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: *SHELXS86* (Sheldrick, 1990*a*); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEP* (Johnson, 1965) in *SHELXTL/PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL93*.

The authors thank the National Science Council for supporting this work through an R & D grant (09-02-03-0004).

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.

References

Enraf–Nonius (1988). *CAD-4 VAX/PC Operator's Manual.* Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Freeman, H. C. (1967). *Adv. Protein Chem.* **22**, 257–421.
Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Lim, M. C. & McCool, B. J. (1984). *Inorg. Chem.* **23**, 1192–1194.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC Users Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Sigel, H. & Martin, R. B. (1982). *Chem. Rev.* **82**, 385–426.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Acta Cryst. (1997). C**53**, 539-543

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

WEI CHEN AND MENG-CHAY LIM

Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia. E-mail: chenwei@kimia.um.edu.my

(*Received 30 August 1996; accepted 12 December 1996*)

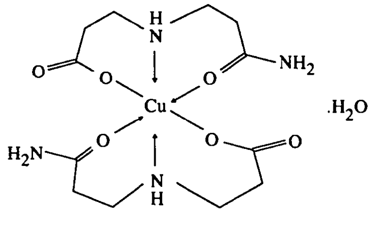
Abstract

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.

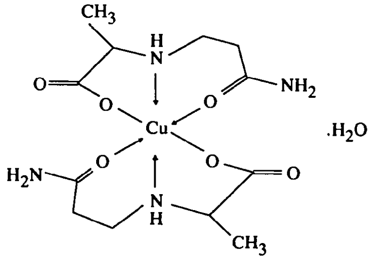
Comment

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

In an acidic medium, the mode of coordination in these complexes is invariably between the copper ion and the carbonyl O atom of the amide group. As the pH increases, however, many, but not all, of these complexes undergo deprotonation and the centre of coordination changes from the carbonyl O atom to the deprotonated amide N atom. The process is accompanied by a spectacular colour change from blue to purple (Freeman, 1967; Sigel & Martin, 1982; Lim & McCool, 1984). Crystallographic studies have shown that most of these deprotonated complexes are mononuclear with the copper ion in the centre of a distorted pyramid. In contrast, the structures of the complexes formed prior to deprotonation have been less well studied, but in a number of cases they are known to be polynuclear. In a previous study (Lim, Chen & Hapipah, 1994), we have shown that it is possible to produce different types of structures for the carbonyl O atom coordinated complexes by careful adjustment of the pH of the solutions. In this paper, we present two more structures of similar complexes, namely, bis(*N*-propionamido-β-alaninato)copper(II) hydrate, (1), and bis(*N*-propionamido-α-alaninato)copper(II) hydrate, (2).



(1)



(2)

In the α-alaninato analogue (2), the molecular structure is similar to that of the β analogue, except the Cu atom no longer sits on a centre of inversion. The Cu—O4 bond is exceptionally long [2.843 (5) Å] and the torsion angle C12—C10—N3—C7 differs from C6—C4—N1—C1 [−138.4 (4) *versus* 46.7 (7)°]. Atom C12 bends towards $O5^i$ forming a weak intermolecular hydrogen bond (3.030 Å). However, no such bond exists between C6 and O2.

The β-alaninato analogue, (1), is isostructural with its glycinato analogue (Lim, Chen & Hapipah, 1994). Bond parameters in the two structures are comparable, except

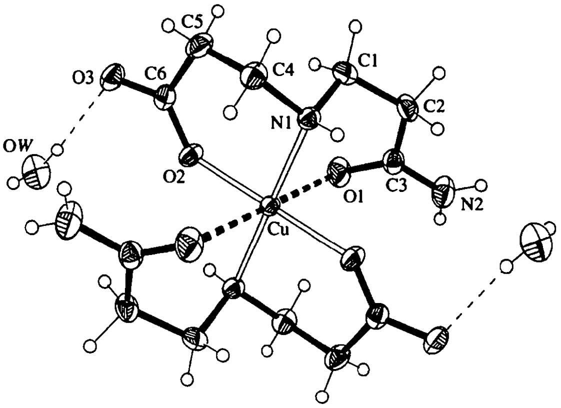


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the β analogue drawn at the 40% probability level. H atoms are drawn as spheres of arbitrary radii.

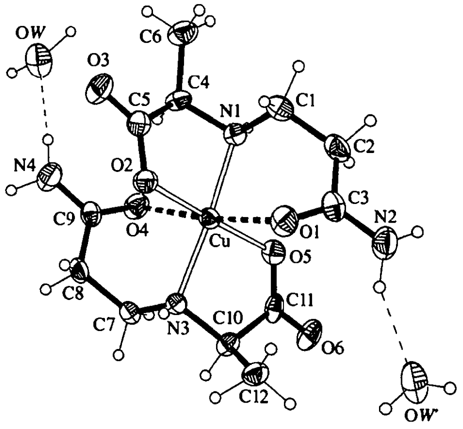


Fig. 2. *ORTEP*II (Johnson, 1976) plot of the α analogue drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

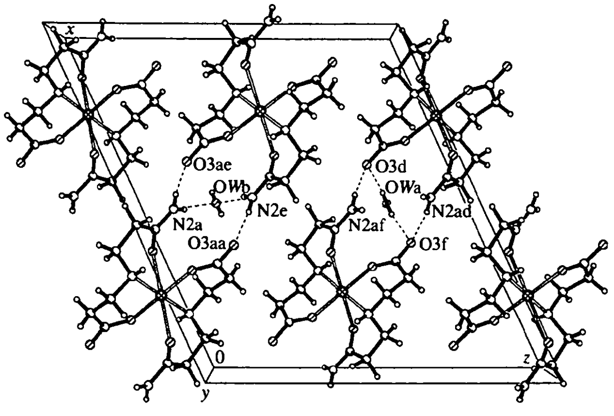


Fig. 3. Packing diagram of the β analogue viewed down the *b* axis.

for the axial Cu—O1 bond which is slightly longer in (2) [2.662 (3) compared with 2.489 (1) Å]. The increase in ring size does not seem to have much effect on the molecular and crystal structures. Hydrogen bonds exist between atoms N1 and O1^{i} (2.985 Å), N2 and OW^{ii} (2.874 Å), N2 and O3^{iii} (2.965 Å), and OW and O3 (2.755 Å) [symmetry codes: (i) x, $1+y$, z; (ii) $\frac{1}{2}-x$, $-\frac{1}{2}-y$, $-z$; (iii) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$].

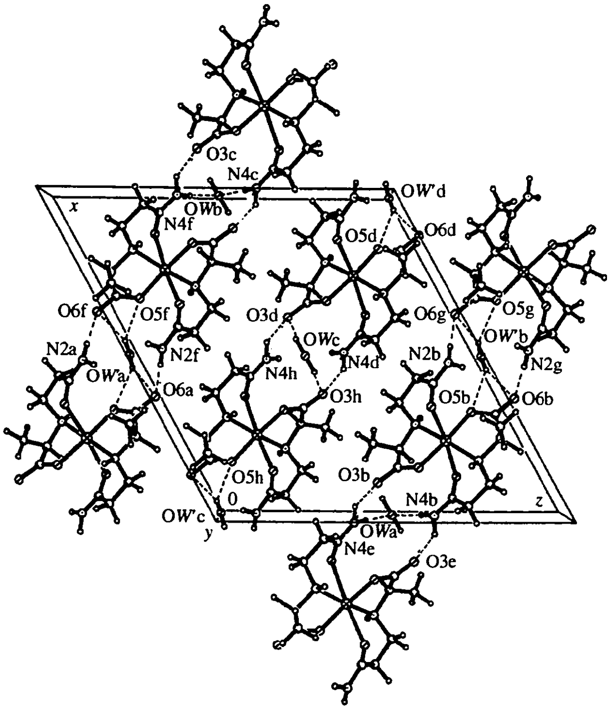


Fig. 4. Packing diagram of the α analogue viewed down the b axis.

Experimental

The ligands in both complexes were synthesized according to a previously reported method (Lim, Chen & Hapipah, 1994) with replacement of glycine by α- and β-alanine. The complexes were synthesized according to the same procedure.

Compound (1)

Crystal data

$[Cu(C_6H_{11}N_2O_3)_2].H_2O$
$M_r = 399.89$
Monoclinic
$C2/c$
$a = 18.520 (2)$ Å
$b = 5.7602 (7)$ Å
$c = 16.788 (2)$ Å
$\beta = 114.78 (2)°$
$V = 1626.0 (4)$ Å^3
$Z = 4$
$D_x = 1.634$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6–8°$
$\mu = 1.387$ mm^{-1}
$T = 300 (2)$ K
Plate
$0.32 \times 0.18 \times 0.03$ mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.8393$, $T_{max} = 0.9993$
2836 measured reflections
1420 independent reflections

1091 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0486$
$\theta_{max} = 24.97°$
$h = -21 \rightarrow 21$
$k = -6 \rightarrow 0$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0339$
$wR(F^2) = 0.1054$
$S = 0.756$
1420 reflections
147 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 5.5P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.308$ e Å^{-3}
$\Delta\rho_{min} = -0.305$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

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

	x	y	z	U_{eq}
Cu	1/4	1/4	0	0.0217 (2)
O1	0.3660 (2)	−0.0466 (5)	0.0178 (2)	0.0410 (7)
O2	0.1799 (2)	0.1544 (5)	−0.1192 (2)	0.0289 (6)
O3	0.1120 (2)	0.1671 (5)	−0.2623 (2)	0.0375 (7)
N1	0.3060 (2)	0.4758 (6)	−0.0438 (2)	0.0248 (7)
N2	0.4835 (2)	0.0068 (8)	0.1323 (2)	0.0446 (9)
C1	0.3707 (2)	0.3750 (8)	−0.0625 (3)	0.0323 (9)
C2	0.4400 (2)	0.2966 (7)	0.0206 (3)	0.0327 (9)
C3	0.4265 (2)	0.0707 (7)	0.0574 (2)	0.0303 (8)
C4	0.2487 (2)	0.6089 (7)	−0.1199 (2)	0.0316 (9)
C5	0.2071 (3)	0.4616 (8)	−0.2008 (2)	0.0347 (9)
C6	0.1632 (2)	0.2466 (7)	−0.1931 (2)	0.0267 (7)
OW1	0	−0.1278 (8)	−1/4	0.045 (1)

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

Cu—O2^{i}	1.954 (2)	N1—C1	1.478 (5)
Cu—O2	1.954 (2)	N1—C4	1.487 (5)
Cu—N1^{i}	1.987 (3)	N2—C3	1.311 (5)
Cu—N1	1.987 (3)	C1—C2	1.515 (5)
O1—C3	1.237 (4)	C2—C3	1.505 (5)
O2—C6	1.263 (4)	C4—C5	1.510 (5)
O3—C6	1.239 (4)	C5—C6	1.516 (6)
O2^{i}—Cu—O2	180.0	N1—C1—C2	111.8 (3)
O2^{i}—Cu—N1^{i}	91.78 (11)	C3—C2—C1	114.4 (3)
O2—Cu—N1^{i}	88.22 (11)	O1—C3—N2	123.1 (4)
O2^{i}—Cu—N1	88.22 (11)	O1—C3—C2	121.4 (3)
O2—Cu—N1	91.78 (11)	N2—C3—C2	115.5 (4)
N1^{i}—Cu—N1	180.0	N1—C4—C5	113.2 (3)
C6—O2—Cu	132.2 (2)	C6—C5—C4	118.2 (3)
C1—N1—C4	111.7 (3)	O3—C6—O2	122.8 (4)
C1—N1—Cu	114.6 (3)	O3—C6—C5	116.7 (3)
C4—N1—Cu	111.1 (2)	O2—C6—C5	120.5 (3)

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

Compound (2)

Crystal data

$[Cu(C_6H_{11}N_2O_3)_2].H_2O$
$M_r = 399.89$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$C2$
$a = 18.357\ (3)$ Å
$b = 5.7887\ (4)$ Å
$c = 17.728\ (3)$ Å
$\beta = 119.52\ (2)°$
$V = 1639.3\ (4)$ Å^3
$Z = 4$
$D_x = 1.620$ Mg m^{-3}
D_m not measured

Cell parameters from 20 reflections
$\theta = 4–15°$
$\mu = 1.376$ mm^{-1}
$T = 300\ (2)$ K
Rectangular plate
$0.3 \times 0.2 \times 0.15$ mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.734$, $T_{\max} = 0.814$
1554 measured reflections
1554 independent reflections

1413 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 24.97°$
$h = -21 \rightarrow 0$
$k = -6 \rightarrow 0$
$l = -17 \rightarrow 21$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0338$
$wR(F^2) = 0.0776$
$S = 1.113$
1554 reflections
217 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 1.66P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.336$ e Å^{-3}
$\Delta\rho_{\min} = -0.284$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.01 (2)

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	$U_{\rm eq}$
Cu	0.24685 (3)	0.0012	0.76316 (4)	0.0249 (2)
O1	0.3517 (2)	0.3132 (8)	0.7679 (2)	0.037 (1)
O2	0.1681 (2)	0.0885 (7)	0.6460 (2)	0.031 (1)
O3	0.1194 (2)	−0.019 (1)	0.5096 (2)	0.041 (1)
O4	0.1305 (2)	−0.3495 (8)	0.7441 (2)	0.039 (1)
O5	0.3317 (2)	−0.0721 (7)	0.8793 (2)	0.029 (1)
O6	0.3732 (2)	−0.001 (1)	1.0177 (2)	0.0413 (9)
N1	0.2922 (2)	−0.2098 (8)	0.7063 (3)	0.024 (1)
N2	0.4819 (3)	0.286 (1)	0.8821 (3)	0.043 (1)
N3	0.1911 (2)	0.1745 (8)	0.8198 (3)	0.022 (1)
N4	0.0110 (3)	−0.304 (1)	0.6187 (3)	0.044 (1)
C1	0.3585 (3)	−0.105 (1)	0.6920 (4)	0.032 (1)
C2	0.4323 (3)	−0.020 (2)	0.7768 (3)	0.036 (1)
C3	0.4186 (3)	0.206 (1)	0.8087 (4)	0.031 (1)
C4	0.2157 (3)	−0.273 (1)	0.6235 (3)	0.030 (1)
C5	0.1644 (3)	−0.052 (1)	0.5885 (3)	0.027 (2)
C6	0.2303 (4)	−0.402 (1)	0.5575 (4)	0.041 (2)
C7	0.1179 (3)	0.057 (1)	0.8172 (3)	0.028 (2)
C8	0.0508 (3)	−0.008 (2)	0.7264 (3)	0.029 (1)
C9	0.0675 (3)	−0.235 (1)	0.6966 (3)	0.028 (1)
C10	0.2576 (3)	0.213 (1)	0.9123 (3)	0.027 (1)
C11	0.3258 (3)	0.029 (1)	0.9398 (3)	0.029 (1)
C12	0.2953 (3)	0.450 (1)	0.9223 (3)	0.033 (2)
O*W*	0	−0.677 (1)	1/2	0.049 (2)
O*W*′	1/2	0.678 (1)	1	0.055 (2)

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

Cu—O5	1.920 (4)	N1—C4	1.493 (6)
Cu—O2	1.923 (4)	N2—C3	1.328 (7)
Cu—N1	2.006 (4)	N3—C7	1.487 (7)
Cu—N3	2.019 (4)	N3—C10	1.501 (6)
Cu—O1	2.610 (4)	N4—C9	1.317 (7)
Cu—O4	2.843 (5)	C1—C2	1.526 (8)
O1—C3	1.242 (7)	C2—C3	1.494 (11)
O2—C5	1.281 (6)	C4—C6	1.519 (8)
O3—C5	1.239 (6)	C4—C5	1.525 (8)
O4—C9	1.237 (6)	C7—C8	1.514 (7)
O5—C11	1.272 (7)	C8—C9	1.503 (10)
O6—C11	1.230 (6)	C10—C12	1.507 (8)
N1—C1	1.491 (7)	C10—C11	1.528 (8)
O5—Cu—O2	175.6 (2)	C10—N3—Cu	106.2 (3)
O5—Cu—N1	95.0 (2)	N1—C1—C2	111.5 (4)
O2—Cu—N1	84.0 (2)	C3—C2—C1	115.0 (5)
O5—Cu—N3	85.3 (2)	O1—C3—N2	122.3 (6)
O2—Cu—N3	96.4 (2)	O1—C3—C2	121.3 (5)
N1—Cu—N3	171.8 (2)	N2—C3—C2	116.5 (5)
O5—Cu—O1	85.58 (14)	N1—C4—C6	116.2 (5)
O2—Cu—O1	90.16 (15)	N1—C4—C5	106.7 (5)
N1—Cu—O1	87.5 (2)	C6—C4—C5	114.1 (5)
N3—Cu—O1	100.8 (2)	O3—C5—O2	123.0 (6)
O5—Cu—O4	97.73 (14)	O3—C5—C4	121.5 (6)
O2—Cu—O4	86.47 (15)	O2—C5—C4	115.4 (4)
N1—Cu—O4	88.8 (2)	N3—C7—C8	113.2 (4)
N3—Cu—O4	83.0 (2)	C9—C8—C7	112.9 (5)
O1—Cu—O4	175.20 (12)	O4—C9—N4	122.5 (6)
C3—O1—Cu	100.1 (4)	O4—C9—C8	121.0 (5)
C5—O2—Cu	114.1 (4)	N4—C9—C8	116.5 (5)
C9—O4—Cu	95.4 (4)	N3—C10—C12	110.1 (5)
C11—O5—Cu	116.2 (3)	N3—C10—C11	110.0 (5)
C1—N1—C4	112.5 (4)	C12—C10—C11	109.8 (4)
C1—N1—Cu	114.4 (4)	O6—C11—O5	125.0 (6)
C4—N1—Cu	102.8 (3)	O6—C11—C10	118.2 (6)
C7—N3—C10	109.7 (4)	O5—C11—C10	116.7 (4)
C7—N3—Cu	115.4 (3)		

The H atoms in the α analogue, (2), were not refined, while those in the β analogue, (1), were refined with fixed displacement parameters of 0.05 Å^2.

For both compounds, data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988); cell refinement: *CAD*-4 *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*II (Johnson, 1976) in *SHELXTL/PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL*93.

The authors thank the National Science Council for supporting this work with an R&D grant (09-02-03-0004).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: DE1046). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1988). *CAD*-4 *Manual*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Freeman, H. C. (1967). *Adv. Protein Chem.* **22**, 257–421.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lim, M. C., Chen, W. & Hapipah, M. A. (1994). *Transition Met. Chem.* **19**, 409–412.
Lim, M. C. & McCool, B. J. (1984). *Inorg. Chem.* **23**, 1192–1194.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sigel, H. & Martin, R. B. (1982). *Chem. Rev.* **82**, 385–426.

Acta Cryst. (1997). C**53**, 543-545

μ-Cyano-bis(2,2′:6′,2″-terpyridine-*N*,*N*′,*N*″)dicopper(II) Perchlorate Acetonitrile, $[Cu_2(CN)(C_{15}H_{11}N_3)_2](ClO_4)_3.CH_3CN$

Véronique Bulach, Hugues Duval, Jean Fischer and Raymond Weiss

Laboratoire de Cristallochimie et Chimie Structurale, UA 424, Université Louis Pasteur, Institut Lebel, 4, rue Blaise Pascal, 67070 Strasbourg Cédex, France. E-mail: fischer@chimie.u-strasbg.fr

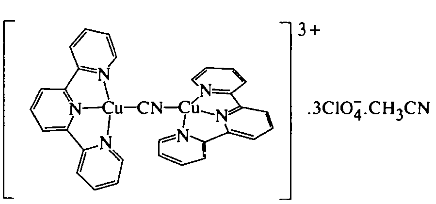
(*Received 24 October 1996; accepted 16 December 1996*)

Abstract

The $[Cu_2(terpy)_2(CN)]^{3+}$ cation (terpy is 2,2′:6′,2″-terpyridine) is non-centrosymmetric and contains two Cu^{II} centres bridged by a disordered cyano group. The overall geometry around both metallic centres can be described as a distorted octahedron. The equatorial coordination plane is occupied by the N atoms of the tridentate terpy ligand and by an atom (C* or N*) of the cyanide bridge. The axial positions for one Cu atom are occupied by O atoms of two perchlorate anions while, for the other Cu atom, a perchlorate ion and an acetonitrile molecule lie in *trans* positions.

Comment

As part of our efforts to synthesize heterobimetallic Fe^{III}–Cu^{II} compounds in which the two metallic centres are bridged by various bidentate ligands (Bulach, Mandon & Weiss, 1991), we have isolated crystals of the dinuclear $[Cu_2(terpy)_2(CN)](ClO_4)_3.CH_3CN$ complex, (I).



(I)

The structure consists of asymmetric dimeric molecules in which the coordination polyhedron around each copper ion is a distorted elongated octahedron (the coordination mode is approximately '4+2' for the Cu1 atom and '4+1+1' for Cu2). A cyanide group acts as a bridging ligand between the two divalent Cu atoms. As a class, Cu^{II}–cyanide complexes are not very common, owing to the tendency of Cu^{II} to oxidize cyanide to cyanogen (Hathaway, 1987). Moreover, the Cu^{II}—CN—Cu^{II} bridge has been previously structurally authenticated for $[Cu_2([14]\text{-}4,11\text{-dieneN4})_2(CN)]^{3+}$ (Jungst & Stucky, 1974) and $[Cu_2(Me_6tren)_2(CN)]^{3+}$ (Scott, Lee & Holm, 1994) in the centrosymmetric trigonal bipyramidal geometry, and for the polymeric complex $[Cu(terpy)(CN)](NO_3).H_2O$ (Anderson, Packard & Wicholas, 1976) in the distorted square-pyramidal geometry.

The equatorial plane around each Cu atom is similar, being composed of the three N atoms of the terpyridine ligand and the cyanide group C* or N* (disordering of the bridging CN group prevented identification of the C and N atoms) (Fig. 1). The environment around the two Cu atoms differs in the nature of the ligands in the apical positions, *i.e.* two O atoms of two perchlorate anions for Cu1 [Cu1—O5 2.564 (3) Å and Cu1—O10 2.543 (4) Å],

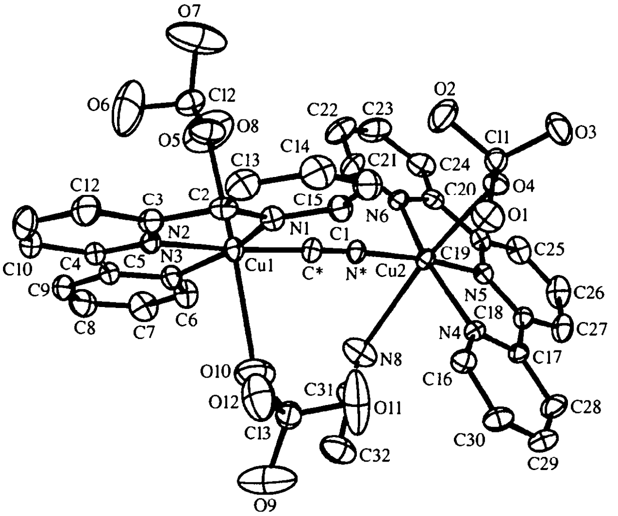


Fig. 1. *ORTEP* (Johnson, 1965) plot of the $[Cu_2(terpy)_2(CN)](ClO_4)_3$.-$CH_3CN$ molecule showing the atom labels. Displacement ellipsoids are drawn at the 50% probability level.