Inorganica Chimica Acta, *105* (1985) 115–120

Revaluation of the Structural Properties of *trans*-Dibenzoato-bis(1,3-diaminopropane)copper(II), $C_{20}H_{30}CuN_4O_4$

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Received March 9, 1985

Abstract

The structure of the title compound was re-determined by X-ray methods and the refinement improved from the earlier *R* value of 0.119 [12] to the value of 0.042. The new cell constants are a = 11.498(2), b = 8.295(2), c = 11.383(2) Å, β = 91.84(1). The symmetry around the Cu(II) ion is near to D_{4h}. The greatest deviation from the symmetry approximated is the tilting of 4.4° of the axial Cu–O bond from the normal perpendicular to the equatorial CuN_4 plane. Another deviation is the endocyclic N–Cu–N angle, which is here 87.09(14)°. Broadening of the ν(N–H) vibrations and their shifting to lower energies in the IR spectrum are indicative of a hydrogen bonding network (which runs diagonally along the *bc* plane). The axial bond length Cu–O1 is statistically short, 2.468(3) Å, and consequently the tetragonality *T* is rather high, 0.825. The two C–O bond lengths in the carboxylate group do not differ significantly: 1.261(5) and 1.247(5) Å.

Electron population analysis, performed by using CNDO, reveals uneven electron distribution on the carboxylic oxygen atoms and slight polarization between the carboxylic group and the aromatic ring, where the electronic charge is evenly distributed. The UV-Vis spectrum shows bands at 580 and 860 (sh) nm. The band at 860 nm may be assigned either to the d–d transition $B_{1g} \rightarrow A_{1g}$ (although this is an unusually high wavelength compared with values obtained for similar compounds), or to a charge transfer between the neighbouring benzoate anions.

Introduction

In the systematic study going on in our laboratory we are investigating monomeric *trans*-ML_2L_2' complexes, where M is a metal ion of the first transition series, L is 1,3-diaminopropane (hereafter tn) and L′ is a substituted benzoate. The most frequently used substituents are methyl, nitro and halide moieties [1–11].

In their paper on the structure of *trans*-dibenzoato-bis(tn)Cu(II), the simplest member of the above named series, Uggla and Klinga reported a relatively short bond length for Cu–O and somewhat anomalous values for N–C and C(arom)–C(arom) bond lengths and for the endocyclic angle **ipso** to the carboxylate group [12]. Because the *R* value of 0.119 was rather high, we undertook a re-investigation of this structure.

Experimental

Crystals of the sample synthesized for the earlier study [12] were recrystallized from a hot ethanol solution and were used for the XRD analysis. The more detailed data are given in Table I. Lattice parameters for the blue single crystal selected were obtained from least-squares refinement of 15 well-centered reflections measured on a NICOLET P3 diffractometer. The new cell constants match fairly well with the old ones [12]. Intensity data were collected at ambient temperature using an ω-scan technique. During the collection two check reflections were measured after every 98 reflections. The intensities of these showed only statistical variation. The data were corrected for Lorentz and polarization factors but not for absorption. Out of 2497 independent reflections measured 1522 had $F_o \geqslant 4\sigma(F_o)$; those were used in the structure refinement. Dispersion correction was applied for the Cu atom [13]. The atomic parameters found in the earlier study were refined anisotropically. The hydrogen atoms were then given the calculated positions with constant bond length 1.0 Å before the last cycles; they were left unrefined with fixed isotropic temperature factor U = 0.06 Å^2. All structure calculations were done by applying the X-RAY 76 system [14] and the neutral atom scattering factors included in the program. The function $\Sigma w(F_o - F_c)^2$ was refined by full-matrix least-squares techniques to the *R* value 0.042 (R_w = 0.044, unit weights). The three largest residual electron densities in the range 0.33–0.47 e Å^{-3} were located about 1.0 Å from the copper atom and were not pointing towards any ligand atom.

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0020-1693/85/$3.30

TABLE I. Crystal and Intensity Collection Data.

Mol. formula	$C_{20}H_{30}CuN_4O_4$
Mol. wt.	454.03
$F(000)$	478
a (Å)	11.498(2)
b (Å)	8.295(2)
c (Å)	11.383(2)
β (deg)	91.84(1)
V (Å^3)	1085.1
Z	2
d_{calc} (g cm^{-3})	1.39
d_{obs}	1.39
Space group	$P2_1/c$
Crystal dimensions (mm)	0.20 × 0.20 × 0.13
Radiation	MoKα (a = 0.71069 Å)
2θ limits	$5° < 2\theta < 55°$
Scan rate	1.9° to 19.9° (min)
Absorption coefficient (cm^{-1})	10.8
Number of independent reflections measured	2497
Unique data used	1522
R	0.042
R_w	0.044, unit weights

A list of the structure factors and anisotropic thermal parameters can be obtained from the authors.

The electronic spectrum was run from a powdered sample in paraffin paste (E. Merck: Uvasol) spread on filter paper, employing a Beckman DK-2A spectrophotometer in the range 360–1200 nm. Paraffin-treated filter paper was used as reference.

The IR spectrum was run from a KBr disc on a Perkin-Elmer grating infrared spectrophotometer 577 in the range 4000–200 cm^{-1}, using the five-fold wavenumber expansion. A polystyrene film was used for calibrations.

Results and Discussion

The atomic coordinates and their standard deviations are given in Table II. The structure obtained here confirms almost all the earlier findings [12]. However, the details of the structure, especially the bond lengths and angles (see Fig. 1) are significantly different due to the better intensity data.

The Equatorial Direction

The bond lengths N–C, 1.480(6) and 1.475(6) Å, are considerably shorter than those reported earlier, 1.54(3) and 1.52(3) Å, and are now quite near to that reported for tn·2HCl, 1.484(4) Å [15]. The geometry of the chelate ring is now similar to that predicted by Gollogly and Hawkins [16], with the exception of the bond lengths Cu–N and the bite angle N–Cu–N. The new bond lengths Cu–N1, 2.028(3) Å, and Cu–N2, 2.043(3) Å, seem to be shorter than the respective old values, 2.05(2) and 2.06(2) Å. The value of the angle N1–Cu–N2, 87.09(14)°, is comparable with the old value of 88.5(7)°, and continues to be clearly smaller than the theoretical value (≥90°) given by Gollogly and Hawkins [16]. The only *trans*-Cu(II)(tn)$_2$X$_2$ compound behaving as predicted is *trans*-dinitratobis(tn)Cu(II) with the N1–Cu–N2 value of 94.4(5)° [17].

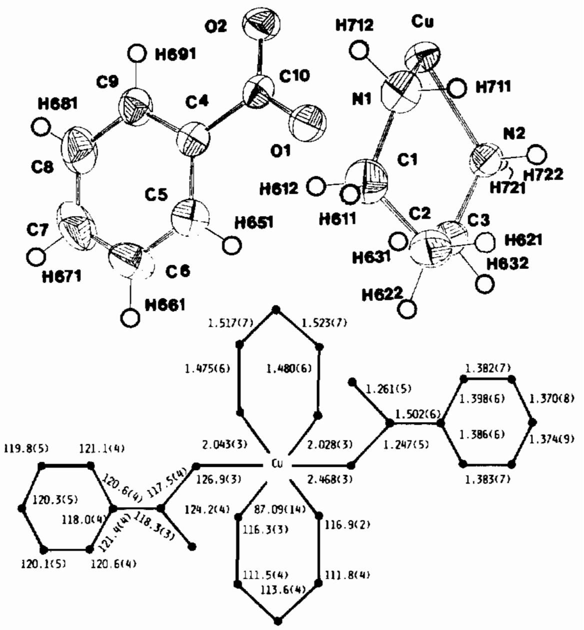


Fig. 1. The bond lengths (Å) and angles (°) with their standard deviations for the non-hydrogen atoms and the numbering scheme.

TABLE II. The Positional Parameters and Averaged Temperature Factors with their Standard Deviations for *trans*-dibenzoato-bis(tn)Cu(II) Chelate. $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$. For H atoms, U is the Unrefined Isotropic Temperature Factor.

Atom	x/a	y/b	z/c	U_{eq} or U
Cu	0.0000	0.0000	0.0000	0.032(1)
N1	−0.0050(3)	0.2385(4)	0.0389(3)	0.039(2)
N2	0.0934(3)	0.0616(4)	−0.1429(3)	0.036(2)
C1	0.1083(4)	0.3233(5)	0.0450(4)	0.047(3)
C2	0.1637(4)	0.3291(6)	−0.0747(4)	0.050(3)
C3	0.1966(4)	0.1645(6)	−0.1213(4)	0.044(2)
C4	0.3064(3)	−0.1457(5)	0.2696(3)	0.036(2)
C5	0.3977(4)	−0.0505(6)	0.2337(4)	0.051(3)
C6	0.5032(4)	−0.0488(7)	0.2955(5)	0.069(4)
C7	0.5180(5)	−0.1414(8)	0.3950(5)	0.074(4)
C8	0.4288(5)	−0.2353(7)	0.4331(4)	0.063(3)
C9	0.3232(4)	−0.2377(6)	0.3716(4)	0.045(2)
C10	0.1927(3)	−0.1484(5)	0.2007(3)	0.035(2)
O1	0.1800(3)	−0.0503(4)	0.1182(3)	0.053(2)
O2	0.1162(2)	−0.2482(4)	0.2300(3)	0.049(2)
H711	−0.055	0.293	−0.023	0.06
H712	−0.041	0.250	0.117	
H721	0.040	0.120	−0.199	
H722	0.120	−0.040	−0.180	
H611	0.096	0.436	0.073	
H612	0.162	0.266	0.102	
H621	0.107	0.380	−0.132	
H622	0.236	0.397	−0.068	
H631	0.238	0.179	−0.197	
H632	0.250	0.110	−0.062	
H651	0.387	0.018	0.162	
H661	0.569	0.020	0.268	
H671	0.594	−0.140	0.440	
H681	0.440	−0.302	0.506	
H691	0.258	−0.306	0.400	

TABLE III. The Distances (r(Å)) and Angles (α(°)) for Hydrogen Bonds in the Title Compound. The Atoms Marked with an Asterisk have been Generated with the Symmetry Operator Indicated.

(i) $\bar{x}, \bar{y}, \bar{z}$		
r(N2–O2*)	r(H721–O2*)	α(N2–H721–O2*)
3.006(4)	2.10	149
(ii) $\bar{x}, 1/2 + y, 1/2 - z$		
r(N1–O2*)	r(H712–O2*)	α(N1–H712–O2*)
2.964(5)	1.97	175
(iii) $x, \bar{y} - 1/2, z - 1/2$		
r(N2–O2*)	r(H722–O2*)	α(N2–H722–O2*)
2.991(5)	2.03	160

The reason for the anomalous behaviour is not yet clear, but possibly there is another atom with lone electron pairs, linked to the axial atom, in the vicinity of the amine nitrogens. Gollogly and Hawkins [16] considered only the case of one separate atom in the axial direction. The presence of a coordinated base containing another lone pair in the vicinity of an amine hydrogen atom has been claimed to be of importance in the kinetics of the blue-to-red interconversion of a macrocyclic Cu(II) complex [18]. Furthermore, hydrogen bonds are known to affect the geometry of barbiturates, which have a ring structure [19]. The following expected values were used in a search for possible hydrogen bonds: H···O 1.96(12), N···O 2.85(9) Å and N–H···O 162(11)° [20]. The boundary values for the search were obtained by applying 3σ as delimiter. A list of the possible hydrogen bonds is given in Table III; the corresponding

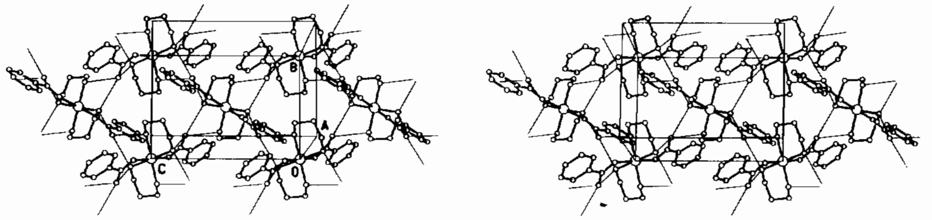


Fig. 2. A stereoview of the packing of the title compound showing the hydrogen bonding network.

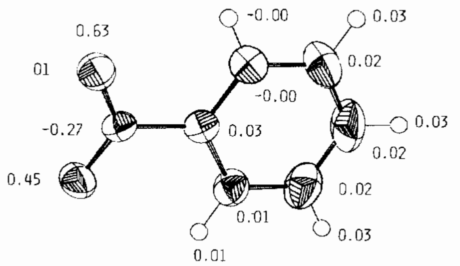
hydrogen bond network runs diagonally along the *bc* plane (Fig. 2). Because all the hydrogen atoms were placed in their calculated positions and not subjected to refinement, we also recorded an IR spectrum to ensure their existence.

Nevertheless, the anomalous value of the bite angle cannot be explained by hydrogen bonding alone, because the above-noted compound *trans*-dinitrato-bis(tn)Cu(II) has a similar arrangement of an oxygen atom next to each amino group and yet has a bite angle larger than 90°. The difference in the basicity of the NO_3^- and the benzoate anions may therefore also be playing a role.

The Axial Direction

The bond lengths in the aromatic ring are in the normal range, 1.370–1.398 Å. The original finding of the endocyclic angle **ipso** to the carboxylate group being considerably greater than 120° has been reversed. The new value of 118.0(4)° is now significantly smaller than the value found in the benzoic acid, 119.9(4)°, [21] and in lithium benzoate–dimethylsulfoxide, 119.3(6)° and 119.3(7)°, (two independent units)†. The bond length C4–C10 remains somewhat long, 1.502(6) Å, relative to the corresponding value of the benzoic acid, 1.484(6) Å [21]. In lithium benzoate–dimethylsulfoxide the bond lengths seem to be even longer: 1.511(10) and 1.511(9) Å†. Possibly the lengthening is related to the hydrogen removal from the COOH group. The lengthening of this bond in turn probably allows the twisting of the carboxylate group relative to the aromatic ring. The most stable theoretical configuration for benzoic acid is coplanar [22] (although the observed value for the torsion angle is 1.5° [21]), whereas in the title compound the torsion angle is 7.2° and in lithium benzoate–dimethylsulfoxide 8.2°. The C10–O bond lengths do not differ significantly. In one of the two independent units of lithium benzoate–dimethylsulfoxide the bonds are significantly different, 1.279(8) and 1.235(9) Å, whereas in the other unit they are nearly similar, 1.259(8) and 1.242(9) Å, respectively. In *trans*-dibenzoato-bis(tn)-Ni(II) the bond lengths were found to be identical, 1.251(6) Å [23].

To evaluate the electronic distribution in the title compound we performed an electron population analysis using CNDO (Scheme 1). The oxygen atom nearest to the Cu(II) ion acquired the largest part of the negative charge. Another polarization seems to have occurred between the carboxylate group and the aromatic ring. Moreover, the additional negative charge is evenly distributed in the aromatic ring.



Scheme 1.

The reason for the variation in the C10–O bonds remains unclear, although we may suspect a second-order Jahn-Teller effect to be of importance.

The axial bond length Cu–O1 is comparable with the old value: now 2.468(3) and then 2.48(2) Å. Among the 45 known coordination polyhedra of the type *trans*-CuN_4O_2 [24], there is only one with a shorter value [25]. Consequently the tetragonal distortion *T* has a very high value, 0.825. The axial elongation of the coordination polyhedron is obvious, however. Another distortion can be seen in the minimum angle between the Cu–O1 bond and the CuN_4 plane, which is 85.6°.

In the IR spectrum of the title compound the N–H stretching vibrations appear as broad bands at 3235(s) and 3100(m) cm^{-1}. In the gas phase (or in dilute solutions) of primary amines two sharp bands are seen in the range 3500–3300 cm^{-1}. Shifting to lower wavenumbers can be explained by hydrogen bonding or chelation or both – in this case probably both, since chelation can hardly explain the broadening of the bands‡. We conclude, therefore, that the

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† The values for the angles are calculated from the atomic parameters reported.

‡ A sharp and narrow band at 3286 cm^{-1} due to ν(N–H) can be seen in the IR spectrum of *trans*-di-3-chlorobenzoato-bis(tn)Cu(II).

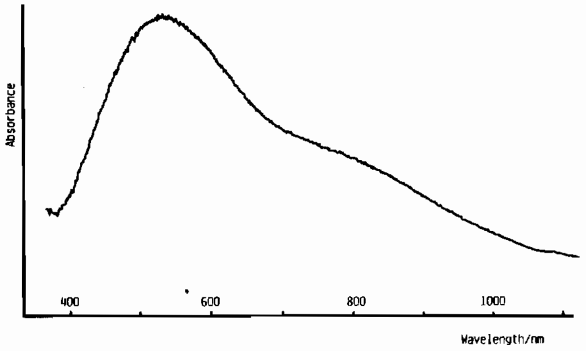

Fig. 3. The UV-Vis spectrum of the title compound.

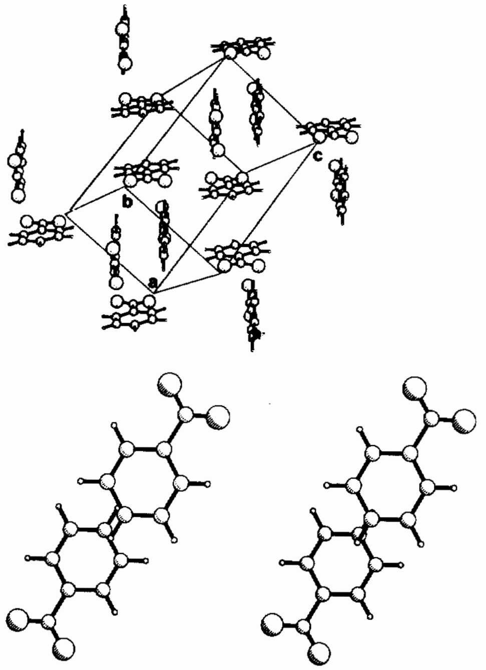

Fig. 4. The stacking of the benzoate anions in the title compound.

hydrogen bonds originating from the two N–H bonds of one amino group are non-equivalent in the title compound. Bellamy and Williams [26] have calculated an expression $\nu_s = 345.5 + 0.876\ \nu_{as}$ for N–H stretching frequencies of hydrogen bonded primary amines (with the standard deviation of 4.8 cm^{-1} for the symmetric frequency calculated). The authors note that when only one N–H bond is hydrogen bonded, asymmetry is introduced and the equation breaks down. The frequencies observed do not obey the equation. The UV/Vis spectrum of the title compound shows a maximum at 580 nm (17 200 cm^{-1}), which is a normal value for monomeric *trans*-CuN_4O_2 complexes [27]. The very broad shoulder with maximum at 860 nm (11 600 cm^{-1}) is interesting (Fig. 3), if we compare it with values for complexes of the type *trans*-Cu(II)$(NH_3)_4X_2$ [28] or *trans*-Cu(II)$(en)_2X_2$ [29]. Among the 24 measured compounds there are only two that have a band (or a shoulder) at wavelengths $\leq$ 13 000 cm^{-1}. The first one, $Cu(NH_3)_4(CuBr_2)_2$, shows in a single crystal spectrum a maximum at 12 400 cm^{-1} (sh). However, the coordination polyhedron of this compound is practically planar, with a very low *T* value (0.34). The other, $Cu(en)_2SO_4$, has an unknown structure, and the corresponding maximum at 13 000 cm^{-1} (sh) (obtained from a polycrystalline sample) is far from the present value. If this band is assigned to a d–d transition, then the $B_{1g} \leftarrow A_{1g}$ transition seems more probable than $B_{1g} \leftarrow B_{2g}$, because the *T* value is rather high, [30]. Nevertheless, this assignment, with the known magnetic properties of the title compound [31], leads to unreasonable molecular orbital coefficients, if the calculations are performed as in ref. 11.

In *trans*-di-4-chlorobenzoato-bis(tn)Cu(II) chelate the band at 860 nm (11 600 cm^{-1}) was tentatively assigned to a possible interaction between the neighbouring 4-chlorobenzoate anions [11]. There is slight overlap in the title compound between the ends of two parallel aromatic rings at discrete equivalent positions (Fig. 4). The perpendicular distance between the neighbouring planes is only 3.25 Å, and the shortest distance between carbons $C7–C7^i$ is 3.384(9) Å (where i is the symmetry operation $1 - x, -y, 1 - z$). These distances are quite short relative to the sum of the Van der Waals radii of aromatic rings, 3.7 Å. However, more data are needed to obtain the final assignment.

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