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The Crystal and Molecular Structure of Bis(*N*-phenyl-2-carbamoyl-5,5′-dimethylcyclohexane-1,3-dionato)copper(II)

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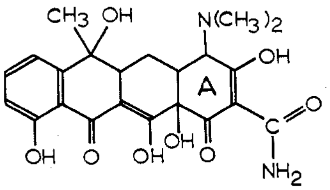
Bis(*N*-phenyl-2-carbamoyl-5,5′-dimethylcyclohexane-1,3-dionato)copper(II) crystallizes as blue, monoclinic plates with cell dimensions of $a = 9.697 \pm 0.006$ Å, $b = 23.07 \pm 0.03$ Å, $c = 6.325 \pm 0.003$ Å, and $\beta = 97.51 \pm 0.04°$. The space group is $P2_1/n$, and with two molecules per unit cell ($d_c = 1.373 \pm 0.004$ g/cm^3 and $d_m = 1.374 \pm 0.005$ g/cm^3), the complex is required to have $\bar{1}$ molecular symmetry. Diffractometer data were collected using the stationary-crystal, stationary-counter technique with Cu Kα radiation and refined by least-squares methods to a final R of 0.096 for the 1315 observed reflections used in the analysis. The copper atom is surrounded by a planar arrangement of oxygen atoms with the two independent Cu–O distances being 1.923 ± 0.008 and 1.865 ± 0.006 Å. A distorted octahedral configuration about the copper is completed by a long Cu–O distance of 3.073 Å to an oxygen atom of a neighboring molecule. The overall configuration of the complex is that of a very flattened chair. There is delocalization of charge in the diketoamide grouping of the ligand similar to that found in the A ring of tetracyclines.

Introduction

The antibacterial action of tetracyclines such as aureomycin and terramycin has been related to the formation of metal complexes.[1,2] Since metal complexes of tetracyclines are difficult to isolate in crystalline form,[3] the coordination site of the metal ion is not definitely known. However, the available data favor coordination of the metal *via* the diketoamide grouping on the A ring of tetracyclines[4] (1). The more simple model system of N-substituted 2-carbamoyldimedone (2) was studied by infrared and magnetic measurements[5] to investigate the coordination of metal ions by the diketoamide grouping. The evidence suggested that the oxygen atoms of one ketone group and of the amide group were coordinated to the metal ion. A crystal structure investigation of bis(*N*-phenyl-2-carbamoyl-5,5′-dimethylcyclohexane-1,3-dionato)copper(II), henceforth CuPCD, was undertaken to establish unequivocally the mode of coordination of the diketoamide group together with a comparison of the distances relative to the tetracyclines.



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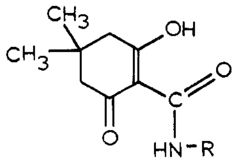

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Experimental Section

Blue plates of CuPCD elongated along $\tilde{a}$ with well-developed (010) faces can be grown from chloroform. Preliminary Weissenberg and precesson photographs indicated monoclinic symmetry with the systematic absences $h0l$ absent if $h + l = 2n + 1$ and $0k0$ absent if $k = 2n + 1$. The most probable space group is therefore $P2_1/n$ (C_{2h}^5), a nonstandard setting for $P2_1/c$. The four equivalent positions are (x, y, z), $(-x, -y, -z)$, $(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$, and $(^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z)$.

A small crystal with dimensions of 0.16 × 0.08 × 0.11 mm (parallel to $\tilde{a}$, $\tilde{b}$, and $\tilde{c}$, respectively) was mounted on a glass fiber. The crystal was aligned on a General Electric single-crystal orienter with a^* parallel to the ϕ axis of the orienter. The cell dimensions were obtained by least-squares methods from the measurement of the 2θ values for the Cu Kβ peak (λ_β 1.39217 Å) for 26 reflections. The final values were $a = 9.697 \pm 0.006$ Å, $b = 23.07 \pm 0.03$ Å, $c = 6.325 \pm 0.003$ Å, $\beta = 97.51 \pm 0.04°$, and $V = 1402.7$ Å^3. The density calculated for two molecules of $Cu(C_{15}H_{16}O_3N)_2$, mol wt 580.11, per unit cell was 1.373 ± 0.004 g/cm^3 compared with 1.374 ± 0.005 g/cm^3 measured by flotation in an aqueous KI solution.

The intensity measurements were made using a wide beam, takeoff angle 4°, of Cu Kα radiation (λ_{α_1} 1.54051 Å) with the stationary-crystal, stationary-counter method. A 20-sec count was taken for each reflection with a 0.7-mil Ni foil at the counter window. Four standard reflections were counted after every 100 reflections and were used to apply a small correction (maximum 4.2%) for a slight decline of intensity over the course of the measurements. A total of 4981 measurements in the region of $2\theta \leq 135°$ were made and reduced to a set of 2538 independent reflections after averaging equivalent reflections. Background corrections were made by measuring the background at various points reasonably free from streaking in the hemisphere and averaging the values obtained at a given 2θ setting. A total of 1315 reflections, where I(total counts) was greater than B(background counts) + $3\sqrt{B}$, were considered to be observed. The $\sqrt{B}$ instead of $\sqrt{B + I}$ was inadvertently used in the data processing but the errors introduced are negligible. The remaining 1233 reflections (entered as $^1/_2(B + 3\sqrt{B})$ and flagged with minus signs) were not used in the analysis. Subsequently, 370 reflections with $k \geq 19$, which were all unobserved, were dropped from further consideration. The value of μ(Cu Kα) is 15.0 cm^{-1} and μt varies from 0.12 to 0.32. Althouh an 18% error in I could result in the extreme case, the variation of intensity as a function of

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(1) A. Albert and C. W. Rees, *Nature (London)*, **177**, 433 (1956).

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(5) E. P. Dudeck and M. L. Snow, *Inorg. Chem.*, **5**, 395 (1966).

ϕ (at $\chi = 90°$) suggests that the average error was much less. The data were reduced to a set of observed amplitudes on an arbitrary scale by the application of Lorentz–polarization corrections.

Determination and Refinement of the Structure

With 2 molecules per unit cell, the copper atoms lie on centers of symmetry which can be chosen as 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$. A Fourier synthesis computed with all positive phases contains the molecule plus the superimposed mirror image. The ketoamide group and the phenyl ring were located in the Fourier synthesis by assuming the usual bond lengths. The remaining atoms were easily located in a subsequent Fourier synthesis phased with the copper atom and 12 other atoms. The position parameters and an individual isotropic thermal parameter for each atom were refined by full-matrix least-squares methods to an R of 0.16. Additional refinement using anisotropic thermal parameters reduced R to 0.097.

A difference Fourier synthesis gave ambiguous positions for the hydrogen atoms. Therefore, all five phenyl hydrogen atoms were placed in idealized positions (all of which were in areas of positive electron density) and included but not refined in subsequent calculations. Two more least-squares cycles reduced R to 0.096. The final positional parameters are given in Table I and the thermal parameters in Table II. The observed and calculated structure factors are presented in Table III.

TABLE I

FINAL FRACTIONAL COORDINATES AND THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[a]

Atoms	x	y	z
Cu[b]	0	0	0
OA6	−708 (7)	705 (4)	1074 (9)
O1	1382 (7)	−64 (4)	2334 (9)
C1	1527 (10)	252 (6)	4037 (16)
CA1	706 (9)	749 (6)	4424 (13)
CA6	−339 (9)	955 (6)	2846 (14)
OA2	1769 (8)	903 (4)	8004 (11)
CA2	906 (10)	1068 (6)	6454 (15)
CA3	11 (13)	1574 (7)	6811 (17)
CA4	−455 (10)	1952 (6)	4746 (19)
CA5	−1159 (10)	1492 (5)	3080 (17)
N1	2548 (7)	82 (4)	5641 (10)
CM1	823 (13)	2253 (7)	3895 (27)
CM2	−1540 (13)	2413 (7)	5184 (23)
CB1	3495 (9)	−375 (6)	5626 (16)
CB2	4303 (11)	−483 (6)	7590 (17)
CB3	5305 (13)	−944 (7)	7741 (23)
CB4	5522 (13)	−1253 (8)	5975 (27)
CB5	4729 (12)	−1133 (6)	4025 (21)
CB6	3728 (10)	−716 (6)	3824 (15)
HB2	414	−022	900
HB3	594	−103	932
HB4	634	−159	614
HB5	491	−140	259
HB6	310	−062	255

[a] The values for Cu–CB6 are ×10^4 and for HB2–HB6 ×10^3.
[b] Value required by space group.

TABLE II

FINAL THERMAL PARAMETERS (×10^4) AND THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	92 (2)	36 (1)	133 (5)	25 (2)	−60 (4)	−7 (4)
OA6	110 (8)	34 (3)	114 (15)	37 (7)	−49 (18)	−19 (10)
O1	131 (9)	27 (2)	139 (16)	33 (8)	−88 (17)	−50 (12)
CO1	104 (12)	48 (5)	323 (32)	−28 (11)	29 (29)	55 (19)
CA1	57 (10)	35 (4)	146 (23)	18 (10)	6 (24)	−8 (16)
CA6	69 (10)	40 (5)	149 (25)	1 (11)	25 (26)	23 (17)
OA2	171 (11)	39 (3)	176 (19)	33 (9)	−115 (23)	−46 (12)
CA2	82 (11)	44 (5)	172 (27)	−24 (12)	20 (29)	−5 (18)
CA3	142 (16)	48 (6)	203 (32)	37 (15)	13 (35)	−14 (21)
CA4	99 (13)	27 (4)	343 (36)	−12 (11)	21 (35)	0 (20)
CA5	84 (11)	18 (4)	315 (33)	1 (10)	−13 (30)	−44 (17)
N1	70 (8)	28 (3)	152 (17)	−5 (9)	−106 (18)	28 (14)
CM1	116 (15)	30 (5)	735 (69)	−28 (14)	133 (51)	105 (29)
CM2	142 (16)	28 (5)	524 (53)	45 (14)	52 (46)	−61 (24)
CB1	64 (10)	23 (3)	258 (31)	−22 (10)	−102 (27)	49 (17)
CB2	100 (13)	33 (4)	239 (30)	−8 (12)	−134 (30)	50 (18)
CB3	119 (16)	34 (5)	405 (46)	−11 (14)	−108 (42)	64 (25)
CB4	105 (15)	42 (6)	509 (60)	38 (14)	21 (50)	108 (29)
CB5	120 (15)	28 (5)	363 (40)	29 (13)	78 (38)	33 (21)
CB6	102 (12)	25 (4)	215 (28)	18 (11)	9 (29)	24 (17)

[a] The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

The least-squares refinement minimized $\Sigma w(\Delta F)^2$ where $\sqrt{w} = F_o/8$ if $F_o < 8$, $\sqrt{w} = 1$ if $8 \leq F_o \leq 32$, and $\sqrt{w} = 32/F_o$ if $F_o > 32$. The scattering factors for O, N, C, and H were from the ref 6. The scattering factor for Cu[7] was corrected for the real part of the anomalous dispersion,[8] but the small imaginary part (0.2 electron) was not included. The atomic numbering and the vibration ellipsoids are illustrated in Figure 1.

Discussion

The CuPCD molecule has molecular symmetry $\bar{1}$ as required by the space group. The copper atom at the center of symmetry is surrounded by four oxygen atoms in a planar arrangement. The remaining atoms of one ligand (excluding the phenyl ring, CA4, CM1, and CM2) are below the plane defined by the Cu–O1–OA6 atoms (see Table IV), resulting in a flattened chair configuration for the complex.

The Cu–OA6 distance of 1.923 (8) Å is significantly different from the Cu–O1 distance of 1.865 (6) Å (t_0 = 5.8).[9] This difference is not surprising since the two oxygen atoms are chemically different. Although the C1–O1 bond is longer than the CA6–OA6 bond, the difference is not significant. The Cu–O and C–O distances are close to the values found in the acetylacetone and salicylaldimine complexes[10] which resemble the ketoamide grouping. The next shortest Cu–O distance of 3.073 (9) Å to OA2 of another molecule is longer than is usually found in the acetylacetone and salicylaldimine complexes.[10] However, the short Cu–O bonds together with the long interaction are consistent with the arguments presented recently for distances in copper complexes.[11]

The two C–C distances CA1–CA6 of 1.409 (13) and CA1–C1 of 1.434 (17) Å are slightly but not significantly longer than the corresponding bonds in

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(6) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

(7) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(8) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(9) D. W. J. Cruickshank and A. P. Robertson, *ibid.*, **6**, 698 (1953).

(10) E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, **88**, 2951 (1966).

(11) H. C. Freeman, "The Biochemistry of Copper," J. Peisach, P. Aisen, and W. E. Blumberg, Ed., Academic Press, New York, N. Y., 1966, p 79.

TABLE III: OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) FOR BIS(*N*-PHENYL-2-CARBAMOYL-5,5′-DIMETHYLCYCLOHEXANE-1,3-DIONATO)COPPER(II)

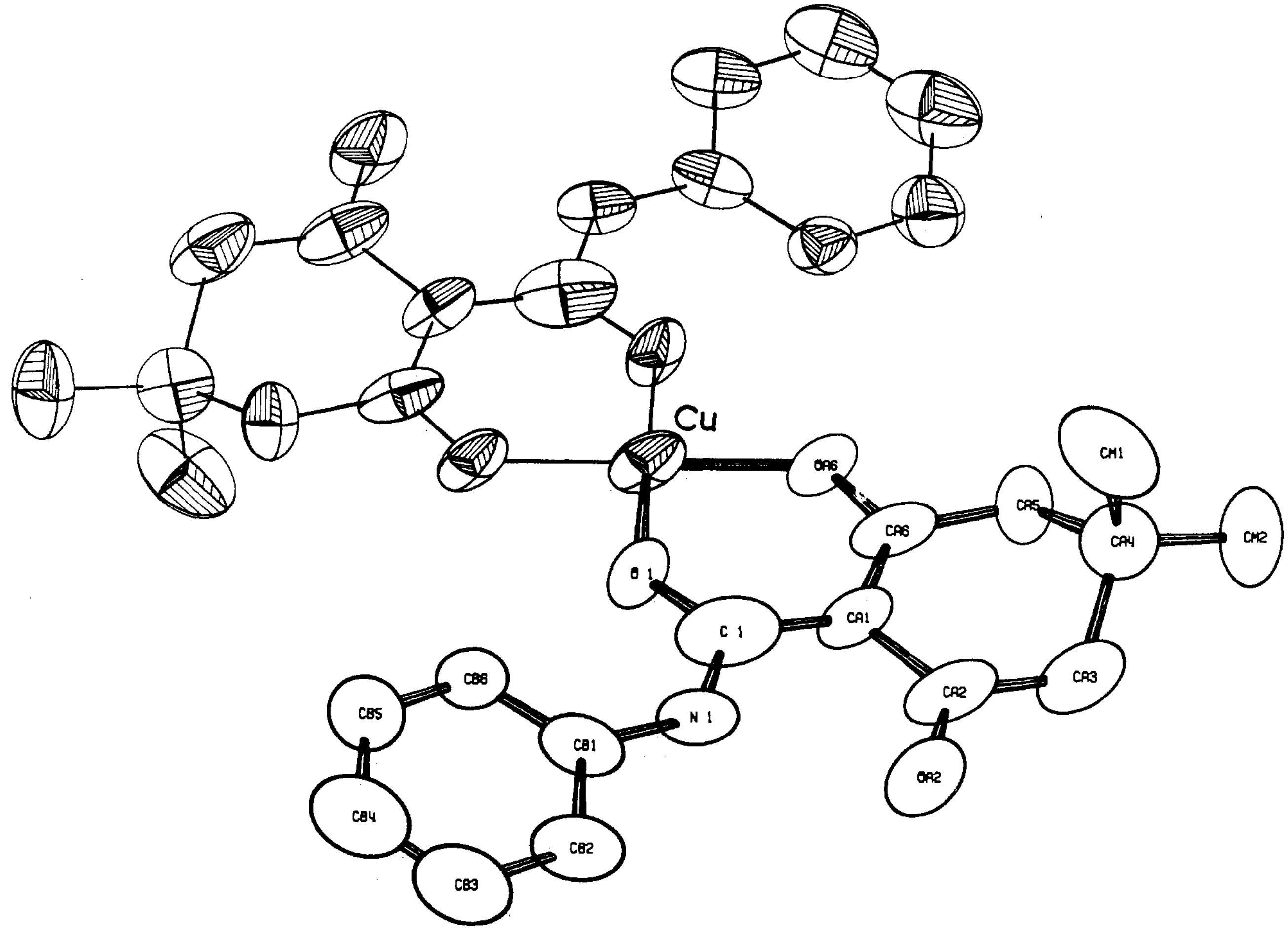

Figure 1.—An ORTEP drawing of the CuPCD molecule illustrating the thermal ellipsoids (50% probability) and the atomic numbering.

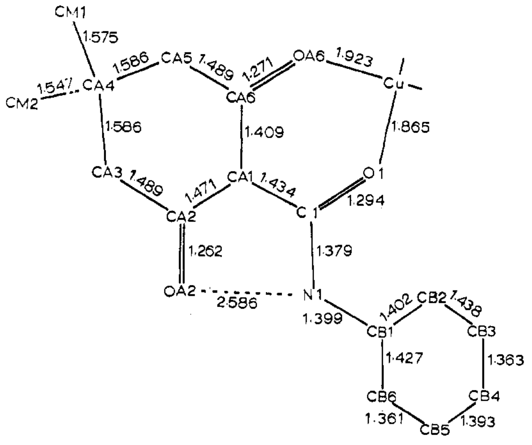

Figure 2.—The intramolecular distances in the CuPCD molecule. The estimated standard deviations of the distances are: Cu-O, 0.007 Å; C-O, 0.013 Å; C-N, 0.012 Å; C-C, 0.012–0.023 Å.

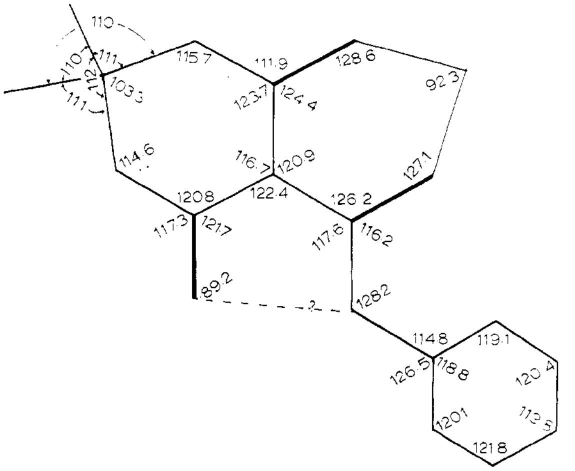

Figure 3.—The bond angles in the CuPCD molecule. The estimated standard deviations are 0.3° for angles involving Cu and 0.3–1.0° for light atom angles.

acetylacetone and salicylaldimine complexes.[10] A lengthening of these bonds is consistent with an interaction with the uncomplexed keto group. The slightly longer C*A*2–O*A*2 distance of 1.262 (13) Å (compared to a normal ketone distance of 1.24 Å) and the slightly shorter C*A*1–C*A*2 distance of 1.471 (15) Å (compared to a normal C(sp^2)–C(sp^2) of 1.48 Å) are consistent with a delocalization of electron density about the diketoamide grouping.

The bond distances in the ligand are surprisingly close to the values found in the A ring of several tetracyclines in spite of being coordinated to a copper ion. A comparison of the bond distances in several related compounds is given in Table V.[12–14] The

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(12) R. Restivo, Ph.D. Thesis, University of Waterloo, 1969.

(13) H. Cid-Dresdner, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **121**, 170 (1965).

(14) J. Donohue, J. D. Dunitz, K. N. Trueblood, and M. S. Webster, *J. Amer. Chem. Soc.*, **85**, 851 (1963).

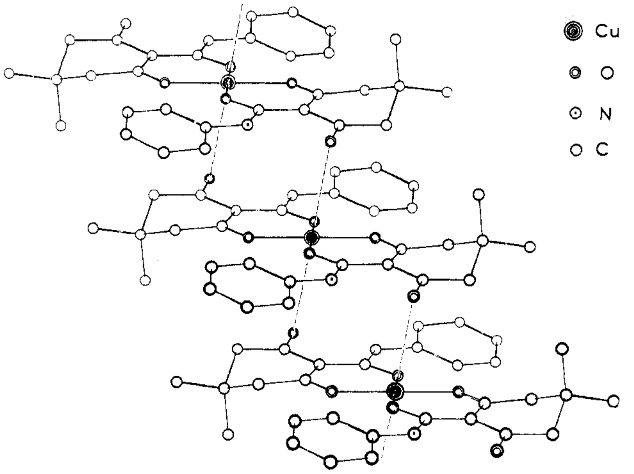

Figure 4.—An arbitrary view of the structure illustrating the molecular packing. The Cu–OA6 interaction of 3.07 Å is shown as a dotted line.

TABLE IV
LEAST-SQUARES PLANES[a]

	Dev from plane[b]				
Atom	I	II	III	IV	V
Cu	0*	−139	−163	−267	
O1	0*	5*	−3*	−53	
OA6	0*	−16*	−23	−99	
OA2	−613	−186	−145	−62	
C1	−133	3*	9*	0*	
CA1	−215	−18*	−3*	1*	
CA2	−427	−81	−49	0*	
CA3	−536	−131	−90	−31	
CA4	366	692	726	749	
CA5	−66	106	122	98	
CA6	−89	26*	33	0*	
N1	−240	−18	−3*	25	
CB1	−160	28	37	63	−2*
CB2					16*
CB3					−16*
CB4					3*
CB5					11*
CB6					−12*
	Parameters for plane[c]				
	I	II	III	IV	V
l	6916	7101	7108	7198	7189
m	5321	5800	5860	5951	6612
n	−4884	−3993	−3891	−3574	−2145
D					0.776

[a] The deviations ($\times 10^3$) from the plane (Å) are given for the specified atom. [b] The atoms used to define the plane are noted by an asterisk following the deviation. [c] Equation of the plane in the form: deviation (Å) $= lX + mY + nZ - D$ where X, Y, and Z are the orthogonal coordinates (in Å) relative to a, b, and c^*, and D, the distance from the origin, is given by the displacement of the Cu atom.

most significant differences are in C1–N1 and in the six-membered ring. The lengthening of C1–N1 may be related to the formation of the copper complex or to an inductive effect involving the phenyl ring. Additional studies are necessary to resolve this point.

The C–C bonds involving C*A*4 are all long and longer than the values observed in the tetracyclines. However, the two methyl groups on C*A*4 are not present in the tetracyclines. Similar bond lengthenings were reported in 1-biapocamphane[15] and related molecules and have been extensively discussed.

TABLE V
A COMPARISON OF BOND DISTANCES IN
BIS(*N*-PHENYL-2-CARBAMOYL-5,5′-DIMETHYLCYCLOHEXANE-1,3-DIONATO)COPPER(II) WITH ANHYDROTETRACYCLINE,
TERRAMYCIN, AND AUREOMYCIN[a]

Atoms	CuPCD	ANHYD	TERRA[b]	AUREO[b]
CA2–OA2	1.26 (1)	1.223 (7)	1.26	1.25
C1–N1	1.38 (1)	1.291 (10)	1.28	1.30
CA6–OA6	1.27 (1)	1.261 (7)	1.26	1.25
CA1–C1	1.43 (2)	1.446 (8)	1.45	1.43
C1–O1	1.29 (1)	1.296 (8)	1.31	1.32
CA1–CA2	1.47 (2)	1.440 (7)	1.41	1.44
CA2–CA3	1.49 (2)	1.541 (7)	1.51	1.57
CA3–CA4	1.59 (2)	1.528 (8)	1.51	1.51
CA4–CA5	1.59 (2)	1.537 (7)	1.55	1.57
CA5–CA6	1.49 (2)	1.532 (7)	1.50	1.54
CA6–CA1	1.41 (1)	1.413 (9)	1.40	1.40

[a] Abbreviations: ANHYD, anhydrotetracycline hydrobromide;[12] TERRA, terramycin hydrochloride;[13] AUREO, aureomycin hydrochloride.[14] [b] Estimated standard deviations of about 0.02 Å.

The phenyl group is planar (Table IV) and makes an angle of 10° 57′ with the amide grouping. The distances and angles average 1.40 ± 0.02 Å and 120 ± 1°, respectively, in agreement with the values usually found in phenyl rings.

The shortest intermolecular distances are summarized in Table VI and there are no unusually short contacts. The molecules are held together by the long Cu–O*A*2 contact 3.073 (9) Å, with the other contacts being normal van der Waals interactions. In spite of the apparently weak intermolecular forces, the crystals have a low solubility in most solvents and a high decomposition point.[5]

TABLE VI
SUMMARY OF THE SHORTEST INTERMOLECULAR DISTANCES[a]

Atom A	Atom B	Position	Distance, Å
Cu	OA2	2	3.07
Cu	CA2	2	3.52
OA6	OA2	2	3.31
O1	OA2	2	3.59
O1	CA2	3	3.36
CA6	N1	3	3.43
OA2	HB3	4	2.63
CB2	HB2	4	2.95
HB2	HB2	4	2.21

[a] The distance is from atom A in position 1 to atom B in the specified position. The positions are: (1) x, y, z; (2) $x, y, \bar{1} + z$; (3) $-x, -y, 1 - z$; (4) $1 - x, -y, 2 - z$.

A number of the thermal ellipsoids shown in Figure 1 appear to be oriented in the same direction, possibly suggesting a systematic error in the data. Alternatively, the molecule may be oscillating about the Cu–O*A*2 vector as well as undergoing rigid-body motions in the phenyl ring and nonrigid body motions in the cyclohexane ring. To examine these possibilities the mean-square displacements and direction cosines of all the atoms were calculated and a careful examination was made of these values. For the atoms C*M*1 and C*M*2 the largest displacements are approximately normal to the corresponding C–C bond (86° and 80° for C*M*1 and 90 and 90° for C*M*2) as would be ex-

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[15] R. A. Alden, J. Kraut, and T. G. Taylor, *J. Amer. Chem. Soc.*, **90**, 74 (1968).

pected for a riding motion. Similarly, the largest mean-square displacement for O*A*2 makes an angle of 97° to the C*A*2–O*A*2 bond. In the phenyl ring, as expected, the smallest displacement is usually normal to the ring. Consequently, many of the mean-square displacements can be interpreted in the usual way, suggesting that no serious systematic errors are present in the data.

In conclusion we see that the diketoamide grouping is capable of functioning as a strong bidentate chelate toward transition elements. The coordination occurs through two oxygen atoms rather than through an oxygen and a nitrogen atom. The tetracycline antibiotics are therefore capable of forming metal complexes involving this grouping although other coordination sites cannot be eliminated.

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The Crystal and Molecular Structure of Bis(*N*-benzoylhydrazine)copper(II) Pentachlorotricuprate(I), a New Complex Containing Copper in Mixed Oxidation States

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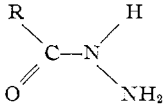
The crystal structure of bis(*N*-benzoylhydrazine)copper(II) pentachlorotricuprate(I) has been determined by three-dimensional X-ray analysis. The crystals are orthorhombic, space group *Pbca*, with unit cell dimensions $a = 9.299$ (2), $b = 16.165$ (3), $c = 28.656$ (6) Å. The intensities of 1754 observed reflections were measured by an automatic four-circle diffractometer. The structure was refined to a conventional *R* factor of 0.051. The two *N*-benzoylhydrazine bidentate chelates are arranged in an equatorial cis configuration around the Cu(II) ion, with chloride ions in the axial positions of a distorted octahedron. All five Cl^- per molecule are involved in bonding to the three Cu(I) ions in an infinite cylinder of distorted tetrahedra. These cylinders run in the *x* direction and are cross-linked in the *y* direction by Cl–Cu(II)–Cl bonds and by an extensive network of N–H···Cl hydrogen bonds. The ··N–N–C–O·· parts of the chelate rings are each planar, though they are not mutually coplanar, and the Cu(II) ion is substantially displaced from both these planes in the direction of the nearer Cl^- ion. The bond lengths and angles around Cu(II) are normal. In the cylinders containing Cu(I) ions the bond lengths range from 2.228 (4) to 3.393 (4) Å, and the Cl–Cu(I)–Cl angles from 84.1 (1) to 140.0 (1)°.

Introduction

Until recently, no systematic investigation of the coordinating properties of *N*-acylhydrazine compounds (I) had been attempted. The isolation of cationic bis complexes of copper(II) with *N*-benzoylhydrazine[1] (R = C_6H_5) and with *N*-acetylhydrazine[2] (R = CH_3)



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was reported many years ago. Both ligands may be presumed to coordinate by the carbonyl oxygen and terminal amino nitrogen atoms forming five-membered chelate rings with a planar configuration about the copper(II) ion.

Following the discovery that *N*-isonicotinoylhydrazine (R = C_5H_4N) has valuable tuberculostatic properties, a number of its transition metal complexes have been prepared, and spectroscopic and conductometric measurements on these have been carried out.[3-5] Chelation could be important in the mode of action of this drug, and though the ligand is capable of bonding as suggested above, the presence of a potentially chelating pyridine nitrogen atom is a complicating factor, which may lead to the formation of polymeric complexes.[4] The crystal structure of isonicotinoylhydrazine itself is known,[6] but no crystal structure of any of its complexes has been published.

As part of a detailed investigation into complex formation by the simple *N*-acylhydrazine ligands,[7] attempts to make bis(*N*-benzoylhydrazine)copper(II) dichloride produced unexpected results. While the required complex can be obtained from ice-cold aqueous solutions of the liquid and copper(II) dichloride, reac-

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