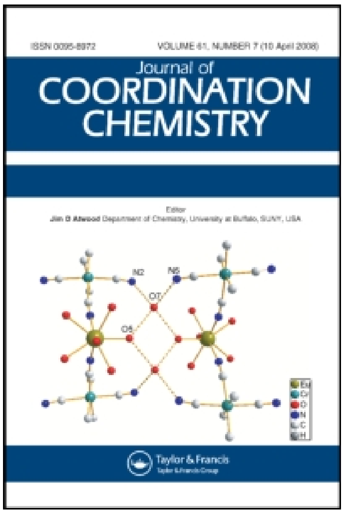

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Synthesis, characterization, and crystal structure determination of Cu(II) coordination compounds with 2,2'-dimethyl-4,4'-bithiazole

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Synthesis, characterization, and crystal structure determination of Cu(II) coordination compounds with 2,2′-dimethyl-4,4′-bithiazole

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$[\{CuCl(dm4bt)\}_2\ \mu\text{-}Cl)_2]$ (**1**) (dm4bt = 2,2′-dimethyl-4,4′-bithiazole) was prepared from the reaction of $CuCl_2 \cdot 2H_2O$ with 2,2′-dimethyl-4,4′-bithiazole in methanol; $[Cu(dm4bt)_2NO_3](NO_3)$ (**2**) was prepared from the reaction of $Cu(NO_3)_2 \cdot 3H_2O$ with 2,2′-dimethyl-4,4′-bithiazole in methanol. Both complexes were characterized by IR, UV–Vis spectroscopy, and single-crystal structure. The structure of **1** consists of centrosymmetric dimeric $[\{CuCl(dm4bt)\}(\mu\text{-}Cl)]$, in which two chloro ligands bridge the coppers forming a four-membered ring; a terminal chloride and a bidentate chelating bithiazole complete five coordination at each Cu(II) in a highly distorted trigonal-bipyramidal geometry. The mononuclear structure **2** consists of a Cu(II), two 2,2′-dimethyl-4,4′-bithiazoles, one monodentate nitrate and one uncoordinated nitrate in a highly distorted square pyramid.

Keywords: Copper; 2,2′-Dimethyl-4,4′-bithiazole; Crystal structure; Jahn-Teller distortion

1. Introduction

Bleomycin (BLM) is an anti-tumor drug employed for treating lymphomas, squamous cell carcinomas, and testicular carcinomas [1]. The bithiazole moiety, one domain of bleomycin, was shown to be responsible for the binding of BLM to DNA, causing interest in design and synthesis of model compounds [2]. Transition metal complexes of bithiazole derivatives have found increasing application. For instance, Ni and Co complexes of 2,2′-diamino-4,4′-bithiazole are effective inhibitors of DNA synthesis in tumor cells [3, 4] and Fe(II), Fe(III), and Cu(II) complexes have found application in soft magnetic materials [5–7].

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Copper plays a role in a number of biological processes with therapeutically administered drugs [8]. Coordination chemistry of Cu(II) complexes is important as building-blocks to construct novel coordination architectures [9].

There are only a few reports in the literature on coordination compounds of Cu(II) with bithiazole [10–12] and we are interested in designing new bithiazole ligands and their coordination chemistry with copper.

We recently introduced the coordination chemistry of 2,2′-dimethyl-4,4′-bithiazole (dm4bt) with Zn(II), Hg(II) [13], Cd(II) [14] and Tl(III) [15], in addition to the nickel bithiazole reported previously [16]. We report here the synthesis and characterization of two copper complexes with dm4bt. These complexes were characterized by spectroscopy and X-ray diffraction.

2. Experimental

2.1. *Materials and instruments*

All reagents and solvents were purchased from chemical sources and used without purification. ^{1}H NMR spectra were recorded on a Bruker AC-300 MHz spectrometer. Infrared spectra (4000–250 cm^{-1}) of solid samples were taken as 1% dispersion in CsI pellets using a Shimadzu-470 spectrometer. UV–Vis spectra were recorded on a Shimadzu 2100 spectrometer using a 1 cm path length cell. Melting points are uncorrected and were obtained by a Kofler Heizbank Rechart type 7841 melting point apparatus. Elemental analyses were performed using a Heraeus CHN-O Rapid analyzer.

2.2. *Synthesis of 2,2′-dimethyl-4,4′-bithiazole (dm4bt)*

2,2′-Dimethyl-4,4′-bithiazole was prepared according to the procedure described previously in [17]. One gram (4.10 mmol) of 1,4-dibromo-2,3-butanedione and 0.62 g (8.20 mmol) of thioacetamide was dissolved in 20 mL of dry methanol. The reaction mixture was refluxed for 3 h. The resulting solution was added to 20 mL of water. Neutralization (pH = 7) with Na_2CO_3 solution produces bright brown solid (yield 0.48 g, 60%, m.p. 171–173°C). ^{1}H NMR δ_H ($CDCl_3$): 7.61 (s, 1H, Ar) and 2.78 (s, 3H, CH_3). ^{13}C NMR δ_C ($CDCl_3$): 166.46, 150.08, 114.52 (Ar) and 19.45 (CH_3). IR (CsI, cm^{-1}): 3450w, 3124s, 3043w (υC–H$_{cycle}$), 3017w (υC–H$_{Me}$), 1541w (υC=C), 1507w (υC=N), 1471s, 1443s (υC–C), 1331w, 1312w, 1261m, 1247w, 1217m, 1158w (υC–N), 1100w, 1075w, 1053m, 1028w, 974s, 910m, 881m (υS–C), 782s, 766s, 726s, 685s, 644s, 620w, 567m. UV–Vis (CH_3OH): λ_{max}: 3.76×10^4 cm^{-1}. Anal. Calcd for $C_8H_8N_2S_2$ (%). C, 48.90; H, 4.07; N, 14.26. Found: C, 48.71; H, 3.96; N, 14.12.

2.3. *Synthesis of [{CuCl(dm4bt)}$_2\mu$-Cl)$_2$] (1)*

2,2′-Dimethyl-4,4′-bithiazole (0.09 g, 0.46 mmol) in methanol (20 mL) was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.04 g, 0.23 mmol) in methanol (10 mL) and the resulting pale green solution was stirred at room temperature for 1 h. After 5 days, pale orange prismatic crystals of compound **1** were isolated (yield 0.058 g, 76% based on $CuCl_2 \cdot 2H_2O$, m.p. 242–243°C). IR (CsI, cm^{-1}): 3468w, 3058s, 3064s (υC–H_{cycle}), 2923w (υC–H_{Me}), 1587m, 1526s, 1487m, 1432, 1376s, 1296s, 1212s, 1162s, 1026m, 973s, 885m, 863m, 795s, 707m, 689w, 642m, 597w, 581m, 370m, 317s (υCu–N), 292s (υCu–$Cl_{terminal}$), 275s, 261s (υCu–Cl_{bridge}). UV–Vis (CH_3OH): λ_{max}: $3.77 \times 10^4\,cm^{-1}$. Anal. Calcd for $C_{16}H_{16}Cl_4Cu_2N_4S_4$ (%): C, 29.02; H, 2.42; N, 8.46. Found: C, 28.88; H, 2.35; N, 8.32.

2.4. *Synthesis of [Cu(dm4bt)$_2$NO$_3$](NO$_3$) (2)*

2,2′-Dimethyl-4,4′-bithiazole (0.06 g, 0.306 mmol) in methanol (5 mL) was added to a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.037 g, 0.153 mmol) in acetonitrile (15 mL) and the resulting green solution was stirred at 40–45°C for 20 min. After 3 weeks, green block crystals of **2** were isolated (yield 0.065 g, 73% based on $CuCl_2 \cdot 2H_2O$, m.p. 178–179°C). IR (CsI, cm^{-1}): 3446w, 3101s, 3072s (υC–H_{cycle}), 2926w (υC–H_{Me}), 1620w, 1528s, 1468s, 1437s, 1346s, 1282s, 1212s, 1170s, 1094w, 1015s, 976s, 887m, 826m, 777s, 714m, 645w, 597m, 458m, 374m, 316s (υCu–N), 285s (υCu–ONO_2). UV–Vis (CH_3OH): λ_{max}: $3.94 \times 10^4\,cm^{-1}$. Anal. Calcd for $C_{16}H_{16}Cu_1N_6O_6S_4$ (%): C, 33.09; H, 2.76; N, 14.48. Found: C, 32.94; H, 2.67; N, 14.39.

2.5. *Crystal structure determination and refinement*

The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo-Kα radiation. For **1**, a pale orange prismatic crystal of $0.38 \times 0.21 \times 0.10\,mm^3$ and for **2**, a deep green block crystal of $0.38 \times 0.2 \times 0.17\,mm^3$ were mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 3055 for **1** and 5308 for **2** unique reflections. Data were collected at a temperature of 120(2) and 293(2) K to a maximum 2θ value of 58.46° and 55.82° for **1** and **2**, respectively and in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [18] software package. The numerical absorption coefficient, μ, for Mo-Kα radiation is $2.709\,mm^{-1}$ for 1 and $1.374\,mm^{-1}$ for **2**. A numerical absorption correction was applied using X-RED [19] and X-SHAPE [20] software. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods [21] and subsequent difference Fourier maps and then refined on F^2 by full-matrix least-squares using anisotropic displacement parameters [22]. All hydrogen atoms were treated as riding. Subsequent refinement then converged with R factors and parameter errors significantly better than for all attempts to model the solvent disorder. Atomic factors are from International Tables for X-ray Crystallography [23]. All refinements were performed using the X-STEP32 crystallographic software package [24]. A summary of the crystal data, experimental details, and refinement results is given in table 1.

Table 1. Crystallographic and structure refinements data for **1** and **2**.

	1	**2**
Formula	$C_{16}H_{16}Cl_4Cu_2N_4S_4$	$C_{16}H_{16}Cu_1N_6O_6S_4$
Formula weight	661.51	580.18
Temperature (K)	120(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space Group	*Pbca*	$P\bar{1}$
Crystal size (mm^3)	0.38 × 0.21 × 0.10	0.38 × 0.20 × 0.17
Unit cell dimensions (Å, °)		
a	10.4975(7)	7.4976(12)
b	13.6568(10)	9.6651(17)
c	15.9335(15)	16.726(3)
α	90	81.499(14)
β	90	79.029(13)
γ	90	73.946(13)
Volume ($Å^3$)	2284.3(3)	1137.6(3)
Z	4	2
Density (Calcd) ($g\,cm^{-1}$)	1.923	1.694
θ ranges for data collection	2.76–29.23	2.20–27.91
$F(000)$	1320	590
Absorption coefficient	2.709	1.374
Index ranges	$-13 \le h \le 14$; $-18 \le k \le 14$; $-14 \le l \le 21$	$-9 \le h \le 9$; $-12 \le k \le 12$; $-21 \le l \le 22$
Data collected	7917	10848
Unique data (R_{int})	3055 (0.0374)	5308 (0.0323)
Parameters, restraints	137, 0	298, 0
Final R_1, wR_2[a] (Obs. data)	0.0333, 0.0852	0.0459, 0.1341
Final R_1, wR_2[a] (All data)	0.0372, 0.0876	0.0500, 0.1380
Goodness-of-fit on F^2 (S)	1.071	1.099
Largest difference peak and hole (e $Å^{-3}$)	0.846, −0.888	1.946, −0.529

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

3. Results and discussion

3.1. *Synthesis of 1 and 2*

Compound **1** was obtained from reaction of one equivalent of $CuCl_2 \cdot 2H_2O$ with two equivalents of 2,2′-dimethyl-4,4′-bithiazole in methanol at room temperature, in 76% yield, as follows:

$$CuCl_2 \cdot 2H_2O + 2dm4bt \xrightarrow[CH_3OH]{\text{room temperature}} \left[\{CuCl(dm4bt)\}_2(\mu\text{-}Cl)_2\right] \tag{1}$$

Compound **2** was prepared in 73% yield similarly except for the replacement of $CuCl_2 \cdot 2H_2O$ with $Cu(NO_3)_2 \cdot 3H_2O$, as follows:

$$Cu(NO_3)_2 \cdot 3H_2O + 2dm4bt \xrightarrow[CH_3OH,\ CH_3CN]{(40\text{–}45)^\circ C,\ 20\ \text{min}} \left[Cu(dm4bt)_2NO_3\right](NO_3). \tag{2}$$

We previously reported the synthesis and crystal structure of dm4bt and also its zinc, cadmium, mercury, and thallium complexes from $ZnCl_2$, $HgCl_2$, $CdCl_2$, $Cd(NO_3) \cdot 4H_2O$, and $Tl(NO_3)_3 \cdot 3H_2O$ [13–15], obtaining $[Zn(dm4bt)Cl_2]$ and $[Hg(dm4bt)Cl_2]$ with one chloride in a semi-bridging position [13]. We also obtained

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

Compound **1**			
Cu(1)–N(1)	2.2010(18)	N(1)–Cu(1)–Cl(1)	124.74(5)
Cu(1)–N(2)	1.9867(18)	N(2)–Cu(1)–Cl(2)	175.19(5)
Cu(1)–Cl(1)	2.2815(6)	N(1)–Cu(1)–Cl(2)	100.92(5)
Cu(1)–Cl(2)	2.2825(6)	Cl(1)–Cu(1)–Cl(2)	91.93(2)
Cu(1)–Cl(2)^{i}	2.4609(6)	N(2)–Cu(1)–Cl(2)^{i}	88.23(5)
Cl(2)–Cu(1)^{i}	2.4609(6)	N(1)–Cu(1)–Cl(2)^{i}	97.26(5)
N(2)–Cu(1)–N(1)	79.75(7)	Cl(1)–Cu(1)–Cl(2)^{i}	137.26(2)
N(2)–Cu(1)–Cl(1)	91.57(6)	Cl(2)–Cu(1)–Cl(2)^{i}	86.96(2)
Compound **2**			
Cu(1)–O(1)	1.997(2)	O(1)–Cu(1)–N(1)	153.22(9)
Cu(1)–N(1)	2.070(2)	N(2)–Cu(1)–N(1)	82.46(9)
Cu(1)–N(2)	2.002(2)	N(3)–Cu(1)–N(1)	99.80(9)
Cu(1)–N(3)	2.004(2)	O(1)–Cu(1)–N(4)	114.89(9)
Cu(1)–N(4)	2.315(2)	N(2)–Cu(1)–N(4)	95.81(9)
O(1)–Cu(1)–N(2)	93.61(9)	N(3)–Cu(1)–N(4)	79.00(9)
O(1)–Cu(1)–N(3)	86.67(9)	N(1)–Cu(1)–N(4)	91.89(8)
N(2)–Cu(1)–N(3)	174.37(9)		

Symmetry transformations used to generate equivalent atoms: i: $-x+2, -y, -z+1$.

a 1-D zig-zag coordination polymer with bridging chloride, $[\mathrm{Cd(dm4bt)Cl_2}]_n$ [14]. We were not able to make complexes bearing two dm4bt ligands for chloride salts of Zn, Cd, Hg, and Cu, but in complexes from nitrate salts two dm4bt ligands coordinated to Cd [14], Tl [15], and Cu.

3.2. *IR and UV–Vis investigation*

The infrared spectral data for dm4bt, **1** and **2** are listed in section 2 and are presented as a table in "Supplementary material". Several bands in the region 800–3400 cm^{-1} are related to the hetero aromatic ring modes related to C–H, C–C, C=N, C–C, C–N, and S–C [25, 26]. Bands at 1541, 1507, 1471, 1261, 1158, 881, and 782 cm^{-1} for the free ligand are shifted to higher frequencies upon coordination, 1587, 1526, 1487, 1296, 1162, 885, and 795 cm^{-1} in **1**. This shift to higher frequencies upon coordination has been observed for bipyridine and other ligands [27–30], and can be explained by changing the geometry of the free ligand from *syn* to *anti* upon coordination. The same trend was observed for **2**. The IR spectra of **1** and **2** are distinguished from that of dm4bt mainly by the metal to ligand bands. Strong peaks at 317 and 316 cm^{-1} were assigned to $\nu(\mathrm{Cu{-}N_{thiazol}})$ for **1** and **2**, respectively [31]. The band at 292 cm^{-1} was assigned to $\nu(\mathrm{Cu{-}Cl_{terminal}})$ and the bands at 275 and 261 cm^{-1} were assigned to $\nu(\mathrm{Cu{-}Cl_{bridge}})$ in **1** [31–36]. The Cu–$\mathrm{ONO_2}$ stretching vibration for **2** is at 285 cm^{-1} [37].

3.3. *Description of the molecular structure of 1 and 2*

Selected bond lengths and angles for **1** and **2** are listed in table 2 and the atomic numbering scheme and atom connectivity for **1** are shown in figure 1. The structure of **1** consists of centrosymmetric dimeric [{CuCl(dm4bt)}(μ-Cl)] units, in which two chlorides bridge copper forming a four-membered ring; a terminal chloride and a bidentate chelating bithiazole complete five coordination. The bridging $\mathrm{Cu_2Cl_2}$ unit is

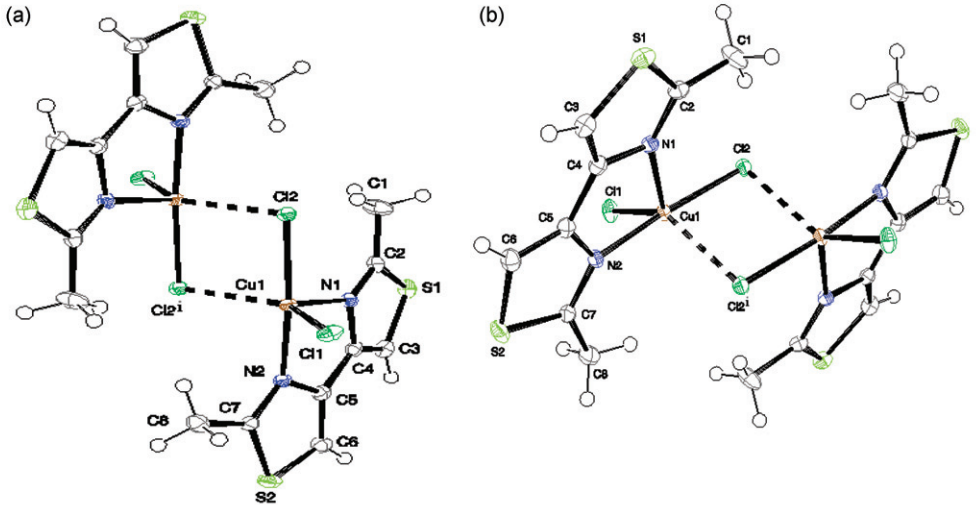

Figure 1. Graphical representation of **1** (a) trigonal-bipyramidal view and (b) square-pyramidal view (50% probability for the thermal ellipsoids). [Symmetry code: i: $-x+2, -y, -z+1$].

strictly planar by the presence of the crystallographic inversion center in the middle of the dimer. In this compound, Cu(II) is a highly distorted trigonal-bipyramidal geometry, with trigonality index $\tau = 0.63$ ($\tau = (\beta - \alpha)/60$, where β is the greatest basal angle and α is the second in magnitude; $\tau = 0$ and 1 for perfect square-pyramidal and trigonal-bipyramidal geometries, respectively) [38]. In this structure, the basal plane is one thiazoline nitrogen N(1), the terminal chloride Cl(1), and the bridging chloride Cl(2)^{i} [symmetry code; (i) $-x+2, -y, -z+1$]; the apical sites are occupied by the other thiazoline nitrogen N(2) and bridging chloride Cl(2). The N(2)– or Cl(2)–metal–basal ligand angles differ from the ideal value for trigonal-bipyramidal (90°), ranging between 79.75(7)° [for N(2)–Cu(1)–N(1)] and 100.92(5)° [for Cl(2)–Cu(1)–N(1)]. Likewise, the basal ligand–metal–basal ligand angles differ from the ideal value of 120°, ranging between 97.26(5)° [for Cl(2)^{i}–Cu(1)–N(1), symmetry code; (i) $-x+2, -y, -z+1$] and 137.26(2)° [for Cl(2)^{i}–Cu(1)–Cl(1), symmetry code; (i) $-x+2, -y, -z+1$]. These differences are due to bridging of the bithiazole. The terminal Cu–Cl(1) distance [Cu–Cl(1) = 2.2815(6) Å] is slightly longer than the calculated average value [2.268(35) Å] for 90 Cu(II) complexes with a $CuCl_3N_2$ chromophore and short Cu–Cl$_{\text{terminal}}$ bond distances (<2.4 Å) according to Orpen *et al.* [39]. These bond lengths were obtained by CONQUEST software [40] from the CSD [41]. Likewise, the bridging Cu–Cl(2) and Cu–Cl(2)^{i} distances [Cu–Cl(2) = 2.2825(6) Å and Cu–Cl(2)^{i} = 2.4069(6) Å, symmetry code; (i) $-x+2, -y, -z+1$] are comparable to the calculated average value [2.309(53) Å] for short Cu–Cl$_{\text{bridging}}$ bond distances (<2.43 Å) [39] of 56 five-coordinate Cu(II) complexes in CSD [41].

From bond distances and Jahn-Teller distortion, it seems that the geometry around copper is square pyramidal with equatorial positions occupied by one nitrogen of the chelating dm4bt nitrogen and three chlorides (two terminal and one bridging) and the apical position occupied by bithiazole nitrogen. The significant difference between bond distance of two nitrogens of chelating bithiazole (2.2 *vs.* 1.9 Å) shows the longer bond bearing Jahn-Teller distortion in the *Z*-direction. Further distortion from ideal

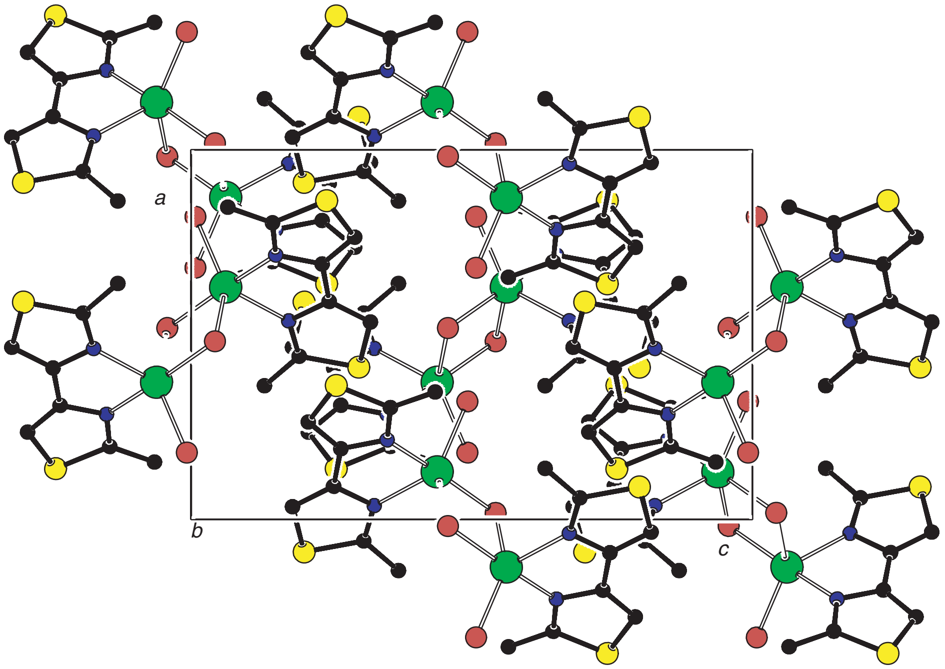

Figure 2. The unit cell-packing diagram of the complex **1** in *b*-direction. Hydrogen atoms are omitted for clarity.

square-based pyramidal geometry arises from the bite angle of the dm4bt nitrogens (N1–Cu1–N2 79.75(7)°), figure 1. The two halves of the dimer are related by inversion, with the inversion center being at the midpoint between the two coppers. The Cl2 atoms bridge the two halves of the complex in a step-wise fashion with the bithiazole rings perpendicular to the Cu2Cl2 bridging plane. The Cu–Cu distance [3.444(5) Å] is slightly shorter than the average value found for 188 dinuclear copper(II) complexes containing two bridging chlorides [3.499(133) Å] in CSD. The five-membered chelating ring Cu(1)–N(1)–C(4)–C(5)–N(2) shows an envelope conformation with the apex at copper. This atom is 0.137 Å out of plane formed by N(1), C(4), C(5), and N(2) [maximum mean-plane deviation for C(4) = 0.026 Å]. The thiazole ring N(1)–C(2)–S(1)–C(3)–C(4) is essentially planar with maximum mean plane deviation for N(1) and C(2) [0.001 Å]. The angle between two thiazoline rings of bithiazole is 9.51°. As shown in figure 2, in **1**, the thiazoline rings form π bonding stacks. The close contact distance between adjacent aromatic rings is 3.617 Å.

Mononuclear **2** consists of a Cu(II), two 2,2′-dimethyl-4,4′-bithiazole ligands, one monodentate nitrate and one uncoordinated nitrate. The structure is depicted in figure 3 together with the numbering scheme. Analysis of the shape determination angles, α and β (the two largest angles around the central atom) yield a value for the trigonality index, τ of 0.35 such that copper can be described as a highly distorted square pyramid. In this structure, the basal plane is made up of three thiazoline nitrogens N(1), N(2), and N(3) and nitrate oxygen O(1) while the apical site is occupied by the other thiazoline nitrogen N(4). Average bond distances of Cu–N in equatorial position is 2.025 Å, while the Cu–N$_{ap}$ distance is 2.315 Å. Again, Jahn-Teller distortion results in significant increase in bond distance in axial position. The N(4)–metal–basal angles differ from the ideal

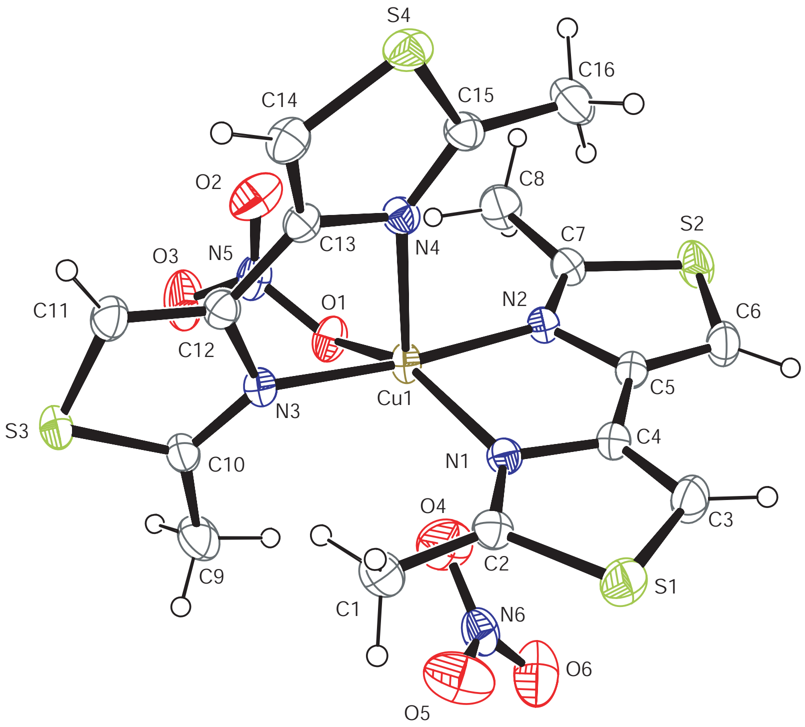

Figure 3. Graphical representation of **2** (30% probability for the thermal ellipsoids).

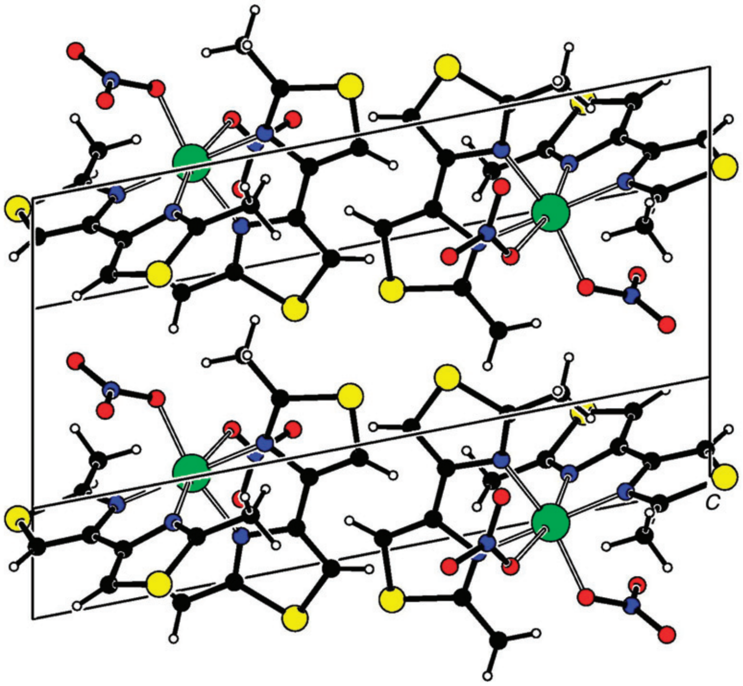

Figure 4. The unit cell-packing diagram of **2**.

value for square-pyramid (90°), ranging between 79.00(9)° [for N(3)–Cu(1)–N(4)] and 114.89(9)° [for O(1)–Cu(1)–N(4)]. Likewise, the basal ligand–metal–basal ligand angles differ from the ideal value of 90°, ranging between 82.46(9)° [for N(1)–Cu(1)–N(2)] and 99.80(9)° [for N(1)–Cu(1)–N(3)].

There are some weak C(thiazole ring)–H ⋯ O(non-coordinated nitrate) [$\mathrm{H3}\cdots\mathrm{O6^{i}} = 2.360(8), \mathrm{C3}\cdots\mathrm{O6^{i}} = 3.226(5)$ Å, and $\mathrm{C3{-}H3}\cdots\mathrm{O6^{i}} = 154.0(3)°$ and $\mathrm{H6}\cdots\mathrm{O6^{i}} = 2.590(7), \mathrm{C6}\cdots\mathrm{O6^{i}} = 3.414(10)$ Å, and $\mathrm{C6{-}H6}\cdots\mathrm{O6^{i}} = 148.0(4)°$, symmetry codes: $\mathrm{i} = -x, 1-y, 1-z$] and C(methyl)–H ⋯ O(non-coordinated nitrate) [$\mathrm{H9C}\cdots\mathrm{O4} = 2.360(7), \mathrm{C9}\cdots\mathrm{O4} = 3.320(5)$ Å and $\mathrm{C9{-}H9C}\cdots\mathrm{O4} = 175.0(4)°$ and $\mathrm{H16A}\cdots\mathrm{O6^{ii}} = 2.580(7), \mathrm{C16}\cdots\mathrm{O6^{ii}} = 3.375(8)$ Å and $\mathrm{C16{-}H16A}\cdots\mathrm{O6^{ii}} = 140.0(3)°$, symmetry code: $\mathrm{ii} = -1 + x, 1 + y, z$] interactions between non-coordinated nitrate and coordinated bithiazole rings that prevents formation of dimeric species. These weak interactions stabilize crystal packing (figure 4).

4. Conclusion

Two new copper complexes containing bithiazole are reported. In the dimeric chloro bridged complex the structure is highly distorted, somewhere between distorted trigonal-bipyramidal and square pyramidal. The monomer is a distorted square pyramid with coordination of four nitrogens of two bithiazole ligands and oxygen from nitrate. Both structures show significant Jahn-Teller distortions for Cu(II).

Supplementary material

The infrared spectral data for dm4bt, **1**, and **2** are presented as a table and CCDC 709025 and 709024 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; or Email: deposit@ccdc.cam.ac.uk

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References

[1] J.P. Henichart, J.L. Bernier, N. Helbecque, R. Houssin. *Nucl. Acids Res.*, **13**, 6703 (1985).
[2] Y.N. Tian, P. Yang, H.F. Wang, Y.L. Feng, S.X. Liu, J.L. Huang. *Polyhedron*, **15**, 2771 (1996).
[3] Y. Tian, P. Yang, Q. Li, S. Liu. *J. Coord. Chem.*, **41**, 223 (1997).
[4] Y. Tian, P. Yang, H.F. Wang, Y.L. Feng, S.X. Liu, J.L. Huang. *Polyhedron*, **15**, 2771 (1996).

[5] W. Sun, X. Gao, F. Lu. *J. Appl. Polym. Sci.*, **64**, 2309 (1997).
[6] J. Weng, W. Sun, L. Jiang, Z. Shen. *Macromol. Rapid Commun.*, **21**, 1099 (2000).
[7] L. Jiang, W. Sun. *Polym. Adv. Technol.*, **16**, 646 (2005).
[8] D. Kovala-Demertzi, A. Theodorou, M.A. Demertzis, C.P. Raptopoulou, A. Terzis. *J. Inorg. Biochem.*, **65**, 151 (1997).
[9] Y.-H. Wen, J.-K. Cheng, Y.-L. Feng, J. Zhang, Z.-J. Li, Y.-G. Yao. *Inorg. Chim. Acta*, **358**, 3347 (2005).
[10] Z.-Y. Wu, D.-J. Xu, Y. Luo, J.-Y. Wu, M.Y. Chiang. *Acta Crystallogr.*, **C59**, m307 (2003).
[11] J.-G. Liu, J.-J. Nie, D.-J. Xu, Y.-Z. Xu, J.-Y. Wu, M.Y. Chiang. *Acta Crystallogr.*, **C57**, 354 (2001).
[12] N.B. Cherif, M. Pierrot, C. Baudrion, J.P. Aune. *Acta Crystallogr.*, **C51**, 72 (1995).
[13] H.R. Khavasi, A. Abedi, V. Amani, B. Notash, N. Safari. *Polyhedron*, **27**, 1848 (2008).
[14] B. Notash, N. Safari, A. Abedi, V. Amani, H.R. Khavasi. *J. Coord. Chem.*, **62**, 1638 (2009).
[15] B. Notash, N. Safari, H.R. Khavasi, V. Amani, A. Abedi. *J. Organomet. Chem.*, **693**, 3553 (2008).
[16] Y.-H. Shen, J.-G. Liu, D.-J. Xu, W.-L. Sun. *J. Coord. Chem.*, **59**, 1983 (2006).
[17] C. Janiak, L. Uhelin, H. Wu, P. Klufers, H.G. Piotrowski, T. Scharmann. *J. Chem. Soc., Dalton Trans.*, 3121 (1999).
[18] Stoe & Cie. *X-AREA*, *Version 1.30: Program for the Acquisition and Analysis of Data*, Stoe & Cie GmbH, Darmstadt, Germany (2005).
[19] Stoe & Cie. *X-RED, Version 1.28b: Program for Data Reduction and Absorption Correction*, Stoe & Cie GmbH, Darmstadt, Germany (2005).
[20] Stoe & Cie. *X-SHAPE, Version 2.05: Program for Crystal Optimization for Numerical Absorption Correction*, Stoe & Cie GmbH, Darmstadt, Germany (2004).
[21] G.M. Sheldrick. *SHELX97*, *Program for Crystal Structure Solution*, University of Göttingen, Germany (1997).
[22] G.M. Sheldrick. *SHELX97*, *Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[23] *International Tables for X-ray Crystallography*, Vol. C, Kluwer Academic Publisher, Dordrecht, The Netherlands (1995).
[24] Stoe & Cie. *X-STEP32*, *Version 1.07b*: *Crystallographic Package*, Stoe & Cie GmbH, Darmstadt, Germany (2000).
[25] M.G. Drew, T.R. Pearson, B.P. Murphy, S.M. Nelson. *Polyhedron*, **2**, 269 (1983).
[26] A. Morsali, M. Payheghader, M.R. Poorheravi, F. Jamali. *Z. Anorg. Allg. Chem.*, **629**, 1627 (2003).
[27] A. Neels, H.S. Evans. *Inorg. Chem.*, **38**, 6164 (1999).
[28] L. Jiang, W. Sun, J. Weng, Z. Shen. *Polymer*, **43**, 1563 (2002).
[29] A.K. Boudalis, C.P. Raptopoulou, A. Terzis, S.P. Perlepes. *Polyhedron*, **23**, 1271 (2004).
[30] V. Amani, N. Safari, H.R. Khavasi. *Polyhedron*, **26**, 4257 (2007).
[31] J.A. Weaver, P. Hambright, P.T. Talbert, E. Kang, A.N. Thorpe. *Inorg. Chem.*, **9**, 268 (1970).
[32] F.J. Barros-García, A. Bernalte-García, F.J. Higes-Rolando, F. Luna-Giles, A.M. Pizarro-Galán, E. Viñuelas-Zahínos. *Z. Anorg. Allg. Chem.*, **631**, 1898 (2005).
[33] K. Nakamato. *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*, 5th Edn, John Wiley & Sons, New York (1997).
[34] B. De Castro, C. Freire, D. Domínguez, J. Gomes. *Polyhedron*, **10**, 2541 (1991).
[35] A. Bernalte-García, F.J. García-Barros, F.J. Higes-Rolando, F. Luna-Giles, R. Pedrero-Marín. *J. Inorg. Biochem.*, **98**, 15 (2004).
[36] Y.J. Weaver, J.A. Weaver. *J. Nucl. Inorg. Chem.*, **37**, 1309 (1975).
[37] J.M. Ramos, R.M. Viana, C.A. Téllez, W.C. Pereira, A. Izolani, M.I. Silva. *Spect. Chim. Acta, Part A*, **65**, 433 (2006).
[38] A.W. Addison, T.N. Rao, J. Reedjik, J. Van Rijn, G.C. Verschorr. *J. Chem. Soc., Dalton Trans.*, 1349 (1984).
[39] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Traylor. *J. Chem. Soc., Dalton Trans.*, S1 (1989).
[40] F.H. Allen. *Acta Crystallogr.*, **B58**, 380 (2002).
[41] Cambridge Structural Database, *Version 5.28*, Cambridge Structural Data Centre, University of Cambridge, Cambridge, UK (2006).