4910 *Inorg. Chem.* **1995,** *34,* 4910−4917

Synthesis, Characterization, Spectroscopy, and Magnetism of Dinuclear Azido- and Alkoxo-Bridged Copper(II) Complexes of Bis(2-benzimidazolyl)alkanes. X-ray Structures of $[Cu_2(tbz)_2(CH_3O)_2](ClO_4)_2(CH_3OH)_2$, $[Cu_2(tbz)_2(NO_3)(CH_3O)_2](NO_3)(CH_3OH)_2$, and $[Cu(tbz)(N_3)_2]_2(CH_3OH)_2$ (tbz = Bis(2-benzimidazolyl)propane)

Gerard A. van Albada,[1a] Miles T. Lakin,[1b] Nora Veldman,[1b] Anthony L. Spek,[1b] and Jan Reedijk*,[1a]

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502,
2300 RA Leiden, The Netherlands, and Bijvoet Center for Biomolecular Research, Vakgroep
Kristal- en Structuurchemie, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received March 16, 1995[⊗]

A group of new compounds with the general formula $Cu(L)(sol^-)(A^-)(Hsol)$, where A = ClO_4^-, $CF_3SO_3^-$, BF_4^-, and NO_3^-, L = bis(2-benzimidazolyl)propane (abbreviated as tbz) and bis(2-benzimidazolyl)butane (abbreviated as qbz), and Hsol = methanol and ethanol, and with the formula $[Cu(tbz)(N_3^-)(Hsol)]$ has been prepared and characterized structurally, magnetically, and spectroscopically. Three representative compounds $[Cu_2(tbz)_2(CH_3O)_2](ClO_4)_2(CH_3OH)_2$ (**1**), $[Cu_2(tbz)_2(NO_3)(CH_3O)_2](NO_3)(CH_3OH)_2$ (**5**), and $[Cu(tbz)(N_3)_2]_2(CH_3OH)_2$ (**13**) were characterized structurally with X-ray diffraction. Crystal data for **1**: monoclinic, space group $P2_1/c$ with $a = 9.6863(10)$ Å, $b = 12.9445(10)$ Å, $c = 19.394(2)$ Å, $\beta = 113.259(10)°$, and $Z = 2$. Crystal data for **5**: monoclinic, space group $P2_1$ with $a = 9.5497(6)$ Å, $b = 12.5073(7)$ Å, $c = 17.5920(12)$ Å, $\beta = 90.996(6)°$, and $Z = 2$. Crystal data for **13**: orthorhombic, space group *Pbca* (No. 61) with $a = 11.3325(7)$ Å, $b = 18.7096(16)$ Å, $c = 19.2011(16)$ Å, and $Z = 4$. The structure refinement converged to $wR2 = 0.1381$, $R1 = 0.0534$ for **1**, $wR2 = 0.0674$, $R1 = 0.0271$ for **5**, and $wR2 = 0.1119$, $R1 = 0.0701$ for **5**. The structures **1** and **5** consist of dinuclear units with bridging methoxo groups and one ligand linked to each copper via the N, providing square planar CuN_2O_2 chromophores. Structure **5** consists of a dinuclear unit in which one of the copper atoms is linked to a nitrate O, to yield a unit with two different copper environments, one square planar and the other square pyramidal. Structure **13** consists also of dinuclear units with the two copper atoms bridged by μ-(1,1)-azido groups. Furthermore each copper is surrounded by two nitrogens of the ligand and a nitrogen of a nonbridging end-on μ-(1,1)-azido moiety resulting in a distorted square pyramidal geometry. The Cu−Cu distances (Å) within the dinuclear units are as follows: **1**, 2.9827(6); **5**, 3.0072(4); **13**, 3.2422(9). The Cu-O-Cu bridging angles (deg) are as follows: **1**, 102.89(14); **5**, 103.97(9), 103.06(9)°. The Cu−N-Cu bridging angle for **13** is 104.66(17)°. Far-infrared spectroscopy shows bands which are characteristic for the bridging $Cu_2O_2N_4$ chromophore; Cu−O vibrations are found at about 457 and 330 cm^{-1} for the ethoxo-bridged compounds and at about 390 and 232 cm^{-1} for the methoxo-bridged compounds. The magnetic susceptibility measurements of the alkoxo-bridged compounds display a diamagnetic behavior below room temperature with an estimated exchange parameter $2J$ of < -600 cm^{-1}. These dinuclear species are EPR silent, and only a weak signal of monomeric impurities is observed. The μ-(1,1)-azido-bridged dimer shows a ferromagnetic behavior with a calculated J value of +23 cm^{-1} and a weak, very broad isotropic EPR signal at $g = 2.14$.

Introduction

Bis(2-benzimidazoles) and some substituted bis(2-benzimidazolyl)alkanes have attracted much interest because of their wide-ranging antivirus activity[2] and also because of the coordination chemistry of azoles acting as ligands in copper(II) compounds. Such compounds are increasingly being studied in the context of modeling biological systems.[3]

Transition-metal compounds with chlorides as a counteranion were reported for bis(2-benzimidazolyl)methane and bis(2-benzimidazolyl)ethane;[4] recently molybdenum(V) compounds of some bis(2-benzimidazolyl)alkanes were reported,[5] but so far only one crystal structure has been published, i.e. a structure showing an ethoxo-bridged dinuclear copper(II) with a square-planar Cu environment.[6] So far no reports concerning the magnetic and spectroscopy properties of copper(II) compounds with bis(2-benzimidazolyl)alkanes have been published.

In view of the limited information and because of our earlier interest in such ligands[7] it was decided to study copper(II)

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1995.

(1) (a) Leiden Institute of Chemistry, Leiden University. (b) Bijvoet Center for Biomolecular Research, Utrecht University.

(2) (a) Akihama, S.; Takahashi, K.; Miyajima, N. *Yakugaku Zasshi* **1974**, *94*, 247 (in Japanese). See also: *Chem. Abstr.* **1974**, *81* (3), 9648x. (b) Çakir, B.; Büyükbingöl, E.; Uçucu, Ü.; Abbasoĝlu, U.; Noyanalpan, N; *J. Fac. Pharm. Gaz.* **1988**, *5*, 71. (c) Tidwell, R. R.; Jones, S. K.; Naiman, N. A.; Berger, L. C.; Brake, W. B.; Dykstra, C. C.; Hall, J. E. *Antimicrobial Agents Chemotherapy* **1993**, *37*, 1713.

(3) (a) Reedijk, J. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: London, **1987**, Vol. 2, p 73. (b) Bouwman, E.; Driessen, W. L.; Reedijk, J. *Coord. Chem. Rev.* **1990**, *104*, 143.

(4) Pujar, M. A.; Bharamgoudar, T. D. *Transition Met. Chem.* **1988**, *13*, 423.

(5) Salunki, N. M.; Revankar, V. K.; Mahak, V. B. *Transition Met. Chem.* **1994**, *19*, 53.

(6) (a) Bernardinelli, G.; Kübel-Pollak, A.; Rüttimann, S.; Williams, A. F. *Chimia* **1992**, *46*, 155. (b) Bernardinelli, G.; Kübel-Pollak, A.; Rüttimann, S.; Williams, A. F. *Z. Kristallogr.* **1993**, *203*, 132.

(7) (a) Sanni, S. B.; Behm, H. J.; Beurskens, P. T.; van Albada, G. A.; Reedijk, J.; Lenstra, A. T. H.; Addison, A. W.; Palandiandavar, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1429. (b) van Albada, G. A.; Reedijk, J.; Hämäläinen, R.; Turpeinen, U.; Spek, A. L. *Inorg. Chim. Acta* **1989**, *163*, 213.

0020-1669/95/1334-4910$09.00/0

Table 1. Crystallographic Data for Compounds **1**, **5**, and **13**

	1	**5**	**13**
formula	$C_{38}H_{46}Cl_2Cu_2N_8O_{12}$	$C_{38}H_{46}Cu_2N_{10}O_{10}$	$C_{36}H_{40}Cu_2N_{20}O_2$
M_r	1004.82	929.94	911.94
space group	$P2_1/c$	$P2_1$	*Pbca*
cryst system	monoclinic	monoclinic	orthorhombic
Z	2	2	4
a, Å	9.6863(10)	9.5497(6)	11.3325(7)
b, Å	12.9445(10)	12.5073(7)	18.7096(16)
c, Å	19.394(2)	17.5920(12)	19.2011(16)
β, deg	113.259(10)	90.996(6)	
V, Å^3	2234.1(4)	2100.9(2)	4071.2(7)
D_{calcd}, g cm^{-3}	1.494	1.470	1.488
$F(000)$	1036	964	1880
$\mu_{MoK\alpha}$, cm^{-1}	11.4	10.8	11.1
no. of refined params	312	547	275
$R1^a$	0.0534 [for 3650, $F_0 > 4.0\sigma F_0$]	0.0271 [for 4728, $F_0 > 4.0\sigma F_0$]	0.0701 [for 2118, $F_0 > 4.0\sigma F_0$]
$wR2^b$	0.1381	0.0674	0.1119

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

compounds of a variety of bis(2-benzimidazolyl)alkanes with both strong and weak coordinating anions and investigate their structural, magnetic, and spectroscopic properties. It appeared also of interest to see whether alkoxo-bridged complexes can be converted into other bridged species.

In the present study a number of copper(II) compounds are reported with the ligand bis(2-benzimidazolyl)propane (hereafter abbreviated as tbz) and bis(2-benzimidazolyl)butane (hereafter abbreviated as qbz) with the general formula [Cu(L)(sol$^-$)(A$^-$)(Hsol)], where A = ClO_4^-, $CF_3SO_3^-$, BF_4^-, and NO_3^-, L = tbz and qbz, and Hsol = methanol and ethanol, and with the formula [Cu(tbz)(N_3^-)(Hsol)], where Hsol = methanol.

The paper includes the crystal structures of three representative complexes from this group, which are discussed in relation to their spectroscopic and magnetic properties.

Experimental Section

Syntheses. 1,3-Propanedicarboxylic acid, 1,4-butanedicarboxylic acid, 1,2-diamino-benzene, metal salts, and solvents were commercially available and used without further purification. The bis(2-benzimidazolyl)alkanes were prepared by heating the appropriate dicarboxylic acid with 1,2-diaminobenzene in ethylene glycol, according to a published method.[8]

Anal. Found (calc) for tbz, $C_{17}H_{16}N_4$: 72.92 (73.89), C; 6.13 (5.84), H; 20.08 (20.27), N. Found (calc) for qbz: 74.40 (74.46), C; 6.53 (6.25), H; 19.27 (19.30), N. ^{1}H NMR (DMSO-d_6, δ): tbz, 2.42 (q, 2H, $-CH_2-$), 3.00 (t, 4H, Im-CH_2), 7.33 (m, 8H, benz-Im); qbz, 1.88 (q, 4H, $-CH_2-$), 2.90 (t, 4H, Im-CH_2), 7.30 (m, 8H, benz-Im).

The coordination compounds were prepared according to the following general procedure for compounds **1**–**12**: 1.2 mmol of Cu(II) salt and 1.2 mmol of the ligand were each dissolved in 10 mL of methanol (or in some cases ethanol). The Cu(II) salt solution was then added slowly to the ligand solution and filtered to remove any undissolved material. Usually after a few days the violet to violet-blue products separate and were isolated by filtration and dried in air. Changing the Cu salt/ligand ratio was found to have no effect on the stoichiometry of the product.

Compound **13** was prepared as follows: 1.2 mmol of $Cu(CF_3SO_3)_2$ and 1.2 mmol of tbz were each dissolved in 10 mL of methanol, and 2.4 mmol of NaN_3 was dissolved in 1 mL of water. The sodium azide solution was added to the copper triflate solution, and the combined solution was slowly added to the ligand solution and filtered to remove any undissolved material. After a few days red-brownish crystals separated, which were isolated by filtration and dried in air.

All given formulas of the compounds in this study agreed with the elemental analysis (see Table S1 of the supporting information).

Physical Measurements. C, H, N, and Cu determinations were performed by the Microanalytical Laboratory of University College, Dublin, Ireland, and the Microanalytical Department, State University, Groningen, The Netherlands.

UV–vis spectra were obtained on a Perkin-Elmer 330 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. X-band powder EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH (g = 2.0036) as a standard. FTIR spectra were obtained on a Bruker 330v infrared spectrophotometer as KBr disks, Nujol mulls, or Kel-F mulls (4000–400 cm^{-1}, mirror velocity 0.166 cm/s, resolution 2 cm^{-1}) or as polyethylene mulls (600–100 cm^{-1}, mirror velocity 0.099 cm/s, resolution 2 cm^{-1}, Mylar 3.5 μ beam splitter). Data for compound **5** were recorded using a Mtech type 200 photoacoustic detector (mirror velocity 0.059 cm/s, resolution 2 cm^{-1}).

Magnetic susceptibilities were measured in the temperature range 20–300 K with a Manics DSM-8 susceptometer. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.[9]

NMR spectra were recorded on a Varian EM360L spectrophotometer with TMS as a standard.

Crystallographic Data Collection and Refinement of the Structures. *X-ray Crystallography on Structures* **1**, **5**, *and* **13**. Crystal data are collected in Table 1. Crystals suitable for X-ray structure determination, 0.25 × 0.50 × 0.75 mm for **1**, 0.25 × 0.50 × 0.75 mm, for **5**, and 0.10 × 0.10 × 0.70 mm for **13**, were covered by an inert oil, glued to the tip of a glass fiber, and immediately placed in the cold dinitrogen stream (150 K) on an Enraf-Nonius CAD4-T diffractometer with rotating anode. Data were collected in the $\omega/2\theta$ mode using λ(Mo Kα) 0.710 73 Å (monochromator), with θ generally in the range 1.1–27.5°. The scan angle was $\Delta\omega = a + 0.35 \tan\theta$ with a = 1.00, 0.58, and 0.68 for **1**, **5**, and **13**, respectively. Unit-cell dimensions and standard deviations were obtained by least-squares fit (SET4)[10] of the setting angles from, generally, 25 reflections. The crystal of compound **1** is slightly twinned: only 21 out of 25 reflections fitted in one lattice (DIRAX).[11] Reduced-cell calculations did not indicate higher lattice symmetry (Lepage).[12] Three standard reflections were monitored periodically and showed approximately 2% (12% for **1**) variation in intensity during data collection. The data were scaled accordingly. Intensity data were corrected for Lorentz, polarization, and absorption effects (an empirical absorption/extinction correction was applied (DIFABS:[13] 0.594–1.000, 0.693–1.000, and 0.822–1.000 transmission ranges for **1**, **5**, and **13**, respectively) and averaged into a unique set of reflections. Total data of 5520, 10 661, and 7595 reflections were

---

(8) (a) Wang, L. L.; Joullié, M. M. *J. Am. Chem. Soc.* **1957**, *79*, 5706. (b) Schubert, H.; Hoffmann, S.; Lehmann, G.; Barthold, I.; Meichsner, H.; Polster, H. *Z. Chem.* **1975**, *15*, 481.

(9) Kolthoff, I. M.; Elving, P. J. *Treatise on Analytical Chemistry*; Interscience Publ.: New York, **1963**; Vol. 4, Part 1.

(10) de Boer, J. L.; Duisenberg, A. J. M. *Acta Crystallogr.* **1984**, *A40*, C410.

(11) Duisenberg, A. J. M. *J. Appl. Crystallogr.* **1992**, *25*, 92.

(12) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.

(13) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

collected of which 5120, 5033, and 4661 were independent (R_{int} = 0.0405, 0.0326 and 0.0632) for **1**, **5**, and **13**, respectively. Data sets range −12:12, −16:0, −25:12 for **1**, −12:12, 0:16, −22:22 for **5**, and 0:14, 0:24, −24:18 for **13**.

Structure **1** was solved by automated direct methods (SHELXS86).[14] The structures **5** and **13** were solved by automated Patterson methods and subsequent difference Fourier syntheses (DIRDIF-92).[15] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93).[16] All reflections were considered observed during refinement. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were included in the refinement cycle at calculated positions, riding on their carrier atoms. A fixed isotropic displacement parameter of 1.5 times the equivalent isotropic displacement parameter of the carrier atom was used for the methyl and hydroxyl hydrogen atoms, with 1.2 times for all other hydrogen atoms. For structure **5** the correct enantiomer was selected on the basis of the final Flack absolute structure parameter (0.052(9)). Weights were introduced in the final refinement cycles. The structure refinements converged to $wR2 = 0.1381$, $R1 = 0.0534$, $S = 1.023$, $w = 1/[\sigma^2(F^2) + (0.0796P)^2]$ for **1**, $wR2 = 0.0674$, $R1 = 0.0271$, $S = 1.048$, $w = 1/[\sigma^2(F^2) + (0.0403P)^2 + 0.20P]$ for **5**, and $wR2 = 0.1119$, $R1 = 0.0701$, $S = 0.891$, $w = 1/[\sigma^2(F^2) + (0.0244P)^2]$ for **13**, where $P = (\max(F^2_o, 0) + 2F^2_c)/3$. Final difference Fouriers showed no residual density outside −0.45 and 0.78, −0.48 and 0.35, and −0.49 and 0.59 e Å^{-3} for **1**, **5**, and **13**, respectively.

Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 17. All geometrical calculations and the ORTEP illustrations were performed with PLATON.[18] Positional parameters for each structure have been listed in Tables 2−4. Computing was conducted on a DEC5000 cluster.

Results and Discussion

Crystal Structure of [$Cu_2(tbz)_2(CH_3O)_2](ClO_4)_2(CH_3OH)_2$ (1). The structure of the dinuclear cationic unit is depicted in Figure 1, with relevant bond length and bond angle information given in Table 5. The unit cell contains two dinuclear methoxo-bridged copper(II) units, four perchlorate molecules, and four methanol molecules. The perchlorate and the methanol molecules are disordered.

The dinuclear unit has a center of symmetry located between two copper ions. The Cu−Cu distance within the dinuclear unit is 2.9827(6) Å; the ligand tbz acts as a didentate ligand with N(13) and N(23) as coordinating atoms.

The Cu atoms are square-planar coordinated with the basal plane formed by the two nitrogens of the ligand (Cu(1)−N(13) 1.955(3) Å, Cu(1)−N(23) 1.973(3) Å) and two oxygens of two methoxo ligands (Cu(1)−O(1) 1.901(3) Å, Cu(1)−O(1)a 1.913(3) Å). The angles (O(1)−Cu(1)−N(13) 170.04(12)°, O(1)a−Cu(1)−N(23) 169.62(13)°) deviate nearly 10° from linearity; the angle of the Cu−O-Cu bridge is 102.89(14)°.

The eight-membered chelate ring (Cul, N13, C12, C1, C2, C3, C22, N23) adopts a stable boat−chair conformation in which the Cu atom has the greatest deviation (0.9563(14) Å) from the least squares plane (total puckering amplitude Q_t = 1.380(3) Å) similar to the geometry described earlier for the compound [$Cu_2(tbz)_2(C_2H_5O)_2](ClO_4)_2(C_2H_5OH)_2$.[6a]

The geometric details are comparable with angles and distances found in the literature for other methoxo-bridged copper(II) dinuclear units[19] and ethoxo-bridged copper(II) dinuclear units;[6b,20] the Cu−N distances are also consistent with Cu−N(imidazole) distances found in the literature.[3b]

Table 2. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for Structure [$Cu_2(tbz)_2(CH_3O)_2](ClO_4)_2(CH_3OH)_2$ (**1**)

atom[a]	x	y	z	U(eq),[b] Å^2
Cu(1)	0.46515(5)	0.11042(3)	0.00816(2)	0.0279(1)
O(1)	0.6152(3)	0.0257(2)	−0.00313(13)	0.0286(7)
N(11)	0.2100(3)	0.2538(2)	0.1040(2)	0.0311(11)
N(13)	0.3103(3)	0.1794(2)	0.0323(2)	0.0314(11)
N(21)	0.7141(3)	0.3660(2)	0.1002(2)	0.0293(8)
N(23)	0.5809(3)	0.2403(2)	0.0277(2)	0.0305(11)
C(1)	0.4417(5)	0.1499(3)	0.1703(2)	0.0428(12)
C(2)	0.5880(5)	0.2123(4)	0.2042(2)	0.0467(14)
C(3)	0.6973(5)	0.2029(3)	0.1646(2)	0.0429(12)
C(12)	0.3214(4)	0.1936(3)	0.1014(2)	0.0335(12)
C(14)	0.1843(4)	0.2356(2)	−0.0134(2)	0.0274(12)
C(15)	0.1203(4)	0.2827(3)	0.0315(2)	0.0294(12)
C(16)	−0.0035(4)	0.3463(3)	0.0024(2)	0.0389(12)
C(17)	−0.0619(4)	0.3619(4)	−0.0734(2)	0.0479(16)
C(18)	0.0000(4)	0.3150(4)	−0.1194(2)	0.0445(14)
C(19)	0.1235(4)	0.2513(3)	−0.0906(2)	0.0356(12)
C(22)	0.6621(4)	0.2689(3)	0.0972(2)	0.0321(12)
C(24)	0.5764(4)	0.3248(2)	−0.0177(2)	0.0259(11)
C(25)	0.6616(4)	0.4041(2)	0.0280(2)	0.0255(12)
C(26)	0.6816(4)	0.4989(2)	−0.0001(2)	0.0275(12)
C(27)	0.6117(4)	0.5116(3)	−0.0769(2)	0.0307(12)
C(28)	0.5257(4)	0.4325(3)	−0.1229(2)	0.0330(12)
C(29)	0.5060(4)	0.3382(3)	−0.0949(2)	0.0319(12)
C(41)	0.7461(5)	0.0576(4)	−0.0118(3)	0.0616(18)
Cl(1)	0.28707(11)	0.40551(7)	0.27220(5)	0.0360(3)
*O(11A)	0.4216(6)	0.4094(4)	0.2575(3)	0.0699(17)
*O(11B)	0.336(3)	0.4536(16)	0.2265(10)	0.035(6)
*O(12A)	0.1912(5)	0.4843(3)	0.2309(3)	0.0768(16)
*O(12B)	0.168(3)	0.474(2)	0.2791(16)	0.067(9)
*O(13A)	0.2157(7)	0.3061(4)	0.2490(3)	0.051(2)
*O(13B)	0.383(2)	0.3922(17)	0.3450(11)	0.033(6)
*O(14A)	0.3260(6)	0.4184(3)	0.3499(2)	0.0545(14)
*O(14B)	0.210(4)	0.315(2)	0.2418(19)	0.07(3)
*O(32B)	0.0987(19)	−0.0285(17)	0.2727(9)	0.070(4)
*C(31B)	0.1086(18)	0.0140(19)	0.2096(9)	0.103(7)
*O(32A)	0.889(2)	0.4377(18)	0.2425(11)	0.077(4)
*C(31A)	0.854(2)	0.4675(16)	0.3017(6)	0.100(7)

[a] Starred atom sites have a population less than 1.0. [b] U(eq) = $^1/_3$ of the trace of the orthogonalized **U**.

The lattice structure is stabilized by stacking between the benzimidazole groups of different units (ring−ring distances of 3.714 Å) and by a hydrogen-bonding network with N···O contacts of 2.77−2.87 Å. Details of the H-bond network are listed in supporting information Table S6.

Crystal Structure of [$Cu_2(tbz)_2(NO_3)(CH_3O)_2](NO_3)(CH_3OH)_2$ (5). The structure of the dinuclear cationic unit is depicted in Figure 2, with relevant bond length and bond angle information given in Table 6. The unit cell contains two dinuclear copper(II) units, four nitrate molecules, and four methanol molecules. The asymmetric dinuclear Cu cluster consists of two crystallographically independent copper(II) ions linked together by two methoxo ligands. The ligand tbz acts as a chelating didentate ligand to each Cu with N(13), N(23), N(33), and N(43) as coordinating atoms as seen in structure **1**.

Unlike structure **1** the two copper(II) atoms slightly differ in their geometry. Cu(1) has a square-pyramidal coordination with

---

(14) Sheldrick, G. M. SHELXS-86 Program for crystal structure determination. University of Göttingen, Germany, 1986.

(15) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.

(16) Sheldrick, G. M. SHELXL-93 Program for crystal structure refinement. University of Göttingen, Germany, 1993.

(17) Wilson, A. J. C., Ed. *International Tables for Crystallography*: Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

(18) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(19) (a) Yamashita, M.; Ito, H.; Ito, T. *Inorg. Chem.* **1983**, *22*, 2102. (b) Wrobleski, D. A.; Rauchfuss, T. B.; Rheingold, A. L.; Lewis, K. A. *Inorg. Chem.* **1984**, *23*, 3124. (c) Voronkova, V. K.; Mosina, L. V.; Yablokov, Y. V.; Yampolskaya, M. A.; Matuzenko, G. S.; Simenov, Y. A.; Kuyavskaya, B. Y.; Gerbeleu, N. V.; Belskii, V. K. *Zh. Strukt. Khim.* **1986**, *27*, 69. (d) Demartin, F.; Manassero, M.; Naldini, L.; Panzanelli, A.; Zoroddu, M. A. *Inorg. Chim. Acta* **1990**, *171*, 229.

(20) Drillon, M.; Grand, A.; Rey, P. *Inorg. Chem.* **1990**, *29*, 771.

Table 3. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen atoms for Structure $[Cu_2(tbz)_2(NO_3)(CH_3O)_2](NO_3)(CH_3OH)_2$ (**5**)

atom	*x*	*y*	*z*	*U*(eq),[a] Å^2
Cu(1)	0.78015(3)	0.30537(2)	0.31776(2)	0.0181(1)
Cu(2)	0.72226(3)	0.51182(2)	0.23542(2)	0.0204(1)
O(1)	0.6340(2)	0.3837(2)	0.26523(12)	0.0227(6)
O(2)	0.8699(2)	0.4372(2)	0.28470(12)	0.0256(6)
O(21)	0.6905(3)	0.5391(3)	0.4921(2)	0.0616(12)
O(22)	0.8866(3)	0.4629(2)	0.4683(2)	0.0457(10)
O(23)	0.6907(2)	0.3883(2)	0.43404(13)	0.0317(7)
N(2)	0.7572(3)	0.4636(2)	0.46486(15)	0.0298(9)
N(11)	1.1193(3)	0.1336(2)	0.40057(14)	0.0237(7)
N(13)	0.9548(3)	0.2323(2)	0.34632(13)	0.0207(7)
N(21)	0.6088(2)	0.0079(2)	0.36033(13)	0.0204(6)
N(23)	0.6774(3)	0.1689(2)	0.32408(13)	0.0204(7)
N(31)	0.8852(3)	0.7749(2)	0.12823(15)	0.0262(7)
N(33)	0.8292(3)	0.6395(2)	0.20291(15)	0.0258(8)
N(41)	0.3929(3)	0.6592(3)	0.1258(2)	0.0372(12)
N(43)	0.5491(3)	0.5832(2)	0.2015(2)	0.0267(8)
C(1)	0.9304(3)	0.1917(3)	0.4863(2)	0.0273(10)
C(2)	0.8171(3)	0.1072(3)	0.4987(2)	0.0273(9)
C(3)	0.6711(3)	0.1337(3)	0.4646(2)	0.0257(9)
C(4)	0.8282(4)	0.6039(3)	0.0626(2)	0.0346(12)
C(5)	0.6822(4)	0.6076(3)	0.0238(2)	0.0417(12)
C(6)	0.5681(4)	0.5425(3)	0.0631(2)	0.0368(12)
C(12)	1.0000(3)	0.1876(2)	0.4110(2)	0.0227(8)
C(14)	1.0503(3)	0.2026(2)	0.2914(2)	0.0204(8)
C(15)	1.1546(3)	0.1407(2)	0.3253(2)	0.0246(8)
C(16)	1.2645(3)	0.0971(3)	0.2845(2)	0.0318(11)
C(17)	1.2650(4)	0.1178(3)	0.2075(2)	0.0362(12)
C(18)	1.1598(4)	0.1805(3)	0.1729(2)	0.0342(12)
C(19)	1.0505(3)	0.2231(3)	0.2130(2)	0.0279(10)
C(22)	0.6526(3)	0.1055(2)	0.3829(2)	0.0209(8)
C(24)	0.6511(3)	0.1067(2)	0.2595(2)	0.0198(8)
C(25)	0.6071(3)	0.0058(3)	0.2815(2)	0.0202(7)
C(26)	0.5731(3)	−0.0739(3)	0.2294(2)	0.0261(10)
C(27)	0.5872(3)	−0.0481(3)	0.1532(2)	0.0293(12)
C(28)	0.6322(3)	0.0533(3)	0.1312(2)	0.0303(11)
C(29)	0.6643(3)	0.1327(3)	0.1827(2)	0.0268(10)
C(32)	0.8454(3)	0.6716(3)	0.1317(2)	0.0260(10)
C(34)	0.8582(3)	0.7278(2)	0.2482(2)	0.0226(8)
C(35)	0.8947(3)	0.8140(3)	0.2016(2)	0.0230(8)
C(36)	0.9298(3)	0.9132(3)	0.2307(2)	0.0275(9)
C(37)	0.9263(3)	0.9242(3)	0.3082(2)	0.0305(11)
C(38)	0.8895(3)	0.8393(3)	0.3559(2)	0.0291(11)
C(39)	0.8547(3)	0.7402(3)	0.3273(2)	0.0261(10)
C(42)	0.5039(3)	0.5938(3)	0.1302(2)	0.0304(12)
C(44)	0.4623(3)	0.6462(3)	0.2457(2)	0.0275(10)
C(45)	0.3626(4)	0.6938(3)	0.1977(2)	0.0338(12)
C(46)	0.2613(4)	0.7642(3)	0.2247(3)	0.0447(14)
C(47)	0.2657(4)	0.7852(3)	0.3010(3)	0.0475(14)
C(48)	0.3666(4)	0.7390(3)	0.3497(2)	0.0454(12)
C(49)	0.4650(3)	0.6676(3)	0.3233(2)	0.0333(12)
C(51)	0.4903(3)	0.3581(3)	0.2575(2)	0.0388(12)
C(52)	1.0100(3)	0.4723(3)	0.2974(2)	0.0295(10)
O(62)	0.0947(3)	0.3583(3)	0.0163(2)	0.0494(11)
C(61)	0.1713(5)	0.4348(4)	0.0582(3)	0.0569(16)
O(72)	0.4332(3)	0.3812(2)	0.50966(15)	0.0454(10)
C(71)	0.3455(4)	0.3126(4)	0.4672(2)	0.0476(12)
O(12)	0.8276(3)	0.3375(2)	0.07370(14)	0.0393(8)
O(13)	0.6332(3)	0.2783(2)	0.0239(2)	0.0502(11)
O(14)	0.8269(4)	0.2299(3)	−0.0226(2)	0.0637(12)
N(1)	0.7623(4)	0.2827(2)	0.0248(2)	0.0366(9)

[a] *U*(eq) = $^1/_3$ of the trace of the orthogonalized U.

the basal plane comprised of two nitrogens from the tbz ligand (Cu(1)−N(13) 1.960(3) Å, Cu(1)−N(23) 1.973(3) Å) and the oxygens of two methoxo ligands (Cu(1)−O(1) 1.928(2) Å, Cu(1)−O(2) 1.952(2) Å). The *trans*-angles deviate more from linearity than in structure **1** (O(1)−Cu(1)−N(13) 164.95(9)°, O(2)−Cu(1)−N(23) 165.73(9)°), as one would expect with such geometrical constraints. The axial atom of the square pyramid is the oxygen of the nitrate anion with a distance of Cu(1)−O(23) = 2.460(2)Å; the Cu atom lies 0.214(0) Å above the square plane toward the axial atom.

Table 4. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen atoms for Structure $[Cu(tbz)(N_3)_2]_2(CH_3OH)_2$ (**13**)

atom	*x*	*y*	*z*	*U*(eq),[a] Å^2
Cu(1)	0.12613(5)	0.01953(3)	0.03499(3)	0.0132(2)
N(1)	0.0091(3)	−0.0633(2)	0.0204(2)	0.0157(14)
N(2)	0.0203(3)	−0.1221(2)	0.0447(2)	0.0170(14)
N(3)	0.0314(4)	−0.1776(2)	0.0692(3)	0.0313(19)
N(4)	0.2034(4)	−0.0357(2)	0.1097(2)	0.0190(16)
N(5)	0.3069(4)	−0.0300(3)	0.1162(3)	0.0280(17)
N(6)	0.4089(5)	−0.0275(4)	0.1207(3)	0.064(3)
N(11)	0.2897(4)	0.2092(2)	0.0964(2)	0.0203(16)
N(13)	0.1831(4)	0.1141(2)	0.0692(2)	0.0157(12)
N(21)	0.3308(4)	0.0022(2)	−0.1547(2)	0.0180(14)
N(23)	0.2477(4)	−0.0041(2)	−0.0497(2)	0.0147(14)
C(1)	0.2800(5)	0.1185(3)	−0.0976(3)	0.0183(17)
C(2)	0.3850(5)	0.1479(2)	−0.0561(2)	0.0197(17)
C(3)	0.3898(5)	0.1217(3)	0.0204(3)	0.0223(19)
C(12)	0.2882(5)	0.1460(3)	0.0615(3)	0.0197(17)
C(14)	0.1155(5)	0.1596(2)	0.1123(3)	0.0173(16)
C(15)	0.1829(5)	0.2193(3)	0.1293(3)	0.0203(17)
C(16)	0.1388(5)	0.2738(3)	0.1708(3)	0.0257(19)
C(17)	0.0253(5)	0.2658(3)	0.1948(3)	0.029(2)
C(18)	−0.0421(5)	0.2060(3)	0.1784(3)	0.027(2)
C(19)	0.0022(5)	0.1520(3)	0.1368(3)	0.0187(17)
C(22)	0.2820(4)	0.0379(2)	−0.1007(3)	0.0130(17)
C(24)	0.2822(4)	−0.0731(3)	−0.0707(3)	0.0140(17)
C(25)	0.3326(4)	−0.0689(3)	−0.1369(3)	0.0187(19)
C(26)	0.3752(5)	−0.1292(3)	−0.1712(3)	0.0237(17)
C(27)	0.3687(5)	−0.1935(3)	−0.1362(3)	0.0230(17)
C(28)	0.3206(4)	−0.1966(3)	−0.0698(3)	0.0203(19)
C(29)	0.2754(4)	−0.1374(2)	−0.0350(3)	0.0167(16)
O(32)	−0.0740(4)	0.4315(2)	0.2714(2)	0.0303(16)
C(31)	0.0435(5)	0.4475(3)	0.2910(3)	0.047(3)

[a] *U*(eq) = $^1/_3$ of the trace of the orthogonalized U.

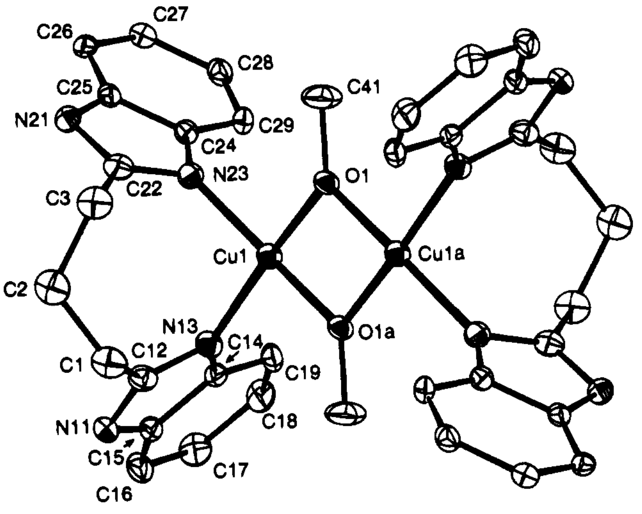

Figure 1. ORTEP 30% probability plot of structure **1** (PLATON) with atom-labeling scheme. H atoms and noncoordinating methanol and perchlorate molecules are omitted for clarity. Atoms marked with an "a" are generated by an inversion center.

Cu(2) is square planar coordinated as in structure **1**. The plane consists of two nitrogens of the ligand (Cu(2)−N(33) 1.985(3) Å, Cu(2)−N(43) 1.963(3) Å) and the oxygens of the two methoxo ligands (Cu(2)−O(1) 1.889(2) Å, Cu(2)−O(2) 1.889(2) Å). The angles in the square plane deviate about 10° similar to structure **1** (O(1)−Cu(2)−N(33) 175.30(10)°, O(2)−Cu(2)−N(43) 169.22(12)°).

An oxygen atom of the second, noncoordinating nitrate ion is at a very long contact distance (Cu(2)−O(12) 3.736(3) Å).

Table 5. Relevant Bond Distances (Å) and Bond Angles (deg) for Structure $[Cu_2(tbz)_2(CH_3O)_2](ClO_4)_2(CH_3OH)_2$ (**1**)[a]

Cu(1)−O(1)	1.901(3)	Cu(1)−Cu(1)a	2.9827(6)
Cu(1)−O(1)a	1.913(3)	Cu(1)−N(13)	1.955(3)
O(1)−C(41)	1.405(6)	Cu(1)−N(23)	1.973(3)
O(1)−Cu(1)−N(13)	170.04(12)	Cu(1)a−Cu(1)−N(23)	134.58(9)
O(1)−Cu(1)−N(23)	96.39(13)	Cu(1)a−Cu(1)−O(1)	38.70(8)
O(1)−Cu(1)−O(1)a	77.11(12)	N(13)−Cu(1)−N(23)	89.79(13)
Cu(1)a−Cu(1)−N(13)	133.67(8)	O(1)a−Cu(1)−N(13)	95.61(12)
O(1)a−Cu(1)−N(23)	169.62(13)	Cu(1)a−Cu(1)−O(1)a	38.41(9)
Cu(1)−O(1)−C(41)	127.7(3)	Cu(1)−O(1)−Cu(1)a	102.89(14)
Cu(1)a−O(1)−C(41)	129.2(3)	Cu(1)−N(13)−C(12)	123.1(3)
Cu(1)−N(13)−C(14)	130.3(3)	Cu(1)−N(23)−C(22)	120.0(3)
Cu(1)−N(23)−C(24)	132.4(3)		

[a] Atoms marked with an "a" are generated by an inversion center.

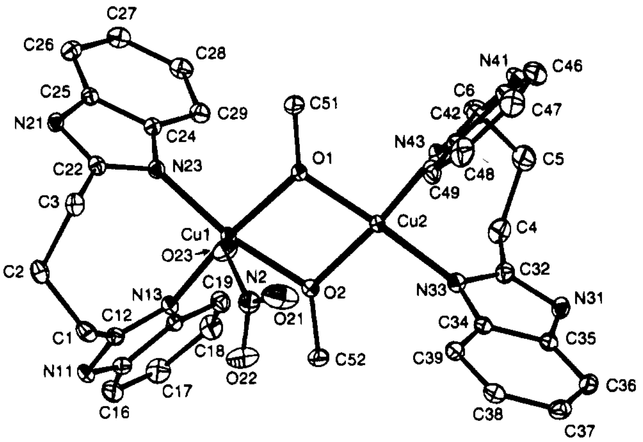

Figure 2. ORTEP 30% probability plot of structure **5** with atom-labeling scheme. H atoms and noncoordinating methanol and nitrate molecules are omitted for clarity.

Table 6. Relevant Bond Distances (Å) and Bond Angles (deg) for Structure $[Cu_2(tbz)_2(NO_3)(CH_3O)_2](NO_3)(CH_3OH)_2$ (**5**)

Cu(1)-Cu(2)	3.0072(4)	Cu(1)-O(1)	1.928(2)
Cu(1)-O(2)	1.952(2)	Cu(1)-O(23)	2.460(2)
Cu(1)-N(13)	1.960(3)	Cu(1)-N(23)	1.973(3)
Cu(2)-O(1)	1.889(2)	Cu(2)-O(2)	1.889(2)
Cu(2)-N(33)	1.985(3)	Cu(2)-N(43)	1.963(3)
O(1)-Cu(1)-O(2)	75.28(9)	Cu(1)-O(2)-C(52)	129.1(2)
O(1)-Cu(1)-O(23)	85.72(8)	Cu(2)-O(2)-C(52)	127.8(2)
O(1)-Cu(1)-N(13)	164.95(9)	Cu(1)-O(23)-N(2)	119.72(18)
O(1)-Cu(1)-N(23)	96.32(11)	Cu(1)-O(2)-Cu(2)	103.06(9)
O(2)-Cu(1)-O(23)	92.99(9)	O(1)-Cu(2)-O(2)	77.68(9)
O(2)-Cu(1)-N(13)	95.40(10)	O(1)-Cu(2)-N(33)	175.30(10)
O(2)-Cu(1)-N(23)	165.73(9)	O(1)-Cu(2)-N(43)	95.31(10)
O(23)-Cu(1)-N(13)	106.84(9)	O(2)-Cu(2)-N(33)	98.40(11)
O(23)-Cu(1)-N(23)	97.91(9)	Cu(1)-O(1)-Cu(2)	103.97(9)
N(13)-Cu(1)-N(23)	90.23(11)	O(2)-Cu(2)-N(43)	169.22(12)
Cu(1)-O(1)-C(51)	128.7(2)	N(33)-Cu(2)-N(43)	88.94(11)
Cu(2)-O(1)-C(51)	127.1(2)		

The Cu(2)−L distances are all significantly shorter than the Cu(1)−L(equatorial) distances in agreement with the square planar geometry.

The Cu−Cu distance within the dinuclear unit is 3.0072(4) Å, and the angles of the Cu−O-Cu bridge are 103.97(9)° [for Cu(1)−O(1)−Cu(2)] and 103.06(9)° [for Cu(1)−O(2)−Cu(2)]. These distances and angles differ only slightly from those found in structure **1**. Unlike structure **1**, there is some torsion in the Cu_2O_2 plane (Cu(1)−O(1)−Cu(2)−O(2)) (torsion angle 1.04(10°)).

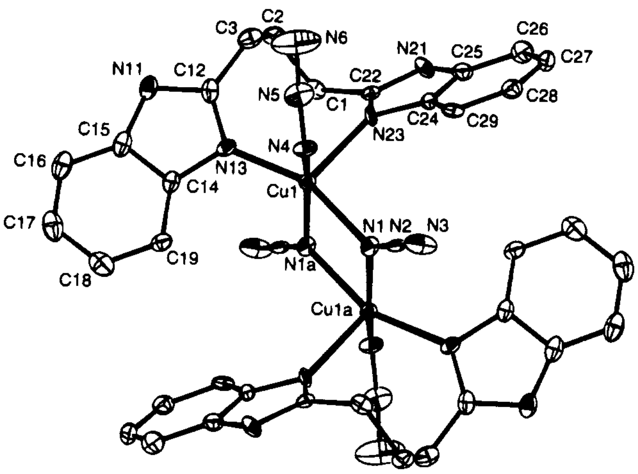

Figure 3. ORTEP 30% drawing probability plot of structure **13** with atom-labeling scheme. H atoms and noncoordinating methanol molecules are omitted for clarity. Atoms marked with an "a" are generated by an inversion center.

Table 7. Relevant Bond Distances (Å) and Bond Angles (deg) for Structure $[Cu(tbz)(N_3)_2]_2(CH_3OH)_2$ (**13**)

Cu(1)−N(1)	2.059(4)	N(1)−N(2)	1.202(5)
Cu(1)−N(4)	1.973(4)	N(2)−N(3)	1.147(6)
Cu(1)−N(13)	1.995(4)	N(4)−N(5)	1.184(6)
Cu(1)−N(23)	2.177(4)	N(5)−N(6)	1.160(7)
Cu(1)−N(1)a	2.037(4)	Cu(1)−(Cu(1)a	3.2422(9)
N(1)−Cu(1)−N(4)	89.46(16)	N(1)a−Cu(1)−N(13)	93.37(16)
N(1)−Cu(1)−N(13)	157.07(16)	N(1)a−Cu(1)−N(23)	99.66(15)
N(1)−Cu(1)−N(23)	98.81(15)	Cu(1)−N(1)−N(2)	124.6(3)
N(1)−Cu(1)−N(1)a	75.34(15)	Cu(1)−N(1)−Cu(1)a	104.66(17)
N(4)−Cu(1)−N(13)	94.68(16)	Cu(1)a−N(1)−N(2)	130.6(3)
N(4)−Cu(1)−N(23)	98.97(16)	N(1)−N(2)−N(3)	178.6(5)
N(1)a−Cu(1)−N(4)	157.52(17)	Cu(1)−N(4)−N(5)	118.0(4)
N(13)−Cu(1)−N(23)	102.79(16)	N(4)−N(5)−N(6)	176.6(7)

[a] Atoms marked with an "a" are generated by an inversion center.

As in structure **1**, the eight-membered chelate ring has a boat−chair conformation in which the Cu atom has the largest deviation (0.8222(11) and 0.9240(12) Å) from the least squares plane (total puckering amplitude Q_t = 1.234(3) and 1.351(3) Å).

The lattice structure is stabilized by stacking between the benzimidazole groups of different units (ring−ring distances of 3.841 Å) and by a hydrogen bonding network with N···O contacts of 2.758(4)−3.144(4) Å and O···O contacts of 2.772(4)−3.172(4) Å. Details on the H-bond network are listed in Table S12 of the supporting information.

Crystal Structure of $[Cu(tbz)(N_3)_2]_2(CH_3OH)_2$ (13). The structure of the dinuclear unit is depicted in Figure 3, with relevant bond length and bond angle information given in Table 7. The unit cell contains four dinuclear copper(II) units, sixteen azido moieties, and eight methanol molecules. The dinuclear units consist of a centrosymmetric pair of copper ions bridged by μ-(1,1)-azido anions. The ligand tbz acts as a didentate ligand with N(13) and N(23) as coordinating atoms like in the structures **1** and **5**. The coordination geometry around Cu can be best described as distorted square pyramidal (N(1)−Cu(1)−N(13) 157.07(16) Å and N(1)a−Cu(1)−N(4) 157.52(17) Å), with N(23) in the apical position (Cu(1)−N(23) 2.177(4) Å),

The Cu−Cu distance in the dinuclear unit is 3.2422(9) Å, i.e. considerably longer than in structures **1** and **5** (2.9827(6) and 3.0072(4) Å). Earlier reports in the literature for dinuclear copper(II) compounds with the same type of azido bonding show Cu−Cu distances varying from 3.120[21] to 3.391 Å.[22] Both

---

(21) Mautner, F. A.; Goher, M. A. S. *Polyhedron* **1993**, *12*, 2823.

(22) Matsumoto, K.; Ooi, S.; Nakatsuka, K.; Mori, W.; Suzuki, S.; Nakahara, A.; Nakao, Y. *J. Chem. Soc., Dalton Trans.* **1985**, 2095.

Table 8. UV–vis/EPR Values[a] for Alkoxo- and Azido-Bridged Cu(II) Dimers

no.	compd	UV–vis (10^3 cm^{-1})	EPR values $g_\perp$, $g_\parallel$, $A_\parallel$ (mT)
1	$[Cu_2(tbz)_2(CH_3O)_2](ClO_4)_2(CH_3OH)_2$[c]	18.4, 28.0	2.05, 2.29, 16.3[b]
2	$[Cu_2(tbz)_2(CH_3O)_2](ClO_4)_2(CH_3OD)_2$	18.0, 27.8	2.06, 2.30, 15.1[b]
3	$[Cu_2(tbz)_2(CD_3O)_2](ClO_4)_2(CD_3OD)_2$	17.9, 27.6	2.06, 2.29,15.7[b]
4	$[Cu_2(tbz)_2(C_2H_5O)_2](ClO_4)_2(C_2H_5OH)_2$[d]	17.9, 27.5	2.05, 2.29, 16.1[b]
5	$[Cu_2(tbz)_2(NO_3)(CH_3O)_2](NO_3)(CH_3OH)_2$[c]	17.9, 27.7	2.07, 2.30, 14.3/15.2[b]
6	$[Cu_2(tbz)_2(NO_3)(C_2H_5O)_2](NO_3)(C_2H_5OH)_2$	17.9, 27.3	2.08, 2.30, 14.6/17.8[b]
7	$[Cu_2(tbz)_2(CH_3O)_2](BF_4)_2(CH_3OH)_2$	18.2, 28.2	2.07, 2.30, 14.3[b]
8	$[Cu_2(tbz)_2(C_2H_5O)_2](BF_4)_2(C_2H_5OH)_2$	18.3, 27.7	2.05, 2.30, 16.4[b]
9	$[Cu_2(qbz)_2(CH_3O)_2](CF_3SO_3)_2(CH_3OH)_2$	16.3, 18.9, 27.8	2.06[b,e]
10	$[Cu_2(qbz)_2(C_2H_5O)_2](CF_3SO_3)_2(C_2H_3OH)_2$	17.7, 27.5	2.05, 2.30, 15.6[b]
11	$[Cu_2(qbz)_2(CH_3O)_2](ClO_4)_2(CH_3OH)_2$	17.5, 28.1	2.06, 2.27, 16.2[b]
12	$[Cu_2(qbz)_2(C_2H_5O)_2](ClO_4)_2(C_2H_5OH)_2$	17.7, 27.4	2.05, 2.30, 16.6[b]
13	$[Cu(tbz)(N_3)_2]_2(CH_3OH)_2$[c]	12.3, 23.6 (19.6) sh	2.14 (vbr)

[a] Abbreviations: vbr = very broad signal, sh = shoulder. [b] These are the results of the monomeric impurities in the spectra (see text). [c] X-ray structure determination done in this work. [d] X-ray structure determination done by ref 6. [e] Signal was too weak to detect the $g_\parallel$ and $A_\parallel$.

terminal and bridging azido to Cu distances are consistent with values found in the literature.[21,23]

The angle of the Cu(1)–N(1)–Cu(1)a bridge is 104.66(17)°; this angle is the largest one, reported for square pyramidal Cu(II) compounds with this type of azido bonding. So far the largest value of 103.7° was reported by Pickardt.[24]

Contrary to structures **1** and **5** the eight-membered chelate ring has in this case a distorted irregular boat-shaped conformation. The propane-ring C atoms (C(3) and C(1)) have the largest deviation (0.769(6) and −0.786(6) Å) from the least squares plane through all atoms (total puckering amplitude Q_t = 1.408(5) Å).

The lattice structure is further stabilized by a hydrogen bonding network with N(ligand)···N(azido) contacts of 2.978(6) Å, N(ligand)···O contacts of 2.779(6) Å, and O···N(azido) contacts of 2.782(6) Å. Unlike structures 1 and **5** there is no stacking between the benzimidazole moieties. Details of the H-bond network are listed in Table S16 of the supporting information.

Ligand Field Spectroscopy. Given the interesting geometries for Cu(II), it was decided to study the ligand field spectra of the solid copper compounds, to compare them with those of known compounds for which X-ray studies were performed. The observed ligand field maxima obtained from diffuse reflectance spectra are tabulated in Table 8, together with some EPR data.

All the methoxo- and ethoxo-bridged dimers (compounds **1**–**12**) have bands at (17.5–18.4) × 10^3 cm^{-1}, which are normal ligand field transitions for a CuN_2O_2 or a CuN_2O_2X' chromophore.[25] In addition a second strong and sharp band is found for all these compounds at (27.5–28.2) × 10^3 cm^{-1}, which is characteristic for dinuclear copper(II) compounds with a square planar $Cu_2O_2N_4$ chromophore, and has been assigned to an O → Cu charge transfer band.[19a,26]

The compound with the bridging azido (compound **13**) exhibits a band at 12.3 × 10^3 cm^{-1}, which is a typical ligand field transition band for square-pyramidal geometry with a short axial ligand distance.[25] The additional band at 23.6 × $10^3$$cm^{-1}$, with a shoulder at 19.6 × 10^3 cm^{-1}, is consistent with observations made earlier[21,27] for dinuclear copper(II) azido compounds with square-pyramidal or distorted square-pyramidal geometry. The band at 23.6 × 10^3 cm^{-1} has been attributed to the Cu–μ-(1,1)-azido charge transfer band.[27c]

Infrared Spectroscopy. In the mid-infrared region the nitrate vibrations (compound **5**) are found at 1400 and 1344 cm^{-1} which indicates monodentate nitrate.[28] For the azido compound (compound **12**) the characteristic asymmetric N_3 stretching vibrations are found at 2075, 2067, 2051, and 2032, (sh) cm^{-1}; these are consistent with the vibrations found in the literature.[28,29] The vibrations at higher frequency (2075, 2067 cm^{-1}) can be assigned to the μ-(1,1)-azido-bridging mode, while the lower frequency bands (2051, 2032 cm^{-1}) can be assigned to the terminal azide mode.[27c]

The far-infrared spectra of the present compounds, especially regarding the Cu–O vibrations, are of particular interest. The spectrum of benzimidazole itself is well characterized with only some torsion vibrations of benzimidazole present in the far-infrared region.[30] So far for planar Cu–alkoxo bridged compounds Cu–O vibrations are reported at 270 cm^{-1}, at 352 cm^{-1} (methoxo-bridged),[19d] and at 324 cm^{-1} (ethoxo-bridged) compounds.[31]

Examination of the far-infrared spectra of the present compounds revealed six metal-dependent vibrations, which are listed in Table 9. From this table we can assign the Cu–O vibrations at around 457 and 330 cm^{-1} for the ethoxo-bridged compounds and at around 390 and 232 cm^{-1} for the methoxo-bridged compounds. These shifts in the Cu–O absorptions, which are the most prominent and broadest bands,[32] are independent of the anion.

The other vibrations, at approximately 440, 356, 285, and 206 cm^{-1}, can be assigned to Cu–N stretching and/or metal–ligand deformation modes.[31,33]

The difference in the Cu–N values with the ligand tbz (compounds **1**–**8**) and the ligand qbz (compounds **9**–**12**) is attributed to a change in geometry, due to the longer carbon chain between the benzimidazole moieties.

The bands at 230 and 330 cm^{-1} are diagnostic for the Cu–O vibrations of the methoxo- and ethoxo-bridged compounds,

---

(23) Goher, M. A. S.; Mautner, F. A. *Z. Naturforsch.* **1991**, *46b*, 687.

(24) Pickardt, J. *Z. Naturforsch.* **1982**, *37b*, 110.

(25) Hathaway, B. J. *Struct. Bonding* **1984**, *57*, 56.

(26) Kida, S.; Nishida, Y.; Sakamoto, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2428.

(27) (a) Goher, M. A. S.; Mak, T. C. W. *Inorg. Chim. Acta* **1984**, *85*, 117. (b) Mak, T. C. W.; Goher, M. A. S. *Inorg. Chim. Acta* **1986**, *115*, 17. (c) Pate, J. E.; Ross, P. K.; Thamann, T. J.; Reed, C. A.; Karlin, K. D.; Sorrell, T. N.; Solomon E. I. *J. Am. Chem. Soc.* **1989**, *111*, 5198.

(28) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986.

(29) Goher, M. A. S.; Mak, T. C. W. *Inorg. Chim. Acta* **1985**, *99*, 223.

(30) (a) Cordes, M. M.; Walter, J. L. *Spectrochim. Acta* **1968**, *24A*, 1421. (b) Drolet, D. P.; Manuta, D. M.; Lees, A. J.; Katnani, A. D.; Coyle, G. J. *Inorg. Chim. Acta* **1988**, *146*, 173.

(31) Ghomashchi, E. *Spectrosc. Lett.* **1994**, *27*, 829.

(32) Ferraro, J. R. *Low Frequency vibrations of Inorganic and Coordination Compounds*; Plenum Press: New York, 1971.

(33) Ferraro, J. R.; Walker, W. R. *Inorg. Chem.* **1965**, *4*, 1382.

Table 9. Far-Infrared Vibrations (cm^{-1})[a] for the Alkoxo-Bridged Cu(II) Compounds

no.	compd	vibrations							
1	$[Cu_2(tbz)_2(CH_3O)_2](ClO_4)_2(CH_3OH)_2$[b]		439, m	390, s, br	351, m		290, m	229, s	207, m
2	$[Cu_2(tbz)_2(CH_3O)_2](ClO_4)_2(CH_3OD)_2$		439, m	387, s, br	354, m		283, s	230, s	205, m
3	$[Cu_2(tbz)_2(CD_3O)_2](ClO_4)_2(CD_3OD)_2$		441, m	385, vs, br	352, s		283, s	229, s	205, m
4	$[Cu_2(tbz)_2(C_2H_5O)_2](ClO_4)_2(C_2H_5OH)_2$[c]	457, s, br	440, s		354, m	329, s, br	285, s		205, m
5	$Cu_2(tbz)_2(NO_3)(CH_3O)_2](NO_3)(CH)$[b]		443, s	386, vs, br	357, s		286, s	231, s	208, m
6	$[Cu_2(tbz)_2(NO_3)(C_2H_5O)_2](NO_3)(C_2H_5OH)_2$	460, s, br	440, s		356, m	330, s, br	285, s		206, m
7	$[Cu_2(tbz)_2(CH_3O)_2](BF_4)_2(CH_3OH)_2$		441, m	390, vs, br	357, s		285, s	231, s	206, m
8	$[Cu_2(tbz)_2(C_2H_5O)_2](BF_4)_2(C_2H_5OH)_2$	454, m, br	441, s		355, s	332, s, br	285, s		207, m
9	$[Cu_2(qbz)_2(CH_3O)_2](CF_3SO_3)_2(CH_3OH)_2$		443, m	395, m	365, m, sh		288, m	235, m	212, m
10	$[Cu_2(qbz)_2(C_2H_5O)_2](CF_3SO_3)_2(C_2H_3OH)_2$	454, s, br[d]	447, m, sh		359, m	328, s, br	260, w		218, s
11	$[Cu_2(qbz)_2(CH_3O)_2](ClO_4)_2(CH_3OH)_2$		437, s	387, s, br	360, s		270, s	235, s	170, s
12	$[Cu_2(qbz)_2(C_2H_5O)_2](ClO_4)_2(C_2H_5OH)_2$	454, s, br[d]	447, m, sh		360, m	331, vs, br	279, w		208, s

[a] Abbreviations: vs = very strong, s = strong, m = medium, br = broad, sh = shoulder. [b] X-ray structure determination done in this work. [c] X-ray structure determination done by ref 6. [d] Triplet of which the peak at 447 cm^{-1} is one of them.

respectively, as in this spectral range no other absorptions are located. Further support has been obtained from the compounds $[Cu_2(mtbz)_2(RO)_2](CF_3SO_3)_2(ROH)_2$ (mtbz = bis(1-methyl-2-benzimidazolyl)propane, and R = CH_3, C_2H_5) in which the Cu−O vibrations have been assigned at 388 and 229 cm^{-1} for methoxo compounds and 454 and 332 cm^{-1} for ethoxo compounds.[34]

Magnetic Measurements. As early as 1980 Merz and Haase[35] reported about a linear relationship between the exchange parameter $2J$ and the Cu−O-Cu angle of alkoxo-bridged copper(II) dimers. The magnetic susceptibility measurements of the present alkoxo-bridged compounds (compounds **1**−**11**) shows a diamagnetic behavior below room temperature (above ca. 360 K the compounds decompose). In general the alkoxo-bridged copper(II) dimers show an antiferromagnetic behavior.[19a,20,36] According to the above-mentioned relationship the exchange parameter $2J$ would be expected < -600 cm^{-1}.[35]

All our alkoxo-bridged compounds are EPR silent and show no triplet spectrum; in fact in many cases a weak but clearly resolved signal of a monomeric impurity, always present on the edges of crystals, is observed (see Table 8). Such a diamagnetic and EPR-silent behavior is also found in the literature.[19a,36c]

The monomeric impurities, which are present <0.01%,[37] have a $g_\perp$ value of about 2.05 and a $g_\parallel$ of about 2.30, with $A_\parallel$ values around 15.0−16.0 mT. The presence of a nitrogen superhyperfine structure for some cases in fact agrees with a CuN_2O_2 chromophore for this species.[38]

The variable magnetic susceptibility measurements of the azido compound (compound **12**) suggest that the copper(II) ions are coupled in a ferromagnetic manner (Weiss constant $\Theta = +15$ K). The maximum in the magnetic susceptibility data occurs at about 22 K, and least-squares fitting with a Bleaney−Bowers equation[39] of the data gives $J = 23$ cm^{-1}. Literature values of J for bis-μ-(1,1)-azido-bridging copper(II) compounds vary from 20 to 105 cm^{-1}.[40,41]

The ferromagnetic behavior is consistent with the spin polarization effect developed by Kahn and co-workers.[42] Such a ferromagnetic behavior has also been found for Mn and Ni complexes with the same type of bis-μ-(1,1)-azido bridges.[43]

The room-temperature EPR signal of this azido compound shows a weak and very broad isotropic signal with a g value of 2.14, with no further splitting, a phenomenon not uncommon for this type of azido-bridged copper(II) dimers.[40,44] EPR spectra from a frozen solution at 77 K could not be obtained, as the compound decomposes in the solvents in which it dissolves (e.g. dimethyl sulfoxide).

Concluding Remarks

The results discussed above have shown that with the ligand tbz and qbz in the presence of weakly coordinating anions in alcoholic solution copper(II) alkoxy dimers are formed. It appears that the ligands are basic enough to dehydronate the alcohol. When stronger coordinating anions are used, like chlorides, only monomeric species are obtained,[45] whereas with the azido anion bis-μ-(1,1)- bridging dimers are formed.

The spectroscopic and magnetic properties of our compounds agree with theoretical expectations. In the far-infrared region two prominent Cu−O bands have been observed with a large difference in energy, for the methoxo and the ethoxo bridge. The origin and understanding of the difference of 100 cm^{-1} between the Cu−O vibrations of the methoxo- and ethoxo-bridged species is not clear yet, as the bridging angle is known

---

(34) van Albada, G. A.; Sànchez Sànchez, M.; Reedijk, J.; Lakin M. T.; Spek, A. L. To be published.

(35) Merz, L.; Haase, W. *J. Chem. Soc., Dalton Trans.* **1980**, 875.

(36) (a) Olejnik, Z.; Grobelny, R.; Jezowska-Trzebiatowsak, B. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1976**, *24*, 883. (b) Willett, R. D.; Breneman, G. L. *Inorg. Chem.* **1983**, *22*, 326. (c) Drew, M. G. B.; Yates, P. C. *J. Chem. Soc., Dalton Trans.* **1988**, 2995. (d) Fukuhara, C.; Tsuneyoshi,K.; Katsura, K.; Matsumoto, N.; Kida, S.; Mori, M. *Bull. Chem. Soc. Jpn* **1989**, *62*, 3939.

(37) This figure is obtained by integration of a weighted sample in comparison with a weighted sample of the monomeric $CuCl_2(tbz)_2$ compound (analyses: see Table S1 of the supporting information).

(38) (a) Uma, R; Palaniandavar, M. *Transition Met. Chem.* **1993**, *18*, 629. (b) Chautemps, P.; Gellon, G.; Morin, B.; Pierre, J.; Provent, C.; Refaif, S.; Beguin, C.; Marzouki, A.; Serratrice, G.; Saint-Aman, E. *Bull. Soc. Chim. Fr.* **1994**, *131*, 434.

(39) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London Ser. A* **1952**, *214*, 451.

(40) Cortés, R.; Lezama, L.; Larramendi, J. I. R.; Insausti, M.; Folgado, J. V.; Madariaga, G.; Rojo, T. *J. Chem. Soc., Dalton Trans.* **1994**, 2573.

(41) Sikorav, S.; Bkouche-Waksman, I.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 490.

(42) (a) Kahn, O. *Inorg. Chim. Acta* **1982**, *62*, 3. (b) Kahn, O.; Sikorav, S.; Gouteron, J.; Jeannin, S. *Inorg. Chem.* **1983**, *22*, 2877. (c) Charlot, M.; Kahn, O.; Chaillet, M.; Larrieu, C. *J. Am. Chem. Soc.* **1986**, *108*, 2574.

(43) (a) Cortés, R.; Pizarro, J. L.; Lezama, L.; Arriortua, M. I.; Rojo, T. *Inorg. Chem.* **1994**, *33*, 2697. (b) Arriortua, M. I.; Cortés, A. R.; Lezam, L.; Rojo, T.; Solans, X.; Font-Bardia, M. *Inorg. Chim. Acta* **1990**, *174*, 263. (c) Cortés, R.; Ruiz de Larramendi, J. I.; Lezama, L.; Rojo, T.; Urtiaga, K.; Arriortua, M. I. *J. Chem. Soc., Dalton Trans.* **1992**, 2723. (d) Vicente, R.; Escuer, A.; Ribas, J.; Salah el Fallah, M.; Solans, X.; Font-Bardia, M. *Inorg. Chem.* **1993**, *32*, 1920.

(44) Comarmond, J.; Plumeré, P.; Lehn, J. M.; Agnus, Y.; Louis, R.; Weiss, R.; Kahn, O.; Morgenstein-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 6330.

(45) Baldwin, M. J.; Root, D. E.; Pate, J. E.; Fujisawa, K.; Kitajima, N.; Solomon, E. I. *J. Am. Chem. Soc.* **1992**, *114*, 10421.

(46) van Albada, G. A.; Unpublished observations.

to be of great influence in the frequency schift of Cu−O vibrations;[45] however, this cannot be the only reason in this case as the ethoxo-bridged dimer (compound **4**) has a Cu−O-Cu angle of 102.4(3)° [6] and the methoxo bridged compounds have angles vary from 102.89(14)−103.97(9)° (compounds **1** and **5**) to 100.9(3)−102.1(3),° [34] so also the mass of the group attached to the bridging O must play an important role; therefore further analysis, e.g. ^{18}O substitution would be required for a complete understanding. This is left for future investigation. The magnetic measurements of the azido dimer confirm the spin polarization effect.[42]

Formation of the dinuclear species is related clearly to the flexibility of the ligand, as with the ligand with a shorter chain between the two benzimidazole moieties (bis(2-benzimidazolyl)-ethane) only monomeric species are formed.[45] The crystal packing of the alkoxo-bridged compounds is determined by hydrogen contacts and stacking interactions of the benzimidazole moieties and only by hydrogen contacts in the case of the azido-bridged compound.

Acknowledgment. This work was supported in part (A.L.S. and N.V.) by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO) and by the award of a postdoctoral fellowship under the EC Human Capital and Mobility Initiative (M.T.L.). Mr. J. Kolnaar is acknowledged for the magnetic susceptibility measurements, and we wish to thank Dr. J. G. Haasnoot for his discussions about the far-infrared spectra. Prof. A. F. Williams (Geneva) is thanked for communications, unpublished results, and useful discussions. The work described in the present paper has been supported by the Leiden University Study group WFMO (Werkgroep Fundamenteel Materialen Onderzoek). Financial support by the European Union, allowing regular exchange of preliminary results with several European colleagues, under contract ERBCHRXCT920080 is thankfully acknowledged. Use of the services and facilities of the Dutch National NWO/SURF Expertise Center CAOS/CAMM, under Grant Nos. SON 326-052 and STW NCH99.1751, is gratefully acknowledged.

Supporting Information Available: Tables giving further details of the structure determination, including atomic coordinates and *U* values for the hydrogen atoms, bond lengths and angles, and thermal parameters of all non-hydrogen atoms for structures **1**, **5**, and **13**, and a table giving the elemental analyses (Tables S1−S16) (13 pages). Ordering information is given on any current masthead page.

IC9503141