Copper Coordination Polymers with Infinite Chloride Ion Channels and Different Directions of the Jahn-Teller Distortion, Built from Tris(1,2,4-triazolyl)borate as a Modified Tris(pyrazolyl)borate Ligand☆

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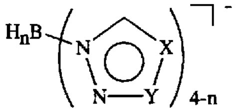
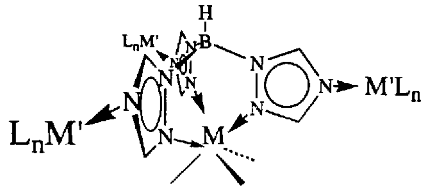
$[Co\{HB(C_2H_2N_3)_3\}_2]$ reacts with an excess of $CuCl_2$ in hot water with formation of ${}^2_\infty[Cu_2Cl_2\{\mu_3\text{-}HB(C_2H_2N_3)_3\}_2 \cdot 2\,H_2O]$ (**7**) or ${}^3_\infty\{[Cu_2\{\mu_4\text{-}HB(C_2H_2N_3)_3\}(\mu\text{-}OH)_2]Cl \cdot 6\,H_2O\}$ (**8**), depending on the reaction time. **8** can also be obtained from $[Cu\{HB(C_2H_2N_3)_3\}_2]$ and $CuCl_2$ in aqueous ammonia. The 2-D double-layer-type coordination polymer **7** crystallizes in the orthorhombic space group $P2_12_12_1$. The two different Cu(II) centers in the lattice are distinguished only be the direction of the Jahn-Teller distortion. The following corresponding distances for the $CuClN_5$ coordination sphere were found Cu1/Cu2–Cl = 2.572(2)/2.328(2), Cu1/Cu2–N = 2.585(5)/2.077(4); 2.000(4)/1.979(5); 2.100(5)/2.734(5); 2.005(4)/1.994(4); 2.024(5)/2.369(5). In the 3-D coordination polymer **8** one of the two different Cu centers is chelated by the three endodentate nitrogen donors, while the other Cu center is coordinated by three exodentate nitrogen atoms. The coordination sphere is completed in both cases by two hydroxo bridges to symmetry-related Cu centers. The metal-ligand connectivity creates infinite channels with helical walls which contain the solvated chloride anions.

The results presented here are part of an investigation of the rational assembly of coordination polymers and polynuclear metal complexes containing modifications of the popular poly(*pyrazolyl*)borate ligands (**1**)[1], such as hydrotris- and dihydrobis(*1,2,4-triazolyl*)borate (**2**, **3**)[2–4] or dihydrobis(tetrazolyl)borate (**4**)[3–5]. The additional donor atoms in **2**–**4** extend the molecular coordination "chemistry" of **1** to the dimension of the solid state by the bridging action of the ligand and/or by the formation of hydrogen bonds with water of crystallization as an important element of the crystal architecture. Depending on the metal, the poly(triazolyl)borate ligands **2** and **3** were found to be able to function either as chelate ligands or as bridges between metal centers[2,4]. We demonstrate here that five or even all six nitrogen donor atoms of the hydrotris(trialzolyl)borate ligand **2** can engage in metal coordination to give a polynuclear complex, schematically shown in **5**, as part of a two- or three-dimensional framework, with additional interesting features. The crystal engineering of materials composed of inifinite two- and three-dimensional frameworks is an area of intense research[6].

When the labile homoleptic cobalt chelate complex **6**[2a,3] is treated with $CuCl_2$ in water a ligand exchange takes place to give cobalt-free copper compounds of **2** as products. The exact nature of the product depends on the reaction and work-up conditions as outlined in Scheme 1. A slow reaction at elevated temperature yields light blue needle-shaped crystals (**7**) with a borate ligand-to-copper-to-chlorine ratio of 1:1:1 directly from the reaction mixture. In contrast, a fast reaction gives a blue precipitate of yet unknown composition (but different from **7**) which was recrystallized from aqueous ammonia to give parallelepipedal deep blue crystals (**8**) with a ligand-to-copper-to-chlorine ratio of 1:2:1. Subsequently, **8** could also be prepared by a ligand comproportionation reaction of the homoleptic tris(triazolyl)borate copper complex (**9**) with $CuCl_2$[6].



Pyrazolyl: X = Y = CH; n = 0, 1, 2 (**1**)
Triazolyl: X = N, Y = CH; n = 1 (**2**)
n = 2 (**3**)
Tetrazolyl: X = Y = N; n = 2 (**4**)



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Compounds **7** and **8** exist as two- and three-dimensional coordination polymers, respectively, with two different copper centers each, according to single-crystal X-ray analyses. In **7** the $CuClN_5$ polyhedra of both copper ions are approximately tetragonally elongated octahedra, as expected due to vibronic Jahn-Teller coupling, and the polyhedra are formed by three endodentate and two exodentate nitrogen atoms from the triazolyl rings and a chlorine atom (Figure 1). Two of the triazolyl rings on each borate ligand bridge

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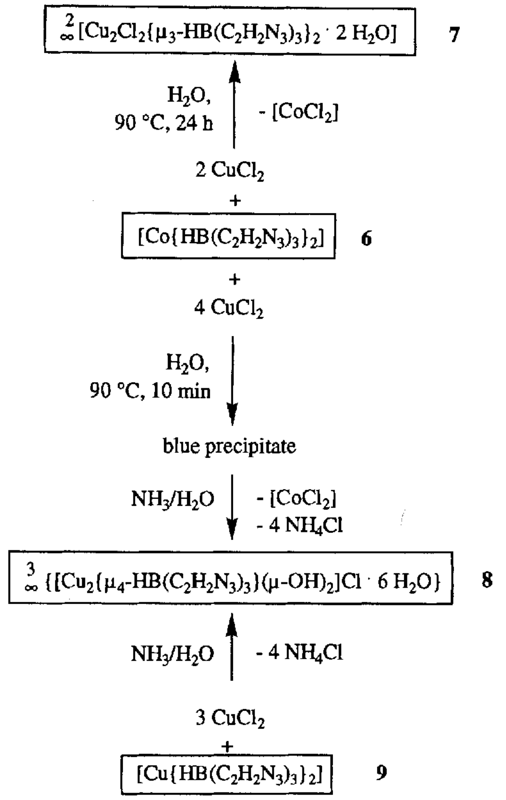
Scheme 1. Synthetic routes to compounds **7** and **8**

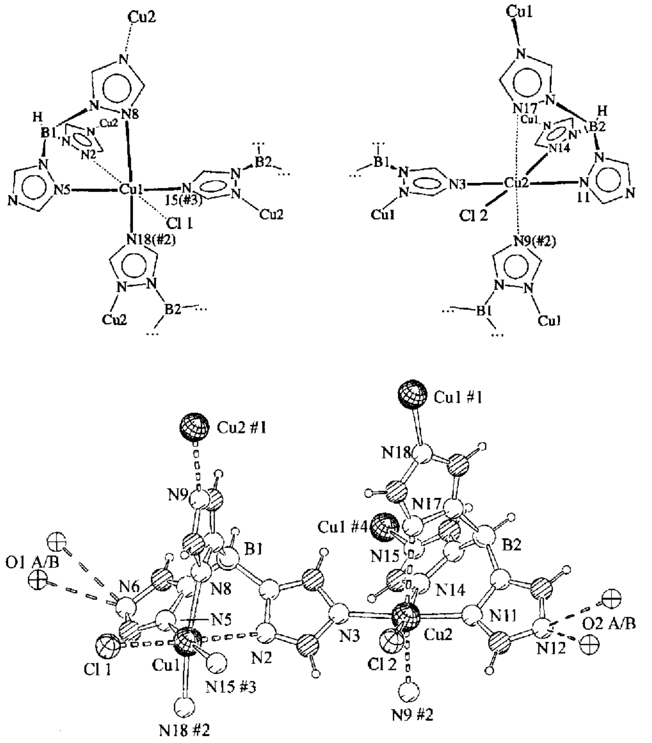


metal centers thereby giving rise to a two-dimensional double-layer network, whose packing is detailed in Figure 2. The donor function of the exodentate nitrogen on the third triazolyl ring is occupied by a disordered solvent water molecule (cf. Figure 1, bottom).

Concerning the type and relative arrangement (*endo*-N *trans* to *exo*-N and Cl etc.) of the coordinating ligands, both copper centers in **7** would behave as image and mirror image (Figure 1) if it were not for a difference in bond lengths: At Cu1 the copper-to-chlorine and the *trans*-lying Cu−N2 bond are longest, whereas at Cu2 the Jahn-Teller distortion of the d^9 ion manifests itself in an elongation of two *trans* Cu−N bonds to N17 and N9(#2). The short Cu−Cl distance is in good agreement with short equatorial contacts of tetragonally elongated $CuCl_6^{4-}$ octahedra[7a]. Initially, a long Cu−Cl bond would be expected in the presence of five nitrogen donor ligands. The Jahn-Teller effect normally leads to an elongation of the bonds towards the spectrochemically weaker ligands. At the same time there are no decisive features, such as O−H···Cl hydrogen bonds, in the "non-bonded" coordination spheres for both chlorine atoms to account for the difference in the Cu−Cl bonds. The Cl···(H-)O contact is rather similar, with 3.25 Å for Cl1 and 3.35 Å for Cl2[7]. The unusual phenomenon where molecules differ only in the length of one or more bonds has been termed bond-stretch isomerism[8]. Also, in the structural chemistry of Cu(II) the potential surface for Cu−X linkages is known to be very soft and much determined by the crystal environment[9]. We are, however, not aware of a distortion isomer of Cu(II) complexes where the direction of the Jahn-Teller distortion is changed to a different bond couple.

As an explanation for the difference in bond lengths we suggest a similar ligand-field strength or comparable σ-bonding capacities towards Cu^{2+} for the chlorine ligand and the nitrogen donors in the bridging triazolyl rings. We ascribe the decrease in ligand-field strength of the nitrogen donors in **7**, compared to those normally seen, to the bridging action and a subsequent decrease or delocalization in electron density. The observation that the non-metal bridging triazolyl rings (coordinated through N5 and N11) show only short Cu−N bonds would support this notion[10].

Figure 1. Top: Schematic representation of the coordination spheres of the two different copper centers. Bottom: Schakal plot[16] of a section of the polymeric network of **7**, showing the unique formula unit. Selected bond lengths [Å] and angles [°]: Cu1−N2 2.585(5), Cu1−N5 2.000(4), Cu1−N8 2.100(5), Cu1−N15(#3) 2.005(4), Cu1−N18(#2) 2.024(5), Cu1−Cl1 2.572(2), Cu2−N3 1.994(4), Cu2−N9(#2) 2.369(5), Cu2−N11 1.979(5), Cu2−N14 2.077(4), Cu2−N17 2.734(5), Cu2−Cl2 2.328(2), *cis*-N−Cu1−N 80.8(2)−92.1(2), *cis*-N−Cu1−Cl1 90.9(1)−97.4(1), N2−Cu1−Cl1 176.7(1), N5−Cu1−N15(#3) 173.6(2), N18(#2)−Cu1−N8 169.3(2), *cis*-N−Cu2−N 76.5(2)−93.9(2), *cis*-N−Cu2−Cl2 89.2(2)−95.4(1), N14−Cu2−Cl2 169.9(2), N11−Cu2−N3 175.4(2), N9(#2)−Cu2−N17 169.9(2). Note that the unique formula unit extends in two directions, vertical and perpendicular to the paper plane to build up a double-layer polymer (cf. Figure 2)



In **8** both copper ions are coordinated by three nitrogen atoms from the triazolyl rings and two hydroxo bridges (Figure 3). The coordination of both CuN_3O_2 polyhedra is approximately an elongated square-pyramid as expected for five-coordinate Cu^{2+} again as a consequence of vibronic Jahn-Teller coupling. The nitrogen coordination sphere around Cu1 is formed by three exodentate donors, while Cu2 is surrounded by three endodentate nitrogen atoms, in each case with two short and one long bond. Thus, the tris(triazolyl)borate ligand utilizes all six nitrogen donors in metal coordination, thereby bridging four copper centers. Each copper atom is further bridged to a symmetry-related copper center by the two hydroxo groups. Overall, the metal-ligand connectivity leads to a three-dimensional array with infinite open channels which contain the solvated chloride anions, as shown in Figure 4. The cross-sectional dimension of these one-dimensional pores is about 4.5 to 5 Å, and the Cl···Cl contact along the chains is 10.56 Å. No chloride ion conductivity could be observed, however. When tracing the borate or hydroxo ligands linking the copper centers that surround

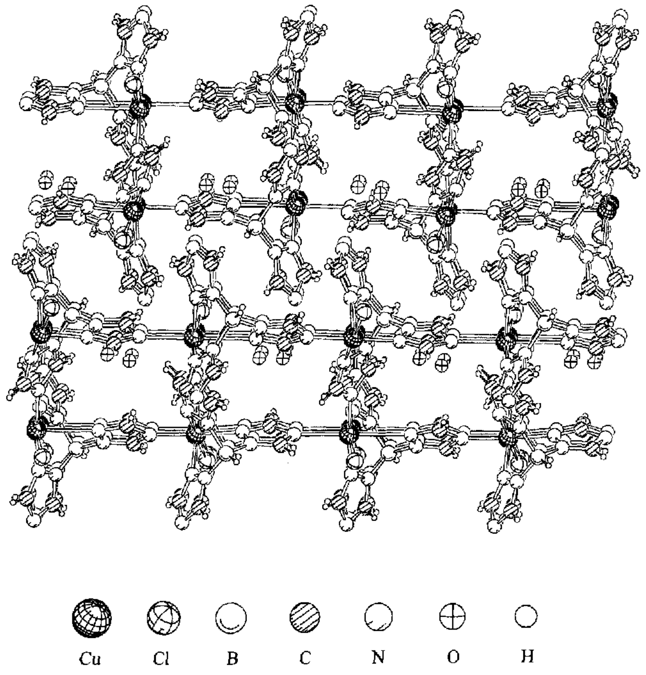


Figure 2. Crystal packing in **7** illustrating the layer-type structure. View along *a* and along the double-layer planes which extend perpendicular to the paper plane (Schakal[16])

the chloride ion channels, these "walls" can be recognized as a helix or spring. Neighboring walls are of opposite helicity. Out of the six water molecules of crystallization four solvate the chloride ions (Cl···O contacts 3.03–3.22 Å)[7] and the remaining two form hydrogen bonds with the hydroxo groups. The small amount of disorder in the water-oxygen centers, together with the notable fact that the crystal phase is stable in air, indicates a rather rigid hydrogen bonding network (cf. ref.[2b,4]).

For **8**, the room-temperature magnetic moment was measured to be $\mu_{\text{eff}} = 1.5\ \mu_B$ per Cu atom which is lower than the value typically observed for magnetically dilute Cu(II) complexes (the spin-only value for Cu^{2+} is 1.73 μ_B). Antiparallel alignment by antiferromagnetic coupling in a through-bond (Cu–OH–Cu or Cu–triazolyl–Cu[11]) interaction can result in a smaller effective magnetic moment which further decreases when the temperature is lowered as can be seen in Figure 5. Because of its two-dimensionality the magnetic properties of **7** would be even more interesting[12], however, they are not as clear, yet, because of small cobalt impurities in the bulk material (see Experimental). A more detailed study of the antiferromagnetic exchange as well as additional spectroscopic investigations will be the subject of future work.

We are currently trying to develop an understanding of the controlling factors in the formation of the coordination polymers with the tris(triazolyl)borate ligand by investigating the possibility of a template effect of the chloride ions in the channel formation. Furthermore, we are elucidating the role of the solid-state network in the chloride enclathration and copper chloride bond-length variation by studying the role of hydrogen bond interactions in these poly(azolyl)borate structures in more detail.

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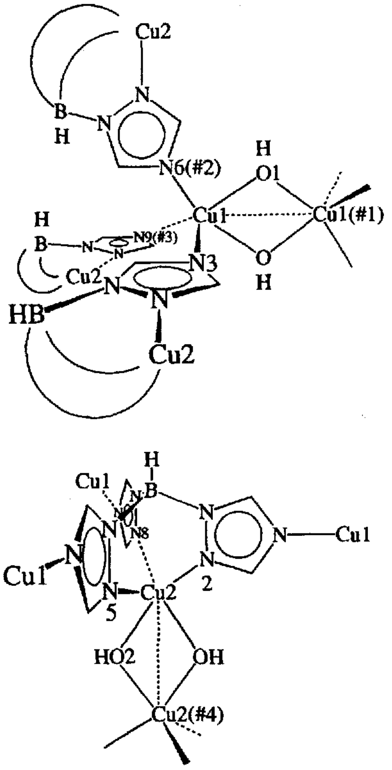


Figure 3. Schematic representation of the coordination spheres of the two different copper centers in **8**. (The position of Cu2 is slightly disordered with about a 10% occupancy for a position having the short Cu–N contacts to N2 and N8 and the long one to N5. This disorder corresponds also to a different direction of the Jahn-Teller distortion.) Selected bond lengths [Å]: Cu1–O1 1.947(5), Cu1–O1(#1) 1.949(5), Cu1–N3 2.002(6), Cu1–N6(#2) 1.996(6), Cu1–N9(#3) 2.297(6), Cu1–Cu1(#1) 2.946(2), Cu2–O2 1.936(5), Cu2–O2(#4) 1.938(6), Cu2–N2 2.452(6), Cu2–N5 2.021(6), Cu2–N8 1.989(6), Cu2–Cu2(#4) 2.878(2)

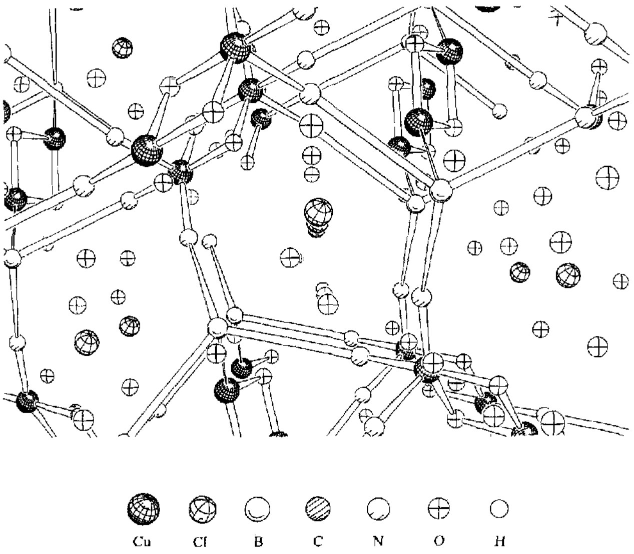
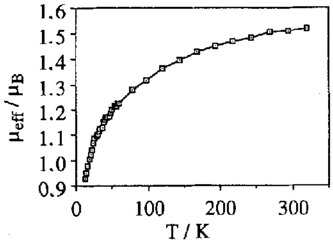


Figure 4. Crystal packing in **8** in a rudimentary view with only the boron, copper, and exodentate nitrogen and oxygen donor atoms left to show the chloride ion channels and to illustrate the helical walls. View along *a* (Schakal[16]). The Cu centers which are tris-chelated by the endodentate nitrogen donors are directly connected to the boron atoms

Figure 5. Temperature variations of the effective magnetic moment μ_{eff} of **8**. From room temperature to 70 K a Faraday balance has been used, from 70 K down to 14 K the magnetic susceptibility has been measured with an AC susceptometer. $\mu_{eff} = 0.798\ \mu_B\ (\chi_{para} T)^{1/2}$ (χ_{para} = paramagnetic molar susceptibility in cm^3/mol; T = temperature in Kelvin)[19]



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Experimental

IR: Nicolet Magna 750 FT-IR. – Susceptibility measurements: Faraday magnetic balance and AC susceptometer Lakeshore Model 7000. – The complexes $[Co\{HB(C_2H_2N_3)_3\}_2]$ (**6**)[2a,3] and $[Cu\{HB(C_2H_2N_3)_3\}_2]$ (**9**)[2a] were prepared as previously described.

$^2_\infty[Cu_2Cl_2\{\mu_3\text{-}HB(C_2H_2N_3)_3\}_2 \cdot 2\ H_2O]$ (**7**)[13]: A slurry of 0.65 g (1.33 mmol) of $[Co\{HB(C_2H_2N_3)_3\}_2]$ (**6**) in 35 ml of water was thermostated to 90°C, overlayered with a hot solution of 0.69 g (4.02 mmol) of $CuCl_2 \cdot 2\ H_2O$ in 15 ml of water and kept at this temp. for 24 h. After this time the light blue microcrystalline precipitate formed was collected. The crystalline character was maintained upon air-drying. Yield: 0.20 g (45%). – IR (KBr): $\tilde{v}$ = 3453 cm^{-1} m, br (O–H), 3135 and 3107 m (C–H), 2512 m (B–H). – $C_{12}H_{18}B_2Cl_2Cu_2N_{18}O_2$ (666.0): calcd. C 21.64, H 2.72, N 37.86; found C 21.85, H 2.75, N 37.54. – AAS and a neutron activation analysis of the bulk material gave a cobalt content of 1.0–1.2% and a copper content of 19.5–20.3% (calcd. 19.1%). An energy-dispersive X-ray analysis showed, however, that the single crystal selected for X-ray diffraction was free of cobalt.

$^3_\infty\{[Cu_2\{\mu_4\text{-}HB(C_2H_2N_3)_3\}(\mu\text{-}OH)_2]Cl \cdot 6\ H_2O\}$ (**8**)[13]. – a) Solid $CuCl_2 \cdot 2\ H_2O$ (0.69 g, 4.02 mmol) was added to a hot solution of 0.65 g (1.33 mmol) of **6** in 50 ml of water. The resulting precipitate was filtered and air-dried to yield 1.24 g of a blue powder. Samples of this powder were dissolved in aqueous ammonia (25%) to afford a deep blue solution. Slow solvent evaporation gave dark blue crystals which were separated from some white or light blue amorphous material.

b) A mixture of 0.20 g (0.40 mmol) of $[Cu\{HB(C_2H_2N_3)_3\}_2]$ (**9**)[2a] and of 0.21 g (1.23 mmol) of $CuCl_2 \cdot 2\ H_2O$ was dissolved in 5 ml of aqueous ammonia (25%) and 1 ml of water to furnish a deep blue solution. Slow solvent evaporation afforded 0.26 g (62%) of dark blue crystals.

The identity of the crystal phase from a) and b) was established by X-ray powder diffractometry. The crystalline character is maintained upon air-drying. – IR (KBr): $\tilde{v}$ = 3420 cm^{-1} vs, br (O–H), 3135 w (C–H), 2530 w (B–H). – $C_6H_{21}BClCu_2N_9O_8$ (520.7): calcd. C 13.84, H 4.07, N 24.21; found C 14.25, H 4.18, N 24.42.

Crystal Structure Analyses: Structure solution was performed by direct methods (SHELXS-86[14]). Refinement: Full-matrix least-squares on F^2 (SHELXS-93[14]); all atomic positions including those of the hydrogen atoms found and refined (non-hydrogen atoms with anisotropic temperature factors). Crystal data are listed in Table 1[15]. The crystal structure of **7** was refined as a racemic twin, upon refinement the twin parameter converged at 0.48(3). The absolute structure was correctly determined since a monoclinic data set had been collected, hence the symmetry equivalents of the antireflections were available for refinement. The space group determination was based on the unequivocal systematic absences *h*00, 0*k*0, and 00*l* = 2*n* + 1; violations were only observed for very weak reflections with $F^2 < 65$. In the structure of **8** the copper atom 2 is partly disordered. The largest difference peak and hole in the structure of **8** were found mostly near the Cu–O bridges.

Table 1. Crystal data for compounds **7** and **8**

Compound	7	8
Formula	$C_{12}H_{18}B_2Cl_2Cu_2N_{18}O_2$	$C_6H_{21}BClCu_2N_9O_8$
Mol. mass [g mol^{-1}]	666.01	520.66
Crystal size [mm]	0.3·0.05·0.05	0.37·0.13·0.13
Temperature [K]	293(2)	293(2)
Diffractometer	Turbo-CAD4 with rotating anode generator	STOE
Radiation; wavelength [Å]	Cu-*K*α; 1.5418	Mo-*K*α; 0.71069
Monochromator	nickel filter	graphite
Scan-type, 2Θ-range	ω, 8-120°	ω, 4-50°
h; *k*; *l* range	-10,10; 0,14; 0,21	0,12; -18,0; -13,13
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$ (Nr. 19)	$P2_1/n$ (Nr. 14)
Unit cell dimensions:		
a [Å]	9.3573(2)	10.562(5)
b [Å]	13.4692(5)	15.66310)
c [Å]	19.4072(8)	11.476(5)
β [°]	90	93.57(4)
V [Å^3]	2446.0(2)	1895(2)
Z	4	4
$D_{calcd.}$ [g cm^{-3}]	1.809	1.825
F(000) [elektrons]	1336	1056
μ[cm^{-1}]	46.3	24.4
Absorption correction:	none	DIFABS [a]
max.; min.	--	1.112; 0.795
Measured reflections	3487	3530
Unique reflections	3230 (R_{int} = 0.028)	3342 (R_{int} = 0.064)
Data for refinement (*n*)	3224	3331
Parameters refined (*p*)	343	283
Δρ [b]: max; min [e Å^{-3}]	0.356; -0.492	0.989; -0.789
R1; *wR2* [c] [$I > 2\sigma(I)$]	0.0360; 0.0869	0.0594; 0.1305
Goodness-of-fit on F^2 [d]	1.084	1.097
Weighting scheme, *w*; *a*; *b* [e]	0.508; 2.0997	0.069; 2.9729
Flack-Parameter [f]	0.00 (racemic twin)	--

[a] Empirical absorption correction[17]. – [b] Largest difference peak and hole. – [c] $R1 = ([\Sigma\|F_o|-|F_c\|)/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. – [d] Gof = $[\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. – [e] $w = 1/[\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$ where $P = [\max(F_o^2 \text{ or } 0) + 2 \cdot F_c^2]/3$. – [f] Absolute structure parameter[18].

☆ Dedicated to Prof. Dr. *Jörn Müller* on the occasion of his 60th birthday.

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[10] Along the same lines we note here that in the Jahn-Teller distorted octahedral structure of complex **9**[2a] the two long Cu–N bonds were to those triazolyl rings which formed additional hydrogen bonds with solvent molecules via the exodentate nitrogen atom.

[11] Antiferromagnetic exchange interactions through 1,2,4-triazole bridges in polynuclear copper(II) compounds are well documented: P. J. van Koningsbruggen, D. Gatteschi, R. A. G. de Graaff, J. G. Haasnoot, J. Reedijk, C. Zanchini, *Inorg. Chem.* **1995**, *34*, 5175–5182; P. J. van Koningsbruggen, J. G. Haasnoot, W. Vreugdenhil, J. Reedij, O. Kahn, *Inorg. Chim. Acta* **1995**, *239*, 5–12; P. J. van Koningsbruggen, J. W. van Hal, R. A. G. de Graaff, J. P. Haasnoot, J. Reedijk, *J. Chem. Soc., Dalton Trans.* **1993**, 2163–2167; P. J. van Koningsbruggen, J. W. van Hal, E. Müller, R. A. G. de Graaff, J. G. Haasnoot, J. Reedijk, *ibid.* **1993**, 1371–1375; D. W. Engelfriet, W. L. Groeneveld, H. A. Groenendijk, J. J. Smit, G. M. Nap, *Z. Naturforsch., Part A*, **1980**, *35*, 115–128; D. W. Engelfriet, W. L. Groeneveld, G. M. Nap, *ibid.* **1980**, *35*, 852–864.

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[13] The connectivity of the flexidentate tris(1,2,4-triazolyl)borate ligand can be indicated with the kappa formalism according to IUPAC: ${}^{2}_{\infty}[Cu_2Cl_2\{\mu_3\text{-}HB(C_2H_2N_3)_3\text{-}1\kappa^3N^{2,2',2''}{:}2\kappa N^4{:}2'\kappa N^{4'}\}\text{-}\{\mu_3\text{-}HB(C_2H_2N_3)_3\text{-}2\kappa^3N^{2,2',2''}{:}1\kappa N^4{:}1'\kappa N^{4'}\}\cdot 2\ H_2O]$ (**7**) and ${}^{3}_{\infty}\{[Cu_2\{\mu_4\text{-}HB(C_2H_2N_3)_3\text{-}1\kappa^3N^{2,2',2''}{:}2'\kappa N^{4'}{:}2'\kappa N^{4'}{:}2''\kappa N^{4''}\}(\mu\text{-}OH\text{-}1{:}1'\kappa^2O)(\mu\text{-}OH\text{-}2{:}2'\kappa^2O)]Cl\cdot 6\ H_2O\}$ (**8**). The number in front of κ is the numerical descriptor of the central atom; 1 and 2 refer to the two different Cu centers present in these structures and 1′,2′ or 2″ indicate the respective symmetry related centers. The colon indicates the bridging mode of the ligand. The exponent at the N atom gives the donor type: N^2 endodentate, N^4 exodentate. For further information see: *Nomenklatur der anorganischen Chemie*, IUPAC recommendations 1990, VCH, Weinheim, **1995**.

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[15] Further details of the crystal structure determinations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen on quoting the depository number CSD-404981 (for **7**) or CSD-404980 (for **8**), the authors, and the journal citation.

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