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Hydrogen-bond-driven self-assembly of bis(3-benzylpentane-2,4-dionato)(nicotinamide)-copper(II) in the solid state

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.007 Å
R factor = 0.052
wR factor = 0.151
Data-to-parameter ratio = 17.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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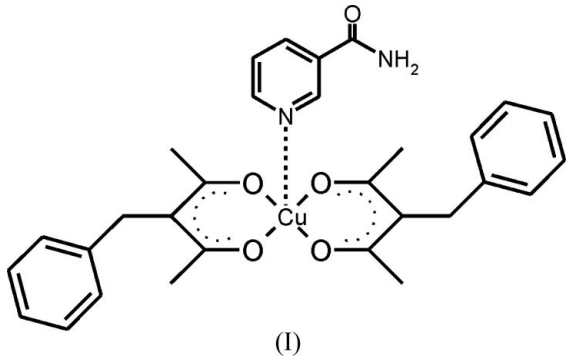
In the title compound, $[Cu(C_{12}H_{13}O_2)_2(C_6H_6N_2O)]$, a nicotinamide adduct of bis(3-benzylpentane-2,4-dionato)copper(II), the metal ion exhibits a square-pyramidal coordination environment. The molecules of the complex self-assemble in the solid state by way of amide-to-amide hydrogen bonds to form one-dimensional polymers.

Comment

Metal complexes of β-diketones have been studied intensively for many years and have proved useful in a wide range of applications (Dash & Mohapatra, 1984; Parkanyl *et al.*, 1981; Soldatov *et al.*, 2003). However, these compounds have not been extensively studied in terms of supramolecular chemistry and solid-state self-assembly involving weak interactions (Aakeröy *et al.*, 2005; Papaefstathiou *et al.* 2004). In this context, copper(II) β-diketonate molecules, being planar and coordinatively unsaturated, are suitable to be used for the exploration of the weak interactions that steer the self-assembly of molecules in solids. In particular, the ability of such molecules to form adducts by binding additional ligands provides a way to construct extended metal-containing motifs in which the assembly and organization of molecules is regulated by weak interactions (*e.g.* hydrogen bonds). Consequently, different choices of addend molecules are expected to result in different solid-state architectures.



(I)

The self-assembly of the bis(3-benzylpentane-2,4-dionato)-copper(II) complex Cu[α(Bzl)acac]$_2$ is driven by weak C—H···O hydrogen bonding and π–π stacking (Judaš & Kaitner, 2006). A suitable bifunctional ligand that would bind to the Cu^{II} ion and also participate in intermolecular hydrogen bonding is expected to affect the morphology of the crystal. We have selected nicotinamide as a template that would construct a metal-containing ribbon-like supramolecular architecture following coordination to Cu[α(Bzl)acac]$_2$ 'hubs'

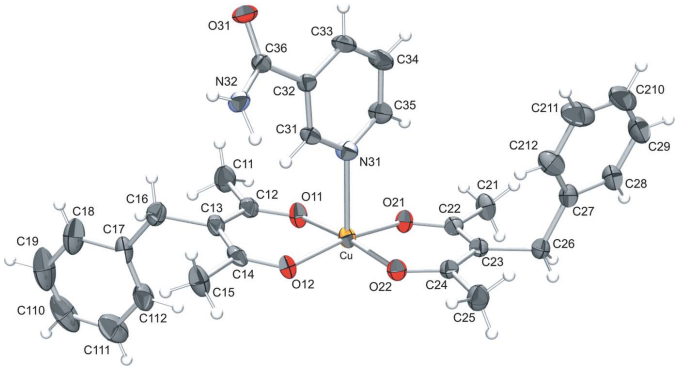


Figure 1
The molecular structure of the nicotinamide adduct of Cu[α(Bzl)acac]$_2$, (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

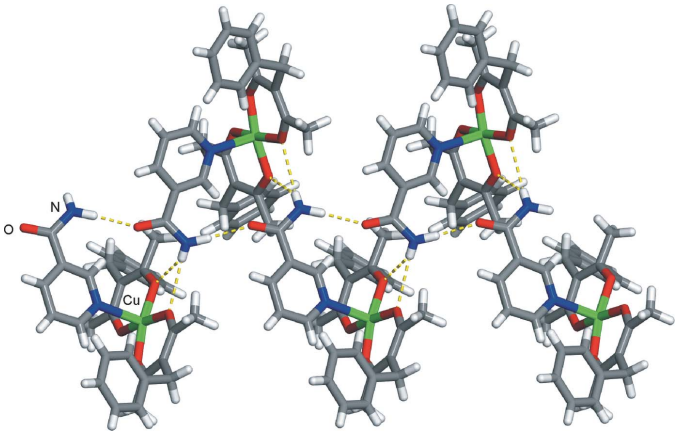


Figure 2
A ball-and-stick representation of the hydrogen-bonded molecular ribbons in the crystal structure of (I)

and present here the crystal structure of such a complex, the title compound, (I).

As expected, the nicotinamide molecule of (I) binds in the apical position of the central metal ion through pyridine atom N31, thus establishing a square-pyramidal coordination environment (Fig. 1 and Table 1). The Cu^{II} ion is displaced from of the chelate plane towards the nicotinamide molecule by 0.151 (1) Å. In comparison, the starting Cu[α(Bzl)acac]$_2$ complex exhibits an approximately square-planar coordination of Cu^{II}. The overall structure of the Cu[α(Bzl)acac]$_2$ hub does not change significantly from the pure compund to the present nicotinamide adduct. In the nicotinamide derivative, the chelate rings of the Cu[α(Bzl)acac]$_2$ unit are more folded along the line defined by the chelate O atoms than in the case of the free complex. Notably, the dihedral angles between the plane of the chelate ring atoms C12, C13 and C14 and the plane defined by atoms Cu, O11 and O12, and between the planes Cu/O21/O22 and C22/C23/C24, amount to 8.3 (5) and 18.4 (5)°, respectively, in the nicotinamide adduct and 2.4 (3)° in the free Cu[α(Bzl)acac]$_2$ complex.

The benzyl groups of the two β-diketonate ligands of the nicotinamide adduct molecule adopt different conformations. Specifically, the difference is best described in terms of the torsion angles C13—C16—C17—C18 = −137.4 (4)° and C23—C26—C27—C28 = 12.8 (7)°. The second value differs significantly from the value of 54.8 (3)° observed in the free Cu[α(Bzl)acac]$_2$ complex. The difference can most probably be explained by the formation of C—H···O hydrogen bonds involving the benzyl group atom C210 and the amide O atom of a neighbouring molecule (Table 2).

As expected, the crystal structure of (I) is characterized by intermolecular hydrogen bonds that form between the amide moieties of adjacent nicotinamide ligands (Table 2). Notably, pairs of N—H···O and C—H···O hydrogen bonds link the nicotinamide fragments of neighbouring molecules to form zigzag molecular ribbons that run parallel to the crystallographic *c* axis. The structure of the ribbons is also supported by intermolecular N—H···O hydrogen bonds, which involve an amide group and O atoms of the β-diketonate ligand (Fig. 2).

The ribbons are further interlinked by C210—H210···O31^{iii} hydrogen bonds and stack on top of each other (Fig. 3*a*) to form sheets parallel to the crystallographic *ac* plane. The sheets are held together by C34—H34···O212^{iv} hydrogen bonds (symmetry codes are given in Table 2), thus forming an extended metal–organic framework that displays narrow channels parallel to the crystallographic *a* axis (Fig. 3*b*).

The replacement of C—H···O hydrogen bonding in the free Cu[α(Bzl)acac]$_2$ complex with a combination of N—H···O and C—H···O interactions in the nicotinamide adduct results in a profound change in the crystal morphology. In particular, whereas the free Cu[α(Bzl)acac]$_2$ complex crystallizes in the form of extremely long and fragile needles, the nicotinamide adduct provides crystals of a more isometric habit. This observation suggests that adduct formation is useful not only as a tool to construct extended architectures, but also a means of modifying the macroscopic properties of the material.

Experimental

The title complex was prepared by reacting the starting Cu[α(Bzl)-acac]$_2$ complex with a threefold excess of nicotinamide in hot acetone. To an almost boiling dark-green solution of Cu[α(Bzl)acac]$_2$ (0.442 g, 1 mmol) in acetone (20 ml), solid nicotinamide (0.370 g, 3 mmol) was added, successively and in small portions. The reaction mixture turned bright green upon the addition of the ligand. The hot mixture was filtered and the mother liquor was left to cool to room temperature. Slow evaporation of the mother liquor over a period of 1 d resulted in the formation of small green plates of the title compound.

Crystal data

$[Cu(C_{12}H_{13}O_2)_2(C_6H_6N_2O)]$
M_r = 564.13
Monoclinic, $P2_1/c$
a = 12.3775 (18) Å
b = 22.5695 (19) Å
c = 10.0534 (12) Å
β = 93.018 (8)°
V = 2804.6 (6) Å^3
Z = 4
D_x = 1.336 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 34 reflections
θ = 10.1–16.4°
μ = 0.82 mm^{-1}
T = 298 (1) K
Plate, green
0.58 × 0.37 × 0.07 mm

Data collection

Philips PW1100 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.688, T_{max} = 0.946
6404 measured reflections
6128 independent reflections
2868 reflections with $I > 2\sigma(I)$

R_{int} = 0.180
θ_{max} = 27.0°
$h = 0 \rightarrow 15$
$k = -28 \rightarrow 0$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: 3.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.151
S = 0.97
6128 reflections
343 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0738P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O11	1.918 (3)	Cu—O21	1.937 (3)
Cu—O12	1.930 (3)	Cu—N31	2.342 (3)
Cu—O22	1.930 (2)		
O11—Cu—O12	91.43 (11)	O22—Cu—O21	90.28 (11)
O11—Cu—O22	169.43 (12)	O11—Cu—N31	93.92 (12)
O12—Cu—O22	88.06 (11)	O12—Cu—N31	95.86 (12)
O11—Cu—O21	88.86 (11)	O22—Cu—N31	96.64 (12)
O12—Cu—O21	172.49 (12)	O21—Cu—N31	91.61 (12)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N32—H1*N*···O31^{i}	1.06	1.95	3.008 (4)	178
N32—H2*N*···O22^{ii}	1.00	2.42	3.174 (4)	131
N32—H2*N*···O12^{ii}	1.00	2.32	3.205 (4)	147
C31—H31···O31^{i}	0.93	2.45	3.096 (5)	126
C210—H210···O31^{iii}	0.93	2.67	3.453 (7)	142
C34—H34···O21^{iv}	0.93	2.56	3.309 (5)	138

Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $x+1, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x, -y, -z+1$.

The coordinates of the H atoms bonded to C atoms were calculated following stereochemical rules, with C—H distances of 0.93 for phenyl H, 0.97 for methylene H and 0.96 Å for methyl groups. The H atoms were included in the refinement using the riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(C) for phenyl and methylene residues and 1.5U_{eq}(C) for the methyl groups. The H atoms of the amino group were located in a difference Fourier map; their coordinates were not refined and U_{iso}(H) = 1.5U_{eq}(N).

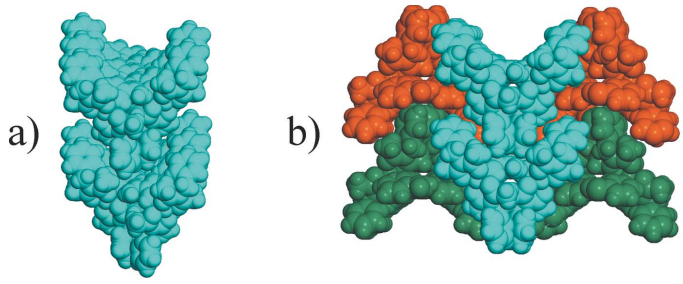


Figure 3
(*a*) A space-filling representation of the molecular sheets in (I). (*b*) A space-filling view illustrating the extended metal–organic framework with narrow channels in (I).

Data collection: *STADI4* (Stoe & Cie, 1995); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997), *MERCURY* (Version 1.2.1; Bruno *et al.*, 2002), *RasTop* (Valadon, 2004) and *POV-RAY* (Persistence of Vision, 2004); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Aakeröy, C. B., Schultheiss, N. & Desper, J. (2005). *Inorg. Chem.* **44**, 4983–4991.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Dash, G. C. & Mohapatra, B. K. (1984). *J. Indian Chem. Soc.* **61**, 830–832.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Judaš, N. & Kaitner, B. (2006). *Acta Cryst.* E**62**, m163–m165.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Papaefstathiou, G. S., Hamilton, T. D., Friščić, T. & MacGillivray, L. R. (2004). *Chem. Commun.* pp. 270–271.
Parkanyl, C., Sturm, P., Jeffries, A. T. & Pannel, K. H. (1981). *J. Coord. Chem.* **11**, 153–158.
Persistence of Vision (2004). *POV-RAY*. Version 3.6. Persistence of Vision Pty. Ltd, Victoria, Australia. URL: http://www.povray.org/.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Soldatov, D. V., Tinnemans, P., Enright, G. D., Ratcliff, C. I., Diamente, P. R. & Ripmeester, J. A. (2003). *Chem. Mater.* **15**, 3826–3840.
Stoe & Cie (1995). *STADI4* (Version 1.05b) and *X-RED* (Version 1.05). Stoe & Cie, Darmstadt, Germany.
Valadon, P. (2004). *RasTop*. Version 2.0.3. Philippe Valadon, PO Box 928064, La Jolla, CA 92192-8064, USA. URL: http://www.geneinfinity.org/rastop/.