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Synthesis, crystal structures and spectroscopic studies on *trans* and *cis* isomers of Co(II) complexes with 1-benzyl-2-hydroxymethylimidazole

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Abstract

By carrying out the synthesis in a special way, two novel cobalt(II) isomers of *trans*(*O*)-[Co(1-Bz-2-$CH_2OHIm)_4](NO_3)_2$ (**1**) and *cis*(*O*)-[Co(1-Bz-2-$CH_2OIm)_4](NO_3)_2 \cdot 1.5H_2O$ (**2**) have been separated. The crystal structures of the Co(II) isomers show the triclinic space group $P\bar{1}$ (**1**) and the monoclinic space group $C2/c$ (**2**). The coordination geometry around the Co atom is approximately octahedral (**1**) or very distorted octahedral (**2**) and the Co(II) ions are surrounded by four nitrogen atoms of the four imidazole rings and two oxygen atoms of the hydroxymethyl group. Two of the ligands act as a monodentate and two as a bidentate, forming the five–membered chelate ring with the central ion. The structural data obtained for the Co(II) isomers were confirmed by IR and UV–Vis spectroscopic methods.

Keywords: *Cis* and *trans* Co(II) isomers; Bidentate ligand; Crystal structure; UV–Vis and IR spectra

1. Introduction

The cobalt(II) ion is frequently used to substitute for zinc ion in proteins, and the cobalt(II)-substituted enzymes often show about as much catalytic activity as the native zinc enzymes. During the last three decades, many efforts have been made to characterize the active centers of these metalloproteins. The use of low molecular weight model compounds of these biological macromolecules has proved to be very useful and in some cases the only possible way to understand better the structure and function of their active sites. From our earlier studies on the coordination behavior of the imidazole ring towards the Co(II) ion in solution it follows that the compounds of Co(II) with 1-alkylimidazoles have octahedral or pseudo-octahedral symmetry [1,2]. However, the derivatives containing alkyl substituents situated in the position 2 or 4 of the imidazole ring, present steric hindrance to complexation and decrease the coordination number of central ion from six to four. It results in the configuration equilibrium of the octahedron↔tetrahedron type [3,4]. Recently, we have found that the CH_2OH group situated in the 2 position of the imidazole ring has no such steric effect. This was explained by an additional interaction between the oxygen atom of the hydroxymethyl group and the Co(II) metal ion [5,6]. This results in the formation of five membered chelate ring. Quantitative analysis of log K_n/log K_{n+1} does not indicate the existence of typical, strong chelates in solution because the metal–oxygen bond is weak and easily broken.

In the light of our previous results we extend our studies to the solid state chemistry of Co(II) complexes with 1-benzyl-2-hydroxymethylimidazole, potentially coordinating not only by nitrogen but also oxygen atoms. Special attention was paid to find direct proof of its chelation role towards the Co(II) ion on the basis of X-ray crystal structure analysis.

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2. Experimental

2.1. Chemicals

1-Bz-2-CH_2OHIm (96–97 °C) was synthesised at the Technical University of Poznan. The purity of 1-Bz-2-CH_2OHIm was additionaly monitored by chromatography.

2.2. Instrumentation

Elemental analyses were run on a model 240 Perkin–Elmer CHN analyzer.

The infrared spectra (4000–400 cm^{-1}) in KBr and FIR spectra (400–30 cm^{-1}) in Nujol, with specimens applied as a suspension of the complexes in Nujol onto a polyethylene window, were recorded on a Perkin–Elmer 180 spectrophotometer.

The absorption spectra were recorded using a Specord M-40 (Carl Zeiss Jena). The reflectance spectra were measured on a Cary 5 UV–Vis–near IR spectrometer. The X-ray patterns of the residues found were obtained on a Kuma KM4CCD k-axis diffractometer.

Conductivity measurements were carried out with a N572 (Mera-Elwro) conductivity meter using 1×10^{-3} mol dm^{-3} solution of the complexes. Magnetic measurements were carried out on a magnetic susceptibility balance (Sherwood Scientific) at room temperature by Guoy's method using $Hg[Co(NCS)_4]$ as the calibrant.

2.3. Spectra in the visible region

The complexes of Co(II) with 1-Bz-2-CH_2OHIm were investigated by a spectral method over the visible range. The ligands' concentration were 2.4×10^{-1} mol dm^{-3} and the concentration ratio of metal–ligand was 1:6. The absorption spectra were recorded after pH adjustment by NaOH or HNO_3, at constant ionic strength ($I = 0.5$ M).

2.4. X-ray crystallography

Measurements of the crystal were performed on a Kuma KM4CCD k-axis diffractometer with a graphite monochromator and Mo Kα radiation. The crystal was positioned at 65 nm from the KM4CCD camera. 612 frames were measured at 0.750 intervals with a counting time of 30 s.

The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma diffraction (Wroclaw) program. The crystallographic data and the refinement procedure details are given in Table 1.

The structures were solved by direct methods with SHELXS-97 [7] and refined by full-matrix least-square methods on all F^2, using the SHELXS-97 [7] program. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included from the delta rho maps and refined with isotropic thermal parameters. Only in the case of water molecules and hydroxymethyl groups, H atoms were not refined.

Table 1
Crystal data and structure refinement for *cis* and *trans* Co(II) complexes with 1-benzyl-2-hydroxymethylimidazole

	Isomer *trans* (**1**)	Isomer *cis* (**2**)
Empirical formula	$C_{44}H_{48}N_{10}O_{10}Co$	$C_{44}H_{51}N_{10}O_{11.5}Co$
Formula weight	935.85	962.88
T (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
Unit cell dimensions		
a (Å)	9.315(2)	37.261(7)
b (Å)	10.930(2)	10.154(2)
c (Å)	12.579(3)	24.408(5)
α (°)	109.79(3)	
β (°)	98.96(3)	97.69(3)
γ (°)	109.35(3)	
V (Å^3)	1084.0(4)	9152(3)
Z	1	8
D_{calc} (g cm^{-3})	1.434	1.398
Crystal size (mm)	$0.15 \times 0.15 \times 0.20$	$0.15 \times 0.20 \times 0.25$
$F(000)$	489	4032
2Θ Range (°)	6.0–57.7	5.2–48.0
Extinction coefficient		0.00006(9)
Range of h, k, l	$-12 \rightarrow 6$,	$-42 \rightarrow 42$,
	$-14 \rightarrow 14$,	$-11 \rightarrow 11$,
	$-16 \rightarrow 16$	$-14 \rightarrow 27$
No. reflections measured/unique	7741/4924 [$R_{int} = 0.0135$]	22 709/7173 [$R_{int} = 0.0238$]
No. reflections observed	4712 [$I > 2\sigma(I)$]	6543 [$I > 2\sigma(I)$]
No. parameters varied	391	781
Goodness-of-fit (on F^2)	1.054	1.111
R_1, wR_2	0.0311, 0.00747	0.0649, 0.1653
R_1, wR_2	0.0325, 0.0764	0.0701, 0.1711
Largest difference peak and hole (e Å^{-3})	0.337 and −0.402	0.635 and −0.496

2.5. Synthesis of the coordination compounds

By carrying out the synthesis in the same way as for the Cu(II) complex with 1-benzyl-2-hydroxymethylimidazole [8] we obtained an oil as a product. It was a mixture of two isomers which have been separated by synthesis in a special way.

2.5.1. *Trans(O)-[Co(1-Bz-2-CH_2OHIm)$_4$](NO_3)$_2$*

A solution of 1-Bz-2-CH_2OHIm (0.5645 g, 3 mmol) in 20 cm^3 of trimethyl orthoformate was added dropwise to a stirred solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.1451 g, 0.5 mmol) in 20 cm^3 of trimethyl orthoformate. The molar ratio Co:L was 1:6. The solution was left to stand at room temperature (r.t.) for a few days and the resulting pale pink crystals were filtered and washed with cold

Et_2O and after that were dried for 3 days in a vacuum box. Under these preparative conditions a complex of definite stoichiometry was formed. *Anal.* Found: C, 56.46; H, 5.30; N, 14.92. Calc.: C, 56.65; H, 5.18; N, 14.96%. The complex has $\Lambda_M = 173$ S cm^2 mol^{-1} in MeOH, consistent with a 2:1 electrolyte.

2.5.2. *Cis(O)-[Co(1-Bz-2-CH$_2$OHIm)$_4$](NO$_3$)$_2$·1.5H$_2$O*

This complex was prepared by a method similar to that described above but a solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.1454 g, 0.5 mmol) in 20 cm^3 of timethyl orthoformate was added dropwise to a stirred solution of 1-Bz-2-CH$_2$OHIm (0.3768 g, 2 mmol) in 20 cm^3 of timethylorthoformate. The molar ratio Co:L was 1:4. The violet crystals of definite stoichiometry, suitable for X-ray analysis were obtained. *Anal.* Found: C, 55.09; H, 5.43; N, 14.65. Calc.: C, 54.77; H, 5.33; N, 14.51%. The complex has the same value of conductivity, $\Lambda_M = 173$ S cm^2 mol^{-1} at 298 K in MeOH, consistent with a 2:1 electrolyte.

3. Results and discussion

3.1. *Description of the structures*

3.1.1. *Crystal structure of trans(O)-[Co(1-Bz-2-CH$_2$OHIm)$_4$](NO$_3$)$_2$*

Trans(*O*)-[Co(1-Bz-2-CH$_2$OHIm)$_4$](NO$_3$)$_2$ crystallizes in the triclinic space group $P\bar{1}$. A perspective drawing of the complex cation is given in Fig. 1 together with a numbering scheme. Selected bond distances and angles are listed in Table 2.

The present complex adopts a six coordinate structure and the coordination geometry around the Co atom which is the center of symetry, is approximately octahedral. The Co atom is surrounded by four nitrogen atoms of the imidazole rings: N(11), N(1$_a$), N(21), N(2$_a$) and two oxygen atoms: O(11), O(11$_a$) of the hydroxymethyl group. Thus, two of the ligands act as monodentate and two as bidentate, forming a five-membered chelate ring with the central ion.

The two hydroxo oxygen atoms of two ligands occupy *trans* positions to each other. Therefore, the structure of the complex (Fig. 1) is assigned to *trans*(*O*)-[Co(1-Bz-2-CH$_2$OHIm)$_4$]·2NO$_3$. The Co–O distances (2.1749(10) Å are shorter than Cu–O distances (2.472 Å) [8] of similar complexes [Cu(1-Bz-2-CH$_2$OHIm)$_4$](NO$_3$)$_2$, apparently for the second one, due to the Jahn–Teller effect. The coordination distances Co–N(11), (2.0905(12) Å) and Co–N(21), (2.1557(15) Å) are longer than the Cu–N distances of *trans*(*O*)-Cu(II) complexes (2.009 and 2.028 Å) [8]. The charge of the cationic complexes is balanced by two nitrate anions which interact by hydrogen bonds with the OH of the hydroxymethyl group of the ligand. There are hydrogen bonds between O(11) and O(21) and O(2), O(1) of the nitrate anions (Table 4) leading to O(11)–H(1)···O(2) (1.820(2) Å), and O(21)–H(13)···O(1) (1.990(3) Å) interactions.

3.1.2. *Crystal structure of cis(O)-[Co(1-Bz-2-CH$_2$OHIm)$_4$](NO$_3$)$_2$·1.5H$_2$O*

Selected bond distances and angles are given in Table 3. Fig. 2 shows the coordination polyhedron around Co(II). The cobalt(II) ion is six coordinated by two oxygen atoms O(11), O(21) of the hydroxymethyl group which occupy *cis* positions to each other and four nitrogen atoms furnished by the imidazole rings, N(11) N(21), N(31), N(41). Two of the ligands act as monodentate and two as bidentate. The stereochemistry of the metal centre is very irregular, and it can be considered a distorted octahedron, with the equatorial plane defined by the O(11), O(21), N(31), N(41) atoms and the axial positions occupied by the N(11) and N(21) atoms. The equatorial metal–ligand distances Co–N(31) (2.135 Å) and Co–N(41) (2.096 Å) which participated in forming five-membered chelate rings with the central ion, are shorter than the cobalt–oxygen; Co–O(21) (2.205 Å) Co–O(11) (2.247 Å). However, due to the differences between Co–N and Co–O distances the chelation is definitely asymmetric. The cobalt–nitrogen axial bond Co–N(11) and Co–N(21) have lengths 2.143 and 2.124 Å, respectively.

The form of distortion in the *cis*-*O*-[Co-(1Bz-2-CH$_2$OH)$_4$]$^{2+}$ cation involves not only bond lengths but also apparent is bond angle distortion (see Table 3). However, the angles at the metal centre are quite far from those at an octahedron, because of the asymmetric chelating effect of two ligands and a *cis* distorting effect.

The crystal structure of the complex is stabilized by a network of hydrogen bonds. There are hydrogen bonds between O–H of the hydroxymethyl group of two imidazole molecules and water oxygen atoms O(11)–H(11)···O(7) and O(41)–H(41)···O(8) (Table 4).

The following two molecules of 1-Bz-2-CH$_2$OH parcitipate in hydrogen bonding interaction with oxygen atoms of the nitrate groups. Additionally, the oxygen atoms of the nitrate groups are engaged in hydrogen bonding with the molecules of H$_2$O (Table 4).

3.2. *Vibration spectra*

The free ligands exhibits a broad absorption band at 3136 cm^{-1} which is assigned to inter- and intramolecular hydrogen bond ν(O···H···N) vibration. The complexes which consist of two kind of ligands, mono- and bidentate, exhibit two absorption bands of O–H vibration, at 3336 and 3119 cm^{-1} for the *cis*-Co(II)-complex and at 3336 and 3123 cm^{-1} for the *trans*-Co(II) complex. The first one owing to a ν(O–H) vibration is assigned to the free OH group of the monodentate ligands which coordinate to the Co(II)

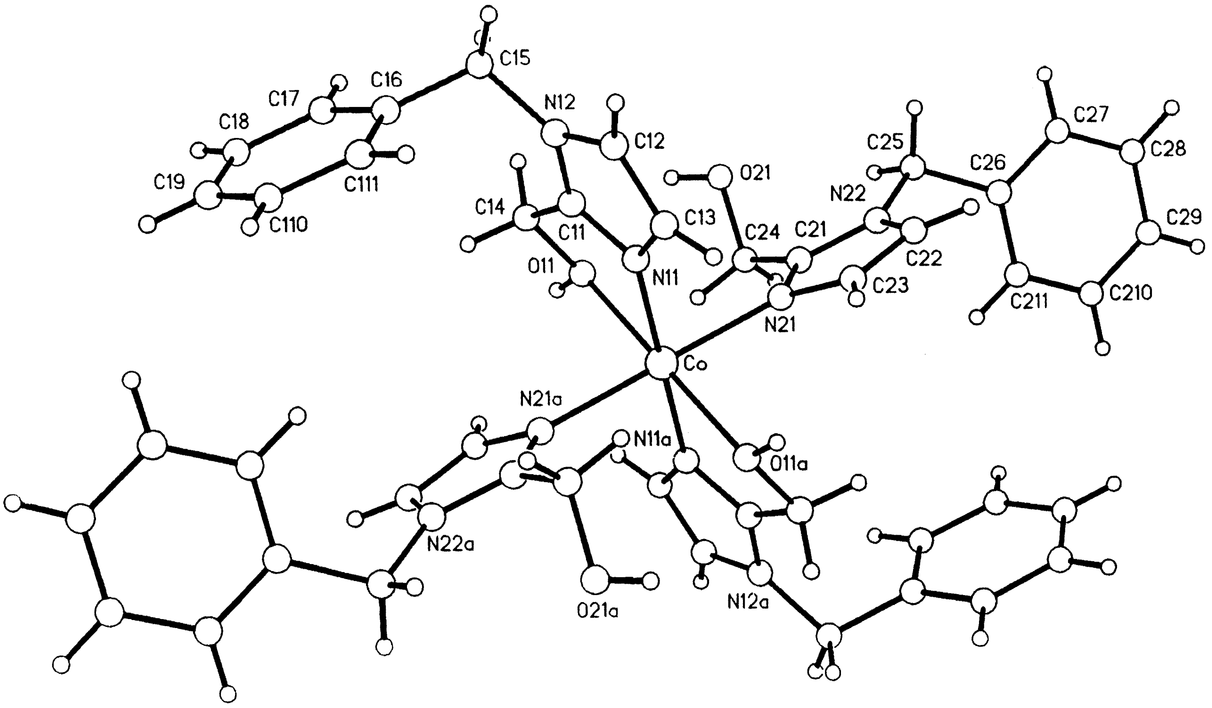

Fig. 1. Atomic numbering scheme and the structure of the complex *trans*(*O*)-[Co(1-Bz-2-CH$_2$OHIm)$_4$](NO$_3$)$_2$.

Table 2
Selected bond lengths (Å) and bond angles (°) for *trans*(*O*)-[Co(1-Bz-2-CH$_2$OHIm)$_4$](NO$_3$)$_2$

Bond lengths			
Co–N(11)	2.0905(12)	Co–N(21)	2.1557(15)
Co–N(11)^a	2.0905(12)	Co–O(11)	2.1749(10)
Co–N(21)^a	2.1557(15)	Co–O(11)^a	2.1749(10)
Bond angles			
N(11)–Co–N(11)^a	180.0	N(11)–Co–O(11)^a	103.20(4)
N(11)–Co–N(21)^a	89.98(5)	N(11)^a–Co–O(11)^a	76.80(4)
N(11)^a–Co–N(21)^a	90.02(5)	N(21)^a–Co–O(11)^a	92.87(5)
N(11)–Co–N(21)^a	90.02(5)	N(21)–Co–O(11)^a	87.13(5)
N(11)^a–Co–N(21)	89.98(5)	O(11)–Co–O(11)^a	180.0
N(21)^a–Co–N(21)	180.0	C(14)–O(11)–Co	113.94(8)
N(11)–Co–O(11)	76.80(4)	C(11)–N(11)–Co	113.51(8)
N(11)^a–Co–O(11)	103.20(4)	C(13)–N(11)–Co	140.22(9)
N(21)^a–Co–O(11)	87.13(5)	C(21)–N(21)–Co	130.72(9)
N(21)–Co–O(11)	92.87(5)	C(23)–N(21)–Co	122.76(9)

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

Table 3
Selected bond lengths (Å) and bond angles (°) for *cis*(*O*)-[Co(1-Bz-2-CH$_2$OHIm)$_4$](NO$_3$)$_2$·1.5H$_2$O

Bond lengths			
Co–N(41)	2.096(3)	Co–N(11)	2.143(3)
Co–N(21)	2.124(3)	Co–O(21)	2.205(2)
Co–N(31)	2.135(3)	Co–O(11)	2.247(2)
Bond angles			
N(41)–Co–N(21)	96.82(11)	N(31)–Co–O(21)	86.82(11)
N(41)–Co–N(31)	102.56(12)	N(11)–Co–O(21)	87.83(10)
N(41)–Co–N(11)	100.66(11)	N(41)–Co–O(11)	88.51(11)
N(41)–Co–N(11)	97.55(11)	N(21)–Co–O(11)	84.39(10)
N(21)–Co–N(11)	153.56(11)	N(31)–Co–O(11)	167.08(10)
N(31)–Co–N(11)	97.72(11)	N(11)–Co–O(11)	73.93(9)
N(41)–Co–O(21)	168.38(10)	O(21)–Co–O(11)	83.07(10)
N(21)–Co–O(21)	74.46(10)		

ion only by the nitogen atom of the imidazole ring and the second to the OH group being sensitive to metal coordination via the oxygen atom.

The spectrum of the free ligand shows a strong band at 1031 cm^{-1} which is attributed to the ν(C–O) frequencies. After coordination, this bond splits into two bands at 1049 and 1028 cm^{-1} for the *cis*-complex and 1052 and 1031 cm^{-1} for the *trans*-complex which are assigned to the ν(C–O) frequencies of the CH$_2$OH group for the mono- and bidentate ligand, respectively. Both of the *cis* and *trans* Co(II) complexes with 1-Bz-2-CH$_2$OHIm show new bands, compared to the ligand spectrum in the far IR area. The IR spectra for both isomers, however, are significantly different. The *trans*-Co(II) complex exhibits single absorption bands of Co–N and Co–O stretching vibrations, at 256 and 461 cm^{-1}, respectively. The complex which has *cis*-distorted octahedral symmetry exhibits two absorption bands of Co–N and Co–O vibrations at 298, 269 and 475, 458 cm^{-1}, respectively. Such spectra are typical of *cis*-isomer complexes [9].

3.3. Electronic d–d spectra and magnetic properties of the complexes

The absorption spectra in aqueous solution of the Co(II) ion with 1-Bz-2-CH$_2$OHIm suggest that the

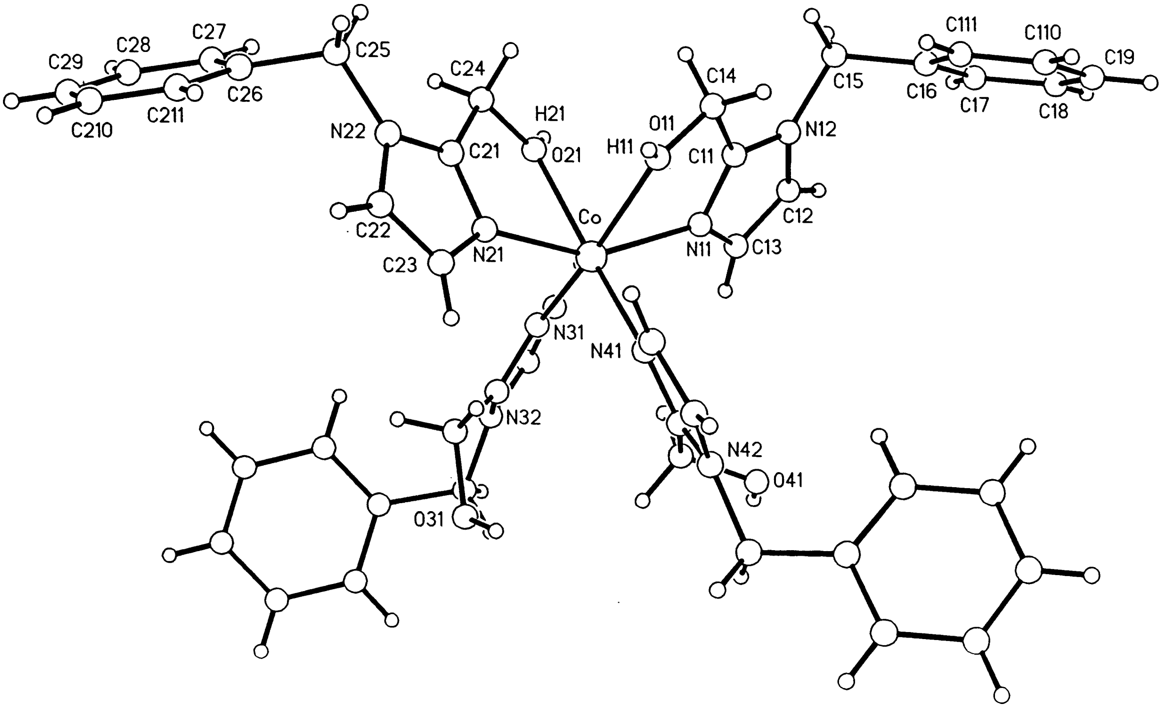

Fig. 2. Atomic numbering scheme and the structure of the complex *cis*(*O*)-[Co(1-Bz-2-CH$_2$OHIm)$_4$](NO$_3$)$_2$·1.5H$_2$O.

Table 4
Hydrogen bond lengths (Å) and bond angles (°)

D–H···A	Lengths			Angles
	D···H	H···A	D···A	DHA
trans(O)-[Co(1-Bz-2-CH$_2$OHIm)$_4$](NO$_3$)$_2$				
O(11)–H(1)···O(2)^a	0.84(2)	1.82(2)	2.647(2)	167(2)
O(21)–H(13)···O(1)^b	0.81(3)	1.99(3)	2.763(2)	160(2)
cis(O)-[Co(1-Bz-2-CH$_2$OHIm)$_4$](NO$_3$)$_2$·1.5H$_2$O				
O(11)–H(1)···O(7)	0.93	1.75	2.593(4)	148.6
O(21)–H(21)···O(3)^b	0.93	1.79	2.681(5)	158.4
O(31)–H(31)···O(4)	1.02	1.76	2.739(5)	159.2
O(41)–H(41)···O(8)	0.83	2.15	2.803(11)	135.2
O(8)–H(82)···O(1)	0.73	2.46	2.808(10)	111.4
O(7)–H(71)···O(5)^c	0.94	2.29	3.229(6)	177.2
O(7)–H(71)···O(6)^c	0.94	2.37	3.022(6)	126.4
O(7)–H(72)···O(6)^b	0.99	2.01	2.998(6)	174.5

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

Co(II) ion is in a pseudooctahedral environment. The spectrum of the complex shows a maximum at 511 nm ($^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$) at pH 4.78 and has a low value for the molar absorption coefficient ($\bar{\varepsilon} = 8.91$ dm^3 mol^{-1} cm^{-1}). The complex at higher pH appeared to be insoluble in water. The solid state *cis*(*O*)- and *trans*(*O*)-[Co(1-Bz-2-CH$_2$OHIm)$_4$](NO$_3$)$_2$·1.5H$_2$O complexes dissolved in methanol shows identical absorption spectra which are similar to the aqueous complex of Co(II) with 1-Bz-2-CH$_2$OHIm. The $\lambda_{\max}$ at 520 nm and $\bar{\varepsilon}_{\max} = 25.77$ dm^3 cm^{-1} mol^{-1} confirmed the octahedral structure of the complexes. The change of the color from pale pink of the *trans*(*O*)-complex to violet after the dissolution suggested that the *trans* isomer is unstable in solution and isomerised to the *cis*-complex which has violet color [10].

The electronic spectrum of the solid *trans*(*O*)-[Co(1-Bz-2-CH$_2$OHIm)$_4$](NO$_3$)$_2$ complex is typical of six coordinate complexes [11] and shows two d–d strong bands and one band of weaker intensity. The first band ($\nu_1 = 9340$ cm^{-1}) is assigned to the transition $^4T_{2g} \rightarrow {}^4T_{1g}(F)$, the second band ($\nu_2 = 15698$ cm^{-1}) is a weak one, assigned to the transition $^4A_{2g} \rightarrow {}^4T_{1g}(F)$, the third band ($\nu_3 = 20660$ cm^{-1}) which is split into three components is assigned to the transition $^4T_{1g}(P) \rightarrow {}^4T_{1g}(F)$. The spectra of the studied complex are diffuse and asymmetric, thus indicating overlap of several bands. For closer examination of these spectra a Gauss distribution could be applied. The positions of individual bands for the complexes, obtained from such an analysis, are shown in Table 5. The reasonable values of $Dq = 1021$ cm^{-1}, $B = 834$ cm^{-1}, $Dq/B = 1{,}22$ for O_h symmetry of a CoN$_4$O$_2$ chromophore were calculated [12] from the absorption maxima of the *trans*(*O*)-Co(II) complex.

Absorption bands due to d–d electronic transitions for *cis*(*O*)-[Co(1-Bz-2-CH$_2$OHIm)$_4$](NO$_3$)$_2$·1.5H$_2$O are presented in Table 5. However, the calculated B value is not reliable. This electronic spectrum may be the outcome of the high degree of distortion from an ideal octahedron (vide supra), which is due to both the unsymmetrical Co–N and Co–O bonds distances and the angles at the metal centre.

Table 5
Ligand field absorption bands (cm^{-1}) and magnetic properties of the complexes

Compound	Colour	Electronic spectra			μ_{eff}
		$\Lambda_{everaged}$	Gauss analysis		
trans(*O*)-$[CoL_4](NO_3)_2$	light pink	20 660	24 570	ν_3	
			20 325	ν_3	
			18 690	ν_3	4.97
			15 686	ν_2	
			9340	ν_1	
cis(*O*)-$[CoL_4](NO_3)_2 \cdot 1.5H_2O$	violet	19 048	21 142	ν_3	
			18 727	ν_3	
			15 674	ν_2	4.81
			8305	ν_1	

Effective magnetic central moments of the cobalt (II) complexes at room temperature are 4.97 and 4.81 μ_B for the *trans* and *cis* isomers, respectively. These values are consistent with high-spin six coordinate complexes.

3.4. Comparison with related structures

The molecular structures of the described compounds have made clear that the 1-Bz-2-CH_2OHIm is an interesting chelating agent which coordinates bidentately through the oxygen atom of the hydroxymethyl group and the imidazole nitrogen. The structure of Co(II) complexes with these compounds resemble the structure of ML_2X_2 with L = 4(5)-propylmercaptomethylimidazole, 2-propylmercaptomethylpyridine [13,14], 5-methyl-4-(ethylmercaptomethyl)imidazole [15] containing N, S-donor atoms instead of N,O. All compounds contain metal ions which are six coordinated with two ligands and two anions or solvent molecules with sulfur-donor atoms in *trans* positions. The coordination distances, for example Co–N (2.066 and 2.118 Å) in the compound [Co(5-methyl-4-(ethylmercaptomethyl-imidazole)$_2$ (NCS)$_2$] [15], are comparable to those in the *trans*(*O*)-[Co(1-Bz-2-CH_2OHIm)$_4$] (2.0905 and 2.1557 Å) whereas the Co–S distance (2.5504 Å) is much longer than the Co–O distance (2.1749 Å). The coordinating behavior of the 1,6-bis(5-methyl-4-imidazolyl)-2,6-dithiahexane and 1,7-bis(5-methyl-4-imidazolyl)-2,6-dithiaheptane [16,17] which contain N_2,S_2-donor atoms changes dramatically. The sulfur atoms are forced in the *cis* position and compressed octahedral geometries are observed.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 168005 and 168006. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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