

# Structure of 1,3,7-Trimethyl-2,6-dioxopurine Copper(II) *o*-Iodobenzoate

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The crystal structure of  $\text{Cu}_2(\textit{o}\text{-IC}_6\text{H}_4\text{COO})_4(\text{caffeine})_2$  contains Cu(II) atoms bridged by *o*-iodobenzoate groups forming binuclear molecules  $[\text{Cu}_2(\textit{o}\text{-iodobenzoate})_4(\text{caffeine})_2]$ . Copper atoms are surrounded by four oxygen atoms from the *o*-iodobenzoate groups and one nitrogen atom from caffeine in the apices of slightly distorted square pyramids. Mean Cu—O and Cu—N bond lengths are 0.197(1) nm and 0.224(1) nm. The displacements of copper atoms from the basal planes are 0.0246(6) nm and 0.0248(7) nm. The Cu···Cu distances are 0.2713(2) nm.

Caffeine (1,3,7-trimethyl-2,6-dioxopurine) (caf) is one of purine alkaloids showing interesting pharmacological properties. It is used as a stimulating agent to activate the nervous system and also for some cardiovascular diseases. In our previous study [1] we solved the structure of  $\text{Cu}(\text{chloroacetate})_2(\text{caf})$ . So far an abundance in structure material of binuclear acetate complexes of Cu(II) has been gathered. The review [2] presented the crystal structure data of complexes of the class  $(\text{RCOO})\text{Cu} \cdot 2\text{L}$  (R = radical, L = ligand). A typical manifestation of this class dimers is that Cu(II) atom shows pyramidal coordination. Four oxygen atoms are in the basal plane, nitrogen or another oxygen in the apex, the central atom being shifted out of the basal plane towards the apex.

The bond-valence method [3, 4] can also be used to identify such structural models of binuclear complexes that cannot be distinguished by X-ray diffraction. According to our knowledge only two organic substrates containing *ortho*-substituents of benzoic acid [5, 6] have been studied. The crystal structures of two organic substrates containing iodine as compound of Cu(II) *o*-iodobenzoate with caffeine ligand using X-ray analysis methods have not been studied, thus we decided to take this compound as the subject of our study.

## EXPERIMENTAL

The green  $[\text{Cu}_2(\textit{o}\text{-IC}_6\text{H}_4\text{COO})_4(\text{caf})_2]$  was prepared by combining a warm methanol solution of copper(II) *o*-iodobenzoate monohydrate (together with

a small amount of corresponding free acid) and caffeine in a mole ratio of 1:1:2. The mixture was left to stand at room temperature. The final green product which precipitated was filtered off, washed with cold methanol, and dried at room temperature. The compound was purified by recrystallization from methanol. Recrystallization in methanol yielded bright green prismatic monocrystals of the compound under investigation of the size 0.4 mm × 0.3 mm × 0.05 mm. Density of crystals was measured by flotation in  $\text{CHBr}_3\text{—CCl}_4$ .

X-Ray structure analysis:

Crystal data:  $\text{C}_{44}\text{H}_{36}\text{O}_{12}\text{N}_8\text{Cu}_2\text{I}_4$ ,  $M_r = 1503.48$ , monoclinic,  $a = 1.4621(6)$  nm,  $b = 1.3700(3)$  nm,  $c = 1.3660(6)$  nm,  $\beta = 116.58(2)^\circ$ ,  $V = 2.451(2)$  nm<sup>-3</sup>,  $Z = 2$ ,  $D_m = 2.01$  g cm<sup>-3</sup>,  $D_x = 2.04$  g cm<sup>-3</sup>, space group  $\text{P}2_1$  (No. 4),  $\text{MoK}\alpha$  radiation,  $\lambda = 0.071069$  nm,  $\mu = 3.5$  mm<sup>-1</sup>,  $F(000) = 1444$ .

As Weissenberg photographs showed, the crystalline phase of  $[\text{Cu}_2(\textit{o}\text{-IC}_6\text{H}_4\text{COO})_4(\text{caf})_2]$  belongs to the monoclinic system. The unconventional space group of  $\text{B}12_11$  ( $\text{B}2_1$ ) was chosen. The unit cell parameters were refined by means of a SYNTEX  $\text{P}2_1$  apparatus (computer-controlled four-circle diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation), applying the least-squares method from angles of ten selected reflections ( $4.0 \leq 2\theta \leq 20.5$ ). 3384 independent reflections were scanned ( $2\theta_{\text{max}} = 38^\circ$ ); 2566 ( $I > 1.96\sigma(I)$ ) were observed;  $hkl$  index in the range of 0/16, 0/14, -30/30; after scanning every 98 reflections integral intensity was remeasured for two standard reflections 1, 1, 3 and 1, -4, 3 (their relative variations

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Table 1. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters with e.s.d.'s in Parentheses

$$U_{eq} = 1/3 \sum_j \sum_i U_{ij} a_i^* a_j^* a_i a_j$$

Atom*	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/(10^{-2} \text{ nm}^2)$
Cu-1	0.7174(2)	0.5351(2)	0.1503(2)	0.0230(5)
Cu-2	0.7813(2)	0.6205(2)	0.3491(2)	0.0303(7)
N-1a	0.641(1)	0.448(1)	-0.313(1)	0.033(4)
C-2a	0.722(1)	0.469(1)	-0.239(2)	0.039(5)
N-3a	0.731(1)	0.471(1)	-0.126(2)	0.049(5)
C-4a	0.646(1)	0.463(1)	-0.111(1)	0.026(4)
C-5a	0.556(1)	0.462(1)	-0.204(1)	0.027(4)
C-6a	0.556(2)	0.429(2)	-0.304(2)	0.049(6)
N-7a	0.486(1)	0.442(1)	-0.1580(9)	0.019(3)
C-8a	0.534(1)	0.469(1)	-0.057(1)	0.027(4)
N-9a	0.636(1)	0.483(1)	-0.018(1)	0.031(4)
C-10a	0.629(2)	0.405(2)	-0.426(2)	0.055(6)
O-11a	0.8102(8)	0.4769(8)	-0.2403(9)	0.030(3)
C-12a	0.835(1)	0.494(2)	-0.030(2)	0.045(5)
O-13a	0.467(1)	0.4231(1)	-0.392(1)	0.044(4)
C-14a	0.371(1)	0.453(1)	-0.224(1)	0.034(4)
N-1b	0.868(1)	0.723(1)	0.817(1)	0.033(4)
C-2b	0.762(1)	0.702(1)	0.719(1)	0.025(4)
N-3b	0.763(1)	0.688(1)	0.624(1)	0.017(3)
C-4b	0.849(1)	0.689(1)	0.617(1)	0.030(5)
C-5b	0.945(1)	0.719(1)	0.700(1)	0.024(4)
C-6b	0.965(1)	0.721(1)	0.812(1)	0.014(3)
N-7b	1.019(1)	0.700(1)	0.662(1)	0.044(5)
C-8b	0.957(2)	0.704(2)	0.545(2)	0.048(6)
N-9b	0.861(1)	0.689(1)	0.520(1)	0.021(3)
C-10b	0.862(1)	0.728(1)	0.921(1)	0.038(5)
O-11b	0.698(1)	0.704(1)	0.745(1)	0.063(5)
C-12b	0.665(1)	0.691(2)	0.528(1)	0.038(5)
O-13b	1.040(1)	0.746(1)	0.890(1)	0.050(4)
C-14b	1.128(2)	0.735(2)	0.727(2)	0.048(5)
I-c	1.0457(1)	0.7607(1)	0.2673(1)	0.0571(5)
O-1c	0.7597(8)	0.662(1)	0.107(1)	0.041(3)
O-2c	0.806(1)	0.724(1)	0.267(1)	0.048(4)
C-3c	0.788(1)	0.729(2)	0.168(2)	0.043(5)
C-4c	0.819(1)	0.8193(9)	0.1309(9)	0.004(3)
C-5c	0.922(1)	0.850(1)	0.166(1)	0.025(4)
C-6c	0.933(2)	0.948(2)	0.129(2)	0.050(6)
C-7c	0.867(1)	0.997(1)	0.068(1)	0.033(5)
C-8c	0.765(2)	0.979(2)	0.023(2)	0.075(8)
C-9c	0.748(1)	0.877(1)	0.059(1)	0.019(4)
I-d	0.4554(1)	0.3966(1)	0.2339(1)	0.0560(5)
O-1d	0.6893(8)	0.4266(9)	0.2270(8)	0.023(3)
O-2d	0.7410	0.499(1)	0.396(1)	0.036(3)
C-3d	0.697(1)	0.433(1)	0.323(1)	0.015(4)
C-4d	0.664(2)	0.341(2)	0.355(2)	0.061(7)
C-5d	0.575(1)	0.303(2)	0.324(2)	0.034(5)
C-6d	0.547(1)	0.219(2)	0.356(2)	0.038(5)
C-7d	0.638(2)	0.147(2)	0.433(2)	0.065(8)
C-8d	0.734(1)	0.193(1)	0.473(1)	0.021(4)
C-9d	0.765(2)	0.280(2)	0.444(2)	0.062(7)
I-e	1.0750(1)	0.4437(1)	0.5694(1)	0.0568(5)
O-1e	0.8595(8)	0.4998(8)	0.2025(8)	0.030(3)
O-2e	0.9148(9)	0.567(1)	0.370(1)	0.039(3)
C-3e	0.929(1)	0.512(2)	0.302(2)	0.034(5)
C-4e	1.036(2)	0.487(2)	0.332(2)	0.050(6)
C-5e	1.113(1)	0.456(1)	0.435(1)	0.029(4)
C-6e	1.207(1)	0.433(1)	0.443(1)	0.032(4)
C-7e	1.237(2)	0.430(2)	0.379(2)	0.050(6)

Table 1 (Continued)

Atom*	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> /(10 <sup>-2</sup> nm <sup>2</sup> )
C-8e	1.161(2)	0.462(2)	0.252(2)	0.073(8)
C-9e	1.063(1)	0.473(1)	0.249(1)	0.036(5)
I-f	0.4237(1)	0.7125(1)	-0.0704(1)	0.0587(5)
O-1f	0.5896(9)	0.6033(9)	0.1292(9)	0.029(3)
O-2f	0.6406(8)	0.6808(9)	0.2884(9)	0.031(3)
C-3f	0.575(1)	0.647(2)	0.202(1)	0.025(4)
C-4f	0.470(1)	0.680(1)	0.174(1)	0.015(4)
C-5f	0.399(2)	0.700(2)	0.065(2)	0.050(6)
C-6f	0.292(2)	0.732(2)	0.032(2)	0.051(6)
C-7f	0.267(2)	0.717(2)	0.139(2)	0.045(5)
C-8f	0.333(1)	0.702(1)	0.226(1)	0.024(4)
C-9f	0.436(1)	0.664(2)	0.262(2)	0.050(8)

\*For the atom numbering see Fig. 1.

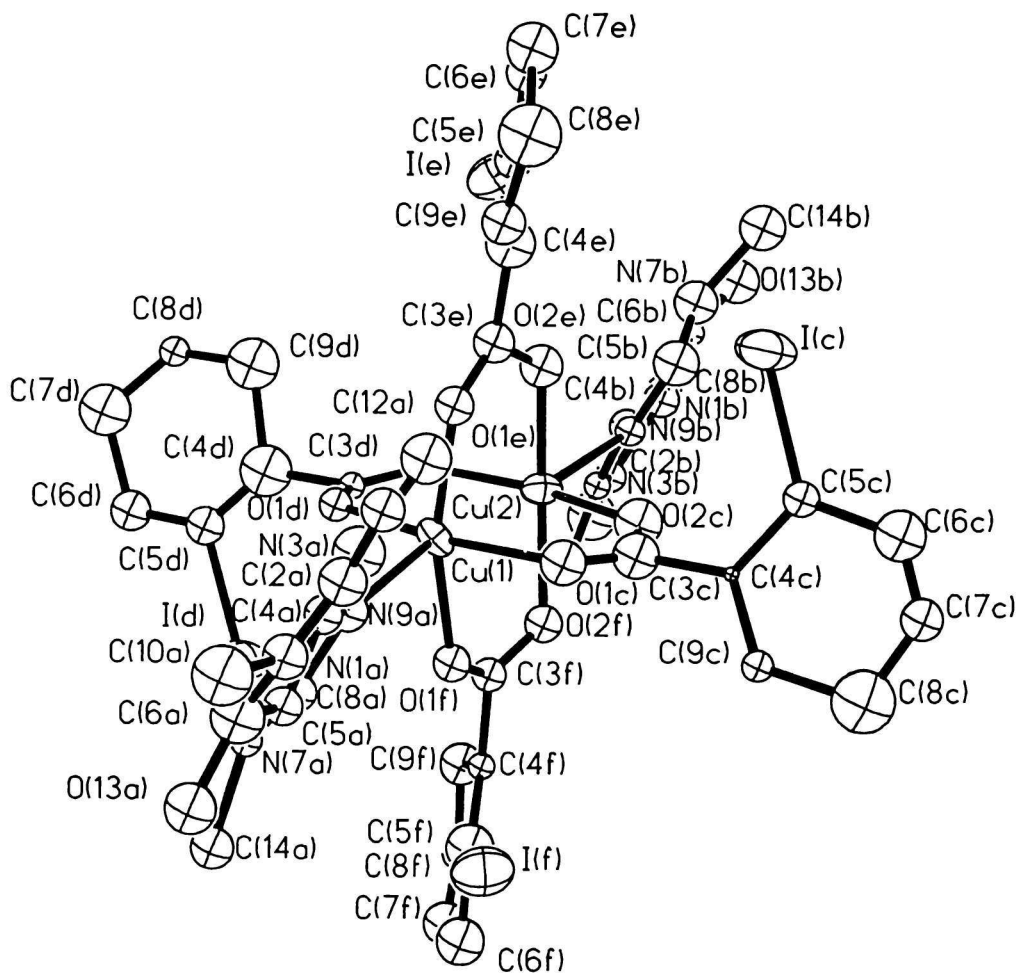


Fig. 1. Structure of the  $[\text{Cu}_2(\text{o-IC}_6\text{H}_4\text{COO})_4(\text{caffeine})_2]$  unit showing the atom numbering.

being 1.35 % and 1.01 %); the reflections intensities were corrected for the Lorentz polarization factor; absorption correction ( $\psi$ -scan) [7, 8] was applied.

The structure was solved by means of the program MULTAN 80 [9], using molecule scattering factors for the calculation of  $E$  values. After localization of all nonhydrogen atoms the structure was

transformed into the primitive unit cell with conventional space group  $P2_1$ ,  $hkl$  index range  $-15/8, 0/14, -7/15$ , and  $2\theta_{\text{max}} = 53^\circ$ . Refinement of 323 crystal structure parameters was performed by the program SHELXL-93 [10]. Temperature parameters of the copper and iodine atoms were refined anisotropically. The positions of hydrogen atoms except two

**Table 2.** Bond Distances/(10<sup>-1</sup> nm) and Angles/° with e.s.d.'s in Parentheses

Cu-1 atom surrounding: —O-1c 2.02(2), —O-1e 1.94(1), —N-9a 2.18(1)

—O-1d 1.96(1), —O-1f 1.99(1)

Cu-2 atom surrounding: —O-2c 1.94(2), —O-2e 1.98(1), —N-9b 2.30(1)

—O-2d 1.96(1), —O-2f 2.02(1)

Caffeine molecules:

Bond	a	b	Bond	a	b
N-1—C-2	1.20(2)	1.55(2)	C-4—N-9	1.36(2)	1.41(2)
N-1—C-6	1.33(2)	1.45(2)	C-5—C-6	1.45(3)	1.43(2)
N-1—C-10	1.58(3)	1.47(2)	C-5—N-7	1.44(2)	1.41(2)
C-2—N-3	1.50(3)	1.30(2)	C-6—O-13	1.33(2)	1.20(2)
C-2—O-11	1.30(2)	1.15(2)	N-7—C-8	1.29(2)	1.45(2)
N-3—C-4	1.35(2)	1.33(2)	N-7—C-14	1.53(2)	1.51(2)
N-3—C-12	1.54(2)	1.45(2)	C-8—N-9	1.36(2)	1.31(2)
C-4—C-5	1.36(2)	1.42(2)			

*o*-Iodobenzoate molecules:

Bond	c	d	e	f
I—C-5	2.11(2)	2.08(2)	2.14(2)	2.04(2)
O-1—C-3	1.19(2)	1.27(2)	1.29(2)	1.25(2)
O-2—C-3	1.26(2)	1.28(2)	1.29(2)	1.24(2)
C-3—C-4	1.48(3)	1.49(3)	1.48(3)	1.48(2)
C-4—C-5	1.42(2)	1.29(3)	1.42(3)	1.42(3)
C-4—C-9	1.32(2)	1.65(3)	1.37(3)	1.51(2)
C-5—C-6	1.47(3)	1.36(3)	1.37(2)	1.50(3)
C-6—C-7	1.17(3)	1.60(3)	1.14(3)	1.66(3)
C-7—C-8	1.36(3)	1.42(3)	1.65(3)	1.17(2)
C-8—C-9	1.55(3)	1.39(3)	1.41(3)	1.46(2)

Cu-1 atom surrounding:

N-9a—Cu-1—O-1c	93.7(6)	O-1c—Cu-1—O-1e	84.5(5)
N-9a—Cu-1—O-1d	99.8(5)	O-1c—Cu-1—O-1f	86.8(5)
N-9a—Cu-1—O-1e	107.3(5)	O-1d—Cu-1—O-1e	93.4(5)
N-9a—Cu-1—O-1f	88.0(5)	O-1d—Cu-1—O-1f	91.6(5)
O-1c—Cu-1—O-1d	166.4(5)	O-1e—Cu-1—O-1f	162.8(5)

Cu-2 atom surrounding:

N-9b—Cu-2—O-2c	98.7(5)	O-2c—Cu-2—O-2e	85.7(6)
N-9b—Cu-2—O-2d	96.1(5)	O-2c—Cu-2—O-2f	83.3(5)
N-9b—Cu-2—O-2e	89.0(5)	O-2d—Cu-2—O-2e	94.7(4)
N-9b—Cu-2—O-2f	102.2(5)	O-2d—Cu-2—O-2f	93.5(5)
O-2c—Cu-2—O-2d	165.2(6)	O-2e—Cu-2—O-2f	165.3(5)

*o*-Iodobenzoate molecules:

Bond angle	c	d	e	f
Cu-1—O-1—C-3	121(1)	124(1)	125(1)	126(1)
Cu-2—O-2—C-3	131(1)	118(1)	125(1)	117(1)
O-1—C-3—O-2	123(2)	129(2)	122(2)	127(2)
O-1—C-3—C-4	118(2)	110(2)	120(2)	118(2)
O-2—C-3—C-4	118(2)	120(2)	115(2)	114(2)
C-3—C-4—C-5	125(1)	131(2)	128(2)	121(2)
C-3—C-4—C-9	119(1)	110(2)	118(2)	116(1)
C-5—C-4—C-9	116(1)	118(2)	113(2)	122(2)
C-4—C-5—C-6	114(2)	130(2)	118(2)	123(2)
C-4—C-5—I	121(1)	114(2)	119(1)	129(2)
C-6—C-5—I	124(1)	115(1)	123(1)	107(1)

Table 2 (Continued)

*o*-Iodobenzoate molecules:

Bond angle	c	d	e	f
C-5—C-6—C-7	126(2)	116(2)	132(2)	108(2)
C-6—C-7—C-8	128(2)	112(2)	118(2)	121(2)
C-7—C-8—C-9	109(2)	131(2)	105(2)	132(2)
C-4—C-9—C-8	126(2)	110(2)	130(2)	110(2)

Caffeine molecules:

Bond angle	a	b
C-2—N-1—C-6	126(2)	125(1)
C-2—N-1—C-10	123(2)	112(1)
C-6—N-1—C-10	108(2)	122(1)
N-1—C-2—O-11	129(2)	112(2)
N-1—C-2—N-3	118(2)	116(1)
O-11—C-2—N-3	112(2)	132(2)
C-2—N-3—C-4	120(2)	120(1)
C-2—N-3—C-12	119(2)	118(1)
C-4—N-3—C-12	121(2)	121(1)
N-3—C-4—C-5	115(2)	126(2)
N-3—C-4—N-9	127(2)	127(2)
C-5—C-4—N-9	114(2)	105(2)
C-4—C-5—N-7	100(1)	108(2)
C-4—C-5—C-6	119(2)	121(2)
C-6—C-5—N-7	130(2)	125(1)
N-1—C-6—C-5	115(2)	109(1)
N-1—C-6—O-13	121(2)	118(1)
C-5—C-6—O-13	118(2)	130(2)
C-5—N-7—C-8	105(1)	101(1)
C-5—N-7—C-14	122(1)	121(2)
C-8—N-7—C-14	122(1)	128(2)
N-7—C-8—N-9	116(2)	111(2)
C-4—N-9—C-8	99(1)	109(1)
Cu-1—N-9—C-4	144(1)	
Cu-1—N-9—C-8	117(1)	
Cu-2—N-9—C-4	138(1)	
Cu-2—N-9—C-8	109(1)	

H atoms from each methyl group of caffeine were found from the difference map. Remaining hydrogen atoms of methyl groups were calculated. The parameters of hydrogen atoms were not refined. The final  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.057$  for 2536 reflections ( $|F_o| > 4\sigma(F_o)$ ), and  $R = 0.071$ , goodness of fit  $S = 0.868$ ,  $Rw = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0.170$  for all 3384 reflections. In the last refining cycles the weighting scheme  $w = 1.0/\sigma^2(F_o^2)$  was applied; in the last least-squares cycles  $(\Delta/s)_{\max} = 0.021$ ; the maximum and minimum values of the electron density difference map are  $1200 \text{ nm}^{-3}$  and  $-920 \text{ nm}^{-3}$ . The final atom parameters are listed in Table 1.

## RESULTS AND DISCUSSION

The structure of the studied complex consists of isolated units of  $[(o\text{-IC}_6\text{H}_4\text{COO})_4\text{Cu}_2(\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2)_2]$  (Fig. 1), mutually held together by van der Waals forces. Each of the copper(II) atoms is coordinated

by four oxygen atoms from the *o*-iodobenzoate groups and one nitrogen atom from the caffeine ligand, localized in the apex of a slightly distorted square pyramid. The bond lengths and angles of the compound studied here are presented in Table 2. The angle between the basal planes is small ( $2.3(6)^\circ$ ), thus the value of the distance basal plane—basal plane (Fig. 2) obtained by subtraction of the distance Cu···basal plane from the distance of Cu···Cu may be compared with the average values in Table 3. Copper(II) complexes with chloroacetate and *ortho*-iodobenzoate (Table 3) slightly differ in the displacement of the central atom from the basal plane. The complex studied here exhibits significant differences from the average values only in one bond length, *viz.* Cu-2—N-9b ( $0.230(1) \text{ nm}$ ).

In the studied compound caffeine appears as a monodentate donor ligand. The dihedral angle between pyridine and imidazole rings is  $0.4(5)^\circ$  for the caffeine ligand bonded to Cu-1 and  $3.55(4)^\circ$  for caf-

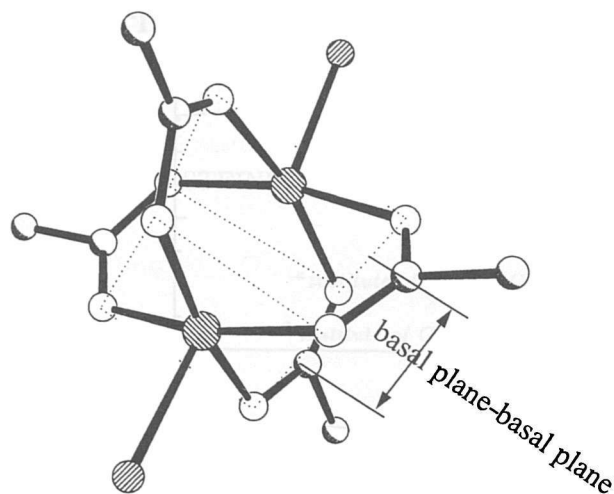


Fig. 2. Schematic drawing of the basal plane—basal plane distance.

caffeine coordinated to Cu-2.

Average bond valence sum around the copper atoms calculated by the formula

$$s = \frac{a_1}{R} + \frac{a_2}{R^2} + \frac{a_3}{R^3} + \frac{a_4}{R^4} + \frac{a_5}{R^5}$$

( $s$  is bond valence,  $R$  is bond length, and  $a_i$  are fitted parameters for Cu—O and Cu—N bonds [12, 13]) neglecting the Cu··Cu bond valence is 2.0. Supposing the fixed Cu—O bond length being 0.197 nm (Table 3), the bond valence sum ( $V$ ) around the central atom (copper atom valence [3, 4]) of CuO<sub>4</sub>N chromophore exhibits the dependence on Cu—N bond

length shown in Fig. 3, curve *a*. The most stable bond length Cu—N showing the minimum of the derivative  $dV/dR$  (Fig. 3, curve *b*) at 0.205 nm belongs to the inflection point A. But for such binuclear complex the valence sums around the copper atoms should be 2.18. The observed bond lengths Cu-1—N-9a and Cu-2—N-3b are slightly displaced from minimum into the points B and C, which could be due to the displacements of Cu-1 and Cu-2 atoms from the basal planes resulting in the stress within both CuO<sub>4</sub>N chromophores.

In the crystal structure of triaqua(caf)nitrocopper(II) nitrate [14] the caffeine molecule was found planar, while, however, in other adducts the caffeine molecules show a deviation from planarity: triphenylmethylphosphonium trichloro-(caf)-Pt(II) [15]; bis(caf)-hexaaqua-Mg(II) dibromide [16]; bis(caf)-hexaaqua-Mn(II) triiodide [16]; caffeine monohydrate hydrogen triiodide [17]; bis(barbital)-caffeine complex [18]; caffeine chloride dihydrate [19]; aqua-dichloro-caf-Cu(II) [20]; dichloro-triamine-(caf-8-yl)-Ru(III) chloride monohydrate [21]; caffeine monohydrate [22]; caffeine-5-chlorosalicylic acid complex, and *N*-acetylsulfanilamide-caffeine [23].

The benzene rings of *o*-iodobenzoates are planar. The iodine atoms are significantly deviated from the least-squares planes of benzene rings in *d*-ring (0.028(3) nm) and *f*-ring (0.017(4) nm). In the structures of *o*-iodobenzoic acid [6] and *o*-iodobenzonitrile [5] the benzene rings are almost planar. In the structure studied the carbon—carbon bond distances are in the range of 0.120(4)—0.164(4) nm (Table 2). On C-3 atoms the SP<sup>2</sup> hybridization may be proposed (sum of bond angles is in the range 357(3)—359(2)<sup>o</sup>).

Table 3. Structure and Geometric Data of Binuclear Cu(II) Complexes with CuO<sub>4</sub>N Chromophore

	[Cu <sub>2</sub> (ClCH <sub>2</sub> COO) <sub>4</sub> -(caffeine) <sub>2</sub> ]	[Cu <sub>2</sub> ( <i>o</i> -IC <sub>6</sub> H <sub>4</sub> COO) <sub>4</sub> -(caffeine) <sub>2</sub> ]	[Cu <sub>2</sub> (CH <sub>3</sub> COO) <sub>4</sub> -(4-pymet) <sub>2</sub> ]**	Mean value
Cu··Cu/(10 <sup>-1</sup> nm)	2.711(3)	2.713(2)	2.647(1)	2.67 ± 0.07
Cu—O/(10 <sup>-1</sup> nm*)	1.97 ± 0.04	1.97 ± 0.01	1.982(2)	1.97 ± 0.01
Cu—N/(10 <sup>-1</sup> nm)	2.23(4)	2.18(1) 2.30(1)	2.160(3)	2.17 ± 0.05
Cu—basal plane (10 <sup>-1</sup> nm)	0.236(1)	0.222(7) 0.253(6)	0.211(1)	0.25 ± 0.03
Sum of bond lengths Cu—O—C—O—Cu (10 <sup>-1</sup> nm)*	6.46 ± 0.05	6.47 ± 0.04	6.48(3)	6.44 ± 0.03
Sum of bond angles Cu—O—C—O—Cu (°)*	374 ± 1	372 ± 3	375.6(5)	373 ± 2
Basal plane—basal plane (10 <sup>-1</sup> nm)	2.23(1)	2.24(1)	2.226(2)	2.20 ± 0.06
References	[1]	This paper	[11]	[2]

\*Where more than two chemically equivalent distances or angles are present, the mean value is tabulated.

\*\*4-pymet = 4-pyridylmethanol.

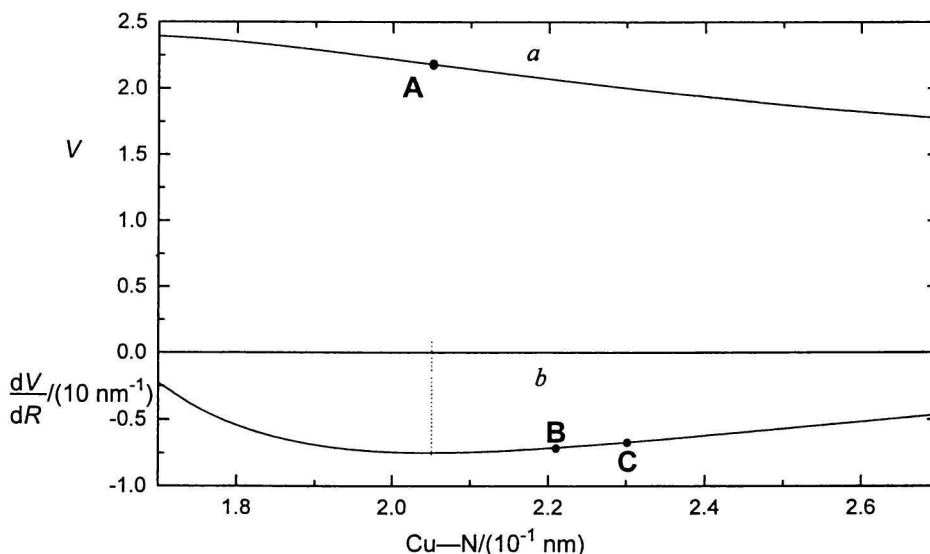


Fig. 3. Dependence of the central atom valence (a) and the derivative of central atom valence (b) of  $\text{CuO}_4\text{N}$  chromophore on the bond length  $\text{Cu—N}$ .

Small temperature vibrations of C-4c atom are probably caused by the rigidity of attached carboxylato group and the packing of binuclear structure units.

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