu1-N33	2.040 (4)	Cu2-N31	2.084 (4)
Cu1-N1	2.230 (4)	Cu2-N4	2.053 (4)
Cu1-N2	2.076	Cu2-N5	2.086 (4)
Cu1-N3	2.067	Cu2-N6	2.236 (4)
Cu1-N13	2.944 (6)	Cu2-N23	2.709 (6)
N11-N12	1.193 (7)	N21-N22	1.198 (6)
N12-N13	1.153 (7)	N22-N23	1.155 (6)
Cu1-Cu2	4.803 (2)	N31-N32	1.167 (6)
		N32-N33	1.183 (6)
N21-Cu1-N33	91.8 (3)	N21-Cu1-N2	90.6 (2)
N33-Cu1-N1	99.1 (2)	N33-Cu1-N3	92.7 (2)
N1-Cu1-N3	83.6 (2)	N21-Cu1-N3	173.6 (3)
N21-Cu1-N1	99.8 (3)	N1-Cu1-N2	83.1 (2)
N33-Cu1-N2	176.3 (4)		
N2-Cu1-N3	84.7 (2)		
N11-Cu2-N31	91.8 (2)	N11-Cu2-N5	91.4 (2)
N31-Cu2-N4	93.2 (2)	N31-Cu2-N6	96.7 (2)
N4-Cu2-N6	84.2 (2)	N11-Cu2-N6	98.4 (2)
N11-Cu2-N4	174.3 (3)	N4-Cu2-N5	83.7 (2)
N31-Cu2-N5	177.4 (5)		
N5-Cu2-N6	83.5 (2)		
Cu1-N21-N22	121.5 (3)	N11-N12-N13	177.6 (9)
Cu2-N31-N32	121.4 (4)	N21-N22-N23	176.5 (8)
Cu1-N33-N32	122.6 (3)	N31-N32-N33	176.6 (8)
Cu2-N11-N12	123.8 (4)		
Cu1-N13-N12	100.2 (3)		
Cu2-N23-N22	104.5 (3)		

Table VIII. Bond Distances (Å) and Angles (deg) in **2**

Cu-N1	1.980 (5)	N1-N2	1.185 (8)
Cu-N4	2.290 (5)	N2-N3	1.153 (8)
Cu-N5	2.093 (5)	N7-N8	1.167 (8)
Cu-N6	2.119 (5)	N8-N9	1.156 (8)
Cu-N7	2.005 (5)		
Cu-N9'	2.752 (6)	Cu-Cu'	5.774 (1)
N4-Cu-N5	83.3 (2)	N4-Cu-N6	81.9 (2)
N5-Cu-N6	83.2 (2)	N5-Cu-N1	172.5 (3)
N6-Cu-N7	176.0 (5)	N1-Cu-N7	93.9 (3)
N4-Cu-N1	99.7 (3)	N5-Cu-N7	92.6 (3)
N4-Cu-N7	97.1 (3)	N4-Cu-N9'	168.5 (2)
N6-Cu-N1	90.3 (3)	N5-Cu-N9'	86.5 (3)
N1-Cu-N9'	89.9 (3)		
N7-Cu-N9'	88.3 (3)		
Cu-N7-N8	123.9 (4)	N8-N9	175.5 (10)
N8-N9-Cu'	144.1 (7)		
Cu-N1-N2	124.3 (5)	N1-N2-N3	176.8 (11)

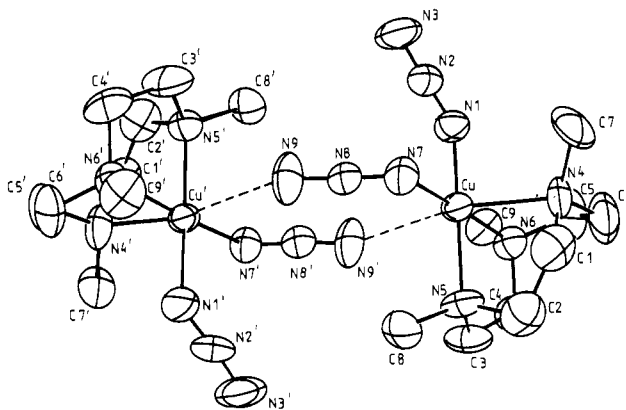
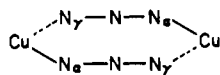


Figure 2. Molecular geometry and atomic labeling scheme of a pair of $\text{LCu}(\text{N}_3)_2$ molecules in **2**. The dotted lines indicate weak $\text{Cu}\cdots\text{N}$ interactions.

complex three end-to-end azido bridges are observed with the nickel(II) in a distorted-octahedral environment.

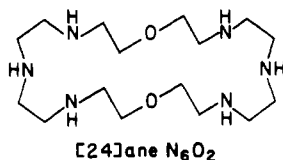
(24) Chaudhuri, P.; Guttman, M.; Ventur, D.; Wieghardt, K.; Nuber, B.; Weiss, J. *J. Chem. Soc., Chem. Commun.* **1985**, 1618-1620.

Description of the Structure of 2. Figure 2 shows a perspective view of the neutral complex **2**, and in Table VIII bond distances and angles are summarized. The geometry around the copper center is again square-based pyramidal. Three nitrogen atoms of the macrocycle and two of the two terminal azido ligands are bonded to the Cu(II) ion; one nitrogen atom of the tridentate macrocycle occupies the apical site of the square pyramid ($\text{Cu-N}_4 = 2.290$ (5) Å). The most remarkable feature of the structure of **2** is the fact that two neutral molecules, $\text{LCu}(\text{N}_3)_2$, are related by a crystallographic center of symmetry leading to pairs of monomers in the solid state. The $\text{Cu}\cdots\text{Cu}'$ distance within such a pair is 5.774 (1) Å. Is this pairing governed by packing effects or are we dealing with a genuine dimer, where the two Cu(II) centers are connected via two asymmetrical end-to-end azido bridges?



The pertinent structural details of this $\text{Cu}_2(\text{N}_3)_2$ moiety are as follows: (i) the two Cu-N distances of each μ -azido bridge consist of one short bond of 2.005 (5) Å, Cu-N7 (and a Cu-N7-N8 bond angle of 123.9 (4)°), and one very weak interaction of 2.753 (6) Å, Cu-N9' (and a Cu-N9'-N8' angle of 144.1 (7)°); (ii) the eight-membered $\text{Cu}_2(\mu\text{-N}_3)_2$ ring is planar, and the two linear ($\mu\text{-N}_3$) ligands are aligned parallel to the $\text{Cu}\cdots\text{Cu}$ axis; (iii) the $\text{Cu}\cdots\text{N}$ vector coincides approximately with the respective tetragonal axis of the CuN_5 square-based pyramidal polyhedron. The geometry around the Cu(II) centers may therefore be considered tetragonally elongated octahedral (CuN_6).

It is of interest to compare the present situation with two similar complexes described in the literature. In discrete $[\text{Cu}(\text{N}_3)_2]_2^{2-}$ ($\text{C}_{16}\text{H}_{38}\text{N}_6\text{O}_2$) molecules¹⁰ two $\text{Cu}(\text{N}_3)_2$ moieties are bonded into the macrocyclic ligand [24]ane N_6O_2 . The $\text{Cu}\cdots\text{Cu}$ distance is 5.973 (1) Å; the two independent Cu(II) centers are of the CuN_5



type (square pyramidal). One azide ligand of each Cu(II) is inside the cavity parallel to the $\text{Cu}\cdots\text{Cu}$ axis, and the configuration of this $\text{Cu}_2(\text{N}_3)_2$ unit is as in **2**. The Cu-N_α bond length is 1.963 (3) Å (shorter by 0.042 Å), whereas the $\text{Cu}\cdots\text{N}_\gamma$ interaction at 2.999 (4) Å (longer by 0.226 Å than in **2**) is considered to be essentially nonbonding. In this case the two paramagnetic Cu centers are held together by a binucleating macrocyclic ligand; no magnetic exchange interaction between the two Cu centers has been detected.

In $[\text{Cu}(\text{tmen})(\text{N}_3)_2]^{16}$ two asymmetric end-to-end azido bridges are observed ($\text{Cu-N}_\alpha = 1.979$ (5) Å, $\text{Cu-N}_\gamma = 2.456$ (6) Å); the geometry around the two copper(II) centers is square-based pyramidal. The $\text{Cu}_2(\text{N}_3)_2$ ring is not planar. Negligible magnetic interaction of the two Cu(II) atoms is observed. The asymmetry of the azido bridges is less than in **2** but more pronounced than in Weiss' complex.¹⁰ Finally, in Hendrickson's complex this asymmetry is even less; in $[\text{Cu}_2(\text{Me}_5\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2^{17}$ the Cu-N_α distance is 1.985 (4) Å and Cu-N_γ is 2.252 (5) Å but the geometry around the Cu(II) centers has been described as distorted trigonal bipyramidal and a weak antiferromagnetic coupling has been observed ($J = -6.5 \text{ cm}^{-1}$). The $\text{Cu}_2(\text{N}_3)_2$ ring is planar.

It therefore would appear that quite a range of Cu-N distances in doubly end-to-end-bridged μ -azido copper(II) complexes is observed. In **2** the Cu-N_γ distance of 2.752 (5) Å is borderline between weakly bonding and nonbonding.

Description of the Structure of 3. The structure consists of discrete $[\text{Cu}_2\text{L}_2(\mu\text{-N}_3)_2(\text{ClO}_4)_2]$ molecules, resulting from the

Table IX. Bond Distances (Å) and Angles (deg) of **3**

Cu1-N11	2.010 (7)	Cl1-O11	1.385 (8)
Cu1N13A	2.009 (7)	Cl1-O12	1.407 (12)
Cu1-N1	2.052 (7)	Cl2-O13	1.365 (9)
Cu1-N2	2.067 (6)	Cl2-O14	1.389 (9)
Cu1-N3	2.245 (7)	N11-N12	1.165 (10)
Cu1-O12A	2.836 (11)	N12-N13	1.151 (10)
Cu1...Cu1A	5.062 (2)		
N11-Cu1-N13A	92.9 (4)	N11-Cu1-N1	90.0 (4)
N13A-Cu1-N1	177.0 (8)	N13A-Cu1-N2	91.4 (4)
N1-Cu1-N3	84.2 (3)	N2-Cu1-N3	85.3 (4)
N11-Cu1-N2	174.4 (5)	N3A-Cu1-N3	96.8 (4)
N11-Cu1-N3	98.5 (4)	N1-Cu1-N2	85.7 (4)
Cu1-N11-N12	131.6 (6)	N11-N12-N13	173.2 (8)
Cu1A-N13-N12	127.6 (7)	O12A-Cu1-N11	81.5 (4)
O12A-Cu1-N13A	83.1 (5)	O12A-Cu1-N1	96.0 (5)
O12A-Cu1-N2	94.8 (5)	O12A-Cu1-N3	179.3 (8)

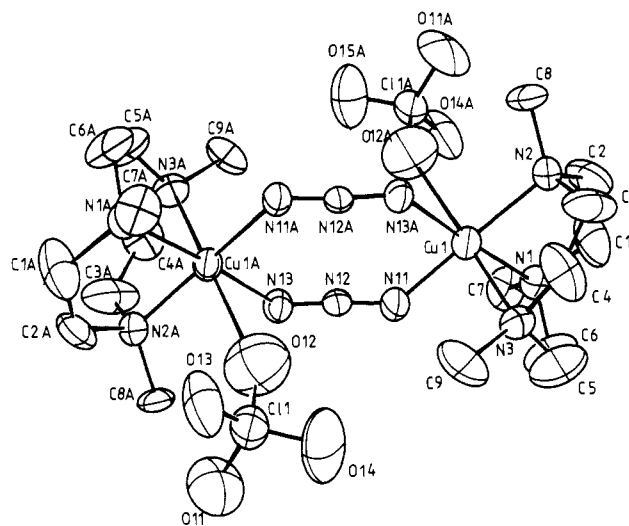


Figure 3. Molecular geometry and atomic labeling scheme of $[\text{L}_2\text{Cu}_2(\mu\text{-N}_3)_2(\text{ClO}_4)_2]$ (**3**).

binding of a $\text{Cu}_2(\text{N}_3)_2$ unit to two macrocyclic ligands, L, and two perchlorate anions. Bond distances and angles are summarized in Table IX. The structure of the complex and its atomic labeling scheme are shown in Figure 3. The halves of the molecule are related by a crystallographic center of symmetry. The eight-membered $\text{Cu}_2(\mu\text{-N}_3)_2$ ring is planar; the $\text{Cu1}\cdots\text{Cu1A}$ distance is 5.062 (2) Å.

The two end-to-end-coordinated azido bridges are symmetrical; they are bonded to two metal centers via two covalent Cu-N and two Cu'-N bonds (2.010 (7) and 2.009 (7) Å), respectively. Each copper(II) ion is bonded to five nitrogen atoms, three of which belong to the cyclic ligand and two to the azido bridges. The geometry around each Cu(II) is square pyramidal with the azide nitrogen atoms in the basal plane. The two CuN_4 planes are not exactly coplanar, in contrast to $\text{Cu}_2(\text{N}_3)_4(\text{C}_{18}\text{H}_{38}\text{N}_2\text{S}_4)^{14}$ a diamagnetic complex with two symmetrical $\mu\text{-N}_3$ bridges.

Two perchlorate anions are each very weakly coordinated via one oxygen atom to one Cu(II) center. These monodentate ClO_4^- groups are only very weakly bound, the Cu-O distance is 2.836 (11) Å, and, consequently, the geometry of each Cu(II) may be described as tetragonally elongated octahedral. It should be noted that this Cu-O distance is rather long as compared to those found in other copper(II) complexes with monodentate perchlorate ligands. Thus in $\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{SCH}_3)_2(\text{ClO}_4)_2$ a Cu-O bond length of 2.599 Å has been reported and Cu-O distances of 2.61 (2) and 2.575 (6) Å have been found for $\text{Cu}(\text{en})_2(\text{ClO}_4)_2^{26}$ and $\text{Cu}(\text{CH}_3\text{NHCH}_2\text{CH}_2\text{NH}_2)_2(\text{ClO}_4)_2^{24}$. Cu-O distances of 2.606

(25) Ou, C. C.; Miskowski, V. M.; Lalancette, R. A.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **1976**, *15*, 3157-3161.

(26) Pajunen, A. *Ann. Acad. Sci. Fenn., Ser. A2* **1967**, *138*, 2-28. *Struct. Rep.* **1967**, *32B*, 379 (International Committee of Crystallography).
(27) Luukkonen, E.; Pajunen, A.; Lehtonen, M. *Suom. Kemistil. B* **1970**, *43*, 160.

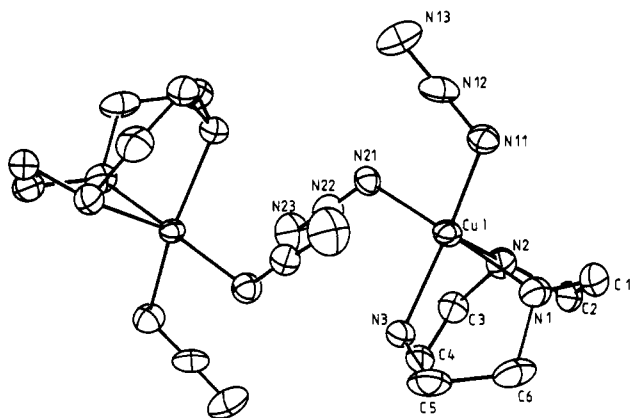


Figure 4. Molecular geometry and atomic labeling scheme of a pair of $L'Cu(N_3)_2$ molecules in **4**.

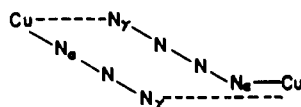
Table X. Bond Distances (Å) and Angles (deg) of **4**

Cu1-N1	2.035 (2)	N11-N12	1.193 (3)
Cu1-N2	2.238 (2)	N12-N13	1.151 (3)
Cu1-N3	2.072 (2)	N21-N22	1.202 (3)
Cu1-N11	1.991 (2)	N22-N23	1.158 (3)
Cu1-N21	1.983 (2)	Cu1-Cu1'	4.933 (1)
Cu1-N23'	3.126 (3)		
N1-Cu1-N2	81.9 (1)	N1-Cu1-N3	84.5 (1)
N2-Cu1-N3	82.7 (1)	N2-Cu1-N11	115.4 (2)
N3-Cu1-N21	95.2 (1)	N11-Cu1-N21	90.7 (1)
N1-Cu1-N11	89.5 (1)	N1-Cu1-N21	178.7 (3)
N2-Cu1-N21	98.4 (1)	N3-Cu1-N11	159.9 (5)
Cu1-N21-N22	122.2 (2)	N11-N12-N13	176.7 (5)
Cu1-N11-N12	120.5 (2)	N21-N22-N23	176.2 (5)
N21-Cu1-N23'	80.3 (1)	N2-Cu1-N23'	162.7 (6)
N3-Cu1-N23'	80.3 (1)	N1-Cu1-N23'	99.4 (1)
N11-Cu1-N23'	81.7		

and 2.594 Å have been reported for a copper(II) dimer containing a bridging μ -ClO₄ group.²⁸

The Cu-N bond distances in the equatorial plane range from 2.009 (7) to 2.067 (6) Å and are considered normal covalent bonds; the axial Cu-N bond is longer (2.245 (7) Å) as is expected for square-pyramidal complexes of copper(II).

Description of the Structure of 4. A perspective view of the molecule $L'Cu(N_3)_2$ is given in Figure 4. Bond distances and angles are given in Table X. As has been described for **2**, two molecules are related by a crystallographic center of symmetry resulting in a pairwise packing of $L'Cu(N_3)_2$ molecules in the unit cell, but in contrast to **2**, the $Cu_2(N_3)_2$ core of such a pair is not planar; a chair conformation is adopted instead. The Cu-N_α bond distance is a normal covalent Cu-N bond (1.983 (2) Å) whereas the Cu...N_γ interaction is very weak and is essentially nonbonding (Cu...N = 3.126 (3) Å). It is noted that two azido ligands, one from each molecule, are aligned parallel with respect to each other.



If the Cu...N_γ distances are considered nonbonding, the geometry of the Cu(II) center is square-pyramidal with the metal center bonded to three nitrogen atoms of 1,4,7-triazacyclononane and two terminal azido groups, both of which are in the basal plane. One nitrogen atom of the cyclic amine occupies the apical site (Cu-N₂ = 2.238 Å). Interestingly, in $L'CuCl_2$ ²⁹ the geometry around the copper(II) center is also square-pyramidal as is in $L'CuBr_2$.³⁰ The Cu1-Cu1' distance is 4.933 (1) Å, which is

(28) Coughlin, P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 3228-3229.

(29) Schwindinger, W. F.; Fawcett, T. G.; Lalancette, R. A.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **1980**, *19*, 1379-1381.

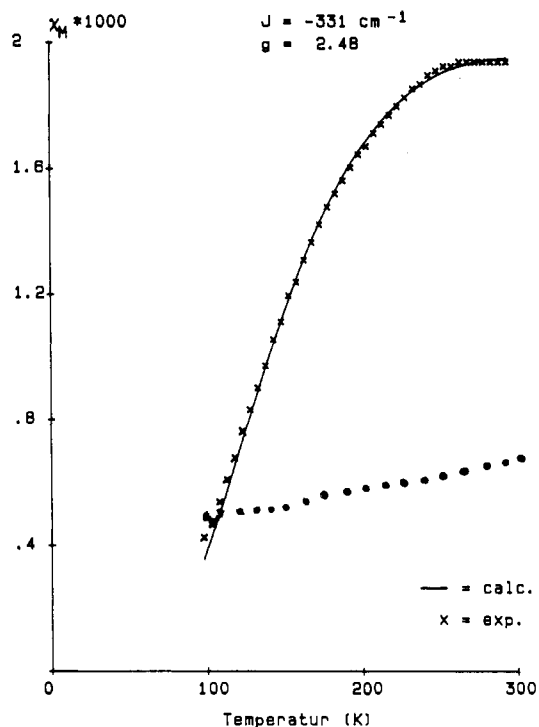


Figure 5. Plot of the magnetic susceptibility vs. the temperature of **1** (experimental data (x) and calculated curve (—) (see text)) and **3** (experimental data (●)).

significantly shorter than that in **2**.

Magnetic Susceptibility. Variable-temperature magnetic susceptibility data for complexes **1-4** were measured between 100 and 300 K with use of the Faraday method. A representative plot of magnetic susceptibility vs. temperature is shown in Figure 5 for **1**. The susceptibility decreases strongly with decreasing temperature. A plateau is reached at 250-300 K. The magnetic moment per Cu ion varies from 1.51 μ_B at 293 K to 0.44 μ_B at 103 K. Least-squares fitting of the susceptibility data to the Bleaney-Bowers equation (1) gives $J = -331$ (10) cm^{-1} with g

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

= 2.48. The solid line in Figure 4 represents this fit. Thus the spins of the two copper(II) centers in the dimeric cation of **1** are strongly antiferromagnetically coupled.

Magnetic susceptibility data for **2** (100-300 K) adhere closely to the Curie-Weiss law. Magnetic moments in this temperature range are independent of the temperature (1.92 μ_B), and the Weiss constant is very small ($\theta = +0.45$ K). From our measurements we cannot rule out a very weak ferromagnetic coupling, which would only be detected unambiguously at temperatures below 20 K. This indicates that the two Cu(II) ions in a pair of $L'Cu(N_3)_2$ moieties are essentially noncoupled. Variable-temperature magnetic susceptibility measurements between 100 and 300 K show that **3** is very strongly antiferromagnetic ($J < -400$ cm^{-1}). χ_M varies from 6.8×10^{-4} cm^3 mol^{-1} at 293 K to 4.9×10^{-4} cm^3 mol^{-1} at 98 K, which is largely due to the usual 1-2% monomeric paramagnetic impurity. The measured values of χ_M varied with samples from different preparations. The magnetic behavior of **3** parallels closely that reported for $Cu_2(N_3)_4(C_{18}H_{38}N_2S_4)$.¹⁴

Finally, the magnetic data of **4** adhere again closely to the Curie-Weiss law (108-298 K). Magnetic moments vary from 1.95 μ_B/Cu^{2+} at 293 K to 1.92 μ_B at 108 K. A Weiss constant, θ , of -14 K may indicate a small intermolecular antiferromagnetic exchange coupling between two Cu(II) atoms in a pair of $L'Cu(N_3)_2$ molecules. J was tentatively calculated to be -3 cm^{-1} .

(30) Bereman, R. D.; Churchill, M. R.; Schaber, P. M.; Winkler, M. E. *Inorg. Chem.* **1979**, *18*, 3122-3125.

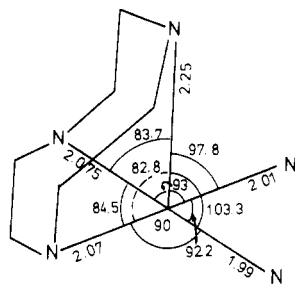


Figure 6. Schematic representation of the square-based pyramidal geometry around the Cu(II) centers in **1–4** with averaged bond distances (Cu–N) and angles (N–Cu–N). Averaged deviations from the mean values are 0.01 Å and 0.2°, respectively.

Discussion

The geometries around the copper(II) centers in structures **1–4** are very similar. This is shown in Figure 6, where average bond distances and angles of the CuN_5 polyhedron are given. To a first approximation a common square-based pyramid is encountered in all four complexes. Due to the steric constraints of the macrocyclic ligand the three respective N–Cu–N bond angles are smaller than 90° (average 83.5°). The Cu–N distances of coordinated amine and azide groups in the basal plane range from 1.98 to 2.04 Å, which correspond to normal Cu(II)–N single bonds; the apical Cu–N bond is in all cases a copper(II)–amine bond and is significantly elongated (average Cu–N = 2.25 Å). The azide groups are always bonded to the Cu(II) ions in the basal plane and are in cis positions with respect to each other. Significant differences between the structures of **1**, **2**, **3**, and **4** arise from different modes of linkage of two such square pyramids. One symmetrical end-to-end μ -azido bridge (in combination with possibility two further asymmetric end-to-end azido bridges) connects two basal planes in **1** (Figure 7, type A). Two symmetrical end-to-end μ -azido bridges are found in **3**, which align the two basal planes in one plane (Figure 7, type C). In **2** strongly asymmetrical bridging by two end-to-end μ -azido bridges may be envisaged, in which case the coordination spheres of the Cu(II) centers are expanded to the coordination number 6 (Figure 7, type B). In **4** only terminal azide ligands prevail and no linkage via azide bridges is found. Nevertheless, in the solid state two monomeric $\text{L}'\text{Cu}(\text{N}_3)_2$ units are packed pairwise (Figure 7, type D). Finally, it is noted that two square pyramids may also be linked together via a symmetrical end-to-end azide bridge, where the N_α and N_β atoms of the bridge occupy apical positions (Figure 7, type E). This mode has previously been observed in $[\text{Cu}_2(\text{N}_3)_3(\text{C}_{30}\text{H}_{42}\text{N}_6\text{O}_4)](\text{ClO}_4)_8$ and in $[\text{Cu}_2(\text{N}_3)_3(\text{C}_9\text{H}_9\text{N}_2\text{O}_2)_2]\text{Cl}\cdot 2\text{H}_2\text{O}$.¹⁵

The interpretation of the observed magnetism of complexes of types A–E is straightforward. The close to square-pyramidal stereochemistry of d^9 copper(II) atoms in the dimers discussed here suggests that they have $(d_{x^2-y^2})^1$ ground states. The major σ pathway for the interaction of these magnetic orbitals containing the unpaired electron involves azide ligands, which bridge these $d_{x^2-y^2}$ orbitals. Strong antiferromagnetic coupling is therefore observed in **1** ($J = -331$ (10 cm^{-1})) and **3** ($J < 400\text{ cm}^{-1}$), where two $d_{x^2-y^2}$ orbitals are linked via one (1) or two (3) symmetrical azide bridges. In **3** the planes containing the lobes of the $d_{x^2-y^2}$ orbitals of both Cu(II) ions are in one plane, which effectively leads to diamagnetism of this complex at room temperature, whereas in **1** these basal planes are not coplanar.

In **2** and **4** the $d_{x^2-y^2}$ orbital of one Cu(II) ion is weakly interacting with a d_{z^2} orbital of the second Cu(II) ion and vice versa

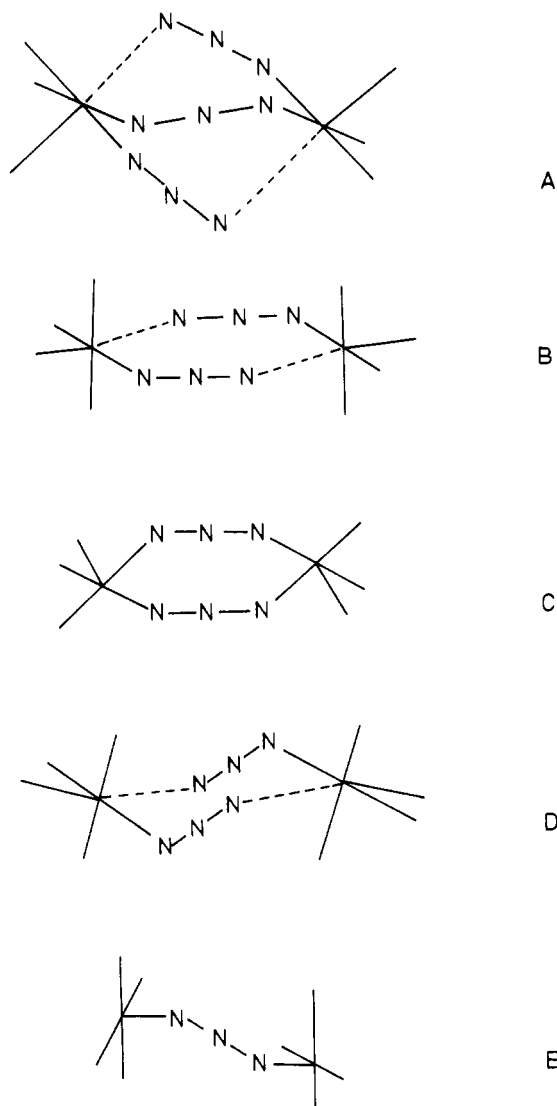


Figure 7. Modes of μ -azido bridging of two square pyramids.

via two very asymmetrical μ - N_3 bridges. In **4** it is probably more realistic to say that no bonding interaction between the two copper(II) ions of a pair of $\text{L}'\text{Cu}(\text{N}_3)_2$ molecules exists. Consequently, no intramolecular magnetic exchange coupling is observed. At least in the temperature range 100–300 K **2** and **4** exhibit normal paramagnetism. We cannot at present rule out very weak intramolecular ferromagnetic (in **2**) or antiferromagnetic (in **4**) coupling.

Finally, it is noted that in complexes of structure type E, where d_{z^2} orbitals are linked via a symmetrical azide bridge, very weak antiferromagnetic behavior or no coupling at all^{8,15} is observed.

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Supplementary Material Available: Tables of intraligand bond distances, anisotropic thermal parameters, and calculated positional parameters of H atoms for **1–4** (9 pages). Ordering information is given on any current masthead page.