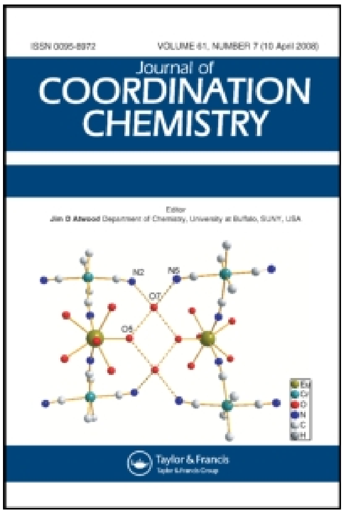

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Synthesis, structures, and magnetic properties of two pyrazolato-bridged trinuclear copper(II) complexes

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One nonlinear and one linear trinuclear copper(II) complex $[Cu_3(dien)_2(pdc)_2CH_3OH]_2 \cdot 6CH_3OH$ (**1**) and $[Cu_3(pdc)_2(CH_3OH)_6(H_2O)_4]$ (**2**) were prepared and characterized structurally, where dien is diethylenetriamine and pdc^{3-} the trianion of 3,5-pyrazoledicarboxylic acid. Both complexes consist of 3,5-pyrazoledicarboxylato-bridged trinuclear copper(II) centers. In **1**, copper(II) ions are five-coordinate in distorted square pyramids with bond angles 164.78° for Cu(1)–Cu(2)–Cu(3) and 164.51° for Cu(4)–Cu(5)–Cu(6). In **2**, the three copper(II) ions are six-coordinate with elongated octahedral geometry. The trinuclear units of **1** and **2** interact through hydrogen bonds to form 3-D and 2-D supramolecular networks, respectively. Variable temperature magnetic susceptibility measurements show that **1** and **2** are antiferromagnetically coupled with J values of -11.2 and $-13.3\,cm^{-1}$.

Keywords: Copper(II) complex; 3,5-Pyrazoledicarboxylic acid; Crystal structure; Magnetic property

1. Introduction

Polynuclear metal complexes attract interest due to their interesting magnetic properties [1], their roles as catalysts for organic reactions [2] and structural components for the synthesis of metallo-supramolecular structures. 3,5-Pyrazoledicarboxylic acid (H_3pdc) has potential coordination sites involving both nitrogens of pyrazole and the carboxylate oxygens. It can coordinate in a variety of coordination modes [3–5] and provide several possibilities in creating supramolecular architectures through hydrogen bonds and π–π interactions; it has been widely used to synthesize mononuclear [3], dinuclear [6–8], trinuclear [9–11], and coordination polymeric compounds [5, 12–15]. Most compounds were prepared by hydrothermal methods [3, 5, 7, 8, 10–14], but several were synthesized by conventional solution methods [6, 15]. Studies of trinuclear copper(II) complexes with H_3pdc are relatively rare [9–11]; only one discrete trinuclear copper(II) complex $[Cu_3(L)_2(Me_2en)_2(H_2O)_2] \cdot (H_2O)_8$ ($L = pdc^{3-}$) containing Me_2en as ancillary ligand was reported [9]. Another complex containing trinuclear copper,

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$[Cu_3(pdc)_2(phen)_2(H_2O)_2]$, is a coordination polymer with phen as ancillary ligand [13]. Both the above two trinuclear compounds contain linear tricopper centers.

In this study, a nonlinear pyrazolato-bridged trinuclear copper(II) complex containing dien as ligand, $[Cu_3(dien)_2(pdc)_2CH_3OH]_2 \cdot 6CH_3OH$ (**1**), was prepared, a rare example that contains nonlinear copper centers. A linear trinuclear copper(II) complex $[Cu_3(pdc)_2(CH_3OH)_6(H_2O)_4]$ (**2**) was also prepared, in which *N*,*N*-dimethylethylenediamine was not coordinated, but it acted as a base in the reaction to remove the third proton of 3,5-pyrazoledicarboxylic acid. The X-ray crystal structure of **2** was reported previously, which was prepared by the copper(II) induced amide hydrolysis of precursor ligand [9]. In our study, **2** is prepared by a different method.

2. Experimental

2.1. *Materials and measurements*

All reagents and chemicals were purchased from commercial sources and used without purification. Elemental analyses for C, H, and N were carried out on an Elemental Vario MICRO CUBE (Germany) elemental analyzer. Infrared (IR) spectra were recorded on Perkin Elmer-1730 FT-IR with KBr pellets from 4000 to 400 cm^{-1}. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

Caution! Salts of perchlorate and their metal complexes are potentially explosive and should be handled with great care and in small quantities.

2.2. *Synthesis of the complexes*

2.2.1. Synthesis of $[Cu_3(dien)_2(pdc)_2CH_3OH]_2 \cdot 6CH_3OH$ (1). Diethylenetriamine (0.103 g, 1 mmol) in methanol (20 mL) was added to a stirred methanol (20 mL) solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.561 g, 1.5 mmol). Then, 3,5-pyrazoledicarboxylic acid monohydrate (0.174 g, 1 mmol) and triethylamine (0.202 g, 2.0 mmol) in methanol (10 mL) were added. The solution was stirred for 2 h. Slow evaporation of the resulting solution at room temperature yielded blue crystals after 20 days. Yield: 0.465 g (56%). Anal. Calcd for $C_{22}H_{44}Cu_3N_{10}O_{12}$: C, 31.79; H, 5.34; and N, 16.85. Found: C, 31.35; H, 5.04; and N, 17.24. FT-IR (KBr pellet, cm^{-1}): 3425 s/br, 3251 s, 2938 m, 1612 s, 1509 s, 1386 s, 1351 s, 1256 m, 1145 m, 1090 s, 1052 m, 1030 m, 840 m, and 787 m.

2.2.2. Synthesis of $[Cu_3(pdc)_2(CH_3OH)_6(H_2O)_4]$ (2). *N*,*N*-dimethylethylenediamine (0.088 g, 1 mmol) in methanol (20 mL) was added to a stirred methanol (20 mL) solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.561 g, 1.5 mmol). Then, methanol (10 mL) solution containing 3,5-pyrazoledicarboxylic acid monohydrate (0.174 g, 1 mmol) and triethylamine (0.202 g, 2.0 mmol) was added. The solution was stirred for 2 h. Slow evaporation of the solution at room temperature produced blue crystals. Yield: 0.342 g (45%). Anal. Calcd for $C_{16}H_{34}Cu_3N_4O_{18}$: C, 25.25; H, 4.50; and N, 7.36. Found: C, 24.96; H, 4.31; and N, 7.66. FT-IR (KBr pellet, cm^{-1}): 3425 s/br,

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

Complex	**1**	**2**
Empirical formula	$C_{22}H_{44}Cu_3N_{10}O_{12}$	$C_{16}H_{34}Cu_3N_4O_{18}$
Formula weight	831.29	761.62
Temperature (K)	293(2)	113(2)
Shape	Block	Block
Color	Blue	Blue
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Unit cell dimensions (Å, °)		
a	13.287(3)	8.9518(18)
b	15.700(3)	8.6608(17)
c	17.883(4)	18.678(4)
α	97.16(3)	90.00
β	94.06(3)	96.70(3)
γ	114.92(3)	90.00
Volume (Å^3), Z	3325.0(12), 4	1438.2(5), 2
Dimension (mm^3)	$0.10 \times 0.08 \times 0.06$	$0.14 \times 0.12 \times 0.08$
D_c (g cm^{-3})	1.661	1.758
μ (mm^{-1})	1.974	2.282
$F(000)$	1716	778
2θ range for data collection (°)	1.70–25.02	2.20–27.84
Limiting indices	$-15 \le h \le 15$; $-18 \le k \le 18$; $-21 \le l \le 21$	$-11 \le h \le 11$; $-11 \le k \le 11$; $-24 \le l \le 24$
Reflections collected	33,591	15,246
Independent reflection	11,560 [R(int) = 0.0898]	3414 [R(int) = 0.0461]
Goodness-of-Fit on F^2	1.000	0.963
Data/restraints/parameters	11,560/0/860	3414/9/215
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0896$, $wR_2 = 0.2272$	$R_1 = 0.0287$, $wR_2 = 0.0709$
R indices (all data)	$R_1 = 0.1089$, $wR_2 = 0.2460$	$R_1 = 0.0341$, $wR_2 = 0.0737$
Largest difference peak and hole (e nm^{-3})	898 and −761	613 and −542

1630 s, 1518 s, 1390 s, 1339 m, 1322 m, 1291 m, 1120 s, 1064 s, 1018 m, 850 m, 782 m, and 626 m.

2.3. *X-ray crystal analysis*

Crystals of the two complexes were mounted on glass fibers. Determination of the unit cell and data collection were performed using monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) on a Bruker SMART 1000 diffractometer equipped with a CCD camera for **1** and Saturn724+ diffractometer for **2**. The ω–2θ scan technique was employed. The structures were solved primarily by direct methods and secondarily by Fourier difference techniques and refined using full-matrix least squares. Computations were performed with the SHELXS-97 and the SHELXL-97 programs [16, 17]. All nonhydrogen atoms were refined anisotropically. All hydrogens were located on calculated positions and refined as riding with common fixed isotropic thermal parameters. The crystal data and structure refinements of **1** and **2** are given in table 1. Selected bond lengths and angles of **1** and **2** are given in tables 2 and 3.

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

Cu(1)–N(4)	1.957(6)	Cu(2)–N(6)	1.946(6)	Cu(3)–N(9)	1.988(6)
Cu(1)–N(2)	1.980(6)	Cu(2)–N(5)	1.961(6)	Cu(3)–O(7)	2.003(5)
Cu(1)–N(3)	2.013(6)	Cu(2)–O(3)	1.964(5)	Cu(3)–N(8)	2.010(6)
Cu(1)–N(1)	2.030(7)	Cu(2)–O(5)	1.976(5)	Cu(3)–N(10)	2.019(6)
Cu(1)–O(1)	2.260(5)	Cu(2)–O(9)	2.308(5)	Cu(3)–N(7)	2.237(6)
Cu(1)–Cu(2)	4.2090(2)	Cu(2)–Cu(3)	4.6527(2)		
N(4)–Cu(1)–N(2)	178.9(3)	N(6)–Cu(2)–N(5)	162.5(2)	N(9)–Cu(3)–O(7)	177.5(2)
N(4)–Cu(1)–N(3)	95.2(2)	N(6)–Cu(2)–O(3)	94.0(2)	N(9)–Cu(3)–N(8)	84.7(2)
N(2)–Cu(1)–N(3)	84.1(2)	N(5)–Cu(2)–O(3)	82.5(2)	O(7)–Cu(3)–N(8)	93.9(2)
N(4)–Cu(1)–N(1)	95.5(2)	N(6)–Cu(2)–O(5)	83.5(2)	N(9)–Cu(3)–N(10)	84.3(2)
N(2)–Cu(1)–N(1)	84.8(2)	N(5)–Cu(2)–O(5)	99.6(2)	O(7)–Cu(3)–N(10)	95.9(2)
N(3)–Cu(1)–N(1)	155.0(3)	O(3)–Cu(2)–O(5)	177.3(2)	N(8)–Cu(3)–N(10)	151.7(2)
N(4)–Cu(1)–O(1)	76.5(2)	N(6)–Cu(2)–O(9)	102.9(2)	N(9)–Cu(3)–N(7)	103.6(2)
N(2)–Cu(1)–O(1)	104.6(2)	N(5)–Cu(2)–O(9)	94.5(2)	O(7)–Cu(3)–N(7)	78.8(2)
N(3)–Cu(1)–O(1)	116.1(2)	O(3)–Cu(2)–O(9)	94.3(2)	N(8)–Cu(3)–N(7)	110.0(2)
N(1)–Cu(1)–O(1)	88.5(2)	O(5)–Cu(2)–O(9)	87.3(2)	N(10)–Cu(3)–N(7)	97.9(2)
Cu(4)–O(10)	1.967(5)	Cu(5)–N(16)	1.932(6)	Cu(6)–O(16)	1.993(6)
Cu(4)–N(12)	1.992(6)	Cu(5)–N(15)	1.939(6)	Cu(6)–N(18)	2.001(7)
Cu(4)–N(13)	2.010(6)	Cu(5)–O(14)	2.007(5)	Cu(6)–N(20)	2.016(7)
Cu(4)–N(11)	2.019(7)	Cu(5)–O(12)	2.008(5)	Cu(6)–N(19)	2.024(7)
Cu(4)–N(14)	2.209(6)	Cu(5)–O(18)	2.324(5)	Cu(6)–N(17)	2.152(6)
Cu(4)–Cu(5)	4.6044(2)	Cu(5)–Cu(6)	4.5076(2)		
O(10)–Cu(4)–N(12)	174.5(2)	N(16)–Cu(5)–N(15)	163.7(3)	O(16)–Cu(6)–N(18)	95.5(3)
O(10)–Cu(4)–N(13)	93.7(2)	N(16)–Cu(5)–O(14)	82.7(2)	O(16)–Cu(6)–N(20)	93.6(3)
N(12)–Cu(4)–N(13)	85.0(2)	N(15)–Cu(5)–O(14)	96.7(2)	N(18)–Cu(6)–N(20)	158.8(3)
O(10)–Cu(4)–N(11)	94.2(2)	N(16)–Cu(5)–O(12)	95.7(2)	O(16)–Cu(6)–N(19)	170.2(2)
N(12)–Cu(4)–N(11)	85.0(2)	N(15)–Cu(5)–O(12)	83.5(2)	N(18)–Cu(6)–N(19)	84.0(3)
N(13)–Cu(4)–N(11)	156.6(3)	O(14)–Cu(5)–O(12)	175.3(3)	N(20)–Cu(6)–N(19)	83.8(3)
O(10)–Cu(4)–N(14)	80.0(2)	N(16)–Cu(5)–O(18)	98.1(2)	O(16)–Cu(6)–N(17)	79.4(2)
N(12)–Cu(4)–N(14)	105.5(2)	N(15)–Cu(5)–O(18)	98.2(2)	N(18)–Cu(6)–N(17)	102.6(3)
N(13)–Cu(4)–N(14)	104.4(2)	O(14)–Cu(5)–O(18)	91.84(19)	N(20)–Cu(6)–N(17)	97.8(2)
N(11)–Cu(4)–N(14)	98.7(2)	O(12)–Cu(5)–O(18)	92.8(2)	N(19)–Cu(6)–N(17)	110.3(3)

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Cu(1)–O(5)	1.9441(14)	O(5)–Cu(1)–O(6)	90.25(6)	O(3)#1–Cu(2)–N(2)	97.76(6)
Cu(1)–O(1)	1.9698(13)	O(1)–Cu(1)–O(6)	83.64(6)	O(3)–Cu(2)–N(2)	82.24(6)
Cu(1)–O(6)	1.9793(15)	O(5)–Cu(1)–N(1)	103.75(6)	N(2)#1–Cu(2)–N(2)	180.0
Cu(1)–N(1)	2.0002(17)	O(1)–Cu(1)–N(1)	82.38(6)	O(3)#1–Cu(2)–O(8)	88.94(6)
Cu(1)–O(7)	2.3052(15)	O(6)–Cu(1)–N(1)	166.00(6)	O(3)–Cu(2)–O(8)	91.06(6)
Cu(2)–O(3)#1	1.9788(14)	O(5)–Cu(1)–O(7)	89.76(6)	N(2)#1–Cu(2)–O(8)	92.25(6)
Cu(2)–O(3)	1.9789(14)	O(1)–Cu(1)–O(7)	94.38(6)	N(2)–Cu(2)–O(8)	87.75(6)
Cu(2)–N(2)#1	1.9882(15)	O(6)–Cu(1)–O(7)	90.27(6)	O(3)#1–Cu(2)–O(8)#1	91.06(6)
Cu(2)–N(2)	1.9883(15)	N(1)–Cu(1)–O(7)	90.07(6)	O(3)–Cu(2)–O(8)#1	88.94(6)
Cu(2)–O(8)	2.4330(17)	O(3)#1–Cu(2)–O(3)	180.0	N(2)#1–Cu(2)–O(8)#1	87.75(6)
Cu(2)–O(8)#1	2.4330(17)	O(3)#1–Cu(2)–N(2)#1	82.24(6)	N(2)–Cu(2)–O(8)#1	92.25(6)
Cu(1)–Cu(2)	4.4369(10)	O(3)–Cu(2)–N(2)#1	97.76(6)	O(8)–Cu(2)–O(8)	180.0
O(5)–Cu(1)–O(1)	172.62(6)				

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

3. Results and discussion

3.1. *IR spectra*

IR spectra of **1** and **2** show broad absorptions at 3600–3200 $\mathrm{cm^{-1}}$, characteristic of ν(N–H) and ν(O–H) in dien, methanol, and water [18]. Strong absorptions around 1640–1580 $\mathrm{cm^{-1}}$ and 1560–1400 $\mathrm{cm^{-1}}$ of **1** and **2** are characteristic for asymmetric and

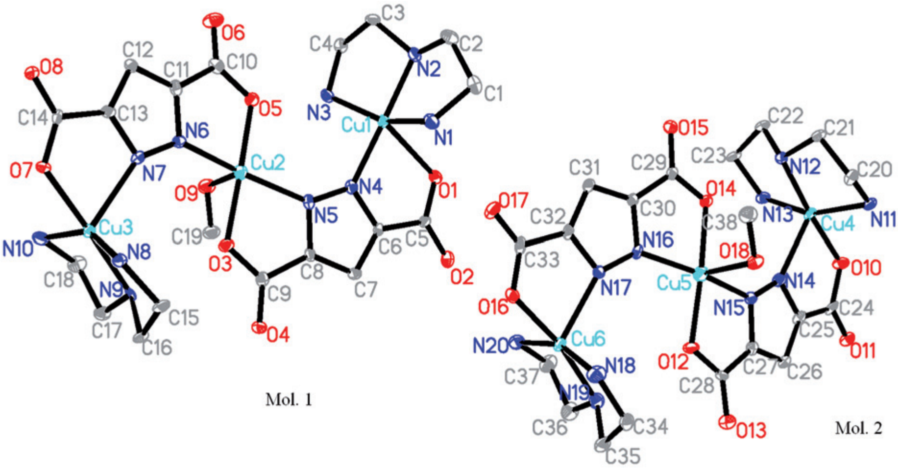

Figure 1. Perspective views of two crystallographically independent structural units of **1**; six lattice methanols were omitted for clarity (30% displacement ellipsoids).

symmetric vibrations of the carboxylate of 3,5-pdc trianion; these bands are proximate to that of reported copper(II) complexes [5, 9]. The main bands in the two complexes are in agreement with the reported copper(II) complexes containing pdc^{3-} [9], demonstrating bidentate u_2-O, N-chelating mode of pdc^{3-} which is also verified by X-ray crystallography.

3.2. *Description of the crystal structures*

3.2.1. Structure of $[Cu_3(dien)_2(pdc)_2CH_3OH]_2 \cdot 6CH_3OH$ (1). Complex **1** was obtained by reaction of $Cu(ClO_4)_2 \cdot 6H_2O$, diethylenetriamine and twice deprotonated 3,5-pyrazoledicarboxylic acid monohydrate at 3 : 2 : 2 ratio in methanol. Complex **1** is comprised of two crystallographically independent trinuclear copper(II) units and six lattice methanols. The two units are slightly different in bond angles and bond distances. Figure 1 shows the two units identified as Mol. 1 and Mol. 2.

In Mol. 1, the trinuclear unit contains three, five-coordinated copper(II) ions chelated by 3,5-pyrazoledicarboxylic acid (pdc^{3-}) in distorted square pyramidal geometry with the Addison parameter τ value of 0.40, 0.25, and 0.43 for Cu(1), Cu(2), and Cu(3) [19]. The copper(II) ions are arranged asymmetrically with bond distances 4.2090(2) Å for Cu(1) ⋯ Cu(2) and 4.6527(2) Å for Cu(2) ⋯ Cu(3). The Cu(1)–Cu(2)–Cu(3) bond angle is 164.78°, not 180° as observed in other complexes [9, 11, 13]. The central Cu(2) is coordinated by two pyrazole nitrogens [Cu(2)–N(5) 1.961(6) Å, Cu(2)–N(6) 1.946(6) Å] and two carboxylate oxygens [Cu(2)–O(3) 1.964(5) Å, Cu(2)–O(5) 1.976(5) Å] from two pdc^{3-} ligands in the equatorial plane. The axial site is occupied by methanol O(9) [Cu(2)–O(9) 2.308(5) Å]. Deviation of Cu(2) from the mean plane [N(5), O(5), N(6), O(3)] is 0.158 Å and equatorial plane angles are 82.5(2)–99.6(2)° [N(5)–Cu(2)–O(3) 82.5(2)°, N(5)–Cu(2)–O(5) 99.6(2)°, N(6)–Cu(2)–O(3) 94.0(2)°, N(6)–Cu(2)–O(5) 83.5(2)°].

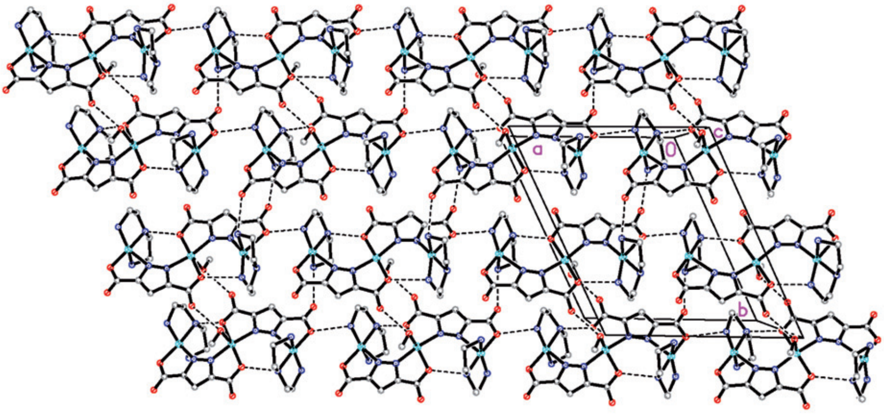

Figure 2. Hydrogen bonding interactions in **1**.

Cu(1) is coordinated by three nitrogens of dien [Cu(1)–N(1) 2.030(7) Å, Cu(1)–N(2) 1.980(6) Å, Cu(1)–N(3) 2.013(6) Å] and one pyrazole nitrogen [Cu(1)–N(4) 1.957(6) Å] of pdc^{3-} in the equatorial plane. The axial position is occupied by O(1) of pdc^{3-} [Cu(1)–O(1) 2.260(5) Å]. Cu(1) deviates 0.204 Å from the plane of N(1), N(2), N(3), and N(4); the equatorial plane angles are in the range of 84.1(2)–95.5(2)°, all close to 90°. Cu(3) is also coordinated by three nitrogens of dien [Cu(3)–N(8) 2.010(6) Å, Cu(3)–N(9) 1.988(6) Å, Cu(3)–N(10) 2.019(6) Å] and one carboxylate of pdc^{3-} [Cu(3)–O(7) 2.003(5) Å] in the square plane. In this case, the axial site is occupied by the pyrazole [Cu(3)–N(7) 2.237(6) Å] of pdc^{3-}. Cu(3) is 0.248 Å above the square plane [N(8), N(9), N(10), and O(7)]. Bond angles of the equatorial plane are of the range 84.3(2)–95.9(2)°. The pdc^{3-} bite angles at the three copper(II) ions are similar, N(4)–Cu(1)–O(1) 76.5(2)°, N(5)–Cu(2)–O(3) 82.5(2)°, N(6)–Cu(2)–O(5) 83.5(2)°, N(7)–Cu(3)–O(7) 78.8(2)°, implying that pdc^{3-} is a fairly rigid ligand and retains its integrity on metal chelation.

Cu(4), Cu(5), and Cu(6) in Mol. 2 have the same coordination environment with the three copper(II) ions in Mol. 1. They are all five-coordinate in distorted square pyramidal geometry with τ value of 0.19 for Cu(5) and Cu(6) and 0.30 for Cu(4); bond distance of adjacent copper(II) ions are 4.6044(2) Å for Cu(4) $\cdots$ Cu(5) and 4.5076(2) Å for Cu(5) $\cdots$ Cu(6) and the bond angle of Cu(4)–Cu(5)–Cu(6) is 164.51°. Other structural features are similar to Mol. 1.

Other than the complicated hydrogen bonds formed by lattice methanol molecules in **1**, two types of N–H $\cdots$ O, O–H $\cdots$ O intermolecular hydrogen bonds exist. First, each crystallographically independent Mol. 1 and Mol. 2 trinuclear unit is connected through hydrogen bonds of type N–H $\cdots$ O to form a 1-D chain structure along the a axis. Crystallographically independent trinuclear units are interlinked to form the 2-D network structure (figure 2) through two types of N–H $\cdots$ O, O–H $\cdots$ O intermolecular hydrogen bonds. The first type (N–H $\cdots$ O) is formed between the terminal NH groups of dien as hydrogen donors and uncoordinated carboxylate oxygen of pdc^{3-} in adjacent units as proton acceptors with bond distances in the range 2.829–2.964 Å. The second type (O–H $\cdots$ O) is formed between coordinated methanol as hydrogen donors and uncoordinated carboxylate oxygen of pdc^{3-} in the adjacent unit as proton acceptors

Table 4. Hydrogen bonding parameters within **1** and **2**.

D–H···A	d(D–H)	d(H···A)/Å	∠(DHA)/°	d(D···A)/Å	Symmetry codes
1					
N1–H1A···O21	0.900	2.127	173.93	3.023	$1-x, 1-y, 1-z$
N1–H1B···O17	0.900	1.972	158.73	2.829	x, y, z
N2–H2···O7	0.910	2.120	162.18	3.000	$1+x, y, z$
N3–H3B···O5	0.900	2.031	155.12	2.872	x, y, z
N8–H8A···O23	0.900	2.065	166.82	2.949	$-1+x, y, z$
N8–H8B···O1	0.900	1.995	156.54	2.844	$-1+x, y, z$
O9–H9···O13	0.930	2.227	115.63	2.759	$-1+x, -1+y, z$
N9–H9A···O3	0.910	1.926	170.71	2.828	x, y, z
N10–H10A···O22	0.900	2.141	163.81	3.015	$-x, 1-y, 1-z$
N10–H10B···O11	0.900	2.066	152.88	2.896	$-2+x, -1+y, z$
N11–H11A···O8	0.900	2.149	150.23	2.964	$2+x, 1+y, z$
N11–H11B···O19	0.900	2.067	169.11	2.955	$2-x, 1-y, 1-z$
N12–H12···O14	0.910	1.956	170.23	2.857	x, y, z
N13–H13A···O16	0.900	2.114	162.85	2.986	$1+x, y, z$
N13–H13B···O24	0.900	2.148	161.62	3.016	$1+x, y, z$
O18–H18···O6	0.930	2.260	106.00	2.678	$1+x, 1+y, z$
N18–H18B···O10	0.900	1.993	168.86	2.881	$-1+x, y, z$
N19–H19···O12	0.910	2.001	163.66	2.885	x, y, z
O20–H20···O11	0.820	2.021	145.07	2.734	$-1+x, -1+y, z$
N20–H20A···O20	0.900	2.070	152.75	2.899	$1-x, 1-y, 1-z$
N20–H20B···O2	0.900	2.153	145.79	2.941	x, y, z
O22–H22···O2	0.820	2.012	154.04	2.772	x, y, z
O23–H23···O15	0.820	1.985	171.93	2.799	x, y, z
O24–H24···O4	0.820	1.915	163.34	2.711	x, y, z
2					
O5–H5A···O3	0.858	1.757	178.20	2.614	$-x, 2-y, -z$
O5–H5B···O1	0.856	1.866	171.02	2.715	$1/2-x, 1/2+y, 1/2-z$
O6–H6A···O9	0.856	1.940	171.49	2.789	$1/2-x, -1/2+y, 1/2-z$
O6–H6B···O2	0.848	1.847	177.06	2.695	$1/2-x, 1/2+y, 1/2-z$
O7–H7···O4	0.841	1.883	172.36	2.719	$-x, 1-y, -z$
O8–H8···O2	0.840	1.948	166.63	2.772	$x, 1+y, z$
O9–H9···O4	0.836	1.987	168.16	2.811	$1/2+x, 3/2-y, 1/2+z$

with bond distances in the range 2.844–3.001 Å. The trinuclear units are further connected through lattice methanols by hydrogen bonds to form the final 3-D architecture. Details of the hydrogen bond parameters are summarized in table 4.

3.2.2. Structure of $[Cu_3(pdc)_2(CH_3OH)_6(H_2O)_4]$ (2). Complex **2** was reported before by Driessen *et al.* [9] prepared by copper induced amide hydrolysis of a precursor ligand. The direct preparation of this complex was not successful. In our study, **2** was synthesized by the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$, *N*,*N*-dimethylethylenediamine and twofold deprotonated 3,5-pyrazoledicarboxylic acid. We planned to incorporate *N*,*N*-dimethylethylenediamine as an ancillary ligand in the preparation of **2** as dien in **1**; unfortunately, *N*,*N*-dimethylethylenediamine was not coordinated with copper(II) in the formed complex; instead it acts as a base to remove the third proton of 3,5-pyrazoledicarboxylic acid, resulting in the formation of **2**, $[Cu_3(pdc)_2(CH_3OH)_6(H_2O)_4]$. Complex **2** and the previous reported complex by Driessen *et al.* [9] are distortion isomers which only differ slightly in bond lengths and bond angles.

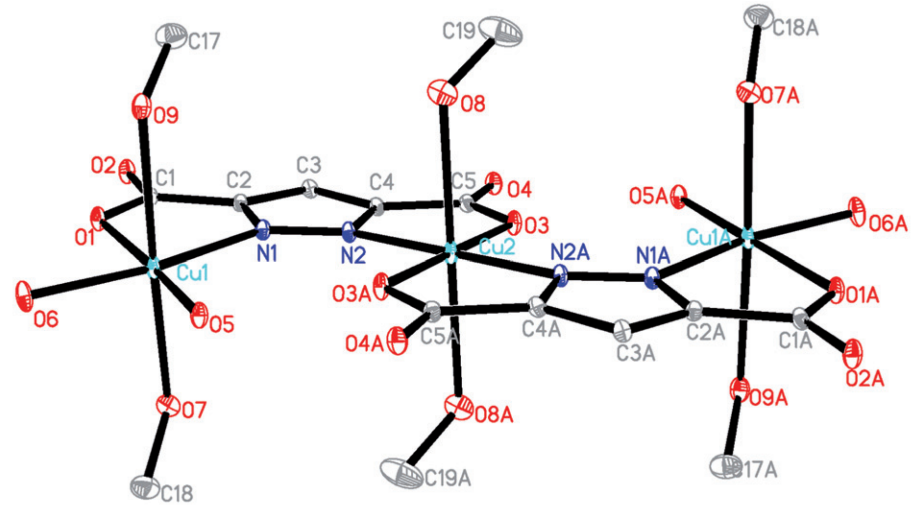

Figure 3. Perspective view of **2** (30% displacement ellipsoids).

The structure of **2** consists of trinuclear copper(II) [$Cu_3(pdc)_2(CH_3OH)_6(H_2O)_4$] (figure 3). The planar trinuclear unit contains three six-coordinate copper(II) ions chelated by two pdc^{3-} trianion ligands. The three copper(II) ions are linear with Cu(1)–Cu(2)–Cu(1)A bond angle of 180°. Cu(2) is on a crystallographic inversion center and the Cu(1) $\cdots$ Cu(2) distance is 4.437 Å.

All copper ions are six-coordinate in elongated octahedra. Cu(2) ion is coordinated by N(2), N(2)′, and O(3), O(3)′ of each carboxylato-pyrazolato group in the equatorial plane. The axial positions are occupied by O(8), O(8)′ of two methanols with bond angle of 180° for O(8)–Cu(2)–O(8)′. The bond distances are 1.9883(15) Å for Cu(2)–N(2), 1.9789(14) Å for Cu(2)–O(3), and 2.4330(17) Å for Cu(2)–O(8). The terminal copper ions are coordinated by carboxylate O(1) and pyrazole N(5) of pdc^{3-} trianion and two oxygens of two waters in the equatorial plane with bond distances to be 1.9698(13) Å for Cu(1)–O(1), 2.0002(17) Å for Cu(1)–N(1), 1.9441(14) Å for Cu(1)–O(5), and 1.9793(15) Å for Cu(1)–O(6); equatorial plane bond angles are in the range 82.38(6)–103.75(6)°. Axial positions are O(7) and O(9) of two methanols with bond lengths 2.3052(15) Å for Cu(1)–O(7) and 2.566 Å for Cu(1)–O(9), weak bonds. The very long axial Cu–O(methanol) bond distances are due to the Jahn–Teller effect. For the complex reported by Driessen *et al.* [9] the Cu–O(methanol) bond lengths are 2.341(6) Å and 2.599(5) Å, a little bit longer than those of **2**. Also, the orientations of the weakly coordinated methanols are different from that of **2** with bond angle of 177.31° (178.40° for **2**). This might be the reason for the different crystal parameters of **2**.

Extensive hydrogen bonds are present in **2**. Each trinuclear copper unit interacts with six neighboring units through hydrogen bonds to form a 2-D network (figure 4). There are seven unique hydrogen bonds, and details of these are given in table 4.

The coordinated water, O(5), forms one intramolecular H-bond with the coordinated carboxylate O(3) of pdc^{3-}, and one intermolecular hydrogen bond with the coordinated carboxylate O(1) of pdc^{3-} on an adjacent complex, while coordinated water O(6) forms one intermolecular hydrogen bond with the uncoordinated carboxylate O(2) of pdc^{3-}

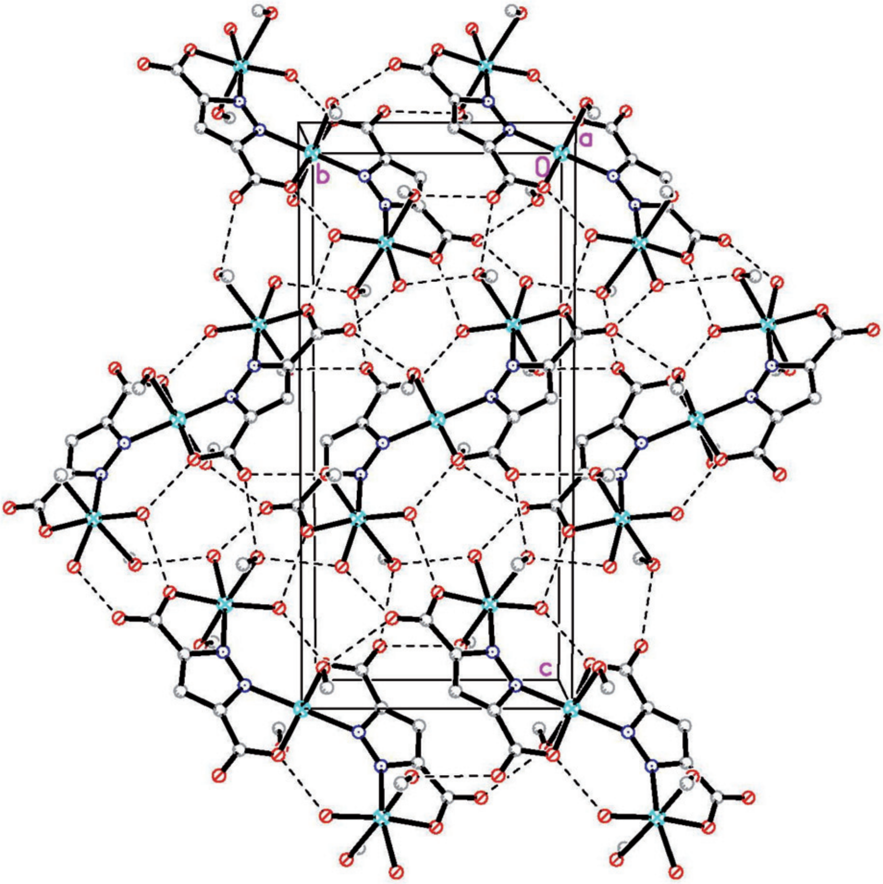

Figure 4. View of hydrogen bond interactions in **2**.

and another H-bond with the coordinated methanol O(9) on an adjacent complex, respectively. The uncoordinated carboxylate O(2) of pdc^{3-} is hydrogen bonded further with a methanol O(8) The uncoordinated carboxylate O(4) of pdc^{3-} is hydrogen bonded to O(7) and O(9) of two methanols on different trinuclear neighbors. The crystal packing (figure 5) shows the presence of the stacked pyrazolato groups, with the shortest ring–ring distances of 3.808 Å along the *b*-axis. The crystal packing of the previously reported complex by Driessen *et al.* [9] is exactly the same as that of **2**, also showing the stacking of the pyrazolato groups along the *b*-axis with the shortest ring–ring distance of 3.958 Å.

3.3. *Magnetic properties of the trinuclear copper(II) complexes*

Variable-temperature magnetic susceptibilities of **1** and **2** were measured from 2 to 300 K at a magnetic field of 1000 Oe. The effective magnetic moment (μ_{eff}) and the

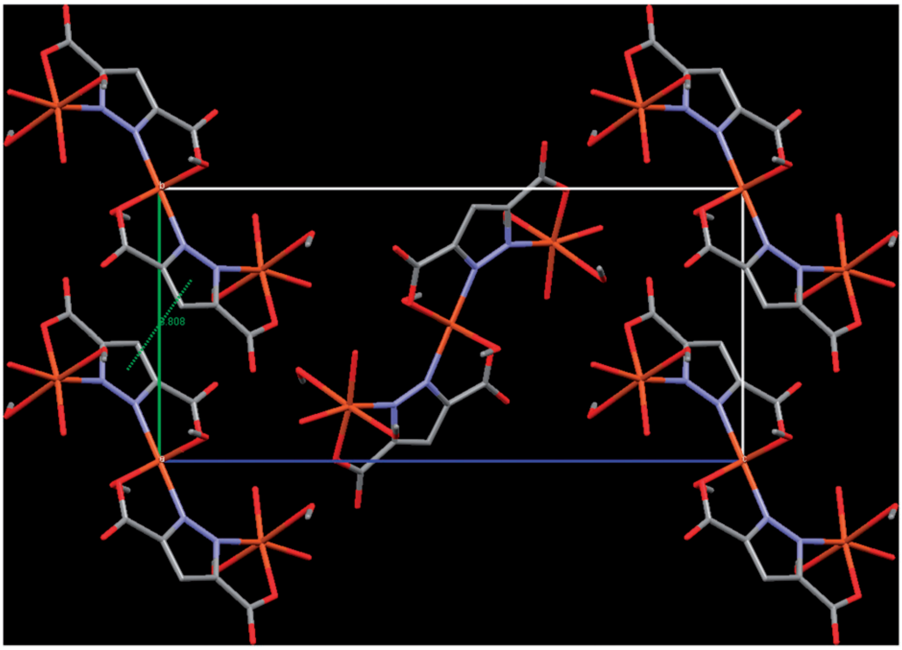

Figure 5. Unit cell showing the π–π stacking interactions in **2**.

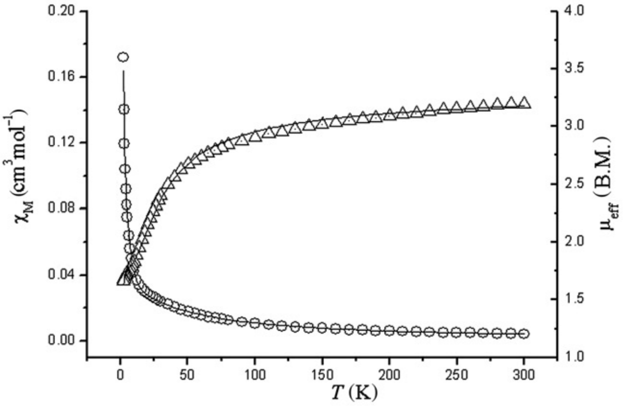

Figure 6. Plots of χ_M and μ_{eff} *vs.* T of **1**. Solid lines represent the best theoretical fits.

molar magnetic susceptibilities (χ_M) *versus* T of **1** are plotted in figure 6, and of **2** in figure 7.

At 300 K, the μ_{eff} value of **1** is 3.19 μ_B, while that of **2** is 3.17 μ_B. Upon cooling, the μ_{eff} value of both monotonously decrease, suggesting dominant antiferromagnetic interactions between adjacent Cu(II) centers [9, 10]. The experimental magnetic susceptibilities data were analyzed with equation (1), the Heisenberg–Hamiltonian expression $[\hat{H} = -2J(\hat{S}_{Cu1}\hat{S}_{Cu2} + \hat{S}_{Cu2}\hat{S}_{Cu3})]$ for a symmetrical linear trinuclear

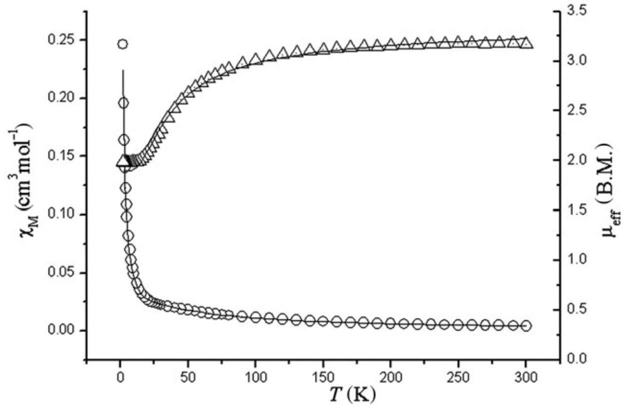

Figure 7. Plots of χ_M and μ_{eff} *vs*. T of **2**. Solid lines represent the best theoretical fits.

copper(II) complex, assuming that the exchange integrals between neighboring copper(II) ions are identical and the integral between the terminal copper ions is neglected, because of their large separation of 8.784 Å for Cu(1) ··· Cu(3) and 9.029 Å for Cu(4) ··· Cu(6) in **1** and 8.874 Å for Cu(1) ··· Cu(1)A in **2**, respectively. For **1**, the intertrimer magnetic interactions were taken into account by using the molecular-field approximation equation (2).

$$\chi_M = \frac{Ng^2\beta^2}{4KT}\left[\frac{5+\exp(-3J/KT)}{1+\exp(-3J/KT)}\right] + N_\alpha, \quad N_\alpha = 120 \times 10^{-6} \tag{1}$$

$$\chi'_M = \frac{\chi_M}{1-(2zj'/Ng^2\beta^2)\chi_M} \tag{2}$$

where χ'_M is the magnetic susceptibility per tricoppper(II) and zj'' the intertrimer exchange parameter. The best fitting for the experimental data gives $J = -11.2\,\mathrm{cm}^{-1}$, $g = 2.15$, $zj' = -0.89\,\mathrm{cm}^{-1}$ for **1**, and $J = -13.3\,\mathrm{cm}^{-1}$, $g = 2.19$ for **2**. The agreement factor $R = \sum(\chi_{\mathrm{obsd}} - \chi_{\mathrm{Calcd}})^2/\sum \chi^2_{\mathrm{obsd}}$ is 6.80×10^{-4} for **1**, and 6.67×10^{-3} for **2**. The negative exchange coupling constant (J) indicates that dominant antiferromagnetic interactions exist between adjacent Cu(II)'s, consistent with that of the similar pyrazolato-bridged trinuclear copper(II) complexes reported by Driessen *et al.* [9].

4. Conclusion

Two pyrazolato-bridged trinuclear copper(II) complexes $[Cu_3(dien)_2(pdc)_2CH_3OH]_2 \cdot 6CH_3OH$ (**1**) and $[Cu_3(pdc)_2(CH_3OH)_6(H_2O)_4]$ (**2**) were synthesized and structurally characterized. Complex **1** consists of nonlinear trinuclear units with copper(II) bond angles 164.78° and 164.51°. Complex **2** has been reported, but the synthesis and structural data in this study are different from the published method. The antiferromagnetic interactions of the adjacent Cu(II) ions in both complexes confirm the relatively small magnetic exchange coupling propagated by 3,5-pyrazoledicarboxylic acid.

Supplementary material

Crystallographic data for the two complexes reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC 688728 for **1** and CCDC 704916 for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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