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The Crystal and Molecular Structure of *Catena*-3,5-dimethylisoxazole-μ-dichloro-dicopper(I), a Compound Reacting with Molecular Oxygen

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The title compound has been prepared by an in situ *method involving the reduction of cupric ions and the cyclisation of 2,4-pentanedioxime. The colourless crystals were found to be sensitive to molecular oxygen and the initial dark brown product formed on exposure to the gas has a new i.r. band at 1083 cm*$^{-1}$ *taken as indicative of dioxygen bonding. An X-ray structural determination of the colourless compound (*a = *3.8660,* b = *18.543,* c = *11.888Å,* β = *92.65°,* $P2_1/c$*, 4 molecules of* $L(CuCl)_2$*) revealed a linear polymeric structure with the metal atoms bound by chlorine bridges. Each copper has a distorted tetrahedral donor arrangement but only half of them have the organic group, found to be 3,5-dimethylisoxazole, as a ligand. The stoichiometry is thus* $L(CuCl)_2$ *and it seems likely that the sensitivity to dioxygen is a consequence of the compound's relationship with CuCl rather than to the influence of the isoxazole.*

Introduction

During an investigation of the complexation of 2,4-pentanedioxime (acetylacetonedioxime ≡ AAD) with cupric ions the preparation of a colourless crystalline compound was achieved by heating a solution of $Cu(AAD)Cl_2$ to near boiling in water. This new compound was found to interact with the atmosphere – specificially with molecular oxygen – initially turning dark brown but finally, after some days, crumbling to a green powder. Qualitative interpretation of physical measurements – i.r., u.v., magnetic moments, e.s.r. – confirmed that the colourless species contained cuprous copper, that it did not contain an oxime function but that it retained an organic moiety. Because of the reactivity towards dioxygen and the possible implications for biological models we determined the composition and structure of the compound by X-ray diffraction methods. When we had completed this work we were able to establish its similarity with bromide analogues and derivatives recently reported [1, 2].

Experimental

Preparation

A solution of $CuCl_2 \cdot 2H_2O$ (0.5 g) in methanol (10 ml) was added to AAD (1.0 g) – the stoichiometry is not important so long as the ligand is in excess in methanol (20 ml). An immediate precipitate of a green microcrystalline product was obtained. Expected for $Cu(AAD)Cl_2$, $C_5H_{10}Cl_2CuN_2O_2$: C, 22.7; H, 3.8; N, 10.6; found, C, 22.7; H, 3.9; N, 10.7. Water (200 ml) was added to form a solution of the precipitate in its mother liquor and the mixture held near the boiling point for a few minutes. It then became bright orange in colour, a gas was evolved and, on cooling, white needles of a new compound were deposited. Expected for $C_5H_7Cl_2Cu_2NO$ (as determined by X-ray analysis): C, 20.3; H, 2.4; N, 4.7; found C, 19.7; H, 2.4; N, 4.9.

The cuprous compound is diamagnetic but $Cu(AAD)Cl_2$ was found to have a μ_{eff} of 2.1 Bohr magnetons at 18 °C.

Crystal data

$C_5H_7Cl_2Cu_2NO$, $M = 295.1$; monoclinic, $a = 3.8860(5)$, $b = 18.543(2)$, $c = 11.888(1)$Å, $\beta = 92.659(8)°$ (standard deviations from the least squares fit to the diffractometer co-ordinates of twelve reflexions), $U = 856$Å^3, CuK_α radiation $\lambda = 1.5418$Å; $D_m = 2.27$ g cm^{-3}, $D_c = 2.29$ g cm^{-3}, $Z = 4$ for the stoichiometry given, space group $P2_1/c$; μ (for CuK_α) = 114.3 cm^{-1}.

Since the compound reacted with the atmosphere it was necessary to seal crystals by spraying them with a polyurethane aerosol. After preliminary photography an approximately rectangular crystal of dimensions 0.30 × 0.12 × 0.08 mm was selected for data collection on a Hilger–Watts Y290 four-circle computer-controlled diffractometer. Reflexions were recorded over the range $0 < \theta < 55°$, a total of 1072 independent values being obtained, 855 with an intensity $>3\sigma(I)$. A primary beam collimator of 0.5 mm diameter was used at a take-off angle of 3°. The appropriate secondary collimator size was experimen-

TABLE I. Atomic Positions

Atom	x/a	y/b	z/c
Cu(1)	−0.0035(4)	0.1312(1)	0.0720(1)
Cu(2)	0.4916(4)	0.0099(1)	0.1315(1)
Cl(1)	0.4910(4)	0.4000(1)	0.4594(1)
Cl(2)	0.0107(5)	0.0421(1)	0.2232(1)
O(1)	0.825(1)	0.2829(2)	0.0457(4)
N(2)	−0.011(1)	0.2321(3)	0.1192(5)
C(3)	0.092(2)	0.2675(4)	0.2083(5)
C(4)	0.000(2)	0.3402(4)	0.1977(7)
C(5)	0.838(2)	0.3472(4)	0.0976(6)
C(6)	0.684(3)	0.4081(5)	0.0316(8)
C(7)	0.276(2)	0.2300(5)	0.3039(7)

tally found to be 2.0 mm. A scan range of $\theta = 0.72^\circ$ was determined as being suitable and the machine was operated in the $2\theta/\omega$ mode using $\theta = 0.01^\circ$ steps counting for 1 second. Backgrounds were counted for 18 seconds at each end of the scan. The reflexions $0\,0\,6$, $0\,8\,0$ and $1\,\bar{3}\,\bar{6}$ were monitored throughout data collection but each gave constant counts with 3%. Crystal decomposition was not, therefore, a problem a conclusion reinforced by the observation that discoloration did not occur during diffractometry. Data were corrected for L_p effects in the usual way and a p factor [3] of 0.04 was incorporated into the estimation of their standard deviations. Absorption corrections were not applied because of the difficulty in accounting for the non-uniform polyurethane coating. Since the structure refined satisfactorily (R = 0.046) and since interest lies in the overall atomic arrangement and not bonding details this omission is not serious. As a systematic error it will, however, lower the accuracy claimed for the structural parameters.

Normal Patterson and heavy-atom techniques were used to overcome the phase problem. Once the positions of the chlorine atoms had been established the identity of the organic ligand became clear. Atomic scattering factors were selected from those currently in use [4], applying only the real correction to the values for copper, and full-matrix least-squares refinement was begun using a local variant [5] of ORFLS [6]. At the point where individual isotropic temperature parameters were to be replaced by anisotropic values an electron density difference synthesis was calculated and searched for hydrogen atom positions. All but two – on C(6) – were clearly seen and were then incorporated into the model, where possible at calculated co-ordinates. When the positions of the two missing methyl hydrogens were determined from the known location of the third they were found to fall on regions of positive density and were also included. All these atoms were given isotropic temperature factors of $B = 5.5 Å^2$. Neither their thermal nor positional parameters were refined. Convergence occurred at a conventional R factor, R_1, of 0.046 ($R_2 = 0.061$) all parameter shifts then being less than 0.4 of their respective standard deviations.

The atom parameters are listed in Table I, temperature factors in Table II and calculated bond lengths and angles in Table III and IV. The structure factor data are listed in Table V. Figure 1 is an ORTEP diagram of repeating units along the *a* axis and gives the atom numbering scheme; Figure 2 shows a unit cell viewed along the *a* axis.

Discussion

The compound is seen to be a polymeric complex of cuprous copper (Figures 1 and 2) involving bridging chlorine atoms and 3,5-dimethylisoxazole molecules as ligands. It is therefore analogous, at least in stoichiometry, to the isoxazole complexes prepared by Ponticelli, Preti and co-workers [1, 2]. Their syntheses differ, however, from our *in situ* aproach by requiring the initial preparation of the isoxazole. Our synthesis can be visualised as occurring through the elimination of hydroxylamine and the reduction of the metal ions, associated with, or followed by, ring closure. The reaction does not occur in the absence of metal to that co-ordination processes are probably involved. We also made the bromide and iodide by adding a large excess of the potassium salt of these halides just before crystallisation of the colourless compound began. Both proved more insoluble than the chloride. Presumably other substituted isoxazoles could be prepared from the appropriate oxime.

The polymer is one-dimensional, the chain running in the direction of the *a* axis of the crystal and can be described as a stepped or pleated double chain cross-linked by bonds between chlorine atoms and one of the two crystallographically independent copper atoms, Cu(2). A distorted tetrahedral co-ordination sphere is completed about this metal centre, the other, Cu(1), achieving a similar, but less distorted arrangement by binding the organic ligand. The compound is thus a new example in the general $L_m(CuX)_n$ classification [7] in which m = 1 and n = 2. One chlorine atom, Cl(1), also has four bonding groups – the adjacent copper atoms – but Cl(2) has only three. The copper–chlorine bond lengths cover a wide range from 2.286(2) to 2.641(2)Å, a larger spread than that quoted for tetrahedral copper in other compounds of the $L_m(CuX)_n$ type [7]. It is interesting that the bond of 2.641Å from Cu(2) to Cl(1) could be described as being to the axial position of a very distorted trigonal pyramid with angles in the "base" (between Cl(1"), Cl(2) and Cl(2')) of 113.7, 114.8 and 119.7° and angles between base ligands and the axial ligand (Cl(1)) of 99.8, 101.2

TABLE II. Anisotropic Thermal Parameters (× 10^4).

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	1370(20)	24(1)	105(1)	10(2)	-69(3)	-13(1)
Cu(2)	1020(10)	40(1)	113(1)	19(2)	15(3)	-9(1)
Cl(1)	580(10)	19(1)	52(1)	-9(2)	-6(3)	0(1)
Cl(2)	610(10)	22(1)	57(1)	2(2)	6(4)	-1(1)
O(1)	900(40)	20(2)	49(3)	-4(7)	-20(10)	-2(2)
N(2)	660(50)	21(2)	53(4)	-2(8)	-10(10)	1(2)
C(3)	530(50)	21(2)	47(5)	-21(9)	40(1)	0(3)
C(4)	750(70)	24(3)	67(7)	-10(10)	30(2)	-10(3)
C(5)	590(60)	23(2)	62(6)	-10(10)	50(2)	1(3)
C(6)	710(80)	33(3)	110(10)	30(10)	-30(2)	16(4)
C(7)	800(80)	30(3)	59(6)	0(10)	-20(2)	-3(4)

TABLE III. Bond Lengths.

Bond	Distance (Å)
Cu(1)-Cl(1)	2.461(2)
Cu(1)-Cl(1')	2.396(2)
Cu(1)-Cl(2)	2.440(2)
Cu(1)-N(2)	1.954(5)
Cu(2)-Cl(1)	2.641(2)
Cu(2)-Cl(1")	2.309(2)
Cu(2)-Cl(2)	2.286(2)
Cu(2)-Cl(2')	2.326(2)
O(1)-N(2)	1.416(7)
O(1)-C(5)	1.342(8)
N(2)-C(3)	1.294(9)
C(3)-C(4)	1.399(10)
C(3)-C(7)	1.487(11)
C(4)-C(5)	1.327(11)
C(5)-C(6)	1.485(12)

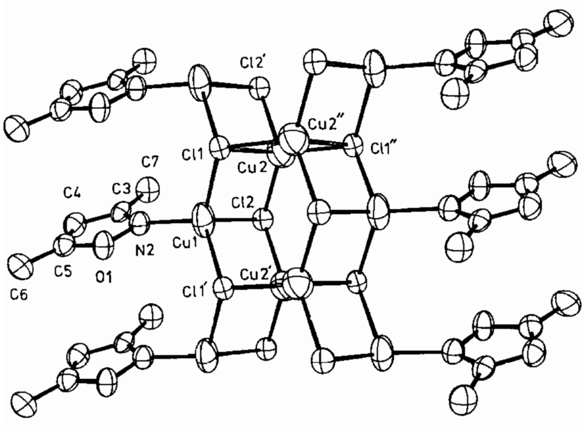

Figure 1. The molecular structure viewed down the *c* axis. Six L(CuCl)$_2$ units are shown, the repeat distance down the page defines the *a* axis.

and 103.5°. This leaves the co-ordination sphere of the copper somewhat "open" in the direction away from Cl(1).

TABLE IV. Bond Angles.

Atoms	Angle (°)
N(2)-Cu(1)-Cl(1')	111.6(2)
N(2)-Cu(1)-Cl(2)	115.9(2)
N(2)-Cu(1)-Cl(1)	113.8(2)
Cl(1')-Cu(1)-Cl(2)	103.8(1)
Cl(1')-Cu(1)-Cl(1)	106.3(1)
Cl(2)-Cu(1)-Cl(1)	104.5(1)
Cl(2)-Cu(2)-Cl(1")	119.7(1)
Cl(2)-Cu(2)-Cl(2')	114.8(1)
Cl(2)-Cu(2)-Cl(1)	103.5(1)
Cl(1")-Cu(2)-Cl(2')	113.7(1)
Cl(1")-Cu(2)-Cl(1)	101.2(1)
Cl(2')-Cu(2)-Cl(1)	99.8(1)
Cu(2")-Cl(1)-Cu(1')	115.7(1)
Cu(2")-Cl(1)-Cu(1)	120.2(1)
Cu(2")-Cl(1)-Cu(2)	78.8(1)
Cu(1')-Cl(1)-Cu(1)	106.3(1)
Cu(1')-Cl(1)-Cu(2)	75.4(1)
Cu(I)-Cl(1)-Cu(2)	72.6(1)
Cu(2)-Cl(2)-Cu(2')	114.8(1)
Cu(2)-Cl(2)-Cu(1)	79.4(1)
Cu(2')-Cl(2)-Cu(1)	80.7(1)
N(2)-O(1)-C(5)	107.5(5)
C(3)-N(2)-O(1)	106.3(5)
C(3)-N(2)-Cu(1)	135.5(4)
O(1)-N(2)-Cu(1)	118.1(3)
N(2)-C(3)-C(4)	110.3(6)
N(2)-C(3)-C(7)	120.5(6)
C(4)-C(3)-C(7)	129.1(7)
C(3)-C(4)-C(5)	106.5(7)
C(4)-C(5)-O(1)	109.4(6)
C(4)-C(5)-C(6)	135.3(7)
O(1)-C(5)-C(6)	115.3(6)

The isoxazole ligand is planar. The χ^2 value for the plane of best fit through the five ring atoms C(3), C(4), C(5), N(2) and O(1), *i.e.* $0.8918x + 0.1919y - 0.4096z + 0.1529 = 0$ referred to the cell axes is 1.169 and the largest deviation from this plane

TABLE V. Structure Feactors.

H	K	L	|FOBS|	|FCALC|
0	0	-2	47.5	50.1
0	0	-4	21.7	24.3
0	0	-6	55.2	54.1
0	0	-8	16.9	17.2
0	0	10	13.8	13.9
0	0	-12	33.2	34.5
0	1	-1	113.4	147.0
0	1	-2	97.7	110.7
0	1	-3	52.0	56.1
0	1	-4	49.4	51.9
0	1	5	34.0	35.2
0	1	-6	11.9	12.2
0	1	-7	16.4	17.0
0	1	-8	34.2	33.2
0	1	9	8.8	7.8
0	1	-11	34.7	36.4
0	2	0	65.8	59.4
0	2	-1	37.1	35.3
0	2	-2	17.7	17.1
0	2	-3	12.4	14.4
0	2	-4	23.4	26.1
0	2	-7	45.0	44.7
0	2	-8	41.4	42.2
0	2	-9	29.9	29.8
0	2	-10	16.0	15.7
0	2	-11	20.5	19.3
0	3	-1	25.5	25.3
0	3	-2	36.4	37.9
0	3	-3	109.4	119.1
0	3	-4	26.2	25.1
0	3	-5	30.6	30.3
0	3	-6	6.3	6.3
0	3	-7	31.8	34.1
0	3	-8	45.5	46.1
0	3	-9	40.4	39.9
0	3	-10	14.3	13.3
0	3	-11	18.1	16.9
0	3	-12	9.6	9.9
0	4	0	10.9	10.9
0	4	-1	64.9	63.7
0	4	-2	129.9	141.3
0	4	-3	53.6	54.6
0	4	-4	54.1	55.4
0	4	5	7.8	6.4
0	4	-6	47.3	48.1
0	4	-7	28.7	28.4
0	4	-8	62.8	61.5
0	4	-9	7.8	6.4
0	4	-10	8.9	8.7
0	4	-12	15.7	14.9
0	5	-1	42.6	40.7
0	5	-2	14.4	14.8
0	5	-3	83.1	86.2
0	5	-4	58.8	60.9
0	5	5	25.9	23.7
0	5	-6	6.6	8.0
0	5	7	67.7	67.4
0	5	-9	37.5	36.7
0	5	-10	44.0	43.4
0	5	-12	8.6	9.7
0	6	0	13.0	15.1
0	6	-1	59.4	53.5
0	6	-2	38.8	37.1
0	6	-3	72.9	72.0
0	6	-4	77.9	77.0
0	6	-5	30.8	32.8
0	6	-6	4.8	4.6
0	6	-7	13.2	12.8
0	6	8	23.4	22.4
0	6	-9	30.6	28.7
0	6	10	6.4	4.6
0	6	-11	25.0	24.1
0	6	12	10.2	11.8
0	7	-1	104.3	103.4
0	7	-2	30.2	27.6
0	7	-3	12.5	13.6
0	7	-4	30.5	30.7
0	7	-5	34.2	33.9
0	7	-6	30.7	29.2
0	7	-7	7.6	6.8
0	7	-9	17.8	17.9
0	7	-10	31.5	30.6
0	7	-11	6.9	6.7
0	8	0	137.6	137.4
0	8	-1	56.5	52.7
0	8	-2	52.8	51.9
0	8	-3	35.6	36.7
0	8	-4	70.0	69.4
0	8	-5	67.3	65.8
0	8	6	21.4	18.7
0	8	-7	26.7	26.2
0	8	-8	7.3	6.6
0	8	-9	29.4	28.4
0	8	-10	6.3	6.6
0	9	-1	75.4	72.2
0	9	-2	100.4	98.8
0	9	-3	17.5	16.4
0	9	-4	39.5	39.1
0	9	-5	61.2	59.2
0	9	-6	18.5	18.0
0	9	-7	23.9	24.0
0	9	-8	21.9	19.0
0	9	9	10.5	10.8
0	9	-10	7.8	8.8
0	10	0	8.2	9.0
0	10	-1	70.2	69.6
0	10	-2	57.7	54.0
0	10	-3	54.5	53.5
0	10	-4	20.7	21.8
0	10	-5	7.8	7.5
0	10	-6	32.0	32.2
0	10	-7	22.0	21.4
0	10	-8	11.7	11.2
0	10	-9	11.8	9.4
0	10	-10	23.7	23.6
0	11	-2	24.2	25.1
0	11	-3	9.3	10.9
0	11	-4	4.6	4.1
0	11	-5	9.2	9.6
0	11	-6	20.8	20.1
0	11	-7	38.8	38.8
0	11	-8	10.5	8.7
0	11	9	12.5	13.2
0	12	0	23.2	23.8
0	12	-1	6.4	6.2
0	12	-3	19.3	19.5
0	12	-4	26.9	26.6
0	12	-5	38.8	38.6
0	12	-6	41.6	40.5
0	12	-7	25.1	25.1
0	12	-8	18.6	17.9
0	13	-1	16.6	16.8
0	13	-2	24.0	22.9
0	13	-4	52.9	54.4
0	13	-5	27.7	25.9
0	13	-6	46.0	48.3
0	13	-7	45.6	44.5
0	13	-9	6.8	7.6
0	14	0	12.2	12.4
0	14	-1	20.9	19.6
0	14	-2	18.1	18.1
0	14	-3	15.0	13.5
0	14	-4	36.5	35.0
0	14	-5	50.8	52.6
0	14	-7	14.6	15.2
0	15	-1	19.5	18.9
0	15	-2	17.2	17.2
0	15	-3	16.5	15.1
0	15	-4	10.8	10.9
0	15	-5	18.7	17.0
0	15	-6	11.2	11.6
0	15	-8	15.3	15.8
0	16	0	9.5	10.1
0	16	-3	35.0	35.4
0	16	-4	30.7	29.5
0	16	-5	6.1	5.6
0	16	-6	9.4	7.5
0	16	-7	11.9	12.7
0	17	-1	10.6	10.0
0	17	-2	25.9	26.6
0	17	-3	8.2	7.0
0	17	-4	37.0	37.0
0	17	-5	18.6	18.1
0	18	-1	11.9	12.2
0	18	-2	9.6	8.8
0	18	-3	49.7	52.0
0	18	-5	5.8	6.3
0	19	-1	8.3	9.5
0	19	-2	10.6	12.4
-1	0	0	57.9	58.8
-1	0	-2	15.5	13.7
-1	0	2	89.9	92.9
-1	0	-4	68.4	70.5
-1	0	4	19.3	20.5
-1	0	6	86.6	89.9
-1	0	-6	56.3	57.9
-1	0	-8	29.5	30.1
-1	0	8	42.4	41.8
-1	0	-10	24.4	24.7
-1	0	10	28.4	28.7
-1	0	12	6.7	6.5
-1	0	-12	18.3	17.6
-1	1	0	13.3	12.4
-1	1	1	27.7	24.8
-1	1	-1	53.8	54.8
-1	1	2	134.1	154.1
-1	1	-2	52.0	55.1
-1	1	3	37.9	42.1
-1	1	-3	14.7	16.3
-1	1	4	39.0	40.8
-1	1	-4	51.0	52.8
-1	1	-5	12.2	12.5
-1	1	5	26.9	27.8
-1	1	-6	57.3	57.8
-1	1	6	38.2	38.4
-1	1	-7	67.6	70.1
-1	1	7	64.5	67.5
-1	1	-8	14.0	14.0
-1	1	8	10.6	9.4
-1	1	-9	8.8	9.2
-1	1	9	12.7	13.5
-1	1	-10	8.2	9.8
-1	1	-11	8.8	7.8
-1	1	11	12.7	11.4
-1	2	0	114.8	115.6
-1	2	1	11.0	10.6
-1	2	-1	76.2	77.2
-1	2	2	26.6	25.7
-1	2	-2	73.5	73.9
-1	2	3	56.0	59.7
-1	2	-3	94.3	98.5
-1	2	-4	78.5	82.1
-1	2	4	86.5	91.5
-1	2	5	83.7	88.0
-1	2	-5	78.7	83.1
-1	2	6	11.5	11.5
-1	2	-6	23.5	24.2
-1	2	7	21.8	20.3
-1	2	-7	17.0	17.1
-1	2	8	15.5	15.3
-1	2	-8	17.8	17.6
-1	2	9	7.2	4.6
-1	2	-10	8.8	9.3
-1	2	10	9.7	9.4
-1	2	-11	13.1	11.3
-1	2	12	15.7	14.7
-1	2	-12	12.2	12.7
-1	3	0	25.2	24.4
-1	3	-1	67.9	68.0
-1	3	1	83.0	83.8
-1	3	-2	41.9	42.6
-1	3	2	9.7	9.7
-1	3	3	11.4	12.8
-1	3	-3	38.4	41.3
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-3	1	2	18.6	14.9
-3	1	-2	14.3	15.8
-3	1	-4	16.1	17.6
-3	1	-5	6.7	7.2
-3	1	6	13.0	11.7
-3	1	-6	11.8	11.1
-3	1	7	24.6	28.4
-3	1	9	11.5	12.6
-3	2	0	13.3	13.5
-3	2	1	17.5	18.0
-3	2	-1	18.8	19.7
-3	2	2	10.1	10.3
-3	2	-2	11.2	11.8
-3	2	3	21.2	21.4
-3	2	-3	23.9	23.8
-3	2	4	33.3	34.6
-3	2	-4	26.2	27.1
-3	2	-5	32.9	32.2
-3	2	5	27.3	26.7
-3	2	6	21.1	19.6
-3	2	7	8.0	6.0
-3	2	-7	8.0	5.1
-3	2	8	6.1	5.9
-3	2	-8	5.7	6.5
-3	3	0	5.5	4.7
-3	3	1	16.9	15.4
-3	3	-1	33.8	32.3
-3	3	2	13.1	12.7
-3	3	-2	18.4	18.6
-3	3	3	6.8	7.6
-3	3	-3	7.5	7.4
-3	3	4	12.9	12.6
-3	3	-4	20.3	20.5
-3	3	5	27.5	32.2
-3	3	-5	27.0	29.7
-3	3	6	37.8	36.7
-3	3	-6	37.3	38.8
-3	3	7	14.7	14.4
-3	3	-7	10.5	9.3
-3	4	0	13.8	12.9
-3	4	1	7.1	8.1
-3	4	-1	11.9	12.0
-3	4	-2	13.4	14.3
-3	4	3	19.1	19.5
-3	4	-3	20.6	20.5
-3	4	4	16.1	18.1
-3	4	-4	26.4	26.0
-3	4	5	12.3	11.9
-3	4	-5	15.8	15.5
-3	4	-6	7.3	4.7
-3	4	7	7.4	8.7
-3	5	0	6.2	6.3
-3	5	1	6.1	6.5
-3	5	-1	6.5	6.1
-3	5	-2	10.5	9.5
-3	5	3	33.5	33.7
-3	5	-3	20.6	20.5
-3	5	4	14.4	15.8
-3	5	-4	10.8	10.4
-3	5	-5	13.6	15.0
-3	5	5	15.7	16.6
-3	5	7	10.2	10.0
-3	5	-7	6.5	6.4
-3	5	8	13.4	11.0
-3	6	0	6.4	5.6
-3	6	1	8.1	8.0
-3	6	-1	5.4	5.7
-3	6	2	13.6	11.9
-3	6	-2	9.4	9.0
-3	6	3	32.0	32.1
-3	6	-3	38.0	36.8
-3	6	4	30.9	31.8
-3	6	-4	15.7	18.7
-3	6	-7	6.8	7.1
-3	6	8	11.8	11.8
-3	7	1	9.7	8.9
-3	7	2	15.4	13.9
-3	7	-2	24.2	22.5
-3	7	3	24.0	21.5
-3	7	-3	19.0	17.8
-3	7	4	27.0	29.2
-3	7	-4	32.2	32.0
-3	7	6	8.0	8.5
-3	7	7	8.0	7.5
-3	8	0	13.2	13.1
-3	8	2	15.2	14.6
-3	8	-2	11.3	10.3
-3	8	3	17.7	17.3
-3	8	-3	22.2	21.9
-3	8	-6	7.5	6.9
-3	8	7	11.4	11.7
-3	9	-1	5.8	6.9
-3	9	1	21.1	21.1
-3	9	-2	7.7	5.8
-3	9	3	8.4	7.7
-3	9	4	6.1	7.4
-3	9	5	12.1	11.5
-3	9	6	9.5	7.5
-3	9	-6	5.8	4.6
-3	10	0	41.2	41.1
-3	10	-1	9.6	9.8
-3	10	1	12.6	13.1
-3	10	4	6.4	6.1
-3	10	-4	8.5	8.5
-3	10	5	15.7	14.1
-3	10	5	15.7	14.1
-3	10	-5	18.9	17.5
-3	11	-1	38.8	38.9
-3	11	1	30.7	30.7
-3	11	-4	10.1	9.3
-3	11	4	9.4	9.0
-3	11	5	6.1	5.9
-3	12	0	29.5	27.0
-3	12	1	11.2	10.2
-3	12	-1	7.1	6.1
-3	12	2	6.8	7.1
-3	12	3	6.1	5.9
-3	13	2	7.4	7.4
-3	13	2	7.4	7.4
-4	0	0	33.7	36.6
-4	1	1	19.7	20.8
-4	1	-1	16.6	18.6
-4	1	3	6.4	6.5
-4	2	0	17.5	18.6
-4	2	1	8.5	8.8
-4	2	2	7.8	8.2
-4	3	2	6.4	5.0
-4	3	3	14.4	13.4
-4	4	-1	9.7	10.1
-4	4	2	15.9	15.7

is 0.03Å shown by N(2). The bond lengths and angles within the ring are in good agreement with those found in 5-diacetylamino-3,4-diphenylisoxazole [8].

As mentioned earlier a feature of the solid is the darkening which occurs on exposure to molecular oxygen. An i.r. spectrum of a freshly prepared dark sample is identical with that of the colourless parent material except for the appearance of a clear absorption band at 1083 cm^{-1} which we take to signify the present of co-ordinated dioxygen [9]. If this be so there is no reason to assume that the binding of this ligand is any different from that occurring in cuprous chloride itself [10], the reaction probably proceeding in the solid as a consequence of the more open structure dictated by the insertion of dimethylisoxazole.

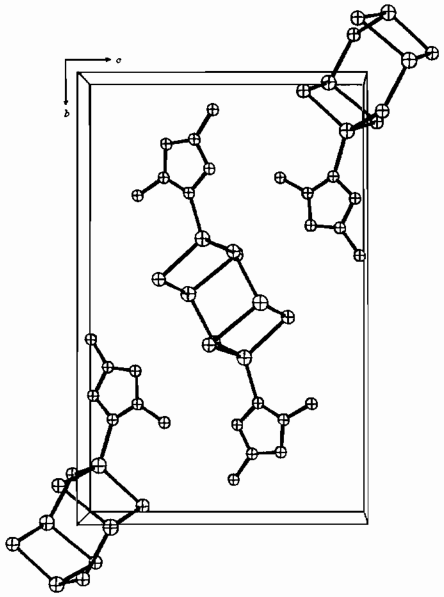

Figure 2. The contents of the unit cell viewed down the *a* axis.

Nor is it clear where the dioxygen might attach itself although the "open" site of Cu(2) comes to mind since it faces away from the cage-like structure of the chains into the channels between them. We speculate that the reaction proceeds to an identifiable dioxygen species because the structure of the solid allows oxygen penetration, *cf.* the active forms of N,N'-ethylenebis(salicylaldiminato)cobalt(II) [11], and provides a protective environment for stability.

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