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Bis(*o*-phenylenebis(acetylacetonato))dicopper(II): A Strained Copper(II) Dimer Exhibiting a Wide Range of Colors in the Solid State

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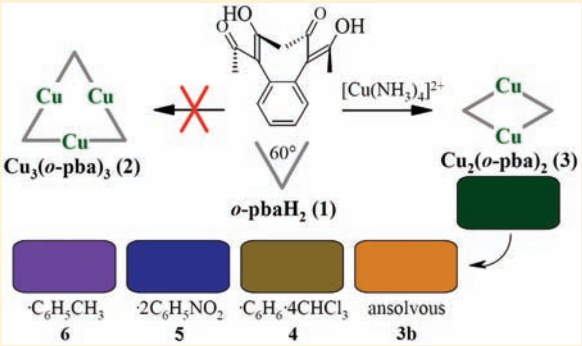
Supporting Information

ABSTRACT: The bis(β-diketone) *o*-pbaH$_2$ (*o*-phenylenebis(acetylacetone), **1**) reacts readily with Cu^{2+}. Although this reaction was expected to yield a trimeric product (**2**) on geometric grounds, the binuclear complex Cu$_2$(*o*-pba)$_2$ (**3**) is obtained instead. Materials containing Cu$_2$(*o*-pba)$_2$ adopt a variety of colors, depending on the solvents used in preparation: dark green (microcrystalline, **3a**), golden-brown (ansolvous, **3b**), green-brown (CHCl$_3$−C$_6$H$_6$ solvate, **4**), dark blue (nitrobenzene solvate, **5**), or violet (toluene solvate, **6**). Complexes **5** and **6** contain 1D chains of Cu$_2$(*o*-pba)$_2$ molecules joined by weak Cu···O interactions. Crystalline adducts [Cu$_2$(*o*-pba)$_2$L]$_n$ (**7** and **8**) containing 1D polymeric chains are also obtained upon reaction of **3** with bridging ligands (L = 1,2-bis(4-pyridyl)ethane or 4,4′-bipyridine, respectively). All of the new metal complexes except for **3a** have been characterized by X-ray analysis.



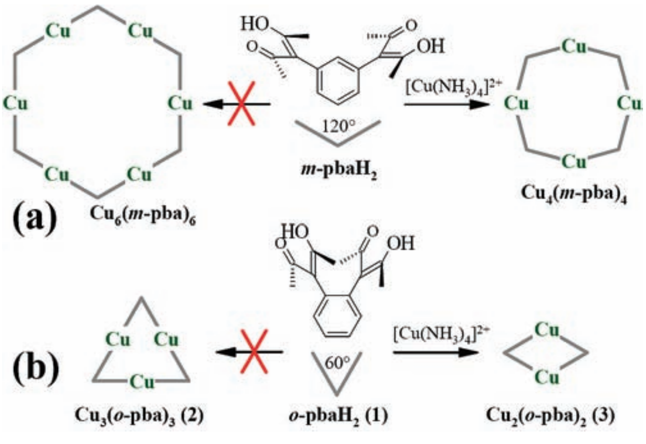
INTRODUCTION

Metal−organic supramolecules constructed from Cu^{2+} and organic linkers continue to be developed at a rapid rate owing to their diverse structures and range of applications.[1] Our group and others have been interested in using β-diketones as organic linkers.[2] We recently described the bis(β-diketone) *meta*-phenylenebis(acetylacetone) (*m*-pbaH$_2$), whose β-diketone moieties make an angle of 120°. Although this linker appeared to be well suited for the construction of a "molecular hexagon", Cu$_6$(*m*-pba)$_6$, we found no evidence for this product, obtaining instead the square Cu$_4$(*m*-pba)$_4$ in high yield (Scheme 1).[3]

We now report the chemistry of the ortho isomer, *o*-pbaH$_2$, with Cu^{2+}. On the basis of the ~60° angle between the β-diketone moieties in *o*-pbaH$_2$, we expected a trinuclear product, Cu$_3$(*o*-pba)$_3$ (**2**). Other linkers with donor groups at 60° angles, and related multidentate ligands, have been used successfully to prepare trinuclear species.[4] However, the sole product in the Cu^{2+}−*o*-pba^{2-} reaction is the cyclic *dimer*, Cu$_2$(*o*-pba)$_2$ (**3**).

Other investigators have reported the formation of unexpectedly small cyclic metal−organic structures. For example, right-angle "corners" such as *cis*-disubstituted Pd(II) complexes usually react with a linear linker such as 4,4′-bpy to produce the square [Pd$_4$(4,4′-bpy)$_4$], but a number of examples of trinuclear products [Pd$_3$(4,4′-bpy)$_3$] have been observed.[5] The formation of a triangle instead of the expected square requires a distortion of ca. 30° at each metal ion, just like the formation of a square instead of the expected hexagon (as we saw in the formation of Cu$_4$(*m*-pba)$_4$[3]). In contrast, the amount of distortion required to assemble Cu$_2$(*o*-pba)$_2$ is twice as large, ca. 60° at each metal ion. In the present work, we show that this dimer forms solids of a variety of colors, ranging from blue to green to golden-brown, depending on the solvents used in preparation.

Scheme 1. Preparation of Supramolecular Cu Complexes from the Meta (a) and Ortho (b) Isomers of the Bis(β-diketone) pbaH$_2$



EXPERIMENTAL SECTION

All reagents were used as received. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona.

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Table 1. X-Ray Crystallographic and Structure Refinement Data for 3b, 4−8

Compound	3b	4	5
empirical formula	$C_{32}H_{32}Cu_2O_8$	$C_{32}H_{32}Cu_2O_8 \cdot C_6H_6 \cdot 4CHCl_3$	$C_{32}H_{32}Cu_2O_8 \cdot 2C_6H_5NO_2$
fw	671.66	1227.24	917.88
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	7.5200(14)	11.7288(10)	7.7190(5)
b, Å	9.200(3)	20.790(2)	11.6921(9)
c, Å	10.728(3)	12.0788(11)	12.1682(10)
α, deg	90.484(13)	90	79.475(4)
β, deg	91.742(16)	119.005(4)	80.666(5)
γ, deg	105.265(16)	90	72.687(6)
V, Å^3	715.6(3)	2575.9(4)	1023.98(13)
Z	1	2	1
T, K	115	115	90
D_{calcd}, g cm^{-3}	1.559	1.582	1.488
cryst dimenions, mm	0.12 × 0.02 × 0.02	0.40 × 0.30 × 0.18	0.42 × 0.15 × 0.12
θ limits, deg	$2.8 < \theta < 25.1$	$2.7 < \theta < 35.0$	$2.7 < \theta < 36.4$
reflns, measd/unique/obsd	9333/2423/1056	62001/10919/8596	33966/9553/8515
data/param	2423/194	10 919/294	9553/276
μ, mm^{-1}	1.538	1.496	1.106
R ($I > 2\sigma(I)$)	0.117	0.036	0.034
R_w (all data)	0.282	0.094	0.092
GOF	1.074	1.029	1.046

compound	6	7	8
empirical formula	$C_{32}H_{32}Cu_2O_8 \cdot C_7H_8$	$C_{32}H_{32}Cu_2O_8 \cdot C_{12}H_{12}N_2 \cdot 1.5C_7H_8$	$C_{32}H_{32}Cu_2O_8 \cdot C_{10}H_8N_2 \cdot C_7H_8$
fw	763.79	994.09	919.97
cryst syst	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$Cmma$ (No. 67)
a, Å	7.5492(10)	8.670(3)	20.978(9)
b, Å	11.4219(15)	11.963(5)	11.525(4)
c, Å	11.9423(15)	12.116(8)	16.980(6)
α, deg	116.990(6)	101.86(2)	90
β, deg	93.970(8)	110.69(2)	90
γ, deg	105.046(8)	101.23(2)	90
V, Å^3	864.94(19)	1100.4(9)	4105(3)
Z	1	1	4
T, K	115	115	115
D_{calcd}, g cm^{-3}	1.466	1.500	1.488
cryst dimensions, mm	0.43 × 0.10 × 0.02	0.20 × 0.15 × 0.05	0.45 × 0.08 × 0.07
θ limits, deg	$2.8 < \theta < 30.0$	$2.5 < \theta < 24.3$	$3.0 < \theta < 22.1$
reflns, measd/unique/obsd	18674/5043/4420	19243/6513/4847	16670/1392/939
data/param	5043/245	6513/143	1392/158
μ, mm^{-1}	1.283	1.029	1.096
R ($I > 2\sigma(I)$)	0.032	0.123	0.097
R_w (all data)	0.079	0.350	0.286
GOF	1.057	1.341	1.589

Preparation of Compounds. *Cu_2(o-pba)$_2$ (**3a**).* $CuSO_4 \cdot 5H_2O$ (0.500 g, 2.00 mmol) was dissolved in 10 mL of H_2O and converted to $[Cu(NH_3)_4]SO_4$(aq) by the dropwise addition of conc. NH_3(aq). To this blue-violet solution, a solution of *o*-pbaH_2 (0.275 g, 1.00 mmol) in 20 mL of CH_2Cl_2 was added slowly, and the mixture was stirred for 6 h. CH_2Cl_2 (20 mL) was added, and the organic layer was separated, dried over $MgSO_4$, and evaporated to give a dark green powder. This residue was washed with hexane (2 × 10 mL) and dried in the air. Yield: 0.325 g (96%), mp > 210 °C. Anal. Calcd for $C_{32}H_{32}Cu_2O_8$: C, 57.22; H, 4.80. Found: C, 57.11; H, 4.93.

*Cu_2(o-pba)$_2$ (**3b**).* A solution of Cu_2(*o*-pba)$_2$ (**3a**, 0.050 g, 0.074 mmol) in 1.5 mL of $CHCl_3$ was layered with acetone. Small golden-brown crystals of **3b** were obtained after ca. 48 h. This product was collected and dried in the air. Yield: 0.039 g (78%). Anal. Calcd for $C_{32}H_{32}Cu_2O_8$: C, 57.22; H, 4.80. Found: C, 57.46; H, 4.56.

*Cu_2(o-pba)$_2 \cdot C_6H_6 \cdot 4CHCl_3$ (**4**).* A solution of Cu_2(*o*-pba)$_2$ (**3a**, 0.050 g) in 1.5 mL of $CHCl_3$ was layered with benzene. Green-brown dichroic crystals of **4** were obtained after ca. 72 h. Yield: 0.053 g (58%). These crystals slowly become opaque on standing, suggesting a loss of

solvent; microanalysis results were in agreement with the ansolvous material. Anal. Calcd for Cu_2(*o*-pba)$_2$ ($C_{32}H_{32}Cu_2O_8$): C, 57.22; H, 4.80. Found: C, 57.12; H, 4.65.

*Cu_2(o-pba)$_2$·$2C_6H_5NO_2$ (**5**).* A solution of Cu_2(*o*-pba)$_2$ (**3a**, 0.050 g) in 1.5 mL of $CHCl_3$ was layered with nitrobenzene. Dark blue crystals of **5** were obtained in ca. 4 days. This product was collected and dried in the air. Yield: 0.047 g (65%). Anal. Calcd for $C_{44}H_{42}Cu_2N_2O_{12}$: C, 57.57; H, 4.61, N, 3.05. Found: C, 57.48; H, 4.72; N, 3.11.

*Cu_2(o-pba)$_2$·$C_6H_5CH_3$ (**6**).* A solution of Cu_2(*o*-pba)$_2$ (**3a**, 0.050 g) in 1.5 mL of $CHCl_3$ was layered with toluene. Violet crystals of **6** were obtained in ca. 4 days. This product was collected and dried in the air. Yield: 0.042 g (74%). Anal. Calcd for $C_{39}H_{40}Cu_2O_8$: C, 61.32; H, 5.29. Found: C, 61.50; H, 5.50.

Coordination Polymers of Cu_2(*o*-pba)$_2$. *[Cu_2(o-pba)$_2$(dpea)]·$1.5C_6H_5CH_3$ (**7**).* A solution of Cu_2(*o*-pba)$_2$ (**3a**, 0.025 g, 0.037 mmol) in 1.0 mL of $CHCl_3$ turned bluish-green when 1,2-bis(4-pyridyl)ethane (dpea; 0.010 g, 0.054 mmol, in 0.5 mL $CHCl_3$) was added; the resulting mixture was layered with toluene. Bluish-green crystals of **7** were obtained in 2 days. These crystals slowly become opaque on standing, suggesting a loss of solvent; microanalysis results were in agreement with the ansolvous material. Yield: 0.026 g (82%). Anal. Calcd for Cu_2(*o*-pba)$_2$(dpea) ($C_{44}H_{44}N_2Cu_2O_8$): C, 61.69; H, 5.18, N, 3.27. Found: C, 61.99; H, 5.23; N, 3.43.

*[Cu_2(o-pba)$_2$(4,4′-bpy)]·$C_6H_5CH_3$ (**8**).* A solution of Cu_2(*o*-pba)$_2$ (**3a**, 0.025 g, 0.037 mmol) in 1.0 mL of $CHCl_3$ turned bluish-green when 4,4′-bipyridine (0.009 g, 0.058 mmol, in 0.5 mL $CHCl_3$) was added; the resulting mixture was layered with toluene. Bluish-green crystals of **8** were obtained in 2 days. These crystals slowly become opaque on standing, suggesting a loss of solvent; microanalysis results were in agreement with the ansolvous material. Yield: 0.027 g (88%). Anal. Calcd for Cu_2(*o*-pba)$_2$(4,4′-bpy) ($C_{42}H_{40}N_2Cu_2O_8$): C, 60.88; H, 4.87, N, 3.38. Found: C, 60.75; H, 4.90; N, 3.44.

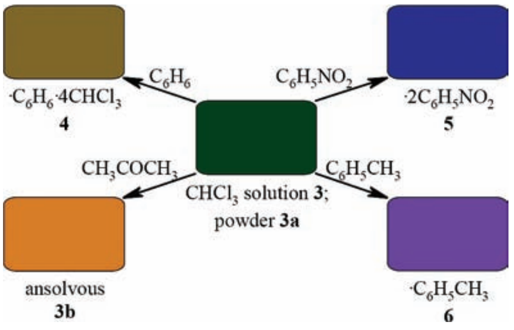
X-Ray Structure Determinations. Intensity data were collected at low temperatures on a Nonius KappaCCD diffractometer equipped with an Oxford Cryosystems Cryostream sample cooler and a graphite monochromated Mo Kα X-ray source (λ = 0.71073 Å). Data were corrected for absorption using the multiscan method using DENZO and SCALEPACK.[6] Structures were solved by direct methods using SIR[7] and refined on F^2 using SHELXL.[8] Crystal quality for **4**, **5**, and **6** was excellent, less so for **3b**, **7**, and **8**. The toluene solvent in **6** was disordered about an inversion center. The toluene solvent in **8** was also disordered into two orientations, and a common isotropic displacement parameter was refined for its C atoms. Contribution from disordered solvent in **7**, assumed to be toluene, was removed using SQUEEZE.[9] For **7**, only Cu and O were treated as anisotropic. For all structures, hydrogen atoms were frequently visible in difference maps but were placed in idealized positions, and torsional parameters were refined for methyl groups. Crystal data and refinement details are given in Table 1.

Powder diffraction data were collected by using a Bruker D8 Advance instrument.

■ RESULTS AND DISCUSSION

The bis(β-diketone) *o*-pbaH_2 was synthesized according to the literature procedure[10] and converted to dark green Cu_2(*o*-pba)$_2$ (**3**) in a CH_2Cl_2 solution by treatment with $[Cu(NH_3)_4]^{2+}$ (aq). The transformations of **3** are illustrated in Scheme 2. The initial product is a dark green powder (**3a**) which dissolves readily in $CHCl_3$ or CH_2Cl_2 but not in most other solvents. For example, **3a** dissolves in acetone to give a green solution, but this solution deposits a golden-brown powder within a few seconds. Slow evaporation of a $CHCl_3$/acetone solution yields crystalline golden-brown Cu_2(*o*-pba)$_2$ (**3b**; Figure 1) over a period of several days. Complex **3a** is microcrystalline, as determined by powder X-ray diffraction, and its diffraction pattern is quite different from that of **3b** (see Figure S1, Supporting Information).

Scheme 2. Transformations of Cu_2(*o*-pba)$_2$



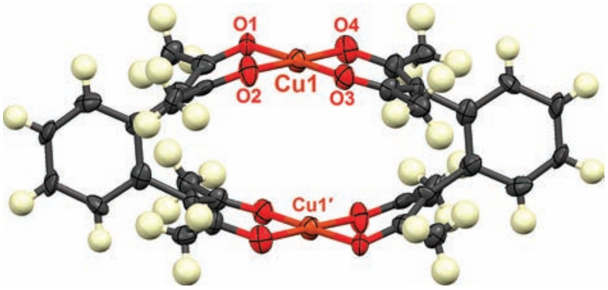


Figure 1. Crystal structure of Cu_2(*o*-pba)$_2$ (**3b**) (Cu1···Cu1′ = 4.551(2) Å), with 50% ellipsoids for non-hydrogen atoms.

The other crystalline materials described here were all prepared from $CHCl_3$ solutions of **3** by layering and have been characterized by X-ray analysis: with benzene, green-brown Cu_2(*o*-pba)$_2$·C_6H_6·$4CHCl_3$ (**4**; Figure 2); with nitrobenzene, dark blue Cu_2(*o*-pba)$_2$·$2C_6H_5NO_2$ (**5**; Figure 3); with toluene, violet Cu_2(*o*-pba)$_2$·$C_6H_5CH_3$ (**6**; Figure 4). All of the crystalline materials (**3b**, **4**, **5**, and **6**) dissolve in $CHCl_3$ or CH_2Cl_2 to give green solutions which are indistinguishable from those prepared using **3a**. (Complex **3b** dissolves less readily than the other materials; this may be for thermodynamic reasons, as suggested by the fact that solid **3a** spontaneously converts to solid **3b** in solvents such as acetone.)

Compounds **3a** and **3b** have the same composition but different colors. The absorption spectrum of dark green solid **3a** is nearly identical to that of its $CHCl_3$ solution, as illustrated by the spectra in Figure 5 (for the solid) and in Figure S2 (for the solution), with maxima at 690−700 and 580−590 nm and a rising absorbance below 500 nm. (The spectra in Figure 5 were recorded for Nujol mulls of the solids, because their solutions are all dark green.) These spectra are similar to those of Cu complexes of other 3-substituted acetylacetonates (d−d bands above 500 nm, and CT and intraligand transitions at shorter wavelengths), suggesting that **3a** contains isolated molecules.

Ansolvous crystalline **3b**, on the other hand, is golden-brown, with intense absorption at shorter wavelengths in addition to the features in the 550−700 nm region. The CuO_4 coordination environment in **3b** is nearly planar (the Cu atom is 0.005 Å from the O_4 plane), and the CuO_4 and two crystallographically independent β-diketonate planes make angles of 15.9° and 30.3° with the CuO_4 coordination plane.

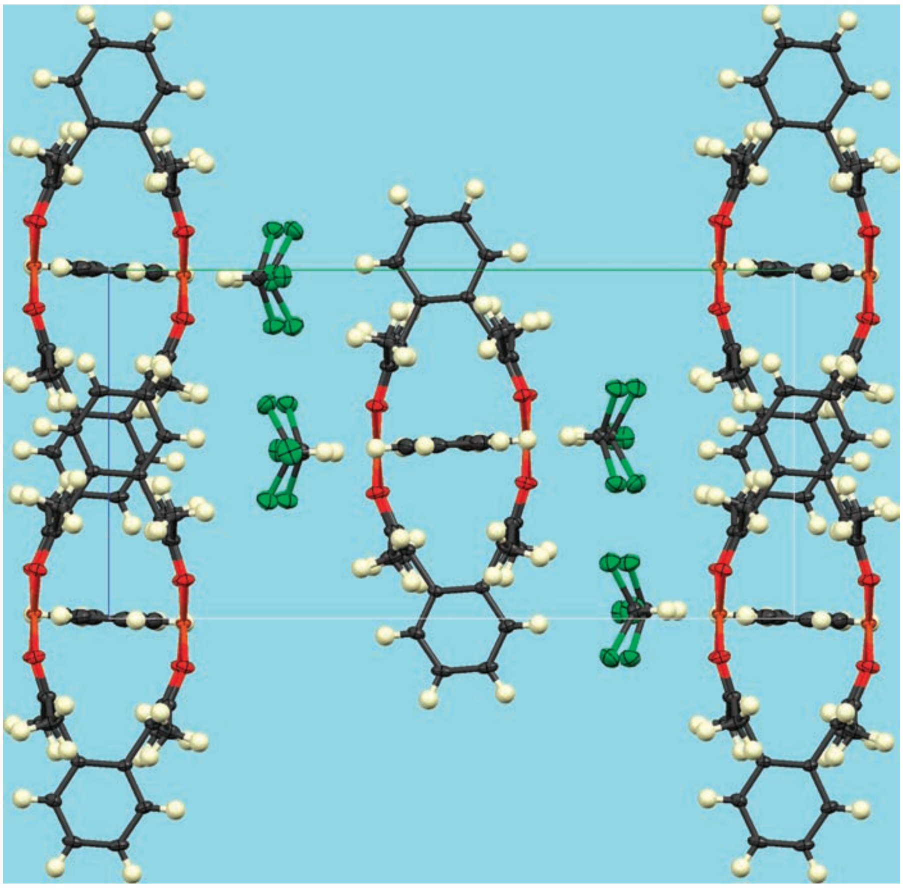


Figure 2. Crystal structure of $Cu_2(o\text{-pba})_2 \cdot C_6H_6 \cdot 4CHCl_3$ (**4**; Cu1···Cu1′ 4.5482(5) Å), showing one unit cell, viewed along the crystallographic *a* direction; *b* is horizontal (50% ellipsoids for non-hydrogen atoms).

The $C_6H_6-CHCl_3$ solvate **4** is green-brown, and individual crystals frequently show a well-developed dichroic face, with green and brown colors in polarized light (Figure 6). These green and brown colors are similar to those of **3a** and **3b**, respectively. We could not obtain spectra of this material in the two polarizations for a more quantitative comparison, owing to a rapid loss of solvent from the crystals. X-ray analysis of **4** (Figure 2) reveals molecules that are almost identical to those in **3b** (Cu···Cu = 4.5482(5) Å; Cu atom 0.012 Å from O_4 plane; 26.0° and 20.7° between the CuO_4 and β-diketonate planes). The Bruker Apex2 face-indexing software[11] identified the prominent face in crystals of **4** as (100), as illustrated in Figure 7. The location of the *b* axis enabled us to assign the polarizations in Figure 6.

The brown colors in **3b** and **4** are similar, but their cause remains puzzling. We considered the severe structural distortions that occur in the $Cu_2(o\text{-pba})_2$ molecules as a possible cause for the unusual colors. If **3a** contained polymeric $[Cu(o\text{-pba})]_n$, for example, it might be unstrained and show the "normal" dark green color. However, this is unlikely, because it would require that the polymer and dimer interconvert rapidly as the solids are dissolved and precipitated. Such an interconversion could only occur by dissociation of the chelating ligands, which is unfavorable in nonpolar solvents. Also, **3a** and **3b** interconvert to some extent even in the solid state: dark green **3a** slowly turns brownish-green on standing, and grinding golden-brown crystalline **3b** gives it a slight green color. Thus, **3a**, like **3b**, consists of discrete $Cu_2(o\text{-pba})_2$ molecules.

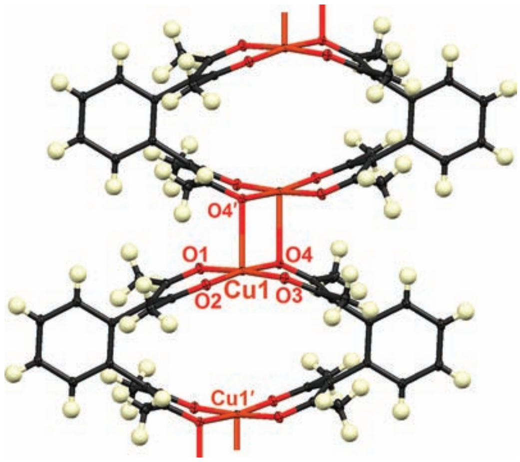


Figure 3. Crystal structure of $Cu_2(o\text{-pba})_2 \cdot 2C_6H_5NO_2$ (**5**), showing a portion of the 1D chain of $Cu_2(o\text{-pba})_2$ units: Cu1···Cu1′ = 4.9636(4) Å; Cu1···O4′ = 2.422(1) Å. Solvent molecules omitted for clarity; 50% ellipsoids for non-hydrogen atoms.

The orientation of the molecules in crystals of **4** is shown in Figure 2. The $Cu_2(o\text{-pba})_2$ molecules are aligned so that their Cu···Cu vectors are almost exactly along the *b* axis. The intense brown color in the micrographs in Figure 6 appears only in polarization perpendicular to *b*. This information limits the transitions that could be responsible: the intensity of the color suggests a charge-transfer assignment, and LMCT transitions originating in the π system of the β-diketonate ligands are possible. These transitions normally lie in the ultraviolet region.

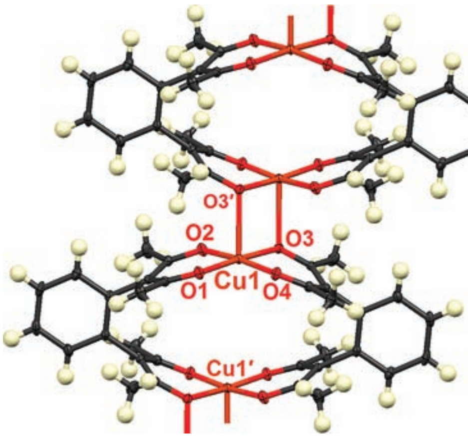


Figure 4. Crystal structure of $Cu_2(o\text{-pba})_2 \cdot C_6H_5CH_3$ (**6**), showing a portion of the 1D chain of $Cu_2(o\text{-pba})_2$ units: Cu1···Cu1′ = 4.7575(7), Cu1···O3′ = 2.443(1) Å. Solvent molecules omitted for clarity; 50% ellipsoids for non-hydrogen atoms.

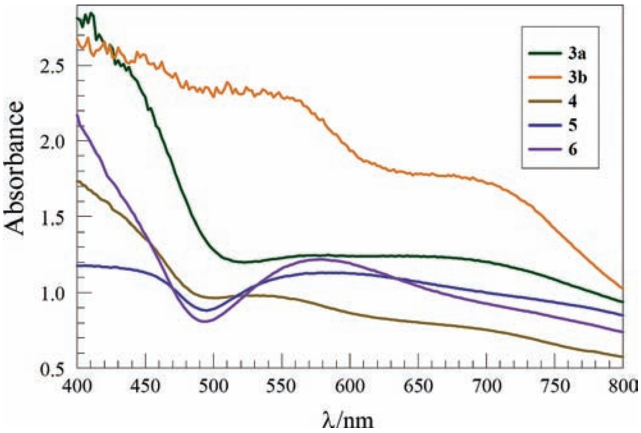


Figure 5. Absorption spectra of the five forms of $Cu_2(o\text{-pba})_2$ (**3a**, **3b**, **4**, **5**, and **6**) in the solid state, recorded as Nujol mulls.

The β-diketonates in $Cu_2(o\text{-pba})_2$ are noticeably distorted from planarity, and this distortion could lead to a red-shift in the LMCT transition(s) and the observed brown color. However, the structure of the $Cu_2(o\text{-pba})_2$ unit is almost identical in all of the crystalline solids studied here, so we would expect to see similar intense transitions in the other materials as well; but only **3b** and **4** show them. Intermolecular interactions in **3b** and **4** could produce the brown color, but no unusual interactions were apparent in their crystal structures.[12] Thus, we do not have a complete explanation of the origin of the brown color.

The solvated compounds **5** and **6** both contain separate one-dimensional stacks of $Cu_2(o\text{-pba})_2$ molecules and solvent molecules. In the $Cu_2(o\text{-pba})_2$ stacks, adjacent molecules make close approaches, with intermolecular Cu···O distances of 2.422(1) Å (in **5**; Figure 3) and 2.443(1) Å (in **6**; Figure 4). This close approach leads to pyramidal distortions and effective five-coordination at the Cu atoms. The dark blue and violet colors of **5** and **6**, respectively, and their spectra in Figure 5 are consistent with the change to five-coordination.

Solutions of $Cu_2(o\text{-pba})_2$ turn greenish-blue on reaction with nitrogen-donor ligands, as expected for the formation of 5-coordinate adducts at Cu. We have crystallized two such adducts, with 1,2-bis(4-pyridyl)ethane (**7**, Figure 8) and 4,4′-bipyridine (**8**, Figure 9), both of which are 1-D coordination polymers.

Binding of adjacent O or N atoms to $Cu_2(o\text{-pba})_2$ leads to pyramidal environments about Cu and increased Cu···Cu distances: 4.9636(4), 4.7575(7), 5.287(1), and 5.318(3) Å in

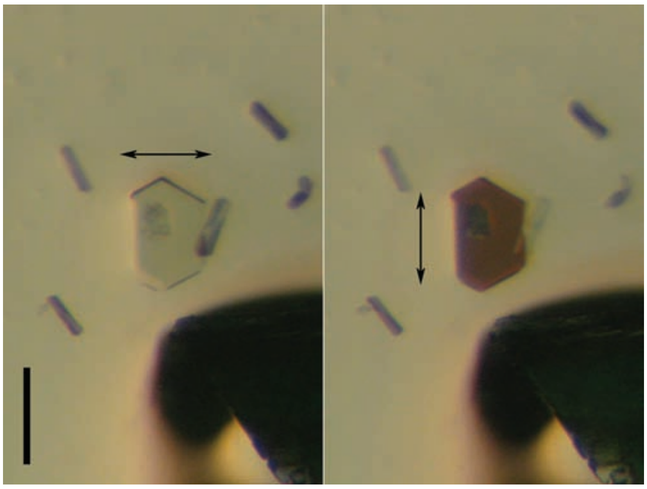


Figure 6. Photographs of the (100) face of a crystal of $Cu_2(o\text{-pba})_2 \cdot C_6H_6 \cdot 4CHCl_3$ (**4**) in polarized light. Left, horizontal polarization (parallel to *b*); right, vertical (perpendicular to *b*). Scale bar (black bar on left) = 0.25 mm. [This view is slightly different from that in Figure 2, which is along the *a* axis. However, *b* is still horizontal, and the vertical direction is approximately along *c*.]

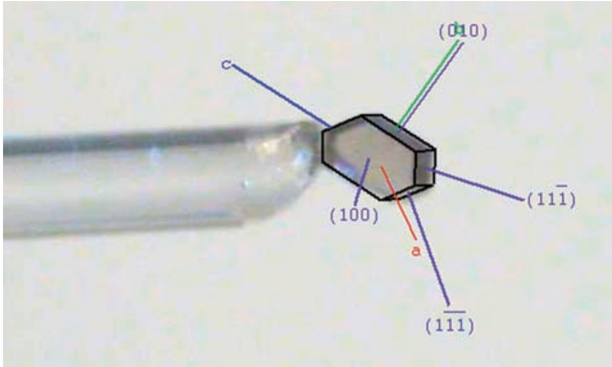


Figure 7. Face indexing performed for a crystal of $Cu_2(o\text{-pba})_2 \cdot C_6H_6 \cdot 4CHCl_3$ (**4**).

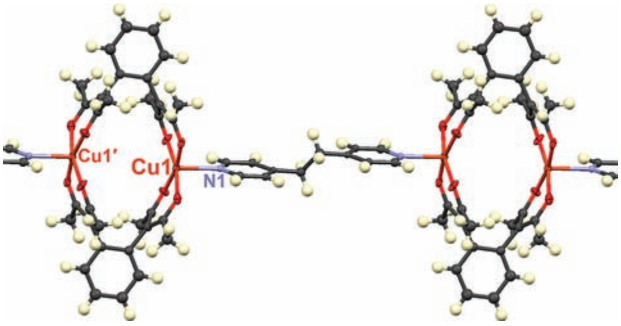


Figure 8. Crystal structure of $Cu_2(o\text{-pba})_2L \cdot 1.5C_6H_5CH_3$ (**7**; L = 1,2-bis(4-pyridyl)ethane), showing a portion of the 1D polymeric chain of $Cu_2(o\text{-pba})_2L$ units: Cu1···Cu1′ = 5.287(1) Å; Cu1···N1 = 2.292(6) Å (50% ellipsoids for non-hydrogen atoms).

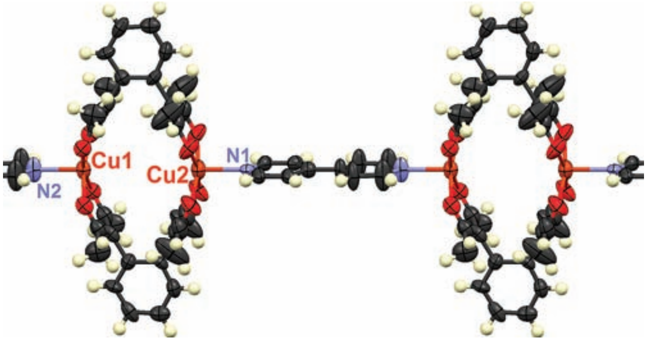


Figure 9. Crystal structure of $Cu_2(o\text{-pba})_2L\cdot1.5C_6H_5CH_3$ (**8**; L = 4,4′-bipyridine), showing a portion of the 1D polymeric chain of $Cu_2(o\text{-pba})_2L$ units: Cu1···Cu2 = 5.318(3) Å (50% ellipsoids for non-hydrogen atoms).

5, **6**, **7**, and **8**, respectively. The greater elongation in **7** and **8** is also accompanied by greater displacements of the Cu atoms away from the O4 planes (0.096, 0.087, 0.194, and 0.179 and 0.217 Å in **5**, **6**, **7**, and **8**, respectively); both of these trends reflect the stronger coordination of N donors to the Cu centers. Formation of square pyramidal adducts may be favored in the $Cu_2(o\text{-pba})_2$ system, because the orientation of the β-diketone moieties is more compatible with pyramidal geometry at the Cu atom than with planar geometry.

CONCLUSIONS

The reaction of the bis(β-diketone) o-pbaH_2 with Cu^{2+} yields the cyclic dimer $Cu_2(o\text{-pba})_2$, rather than the trimer that was expected on the basis of ligand geometry. This reaction proceeds in high yield despite the severe distortion required in the product; the distortion occurs primarily in the dihedral angles between the β-diketonate and CuO_4 planes. $Cu_2(o\text{-pba})_2$ forms solids with a wide range of colors, depending on the solvents used in preparation, and it also binds to bidentate N donors to give 1-D coordination polymers.

ASSOCIATED CONTENT

S Supporting Information. Powder X-ray diffraction results for **3a** and **3b** (Figure S1). Absorption spectrum of **3** in solution (Figure S2). X-ray crystallographic data for **3b**, **4**, **5**, **6**, **7**, and **8**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The crystal structures were determined on the basis of low-temperature data, while the color observations and spectral measurements were performed at room temperature. However, we saw no evidence for phase changes upon cooling the crystals for data collection. Thus, we believe the low-temperature structures give good indications of the presence or absence of intermolecular interactions in the solids at room temperature.