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ORIGINAL PAPER

Dinuclear Complexes and a One-dimensional Chain Involving Difunctional Ligands Containing the Acetylacetonate Functionality

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Abstract Systems containing two acetylacetonate (acac) ligands separated by an aromatic spacer (**1**–**3**) react with Cu(II) in the presence of bidentate nitrogen ligands to form crystalline, capped, dinuclear (zero-dimensional) structures (**6**–**8**). Noncovalent interactions between stacked aromatic ligands on adjacent molecules in **7** and **8** produce one-dimensional chains in the crystal. Molecules **1**–**3** fail to produce crystalline, one-dimensional chains with covalent metal-organic bonding on reaction with Cu(II) alone. System **5**, which contains a single acac ligand and a pyridyl nitrogen, forms a crystalline, one-dimensional chain on reaction with Cu(II) in the presence of a bidentate nitrogen ligand (**9**). The covalent bonding ribbon of the chain passes from acac to Cu(II) to the pyridyl nitrogen and back to acac. The phenanthroline ligands in **9** provide noncovalent bonding with adjacent chains in the crystal to produce a two-dimensional layered structure.

Keywords Acetylacetonate ligands · Aromatic stacking · Noncovalent bonding · One-dimensional chains

Introduction

Metal-organic bonds [1–3], like hydrogen bonds [4, 5], are used commonly as the basis for the formation of organized solids that are held together by noncovalent bonds. The low energy of the hydrogen bond, however, leads to two negative factors not shared by metal-organic bonds. First, during the process of recrystallization, hydrogen bonds can form, break, and reform, with the result that multiple, interpenetrating, multidimensional structures can grow around and through each other and fill crystalline voids. The resulting materials are nonporous. In one example from our own work, the tetracarboxylic acid Si[4-$(CO_2H)C_6H_4]_4$ crystallizes as six separate, interpenetrating hydrogen-bonded networks [6]. Second, even when voids are left during crystallization, they usually are filled with solvent or other guests. Attempts at thermal removal of the guests often result in collapse of a crystal based on hydrogen bonding connections, with concomitant loss of porosity. Architectures based on hydrogen bonds thus are not ideally suited for forming robust, porous solids, which may be suitable for catalysis and separations.

The intermediate strength of many metal-organic bonds has made them the frequent basis for the formation of porous materials such as metal-organic frameworks [1–3]. The carboxylic acid functionality again is the most common organic connector, but now in its ionized carboxylate form, bonded to a metal. When translated into two and three dimensions, such motifs can create complex structures containing significant voids. Such systems often are robust to heating, for example, during the process of solvent removal. Thus metal-organic frameworks have proved to be superior to hydrogen-bonded networks in creating solids with large voids.

The vast majority of metal-organic frameworks has contained the carboxylate building block, and the remaining examples usually contained pyridine functionalities. In 1984, Maverick and co-workers [7–9] reported that organic-connected acetylacetonate (acac) ligands

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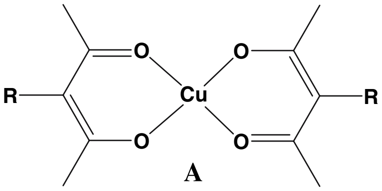
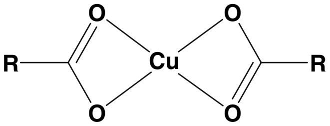
form dinuclear complexes with copper in macrocyclic structures reminiscent of the pyridine-based structures of Fujita, Stang, and others [10]. By placing two acac groups onto a single molecule with a bent geometry, Maverick et al. prepared dimers linked by copper ions. These dimers proved to be soluble in organic solvents and capable of serving as molecular hosts. A pair of acac ligands (**A**) bear a formal similarity to a pair of carboxylates (**B**) in their copper complexes. The group R serves as a connector to a second acac ligand, so that either cyclic or infinite arrays could be formed. Maverick's bent molecules [7–9] led to cyclic (finite) arrays, which might be termed the zeroth order structure of a topological family.

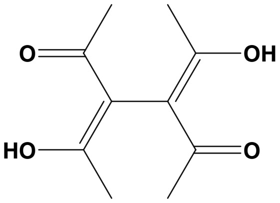


A



B

The structural key is the presence of two acac groups in the same molecule. The most studied example of this motif also has been the simplest, tetraacetylethane (**C**, shown in its dihydroxy tautomer), in which the two acac groups are attached to each other directly at their 3 positions [11–13]. In one case [11] noncrystalline materials were obtained with Cu(II), in a second example [12] a molecular square was obtained with Co(II), and in a third [13] a hydrogen-bonded chain structure was obtained with Cu(II) and dipyridyl co-reactants. Domasevitch [14], Maverick [15, 16], and their co-workers have used acac linked to pyridine to produce two-dimensional metal-organic polymers. In the present study, we used linear molecules containing acac and a second ligating functionality to explore whether acac can participate in dinuclear and higher order (infinite) arrays.



C

Experimental

Chemicals

4,4′-Diformylbiphenyl [17], 2,2,2-trimethoxy-4,5-dimethyl-1,3-dioxaphospholene [18, 19], and 4-(3′-acetylacetonato)pyridine (**5**) [15] were synthesized according to the literature and were characterized by GC-MS and NMR spectra, which matched the reported data. Other cited materials were available commercially.

Synthesis of Monomers

1,4-Di-(3′-acetylacetonato)benzene ***(1)*** *[20, 21]*

A 250 mL flask containing a magnetic stirrer and terephthalaldehyde (13.4 g, 0.1 mol) was placed in an ice bath, subjected to vacuum, and refilled with nitrogen for three cycles. Anhydrous dichloromethane (100 mL) was transferred into the flask by a cannula. Freshly prepared 2,2,2-trimethoxy-4,5-dimethyl-1,3-dioxaphospholene (50 g, 0.24 mol) was added dropwise. The ice bath was removed, and the mixture was stirred overnight. The volatiles were removed by vacuum, and anhydrous CH_3OH (150 mL) was admitted through a cannula. The mixture was heated to reflux for 24 h and cooled. The volatiles were removed under vacuum, and the solid was recrystallized in benzene to give a white solid: 18.5 g (67%); GC-MS, *m/z* 274 (M^+); NMR δ_H (400 MHz; $CDCl_3$; Me_4Si) 16.68 (2 H, s), 7.20 (4 H, s), 1.91 (12 H, s); δ_C (100 MHz; $CDCl_3$; Me_4Si) 190.7, 136.3, 131.6, 114.8, 24.4.

1,4-Di-[methylene-3′-(acetylacetonato)]benzene ***(2)*** *[22, 23]*

To a stirred mixture of chlorotrimethylsilane (25.6 mL, 0.2 mol), NaI (30 g, 0.2 mol), 2,4-pentanedione (4 g, 0.04 mol), and acetonitrile (200 mL) in a 500 mL flask at 0 °C was added dropwise an acetonitrile solution of terephthalaldehyde (2.68 g, 0.02 mol). The mixture was stirred for 10 h at room temperature and then for 24 h at 68 °C. After addition of water (200 mL), the mixture was extracted with ether. The combined ether extracts were washed with aqueous $Na_2S_2O_3$ solution to remove the liberated iodine, washed with brine and fresh water, and dried ($MgSO_4$). Solvents were removed by rotary evaporation at room temperature. The white solid was recrystallized from *tert*-butanol to give white plate-like crystals: 5.0 g (83%). Spectra were in agreement with the literature [23].

4,4′-Di-(3′-acetylacetonato)biphenyl ***(3)***

A 250 mL flask containing a magnetic stirrer and 4,4′-diformylbiphenyl (5 g, 24 mmol) was placed in an ice bath, subjected to vacuum, and refilled with nitrogen for three cycles. Anhydrous dichloromethane (50 mL) was transferred into the flask by a cannula. Freshly prepared 2,2,2-trimethoxy-4,5-dimethyl-1,3-dioxaphospholene (15 g, 71 mmol) was added dropwise. The ice bath was removed, and the mixture was stirred overnight. The volatiles were removed under vacuum, and anhydrous CH_3OH (50 mL) was admitted through a cannula. The mixture was heated to reflux for 24 h and cooled. The volatiles were removed by rotary evaporation, and the residue was dried at 80 °C (0.5 torr) for 24 h. A white solid was collected, and the remaining residue was discarded. The solid was recrystallized from benzene to give white crystals: 1.5 g (18%); GC-MS, *m/z* 350 (M^+); NMR, δ_H (400 MHz; $CDCl_3$; Me_4Si) 16.72 (1 H, s), 7.67 (4 H, m), 7.28 (4 H, m), 1.95 (12 H, s); δ_C (100 MHz; $CDCl_3$; Me_4Si) 191.1, 139.7, 136.4, 131.8, 127.6, 115.0, 24.6. Anal. Calcd. (found) for $C_{22}H_{22}O_4$: C, 75.41 (75.49); H, 6.33 (6.41); N, 0.00 (0.01).

Methyl 4-(3′-acetylacetonato)benzoate

A 250 mL flask containing a magnetic stirrer and methyl 4-formylbenzoate (11 g, 67 mmol) was placed in an ice bath, subjected to vacuum, and refilled with nitrogen for three cycles. Anhydrous dichloromethane (150 mL) was transferred into the flask by a cannula. Freshly prepared 2,2,2-trimethoxy-4,5-dimethyl-1,3-dioxaphospholene (28 g, 133 mmol) was added dropwise. After 2 h, the ice bath was removed, and the solution was stirred overnight. The volatiles were removed by vacuum, and anhydrous CH_3OH (150 mL) was admitted through a cannula. The mixture was heated to reflux for 3 h. The volatiles were removed by rotary evaporation, and the residue was dried at 80 °C (0.5 torr) for 24 h. A white solid was collected, and the remaining residue was discarded. The solid was recrystallized from benzene to give white crystals: 8.1 g (55%); GC-MS, *m/z* 234 (M^+); NMR, δ_H (400 MHz; $CDCl_3$; Me_4Si) 16.66 (1 H, s), 8.01 (2 H, d), 7.23 (2 H, d), 3.88 (3 H, s), 1.85 (6 H, s); δ_C (100 MHz; $CDCl_3$; Me_4Si) 190.8, 166.9, 142.1, 131.5, 130.3, 129.6, 114.5, 52.4, 24.3.

4-(3′-Acetylacetonato)benzoic acid ***(4)*** *[24]*

A 100 mL flask containing a magnetic stirrer, 4-(3′-acetylacetonato)benzoate (0.2 g, 0.85 mmol) in acetone (5 mL), pig liver esterase (60 mg, 1440 units), and a buffer solution (50 mL, 0.05 M, pH = 6.5) of KH_2PO_4/KOH was placed into a water bath (32 °C). The mixture was stirred for 4 h, and the volume of the solution was reduced under vacuum. The resulting solid was extracted by ether. The product was purified by flash chromatography (hexane/ether) to give a white solid: 140 mg (75%); mp 197.5 °C; GC-MS, *m/z* 220 (M^+); NMR, δ_H (400 MHz; acetone-d_6; Me_4Si) 16.90 (1 H, s), 8.10 (2 H, d), 7.46 (2 H, d), 1.90 (6 H, s); δ_C (100 MHz; acetone-d_6; Me_4Si) 191.6, 167.5, 142.8, 132.4, 130.9, 129.6, 115.4, 24.3. Anal. Calcd. (found) for $C_{12}H_{12}O_4$: C 64.45 (65.39); H 5.49 (5.47).

Synthesis of Polymers

Attempted Chelate Polymer Formation of 1,4-di-(3′-acetylacetonato)benzene ***(1)****, 1,4-di-[methylene-3′-(acetylacetonato)]benzene* ***(2)****, and 4-(3′-acetylacetone)benzoic acid* ***(4)***

To a 250 mL flask containing a magnetic stirrer was added 1,4-di-[methylene-3′-(acetylacetonato)]benzene (2) (0.6 g, 2 mmol) in dichloromethane (15 mL). Tetraamminecopper(II) sulfate (0.46 g, 2 mmol) in water (15 mL) was added dropwise [25, 26]. After the solution had been stirred for 30 min, a gray, noncrystalline precipitate was collected by filtration and washed with water. Chelate polymerizations of 1,4-di-(3′-acetylacetonato)benzene ***(1)*** and of 4-(3′-acetylacetonato)benzoic acid ***(4)*** with tetraamminecopper(II) sulfate were carried out in a similar fashion [27]. The products were amorphous materials that did not dissolve in water or in common organic solvents. Single crystals of these materials failed to grow by slow diffusion of the reactants in two solutions.

Dinuclear Copper Complex of 1,4-di-(3′-acetylacetonato)benzene with Tetramethylethylenediamine ***(6)***

To a 50 mL flask containing a magnetic stirrer and acetone (10 mL) was added dropwise first copper perchlorate hexahydrate (185 mg, 0.5 mmol) and then tetramethylethylenediamine (58 mg, 0.5 mmol) in acetone (10 mL). After addition was complete, the mixture was stirred for another 5 min, and 1,4-di-(3′-acetylacetonato)benzene (**1**, 69 mg, 0.25 mmol) in acetone (5 mL) was added slowly and dropwise. The mixture was stirred for another 10 min, and NaOH (20 mg) in CH_3OH was added. A blue precipitate appeared. The mixture was subjected to ultrasonic sound for several hours until the solution became clear blue. The solution was reduced to 3 mL under vacuum. Ether was added, and a dark blue precipitate was collected and dried by vacuum: 154 mg (74%). A sample of the product (30 mg) was dissolved in the minimum amount of acetone and was transferred to a small vial, which was placed in a large capped vial with ether/dimethylformamide. After several days, dark purple crystals were collected. Anal. Calcd. (found) for $(C_{16}H_{16}O_4)Cu_2(C_6H_{16}N_2)_2(ClO_4)_2$: C, 40.48 (40.63); H, 5.82 (5.71); N, 6.74 (6.50).

Dinuclear Copper Complex of 1,4-di-(3′-acetylacetonato)benzene with 2,2′-bipyridine ***(7)***

To a 50 mL flask containing a magnetic stirrer and acetone (10 mL) was added dropwise first copper perchlorate hexahydrate (185 mg, 0.5 mmol) and then an acetone solution (10 mL) of 2,2′-bipyridine (78 mg, 0.5 mmol). After addition was complete, the mixture was stirred for another 5 min, and 1,4-di-(3′-acetylacetonato)benzene (**1**, 69 mg, 0.25 mmol) in acetone (5 mL) was added slowly and dropwise. The mixture was stirred for another 10 min, and NaOH (20 mg) in CH_3OH was added. The precipitate was collected and dried by vacuum: 195 mg (86%). A portion of the product (30 mg) was dissolved in the minimum amount of dimethyl sulfoxide (DMSO) and was transferred to a small vial. The vial was placed in a large capped vial with acetone/DMSO. One week later, dark blue single crystals were collected for X-ray crystallography. The crystals were dried under vacuum for 24 h to remove acetone and DMSO prior to elemental analysis. Anal. Calcd. (found) for $(C_{16}H_{16}O_4)Cu_2(C_{10}H_8N_2)_2(ClO_4)_2$: C, 47.48 (47.34); H, 3.54 (3.50); N, 6.15 (5.97).

Dinuclear Copper Complex of 4,4′-di-(3′-acetylacetonato)biphenyl with 2,2′-bipyridine ***(8)***

To a 50 mL flask containing a magnetic stirrer and acetone (10 mL) was added dropwise first copper perchlorate hexahydrate (185 mg, 0.5 mmol) and then an acetone solution (10 mL) of 2,2′-bipyridine (78 mg, 0.5 mmol). After addition was complete, the mixture was stirred for another 5 min and 4,4′-di-(3′-acetylacetonato)biphenyl (87 mg, 0.25 mmol) in acetone (5 mL) was added slowly and dropwise. The mixture was stirred for another 10 min, and NaOH (20 mg) in CH_3OH was added. The precipitate was collected and dried under vacuum: 204 mg (83%). A portion of the product (30 mg) was dissolved in the minimum amount of dimethylformamide (DMF) and was transferred to a small vial. The vial was put in a large capped vial with ether/DMF. Four days later, dark blue single crystals were collected. Anal. Calcd. (found) for $(C_{22}H_{20}O_4)Cu_2(C_{10}H_8N_2)_2(C_3H_7NO)_{1.5}(ClO4)_2$: C, 50.94 (50.81); H, 4.27 (4.39); N, 7.03 (7.03).

Table 1 Crystal data and structure refinement for **6**

Identification code	92q
Empirical formula	C56 H96 Cl4 Cu4 N8 O24
Formula weight	1661.37
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 27.8046(17) Å, b = 9.7529(6) Å, β = 90.3700(10)°, c = 13.2329(8) Å
Volume	3588.4(4) Å^3
Z, Calculated density	2, 1.538 mg/m^3
Absorption coefficient	1.397 mm^{-1}
F(000)	1728
Crystal size	0.452 × 0.442 × 0.088 mm
Theta range for data collection	1.46 to 29.17°
Limiting indices	–37 ≤ h ≤ 37, –12 ≤ k ≤ 13, –18 ≤ l ≤ 18
Reflections collected/unique	21531/4473 [R(int) = 0.0613]
Completeness to theta = 29.17	92.1%
Absorption correction	Integration
Transmission factors	0.8792 (maximum) and 0.5466 (minimum)
Refinement method	Full-matrix least-squares on F2
Data/restraints/parameters	4473/0/223
Goodness-of-fit on F^2	1.033
Final R indices [I > 2sigma(I)]	R1 = 0.0355, wR2 = 0.0909
R indices (all data)	R1 = 0.0446, wR2 = 0.0939
Largest diff. peak and hole	0.454 and –0.487 e-/Å^{-3}

Table 2 Crystal data and structure refinement for **7**

Identification code	s51q1m
Empirical formula	C23 H28 Cl Cu N2 O8 S
Formula weight	591.52
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 11.0425(9) Å, α = 104.8720(10)°, b = 11.3196(10) Å, β = 101.6620(10)°, c = 12.0961(10) Å, γ = 108.1070(10)°
Volume	1321.94(19) Å^3
Z, Calculated density	2, 1.486 Mg/m^3
Absorption coefficient	1.055 mm^{-1}
F(000)	612
Crystal size	0.322 × 0.214 × 0.082 mm
Theta range for data collection	1.83 to 29.28°
Limiting indices	$-14 \le h \le 14$, $-15 \le k \le 14$, $-16 \le l \le 15$
Reflections collected/unique	11965/6254 [R(int) = 0.0657]
Completeness to theta = 29.28	86.6%
Absorption correction	Integration
Transmission factors	0.9221 (maximum) and 0.7400 (minimum)
Refinement method	Full-matrix least-squares on F2
Data/restraints/parameters	6254/0/331
Goodness-of-fit on F^2	1.094
Final R indices [I > 2sigma(I)]	R1 = 0.0762, wR2 = 0.2119
R indices (all data)	R1 = 0.1124, wR2 = 0.2733
Largest diff. peak and hole	1.331 and –1.360 e-/Å^{-3}

*One-dimensional Polymer of 4-(3′-acetylacetonato)pyridine **(9)** with 1,10-phenanthroline and Cu(II)*

Copper perchlorate hexahydrate (91 mg, 0.246 mmol) and 1,10-phenanthroline (45 mg, 0.25 mmol) were dissolved in a combinatory solution of CH_3OH (15 mL) and DMF (5 mL). The clear blue-green solution was subjected to ultrasonic sound for 10 min. 4-(3′-Acetylacetonato)pyridine (**5**, 44 mg, 0.25 mmol) was dissolved in CH_3OH (20 mL). In five glass tubes, the CH_3OH solution (4 mL) of the acetylacetone derivative **5** was carefully layered upon the combinatory solution. After one week, green crystals appeared at the interface and fell to the bottom.

Crystal Structures

Crystal data are presented in Table 1 for **6**, Table 2 for **7**, Table 3 for **8**, and Table 4 for **9**. Experimental details are given in the Supplementary Materials.

Results and Discussion

We prepared five molecules that contain one or two acac functionalities that are positioned at opposite ends (1,4 or para) of a connector (Scheme 1). Such a juxtaposition is intended to discourage finite cyclic arrays in favor of infinite linear arrays. In contrast to tetraacetylethane (**C**), the acac groups here are separated by a spacer: 1,4-phenylene in **1**, 1,4-phenylenebismethylene in **2**, and 4,4′-biphenylene in **3**. Molecule **4** contains acac and the carboxylic acid functionality separated by 1,4-phenylene, and **5** contains acac para to a pyridine nitrogen [14–16]. Reaction with Cu(II) salts failed to yield crystalline polymer. Only amorphous materials formed, as previously observed for **1** [20]. The simple phenylene compound **1**, however, reacted with Cu(II) in the presence of bidentate nitrogen bases (either *N,N,N′,N′*-tetramethylethane-1,2-diamine or 2,2′-bipyridine) to form dinuclear complexes, **6** (Fig. 1) and **7** (Fig. 2). No useful products were isolated from the substrate **2** in the presence of a chelate. The biphenylene substrate **3** also produced a dinuclear complex, **8** (Fig. 3), on reaction with 2,2′-bipyridine. These finite complexes are considered to be zero dimensional. No materials were isolated from the reaction of the mixed carboxylate/acac substrate **4** in the presence of a chelate. The mixed pyridine/acac substrate **5** formed an infinite one-dimensional zigzag chain with the unit structure **9** (Fig. 4) in the presence of 1,10-phenanthroline.

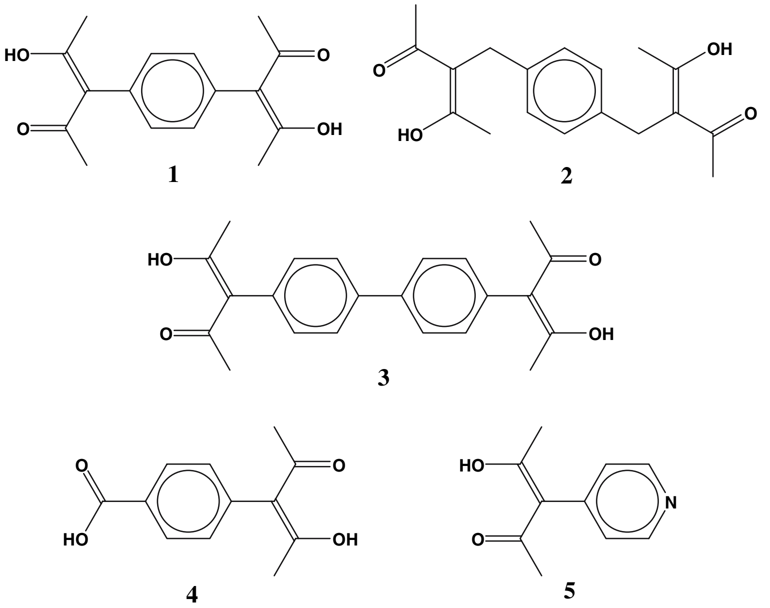
Table 3 Crystal data and structure refinement for **8**

Identification code	s81q1m
Empirical formula	C24 H25 Cl Cu N3 O7
Formula weight	566.46
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.832(3) Å, α = 88.258(5)°, b = 10.876(3) Å, β = 83.332(5)°, c = 11.551(4) Å, γ = 69.298(4)°
Volume	1264.2(7) $Å^3$
Z, Calculated density	2, 1.488 Mg/m^3
Absorption coefficient	1.018 mm^{-1}
F(000)	584
Crystal size	0.410 × 0.376 × 0.030 mm
Theta range for data collection	1.78 to 28.58°
Limiting indices	$-14 \le h \le 13$, $-14 \le k \le 14$, $-14 \le l \le 15$
Reflections collected/unique	11286/5738 [R(int) = 0.0253]
Completeness to theta = 28.58	88.7%
Absorption correction	Integration
Transmission factors	0.9696 (maximum) and 0.6891 (minimum)
Refinement method	Full-matrix least-squares on F2
Data/restraints/parameters	5738/0/336
Goodness-of-fit on F^2	1.041
Final R indices [I > 2sigma(I)]	R1 = 0.0446, wR2 = 0.1173
R indices (all data)	R1 = 0.0584, wR2 = 0.1282
Largest diff. peak and hole	0.983 and –0.673 e-/$Å^{-3}$

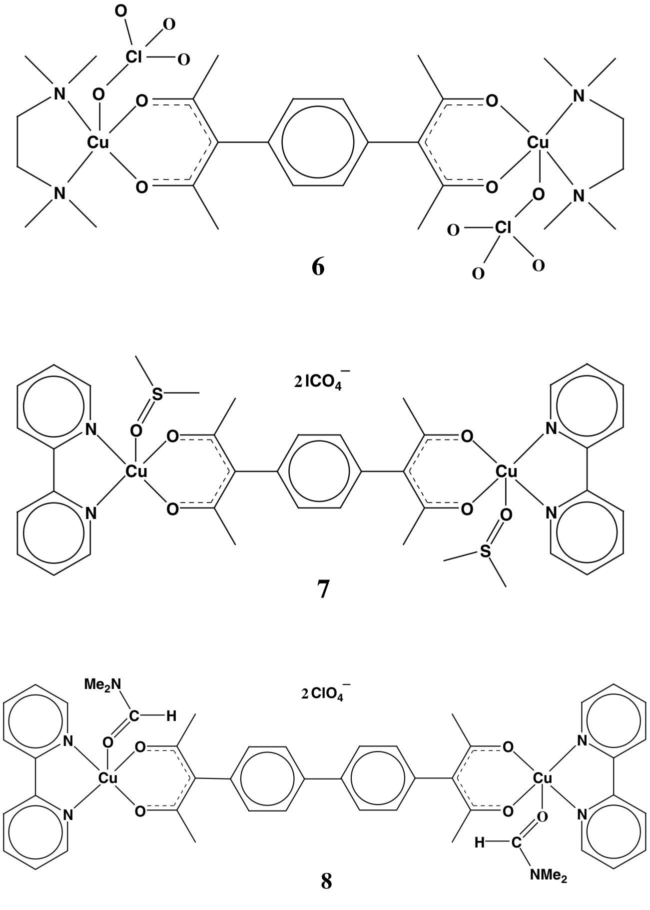
Table 4 Crystal data and structure refinement for **9**

Identification code	s20r1m
Empirical formula	C22 H18 Cl Cu N3 O6
Formula weight	519.38
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Cmca
Unit cell dimensions	a = 11.3015(8) Å, b = 25.3610(18) Å, c = 15.2995(11) Å
Volume	4385.1(5) $Å^3$
Z, Calculated density	8, 1.573 Mg/m^3
Absorption coefficient	1.163 mm^{-1}
F(000)	2120
Crystal size	0.160 × 0.142 × 0.082 mm
Theta range for data collection	1.61 to 28.70°
Limiting indices	$-14 \le h \le 14$, $-32 \le k \le 34$, $-20 \le l \le 19$
Reflections collected/unique	19818/2858 [R(int) = 0.1070]
Completeness to theta = 28.70	96.1%
Absorption correction	Integration
Transmission factors	0.9194 (maximum) and 0.8152 (minimum)
Refinement method	Full-matrix least-squares on F2
Data/restraints/parameters	2858/0/218
Goodness-of-fit on F^2	1.033
Final R indices [I > 2sigma(I)]	R1 = 0.0457, wR2 = 0.1194
R indices (all data)	R1 = 0.0758, wR2 = 0.1353
Largest diff. peak and hole	0.587 and –0.929 e-/$Å^{-3}$

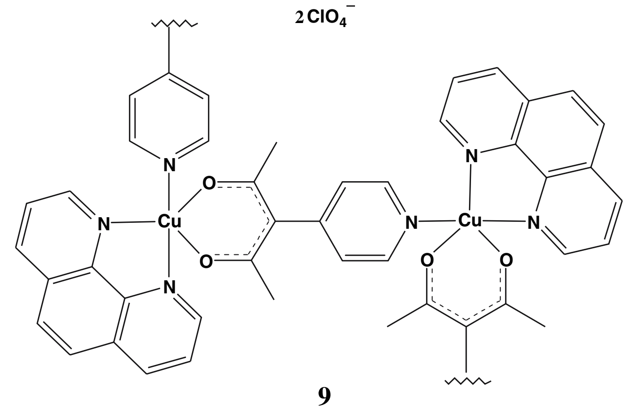
Scheme 1



1 2 3 4 5



6 7 8



9

The acetylacetonate functionality, in contrast to carboxylate, exhibited little ability in this study to form infinite chains as isolable, crystalline substances. Crystal formation of infinite chains or networks is a delicate function of the strengths of the bonds forming between the organic and inorganic components. Reversibility is a critical characteristic of the crystallization process, in order that errors in the crystal may be repaired. When bonds that connect portions of the solid are quite strong, incorrect structures (those that do not match the overall crystal lattice) cannot be repaired. Such errors, when propagated, lead to amorphous materials. One measure of bond strength in the present context is the stability constant between the metal ion and the organic ligand. For extremely large

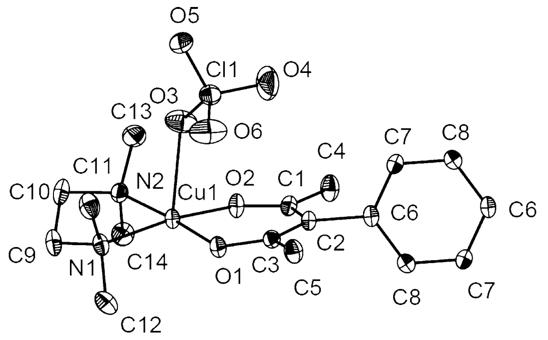


Fig. 1 The crystal structure of **6** (50% probability level thermal ellipsoids)

constants, the dissociation rate is much slower than the association rate. As a result, incorrectly formed substructures that cannot be repaired promote noncrystallinity. The binding constant of copper to carboxylate is about six orders of magnitude smaller than that of copper to acetylacetonate [28]. This difference provides an explanation for the inability of acac to form infinite chains or networks in this study, whereas similar structures are common for the carboxylate function [29].

Such limitations do not apply to single crystals of small complexes, such as the dinuclear complexes **6**–**8** that were prepared in this work. The bidentate nitrogen ligands were necessary to cap the copper centers. Rather than reacting with acac in another molecule to form oligomers and eventually amorphous materials containing infinite chains, the copper centers reacted with the nitrogen base and crystallized as small molecules. All these materials have solvent or anion as a fifth coordination on copper. This result suggested to us that higher coordination could offer a mechanism for the successful formation of crystalline, infinite chains. Molecule **5** has been studied in this context [14–16]. The pyridine ligand might fulfill the same role as solvent/anion in **6**–**8**. If so, infinite chains could be formed that included acac as a part of the chain. Domasevitch and co-workers [14] obtained a mixed metal Cu(Co)/Be two-dimensional array with this ligand. Maverick and co-workers [15, 16] obtained Cu and Cu/Co two-dimensional arrays with this ligand. A novel one-dimensional chain was realized in the present study with **9**, in which the chain leads from acac to copper (ligated to the bidentate phenanthroline) to the pyridyl nitrogen and back to acac at the other end of the pyridine ring.

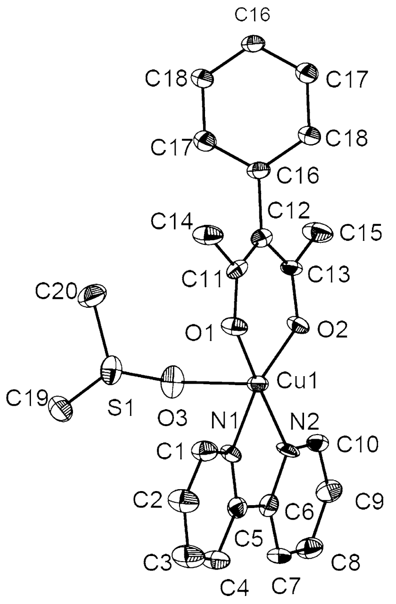


Fig. 2 The crystal structure of **7** (50% probability level thermal ellipsoids)

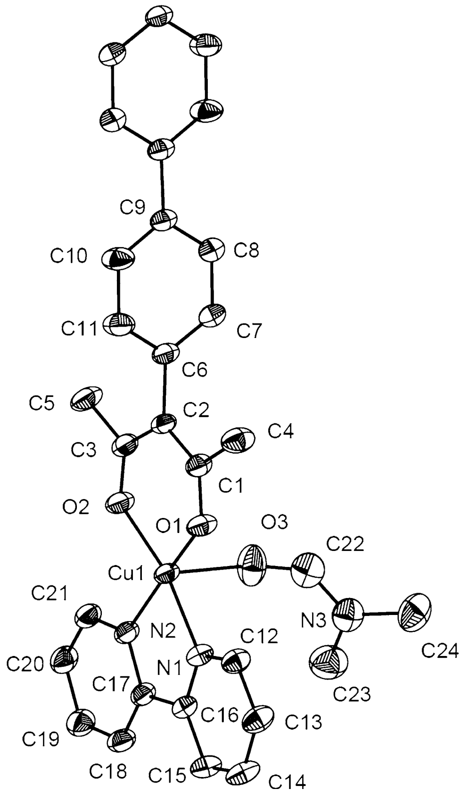


Fig. 3 The crystal structure of **8** (50% probability level thermal ellipsoids)

Complexes **7**–**9**, which contain the bipyridine or phenanthroline ligands, exhibit interesting noncovalent interactions in the solid. By means of π–π stacking or distant π-Cu coordination, these complexes exist as higher order arrays. Figures 5 and 6 show the packing of molecular pairs in the dinuclear complexes **7** and **8**. In both cases, the bipyridine group is arranged parallel to the bipyridine group of another molecule and is offset slightly in order to fill the role of a distant sixth ligand for nearly octahedral copper. The square formed by the two acac oxygens and the two bipyridyl nitrogens around copper in one molecule is parallel to the analogous square in the adjacent molecule.

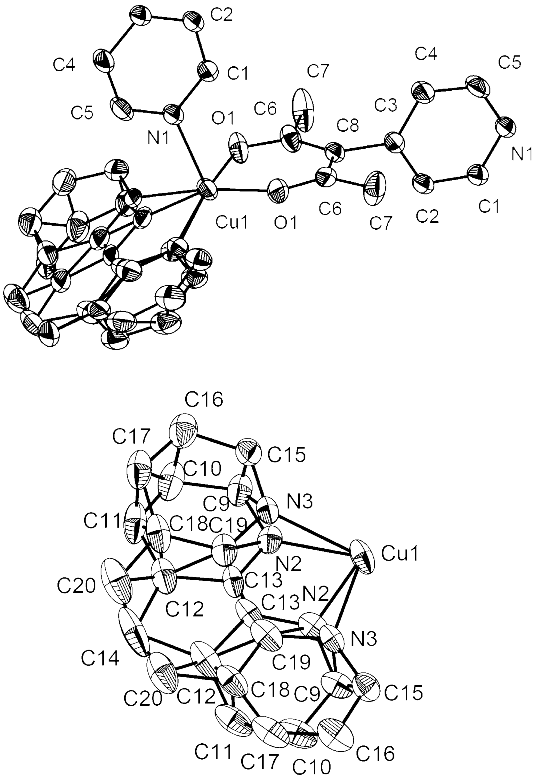


Fig. 4 The crystal structure of **9** (50% probability level thermal ellipsoids). Labels for the disordered phenathroline ring are given in an expansion below the structure

In both cases, noncovalent bonding between the squares and the bipyridine ligands on one molecule with the same entities on the parallel molecule generate an infinite one-dimensional chain in the solid. Such a material based on noncovalent bonded does not qualify as a metal-organic framework.

The phenanthroline ligands in the one-dimensional chain of **9** also engage in noncovalent binding with an adjacent chain, as illustrated in Fig. 7, which contains portions of two zigzag chains. There is some disorder in the phenanthroline pieces, but it is clear that the structure in the crystal is controlled by π–π stacking between two aromatic rings. The zigzag chain is arranged in such a way that alternate phenanthrolines (let us call them the even ligands) face in one direction to bind noncovalently with alternate phenanthrolines on the adjacent chain. Then the odd ligands on that chain bind with an adjacent chain in the opposite direction. The result is a planar, two-dimensional array held together by noncovalent interactions.

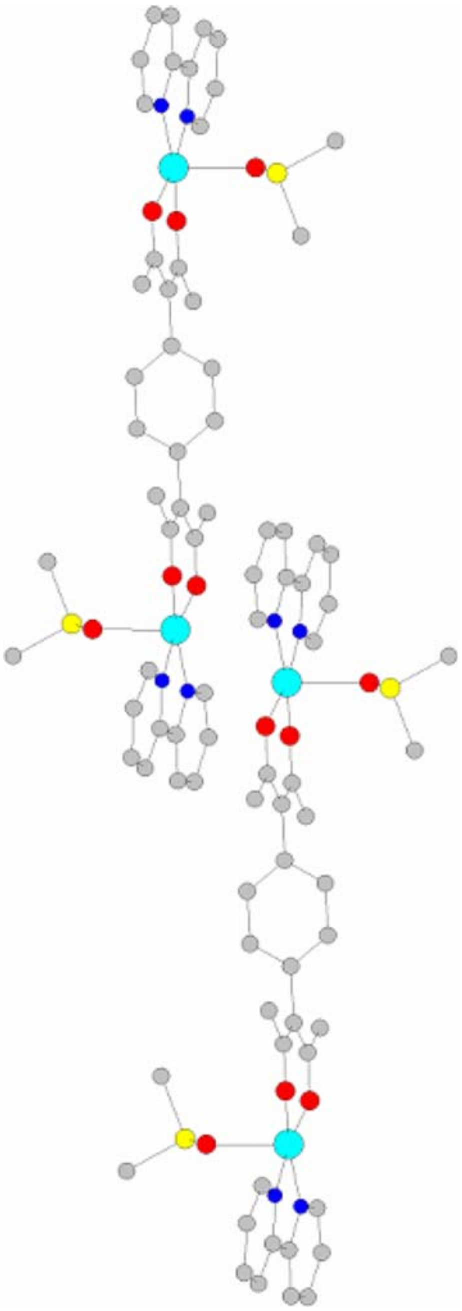


Fig. 5 Crystal packing of **7**, showing π–π stacking between adjacent molecules to create a noncovalent, one-dimensional chain. Copper (cyan), nitrogen (blue), carbon (gray), oxygen (red), and sulfur (yellow)

Summary

Aromatic systems (**1–3**) containing two acetylacetonate (acac) substituents facing in opposite directions (examples of so-called Janus molecules) fail to form crystalline metal-organic frameworks with Cu(II) salts in this study. We attribute this result to the relatively strong oxygen-copper bonds in acac complexes, in comparison with carboxylate systems, which prohibit the free formation, breaking, and reformation of bonds during crystallization. In the presence of bidentate nitrogen ligands, these systems form dinuclear, capped systems (**6–8**) (organic/copper ratio of 1/2), in which copper has distorted pentacoordination to two

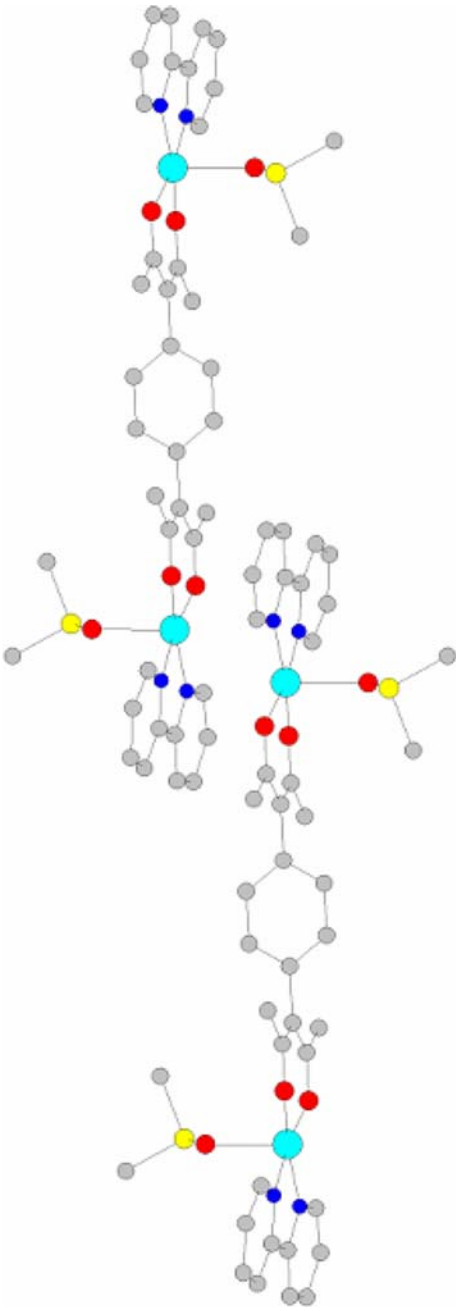


Fig. 6 Crystal packing of **8** showing π–π stacking between adjacent molecules to create a noncovalent, one-dimensional chain. Copper (cyan), nitrogen (blue), carbon (gray), and oxygen (red)

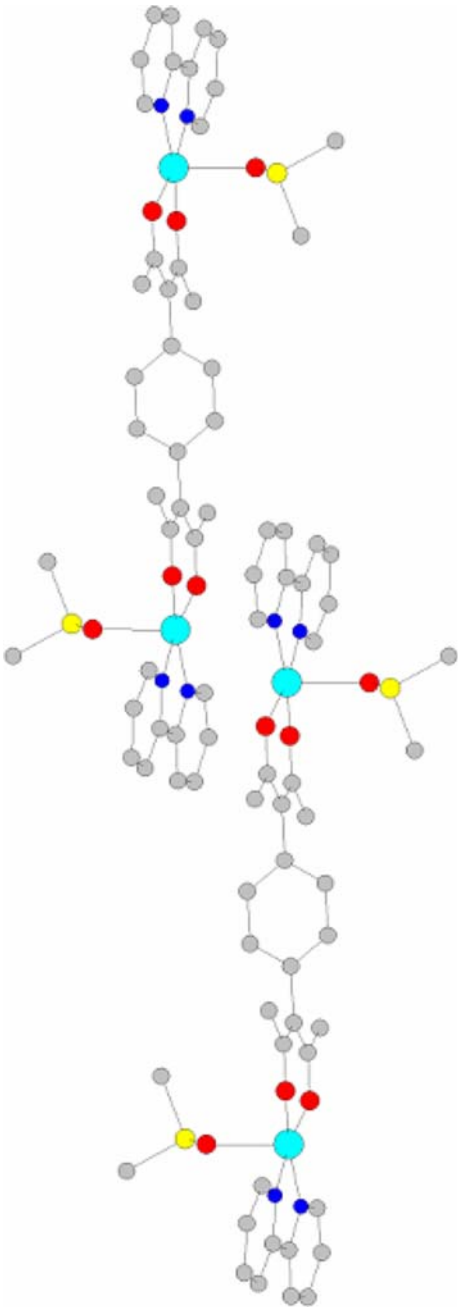


Fig. 7 Crystal packing of **9,** showing π–π stacking between adjacent molecules to create a noncovalent layer. Copper (cyan), nitrogen (blue), carbon (gray), and oxygen (red)

oxygens of acac, two nitrogens of the amine ligand, and one oxygen of solvent or anion. These may be considered zero-dimensional systems. Complexes **7** and **8** include bipyridine as the bidentate nitrogen ligand. In the crystal, an aromatic ring of one molecule stacks with an aromatic ring of another, providing a noncovalently bound sixth ligand for copper. Since each molecule contains two bipyridines, at opposite ends, aromatic stacking results in an infinite one-dimensional chain in the crystal, held together by these noncovalent bonding arrangements (Fig. 5 and 6).

Because copper complexes **7** and **8** contain fifth coordination from solvent, we considered whether a modified acac complex, in which the second acac of **1–3** is replaced by a more loosely coordinating pyridine entity, could form covalent one-dimensional chains. The dual functionalities of molecule **5** thus are acac and the pyridyl nitrogen.

Indeed, reaction of **5** with Cu(II) salts produced a covalent, infinite, one-dimensional chain in which the polymerizing ribbon included acac (**9**). This material contained phenanthroline to provide two ligands on copper. Noncovalent bonding of phenanthroline rings on adjacent chains creates a two-dimensional layered structure (Fig. 7). Interpenetration is not present in any of these structures.

Supplementary Materials

Crystallographic details for compounds **6–9.** The .cif files have been deposited as CCDC-619531, CCDC-619532, CCDC-619533, and CCDC-619534. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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