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3-(4-Cyanophenyl)pentane-2,4-dione and its copper(II) complex

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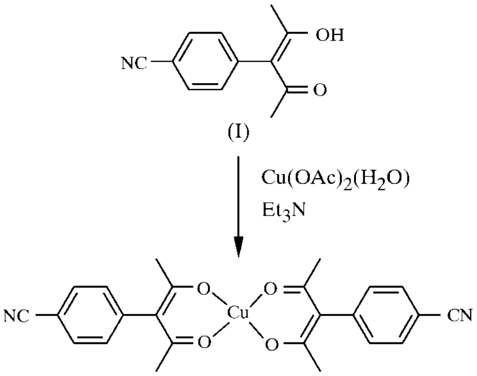
The β-diketone 3-(4-cyanophenyl)pentane-2,4-dione crystallizes as the enol tautomer 4-(2-hydroxy-4-oxopent-2-en-3-yl)benzonitrile, $C_{12}H_{11}NO_2$, (I), with an intramolecular O—H···O hydrogen bond [O···O = 2.456 (2) Å]. Reaction of (I) with copper acetate monohydrate in the presence of triethylamine leads to the formation of the copper(II) complex bis[3-(4-cyanophenyl)pentane-2,4-dionato-κ^2O,O]copper(II), $[Cu(C_{12}H_{10}NO_2)_2]$, (II). In the structure of (II), the Cu atom is coordinated by four β-diketonate O atoms in a slightly distorted square-planar geometry, with Cu—O distances in the range 1.8946 (11)–1.9092 (11) Å. The nitrile moieties in (II) make it a candidate for reaction with other metal ions to produce supramolecular structures.

Comment

Metal–β-diketonate complexes are of interest for their host–guest chemistry (Soldatov & Ripmeester, 2001) and their application in chemical vapor deposition (CVD) of metal films (Borgharkar *et al.*, 1999; Maverick *et al.*, 2002). Our previous studies of metal–β-diketonate supramolecules (Maverick *et al.*, 1986, 2001) have shown that the metal centers in these supramolecules can bind a variety of different guest molecules, making these kinds of compounds potentially useful in separation and sensors. The structures of 3-(4-cyanophenyl)-pentane-2,4-dione (Hacac-C_6H_4CN), (I), and its copper(II) complex, (II), are reported here. We are now attempting to utilize coordination of the CN moieties in (II) to other metal atoms in order to construct nanoporous materials.

The structure of (I) is shown in Fig. 1, and selected bond distances and angles are listed in Table 1. The observation that (I) exists as the enol tautomer is consistent with a solution NMR study (Dell'Erba *et al.*, 1991). The bond distances, angles and hydrogen-bonding distance [2.456 (2) Å; Table 2] for the O1···O2 interaction are comparable to those reported for other 3-phenylpentane-2,4-dione derivatives (Emsley *et al.*, 1989). The dihedral angle between the β-diketone plane and the phenyl ring is 78.28 (4)°, and the H atoms on methyl group C5 are disordered over two sets of sites.



In (II) (Fig. 2), although the two β-diketonate moieties are almost coplanar with the Cu atom, they make an angle of 24.74 (6)° with each other. This conformation represents a twisting distortion of the two ligands, away from square-planar and towards tetrahedral geometry. Few four-coordinate copper(II) β-diketonate complexes show this type of distortion; of 59 such compounds for which coordinates are available in the Cambridge Structural Database (Allen *et al.*, 1979), eight showed a noticeable amount [refcodes BIBFIB10 (Wrobleski *et al.*, 1984), CAXRUO (Prokop *et al.*, 1999), JOXGIM (Rees *et al.*, 1992), NILMUQ (Schilde *et al.*, 1997), PENTUX (Baidini *et al.*, 1992), SOJXIY01 (Polyanskaya *et al.*, 1993), TIRGIK (Schilde *et al.*, 1996) and ZUVSOY (Hirsch *et al.*, 1996)]. The analogous dihedral angles for these structures range from 4.33 to 24.5°, the largest value being for JOXGIM. In the case of BIBFIB10 (20.2°), the distortion at the Cu atom is probably attributable to ring strain, which results from the Pt atom linking the two phosphino-β-diketone ligands. In the other structures, there are no obvious intermolecular interactions causing the distortions.

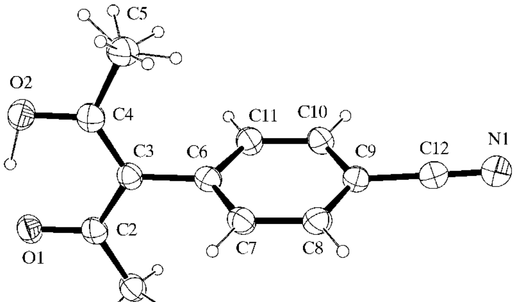


Figure 1
The structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

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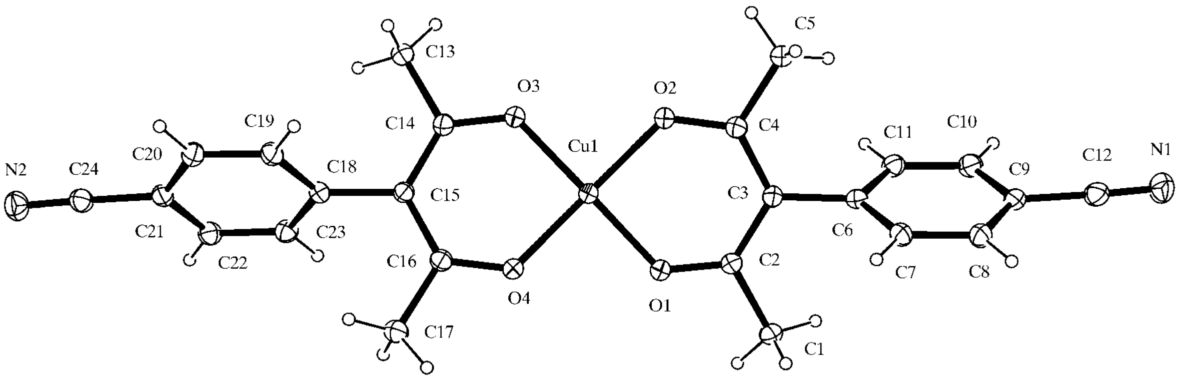

Figure 2
The structure of (II), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

The average Cu—O distance in (II) [1.900 (6) Å; Table 3] is slightly shorter than those found in two other copper(II) cyano-β-diketone complexes, *viz*. Cu(acac-CN)$_2$ [1.920 (2) Å; Hacac-CN is 3-cyanopentane-2,4-dione; Angelova *et al.*, 1989] and Cu(dpm-CN)$_2$ [1.924 (3) Å; Hdpm-CN is 4-cyano-2,2,6,6-tetramethylheptane-3,5-dione; Silvernail *et al.*, 2001]. The dihedral angles between the β-diketone planes and the phenyl rings are 71.07 (5) (O1/O2/C1–C5 and C6–C11) and 67.54 (5)° (O3/O4/C13–C17 and C18–C23). The intramolecular N1···N2 distance is 20.286 (2) Å, making (II) a very long building block for construction of nanometer-sized porous materials.

It is of interest to compare the packing of (II), Cu(acac-C$_6$H$_4$-CN)$_2$, with that of other related metal-β-diketonate building blocks. Unlike bis[3-(4-pyridyl)pentane-2,4-dionato]copper(II), which crystallizes in two- and three-dimensional metal-organic frameworks because of intermolecular Cu···N coordination (Turner *et al.*, 1997; Chen *et al.*, 2003), (II) is a molecular solid without any intermolecular Cu···N(C) coordination. Structures have been reported for three other bis(cyano-β-diketonato)metal(II) compounds. In the structure of Cu(acac-CN)$_2$ (Angelova *et al.*, 1989), a fifth coordination site at the Cu atom is occupied by an N atom from an adjacent Cu(acac-CN)$_2$ group, leading to the formation of one-dimensional Cu(acac-CN)$_2$ chains. On the other hand, in the structures of Cu(dpm-CN)$_2$ (Silvernail *et al.*, 2001) and Co(acac-CN)$_2$ (Angelova *et al.*, 1991), nitrile N atoms occupy both the fifth and the sixth coordination sites, forming two-dimensional Cu(dpm-CN)$_2$ and three-dimensional Co(acac-CN)$_2$ frameworks. These structural variations occur mainly because metal–nitrile coordination is weak. Thus, slight changes in the β-diketone ligands and metal centers can cause substantial changes in intermolecular interactions in the crystal. We are now exploring the use of these metal-functionalized β-diketonate 'building blocks' in the construction of nanometer-sized porous materials.

Experimental

3-(4-Cyanophenyl)pentane-2,4-dione, (I), was synthesized according to the procedure of Dell'Erba *et al.* (1991) and crystallized from ether–dichloromethane (4:1 volume ratio). A solution of (I) (0.05 g, 0.25 mmol) in ethanol (5 ml) was mixed with [Cu(CH$_3$COO)$_2$(H$_2$O)] (0.05 g, 0.25 mmol) in H$_2$O (5 ml), and several drops of triethylamine were added. Compound (II) precipitated and was collected in 65% yield. Recrystallization of the crude product from acetonitrile produced crystals suitable for X-ray analysis.

Compound (I)

Crystal data

$C_{12}H_{11}NO_2$
$M_r = 201.22$
Monoclinic, $P2_1/c$
$a = 7.070$ (5) Å
$b = 11.644$ (9) Å
$c = 12.2430$ (11) Å
$\beta = 94.035$ (3)°
$V = 1005.4$ (11) Å^3
$Z = 4$
$D_x = 1.329$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1990 reflections
$\theta = 2.5$–26.0°
$\mu = 0.09$ mm^{-1}
$T = 100$ K
Plate fragment, colorless
0.20 × 0.10 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer (with an Oxford Cryosystems Cryostream cooler)
ω scans with κ offsets
8931 measured reflections
1969 independent reflections

1396 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\rm max} = 26.0$°
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C2	1.276 (2)	C2—C3	1.427 (3)
O2—C4	1.314 (2)	C3—C4	1.389 (3)
N1—C12	1.150 (3)		
O1—C2—C3	120.99 (18)	O2—C4—C3	121.28 (18)
C4—C3—C2	119.00 (17)	N1—C12—C9	178.9 (2)
C2—C3—C6—C7	−79.7 (2)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O1	1.08 (3)	1.44 (3)	2.456 (2)	153 (2)

m148 Banglin Chen et al. • $C_{12}H_{11}NO_2$ and [Cu($C_{12}H_{10}NO_2$)$_2$] Acta Cryst. (2004). C60, m147–m149

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.138$
$S = 1.02$
1969 reflections
140 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0764P)^2 + 0.1248P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Compound (II)

Crystal data

$[Cu(C_{12}H_{10}NO_2)_2]$
$M_r = 463.96$
Triclinic, $P\overline{1}$
$a = 7.6087$ (10) Å
$b = 9.260$ (2) Å
$c = 15.198$ (3) Å
$\alpha = 91.327$ (8)°
$\beta = 92.814$ (8)°
$\gamma = 107.509$ (12)°
$V = 1019.1$ (3) Å^3

$Z = 2$
$D_x = 1.512$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6559 reflections
$\theta = 2.5$–32.0°
$\mu = 1.11$ mm^{-1}
$T = 100$ K
Fragment, blue–green
0.22 × 0.10 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer (with an Oxford Cryosystems Cryostream cooler)
ω scans with κ offsets
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.793$, $T_{\max} = 0.927$

31 552 measured reflections
7082 independent reflections
5681 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 32.1$°
$h = -10 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.087$
$S = 1.04$
7082 reflections
285 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0230P)^2 + 0.7093P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.53$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0019 (6)

Table 3
Selected geometric parameters (Å, °) for (II).

Cu1—O1	1.8946 (11)	O2—C4	1.2823 (18)
Cu1—O3	1.8954 (11)	O3—C14	1.2809 (18)
Cu1—O2	1.9028 (11)	O4—C16	1.2757 (18)
Cu1—O4	1.9092 (11)	N1—C12	1.147 (2)
O1—C2	1.2751 (18)	N2—C24	1.148 (2)
O1—Cu1—O3	166.74 (5)	O3—Cu1—O4	92.28 (5)
O1—Cu1—O2	92.44 (5)	O2—Cu1—O4	166.07 (5)
O3—Cu1—O2	89.28 (5)	N1—C12—C9	177.52 (18)
O1—Cu1—O4	89.21 (5)	N2—C24—C21	177.47 (19)
C2—C3—C6—C7	−70.1 (2)	C14—C15—C18—C19	−68.1 (2)

The hydroxy H-atom positional parameters for (I) were refined. All other H atoms were treated as riding in idealized positions, with C—H distances of 0.95–0.98 Å, depending on atom type. A torsional parameter was refined for each methyl group. Methyl group C5 in (I) is disordered and was modeled as six equally spaced half-occupied positions in the expected torus. $U_{\rm iso}$(H) values were taken to be $1.2U_{\rm eq}$ of the attached atom ($1.5U_{\rm eq}$ for hydroxy and methyl atoms).

For both compounds, data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1000). Services for accessing these data are described at the back of the journal.

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