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2D and 3D Supramolecular Structures *of trans*- and *cis*-Octahedral Coordination Compounds of Ethyl-5-methyl-4-imidazolecarboxylate with Transition Metal Ions

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Dedicated to Estela Sánchez Quintanar, friend and colleague, in recognition of her contribution to the biochemistry of maize

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Abstract. Ethyl-5-methyl-4-imidazolecarboxylate (emizco) is an important intermediate in the synthesis of pharmacological active compounds. In this work, there were synthetized and characterized the following coordination compounds with emizco: *trans*-$[Co(emizco)_2(H_2O)_2](NO_3)_2$ **1**, *trans*-$[Ni(emizco)_2(H_2O)_2](NO_3)_2$ **2**, *trans*-$[Cd(emizco)_2(H_2O)_2](NO_3)_2$ (**3**) and *cis*-$[Cd(emizco)_2Br_2]$ (**4**). 2D or 3D supramolecular arrangements were stabilized. All nitrate *trans* octahedral compounds stabilized a 3D supramolecular arrangement *via* hydrogen bonding, throughout the nitrate anions, the ligand and the coordinated water molecules; the *cis*-octahedral halide complex formed a 2D pleated sheet arrangement, by intermolecular π stacking and halide-hydrogen bonding.
Key words: Emizco, cobalt(II), nickel(II), cadmium(II), coordination compounds, supramoleular arrangements.

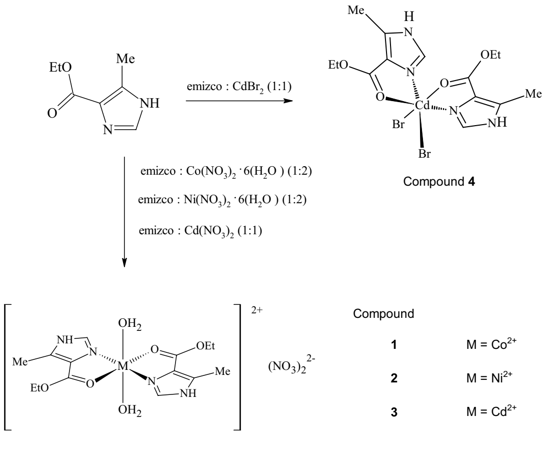
Resumen. El etil 5-metil-4-imidazolcarboxilato (emizco) es un intermediario importante en la síntesis de compuestos con actividad farmacológica. En el presente trabajo se sintetizaron y caracterizaron los siguientes compuesto de coordinación con emizco: *trans*-$[Co(emizco)_2(H_2O)_2](NO_3)_2$ **1**, *trans*-$[Ni(emizco)_2(H_2O)_2](NO_3)_2$ **2**, *trans*-$[Cd(emizco)_2(H_2O)_2](NO_3)_2$ (**3**) y *cis*-$[Cd(emizco)_2Br_2]$ (**4**). Estos compuestos estabilizan estructuras supramoleculares en 2D ó 3D; todos los compuestos de nitrato con geometría *trans* octaédrica estabilizan arreglos en 3D por medio de puentes de hidrógeno entre los iones nitrato, emizco y las moléculas de H_2O; mientras que el compuesto de coordinación del haluro *cis* octaédrico tiene un arreglo en forma de hoja plegada en 2D, por medio de interacciones intermoleculares de tipo apilamiento-π y puente de hidrógeno-haluro.
Palabras clave: Emizco, cobalto(II), niquel(II), cadmio(II), compuesto de coordinación, arreglos supramoleculares.

Introduction

The interaction of imidazole derivatives with metal ions is a subject of continuous interest. It is well known that a number of imidazole derivatives have biological activity, *e.g.* presenting pharmaceutical, antibacterial or fungicidal properties [1-3], among others. Within this class of compounds, nitroimidazoles have been used in the treatment of tropical diseases, in protozoal, anaerobic bacteria and the eradication of *Helicobacter pylori* infections [4-9], as in medical creams for treating acne, seborrheic dermatitis, rosacea and folliculitis [10]. Their biological activity as radiosensitizers, or as hypoxic cytotoxins has been studied [11-19]. Furthermore, these molecules may easily coordinate to transition metal ions, giving stable coordination compounds. The nitro group adjacent to an imidazolic nitrogen may occupy a coordination site, stabilizing chelate metal complexes, while the hydroxyethyl and nitro groups act as supramolecular synthons, with the option to generate hydrogen-bonded networks of different dimensions. The number, orientation and type of hydrogen bonding drive the formation of mono and two dimensional networks. The contribution of metal ions in metronidazole coordination compounds is shown in the stabilization of different aggregate structures, as we have informed [20]. Ethyl 5-methyl-4-imidazolecarboxylate (hereafter abbreviated emizco), is used as an intermediate in the synthesis of a variety of imidazolic compounds with pharmacological properties [21, 22]. Previously, we have investigated the coordination compounds of emizco with copper(II) [23], and the biological activity of its transition metal complexes on photosynthesis. They showed to be inhibitors of the photosynthetic electron flow and ATP-synthesis [24, 25]. In the copper(II) coordination compounds, the imidazole nitrogen atom and its neighbouring ester group are active sites for binding the Cu^{2+} atom, giving place to mono- or bi-dentate coordination modes, therefore stabilizing tetrahedral or octahedral geometries. In this paper we present the synthesis and the structural characterization of coordination compounds of emizco with cobalt(II), nickel(II) and cadmium(II) salts. This work was undertaken to contribute to a better understanding of the coordination behavior of this biologically relevant compound towards metal ions, the geometries and isomers that the metal atoms may adopt in these compounds, as the contribution of the counterion on the stabilization of 2D and 3D molecular aggregates.

Results and Discussion

When the reaction syntheses of emizco was carried out with the corresponding nitrate salts, the octahedral *trans* complexes: **1**, **2** and **3** were obtained, while with cadmium bromide the *cis* compound **4** was isolated. These reactions are summarized in Scheme 1.



Scheme 1. Synthesis of compounds **1**-**4**.

Spectroscopic characterization

In Table 1, spectral and magnetic data of emizco and its coordination compounds are presented. The IR spectrum of emizco showed absorption bands corresponding to the stretching modes ν(C=O), ν_{as}(C-O-C), ν_s(C-O-C) of the ester functional group at 1693, 1321 and 1180 cm^{-1} respectively, and for the ν(C=N) at 1508 cm^{-1}. For compounds **1-4**, the ester bands are shifted, upon coordination, with respect to the respective bands in the free ligand; the ν(C=O) stretching band is shifted to lower energies (1644-1678 cm^{-1}), while ν(C=N) is shifted to higher energy (1509-1528 cm^{-1}), indicating that the emizco ligands are coordinated to the metal ion in a bidentate mode, through the C=O of the ester group and the imidazolic nitrogen, in agreement with their X-ray structures.

Reflectance spectrum of [Co(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ **1** is characteristic of a cobalt(II) in an octahedral geometry, with a band centered at 9100 cm^{-1} assigned as ν_1 $^4T_{2g}(F)\leftarrow{}^4T_{1g}(F)$, in addition to a band at 20892 cm^{-1} corresponding to ν_3 $^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$ [27]. The [Ni(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ **2** compound exhibits three bands at 9803 cm^{-1}, $\nu_1 = {}^3T_{2g}(F)\leftarrow{}^3A_{2g}(F)$, 15852 cm^{-1}, $\nu_2 = {}^3T_{1g}(F)\leftarrow{}^3A_{2g}(F)$, and 25809 cm^{-1}, $\nu_3 = {}^3T_{1g}(P)\leftarrow{}^3A_{2g}(F)$. These transitions are within the expected range for a nickel(II) ion with an octahedral geometry [26]. In this compound the first transition (9803 cm^{-1}) corresponds to the 10 Dq, indicative of a weak crystal field splitting.

In summary, a chelating coordination behavior of emizco towards the transition metal ions was observed in these compounds, where the metal ions adopted an octahedral geometry.

Magnetic susceptibility and electrical conductivity

For [Co(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$, an effective magnetic moment of 4.82 B.M. was observed, which is within the expected range for a high spin Co^{2+} ion with three unpaired electrons. The nickel(II) compound [Ni(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$, presented a magnetic moment of 3.17 B.M., as expected for this metal ion in an octahedral geometry. Their molar conductivities are characteristic for 1:2 electrolytes, for the nitrate complexes **1** and **2** are within the range of 222-257 μS/cm (in water), and for compound **3** a conductivity of 78 μS/cm (in DMSO) was found.

X-ray crystal structures of compounds 1-4

Suitable crystals for X-ray diffraction studies were obtained for the coordination compounds **1**-**4**. The nitrate complexes **13** correspond to a centrosymmetric *trans*-octahedral geometry (Fig. 1), and the bromide compound **4** to a *cis*-octahedral geometry (Fig. 2).

The stabilization of these isomers was controlled by the counterion used in the reaction synthesis. The nitrate anions favors the centrosymmetric *trans*-octahedral cationic complexes [M(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$, where M = Co^{2+}, Ni^{2+} and Cd^{2+}

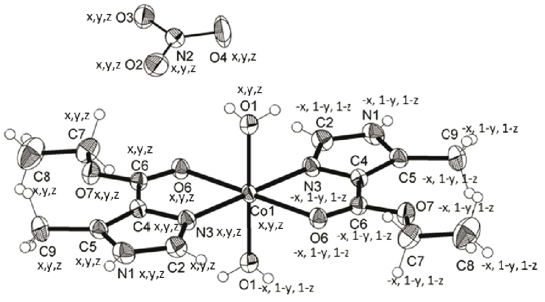


Fig. 1. Crystal structure of compound [Co(emizco)$_2$(H$_2$O)$_2$] (NO$_3$)$_2$ **1** with symmetry operator labels and thermal ellipsoids for non-H atoms at the 30% probability level.

Table 1. Spectral and magnetic data for emizco and its coordination compounds **1-4**.

Compound	$\mu_{eff}{}^a$ (MB)	UV-Vis-NIR^b (cm^{-1})	IR^c ν_{max}/cm^{-1}				
			ν(C=O)	ν(C=N)	ν_{as}(COC)	ν_s(COC)	ν(NO$_3$)
emizco	—	—	1693	1508	1321	1180	—
1. *trans*-[Co(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$	4.82	ν_1 9100, ν_3 20892	1678	1509	1316	1214	1384
2. *trans*-[Ni(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$	3.17	ν_1 9803, $\nu_2$15852, ν_3 25809	1644	1528	—	1217	1384
3. *trans*-[Cd(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$	—	—	1655	1525	1335	1163	1384
4. *cis*-[Cd(emizco)$_2$Br$_2$]	—	—	1679	1522	1324	1206	—

^{a}25 °C; ^{b}diffuse reflectance; centered band; ^{c}KBr pellets, range 4000-600 cm^{-1}.

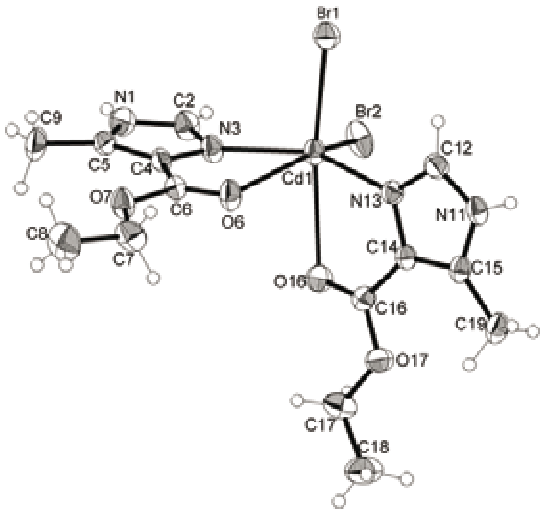


Fig. 2. Crystal structure of [Co(emizco)$_2$Br$_2$] **4** with thermal ellipsoids for non-H atoms at the 30% probability level.

(compounds **1**, **2** and **3)**, whereas the bromide favor the *cis* geometry, [Cd(emizco)$_2$Br$_2$] **4**, as it was previously observed for the copper(II) complexes *trans*-[Cu(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ and *cis*-[Cu(emizco)$_2$X$_2$] (X$^-$ = Cl, Br) [27]. The stabilization of the *cis* or *trans* geometry is driven by steric factors.

In the *trans*-octahedral compounds, two emizco ligands are coordinated in a bidentate mode to the central metal ion, the donor atoms N3 and O6 are in equatorial positions and the axial positions are occupied by two acua ligands completing the coordination sphere. This is a common geometry for this kind of compounds [27], whereas *cis*-coordination is rarely observed [28]. The coordination bond distances in the *trans*-octahedral compounds are shown in Table 2.

For the *trans* compounds **1**-**3**, [Cd(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ **3** presents the longest coordination bond lengths and the smallest chelate angle 73.22(5)°, whereas for the cobalt(II) and nickel(II) compounds as the coordination bond lengths get shorter, the chelate angle increases (Tables 2 and 3). Two intramolecular hydrogen bonds in the emizco ligand, O6···C7 2.707 Å and O7···C9 3.078 Å, [23] are conserved in all coordination compounds, as depicted for [Co(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ **1** (Fig. 3).

Table 2. Selected bond lengths [Å] for *trans*-octahedral compounds **1**-**3**, and *cis*-octahedral compound **4**.

Compound	M-O1	M-N3	M-O6
[Co(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ **1**	2.075(2)	2.088(2)	2.213(1)
[Ni(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ **2**	2.068(2)	2.030(2)	2.114(2)
[Cd(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ **3**	2.306(2)	2.243(2)	2.415(2)
[Cd(emizco)$_2$Br$_2$] **4**	—	2.218(3)	2.757(3)

A partial electronic delocalization on the chelate ring is observed, N3=C4 1.377(3) Å, C4-C6 1.450(3) Å, C6=O6 1.224(3) Å. The angles O1-M-O6 and N3-M-O1 have values in the range of 87-94°, as expected for this geometry.

The compound *cis* [Cd(emizco)$_2$Br$_2$] **4**, has the smallest chelate angles, O6-Cd1-N3 66.58(9)° and O16-Cd1-N13 68.11(9)° (table 3), with the longest coordination bond lengths, N3-Cd 2.218(3) Å, O6-Cd 2.757(3) Å, N13-Cd 2.227(3) Å and O16-Cd 2.645(3) Å (figure 4, table 2).

In the previously reported analogous copper(II) compound *cis* [Cu(emizco)$_2$Br$_2$], the chelate angles are larger, O6-Cu1-N3 75.91(15)° and O16-Cu1-N13 74.44(14)°, while the coordination bond lengths are shorter when changing cadmium(II) for copper(II) [23]. The smaller chelate angles are those of the *cis*-octahedral compound **4**, compared with the *trans*-octahedral **3** (Fig. 4).

Supramolecular arrangements

Trans-octahedral compounds 1-3

A 2D ribbon is build up by hydrogen bonds between the nitrate ions, the amino group of emizco ligands and the water molecules, in figures 5 and 6 these is shown for the cobalt(II)

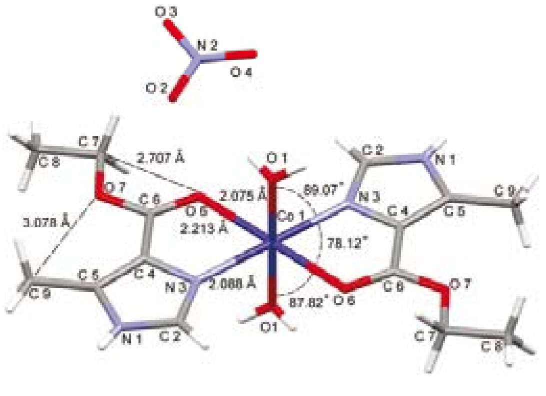


Fig. 3. Chelate angles (°), bond lengths (Å) and intramolecular hydrogen bonding in compound [Co(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ **1**.

Table 3. Selected bond angles [°] of the trans-octahedral compounds **1**-**3** and cis-octahedral compound **4**.

Compound	N3x,y,z-Mx,y,z-O6x,y,z	O1x,y,z-Mx,y,z-N3x,y,z	O6x,y,z-M x,y,z-O1x,y,z
[Co(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ **1**	78.12(5)	89.07(7)	87.81(7)
[Ni(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ **2**	79.99(9)	89.06(10)	88.17(8)
[Cd(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ **3**	73.22(5)	91.20(8)	94.30(8)
	N3-M-O6	N13-M-O16	
[Cd(emizco)$_2$Br$_2$] **4**	66.58(9)	68.11(9)	—

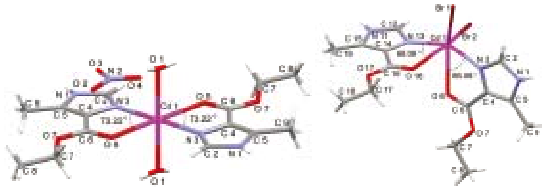


Fig. 4. Chelate angles in the cadmium(II) compounds **3** and **4**.

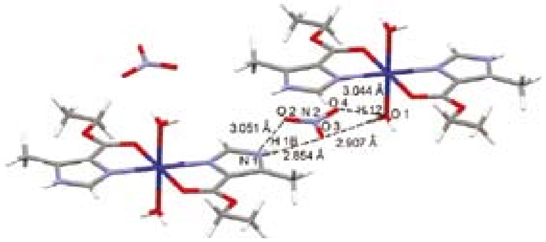


Fig. 5. Intermolecular hydrogen bonding between the nitrate ions and compound **1**.

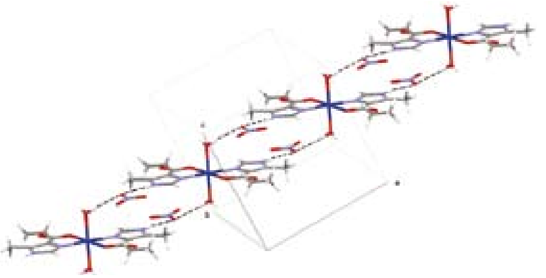


Fig. 6. 2D arrangement in the ab plane, in $[Co(emizco)_2(H_2O)_2](NO_3)_2$ **1**.

Table 4. Intermolecular hydrogen bond lengths (Å) of trans-octahedral **1**- **3** compounds (heavy atoms distances).

Compound	N1···O2	O1···O3	N1···O3
$[Co(emizco)_2(H_2O)_2](NO_3)_2$**1**	3.051(2)	2.907(3)	2.854(2)
$[Ni(emizco)_2(H_2O)_2](NO_3)_2$**2**	2.997(4)	2.897(4)	2.848(3)
$[Cd(emizco)_2(H_2O)_2](NO_3)_2$**3**	3.073(3)	2.986(3)	2.794(3)

compound **1**. The NH of the imidazolic rings form bifurcated hydrogen bonds with the nitrate ion, N1-H1B···O2N2 (N1···O2 3.051 Å) and N1-H1B···O3N2 (N1···O3 2.854 Å), forming a chain, that grows in the a axis direction. Additionally, one coordinated water molecule forms bifurcated hydrogen bonds with the ionic nitrate, O1···O3N2, (2.907 Å, 172.85°) and O1···O4-N2 (3.044 Å, 134.91°), Figure 5.

In tables 4 and 5 are included the intermolecular hydrogen bond lengths and angles for the nitrate *trans* compounds.

A 3D supramolecular structure is built up by parallel planes, linked by hydrogen bonds between the axial acua ligands and the nitrate ions, Figure 7.

Cis-octahedral compound 4

In this compound, there are two types of intermolecular interactions: hydrogen bonding and π stacking. The intermolecular hydrogen bonds are formed between N1-H of imidazole ring and the Br2 of a neighbouring molecule, which is shorter than the sum of van der Waals radii of Br and N atoms (Σ_{rvw}Br-N: 3.51 Å) [29]. In Figure 8 is shown the π stacking and hydrogen bonding, which extend the crystal lattice in the bc crystallographic plane, stabilizing a 2D supramolecular arrangement. Similar interactions were found in the analogous copper(II) compound [23].

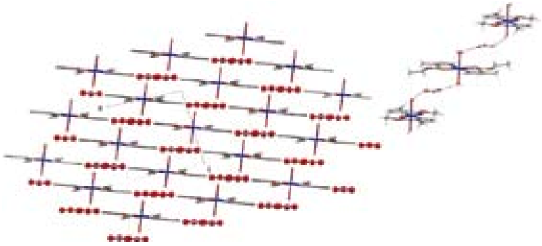
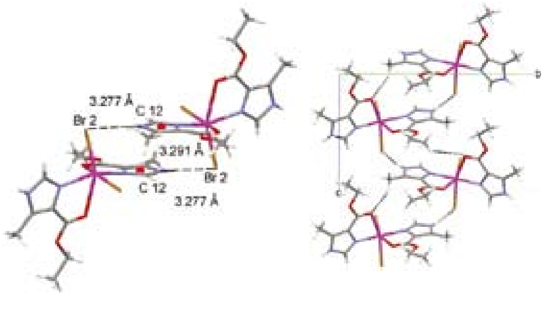


Fig. 7. 3D supramolecular arrangement in compounds **1**-**3**.



(a) (b)

Fig. 8. (a) Hydrogen bonding and π stacking in compound **4**; (b) 2D supramolecular arrangement in the bc plane.

Table 5. Intermolecular hydrogen bond angles of trans-octahedral compounds.

Compound	N1-H1B···O2	O1-H12···O4	N1-H1B···O3
$[Co(emizco)_2(H_2O)_2](NO_3)_2$ **1**	133.47 °	172.85 °	172.72 °
$[Ni(emizco)_2(H_2O)_2](NO_3)_2$ **2**	162.00 °	178.61 °	162.00 °
$[Cd(emizco)_2(H_2O)_2](NO_3)_2$ **3**	130.76 °	150.86°	172.22 °

Concluding remarks

All *trans*-octahedral nitrate compounds stabilized a 3D supramolecular arrangement *via* hydrogen bonding, between the nitrate anions, the N-H from the ligand and the coordinated water molecules. The *cis*-octahedral halide complex forms a 2D pleated sheet arrangement, by intermolecular π stacking and halide-hydrogen bonding. A similar behavior was observed previously for similar nitrate and halide copper(II) compounds, which implies that an anion directed assembly allows the formation of 2D or 3D supramolecular structures.

Experimental

Reagents

Emizco, metal salts: $CdBr_2$, $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2$, and solvents were purchased from Aldrich Chem., Merck and J.T. Baker and were used as received.

Spectroscopic measurements

IR spectra in the range 4000-400 cm^{-1} were recorded in KBr pellets (Perkin Elmer FTIR 1605). Electronic spectra of powdered crystalline samples were measured by the diffuse reflectance method on a CARY-5000 Varian spectrometer, over the range 250-2000 nm (40,000-5,000 cm^{-1}). Elemental analyses were carried out with a Fisons EA 1108 analyzer (CHNS-O) using a cystine standard. Magnetic susceptibility measurements at room temperature of powdered samples were recorded on a Johnson-Matthey type MSB model MK II 13094-3002, using the Gouy method at a temperature of 297 +/– 2 K.

Crystallography

Suitable single crystals of compounds **14** were mounted on a glass fiber. Data were colleted at 293 K. Crystal data, data collection and structure refinement details are given in Table 6. All data were measured using standard procedures on a Oxford Diffraction Gemini “A” instrument with CCD area detector using graphitemonochromated Mo Kα radiation at 293 K. Intensities were measured using $\varphi + \omega$ scans. A summary of data collection and refinements is given in Table 6. All structures were solved using direct methods, using SHELX97 program [30] and the refinement (based on F^2 of all data) was performed by full-matrix least squares techniques with SHELX97 program [30]. All non hydrogen atoms were refined anisotropically. For all compounds, all non aromatic hydrogen atoms were found in the difference map and their positions refined, whereas all the aromatic hydrogen atoms were localized in the difference map and allowed to ride on their respective atoms.

Synthesis of coordination compounds: general procedure

Coordination compounds were prepared in all cases using methanol as solvent and employing a 2:1 (ligand:M^{2+}) ratio for the cobalt(II) and nickel(II) compounds, and a 1:1 ratio for the cadmium(II) compounds. The emizco ligand was dissolved in 5 mL of hot methanol, and the metallic salts were dissolved separately in 10 mL of hot methanol. The metal salt solution was added to the ligand solution and refluxed, after that the solution was allowed to stand at RT. The resulting crystals were washed with methanol and dried *in vacuo.*

[Co(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ **(1)**
Cobalt(II) nitrate hexahydrate (0.580 g, 2 mmol) was dissolved in hot methanol (10 mL) and added to a solution of emizco (0.154 g, 1 mmol) in hot methanol (5 mL). The red solution was refluxed for 6 h and then allowed to stand for 4 weeks. The resulting red crystals were filtered off, washed with methanol and dried *in vacuo*. Yield: 99.43%.

Molar conductivity (H_2O): [μS/cm] 257. IR ν_{max} [cm^{-1}] 1678 (C=O), 1509 (C=N), 1316 (COO_{as}), 1214 (COO_s), 1384 (NO_3). Anal. Found: C, 31.46; H, 4.69; N, 15.88%. Calcd. for $C_{14}H_{24}CoN_6O_{12}$:C, 31.88; H, 4.58; N, 15.93%.

*[Ni(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$·***(2)**
Nickel(II) nitrate hexahydrate (0.290 g, 1 mmol) was dissolved in hot methanol (10 mL) and added to a solution of emizco (0.308 g, 2 mmol) in hot methanol (5 mL). The green solution was refluxed for 6 h and then allowed to stand for 5 weeks. The resulting lime green crystals were filtered off, washed with methanol and dried *in vacuo*. Yield: 30.13%. Molar conductivity (H_2O): [μS/cm] 222. IR ν_{max} [cm^{-1}] 1644 (C=O), 1528 (C=N), 1217 (COO_s), 1384 (NO_3). Anal. Found: C, 31.63; H, 4.65; N, 16.22%. Calcd. for $C_{14}H_{24}NiN_6O_{12}$: C, 31.90; H, 4.59; N, 15.94%.

[Cd(emizco)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ **(3)**
Cadmium(II) nitrate (0.236 g, 1 mmol) was dissolved in hot methanol (10 mL) and added to a solution of emizco (0.154 g, 1 mmol) in hot methanol (5 mL). The colorless solution was refluxed for 6 h and then allowed to stand for 4 weeks. The resulting colorless crystals were filtered off, washed with methanol and dried *in vacuo*. Yield: 32.38%. Molar conductivity (DMSO): [μS/cm] 78.8. IR ν_{max} [cm^{-1}] 1655 (C=O), 1525 (C=N), 1335 (COO_{as}), 1163 (COO_s), 1384 (NO_3). Anal. Found: C, 28.75; H, 4.30; N, 14.12%. Calcd. for $C_{14}H_{24}CdN_6O_{12}$: C, 28.95; H, 4.16; N, 14.47%.

4 [Cd(emizco)$_2$Br$_2$] (**4**)
Cadmium(II) bromide (0.272 g, 1 mmol) was dissolved in hot methanol (10 mL) and added to a solution of emizco (0.154 g, 1 mmol) in hot methanol (5 mL). The colorless solution was refluxed for 6 h and then allowed to stand for 4 weeks. The resulting colorless crystals were filtered off, washed with methanol and dried *in vacuo*. Yield: 21.5%. IR ν_{max} [cm^{-1}] 1679 (C=O), 1522 (C=N), 1324 (COO_{as}), 1206 (COO_s). Anal. Found: C, 28.80; H, 3.67; N, 9.40%. Calcd. for $C_{14}H_{20}CdN_4O_4Br_2$: C, 28.96; H, 3.47; N, 9.65%.

Table 6. Crystal data, data collection and refinement details for **1**, **2**, **3** and **4**.

Chemical Formula	$C_7H_{10}CoN_4O_8$ (**1**)	$C_{14}H_{24}NiN_6O_{12}$ (**2**)	$C_7H_{10}Br_2CdN_2O_2$ (**3**)	$C_{14}H_{24}CdN_4O_6$ (**4**)
Formula weight (g mol^{-1})	337.12	527.1	426.39	456.77
Crystal colour	Red	Green	Colourless	Colourless
Crystal size (mm)	0.25 × 0.15 × 0.1	0.3 × 0.2 × 0.1	0.35 × 0.25 × 0.5	0.32 × 0.21 × 0.13
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$
Unit cell dimensions				
a (Å)	10.1001(3)	10.008(2)	8.5728(3)	10.2217(3)
b (Å)	10.7338(4)	10.668(4)	26.0312(7)	10.7087(3)
c (Å)	10.3588(4)	10.223(3)	9.7355(4)	10.4492(4)
β (°)	94.341(3)	94.05(2)	106.985(4)	94.429(3)
V	1119.80(7)	1088.8(5)	2077.8(1)	1140.37(6)
Z	4	2	8	4
D_{calc} (g/cm^3)	2.0	1.608	2.726	2.661
μ (mm^{-1})	1.584	0.965	9.768	1.975
F(000)	684	548	1600	928
T (K)	293(2)	293(2)	294(2)	293(2)
θ_{min}	3.31	3.52	3.2	3.29
θ_{max}	26.05	26.33	26.07	26.06
Index range	$-12 \leq h \leq 9$	$-11 \leq h \leq 12$	$-10 \leq h \leq 6$	$-12 \leq h \leq 12$
	$-13 \leq k \leq 11$	$-13 \leq k \leq 10$	$-31 \leq k \leq 32$	$-10 \leq l \leq 12$
	$-12 \leq l \leq 12$	$-12 \leq l \leq 12$	$-13 \leq k \leq 10$	$-12 \leq l \leq 9$
Measured reflections	4680	5814	9634	5017
Independent reflections [a]	2137	1800	4077	2258
Observed reflections	1648	1056	2923	1771
Number of parameters	164	161	284	170
R [a]	0.0297	0.0543	0.0323	0.027
R_w [a]	0.0836	0.0697	0.0632	0.0674
Goodness-of-fit on F^2, S[a]	1.022	0.851	0.95	0.967
Maximum Δ/σ	0.011	0.001	0.001	0
$\Delta\rho$ Maximum (e Å^3)	0.231	0.346	0.484	0.394
$\Delta\rho$ Minimum (e Å^3)	−0.282	−0.307	−0.677	−0.317

[a] R_{int}, R_1, wR_2 and S are defined as follows:

Supplementary material

Supplementary crystallographic data for this paper have been deposited with the CCDC: 810798 to 810801. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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References

1. Gilman, A.; Goodman Gilman, L.S.; Rall, T.W.; Murad, F., in: *Goodman and Gilman's The Pharmacological Basics of Therapeutics*. 7th Ed., Mc-Graw Hill, New Jersey, **1986**, pp. 1166-1168.
2. Sunkyung, L.; Kyu, Y. Y.; Sung, J. Y.; Byung, H. L.; Sung-Eun, Y. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 1329-1331.
3. Abhishek, K. J.; Ravichandranb, V; Madhvi, S; Agrawala, R. K. *J. Trop. Med.* **2010**, *3*, 471-474.
4. Castelli, M.; Malagoli, M.; Lupo, L.; Bofia, S.; Paloucci, C.; Zanca, A.; Baggio, G. *J. Antimicro. Chemoth.* **2000**, *46*, 541-550.
5. Britzi, M.; Gross, M.; Lavy, E.; Soback, S.; Steinman, A. *J. Vet. Pharmacol. Ther.* **2010**, *33*, 511-514.
6. Silvestri, R.; Artico, M.; Marceddu, S. T.; DeMontis, F.; LaColla, P. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 253-256.

7. Hu, J.; McDougald, L. R. *Vet. Parasitol.* **2004**, *121*, 233-238.
8. Demirayak, S.; Karaburun, A.C.; Kiraz, N. *Eur. J. Med. Chem.* **1999**, *34*, 275-278.
9. Tong, L.; Perez, S.; Goncalves, C.; Alpendurada, F.; Wang, Y.; Barcelo, D. *Anal. Bioanal. Chem.* **2011**, *399*, 421-428.
10. Weijun, L. Chinese Patent, CODEN: CNXXEV CN 101884642 A 20101117 **2010**. Appl.: CN **2010**-10240918 20100730. Priority: CN 2010-10240918 20100730. CAN 153:651461 AN 2010:1447071.
11. Macdonald, F. M.; Sadler, P.S. *Polyhedron* **1991**, *10*, 1443-1448.
12. Macdonald, F. M., Sadler P.S. *Magn. Reson. Chem.* **1991**, *29*, S52-59
13. Rochon, B. D.; Melanson R.; Farrel, N. *Acta Cryst.* **1993**, *C49*, 1706-1715.
14. Dyson, T. M.; Morrison, E. C.; Tocher, D.A.; Dale, L. D.; Edwards, D. I. *Inorg. Chim. Acta* **1990**, *169*, 127-131.
15. Roy, M. B.; Mandal, P. C.; Bhattacharyya, S. N. *Int. J. Radiat. Biol.* **1996**, *69*, 471-480.
16. Roy, M. B.; Mandal, P. C.; Bhattacharyya, S. N. *J. Radioanal. Nucl. Chem.***1995**, *191*, 337-348.
17. Roy, M. B.; Mandal, P. C.; Bhattacharyya, S.N. *J. Chem. Soc., Dalton Trans.* **1993**, 2485-2490.
18. Roy, M. B.; Mandal, P. C.; Bhattacharyya, S.N. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2975-2980.
19. Rachna, K.; Singh, P. *Asian J. Chem.* **2000**, *12*, 23-26.
20. Galván-Tejada, N.; Bernès, S.; Castillo-Blum, S. E.; Nöth, H.; Vicente, R.; Barba-Behrens, N. *J. Inorg. Biochem.* **2002**, *91*, 339-348.
21. Gant, T. G.; Sarshar, S. US patent CODEN:USXXCO US 20100113478 A1 **2010**.
22. Heim-Riether, A.; Healy, J. *J. Org. Chem.* **2005**, *70* (18), 7331-7337.
23. Montes-Ayala, J.; Escartín-Guzmán, C.; Castillo-Blum, S. E.; Rodríguez-Hernández, E. O.; Bernès, S.; Rosales-Hoz, Ma. J.; Barba-Behrens, N. *J. Inorg. Biochem.* **2005**, *99*, 1676-1684.
24. King-Díaz, B.; Barba-Behrens, N.; Montes-Ayala, J.; Castillo-Blum, S. E.; Escartín-Guzmán, C.; Iglesias-Prieto, R.; Lotina-Hennsen, B. *Z. Naturforsch* **1998**, *53C*, 987-994.
25. King-Díaz, B.; Montes-Ayala, J.; Escartín-Guzmán, C.; Castillo-Blum, S. E.; Iglesias-Prieto, R.; Lotina-Hennsen, B.; Barba-Behrens, N. *Bioinorg. Chem. & Appl.* **2005**, *3(1-2)*, 93-108.
26. Lever, A.B.P., in: *Inorganic Electronic Spectroscopy,* 2nd Ed. Elsevier, New York, **1986, pp.** 507-511.
27. Acuña-Cueva, E. R.; Faure, R.; Illán-Cabeza, N. A.; Jiménez-Pulido, S. B.; Moreno-Carretero, M. N.; Quirós-Olozábal, M. *Polyhedron* **2002**, *21*, 19611968
28. Acuña-Cueva, E. R.; Faure, R.; Illán-Cabeza, N. A.; Jiménez-Pulido, S. B.; Moreno-Carretero, M. N.; Quirós-Olozábal, M. *Inorg. Chim. Acta* **2003**, *342*, 209218.
29. Batsanov, S. S. *Inorganic Materials*, **2001**, *37*, 871885.
30. Sheldrick, G. M. *Acta Crystallogr.*, **2008** Sect. A 64 112-122.