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Effect of hydrogen bonding on coordination in *trans*-di(*Z*-aminobenzoato-*O*)di(1,3-diaminopropane-*N,N'*)copper(II) (Z=2, 3 or 4) complex units

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Abstract

The crystal structures of the series of compounds containing the di(*Z*-aminobenzoato-*O*)di(1,3-diaminopropane-*N,N'*)copper(II) ($Z=2$, 3 or 4) coordination units were determined by single-crystal X-ray methods. In the *ortho*- and *meta*-aminobenzoate analogues the structures are composed of monomeric complex units, where a copper(II) cation is located at a centre of symmetry and the chelate rings display a chair conformation. The benzoate anions in the axial positions are coordinated via one oxygen only. In the *para*-aminobenzoate analogue the complex units are similar, but there are two additional crystal water molecules in the asymmetric unit. The main differences between the three coordination units are seen in the bite angle of a chelate ring and the declination value of a benzoate anion. The differences are likely due to variation in the participation of an amine group of a chelate ring and a carboxylate group of a benzoate anion to form a hydrogen bonding network. Intramolecular hydrogen bonding seems to be correlated with inclination of a benzoate anion. Small inclination and absolute declination values for a benzoate anion seem to be related with bifurcated intramolecular hydrogen bonding and narrowing of a bite angle N–Cu–N. The hydrogen bonding to the coordinated oxygen atom changes its hybridisation from approximate sp^2 towards sp^3. The existence of hydrogen bonding is supported by IR spectra. The crystallographic data are as follows (tn: 1,3-diaminopropane; bzO: a benzoate anion): [Cutn$_2$(2NH$_2$bzO)$_2$], C$_{20}$H$_{32}$CuN$_6$O$_4$, monoclinic, space group $P2_1/a$ No. 14, $a=10.513(2)$, $b=9.1789(12)$, $c=12.126(2)$ Å, $\beta=99.82(2)°$, $V=1153.0(4)$ Å^3; [Cutn$_2$(3NH$_2$bzO)$_2$], C$_{20}$H$_{32}$CuN$_6$O$_4$, monoclinic, space group $P2_1/n$ No. 14, $a=6.7128(12)$, $b=16.503(4)$, $c=10.268(2)$ Å, $\beta=92.022(15)°$, $V=1136.8(4)$ Å^3; [Cutn$_2$(4NH$_2$bzO)$_2$]·2H$_2$O, C$_{20}$H$_{36}$CuN$_6$O$_6$, monoclinic, space group $P2_1/n$ No. 14, $a=9.484(2)$, $b=8.938(2)$, $c=16.301(3)$ Å, $\beta=103.910(14)°$, $V=1334.6(5)$ Å^3.

Keywords: Copper complexes; Hydrogen bonding; Crystal structures; Bidentate amine complexes

1. Introduction

The coordination mode in a series of Cutn$_2$(ZbzO)$_2$ (where ZbzO is either unsubstituted or substituted benzoate anion; tn is 1,3-diaminopropane) has been examined in a large number of structural studies [1]. Usually the complex units display centrosymmetric *trans*-bis coordination mode with the two six-membered chelate rings in chair conformation and the two axial sites coordinated by one oxygen of a benzoate anion. In an earlier study, Klinga [2] suggested that the complex units in the Cutn$_2$(ZbzO)$_2$ series would usually be connected by a 2D hydrogen bonding network.

It is well known that hydrogen bonding plays an important role in bioinorganic chemistry. The very existence or non-existence of hydrogen bonding is correlated with the coordination number in bacteriochlorophyll **a** [3]. In ferric P450 enzymes hydrogen bonding affects the circular dichroism spectra [4]. Also, the *cis*-platinum coordination to DNA is dependent on hydrogen bonding [5].

On the other hand, the effect of hydrogen bonding on the coordination properties has been a topic only in some papers. Stabilisation of an oxo-hydroxo bridge by hydrogen bonding has been studied in diiron complexes [6]. Intramolecular hydrogen bonding has been found to stabilise tetrafluoroborate coordination to copper(II) ion [7].

So far, the substituents in the benzoate anions have not been capable of marked hydrogen bonding in the Cutn$_2$(XbzO)$_2$ series. Since hydrogen bonding is a gateway to molecular organisation [8] and even to crystal engineering, it was considered appropriate to use a potentially active sub-

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stituent as a suitable probe to study the packing effects in the present series. Accordingly, a new series of copper(II) complexes formed by tn as well as *ortho-*, *meta-* and *para-*substituted aminobenzoate anions was synthesised and their respective structures were determined by single-crystal X-ray methods. The compounds are hereafter referred to as CUORAM, CUMEAM and CUPAAM, respectively. IR spectra were recorded to establish any hydrogen bonding in the complexes.

2. Experimental

2.1. Syntheses

Both CUORAM and CUPAAM were synthesised by the same method. First, 20 mmol of an aromatic acid (*ortho-*aminobenzoic acid, Fluka AG, pur.; *meta*-aminobenzoic acid, Merck, p.a.; *para*-aminobenzoic acid, Fluka AG, pur.) and 10 mmol of $CuCO_3 \cdot Cu(OH)_2$ (Baker's Analyzed) were dispersed in aqueous EtOH (100 ml H_2O, 50 ml EtOH). In the case of CUORAM and CUPAAM the suspension was heated and stirred until a homogeneous precipitate was formed after removal of CO_2. When 20 mmol of tn (Fluka, purum) was added into the suspension, a deep violet solution formed. The deep blue crystals were formed upon cooling and were separated by filtration.

As for CUMEAM, it was necessary to carry out the synthesis by a modified technique. Otherwise the product was a brownish oily substance. At first, 1.10 g (4.97 mmol) of $CuCO_3 \cdot Cu(OH)_2$ and 2.74 g (20.0 mmol) of 3-aminobenzoic acid (Fluka AG, pur.) were added to 100 ml of MeOH and heated, whereupon a precipitate formed. The flask was equipped with a condenser, and vacuum and argon inlets. The flask was evacuated and purged with argon four times. To the stirred mixture was added 1.7 ml (20 mmol) of 1,3-diaminopropane with a syringe. The colour changes slowly from green to grey and blue and some grey precipitate was formed. The solution was refluxed for 3 h and then stirred overnight. The precipitate was removed from the blue solution by filtration by means of a canula. MeOH was evaporated in vacuo and the black residue was refluxed with PrOH until dissolved. The flask was transferred to the freezer (−20 °C). The precipitate was separated from the solution by decantation under argon. The resulting bluish black solid (3.75 g) was dried in vacuo.

2.2. X-ray structure determination

Suitable single crystals were selected after careful investigation under a polarising microscope for each determination. All the measurements were performed on a Nicolet P3F diffractometer using graphite monochromatised Mo Kα radiation ($\lambda = 0.710\,69$ Å). The unit cell parameters were obtained by least-squares refinement of 25 well-centred, high-angle reflections. Axial photos were taken to ensure the right axial choice.

The data collections were carried out by the ω-scan technique. The stability of a crystal was confirmed by repeated measurements of three check reflections after every 100 reflections. The data gathered at ambient temperature for the structure determination were corrected for Lorentz and polarisation effects. Further details for the X-ray studies are given in Table 1.

The usual procedure in solving the phase problem was to make use of the SHELXS program [9]. The positions of heavy atoms were then refined by XTAL3.0 programs [10]. The repeated Fourier syntheses and least-squares refinements revealed the positions of the remaining heavy atoms. After this stage, a difference Fourier map was inspected to find the positions of the hydrogen atoms. The anomalous dispersion was applied at the final stage of the refinements; the constants were those included in XTAL 3.0. The final least-squares calculations with full matrix refinements were performed with the XTAL 3.0 program package.

The hydrogen atoms in CUORAM and CUPAAM were found from the difference Fourier map and refined with individual isotropic thermal parameters. The hydrogen atoms connected to the amino nitrogen of the aromatic ring in CUMEAM were found from the difference Fourier map; the other hydrogens were placed in their calculated positions. The hydrogen atoms were refined with an overall isotropic thermal parameter.

The coordinates for the compounds are listed as Supplementary Material and selected bonding parameters in Table 2. The numbering scheme and thermal displacement values for the atoms in the compounds are shown in Fig. 1.

2.3. EI-MS

Mass spectra were recorded on a JEOL JMS-SX102 instrument, 70 eV, 300 μA, operating under the electron impact (EI) mode. The solid samples were introduced by a direct inlet probe and heated in the range 50–350 °C. All of the spectra contain the normal mass spectra of the aminobenzoic acids (137, 120, 92, 65 and 39 *m/e*) for the *meta-* and *para-*aminobenzoic acids, 119 instead of 120 for the *ortho*-benzoic acid [11]. The rest of the peaks are due to 1,3-diaminopropane (57 and 30 *m/e*) [11].

2.4. IR

The IR spectra were run from KBr discs on a BOMEM MB-100 FT-IR spectrometer with a resolution of 2 cm^{-1}. The final spectra were obtained as averages over 16 scans. The spectra were recorded with the help of the SpectraCalc™ program [12] installed on a local PC.

Table 1
Crystal data and experimental details for the single-crystal determinations

Compound	CUORAM	CUMEAM	CUPAAM
Chemical formula	$C_{20}H_{32}CuN_6O_4$	$C_{20}H_{32}CuN_6O_4$	$C_{20}H_{40}CuN_6O_8$
Formula weight	484.06	484.06	520.08
a (Å)	10.513(2)	6.7128(12)	9.484(2)
b (Å)	9.1789(12)	16.503(4)	8.938(2)
c (Å)	12.126(2)	10.268(2)	16.301(3)
β (°)	99.82(2)	92.022(15)	103.910(14)
V (Å^3)	1153.0(4)	1136.8(4)	1334.6(5)
Z	2	2	2
D_c (g cm^{-3})	1.394	1.414	1.374
Space group	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Crystal dimensions (mm)	0.15 × 0.23 × 0.39	0.18 × 0.21 × 0.45	0.29 × 0.34 × 0.39
Absorption coeff. (cm^{-1})	9.8	10.0	8.6
Absorption corr.	yes	yes	no
2*θ* Limits	5.0–55.0	3.0–55.0	5.0–55.0
Scan speed (° min^{-1})	3.0–30.0	2.0–20.0	2.0–20.0
Reflections collected	2645	2924	3439
Reflections observed	1859	1076	2282
hkl Range	$0 \leq h \leq 13$	$0 \leq h \leq 8$	$0 \leq h \leq 12$
	$0 \leq k \leq 11$	$0 \leq k \leq 19$	$0 \leq k \leq 11$
	$-15 \leq l \leq 15$	$-13 \leq l \leq 13$	$-21 \leq l \leq 20$
Criterion $I_o > x\sigma(I_o)$	5	3	3
R	0.033	0.051	0.031
R_w	0.032	0.035	0.033
No. of variables	206	143	240
S	2.244	1.525	2.660

3. Results and discussion

3.1. General description of the compounds

The compounds have similar overall structures. The coordination polyhedra are elongated pseudo-octahedra with two tn ligands coordinated to a central metal cation. The six-membered chelate rings formed by the copper(II) ion and 1,3-diaminopropane display chair conformation. The axial sites are occupied by two aminobenzoate anions. In CUPAAM there are two additional uncoordinated crystal water molecules in the asymmetric unit. All of the compounds studied here crystallise in the monoclinic crystal system. In this respect CUORAM is exceptional, since so far all previous *ortho*-substituted compounds in the $Cutn_2(XbzO)_2$ series are crystallised in the orthorhombic system [13]. On the other hand, the *ortho*-substituent has always been in the *trans*-position with respect to the coordinated oxygen O1. In CUORAM the amino group lies in the *cis*-position.

There are some notable differences in the bond lengths and angles among the three compounds. The axial bond lengths for CUORAM, CUMEAM and CUPAAM are 2.512(2), 2.574(4) and 2.487(2) Å, respectively. In the six-coordinated bis(*ortho*-aminobenzoato)copper(II) the axial Cu–O bond length is shorter, 2.415(5) Å [14]. Obviously the axial bond is weak and susceptible to changes. The pK_a values for the *ortho*-, *meta*- and *para*-aminobenzoic acids are 4.96(1), 4.76(3) and 4.88(3), respectively [15]. Clearly, the axial bond lengths do not correlate with the pK_a values. In a recent paper it was shown that the structures of *trans*-di(*ortho*-chlorobenzoato-*O*)bis(1,3-diaminopropane-*N*,*N*′)copper(II) and the corresponding bromo derivative have isomorphous structures with the same axial Cu–O bond lengths, in spite of the different anions [13]. Obviously a negative charge on a carboxylate group must be divided between the bond to the copper(II) ion and the hydrogen bonding network.

It is seen from the Fig. 1 that the orientations of the benzoate anions vary clearly with reference to a CuN_4 plane. To describe the orientation, two new parameters (inclination and declination) are introduced. These are defined in Fig. 2. Inclination ς describes bowing of a carboxylate (or the whole benzoate anion) group from (or towards) the equatorial coordination plane. Declination ϑ illustrates the lurching of the benzoate anion. The respective numerical values for the three compounds are clearly different: the absolute values for the declination are 4.80, 28.03 and 38.5°, and the inclination values −125.3, −123.1 and −132.7° for CUORAM, CUMEAM and CUPAAM, respectively. Declination shows clearly more variation than inclination. The declination values for the majority of the $Cutn_2(ZbzO)_2$ complexes are usually in the range of 0.5–12.0° [1]. As mentioned in the Introduction, in the previous compounds the substituents have not been able to play a marked role as donors in hydrogen bonding. The anomalous declination values for the present compounds suggest that the aromatic amino substituent may possibly be involved in the hydrogen bonding.

Because the copper(II) ion lacks spherical symmetry, the eccentricity of the copper(II) ion prolate ellipsoid is variable. The term 'plasticity' has been introduced to describe simultaneous compression and elongation in the equatorial and

Table 2
Selected bond lengths (Å) and angles (°) with their standard deviations for CUORAM, CUMEAM and CUPAAM

	CUORAM	CUMEAM	CUPAAM
Bond lengths			
Cu–N1	2.027(2)	2.029(4)	2.038(3)
Cu–N2	2.042(2)	2.020(6)	2.028(2)
Cu–O1	2.512(2)	2.574(4)	2.487(2)
N1–C1	1.481(4)	1.466(7)	1.478(4)
N2–C3	1.477(4)	1.488(9)	1.471(4)
C1–C2	1.515(5)	1.497(11)	1.501(4)
C2–C3	1.517(4)	1.508(9)	1.496(5)
C4–C5	1.398(4)	1.384(8)	1.401(3)
C4–C9	1.411(3)	1.385(7)	1.390(3)
C4–C10	1.513(4)	1.521(8)	1.495(3)
O1–C10	1.255(3)	1.251(7)	1.260(2)
O2–C10	1.258(3)	1.252(6)	1.259(3)
N3–C9	1.375(4)		
N3–C6		1.404(8)	
N3–C7			1.373(4)
Bond angles			
N1–Cu–N2	86.60(9)	88.6(2)	90.18(9)
Cu–N1–C1	117.2(2)	119.1(3)	118.7(2)
Cu–N2–C3	116.7(2)	118.5(4)	122.0(2)
N1–C1–C2	112.1(2)	112.1(6)	111.5(3)
N2–C3–C2	111.7(3)	111.7(5)	111.5(2)
C5–C6–C7	118.6(3)	119.0(5)	121.3(2)
C6–C7–C8	121.3(4)	119.9(6)	117.9(3)
C4–C9–C8	120.4(5)	120.4(5)	122.2(2)
O1–C10–O2	123.1(3)	125.7(5)	123.6(2)
O1–C10–C4	118.8(2)	117.9(5)	117.9(2)
O2–C10–C4	118.1(2)	116.4(4)	118.6(2)
N3–C9–C4	122.3(3)		
N3–C9–C8	118.9(3)		
N3–C6–C5		119.1(5)	
N3–C8–C7		121.9(5)	
N3–C7–C6			121.3(2)
N3–C7–C8			120.7(2)

axial directions in 4+2 type coordination polyhedra [16]. The tetragonalities ($T = R_s/R_l$, where R_s is equatorial and R_l axial bond length) are 0.811, 0.787 and 0.817 for CUORAM, CUMEAM and CUPAAM, respectively. Accordingly, if there is variation in the axial bond lengths, the equatorial direction should also be susceptible to changes. This is indeed the case in the present compounds. However, it must be also noted that the tetragonalities do not have constant values.

As seen in Table 2, the bite angles N1–Cu–N2 vary from 86.60(9) to 90.18(9)°. The latter value represents the maximum value found so far in the Cutn$_2$(XbzO)$_2$ series. However, an even wider value for the bite angle of 96.8(2)° has been found for diaqua-[μ-1,3-propanenediylbis(oxamato-*O,O′,O″,O‴,N,N′*)](1,3-diaminopropane-*N,N′*)dicopper(II) dihydrate [17]. The narrowest angle (85.9(2)°) in the series has been found for *trans*-di(*para*-methoxybenzoato-*O*)-bis(1,3-diaminopropane-*N,N′*)copper(II) (CUPAMX hereafter) [18].

All of the six-membered chelate rings display chair conformation in the present compounds. It is to be expected that variation in the bite angle would result in change in the total puckering [19] of a chelate ring. Indeed, widening of the bite angle seems to cause flattening of the ring, which is seen in the total puckering values: 0.659, 0.602 and 0.567 Å for CUORAM, CUMEAM and CUPAAM, respectively.

In CUORAM and CUPAAM the C–N bond lengths are almost the same, 1.375(4) and 1.373(4) Å, respectively. However, in CUMEAM the C–N bond seems to be longer, 1.404(8) Å. The respective angles *ipso* to an amino group are similar in CUORAM and CUPAAM, 118.8(3) and 117.9(3)°, whereas in CUMEAM the angle seems to be wider, 120.4(5)°. There is no correlation to be found here with the above mentioned pK_a values. Instead, it seems that the C–N bond lengths and the *ipso* angles are dependent on the protonation (or hydrogen bonding) of the amino group. This is seen in the values found for the *ortho*-aminobenzoic acid (anthranilic acid I). According to the neutron diffraction study, there are two molecules per asymmetric unit in the crystal structure, one is neutral and the other zwitterion. The C–N bond lengths are 1.386(3) and 1.455(4) Å, respectively; the respective angles are 118.4(2) and 121.8(3)° [20]. Therefore, the elongation of the C–N bond in CUMEAM may be interpreted to be caused by hydrogen bonding. Indeed, there is hydrogen bonding involved, as discussed later.

3.2. *The inter- and intramolecular interactions*

The changes in the pK_a values of the acids will certainly manifest themselves in the electronic properties of the carboxylate groups. However, the carboxylate groups have a dual function: one of the two oxygen atoms forms a coordination bond to copper, while the other one is susceptible to form hydrogen bonds. Accordingly, both coordination and hydrogen bonding are likely to affect the geometry of the benzoate anions with respect to a [Cu(tn)$_2$]$^{2+}$ cation. All of the compounds crystallise in the monoclinic system. This strongly suggests that the packing is affected by similar types of intermolecular interactions.

3.2.1. *Hydrogen bonding*

Non-covalent interactions that are selective, directional and strongly attractive can induce the self-assembly of predictable aggregates. An understanding of these interactions may lead via molecular tectonics into crystal engineering [21]. One of the most important interactions is hydrogen bonding. Klinga [2] has shown that, in Ni(II) and Cu(II) complexes formed by tn and methyl- or nitrobenzoates, there are either 1D or 2D hydrogen bonding networks. The dimensionality is not dependent on the central metal cation in these compounds.

Since it was suggested earlier that the hydrogen bonding would be a reason for the deformations in the chelate rings containing tn [22], the hydrogen bonds to the chelate ring are of special interest. The IR spectra of *trans*-di(benzoato-*O*)bis(1,3-diaminopropane-*N,N′*)copper(II) and the *meta*-

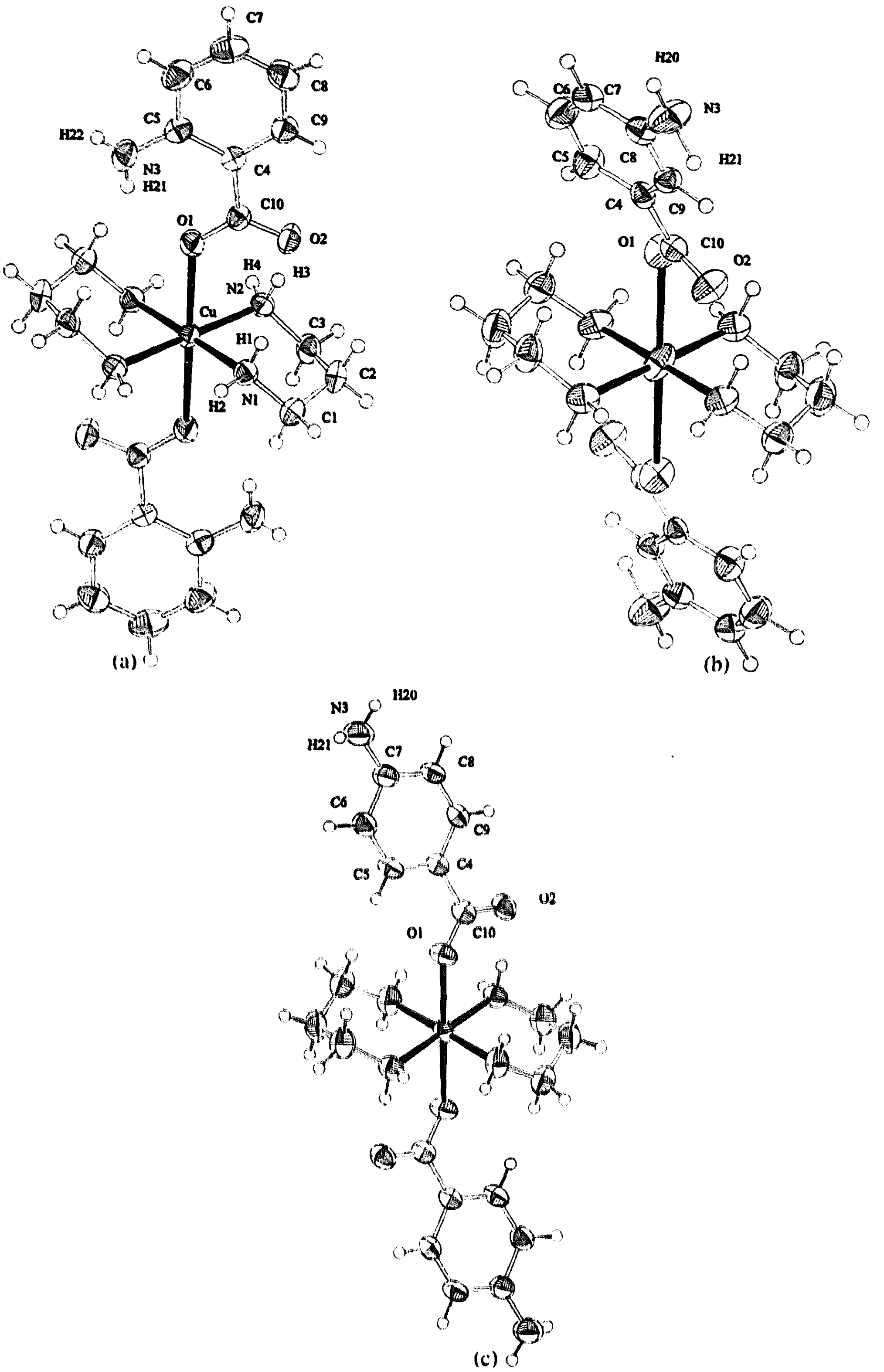

Fig. 1. ORTEP drawings showing the numbering scheme for (a) CUORAM, (b) CUMEAM and (c) CUPAAM. The thermal ellipsoids have been presented at the 50% probability level.

iodobenzoate analogue support the idea of hydrogen bonding [23,24]. The relevant bands in the IR spectra are those related to the amino and carboxylate groups. Listing of the pertinent bands is given in Table 3 for CUORAM, CUMEAM and CUPAAM.

We believe that the bands above 3400 cm^{-1} are due to aromatic N–H stretching, since in aqua-di(1,3-diaminopropane-*N,N′*)copper(II) dichloride the aliphatic N–H stretchings are seen in the range 3349–3129 cm^{-1} as a broad band with three maxima [25] and in [Cu(tn)$_2$](PF6)$_2$ between

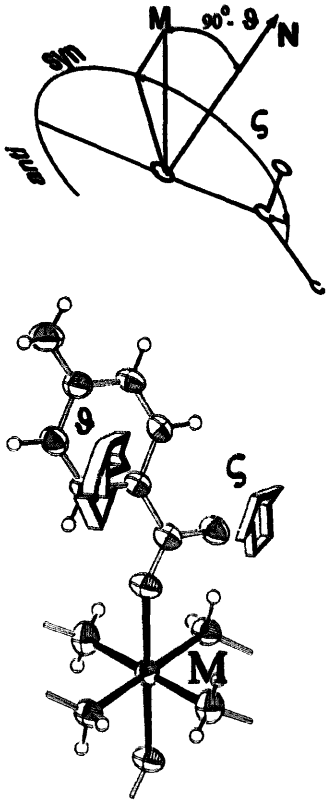

Fig. 2. Definition of declination (ϑ) and inclination (ς). *N* is a normal vector drawn to the carboxylate plane.

3300 and 3200 cm^{-1} as relatively sharp bands [26]. As stated before, CUPAAM also contains uncoordinated water molecules. There are no distinctive bands to be distinguished in the respective IR spectrum owing to overlap with the N–H stretchings. However, there is a very broad band (with the N–H stretchings) appearing as background in the range 3600–3000 cm^{-1}, which may well be due to hydrogen bonding related to water molecules.

The differences between the frequencies of the symmetric and antisymmetric C–O stretching bands are 266, 246 and 255 cm^{-1} for CUORAM, CUMEAM and CUPAAM, respectively. In unidentate acetate groups this difference is in the range 314–523 cm^{-1}, and in bridging carboxylates 159–171 cm^{-1} [27]. The values for the present compounds lie between the two ranges. This suggests that the carboxylate groups do not have 'pure' unidentate coordination mode, but have a slight tendency towards the bridging mode. This can be interpreted as caused by hydrogen bonding. CUMEAM has the smallest difference, which is nicely in accordance with the widest O1–C10–O2 angle.

3.2.2. *The hydrogen bonds formed with the chelate rings*

Because all of the four amine hydrogen atoms of a chelate ring are capable of hydrogen bond formation, their surroundings are studied in detail. Table 4 lists all of the shortest contacts to the hydrogen atoms of the amino groups. The following statistical expectation values with three e.s.d. values may be taken as a criterion to establish a hydrogen bond: H···O 1.96(12), N···O 2.85(9) Å and N–H···O 162(11)° [28][1]. If these values are applied, the following conclusions can be made. There are no compounds displaying 1D networks. Instead, both CUMEAM and CUPAAM display 3D hydrogen bonding, whereas CUORAM may be classified to 2D compounds. In CUPAAM the non-coordinated crystal water molecules are also involved in the network of the hydrogen bonds. It is noteworthy that in CUPAAM the amino group (N1, H1, H2) has no suitable contacts with O2 to be interpreted as hydrogen bonds. So far, in all of the complexes both of the two amino groups in a tn molecule have been hydrogen bonded [11]. This is probably the reason for the non-equivalence of the Cu–N–C angles in CUPAAM; in CUORAM and CUMEAM the angles are the same within three e.s.d. values. Another deviation most probably due to the different hydrogen bonding is the unusually wide bite angle N1–Cu1–N2 of CUPAAM (90.18(9)°) noted above.

Table 4 shows an interesting feature concerning the non-coordinated oxygen O2: it has the tendency to form either two intramolecular or two intermolecular hydrogen bonds. Although the maximum number is accordingly four, the fourth one seems always to be very weak or non-existing. This suggests that the oxygen atom O2 would have an sp^3 electronic configuration with three electron pairs capable of hydrogen bonding formation. Presumably the declination of a benzoate anion should have a marked effect on the hydrogen bonding, as the position of the relevant electron pair changes.

Table 3
Selected IR bands (cm^{-1}) with tentative asssignments for CUORAM, CUMEAM and CUPAAM

Assignment	CUORAM	CUMEAM	CUPAAM
N–H(arom) str	3458(s)	3443(m), 3409(m)	3441(br)
N–H(aliph) str [a]	[3300, 3270, 3238, 3201](s,br)	3312(s)	3313(s), 3256(s), 3217(m,br)
N–H(aliph) str		3279(s)	
N–H(aliph) str		3203(m,br)	
N–H(aliph) str	[3155, 3130](s,br)	3150(s,br)	
N–H(aliph) str	3034(m,br)		3035(w,sh)
C–O as str	1636(sh) 1609(s)	1620(m)	1630(m), 1604(s)
C–O sym str	1370(s)	1374(s)	1375(s)

[a] In CUPAAM the bands due to water molecules also appear here.

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[1] Accordingly, e.g. the range for a N–H···O angle will be 129–180°.

Table 4
The possible hydrogen bonds built by the amine groups in the CUORAM, CUMEAM and CUPAAM. The distances and angles in italics may be too long or narrow, respectively, to indicate significant hydrogen bonding. A = N, O

Hydrogen bond	H···O	A···O	A–H···O	Symmetry operation
CUORAM				
N1–H1···O2	2.20(3)	3.023(3)	155(2)	x, y, z
N1–H2···O2	2.08(3)	2.943(3)	170(3)	$1/2-x, 1/2+y, -z$
N2–H3···O2	*2.43(3)*	3.023(3)	162(2)	x, y, z
N2–H4···O2	2.01(3)	2.970(3)	171(3)	$-1/2+x, -1/2-y, z$
N3–H20···N3	*2.85(3)*	*3.238(4)*	*116(3)*	$-x, -y, -z-1$
N3–H21···O1	2.01(3)	2.658(4)	139(3)	x, y, z
CUMEAM				
N1–H1···O2	2.09(5)	2.904(7)	148(5)	x, y, z
N1–H2···O2	2.49(5)	*3.268(7)*	167(5)	$1-x, -y, -z$
N2–H3···O1	*2.73(5)*	3.123(7)	*111(4)*	x, y, z
N2–H4···O2	2.12(5)	2.948(6)	171(5)	$-1+x, y, z$
N3–H20···O2	*2.61(6)*	*3.146(8)*	130(6)	$1/2+x, 1/2-y, -1/2+z$
N3–H21···O1	2.38(5)	*3.264(8)*	165(4)	$1+x, y, z$
CUPAAM				
N1–H1···O4	*2.95(3)*	3.075(3)	*91(2)*	$-1/2+x, 1/2-y, -1/2-y$
N1–H2···O4	*2.51(3)*	3.075(3)	126(3)	$-1/2+x, 1/2-y, -1/2-y$
N2–H3···O2	1.96(3)	2.922(3)	170(2)	x, y, z
N2–H4···O4	2.32(3)	3.045(4)	167(3)	$1/2-x, -1/2-y, 1/2-z$
N3–H20···O2	*3.06(4)*	*3.622(4)*	123(3)	$-x-1, -y, -z$
N3–H21···O3	2.29(3)	3.008(4)	170(4)	$-x-1, -y+2, -z$
O3–H31···O1	1.98(3)	2.708(3)	170(3)	x, y, z
O3–H32···O2	1.97(3)	2.762(3)	173(3)	$-x, -y+1, -z$
O3–H31···O4	*2.96(3)*	2.746(4)	*66(2)*	$-1/2+x, 1/2-y, -1/2+z$
O4–H41···O3	1.92(3)	2.746(4)	169(3)	$1/2+x, 1/2-y, 1/2+z$
O4–H42···O2	2.16(3)	2.822(3)	172(5)	x, y, z

Indeed, this assumption gets support from the following discussion.

In CUORAM the intramolecular hydrogen bond is bifurcated with the contacts to both amino groups. It means that the oxygen O2 is oriented in between the chelate ring. It is noteworthy that the respective bite angle has the small value of 86.60(9)°. In accordance with this, in CUPAMX the bite angle is 85.9(2)° [18] and the intramolecular contact values suggest even stronger interactions. In general, the orientation of the non-coordinated oxygen atom O2 shows wide variation in the Cutn$_2$(ZbzO)$_2$ series with respect to a six-membered chelate ring. To get a better insight, a new parameter twist

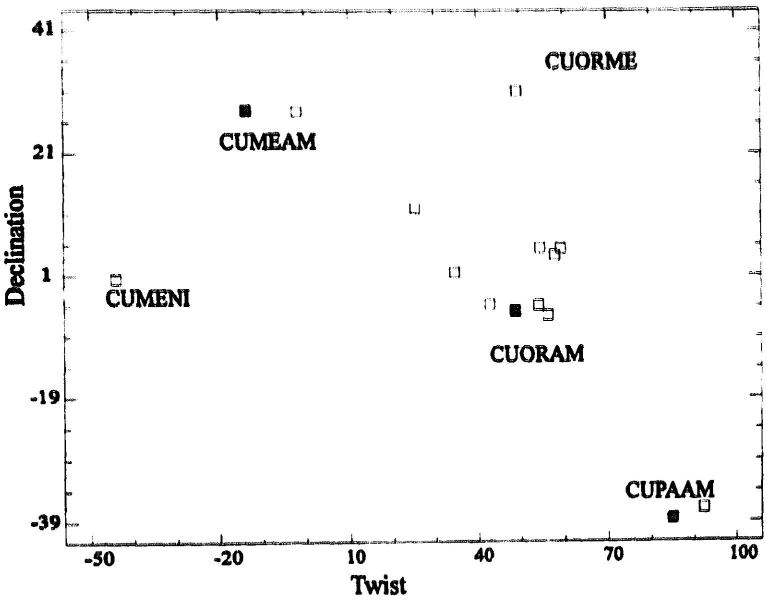

Fig. 3. Scatter plot of twist (ξ) vs. declination (ϑ). CUMENI: *trans*-di(*meta*-nitrobenzoato-*O*)bis(1,3-diaminopropane-*N,N'*)copper(II); CUORME: *trans*-di(*ortho*-nitrobenzoato-*O*)bis(1,3-diaminopropane-*N,N'*)copper(II).

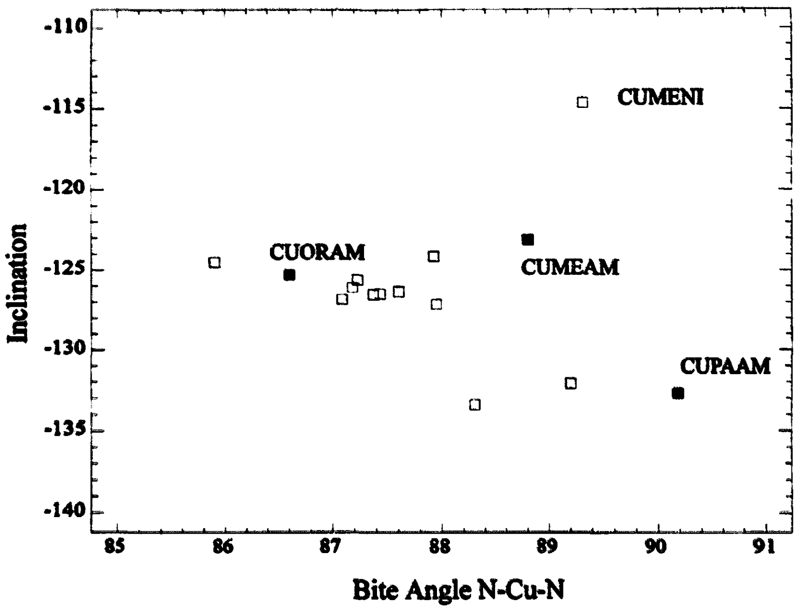

Fig. 4. Scatter plot of inclination vs. bite angle N–Cu–N.

(ξ) is utilised to describe the orientation. It is defined as torsion angle N1–Cu1–O1–C10. A scatter plot is shown in Fig. 3 to study the possible dependence between twist and declination. There seems to be a correlation with the exception of two outliers, CUMENI and CUORME. When the twist values indicate that the oxygen O2 would be projected in between a chelate ring, then the declination also has the smallest values. As for CUMENI, its axial bond length Cu–O1 is the longest one in the series, 2.665(2) Å. According to Klinga [2], it displays only a 1D hydrogen bonding network, while the other complexes in the $\mathrm{Cutn_2(ZbzO)_2}$ series have 2D networks. Although the twist angle for CUORME (49.2°) is suggestive of a bifurcate intramolecular hydrogen bond, the distances are perhaps too long (even the shorter O · H distance is 2.29(6) Å) to indicate any hydrogen bonding [2]. Moreover, the methyl group in the *ortho*-position lies *trans* to the non-coordinated hydrogen and thus may have intramolecular interactions to it diminishing the contribution of the usual interactions.

To evaluate the influence of intramolecular hydrogen bonding on the coordination in the equatorial direction, a new scatter plot was constructed (Fig. 4). There seems to be a linear correlation between inclination and bite angle with one outlier, CUMENI. As a carboxylate group is bending towards the equatorial plane, the bite angle N–Cu–N is getting narrower concomitantly. Obviously this must be due to increased intramolecular interaction.

3.2.3. The hydrogen bonds to the coordinated oxygen O1

In most of the compounds it is the non-coordinated oxygen O2 which participates in the hydrogen bonding. In CUPAAM the water molecules are also mediating the interactions. In the *trans*-di(benzoato-*O*)bis(tn)M(II) complexes studied so far, the coordinated oxygen O1 has played no role in the hydrogen bonding. In the present series, all of the compounds studied here (CUORAM, CUMEAM and CUPAAM) have geometrical parameters which seem to indicate hydrogen bonding into O1.

In CUORAM there is a short intramolecular distance between the amino group and O1. As stated before, in all previous *ortho*-substituted benzoates in the $\mathrm{Cutn_2(XbzO)_2}$ series, the *ortho*-substituent has been in the *trans*-position with respect to the coordinated oxygen atom O1. The *cis*-position in CUORAM has an obvious explanation: the non-coordinated oxygen is not capable of further hydrogen bonding. As is usual in these compounds, the oxygen O2 tends to form three hydrogen bonds. Therefore, the amino group forms the intramolecular hydrogen bond to O1, which has no other hydrogen bonds.

In CUMEAM there is an exceptional hydrogen bonding system (Fig. 5), which is a chain $\mathrm{O1^{i}\cdots H21–N3–H20\cdots O2^{j}–C10^{j}–O1^{j}\cdots}$ ($i = 1+x, y, z$; $j = 1/2+x, 1/2-y, -1/2+z$).

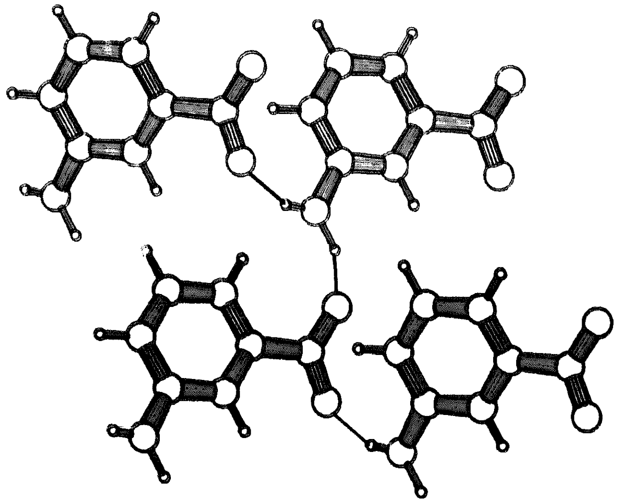

Fig. 5. Hydrogen bonding chain between the carboxylate and amino groups in CUMEAM.

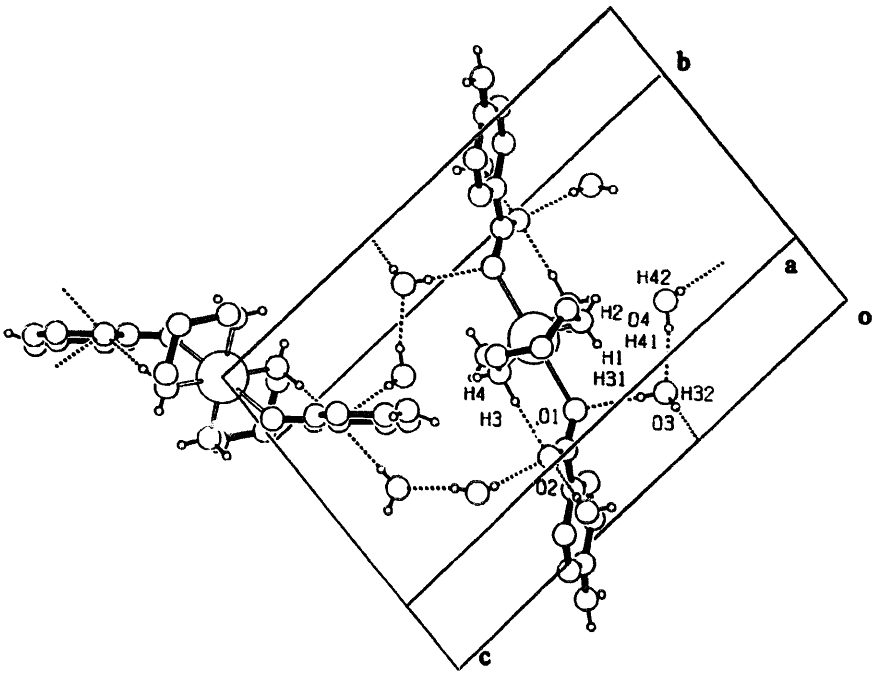

Fig. 6. Simplified packing diagram for CUPAAM illustrating the hydrogen bonding related to the carboxylate groups.

Both the aromatic amino groups as well as the carboxylate groups act like bridges. Here the interaction is intermolecular.

In CUPAAM the hydrogen bonding to O1 is mediated by the water molecules (Fig. 6). The relevant parameters in CUPAAM between O3 and O1 suggest that there is a stronger hydrogen bond to the coordinated oxygen O1 in CUPAAM than in CUMEAM, which is probably correlated with the wider declination value of CUPAAM. This in turn may indicate an increasing change from a sp^2 towards a sp^3 hybridisation of the coordinated oxygen.

A hydrogen bond into a coordinated oxygen O1 is very likely to change the bonding properties to the central metal cation. Indeed, both CUMEAM and CUPAAM have clearly wide declination angles, but not CUORAM. Obviously the intramolecular interaction in CUORAM plays a minor role due to the narrower N3–H21···O1 angle and accordingly also the declination is smaller.

4. Conclusions

The presence of hydrogen bonding in the *trans*-di(Z-aminobenzoato-*O*)di(1,3-diaminopropane-*N,N'*)copper(II) ($Z=2$, 3 or 4) has been established by single-crystal X-ray diffraction and IR spectroscopy. Intermolecular hydrogen bonding to the coordinated oxygen atom of a carboxylate group results in increased declination. Both small inclination and absolute declination values are correlated with bifurcated intramolecular hydrogen bonding and narrow bite angles N–Cu–N. Hydrogen bonding into the coordinated oxygen changes probably its hybridisation from approximate sp^2 towards sp^3.

5. Supplementary material

Complete listings of the structure factors, atomic coordinates, bonding parameters and packing diagrams are available upon request.

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