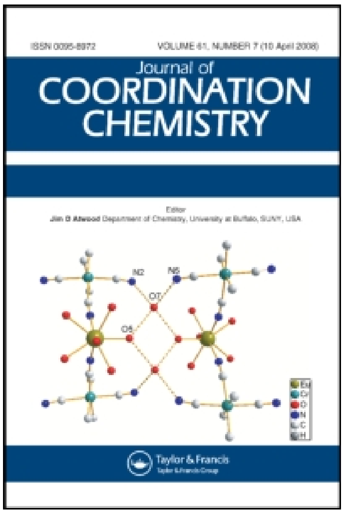

**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# Self-assembly of hydrogen-bonded supramolecular structures of two copper(II) 2-bromobenzoate complexes with 4-pyridylmethanol and nicotinamide

Jan Moncol[a]; Jaroslava Maroszova[a]; Marian Koman[a]; Milan Melnik[a]; Marian Valko[b]; Milan Mazur[b]; Tadeusz Lis[c]
[a] Institute of Inorganic Chemistry, Technology and Materials, Slovak, Technical University, Bratislava, Slovakia [b] Institute of Physical Chemistry and Chemical Physics, Slovak, Technical University, Bratislava, Slovakia [c] Faculty of Chemistry, University of Wrocław, Wrocław, Poland

**To cite this Article** Moncol, Jan , Maroszova, Jaroslava , Koman, Marian , Melnik, Milan , Valko, Marian , Mazur, Milan and Lis, Tadeusz(2008) 'Self-assembly of hydrogen-bonded supramolecular structures of two copper(II) 2-bromobenzoate complexes with 4-pyridylmethanol and nicotinamide', Journal of Coordination Chemistry, 61: 23, 3740 — 3752

**To link to this Article: DOI:** 10.1080/00958970802146031

**URL:** http://dx.doi.org/10.1080/00958970802146031

*Journal of Coordination Chemistry*
Vol. 61, No. 23, 10 December 2008, 3740–3752

Taylor & Francis
Taylor & Francis Group

# Self-assembly of hydrogen-bonded supramolecular structures of two copper(II) 2-bromobenzoate complexes with 4-pyridylmethanol and nicotinamide

JAN MONCOL*†, JAROSLAVA MAROSZOVA†, MARIAN KOMAN†,
MILAN MELNIK†, MARIAN VALKO‡, MILAN MAZUR‡
and TADEUSZ LIS§

†Institute of Inorganic Chemistry, Technology and Materials, Slovak, Technical University,
Radlinského 9, SK-812 37, Bratislava, Slovakia
‡Institute of Physical Chemistry and Chemical Physics, Slovak, Technical University,
Radlinského 9, SK-812 37, Bratislava, Slovakia
§Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie St, 50-383, Wrocław, Poland

(*Received 22 August 2007; in final form 19 March 2008*)

The structures of [$Cu(2\text{-}Brbz)_2(4PM)_2(H_2O)$] (**1**) and [$Cu(2\text{-}Brbz)_2(NIA)2$] · $2H_2O$ **2** [where 2-Brbz is the 2-bromobenzoate anion, 4-PM is the 4-pyridylmethanol and NIA is nicotinamide] have been determined by X-ray and characterized by EPR spectroscopy. The $Cu^{2+}$ cation in **1** is coordinated by a pair of oxygens from monodentate 2-bromobenzoate anions by a pair of pyridine nitrogens from monodentate 4-pyridylmethanol ligands and finally by a water forming a tetragonal-pyramidal coordination polyhedron. The $Cu^{2+}$ cation in **2** is coordinated by two pairs of oxygens from the asymmetric bidentate 2-bromobenzoate anions and by a pair of pyridine nitrogen atoms from the monodentate nicotinamide in trans positions, forming an extremely elongated bipyramid. The molecules of both complexes are linked by O–H $\cdots$ O, C–H $\cdots$ O and for **2** by N–H $\cdots$ O hydrogen bonds, which create three-dimensional hydrogen-bonding networks. EPR spectra of **1** and **2** are in agreement with X-ray data. Nicotinamide as well as 4-pyridylmethanol are suitable ligands for construction of hydrogen bonding coordination polymers.

*Keywords*: Copper; Carboxylate complexes; Crystal structure; Hydrogen bonds

## 1. Introduction

Carboxylato-copper(II) complexes are interesting from both chemical and biological points of view. The different coordination of carboxyl group to the central atom leads to formation of compounds with distinct crystal structures. Some derivatives of benzoic acid (salicylic acid and its derivatives, fenamates), in particular, possess very interesting pharmaceutical properties and constitute an important group of non-steroid anti-rheumatic drugs [1–3].

---

*Corresponding author. Email: jan.moncol@stuba.sk

*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802146031

Construction of metal-containing supramolecular systems, with coordination complexes connected by hydrogen-bonding motifs, has attracted interest because of their intriguing structural features and potential in catalysis, separation, gas storage, magnetic and non-linear optic materials [4, 5]. The resulting networks of coordination complexes with self-assembly through hydrogen bonds create 1-D (e.g. linear or zig-zag chains), 2-D (e.g. hexagonal or square grids) or 3-D (e.g. cubic or diamondoid lattice) structures [6]. Strong hydrogen bonds such as O–H $\cdots$ O, O–H $\cdots$ N, N–H $\cdots$ O and N–H $\cdots$ N are useful for construction of self-assembly hydrogen-bond networks. The ligands containing $-NH_2$, –OH, $-CO_2H$, $-CONH_2$ and –CONHR form coordination polymers via strong hydrogen bonding [7]. Typical examples of ligands used for the construction of hydrogen-bonded coordination networks are pyridinecarboxylic acid and their derivatives such as pyridinecarboxamide [7]. For example, hydrogen-bonded coordination networks based on nicotinamide, isonicotinamide and its derivatives have been extensively studied [8–23].

In this paper, the results on structural and spectral investigations of two copper(II) 2-bromobenzoate complexes with 4-pyridylmethanol (**1**), and nicotinamide (**2**) are presented.

## 2. Results and discussion

### 2.1. *Description of the structures*

**2.1.1. Crystal structure of [Cu(2-Brbz)$_2$(4PM)$_2$(H$_2$O)].** The coordination polyhedron around copper in **1** (figure 1) is tetragonal pyramidal (4 + 1). The tetragonal plane is built up by a pair of unidentate 2-bromobenzoate anions using carboxyl oxygens [Cu–O3 = 1.965(2) Å and Cu–O5 = 1.981(2) Å] and by a pair of neutral 2-pyridylmethanol molecules using pyridine ring nitrogens [Cu–N1 = 2.026(2) Å and Cu–N2 = 2.033(2) Å] (table 1) in *trans* positions, forming the basal plane. The axial position is occupied by a water molecule [Cu–O1W = 2.220(2) Å]. The O3–Cu–O5 and N1–Cu–N2 bond angles are 177.69(8)° and 173.58(9)°, respectively. The Cu atom lies in the equatorial plane O3–N1–O5–N2. For this type of five-coordinate structure, the parameter $\tau$ [$\tau = (\alpha - \beta)/60$], (where $\alpha$ and $\beta$ are the equatorial angles) was introduced by Addison *et al.* [24]. The $\tau$ value is 0 for perfectly square-pyramidal geometry and 1 for perfectly trigonal-bipyramidal geometry. In the case of **1**, $\tau = 0.07$, indicating tetragonal-pyramidal geometry. The square-pyramidal stereochemistry is known for pyridine nitrogen base adducts of copper(II) benzoates and 4-bromobenzoate, where three complexes, aqua-*bis*(benzoato-*O*)-*bis*(pyridine-*N*)copper(II) [25], aqua-*bis*(benzoato-*O*)-*bis*(4-methylpyridine-*N*) copper(II) [26] and aqua-*bis*(4-bromobenzoato-*O*)-*bis*(pyridine-*N*) copper(II) [27] have the same coordination. All these three complexes have tetragonal geometry with $\tau$ parameters of 0.16, 0.22 and 0.21, respectively.

Complex **1** can be compared with [Cu(clof)$_2$(4PM)$_2$(H$_2$O)] $\cdot$ 2H$_2$O (clof$^-$ = clofibriate anions) [29], which has the same penta-coordination, but the copper atom lies on a twofold rotation axis. A paddle-wheel dinuclear complex [Cu$_2$(CH$_3$CO$_2$)$_4$(4PM)$_2$] [30] is another example with the terminal 4-pyridylmethanol ligand; [CuCl(4PM)$_4$]Cl [31] is also known, containing terminal 4-pyridylmethanol.

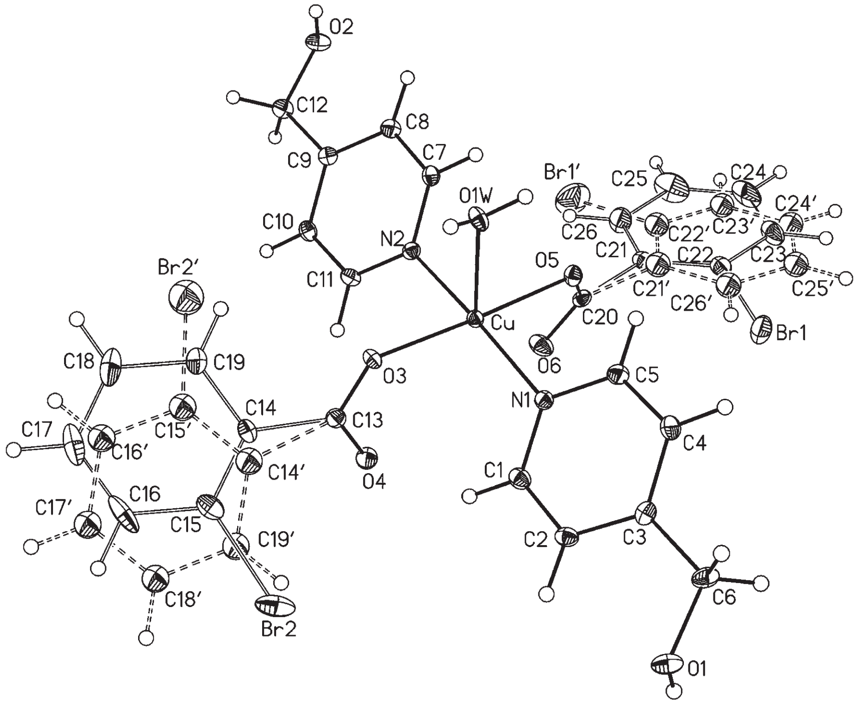

Figure 1. Perspective view of **1**, with the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Open and dashed open lines indicate the main and side populations, respectively, of disordered 2-bromophenyl groups.

Table 1. Selected bond lengths (Å) and angles (°) for **1** and **2**.

| | | | | | |
|---|---|---|---|---|---|
| **1** | | | | | |
| Cu–O3 | 1.964(2) | Cu–N2 | 2.033(2) | Cu–O5 | 1.981(2) |
| Cu–O1W | 2.220(2) | Cu–N1 | 2.026(2) | | |
| O3–Cu–O5 | 177.69(8) | N1–Cu–N2 | 173.58(9) | O3–Cu–N1 | 91.70(8) |
| N1–Cu–N2 | 173.58(9) | O3–Cu–N1 | 91.70(8) | O3–Cu–O1W | 88.31(6) |
| O5–Cu–N1 | 90.19(8) | O5–Cu–O1W | 90.21(6) | O3–Cu–N2 | 89.41(8) |
| N1–Cu–O1W | 94.37(8) | O5–Cu–N2 | 88.85(8) | N2–Cu–O1W | 91.98(8) |
| **2** | | | | | |
| Cu–O1 | 1.947(2) | Cu–O2 | 2.950(2) | Cu–N1 | 2.025(2) |
| O1–Cu–N1 | 90.20(7) | N1–Cu–O2 | 75.22(6) | O1–Cu–O2 | 49.07(6) |

The molecules of **1** are linked to adjacent molecules by O–H···O and C–H···O hydrogen bonds, creating a 3-D hydrogen bonding network (table 2), consisting of 2-D sheets, approximately along the *b* axis (figure 2). The packing diagram of **1** in the 2-D sheet is shown in figure 3. The coordinated water hydrogen atoms are linked to hydroxyl oxygen atoms of the 4-pyridylmethanol ligands of the adjacent complex by hydrogen bonds [O1W–H1W···O2 and O1W–H2W···O1] with interatomic O···O distance of 2.723(2) and 2.768(2) Å, respectively. The hydroxyl hydrogen atoms of 4-pyridylmethanol are linked to the uncoordinated carboxyl oxygen atoms of 2-bromobenzoate anions of adjacent molecules by other hydrogen bonds

Table 2. Hydrogen bond geometries (Å, °) for **1** and **2**.

| *D*–H···*A* | H···*A* | *D*···*A* | *D*–H···*A* | |
|---|---|---|---|---|
| **1** | | | | |
| O1–H1O···O4 | $(-x+1, -y+1, z-1/2)$ | 1.81 | 2.650(2) | 173 |
| O2–H2O···O6 | $(-x+3/2, y-1/2, z+1/2)$ | 1.84 | 2.642(2) | 160 |
| O1W–H1W···O2 | $(-x+3/2, y-1/2, z-1/2)$ | 1.89 | 2.723(2) | 171 |
| O1W–H2W···O1 | $(-x+1, -y, z+1/2)$ | 1.93 | 2.768(2) | 172 |
| C6–H6B···O3 | $(-x+1, -y, z-1/2)$ | 2.43 | 3.317(3) | 149 |
| C12–H12A···O5 | $(-x+3/2, y+1/2, z+1/2)$ | 2.51 | 3.365(3) | 145 |
| **2** | | | | |
| N2–H2A···O3 | $(-x+1, -y, -z+1)$ | 2.11 | 2.939(2) | 157 |
| N2–H2B···O4 | $(x-1/2, -y+1/2, z-1/2)$ | 2.16 | 3.032(3) | 170 |
| O4–H1W···O2 | $(x+1, y, z)$ | 1.94 | 2.760(3) | 164 |
| O4–H2W···O2 | $(-x+1, -y+1, -z+1)$ | 2.03 | 2.864(3) | 171 |
| C11–H11···O3 | $(x-1/2, -y+1/2, z-1/2)$ | 2.24 | 3.149(3) | 159 |
| C10–H10···O4 | $(x-1/2, -y+1/2, z-1/2)$ | 2.49 | 3.328(3) | 147 |

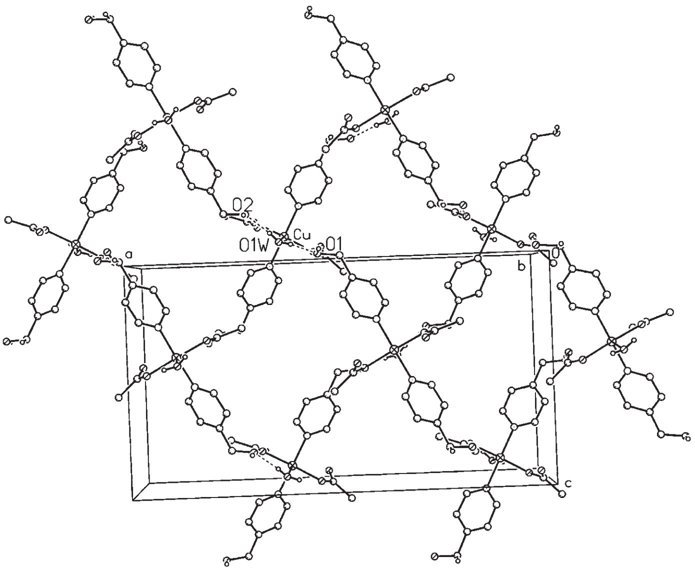

Figure 2. View of the three-dimensional (4, 4) grid net formed by **1**. The two-dimensional sheets of **1** lie parallel and perpendicular in the three-dimensional (4, 4) grid net. Dashed lines indicate O–H···O hydrogen bonds. The 2-bromophenyl groups are omitted for clarity.

[O1–H1O···O4 and O2–H2O···O6] with interatomic O···O distance of 2.650(3) and 2.642(3) Å, respectively. The O–H···O hydrogen bonds in **1** are supplemented by very weak C–H···O hydrogen bonds between methylene hydrogen atoms of 4-pyridylmethanol ligands and coordinated carboxyl oxygen atoms of 2-bromobenzoate anions of adjacent molecules [C6–H6B···O3 and C12–H12A···O5] with interatomic C···O distance of 3.317(3) and 3.365(3) Å, respectively. This system of hydrogen bonds is different from that found for [Cu(clof)$_2$(4PM)$_2$(H$_2$O)]·2H$_2$O, reported recently by our group [29]. Only a few structures of metal complexes with 4-pyridylmethanol have been

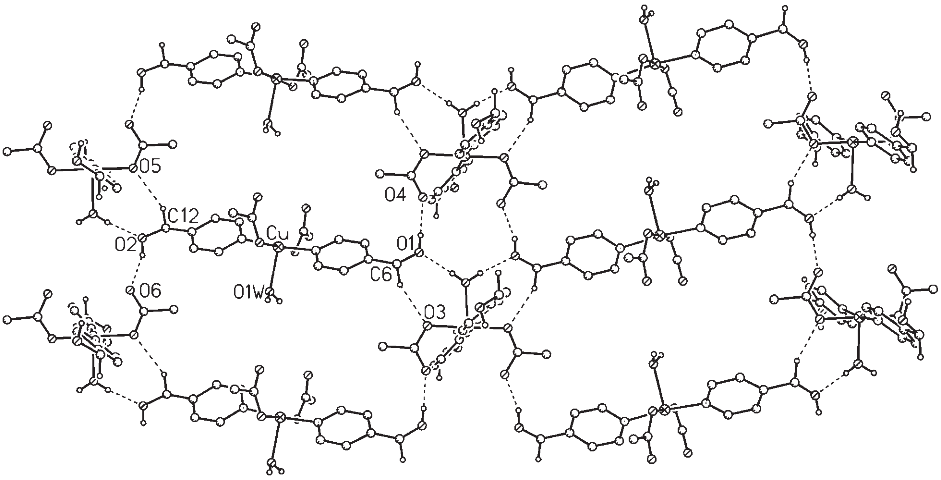

Figure 3. View of the two-dimensional sheet of **1**. Dashed lines indicate O–H ··· O and C–H ··· O hydrogen bonds. The 2-bromophenyl groups are omitted for clarity.

reported [30–34]. The hydroxyl group of 4-pyridylmethanol in these structures is linked through hydrogen bonds to acceptors from coordinated anionic groups (carboxylate [30, 32], phosphate [33], or chlorides [34]) or water molecules [29]. Formation of hydrogen bonds through 4-pyridylmethanol has previously been observed in similar systems of copper(II) carboxylates with terminal 3-pyridylmethanol [35, 36]; in these complexes 1-D or 2-D hydrogen-bonding networks have been observed.

### 2.1.2. Crystal structure of [Cu(2-Brbz)$_2$(NIA)$_2$] • 2H$_2$O (2).

The molecular structure of **2** is shown in figure 4. The Cu is located on an inversion center and has an extreme elongated tetragonal bipyramidal (4 + 2) coordination geometry. The tetragonal plane is built up by a pair of asymmetric bidentate 2-bromobenzoate anions using carboxyl oxygen atoms [Cu–O1 = 1.947(2) Å] and by a pair of neutral nicotinamide molecules using pyridine ring nitrogen atoms [Cu–N1 = 2.025(2) Å] (table 1) in *trans* positions. The axial positions are occupied by a second pair of oxygen atoms originating from the 2-bromobenzoate anions [Cu–O2 = 2.950(2) Å], significantly longer (by 1.003(3) Å) than the Cu–O1 bond distance. The N1–Cu–O2 and O1–Cu–O2 bond angles are 75.22(6)° and 49.07(6)°, respectively. The value of the $T$ parameter (parameter tetragonality, $T = R_S/R_L$) [37] indicating the degree of tetragonally elongated octahedron with further rhombic distortion about Cu$^{2+}$ is 0.67, in agreement with the small bond angle O1–Cu–O2 as a consequence of the Jahn-Teller effect [38].

Complex **2** can be compared with [Cu(2-chloro-6-fluorobenzoato-*O*)$_2$(NIA)$_2$] [39], where Cu–O2 distance is as high as 3.141(3) Å, indicating that O2 carboxyl is not coordinated to copper. On the other hand, the same bond distances (Cu–O2) in the structures of monoclinic [40] and orthorhombic [41] forms of [Cu(sal-$O,O'$)$_2$(NIA)$_2$] (sal$^-$ = salicylate anion), [Cu(clof-$O,O'$)$_2$(NIA)$_2$] [42], [Cu(valerato-$O,O'$)$_2$(NIA)$_2$] [43] and [Cu(acetylsalicylate-$O,O'$)$_2$(NIA)$_2$] [44] show lower values, 2.766(2), 2.609(6), 2.614(2) and 2.621(2) Å, respectively. The extremely low value of Cu-O2 distance has been observed for [Cu(bz-$O,O'$)$_2$(NIA)$_2$] (bz$^-$ = benzoate anion) [45]. The carboxyl

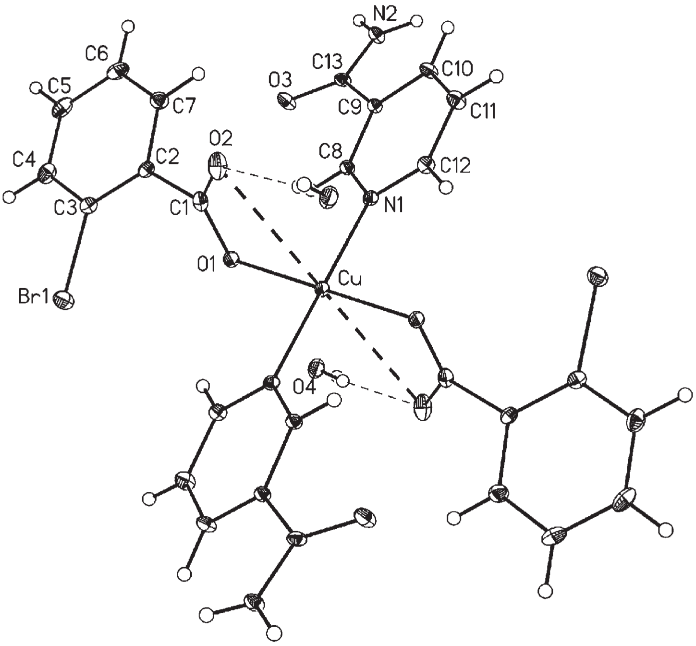

Figure 4. Perspective views of **2**, with the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

groups in this structure are symmetrically bonded with Cu–O bond lengths being 2.180(3) and 2.209(3) Å, respectively. The water molecules are not coordinated to Cu, but the distance between copper and water oxygen atoms of 3.069(2) Å is close to the Cu–O2 bond distance. The Cu–$O_{water}$ distances for the directly coordinated water in [Cu(4-hydroxybenzoato-*O*)$_2$(NIA)$_2$($H_2O$)$_2$] [46], [Cu(sal-*O*)$_2$(NIA)$_2$($H_2O$)$_2$] [47], [Cu(2-nitrobenzoato-*O*)$_2$(NIA)$_2$($H_2O$)$_2$] [48], [Cu(3-hydroxybenzoato-*O*)$_2$(NIA)$_2$ ($H_2O$)$_2$] [49] and [Cu(2-fluorobenzoato-*O*)$_2$(isonicotinamide)$_2$($H_2O$)$_2$] [50] are shorter and lie in the range 2.33–2.89 Å. A search through the Cambridge Structural Database (CSD) [28] revealed that for copper(II) carboxylates with two pyridine-like ligands, (4 + 1) coordination of [Cu($RCO_2$)$_2$$L_2$($H_2O$)] is preferred. However, there are two types of (4 + 2) coordination geometries: [Cu($RCO_2$)$_2$$L_2$($H_2O$)$_2$] (carboxylate coordinated as a monodentate ligand) and [Cu($RCO_2$)$_2$$L_2$] (carboxylate coordinated bidentate). Exact results for CSD version 5.29 shows 111 entries for (4 + 1) geometry, and 34 and 39 entries for both types of (4 + 2) geometries. On the other hand, mononuclear copper(II) carboxylates with nicotinamide and/or isonicotinamide prefer one of two possible 4 + 2 coordination modes. The nicotinamide and isonicotinamide prefer coordination through pyridine nitrogen (more than 100 entries of metal complexes with nicotinamide or nicotinamide are reported), however, only fifteen examples where nicotinamide and isonicotinamide are bridging have been reported [51–61].

The water molecules of **2** are linked to adjacent molecules by O–H ··· O and N–H ··· O hydrogen bonds in 2-D hydrogen bonding sheets, which are connected by another N–H ··· O and C–H ··· O hydrogen bond forming a 3-D hydrogen bonding network (table 2). The uncoordinated water molecules are linked to Cu(2-Brbz)$_2$(NIA)$_2$ by O–H ··· O hydrogen bonds in chains along the *a* axis (figure 5). The hydrogen bonds originate between both hydrogens of water and carboxyl oxygen atoms [O4–H1W ··· O2 and O4–H2W ··· O2], with interatomic O ··· O distances of 2.760(3) and 2.864(3) Å, respectively. Adjacent carboxamide groups are connected by a hydrogen bond [N2–H2A ··· O3], with interatomic O ··· O distance of 2.939(2) Å, creating *zigzag* chains approximately along *b*. Such amide ··· amide hydrogen bonds $R_2^2(8)$ [62] are frequently seen in coordination compounds with nicotinamide or isonicotinamide [7–23]. A search through the Cambridge Structural Database [28] revealed that the majority of metal complexes with coordinated nicotinamide/isonicotinamide exhibit amide ··· amide hydrogen bonds with graphical set $R_2^2(8)$ [62]. Other amide ··· amide hydrogen bonds exhibit chains $C(4)$ [62], but rarely rings of four amide groups $R_4^4(16)$ [8] or $R_4^2(8)$ [63]. The two-dimensional sheets are linked by N–H ··· O and C–H ··· O hydrogen bonds (figure 6). The carboxamide and pyridine hydrogens of nicotinamide are linked to water [N2–H2B ··· O4 and C10–H10 ··· O4], with donor and acceptor distanc es of 3.032(3) and 3.328(3) Å, respectively. Additional hydrogen bonds between the two-dimensional sheets observed are C–H ··· O which connect pyridine hydrogens and carboxamide oxygens [C11–H11 ··· O3], with interatomic C ··· O distance of 3.149(3) Å.

## 2.2. *EPR analysis*

The EPR spectrum of **1** (figure 7) taken in polycrystalline form is of axial symmetry, showing rather broad parallel part of the spectrum. The parallel part exhibits very weak hyperfine splitting and therefore this term has been included in the simulation. A good match between experimental spectrum and simulated spectrum has been achieved using $A_{\|} = 170$ Gauss and $g_{\|} = 2.301$, $g_{\perp} = 2.081$, however, with rather large value of parallel

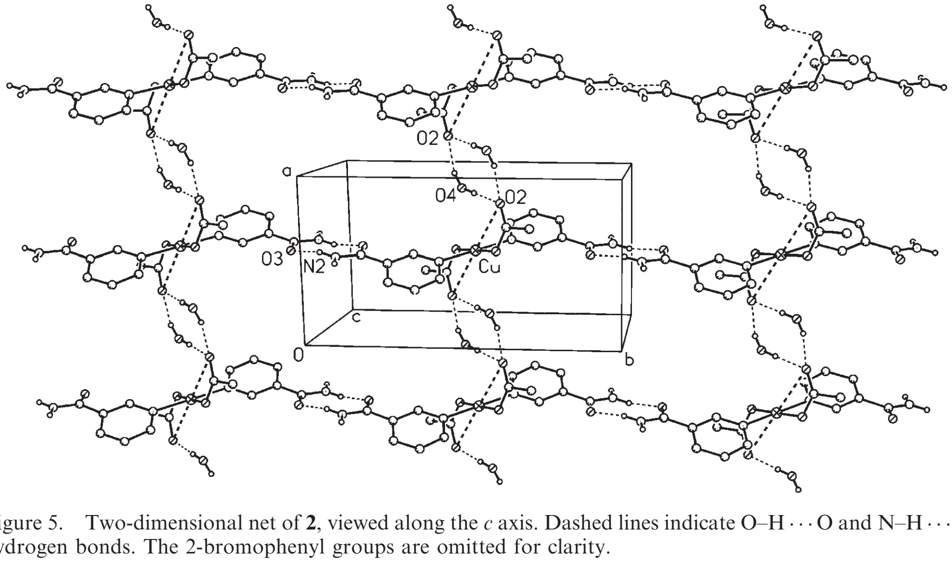

Figure 5. Two-dimensional net of **2**, viewed along the *c* axis. Dashed lines indicate O–H ··· O and N–H ··· O hydrogen bonds. The 2-bromophenyl groups are omitted for clarity.

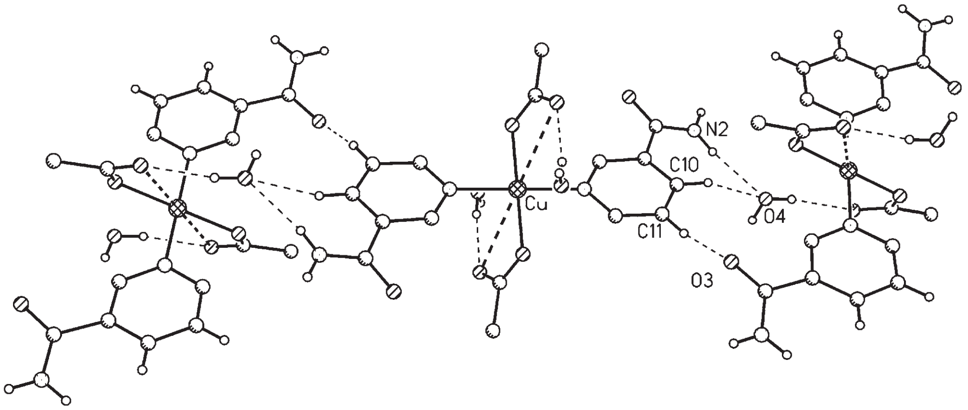

Figure 6. Hydrogen bonds (dashed lines) in crystal structure of **2**. The 2-bromophenyl groups are omitted for clarity.

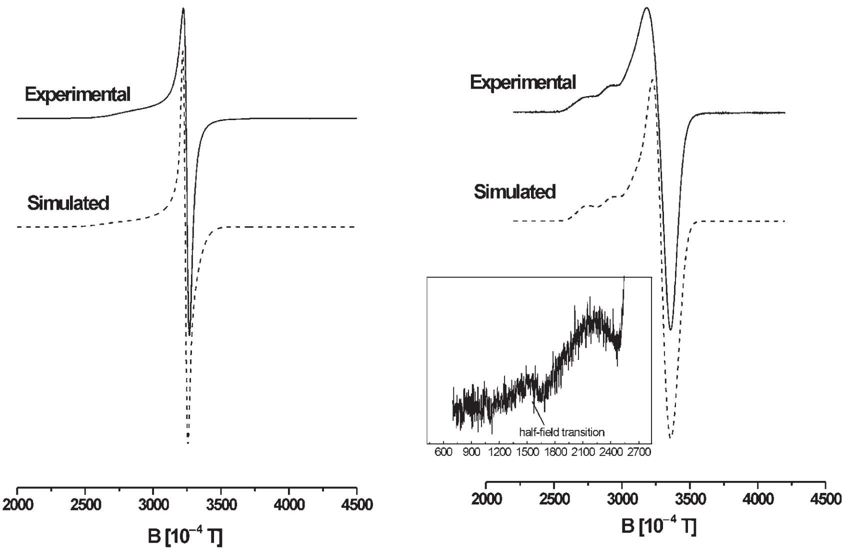

Figure 7. EPR spectra of **1** (left) and **2** (right) taken in polycrystalline form. Inset shows half-field transition.

half-width ($\Delta B_{\|} = 230$ Gauss). The EPR data points to a $d_{x^2-y^2}$ ground electronic state of copper(II) and agree with the X-ray data for tetragonal-pyramidal coordination around copper. No half-field transitions have been observed even at high gain/field-modulation showing that there is extremely weak or no magnetic interaction between copper ions, probably because of rather long copper-copper distance and/or ligand shielding.

The EPR spectrum of **2** in polycrystalline form is of axial symmetry and shows well resolved parallel hyperfine splitting with $A_{\|} = 185$ Gauss and $g_{\|} = 2.240$, $g_{\perp} = 2.053$. It has been well established that tetrahedral distortions of a planar $CuX_4$ moiety markedly reduces $A_{\|}$ whilst simultaneously increasing $g_{\|}$. The tetrahedral distortion arising from the dependence of $g_{\|}$ on the dihedral angle led to the introduction of the quotient $g_{\|}/|A_{\|}|$ as a convenient measure of the degree of tetrahedral distortion [64]. The EPR data for **2** gives a value of $g_{\|}/|A_{\|}|$ ~125 cm which suggests a marked tetragonal distortion around the copper ion.

## 3. Experimental

### 3.1. *Syntheses*

**3.1.1. [Cu(2-Brbz)$_2$(4PM)$_2$(H$_2$O)] (1).** A green copper(II) 2-bromobenzoate monohydrate was prepared by adding aqueous solution of cupric sulfate to sodium 2-bromobenzoate obtained by addition of an aqueous solution of NaOH (0.05 mol) to 2-bromobenzoic acid (0.05 mol) in water. The crystals of **1** were prepared by adding 20 mL of a methanol solution of 4-pyridylmethanol (0.02 mol) to 100 mL of a methanol solution of the copper(II) 2-bromobenzoate monohydrate (0.01 mol). After heating to boiling, the solution was left to cool and stand at room temperature. A blue product precipitated, was filtered, washed with cold water and dried in air. Crystals of **1**, suitable for X-ray analysis, were obtained from the mother liquor after slow room-temperature crystallization. Yield: 80%. Anal. Calcd for $C_{26}H_{24}Br_2CuN_2O_7$: C, 44.62; H, 3.46; N, 4.00%. Found: C, 44.43; H, 3.49; N, 4.03%. IR data (KBr, cm$^{-1}$): 3407s $\nu(O{-}H)_{H_2O}$, 3214s $\nu(O{-}H)_{4PM}$, 1609vs $\nu_{as}(COO^-)$, 1396vs $\nu_s(CO\ O^-)$, 1061s $\nu(C{-}O)_{4PM}$.

**3.1.2. [Cu(2-Brbz)$_2$(NIA)$_2$] • 2H$_2$O (2).** Crystals of **2** were prepared by adding 20 mL of a methanol solution of the nicotinamide (0.02 mol) to 100 mL of a methanol solution of the copper(II) 2-bromobenzoate monohydrate (0.01 mol). After heating to boiling the solution was left to cool and stand at room temperature. A violet-blue product precipitated, was filtered, washed with cold water and dried in air. Crystals of **2**, suitable for X-ray analysis, were obtained from the mother liquor after slow room-temperature crystallization. Yield: 75%. Anal. Calcd for $C_{26}H_{24}Br_2CuN_4O_8$: C, 41.98; H, 3.25; N, 7.53%. Found: C, 41.83; H, 3.36; N, 7.53%. IR data (KBr, cm$^{-1}$): 3379s $\nu_{as}(N{-}H)_{NIA}$, 3307br $\nu(O{-}H)_{H_2O}$, 3204s $\nu_s(N{-}H)_{NIA}$, 1684vs $\nu(C{=}O)_{NIA}$, 1606s $\nu_{as}(COO^-)$, 1394vs $\nu_s(COO^-)$.

### 3.2. *Analysis and spectral measurements*

Carbon, hydrogen and nitrogen analyses were carried out on a CHNSO FlashEA 1112 (ThermoFinnigan) elemental analyzer.

Electronic spectra (190–1100 nm) of the complexes were measured in Nujol suspension with a SPECORD 200 (Carl Zeiss Jena) spectrometer, and infrared spectrum in the region of 4000–100 cm$^{-1}$ were measured with a Nicolet MAGNA 750 IR spectrometer using KBr pellets for 4000–400 cm$^{-1}$ region and polyethylene pellet for 400–100 cm$^{-1}$ region. The X-band EPR spectra in polycrystalline solid state were recorded on a Bruker EMX spectrometer equipped with a Bruker variable temperature unit. Line positions were measured by an NMR gaussmeter, while the microwave frequency was measured by a microwave frequency counter; 100 kHz magnetic field modulation (peak-to-peak amplitude 3 G) was used. For additional details see elsewhere [64]. The simulations of the EPR spectra were performed using the commercially available program SimFonia [65].

### 3.3. *Crystallography*

The crystal data and details of data collections for all structures are given in table 3. Intensity data for both complexes were collected using a Kuma KM-4CCD with graphite monochromated Mo-K$\alpha$ radiation at 100 K. The diffraction intensities were corrected for Lorentz and polarization effects. Analytical absorption corrections were applied using the program CrysAlis-RED [66]. The structures were solved by direct methods using the programs SIR-97 [67] **1** or SHELXS-97 [68] **2** and refined by full-matrix least-squares on all $F^2$ data using the program SHELXL-97 [68]. Geometrical analyses were performed using SHELXL-97. The structures were drawn by XP in SHELXTL [68].

The 2-bromobenzoate anions of **1** have orientational disorders and the refined site-occupancy factors of the disordered parts (bromophenyl groups: Br2/C14–C19; Br2′/C14′–C19′; Br1/C21–C26; Br1′/C21′–C26′ and associated H atoms) are 0.912(1), 0.088(1), 0.976(1) and 0.024(1), respectively. The benzene rings (C21′–C26′) and (C14′–C19′) (in figure 1 dashed open lines) of the disordered anions were refined only as rigid ideal hexagons with C–C = 1.39 Å and constrained with the same isotropic displacement parameters. The Flack parameter [69] of non-centrosymmetric structure

Table 3. Crystal data and structure refinement parameters for **1** and **2**.

| Complex | **1** | **2** |
|---|---|---|
| Chemical formula | $C_{26}H_{24}Br_2CuN_2O_7$ | $C_{26}H_{24}Br_2CuN_4O_8$ |
| $M_r$ | 699.83 | 743.84 |
| Cell setting | Orthorhombic | Monoclinic |
| Space group | $Pna2_1$ | $P2_1/n$ |
| Temperature (K) | 100(2) | 100(2) |
| Unit cell dimention (Å, °) | | |
| $a$ | 24.788(6) | 7.911(3) |
| $b$ | 8.246(2) | 14.241(5) |
| $c$ | 13.650(3) | 12.498(5) |
| $\alpha$ | 90 | 90 |
| $\beta$ | 90 | 102.01(3) |
| $\gamma$ | 90 | 90 |
| $V$ (Å$^3$) | 2790.1(11) | 1377.2(9) |
| $Z$ | 4 | 2 |
| $D_x$ (Mg m$^{-3}$) | 1.666 | 1.794 |
| Radiation type | Mo-K$\alpha$ | Mo-K$\alpha$ |
| $\mu$ (mm$^{-1}$) | 3.69 | 3.75 |
| Crystal form, color | Block, blue | Block, violet-blue |
| Crystal size (mm$^3$) | $0.46 \times 0.36 \times 0.29$ | $0.50 \times 0.38 \times 0.36$ |
| $T_{\min}$, $T_{\max}$ | 0.144, 0.378 | 0.170, 0.374 |
| No. of measured, independent and observed reflections | 28240, 8019, 6334 | 17836, 4349, 3630 |
| $R_{\text{int}}$ | 0.047 | 0.039 |
| $\theta_{\max}$ (°) | 31.0 | 31.0 |
| Refinement on | $F^2$ | $F^2$ |
| $R[F^2 > 2\sigma(F^2)]$, w$R(F^2)$, $S$ | 0.033, 0.062, 1.01 | 0.036, 0.094, 1.05 |
| No. of reflections/parameters | 8019/368 | 4349/194 |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å$^{-3}$) | 0.41, −0.64 | 0.89, −0.88 |

of **1** was refined explicitly, with both TWIN and BASF instructions of SHELXL-97 program; its value was 0.237(6).

## 4. Conclusion

Two hydrogen-bonded coordination polymers formed by copper(II) 2-bromobenzoate with 4-pyridylmethanol and nicotinamide have been prepared and characterized. The crystal structure of **1** consists of a 3-D hydrogen-bonded framework, formed by O–H$\cdots$O hydrogen bonds of hydroxyl and water donor oxygen atoms. The crystal structure of **2** consists of a 3-D hydrogen-bonded framework, formed by N–H$\cdots$O hydrogen bonds of amide donor nitrogens and O–H$\cdots$O hydrogens of water. The weak C–H$\cdots$O hydrogen bonds supplemented the system of hydrogen bonds in the frameworks of both complexes. Nicotinamide and 4-pyridylmethanol can conveniently be used as terminal ligands for construction of hydrogen-bonded coordination networks.

### Supporting information

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-634177 **1** and CCDC-634178 **2**. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44 1223/336033; Email: deposit@ccdc.cam.ac.uk].

## Acknowledgements

We thank the Scientific Grant Agency of the Ministry of Education of Slovak Republic and the Slovak Academy of Sciences for financial support (1/4454/07, 1/0353/08 and 1/0575/08), and the Research and Development Agency of the Slovak Republic (contract No. APVT-20-004504) for financial support.

## References

[1] J.R.J. Sorenson. *J. Med. Chem.*, **19**, 135 (1976).
[2] J.R.J. Sorenson. *Progr. Med. Chem.*, **26**, 437 (1989).
[3] J.E. Weder, C.T. Dillon, T.W. Hambley, B.J. Kennedy, P.A. Lay, J.R. Biffin, H.L. Regtop, N.M. Davies. *Coord. Chem. Rev.*, **232**, 95 (2002).
[4] A.M. Beatty. *Coord. Chem. Rev.*, **246**, 131 (2003).
[5] A.D. Burrows. *Structure Bonding*, **108**, 55 (2004).
[6] A.M. Beatty. *Cryst. Eng. Comm.*, **3**, 243 (2001).
[7] G.R. Desiraju. *J. Chem. Soc., Dalton Trans.*, 3745 (2000).
[8] C.B. Aakeröy, A.M. Beatty, D.S. Leinen. *Angew. Chem. Int. Ed.*, **38**, 1815 (1999).
[9] J.C. Mareque-Rivas, L. Brammer. *New J. Chem.*, **22**, 1315 (1998).
[10] L. Brammer, J.C. Mareque-Rivas, R. Antencia, S. Fang, F.C. Pigge. *J. Chem. Soc., Dalton Trans.*, 3855 (2000).

[11] Z. Qin, M.-C. Jennings, R.J. Puddephat. *Inorg. Chem.*, **40**, 6220 (2001).
[12] G. Yang, H.-G. Zhu, B.-H. Liang, X.-M. Chen. *J. Chem. Soc., Dalton Trans.*, 580 (2001).
[13] C.B. Aakeröy, A.M. Beatty. *Cryst. Eng.*, **1**, 39 (1998).
[14] K. Bera, T.-T. Vo, R.A. Walton, K.R. Dunbar. *Polyhedron*, **22**, 3009 (2003).
[15] C.B. Aakeröy, A.M. Beatty, A. Helfrich. *J. Chem. Soc., Dalton Trans.*, 1943 (1998).
[16] C.B. Aakeröy, A.M. Beatty. *Chem. Commun.*, 1067 (1998).
[17] C.B. Aakeröy, A.M. Beatty, D.S. Leinen, K.R. Lorimer. *Chem. Commun.*, 935 (2000).
[18] C.J. Kuehl, F.M. Tabellion, A.M. Arif, P.J. Stang. *Organometallics*, **20**, 1956 (2001).
[19] C.-H. Chen, J. Cai, X.-L. Feng, X.-M. Chen. *Polyhedron*, **21**, 689 (2002).
[20] M.D. Selby, B.K. Roland, M.D. Carducci, Z. Zheng. *Inorg. Chem.*, **42**, 1656 (2003).
[21] C.-H. Chen, J.-W. Cai, C.-Z. Liao, X.-L. Feng, X.-M. Chen, S.W. Ng. *Inorg. Chem.*, **41**, 4967 (2002).
[22] C.B. Aakeröy, J. Desper, J. Valdes-Martinez. *CrystEngComm*, **6**, 41 (2004).
[23] B.R. Bhogala, P.K. Thallapally, A. Nangia. *Cryst. Growth Des.*, **4**, 215 (2004).
[24] A.W. Addison, T.N. Rao, J. Reedijk, J. Rija, G.C. Verchoors. *J. Chem. Soc., Dalton Trans.*, 1349 (1984).
[25] W.M. Willingham, J.R.J. Sorenson, F. Yarberry, W. Cordes. *J. Cryst. Spectr. Res.*, **23**, 505 (1993).
[26] M.-M. Borel, L. Boniak, F. Busnot, A. Leclaire. *Rev. Chim. Min.*, **15**, 397 (1978).
[27] R.E. Del Sesto, A.M. Arif, J.S. Miller. *Inorg. Chem.*, **39**, 4894 (2000).
[28] F.A. Allen. *Acta Crystallogr.*, **B58**, 380 (2002); Searches of CSD version 5.29 (November 2007) were conducted using the CONQUEST software.
[29] J. Moncol, B. Kaliňaková, J. Švorec, M. Kleinová, M. Koman, D. Hudecová, M. Melník, M. Mazúr, M. Valko. *Inorg. Chim. Acta*, **357**, 3211 (2004).
[30] N.N. Hoang, F. Valach, M. Melník. *Acta Crystallogr.*, **C49**, 467 (1993).
[31] J. Moncol, M. Múdra, P. Lönnecke, M. Koman, M. Melník. *J. Chem. Crystallogr.*, **34**, 423 (2004).
[32] T.C. Stamatatos, D. Foguet-Albiot, S.P. Perlepes, C.P. Raptopoulou, A. Terzis, C.S. Patrickios, G. Christou, A.J. Tasiopoulos. *Polyhedron*, **25**, 1737 (2006).
[33] R. Murugavel, S. Kuppuswamy, R. Boomishankar, A. Steiner. *Angew. Chem. Int. Ed.*, **45**, 5536 (2006).
[34] F.J. Ramos-Lima, O. Vrana, A.G. Quiroga, C. Navarro-Ranninger, A. Halamikova, H. Rybnickova, L. Hejmalova, V. Bravec. *J. Med. Chem.*, **49**, 2624 (2006).
[35] J. Moncol, P. Segl'a, D. Mikloš, M. Mazúr, M. Melník, T. Głowiak, M. Valko, M. Koman. *Polyhedron*, **25**, 1561 (2006).
[36] P. Stachová, M. Korabik, M. Koman, M. Melník, J. Mrozinski, T. Glowiak, M. Mazúr, D. Valigura. *Inorg. Chim. Acta*, **359**, 1275 (2006).
[37] B.J. Hathaway, P.G. Hodgson. *J. Inorg. Nucl. Chem.*, **35**, 4071 (1973).
[38] J. Moncol, M. Múdra, P. Lönnecke, M. Koman, M. Melník. *J. Coord. Chem.*, **57**, 1065 (2004).
[39] N.N. Hoang, F. Valach, M. Dunaj-Jurčo. *Acta Crystallogr.*, **C51**, 1095 (1995).
[40] I. Leban, B. Kozlevčar, J. Sieler, P. Šegedin. *Acta Crystallogr.*, **C53**, 1420 (1997).
[41] N.N. Hoang, F. Valach, M. Melník. *Z. Kristallogr.*, **208**, 27 (1993).
[42] M. Melník, M. Koman, D. Hudecová, J. Moncol, B. Dudová, T. Głowiak, J. Mroziński, C.E. Holloway. *Inorg. Chim. Acta*, **308**, 1 (2000).
[43] A.S. Antsyshkina, G.G. Sadikov, T.V. Koksharova, I.S. Gritsenko, V.S. Sergienko. *Russ. J. Inorg. Chem.*, **51**, 1571 (2006).
[44] Z. Ma, B. Moulton. *Cryst. Growth Des.*, **7**, 196 (2007).
[45] I. Leban, P. Šegedin, K. Gruber. *Acta Crystallogr.*, **C52**, 1096 (1996).
[46] T. Hökelek, K. Bukak, K. Sendil, H. Necefoğlu. *Acta Crystallogr.*, **C54**, 347 (1998).
[47] N. Petrovčič, B. Kozlevčar, L. Golič, I. Leban, P. Šegedin. *Acta Crystallogr.*, **C55**, 176 (1999).
[48] P. Stachová, M. Melník, M. Korabik, J. Mrozinski, M. Koman, T. Głowiak, D. Valigura. *Inorg. Chim. Acta*, **360**, 1517 (2007).
[49] O. Sahir, O. Buyukgungor, D.A. Kose, H. Necefoglu. *Acta Crystallogr.*, **C63**, m510 (2007).
[50] C.B. Aakeröy, A.M. Beatty, J. Desper, M. O'Shea, J. Valdés-Martinez. *Dalton Trans.*, 3956 (2003).
[51] B. Kozlevčar, I. Leban, I. Turel, P. Šegedin, M. Petrič, F. Pohleven, A.J.P. White, D.J. Williams, J. Sieler. *Polyhedron*, **18**, 755 (1999).
[52] S. Cakir, I. Bulut, K. Aoki. *J. Chem. Crystallogr.*, **33**, 875 (2003).
[53] X.-L. Zhao, T.C.W. Mak. *Dalton Trans.*, 3212 (2004).
[54] D. Valigura, J. Moncol, M. Korabik, Z. Pučeková, T. Lis, J. Mrozinski, M. Melník. *Eur. J. Inorg. Chem.*, 3813 (2006).
[55] J. Moncol, M. Múdra, P. Lönnecke, M. Hewitt, M. Valko, H. Morris, J. Svorec, M. Melnik, M. Mazur, M. Koman. *Inorg. Chim. Acta*, **360**, 3213 (2007).
[56] Z.-X. Lian, J. Cai, C.-H. Chen, H.-B. Luo. *CrystEngComm*, **9**, 319 (2007).
[57] H.H. Monfared, Z. Kalantari, M.-A. Kamyabi, C. Janiak. *Z. Anorg. Allg. Chem.*, **633**, 1945 (2007).
[58] Ľ. Žurková, E. Rakovský. *ChemZi*, **3/1**, 238 (2007).
[59] M.M. Najafpour, V. McKee. *Anal. Sci.: X-Ray Struct. Anal. Online*, **23**, x23 (2007).
[60] P. Naumov, S. Cakir, I. Bulut, E. Bicer, O. Cakir, G. Jovanovski, A.R. Ibrahim, A. Usman, H.-K. Fun, S. Chantrapromma, S.W. Ng. *Main Group Metal Chemistry*, **25**, 175 (2002).
[61] M.M. Najafpour, T. Lis, M. Hołynska. *Inorg. Chim. Acta*, **360**, 3452 (2007).

[62] J. Bernstein, R.E. Davis, L. Shimoni, N.-L. Chang. *Angew. Chem., Int. Ed. Engl.*, **34**, 1555 (1995).
[63] C. Nather, J. Jess. *Acta Crystallogr.*, **C58**, m19 (2002).
[64] M. Valko, H. Morris, M. Mazur, J. Telser, E.J.L. McInnes, F.E. Mabbs. *J. Phys. Chem. B*, **103**, 5591 (1999).
[65] SimFonia: Simulation Program, Ver. 1.0, Bruker EPR (1996).
[66] Oxford Diffraction, CrysAlis CCD and CrysAlis RED, Oxford Diffraction Poland, Wrocław, Poland (2003).
[67] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna. *J. Appl. Crystallogr.*, **32**, 115 (1999).
[68] G.M. Sheldrick. *Acta Crystallogr.*, **A64**, 112 (2008).
[69] H.D. Flack. *Acta Crystallogr.*, **A39**, 876 (1983).