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Bond-valence approach to the copper–copper and copper–nitrogen bonding in binuclear copper(II) complexes: Structure of tetrakis(2-iodobenzoato)bis(caffeine)dicopper(II) at 210 K

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Abstract

The crystal structure of tetrakis(2-iodobenzoato)bis(caffeine)dicopper(II) at 210 K is monoclinic, space group $P2_1/n$ (No.14), unit cell parameters $a = 13.6090(4)$, $b = 13.5900(2)$, $c = 14.5370(4)$ Å, $\beta = 116.394(1)°$, $Z = 2$ and $D_{calc} = 2.07$ g cm^{-3}. The structure consists of centrosymmetric $[Cu_2(2IbzO)_4(caf)_2]$ units (2IbzO = 2-iodobenzoate, caf = caffeine). These binuclear units are mutually held by van der Waals forces. Cu atoms are pentacoordinated by four carboxylic O atoms in the basal plane and one apical N atom from the caffeine molecule. Cu–O bond lengths are 1.961(3), 1.969(3), 1.969(2), 1.974(3) Å, and Cu–N bond length is 2.238(3) Å. The displacement of Cu atom from the basal plane is 0.2354(4) Å. The calculated Cu(II)–N bond length by bond-valence sum model is 2.31 Å. The Cu...Cu distance is 2.7041(6) Å. The non-bonding character of Cu(II)...Cu(II) contact in 26 binuclear carboxylic complexes with CuO_4N chromophores is proved. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Bond-valence sum model; Crystal structure; Copper complex; 2-Iodobenzoate; Caffeine

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1. Introduction

Bond-valence sum model [1–8] is based on Eq. (1) introduced originally by Pauling [9,10] which holds for all atoms of the crystal structure:

$$V_i = \sum_j s_{ij} \tag{1}$$

V_i is the valence of atom i and s_{ij} is the valence of a bond between atoms i and j. For Cu–N and Cu–O bonds the bond valence can be calculated by Eq. (2) [11]:

$$s_{ij} = \frac{\alpha_1}{r_{ij}} + \frac{\alpha_2}{r_{ij}^2} + \frac{\alpha_3}{r_{ij}^3} + \frac{\alpha_4}{r_{ij}^4} + \frac{\alpha_5}{r_{ij}^5} \tag{2}$$

where r_{ij} is internuclear distance and α_i are fitted constants dependent on the types of bonded atoms. Metal–metal interactions in binuclear complexes range from non-bonding to covalent to very short metal–metal bonds found in isolated molecules [12]. In the oxo-bridged dimers Cu(II) atoms show pyramidal coordination [13,14].

Caffeine (1,3,7-trimethyl-2,6-dioxopurine) as a ligand in copper compounds was studied by X-rays in Refs. [15–22]. In our previous work [23] we studied Cu(II)...Cu(II) and Cu(II)–O bonding in binuclear complexes. The diversity of atomic temperature vibrations [24] led us to redetermine entitled structures at temperatures lower than room temperature. The bond–valence sum model may be a suitable approach to resolve the character of interatomic contacts in coordination and organometallic compounds. In this paper the apical Cu(II)–N bond length of binuclear complexes with CuO_4N chromophores are predicted.

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2. Experimental

The green–blue crystals of $C_{44}H_{36}Cu_2I_4N_8O_{12}$ compound were prepared by the method described in [24]. Intensity data of selected crystal ($0.20 \times 0.20 \times 0.30$ mm) were measured at 210 K on Enraf–Nonius DIP2020 diffractometer with graphite monochromated Mo–K_α radiation, $\lambda = 0.7107$ Å. A total of 4972 diffraction data were measured up to $\Theta_{max} = 26.6°$; $R_{int} = 0.04$. A sum of 4921 data from this set were unique and satisfying the condition $I \geq 3\sigma(I)$. Multiscan absorption correction was used [25]. The structure was solved by direct methods using program SIR 92 [26] and was refined by applying full matrix least-squares method based on F values. The calculations were done with the program system CRYSTALS [27]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were found in difference Fourier map, but not refined, in the course of further refinement of 317 parameters. The refinement converged at $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.053$ and $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2} = 0.039$. The coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms are collected in Table 1.

Table 1
Fractional atomic coordinates and U_{eq} values for $[Cu_2(2IbzO)_4(caf)_2]$ at 210 K

Atom	x	y	z	U_{eq} [a]
Cu	1.09927(3)	−0.04325(3)	0.03204(3)	0.0127(2)
I(1)	1.01551(2)	−0.18265(2)	0.29532(2))	0.0313(2)
I(2)	0.67897(2)	−0.13413(2)	−0.32612(2)	0.0325(2)
O(1)	1.0199(2)	−0.15057(1)	0.0598(2)	0.023(1)
O(2)	0.8558(2)	−0.0800(2)	0.0097(2)	0.024(1)
O(3)	1.0430(2)	−0.0913(2)	−0.11009(1)	0.022(1)
O(4)	0.8806(2)	−0.0171(2)	−0.16278(1)	0.022(1)
O(5)	1.4923(2)	−0.1092(2)	−0.0577(2)	0.0356(2)
O(6)	1.6417(2)	−0.1633(2)	0.2875(2)	0.029(2)
N(1)	1.2693(2)	−0.1043(2)	0.1133(2)	0.018(1)
N(2)	1.4110(2)	−0.1309(2)	0.2671(2)	0.020(2)
N(3)	1.3755(2)	−0.1079(2)	0.0146(2)	0.018(1)
N(4)	1.5651(2)	−0.1373(2)	0.1141(2)	0.023(2)
C(1)	0.9223(3)	−0.1488(3)	0.0461(2)	0.016(2)
C(2)	0.8817(3)	−0.2421(3)	0.0726(3)	0.018(2)
C(3)	0.8056(3)	−0.2998(3)	−0.0062(3)	0.020(2)
C(4)	0.7743(3)	−0.3903(3)	0.0150(3)	0.025(2)
C(5)	0.8157(3)	−0.4245(3)	0.1151(3)	0.029(2)
C(6)	0.8875(3)	−0.3658(3)	0.1952(3)	0.025(2)
C(7)	0.9196(3)	−0.2754(3)	0.1730(3)	0.019(2)
C(8)	0.9491(3)	−0.0672(2)	−0.1775(3)	0.018(2)
C(9)	0.9202(3)	−0.0990(3)	−0.2853(3)	0.012(2)
C(10)	0.8145(3)	−0.1247(3)	−0.3581(3)	0.019(2)
C(11)	0.7946(3)	−0.1491(3)	−0.4580(3)	0.024(2)
C(12)	0.8786(4)	−0.1456(3)	−0.4866(3)	0.031(2)
C(13)	0.9834(4)	−0.1208(3)	−0.4155(3)	0.0347(2)
C(14)	1.0040(3)	−0.0988(3)	−0.3160(3)	0.026(2)
C(15)	1.3032(3)	−0.1157(3)	0.2144(3)	0.022(2)
C(16)	1.4747(3)	−0.1401(4)	0.3784(3)	0.0328(2)
C(17)	1.4518(3)	−0.1289(3)	0.1959(3)	0.019(2)
C(18)	1.3641(3)	−0.1128(2)	0.1027(3)	0.016(2)
C(19)	1.2793(3)	−0.1006(3)	−0.0858(3)	0.0273(2)
C(20)	1.4779(3)	−0.1168(3)	0.0182(3)	0.021(2)
C(21)	1.6716(3)	−0.1580(4)	0.1153(4)	0.0365(2)
C(22)	1.5605(3)	−0.1454(3)	0.2078(3)	0.019(2)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j\ a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j^*$.

3. Discussion

The structure consists of centrosymmetric binuclear $[Cu_2(2IbzO)_4(caf)_2]$ units mutually held by van der Waals forces (Fig. 1). The structure of one $[Cu_2(2IbzO)_4(caf)_2]$ unit with atomic labelling is shown in Fig. 2. Bond distances and angles are listed in Tables 2 and 3. Within each unit two copper atoms are coordinated by four oxygen atoms from the 2-iodobenzoate groups. The Cu...Cu[1] distance is 2.7041(6) Å. Regarding such contact as non-bonding and oxidation state of both central atoms having a value of 2, the rule (Eq. (1)) for both copper atoms implies the relation $V_o + s_{Cu-N} = 2$. V_o is the bond-valence sum calculated by Eqs. (1) and (2) using bond lengths Cu–O(1), Cu–O(2)^i, Cu–O(3), Cu–O(4)^i. The quantity s_{Cu-N} is bond valence for apical Cu–N(1) bond. Inserting the function (2) for s_{Cu-N} we get the following equation:

$$V_o + \frac{\alpha_1}{r} + \frac{\alpha_2}{r^2} + \frac{\alpha_3}{r^3} + \frac{\alpha_4}{r^4} + \frac{\alpha_5}{r^5} = 2 \qquad (3)$$

The constants α_i for the Cu–N bond are tabulated in [11]. r is the predicted Cu(II)–N(1) bond length. Rearrangement of the Eq. (3) leads to the polynomial equation for r:

$$(V_o - 2)r^5 + \alpha_1 r^4 + \alpha_2 r^3 + \alpha_3 r^2 + \alpha_4 r + \alpha_5 = 0 \qquad (4)$$

Solutions of Eq. (4) for binuclear carboxylic compounds with CuO_4N chromophores found in Cambridge Structural Database System [28] are collected in Table 4. Refcodes of the compounds are listed in Table 5. Only the structures with no disordered non-hydrogen ligand atoms were accepted. Structures with at least one disordered non-hydrogen ligand atom were excluded. To avoid the experimental errors only the structures with R values less then 0.06 are included. The reliability factor[2] for the calculated Cu(II)–N bond lengths 0.044 demonstrates the non-bonding character of

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[1] Operation of symmetry (i) is defined throughout the paper as $-x+2,\ -y,\ -z$.

[2] $\rho = \Sigma|r_o - r_c|/\Sigma r_o$.

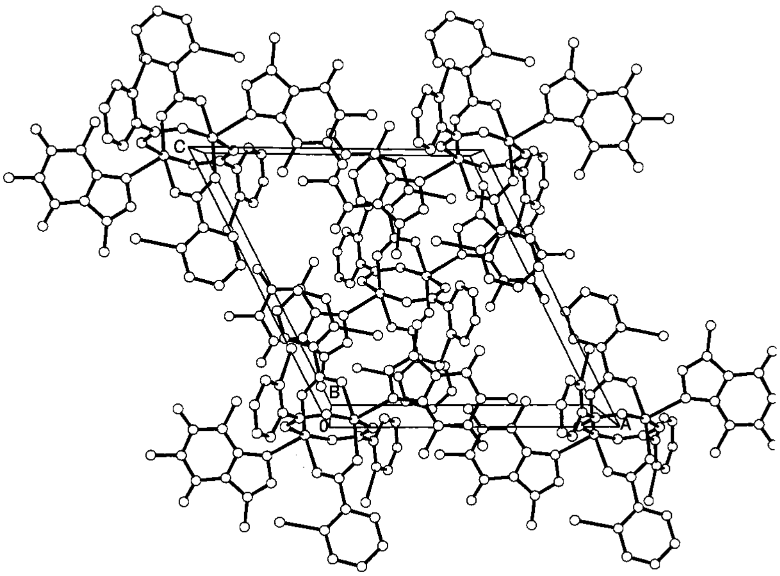

Fig. 1. Crystal structure of [$Cu_2(2IbzO)_4(caf)_2$] at 210 K viewed along the *b* axis.

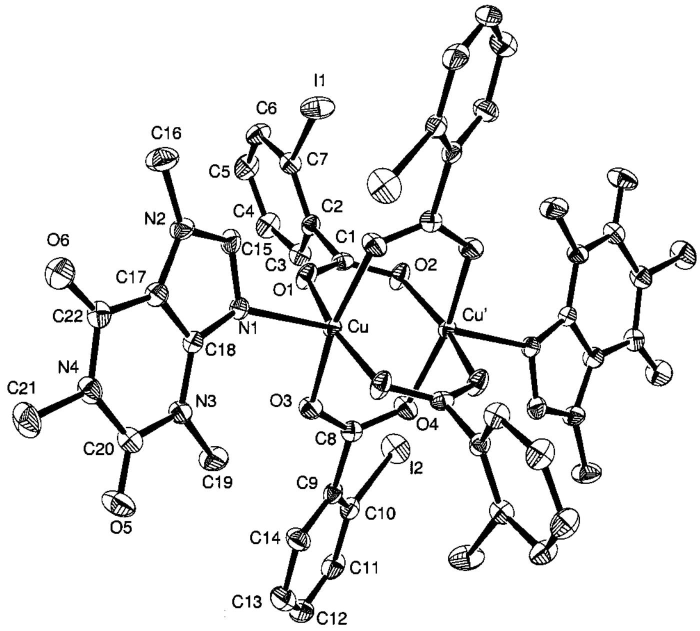

Fig. 2. Molecular structure of [$Cu_2(2IbzO)_4(caf)_2$] at 210 K (with thermal ellipsoids at the 50% probability level). H atoms are omitted.

Cu(II)…Cu(II) contacts in the studied set of compounds. This value is greater than the reliability factor 0.016 [23] for predicted apical Cu(II)–O bond lengths of binuclear complexes with Cu(II)O_5 chromophores. Such difference of reliability factors is caused by a greater slope in the bond valence curve for the Cu–N bond as compared with the Cu–O bond within the studied range of internuclear distances (2.05–2.31 Å) and by greater structural stability of the central atom valence for CuO_5 chromophore than for the CuO_4N chromophore [11]. All calculated copper atom bond valence sums in Table 4 are greater or very close to 2 which indicates the non-significant contribution of Cu…Cu contacts to the central atom valences. The mean copper atom valence

Table 2
Bond lengths (Å) for $[Cu_2(2IbzO)_4(caf)_2]$ at 210 K

Cu–O(1)	1.961(3)	N(1)–C(15)	1.339(5)	C(3)–C(4)	1.380(6)
Cu–O(2)^{i}	1.969(3)	N(1)–C(18)	1.371(5)	C(4)–C(5)	1.386(6)
Cu–O(3)	1.969(2)	N(2)–C(15)	1.335(5)	C(5)–C(6)	1.391(6)
Cu–O(4)^{i}	1.974(3)	N(2)–C(16)	1.462(5)	C(6)–C(7)	1.389(6)
Cu–N(1)	2.238(3)	N(2)–C(17)	1.375(5)	C(8)–C(9)	1.500(6)
Cu…Cu^{i}	2.7041(6)	N(3)–C(18)	1.358(5)	C(9)–C(10)	1.399(6)
O(1)–C(1)	1.253(5)	N(3)–C(19)	1.468(5)	C(9)–C(14)	1.397(6)
O(2)–C(1)	1.244(5)	N(3)–C(20)	1.376(5)	C(10)–C(11)	1.394(6)
O(3)–C(8)	1.260(5)	N(4)–C(20)	1.399(5)	C(11)–C(12)	1.380(7)
O(4)–C(8)	1.247(5)	N(4)–C(21)	1.469(6)	C(12)–C(13)	1.380(7)
O(5)–C(20)	1.208(5)	N(4)–C(22)	1.395(5)	C(13)–C(14)	1.378(6)
O(6)–C(22)	1.218(5)	C(1)–C(2)	1.500(6)	C(17)–C(18)	1.368(6)
I(1)–C(7)	2.095(4)	C(2)–C(3)	1.395(6)	C(17)–C(22)	1.429(6)
I(2)–C(10)	2.097(5)	C(2)–C(7)	1.390(6)		

is 2.05 ± 0.05. For both kinds of binuclear complexes with Cu(II)O$_5$ and Cu(II)O$_4$N chromophores all copper atom electrons sharing the bonds are involved in Cu–O and Cu–N bonds.

Within each $[Cu_2(2IbzO)_4(caf)_2]$ unit the atoms O(1), O(3), O(2)^1 and O(4)^1 do not deviate significantly from planarity. Two nitrogen atoms of two caffeine ligands complete the coordination polyhedrons of copper atoms to the deformed tetragonal pyramids. The copper atoms are displaced 0.2354(4) Å from the basal plane toward the apical Cu–N(1) bonds. The benzene rings of both 2IbzO ligands are slightly deviated from planarity. Atoms I(1) and I(2) are deviated from the least-square planes of their benzene rings 0.2370(3) and 0.0375(3) Å. The torsion angles O(2)–C(1)–C(2)–C(7) and O(4)–C(8)–C(9)–C(10) are –113.9(4) and −35.3(5)°. The caffeine molecule is weakly deviated from planarity. The dihedral angle created by the least-squares planes of the caffeine pyridine and imidazole rings is 1.1(1)°. The torsion angle O(1)–Cu–N(1)–C(15) is −62.6(3)°. The lengths of bonds N(1)–C(18), N(3)–C(18), N(3)–C(19) and O(6)–C(22) slightly differ within the range 0.032–0.062 Å from the same bonds in the structure of caffeine [45].

4. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 139 369 for compound tetrakis(2-iodobenzoato)bis(caffeine)dicopper(II). Copies of this information maybe obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 3
Selected bond angles (°) for $[Cu_2(2IbzO)_4(caf)_2]$ at 210 K

O(1)–Cu–O(3)	88.7(1)	O(1)–C(1)–O(2)	127.0(4)
O(2)^{i}–Cu–O(3)	89.3(1)	O(1)–C(1)–C(2)	115.4(3)
O(1)–Cu–N(1)	98.7(1)	O(2)–C(1)–C(2)	117.6(4)
O(3)–Cu–N(1)	105.0(1)	I(1)–C(7)–C(2)	119.7(3)
Cu^{i}…Cu–O(1)	80.60(8)	I(1)–C(7)–C(6)	118.5(3)
Cu^{i}…Cu–O(3)	85.40(9)	C(2)–C(7)–C(6)	121.6(4)
Cu^{i}…Cu–O(2)	85.62(9)	O(3)–C(8)–O(4)	125.8(4)
Cu^{i}…Cu–O(4)	80.84(8)	O(3)–C(8)–C(9)	116.2(4)
Cu–O(1)–C(1)	126.5(3)	O(4)–C(8)–C(9)	117.9(4)
Cu^{i}–O(2)–C(1)	120.2(3)	I(2)–C(10)–C(9)	123.9(3)
Cu–O(3)–C(8)	121.1(3)	I(2)–C(10)–C(11)	115.7(3)
Cu^{i}–O(4)–C(8)	126.7(3)	N(1)–C(15)–N(2)	113.7(4)
Cu–N(1)–C(18)	140.9(2)	N(2)–C(17)–C(22)	130.4(4)
Cu–N(1)–C(15)	113.1(3)	N(2)–C(17)–C(18)	106.4(4)
C(18)–N(1)–C(15)	103.4(3)	C(22)–C(17)–C(18)	123.1(4)
C(17)–N(2)–C(15)	105.9(3)	N(1)–C(18)–C(17)	110.7(4)
C(17)–N(2)–C(16)	126.5(3)	N(3)–C(18)–N(1)	127.6(3)
C(15)–N(2)–C(16)	127.4(3)	N(3)–C(18)–C(17)	121.8(4)
C(19)–N(3)–C(20)	119.0(3)	O(5)–C(20)–N(3)	122.0(4)
C(19)–N(3)–C(18)	121.0(3)	O(5)–C(20)–N(4)	121.1(4)
C(20)–N(3)–C(18)	119.9(3)	N(3)–C(20)–N(4)	116.8(3)
C(20)–N(4)–C(22)	127.0(3)	O(6)–C(22)–N(4)	121.9(4)
C(20)–N(4)–C(21)	116.4(3)	O(6)–C(22)–C(17)	126.8(4)
C(22)–N(4)–C(21)	116.5(3)	N(4)–C(22)–C(17)	111.3(3)

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Table 4
Cu…Cu distances of selected binuclear carboxylic copper(II) complexes with experimental and observed apical Cu(II)–N bond lengths

Ref. code	Cu…Cu contact length (Å)	Experimental apical Cu–N bond length (Å)	Calculated apical Cu(II)–N bond length (Å)	Copper atom bond valence sum
ACAPU01	2.673(1)	2.246(4)	2.26	2.01
CIBHEA	2.685(1)	2.151(4)	2.23	2.06
JITGAU	2.634(2)	2.217(5)	2.32	2.07
JOGMUN	3.087(1)	2.054(4), 2.062(4)	1.98, 2.06	1.94, 2.00
JOSROY	2.683(2)	2.229(5)	2.28	2.04
KUHFUO	3.062(7)	2.045(3)	2.13	2.06
KUHGID	2.951(1)	2.120(5), 2.114(5)	2.18, 2.23	2.04, 2.08
MQCUAC20	2.651(2)	2.226(6)	2.26	2.02
NEHSUO	2.651(1)	2.217(3)	2.32	2.07
RERTAJ	2.735(1)	2.131(3)	2.32	2.14
RERTEN	2.757(1)	2.162(3)	2.28	2.08
RERTIR	2.725(1)	2.123(4), 2.121(4)	2.24, 2.25	2.09, 2.09
RERTOX	2.729(2)	2.128(7)	2.26	2.10
SIZSAV	2.736(1)	2.182(2)	2.24	2.04
SIZSEZ	2.694(1)	2.148(2), 2.141(2)	2.27, 2.26	2.09, 2.09
SIZSID	2.665(1)	2.166(2)	2.28	2.08
SIZSUP	2.621(2), 2.634(2)	2.175(8), 2.178(7)	2.24, 2.28	2.05, 2.07
SIZTAW	2.641(2)	2.185(3)	2.28	2.07
VEYGOV	2.658(1)	2.155(3)	2.27	2.08
VUBSIU	2.679(1)	2.152(6), 2.147(6)	2.24, 2.31	2.07, 2.11
WABNUI	2.648(1)	2.160(3)	2.23	2.05
WAZTIA	2.907(1)	2.286(4), 2.306(4)	2.23, 2.18	1.96, 1.91
ZAHLUP	2.678	2.161, 2.134	2.28, 2.28	2.09, 2.10
ZENFAZ	2.611(1)	2.163(6)	2.28	2.08
ZEZHOB	2.689(1)	2.176(4)	2.28	2.07
Present structure	2.7041(6)	2.238(3)	2.31	2.05

Table 5
Refcodes for binuclear copper(II) complexes

Ref. code	Compound	Reference
ACAPU01	Bis(bis(μ-acetato-*O*,*O*′)-(alpha-picolinato)-copper(II))	[29]
CIBHEA	Tetrakis(μ-phenylthio-acetato)-bis(pyridine-copper(II))	[30]
JITGAU	Catena-(tetrakis(μ-acetato-*O*,*O*′)-(2-amino-pyrimidine-*N*,*N*′)-di-copper(II))	[31]
JOGMUN	Tetrakis(*μ*-triphenylacetato-*O*,*O*′)-bis(pyridine)-di-copper(II) benzene solvate	[32]
JOSROY	Catena(tetrakis(μ-acetato-*O*,*O*′)-(μ-1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane-*N*,*N*′)-di-copper(II))	[33]
KUHFUO	Tetrakis(μ-trichloroacetato-*O*,*O*′)-bis(caffeine)-di-copper(II)	[34]
KUHGID	Tetrakis(μ-trichloroacetato)-bis(2,5-dichloropyridine)-di-copper(II)	[34]
MQCUAC20	Tetrakis(μ-acetato)-bis(quinoline-copper(II))	[35]
NEHSUO	Tetrakis(μ-acetato)-bis((1-(pyridine-2-thio)-2-(2-pyridyl)ethane)-copper(II))	[36]
RERTAJ	Tetrakis(μ-benzoylformato-*O*,*O*′)-bis(pyridine)-di-copper(II)	[37]
RERTEN	Tetrakis(μ-benzoylformato-*O*,*O*′)-bis(2-picoline)-di-copper(II)	[37]
RERTIR	Tetrakis(μ-benzoylformato-*O*,*O*′)-bis(3-picoline)-di-copper(II) monobenzene solvate	[37]
RERTOX	Tetrakis(μ-benzoylformato-*O*,*O*′)-bis(4-picoline)-di-copper(II)	[37]
SIZSAV	Bis(bis(μ-acetato-*O*,*O*′)-(alpha-picolinato)-copper(II))	[29]
SIZSEZ	Bis(bis(μ-acetato-*O*,*O*′)-(alpha-picolinato)-copper(II))	[29]
SIZSID	Bis(bis(μ-acetato-*O*,*O*′)-(alpha-picolinato)-copper(II))	[29]
SIZSUP	Bis(bis(μ-acetato-*O*,*O*′)-(alpha-picolinato)-copper(II))	[29]
SIZTAW	Bis(bis(μ-acetato-*O*,*O*′)-(alpha-picolinato)-copper(II))	[29]
VEYGOV	Tetrakis(μ-acetato)-bis(2-aminothiazole)-di-copper	[38]
VUBSIU	Tetrakis(μ-2-chlorobenzoato-*O*,*O*′)-bis(pyridine-copper(II)) carbon tetrachloride solvate	[39]
WABNUI	Tetrakis(μ-acetato-*O*,*O*′)-bis(4-pyridylmethanol-*N*)-di-copper(II)	[40]
WAZTIA	Bis(2,6-dimethylpyridine)-tetrakis(μ-2-methyl-2-phenylpropanoato-*O*,*O*′)-di-copper(II) benzene solvate	[41]
ZAHLUP	Tetrakis(μ-benzoato-*O*,*O*′)-bis(2-aminothiazole-*N*)-di-copper(II)	[42]
ZENFAZ	Tetrakis(μ-benzoato-*O*,*O*′)-bis(*N*,*N*-diethylnicotinamide-*N*′)-dicopper(II)	[43]
ZEZHOB	Tetrakis(μ-benzoato-*O*,*O*′)-bis(2-aminopyridyl)-di-copper(II) tetrahydrofuran solvate	[44]

References

[1] G. Donnay, R. Allmannn, Am. Mineral. 55 (1970) 1003.
[2] G. Donnay, J.D.H. Donnay, Acta Crystallogr. Sect. B 29 (1966) 1417.
[3] I.D. Brown, I.D. Shannon, Acta Crystallogr. Sect. A 29 (1973) 266.
[4] I.D. Brown, Chem. Soc. Rev. 7 (1978) 359.
[5] I.D. Brown, The bond-valence method: An empirical approach to chemical structure and bonding, in: M. O'Keefe, A. Navrotsky (Eds.), Structure and Bonding in Crystals, vol. 2, Academic Press, New York, 1981, pp. 1–30 and references therein.
[6] M. O'Keefe, Struct. Bonding (Berlin) 71 (1989) 161 and references therein.
[7] I.D. Brown, Acta Crystallogr. Sect. B 48 (1992) 553.
[8] N.E. Brese, M. O'Keefe, Acta Crystallogr. Sect. B 47 (1991) 192.
[9] L. Pauling, J. Am. Chem. Soc. 51 (1929) 1010.
[10] L. Pauling, J. Am. Chem. Soc. 69 (1947) 542.
[11] F. Valach, Polyhedron 18 (1999) 699.
[12] F.A. Cotton, R.A. Walton, Multiple Bonds Between Metal Atoms, Wiley, New York, 1982.
[13] M. Melník, Coord. Chem. Rev. 42 (1982) 259.
[14] M. Melník, M. Kabešová, M. Dunaj-Jurčo, C.E. Holloway, J. Coord. Chem. 41 (1997) 35.
[15] M.B. Cingi, A.C. Willa, A.G. Manfredotti, C. Gaustini, Cryst. Struct. Commun. 1 (1972) 363.
[16] G. Bandoli, M.C. Biagini, D.A. Clemente, G. Rizzardi, Inorg. Chem. 20 (1976) 71.
[17] B. Koreň, F. Valach, P. Sivý, M. Melník, Acta Crystallogr. Sect. C 41 (1985) 1160.
[18] H. Horie, S. Husebye, M. Kato, E.A. Meyers, Y. Muto, I. Suzuki, T. Tokii, R.A. Zingaro, Acta Chem. Scand. A40 (1986) 579.
[19] M. Melník, M. Koman, T. Glowiak, Polyhedron 17 (1998) 1767.
[20] T. Kawata, H. Uekusa, S. Ohba, T. Furukawa, T. Tokii, Y. Muto, M. Kato, Acta Crystallogr. Sect. B 48 (1992) 253.
[21] H. Uekusa, S. Ohba, T. Tokii, Y. Muto, M. Kato, S. Husebye, O.W. Steward, S.-C. Chang, J.P. Rose, J.F. Pletcher, I. Suzuki, Acta Crystallogr. Sect. B 48 (1992) 650.
[22] A. Harada, M. Tsuchimoto, S. Ohba, K. Iwasawa, T. Tokii, Acta Crystallogr. Sect. B 53 (1997) 654.
[23] F. Valach, M. Tokarčík, T. Maris, D.J. Watkin, C.K. Prout, Z. Kristallogr. 215 (2000) 56.
[24] F. Valach, B. Koreň, M. Tokarčík, M. Melník, Chem. Papers 52 (1998) 140.
[25] D.J. Watkin, C.K. Prout, P.M. de Q. Lilley, RC93, Chemical Crystallography Laboratory, Oxford, UK, 1994.
[26] A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Cryst. (1994) 435.
[27] D.J. Watkin, C.K. Prout, J.R. Currathers, P.W. Betteridge, CRYSTALS Issue 10, Chemical Crystallography Laboratory, Oxford, UK, 1996.
[28] F.H. Allen, O. Kennard, Chem. Design Automation News. 8 (1993) 31.
[29] M. Yamanaka, H. Uekusa, S. Ohba, Y. Saito, S. Iwata, M. Kato, T. Tokii, Y. Muto, O.W. Steward, Acta Crystallogr. Sect. B 47 (1991) 344.
[30] E.J. O'Reilly, G. Smith, C.H.L. Kennard, T.C.W. Mak, W.-H. Yip, Inorg. Chim. Acta 83 (1984) L63.
[31] G. Smith, C.H.L. Kennard, H.L. Colin, K.A. Byriel, Polyhedron 10 (1991) 873.
[32] O.W. Steward, M. Kato, S.-C. Chang, M. Sax, C.-H. Chang, C.F. Jury, Y. Muto, T. Tokii, T. Taura, J.F. Pletcher, C. Soo Yoo, Bull. Chem. Soc. Jpn. 64 (1991) 3046.
[33] W.G. Haanstra, W.L. Driessen, J. Reedijk, J.S. Wood, Acta Crystallogr. Sect. C 48 (1992) 1405.
[34] H. Uekusa, S. Ohba, T. Tokii, Y. Muto, M. Kato, S. Husebye, O.W. Steward, S.-C. Chang, J.P. Rose, F. Pletcher, I. Suzuki, Acta Crystallogr. Sect. B 48 (1992) 650.
[35] Y.A. Simonov, V.I. Ivanov, A.V. Ablov, L.N. Milkova, T.I. Malinovskii, Zh. Strukt. Khim. 17 (1976) 516.
[36] S.C. Davies, M.C. Durrant, D.L. Hughes, K. Leidenberger, C. Stapper, R.L. Richards, J. Chem. Soc., Dalton Trans. (1997) 2409.
[37] A. Harada, M. Tsuchimoto, S. Ohba, K. Iwasawa, T. Tokii, Acta Crystallogr. Sect. B 53 (1997) 654.
[38] A.S. Antsyshkina, M.A. Porai-Koshits, D.A. Garnovskii, A.P. Sadimenko, O.A. Osipov, A.D. Garnovskii, Zh. Strukt. Khim. 30 (1989) 156.
[39] T. Kawata, S. Ohba, T. Tokii, Y. Muto, M. Kato, Acta Crystallogr. Sect. C 48 (1992) 1590.
[40] N.N. Hoang, F. Valach, M. Melni'k, Acta Crystallogr. Sect. C 49 (1993) 467.
[41] T. Fujita, S. Ohba, M. Nagamatsu, T. Tokii, C.F. Jury, O.W. Steward, M. Kato, Acta Crystallogr. Sect. C 49 (1993) 2095.
[42] D.-M. Wang, Y.-M. Hou, R.-N. Yang, X.-Y. Hu, B.-Y. Xuo, D.-M. Jin, L.-R. Chen, B.-S. Luo, J. Huaxue, J. Struct. Chem. 14 (1995) 300.
[43] T. Hokelek, H. Necefoglu, M. Balci, Acta Crystallogr. Sect. C 51 (1995) 2020.
[44] R.-N. Yang, D.-M. Wang, Y.-M. Hou, B.-Y. Xue, D.-M. Jin, L.-R. Chen, B.-S. Luo, Acta Chem. Scand. 49 (1995) 771.
[45] D.J. Sutor, Acta Crystallogr. 11 (1958) 453.