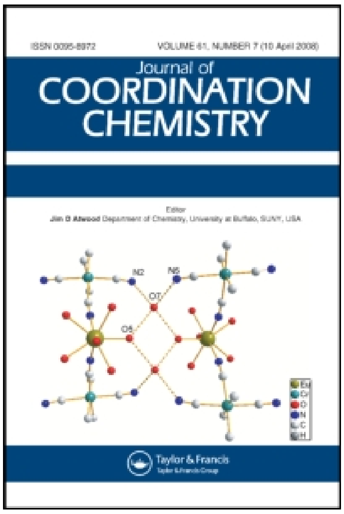

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Coordination properties of 4(5)-hydroxymethylimidazole and 4(5)-hydroxymethyl-5(4)-methylimidazole towards cobalt(II) ions

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Two new complexes of imidazole alcohols, 4-hydroxymethylimidazole (4-CH_2OHim) and 4-hydroxymethyl-5-methylimidazole (4-CH_2OH-5-CH_3im), with cobalt(II) of formula $[CoL_2(H_2O)_2](NO_3)_2$ were obtained. These compounds were described through single X-ray diffraction studies, spectroscopic (Ir. Far-IR, UV-Vis-NIR) and magnetic measurements. In the present complexes imidazole ligands are bidentate coordinating the heterocyclic ring through pyridine-like nitrogen and the oxygen atom of the hydroxymethyl group (chromophore CoN_2O_4). The shape of Co(II) coordination polyhedra is that of a distorted octahedron, with the equatorial plane defined by the 4-CH_2OHim (or 4-CH_2OH-5-CH_3im) bidentate ligands and two water molecules occupying axial positions (i.e. trans to each other). Formation of successive cobalt(II) complexes with 4-CH_2OH-5-CH_3im in aqueous solution was followed quantitatively by potentiometry.

Keywords: Cobalt(II) complexes; Imidazole complexes; Crystal structures; Electronic spectra

1. Introduction

The imidazole residue, present in a side-chain of natural aminoacid L-histidine, plays an important role as a general-acid – general-base catalyst in the active site of hydrolytic enzymes such as ribonuclease A [1], α-chymotrypsin [2] and other serine proteases [3]. This molecule is also essential for the structure and activity of zinc-dependent metalloenzymes including carbonic anhydrase [4] or carboxypeptidase A [5] where the central zinc(II) is coordinated by imidazole residues of active site histidines. The presence of imidazole is also important for the performance of oxygen-binding metalloproteins such as hemoglobin or myoglobin, where the heme moiety is bound to the protein through a coordinate bond between an imidazole ring of so-called proximal histidine and the central iron atom [6].

In order to investigate the mechanism of action of these enzymes, numerous studies were undertaken with imidazole, its alkyl derivatives and transition metal complexes as

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enzyme model systems. Thus, the complexes of tris(imidazoyl) carbinols or bis(imidazolyl) glycolic acid with Zn(II), Co(II) or Ni(II) ions were studied as models of metal binding site of zinc-dependent enzymes [7]. Similarly, macrocyclic molecules containing imidazole complexed with copper(II) ions were used as models of copper-containing enzymes [8] whereas 1-methylimidazole and 1,2-dimethylimidazole complexes of Co(II)–porphyrin were employed as models of cobalt-substituted hemoglobin [9].

The importance of imidazole for biological activity of various metalloproteins prompted us to synthesize complexes of substituted imidazoles with transition metal ions.

The imidazole alcohol has two potential metal-binding sites, the imidazole pyridine-like nitrogen N3 of the heterocyclic ring and the hydroxymethyl oxygen atom (O).

In previous studies coordination properties of 4-CH_2OH-5-CH_3im to copper(II) and nickel(II) in solid state and in aqueous solution were presented [10]. The molecular structure and physico-chemical properties of cobalt(II) complex, of the formula $[Co(4\text{-}CH_2OH\text{-}5\text{-}CH_3im)_4](NO_3)_2$, was described [11]. Thermal stability, kinetics and decomposition mechanism of these complexes were also studied [12]. Coordination properties of the other homologous imidazole alcohol, 4-CH_2OHim, in aqueous solution were given in the study [13]. In this article we present our results on the crystal and molecular structure and spectroscopic properties of two crystalline complexes formed by 4-hydroxymethylimidazole (4-CH_2OHim) and 4-hydroxymethyl-5-methylimidazole (4-CH_2OH-5-CH_3im) with cobalt(II) ions, containing two molecules of these imidazole alcohols in the coordination sphere. The stability constants of the complexes of cobalt(II) with 4-CH_2OH-5-CH_3im in aqueous solution were determined by the potentiometric method.

2. Experimental

2.1. *Reagents and physical measurement*

4(5)-Hydroxymethylimidazole was synthesized at the Institute of Pharmacology, Polish Academy of Sciences, Kraków, Poland [14]. 4-Hydroxymethyl-5-methylimidazole hydrochloride, $Co(NO_3)_2 \cdot 6H_2O$, methanol, propan-2-ol and butan-1-ol were purchased from Aldrich. 4-Hydroxymethyl-5-methylimidazole hydrochloride was neutralized adding a stoichiometric quantity of $KHCO_3$ (14.87 g of 4-CH_2OH-5-CH_3im · HCl was dissolved in 100 cm^3 of water, and, then, 10.01 g of $KHCO_3$ dissolved in 150 cm^3 of water was gradually added to this solution constantly stirring). Free 4-hydroxymethyl-5-methylimidazole was extracted in butan-1-ol.

Elemental analyses were run on a Model 240 Perkin Elmer CHN Analyzer. The IR spectra were recorded on a Perkin Elmer 180 (spectral range 50–4000 cm^{-1}) spectrophotometer in Nujol and in KBr pellets. The far-IR spectra were obtained in Nujol mulls sandwiched between polyethylene plates. The diffuse reflectances spectra (5000–30,000 cm^{-1}) were recorded on a Cary 5 UV-VIS-NIR spectrophotometer in Nujol mulls. Magnetic measurements were carried out on a magnetic susceptibility balance (Sherwood Scientific) at room temperature by using $Hg[Co(NCS)_4]$ as the calibrant.

2.2. *Crystal data*

X-ray measurements were performed on a Kuma KM4 diffractometer. The structures were solved by direct methods using the SHELXS 97 [15] and refined by full-matrix least-squares methods using the SHELXL 97 [16] program. Details of the crystal data and refinement for studied compounds are collected in table 1. Selected bond lengths and angles are given in table 2 and the hydrogen bonding geometry are given in tables 3 and 4.

2.3. *Potentiometric measurements*

Potentiometric measurements of the metal-ion systems were carried out using a PHM-84 pH meter (Radiometer) and a GK 24001 C combination electrode placed in a glass vessel thermostated at 298 K in solution of constant ionic strength $I = 0.5\,\mathrm{mol\,dm^{-3}}$ maintained with KNO_3. The electrode was calibrated by means of a HCl solution of known titre with a KOH solution. The concentration of protonated ligand (HL^+) in stock solutions used in potentiometric titrations was $0.10\,\mathrm{mol\,dm^{-3}}$.

In the three series of measurements the metal/HL^+ molar ratios were 1 : 4, 1 : 6 and 1 : 8. Titration with the base was conducted in triplicate, over the pH range 2.5–7.0. The dissociation constants of the conjugate acid and stability constants, β_n, of the complexes were refined by the SUPERQUAD program [17].

2.4. *Spectroscopic measurements*

The visible-range absorption spectra of the cobalt(II) complexes in aqueous solutions were recorded on a Specord M-500 (Carl Zeiss, Jena) spectrophotometer. The solutions were prepared in an analogous manner to those for the potentiometric titrations. The initial metal concentrations were $0.02\,\mathrm{mol\,dm^{-3}}$. The highest concentration of the ligand was $0.20\,\mathrm{mol\,dm^{-3}}$.

Table 1. Crystal data and structure refinement for $[Co(4\text{-}CH_2OHim)_2(H_2O)_2](NO_3)_2$ (**1**) and $[Co(4\text{-}CH_2OH\text{-}5\text{-}CH_3im)_2(H_2O)_2](NO_3)_2$ (**2**) complexes.

	1	**2**
Empirical formula	$C_8H_{16}N_6O_{10}Co$	$C_{10}H_{20}N_6O_{10}Co$
Molecular weight	415.20	443.25
T (K)	100(1)	100(1)
Radiation	Mo-Kα ($\lambda = 0.71073$ Å)	Mo-Kα ($\lambda = 0.71073$ Å)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	6.816(2)	6.795(2)
b (Å)	10.458(2)	11.716(2)
c (Å)	11.129(2)	10.922(2)
β (°)	92.06(2)	91.16(1)
V (Å^3)	792.8(3)	869.3(1)
Z	2	2
μ (mm^{-1})	1.739	1.693
Reflections collected	5152	14679
Independent reflections	1861, [$R_{(int)} = 0.0323$]	4326 [$R_{(int)} = 0.0302$]
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0269, 0.0629	0.0314, 0.0739
Final R_1, wR_2 (all data)	0.0350, 0.0658	0.0446, 0.0784
Largest difference peak and hole (e Å^{-3})	0.277 and −0.329	0.610 and −0.556

Table 2. Selected bond lengths (Å) and angles (°) for $[Co(4\text{-}CH_2OHim)_2(H_2O)_2](NO_3)_2$ (**1**) and $[Co(4\text{-}CH_2OH\text{-}5\text{-}CH_3im)_2(H_2O)_2](NO_3)_2$ (**2**).

	1	**2**
Co–N(1)	2.068(1)	2.058(1)
Co–O(1)	2.115(1)	2.123(1)
Co–O(2)	2.123(1)	2.124(1)
O(1)–C(4)	1.435(2)	
O(1)–C(5)		1.432(1)
N(1)–C(3)	1.387(2)	1.385(1)
C(3)–C(4)	1.504(2)	
C(3)–C(5)		1.499(1)
O(3)–N(3)	1.276(2)	1.255(1)
O(4)–N(3)	1.234(2)	1.274(1)
O(5)–N(3)	1.259(2)	1.237(1)
N(1)–Co–N(1)[a]	180.0	180.0
N(1)–Co–O(1)[a]	102.64(5)	102.02(3)
N(1)–Co–O(1)	77.36(5)	77.98(3)
N(1)[a]–Co–O(1)	102.64(5)	102.02(3)
O(1)[a]–Co–O(1)	180.0	180.0
N(1)–Co–O(2)	88.82(5)	89.97(3)
N(1)[a]–Co–O(2)	91.18(5)	90.03(30)
O(1)[a]–Co–O(2)	90.36(5)	90.31(3)
O(1)–Co–O(2)	89.64(5)	89.69(3)
N(1)–Co–O(2)[a]	91.18(5)	90.03(3)
O(1)–Co–O(2)[a]	90.36(5)	90.31(3)
O(2)–Co–O(2)[a]	180.0	180.0
C(4)–O(1)–Co	118.09(10)	
C(5)–O(1)–Co		118.38(6)
C(3)–N(1)–Co	115.34(10)	115.26(5)
O(4)–N(3)–O(5)	121.31(13)	119.52(7)
O(4)–N(3)–O(3)	119.76(12)	120.09(8)
O(5)–N(3)–O(3)	118.93(12)	120.39(8)
N(1)–C(3)–C(4)	119.44(13)	
N(1)–C(3)–C(5)		120.34(7)
O(1)–C(4)–C(3)	106.80(13)	
O(1)–C(5)–C(3)		107.12(7)

Symmetry transformations used to generate equivalent atoms: a $= -x, -y, -z$.

2.5. *Preparation of the complexes*

2.5.1. $[Co(4\text{-}CH_2OHim)_2(H_2O)_2](NO_3)_2$ (1). A solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.2910 g, 1 mmol) in methanol (25 cm^3) was slowly added to the solution of 4-hydroxymethylimidazole (0.1643 g, 2 mmol) in the same alcohol (25 cm^3). The molar ratio was 1 : 2. The mixture was placed in the refrigerator. After passive evaporation of the solvent (after about six weeks), apricot-coloured crystals of the complex appeared in thick violet-pink oil. The reaction efficiency was 8%. The results of the elemental analysis were as follows (%): C; 23.3, H; 3.9, N; 20.1, calculated for $Co(4\text{-}CH_2OHim)_2(H_2O)_2(NO_3)_2$: C; 23.14, H; 3.88, N; 20.24.

2.5.2. $[Co(4\text{-}CH_2OH\text{-}5\text{-}CH_3im)_2(H_2O)_2](NO_3)_2$ (2). Solutions of 4 mmol of 4(5)-CH_3-5(4)-CH_2OHim in 20 cm^3 of 2-propanol and of 2 mmol of $Co(NO_3)_2 \cdot 6H_2O$ in 20 cm^3 of the same alcohol were prepared. The solutions were mixed slowly adding the solution of cobalt nitrate to the solution of the ligand. The mixture was left to crystallize at 10°C. After a fortnight pink crystals of the complex crystallized from the blue solution. The crystals were collected in 28% yield. The results of the elemental analysis were as follows: (%): C; 27.1, H; 4.7, N; 19.1, calculated for Co(4-CH_2OH-5-CH_3im$)_2(H_2O)_2(NO_3)_2$: C; 27.10, H; 4.55, N; 18.96.

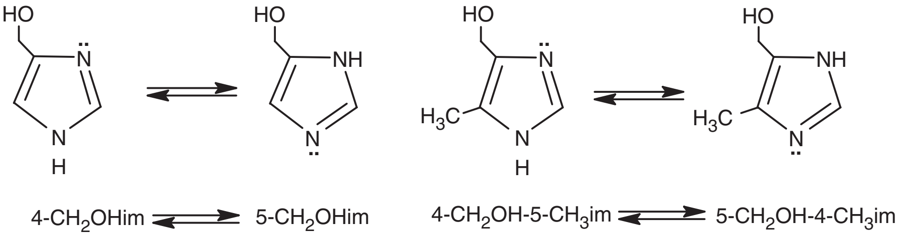
2.6. *Theoretical calculation*

Calculations were carried out with the GAUSSIAN 98W program running on a PC Pentium IV computer [18].

3. Results and discussion

3.1. *Molecular structures of the cobalt(II) complexes*

Imidazole derivatives containing the substituent at position 4 of the ring or two different substituents at positions 4 and 5 occur in tautomeric equilibria:



The previous studies showed that the form containing the hydroxymethyl substituent adjacent to the donor nitrogen atom of the ring (4-CH_2OHim and 4-CH_2OH-5-CH_3im) is privileged in coordination reactions [10–13]. Apart from the nitrogen atom, the oxygen atom of this group can be another donor in the co-ordination bond. In such complexes as [M(4-CH_2OH-5-CH_3im$)_4](NO_3)_2$, where M = Cu(II), Ni(II) and Co(II), the above-mentioned alcohol is of dual nature. Two molecules act as monodentate ligands co-ordinating through the pyridine "3" nitrogen atom of the heterocyclic ring, whereas the remaining two are chelating ligands additionally bonding through the oxygen atom of the hydroxymethyl group [11].

The present cobalt(II) compounds with 4-hydroxymethylimidazole (4-CH_2OHim) and 4-hydroxymethyl-5-methylimidazole (4-CH_2OH-5-CH_3im) are cation complexes containing two molecules of imidazole base and two molecules of water in the co-ordination sphere of the central ion, $[CoL_2(H_2O)_2](NO_3)_2$. These ligands occupy *trans* positions in the coordination polyhedron (the molecular structure of these compounds is shown in figures 1 and 2).

Both 4-CH_2OHim and 4-CH_2OH-5-CH_3im are chelating ligands here. "Pyridine" nitrogen atoms of imidazole rings and oxygen atoms of hydroxymethyl groups are donor atoms. Consequently, in the present complexes the immediate surrounding of the central ion is made up of two nitrogen atoms and four oxygen atoms

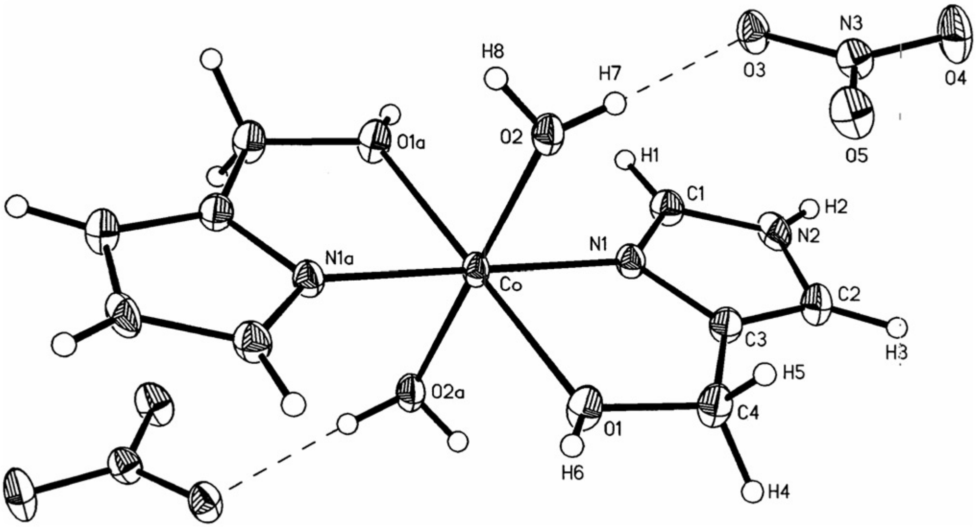


Figure 1. Molecular structure of $[Co(4\text{-}CH_2OHim)_2(H_2O)_2](NO_3)_2$ (**1**) with the atom numbering scheme.

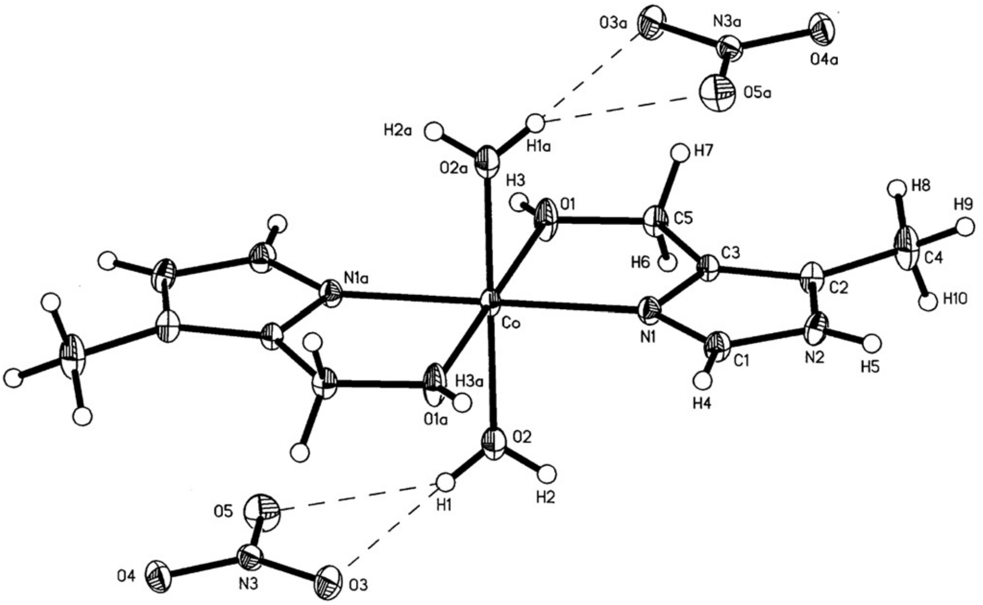


Figure 2. Molecular structure of $[Co(4\text{-}CH_2OH\text{-}5\text{-}CH_3im)_2(H_2O)_2](NO_3)_2$ (**2**) with the atom numbering scheme.

(CoN_2O_4 chromophore). As a result of coordination, five-member chelating rings are formed. The nitrogen–cobalt–oxygen angles in these rings are 77.36(5) and 77.98(3)° in complexes **1** and **2**. In the complex with four $4\text{-}CH_2OH\text{-}5\text{-}CH_3im$ molecules studied earlier [11] the angle was 78.82(4)°, whereas in the Co(II) complex with the anion of imidazole-4-acetic acid (also CoN_2O_4 chromophore) the angle was 84.5(1)° [19].

Table 3. Hydrogen-bonds for $[Co(4\text{-}CH_2OHim)_2(H_2O)_2](NO_3)_2$ (**1**) (Å and °).

D–H···A	d(D–H)	d(H···A)	d(H···A)	∠(DHA)
N(2)–H(2)···O(5)^b	0.83(2)	2.21(2)	2.9042(19)	142(2)
N(2)–H(2)···O(2)^b	0.83(2)	2.47(2)	3.0818(18)	131(2)
O(1)–H(6)···O(3)^c	0.76(2)	2.05(2)	2.7873(16)	166(2)
O(2)–H(7)···O(3)	0.84(3)	1.92(3)	2.7572(16)	175(2)
O(2)–H(8)···O(5)^d	0.82(2)	1.99(2)	2.8030(18)	174(2)

Symmetry transformations used to generate equivalent atoms: $a = -x, -y, -z$; $b = x + 1/2, -y + 1/2, z + 1/2$; $c = x - 1, y, z$; $d = -x + 1/2, y - 1/2, -z - 1/2$.

Table 4. Hydrogen-bonds for $[Co(4\text{-}CH_2OH\text{-}5\text{-}CH_3im)_2(H_2O)_2](NO_3)_2$ (**2**) (Å and °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(2)–H(1)···O(3)	0.82(2)	2.16(2)	2.978(1)	170.7(16)
O(2)–H(1)···O(5)	0.82(2)	2.54(2)	3.166(1)	134.1(15)
O(2)–H(2)···O(4)^b	0.79(2)	2.00(2)	2.779(1)	172.0(17)
O(1)–H(3)···O(4)^c	0.77(2)	2.10(2)	2.848(1)	164.9(17)
O(1)–H(3)···O(5)^c	0.77(2)	2.43(2)	3.045(1)	137.3(16)
N(2)–H(5)···O(3)^d	0.88(2)	2.07(2)	2.833(1)	144.9(13)

Symmetry transformations used to generate equivalent atoms: $a = -x, -y, -z$; $b = -x + 1/2, y + 1/2, -z - 1/2$; $c = -x - 1/2, y + 1/2, -z - 1/2$; $d = -x + 1, -y, -z$.

The remaining angles and bond lengths of chelating rings are very close in both complexes **1** and **2** (table 2).

The cobalt(II)–nitrogen bond lengths are 2.068(1) and 2.058(1) Å in complexes **1** and **2**, respectively, similar to the corresponding cobalt–nitrogen bond lengths in $[Co(4\text{-}CH_2OH\text{-}5\text{-}CH_3im)_4](NO_3)_2$ studied earlier [11]. The bonds of the cobalt with oxygen are slightly longer than those with nitrogen, namely 2.115(1) and 2.122(1) Å in complex **1**, and 2.123(1) and 2.124(1) Å in complex **2**. They are then about 0.07 Å as short as the corresponding bonds in $[Co(4\text{-}CH_2OH\text{-}5\text{-}CH_3im)_4](NO_3)_2$ [11]. The stereochemistry of the coordination polyhedron is described as distorted *trans*-octahedral. The distortion concerns, first of all, the nitrogen-cobalt-oxygen bond angles in the chelating molecules of azole ligands. As a result of chelation the N(1)–Co–O(1) bond angle differs from 90° by −22.6° in complex **1** and by −22.0° in complex **2**.

In both complexes the nitrate group is outside the coordination sphere of the central ion and is bound by hydrogen bonds with the hydrogen atom of the water molecule. In complex **2** the two oxygen atoms of the nitrate group O(3) and O(5) form intramolecular hydrogen bonds with the H(1) atom of the water molecule, whereas in complex **1** only one O(3) atom forms a bond with the water molecule. The lengths and angles of these bonds are given in tables 3 and 4.

The nitrogen–oxygen bond lengths of the nitrate group are: 1.23(2), 1.26(2) and 1.28(2) Å in complex **1**, and 1.24(1), 1.25(1) and 1.27(1) Å in complex **2**. The oxygen–nitrogen–oxygen bond angles of complex **1** are 120.4(1), 119.5(1), 120.1(1)°, whereas in complex **2** the O(5)–N(3)–O(3) angle differs from the trigonal value 120° by −1.1°, being 118.9(1)°, as a result of the presence of the oxygen atoms O(3) and O(5) in the hydrogen bond.

The crystal structure of the present complexes is stabilized by intermolecular hydrogen bonds (tables 3 and 4). The molecular packings of the

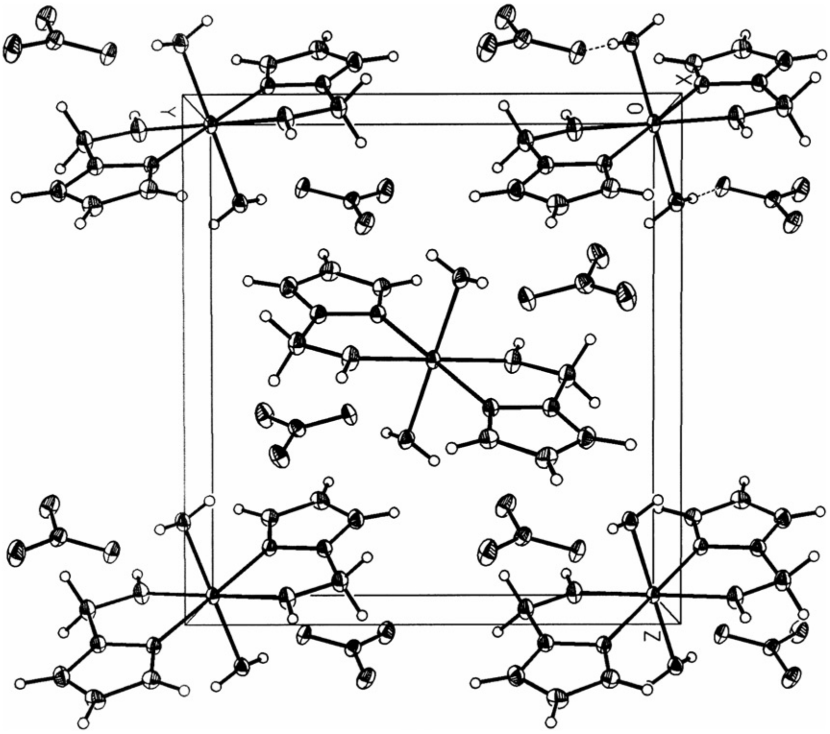


Figure 3. Molecular packing of $[Co(4\text{-}CH_2OHim)_2(H_2O)_2](NO_3)_2$ (**1**) in the unit cell.

$[Co(4\text{-}CH_2OH)_2(H_2O)_2](NO_3)_2$ complex **1** and the $[Co(4\text{-}CH_2OH\text{-}5\text{-}CH_3im)_2(H_2O)_2](NO_3)_2$ complex **2** in the unit cell are shown in figures 3 and 4.

3.2. *Spectroscopic and magnetic properties*

The IR and far-IR spectra are in accord with the above-mentioned structures of the complexes. Coordinate metal–nitrogen and metal–oxygen bonds of the complexes under investigation are signalled in far-IR spectra where new bands, absent from spectra of free imidazole ligands, are observed. In the cobalt(II) complexes with $4\text{-}CH_2OHim$ (**1**) and $4\text{-}CH_2OH\text{-}5\text{-}CH_3im$ (**2**) these bands are placed at $\nu_{Co\text{–}N}$ 269 and $275\,cm^{-1}$, $\nu_{Co\text{–}O}$ 331 and $327\,cm^{-1}$, respectively. The "non-coordinated" character of the nitrate group in the present complexes is reflected in the IR spectra by the position of the sharp and strong band at $1385\,cm^{-1}$ and of the considerably weaker one at $812\,cm^{-1}$.

In the IR spectra a broad and complicated band between 3300 and $2700\,cm^{-1}$ is also noteworthy. It results from the presence of water and hydrogen bonds in the molecules of the present coordination compounds [20].

Visible-range and near IR absorption spectra are characteristic of hexacoordinate, octahedral coordination complexes of the central ion of cobalt(II) since three absorption maxima connected with such electronic transitions as ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) [21, 22] are observed, in accord with ligand field theory. The electronic spectra of both complexes,

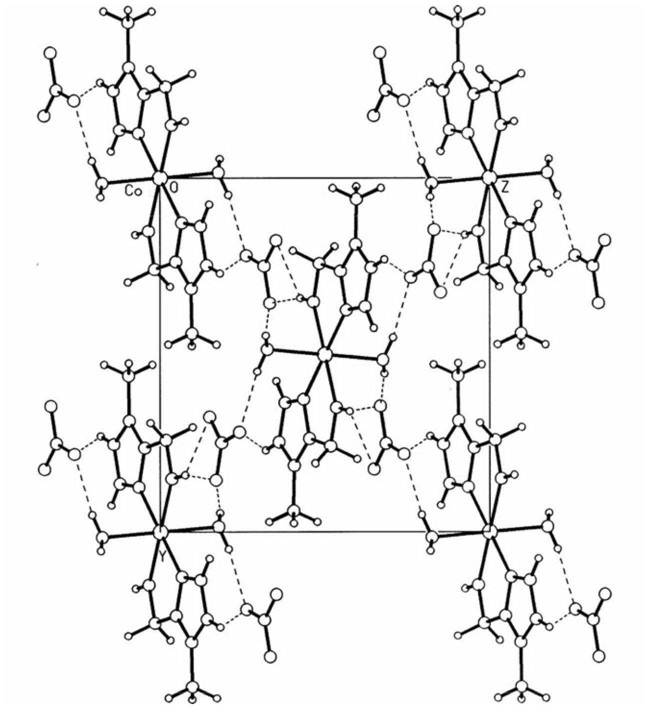


Figure 4. Molecular packing of $[Co(4\text{-}CH_2OH\text{-}5\text{-}CH_3im)_2(H_2O)_2](NO_3)_2$ (**2**) in the unit cell.

$[Co(4\text{-}CH_2OHim)_2(H_2O)_2](NO_3)_2$ and $[Co(4\text{-}CH_2OH\text{-}5\text{-}CH_3im)_2](NO_3)_2$, are very similar, expected with similar structures of both CoN_2O_4 chromophores.

A weak absorption band, at $\nu_1 = 11{,}000\,\mathrm{cm}^{-1}$ is observed for both complexes in the IR range. The strongest absorption band of both complexes is at $20{,}300\,\mathrm{cm}^{-1}$, asymmetric and broad at lower energies. Such a shape results from the superposition of several component bands. The diagram of this absorption range is divided by the Gauss distribution into two individual bands. The positions of the maxima of individual bands are at $\nu_2\ ({}^4T_{1g}(F) \rightarrow {}^4A_{2g}) = 19{,}200\,\mathrm{cm}^{-1}$ and $\nu_3\ ({}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)) = 23{,}000\,\mathrm{cm}^{-1}$.

The picture of the d–d spectra corresponds with the CoN_2O_4 chromophore of distorted octahedral because the presence of two chelating imidazole alcohols in the coordination sphere results in the deformation of bond angles in the equatorial plane of the polyhedron determined by donor atoms N_{ring} and O_{-CH_2OH}.

The effective magnetic moments of the cobalt(II) complexes at room temperature are 4.85 and 4.92 M.B. for **1** and **2**, respectively. These values are consistent with high-spin six-coordinate complexes.

3.3. *Investigation in aqueous solution*

Coordination properties and stability of complexes with metal ions depend on such essential physico-chemical properties of ligands as basicity, nucleophility, steric effect, distribution of electron density on atoms etc. In the present molecules with imidazole ligands, i.e. 4-hydroxymethylimidazole and

4-hydroxymethyl-5-methylimidazole as well as their alkyl derivatives, 4-methylimidazole and 4,5-dimethylimidazole, steric conditions in coordination reactions with metal ions are very similar because positions of substituents in relation to the donor nitrogen atom N3 are the same. The difference in coordination properties of these azoles result mainly from their different electronic properties.

Employing DFT theoretical calculation with the B3PW91 functional and 6-311++G** basic set, we established the charge density on each atom. The obtained values are shown in figure 5.

Substitution of the methyl group by the hydroxymethyl group results in decreasing charge density on the pyridine-like nitrogen atom. It is reflected in the basicity of the present imidazoles, i.e. alcohol derivatives are weaker bases by one order of magnitude than methylimidazoles, e.g. pK_a for 4,5-dimethylimidazole is 8.19, for 4-hydroxymethyl-5-methylimidazole 7.14 (table 5). Although the basicity of 4-hydroxymethyl-5-methylimidazole is lower, stability constants of its complexes with cobalt(II) ions ($\log \beta_1 = 1.90$) are higher than compounds of 4,5-dimethylimidazole ($\log \beta_1 = 1.17$) (table 5).

Coordination of cobalt(II) ions with 4-hydroxymethyl-5-methylimidazole in aqueous solution is described by stability constants (β_n) listed in table 5. On the basis of these constants, curves of percentile molar contributions of successive complexes being formed in aqueous solution are plotted in figure 6.

Quantities of constants of substituting the proton for the central metal ion, expressed by the dependence $\log^*\beta_1 = \log \beta_1 - pK_a$ (table 5), are useful in analysis of the coordination. This parameter eliminates the influence of the basicity of the ligand on the stability of its complexes with metal ions. $\text{Log}^*\beta_1$ for cobalt(II) complexes with 4,5-dimethylimidazole is −7.02, whereas for 4-hydroxymethyl-5-methylimidazole complexes it is higher, $\log^*\beta_1 = -5.34$. The substitution constant for 4-hydroxymethylimidazole is also higher than for 4-methylimidazole. An increase in the stability constant of cobalt(II) complexes resulting from the substitution of the methyl group by hydroxymethyl group can only be accounted for by the interaction

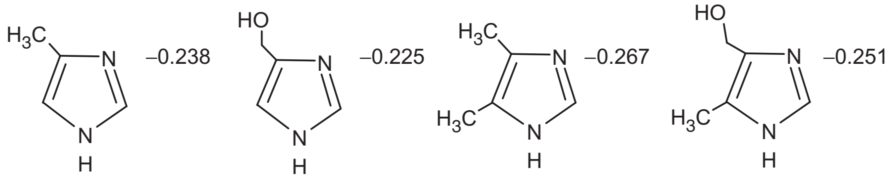


Figure 5. Calculated values of charge density for 4-methylimidazole, 4-hydroxymethylimidazole, 4,5-dimethylimidazole, 4-hydroxymethyl-5-methylimidazole.

Table 5. Stability constants and substitution constants of some imidazole derivatives with cobalt(II) ion in aqueous solution at 298 K and $I = 0.5\,\text{mol dm}^{-3}$ (KNO_3).

Ligand	pK_a	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	$\log^*\beta_1$	Ref.
4(5)-Methylimidazole	7.80	2.34	4.09	5.33	6.67	−5.46	[23]
4(5)-Hydroxymethylimidazole	6.67	1.88	3.60	4.62	5.98	−4.79	[12]
4,5-Dimethylimidazole	8.19	1.17				−7.02	[24]
4(5)-Hydroxymethyl-5(4)-methylimidazole	7.14	1.80(2)	3.60(3)	4.91(3)		−5.34	This work

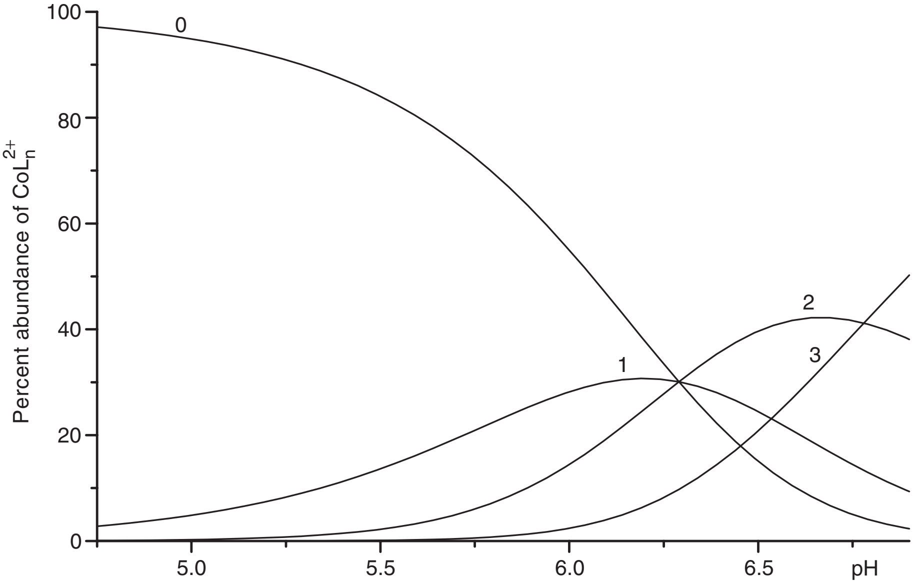


Figure 6. Distribution diagrams of complexes formed in the Co^{2+} – 4-hydroxymethyl-5-methylimidazole systems as a function of pH at 298 K and $I = 0.5\,\mathrm{mol\,dm^{-3}}$. The number in the diagrams mean n in CoL_n^{2+}.

of the oxygen atom in the donor bond and the central ion. This parameter is not high enough to assume that chelates of two stable bonds with the central ion are formed in the present solutions. The quantitative analysis of changes in stability constants of successive complexes $\log(K_2/K_1)$ shows no indication of the existence of typical strong chelate bonds. The bond with the oxygen atom is weak and easily broken because it is not accompanied by loss of the proton from the hydroxymethyl group and leads to the establishment of equilibrium between, for example, the first cobalt(II) complex with 4-hydroxymethyl-5-methylimidazole as a monodentate ligand and the first chelate complex where, apart from the donor nitrogen atom of the heterocyclic ring N3, the oxygen atom of the group $-CH_2OH$ is involved:

$$[Co(H_2O)_5L]^{2+} \leftrightarrow [Co(H_2O)_4L]^{2+} + H_2O$$

The dual character of 4-hydroxymethyl-5-methylimidazole as a ligand in coordination reactions is confirmed by X-ray structural studies of its $[Co(4\text{-}CH_2OH\text{-}5\text{-}CH_3im)_4](NO_3)_2$ complexes where two alcohol molecules are bidentate and the remaining two are monodentate ligands [11].

This type of 4-hydroxymethyl-5-methylimidazole coordination with cobalt(II) ions in aqueous solution is confirmed by visible-range absorption spectra. With increasing azole ligand concentration, the bathochromic shift of the absorption maximum from $19{,}600\,\mathrm{cm^{-3}}$ for cobalt(II) aquacomplexes to $17{,}900\,\mathrm{cm^{-1}}$ for 4-hydroxymethyl-5-methylimidazole complexes is observed. At the analytic concentration of cobalt(II) ions $0.02\,\mathrm{mol\,dm^{-3}}$, $\mathrm{pH} = 7.50$, the mean molar coefficient of extinction is $138\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$.

A similar spectral pattern and a similar value of the extinction coefficient were observed for cobalt(II) complexes with dipivaloymethane [22] and diketones [25].

In such systems the authors suggested a similar coordination mechanism, i.e. interaction of the oxygen atom with the central ion.

Supplementary data

Tables of crystal data and structure refinement, anisotropic displacement coefficients, atomic coordinates and equivalent isotropic displacement parameters for nonhydrogen atoms, H-atom coordinates and isotropic displacement parameters, bond lengths and interbond angles have been deposited with the Cambridge Crystallographic Data Centre under No. CCDC 609822 and CCDC 609823 for compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge from Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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