

Crystal structure and EPR spectrum of dimeric di- μ -azide-bis[cyanide(N,N-diethylethylenediamine)]-copper(II), $[\text{Cu}(\text{N}_3)(\text{NCO})(\text{diEten})]_2$

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The title compound, $[\text{Cu}(\text{N}_3)(\text{NCO})(\text{C}_6\text{H}_{16}\text{N}_2)]_2$, crystallizes in the space group $P2_1/n$, with $a = 8.336(1)$, $b = 17.405(3)$, $c = 8.376(1)$ Å, $\beta = 109.73(2)^\circ$ and $Z = 4$. The molecules are arranged as centrosymmetric dimers in which two azide ligands bridge neighboring copper ions in an asymmetric head-on fashion. The Cu(II) ion is coordinated to five nitrogen atoms which form a distorted tetragonal pyramid. At the pyramid base are the two N atoms of a diEten molecule [Cu–N = 2.00(1), 2.130(9) Å], an azide end atom [Cu–N = 1.99(1) Å] and a NCO group [Cu–N = 1.93(1) Å]. At the pyramid apex is the other, inversion related, azide N atom in the dimer [Cu–N = 2.38(1) Å]. This Cu–N contact links the monomers within a dimer. Neighboring dimers are coupled by weak N–H...O contacts. Single crystal EPR data at X-band show that the pair of resonances expected for neighboring, magnetically nonequivalent dimers, collapse into a single line, a signature of inter-dimers superexchange coupling. The observed crystal gyromagnetic tensor is used to disclose the electronic and magnetic structure around Cu(II) ions.

KEY WORDS: Crystal structure; copper(II) dimer; EPR spectrum.

Introduction

Dimeric Cu(II) complexes are of continuous interest, in particular because they provide simple model systems of the active site in dinuclear copper-containing proteins.^{1,2} These model systems are amenable to many detailed studies by solid state techniques.

Also, they are the simplest of magnetically coupled Cu(II) systems to study superexchange interactions and the relation of these interactions with crystal structure and the nature of the bridging groups.

There have been several crystallographic and magnetic studies on azide-bridged Cu(II) dimers. The bridging occurs basically in either the end-to-end or the head-on fashions, which can in turn be classified as symmetric, when both Cu–N bond distances are similar and asymmetric when these distances are appreciably different.

Symmetric end-to-end azide-bridged Cu(II) dimers with Cu–N bond distances of about 2.0 Å have been reported to present a strong antiferromagnetic coupling between the Cu(II) unpaired electrons.^{3,4} As expected, weak antiferromagnetic coupling has been found in Cu(II) dimers with this kind of symmetric bridging but longer Cu–N distances.^{5,6} On the other hand, asymmetric end-to-end azide-bridged binuclear

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Cu(II) complexes with one short Cu–N bond distance of about 2.0 Å and a second, much weaker, Cu–N interaction have been reported as consisting of practically uncoupled copper ions.^{1,3}

Symmetric head-on azide-bridged Cu(II) dimers with Cu–N bond distances of about 2.0 Å have been reported as strongly ferromagnetically coupled.^{3,7,8} A ferromagnetic ground state has been reported for a double asymmetric head-on azide-bridged Cu(II) dimer with Cu–N distances of 1.975 and 2.536 Å.⁶

As part of our studies dealing with the effect of pseudohalogen substitutions in Cu(II) complexes on its chemical, structural^{9,10} and magnetic properties, we are reporting here the crystal structure and EPR data of [Cu(N₃)(NCO)(C₆H₁₆N₂)₂], a new double asymmetric head-on azide-bridged Cu(II) dimer.

Experimental

X-ray diffraction data and crystal structure determination and refinement

Crystal data, data collection procedure, structure determination methods and refinement results are summarized in Table 1. The amine, secondary CH₂ and methyl hydrogen atoms were positioned on stereochemical grounds. The CH₃ groups were rotationally positioned as to fit the residual electron density at bond distances from the corresponding carbon atom. All H atoms were included in the structure factor calculation with a common fixed temperature parameter, which in the final refinement run converged to $U = 0.1 \text{ \AA}^2$ ($B = 3.95 \text{ \AA}^2$).

EPR data

Single crystal EPR data were collected at room temperature with an ER-200 Bruker spectrometer, using a cylindrical cavity working in the TE011 mode at 9.7 GHz with 100 KHz magnetic field modulation and a rotating 12" electromagnet. The crystal samples were glued to an L-shaped sample holder and oriented along an orthogonal system (*xyz*) of axes defined in the sample holder. The *b* axis was oriented parallel to the *y* direction and the crystal $[-101]$ direction parallel to the *z* axis of the reference frame. The sample holder was fastened to a horizontal plane at the top of a pedestal which was then positioned inside the microwave cavity. The spectral position and the peak-to-

Table 1. Crystal data and summary of intensity data collection and structure refinement for [Cu(N₃)(NCO)(diEten)]₂

Formula	C ₇ H ₁₆ N ₆ OCu
Color/shape	Blue-green/fragment
Formula weight	261.54
Space group	<i>P</i> 2 ₁ / <i>n</i>
Temp., °C	22
Cell constants ^a	
<i>a</i> , Å	8.336(1)
<i>b</i> , Å	17.405(3)
<i>c</i> , Å	8.376(1)
β, deg	109.73(2)
Cell volume, Å ³	1143.97(5)
Formula units/unit cell	4
<i>D</i> _{calc.} , g·cm ⁻³	1.52
<i>μ</i> _{calc.} , cm ⁻¹	18.0
Diffractometer/scan	Enraf-Nonius CAD-4/ω-2θ
Radiation, graphite monochromator	Mo Kα(λ = 0.71069 Å)
Max. crystal dimens., mm	0.15 × 0.30 × 0.45
Scan width	0.8 + 0.35 tan θ
Standard reflections	(1,0,16); (2,5,1)
Decay of standards	±2%
Reflections measured	2232
2θ range, deg	2 ≤ 2θ ≤ 50 °
Range of <i>h</i> , <i>k</i> , <i>l</i>	+9, +20, ±9
Reflections observed	
[<i>F</i> _o ≥ 6σ(<i>F</i> _o)] ^b	1484
Computer programs ^c	SHELX, ¹¹ SDP ¹²
Structure solution ^d	SHELX ¹¹
No. of parameters varied	136
Minimized function	Σw(<i>F</i> _o − <i>F</i> _c) ²
Weights, <i>w</i>	[σ(<i>F</i> _o) ² + 0.001 <i>F</i> _o ²] ⁻¹
GOF	3.5
$R = \sum F_o - F_c / \sum F_o $	0.075
$R_w = [\sum w (F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.075
Largest feature final diff.map	1.1 e ⁻ Å ⁻³

^a Least-squares refinement of [(sinθ)/λ]² values for 25 reflections in the 11.2 < 2θ < 36.2 ° range.

^b Corrections: Lorentz and polarization.

^c Neutral scattering factors and anomalous dispersion corrections.

^d Structure solved by Patterson and Fourier methods and the final molecular model obtained by anisotropic full-matrix least-squares refinement of nonhydrogen atoms.

peak linewidth of the single resonance observed were measured as a function of the orientation of the magnetic field **B** in the three perpendicular planes *xy*, *xz*, and *zy*.

Low temperature powder EPR data were recorded at X-band (CW) in a home-made spectrometer, using a rectangular cavity working in the TE102 mode and a 85 KHz magnetic field modulation. The sample temperature was varied from room temperature down to

about 6K employing a liquid transfer HELI-TRAN refrigerator (Model LTR-3; APD Cryogenics Inc.).

Results and discussion

Crystallographic results

Fractional coordinates and equivalent isotropic temperature parameters according to Hamilton¹³ for the non-H atoms in [Cu(N₃)(NCO)(diEten)]₂ are given in Table 2. Relevant bond distances and angles around the copper ion and for the organic, cyanide and azide molecules are in Table 3. Figure 1 is an ORTEP¹⁴ projection of a dimer showing the labeling of the non-H-atoms. The Cu(N₃)(NCO)(diEten) monomers are arranged in the lattice as bonded pairs. The monomers in a dimer are related to each other by a crystallographic inversion center (see Fig. 1).

Bond distances and angles within the organic molecule and angles around diEten nitrogen atoms involving the bound Cu(II) ion conform to a single-bond *sp*³ hybridization scheme for all the diEten backbone atoms. These structural results are similar to those in the related double asymmetric head-on cyanate-bridged [Cu(NCO)₂(diEten)]₂ dimer.¹⁰

The ligands around the Cu(II) ion form a distorted tetragonal pyramidal polyhedron. The strongest covalent bonds involving mainly the copper *d*(*x*² - *y*²) orbital occur with three of the four nitrogen atoms at

Table 2. Fractional atomic coordinates and isotropic temperature parameters (Å²) of [Cu(N₃)(NCO)(diEten)]₂

Atom	X/a	Y/b	Z/c	B _{iso} ^a
Cu	0.9409(2)	0.0938(1)	0.4782(2)	2.62(4)
N(1)	1.141(1)	0.0329(5)	0.474(1)	3.3(3)
N(2)	0.849(1)	0.1119(5)	0.211(1)	2.8(3)
N(3)	0.720(1)	0.1421(6)	0.468(1)	3.7(3)
N(4)	1.051(2)	0.1399(6)	0.698(1)	4.9(4)
N(5)	1.281(1)	0.0575(6)	0.522(1)	3.7(3)
N(6)	1.422(2)	0.0800(9)	0.569(2)	6.7(5)
C(1)	0.699(2)	0.1620(7)	0.176(2)	3.8(4)
C(2)	0.597(2)	0.1421(7)	0.290(2)	4.0(4)
C(3)	0.807(2)	0.0351(7)	0.128(2)	3.8(4)
C(4)	0.739(2)	0.0370(8)	-0.067(2)	5.1(5)
C(5)	0.989(2)	0.1514(7)	0.162(2)	3.5(3)
C(6)	1.068(2)	0.2187(8)	0.274(2)	5.0(5)
C(7)	1.156(2)	0.1569(7)	0.826(2)	3.5(4)
O(1)	1.262(1)	0.1777(6)	0.954(1)	6.0(4)

^a B_{iso} defined as: B_{iso} = 8π²/3 Σ_i Σ_j U_{ij} a_i^{*} a_j^{*} · a_i^{*} · a_j^{*}.

Table 3. Interatomic bond distances (Å) and angles (°) in [Cu(N₃)(NCO)(diEten)]₂

(a) Bond distances ^a	
Cu-N(1)	1.99(1)
Cu-N(1')	2.38(1)
Cu-N(2)	2.130(9)
Cu-N(3)	2.00(1)
Cu-N(4)	1.93(1)
N(1)-N(5)	1.18(2)
N(2)-C(1)	1.47(2)
N(2)-C(3)	1.49(1)
N(2)-C(5)	1.53(2)
N(3)-C(2)	1.50(2)
N(4)-C(7)	1.17(2)
N(5)-N(6)	1.17(2)
C(1)-C(2)	1.52(2)
C(3)-C(4)	1.54(2)
C(5)-C(6)	1.51(2)
C(7)-O(1)	1.19(2)
(b) Bond angles ^a	
N(1)-Cu-N(2)	93.8(4)
N(1)-Cu-N(3)	171.9(4)
N(1)-Cu-N(4)	96.1(5)
N(2)-Cu-N(3)	83.9(4)
N(2)-Cu-N(4)	145.7(4)
N(3)-Cu-N(4)	90.0(5)
N(1)-Cu-N(1')	78.4(3)
N(2)-Cu-N(1')	107.0(2)
N(3)-Cu-N(1')	94.8(3)
N(4)-Cu-N(1')	107.2(4)
Cu-N(1)-Cu'	101.6(4)
Cu-N(1)-N(5)	122.7(9)
Cu'-N(1)-N(5)	125.9(7)
Cu-N(2)-C(1)	106.1(7)
Cu-N(2)-C(3)	107.5(7)
Cu-N(2)-C(5)	108.2(7)
C(1)-N(2)-C(3)	112.8(9)
C(1)-N(2)-C(5)	110.8(9)
C(3)-N(2)-C(5)	111.0(9)
Cu-N(3)-C(2)	110.7(8)
Cu-N(4)-C(7)	161(1)
N(1)-N(5)-N(6)	178(1)
N(2)-C(1)-C(2)	111(1)
N(3)-C(2)-C(1)	107(1)
N(2)-C(3)-C(4)	115(1)
N(2)-C(5)-C(6)	113(1)
N(4)-C(7)-O(1)	177(1)

^a Cu' and N(1') are related to Cu and N(1) by the inversion symmetry operation 2-x, -y, 1-z.

the corners of the pyramid base, namely, with the nitrogen atom of the NCO group [d(Cu-N) = 1.93(1) Å], with an end azide nitrogen [d(Cu-N) = 1.99(1) Å] and with the diEten amino nitrogen [d(Cu-N) = 2.00(1) Å], *trans* to the azide nitrogen atom. The Cu(II) ion practically lays on the equatorial plane defined by

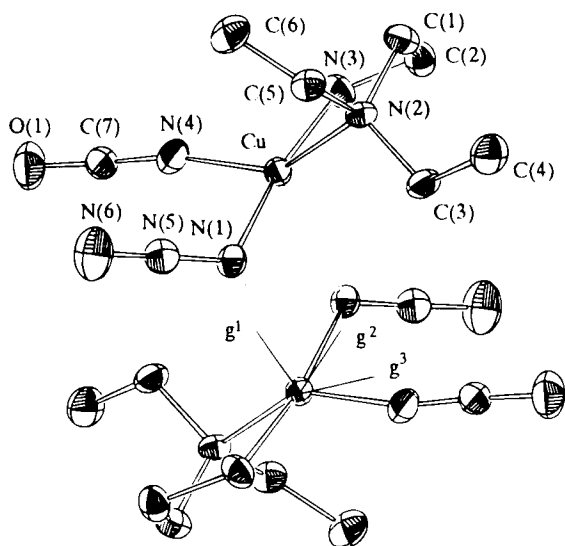


Fig. 1. ORTEP view of a $[\text{Cu}(\text{N}_3)(\text{NCO})(\text{diEten})]_2$ dimer showing the numbering scheme for the nonhydrogen atoms and their thermal ellipsoids at 30% probability. The molecule is sited on a crystallographic inversion center. The drawing also shows the principal directions of the molecular g tensor.

the above three nitrogen atoms [at 0.085(1) Å]. The fourth corner of the pyramid base is occupied by the other diEten nitrogen atom. This last atom participates in a bent, strained Cu–N bond [$d(\text{Cu}–\text{N}) = 2.130(9)$ Å] whose direction is out of the equatorial plane in about 36°. This weaker bond is probably favored because of the failure of diEten molecule to conform both Cu–N bonds in the equatorial plane due to steric hindrance. The fivefold coordination is completed with the symmetry related coordinated azide nitrogen in the dimer [$d(\text{Cu}–\text{N}) = 2.38(1)$ Å] located at the pyramid apex, 2.14(1) Å apart from the equatorial plane.

A given dimer is linked to four other neighboring dimers through weak N–H...O bonds [$d(\text{N}...O) = 3.15(1)$ Å, $d(\text{H}...O) = 2.13(1)$ Å and $\text{ang}(\text{N}–\text{H}...O) = 155(1)^\circ$].

OCN⁻ and N₃⁻ electronic structure and bonding to the transition metal

The double bond configuration of $\text{O}=\text{C}=\text{N}^-$ and $^-\text{N}=\text{N}^+=\text{N}^-$ ions can be described in the Valence Bond (VB) picture by σ bonds between adjacent atoms involving $2s2p$ hybrid ($2sp\sigma$) orbitals and additional π bonds resulting from overlapping $2p$ orbitals centered on the pair of nearest neighbor atoms. The eight valence electrons not participating

in the double bonds fill the two lone-pair nonbonding orbitals (one of the $sp\sigma$ type and the other of the $p\pi$ kind) located on each of the end atoms in the molecule. An alternative VB description involves the replacement of the $sp\sigma$ and nonbonding $p\pi$ orbitals on the end atoms by $sp^2\sigma$ hybrids; the corresponding two lone-pair lobes on each end atom become equivalent, nonbonding orbitals subtending an angle of 120° with each other and with the molecular axis. In each of the above VB descriptions there are two equivalent bonding arrangements, related to each other by a 90° rotation around the molecule axis. Resonance between them makes the molecule symmetric about this axis and stabilizes the molecule relative to any one of the two possible bonding schemes. In the simplest LCAO-MO picture, the ground state configuration of both ions can be described similarly to the case of the CO_2 molecule¹⁵ by $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(1\pi_g)^4: ^1\Sigma_g$.

The nonbonding $2\sigma_g$, $2\sigma_u$, and the doubly degenerate $1\pi_g$ orbitals correspond to the four lone-pair lobes of the VB picture. In either description, these lone-pair lobes are the relevant orbitals participating in the azide–Cu(II) and cyanide–Cu(II) bondings.

In $[\text{Cu}(\text{N}_3)(\text{NCO})(\text{diEten})]_2$, the Cu–N–CO bond angle of 161(1)° (see Table 3) suggests that the –NCO ion behaves mainly as a σ donor, similarly to the case of the closely related thiocyanate ligand in metal–NCS bonding.¹⁶ In the first of the two VB pictures considered above, this corresponds to a dominant participation in the Cu–NCO bond of the nitrogen $sp\sigma$ lone-pair lobe and a relatively smaller contribution of the $p\pi$ lone-pair orbital. In contrast, the appreciably bent Cu–N₃ bond [Cu–N–N angle of 122.7(9)°] indicates that the azide ligand acts as both, σ and π donors, similarly to thiocyanate in the metal–SCN bonding.¹⁶ This can be better rationalized in the frame of the second of the VB pictures mentioned above. In this description, one of the azide end nitrogen $sp^3\sigma$ lone-pair orbitals strongly overlaps with a Cu(II) $d(x^2 - y^2)$ lobe to form an essentially σ bond whose direction subtends an angle of about 120° with the N₃ axis. The other nitrogen $sp^3\sigma$ lone-pair lobe overlaps with $3d$ orbitals of another, inversion related, copper ion [$d(\text{N}–\text{Cu}) = 2.38$ Å]. This interaction accounts for most of the bonds linking the molecules in a dimer and also provides a possible path for superexchange coupling between the corresponding pair of Cu(II) ions [$d(\text{Cu}–\text{Cu}) = 3.395(2)$ Å]. Metal–N₃ bonds bent at about 120° are also observed in other Cu(II)-containing complexes, namely $\text{Cu}(\text{N}_3)_2$ (aver-

age Cu–N–N bond angle of 127.5° ¹⁷) and *trans*- $[\text{Cu}(\text{N}_3)_2(\text{NH}_3)_2]$ (average Cu–N–N bond angle of 119° ¹⁸) and in other transition metal complexes, including $[\text{Co}(\text{N}_3)(\text{NH}_3)_5](\text{N}_3)_2$ [(Co–N–N) = 125.2° ¹⁹] and $[\text{Co}(\text{N}_3)(\text{CN})_5] \cdot 2\text{H}_2\text{O}$ [(Co–N–N) = 116.3° ²⁰]. The covalent Metal–N₃ bond gives rise to an asymmetry in the azide N–N bond lengths (see, for example, Ref. 20 and references therein). This effect is only marginally appreciated in the crystal data of $[\text{Cu}(\text{N}_3)(\text{NCO})(\text{diEten})]_2$ as it is of the order of experimental error (see Table 3).

EPR results

The two $\text{Cu}(\text{N}_3)(\text{NCO})(\text{diEten})$ molecules of each dimer are related by an inversion symmetry operation and are, therefore, magnetically equivalent. In the crystal, there are two magnetically unequal types of dimers related by a twofold screw axis. Assuming independent molecular response, two symmetry related EPR spectra are expected. However, the exchange interaction between neighboring, magnetically inequivalent dimers, produces the collapse of their EPR resonances into a single band. This interaction is also responsible for the collapse of EPR fine structure bands due to hyperfine and superhyperfine coupling of the unpaired electron with the copper nucleus ($I_{\text{Cu}} = 3/2$) and with the coordinated nitrogen nuclei ($I_{\text{N}} = 1$), respectively.

The variation in the spectral position of the observed EPR line with the orientation of the applied magnetic field \mathbf{B} (see Fig. 2), can be described with the spin hamiltonian

$$H = \mu_{\text{B}} \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S}$$

where μ_{B} is the Bohr magneton and \mathbf{g} is the gyromagnetic tensor corresponding to the single collapsed line. The components of the second-order tensor \mathbf{g}^2 were evaluated by least-squares with the data of Fig. 2. The values obtained are given in Table 4. The angular variation of g^2 in the three orthogonal planes calculated with these least-squares parameters are compared in Fig. 2 with the experimental data.

Following the decoupling procedure described in Ref. 21, we calculated the principal values and directions of the molecular gyromagnetic tensor from the determined crystal \mathbf{g}^2 tensor (Table 4). To this purpose, it was assumed that one of the eigenvectors of the molecular g -tensor (namely, the one associated with the g^1 eigenvalue) is parallel to the bisector of Cu–

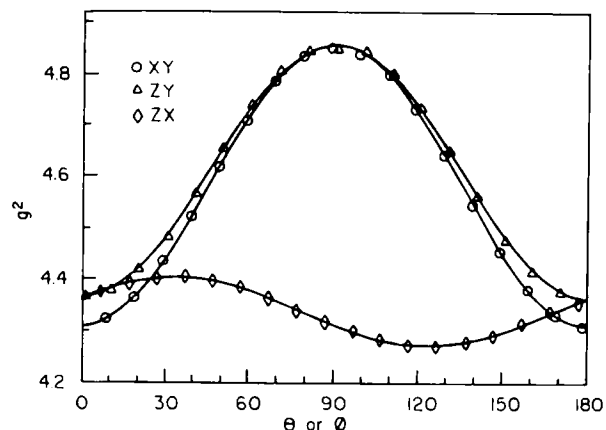


Fig. 2. Angular variation of the squared gyromagnetic factor measured at 300 K and 9.7 GHz in three orthogonal planes of $[\text{Cu}(\text{N}_3)(\text{NCO})(\text{diEten})]_2$ single crystal. The curves were obtained by least squares fitting of the data with a symmetric g^2 second-order tensor. The relevant parameters are included in Table 4.

N(1)–N(4) and Cu–N(2)–N(3) plane normals. The results of these calculations are included in Table 4. The orientation of the eigenvectors relative to the CuN_5 molecular group is shown in Fig. 1.

The obtained eigenvalues of the molecular g tensor have nearly axial symmetry, with $g_{\parallel} = 2.26$ and $g_{\perp} = 2.05$. These values confirm that the ground state of the unpaired electron is mainly a $d(x^2 - y^2)$ orbital. Besides, the in-plane principal directions are close to the directions of the equatorial Cu–N bonds (see Fig. 1), a result which is also consistent with a $d(x^2 - y^2)$ ground orbital state. The anisotropy of the in-plane principal g -values indicates some admixture of the excited states into the ground state. This is to be expected as the N(2) ligand is appreciably out (in about 1.3 Å) of the mean square plane CuN(1)N(3)N(4).

Table 4. EPR parameters for $[\text{Cu}(\text{N}_3)(\text{NCO})(\text{diEten})]_2$

(a) $(g^2)_{xx} = 4.310(1)$	$(g^2)_{xy} = 0.000(1)$
$(g^2)_{yy} = 4.857(1)$	$(g^2)_{xz} = 0.612(1)$
$(g^2)_{zz} = 4.364(1)$	$(g^2)_{yz} = 0.000(1)$
(b) $g^1 = 2.26(1)$	$(-0.468, -0.87, 0.157)$
$g^2 = 2.01(1)$	$(0.878, -0.478, -0.031)$
$g^3 = 2.09(1)$	$(0.102, 0.123, 0.987)$

^a Values of the components of the tensor g^2 .

^b Eigenvalues and eigenvectors of the molecular g -tensor in the orthogonal reference system defined by the \mathbf{a} , \mathbf{b} , and $\mathbf{c}' = \mathbf{a} \times \mathbf{b}$ vectors.

Table 5. Anisotropic thermal parameters (\AA^2)^a for the nonhydrogen atoms in $[\text{Cu}(\text{N}_3)(\text{NCO})(\text{diEten})]_2$ ^b

Atom	U(1,1)	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
Cu	0.0328(7)	0.0333(7)	0.0334(7)	0.0016(7)	0.0109(5)	-0.0009(7)
N(1)	0.032(5)	0.042(6)	0.052(6)	0.001(5)	0.017(4)	-0.007(4)
N(2)	0.046(5)	0.027(5)	0.036(5)	0.000(4)	0.019(4)	0.004(4)
N(3)	0.030(5)	0.055(6)	0.054(6)	0.010(5)	0.013(5)	0.006(5)
N(4)	0.073(8)	0.042(6)	0.055(7)	0.001(6)	-0.001(6)	-0.016(6)
N(5)	0.052(7)	0.051(6)	0.042(6)	0.007(5)	0.021(5)	-0.003(5)
N(6)	0.058(8)	0.11(1)	0.09(1)	-0.011(9)	0.037(7)	-0.022(8)
C(1)	0.052(7)	0.044(7)	0.046(7)	0.005(6)	0.014(6)	0.012(6)
C(2)	0.041(7)	0.056(8)	0.051(8)	-0.010(6)	0.011(6)	0.007(6)
C(3)	0.069(8)	0.031(6)	0.042(7)	-0.004(5)	0.013(6)	-0.001(6)
C(4)	0.08(1)	0.063(9)	0.051(8)	-0.010(7)	0.018(7)	-0.001(8)
C(5)	0.048(7)	0.042(7)	0.048(7)	0.007(6)	0.025(6)	-0.003(6)
C(6)	0.065(9)	0.051(8)	0.08(1)	0.006(8)	0.035(8)	-0.020(7)
C(7)	0.052(7)	0.045(7)	0.034(7)	0.005(6)	0.013(6)	-0.001(6)
O	0.070(7)	0.089(8)	0.055(6)	0.002(6)	0.002(5)	-0.024(6)

^a The Debye-Waller temperature factor is defined by: $\exp[-4\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

^b To be deposited.

Table 6. Fractional atomic coordinates for the hydrogen atoms in $[\text{Cu}(\text{N}_3)(\text{NCO})(\text{diEten})]_2$ ^a

Atom	X/a	Y/b	Z/c
H(C1)	0.7652	0.2150	0.2161
H'(C1)	0.6059	0.1670	0.0525
H(C2)	0.4730	0.1637	0.2186
H'(C2)	0.5976	0.0794	0.2632
H(C3)	0.9203	0.0053	0.2111
H'(C3)	0.6962	0.0108	0.1465
H(C4)	0.7149	-0.0177	-0.1264
H'(C4)	0.8280	0.0691	-0.1129
H''(C4)	0.6221	0.0700	-0.0975
H(C5)	0.9295	0.1687	0.0314
H'(C5)	1.0864	0.1103	0.1733
H(C6)	1.1570	0.2618	0.2745
H'(C6)	1.0992	0.1933	0.4004
H''(C6)	0.9400	0.2420	0.2380
H(N3)	0.6964	0.2035	0.4633
H'(N3)	0.6640	0.1159	0.5536

^a To be deposited.

The EPR linewidth showed an angular variation similar to that of g^2 . This suggests that the main source of line broadening arises from the hyperfine and super-hyperfine structures collapsed by the exchange interaction between neighboring dimers.

EPR band intensity of powdered samples increases with decreasing temperature following approximately a Curie behavior down to about 6K. This suggests a triplet ($S = 1$) ground state, in agree-

ment with the reported ferromagnetic ground state for $[\text{Cu}(\text{N}_3)(\text{L})]_2(\text{ClO}_4)_2$ {L = 1-(imidazol-4-yl)-2-[(2-pyridylmethylene)amino]ethane}, a Cu(II) dinuclear complex with a bonding structure around Cu(II) similar to that of $[\text{Cu}(\text{N}_3)(\text{NCO})(\text{diEten})]_2$. However, EPR and magnetic susceptibility measurements below 6K are necessary to confirm a dimer ferromagnetic ground state for this latter compound.

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Supplementary material. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/5125. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: teched@chemcrs.cam.ac.uk).

Table 7. Least-squares planes^a and dihedral angles around Cu(II) ion in $[\text{Cu}(\text{N}_3)(\text{NCO})(\text{diEten})]_2$ ^b

Pl. No	Atoms used in the fitting	A	B	C	D	χ^2
I	N(1)N(2)N(3)N(4)	0.4858	0.8622	-0.1435	4.2492	5068
II	N(1)N(2)N(3)N(4)Cu	0.4876	0.8617	-0.1406	4.2250	22482
III	N(1)N(3)N(4)	0.4249	0.7689	-0.4778	2.1261	—
IV	N(1)N(3)N(4)Cu	0.4272	0.7740	-0.4672	2.2177	1867
Deviation (Å) from						
Atom ^c	Plane I	Plane II	Plane III	Plane IV		
N(1)	-0.32(1)	-0.27(1)	0.00(1)	-0.03(1)		
N(2)	0.34(1)	0.38(1)	1.33(1)	1.28(1)		
N(3)	-0.37(1)	-0.33(1)	0.00(1)	-0.03(1)		
N(4)	0.36(1)	0.41(1)	0.00(1)	-0.00(1)		
Cu	-0.230(1)	-0.183(1)	0.085(1)	0.059(1)		
N(1 ⁱ)	-2.58(1)	-2.53(1)	-2.14(1)	-2.17(1)		
Dihedral angles (°) between planes: $\text{ang}(\text{I,II}) = 0(6)$; $\text{ang}(\text{III,IV}) = 0(6)$; $\text{ang}(\text{I,III}) = 20.3(7)$; $\text{ang}(\text{II,IV}) = 19.8(7)$						

^a The equation of the plane is $Ax + By + Cz + D = 0$, where A, B, C, and D are constants and x, y and z are orthogonalized coordinates.

^b To be deposited.

^c Symmetry code: (i) $2-x, -y, 1-z$.

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