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An X-Ray Investigation of DL-(ethylvalinate-N,N-diacetato)diaquocopper(II)

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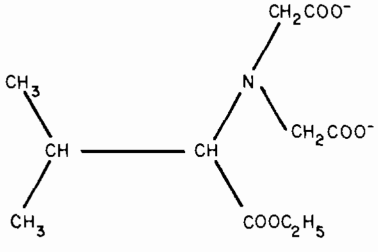
A single-crystal X-ray structure investigation of the DL form of (ethylvalinate-N,N-diacetato)diaquocopper(II) has been carried out. The compound crystallizes in the monoclinic space group $P2_1/n$, with a = 7.50 ± 0.01, b = 28.60 ± 0.01, c = 7.50 ± 0.01 Å, β = 91.27 ± 0.01°, and Z = 4. Least-squares refinement on 1252 reflections with $|F_o| > 3\sigma(F)$ resulted in a final discrepancy factor of 0.130. The stereochemistry around the copper is distorted octahedral, the equatorial co-ordination consisting of the tertiary nitrogen, the two acetate oxygens, and a water molecule. Here, the bonding distances to the metal range from 1.94(1) to 2.04(1) Å. The second water molecule occupies an axial position at a greater distance from the metal (2.32(1) Å), while the ether oxygen of the ester linkage occupies an opposite axial position, lying at 2.84(2) Å from the metal. The ester carbonyl group is not co-ordinated. The ester chain is partially disordered, corresponding to a randomness of the two isomers.

Introduction

Most of the mechanisms suggested[1] for the hydrolysis of α-amino acid esters by transition metal ions involve a complex intermediate in which the ester group is activated to nucleophilic attack by co-ordination to the metal. Specifically, the ester studied here, DL-ethylvalinate-N,N-diacetate (EVDA),



EVDA

has four potential co-ordinating sites: the two acetate groups, the tertiary nitrogen atom, and the ester group. Although it appears fairly certain that EVDA co-ordinates as a tridentate ligand,[1] attempts to substantiate co-ordination of the ester linkage in this and similar molecules have been largely inconclusive. Thus, for ethylglycinate-N,N-diacetate (EGDA), the ester carbonyl absorption in the complex Cu(EGDA) in D_2O occurred at 1725 cm^{-1}, showing no significant shift from that of the free ester (at 1723 cm^{-1}).[2] Normally, it has been observed[3] that carbonyl co-ordination to Cu(II) lowers the stretching frequency by about 100 cm^{-1}.

Similarly, the formation constant ratio K_1/K_2 of 8,800 for EVDA with Cu(II)[1] is much smaller than the expected value[4] of at least 10^6 for tetradentate co-ordination to Cu(II). These results suggest that the ester group is not or only slightly co-ordinated. However, the fact that metal catalysis occurs at all is evidence of ester interaction, since it is difficult to see how activation to nucleophilic attack could occur *via* the co-ordinated nitrogen.

It has been observed[5] that carbonyl oxygen exchange occurs during the cupric ion catalyzed hydrolysis of DL-phenylalanine ethyl ester *carbonyl*-O^{18}. This would indicate the formation of an addition intermediate which is symmetric with respect to the isotopic oxygen atom. The mechanism suggested for achieving this intermediate involved a transient interaction of an ester oxygen with the metal ion, but the question was posed as to whether this interaction occurs *via* the carbonyl oxygen or the ether oxygen of the ester group.

The present structural investigation was undertaken to establish whether EVDA can in fact function in a tetradentate manner, and if so, what is the ester group's mode of co-ordination.

Experimental

A quantity of Na_2EVDA was kindly supplied by B.E. Leach and R.J. Angelici. On mixing aqueous solutions containing equimolar amounts of $CuCl_2$ and Na_2EVDA, an intense blue color formed immediately. The resulting solution was treated with ethanol and allowed to stand; bright blue platelets of the copper complex separated. These showed a marked tendency to cleave along the (010) planes, corresponding to the faces of the platelets. Elemental analysis was consistent with the formula Cu(EVDA)$(H_2O)_2$. Because they appeared quite stable in the atmosphere, single crystals of the complex were mounted on thin glass fibers for the X-ray investigation.

Approximate unit cell dimensions and the space group were determined from Weissenberg photographs, taken with CuKα radiation. The Laue symmetry shown was 2/m, indicating a monoclinic system.

Crystal Data

$C_{11}H_{21}NO_8Cu$, M = 358.8, monoclinic, a = 7.50 ± 0.01, b = 28.60 ± 0.01, c = 7.50 ± 0.01 Å, β = 91.27 ± 0.01°, V = 1608 Å^3, D_m = 1.50 (by flotation in n-pentane/CCl_4), Z = 4, D_c = 1.48, F(000) = 748, μ = 22.9 cm^{-1} for CuKα radiation. Space group $P2_1/n$ (C_{2h}^5 no. 14) from systematic absences $h0l$ for $h + l = 2n + 1$, $0k0$ for $k = 2n + 1$.

The quoted cell parameters were obtained by a least-squares fit[6] to the 2Θ angles of 31 independent reflections in the 2Θ range 135°–145°. The Kα_1 and Kα_2 peaks were well resolved for Cu radiation in this range, and the 2Θ values of both were used in the least-squares refinement.

Complete three-dimensional intensity data were taken at room temperature using Ni-filtered CuKα radiation on a GE Single Crystal Orienter (SCO) equipped with a scintillation counter. A well-formed crystal of dimensions 0.24 × 0.28 × 0.14 mm^3 was mounted with its c* axis coincident with the Φ axis. All reflections in the hkl and $\bar{h}$kl octants within a Cu-radiation sphere of radius ($\sin\Theta/\lambda$) = 0.4586 (2Θ = 90°) were measured. For data collection, the moving-crystal–moving-counter technique (Θ–2Θ coupling) was employed, and a chart trace was taken simultaneously to verify that each reflection had a normal profile. In all, 1653 reflections were collected in this way. A repeat scan was carried out on 200 representative reflections with an appropriate offset in ω to obtain backgrounds. These were used to prepare a curve of background versus 2Θ. A further plot indicated that the backgrounds had negligible χ dependence. During the course of the data taking, several reflections were checked regularly to monitor electronic and crystal stability. The maximum decrease in any of the standards was 5% of the original count.

In addition to Lorentz-polarization, the intensity data were corrected for absorption,[7] and streaking effects.[8] The estimated standard deviation in the structure factor σ(F) was calculated as described previously.[9] Of the reflections measured, 1263 had $|F_o| > 3\sigma(F)$. The remainder were considered unobserved, and were not used in the refinement.

Solution and Refinement of the Structure

The co-ordinates (x,y,z) of the Cu atom were readily determined from an analysis of the Patterson map. Several cycles of full-matrix least squares[10] resulted in $R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.49$. The scattering factors used in the refinement were those of Hanson *et al.*[11] with copper modified for the real and imaginary parts of anomalous dispersion.[12] Weights were based on $1/\sigma^2(F)$. Successive difference electron density maps and least-squares cycles readily permitted the location of all the atoms in the molecule except the –COOEt linkage. At this stage in the refinement, R was 0.21. It appeared from an examination of an electron density map that the ester group was disordered. Eight unassigned peaks occurred on the difference electron density map in the region expected for the ester. These were explained by assuming that the ester carbonyl group can lie in either of the two possible tetrahedral positions of the asymmetric carbon atom C(5). The situation was treated by assigning four of the peaks as two carbonyl groups, giving each atom an occupancy factor of 0.5. The penultimate carbon in the ester chain was also inserted as two half atoms. The ether oxygen of the ester and the terminal carbon were given the usual unit atom occupancy. The correctness of this interpretation was supported by a decrease of the R factor to 0.142 after several cycles of least-squares refinement, and by no large positive or negative regions appearing on a difference electron density map.

Suspect data were now examined. Five reflections which had abnormal chart profiles, and six (of $2\Theta < 15°$) suspected of suffering from extinction effects, were removed from the refinement. The weighting scheme was also adjusted slightly so that a more constant value of $\overline{w\Delta^2}$ was obtained for groups of reflections over different ranges of $|F_o|$. New values of w were derived from a smooth curve fit to the variation in $\overline{w\Delta^2}$.

For the final cycles of least squares, the copper atom was refined anisotropically. The temperature factors of the light atoms were kept isotropic. Final convergence was reached at an R value of 0.130. The average shift/error for the last cycle was 0.03. No attempt was made to include hydrogen parameters. The highest peak observed on a final difference electron density map was 1.2 e/Å^3. This occurred in the vicinity of the nitrogen atom.

Discussion

The unit cell consists of four discrete molecules of the complex. Table I lists the final atomic parameters and their standard deviations, and observed and calculated structure factors are given in Table II.

As can be seen from an illustration of the molecule, Figure 1, the stereochemistry around the metal ion is distorted octahedral. The tertiary nitrogen atom N, the two acetate oxygens O(3) and O(6), and a water

TABLE I. Final Positional Parameters (× 10^4) and Thermal Parameters from Least-squares Refinement.[a]

Atom	x	y	z	B[b]
Cu	−937(3)	1789(1)	1462(3)	–
O(1)	−847(13)	2599(4)	1522(13)	3.67(25)
O(2)	−2768(16)	1705(4)	−397(17)	5.11(30)
O(3)	−2579(14)	1799(3)	3416(15)	3.23(24)
O(4)	−2590(15)	1969(4)	6254(16)	4.22(26)
O(5)	3867(15)	1963(4)	−237(15)	3.87(25)
O(6)	1033(15)	1794(3)	−192(15)	3.50(25)
O(7)	−944(17)	797(5)	1524(19)	6.70(36)
O(8)[c]	−1589(32)	785(8)	4582(34)	5.04(55)
O(8′)[c]	2090(37)	784(9)	776(38)	6.66(67)
N	976(12)	1666(3)	3377(13)	0.81(22)
C(1)	−1785(18)	1869(4)	4892(19)	1.74(29)
C(2)	261(22)	1866(5)	5037(22)	3.29(36)
C(3)	2613(21)	1849(5)	2685(21)	2.80(34)
C(4)	2454(21)	1867(5)	640(20)	2.51(33)
C(5)	1186(22)	1103(6)	3596(23)	4.02(39)
C(6)	2483(33)	919(9)	4856(35)	8.38(64)
C(7)	3657(32)	1176(9)	6113(34)	8.31(64)
C(8)	2511(35)	382(10)	4981(36)	9.52(72)
C(9)[c]	−544(53)	905(14)	3448(56)	5.37(90)
C(9′)[c]	926(51)	887(13)	1822(52)	4.95(86)
C(10)[c]	−1135(56)	602(15)	−500(58)	6.29(102)
C(10′)[c]	−3126(61)	662(17)	1376(66)	7.46(115)
C(11)	−2959(38)	454(11)	−348(39)	10.20(80)

[a] In this and succeeding tables, standard deviations are given in parentheses. [b] Anisotropic Thermal Parameters: $\beta_{11}, \beta_{22}, \beta_{33}, \beta_{12}, \beta_{13}, \beta_{23}$. Cu: 0.0073(6), 0.0015(0), 0.0078(6), 0.0003(1), 0.0014(4), 0.0002(1). The form of the anisotropic temperature factor expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Atoms refined with an occupancy factor of 0.5.

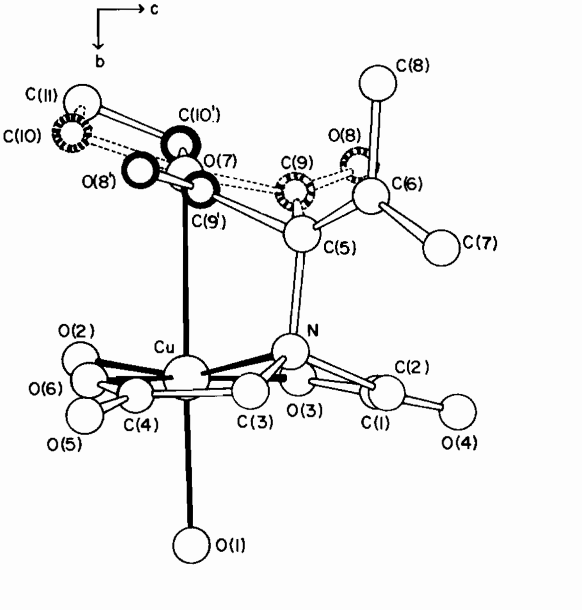


Figure 1. Illustration of the molecule (those atoms with heavy outlines were refined at half occupancy).

oxygen O(2) lie in an approximate equatorial plane. The internal bond distances and angles of the molecule are given in Table III. The Cu–O distances in the equatorial plane are, within experimental error, identical, the Cu–N distance being somewhat longer. Angular distortion in the equatorial plane appears to be dictated by the geometry of the ligand. For example, the angles O(3)–Cu–N and O(6)–Cu–N are 85.4° and 85.2° respectively, the reduction from 90° being due to the requirements of the chelate rings. An examination of the atomic parameters for the ester linkage shows the effects of the disorder. Here the standard deviations on bond lengths increase to about 0.05 Å, and the isotropic temperature factors are all somewhat larger for the disordered atoms with a reduction in the nitrogen temperature factor.

Common to many octahedral complexes of Cu(II), the axial bond lengths are elongated relative to those in the equatorial plane. The axial water oxygen O(1) lies at a distance of 2.32 Å from the metal, compared to 1.95 Å for the equatorial water oxygen O(2). Although the ether oxygen O(7) of the ester linkage lies in an approximate axial position (angle O(1)–Cu–O(7) is 177.5°) the distance of 2.84 Å from Cu clearly re-

TABLE II. Observed and Calculated Structure Factors for Cu(EVDA)·$2H_2O$.

**** L = 0 ****

H	K	FO	FC
2	0	94	-84
4	0	48	-47
2	1	81	90
3	1	6	-8
4	1	42	48
5	1	47	-46
6	1	30	-23
2	2	23	-10
3	2	6	8
4	2	19	18
5	2	18	11
6	2	58	51
1	3	111	-121
2	3	30	-31
3	3	13	6
4	3	6	-6
5	3	69	65
6	3	11	4
1	4	50	-52
2	4	8	4
3	4	44	39
4	4	21	22
5	4	21	-21
6	4	12	10
1	5	42	35
2	5	15	9
3	5	23	13
4	5	8	7
5	5	35	-34
6	5	10	4
0	6	120	122
1	6	57	58
2	6	31	-24
3	6	7	7
4	6	5	-4
5	6	7	-3
6	6	53	-48
1	7	22	-21
2	7	22	27
3	7	7	4
4	7	22	22
5	7	11	-9
6	7	27	-22
0	8	237	-283
1	8	46	43
2	8	61	58
3	8	5	5
4	8	12	5
5	8	8	4
6	8	61	53
1	9	104	-96
2	9	50	-53
3	9	11	11
4	9	19	-16
5	9	59	60
6	9	17	16
0	10	99	99
1	10	80	-79
2	10	21	-19
3	10	43	-45
4	10	7	3
5	10	10	-3
6	10	17	-14
1	11	123	126
2	11	7	-4
3	11	20	-20
4	11	18	-18
5	11	55	-54
6	11	8	3
0	12	111	111
1	12	9	7
2	12	25	18
3	12	17	14
4	12	28	-27
5	12	11	11
6	12	34	-34
1	13	11	-14
2	13	26	23
3	13	13	-14
4	13	22	21
5	13	12	10
0	14	150	-153
1	14	14	-9
2	14	16	8
3	14	5	5
4	14	18	17
5	14	7	-4
1	15	24	-29
2	15	32	-32
3	15	7	8
4	15	18	-17
5	15	27	30
6	15	12	8
0	16	71	95
1	16	9	-7
2	16	16	-8
3	16	7	6
4	16	11	-7
5	16	8	-5
1	17	35	39
2	17	39	47
3	17	6	-8
4	17	12	9
5	17	32	-36
0	18	14	-23
1	18	29	24
2	18	13	12
3	18	21	18
4	18	14	-17
5	18	5	-2
1	19	35	-34
2	19	5	-6
3	19	14	9
4	19	8	5
0	20	44	-51
1	20	7	-2
2	20	13	-4
3	20	25	-20
4	20	15	16
1	21	11	-10
2	21	24	-21
3	21	7	6
4	21	14	-11
0	22	40	48
1	22	13	-13
2	22	9	-4
3	22	14	-12
4	22	8	4
1	23	28	33
2	23	12	15
3	23	10	-6
0	24	7	-13
1	24	19	18
2	24	6	5
3	24	22	23
1	25	22	-26
2	26	7	-8

**** L = 1 ****

H	K	FO	FC
-5	0	51	-57
-3	0	84	-91
-1	0	16	8
1	0	47	54
3	0	95	101
5	0	48	-49
-6	1	19	-15
-5	1	52	50
-4	1	34	-42
-3	1	46	-34
-2	1	7	3
-1	1	130	-128
1	1	105	-122
2	1	27	29
3	1	88	82
4	1	8	-5
5	1	72	71
6	1	17	-15
-6	2	60	58
-5	2	25	26
-4	2	27	-20
-3	2	59	62
-2	2	37	-37
-1	2	4	-3
1	2	21	-26
2	2	14	10
3	2	50	-51
4	2	81	83
5	2	27	22
6	2	27	23
-6	3	33	30
-5	3	9	-6
-4	3	60	63
-3	3	30	32
-2	3	26	23
-1	3	89	-86
0	3	38	-43
1	3	71	59
2	3	41	-48
3	3	19	-16
4	3	18	16
5	3	9	-7
6	3	37	37
-6	4	50	-47
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-1	4	4	-3
0	4	65	59
1	4	6	-3
2	4	55	-47
3	4	16	14
4	4	48	-47
5	4	6	4
6	4	29	-29
-6	5	20	-17
-5	5	25	-27
-4	5	59	-61
-3	5	13	14
-2	5	35	-37
-1	5	11	4
0	5	73	67
1	5	53	47
2	5	51	58
3	5	40	-37
4	5	33	-36
5	5	20	-23
6	5	33	-33
-6	6	21	20
-5	6	29	-27
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-3	6	23	-28
-2	6	18	-16
-1	6	4	3
1	6	5	4
2	6	32	23
3	6	17	21
4	6	27	30
5	6	31	-29
6	6	13	5
-5	7	24	24
-4	7	29	30
-3	7	20	-18
-2	7	4	-3
-1	7	13	-8
1	7	30	-40
2	7	31	-29
3	7	26	26
4	7	15	17
5	7	43	43
6	7	8	7
-5	8	30	32
-4	8	7	-5
-3	8	50	51
-2	8	14	-12
-1	8	4	2
1	8	11	-15
2	8	9	8
3	8	58	-58
4	8	23	24
5	8	35	39
6	8	13	15
-5	9	20	-20
-4	9	41	47
-3	9	27	21
-2	9	56	57
-1	9	26	-23
0	9	98	-93
1	9	105	108
2	9	46	-45
3	9	36	-36
4	9	7	2
5	9	30	-27
6	9	33	33
-5	10	8	6
-4	10	27	17
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0	10	140	136
1	10	26	-29
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4	10	64	-70
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-3	11	12	12
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-1	11	54	58
1	11	19	-9
2	11	73	77
3	11	10	-10
4	11	9	-6
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0	12	66	-70
1	12	59	64
2	12	29	21
3	12	20	18
4	12	35	37
5	12	19	-16
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-3	13	21	-15
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2	13	34	-38
3	13	38	35
4	13	13	14
5	13	43	47
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-3	14	36	37
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0	14	21	-21
1	14	44	-42
2	14	14	-16
3	14	24	-27
4	14	6	1
5	14	25	23
-5	15	25	-25
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-1	15	36	34
0	15	14	4
1	15	24	24
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5	15	25	-27
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2	16	8	-7
3	16	28	31
4	16	19	-17
5	16	18	-21
-5	17	7	1
-4	17	16	-15
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-2	17	23	-18
-1	17	32	39
0	17	31	27
1	17	52	-52
2	17	7	5
3	17	22	19
4	17	10	6
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-3	18	17	20
-2	18	12	11
-1	18	8	6
0	18	42	-43
1	18	9	9
2	18	15	13
3	18	19	-23
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-4	19	29	31
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2	19	34	-36
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1	20	39	-46
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3	20	13	-6
4	20	6	2
-4	21	9	-12
-3	21	15	9
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2	21	7	11
3	21	12	-13
-3	22	25	-26
-2	22	12	9
-1	22	6	1
0	22	24	27
1	22	26	31
2	22	8	6
3	22	15	14
-3	23	12	-12
-2	23	16	-17
-1	23	5	10
0	23	19	20
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2	23	28	22
3	23	6	4
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-1	24	5	2
0	24	26	-30
1	24	5	-2
2	24	12	3
-1	25	15	-23
0	25	18	-17
1	25	10	10

**** L = 2 ****

H	K	FO	FC
-6	0	47	46
-4	0	66	-56
-2	0	152	-176
0	0	105	98
2	0	86	74
4	0	77	77
6	0	7	-8
-6	1	42	43
-5	1	16	12
-4	1	48	52
-3	1	55	-54
-2	1	16	-18
-1	1	18	-21
0	1	77	-83
1	1	13	4
2	1	46	-42
3	1	60	52
4	1	14	12
5	1	13	12
6	1	23	27
-6	2	21	-21
-5	2	32	37
-4	2	45	45
-3	2	37	29
-2	2	47	44
-1	2	21	-16
0	2	29	5
1	2	39	-44
2	2	96	-90
3	2	27	-27
4	2	26	-28
5	2	14	13
6	2	8	-2
-6	3	14	-12
-5	3	27	-23
-4	3	19	-16
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1	12	32	31
2	12	5	-2
-2	14	27	-27
0	14	37	-38
2	14	11	8
0	15	22	-22
0	16	18	16

TABLE III. Selected Bond Distance and Angles in Cu(EVDA)·$2H_2O$.

Distances (Å)			
Cu–O(1)	2.32(1)	C(4)–O(6)	1.24(2)
Cu–O(2)	1.95(1)	N–C(5)	1.63(2)
Cu–O(3)	1.94(1)	C(5)–C(6)	1.44(3)
Cu–O(6)	1.95(1)	C(6)–C(7)	1.47(4)
Cu–N	2.04(1)	C(6)–C(8)	1.54(4)
Cu–O(7)	2.84(2)	C(5)–C(9)	1.42(4)
		C(9)–O(8)	1.22(5)
C(1)–O(3)	1.26(2)	C(9)–O(7)	1.50(4)
C(1)–O(4)	1.23(2)	C(5)–C(9′)	1.48(4)
C(1)–C(2)	1.54(2)	C(9′)–O(8′)	1.22(5)
C(2)–N	1.48(2)	C(9′)–O(7)	1.44(4)
N–C(3)	1.44(2)	O(7)–C(10)	1.62(5)
C(3)–C(4)	1.54(2)	C(10)–C(11)	1.44(5)
C(4)–O(5)	1.29(2)	O(7)–C(10′)	1.68(5)
		C(10′)–C(11)	1.43(6)
Angles (°)			
O(2)–Cu–O(3)	95.3(5)	N–C(3)–C(4)	108.8(12)
O(3)–Cu–N	85.4(4)	C(3)–C(4)–O(5)	118.0(13)
N–Cu–O(6)	85.2(4)	O(5)–C(4)–O(6)	119.1(14)
O(6)–Cu–O(2)	94.5(5)	C(3)–C(4)–O(6)	112.9(14)
O(1)–Cu–O(2)	99.1(4)	N–C(5)–C(6)	119.4(16)
O(1)–Cu–O(3)	89.4(4)	N–C(5)–C(9)	107.5(19)
O(1)–Cu–N	98.0(4)	N–C(5)–C(9′)	108.2(18)
O(1)–Cu–O(6)	89.1(4)	C(6)–C(5)–C(9)	120.6(23)
O(1)–Cu–O(7)	177.5(4)	C(6)–C(5)–C(9′)	120.7(22)
O(7)–Cu–O(2)	83.5(5)	C(5)–C(6)–C(7)	128.4(22)
O(7)–Cu–O(3)	90.1(4)	C(5)–C(6)–C(8)	114.4(21)
O(7)–Cu–N	79.5(4)	C(7)–C(6)–C(8)	117.0(22)
O(7)–Cu–O(6)	91.0(4)	C(5)–C(9)–O(8)	131.3(36)
N–Cu–O(2)	162.9(5)	O(8)–C(9)–O(7)	119.7(32)
O(3)–Cu–O(6)	170.2(5)	C(5)–C(9)–O(7)	108.7(28)
O(3)–C(1)–O(4)	122.3(13)	C(5)–C(9′)–O(8′)	126.7(33)
O(4)–C(1)–C(2)	116.7(13)	O(8′)–C(9′)–O(7)	124.4(33)
O(3)–C(1)–C(2)	120.9(13)	C(5)–C(9′)–O(7)	108.9(27)
C(1)–C(2)–N	108.8(12)	C(9)–O(7)–C(10)	169.8(23)
C(2)–N–C(3)	119.3(11)	C(9′)–O(7)–C(10′)	174.1(25)
C(2)–N–C(5)	109.5(10)	O(7)–C(10)–C(11)	95.3(27)
C(3)–N–C(5)	108.3(10)	O(7)–C(10′)–C(11)	92.9(28)

presents only a very weak interaction with the metal, but co-ordination of the carbonyl oxygen of the ester group does not occur in this compound, at least in the solid state. The Cu–O(7)–C(9) angle is approximately 80° which would also be indicative of a weak interaction of the metal with the *p*-orbital on O(7). Rotation about C(9)–C(5) would essentially interchange O(7) and O(8) in space, but metal interaction with the double bond π-orbitals in C(9)–O(8) would likely be even less favorable.

Those molecules in the unit cell which are related by the inversion center have their ester groups as points of closest-contact. Between these, in the *b* direction, only weak van der Waals forces operate (the closest intermolecular contact is 3.42 Å). However, parallel to the *a c* plane, the crystal has high dimensional stability, due to an infinite network of hydrogen bonds linking molecules of coordinates (x,y,z) and ($^1/_2$ + x, $^1/_2$–y, $^1/_2$ + z). The hydrogen atoms of the water molecules are fully utilized in this hydrogen bonding, which is illustrated in Figure 2. For clarity, only the iminodiacetate group of the ligand is shown. The equatorial water oxygen atom O(2) is hydrogen bonded to the carboxyl oxygens O(5) and O(4) of those molecules one cell away in the –*a* and –*c* directions, respectively. The network is completed by a water oxygen O(1) of the molecule at ($^1/_2$ + x, $^1/_2$–y, $^1/_2$ + z). The displacement of O(2) from the equatorial plane of the molecule (see Figure 1) is presumably necessary to optimize the distances and angles involved in the hydrogen bonding.

These observations on packing explain the observed tendency of the crystals to cleave parallel to the (010) planes. The absence of close intermolecular contacts

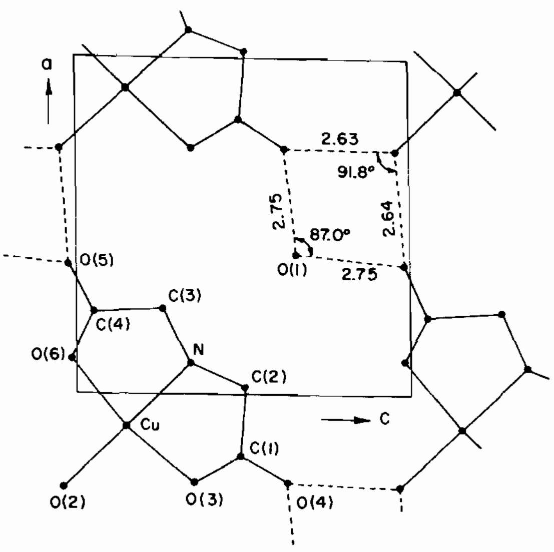

Figure 2. Intermolecular hydrogen bonding.

for the ester suggest that the disorder is simply due to a random insertion of the D and L forms of the molecule, since sterically neither is unfavorable.

The present structure verifies that EVDA can function as a tetradentate ligand, although rather surprisingly the ester is weakly bonded to the metal via the ether oxygen, rather than the carboxyl oxygen. Of course, it cannot be certain that this is the complex intermediate which in solution is responsible for hydrolysis. However, it was isolated at neutral pH, and under these conditions the hydrolysis of EVDA is slow[1], which argues that the intermediate is fairly stable in the absence of the OH^- nucleophile.

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