

Preparation of Single Crystals of Coordination Solids in Silica Gels: Synthesis and Structure of $\text{Cu}^{\text{II}}(1,4\text{-C}_4\text{H}_4\text{N}_2)(\text{C}_4\text{O}_4)(\text{OH}_2)_4$

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The title compound, $\text{Cu}^{\text{II}}(1,4\text{-C}_4\text{H}_4\text{N}_2)(\text{C}_4\text{O}_4)(\text{OH}_2)_4$, was synthesized at room temperature using a silica gel medium to grow single crystals that have been analyzed by X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/n$, with $a = 6.887(3) \text{ \AA}$, $b = 11.141(4) \text{ \AA}$, $c = 7.545(3) \text{ \AA}$, $\beta = 90.68(3)^\circ$, $V = 578.9(4) \text{ \AA}^3$, $Z = 2$, and $R(R_w) = 0.0263 (0.0393)$. The structure is composed of a linear chain of $\text{Cu}^{\text{II}}(1,4\text{-C}_4\text{H}_4\text{N}_2)(\text{OH}_2)_4$ that is closely hydrogen bonded to squarate anions which link the chains together in a 3-D framework. This material was found to be insoluble in most common solvents; thus it was difficult to obtain large crystals without employing the gel as a diffusion medium. This method might serve as a route to accessing new crystalline solids that are constructed from soluble molecular building blocks. © 1995

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INTRODUCTION

The design and construction of three-dimensional solid networks at room temperature remains a challenge due to at least two issues: (i) controlling the orientation of the molecular components in the solid state is difficult due to the large number of possible orientations a molecule may have, and (ii) obtaining the ultimate product in single crystal form is often difficult or at best fortuitous in nature (1). In an effort to express control over the resulting structure, we and others have exploited symmetry and chemical functionality of molecules in building extended solid frameworks (2, 3). However, in most cases, the products of such assembly reactions are found to be amorphous or microcrystalline and thus are not suited for single crystal diffraction studies. This report shows how single crystals of a coordination solid may be prepared by utilizing gels for crystal growth. Although the use of polymeric matrices as reaction and diffusion media in the achievement of single crystals of ionic solids has been reported (4), their application to the assembly of coordination solids remains largely unexplored. In this study, we have chosen silica gels to obtain single crystals of a 3-D polymeric com-

pound, $\text{Cu}^{\text{II}}(1,4\text{-C}_4\text{H}_4\text{N}_2)(\text{C}_4\text{O}_4)(\text{OH}_2)_4$, which otherwise is produced in microcrystalline form. This compound was isolated during the course of investigating the possible use of squarate anions in linking polymeric metal-pyrazine chains to form open-framework solids. Pyrazine was chosen because of its well-known ability to react with metal ions to form pyrazine-bridged linear and 2-D polymers. The squarate anion was employed in this study for its symmetrical, planar, and rigid properties which provide a minimal amount of hindrance to hydrogen bonds originating from the metal-water centers. In an earlier study (5), we have observed that the formation of hydrogen bonds not only aid in directing the structure but also contribute to crystal stability. Herein, the preparation of the title compound in silica gels and its X-ray single crystal structure are described.

EXPERIMENTAL

Synthesis. Equal volumes of equimolar aqueous solutions of copper(II) acetate monohydrate ($\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$) and pyrazine ($1,4\text{-C}_4\text{H}_4\text{N}_2$) were mixed to give a clear blue solution. To this mixture, 5 ml of 0.05 M aqueous squaric acid ($\text{H}_2\text{C}_4\text{O}_4$) solution was added to give an immediate yellow-green precipitate, which was collected and washed with water ($3 \times 10 \text{ ml}$) followed by acetone ($3 \times 10 \text{ ml}$) and air-dried to give 0.048 g (58% yield). This material is insoluble in water and common organic solvents. Repeated attempts to obtain single crystals from this reaction produced very thin and tiny crystals (Fig. 1, top). Eventually, large single crystals (Fig. 1, bottom) were obtained by employing silica gel as the reaction medium. The $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.10 g, 0.50 mmole) was dissolved in sodium silicate solution (1.06 g/ml, 30 ml) before it gels. Then the mixture was placed in a test tube (25 mm i.d.), where after 24 hr, the gel is set. At this point, an aqueous solution (30 ml) containing $\text{H}_2\text{C}_4\text{O}_4$ (0.057 g, 0.50 mmole) and $1,4\text{-C}_4\text{H}_4\text{N}_2$ (0.040 g, 0.50 mmole) was placed on top of the gel and allowed to diffuse into it. Rod-like green crystals begin to form at the solution/gel interface within 6 hr.

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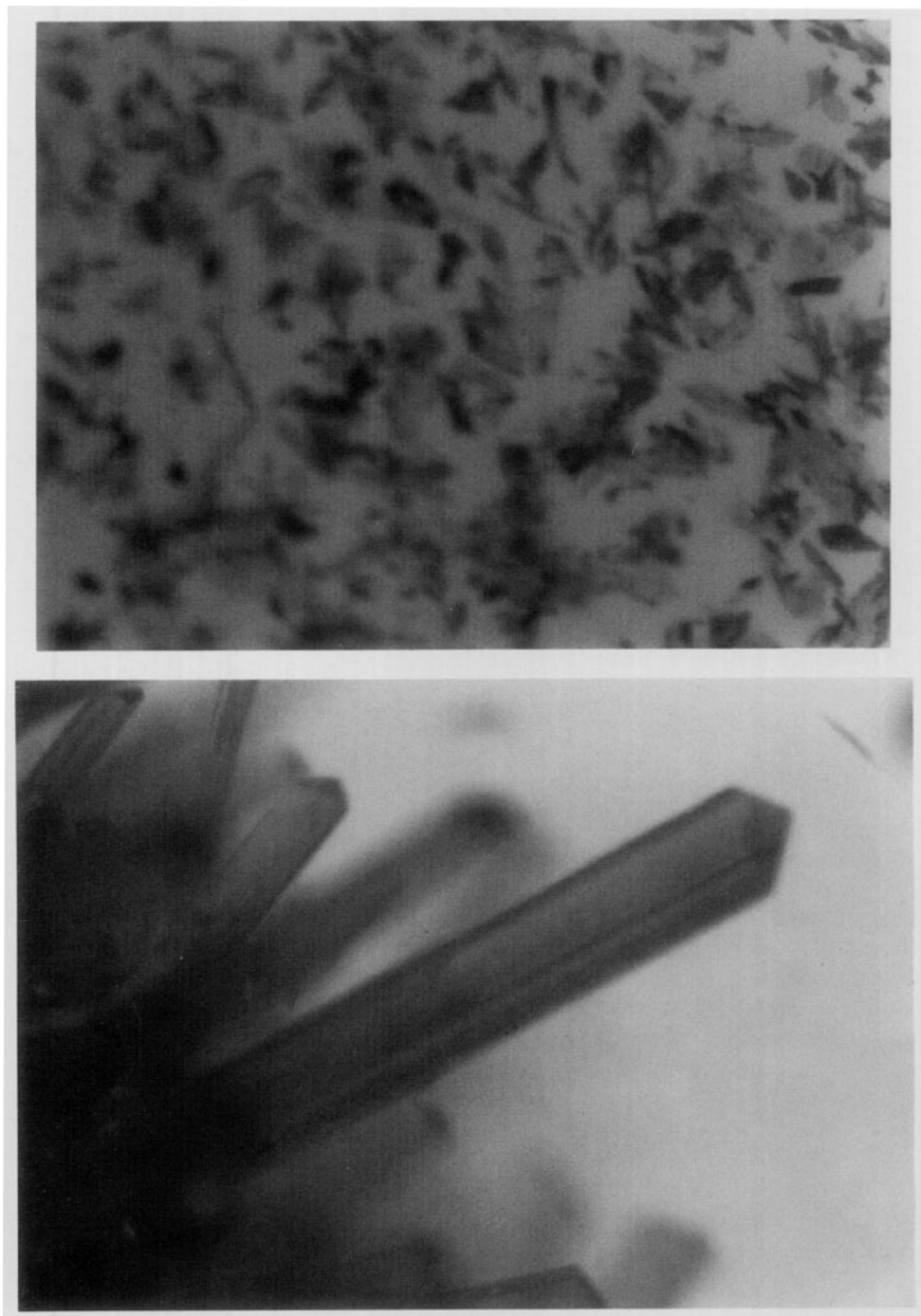


FIG. 1. The differences in crystal morphology of $M^{\text{II}}(1,4\text{-C}_4\text{H}_4\text{N}_2)(\text{C}_4\text{O}_4)(\text{OH}_2)_4$ grown without (top) and with the gel as a diffusion medium (bottom).

Single crystals suitable for X-ray study were chosen from such samples by crushing the tube containing the hardened gel and mechanically isolating them. The homogeneity of the bulk product was confirmed by comparison of the observed X-ray powder diffraction (XRD) pattern with that calculated using single crystal diffraction pattern *vide infra*. In addition, the XRD pattern observed for the product obtained from the gel is in full agreement with that

recorded for the powder material obtained from solution without employing silica gel in the reaction.

We have since found that the Fe, Co, Ni, and Zn analogues may be prepared following the procedure outlined above but without using the gel. Elemental analysis data of these compounds are presented in Table I.

Crystallography. A green crystal of $\text{Cu}^{\text{II}}(1,4\text{-C}_4\text{H}_4\text{N}_2)(\text{C}_4\text{O}_4)(\text{OH}_2)_4$, prepared using the silica gel, with dimen-

TABLE 1

Calculated and Found Elemental Analyses for $M^{II}(1,4-C_4H_4N_2)(C_4O_4)(OH_2)_4$ ($M = Fe, Co, Ni, Cu, \text{ and } Zn$)

<i>M</i>	C	H	N	M
Fe	30.02	3.78	8.75	17.45
	30.05	4.04	8.68	17.46
Co	29.74	3.74	8.67	18.24
	29.07	3.36	8.51	16.97
Ni	28.18	4.14	8.22	17.22
	28.60	4.08	7.90	17.18
Cu	29.32	3.69	8.55	19.39
	29.61	3.74	8.72	19.49
Zn	29.16	3.67	8.50	19.84
	29.18	3.73	8.34	19.10

sions $0.20 \times 0.10 \times 0.25 \text{ mm}^3$ was selected for the structure determination. Crystal data, data collection, solution, and refinement information are presented in Table 2. Atomic positional parameters, and selected interatomic distances and angles are given, respectively, in Tables 3 and 4. The Fe, Co, Ni, and Zn analogues were found to be isomorphous with the Cu compound.

RESULTS AND DISCUSSION

Description of structure. X-ray single crystal analysis performed on the title compound reveal the presence of squarate anions ($C_4O_4^{2-}$) hydrogen bonded to $Cu(1,4-C_4H_4N_2)(OH_2)_4$ polymeric chains to form a 3-D solid network. Each of the pyrazine ligands bridge two copper centers through the nitrogen ($Cu1-N1p = 2.057(3) \text{ \AA}$) to form linear chains along the crystallographic *x*-axis. Four water molecules are bonded in the equatorial positions, with respect to the chains, where two (O1w and O1wA) form significantly longer bonds to copper ($Cu1-O1w = 2.320(2) \text{ \AA}$) than the remaining two (O2w and O2wA) where $Cu1-O2w = 1.996(2) \text{ \AA}$. Thus leading to a copper center that has an orthorhombically distorted geometry with three different bonded distances to pyrazine and water, with the angles all close to 90° ($N1p-Cu1-O1w = 93.6(1)^\circ$, $N1p-Cu1-O2w = 89.9(1)^\circ$, $N1p-Cu1-O1wA = 86.4(1)^\circ$, $O1w-Cu1-O2w = 88.3(1)^\circ$, $O1wA-Cu1-O2w = 91.7(1)^\circ$). The pyrazine ligands are twisted, relative to the diagonal containing O2w, Cu1, O2wA, to make a dihedral angle $C1p-N1p-Cu1-O2w$ of $32.0(2)^\circ$.

In the overall structure, each squarate anion forms a total of eight hydrogen-bonded contacts to four such chains, where every squarate oxygen forms two hydrogen bonds to two different water hydrogens belonging to different chains as shown in Fig. 2b. Although the hydrogen-bonding distances (four symmetry inequivalent distances are: $O1W-H \cdots O1S = 2.803(3)$, $O2W-H \cdots O1S =$

TABLE 2
Experimental Crystallographic Data

A. Crystal data	
Empirical formula	$C_8H_{12}CuN_2O_8$
Crystal size (mm)	$0.20 \times 0.10 \times 0.25$
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 6.887(3) \text{ \AA}$ $b = 11.141(4) \text{ \AA}$ $c = 7.545(3) \text{ \AA}$ $\beta = 90.68(3)^\circ$
Volume	$578.9(4) \text{ \AA}^3$
Z	2
Formula weight	327.7
Density (calc.)	1.880 Mg/m^3
Absorption coefficient	1.927 mm^{-1}
B. Data collection	
Diffractometer used	Siemens R3m/V
Radiation	$MoK\alpha$ ($\lambda = 0.71073 \text{ \AA}$)
Temperature (K)	298
Scan type	ω
Scan speed	Variable; 1.50 to $14.65^\circ/\text{min}$.
Scan range (ω)	1.60°
Background measurements	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	3 measured every 47 reflections
Index ranges	$-8 \leq h \leq 8$, $-1 \leq k \leq 13$, $0 \leq l \leq 8$
Reflections collected	1217
Independent reflections	1016 ($R_{\text{int}} = 1.59\%$)
Observed reflections	874 ($F > 4.0\sigma(F)$)
Absorption correction	Psi scan of 6 reflections
C. Solution and refinement	
System used	Siemens SHELXTL PLUS (PC Version)
Solution	Direct methods
Refinement method	Full-matrix least-squares
Quality minimized	$\sum w(F_o - F_c)^2$
Hydrogen atoms	Riding model, isotropic <i>U</i> fixed at 1.2 times bonding partner's isotropic <i>U</i>
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0006F^2$
Number of parameters	89
Refined	
Final <i>R</i> indices (obs. data)	$R = 2.63\%$, $wR = 3.93\%$
<i>R</i> indices (all data)	$R = 3.32\%$, $wR = 4.11\%$
Goodness-of-fit	1.28
Largest and mean Δ/σ	0.000, 0.000
Date-to-parameter ratio	9.8:1
Largest difference peak	0.29 e\AA^{-3}
Largest difference hole	-0.29 e\AA^{-3}

$2.680(3)$, $O1W-H \cdots O2S = 2.747(3)$, and $O2W-H \cdots O2S = 2.658(3)$, of this compound are considered to be medium to weak in their strength (6), this arrangement results in a tightly held 3-D network that is found to be insoluble in aqueous and common nonaqueous media, which made it difficult to obtain large crystals without employing silica gel as the reaction medium.

TABLE 3
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for $\text{Cu}(\text{C}_4\text{O}_4)(1,4\text{-C}_4\text{H}_4\text{N}_2)(\text{OH}_2)_4$

	x	y	z	U(eq)
Cu(1)	5000	5000	5000	20(1)
O(1W)	4816(3)	6366(2)	2682(3)	31(1)
O(2W)	5066(3)	3686(2)	3203(2)	26(1)
N(1P)	7986(3)	5019(2)	5085(3)	21(1)
C(1P)	9005(4)	6007(3)	4674(4)	25(1)
C(2P)	8992(4)	4018(3)	5412(4)	25(1)
O(1S)	7163(3)	6055(2)	-293(3)	33(1)
C(1S)	8717(4)	5474(3)	-140(3)	24(1)
O(2S)	8441(3)	3524(2)	1547(3)	32(1)
C(2S)	9288(4)	4336(2)	699(3)	24(1)

Crystal growth. The success of the gel method for crystal growth is believed to be due to at least two factors (4g). First, since the crystals are grown by diffusion, the concentration gradient of solutes at the interface is self-regulated, as required by the crystal growth process. A second key factor is that the presence of small cavities within the gel allows the isolation of solute molecules

TABLE 4
Selected Bond Lengths (\AA) and Angles ($^\circ$)

Bond lengths			
Cu(1)–O(1W)	2.320(2)	Cu(1)–O(2W)	1.996(2)
Cu(1)–N(1P)	2.057(3)	N(1P)–C(1P)	1.343(3)
N(1P)–C(2P)	1.335(3)	C(1P)–C(2PA)	1.381(4)
O(1S)–C(1S)	1.255(4)	C(1S)–C(2S)	1.469(4)
Angles			
O(1W)–Cu(1)–O(2W)	88.3(1)	O(1W)–Cu(1)–N(1P)	93.6(1)
O(2W)–Cu(1)–N(1P)	89.9(1)	O(1W)–Cu(1)–O(1WA)	180.0(1)
O(2W)–Cu(1)–O(1WA)	91.7(1)	N(1P)–Cu(1)–O(1WA)	86.4(1)
N(1P)–Cu(1)–O(2WA)	90.1(1)	N(1P)–Cu(1)–N(1PA)	180.0(1)
O(1WA)–Cu(1)–N(1PA)	93.6(1)	Cu(1)–N(1P)–C(1P)	121.7(2)
Cu(1)–N(1P)–C(2P)	120.9(2)	C(1P)–N(1P)–C(2P)	117.1(2)

leading to suppressed nucleation, thus leading to controlled crystal growth. We find that the gel method for crystal growth is well suited for the crystal growth of coordination solids and other assembled materials for the following reasons: (a) the gels could be prepared from silica materials or organic polymers using aqueous and nonaqueous techniques under aerobic or anaerobic conditions; (b) a large number of polymers exist which can be prepared as gels and thus an inert gel can be employed as a diffusing medium or a reaction medium; (c) many

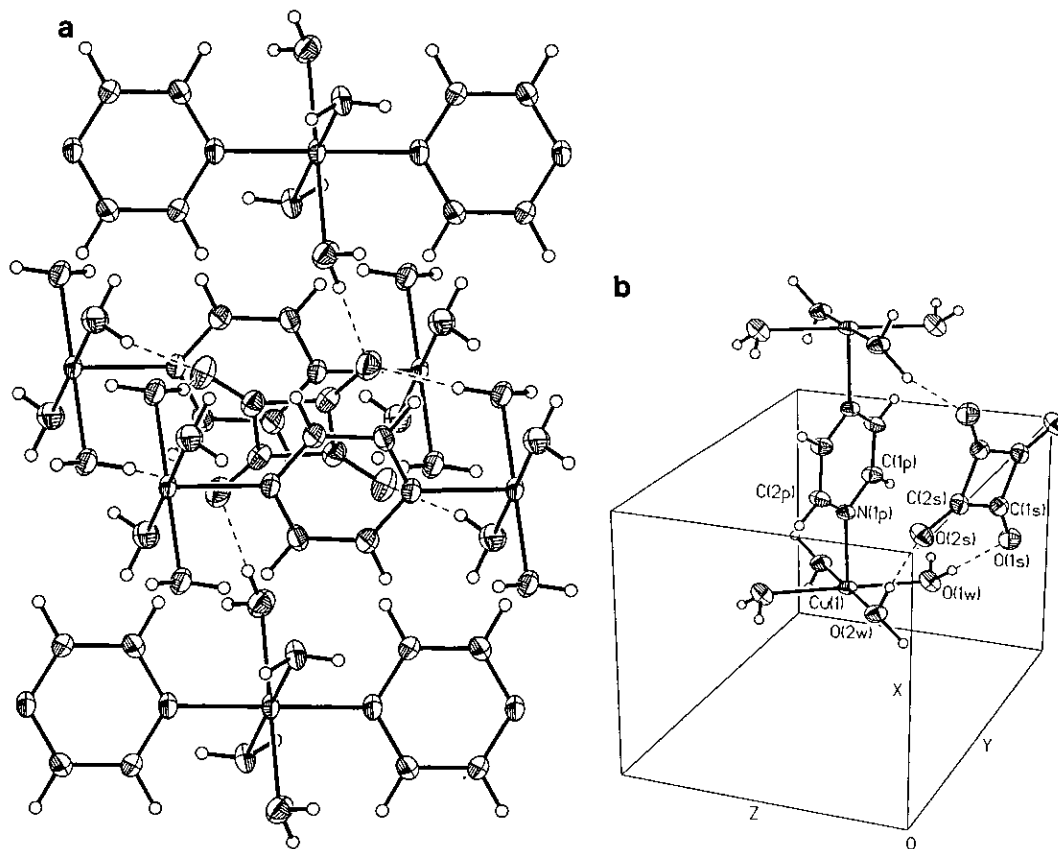


FIG. 2. (a) Perspective view of $\text{M}^{\text{II}}(1,4\text{-C}_4\text{H}_4\text{N}_2)(\text{C}_4\text{O}_4)(\text{OH}_2)_4$ showing the atom labeling scheme for the crystallographically distinct unit. (b) A plot showing how the squarate anion is hydrogen bonded to four chains. Thermal ellipsoids at the 50% probability level. Hydrogen bonding is indicated by dashed lines.

conditions, such as type of gel, porosity of the gel, concentration gradients, solvents, diffusion rates, and temperature can be controlled to provide the appropriate medium for the formation of crystalline materials; (d) the starting materials for the synthesis of the desired solid are soluble and compose a two-component assembly system, where the components are retained in the product and do not decompose as a result of the crystallization process.

CONCLUDING REMARKS

This study illustrates the use of polymeric matrices in the room-temperature preparation of covalently linked solids. The attainment of large single crystals of $\text{Cu}(1,4\text{-C}_4\text{H}_4\text{N}_2)(\text{C}_4\text{O}_4)(\text{OH}_2)_4$ in silica gel, which otherwise was not possible, points to the possible extension of this technique to designed solids with predetermined topologies, such as microporous materials. Recent experiments in this direction revealed that replacing two of the water ligands on the metal center with ligands incapable of hydrogen bonding results in the formation 3-D cage solid networks (5, 7). Given that pyrazine-bridged materials have been widely studied (8) for their magnetic exchange, we are currently attempting to evaluate such properties in the presence of the squarate anions.

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