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Three complexes of bis(*N*-methylbenzohydroxamato-*O*,*O*′)copper(II)

Russell G. Baughman,* Daniel J. Brink, Jill M. Butler and Pamela R. New†

Division of Science, Truman State University, Kirksville, MO 63501-4221, USA
Correspondence e-mail: baughman@truman.edu

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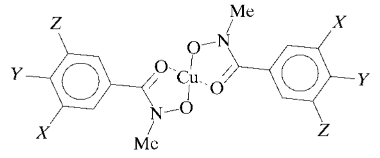
The first single-crystal studies of three bis-*transoid* Cu–hydroxamate salts, bis(3-methoxy-4,*N*-dimethylbenzohydroxamato-*O*,*O*′)copper(II), [$Cu(C_{10}H_{12}NO_3)_2$], bis(4-chloro-*N*-methylbenzohydroxamato-*O*,*O*′)copper(II), [$Cu(C_8H_7ClNO_2)_2$], bis(*N*-methyl-3,5-dinitrobenzohydroxamato-*O*,*O*′)copper(II)–chloroform (1/2), [$Cu(C_8H_6N_3O_6)_2$]·2$CHCl_3$, are presented. The Cu atom in each of the title compounds sits at a center of inversion and displays a nearly square-planar geometry with the hydroxamate-O atoms connected to it in a *syn* configuration. The N atoms are in a *transoid* configuration. Each five-membered Cu–hydroxamate ring is planar, thus providing evidence that a planar N atom is present in each ring. The phenyl groups are twisted with respect to the hydroxamate group by ~40–54°. The angular strain of the *sp*^{2} carbonyl oxygen is significant (~10° from ideal).

Comment

Copper complexes containing derivatives of the *N*-methylbenzohydroxamate ligand have been prepared for the study of the organic ligand as an α nucleophile [see, for example, Carey & Sundberg (1990) for a discussion on the α effect]. Unlike the only other previous single crystallographic studies involving Cu hydroxamates [a dimer by Barclay & Raymond (1986) and metallocrown compounds by Stemmler *et al.* (1999)], we are interested in how the presence of a transition metal will affect the role of the α nucleophile in substitution reactions. Crystal structure determinations were performed to determine the bonding mode of the organic ligands to the copper center, as well as to serve as a starting point for future molecular modeling studies.

All three of the title compounds have a Cu atom at a center of inversion so the hydroxamate-N atoms are in the *transoid* configuration, thus making this the first report of bis*transoid* Cu–hydroxamate structures. The five-membered Cu—O1—N1—C2—O2 groups are planar for (I), (II), and (III) (r.m.s. deviations = 0.010, 0.005, 0.005 Å, respectively). The r.m.s. distances of C1 and C3 from this plane in (I), (II), and (III) are, respectively, 0.062 and −0.030, 0.114 and −0.023, and 0.112 and 0.038 Å. Thus, each N1 atom is essentially planar. The O atoms assume a *syn* configuration yielding O1—Cu—O2 and supplementary angles of ~84 and ~96° (Table 1), respectively, thus making a nearly square-planar geometry about the Cu atom.



Compound	*X*	*Y*	*Z*	Solvate
(I)	−H	−Me	−OMe	None
(II)	−H	−Cl	−H	None
(III)	$-NO_2$	−H	$-NO_2$	2$CHCl_3$

While most of the selected distances and angles noted in Table 1 are comparable, some significant (>4σ) ones are noteworthy. In (III), the Cu—O1 distance is longer than in complexes (I) or (II), while the Cu—O2 distance is concomitantly shorter than its counterparts. Similarly, in (I), the O1—N1—C1 angle is smaller than for (II) or (III); C1—N1—C2 is larger.

For the most part, the Cu—O1 distances in the three title complexes are shorter than in a few other five-membered, though not hydroxamate, rings. Singly bonded Cu—O distances of 1.902 (2) and 1.892 (2) Å (with cupferron; Elerman *et al.*, 1995); 2.011 (2) and 2.013 (2) Å (with 2-amino-2-thiazoline-4-carboxylic acid; Stocker *et al.*, 1999); 1.936 (3) and 1.959 (3), and 1.935 (5) and 1.967 (4) Å (with picolinamide hydrazone:alanine and picolinamide hydrazone:glycine, respectively; Thompson *et al.*, 1998) have been reported.

Stemmler *et al.* (1999) reported an average oxime O—Cu distance for the five metallocrown complexes in their study as 1.934 (6) Å, a difference of ~6σ greater than this work. The average carbonyl O—Cu distance of 1.947 (6) Å is just slightly (>3σ) longer than those in this report. In each of their structures, the oxime-O atoms have a third coordination to a lanthanide facilitating a bridging of Cu atoms to the Ln atom. The hydroxamate-N atoms are also coordinated to a Cu atom aiding in the formation of the metallocrown complexes. They also reported an average value for the O1—Cu—O2 angle (present notation) of 85.8 (2)°, a difference of >7σ from this work. Barclay & Raymond (1986) reported a single dimeric complex in which the N atoms are *cisoid*, all of which is different from that reported in this work. Their distances for oxime O—Cu [1.885 (4) Å] and carbonyl O—Cu [1.915 (4) Å] are both <2σ of the present work. Additionally, their average O1—Cu—O2 angle of 84.2 (2)° is <1σ from this work. The stronger similarity of Barclay & Raymond's (1986) complex to the three structures reported here is likely due to the hydroxamate groups being less constrained in all four complexes than in the work of Stemmler *et al.* (1999).

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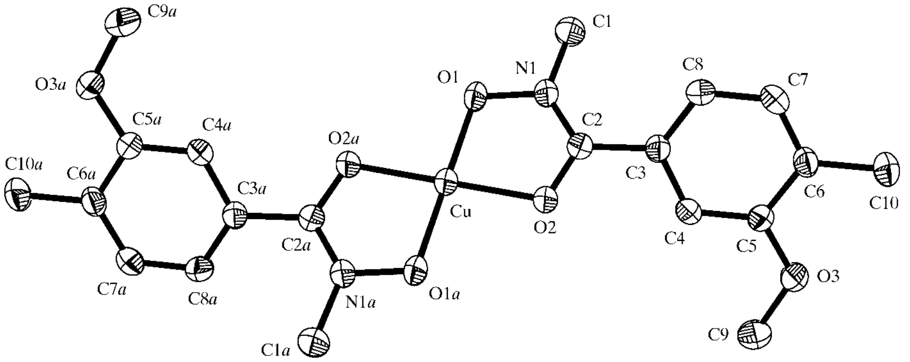
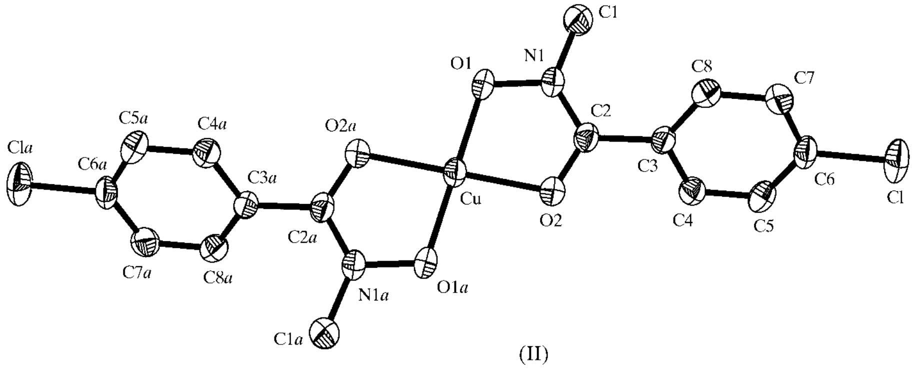
† Current address: Department of Chemistry, University of Central Oklahoma, Edmond, OK 73034-5209, USA.

Although the angles about O1 and O2 in this work are all ~110°, Cu—O2—C2 is significantly (>7σ) larger than Cu—O1—N1 (*cf.* Table 1). Additionally, the deviation of these angles from that anticipated from the hybridization at each oxygen would indicate more strain at O2. Consistent with this is the average C2=O2 distance of 1.281 (4) Å which is significantly longer than the values of 1.20 (2) to 1.25 (1) Å for three free hydroxamic acids (Baughman, 1982) and the average of 1.23 (1) Å cited in the *International Tables for Crystallography*, thus confirming a concomitant weakening of the C2=O2 bond as O2 donates electron density to the Cu atom. Similar comparisons of the N1—O1 distances in (I)–(III) would best be performed with the 'free' hydroxamate anion. These studies are currently in progress and will be reported in a future paper.

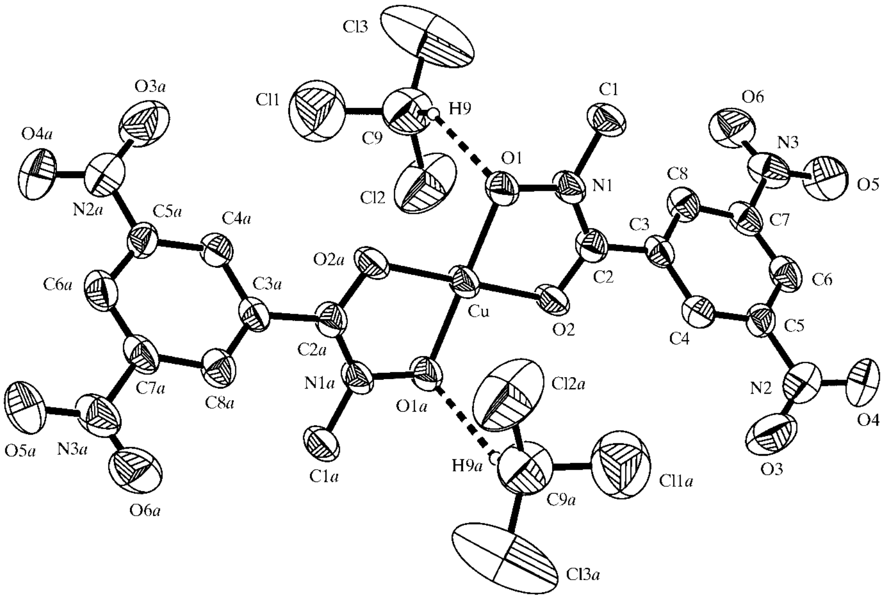
For (I), the methoxy group is coplanar with the phenyl ring as the dihedral angle is 2.2 (2)°. However, the phenyl rings for (I), (II) and (III) are not coplanar with the hydroxamate group, thus reducing delocalization throughout all three systems. The reason for the twisting of the phenyls to comparable dihedral angles [40.86 (7), 54.37 (8) and 46.26 (9)° for (I), (II) and (III), respectively] is primarily due to the steric interference of the H on C8 with the C1 methyl group (Table 3). No close (van der Waals) intermolecular contact



(I)



(II)



(III)

Figure 1

Views of (I), (II) and (III) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels. For (III), H9*a* is drawn as a small sphere of arbitrary radius.

with the phenyl is noted for (I); a few are noted for (II) and (III) (Table 3), perhaps explaining why the dihedral angles for (II) and (III) are larger than for (I).

In (III), a molecule of $CHCl_3$ is hydrogen bonded to O1 (H$\cdots$O1 = 2.34, C9$\cdots$O1 = 3.18 Å, N1—O1$\cdots$H9 = 107, C9—H9$\cdots$O1 = 146°). Both nitro groups (O5/N3/O6 and O3/N2/O4) are slightly twisted with respect to the phenyls as the dihedral angles are 9.6 (6) and 19.7 (4)°, respectively, likely due to numerous close contacts noted in Table 2.

Experimental

Compound (I): in a method similar to that of Bhattacharyya & Dhar (1982), $Cu(NO_3)_2\cdot3H_2O$ (0.5 mmol) in H_2O (30 ml) was added to 3-methoxy-4-methyl-*N*-methylbenzohydroxamic acid (1.1 mmol) in EtOH (20 ml). To this mixture, NaOH (1 ml of 1 *M*) was added dropwise with stirring. The precipitate that formed quickly was filtered off, washed and recrystallized (slow evaporation, ~1 week) from a minimal amount of $CHCl_3$ and ten drops of benzene. Compound (II): $Cu(NO_3)_2\cdot3H_2O$ (0.5 mmol) in H_2O (30 ml) was added to sodium 4-chloro-*N*-methylbenzohydroxamate (1.1 mmol) in EtOH (30 ml) with constant stirring. This quickly produced a precipitate which was filtered off, and washed and recrystallized (slow evaporation, ~1 week) from a minimal amount of $CHCl_3$. Compound (III): $Cu(NO_3)_2\cdot3H_2O$ (0.5 mmol) in H_2O (25 ml) was combined with sodium 3,5-dinitro-*N*-methylbenzohydroxamate (1.1 mmol) in EtOH (40 ml) with constant stirring. The quickly appearing resultant yellow powder was recrystallized from a minimal amount of $CHCl_3$ yielding green crystals in ~3 d.

Compound (I)

Crystal data

$[Cu(C_{10}H_{12}NO_3)_2]$
$M_r = 451.97$
Monoclinic, $P2_1/n$
$a = 7.532$ (2) Å
$b = 9.073$ (3) Å
$c = 14.654$ (4) Å
$\beta = 99.07$ (2)°
$V = 988.9$ (5) Å^3
$Z = 2$

$D_x = 1.518$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
$\theta = 5.5$–21.9°
$\mu = 1.145$ mm^{-1}
$T = 288$ (2) K
Near octahedron, dark green
0.50 × 0.34 × 0.28 mm

Data collection

Siemens *P*3 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (*XDISK*; Siemens, 1991*a*)
$T_{min} = 0.588$, $T_{max} = 0.726$
3051 measured reflections
1735 independent reflections
1384 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$

$\theta_{max} = 25.04°$
$h = -2 \rightarrow 8$
$k = -2 \rightarrow 10$
$l = -17 \rightarrow 17$
3 standard reflections every 50 reflections intensity decay: average of 0.65% in $\sigma(I)$'s

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.087$
$S = 1.112$
1729 reflections
133 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.6217P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

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

	(I)	(II)	(III)
Cu—O1	1.888 (2)	1.888 (2)	1.901 (3)
Cu—O2	1.935 (2)	1.932 (2)	1.916 (3)
O1—N1	1.381 (3)	1.376 (3)	1.372 (4)
O2—C2	1.283 (3)	1.278 (3)	1.281 (4)
N1—C1	1.447 (4)	1.446 (4)	1.450 (5)
N1—C2	1.307 (3)	1.311 (3)	1.303 (5)
O1—Cu—O2	84.21 (8)	84.39 (8)	84.3 (1)
Cu—O1—N1	109.1 (2)	108.9 (1)	108.6 (2)
Cu—O2—C2	110.6 (2)	110.3 (2)	110.5 (2)
O1—N1—C1	111.8 (2)	113.1 (2)	113.4 (2)
O1—N1—C2	117.4 (2)	117.2 (2)	117.1 (3)
C1—N1—C2	130.8 (2)	129.5 (2)	129.4 (3)
O2—C2—N1	118.6 (2)	119.2 (2)	119.5 (4)

Compound (II)

Crystal data

$[Cu(C_8H_7ClNO_2)_2]$
$M_r = 432.74$
Monoclinic, $P2_1/n$
$a = 6.5953$ (9) Å
$b = 19.503$ (2) Å
$c = 7.387$ (1) Å
$\beta = 116.454$ (9)°
$V = 850.7$ (2) Å^3
$Z = 2$

$D_x = 1.689$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
$\theta = 7.22$–23.63°
$\mu = 1.622$ mm^{-1}
$T = 288$ (2) K
Prism, dark green
0.43 × 0.38 × 0.33 mm

Data collection

Siemens *P*3 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (*XDISK*; Siemens, 1991*a*)
$T_{min} = 0.527$, $T_{max} = 0.586$
1616 measured reflections
1487 independent reflections
1269 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$

$\theta_{max} = 25.00°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 23$
$l = -8 \rightarrow 7$
3 standard reflections every 50 reflections intensity decay: average of 0.92% in $\sigma(I)$'s

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.076$
$S = 1.117$
1478 reflections
115 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2 + 0.5359P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Compound (III)

Crystal data

$[Cu(C_8H_6N_3O_6)_2]\cdot2CHCl_3$
$M_r = 782.61$
Monoclinic, $P2_1/c$
$a = 11.197$ (2) Å
$b = 9.571$ (1) Å
$c = 14.676$ (2) Å
$\beta = 107.21$ (1)°
$V = 1502.4$ (4) Å^3
$Z = 2$

$D_x = 1.730$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
$\theta = 6.3$–18.2°
$\mu = 1.327$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, green
0.44 × 0.40 × 0.15 mm

Data collection

Siemens *P*3 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (*XDISK*; Siemens, 1991*a*)
$T_{\rm min} = 0.647$, $T_{\rm max} = 0.820$
2750 measured reflections
2611 independent reflections
1770 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\rm max} = 25.04°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 11$
$l = -17 \rightarrow 16$
3 standard reflections every 50 reflections intensity decay: average of 1.1% in $\sigma(I)$'s

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.113$
$S = 1.130$
2597 reflections
241 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0583P)^2 + 1.1817P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.39$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}

Table 2
Close intermolecular contacts (Å) to nitro-O atoms (O3, O4, O5, O6) in (III).

Contact	Distance	Σ van der Waals radii (Pauling, 1960)
O3···H1*E*$^{\rm i}$	2.47	2.6
O4···Cl2*A*$^{\rm ii}$	3.07 (1)	3.2
O5···H1*A*$^{\rm iii}$	2.68	2.6
O5···H1*B*$^{\rm iii}$	2.57	2.6
O5···Cl3*A*$^{\rm iv}$	3.43 (1)	3.2
O6···Cl3*B*$^{\rm v}$	3.303 (8)	3.2
O6···N3$^{\rm iii}$	3.121 (6)	2.9
O6···O6$^{\rm iii}$	2.855 (8)	2.8

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

Table 3
Close inter- and intramolecular contacts to the phenyl-C atoms in (I), (II) and (III).

Contact	Distance	Σ van der Waals radii (Pauling, 1960)
(I)		
H8*A*···H1*A*	2.11	2.4
H8*A*···C1	2.74	3.2
(II)		
H8*A*···H1*A*	2.43	2.4
H8*A*···C1	2.96	3.2
C8···Cl$^{\rm i}$	3.483 (3)	3.5
(III)		
H8···H1*A*	2.13	2.4
H8···H1*B*	2.59	2.4
H8···C1	2.92	3.2
C4···O4$^{\rm ii}$	3.076 (5)	3.1
C5···O2$^{\rm iii}$	3.131 (5)	3.1

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

For (III), H1*A*, H1*B* and H1*C* were first selected by *SHELXL*93 (Sheldrick, 1993). When difference peaks exactly between these H atoms were noted, three additional H atoms were added. All six were assigned a multiplicity of 0.5 and were placed in ideal positions. The presence of peaks in the difference map indicated disordered chlorines in the $CHCl_3$ librating approximately about the C9—H9 bond. Six chlorines, each with a multiplicity of 0.5, were refined without any constraints. As the data reduction program (*XDISK*; Siemens, 1991*a*) gave a lower figure of merit for the space group *Pc*, an alternate refinement in *Pc* was performed, though the test for the presence of an inversion center indicated a centrosymmetric space group. The refinement in *Pc* led to many elongated displacement ellipsoids and a higher R_1 than the refinement in which $P2_1/c$ was used.

For all compounds, data collection: *P*3/*P*4-*PC Diffractometer Program* (Siemens, 1991*b*); cell refinement: *P*3/*P*4-*PC Diffractometer Program*; data reduction: *XDISK* (Siemens, 1991*a*); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXTL*/*PC* and *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1108). Services for accessing these data are described at the back of the journal.

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