METAL-ORGANIC COMPOUNDS

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Bromo(n-propionamido-α-alaninato)-copper(II) and its Hydrate

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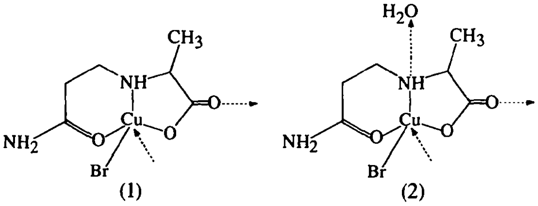
Abstract

The title compound, bromo[N-(carbamoylethyl)-α-alaninato-O^1,N,O^3]copper(II) complex, $[CuBr(C_6H_{11}N_2O_3)]$, (1), and its hydrate, $[CuBr(C_6H_{11}N_2O_3)].H_2O$, (2), both crystallize in the $P2_12_12_1$ space group. The crystals used for the structure analyses were enantiomorphic. There is a distinct difference in the coordination of the bromide to the copper ion with respect to the tridentate ligand. The bromide ion is *syn* with respect to the H1 atom in (1), while it is *anti* to H1 in (2).

Comment

The structures of copper–amide complexes depend strongly on the pH of the solutions. Although many of these complexes undergo deprotonation of the amide group at high pH, with a corresponding change of coordination centres and structures, it has been noted that at lower pH where coordination is confined to the carbonyl O atom, subtle changes in the structure can still be induced by careful adjustment of the pH (Freeman, 1967; Sigel & Martin, 1982; Lim & McCool, 1984). This paper provides further examples, namely bromo(n-propionamido-α-alaninato)copper(II), (1), and its hydrate, (2), of this interesting observation.



(1) (2)

The copper ion in both samples has a trigonal bipyramidal geometry with the O1 and O2 atoms in axial positions. The percentages of trigonal bipyramidal geometry in (1) and (2) are 91 and 66%, respectively (Spek, 1990). The equatorial girdle consists of atoms N1 and Br, and the O3^i atom from a neighbouring molecule forming a polymeric helical chain running parallel to the *a* axis (Fig. 3). A water molecule is found in compound (2) and is hydrogen bonded to the N1 atom [2.883 (10) Å]. This results in the tridentate ring being puckered in the opposite direction to that in compound (1). The torsion angle H1—N1—Cu—Br is 176.06° in (2) compared with 16.0° in (1). Weak hydrogen bonds [in the range 3.33 (7)–3.53 (7) Å] also exist between the Br and N2 atoms in both complexes. Intramolecular bond distances are comparable in (1) and (2). The largest deviations are observed for the angles O1—Cu—O2 [167.3 (2) and 176.6 (2)° for (1) and (2), respectively], O3^i—Cu—N1 [161.3 (2) and 153.7 (2)°] and O2—Cu—Br [100.2 (1) and 91.9 (2)°].

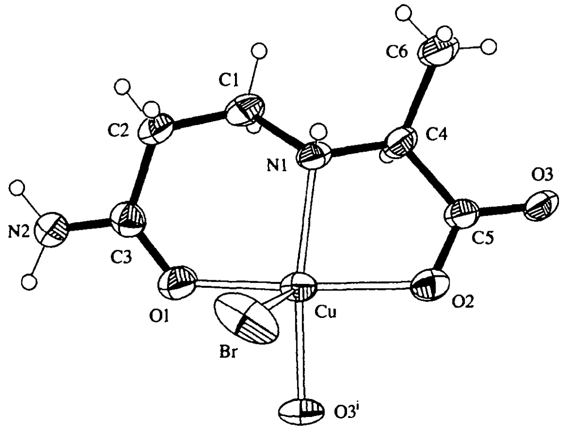


Fig. 1. *ORTEP* (Johnson, 1965) plot of (1) drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry code: (i) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$.]

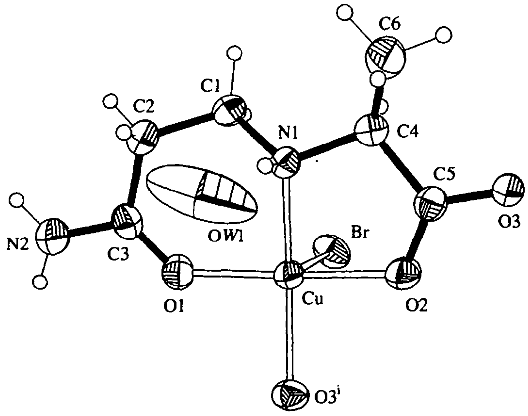


Fig. 2. *ORTEP* (Johnson, 1965) plot of (2) drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 2-z$.]

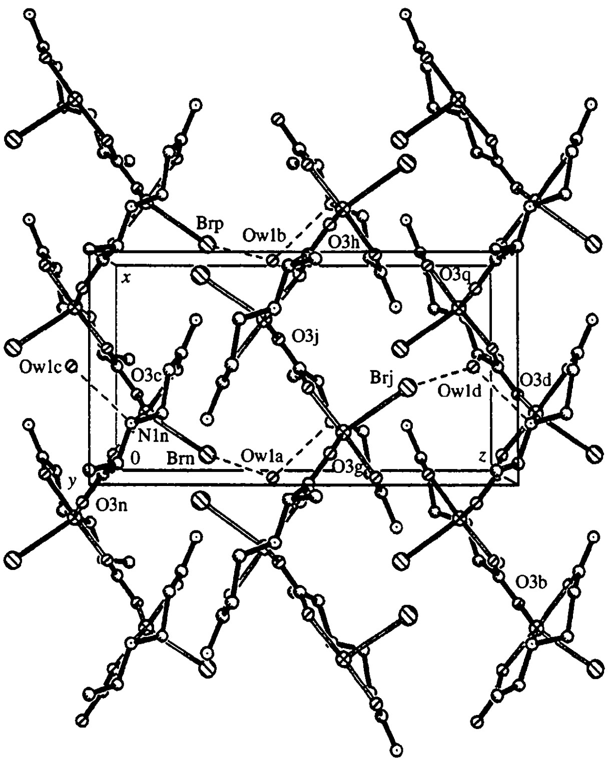


Fig. 3. Packing diagram of (2) viewed down the *b* axis.

Experimental

To a suspension of 5.0 g (0.0125 mmol) of bis(*n*-propionamido-α-alaninato)copper(II) hydrate in 10 ml of water was added dropwise 1.0 ml of concentrated HBr. The solution was evaporated to dryness. The solid was extracted with methanol and the methanolic solution left to evaporate slowly whereupon two types of crystals were formed. Darker blue crystals of (2) were obtained from the base of the container, while lighter blue crystals of (1) were found clinging to the side of the container.

Compound (1)

Crystal data

[CuBr($C_6H_{11}N_2O_3$)]
$M_r = 302.62$
Orthorhombic
$P2_12_12_1$
$a = 6.8175\,(8)$ Å
$b = 10.762\,(2)$ Å
$c = 13.710\,(2)$ Å
$V = 1006.0\,(3)$ Å^3
$Z = 4$
$D_x = 1.998$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 6$–$12°$
$\mu = 6.120$ mm^{-1}
$T = 300\,(2)$ K
Rectangular plate
0.30 × 0.15 × 0.10 mm
Pale blue

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.430$, $T_{\max} = 0.542$
1333 measured reflections
1216 independent reflections

1066 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0190$
$\theta_{\max} = 24.96°$
$h = -1 \rightarrow 8$
$k = -12 \rightarrow 1$
$l = -1 \rightarrow 16$
3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0292$
$wR(F^2) = 0.0545$
$S = 1.096$
1216 reflections
162 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.018P)^2 + 1.1P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.374$ e Å^{-3}
$\Delta\rho_{\min} = -0.390$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.03 (2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Br	0.0861 (1)	0.78021 (7)	0.21077 (5)	0.0548 (2)
Cu	0.2350 (1)	0.81541 (6)	0.39024 (5)	0.0304 (2)
O1	0.4933 (6)	0.8598 (4)	0.3387 (3)	0.042 (1)
O2	0.0026 (6)	0.7795 (4)	0.4700 (3)	0.035 (1)
O3	−0.1688 (6)	0.8560 (3)	0.5927 (3)	0.032 (1)
N1	0.1592 (9)	0.9908 (5)	0.4191 (4)	0.028 (1)
N2	0.726 (1)	0.9748 (6)	0.2733 (4)	0.041 (2)
C1	0.316 (1)	1.0831 (6)	0.4120 (6)	0.040 (2)
C2	0.422 (1)	1.0751 (6)	0.3170 (6)	0.041 (2)
C3	0.551 (1)	0.9623 (6)	0.3099 (4)	0.030 (2)
C4	0.058 (1)	0.9901 (5)	0.5149 (4)	0.031 (2)
C5	−0.0458 (9)	0.8675 (5)	0.5259 (4)	0.027 (1)
C6	−0.077 (2)	1.1005 (7)	0.5300 (7)	0.055 (3)

Table 2. *Selected geometric parameters (Å, °) for (1)*

Br—Cu	2.6886 (11)	Cu—O3$^{\rm i}$	1.972 (4)
Cu—O1	1.956 (4)	Cu—N1	1.996 (5)
Cu—O2	1.964 (4)		
O1—Cu—O2	167.3 (2)	O3$^{\rm i}$—Cu—N1	161.3 (2)
O1—Cu—O3$^{\rm i}$	88.4 (2)	O1—Cu—Br	92.52 (14)
O2—Cu—O3$^{\rm i}$	91.0 (2)	O2—Cu—Br	100.19 (12)
O1—Cu—N1	94.2 (2)	O3$^{\rm i}$—Cu—Br	95.89 (12)
O2—Cu—N1	82.4 (2)	N1—Cu—Br	102.5 (2)

Symmetry code: (i) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$.

Compound (2)

Crystal data

[CuBr($C_6H_{11}N_2O_3$)].H_2O
$M_r = 320.63$
Orthorhombic
$P2_12_12_1$
$a = 7.6203\,(4)$ Å
$b = 10.2094\,(9)$ Å
$c = 14.045\,(2)$ Å
$V = 1092.7\,(2)$ Å^3
$Z = 4$
$D_x = 1.949$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6$–$12°$
$\mu = 5.647$ mm^{-1}
$T = 300\,(2)$ K
Polyhedron
0.50 × 0.43 × 0.43 mm
Deep blue

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.074$, $T_{\max} = 0.088$
2263 measured reflections
1919 independent reflections
1784 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0627$
$\theta_{\max} = 24.98°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 12$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0478$
$wR(F^2) = 0.1167$
$S = 1.074$
1919 reflections
127 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.09P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.714$ e Å^{-3}
$\Delta\rho_{\min} = -0.654$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.03 (3)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Br	0.58779 (9)	0.25430 (6)	0.74957 (5)	0.0404 (2)
Cu	0.7866 (1)	0.20018 (6)	0.90495 (5)	0.0280 (2)
O1	0.9906 (6)	0.1667 (4)	0.8243 (3)	0.034 (1)
O2	0.5877 (6)	0.2247 (4)	0.9901 (3)	0.038 (1)
O3	0.3710 (6)	0.1220 (4)	1.0622 (3)	0.034 (1)
O*W*1	1.004 (1)	−0.0332 (9)	1.0777 (7)	0.134 (5)
N1	0.7450 (6)	0.0118 (5)	0.9316 (3)	0.026 (1)
N2	1.2213 (8)	0.0586 (6)	0.7722 (5)	0.050 (2)
C1	0.793 (1)	−0.0728 (6)	0.8504 (5)	0.038 (2)
C2	0.989 (1)	−0.0703 (7)	0.8333 (7)	0.043 (2)
C3	1.0640 (8)	0.0622 (7)	0.8091 (4)	0.030 (1)
C4	0.562 (1)	−0.0048 (6)	0.9649 (5)	0.033 (1)
C5	0.5044 (9)	0.1220 (7)	1.0104 (5)	0.030 (1)
C6	0.538 (1)	−0.1236 (8)	1.0268 (8)	0.061 (3)

Table 4. *Selected geometric parameters (Å, °) for (2)*

Br—Cu	2.714 (1)	Cu—O3$^{\rm i}$	1.980 (5)
Cu—O2	1.947 (4)	Cu—N1	1.985 (5)
Cu—O1	1.954 (5)		
O2—Cu—O1	176.6 (2)	O3$^{\rm i}$—Cu—N1	153.7 (2)
O2—Cu—O3$^{\rm i}$	89.5 (2)	O2—Cu—Br	91.9 (2)
O1—Cu—O3$^{\rm i}$	92.1 (2)	O1—Cu—Br	90.79 (14)
O2—Cu—N1	83.4 (2)	O3$^{\rm i}$—Cu—Br	100.50 (13)
O1—Cu—N1	93.8 (2)	N1—Cu—Br	105.05 (15)

Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, 2 - z$.

For both compounds, data collection: *CAD*-4 *VAX/PC Operator's Manual* (Enraf–Nonius, 1988); cell refinement: *CAD*-4 *VAX/PC Operator's Manual*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990*a*); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP* (Johnson, 1965) in *SHELXTL/PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: DE1047). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Isomeric Bis(*n*-propionamidoalaninato)copper(II) Hydrate Complexes, $[Cu(C_6H_{11}N_2O_3)_2].H_2O$

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Abstract

The two isomeric complexes, bis[*N*-(carbamoylethyl)-β-alaninato-O^1,*N*,O^3]copper(II) hydrate, (1), and bis[*N*-(carbamoylethyl)-α-alaninato-O^1,*N*,O^3]copper(II) hydrate, (2), both $[Cu(C_6H_{11}N_2O_3)_2].H_2O$, were found to crystallize in different space groups. The structure containing a chiral C atom, (2), crystallizes in the polar *C*2 space group, while the structure with no chiral centre, (1), crystallizes in the centrosymmetric *C*2/*c* space group.

Comment

Amides, including naturally occurring peptides, form complexes with copper ions. The structures of the complexes formed depend on the pH of the solutions.

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