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Crystal Studies of the Reaction Products of Chelate Complexes. I. The Structure of Bis(dihydro-1*H*,3*H*,5*H*-oxazolo[3,4-*c*]oxazole-7a-carboxylato)copper(II)

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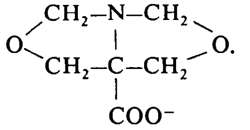
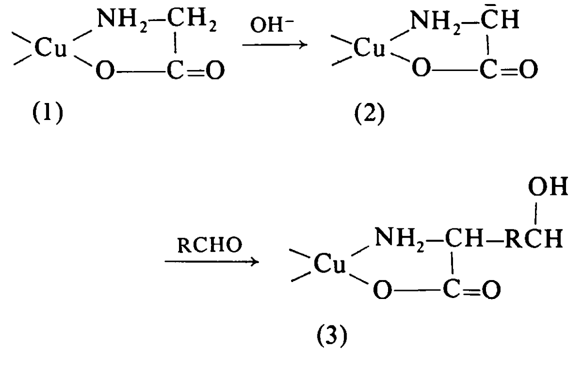
The reaction of bis[(*S*)-serinato]copper(II) with excess formaldehyde at *p*H 7–9 results in the formation of the crystalline product bis(dihydro-1*H*,3*H*,5*H*-oxazolo[3,4-*c*]oxazole-7a-carboxoxylate)cper(II), Cu(dioxc)$_2$. The ligand has the structure



Coordination to Cu is *via* the N and carbonyl O atoms. The structure of Cu(dioxc)$_2$ has been determined from 2035 diffractometer-collected data and refined by full-matrix least squares to an R value of 0·038. The compound forms deep-blue monoclinic crystals having space group $P2_1/c$ with $a = 18·559$ (1), $b = 10·142$ (1), $c = 7·345$ (1) Å, $\beta = 101·60$ (1)° and $Z = 4$. The formula unit of the complex has approximate square-planar geometry with the N atoms occupying *trans* positions. These subunits are connected in the crystal by an apical bond between the Cu atom and a glide-related carbonyl O to form infinite molecular chains parallel to **c**. The Cu–O distance for this bond is 2·354 (4) Å compared with 1·904 (4) and 1·939 (4) Å for the Cu–O bonds in the chelate rings. The complex has a distorted square-pyramidal coordination geometry in the crystal. The two chelate rings have considerably different degrees of puckering because of the apical interaction. The substituted oxazolidine rings adopt envelope conformations which fold toward each other in each ligand.

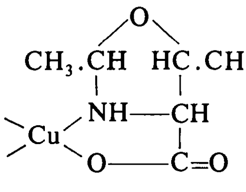
Introduction

The condensation of bis(glycinato)copper(II) with aldehydes in basic solution was thought (Basolo & Pearson, 1967; Akabori, Otani, Marshall, Winitz & Greenstein, 1959) to occur as follows.



(1) (2) (3)

The exchange rate of the α-carbon H atoms in alkaline solution has been studied (Williams & Busch, 1965; Buckingham, Marzilli & Sargeson, 1967) for several α-amino acidato complexes and found to be sufficiently high to indicate ready formation of the α-carbanion under basic conditions. Treatment of (3) with H_2S under acid conditions releases the α-hydroxyalkyl-substituted amino acid in the aqueous solution and the Cu is precipitated as CuS. The Cu^{II} ion may thus be employed as a catalyst in the preparation of α-hydroxyalkyl-substituted amino acids. Only recently has the nature and structure of the intermediate (with $R = CH_3$) been sufficiently characterized to suggest a scheme for the mechanism of the Cu^{II}-catalyzed aldehyde–amino acid condensations in basic solution. Glycine was reacted with acetaldehyde in aqueous base in the presence of basic copper(II) carbonate and the product, (4), was treated with H_2S in an acid medium to produce R,S-threonine. The structure of the Cu^{II} intermediate, (4), was determined (Larcheres & Pierrot, 1971) by an X-ray analysis and led to the suggestion of a reaction mechanism for the threonine synthesis.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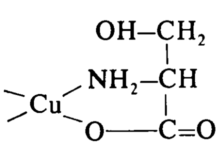
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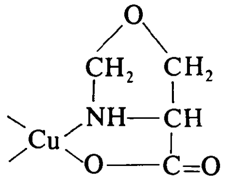
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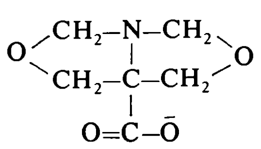
(7)

The Cu^{II} complex formed from the reaction of bis(*S*-serinato)copper(II), (5), with excess formaldehyde in base (*p*H 7–9) was isolated by O'Connor and Teo (Brush, Magee, O'Connor, Teo, Geue & Snow, 1973). Both the composition, $Cu(C_{12}H_{16}N_2O_8)$, and the structure of the complex were determined by the X-ray structural analysis described here, and it was found that two units of the bis(oxazolidine)carboxylate, (dioxc, 7), were coordinated to Cu^{II}. A brief report of this structure and the mechanism of its formation have been published (Brush *et al.*, 1973; Teo, 1975). The full details of the structure analysis appear below.

Experimental

Deep-blue tabular crystals of $Cu(dioxc)_2$ were kindly supplied by M. J. O'Connor of La Trobe University, Victoria, Australia. The forms {100}, {010}, {001}, and {011} were evident from the crystal morphology. The crystal system and space group were determined from preliminary precession photographs with Mo *Kα* radiation. The cell constants were refined from the setting angles of 12 high-angle reflexions, determined on a Picker four-circle diffractometer with monochromatic Cu *Kα* radiation. The crystal data are given in Table 1.

Intensity data were collected on a Picker automated four-circle diffractometer fitted with a Furnas monochromator. Cu *Kα* radiation was used for the intensity measurements on a crystal with dimensions 0·12 × 0·20 × 0·25 mm by the 2θ scan technique. A total of 2395 reflexions were recorded out to $2\theta = 127°$ and three standard reflexions, which showed no systematic change during data collection, were measured after every 60 reflexions. The data were reduced and Lorentz and polarization corrections were applied, but no absorption corrections were made. The transmission factors ranged from 0·65 to 0·80. The standard deviations in the structure factors were initially assigned from counting statistics and later modified as described below. Reflexions with $I_o < 3\sigma(I_o)$ numbering 360 were designated weak and subsequently excluded from the least-squares refinement.

Table 1. *Crystal data*

$C_{12}H_{16}CuN_2O_8$
Monoclinic
$a = 18{\cdot}559\ (1)$ Å
$b = 10{\cdot}142\ (1)$
$c = 7{\cdot}345\ (1)$
$\beta = 101{\cdot}60\ (1)°$
$U = 1354\ (1)$ Å^3

F.W. 379·81
Space group $P2_1/c$
$F(000) = 780$
$D_m = 1{\cdot}86\ (2)$ g cm^{-3}
$D_c = 1{\cdot}863$
$Z = 4$
$\mu(\mathrm{Cu}\ K\alpha) = 27{\cdot}0$ cm^{-1}

[$\lambda(\mathrm{Cu}\ K\alpha_1) = 1{\cdot}5405$ Å]

Structure solution and refinement

The structure was solved by standard heavy-atom techniques. The least-squares refinement of all non-hydrogen atoms with anisotropic temperature factors converged with $R_1 = 0{\cdot}060$. The positions of the H atoms were calculated (C–H = 1·02 Å, H–C–H = 109° 28′) and included in the refinement with fixed isotropic thermal parameters of 3·0 Å^2. The refinement was continued in blocks because of computer storage restrictions on the size of the matrix of parameter coefficients. All coordinates, including those for the H atoms, were refined in one cycle, and the non-hydrogen coordinates and anisotropic temperature factors in the following cycle. The scale factor was always included. This mode of refinement converged with $R_1 = 0{\cdot}041$. The weighting scheme, derived from statistical errors in the observed intensity counts, was at this stage judged to be unsatisfactory from an analysis of the average $w(|F_o| - |F_c|)^2$ in ranges of $|F_o|$. A new relative weighting scheme designed to flatten the $w(|F_o| - |F_c|)^2$ *vs* $|F_o|$ curve was determined from a least-squares fit of $\omega(|F_o| - |F_c|)^2$ to $A + B|F_o| + C|F_o|^2$. All existing weights, $\omega(|F_o|)$, were then multiplied by $1/(1{\cdot}274 + 0{\cdot}037|F_c| + 0{\cdot}002|F_o|^2)$ to place them on the same relative scale. A final two cycles of refinement incorporating the new weighting scheme reduced R_1 to 0·038 and the final R_2 was 0·050. The error in an observation of unit weight was estimated after the final coordinate refinement cycle to be 5·41, showing that the weights are not on an absolute scale. As required by the scheme, the curves of average $\omega(|F_o| - |F_c|)^2$ *vs* $|F_o|$ and $\sin\theta/\lambda$ were relatively flat, showing no systematic variations. Atomic scattering factors for Cu^+, O, N and C were obtained from *International Tables for X-ray Crystallography* (1968) as were the anomalous components $\Delta f'$ and $\Delta f''$ for Cu and Cl. Cl^- and H scattering factors were taken from Doyle & Turner (1968) and Stewart, Davidson & Simpson (1965). Computer programs used were the

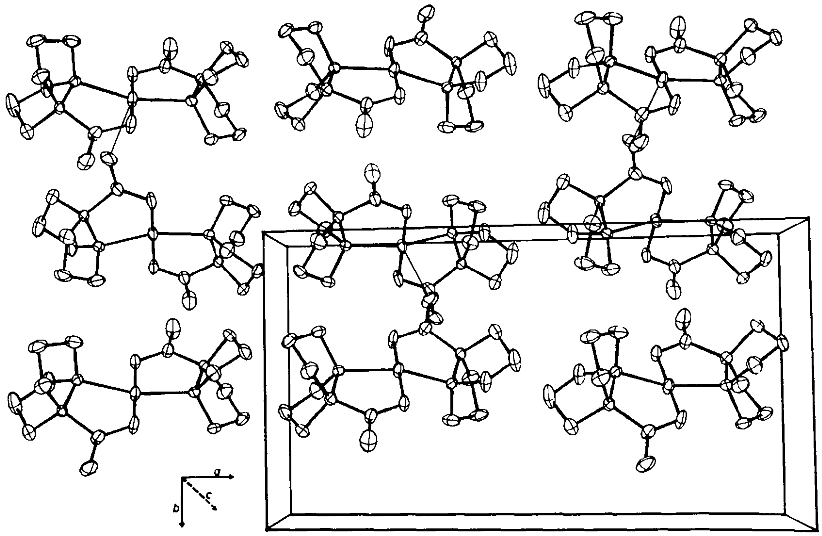

Fig. 1. Projection of the unit cell of Cu(dioxc)$_2$ down **c**. The thermal ellipsoids enclose 50% probability.

Table 2. *Positional* ($\times 10^4$; *for* H $\times 10^3$) *and thermal* ($\times 10^5$) *parameters*

The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. For hydrogen $B = 3{\cdot}0$ Å^2.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	2525 (0)	335 (1)	4927 (1)	86 (3)	589 (10)	912 (19)	33 (3)	−33 (6)	−233 (10)
N(1)	1446 (2)	326 (4)	3705 (6)	100 (13)	345 (44)	921 (93)	−8 (19)	34 (29)	−116 (53)
N(2)	3498 (2)	−155 (4)	6578 (6)	101 (13)	392 (44)	743 (88)	29 (20)	13 (28)	−49 (53)
O(1)	2671 (2)	−763 (4)	2930 (5)	83 (11)	628 (42)	1033 (81)	7 (18)	21 (25)	−208 (50)
O(2)	2081 (2)	−1926 (5)	509 (6)	171 (14)	1148 (60)	1728 (104)	67 (23)	24 (32)	−925 (71)
O(3)	2386 (2)	1392 (4)	7029 (6)	95 (11)	852 (50)	1383 (94)	92 (20)	−38 (28)	−479 (58)
O(4)	3079 (2)	2749 (4)	9026 (6)	221 (14)	568 (47)	1738 (103)	136 (21)	−138 (32)	−541 (60)
O(6)	441 (2)	−1026 (4)	3746 (6)	126 (12)	663 (45)	1760 (101)	−89 (19)	195 (29)	−148 (59)
O(7)	652 (2)	1304 (4)	1210 (6)	173 (13)	495 (43)	1496 (97)	109 (19)	−69 (30)	95 (53)
O(8)	4699 (2)	595 (5)	6819 (6)	116 (12)	1320 (64)	1721 (107)	−93 (23)	147 (31)	−446 (71)
O(9)	3978 (2)	−1261 (4)	9293 (6)	282 (15)	415 (41)	1279 (95)	83 (20)	−87 (32)	168 (53)
C(1)	2092 (3)	−1155 (6)	1803 (8)	106 (16)	584 (59)	1066 (118)	42 (26)	43 (37)	−69 (76)
C(2)	1361 (3)	−582 (5)	2045 (7)	97 (15)	423 (51)	734 (103)	21 (23)	−2 (32)	−107 (64)
C(3)	2991 (3)	1762 (5)	8047 (8)	128 (17)	531 (60)	922 (113)	55 (25)	16 (36)	−69 (69)
C(4)	3660 (3)	868 (5)	8092 (7)	94 (15)	359 (51)	741 (102)	22 (23)	3 (32)	−95 (63)
C(5)	812 (3)	−1632 (5)	2444 (8)	139 (17)	472 (57)	1375 (131)	−40 (26)	21 (39)	−103 (74)
C(6)	1046 (3)	329 (6)	410 (9)	198 (21)	729 (71)	1031 (124)	61 (31)	1 (42)	107 (79)
C(7)	999 (3)	−318 (6)	4939 (9)	177 (19)	712 (69)	1168 (125)	−43 (29)	170 (41)	−4 (77)
C(8)	1117 (3)	1606 (5)	2931 (9)	164 (18)	345 (54)	1680 (142)	37 (26)	−36 (42)	−49 (74)
C(9)	4335 (3)	1577 (6)	7695 (8)	125 (17)	668 (63)	1426 (136)	−77 (28)	33 (41)	−60 (80)
C(10)	3828 (3)	31 (6)	9901 (8)	207 (21)	654 (64)	836 (119)	24 (30)	10 (40)	29 (74)
C(11)	4143 (3)	−110 (7)	5633 (8)	105 (17)	979 (76)	1165 (131)	17 (30)	104 (40)	−253 (84)
C(12)	3464 (3)	−1407 (5)	7607 (9)	275 (22)	338 (55)	1379 (138)	−38 (28)	−32 (45)	−33 (73)

	x	y	z		x	y	z
H(1)	47 (9)	−177 (16)	131 (22)	H(9)	414 (8)	231 (16)	669 (21)
H(2)	109 (8)	−242 (16)	310 (21)	H(10)	471 (8)	189 (16)	886 (21)
H(3)	69 (9)	−13 (16)	−53 (22)	H(11)	335 (9)	−10 (15)	1047 (21)
H(4)	151 (9)	77 (16)	−7 (21)	H(12)	427 (9)	40 (16)	1073 (21)
H(5)	73 (8)	43 (16)	576 (21)	H(13)	398 (8)	48 (16)	448 (22)
H(6)	137 (9)	−100 (16)	578 (21)	H(14)	433 (8)	−111 (16)	539 (21)
H(7)	156 (9)	220 (16)	279 (21)	H(15)	355 (9)	−219 (16)	703 (21)
H(8)	77 (8)	198 (16)	383 (21)	H(16)	291 (9)	−145 (16)	775 (21)

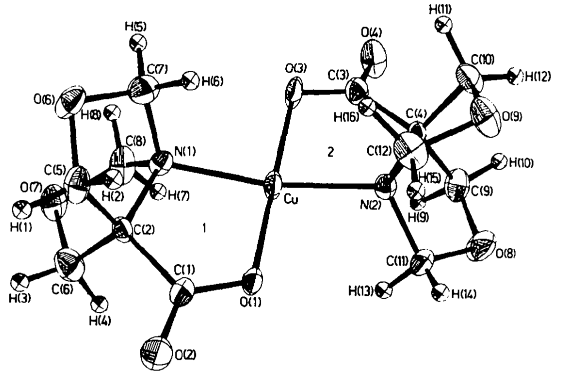

Fig. 2. The $Cu(dioxc)_2$ labelling scheme. The thermal parameters of the non-hydrogen atoms enclose 50% probability.

same as employed previously (Snow, 1974).* The atomic parameters are listed in Table 2 with their estimated standard deviations.

Results and discussion

A projection of the structure down the **c** direction is shown in Fig. 1 and the molecular structure is shown in Fig. 2. The Cu atom is seen to be five-coordinate and the coordination geometry is pseudo square-pyramidal. The dioxo ligands coordinate in the basal plane of the square pyramid, and the apical bond occurs between the Cu atom of one $Cu(dioxc)_2$ formula unit and the carbonyl O of a glide-related unit along the *c* axis. The structure thus consists of infinite molecular chains of $Cu(dioxc)_2$ units along **c**. The apical Cu–O interaction has a distance of 2·354 (4) Å (Table 3). Similar coordination geometries and apical Cu–O distances have been observed in other bis(α-amino acidato)copper(II) complex structures. The *cis*-bis(*R*-α-alaninato)-copper(II) structure (Gillard, Mason, Payne & Robertson, 1969) has such a square-pyramidal coordination sphere around the Cu atom. Here the *cis* arranged α-amino acidato ligands coordinate in the basal plane and a screw-related carbonyl O forms the apical bond with the Cu atom, thus forming infinite spiral molecular chains similar to those of $Cu(dioxc)_2$. The apical Cu–O distance in this structure is 2·390 (7) Å. *trans*-Bis(*S*-tyrosinato)copper(II) (van der Helm & Tatsch, 1972) also forms infinite chains coiled around crystallographic screw axes and the five-coordinate Cu again has an apical bonding interaction of 2·39 Å with the carbonyl O of a screw-related $Cu(S\text{-tyro})_2$ unit. In the aquabis(*N*,*N*-dimethylglycinato)copper(II) dihydrate structure (Cameron, Prout, Rossotti & Steele, 1973), the Cu coordination sphere is square-pyramidal but the apical Cu–O bond is between the Cu atom and a water molecule ligand, and has the relatively short value of 2·28 (2) Å. The complex *cis*-bis(glycinato)diaqua-copper(II) in the structure of $Cu(gly)_2H_2O$ (Freeman, Snow, Nitta & Tomita, 1964) has an essentially similar coordination geometry with the aqua ligand at the apex of the square pyramid and 2·40 (1) Å from the Cu atom. The above values are within the ranges 2·30 to 2·74 and 2·30 to 2·53 Å listed by Freeman (1967) for

Table 3. *Bond lengths* (Å) *and angles* (°)

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

Ligand 1		Ligand 2	
Cu–O(1)	1·904 (4)	Cu–O(3)	1·939 (4)
Cu–N(1)	2·024 (4)	Cu–N(2)	2·024 (4)
O(1)–C(1)	1·280 (6)	O(3)–C(3)	1·274 (6)
C(1)–O(2)	1·228 (7)	C(3)–O(4)	1·225 (7)
C(1)–C(2)	1·520 (7)	C(3)–C(4)	1·532 (7)
C(2)–N(1)	1·510 (6)	C(4)–N(2)	1·506 (6)
C(2)–C(5)	1·542 (7)	C(4)–C(10)	1·554 (7)
C(5)–O(6)	1·425 (7)	C(10)–O(9)	1·430 (7)
O(6)–C(7)	1·410 (7)	O(9)–C(12)	1·411 (7)
C(7)–N(1)	1·496 (7)	C(12)–N(2)	1·485 (7)
C(2)–C(6)	1·534 (8)	C(4)–C(9)	1·523 (7)
C(6)–O(7)	1·425 (7)	C(9)–O(8)	1·427 (7)
O(7)–C(8)	1·414 (7)	O(8)–C(11)	1·405 (7)
C(8)–N(1)	1·497 (7)	C(11)–N(2)	1·499 (7)
Cu–O(1)–C(1)	116·72 (34)	Cu–O(3)–C(3)	112·74 (34)
O(1)–C(1)–C(2)	117·28 (48)	O(3)–C(3)–C(4)	116·98 (47)
C(1)–C(2)–N(1)	112·09 (42)	C(3)–C(4)–N(2)	110·56 (40)
C(2)–N(1)–Cu	107·16 (30)	C(4)–N(2)–Cu	107·13 (29)
N(1)–Cu–O(1)	86·35 (16)	N(2)–Cu–O(3)	84·52 (16)
O(1)–C(1)–O(2)	125·45 (51)	O(3)–C(3)–O(4)	125·61 (52)
O(2)–C(1)–C(2)	117·23 (49)	O(4)–C(3)–C(4)	117·38 (48)
N(1)–C(2)–C(5)	103·50 (42)	N(2)–C(4)–C(10)	103·35 (40)
C(2)–C(5)–O(6)	104·82 (43)	C(4)–C(10)–O(9)	104·57 (44)
C(5)–O(6)–C(7)	104·10 (41)	C(10)–O(9)–C(12)	103·31 (42)
O(6)–C(7)–N(1)	105·85 (46)	O(9)–C(12)–N(2)	105·44 (43)
C(7)–N(1)–C(2)	104·02 (39)	C(12)–N(2)–C(4)	103·65 (41)
N(1)–C(2)–C(6)	103·11 (41)	N(2)–C(4)–C(9)	103·47 (42)
C(2)–C(6)–O(7)	103·96 (47)	C(4)–C(9)–O(8)	103·83 (44)
C(6)–O(7)–C(8)	104·29 (41)	C(9)–O(8)–C(11)	106·25 (42)
O(7)–C(8)–N(1)	106·30 (42)	O(8)–C(11)–N(2)	106·46 (46)
C(8)–N(1)–C(2)	104·68 (41)	C(11)–N(2)–C(4)	105·19 (40)
C(1)–C(2)–C(6)	110·30 (47)	C(3)–C(4)–C(9)	114·25 (44)
C(1)–C(2)–C(5)	113·43 (45)	C(3)–C(4)–C(10)	111·37 (45)
C(5)–C(2)–C(6)	113·76 (46)	C(10)–C(4)–C(9)	112·96 (44)
Cu–N(1)–C(8)	117·09 (32)	Cu–N(2)–C(11)	114·45 (35)
Cu–N(1)–C(7)	110·68 (35)	Cu–N(2)–C(12)	112·99 (34)
C(7)–N(1)–C(8)	112·06 (43)	C(12)–N(2)–C(11)	112·36 (45)

Apical interaction with Cu

Cu–O(4^{i})	2·354 (4)

Interligand angles at Cu

O(1)–Cu–N(2)	94·03 (16)	O(4^{i})–Cu–N(1)	109·16 (16)
O(3)–Cu–N(1)	94·44 (16)	O(4^{i})–Cu–O(1)	97·38 (16)
N(1)–Cu–N(2)	161·58 (18)	O(4^{i})–Cu–N(2)	89·08 (16)
O(1)–Cu–O(3)	177·66 (17)	O(4^{i})–Cu–O(3)	84·45 (17)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32073 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Cu—O(carbonyl) and Cu—O(apical aqua) bond distances respectively. There are no interchain contact distances significantly less than the sum of the literature values (Bondi, 1964) for the van der Waals radii. Apart from the Cu—O(4^{i}) apical interaction, the only significant intrachain close contact is that involving the C(8) hydrogen, H(7), and the chelated oxygen, O(3^{i}), of the carboxylate group containing O(4^{i}). In fact the C(8)—H(7)$\cdots$O(3^{i}) interaction, with a C$\cdots$O distance of 3·276 (7) Å, an O$\cdots$H distance of less than 2·25 (6) Å (owing to the reduced X-ray C—H distance) and a C—H$\cdots$O angle of 169°, has a geometry which is very similar to that found (Hamilton & Ibers, 1968) for previously postulated C—H$\cdots$O hydrogen bonds.

The Cu(dioxc)$_2$ formula unit (Fig. 2) is composed of two dioxc ligands chelated to Cu in the *trans* configuration. Each ligand consists of a glycinato substrate in which the N—C$^{\alpha}$ bond is common to two oxazolidine rings formed by the cyclization of substituents on the N and C$^{\alpha}$ atoms. The oxazolidine rings are similar to those found in *R,S*-bis(2,5-dimethyloxazolidine-4-carboxylato)copper(II) dihydrate (Aune, Maldonado, Larcheres & Pierrot, 1970; Larcheres & Pierrot, 1971).

The Cu—O(chelate) bond lengths of 1·904 (4) [Cu—O(1)] and 1·939 (4) Å [Cu—O(3)] are significantly different. This probably results partly from differences in the bonding properties of O(1) and O(3), and partly from the C(8)—H(7)$\cdots$O(3^{i}) type interaction if O(3^{i}) is an acceptor in a C—H$\cdots$O hydrogen bond [a repulsive contact would decrease the Cu—O(3) distance]. The short Cu—O(chelate) distance found here is less than that observed in most other copper–amino acid complexes, and considerably less than the means of 1·98 (1) and 1·96 Å recorded by Freeman (1967) and Muir (1973) for copper–amino acid and copper–carboxylato complexes. The remaining interatomic bond distances are not unusual and are similar to those found for the analogous bonds in other *trans*-bis(α-amino acidato)copper(II) complexes (Larcheres & Pierrot, 1971; Mathieson & Welsh, 1952; van der Helm & Tatsch, 1972; Cameron *et al.*, 1973). The C—H bond distances are all similar to within 3σ and the mean C—H distance is 1·04 (2) Å. This is significantly larger than the optimal value of 0·95 Å determined by Churchill (1973) over a very limited range of metal complexes, and justifies the earlier inclusion of the H

Table 4. *Least-squares planes and atom deviations*

Plane equations are in the form $LX + MY + LZ = P$. X, Y and Z are orthogonal coordinates (Å) referred to an orthonormal base system with axes parallel to **a**, **b** and **c***. The atoms were assigned weights based on their standard deviations. The mean isotropic e.s.d.'s for Cu, N, O and C coordinates are 8×10^{-4}, 4×10^{-3}, 4×10^{-3} and 6×10^{-3} Å respectively.

Plane	L	M	N	P	Symbol
N(1)O(1), Cu, O(3), N(2)	0·3884	0·8059	−0·4469	0·2075	1
N(1), O(4^{i}), N(2), Cu	0·3978	−0·5011	−0·7686	−1·3233	2
O(1), O(4^{i}), O(3), Cu	−0·7950	0·2988	−0·5280	−4·9195	3
Cu, N(1), C(2), C(1), O(1)	0·2414	0·7990	−0·5508	−0·7238	4
Cu, N(2), C(4), C(3), O(3)	0·4794	0·7399	−0·4719	0·4715	5
C(2), C(1), O(1), O(2)	0·2290	0·7597	−0·6109	−0·8392	6
C(4), C(3), O(3), O(4)	0·3884	0·5165	−0·7631	−1·8113	7
N(1), C(2), C(5), C(7)	−0·7058	0·5533	−0·4424	−2·5912	8
N(1), C(2), C(6), C(8)	0·9532	0·2828	−0·1066	1·8225	9
N(2), C(4), C(10), C(12)	0·9923	−0·1184	−0·0368	5·2870	10
N(2), C(4), C(9), C(11)	−0·4174	0·6326	−0·6524	−5·5294	11

Distances from the planes (Å)

Chelate ring and metal, donor atom planes

	1	2	3		4	6		5	7
Cu	0·020	0·003	0·002	Cu	−0·001	−0·162	Cu	0·006	0·820
N(1)	−0·304	−0·042	1·915	N(1)	0·035	−0·050	N(2)	−0·173	0·263
N(2)	−0·304	−0·040	−2·017	O(1)	0·037	0·002	O(3)	−0·188	−0·002
O(1)	−0·015	1·890	−0·022	O(2)	−0·124	0·003	O(4)	0·629	−0·002
O(3)	−0·013	−1·923	−0·024	C(1)	−0·053	−0·012	C(3)	0·212	0·011
O(4^{i})	2·327	−0·010	−0·001	C(2)	−0·021	0·003	C(4)	0·117	−0·003

Oxazolidine ring planes

	8		9		10		11
N(1)	0·017	N(1)	0·021	N(2)	0·038	N(2)	0·037
C(2)	−0·024	C(2)	−0·030	C(4)	−0·049	C(4)	−0·050
C(5)	0·019	C(6)	0·029	C(10)	0·048	C(9)	0·044
C(7)	−0·023	C(8)	−0·026	C(12)	−0·050	C(11)	−0·049
O(6)	0·564	O(7)	−0·560	O(9)	0·585	O(8)	−0·510

atoms at the positions calculated by assuming a C—H distance of 1·02 Å.

Apart from the Cu—O—C and the N—Cu—O(chelate) angles, the two ligands have identical angular geometries to within the accuracy of the structural determination. The difference in Cu—O—C and N—Cu—O(chelate) angles is probably induced by the ligating function of O(4) and the close contacts with O(3) as inferred above. The remaining chelate ring angles compare well with those found in the copper–α-amino acidato structures cited above, although the large standard deviations in some cases make detailed comparisons somewhat tenuous. The angular dimensions of the four oxazolidine rings do not differ significantly from each other or from those observed for the analogous rings in the Cu-*R*,*S*-(dimoxc)$_2$(H$_2$O)$_2$ structure.

The coordination polyhedron is distorted significantly from square-pyramidal geometry with the O(4^i) apical donor atom being displaced toward ligand 2, as indicated by the inter-donor atom angles at the Cu atom (Table 3). Close contacts between the formula units brought about by the apical bond also result in the N donors being forced below the basal plane of the square pyramid. This is shown by the N—Cu—N angle of 161·58 (18)° and the large deviations of the N atoms (0·304 Å) from the weighted least-squares basal plane through Cu, N(1), O(1), N(2) and O(3) (plane 1, Table 4). Similar steric distortions occur in other pseudo square-pyramidal complexes of Cu^{II} and α-amino acids and generally increase with increasing substitution on the N and α-C atoms of the amino acid chelates.

The chelate rings of the Cu(dioxc)$_2$ complex differ considerably in planarity and the nature of the puckering is unusual compared to that found in many other copper–amino acidato chelate systems (Cameron *et al.*, 1973; Freeman, 1967). The relatively planar nature of the chelate ring of ligand 1 may be seen by comparing least-plane atom deviations (0·001 → 0·053 Å, plane 4, Table 4) and torsion angles (1·3 → 6·8°, Table 5) for this ring with those for the chelate ring of ligand 2 (0·006 → 0·212 Å, plane 5 and 9·3 → 28·5°). This difference is caused principally by the distortion of ligand 2 resulting from the Cu bonding requirements of O(4). Of particular interest is the closely planar nature of the Cu—N—C—C sections in the chelate rings. The Cu—N—C—C torsion angle is 1·3 (5)° for ligand 1 and 9·3 (5)° for ligand 2 and in both cases is the lowest torsion angle in the chelate ring. The analogous torsion angles in other amino acid chelates are often found to be the largest in the rings. These observations indicate the high stability of the envelope conformations of the oxazolidine rings in Cu(dioxc)$_2$ which impose the planar Cu—N—C—C linkages. Another special effect of the distortion associated with the apical bond relates to the relative twist of the chelate ring planes 4 and 5 which have an interplanar angle of 14·8°. This twist leads to a reduction of the distance between oxazolidine rings below the basal plane of the square pyramid, and may block access to the sixth coordination site. A similar effect has been noted in the Cu(dimgly)$_2$-H$_2$O.2H$_2$O structure (Cameron *et al.*, 1973).

As mentioned above the four oxazolidine rings adopt envelope conformations, and in each ligand the envelope tips formed by the C—O—C linkages fold toward each other (Fig. 2). The small atom deviations from the least-squares planes through the C—C—N—C section of the rings (planes 8, 9, 10, 11, Table 4) and the low C—C—N—C torsion angles (Table 5) illustrate the closely planar nature of the envelope bases. The dihedral angles between these planes and the envelope tips range from 36·9 to 41·9°. The envelope conformations may be explained by the minimization of inter and intra-oxazolidine-ring non-bonding interactions. Either half-chair or alternative envelope conforma-

Table 5. *Torsion angles in the ligands* (°)

The torsion angle about the *j–k* bond of the atomic sequence *i–j–k–l* is positive if the skew lines *i*→*l* and *j*→*k* form a right-handed helix.

N(1)—Cu—O(1)—C(1)	−6·1 (4)	N(2)—Cu—O(3)—C(3)	+27·1 (4)
Cu—O(1)—C(1)—C(2)	+6·8 (7)	Cu—O(3)—C(3)—C(4)	−28·5 (6)
O(1)—C(1)—C(2)—N(1)	−3·3 (7)	O(3)—C(3)—C(4)—N(2)	+12·0 (7)
C(1)—C(2)—N(1)—Cu	−1·3 (5)	C(3)—C(4)—N(2)—Cu	+9·3 (5)
C(2)—N(1)—Cu—O(1)	+3·6 (3)	C(4)—N(2)—Cu—O(3)	−18·6 (3)
N(1)—C(2)—C(5)—O(6)	+20·9 (5)	N(2)—C(4)—C(10)—O(9)	+17·6 (5)
C(2)—C(5)—O(6)—C(7)	−39·3 (5)	C(4)—C(10)—O(9)—C(12)	−38·7 (6)
C(5)—O(6)—C(7)—N(1)	+42·7 (5)	C(10)—O(9)—C(12)—N(2)	+45·7 (6)
O(6)—C(7)—N(1)—C(2)	−28·2 (5)	O(9)—C(12)—N(2)—C(4)	−33·4 (5)
C(7)—N(1)—C(2)—C(5)	+4·0 (5)	C(12)—N(2)—C(4)—C(10)	+8·9 (5)
N(1)—C(2)—C(6)—O(7)	−28·4 (5)	N(2)—C(4)—C(9)—O(8)	−28·8 (5)
C(2)—C(6)—O(7)—C(8)	+42·2 (6)	C(4)—C(9)—O(8)—C(11)	+39·6 (6)
C(6)—O(7)—C(8)—N(1)	−39·4 (6)	C(9)—O(8)—C(11)—N(2)	−34·3 (6)
O(7)—C(8)—N(1)—C(2)	+20·3 (6)	O(8)—C(11)—N(2)—C(4)	+14·7 (6)
C(8)—N(1)—C(2)—C(6)	+5·1 (5)	C(11)—N(2)—C(4)—C(9)	+8·7 (5)

tions would introduce much closer C · · · H and/or H · · · H repulsive contacts between the rings, as suggested by an examination of a Dreiding molecular model of the complex. In the observed structure, these inter-ring C · · · H and H · · · H close contacts (those less than the van der Waals radii sum) range from 2·48 to 2·70 Å and 2·13 to 2·33 Å.

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The Crystal and Molecular Structure of 3-Methyl-mono-*o*-benzylautumnaline

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The title compound ($C_{30}H_{37}NO_5$) crystallizes in space group $P\bar{1}$ with $a = 21\cdot657$ (4), $b = 13\cdot193$ (2), $c = 5\cdot291$ (1) Å; $\alpha = 105\cdot52$ (1), $\beta = 89\cdot39$ (1), $\gamma = 113\cdot03$ (1)°; $Z = 2$. The structure was solved by direct methods from diffractometer data and refined anisotropically to $R = 0\cdot05$. A comparison of three automatic direct-methods computer systems, *MULTAN*, *SHELX* and *XCSD*, is presented. The analysis establishes that the compound is the *cis*-1,3 isomer. The molecule is considerably distorted from planarity through the combined effects of intra- and intermolecular forces.

Introduction

Biosynthetic studies of colchicine, the major alkaloid of *Colchicum autumnale* have shown that it is derived from the aromatic amino acids phenylalanine and tyrosine *via* the formation of autumnaline (Battersby, Herbert, McDonald, Ramage & Clements, 1972). To study the steric requirements of the enzyme-active sites in autumnaline the two stereoisomers of 3-methyl-mono-*o*-benzlyautumnaline (ratio 9:1) were prepared (Stachulski, 1974). We have undertaken the X-ray analysis of the minor isomer (I) to establish the relative stereochemistry of the active sites.

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