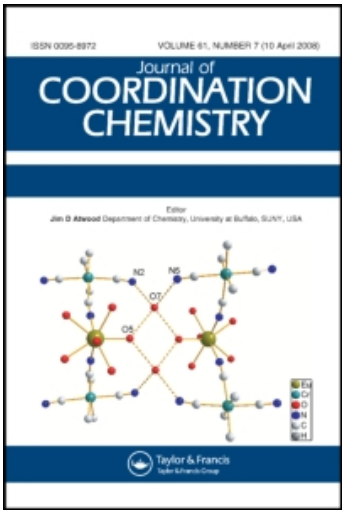

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Distortion isomerism and plasticity of the coordination sphere of binuclear Cu(II) complexes: Crystal structure of the monoclinic isomer of $[Cu_2(2\text{-bromopropionato})_4(caffeine)_2]$

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Distortion isomerism and plasticity of the coordination sphere of binuclear Cu(II) complexes: Crystal structure of the monoclinic isomer of $[Cu_2(2\text{-bromopropionato})_4(caffeine)_2]$

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The crystal and molecular structure of monoclinic [di(caffeine)tetrakis(2-bromopropionato)dicopper(II)] · 0.8 water was determined using direct methods and Fourier techniques. The complex crystallizes in space group *C2/c* and is dimeric with square pyramidal geometry at each copper(II) center. The Cu · · · Cu distance is 2.674(1) Å. Experimental data are compared with those found in a similar triclinic $[Cu_2(2\text{-bromopropionato})_4(caffeine)_2]$ complex. The isomers differ in the geometry of copper(II) and the inter-aromatic interaction of caffeine molecules. The correlation of Cu · · · Cu distances *vs.* apical Cu–O bond length for dimeric copper(II) carboxylate complexes were interpreted by the bond-valence model. Minimum lengths of apical Cu–O bond and Cu · · · Cu separation were predicted.

Keywords: Copper(II); Halogenopropionate; Caffeine; Crystal structure; Distortion isomers

1. Introduction

The relationship between plasticity of the coordination sphere and distortion isomerism of copper(II) compounds was the subject of earlier study [1]. Binuclear Cu(II) carboxylates were not chosen as suitable subjects for study of coordination sphere plasticity because of the relative rigidity of their "paddle-wheel" structure, avoiding larger deformations of the Cu(II) coordination sphere. Recently, we reported the crystal structure of the triclinic $[Cu_2(2\text{-bromopropionato})_4(caffeine)_2]$ complex and structural correlations for complexes with CuO_4N chromophores and weak Cu · · · Cu interactions [2]. The deformations within their binuclear cages are consistent with the bond-valence model [3].

Many binuclear copper(II) carboxylates have been isolated and their magnetostructural correlations studied [4-6]. Caffeine (3,7-dihydro-1,3,7-trimethyl-1,4-purine-2,6-dione) (figure 1) is a purine alkaloid possessing pharmacological

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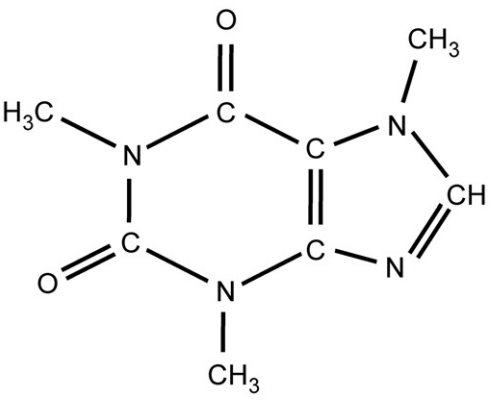

Figure 1. Caffeine molecule.

behavior as a therapeutic agent with analeptic activity. Several crystal structures of caffeine with organic substrates have been determined (5-chlorosalicylic acid [7], barbital [8] and also hydrochloride dihydrate [9]).

A few crystal structures of copper(II) compounds with nitrogen-coordinated caffeine have been described. Two monomeric examples are triaqua(caffeine)nitro-copper(II) nitrate [10] and aqua(caffeine)dichloro-copper(II) [11] with five-coordinate copper(II).

Ten binuclear copper(II) carboxylates with caffeine, $Cu_2(RCOO)_4(caf)_2$ [2, 12–18] and $Cu_2(naproxenato)_4(caffeine)_2(H_2O)$ [19], have been studied. In $Cu_2(RCOO)_4(caffeine)_2$, two copper(II) atoms are bonded by four carboxylate groups in *syn–syn* arrangement, while the apical ligands are caffeine molecules and in the naproxenato complex caffeine and water. Recently the structure of $Cu_2(3,5\text{-dinitrobenzoato})_4(caffeine)_2$ with an oxygen-coordinated caffeine has been reported [20].

As a part of our investigation of copper(II) carboxylates with caffeine, in this article we report the crystal and molecular structure of monoclinic $Cu(CH_3CHBrCOO)_2(caffeine)\cdot 0.4(H_2O)$. A comprehensive view on Cu(II) coordination sphere plasticity in dimeric structures of $Cu_2(RCOO)_4L_2$ compounds is discussed.

2. Experimental

2.1. *Preparation of the complex*

$Cu(CH_3CHBrCOO)_2$ was prepared as described earlier [21]. The complex $Cu(CH_3CHBrCOO)_2(caf)$ (caf = caffeine) was prepared by adding an ethanolic solution of caffeine to a stirred ethanolic solution of $Cu(CH_3CHBrCOO)_2$ in equimolar ratio. After heating and boiling, the solution was left to cool and stand at room temperature. The green product that precipitated was isolated and washed with cold ethanol and dried at room temperature. Anal. Calcd for $Cu(CH_3CHBrCOO)_2(caf)\cdot 0.4(H_2O)$ (%): Cu, 11.28; C, 29.85; H, 3.97; N, 9.95. Found: Cu, 11.25; C, 29.8; H, 3.9; N, 10.0.

2.2. *Crystallography*

The deep green prismatic crystal ($0.21 \times 0.15 \times 0.05\,mm^3$) was scanned on an Oxford Diffraction Xcalibur diffractometer at 270 K with Mo radiation, $\lambda = 0.71073$ Å. The compound crystallized in the space group *C2/c*, monoclinic with lattice parameters $a = 16.4407(9)$ Å, $b = 19.695(1)$ Å, $c = 13.5735(7)$ Å, $\beta = 104.835(3)^\circ$, $V = 4248.5(4)$ Å^3. Density measured by flotation is $D_m = 1.76(2)\,g\,cm^{-3}$ and calculated density for $Z = 8$, $D_x = 1.779\,g\,cm^{-3}$. 11,102 independent reflections were measured, $R_{int} = 0.036$. Absorption correction was applied ($\mu = 4.8\,mm^{-1}$). The calculations were made by CrysAlis software [22]. The structure was solved through direct methods using SHELXS [23]. The parameters of structure were refined on F^2 by full-matrix, least-squares using SHELXL-97 [23] (229 parameters). Occupation parameters of disordered groups and the parameters of hydrogens were refined with restraints and blocked in the last cycles. The final $R = 0.068$ and $R_w = 0.093$ for 5870 observed data. The structure was drawn by ORTEP-3 for Windows [24] and MERCURY [25]. The Crystallographic Information File (CIF) has been deposited at the Cambridge Crystallographic Data Center under deposition number CCDC 671495.

2.3. *Physical measurements*

Electronic spectrum was recorded on a Specord 200 and EPR spectrum on a Bruker ESP 300 spectrometer equipped with the Bruker NMR gaussmeter ER 035M and Hewlet Packard microvave frequency counter HP 5350 B. Magnetic measurements in the temperature range 80–300 K were carried out on a Quantum Design SQUID Magnetometer (type MPMS-XL15). Measurement conditions and evaluation methods of experimental data have been described [2].

3. Results and discussion

The crystal structure of monoclinic $Cu(CH_3CHBrCOO)_2(caf) \cdot 0.4(H_2O)$ is composed of centrosymmetric [Cu_2(2-bromopropionato)$_4$(caf)$_2$] dimers. Four bidentate 2-bromopropionato anions form *syn–syn* bridges between isolated pairs of copper(II) separated by 2.6736(1) Å. An ORTEP diagram of the complex is in figure 2. Selected bond lengths and angles are collected in table 1. Each copper(II) atom has a slightly deformed square-pyramidal arrangement with caffeine in an apical position. The copper(II) to carboxylate oxygen atom distances are 1.941(1) to 1.945(1) Å (av. 1.943 Å) and the copper(II) atom to nitrogen of caffeine distance is 2.1830(1) Å. The copper is displaced 0.2216(1) Å toward the N atom of caffeine from the plane containing the four oxygens. Maximum deviation from the mean plane passing through the basal oxygens is 0.002(2) Å. The eight oxygen atoms of the four carboxylate groups create an oblique parallelepiped.

Selected geometrical parameters for monoclinic and triclinic Cu_2(2-bromopropionato)$_4$(caf)$_2$ isomers are compared in table 2. The monoclinic dimer (I) is more crowded and somewhat less distorted than the triclinic dimer (II); the deviation of Cu(II) from the basal O_4 plane in both isomers is almost equal. All parameters are in the ranges found in the series of copper(II) carboxylate dimers [26, 27]. Within the inner Cu(II)

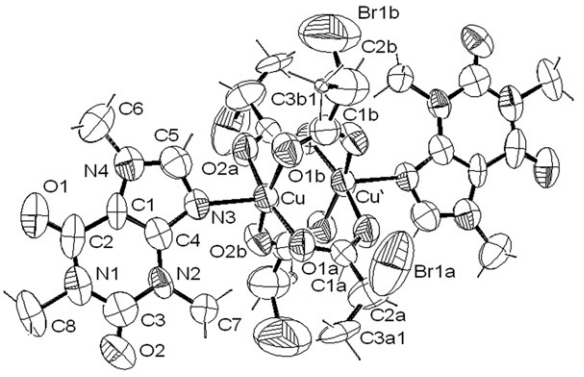

Figure 2. Molecular structure of monoclinic $[Cu_2(2\text{-bromopropionato})_4(caffeine)_2]\cdot 0.8(H_2O)$ showing the atom numbering of the asymmetric unit. Only one half of the disordered 2-bromopropionates are shown for clarity.

Table 1. Selected bond distances (Å) and angles (°) for monoclinic $[Cu_2(2\text{-bromopropionato})_4(caffeine)_2]\cdot 0.8(H_2O)$ with e.s.d's in parentheses.

O(1a)–C(1a)	1.250(8)	O(1b)–C(1b)	1.235(5)
C(1a)–C(2a)	1.55(1)	C(1b)–C(2b)	1.651(4)
C(2a)–C(3a1)	1.48(2)	C(2b)–C(3b1)	1.678(3)
C(2a)–C(3a2)	1.60(2)	C(2b)–C(3b2)	1.491(4)
C(2a)–Br(1a)	1.942(8)	C(2b)–Br(1b)	1.929(4)
C(2a)–Br(2a)	1.968(9)	C(2b)–Br(2b)	1.832(3)
O(1a)–Cu–O(2b)	89.9(2)	O(1b)–Cu–O(1a)	90.0(2)
N(3)–Cu–O(1b)	93.6(2)	N(3)–Cu–O(1a)	102.1(2)
O(1a)–C(1a)–C(2a)	116.8(6)	O(1b)–C(1b)–C(2b)	121.9(3)
C(1a)–C(2a)–Br(1a)	104.7(5)	C(1b)–C(2b)–Br(1b)	100.6(2)
C(1a)–C(2a)–Br(2a)	102.0(5)	C(1b)–C(2b)–Br(2b)	104.3(2)
C(1a)–C(2a)–C(3a1)	116.2(9)	C(1b)–C(2b)–C(3b1)	113.5(2)
C(1a)–C(2a)–C(3a2)	117.2(6)	C(1b)–C(2b)–C(3b2)	111.8(3)

Table 2. Comparison of selected geometrical parameters for monoclinic $[Cu_2(2\text{-bromopropionato})_4(caffeine)_2]\cdot 0.8(H_2O)$ (**I**) and triclinic $[Cu_2(2\text{-bromopropionato})_4(caffeine)_2]$ [2] (**II**).

Parameter	**I**	**II**
Mean Cu–O(basal) (Å)	1.943 ± 0.002*	1.97 ± 0.01
Cu···Cu–N(apical) (°)	173.2(2)	166.73(1)
Cu–N(apical) (Å)	2.183(5)	2.231(4)
Cu···Cu′ (Å)	2.674(1)	2.694(1)
Cu– out of O_4 plane (Å)	0.2216(1)	0.2211(1)
Mean Cu–O–C (°)	123 ± 2	123 ± 4
Cu–O–C–O (°)	3.9(8)	3.0(8)
	−3.4(7)	9(1)

*Maximum deviation from the mean.

coordination sphere, the greatest geometrical difference is Cu–N bond length and N–Cu···Cu angle. The square pyramidal geometry around Cu(II) ion of both isomers is almost regular. The solvent water molecule ($0.8H_2O$) is disordered in the space between the binuclear units. In the monoclinic form, both 2-bromopropionato ligands

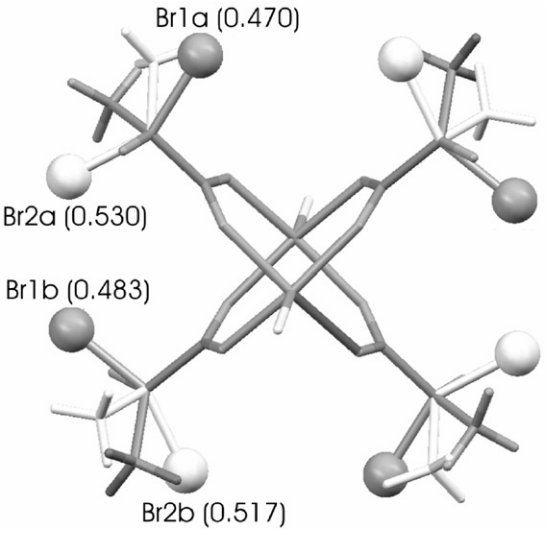

Figure 3. Perspective view of the crystal structure of the monoclinic [Cu_2(2-bromopropionato)$_4$(caffeine)$_2$]. Bromine atoms are represented by spheres. The population parameters of the disordered atoms are reported in parenthesis.

show disorder. The refinement (figure 3) gave final occupation parameter ratios of 0.470(3)/0.530(3) and 0.483(3)/0.517(3) for bromopropionate **a** and **b**, respectively. These parameters are smaller than those found in triclinic form, with values of 0.907(4)/0.093(4) and 0.650(4)/0.350(4). Refinement in the space group Cc led to similar population parameters and a Flack parameter [28] [$x = 0.43(2)$] confirming that the structure is centrosymmetric. This parameter is comparable with that found in triclinic form [$x = 0.48(7)$].

The dihedral angle between the caffeine mean plane and the basal plane of copper(II) of 76.7(1)° is less than that in the triclinic form (87.7(9)°). The dihedral angle between the pyrimidine and pyrazole rings of the caffeine (1.52(9)°) does not differ significantly from that found in the triclinic form (2.1(4)°). Each caffeine molecule in the monoclinic form deviates slightly from planar geometry, with maximum deviation 0.0218(1) Å for N(3) and 0.037(1) Å for O(2). The two oxygen atoms of caffeine also deviate slightly from the pyrimidine ring. The torsion angles O(1)–C(2)–C(1)–C(4) and O(2)–C(3)–N(1)–C(2) are 3.4(5) and 3.6(6)°.

The crystal structures of both forms differ also in the packing of [Cu_2(2-bromopropionato)$_4$(caf)$_2$] units. In the monoclinic form each caffeine is intercalated between two symmetry related caffeine moieties (figure 4). The binuclear units are linked by these $\pi \cdots \pi$ interactions [29] into the infinite 3-D skeleton. The mean inter-plane distance is 3.32081(6) Å, less than that found in the triclinic form (3.56(3) Å). In the triclinic form $\pi \cdots \pi$ interactions between the caffeine molecules connect the [Cu_2(2-bromopropionato)$_4$(caf)$_2$] units into the infinite chains.

No significant differences were found for the magnetic data: μ_{eff} value 1.50(1) B.M. at room temperature and 0.45(1) B.M. at 80 K (monoclinic); against 1.48(1) B.M. at room temperature and 0.42(1) B.M. at 80 K (triclinic) correspond quite well with the respective X-ray data. Energy separation ($-2J$) between the triplet and singlet state of both forms, 290 cm^{-1} (monoclinic) and 310 cm^{-1} (triclinic), are similar to those found in

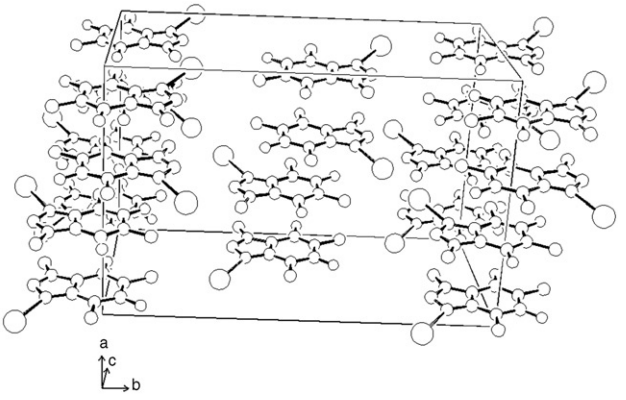

Figure 4. Schematical drawing of caffeine intercalation in the crystal structure of monoclinic $[Cu_2(2\text{-bromopropionato})_4(caffeine)_2]\cdot 0.8(H_2O)$.

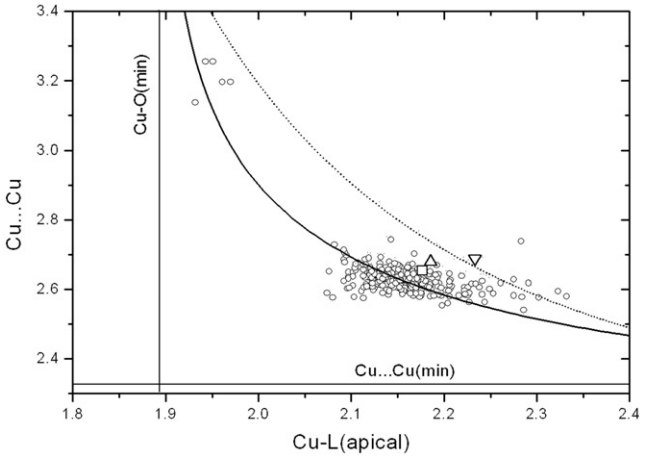

Figure 5. Dependence of Cu···Cu separation (in Å) on apical Cu–O bond length (full line) with the scatterogram of compounds from CSD. Spearman rank correlation coefficient [34] is $\rho = -0.545$. The dependence of Cu···Cu separation on apical Cu–O bond length [2] is shown by the dotted line. Δ-monoclinic $[Cu_2(2\text{-bromopropionato})_4(caffeine)_2]\cdot 0.8(H_2O)$, ∇-triclinic $[Cu_2(2\text{-bromopropionato})_4(caffeine)_2]$, □–$[Cu_2(3,5\text{-dinitratobenzoato})_4(caffeine)_2]$.

binuclear copper(II) carboxylates [27]. The broad absorption $d_{x^2-y^2} \rightarrow d_{x^2-y^2}$ in the visible region and LMCT band (13,500 and 26,000 cm^{-1}) of the monoclinic form are slightly shifted from 13,700 cm^{-1} and 25,000 cm^{-1} in the triclinic form. The EPR spectra of both forms do not show significant differences, with values of $g_\perp = 2.040$, $g_\parallel = 2.310$ and $|D| = 0.340\,cm^{-1}$ (monoclinic) and $g_\perp = 2.045$, $g_\parallel = 2.325$ and $|D| = 0.332\,cm^{-1}$ (triclinic).

Using the Cambridge Structural Database (CSD) [30], Version 2.3.8, the inter-atomic Cu···Cu distances and apical Cu–O bond lengths for $Cu_2(COO)_4O_2$ cages were correlated. The structures with a crystallographic R factor greater than 0.075 and structures solved from powder data were not included. Figure 5 presents such a correlation of 250 hits compared with the similar dependence for $Cu_2(COO)_4N_2$ cage

with caffeine in the apical position (dotted curve). If the basal Cu–O bond length is kept constant, relation (1) holds, as derived from the bond-valence model [3]. The best fit of correlation in figure 5 (full curve) was achieved using the formula based on orbital metal-ligand interaction [31] for the bond valence of apical Cu–O bond and exponential formula [32] for the bond valence of Cu···Cu contact

$$r_{\mathrm{Cu\cdots Cu}} = R^* - b\ln\left(V^* - \frac{\alpha_1}{r_{\mathrm{Cu}-O}} - \frac{\alpha_2}{r^2_{\mathrm{Cu}-O}} - \frac{\alpha_3}{r^3_{\mathrm{Cu}-O}} - \frac{\alpha_4}{r^4_{\mathrm{Cu}-O}} - \frac{\alpha_5}{r^5_{\mathrm{Cu}-O}}\right) \quad (1)$$

where $r_{\mathrm{Cu}\cdots\mathrm{Cu}}$ and $r_{\mathrm{Cu–O}}$ are internuclear distances of Cu–O and Cu···Cu contact and α_i are tabulated constants for the Cu–O bond [31]. Variables R^* and V^* are bond valence parameters [32] of Cu···Cu contact and mean free valence [33] of the apical donor atom. b is a commonly accepted constant equal to 0.37 Å. The fitted parameters are $R^* = 2.086(7)$ Å and $V^* = 0.513(4)$. The standard statistical procedure to test correlation significance and goodness of fit was used [34].

Within the observed Cu–L and Cu···Cu distances, the curve in figure 5 for apical Cu–O bonds lies under the analogous curve for Cu–N that explains why the bonding of caffeine *via* an O atom in $[Cu_2(3,5\text{-dinitrobenzoato})_4(caf)_2]$ [20] results in a smaller Cu···Cu distance compared with compounds with caffeine as an N-donor ligand. Since the interplanar basal plane-basal plane distance for dimeric Cu(II) carboxylates is kept constant [5], the subsequent bonding of caffeine *via* an O atom results in a smaller distance from Cu of the basal plane. Both curves approach asymptotically to the common minimum Cu···Cu(min) = 2.334(3) Å. The asymptotical value for apical bond length is Cu–O(min) = 1.896(3) Å. The apical Cu–O bond lengths in $[Cu_2(Cl_3COO)_4L_2]$ (L = 2,2,6,6-tetramethylpyperidinyl-1-oxy, 2,2,5,5-tetramethylpyrrolinyl-1-oxy) [36] and $[Cu_2(pfpr)_4(NITmNO_2)_2]$ (pfpr = pentafluoropropionate, $NITmNO_2$=2-(3-nitrophenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) approach this value [35]. Cu(II) coordination geometry of both compounds may be described as a distorted trigonal bipyramidal. Each carboxylate ligand bridge extends from an axial coordination site on one copper to an equatorial position on the other copper. Such a bridging arrangement stabilizes substantially longer Cu···Cu and shorter Cu–O(donor) distances, caused by the plasticity of the Cu(II) coordination sphere, than those of remaining dimeric compounds shown in figure 5. When the Cu–O(donor) distance is about 1.95 Å, and remaining Cu–O distances of chromophore are kept within the observed range, there is practically no Cu···Cu interaction.

4. Conclusions

A monoclinic isomer of 2-bromopropionato copper(II) complex with caffeine has been prepared and characterized. Triclinic and monoclinic forms of these compounds are a classic example of distortion isomerism, which prevails in the chemistry of copper(II) complexes [37, 38]. The crystal structures of both isomers differ in the interaromatic interactions between the molecules of caffeine and the deformations of the coordination polyhedron around Cu(II). For $Cu_2(COO)_4O_2$ cages, an increase of Cu–O(apical) interatomic distances leads to strengthening of chemical bonds, and consequently, to shortening of Cu···Cu interatomic distances. A manifestation of the plasticity of

the coordination sphere of Cu(II) is that shortening of Cu···Cu contact brings elongation of apical Cu–O bonds [1]. This dependence is expressed by equation (1). Continual transition between tetragonal pyramidal and trigonal bipyramidal coordinations exists.

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