# Synthesis, Structure and Characterization of Two New Complexes $[Cu_2(C_3H_2O_4)_2(C_4H_4N_2)]\cdot 2H_2O$ and $[Zn_2(OH_2)_2(C_3H_2O_4)_2(C_4H_4N_2)]$

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Two new complexes with three-dimensional extended frameworks linked by pyrazine and malonate ligands, namely $[Cu_2(C_3H_2O_4)_2(C_4H_4N_2)]\cdot 2H_2O$ and $[Zn_2(OH_2)_2(C_3H_2O_4)_2(C_4H_4N_2)]$, have been prepared and characterized by X-ray crystallography, IR, EPR and UV/Vis spectroscopy, their magnetic properties and electrical conductivity.

## Introduction

In the past decade, transition metal complex polymers in which a ligand bridges two or more metal centers have received increasing attention due to the potential applications of their physical and/or chemical properties.[1] It is well-known that pyrazine and $RCO_2^-$ can act as excellent bridging ligands for the syntheses of such compounds.[2] Most compounds, however, have either chain-like structures or two-dimensional layer-like structures.[3] For three-dimensional coordination frameworks, it is often difficult to predict the structures and obtain single crystals for X-ray structural analysis. Recently, we have chosen pyrazine and malonate as ligands and attempted to explore the synthetic strategies and structural features. In this paper, the syntheses and structural characterization of two new complexes with 3-D coordination frameworks, $[Cu_2(C_3H_2O_4)_2(C_4H_4N_2)]\cdot 2H_2O$ (**1**) and $[Zn_2(OH_2)_2(C_3H_2O_4)_2(C_4H_4N_2)]$ (**2**), are reported. The magnetic behavior and temperature dependence of the electric conductivity of complex **1** are also described.

## Results and Discussion

Blue crystalline blocks of **1** were obtained from the reaction of $Cu(C_3H_2O_4)\cdot 2H_2O$, malonic acid and pyrazine, and its structure determined by a single crystal X-ray diffraction study. An ORTEP diagram of **1** is shown in Figure 1 with selected bond distances and angles listed in Table 1. The crystal structure reveals that the copper(II) ion is pentacoordinate with four oxygen atoms from three malonate ligands and a nitrogen atom from the pyrazine ligand. The coordination geometry of the $Cu^{II}$ ion can be described as square-based pyramidal, the square plane being defined by O(1), O(3), O(4), and N(1) with an average Cu−O bond length of 1.950 Å. The Cu−N distance is 2.045(3) Å, while the Cu−O(2) distance is slightly longer at 2.252 Å. The $Cu^{II}$ center and the four atoms forming the base are displaced from the least-squares plane by −0.0338, +0.0346, −0.0343, +0.0334, and +0.1151 Å respectively, while the capping atom O(2) is 2.3553 Å away from the corresponding least-squares plane. As described in previous reports,[4] each malonate ligand has two different coordination modes both of which are seen in compound **1**. In the first mode, each malonate acts as a bridge for three $Cu^{II}$ ions, whilst in the second mode each malonate forms a six-membered chelate ring with one $Cu^{II}$ ion in a boat-type configuration. As shown in Figure 2, four $Cu^{II}$ ions are bridged by malonate ligands forming a square 4.848×4.848 Å in size which is slightly bigger than that previously reported.[4] Such square arrangements are then linked by four pyrazines forming a two-dimensional network, leaving a much bigger square (11.685×11.685 Å) in the same plane. Finally, the two-dimensional network is further linked into a three-dimensional structure via malonate ligands (Figure 3). Interestingly, the interstices of the structure are filled with water molecules.

Colorless rhombohedral crystals of **2** were obtained by a similar method to those of **1**. The molecular structure has been determined by a single crystal X-ray diffraction study and an ORTEP diagram of the structure is shown in Figure 4. Selected distances and angles are listed in Table 2. The crystal structure reveals that each $Zn^{II}$ ion is six-coordinate and the coordination geometry of the $Zn^{II}$ centers is octahedral. Each $Zn^{II}$ ion is chelated by two oxygen atoms from one malonate, two oxygen atoms from two neighbor-

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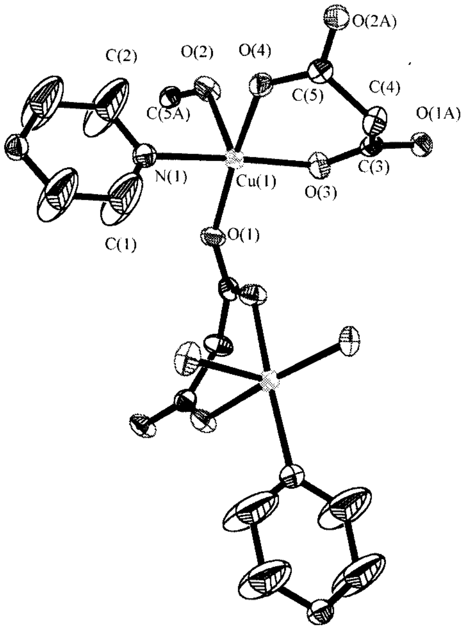

Figure 1. ORTEP diagram of $[Cu_2(C_3H_2O_4)_2(C_4H_4N_2)]\cdot 2H_2O$ **1**

Table 1. Selected bond lengths [Å] and angles [°] in complex **1**

| | | | |
|---|---|---|---|
| Cu(1)−O(1) | 1.956(3) | Cu(1)−O(4) | 1.927(3) |
| Cu(1)−O(2) | 2.252(3) | Cu(1)−N(1) | 2.045(3) |
| Cu(1)−O(3) | 1.968(3) | | |
| O(4)−Cu(1)−O(1) | 171.19(12) | O(3)−Cu(1)−N(1) | 175.37(13) |
| O(4)−Cu(1)−O(3) | 92.03(12) | O(4)−Cu(1)−O(2) | 89.14(12) |
| O(1)−Cu(1)−O(3) | 87.76(12) | O(1)−Cu(1)−O(2) | 99.67(11) |
| O(4)−Cu(1)−N(1) | 87.66(13) | O(3)−Cu(1)−O(2) | 90.10(11) |
| O(1)−Cu(1)−N(1) | 91.84(13) | N(1)−Cu(1)−O(2) | 94.52(12) |

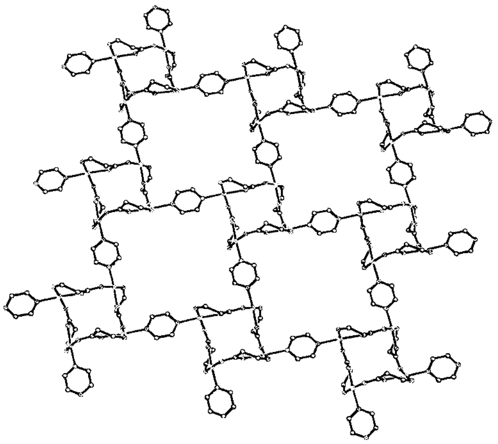

Figure 2. View of the two-dimensional network of **1**

ing malonates, one water molecule, and one nitrogen atom from the pyrazine ligand. The Zn−O bond lengths are in the range 2.065(2)−2.181(3) Å and the Zn−N distance is 2.251(3) Å. The equatorial plane is defined by O(2), O(3), O(5), and N(1) and the deviations of those atoms and the $Zn^{II}$ center from this plane are −0.0045, +0.0046, −0.0049, +0.0047, and −0.1077 Å, respectively, while the axial atoms O(1) and O(4) are −2.1704 and +1.9738 Å away from the corresponding least-squares plane. As in compound **1**, the malonate in complex **2** displays similar coordination modes. As shown in Figure 5, the two-dimensional layer that can be seen is formed in the following way: $Zn^{II}$ ions are first coordinated by malonate ligands to form a chain along the *x*-axis, such chains are then linked by pyrazine units along the *y*-axis to form a wall-like layer. Finally, these layers are

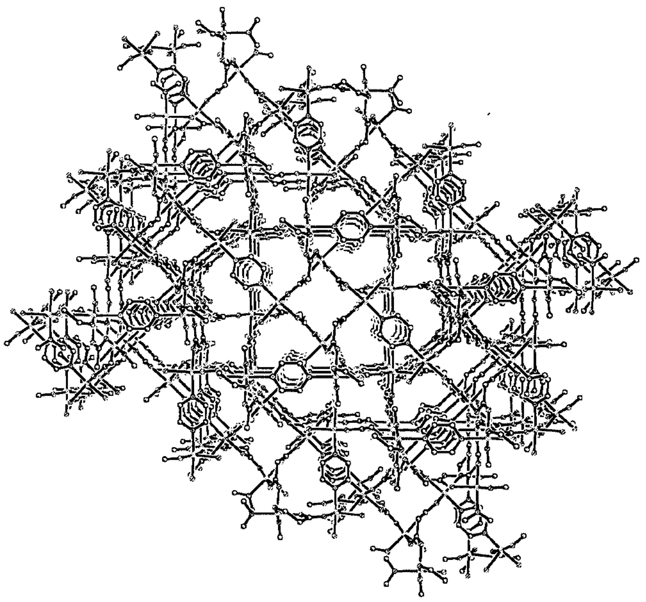

Figure 3. Packing diagram of **1** along the *z*-axis

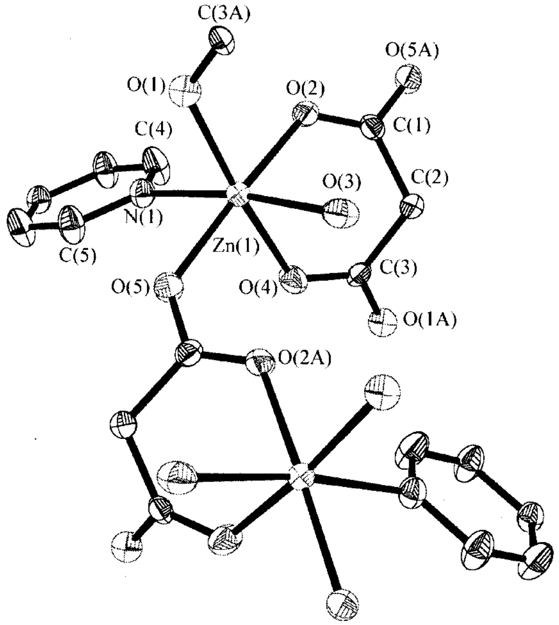

Figure 4. ORTEP diagram of $[Zn_2(OH_2)_2(C_3H_2O_4)_2(C_4H_4N_2)]$ (**2**)

Table 2. Selected bond lengths [Å] and angles [°] in complex of **2**

| | | | |
|---|---|---|---|
| Zn(1)−O(5) | 2.065(2) | Zn(1)−O(2) | 2.085(2) |
| Zn(1)−O(1) | 2.075(3) | Zn(1)−O(3) | 2.181(3) |
| Zn(1)−O(4) | 2.082(3) | Zn(1)−N(1) | 2.251(3) |
| O(5)−Zn(1)−O(1) | 98.68(10) | O(4)−Zn(1)−O(3) | 87.33(11) |
| O(5)−Zn(1)−O(4) | 88.80(11) | O(2)−Zn(1)−O(3) | 92.20(10) |
| O(1)−Zn(1)−O(4) | 172.06(10) | O(5)−Zn(1)−N(1) | 84.91(10) |
| O(5)−Zn(1)−O(2) | 173.69(10) | O(1)−Zn(1)−N(1) | 91.00(10) |
| O(1)−Zn(1)−O(2) | 86.90(10) | O(4)−Zn(1)−N(1) | 86.99(11) |
| O(4)−Zn(1)−O(2) | 85.50(10) | O(2)−Zn(1)−N(1) | 92.08(10) |
| O(5)−Zn(1)−O(3) | 90.23(10) | O(3)−Zn(1)−N(1) | 172.60(10) |
| O(1)−Zn(1)−O(3) | 95.26(10) | | |

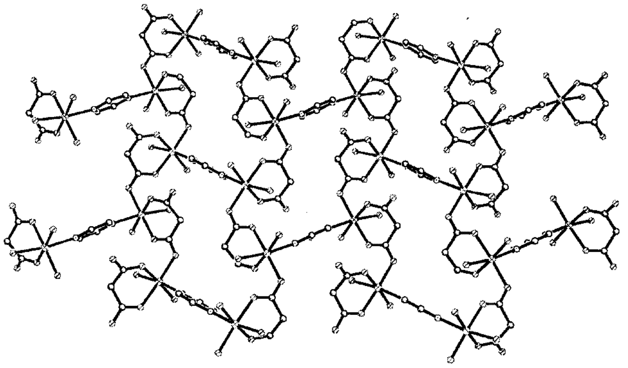

Figure 5. View of the two-dimensional network of **2** in the *ab* plane

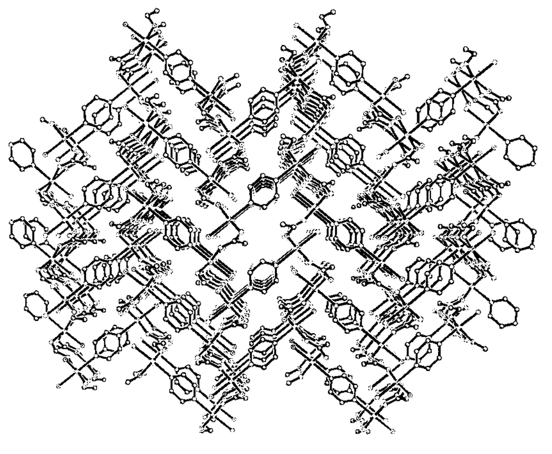

Figure 6. Network structure for complex **2** viewed along the *z*-axis

linked by malonate ligands to form a three-dimensional network possessing polygonal channels (Figure 6).

The magnetic susceptibility of a powder sample of compound **1** was measured using a Quantum Design SQUID magnetometer on the MPMS-7 system with a 10000Qe magnetic field in the temperature range of 5.0−300 K. Its magnetic behavior is highlighted by plots of $\chi_M T$ vs. $T$ and

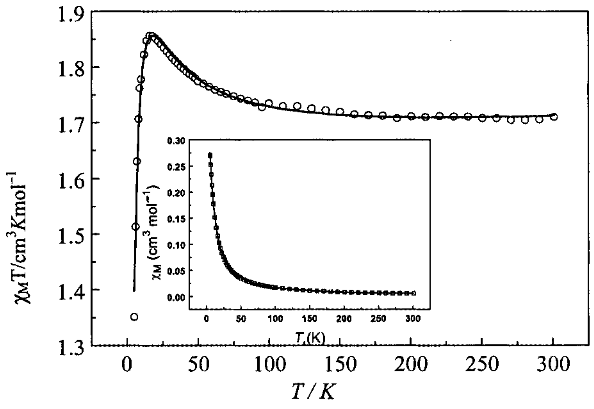

Figure 7. Plots of the experimental temperature dependence of $\chi_M T$ and $\chi_M$ for **1**

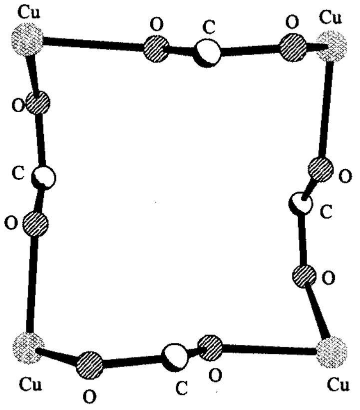

Figure 8. The magnetic exchange path of Cu−O−C(R)−O′−Cu′ in the tetranuclear “Cu$_4$” mini-square

$\chi_M$ vs. $T$ as shown in Figure 7. The temperature dependence of $\chi^{-1}$ is in good agreement with the Curie−Weiss law with $C$ = 0.42(1) cm$^3$·K·mol$^{-1}$ and $\Theta$ = 1.51(1) K, indicating that overall, complex **1** displays ferromagnetic behavior. As the temperature decreases, the $\chi_M T$ values increase gradually from 1.71 cm$^3$·K·mol$^{-1}$ at 300 K, reaching 1.856 cm$^3$·K·mol$^{-1}$ at 16 K, and then drop rapidly to 1.351 cm$^3$·K·mol$^{-1}$ at 5 K. On the basis of the geometrical structure, the magnetic exchange involves a Cu−O−C(R)−O′−Cu′ superexchange path through *syn-anti* bridging binary carboxylate groups in the tetranuclear “Cu$_4$” mini-square (Figure 8) and a Cu−L−Cu (L = pyrazine) interaction between the “Cu$_4$” clusters. Using the Van Vleck equation results in Equations (1) and (2) for $\chi_M'$ and $\chi_M$.

$$\chi_M' = \frac{2Ng^2\beta^2}{kT}\times\frac{e^{2x}+2e^{4x}+5e^{6x}}{1+3e^{2x}+7e^{4x}+5e^{6x}}, \text{ where } x = J/k \tag{1}$$

$$\chi_M = \frac{\chi_M'}{1-\dfrac{2zj\chi_M'}{Ng^2\beta^2}} + \text{TIP} \tag{2}$$

$J$ is the exchange constant for Cu−O−C(R)−O′−Cu′. $j$ and $z$ are the exchange constant for Cu−L−Cu and the number of nearest neighbors respectively. TIP is temperature-independent paramagnetism. A good agreement of $R = 8.55\cdot10^{-5}$ [$R = [(\chi_M T)_{obs} - (\chi_M T)_{cal}]^2/(\chi_M T)^2_{obs}$] is obtained with $J = 5.62(3)$ cm$^{-1}$, $j = -0.284$ cm$^{-1}$ [for $zj = -1.138(8)$cm$^{-1}$, $z = 4$, $g = 2.092(4)$, $TIP = 0.00015(3)$]. These results indicate that there is ferromagnetic exchange between Cu$^{II}$ through the *syn-anti* [Cu−O−C(R)−O′−Cu′] bridge, and the whole [Cu−O−C(R)−O′−Cu′]$_n$ chain skeleton is non-planar. This is consistent with the results of the magnetic properties of the compounds [$Cu_4$(DZB)$_3$(DZBH)($NO_3$)($H_2O$)]·$2H_2O$[5] and [CuL($H_2O$)]$_n$,[6] reported previously. The exchange interaction between the Cu$^{II}$ centers through pyrazine is more complicated. When the dihedral angle between the pyrazine plane and the coordination plane of Cu$^{II}$ in the reported complex [Cu($NO_3$)(pyz)]$_x$,[7] is around 50°, the antiferromagnetic exchange interaction parameter $j$ is about −7.4 cm$^{-1}$. The corresponding dihedral angle in compound **1** is about 65.3°, and the exchange constant $j = -0.2845$, indicating the antiferromagnetic exchange between Cu$^{II}$ through pyrazine is very weak.

It is worthwhile noting that the $g$ value of 2.092(4) mentioned above corresponds well with the results from the EPR measurements at room temperature and at liquid nitrogen temperature ($g = 2.152$ and 2.155, respectively).

In recent years, polymeric unconventional semiconductors have been of much interest.[8] Consequently, we were prompted to investigate the temperature dependence of the electrical conductivity of **1**. Measurements were been carried out using a small pressed disc of the powdered sample on a ZL5-LCR conductometer, giving conductivity values from $2.500\cdot10^{-5}$ S·cm$^{-1}$ to $7.095\cdot10^{-5}$ S·cm$^{-1}$ as the temperature was increased from 298 K to 353 K (Figure 9). These results indicate that complex **1** belongs to the class of semiconductors[9] and this might be mainly due to the interesting structural feature of the copper(II) being linked by aromatic pyrazine and RCOO$^-$ (possessing delocalized π bonding[10]) units.

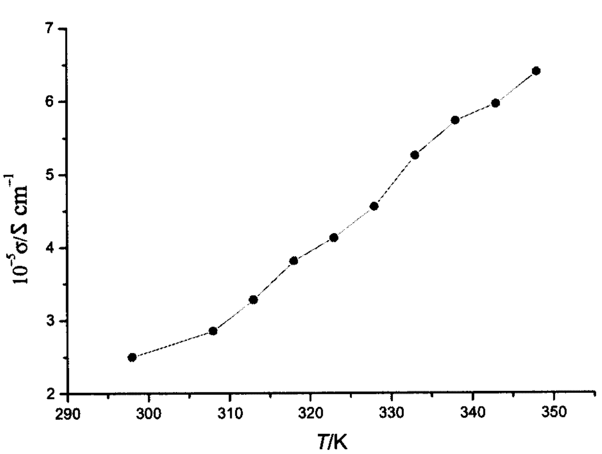

Figure 9. Temperature-dependent electrical conductivity of **1**

Crystalline samples of **1** and **2** were heated from 30 °C to 830 °C. For **1**, TGA showed that the first weight loss, estimated at about 8.15%, occurred between 80 °C and 110 °C which is consistent with the loss of two $H_2O$ molecules (calcd. 8.05% for **1**). The other ligands in **1** (pyrazine and malonate) were lost gradually from 215 °C. In **2**, the loss of two coordinated water molecules and other ligands occurred from 195 °C.

## Experimental Section

### Syntheses

**Preparation of Complex 1:** 1) A solution of basic cupric carbonate [$CuCO_3$·Cu$(OH)_2$·$x$$H_2O$, ca. 0.05 mol] and malonic acid (0.1 mol) in $H_2O$ (200 mL) was heated to reflux for 10 minutes and then filtered. The filtrate was concentrated to approximately 10 mL and filtered again. The resultant precipitates from the filtrations were then dried. 2) To a solution of the dry precipitates (0.2 g) in $H_2O$ (30 mL), was added, dropwise, a solution of pyrazine (0.08 g, 2 mmol) in EtOH (15 mL). The solution was filtered and then evaporated slowly in air. Blue crystalline blocks were obtained after several hours. Yield 0.29 g. Analysis: found C 26.88, H 2.57, N 6.30, Cu 28.34; calcd. C, 26.85, H 2.70, N 6.26, Cu 28.41%. IR (KBr, cm$^{-1}$): ν(OH) 3431−3587, ν(−C−H, =C−H) 3053−3132, δ(OH) 1647, ν(COO) 1558~1429, ν(Cu−O, Cu−N) 228−482.

**Preparation of Complex 2:** 1) A solution of zinc carbonate (0.1 mol) and malonic acid (0.1 mol ) in $H_2O$ (200 mL) was heated to reflux for 10 minutes and then filtered. The filtrate was concentrated to ca. 10 mL and filtered again. The resultant precipitates were then dried. 2) To a solution of the above dry precipitates (0.2 g) in $H_2O$ (30 mL) was added, dropwise, a solution of pyrazine (0.08 g, 2 mmol) in EtOH (15 mL). The solution was filtered and the filtrate was sealed in flask. Colorless rhombohedral crystals were obtained after several days. Yield 0.26 g. Analysis: found C 26.68, H 2.18, N 6.10; Zn, 29.10; calcd. C, 26.63, H 2.23, N 6.21; Zn, 29.00%. IR (KBr, cm$^{-1}$): ν(OH) 3248, ν(−C−H, =C−H) 3053−3122, δ(OH) 1626, ν(COO) 1574~1417, ν(Zn−O, Zn−N) 239−463.

### X-ray Crystallography

**Crystal Data for 1:** Crystal dimensions 0.26 × 0.10 × 0.06 mm, $Cu_2C_{10}H_{12}N_2O_{10}$, $M$ = 447.30, tetragonal, space group $P$-42(1)$c$, $a$ = 12.6075(4), $c$ = 9.1944(4) Å, $V$ = 1461.44(9) Å$^3$, $Z$ = 4, $D_{calcd.}$ =2.033 g·cm$^{-3}$,μ(Mo-$K_\alpha$) = 2.969 mm$^{-1}$, $T$ = 293(2) K. The data were collected on a Siemens SMART CCD diffractometer over the range $2.28 < \theta < 25.04°$. 4349 Reflections were collected of which 1291 were considered to be observed [$I > 2\sigma(I)$]. The structure solution by Patterson methods and full-matrix least-squares refinement were carried out using the SHELXL-97 software package[11] with anisotropic thermal parameters for all skeleton non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms of dissociated water were placed in calculated positions and not refined. It should be pointed out that the $U$(eq) values for C(1) and C(2) are relatively large and could not be improved with an alternative data set from another crystal. The final agreement factors are $R$ [$I > 2\sigma(I)$] = 0.0279, $R_w$ = 0.0719 and GOF = 1.059.

**Crystal Data for 2:** Crystal dimensions 0.46 × 0.24 × 0.06 mm, $Zn_2C_{10}H_{12}N_2O_{10}$. $M$ = 450.99, monoclinic, space group $P2_1/n$, $a$ = 6.9659(5), $b$ = 14.3405(9), $c$ = 7.4477(5) Å, β = 92.179(2)°, $V$ = 743.45(9) Å$^3$, $Z$ = 2, $D_{calcd.}$ =2.014 g·cm$^{-3}$, μ(Mo-$K_\alpha$) = 3.284

mm$^{-1}$, $T = 293(2)$ K. Data were collected on a Siemens SMART CCD diffractometer over the range $2.84 < \theta < 25.01°$. 2428 reflections were collected of which 1117 were considered observed $[I > 2\sigma(I)]$. The structure solution by direct methods and the full-matrix least-squares refinement were carried out using the SHELXL-97 software package[11] with anisotropic thermal parameters for all skeleton non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms of coordinated water molecules were placed in calculated positions and not refined. The final agreement factors are $R\ [I > 2\sigma(I)] = 0.0350$, $R_w = 0.0943$ and GOF = 1.053.

CCDC-184200 and CCDC-184201 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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