

Vanadium(III) chloride complexes of 1,2-bis-(5-H/methyl/chloro/nitro-1*H*-benzimidazol-2-yl)-1,2-ethanediols

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Abstract. The complexes of 1,2-bis-(5-H/methyl/chloro/nitro-1*H*-benzimidazol-2-yl)-1,2-ethanediols (**L1-L4**) with VCl_3 were synthesized and characterized by elemental analyses, molar conductivity, FTIR and 1H -NMR spectroscopy. The ligands act as bidentate coordinating through both of the hydroxyl group oxygen atoms in the complexes. The ionic and diamagnetic complexes have the empirical formula $[V(L)_2]Cl_3$. The $[V(L4)_2]Cl_3$ complex has two isomeric structures according to the 1H -NMR spectral data.

Keywords: benzimidazole, 1,2-ethanediols, VCl_3 complexes, characterization.

INTRODUCTION

Bis-benzimidazoles are known to be strong chelating agents coordinating through both the C=N nitrogen atoms. In addition, bis-benzimidazoles have a polymer-forming characteristic.^{1–4}

In addition, bis-benzimidazoles have various pharmacological activities. For example, 1,2-bis-(2-benzimidazolyl)-ethane has antipoliiovirus⁵ and antifungal effects.⁶ 1,3-Bis-(2-benzimidazolyl)-propane shows and antiviral effect; and its nitro and hydroxyl derivatives show antifungal character and considerable activity towards poliovirus formation.⁷ Bis-(5-chlorobenzimidazoles) and some bis-(benzimidazolyl)-alkane/hydroxyalkane derivatives have antifungal, antitumor, antiviral, yeast inhibition, antibacterial, sedative, diuretic and anthelmintic activity.^{6,8} 1,2-Bis-(1*H*-benzimidazol-2-yl)-1,2-ethanediol (**L1**) shows antifungal and anti-poliiovirus effects.^{6,9,10} It is believed that metal complexes of bis-benzimidazole may also be biologically active because of their strong chelating characteristics.

Vanadium has a biological role in the human body. During the last few decades, the facade of vanadium as a “slightly” toxic and carcinogenic element was eventually ratified to an essential trace element with anti-diabetic and anti-carcinogenic properties.¹¹ Vanadium complexes with certain amino acids have been pro-

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posed as anti-tumour and anti-leukemic agents.¹² They initiate the photo-cleavage of DNA.¹³ In addition, vanadium complexes play a very important role in catalytic organic chemistry.^{14,15}

The aim of this study was to prepare the vanadium(III) chloride complexes of 1,2-bis-(1*H*-benzimidazol-2-yl)-1,2-ethanediol (**L1**), 1,2-bis-(5-methyl-1*H*-benzimidazol-2-yl)-1,2-ethanediol (**L2**), 1,2-bis-(5-chloro-1*H*-benzimidazol-2-yl)-1,2-ethanediol (**L3**) and 1,2-bis-(5-nitro-1*H*-benzimidazol-2-yl)-1,2-ethanediol (**L4**) and characterise them using modern spectroscopic methods.

EXPERIMENTAL

Materials

All chemicals and solvents were of reagent grade. The IR spectra (KBr pellets) were recorded on a Mattson 1000 Fourier Transform spectrometer. Routine solution ¹H-NMR spectra were run on a Varian Unity Inova 500 NMR spectrometer. Analytical data were obtained with a Thermo Finnigan Flash EA 1112 microanalyser and a Varian SpectrAA 220/SS atomic absorption spectrometer. The molar conductance of the compounds was measured on a WPA CMD750 conductivity meter in DMSO.

Synthesis of the ligands

The ligands were synthesized using dl-tartaric acid and 4-R-1,2-phenylenediamines (R = H, CH₃, Cl, NO₂) according to literature procedures.^{16,17} The structure of the ligands is shown in Fig. 1.

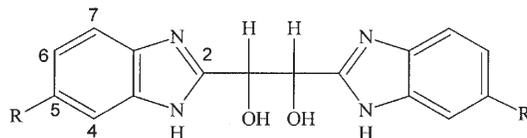


Fig. 1. The structure of the ligands (R=H, **L1**; R=CH₃, **L2**; R=Cl, **L3**; R=NO₂, **L4**).

Preparation of the complexes

Preparation of V(**L1**)₂Cl₃: Anhydrous VCl₃ (75 mg, 0.48 mmole) was dissolved in ethanol (25 cm³) under a nitrogen atmosphere, and then the ligand, **L1**, (140 mg, 0.48 mmole) was added to this solution. The mixture was refluxed for 4 h and then filtered. The filtered solution volume was decreased in volume to 10 cm³ by evaporating and then cooled to under +4 °C in a refrigerator. The dirty white precipitate which formed was filtered, washed with diethylether and dried at 70–80 °C.

The other complexes, V(**L2**)₂Cl₃, V(**L3**)₂Cl₃, V(**L4**)₂Cl₃ were synthesized in a similar manner to that employed for V(**L1**)₂Cl₃.

RESULTS AND DISCUSSION

General Properties

The elemental analysis results, yields, melting points, and molar conductivities are given in Table I.

TABLE I. Analytical data and some physico-chemical properties of the ligands and the complexes

Compound	El. Analysis; Found (Calcd.)				Yield %	m.p. °C ^a	Λ ^b
	%C	%H	%N	%V			
L1 C ₁₆ H ₁₄ N ₄ O ₂	65.3 (65.3)	4.8 (4.7)	19.0 (18.9)	–	80	268	0
V(L1) ₂ Cl ₃ C ₃₂ H ₂₈ Cl ₃ N ₈ O ₄ V	51.3 (51.5)	3.9 (3.7)	9.7 (9.9)	7.0 (6.8)	70	274	135

TABLE I. Continued

Compound	El. Analysis; Found (Calcd.)				Yield %	m.p. °C ^a	Λ^b
	%C	%H	%N	%V			
L2 C ₁₈ H ₁₈ N ₄ O ₂	67.3 (67.1)	5.7 (5.6)	17.2 (17.4)	–	65	233	0
V(L2) ₂ Cl ₃ C ₃₆ H ₃₆ Cl ₃ N ₈ O ₄ V	53.7 (53.9)	4.6 (4.5)	13.8 (4.5)	6.6 (6.3)	70	268	133
L3 C ₁₆ H ₁₂ N ₄ Cl ₂ O ₂	53.1 (52.9)	3.4 (3.3)	15.3 (15.4)	–	65	223	0
V(L3) ₂ Cl ₃ C ₃₂ H ₂₄ Cl ₇ N ₈ O ₄ V	43.7 (43.5)	2.9 (2.7)	12.5 (12.7)	6.0 (5.9)	70	285	150
L4 C ₁₆ H ₁₂ N ₆ O ₆	50.2 (50.0)	3.3 (3.1)	21.7 (21.9)	–	60	176	0
V(L4) ₂ Cl ₃ C ₃₂ H ₂₄ Cl ₃ N ₁₂ O ₁₂ V	41.6 (41.5)	2.7 (2.6)	17.9 (18.1)	5.7 (5.5)	75	241	141

^a Decomposed; ^b Molar conductivity, measured in DMSO at 25 ± 1 °C, S cm²mol⁻¹

The ligands were soluble in polar solvents such as methanol, ethanol, acetic acid and dimethyl sulfoxide, and insoluble in water and diethylether. The dirty white colored complexes were soluble in polar solvents and insoluble in common organic solvents such as toluene and tetrahydrofurane.

The molar conductivities of V(**L1**)₂Cl₃, V(**L2**)₂Cl₃, V(**L3**)₂Cl₃ and V(**L4**)₂Cl₃, in DMSO at 25 ± 1 °C, were 135, 133, 150 and 141 S cm² mol⁻¹, respectively. These values indicate the ionic structures of the complexes and 1:3 type of electrolytes.

VCl₃ is a paramagnetic compound and its color is blue. However, the complexes in this study were dirty white and diamagnetic. This observation shows that the complexes are low-spin.

It is reported that the above mentioned ligands gave the 1:1 M : L complexes with PdCl₂,¹⁷ AgNO₃,¹⁸ HgCl₂.¹⁹ In the present study, according to the analytical data, the M : L ratio in the VCl₃ complexes with the ligands was 1:2.

IR Spectra

The IR spectral data of the ligands and the corresponding complexes are given in Table II.

TABLE II. IR spectral data of the ligands and the complexes

Compound	Frequencies/cm ⁻¹ *
L1	3431 <i>s</i> , 3184 <i>br</i> , 3061 <i>m,br</i> , 2815 <i>m</i> , 1623 <i>m</i> , 1600 <i>sh</i> , 1531 <i>m</i> , 1438 <i>s</i> , 1323 <i>m</i> , 1277 <i>s</i> , 1115 <i>m</i> , 1069 <i>m</i> , 846 <i>m</i> , 746 <i>s</i> , 584 <i>m</i>
V(L1) ₂ Cl ₃	3210 <i>s,br</i> , 3037 <i>m,br</i> , 2875, 1628 <i>s</i> , 1605 <i>sh</i> , 1485 <i>m</i> , 1312 <i>m</i> , 1224 <i>m</i> , 1096 <i>m</i> , 1078 <i>m</i> , 912 <i>m</i> , 762 <i>s</i> , 658 <i>m</i> , 619 <i>m</i>
L2	3400 <i>s, br</i> , 3231 <i>br</i> , 3054 <i>m,br</i> , 2923 <i>m</i> , 2841 <i>m</i> , 1631 <i>m</i> , 1600 <i>sh</i> , 1538 <i>m</i> , 1454 <i>s</i> , 1308 <i>m</i> , 1231 <i>m</i> , 1115 <i>s</i> , 1069 <i>s</i> , 1038 <i>s</i> , 869 <i>m</i> , 808 <i>m</i> , 608 <i>m</i>
V(L2) ₂ Cl ₃	3392 <i>s,br</i> , 3234 <i>m,br</i> , 3033 <i>m,br</i> , 2922 <i>m</i> , 2864, 1624 <i>s</i> , 1612 <i>sh</i> , 1570 <i>m</i> , 1493 <i>s</i> , 1312 <i>m</i> , 1120 <i>m</i> , 1085 <i>m</i> , 870 <i>w</i> , 812 <i>s</i> , 600 <i>m</i>

TABLE II. Continued

Compound	Frequencies/cm ⁻¹ *
L3	3415 <i>s</i> , 3269 <i>s,br</i> , 3077 <i>m,br</i> , 2861 <i>m,br</i> , 1624 <i>m</i> , 1589 <i>m</i> , 1446 <i>s</i> , 1423 <i>s</i> , 1300 <i>m</i> , 1223 <i>m</i> , 1131 <i>m</i> , 1069 <i>s</i> , 931 <i>m</i> , 861 <i>m</i> , 808 <i>s</i> , 600 <i>m</i>
V(L3) ₂ Cl ₃	3430 <i>s,br</i> , 3230 <i>m</i> , 3003 <i>m</i> , 2883 <i>m</i> , 1632 <i>m</i> , 1620 <i>s</i> , 1505 <i>m</i> , 1447 <i>m</i> , 1382 <i>m</i> , 1231 <i>m</i> , 1201 <i>m</i> , 1103 <i>m</i> , 1078 <i>m</i> , 1062 <i>m</i> , 931 <i>m</i> , 869 <i>m</i> , 812 <i>s</i> , 600 <i>m</i>
L4	3407 <i>m,br</i> , 3199 <i>m, br</i> , 3114 <i>m</i> , 2856 <i>w</i> , 1628 <i>m</i> , 1601 <i>w</i> , 1509 <i>s</i> , 1470 <i>m</i> , 1451 <i>m</i> , 1354 <i>s</i> , 1312 <i>m</i> , 1289 <i>m</i> , 1224 <i>m</i> , 1116 <i>m</i> , 1074 <i>m</i> , 885 <i>m</i> , 835 <i>m</i> , 739 <i>m</i> , 696 <i>m</i>
V(L4) ₂ Cl ₃	3410 <i>s,br</i> , 3241 <i>br</i> , 3110 <i>br</i> , 2891 <i>m</i> , 1632 <i>s</i> , 1612 <i>sh</i> , 1536 <i>s</i> , 1451 <i>m</i> , 1385 <i>m</i> , 1351 <i>s</i> , 1228 <i>m</i> , 1097 <i>m</i> , 1074 <i>m</i> , 997 <i>m</i> , 892 <i>m</i> , 831 <i>m</i> , 734 <i>m</i> , 692 <i>m</i>

* *s* = Strong, *m* = medium, *br* = broad, *sh* = shoulder

L1 and **L3** show a sharp strong NH stretching vibrational frequency band at 3431 and 3415 cm⁻¹, respectively, which is broadened considerably on complexation. In **L2** and **L4** it appears around 3400 cm⁻¹ as a broad band. The broad band between 3270 and 3184 cm⁻¹ in the IR spectra of the ligands belongs to the OH stretching vibrational frequency. The weak or medium bands between 1592 – 1601 cm⁻¹ in the spectra of the ligands are attributed to $\nu(\text{C}=\text{N})$. The medium bands at around 1115 cm⁻¹ are due to $\nu(\text{C}-\text{O})$. On complexation these bands shift to the lower frequencies, except for V(**L2**)₂Cl₃. In the V(**L2**)₂Cl₃ complex, $\nu(\text{C}-\text{O})$ is changed from a strong (1115 cm⁻¹) to a medium (1120 cm⁻¹) band.

Intra-molecular hydrogen bonding is observed in the 2600–3450 cm⁻¹ regions as broad bands at the spectra of the ligands. However, the hydrogen bonding is weakened in the complexes, probably due to the participation of hydroxyl oxygen atoms in coordination. More intense hydrogen bonding is seen in the IR spectra of V(**L4**)₂Cl₃ and **L4** than the other ligands and complexes. The reason for this is intermolecular hydrogen bonding between the NO₂ and OH, NH groups.

In the spectra of the ligands, the aromatic C=C stretching vibrations are observed in the range 1623–1632 cm⁻¹ as a medium band changing to a strong band in the complexes. The medium or strong bands between 1470 and 1445 cm⁻¹ are due to the aromatic system in the ligands and the complexes. The *o*-substitution out-of-plane C–H bendings appear about 750 cm⁻¹ as a strong band in **L1**, however, the out-of-plane of the trisubstituted aromatic C–H bendings are at 808, 808 and 835 cm⁻¹ as strong bands for **L2**, **L3** and **L4**, respectively.

The aliphatic CH vibrational stretching bands are observed as medium or weak bands in the range 2815–2891 cm⁻¹ in the IR spectra of the ligands and the complexes. In the spectra of **L2** and V(**L2**)₂Cl₃, $\nu(\text{CH}_3)$ appears around 2920 cm⁻¹ as a weak band. The medium C–Cl stretching vibration frequency is observed at 600 cm⁻¹ in the spectra of **L3** and V(**L3**)₂Cl₃. Two sharp bands are observed at 1354 and 1509 cm⁻¹ for $\nu(\text{NO}_2)$ in the IR spectra of **L4** and at 1351 and 1536 cm⁻¹ in case of the vanadium(III) complex of **L4**.

¹H-NMR Spectra

The ¹H-NMR spectral data of the ligands and the complexes are given in Table III.

TABLE III. Chemical shift values and coupling constants of **L1–L4** and their complexes with VCl₃

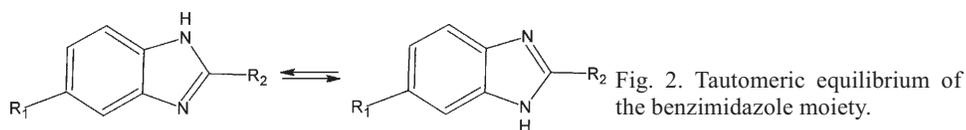
Chemical shifts δ /ppm, and coupling constants J /Hz, (in DMSO-d ₆)							
Compounds	CHOH	OH	H-4	H-5	H-6	H-7	NH
L1	5.35 <i>d</i> $J = 5.0$	5.94 <i>d</i> $J = 5.0$	in 7.53 <i>m</i>	in 7.14 <i>m</i>	in 7.14 <i>m</i>	in 7.53 <i>m</i>	12.30 <i>s,br</i>
V(L1) ₂ Cl ₃	5.94 <i>d</i> $J = 18$ Hz	---	in 7.80 <i>m</i>	in 7.54 <i>m</i>	in 7.54 <i>m</i>	in 7.80 <i>m</i>	---
L2	5.28 <i>d</i> $J = 4.7$	5.90 <i>s,br</i>	7.32 <i>s</i>	2.40 <i>s*</i>	6.96 <i>d</i> $J = 8.1$	7.39 <i>d</i> $J = 7.9$	12.15 <i>s,br</i>
V(L2) ₂ Cl ₃	5.85 <i>d</i> $J = 16$ Hz	---	7.56 <i>s</i>	2.47 <i>s*</i>	7.37 <i>d</i> $J = 8.0$	7.69 <i>d</i> $J = 8.0$	---
L3	5.33 <i>d</i> $J = 5.8$	6.06 <i>d</i> $J = 6.1$	7.53 <i>d,br</i>	---	7.53 <i>d,br</i>	7.17 <i>d-d</i> $J = 8.5, 1.8$	12.49 <i>s,br</i>
V(L3) ₂ Cl ₃	5.77 <i>s</i>	---	7.81 <i>d</i> $J = 2.1$	---	7.77 <i>d</i> $J = 8.8$	7.52 <i>d-d</i> $J = 8.8, 2.1$	---
L4	5.46 <i>d</i> $J = 6.1$	6.37 <i>d</i> $J = 6.2$	8.42 <i>d</i> $J = 10.0$	---	8.15 <i>d</i> $J = 8.8$	7.71 <i>d-d</i> $J = 10.1, 8.9$	12.81 <i>s,br</i>
V(L4) ₂ Cl ₃ iso- mer A (70 %)	5.57 <i>s</i>	---	8.49 <i>s</i>	---	8.19 <i>d-d</i> $J = 8.8, 1.9$	7.79 <i>d</i> $J = 8.8$	---
V(L4) ₂ Cl ₃ iso- mer B (30 %)	5.53 <i>s</i>	---	8.45 <i>s</i>	---	8.16 <i>d-d</i> $J = 8.8, 1.8$	7.73 <i>d</i> $J = 8.8$	---

* 3H(CH₃), *d* = doublet, *s* = singlet, *br* = broad, *m* = multiplet

In the ¹H-NMR spectra of the ligands, the aliphatic protons gave doublets in the δ 5.28 – 5.46 ppm range. They change to singlets shifting considerably to lower fields (δ 5.53 – 5.94 ppm) in the vanadium(III) complexes.

The chemical shifts of the OH protons are at δ 5.94 (*d*), 5.90 (*s, br*), 6.06 (*s, br*) and 6.37 ppm (*s, br*) for the ligands **L1–L4**, respectively. The OH proton signal is not detected in the spectra of the complexes, probably due to the increasing acidic character of the OH protons as a result of the coordination of the hydroxyl oxygen atom in the complexes.

The aromatic protons (H4–H7) show a complex pattern in the aromatic region in the spectra of **L1** and V(**L1**)₂Cl₃. In the ¹H-NMR spectra of **L2**, the aromatic protons, H(4), H(6) and H(7), appear at a higher field (δ 6.96 – 7.39 ppm range) with respect to those in **L3** and **L4** because of the δ^+ effect of the methyl groups. However, in the spectra of **L3** and **L4**, the Cl and NO₂ groups cause the signals of the aromatic protons to shift to lower fields (δ 7.17 – 7.53 ppm and δ 7.71 – 8.42 ppm range for **L3** and **L4**, respectively). H4 appears as a doublet in the spectrum of **L4**, because of interaction with H7 ($J = 10.0$ Hz). H6 and H7 show doublets or doublets of doublets in the spectra of **L2**, **L3** and **L4** and their vanadium(III) complexes. The *d-d* system is due to the interaction of H6 and H7 with H4.



The NH signal gives considerable evidence for the coordination site in the complexes. The N–H proton exhibits a broad signal due to its fluxional behaviour because of resonance through the $N \cdots C \cdots N$ system between δ 12.15 – 12.81 ppm in the spec-

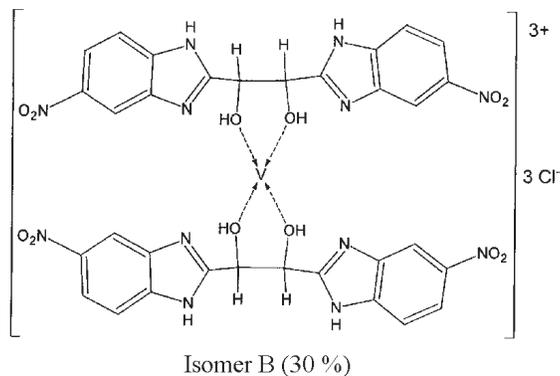
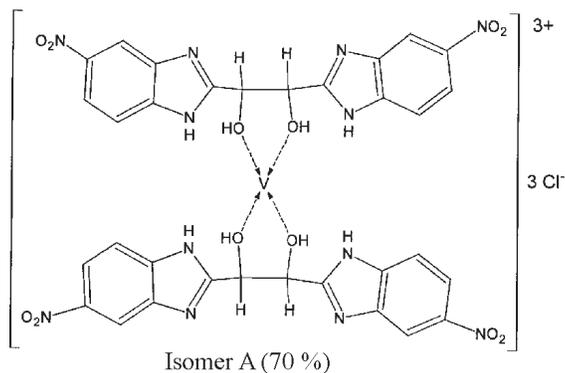
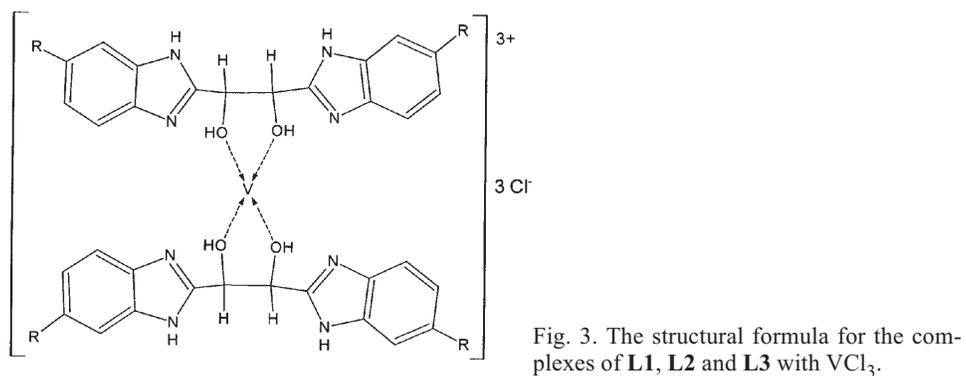


Fig. 4. The two isomeric structural formulas for the $V(L4)_2Cl_3$ complex.

tra of the ligands. In the complexes, the signal of the NH proton was absent, however, in their IR spectra, the broad bands around 3400 cm^{-1} , assigned to $\nu(\text{NH})$, indicate that the NH hydrogen is not eliminated. This shows that the C=N nitrogen was not coordinated to the vanadium(III) ion. If this had occurred, the $\text{N}\cdots\text{C}\cdots\text{N}$ system would have changed to the $\text{N}=\text{C}=\text{N}$ system and, consequently, the NH signal would appear as a sharper peak in comparison with the ligands.^{17,19} In the present study, the NH signal disappeared upon complexation because of the very fast tautomeric equilibrium of the imine hydrogen²⁰ (Fig. 2). This means the fluxionality and, consequently, the acidity of the NH proton are significantly increased in the complexes due to the coordination of the OH oxygen only. A similar complexation was observed in the Ag(I) ¹⁸ and Hg(II) complexes¹⁹ of the mentioned ligands.

In the $^1\text{H-NMR}$ spectra of $\text{V(L4)}_2\text{Cl}_3$ complex, two isomers were observed (Table III). This isomerisation may be caused by the position of the nitro group as shown in Fig. 4. Taking steric hindrance into consideration, it may be proposed that the content of the isomer A is 70 %.

In conclusion, considering the analytical data of the complexes and by comparing the molar conductance data, IR and $^1\text{H-NMR}$ spectra evidence, the structures presented in Figs. 3 and 4 are assigned for the ionic complexes of **L1–L4** with VCl_3 .

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ИЗВОД

КОМПЛЕКСИ ВАНАДИЈУМ(III) ХЛОРИДА СА 1,2-БИС(5-Н/МЕТИЛ/ХЛОРО/НИТРО-1Н-БЕНЗИМИДАЗОЛ-2-ИЛ)-1,2-ЕТАНДИ- ОЛИМА

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Изоловани су комплекси 1,2-бис-(5-Н/метал/хлоро/нитро-1Н-бензимидазол-2-ил)-1,2-етандиолима (**L1–L4**) са VCl_3 и окарактерисани елементалном анализом, моларном проводљивошћу, FTIR и $^1\text{H-NMR}$ спектрима. Лиганд се у комплексима координује као бидентат преко оба кисеоникова атома хидроксилних група. Јонски и дијамагнетни комплекси имају емпиријску формулу $[\text{V(L)}_2]\text{Cl}_3$. Комплекс $[\text{V(L4)}_2]\text{Cl}_3$ има две изомерне структуре на основу $^1\text{H-NMR}$ спектралних података.

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