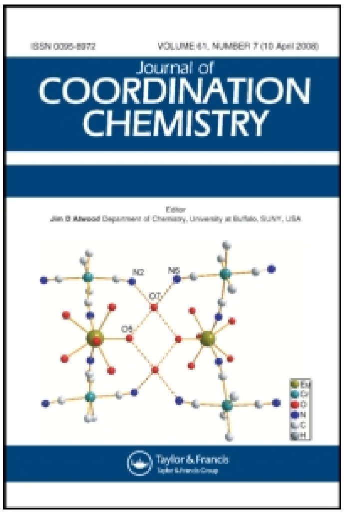

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses, spectral, thermal and structural characterization of copper(II) complexes of 2,3-pyrazinedicarboxylate with <i>N</i>, <i>N</i>'-dimethylethylenediamine and 1,10-phenanthroline

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To cite this Article Yeşiel, Okan Zafer , Mutlu, Aylin and Büyükgüngör, Orhan(2008) 'Syntheses, spectral, thermal and structural characterization of copper(II) complexes of 2,3-pyrazinedicarboxylate with **<i>N</i>**, **<i>N</i>**'-dimethylethylenediamine and 1,10-phenanthroline', Journal of Coordination Chemistry, 61: 20, 3267 — 3275

To link to this Article: DOI: 10.1080/00958970802029823

URL: http://dx.doi.org/10.1080/00958970802029823

Journal of Coordination Chemistry
Vol. 61, No. 20, 20 October 2008, 3267–3275

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Syntheses, spectral, thermal and structural characterization of copper(II) complexes of 2,3-pyrazinedicarboxylate with *N*, *N*′-dimethylethylenediamine and 1,10-phenanthroline

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(*Received 28 October 2007; revised 20 December 2007; in final form 2 January 2008*)

Two copper(II) complexes of 2,3-pyrazinedicarboxylate (pzdca) with *N*,*N*′-dimethylethylenediamine (dmen), $[Cu_2(pzdca)_2(H_2O)_2(dmen)_2]\cdot 6H_2O$ (**1**) and 1,10-phenanthroline (phen), $[Cu(pzdca)(phen)_2]\cdot 5.5H_2O$ (**2**), have been prepared and characterized by elemental analyses, IR, UV/vis, magnetic measurement and single crystal X-ray diffraction. The complexes crystallize in the monoclinic space group $P2_1/c$ and triclinic space group $P\bar{1}$, respectively. In both complexes the copper coordinates pyrazine nitrogen and carboxylate oxygen as a bidentate ligand. The coordination sphere around Cu(II) is completed by two N atoms from dmen and four N atoms from phen groups and one axial position occupied by the carboxyl O atom from the symmetry related molecule in **1**. The coordination sphere should be described as a distorted octahedral and (5 + 1)-geometry in **1** and distorted octahedral geometry in **2**. While **1** shows a first dimeric arrangement, **2** is a monomer. The thermal analyses show that **1** and **2** decompose completely in four and five step thermal processes at 20–600°C temperature intervals.

Keywords: Copper(II) complexes; N,N′-dimethylethylenediamine complex; 1, 10-Phen anthroline complex; 2,3-Pyrazinedicarboxylato complexes

1. Introduction

The 2,3-pyrazinedicarboxylate (pzdca) with a number of potential donor atoms commonly ligate to transition metals by two carboxylic groups together with two pyrazine nitrogens, coordinating with versatile modes as a polymer. More than ten polynuclear Cu(II) complexes with pzdca [1–10] and only two monomeric Cu(II) complexes with pzdca have been reported [11, 12]. In the polymeric complexes, copper(II) ions are bidentate coordinated to nitrogen of pyrazine and oxygen of carboxylate and to the symmetry related oxygen of the other

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970802029823

carboxylate group. In the monomeric $Na_2K_2[\textit{trans}\text{-}Cu(pzdca)_2](SCN)_2 \cdot 2H_2O$ [11] and $K_2[Cu(pzdca)_2(H_2O)] \cdot 6H_2O$ [12] complexes, pzdca coordinates to copper(II) through nitrogen of pyrazine ring and oxygen of carboxylate group as a chelate.

We report the syntheses, X-ray structures, FT-IR and thermal properties of two monomeric copper(II) complexes of 2,3-pyrazinedicarboxylate with *N*,*N*′-dimethylethylenediamine, $[Cu_2(pzdca)_2(H_2O)_2(dmen)_2] \cdot 6H_2O$ (**1**) and 1,10-phenanthroline, $[Cu(pzdca)(phen)_2] \cdot 5.5H_2O$ (**2**).

2. Experimental

2.1. *Materials and instrumentation*

All chemicals were analytical reagent and commercially available. IR spectra were obtained with a Bruker Tensor 27 FT-IR spectrometer using KBr pellets from 4000–400 cm^{-1}. Elemental analyses for C, H and N were performed using a Carlo Erba 1106 microanalyzer. Magnetic susceptibility measurements at room temperature were performed using a Sherwood Scientific MXI model Gouy magnetic balance. The UV–Vis spectra were obtained for aqueous solutions of the complex (10^{-3} M) with a Unicam UV2 spectrometer in the range 900–190 nm. A Diamond TG/DTA thermal analyzer was used to record simultaneous TG, DTG and DTA curves in static air at a heating rate of $10^{\circ}C\,min^{-1}$ in the temperature range 20–600°C using platinum crucibles.

2.2. *Crystallographic analyses*

Diffraction experiments were carried out at 296 K on a Stoe IPDS diffractometer. The structures were solved by direct methods and refined using SHELXS97 and SHELXL97 [13]. Data collections: X-Area, cell refinement: X-Area, data reduction: X-RED [14]; programs have been used for molecular graphics: ORTEP-III for Windows [15]; software has been used to prepare material for publication: WinGX [16].

2.3. *Synthesis of the complexes*

A solution of 2,3-pyrazinedicarboxylic acid (0.67 g, 4 mmol) in water (10 mL) was added dropwise with stirring at 60°C to a solution of $Cu(CH_3COO)_2 \cdot H_2O$ (0.80 g, 4 mmol) in distilled water (15 mL). The mixture was stirred for 4 h at 50°C and then dmen (0.35 g, 4 mmol) in water (5 mL) or phen (1.81 g, 10 mmol) in ethanol (10 mL) was added. The mixture was stirred for 2 h at 50°C and then cooled to room temperature. Green for **1** and blue for **2** crystals were filtered and washed with 10 mL of water and dried *in air*. Anal. Calcd for $C_{20}H_{44}N_8O_{16}Cu_2$: C, 30.81; H, 5.69; N, 14.37. Found: C, 30.79; H, 5.61; N, 14.47%. Anal. Calcd for $C_{30}H_{29}N_6O_{9.5}Cu$: C, 52.29; H, 4.24; N, 12.19. Found: C, 52.32; H, 4.21; N, 12.17%.

3. Results and discussion

3.1. *UV–Vis spectra and magnetic susceptibility*

The UV–Vis spectrum of **1** in H_2O displays an absorption band at 613 nm ($\varepsilon = 71$ $\mathrm{L\,mol^{-1}\,cm^{-1}}$), while **2** shows an absorption band at 695 nm ($\varepsilon = 129$ $\mathrm{L\,mol^{-1}\,cm^{-1}}$), both assigned to $E_g \rightarrow T_{2g}$. The complexes have magnetic moments of 1.41 and 1.71 BM, respectively, corresponding to one unpaired electron.

3.2. *IR spectra*

The IR spectra show strong bands at 3509 and 3404 $\mathrm{cm^{-1}}$ for **1** and 3400 $\mathrm{cm^{-1}}$ for **2** due to water. The N1–H stretching bands of dmen were clearly observable as strong bands at 3225 and 3195 $\mathrm{cm^{-1}}$. These bands display some variability, depending on their environment. The CH/CH_2 stretching absorptions occur in the 2812–3004 $\mathrm{cm^{-1}}$ range as medium bands. In the spectra of the complexes, the hydrogen bonded carboxylic groups (νOH_{acid}) stretching bands at 2438, 2488, 2610, 2849 and 3265 $\mathrm{cm^{-1}}$ in the free 2,3-pyrazindicarboxylic acid disappeared and a new carboxylate band ($\nu_s COO^-$) appeared in the region 1392–1333 $\mathrm{cm^{-1}}$ for **1** and 1376–1337 for **2** indicating that the carboxylate of 2,3-pyrazinedicarboxylic acid participates in coordination with copper after deprotonation. Several $\nu_{as}COO^-$ strong bands in the range 1753–1690 $\mathrm{cm^{-1}}$ in free H_2pzdca are shifted to lower frequencies 1698, 1652 $\mathrm{cm^{-1}}$ ($\nu_{as}COO^-$) and 1607 $\mathrm{cm^{-1}}$ ($\nu_{as}COO^- + CN$) for **1** and 1653 and 1631 $\mathrm{cm^{-1}}$ for **2** confirming coordination of one of the two carboxylates.

3.3. *Thermal analyses*

The thermal decomposition behavior of the complexes to 600°C in static air show four and five stages of mass loss (Supplementary Data).

3.3.1. $[Cu_2(pzdca)_2(H_2O)_2(dmen)_2]\cdot 6H_2O$ (1). The first endothermic stage ($DTA_{max} = 102$°C) in the temperature range 53–127°C corresponds to the loss of the six crystal waters and two aqua ligands (Found 18.68, Calcd 18.47%). The anhydrous complex is stable to ca 181°C. The second exothermic stage is related to release of two dmen ligands and decarboxylation of pzdca ligands in the range 181–210°C ($DTA_{max} = 208$°C). This behavior of pzdca and dmen molecules in the saccharinate complexes [17] and hydrazinium pyrazine-2,3-dicarboxylate [18] have been reported earlier. In the strong exothermic last stage, remaining organic fragment is abruptly burnt ($DTA_{max} = 415$°C). The final decomposition product CuO was identified by IR spectroscopy (the overall weight loss, Found 80.56, Calcd 79.59%).

3.3.2. $[Cu(pzdca)(phen)_2]\cdot 5.5H_2O$ (2). The first stage is related to endothermic removal of 5.5 moles crystal water molecules in the 51–133°C temperature range ($DTG_{max} = 87$, 117°C, mass loss found 13.34, Calcd 14.37%). The anhydrous complex is stable to 184°C. Based on the second DTG_{max} temperatures of anhydrous complexes,

1 ($DTG_{max} = 208°C$) has higher thermal stability than **2** ($DTG_{max} = 198°C$) due to steric effect of phen. The exothermic second stage of **2** is related to decomposition of two phen ligands and release of two CO_2 of pzdca ligand in the 184–296°C temperature range (Found 32.55, Calcd 32.53%). In the following stages, organic residue is burned as a strong exothermic effect ($DTG_{max} = 524°C$). The final decomposition product is CuO. The total mass loss of all decomposition process is 86.48% (Calcd 88.46%).

3.4. *Crystal structures*

3.4.1. $[Cu_2(pzdca)_2(H_2O)_2(dmen)_2] \cdot 6H_2O$.

The molecular structure of $[Cu_2(pzdca)_2(H_2O)_2(dmen)_2] \cdot 6H_2O$ with atom numbering is shown in figure 1. Details of crystal data, data collection, structure solution and refinement are given in table 1. Selected bond lengths and angles are given in table 2 and the hydrogen bonding geometry is given in table 3. The compound crystallizes in the monoclinic system and $P2_1/c$ space group. The Cu(II) is coordinated by three donors from two bidentate pzdca ligands, two N atoms from one dmen ligand and one O atom from coordinated water molecule, forming a distorted octahedral geometry.

The Cu(II) has a basal plane comprised of three nitrogen atoms [$Cu(1)–N(3)_{dmen} = 1.9979(17)$, $Cu(1)–N(4)_{dmen} = 2.0206(16)$ and $Cu(1)–N(1)_{pzdca} = 2.0283(15)$Å] and the one oxygen atom of pzdca ligands [Cu(1)–O(3) = 1.9801(13)Å]. The apical position is occupied by oxygen of the aqua [Cu(1)–O(5) = 2.3108(15)Å] and in the second coordination sphere the copper ion is weakly bonded to the neighboring pzdca [$Cu(1)–O(4)^{iii} = 2.8868(15)$Å], longer than the equatorial Cu–O bonds due to the Jahn-Teller effect which is well-known for d^9 complexes.

The $Cu–N(1)_{pzdca}$ and $Cu–O(3)_{pzdca}$ bond distances are similar to the corresponding values found in $\{[Cu(pzdca)(H_2O)_2] \cdot H_2O\}_n$ [2.061(3) and 1.978(3)Å] [7], $K_2[Cu(pzdca)_2(H_2O)] \cdot 6H_2O$ [1.994(3) and 1.953(3)Å] [12], but somewhat longer than in $[Cu_4(pzdca)_4(phen)_2(H_2O)_4] \cdot 10H_2O$ [1.983(3) and 1.947(3)Å] [5], $\{[Cu_2(pzdca)_2(pyz)] \cdot 2H_2O\}_n$ [1.990(1) and 1.947(9)Å] [2] and $\{[Cu_2(pzdca)_2(dmttd)(H_2O)_2] \cdot 12H_2O\}_n$ [1.970(4) and 1.932(3)Å] [4]. The bridging $Cu–O(4)^{iii}$ bond distance of 2.887(2)Å is significantly longer than the corresponding bond in $\{[Cu_2(pzdca)_2(pyz)] \cdot 2H_2O\}_n$ [2.21(1)Å] [2]. The Cu ··· Cu distance is 5.233 Å, which is shorter than found in Cu(II)-pzdca complexes.

The carboxylate coordinated to the copper(II) is nearly coplanar with the pyrazine ring [dihedral angles 12.40(8)Å], while the other carboxylate group is twisted by 72.29(9)Å. The complex participates in a supramolecular assembly through hydrogen bonds between crystal water and coordinated ligands forming N–H ··· O and O–H ··· O (figure 2).

3.4.2. $[Cu(pzdca)(phen)_2] \cdot 5.5H_2O$.

The asymmetric unit of **2** is composed of two crystallographically independent Cu(II) ions and eleven crystal water molecules (figure 3). The Cu(II) in $[Cu(pzdca)(phen)_2] \cdot 5.5H_2O$ is coordinated by a bidentate pzdca and two bidentate phen. Distorted octahedral coordination geometry is comprised of N and carboxylate O from a doubly deprotonated bidentate pzdca ligand [Cu(1)–N(6) = 2.372(2)Å and Cu(1)–O(1) = 1.978(2) in molecule A and Cu(2)–N(11) = 2.311(2)Å and Cu(2)–O(5) = 1.972(2) in molecule B (table 4)] and four N atoms from two phen ligands [Cu(1)–N(1) = 2.023(2)Å, Cu(1)–N(2) = 2.061(2)Å,

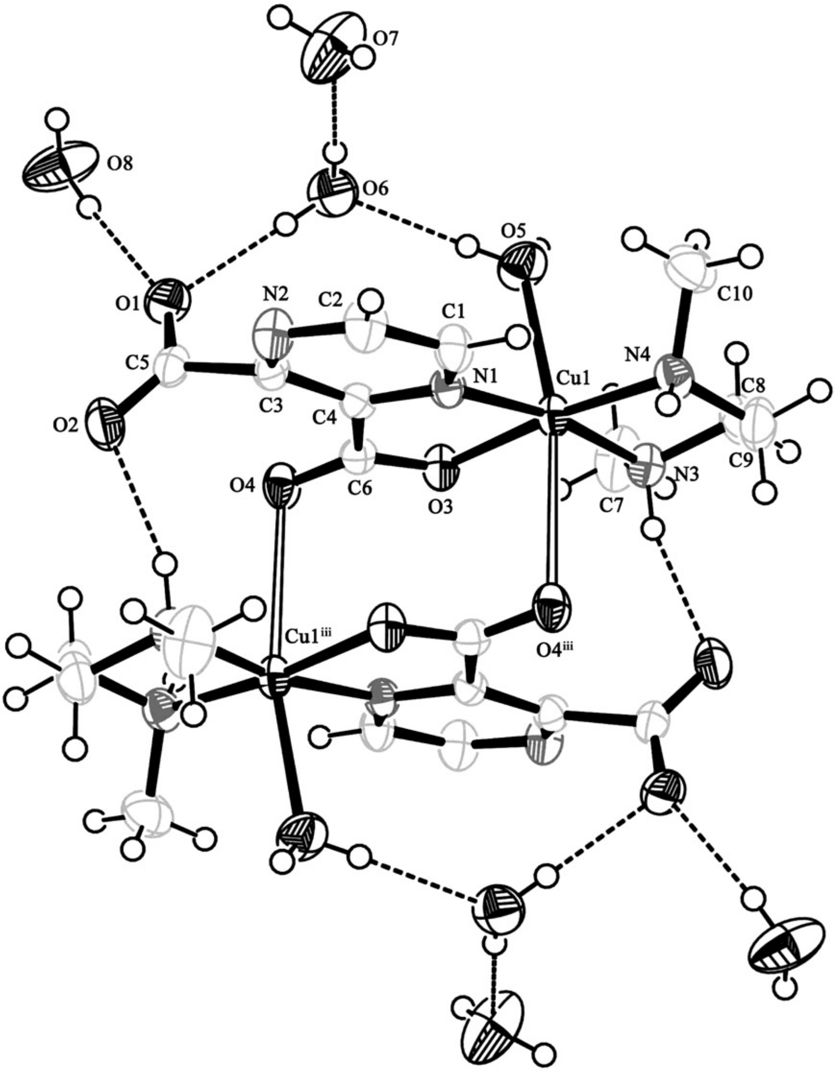

Figure 1. ORTEP III view of **1** with the atom numbering scheme.

Cu(1)–N(3) = 2.021(3)Å and Cu(1)–N(4) = 2.270(2)Å in molecule A and Cu(2)–N(7) = 2.084(2)Å, Cu(2)–N(8) = 2.266(2)Å, Cu(2)–N(9) = 2.058(2)Å and Cu(2)–N(10) = 2.047(2)Å in molecule B]. The angles subtended at the copper(II) by pzdca are 75.23(8)° in molecule A and 77.19(8)° in molecule B, respectively, narrower than previously reported for other pzdca-containing Cu(II) complexes [1, 2, 4–12]. For each crystallographically independent Cu(II), the dihedral angles between pzdca and phen are 80.25 and 65.77° for A and 88.63 and 78.54° for B. It was not possible to locate the H atoms of crystal water.

There are intermolecular O–H $\cdots$ O hydrogen-bonding interactions and face-to-face $\pi \cdots \pi$ stacking interactions between 1,10-phenanthroline ligands of neighboring layers, with distances between the aromatic rings ranging from 3.530(2) to 3.989(2)Å (figure 4).

Table 1. Crystal data and structure refinement parameters for $[Cu_2(pzdca)_2(H_2O)_2(dmen)_2] \cdot 6H_2O$ and $[Cu(pzdca)(phen)_2] \cdot 5.5H_2O$.

	1	**2**
Empirical formula	$C_{20}H_{44}N_8O_{16}Cu_2$	$C_{30}H_{29}N_6O_{9.5}Cu$
Formula weight ($g\,mol^{-1}$)	779.71	689.14
Crystal system, space group	$P2_1/c$, Monoclinic	$P\bar{1}$ Triclinic
Color	Green	Blue
Unit cell dimensions (Å, °)		
a	7.3157(4)	14.7550(6)
b	20.8675(9)	15.1367(7)
c	10.8035(7)	17.3053(7)
α	–	71.251(3)
β	94.926(5)	65.283(3)
γ	–	61.740(3)
Volume (Å^3)	1643.17(16)	3055.4(2)
Z	2	4
Absorption coefficient (mm^{-1})	1.38	0.78
Temperature (K)	296	296
T_{min}, T_{max}	0.4339, 0.6876	0.5603, 0.7542
Reflections collected	20249	44260
Independent reflections	3226	11989
Reflections with $[I > 2\sigma(I)]$	2953	8526
Absorption correction	Integration	Integration
Largest diff. peak and hole (e Å^{-3})	0.55, −0.38	0.76, −0.34
$R[F^2 > 2\sigma(F^2)]$ and $wR(F^2)$	0.027 and 0.071	0.041 and 0.123
R_{int}	0.030	0.045
Goodness-of-fit on F^2	1.05	0.99

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

Cu1–N1	2.0283(15)	Cu1–O3	1.9801(13)
Cu1–N3	1.9979(17)	Cu1–O5	2.3108(15)
Cu1–N4	2.0206(16)	Cu1–O4^{iii}	2.8868(15)
O3–Cu1–N3	93.10(6)	N4–Cu1–N1	98.17(6)
O3–Cu1–N4	173.26(6)	O3–Cu1–O5	89.74(6)
N3–Cu1–N4	86.07(7)	N3–Cu1–O5	100.22(7)
O3–Cu1–N1	81.64(5)	N4–Cu1–O5	97.00(7)
N3–Cu1–N1	170.05(7)	N1–Cu1–O5	88.25(6)

Table 3. Hydrogen bonding interactions in **1**.

D–H···A	d(D–H), (Å)	d(H...A) (Å)	d(D...A) (Å)	∠(DHA)(°)
O5–H5A···O6^{i}	0.812(16)	1.976(17)	2.779(2)	170(2)
O5–H5B···O6	0.819(15)	2.014(16)	2.832(2)	177(2)
O6–H6A···O1	0.795(15)	2.004(17)	2.794(2)	173(2)
O6–H6B···O7	0.813(15)	1.882(16)	2.692(3)	175(3)
O7–H7E···N2^{ii}	0.835(9)	2.208(13)	3.001(3)	159(2)
O7–H7D···O8^{iii}	0.837(9)	1.900(10)	2.732(3)	173(2)
O8–H8C···O1	0.796(15)	2.026(16)	2.819(2)	174(2)
O8–H8D···O2^{ii}	0.803(15)	1.977(16)	2.774(2)	172(3)
N3–H3···O2^{iv}	0.90(3)	2.07(3)	2.936(2)	162(2)
N4–H4···O4^{iii}	0.91(3)	2.11(3)	2.960(2)	155(2)

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $x, -y+1/2, z+1/2$; (iii) $x+1, y, z$; (iv) $-x+1, -y+1, -z+1$.

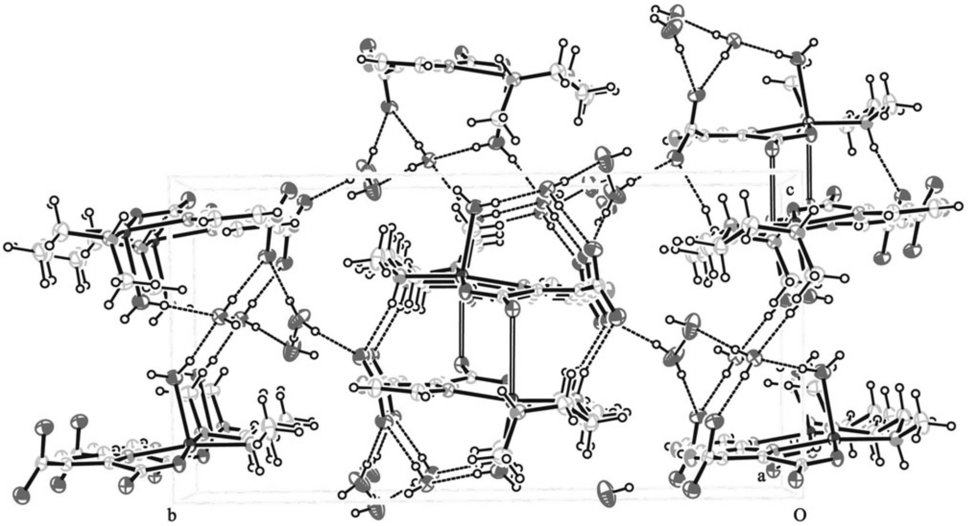

Figure 2. The three-dimensional structure of **1** and hydrogen-bonding interactions.

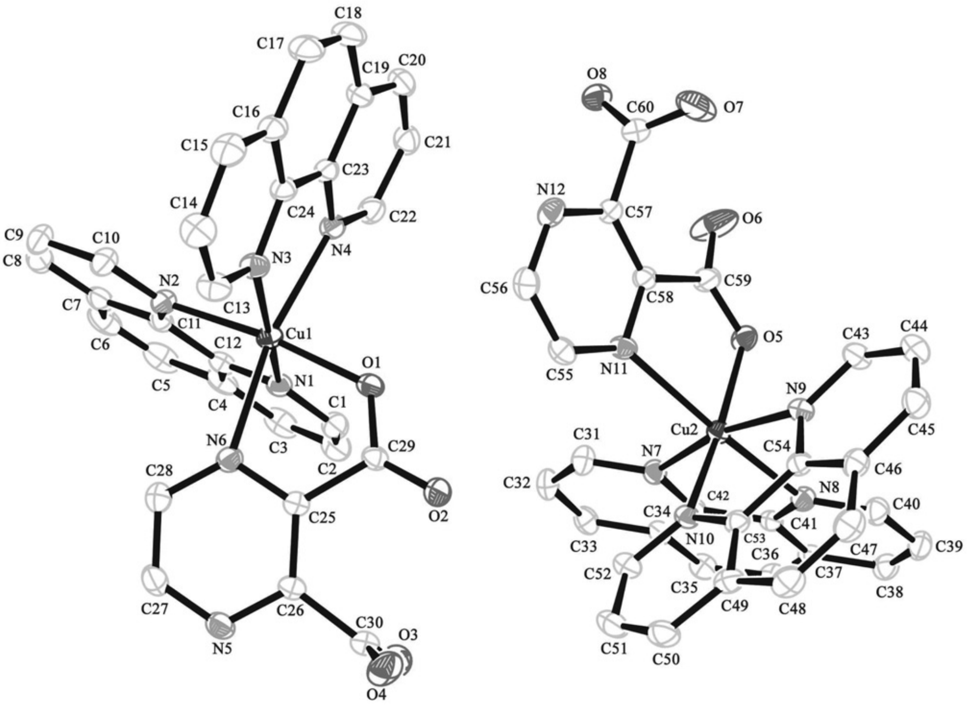

Figure 3. ORTEP III view of **2** with the atom numbering scheme; crystal water molecules omitted for clarity.

Table 4. Selected bond distances (Å) and angles (°) in **2**.

Cu1–N1	2.023(2)	Cu2–N7	2.084(2)
Cu1–N2	2.061(2)	Cu2–N8	2.266(2)
Cu1–N3	2.021(3)	Cu2–N9	2.058(2)
Cu1–N4	2.270(2)	Cu2–N10	2.047(2)
Cu1–N6	2.372(2)	Cu2–N11	2.311(2)
Cu1–O1	1.978(2)	Cu2–O5	1.972(2)
O1–Cu1–N3	94.36(10)	O5–Cu2–N10	167.54(9)
O1–Cu1–N1	93.48(10)	O5–Cu2–N9	92.24(9)
N3–Cu1–N1	168.49(10)	N10–Cu2–N9	80.74(9)
O1–Cu1–N2	172.54(9)	O5–Cu2–N7	92.44(9)
N3–Cu1–N2	91.55(10)	N10–Cu2–N7	96.54(9)
N1–Cu1–N2	81.37(10)	N9–Cu2–N7	167.68(9)
O1–Cu1–N4	91.73(8)	O5–Cu2–N8	91.57(8)
N3–Cu1–N4	78.27(10)	N10–Cu2–N8	98.86(9)
N1–Cu1–N4	93.09(9)	N9–Cu2–N8	91.56(9)
N2–Cu1–N4	93.93(9)	N7–Cu2–N8	76.92(9)
O1–Cu1–N6	75.23(8)	O5–Cu2–N11	77.19(8)
N3–Cu1–N6	96.88(10)	N10–Cu2–N11	93.62(9)
N1–Cu1–N6	93.26(9)	N9–Cu2–N11	98.76(9)
N2–Cu1–N6	99.56(9)	N7–Cu2–N11	93.38(9)
N4–Cu1–N6	165.81(9)	N8–Cu2–N11	164.95(9)

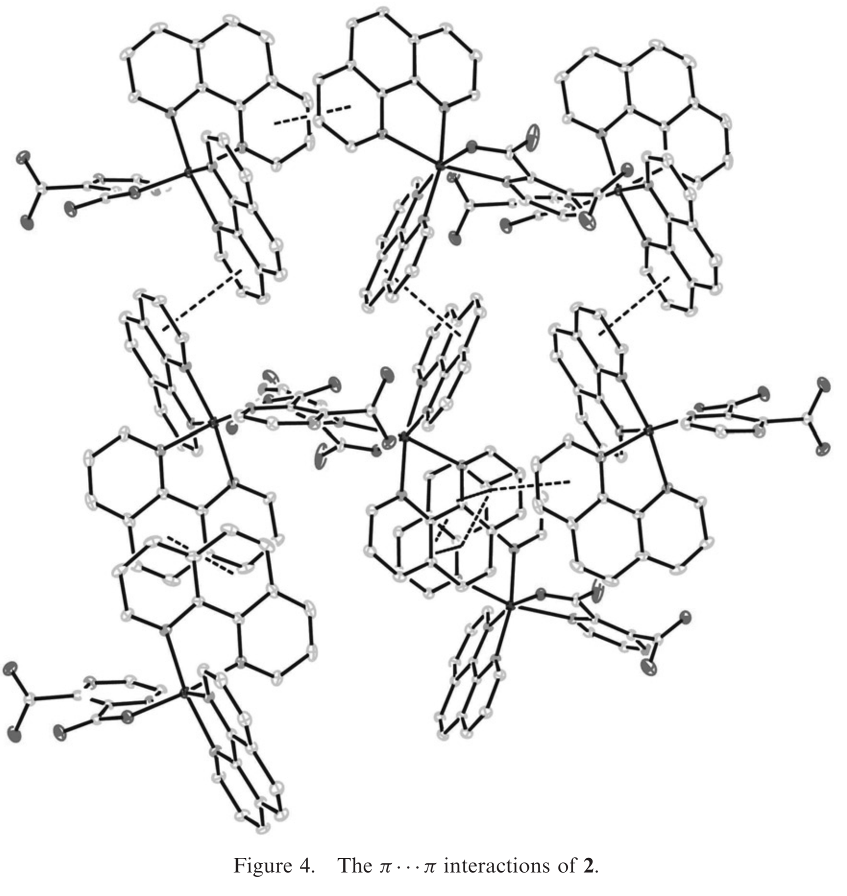

Figure 4. The $\pi\cdots\pi$ interactions of **2**.

4. Conclusion

We have synthesized the first dimeric and a monomeric 2,3-pyrazinedicarboxylate complexes with *N,N′*-dimethylethylenediamine (dmen), $[Cu_2(pzdca)_2(H_2O)_2(dmen)_2] \cdot 6H_2O$ and 1,10-phenanthroline (phen), $[Cu(pzdca)(phen)_2] \cdot 5.5H_2O$. The complexes have been characterized by elemental analyses, spectral (IR and UV/Vis) and thermal and magnetic measurement and single crystal X-ray diffraction.

Supplementary material

CCDC-648980 for **1** and 652134 for **2** contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk].

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