

# Structure of *trans*-Di(3-iodobenzoato)bis(1,3-diaminopropane)copper(II), C<sub>20</sub>H<sub>28</sub>CuI<sub>2</sub>N<sub>4</sub>O<sub>4</sub>

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The structure of the title compound was determined by single-crystal X-ray methods. The compound crystallizes in the monoclinic crystal system (space group *P*<sub>2</sub><sub>1</sub>/*a*, No. 14) with *a* = 11.717(2), *b* = 8.283(2), *c* = 13.000(1) Å, β = 103.79(1)° and *Z* = 2. The copper(II) ion has a centrosymmetric elongated pseudo-octahedral stereochemistry. The equatorial Cu-N bond distances are 2.029(3) and 2.041(3) Å, and the elongated axial Cu-O distance is 2.500(3) Å. The chelate ring, consisting of the 1,3-diaminopropane ligand coordinated to the Cu(II) ion, displays a chair conformation, with puckering parameters close to the ideal values. The carboxylate anion is monodentately coordinated. The uncoordinated oxygen interacts with three amine hydrogen atoms. The hydrogen-bonding system has significance not only in the stabilization of the crystalline state but obviously also in the stabilization of the symmetry of the coordination polyhedron. Along the *c*-direction an intermolecular interaction between the iodine atom and the neighbouring aromatic rings of the 3-iodobenzoate anion is also observed.

The monomeric *trans*-di(XbzO)bis(tn)M(II) chelates (where M is Cu or Ni; bzO is a benzoate anion with X = H, CH<sub>3</sub>, NO<sub>2</sub> or a halide; tn is 1,3-diaminopropane) have been the subject of numerous structural studies.<sup>1</sup> In these compounds the copper(II) ion lies at the centre of symmetry and the benzoate anions are monodentately coordinated. Among the compounds studied, aqua-3-iodobenzoato-bis(tn)Cu(II) 3-iodobenzoate<sup>2</sup> is the only one in which the coordination polyhedron is of the type CuN<sub>4</sub>OO', the other polyhedra representing the type CuN<sub>4</sub>O<sub>2</sub>.

The crystal packing of these compounds is of interest because of possible intermolecular interactions between the benzoate anions.<sup>3,4</sup> The structures of halogen-substituted benzoic acids have also been extensively studied in order to elucidate the possible intermolecular association through halogen-halogen contacts.<sup>5</sup>

This paper presents a method of synthesis and the X-ray crystal structure of the 'normal' *trans*-di(3-iodobenzoato)-bis(tn)Cu(II).

## Experimental

**Syntheses.** The synthetic route employed differed from those described previously, since it was necessary to avoid aqueous conditions. A sample of Cu(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (1.4 mmol, Fluka) was dissolved in 5 ml of acetonitrile (Baker) and 2.9 mmol of tn (Ega-chemie) were added. The resulting dark violet solution was mixed with 5 ml of acetonitrile containing 3.0 mmol 3-iodobenzoic acid (Aldrich). Upon addition of 3.0 mmol triethylamine (Fluka) in 3 ml THF (Fluka) a

pale blue precipitate was formed. The crude product (870 mg, 88%), separated by filtration and washed with THF, obviously contained some free acid as impurity, since the Cu content was too low. (Found: Cu 8.0%; calc. for C<sub>20</sub>H<sub>28</sub>CuI<sub>2</sub>N<sub>4</sub>O<sub>4</sub>: Cu 9.0%.) Crystals of X-ray quality were obtained by recrystallization from a mixture of ethanol and diethyl ether (1:2). The Cu analysis of these gave a satisfactory value of 8.6%.

The synthesis in aqueous solution was performed for comparison. Therefore 20 mmol of 3-iodobenzoic acid and 10 mmol of CuCO<sub>3</sub> (Baker's Analyzed) were dispersed into aqueous ethanol (100 ml H<sub>2</sub>O, 50 ml ethanol). The suspension was heated and stirred until a homogeneous light blue precipitate appeared. Upon addition of 20 mmol of tn a deep violet solution was obtained. Deep blue and light blue crystals were formed after 4 h cooling. The species were identified by the unit-cell determination of suitable single crystals. The light blue compound was found to be the title compound, whereas the dark blue compound had the same unit cell as aqua-3-iodobenzoatobis(tn)Cu(II) 3-iodobenzoate.

**Spectroscopic measurements.** The solid-state UV-VIS spectrum was recorded on a Cary 17D spectrometer using the Nujol mull technique. The spectrum of the title compound exhibited an asymmetric band with a maximum at 558 nm (17900 cm<sup>-1</sup>) in the visible area.

The solid-state IR spectra were recorded on a Mattson Galaxy FT infrared instrument using the Nujol mull technique. The characteristic bands with their tentative assignments are as follows: N-H stretchings at 3293m, 3233s(br), 3140m(sh) and 3100s(br) cm<sup>-1</sup>, NH<sub>2</sub> scissoring at 1588s(br)

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$\text{cm}^{-1}$ ,  $\text{NH}_2$  wagging at  $1263\text{ cm}^{-1}$ ; carbonyl CO stretchings at  $1540$  and  $1362\text{ cm}^{-1}$  and Cu–N stretchings at  $399$  and  $374\text{ cm}^{-1}$ .

**X-Ray crystallographic analyses.** Details from crystal analysis, data collection and structure refinement are given in Table 1. The intensity data were collected on an automatic Rigaku AFC5S diffractometer. The lattice parameters were calculated by least-squares refinements of 25 reflections in the range  $47.7 < 2\theta < 49.8^\circ$ . During data collection, weak reflections [ $F < 10\sigma(F)$ ] were rescanned up to three times. The data were corrected for Lorentz and polarisation effects and for empirical ( $\psi$ -scan) absorption. Direct methods and subsequent difference Fourier syntheses revealed the non-hydrogen atoms. After a least-squares refinement with the non-hydrogen atoms, the hydrogen atoms were also located in the difference Fourier map. In the final cycles the non-hydrogen atoms were refined with anisotropic and the hydrogen atoms with fixed isotropic temperature parameters (1.2 times  $B_{\text{eq}}$  of a carrying non-hydrogen atom). Neutral atomic scattering and dispersion factors were taken from Ref. 6. All calculations were performed with TEXSAN-89 software<sup>7</sup> using a VAXSTATION 3520 computer. The figures were drawn using the ORTEP system.<sup>8</sup> Tables of hydrogen atom coordinates, anisotropic thermal parameters, and observed and calculated structural factors may be obtained from the authors on request.

Table 1. Crystal data and experimental details of the structure determination of *trans*-di(3-iodobenzoato)bis(tn)Cu(II).

Formula	$\text{C}_{20}\text{H}_{28}\text{CuI}_2\text{N}_4\text{O}_4$
$M_r$	705.82
Space group	$P2_1/a$
Cell parameters at 291(1) K	
$a/\text{\AA}$	11.717(2)
$b/\text{\AA}$	8.283(2)
$c/\text{\AA}$	13.000(1)
$\beta/^\circ$	103.79(1)
$V/\text{\AA}^3$	1225.3(4)
Calculated density/ $\text{g cm}^{-3}$	1.913
Measured density/ $\text{g cm}^{-3}$	1.907(5) (floatation)
$Z$	2
$\mu(\text{MoK}\alpha)/\text{cm}^{-1}$	34.2
Crystal description	blue, plates
Crystal size/ $\text{mm}^3$	$0.2 \times 0.3 \times 0.3$
Instrument	Rigaku AFC5S
Data collection	$\omega/2\theta$
Maximum $2\theta/^\circ$	50
$hkl$ ranges	$h = 0-13$ $k = 0-9$ $l = -15-15$
No. of reflections measured	2312 unique
Reflections included	1844 with $I > 3\sigma(I)$
Parameters refined	184
Minimization function	$\sum w( F_o  -  F_c )^2$
Least-squares weights	$w = 1/[\sigma^2(F_o)]$
$R = \sum( F_o  -  F_c ) / \sum F_o $	0.028
$R_w = [\sum w( F_o  -  F_c )^2 / \sum w F_o ^2]^{1/2}$	0.037
Max./min. in final difference map/ $e \text{\AA}^{-3}$	0.68 / -1.35

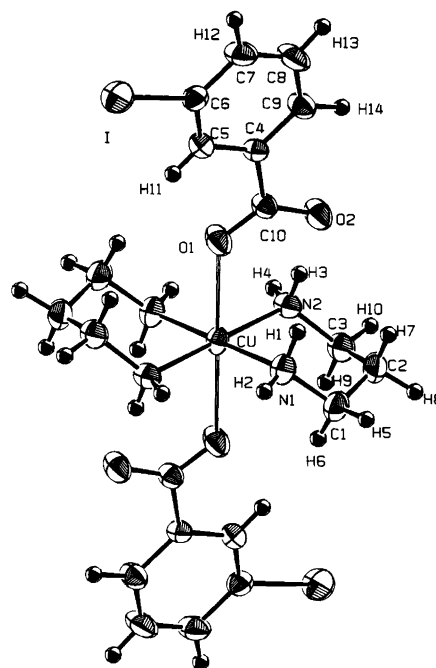


Fig. 1. ORTEP drawing of the title compound showing the labelling scheme. The thermal ellipsoids for the non-hydrogen atoms have been scaled to the 50% probability level.

## Results and discussion

The molecular structure of the title compound is shown in Fig. 1. The atomic coordinates are given in Table 2 and the bond lengths and angles in Table 3. The compound clearly displays the normal configuration of the *trans*-bis-series, the central copper atom lying at the centre of symmetry. The chelate ring, consisting of the Cu(II) ion and the tn molecule, displays the usual chair conformation.

Although structural data on metal complexes of 3-iodobenzoic acid are very scarce [as far as the present authors know, the structure of aqua-3-iodobenzoatobis(tn):Cu(II) 3-iodobenzoate<sup>2</sup> is the only compound characterized by single-crystal analysis], one may say that the bond lengths and angles of the anion fall in the expected range. Compared to the free acid, a notable difference is observed. The distance between the carboxylate carbon C10 and the neighbouring aromatic carbon is  $1.526(5)\text{ \AA}$ , whereas in the free acid it is only  $1.480(6)\text{ \AA}$ .<sup>5</sup> Also, in methyl 4-iodobenzoate the distance is shorter,  $1.496(8)\text{ \AA}$ .<sup>9</sup>

A clear axial elongation is seen in the coordination polyhedron, the axial Cu–O distance being  $2.500(3)\text{ \AA}$ . Because the highest possible site symmetry around the central Cu(II) ion would be  $D_{4h}$ , the first-order Jahn–Teller effect cannot be used to explain the elongation. Assuming the highest site symmetry,  $D_{4h}$ , the second-order Jahn–Teller deformation leads only to a deformation in the  $\text{CuN}_4$  plane.<sup>10</sup> It is well known that  $d-s$  mixing leads to effects of the same order of magnitude as the first-order LF energies. This concept has been used to explain axial elongation in coordination polyhedra of the type  $\text{CuX}_4\text{Y}_2$ .<sup>10-12</sup>

Interestingly,  $d-s$  mixing predicts that the most stabiliz-

Table 2. Atomic positional parameters and equivalent isotropic temperature factors for *trans*-di(3-iodobenzoato)bis(tn)Cu(II).

Atom	x	y	z	$B_{eq}/\text{\AA}^2$ <sup>a</sup>
I	0.28285(3)	-0.05209(4)	0.60497(2)	4.10(2)
Cu	0	0	0	2.30(3)
O(1)	0.15740(3)	-0.0455(4)	0.1648(2)	3.7(1)
O(2)	0.2664(2)	-0.2243(4)	0.10420(2)	3.7(1)
N(1)	-0.0320(3)	-0.2403(4)	0.0054(3)	2.9(1)
N(2)	0.1219(3)	-0.0535(5)	-0.0838(3)	2.6(1)
C(1)	-0.0560(4)	-0.3273(5)	-0.0975(4)	3.4(2)
C(2)	0.0501(4)	-0.3262(6)	-0.1447(4)	3.5(2)
C(3)	0.0849(4)	-0.1618(6)	-0.1763(3)	3.2(2)
C(4)	0.3195(3)	-0.1621(4)	0.2878(3)	2.2(1)
C(5)	0.2834(3)	-0.0979(5)	0.3739(3)	2.5(1)
C(6)	0.3479(3)	-0.1284(5)	0.4757(3)	2.7(1)
C(7)	0.454(4)	-0.2157(6)	0.4936(3)	3.5(2)
C(8)	0.4889(4)	-0.2741(6)	0.4082(4)	3.9(2)
C(9)	0.4232(3)	-0.24950(5)	0.3054(3)	3.0(2)
C(10)	0.2419(3)	-0.1406(5)	0.1764(3)	2.5(1)

<sup>a</sup>The equivalent isotropic temperature factors are of the form  $B_{eq} = 4/3 \sum_i \beta_i a_i \cdot a_i$ .

Table 3. The bond lengths (in Å) and angles (in °) with their standard deviations.<sup>a</sup>

Cu-N1	2.029(3)	C2-C3	1.507(7)
Cu-N2	2.041(3)	C4-C5	1.393(5)
Cu-O1	2.500(3)	C4-C9	1.386(5)
O1-C10	1.246(5)	C4-C10	1.526(5)
O2-C10	1.254(5)	C5-C6	1.382(5)
N1-C1	1.487(5)	C6-C7	1.384(6)
N2-C3	1.479(5)	C7-C8	1.376(6)
I-C6	2.101(4)	C8-C9	1.389(6)
C1-C2	1.513(7)		
N1-Cu-N2	87.9	N2-C3-C2	111.9(4)
N1-Cu-N2'	92.1(1)	O1-C10-O2	125.20(4)
N1-Cu-O1	85.8(1)	O1-C10-C4	117.7(3)
N1-Cu-O1'	94.20(1)	O2-C10-C4	117.0(3)
N1-Cu-N1'	180.00	C5-C4-C9	119.2(3)
N2-Cu-O1	87.6(1)	C5-C4-C10	119.5(3)
N2-Cu-O1'	92.4(1)	C9-C4-C1	121.30(3)
N2-Cu-N2'	180.00	C4-C5-C6	120.0(4)
O1-Cu-O1'	180.00	I-C6-C5	119.5(3)
Cu-N1-C1	116.2(3)	I-C6-C7	119.6(3)
Cu-N2-C3	117.3(3)	C5-C6-C7	120.9(4)
Cu-O1-C10	127.0(3)	C6-C7-C8	118.9(4)
N1-C1-C2	111.4(4)	C7-C8-C9	121.0(4)
C1-C2-C3	114.7(4)	C4-C9-C8	119.9(4)

<sup>a</sup>Symmetry code: (I)  $-x, -y, -z$ .

ing distortion in  $\text{CuN}_4\text{O}_2$ -type polyhedra can be produced by an asymmetric axial elongation.<sup>12</sup> This means that one axial site is weakened more than its antipode, which seems to offer a ready explanation for the symmetry found in the coordination polyhedron of aqua-3-iodobenzoatobis(tn)-Cu(II) 3-iodobenzoate. However, the difference between water and 3-iodobenzoate is large enough to remove the centre of symmetry, and thus the site symmetry around the central copper(II) ion is automatically diminished. Ob-

viously the water molecule is approximately as strong a Lewis base as the 3-iodobenzoate anion; otherwise there would be either a *trans*-diaquabis(tn)Cu(II) or a *trans*-di-3-iodobenzoatobis(tn)-Cu(II) moiety to be found in the presence of water. In a series of 13 'pure' (i.e. with no crystal water) *trans*-di(XbzO)bis(tn)M(II) chelates, there is not a single compound having a coordination polyhedron of the type  $\text{CuN}_4\text{OO}'$ . This apparent controversy might be due to additional hydrogen bonding in the axial direction. Therefore, the intermolecular interactions are of importance and should be examined closely. Alternatively, a sufficiently strong Lewis base has not been used in the series to cause five-coordination.<sup>13</sup>

The following values were used in the search for possible hydrogen bonds:  $\text{H} \cdots \text{O} = 1.96(12)$ ,  $\text{N} \cdots \text{O} = 2.85(9)$  Å and  $\text{N-H} \cdots \text{O} = 162(11)^\circ$ .<sup>14</sup> The threshold values used were  $\pm 3\sigma$ . Possible hydrogen bonds are listed in Table 4. Three of the four hydrogen atoms of the amine nitrogens participate in the hydrogen-bonding network. The uncoordinated oxygen atom participates in three hydrogen bonds. One of these is intramolecular and the other two connect the *trans*-di(3-iodobenzoato)bis(tn)Cu(II) moieties along the *ab*-planes (cf. Fig. 2). This is further corroborated by the IR spectrum, in which four bands are found at 3293, 3233, 3140 and 3107  $\text{cm}^{-1}$ . In the gas phase (or in dilute solutions), primary amines show two sharp bands in the range 3500–3300  $\text{cm}^{-1}$ . The band at 3293  $\text{cm}^{-1}$  is rather sharp compared to the other two bands. Obviously this band refers to N–H stretching, where the hydrogen atom is not hydrogen-bonded. Thus the shift of the band to lower wavenumbers is due to chelation only, whereas the remaining two broad bands at 3233, 3140 and 3100  $\text{cm}^{-1}$  are shifted further owing to hydrogen bonding.

Because the intermolecular hydrogen-bonding network runs along the *ab*-planes, there must be an interaction between the 3-iodobenzoate anions in order to establish the crystalline state. The packing of the anions is shown in Fig. 2. There are no short halogen–halogen contacts as in the corresponding acid.<sup>5</sup> In contrast, there are two aromatic  $\pi$ -stacking interactions. First, two  $\pi$ -faces of the two

Table 4. The distances  $r$  (in Å) and angles  $a$  (in °) for the hydrogen bonds of the title compound. The atoms marked with an asterisk have been generated with the indicated symmetry operators.

(i) $x, y, z$		
$r(\text{O2-N2})$ 2.979(5)	$r(\text{O2-H3})$ 2.16(5)	$a(\text{O2-H3-N2})$ 160(4)
(ii) $1/2-x, -1/2-y, -z$		
$r(\text{O2-N2}^*)$ 3.063(5)	$r(\text{O2-H4}^*)$ 2.18(5)	$a(\text{O2-H4}^*-\text{N2}^*)$ 163(4)
(iii) $1/2+x, -1/2-y, z$		
$r(\text{O2-N1})$ 2.960(5)	$r(\text{O2-H2}^*)$ 2.04(5)	$a(\text{O2-H2}^*-\text{N1}^*)$ 175(4)

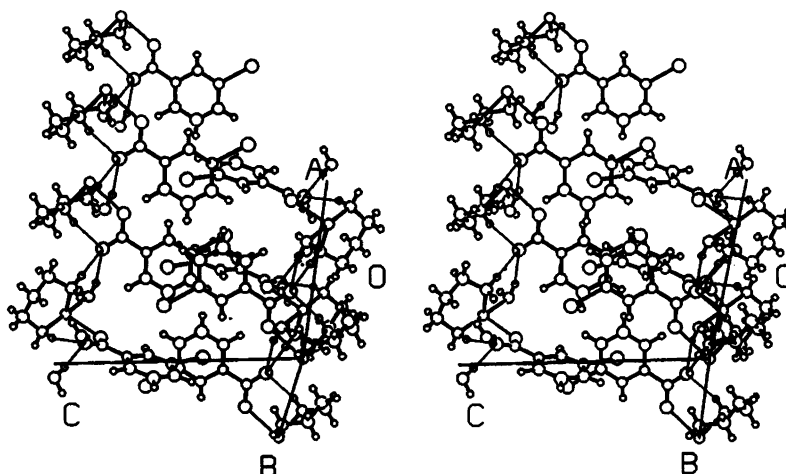


Fig. 2. Stereoscopic ORTEP drawing showing the packing of the 3-iodobenzoate anions along the *b*-axis.

acids interact with  $I \cdots C8^i$ ,  $C6 \cdots C7^i$ ,  $C7 \cdots C6^i$  and  $C8 \cdots I^i$  contacts, the  $I \cdots C$  and  $C \cdots C$  distances being 3.834(5) and 3.656(6) Å, respectively (symmetry operation  $i = 1 - x, -y, 1 - z$ ). Another interaction exists between the iodine atom of a 3-iodobenzoate anion and the aromatic ring of the second anion with  $I \cdots C4^{ii}$ ,  $C5^{ii}$ ,  $C6^{ii}$ ,  $C7^{ii}$ ,  $Cu^{ii}$ ,  $C9^{ii}$  distances of 3.823(4), 3.864(4), 3.872(4), 3.907(5), 3.900(5) and 3.848(4) Å, respectively (symmetry operation  $ii = 0.5 - x, 0.5 - y, 1 - z$ ). The iodine atom of this second anion is connected to the third aromatic ring, etc.

The latter interaction is related to the existence of  $\pi$ -electron clouds and a polar atom. According to Gaultier *et al.*,<sup>15</sup> the periodic bond chain theory predicts the existence of very energetic bonds; these bonds are charge-transfer interactions and in extreme cases polar interactions. Tentative assignment of this kind of charge-transfer band was made earlier for *trans*-di(4-chlorobenzoato)-bis(tn)Cu(II) chelate.<sup>4</sup> It is also important to note that all the attempts to crystallize *trans*-di(alkanoato)bis(tn)Cu(II) chelates have so far been unsuccessful.

According to Orama and Pajunen, the unusual structure of aqua-3-iodobenzoatobis(tn)Cu(II) 3-iodobenzoate may be caused by steric effects.<sup>2</sup> There are two possible major interactions to be inspected. Both of the carboxylate oxygens in the axial direction may interact with the chelate ring. The carbon atoms of the chelate ring are bent away from the  $CuN_4$  plane to the opposite side of oxygen O2, allowing the latter atom to approach. The distance from O2 to the nearest carbon hydrogen is 3.07(5) Å (to H7), so the repulsion must be negligible. The configuration as seen in Fig. 1 suggests attraction rather than repulsion between oxygen O2 and the amine hydrogens H1 and H3. The distances from O2 to H1 and H3 are 2.65(4) and 2.16(5) Å, respectively, and the latter value indicates hydrogen bonding. The distances from the carboxylate oxygen O1 to the hydrogen atoms H1 and H3 are longer than 2.50 Å. Likewise the distances to H6 and H9, 2.68(5) and 2.75(5) Å, respectively, which rule out any noteworthy interaction.

An interaction between the atoms in the axial direction and the equatorial atoms could be expected to cause flat-

tening of the chelate ring. The distances of the carbon atoms C1, C2 and C3 from the  $CuN_4$  plane are 1.037, 0.828 and 1.006 Å, respectively. These values indeed show some flattening, compared to the ideal values of 1.05, 0.75 and 1.05 Å calculated by Gollgoly and Hawkins for  $M(tn)_2b_2$  (where *M* is a metal ion, *a* =  $NH_3$  and *b* =  $OH^-$ ).<sup>16</sup> However, the observed values of 0.85, 0.63 and 0.98 Å for *trans*-di(4-iodobenzoato)bis(tn)Cu(II) are even smaller.<sup>17</sup> Obviously the flexibility of the ring allows an axial approach.

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