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Complexes of 4- and 5-bromo derivatives of 2-(hydroxymethyl)pyridine with copper(II) and cobalt(II) salts. Synthesis and X-ray crystal structures

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ABSTRACT

Four copper(II) complexes (1-4) and a cobalt(II) complex (5) derived from 4-bromo-2-(hydroxymethyl)pyridine (L^1) or 5-bromo-2-hydroxymethyl)pyridine (L^2) with Cu(NO₃)₂·3H₂O, CuCl₂·2H₂O and CoCl₂·6H₂O have been synthesized and their respective crystal structures studied. They show specific influences owing to the different kind of metal cations and counter anions, the hydration as well as the different position of the bromine substitution on both the coordination of the complex unit and the network structure of the crystal lattice. The Cu(II) complexes of L^1 are five-coordinate [Cu(L¹)₂NO₃]- $NO_3 \cdot H_2O(1)$ and $[Cu(L^1)_2Cl]Cl \cdot H_2O(2)$ species with distorted quadratic pyramidal and trigonal bipyramidal coordination geometries of the N_2O_3 and N_2O_2Cl donor atoms around the Cu(II), respectively. The Cu(II) complexes of L^2 are six-coordinate $[Cu(L^2)_2(NO_3)_2]$ (3) and $[Cu(L^2)_2Cl(H_2O)]Cl H_2O$ (4) species with distorted octahedral coordination geometries of the N₄O₂ and N₂O₃Cl donor atoms. A distorted octahedral coordination geometry of the $N_2O_2Cl_2$ donor atoms is also found in the complex unit $[Co(L^2)_2Cl_2]$ of the Co(II) complex 5 but showing the oxygen atoms of the chelating ligand as well as the chloride ions in a cis-position. Depending on the complex, water molecules and chloride anions are shown to act as stabilizing components of the crystal structure. The comparative structural investigation includes also known structures of the bromine-free ligand analogue 2-(hydroxymethyl)pyridine, illustrating the basic implication of the bromine substitution, mostly perceptible in the different modes of crystal packing.

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1. Introduction

Pyridines have been extensively investigated as ligands in coordination compounds [1]. Recently, referring to the important topic of coordination polymers [2], pyridine fragments that bind to different metal centers are becoming increasingly significant in the construction of organic linker molecules [3]. Here, pyridine units frequently benefit from additional donor atoms adjacent to the pyridine nitrogen, thus showing the ability to act as chelating ligands [4]. Typical examples of pyridine moieties modified in this way are 2-(hydroxymethyl)pyridine and 2,6-bis(hydroxymethyl)pyridine having the qualifications to bi- and tridentate complex formation. This has been realized for the two before-mentioned (hydroxymethyl)pyridines with corresponding Cu(II), Co(II) and Ni(II) complexes that depend in their detailed crystal structures on the given anion, the presence of coordinated water molecules or suggest a proton control of framework complexity [5,6].

Another parameter of influence could be a substituent having proven a bearing on the structure of crystalline compounds such as a bromine substituent [7]. Actually, there are two different so-

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called 'supramolecular synthons' created by two approaching bromine atoms, showing a linear or perpendicular contact mode [8]. It is also likely that a bromine substitution should exercise an influence on the $\pi \cdots \pi$ stacking behaviour of pyridine units [9]. Hence, the question arises regarding the concrete consequences of a bromine substitution on the crystal structure of corresponding metal ion complexes, e.g. concerning the plain chelating ligand 2-(hydroxymethyl)pyridine if bromine substituents are present in 4- or 5-position of the pyridine ring such as in the ligands L¹(4-brhmp) and L²(5-brhmp), respectively (Scheme 1). This has given rise to the preparation of complexes of L¹ and L² with different metal salts, including Cu(NO₃)₂·3H₂O, CuCl₂·2H₂O and CoCl₂·6H₂O, namely the complexes and discuss their crystal structures in regard of the posed question.

2. Experimental part

2.1. General

Melting points (uncorrected) were taken on a heating stage microscope PHMK (Rapido, Dresden). Elemental analyses were determined with a Heraeus CHN rapid analyzer.



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3: $[Cu(L^2)_2(NO_3)_2]$ **4**: $[Cu(L^2)_2Cl(H_2O)]Cl \cdot H_2O$ **5**: $[Co(L^1)_2Cl_2]$

Scheme 1. Compounds studied in this paper.

4-Bromo-2-(hydroxymethyl)pyridine (L^1) [10] was synthesized from 2-methylpyridine-*N*-oxide via 4-nitro-2-methylpyridine-*N*oxide [11] and 4-bromo-2-methylpyridine-*N*-oxide [10,12] following the literature procedures. 5-Bromo-2-(hydroxymethyl)pyridine (L^2) was prepared from 2-methylpyridine using the reaction sequence bromination with aluminium chloride and bromine, oxidation with *m*-chloroperbenzoic acid and treatment with trifluoroacetic anhydride, as described in the literature [13]. 2-Methylpyridine, 2-methylpyridine-*N*-oxide as well as the copper(II) and cobalt(II) salts were obtained from usual suppliers.

2.2. General procedure for the synthesis of the complexes 1-5

The respective bromo-2-(hydroxymethyl)pyridine (0.70 mmol) and of the corresponding metal salt (0.35 mmol) were dissolved in ethanol ($30-50 \text{ cm}^{-3}$). The mixture was refluxed for 1 h. The solvent was removed under reduced pressure and the residue recrystallized from a small portion of ethanol.

2.2.1. Bis[4-bromo-2-(hydroxymethyl-kO)-pyridine-kN]nitrato copper(II) nitrate mono-hydrate (1)

 L^1 and copper(II) nitrate trihydrate were used. Turquoise-green crystals (28%) were collected; m.p. 148 °C (dec.). *Anal.* Calc. for C₁₂H₁₄Br₂CuN₄O₉ (FW = 581.62): C, 24.78; H, 2.42; N, 9.63. Found: C, 24.56; H, 2.37; N, 9.31%.

2.2.2. Bis[4-bromo-2-(hydroxymethyl-kO)-pyridine-kN]chloro copper(II) chloride mono-hydrate (**2**)

L¹ and copper(II) chloride dihydrate were used. Turquoisegreen crystals (36%) were collected; m.p. 155 °C (dec.). *Anal.* Calc.

2.2.3. Bis[5-bromo-2-(hydroxymethyl-kO)-pyridine-kN]dinitrato copper(II) (**3**)

 L^2 and copper(II) nitrate trihydrate were used. Blue crystals (42%) were collected; m.p. 168 °C (dec.). *Anal.* Calc. for C₁₂H₁₂Br₂CuN₄O₈ (FW = 563.60): C, 25.57; H, 2.15; N, 9.94. Found: C, 25.64; H, 2.16; N, 9.75%.

2.2.4. Bis[5-bromo-2-(hydroxymethyl-kO)-pyridine-kN]aquochloro copper(II) chloride mono-hydrate (**4**)

 L^2 and copper(II) chloride dihydrate were used. Green crystals (25%) were collected; m.p. 210 °C (dec.). *Anal.* Calc. for C₁₂H₁₆Br₂Cl₂CuN₂O₄ (FW = 546.53): C, 26.37; H, 2.95; N, 5.13. Found: C, 26.58; H, 3.08; N, 5.06%.

2.2.5. Bis[5-bromo-2-(hydroxymethyl-kO)-pyridine-kN]dichloro cobalt(II) (5)

 L^2 and cobalt(II) chloride hexahydrate were used. Violet crystals (35%) were collected; m.p. 182 °C (dec.). *Anal.* Calc. for C₁₂H₁₂Br₂Cl₂CoN₂O₂ (FW = 505.88): C, 28.49; H, 2.39; N, 5.54. Found: C, 28.72; H, 2.20; N, 5.35%.

2.3. X-ray crystallography

Crystals of the complexes **1–5** suitable for structure analysis were grown by slow evaporation of solvent from ethanol solutions.

The intensity data were collected on a Kappa APEX II diffractometer (Bruker-AXS) with graphite monochromated Mo Ka radiation ($\lambda = 0.71073$ Å) using φ and ω sans. Reflections were corrected for background, Lorentz and polarization effects. Preliminary structure models were derived by application of direct methods [14] and were refined by full-matrix least squares calculation based on F^2 values for all unique reflections [15]. Empirical absorption correction based on multi-scans was applied by using the sadabs program [16]. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogens could be derived from the difference Fourier ma. Their O-H bond lengths were restrained to a target value of 0.84 Å. All other hydrogen atoms were included in the models in calculated positions and were refined as constrained to bonding atoms. Crystal and refinement data for the complexes 1–5 are listed in Table 1 and the structural parameters of selected interactions are shown in Tables 2-4.

3. Results and discussion

3.1. Synthesis of L^1 and the complexes 1-5

The ligand L^1 was synthesized using the known route starting from 2-methylpyridine-*N*-oxide which was subjected to a nitration with nitric acid to give 4-nitro-2-methylpyridine-*N*-oxide [11], followed by a bromo substitution of the nitro group using acetyl bromide [10,12]. Reaction of the resulting 4-bromo-2-methylpyridine-*N*-oxide with trifluoroacetic acid yielded 4-bromo-2-(hydroxymethyl)pyridine (L^1) [10]. The ligand L^2 was also prepared according to a known reaction sequence [13]. This involves bromination of 2-methylpyridine with aluminium chloride and bromine, oxidation of the intermediate bromo compound with *m*-chloroperbenzoic acid and subsequent reaction with trifluoroacetic anhydride to yield L^2 . All the complexes **1–5** were prepared by co-crystallization of 2:1 (ligand:salt) stoichiometric amounts of L^1 or L^2 and the respective metal salts [Cu(NO₃)₂·3H₂O, CuCl₂·2H₂O and CoCl₂·6H₂O] from ethanolic solution. Crystals of the complexes

Table 1

Crystallographic and structure refinement data of the compounds studied.

| Compound | 1 | 2 | 3 | 4 | 5 |
|--|---|---|-----------------------------------|---|--|
| Empirical formula | C ₁₂ H ₁₂ N ₄ O ₈ Br ₂ Cu·H ₂ O | C ₁₂ H ₁₂ N ₂ O ₂ Cl ₂ Br ₂ Cu·H ₂ O | C12H12N4O8Br2Cu | $C_{12}H_{12}N_2O_2Cl_2Br_2Cu \cdot H_2O$ | C ₁₂ H ₁₂ N ₄ O ₈ Br ₂ Co |
| Formula weight | 581.63 | 528.50 | 563.61 | 546.53 | 505.87 |
| Crystal system | monoclinic | triclinic | monoclinic | monoclinic | orthorhombic |
| Space group | $P2_1/n$ | ΡĪ | C2/c | $P2_1/n$ | Pbcn |
| a (Å) | 8.2297(3) | 7.9333(3) | 18.2941(4) | 7.5903(2) | 14.4933(3) |
| b (Å) | 13.9737(5) | 11.1019(3) | 7.7840(2) | 33.2879(7) | 9.5820(2) |
| <i>c</i> (Å) | 16.2520(5) | 11.2436(4) | 13.6194(3) | 7.7807(2) | 12.2473(2) |
| α (°) | 90.0 | 102.670(2) | 90.0 | 90.0 | 90.0 |
| β(°) | 101.686(1) | 110.354(2) | 116.488(1) | 115.953(1) | 90.0 |
| γ(°) | 90.0 | 101.724(1) | 90.0 | 90.0 | 90.0 |
| V (Å ³) | 1830.23(11) | 862.52(5) | 1735.84(7) | 1767.66(7) | 1700.84(6) |
| Ζ | 4 | 2 | 4 | 4 | 4 |
| F(000) | 1140 | 514 | 1100 | 1068 | 980 |
| $D_{\rm calc} ({ m mg}{ m m}^{-3})$ | 2.111 | 2.035 | 2.157 | 2.054 | 1.975 |
| μ (mm ⁻¹) | 5.616 | 6.219 | 5.914 | 6.077 | 6.024 |
| Data collection | | | | | |
| T (K) | 153(2) | 90(2) | 153(2) | 173(2) | 173(2) |
| Number of collected reflections | 30311 | 42611 | 31904 | 33668 | 19746 |
| Within the θ -limit (°) | 1.9-32.1 | 2.0-38.6 | 2.5-29.4 | 1.2-35.2 | 2.8-28.4 |
| Index ranges $\pm h$, $\pm k$, $\pm l$ | -12/12, -20/20, -24/ | -13/13, -19/19, -19/19 | -25/25, -10/10, -18/ | -12/12, -53/51, -12/12 | -19/19, -11/12, -16/ |
| | 24 | | 18 | | 16 |
| Number of unique reflections | 6406 | 9745 | 2407 | 7859 | 2131 |
| R _{int} | 0.0339 | 0.1035 | 0.0262 | 0.0321 | 0.0346 |
| Refinement calculations: full-matrix least | -squares on all F ² values | | | | |
| Weighting expression w ^a | $[\sigma^2(F_0^2) + (0.0707P)^2]$ | $[\sigma^2(F_0^2) + (0.0793P)^2]$ | $[\sigma^2(F_0^2) + (0.0523P)^2]$ | $[\sigma^2(F_0^2) + (0.0429P)^2]$ | $[\sigma^2(F_0^2) + (0.0471P)^2]$ |
| | $+ 0.7713P)^{-1}$ | $+ 0.0000P)^{-1}$ | $+ 0.1047P)^{-1}$ | $+ 0.8704P)^{-1}$ | $+ 1.7805P)^{-1}$ |
| Number of refined parameters | 269 | 215 | 128 | 229 | 100 |
| Number of <i>F</i> values used $[I > 2\sigma(I)]$ | 5072 | 6571 | 2125 | 6184 | 1740 |
| Final <i>R</i> -indices | | | | | |
| $R = \sum \Delta F / \sum F_{\rm o})$ | 0.0287 | 0.0562 | 0.0225 | 0.0385 | 0.0289 |
| WR on F^2 | 0.1042 | 0.1453 | 0.0746 | 0.0964 | 0.0845 |
| $S = \text{Goodness-of-fit on } F^2$ | 0.961 | 1.005 | 1.049 | 1.061 | 0.972 |
| Final $\Delta ho_{ m max}/\Delta ho_{ m min}$ (e A ⁻³) | 0.74/-0.57 | 1.99/-1.68 | 0.52/-0.61 | 0.88/-0.89 | 0.80/-0.91 |

^a $P = (F_o^2 + 2F_c^2)/3.$

Table 2

Relevant bond distances (Å), bond angles (°) and torsion angles (°) of 1–5.

| Compound | 1 | 2 | 3 | 4 | 5 |
|-----------------------|----------|----------|----------|----------|----------|
| Bond lengths | | | | | |
| Cu(1)–N(1) | 1.990(2) | 1.972(2) | 1.970(2) | 2.004(2) | |
| Cu(1)-N(2) | 1.976(2) | 1.971(2) | | 2.010(2) | |
| Cu(1)–O(1) | 2.197(2) | 2.179(2) | 1.975(1) | 2.020(2) | |
| Cu(1)-O(2) | 1.978(2) | 2.029(2) | | 2.337(2) | |
| Cu(1)–O(4) | 1.983(2) | | 2.441(2) | | |
| Cu(1)–Cl(1) | | 2.258(1) | | 2.620(1) | |
| Cu(1)-O(1W) | | | | 1.994(2) | |
| Co(1)-N(1) | | | | | 2.125(2) |
| Co(1)-O(1) | | | | | 2.146(2) |
| Co(1)-Cl(1) | | | | | 2.406(1) |
| Bond angles | | | | | |
| N(1)-Cu(1)-N(2) | 170.0(1) | 169.2(1) | | 166.2(1) | |
| N(1)-Cu(1)-N(1) | | | 180.0 | | |
| O(1)-Cu(1)-O(2) | 101.5(1) | 95.5(1) | | | |
| O(1)-Cu(1)-O(1) | | | 180.0 | | |
| N(1)-Cu(1)-Cl(1) | | 94.2(1) | | | |
| N(2)-Cu(1)-Cl(1) | | 95.6(1) | | | |
| O(1)-Cu(1)-Cl(1) | | 109.7(1) | | | |
| O(2)-Cu(1)-Cl(1) | | 154.8(1) | | 174.7(1) | |
| N(1)-Cu(1)-O(4) | 93.4(1) | | 87.7(1) | | |
| N(2)-Cu(1)-O(4) | 96.5(1) | | | | |
| O(1)-Cu(1)-O(4) | 90.4(1) | | 91.6(2) | | |
| O(2)-Cu(1)-O(4) | 168.1(1) | | | | |
| O(1)-Cu(1)-O(1W) | | | | 170.1(1) | |
| N(1)-Co(1)-N(1) | | | | | 155.6(1) |
| O(1)-Co(1)-O(1) | | | | | 86.1(1) |
| Cl(1)-Co(1)-Cl(1) | | | | | 93.9(4) |
| N(1)-Co(1)-Cl(1) | | | | | 97.5(6) |
| O(1)-Co(1)-Cl(1) | | | | | 174.3(1) |
| Torsion angles | | | | | |
| N(1)-C(5)-C(6)-O(1) | -20.8(3) | -15.5(4) | 11.4(2) | 21.8(3) | -6.5(2) |
| N(2)-C(11)-C(12)-O(2) | -8.7(3) | -14.3(3) | | 24.5(4) | |
| | | | | | |

Table 3

Structural parameters (distances (Å), angles (°)) of hydrogen bond type interactions.

| Atoms involved | Symmetry Distance | | Angle | |
|--------------------------------------|--|--------------|--------|------------------|
| D−H···A | | $D \cdots A$ | H····A | $D{-}H{\cdots}A$ |
| 1 | | | | |
| $O(1)-H(1A)\cdots O(6)$ | 1.5 - x, -0.5 + y, 0.5 - z | 3.278(3) | 2.60 | 138 |
| $O(1)-H(1A)\cdots O(7)$ | 1.5 - x, -0.5 + y, 0.5 - z | 2.659(3) | 1.83 | 165 |
| $O(2)-H(2A)\cdots O(1W)$ | 0.5 - x, $-0.5 + y$, $0.5 - z$ | 2.501(3) | 1.65 | 177 |
| $O(1W)-H(1W1)\cdots O(6)$ | x, y, z | 2.740(3) | 1.91 | 174 |
| $O(1W)-H(1W)\cdots O(8)$ | x, y, z | 2.967(3) | 2.41 | 125 |
| $O(1W)-H(1W2)\cdots O(3)$ | -1 + x, y, z | 2.951(3) | 2.15 | 164 |
| $C(1)-H(1)\cdots O(7)$ | x, y, z | 3.282(3) | 2.37 | 161 |
| $C(1)-H(1)\cdots O(8)$ | x, y, z | 3.211(3) | 2.57 | 125 |
| $C(6)-H(6B)\cdots O(3)$ | 1.5 - x, $-0.5 + y$, $0.5 - z$ | 3.280(3) | 2.57 | 128 |
| $C(12)-H(12A)\cdots O(5)$ | -0.5 + x, $0.5 - y$, $-0.5 + z$ | 3.299(3) | 2.48 | 140 |
| 2 | | | | |
| $O(1)-H(1A) \cdot \cdot \cdot O(1W)$ | -1 + x, y, z | 2.628(4) | 1.80 | 171 |
| $O(2)-H(2A)\cdots Cl(2)$ | 1 - x, -y, 1 - z | 2.970(2) | 2.14 | 170 |
| $O(1W)-H(1W)\cdots Cl(2)$ | 1 - x, -y, 1 - z | 3.182(3) | 2.40 | 156 |
| $O(1W)-H(2W)\cdots Cl(2)$ | x, y, -1 + z | 3.184(3) | 2.38 | 162 |
| $C(8)-H(8)\cdots O(2)$ | -1 + x, y, z | 3.314(4) | 2.45 | 151 |
| $C(10)-H(10)\cdots Cl(2)$ | 1 - x, -y, 1 - z | 3.563(3) | 2.69 | 154 |
| 3 | | | | |
| $O(1)-H(1A)\cdots O(3)$ | 1.5 - x, 0.5 + y, 0.5 - z | 2.550(2) | 1.73 | 167 |
| $C(3)-H(3)\cdots O(3)$ | 2 - x, y, 0.5 - z | 3.422(3) | 2.59 | 146 |
| $C(3)-H(3)\cdots O(4)$ | 2 - x, y, 0.5 - z | 3.329(3) | 2.47 | 150 |
| $C(4)-H(4)\cdots O(2)$ | 0.5 + <i>x</i> , 0.5 + <i>y</i> , <i>z</i> | 3.198(2) | 2.52 | 128 |
| $C(4)-H(4)\cdots Br(1)$ | x, 1 + y, z | 3.981(1) | 3.05 | 166 |
| $C(6)-H(6B)\cdots O(3)$ | x, 2 - y, -0.5 + z | 3.374(2) | 2.55 | 141 |
| 4 | | | | |
| $O(1)-H(1A)\cdots Cl(2)$ | 1 + x, y, 1 + z | 2.933(2) | 2.11 | 163 |
| $O(2)-H(2A)\cdots Cl(1)$ | -1 + x, y, z | 3.173(3) | 2.39 | 156 |
| $O(1W)-H(2WA)\cdots Cl(2)$ | 1 + x, y, z | 3.096(2) | 2.27 | 168 |
| $O(1W)-H(1WA)\cdots O(2W)$ | x, y, z | 2.638(3) | 1.80 | 171 |
| $O(2W)-H(1WB)\cdots CI(2)$ | x, y, z | 3.225(3) | 2.44 | 158 |
| $O(2W)-H(2WB)\cdots Cl(1)$ | -1 + x, y, -1 + z | 3.149(2) | 2.32 | 173 |
| $C(6)-H(6A)\cdots Br(1)$ | 2 - x, 1 - y, 2 - z | 3.843(3) | 2.98 | 146 |
| $C(10)-H(10)\cdots Br(2)$ | -1 + x, y, z | 3.792(3) | 2.87 | 164 |
| 5 | | | | |
| $O(1)-H(1A)\cdots Cl(1)$ | x, 2 - y, -0.5 + z | 3.066(2) | 2.23 | 174 |
| $C(4)-H(4)\cdots Cl(1)$ | -0.5 - x, $-0.5 + y$, z | 3.587(2) | 2.87 | 135 |

Table 4

Structural parameters (distances (Å), angles (°)) of bromine involved non-covalent interactions.

| Atoms involv | ved Symmetry | Distanc | e | Angle |
|--|---|---|---|-------------------|
| C−Br···A (A = | = 0,Cl) | C····A | $Br{\cdots}A$ | $C{-}Br{\cdots}A$ |
| 1 C(9)−Br(2)···· | ·O(3) 0.5 + x, 0.5 | − <i>y</i> , −0.5 + <i>z</i> 4.825(3 | 3) 3.02 | 160 |
| $C(3)-Br(1)\cdots$ $C(9)-Br(2)\cdots$ | Cl(1) 1 - x, 1 - y Cl(2) -1 + x, y, z | r, -z 5.353(3 5.303(3 | 3) 3.57 3) 3.52 | 157 157 |
| $C(2)-Br(1)\cdots$ $C(8)-Br(2)\cdots$ 5 $C(2)-Br(1)\cdots$ | $\begin{array}{ll} \text{Cl}(1) & 2 - x, 1 - y \\ \text{Cl}(2) & 1.5 + x, 0.5 \\ \text{Cl}(1) & 0.5 - x, 2.5 \end{array}$ | x, 1 - z 5.156(2 - y, 0.5 + z 5.149(2 - y, -0.5 + z 5.417(2 | 2) 3.26 2) 3.30 2) 3.56 | 177 166 167 |

1–5 suitable for X-ray crystallography were grown by slow evaporation of solvent from solutions in ethanol.

3.2. X-ray structural study

Crystal and refinement data for the complexes **1–5** are listed in Table 1 and the structural parameters of selected interactions are shown in Tables 2–4. Perspective views of the structures including the numbering schemes of atoms are shown in Figs. 1, 3, 5, 7 and 9. Packing illustrations are presented in Figs. 2, 4, 6, 8 and 10.

3.2.1. Crystal structure of the complex $[Cu(L^1)_2NO_3]NO_3 H_2O(1)$

The complex **1** crystallizes in the monoclinic space group $P2_1/n$. The asymmetric entity of the unit cell consists of a $[Cu(L^1)_2NO_3]^+$ cation, one nitrate anion and one molecule of water being associated among each other by weak C–H \cdots O [17] and conventional O–H \cdots O hydrogen bonds [18] (Fig. 1). In the complex unit, the Cu(II) centre adopts a slightly distorted quadratic-pyramidal coordination environment of the structure N_2O_3 with the hydroxy oxygen O(1) occupying the axial position of the polyhedron. The Cu-O_{equatorial} and C-N distances are 1.978(2) [1.983(2)] and 1.976(2) [1.990(2)] Å, respectively, whereas the Cu-O_{axial} distance is 2.197(2) Å. The O-Cu-O coordination angles range between 93.4(1)° and 101.5(1)°. The aromatic rings of the complex are arranged at a dihedral angle of 72.6(1)°. The complex ligands are twisted in different degrees around their hydroxymethyl substituents, which is evident from torsion angles of $20.8(3)^{\circ}$ and $8.7(3)^{\circ}$ for the atomic sequences N(1)-C(5)-C(6)-O(1) and N(2)-C(11)-C(12)-O(2). According to the presence of a two-fold symmetry element, helical supramolecular strands in which $[Cu(L^1)_2NO_3]^+$ cations, water molecules and the non-complexed nitrate ions are interlinked by O-H...O hydrogen bonds $[d(H \cdots O) 1.65 - 2.60 \text{ Å}]$ represent the basic structure elements of 1. As illustrated in Fig. 2, interstrand association is accomplished by the formation of weak C-H···O hydrogen bonds [d(H···O)]2.37–2.57 Å] and Br. O contacts [7a,19]. With reference to this latter contacts, the separation of 3.02 Å between Br(2) and the nitrate oxygen O(3) is significantly shorter than the sum of the van der Waals radii of 3.45 Å [20].



Fig. 1. ORTEP drawing of the complex [Cu(L¹)₂NO₃]NO₃·H₂O) (1). Thermal ellipsoids are drawn at 40% probability level. Broken lines represent hydrogen bonds.



Fig. 2. Packing structure of the complex $[Cu(L^1)_2NO_3)NO_3 \cdot H_2O(1)$ viewed down the *a*-axis. Metal ions are specified as shaded circles; O, N and Br atoms are represented as dotted, hatched and cross-hatched circles, respectively. Dashed lines represent hydrogen bonds.

3.2.2. Crystal structure of the complex $[Cu(L^1)_2Cl]Cl H_2O(2)$

Regarding the complex composition, a situation similar to **1** is found in the solid phase structure of **2** which, however, crystallizes

in the space group $P\overline{1}$. The asymmetric cell unit contains one complex cation of the structure [Cu(L¹)₂Cl]⁺, one separated chloride anion and one molecule of water (Fig. 3). The coordination environment of the copper ion shows a distorted trigonal-pyramidal geometry of the donor structure N₂O₂Cl with the nitrogens occupying the axial positions of the polyhedron. Taking into account experimental error, the Cu-N distances are identical [1.971(2), 1.972(2) Å] while the Cu-O bond lengths differ [2.029(2)] and 2.179(2)Å]. The N(1)–Cu(1)–N(2) bond angle is $169.2(1)^{\circ}$, the angles O(1)-Cu(1)-Cl(1) and O(2)-Cu(1)-Cl(1) are 109.7(1)° and 154.8(1)°, respectively. The dihedral angle between the mean planes of the pyridine rings is 66.6(1)°. A view of the crystal structure of **2** along the *a*-axis (Fig. 4) reveals a complex three-dimensional pattern of non-covalent intermolecular bonding. The chloride ion excluded from complexation acts as an acceptor for the formation of O–H···Cl hydrogen bond type interactions [21] with the hydroxy hydrogen H(2A) of the complex and the hydrogens H(1W) and H(2W) of two neighbouring water molecules. The hydroxy hydrogen of the second complex ligand takes part in hydrogen bonding to the water molecule [O(1)- $H(1A) \cdots O(1W)$ 1.80 Å, 171°]. The distances between the chloride and the bromine atoms of adjacent complex units [3.52, 3.57 Å] are less than the sum of their van der Waals radii (3.60 Å) [20] thus indicating weak interhalogen contacts [7].

3.2.3. Crystal structure of the complex $[Cu(L^2)_2(NO_3)_2]$ (3)

The complex **3** crystallizes in the monoclinic space group C_2/c . The asymmetric cell unit contains one half of the complex moiety, i.e. the Cu(II) cation resides on a symmetry center (Fig. 5). The $Cu(L^2)_2$ part of the complex shows approximate planarity. Only the five-membered chelate ring adopts a slight envelope conformation with the oxygen atom located at a distance of 0.08 Å from the least-squares plane of the ligand molecule. The metal cation forms a distorted octahedral coordination environment with the nitrate ions occupying the axial positions. The bond lengths of Cu-N and Cu–O in the basal plane are 1.970(2) and 1.975(1) Å, while the axial Cu–O distances are 2.441(2) Å. A view of the crystal structure along the crystallographic *b*-axis reveals a layered arrangement of metal complexes (Fig. 6). Within the layer plane, the molecules are crosslinked via $C-H \cdots O_{nitrate}$ [C(3)-H(3)···O(4) 2.47 Å, 150°] and $C-H\cdots$ Br hydrogen bonds [C(4)-H(4)...Br(1) 3.05 Å, 166°] [17], while $O-H \cdots O_{\text{nitrate}} [O(1)-H(1A) \cdots O(3) 1.73 \text{ Å}, 167^{\circ}]$ and aromatic



Fig. 3. ORTEP drawing of the complex [Cu(L¹)₂Cl]Cl·H₂O) (2). Thermal ellipsoids are drawn at 40% probability level. Broken lines represent hydrogen bonds.



Fig. 4. Packing structure of the complex [Cu(L¹)₂Cl]Cl·H₂O (**2**) viewed down the *a*-axis. Metal ions are specified as dark shaded circles; O, N, Br and Cl atoms are represented as dotted, hatched, cross-hatched and light shaded circles, respectively. Dashed lines represent hydrogen bonds.

 $\pi \cdots \pi$ stacking interactions [22] with a distance of 3.63 Å between the centroids of pyridine rings, being in the ordinary range [9], stabilize the packing structure in direction of the *c*-axis.

3.2.4. Crystal structure of the complex $[Cu(\mathbf{L}^2)_2Cl(H_2O)]Cl\cdot H_2O(\mathbf{4})$

The complex crystallizes in the monoclinic space group $P_{1/n}$ with the asymmetric cell unit containing one cation of the structure $[Cu(L^2)_2Cl(H_2O)]^*$, one chloride anion and one molecule of water (Fig. 7). The Cu(II) ion adopts a distorted octahedral coordination environment of the structure N_2O_3Cl with the chloride ion Cl(1) and the hydroxy oxygen O(2) occupying axial positions. Within the basal plane, the Cu–N and Cu–O bonds lengths are 2.004(2) [2.010(2)] and 1.994(2) [2.020(2)] Å, respectively. Due to the Jahn–Teller effect [23], the axial C–O bond is significantly elongated [2.337(2) Å], while the Cu–Cl distance is 2.620(1) Å. The angles be-

tween the atoms in the equatorial plane range between $78.2(2)^{\circ}$ and $94.7(1)^{\circ}$. The *trans*-angles are 166.2 [N(1)–Cu(1)–N(2)], 170.1 [O(1W)–Cu(1)–O(1)] and 174.7° [O(2)–Cu(1)–Cl(1)]. The dihedral angle between the pyridine rings is 58.1° .

The crystal structure of the complex is stabilized by a variety of directed non-covalent interactions. As depicted in Fig. 8, hydrogen bonds of the O-H···O and O-H···Cl type [17] involving chloride ions and water molecules as well as hydroxy hydrogens of the complex ligands primarily contribute to intermolecular cross-linking (cf. Table 3). In this pattern of hydrogen bonding, the water molecules and those chloride ions excluded from complexation form infinite supramolecular strands extending in direction of the crystallographic *c*-axis. Moreover, the bromine atoms take part in the formation of Br···Cl interhalogen contacts [7] and C-H···Br hydrogen bond type interactions [17].



Fig. 5. ORTEP drawing of the complex $[Cu(L^2)_2NO_3)_2]$ (3). Thermal ellipsoids are drawn at 40% probability level.



Fig. 6. Packing excerpt of the complex $[Cu(L^2)_2(NO_3)_2]$ (**3**) viewed down the *b*-axis. For specification of the atom circles see Fig. 2. Dashed lines represent hydrogen bonds, dashed double lines arene–arene interactions.

3.2.5. Crystal structure of the complex $[Co(L^2)_2Cl_2]$ (5)

Crystals of the complex **5** show the orthorhombic space group *Pbcn* with one half of the complex moiety in the asymmetric cell unit (Fig. 9). The Co(II) centre adopts a distorted octahedral coordination environment of the donor set $N_2O_2Cl_2$ with *trans*-positioned nitrogen and *cis*-positioned oxygen atoms of the chelating ligand and the two chloride ions also being in a *cis*-position. The Co–N, Co–O and Co–Cl bond lengths are 2.125(2), 2.146(2) and 2.406(1) Å, respectively. The N(1)–Co(1)–N(1) and O(1)–Co(1)–



Fig. 7. ORTEP drawing of the complex $[Cu(L^2)_2Cl(H_2O)]Cl(H_2O)$ (4). Thermal ellipsoids are drawn at 40% probability level. Dashed lines represent hydrogen bonds.

Cl(1) angles are 155.6(1)° and 174.3(1)°. As shown in Fig. 10, the intermolecular organization is dominated by hydrogen-bond interactions of the O-H···Cl [d(H···Cl) 2.23] and C-H···Cl type [d(H···Cl) 2.87] [17] as well as Br···Cl interhalogen contacts [7]. Furthermore, the crystal structure is stabilized along the *b*-axis by $\pi \cdots \pi$ stacking [22] with a rather close distance of 3.31 Å between pyridine rings of consecutive molecules [9].

4. Structural comparisons and conclusions

The structural characterization of the Cu(II) complexes 1-4 and the Co(II) complex 5 reveals different coordination geometries around the respective metal centers. Although crystal growing of the complexes was carried out under identical conditions using aqueous ethanol as solvent, only three of the complexes (1, 2, 4) crystallize as mono-hydrates. The crystal structures of 1 and 2 are composed of cationic complex species of the structure $[Cu(L^1)_2X]^+$ (X = Cl, NO₃) with five-coordinated Cu(II) cations. The nature of the anion in 1 and 2 affects the molecular structure to a less extent but considerably influences the packing behaviour of the molecules, which can be attributed to different acceptor potentials of the anions. The fact that one of the counter ions is excluded from complexation but acts as highly coordinating crystal component obviously requires the presence of a water molecule to stabilize the crystal structure. As contrasted with 1 and 2, in 4 one of the water molecules participates in complexation resulting in an octahedral coordination environment of the Cu(II) center. Nevertheless, similar to the above mentioned cases, the presence of non-coordinated species with strong donor/acceptor capability, such as a water molecule and chloride anion, appears to be an essential point of the crystal structure of the compound **4**. They give rise to the formation of hydrogen bonded zigzag strands in which the chloride ions allow association of complex units via O-H···Cl hydrogen bonds [17]. Contrary to all expectations, the complex 3 obtained from Cu(NO₃)₂ trihydrate and L² does not contain crystal water. Consequently, the anions participate in complex formation leading to an octahedral coordination sphere of the metal center with a nearly coplanar arrangement of trans-positioned ligand molecules. Also in the complex 5, the Co(II) cation adopts an octahedral coordination environment. However, the configuration of which is basically different from the complex 4, in that ligand oxygens and the chloride ions are arranged in a *cis*-position around the metal cation.

A comparative inspection comprising crystal structures of the present and the corresponding previously studied bromine free analogous ligand compound 2-(hydroxymethyl)pyridine [6]



Fig. 8. Packing structure of the complex [Cu(L²)₂Cl(H₂O)]Cl·H₂O (4) viewed down the *b*-axis. For specification of the atom circles see Fig. 4. Dashed lines represent hydrogen bonds.



Fig. 9. ORTEP drawing of the complex $[{\rm Cu}(L^2)_2{\rm Cl}_2]$ (5). Thermal ellipsoids are drawn at 40% probability level.

reveals that the introduction of a bromine substituent in 4- or 5position of the pyridine ring has a fundamental influence on the crystal packing. In all structures, the bromine atom participates to a more or less degree in the molecular association by forming interhalogen contacts Br...Cl [7], Br...O interactions [7a] or C-H. Br hydrogen bonds [17]. Being more specific, the reported structure of the bromine free copper(II) nitrate complex [6] is composed of O-H···O bonded molecular strands which in turn are associated among each other by C–H···O_{nitrate} [13] and π ··· π arene [22] interactions, resulting in a layered packing arrangement of the complex molecules. In this structure, interlayer interactions are reduced to weak van der Waals forces. In a similar fashion the crystal structure of the corresponding bromine substituted analogous complex 3 consists of supramolecular strands being stabilized by $O{-}H{\cdots}O_{nitrate}$ and $C{-}H{\cdots}O_{nitrate}$ hydrogen bonds. The enhanced acceptor behaviour of nitrate ions as well as the coordinating halogen substituent, however, cause intensive interstrand association leading to the loss of layer formation. Also the copper(II) chloride complex **2** and its bromine free analogue reveal similarities regarding their molecular structures. The crystal of the latter complex is constructed of supramolecular $O-H\cdots$ Cl bonded strands with an alternating order of $[Cu(L)_2CI]^*$ complex units and chloride ions, but shows only poor interstrand association. Introduction of the bromine substituent in 4-position of the pyridine ring as well as the presence of crystal water basically influences the packing behaviour of the molecules. In the structure of **2**, the chloride anion excluded from complexation provides a strong acceptor site for hydrogen bonding to the crystal water and the complex cations resulting in a three-dimensional network of non-covalent interactions.

Apart from the coordination behaviour of the respective anion and the presence of crystal water, which both control the molecular assembly in the crystal structures, the coordination mode of the bromine in the present structures is different depending on its position at the pyridine ring. The linear geometry copper(II) complexes 1 and 2 obviously favour formation of Br...anion contacts, while in complexes 3 and 4 these substituents take part in the formation of C-H(arene)...Br hydrogen bonds. But, surprisingly enough, a pure $Br \cdots Br$ contact, relevant to the crystal structures, is not found in either of the complexes. Another point of interest relates to the $\pi \cdots \pi$ stacking property of the ligands. While in the bromine free complexes $\pi \cdots \pi$ stacking between the pyridine units is a dominating parameter [6], corresponding with an established trend [9], this particular kind of interaction is restraint in the present complexes, possibly caused by the steric hindrance of the bulky bromine substituent. Thus, introduction of a bromine substituent into the pyridine ring of the ligand 2-(hydroxymethyl)pyridine does not really affect the coordination behaviour to the present metal cations Cu(II) and Co(II) but the more the packing structure of the respective complex units. This offers a promising possibility to use the bromine substitution as a controlling function in the



Fig. 10. Packing structure of the complex [Co(L²)₂Cl₂] (5) viewed down the *b*-axis. For specification of the atom circles see Fig. 4. Dashed lines represent hydrogen bonds.

crystal engineering of metal ion complexes involving organic ligands [8,24].

5. Supplementary data

CCDC 757730, 757731, 757732, 757733 and 757734 contains the supplementary crystallographic data for **1–5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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