Crystal structure of bis(pivaloylhydroxamato-κ²O,O′)copper(II)

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Reaction of copper(II) nitrate with pivaloylhydroxamic acid yielded the title compound, [Cu(pivHA)$_2$] (where pivHA$^-$ is pivaloyl hydroxamate, C$_5$H$_{10}$NO$_2$). The centrosymmetric mononuclear complex consists of a Cu^{II} ion, which is located on a center of inversion, with two coordinated pivaloyl hydroxamate monoanions. The Cu^{II} ion has a square-planar coordination environment consisting of four O atoms – two carbonyl O atoms and two hydroxamate O atoms from two hydroxamate pivHA$^-$ ligands. The pivHA$^-$ anions are coordinated to copper(II) in a *trans*-mode, forming two five-membered O,O′-chelate rings.

1. Chemical context

Numerous studies over the past decade of various hydroxamate complexes with 3d and 4f metal ions have been inspired by their potential applications in molecular magnetism, luminescence, adsorption and catalysis (Ostrowska *et al.*, 2016; Pavlishchuk *et al.*, 2015). The ability of further functionalized hydroxamic acids to serve as bridging ligands and to form polynuclear species with different structural motifs has been comprehensively examined in recent years (Mezei *et al.*, 2007; Pavlishchuk *et al.*, 2018; Odarich *et al.*, 2016; McDonald *et al.*, 2014, 2015; Gaynor *et al.*, 2002). Studies of simple unsubstituted hydroxamic acids have been undertaken because of their possible application as mimics of mononuclear iron(III) siderophores (Marmion *et al.*, 2004). As a result of the potentially multiple coordination modes of unsubstituted hydroxamic acids, they can also lead to the formation of polynuclear assemblies (Tirfoin *et al.*, 2014). However, reactions of unsubstituted hydroxamic acids with transition metal ions lead mainly to the formation of octahedral 1:3 (Abu-Dari *et al.*, 1979) or square-planar 1:2 (Baughman *et al.*, 2000) complexes with the hydroxamate in an O,O′-coordination mode. The ability of pivalic acid itself to form polynuclear metallamacrocyclic complexes with various metal ions is well known (Vitórica-Yrezábal *et al.*, 2017; Garlatti *et al.*, 2018). The aim of the current work was to investigate if a *tert*-butyl-substituted hydroxamic acid (*i.e.* the hydroxamate analogue of pivalic acid) could be used as a scaffold for the preparation of polynuclear copper(II) complexes.
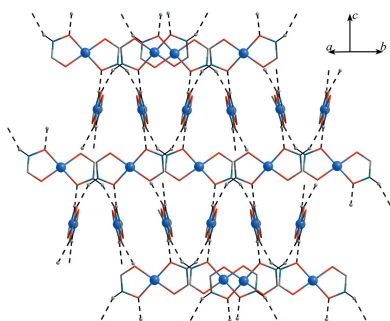
2. Structural commentary

Crystals of the title compound **1** were obtained by reaction of copper(II) nitrate hexahydrate with pivaloylhydroxamic acid in methanol.
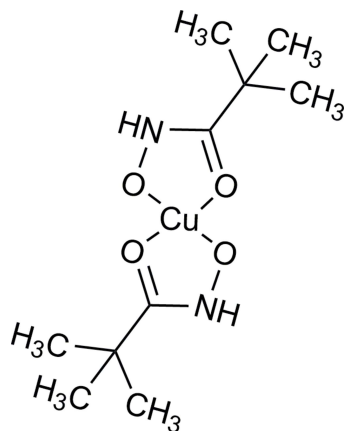
Complex **1** crystallizes in the space group $I4_1/a$, with eight [Cu(pivHA)$_2$] complex molecules per unit cell. The [Cu(pivHA)$_2$] molecules are centrosymmetric, with the copper ion located on an inversion center. Each [Cu(pivHA)$_2$] molecule contains one copper(II) ion in a square-planar coordination environment generated by the coordination of two pivaloylhydroxamate monoanions, forming five-membered chelate rings through both the carbonyl and hydroxamate O atoms (Fig. 1). The centrosymmetric nature of the complex forces the copper(II) ions to be exactly coplanar with the four donor O atoms, O1O2O1^{i}O2^i [symmetry code: (i) $-x$, $1 - y$, $-z$], and the two pivHA$^-$ monoanions in [Cu(pivHA)$_2$] are necessarily mutually *trans*-coordinated. The axial positions of the copper(II) ions remain unoccupied. The Cu—O$_{carbonyl}$ and Cu—O$_{hydroxamate}$ bond lengths are typical for copper(II) hydroxamate or oximate complexes (Buvailo *et al.*, 2012; Pavlishchuk *et al.*, 2017a,b) (Table 1). The hydroxamate N—H groups remain protonated and are not involved in metal coordination. Deprotonation of the N—H groups could
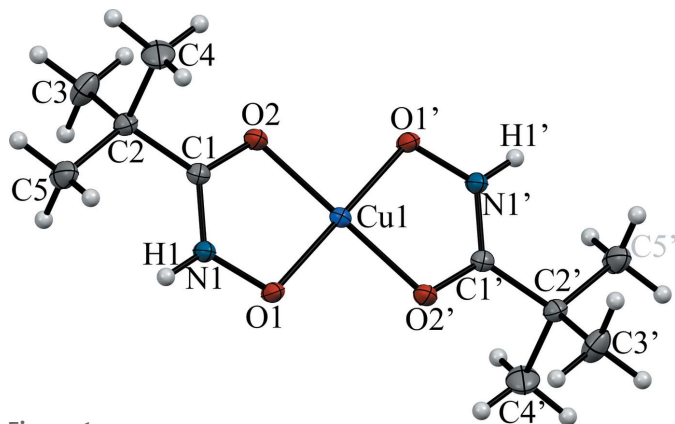
possibly be achieved at higher pH without hydrolysis of hydroxamic acid, which might aid in the formation of polynuclear complexes.

3. Supramolecular features

Adjacent [Cu(pivHA)$_2$] complexes are connected to each other *via* N1–H1···O1^{ii} hydrogen bonds between the hydroxamate N—H group of one complex molecule and a deprotonated hydroxamate oxygen of an adjacent [Cu(pivHA)$_2$] molecule (Table 2, Fig. 2). Four of these N—H···O hydrogen bonds connect molecules into tetramers arranged around a fourfold rotoinversion center. The N—H group of the second hydroxamate ligand of each complex creates an equivalent tetramer *trans* across the copper ion, thus creating an infinite three-dimensional network of corner-connected tetramers (with the copper ions acting as the bridging element, Fig. 3).

Table 1
Selected geometric parameters (Å, °).

C1—O2	1.2821 (13)	O1—Cu1	1.8899 (8)
C1—N1	1.3066 (14)	O2—Cu1	1.9244 (8)
N1—O1	1.3764 (12)		
O1—Cu1—O1^i	180 (5)	O1—Cu1—O2^i	95.16 (3)
O1—Cu1—O2	84.84 (3)	O1^i—Cu1—O2^i	84.84 (3)
O1^i—Cu1—O2	95.16 (3)	O2—Cu1—O2^i	180

Symmetry code: (i) $-x, -y + 1, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{ii}	0.88	1.90	2.7185 (13)	154

Symmetry code: (ii) $y - \frac{1}{4}, -x + \frac{1}{4}, -z + \frac{1}{4}$.

Figure 1
The molecular structure of complex **1** showing the neutral centrosymmetric fragment [Cu(pivHA)$_2$], along with the atom labelling. Displacement ellipsoids are at the 50% probability level. Symmetry code: (') $-x$, $1 - y$, $-z$.

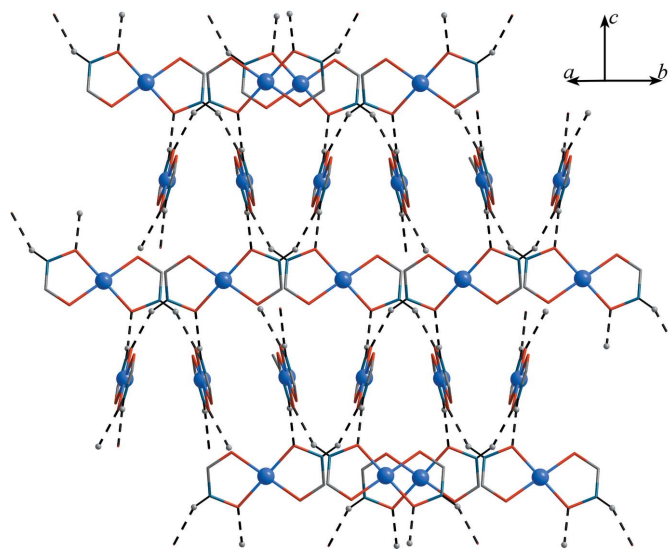**Figure 2**
A fragment of the lattice of complex **1**, showing the intramolecular hydrogen-bonding connections (dashed lines) between the [Cu(pivHA)$_2$] molecules. The *tert*-butyl groups are omitted for clarity.

Figure 3
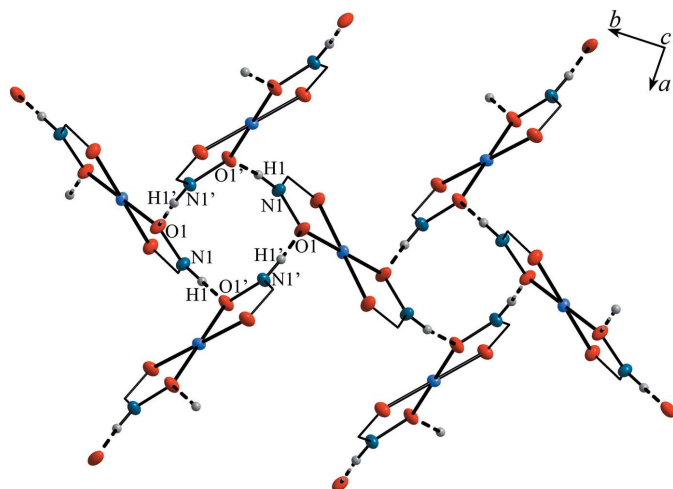A fragment of the packing of complex **1**, showing the formation of supramolecular tetramers [Cu(pivHA)$_2$]$_4$ formed by hydrogen bonds. The *tert*-butyl groups are omitted for clarity.

4. Database survey

The Cambridge Structural Database (CSD, Version 5.27, updated in August 2012; Groom *et al.*, 2016) contains one report with structural information for pivaloylhydroxamic acid (CCDC 1155138; Due *et al.*, 1987). Though the survey did not contain any information about complexes with pivaloyl-hydroxamic acid, there are two reports devoted to structural studies of Th^{4+} (1180613 and 1180614; Smith & Raymond, 1981) and MoO$_2^{2+}$ (763210–763214; Dzyuba *et al.*, 2010) complexes with structurally similar ligands (*N*-isopropyl-2,2-dimethylpropanehydroxamate, *N*-isopropyl-3,3-dimethyl-butanehydroxamate and decano-, *N*-methyl-decano-, *N*-methyl-hexano-, *N*-methyl-1-adamantano- or *N*-*tert*-butyl-hexanohydroxamates, respectively). It should be mentioned that coordination of hydroxamate ligands in the *O*,*O*′-chelating mode is quite typical (Tedeschi *et al.*, 2003; Seitz *et al.*, 2007*a*,*b*; Brewer & Sinn, 1981) and the CSD contains many records with such binding in various mononuclear bis-hydroxamate complexes (*e.g.* Drovetskaia *et al.*, 1996; Li *et al.*, 2004; Fisher *et al.*, 1989; Harrison *et al.*, 1976), which are usually coordinated in the *trans-* mode with respect to each other (Gaynor *et al.*, 2001; Lasri *et al.*, 2012; Casellato *et al.*, 1984).

5. Synthesis and crystallization

A solution of pivaloylhydroxamic acid (23.4 mg, 0.20 mmol) in 5 mL of methanol was added to copper(II) nitrate hexahydrate (29.6 mg, 0.10 mmol) in 5 mL of methanol. The resulting blue solution was stirred for 30 min. at room temperature, filtered and left for slow evaporation. After a week, blue crystals suitable for single crystal X-ray analysis had formed. Yield: 23 mg (78%). Elemental analysis C:H:N Expected (calculated): 40.75 (40.60): 7.03 (6.81): 9.22 (9.47). IR in KBr pellets (cm^{-1}): 3400 (ν_{N-H}); 3196–3040 (ν_{O-H}, likely due to the presence of N1—H1···O1^{ii} hydrogen bonds); 1595

Table 3
Experimental details.

Crystal data	
Chemical formula	[Cu(C$_5$H$_{10}$NO$_2$)$_2$]
M_r	295.82
Crystal system, space group	Tetragonal, $I4_1/a$
Temperature (K)	100
a, c (Å)	12.8059 (5), 17.7051 (8)
V (Å^3)	2903.5 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.51
Crystal size (mm)	0.35 × 0.35 × 0.29
Data collection	
Diffractometer	Bruker D8 Quest CMOS
Absorption correction	Multi-scan (*SADABS*; Krause et al., 2015)
T_{min}, T_{max}	0.656, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24433, 2764, 2444
R_{int}	0.035
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.769
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.074, 1.19
No. of reflections	2764
No. of parameters	82
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.46, −0.48

Computer programs: *APEX2* and, *SAINT* (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *shelXle* (Hübschle *et al.*, 2011), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

and 1503 ($\nu_{amid\ I}$); 1330, 1220 and 1053 (ν_{C-C} and ν_{-C-N}); 963 (ν_{N-O}).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms attached to carbon and nitrogen atoms were positioned geometrically and constrained to ride on their parent atoms: C—H =0.98 Å with $U_{iso}(H)$ = 1.5U_{eq}(C) and N—H = 0.88 Å with $U_{iso}(H)$ = 1.2U_{eq}(N). Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density.

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Crystal structure of bis(pivaloylhydroxamato-κ^2O,O')copper(II)

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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015), *shelXle* (Hübschle *et al.*, 2011); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Bis(pivaloylhydroxamato-κ^2O,O')copper(II)

Crystal data

[Cu(C$_5$H$_{10}$NO$_2$)$_2$]	D_x = 1.353 Mg m^{-3}
M_r = 295.82	Mo $K\alpha$ radiation, λ = 0.71073 Å
Tetragonal, $I4_1/a$	Cell parameters from 9939 reflections
a = 12.8059 (5) Å	θ = 3.2–33.2°
c = 17.7051 (8) Å	μ = 1.51 mm^{-1}
V = 2903.5 (3) Å^3	T = 100 K
Z = 8	Prism, blue
$F(000)$ = 1240	0.35 × 0.35 × 0.29 mm

Data collection

Bruker AXS D8 Quest CMOS diffractometer	T_{min} = 0.656, T_{max} = 0.747
Radiation source: I-mu-S microsource X-ray tube	24433 measured reflections
	2764 independent reflections
Laterally graded multilayer (Goebel) mirror monochromator	2444 reflections with $I > 2\sigma(I)$
	R_{int} = 0.035
ω and phi scans	θ_{max} = 33.2°, θ_{min} = 3.2°
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$h = -19 \rightarrow 19$
	$k = -19 \rightarrow 19$
	$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)]$ = 0.029	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.074	
S = 1.19	H-atom parameters constrained
2764 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0257P)^2 + 3.2993P]$ where $P = (F_o^2 + 2F_c^2)/3$
82 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max}$ = 0.46 e Å^{-3}
	$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.13160 (8)	0.34258 (8)	−0.02113 (6)	0.01465 (18)
C2	0.20901 (9)	0.26772 (9)	−0.05643 (7)	0.01747 (19)
C3	0.30109 (12)	0.33273 (12)	−0.08492 (10)	0.0327 (3)
H3A	0.349813	0.287558	−0.112390	0.049*
H3B	0.337056	0.364691	−0.041874	0.049*
H3C	0.275434	0.387597	−0.118744	0.049*
C4	0.15406 (12)	0.21475 (12)	−0.12341 (8)	0.0284 (3)
H4A	0.130218	0.268097	−0.159159	0.043*
H4B	0.093923	0.174854	−0.105007	0.043*
H4C	0.203005	0.167530	−0.148793	0.043*
C5	0.24745 (12)	0.18527 (12)	−0.00063 (8)	0.0274 (3)
H5A	0.187982	0.144200	0.017576	0.041*
H5B	0.281569	0.219691	0.042206	0.041*
H5C	0.297448	0.139024	−0.025866	0.041*
N1	0.10376 (7)	0.33335 (8)	0.04955 (5)	0.01550 (17)
H1	0.128862	0.282995	0.078083	0.019*
O1	0.03387 (7)	0.40497 (7)	0.07791 (5)	0.01837 (16)
O2	0.09269 (7)	0.41676 (7)	−0.06079 (5)	0.01830 (16)
Cu1	0.000000	0.500000	0.000000	0.01360 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0150 (4)	0.0146 (4)	0.0143 (4)	−0.0005 (3)	0.0017 (3)	0.0009 (3)
C2	0.0180 (5)	0.0179 (5)	0.0166 (5)	0.0020 (4)	0.0038 (4)	0.0011 (4)
C3	0.0242 (6)	0.0314 (7)	0.0424 (8)	−0.0013 (5)	0.0165 (6)	0.0028 (6)
C4	0.0311 (7)	0.0303 (6)	0.0238 (6)	0.0075 (5)	−0.0015 (5)	−0.0098 (5)
C5	0.0321 (7)	0.0275 (6)	0.0227 (6)	0.0144 (5)	0.0056 (5)	0.0046 (5)
N1	0.0168 (4)	0.0156 (4)	0.0142 (4)	0.0034 (3)	0.0031 (3)	0.0026 (3)
O1	0.0227 (4)	0.0186 (4)	0.0138 (3)	0.0077 (3)	0.0063 (3)	0.0033 (3)
O2	0.0241 (4)	0.0172 (4)	0.0136 (3)	0.0045 (3)	0.0037 (3)	0.0035 (3)
Cu1	0.01670 (10)	0.01244 (9)	0.01165 (9)	0.00085 (6)	0.00182 (6)	0.00171 (6)

Geometric parameters (Å, °)

C1—O2	1.2821 (13)	C4—H4B	0.9800
C1—N1	1.3066 (14)	C4—H4C	0.9800
C1—C2	1.5141 (16)	C5—H5A	0.9800
C2—C5	1.5275 (18)	C5—H5B	0.9800

C2—C3	1.5290 (18)	C5—H5C	0.9800
C2—C4	1.5368 (18)	N1—O1	1.3764 (12)
C3—H3A	0.9800	N1—H1	0.8800
C3—H3B	0.9800	O1—Cu1	1.8899 (8)
C3—H3C	0.9800	O2—Cu1	1.9244 (8)
C4—H4A	0.9800		
O2—C1—N1	119.04 (10)	H4A—C4—H4C	109.5
O2—C1—C2	119.84 (10)	H4B—C4—H4C	109.5
N1—C1—C2	121.12 (10)	C2—C5—H5A	109.5
C1—C2—C5	112.43 (10)	C2—C5—H5B	109.5
C1—C2—C3	107.24 (10)	H5A—C5—H5B	109.5
C5—C2—C3	109.95 (12)	C2—C5—H5C	109.5
C1—C2—C4	107.35 (10)	H5A—C5—H5C	109.5
C5—C2—C4	109.97 (11)	H5B—C5—H5C	109.5
C3—C2—C4	109.81 (11)	C1—N1—O1	117.82 (9)
C2—C3—H3A	109.5	C1—N1—H1	121.1
C2—C3—H3B	109.5	O1—N1—H1	121.1
H3A—C3—H3B	109.5	N1—O1—Cu1	108.18 (6)
C2—C3—H3C	109.5	C1—O2—Cu1	110.11 (7)
H3A—C3—H3C	109.5	O1—Cu1—O1^i	180.00 (5)
H3B—C3—H3C	109.5	O1—Cu1—O2	84.84 (3)
C2—C4—H4A	109.5	O1^i—Cu1—O2	95.16 (3)
C2—C4—H4B	109.5	O1—Cu1—O2^i	95.16 (3)
H4A—C4—H4B	109.5	O1^i—Cu1—O2^i	84.84 (3)
C2—C4—H4C	109.5	O2—Cu1—O2^i	180.0
O2—C1—C2—C5	179.56 (11)	C2—C1—N1—O1	179.33 (10)
N1—C1—C2—C5	−0.14 (16)	C1—N1—O1—Cu1	−0.49 (12)
O2—C1—C2—C3	58.59 (15)	N1—C1—O2—Cu1	1.02 (13)
N1—C1—C2—C3	−121.11 (13)	C2—C1—O2—Cu1	−178.69 (8)
O2—C1—C2—C4	−59.37 (14)	N1—O1—Cu1—O2	0.79 (7)
N1—C1—C2—C4	120.94 (12)	N1—O1—Cu1—O2^i	−179.21 (7)
O2—C1—N1—O1	−0.37 (16)		

Symmetry code: (i) −*x*, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{ii}	0.88	1.90	2.7185 (13)	154

Symmetry code: (ii) *y*−1/4, −*x*+1/4, −*z*+1/4.