

# Synthesis, Spectroscopic Studies and X-Ray Diffraction of Heptacoordinated Mn(II) and Co(II) Complexes with Ligands Derived from Carbonohydrazide

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## Abstract

The ligand 1-(1-(pyridin-2-yl)ethylidene)carbonohydrazide ( $H_4L^1$ ) and 1-(pyridin-2-ylmethylene)carbonohydrazide ( $H_4L^2$ ) were prepared by reaction of carbonohydrazide with 2-acetylpyridine or pyridine carbaldehyde respectively in a reflux methanol solution. The complexes are prepared by reaction of the ligand with the appropriate metal salt. These complexes are well characterized by elemental analysis, IR and UV spectroscopies and their structure were determined by single X-ray diffraction technic. In the crystal of the dinuclear complex  $[Mn_2(H_4L^1)_2(H_2O)_4] \cdot Cl_4$ , 1) each Mn(II) center is seven coordinated by two nitrogen atom and one carbonyl atom of the one ligand and one nitrogen atom and one carbonyl oxygen atom of another ligand molecule. The coordination sphere is completed by two water molecules. Each of the carbonyl oxygen atom acts as bridge between the two Mn(II) centers. In the mononuclear complex  $[Co(H_4L^2)(NO_3)(H_2O)_2] \cdot (NO_3)$ ; 2) the Co(II) center is heptacoordinated. The ligand acts in tridentate fashion through two nitrogen atoms and one carbonyl oxygen atom. Two water molecules lie in the apical positions. One nitrate group acts in bidentate manner while the other nitrate group remains uncoordinated. In both complexes the coordination polyhedral are best described as a pentagonal bipyramid. The molecules are linked together in each case by multiple hydrogen bond interaction resulting in a three-dimensional network. The crystallographic data has been deposited in Cambridge Crystallographic Data Centre [CCDC No. 1944387 (complex 1) and 1944386 (complex 2)].

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## Keywords

Carbonohydrazide, Manganese, Cobalt, Complex, X-Ray Diffraction

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## 1. Introduction

Transition metal coordination compounds with Schiff bases continue to attract the attention of researchers because of the easier synthesis, the stability of the molecular structures and the large diverse properties observed [1]-[11]. Indeed catalytic [12] [13] [14], optical [15], magnetic [16] [17], fluorescent [18] [19] and biological activities [8] [20] [21] [22] are reported. The complexes derived from the first row of transition metals can give several models of metalloenzymes [23] [24] and metalloproteins [25] [26]. Heptacoordinated manganese (II) and cobalt (II) structures have also attracted a great deal of interest from chemists in recent years [8] [27] [28] [29]. These kind of structures are present in enzymes: catalase [30] [31], ribonucleotide manganese reductase [32] and arginase [33]. In addition to their interests in biology, these complexes are likely to give very interesting magnetic properties. In the literature, dinuclear compounds of manganese or cobalt which exhibit ferromagnetic or antiferromagnetic interactions are largely reported [34] [35] [36]. In recent years, we have prepared different symmetrical Schiff base types from the condensation of carbon or thiocarbon hydrazide and aldehydes or ketones which are subsequently used to prepare dinuclear or tetranuclear metal complexes [37] [38] [39]. In the absence of any particular precautions, the reaction which is a nucleophilic addition of the primary amine on the carbonyl group, proceeds on both arms of the carbonohydrazide. By controlling the conditions of the reaction we prepared a ligand from the monocondensation of carbonohydrazide and acetyl pyridine or pyridine carbaldehyde. The topologies of these dissymmetric ligands lead it to act in tridentate or tetradentate fashions leading fascinating structures. In this context, we report the isolation and complete characterization of this ligand and its Mn(II) and Co(II) complexes in which the metal centers are heptacoordinated as showed by crystal X-ray diffraction analysis. The structure of the formed crystals has been by single X-ray diffraction analysis and the data have been deposited in CCDC Cambridge crystallographic data centre.

## 2. Experimental

### 2.1. Material and Physical Measurement

Carbonohydrazide (98%), 2-acetylpyridine (99%), 2-pyridinecarboxaldehyde (99%),  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (99%),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99.99%) and analytical grade methanol were supplied from Aldrich. All chemicals and solvents were used directly without further purification. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. The FAB mass spectra were recorded using a Micro-mass Autospec spectrometer using 3-nitrobenzylalcohol as the matrix. Infrared

spectra were obtained on an FTIR Spectrum Two of Perkin Elmer spectrometer in the 4000 - 400  $\text{cm}^{-1}$  region. The UV-Visible spectra was recorded on a Perkin Elmer Lambda UV-Vis spectrophotometer. The molar conductance of  $1 \times 10^{-3}$  M in DMSO solutions of the metal complexes was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Matthey scientific magnetic susceptibility balance (Calibrant: Hg [Co(SCN)<sub>4</sub>]). The voltammetric measurements were recorded using a Palm Sens3 type potentiostat controlled by PSTrace software. A glassy carbon working electrode with a radius of  $2 \pm 0.1$  mm, a stainless steel wire as a counter-electrode and Ag/AgCl electrode as a reference were used. Cyclic voltammetry experiments were performed in acetonitrile solution 0.1 M of tetrabutylammonium hexafluorophosphate (TBAHFP) as a supporting electrolyte.

## 2.2. Synthesis of the Ligand

### 1-(1-(Pyridin-2-yl)Ethylidene)Carbonohydrazide: H<sub>4</sub>L<sup>1</sup>

To a solution of carbonohydrazide (3.0 g, 0.333 mmol) in a mixture of 10 mL of distillate water and 30 mL of methanol was added dropwise a solution of 2-acetylpyridine (4.038 g, 0.330 mmol) in 10 mL of methanol. The mixture was stirred under reflux for 4 hours. A white precipitate appears gradually. On cooling, the precipitate was isolated by filtration and successively washed with  $2 \times 10$  mL of hot methanol and dried under P<sub>4</sub>O<sub>10</sub>. The filtrated was stored at 4 °C. On standing for one week crystals suitable for X-ray analysis were isolated. MP: 222 °C. Yield: 86.4%. Analytical for C<sub>8</sub>H<sub>11</sub>N<sub>5</sub>O: Calc (found) %C = 49.73 (49.43); %H = 5.74 (5.78); %N = 36.25 (36.21). IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3306; 3086; 1671; 1629; 1578; 1506; 1466, 1141. <sup>1</sup>H NMR (dms<sub>o</sub>-d<sub>6</sub>,  $\delta$  (ppm)): 2.36 (s, 3H, -CH<sub>3</sub>); 4.12 (s, 2H, -NH<sub>2</sub>); 7.32 - 8.51 (m, 4H, H<sub>py</sub>); 8.19 (s, 1H, -(C=O)-NH-NH<sub>2</sub>); 9.64 (s, 1H, -(C=O)-NH-(C=N-)). <sup>13</sup>C NMR (dms<sub>o</sub>-d<sub>6</sub>,  $\delta$  (ppm)): 157.32 (CH<sub>3</sub>-C=N-); 155.30 (C=O); 148.37 (C<sub>ipso</sub>); 145.45 (C<sub>py</sub>); 136.43 (C<sub>py</sub>); 123.47 (C<sub>py</sub>); 120.13 (C<sub>py</sub>); 11.03 (-CH<sub>3</sub>).

## 2.3. Synthesis of the Ligand

### 1-(Pyridin-2-ylmethylene)Carbonohydrazide: H<sub>4</sub>L<sup>2</sup>

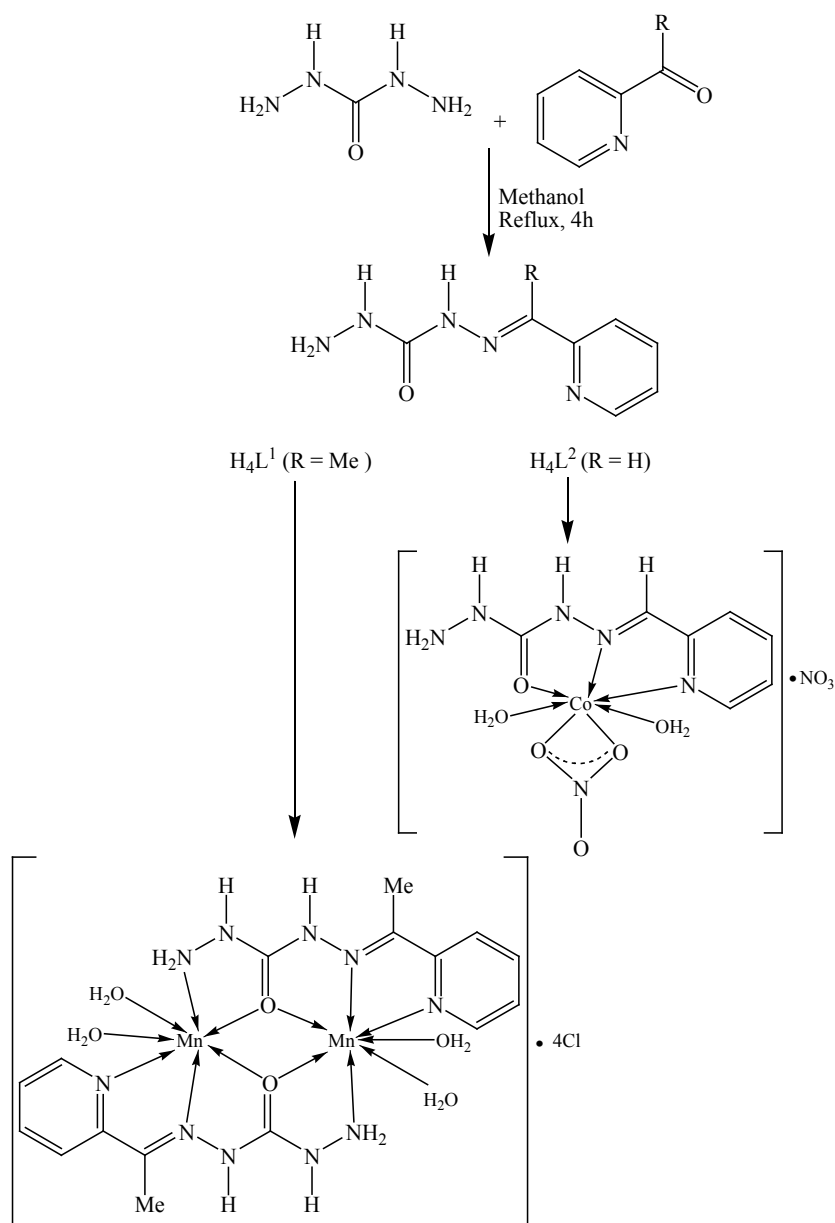
To a solution of carbonohydrazide (3.0 g, 0.333 mmol) in a mixture of 10 mL of distillate water and 30 mL of methanol was added dropwise a solution of 2-pyridinecarboxaldehyde (3.5672 g, 0.330 mmol) in 10 mL of methanol. The mixture was stirred at reflux for 4 hours. After cooling to room temperature, the orange solution was stored in the refrigerator and a precipitate appears overnight. The compound was isolated by filtration and washed successively with  $2 \times 10$  mL of cold methanol and  $2 \times 10$  mL of diethyl ether before being dried over P<sub>4</sub>O<sub>10</sub>. MP: 165 °C - 167 °C. Yield: 62.1%. Analytical for C<sub>7</sub>H<sub>6</sub>N<sub>5</sub>O: Calc (found) %C = 46.92 (46.90); %H = 5.06 (5.04); %N = 39.09 (39.05). IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3304; 3197; 1675; 1634; 1609; 1585; 1519; 1494, 1151. <sup>1</sup>H NMR (dms<sub>o</sub>-d<sub>6</sub>,  $\delta$  (ppm)): 4.08 (s, 2H, -NH<sub>2</sub>); 7.30 - 8.52 (m, 4H, H<sub>py</sub>); 8.21 (s, 1H, H-C=N-NH-C=O); 10.67 (s,

$1\text{H}$ ,  $-(\text{C}=\text{O})-\text{NH}-\text{NH}_2$ ).  $^{13}\text{C}$  NMR (dmso- $d_6$ ,  $\delta$  (ppm)): 156.27 ( $\text{CH}_3-\text{C}=\text{N}$ -); 155.500 ( $\text{C}=\text{O}$ ); 148.79 ( $\text{C}_{\text{ipso}}$ ); 140.46 ( $\text{C}_{\text{py}}$ ); 136.47 ( $\text{C}_{\text{py}}$ ); 123.54 ( $\text{C}_{\text{py}}$ ); 119.50 ( $\text{C}_{\text{py}}$ ) (Scheme 1).

## 2.4. Synthesis of the Complexes

### 2.4.1. $[\text{Mn}_2(\text{H}_4\text{L}^1)_2(\text{H}_2\text{O})_4]\cdot\text{Cl}_4$ (1)

To a suspension of  $\text{L}^1\text{H}_4$  (0.193 g, 1 mmol) in 10 ml of methanol was added  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$  (0.1979 g, 1 mmol). The resulting yellowish mixture was stirred for 30 min. The resulting yellow suspension was stirred at room temperature during one hour. The suspension was filtered and the filtrate was left at room temperature. On standing for one week crystals suitable for X-ray analysis were isolated.



Scheme 1. Preparation of the ligands and the complexes.

Yield: 74.6 (%). SM (ESI-TOF) ( $m/z$ ): 194.1 [(H<sub>5</sub>L)]<sup>+</sup>; 361 [Mn(H<sub>4</sub>L)Cl(H<sub>2</sub>O)<sub>3</sub>Na]<sup>2+</sup>; 440 [Mn(H<sub>4</sub>L)(H<sub>3</sub>L)]<sup>3+</sup>; 602.97 [Mn<sub>2</sub>(H<sub>4</sub>L)<sub>2</sub>(Cl)(H<sub>2</sub>O)<sub>4</sub>]<sup>3+</sup>. IR (cm<sup>-1</sup>): 3276 cm<sup>-1</sup>; 3186 cm<sup>-1</sup>; 3142 cm<sup>-1</sup>; 3070 cm<sup>-1</sup>; 1658 cm<sup>-1</sup>; 1595 cm<sup>-1</sup>; 1557 cm<sup>-1</sup>; 1470 cm<sup>-1</sup>; 1362 cm<sup>-1</sup>; 1185 cm<sup>-1</sup>; 1154 cm<sup>-1</sup>; 1027 cm<sup>-1</sup>; 829 cm<sup>-1</sup>. UV-vis (Solution, DMF, nm): 219; 357; 421.  $\mu_{\text{eff}} = 7.72 \mu_{\text{B}}$ .  $\Lambda$  ( $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ , DMF): 292.

#### 2.4.2. [Co(H<sub>4</sub>L<sup>2</sup>)(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>) (2)

To a suspension of L<sup>2</sup>H<sub>4</sub> (0.1792 g, 1 mmol) in 10 ml of methanol was added Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.2910 g, 1 mmol) dissolved in 5 mL of methanol. The resulting brown mixture was stirred for 60 min at room temperature. The resulting solution was filtered and the filtrate was left at room temperature. On standing for one week crystals suitable for X-ray analysis were isolated. Yield: 36.8 (%). IR (cm<sup>-1</sup>): 3227 cm<sup>-1</sup>; 1637 cm<sup>-1</sup>; 1578 cm<sup>-1</sup>; 1540 cm<sup>-1</sup>; 1455 cm<sup>-1</sup>; 1402 cm<sup>-1</sup>; 1380, 1294 cm<sup>-1</sup>; 1205 cm<sup>-1</sup>; 1116 cm<sup>-1</sup>; 1026 cm<sup>-1</sup>; 936 cm<sup>-1</sup>. UV-vis (Solution, DMF, nm): 225; 321; 421; 530.  $\mu_{\text{eff}} = 4.99 \mu_{\text{B}}$ .  $\Lambda$  ( $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ , DMF): 83.1.

### 2.5. Crystal Structure Determination and Refinement

Crystals suitable for X-diffraction, of the reported compounds, were grown by slow evaporation of MeOH solution of the complex. Details of the X-rays crystal structure solution and refinement are given in **Table 1**. Diffraction data were collected using an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package *SHELXTL* [40]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on  $F^2$  by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [34]. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms (CH and CH<sub>3</sub> groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using *ORTEP-3* [41].

## 3. Results and Discussion

### 3.1. General Study

The infrared spectrum of each molecule ligand shows the presence of two bands in the range 3310 cm<sup>-1</sup> and 3080 cm<sup>-1</sup> attributable to the vibrations  $\nu_{\text{N-H}}$  of the ligand. The vibration bands relative to  $\nu_{\text{C=O}}$  and  $\nu_{\text{C=N}}$  are respectively located at 1671 cm<sup>-1</sup> and 1634 cm<sup>-1</sup> for H<sub>4</sub>L<sup>1</sup> and 1675 cm<sup>-1</sup> and 1639 cm<sup>-1</sup> for H<sub>4</sub>L<sup>2</sup>. Bands assignable  $\nu_{\text{C=N}}$  and  $\nu_{\text{C=C}}$  of the pyridine ring are located between 1460 cm<sup>-1</sup> and 1590 cm<sup>-1</sup> [42]. The vibration of the N-N bond are pointed at *ca.*1146 cm<sup>-1</sup> for both ligands. The <sup>1</sup>H NMR spectra of the ligands recorded in dms<sub>o</sub>-d<sub>6</sub> and show similar signals. The difference is due to the presence of a methyl group on the imino carbon atom for L<sup>1</sup>H<sub>4</sub> instead of imino hydrogen atom as for L<sup>2</sup>H<sub>4</sub>. The

**Table 1.** Crystal data and data collection details of the complexes (1) and (2).

Chemical formula	C <sub>16</sub> H <sub>30</sub> Mn <sub>2</sub> N <sub>10</sub> O <sub>6</sub> ·4(Cl) (1)	C <sub>7</sub> H <sub>13</sub> CoN <sub>6</sub> O <sub>6</sub> ·NO <sub>3</sub> (2)
$M_r$	710.18	398.16
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
Temperature (K)	293	293
<i>a</i> (Å)	8.7932 (2)	8.4248 (2)
<i>b</i> (Å)	9.1070 (2)	8.7674 (2)
<i>c</i> (Å)	9.9348 (3)	10.6885 (2)
$\alpha$ (°)	75.460 (2)	82.151 (2)
$\beta$ (°)	67.174 (2)	86.273 (2)
$\gamma$ (°)	81.729 (2)	81.732 (2)
<i>V</i> (Å <sup>3</sup> )	708.83 (3)	773.14 (3)
<i>Z</i>	1	2
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.32	1.17
Crystal size (mm)	0.40 × 0.30 × 0.15	0.34 × 0.22 × 0.10
$T_{\min}$ , $T_{\max}$	0.574, 1.000	0.763, 1.000
No. of measured reflections	15348	29332
Independent reflections	3394	3611
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	3030	3296
$R_{\text{int}}$	0.048	0.027
$R[F^2 > 2\sigma(F^2)]$	0.026	0.045
$wR(F^2)$	0.069	0.130
Data/parameters/restraints	3389/192/5	3611/269/0
<i>GOF</i>	1.07	1.07
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e·Å <sup>-3</sup> )	0.28, -0.28	1.00, -0.57

presence of a singlet signal incorporating two protons attributable to NH<sub>2</sub> at 4.08 ppm for both spectra is indicative of the mono condensation of the carbonyl hydrazide with the ketoprecursors. The <sup>13</sup>C NMR spectra are similar except the presence of a signal at 11.03 ppm relative to the presence of a methyl group in H<sub>4</sub>L<sup>1</sup>. The FAB mass spectrometry of the compound [Mn<sub>2</sub>(H<sub>4</sub>L<sup>1</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>].Cl<sub>4</sub> gave clear evidence of fragmentation of the complex. The parent ion expected at 710.16 amu was not observed. The observed mass/charge ratio of 602.97 amu, 440 amu, 361 amu and 194.10 amu compared to the calculated exact mass of 603.08 amu, 440.12 amu, 360.63 amu and 194.21 amu are respectively due to the fragments [Mn<sub>2</sub>(H<sub>4</sub>L)<sub>2</sub>(Cl)(H<sub>2</sub>O)<sub>4</sub>]<sup>3+</sup>, [Mn(H<sub>4</sub>L)(H<sub>3</sub>L)]<sup>3+</sup>, [Mn(H<sub>4</sub>L)Cl(H<sub>2</sub>O)<sub>3</sub>Na]<sup>2+</sup>, and [(H<sub>5</sub>L)]<sup>+</sup>. Upon coordination the  $\nu_{\text{C=O}}$  and the  $\nu_{\text{C=N}}$  were strongly shifted to low frequencies in both spectra. For the Mn(II) complex the  $\nu_{\text{C=O}}$  and the  $\nu_{\text{C=N}}$

are respectively pointed at  $1658\text{ cm}^{-1}$  and  $1595\text{ cm}^{-1}$  while the spectrum of the Co(II) complex show the  $\nu_{\text{C=O}}$  and the  $\nu_{\text{C=N}}$  band at  $1637\text{ cm}^{-1}$  and  $1578\text{ cm}^{-1}$ . These shifts are indicative of the involvement of the carbonyl oxygen atom and the nitrogen atom of the azomethine in the complexation with Mn(II) and Co(II) in both cases [43] [44]. In both spectrum broad absorption bands appear at  $3276\text{ cm}^{-1}$  and  $3227\text{ cm}^{-1}$  for the complexes of Mn(II) and Co(II) respectively. These bands are due to the presence of a coordinated water molecule [45]. Additional bands due to the nitrate moieties appears. The sharp and intense band at  $1380\text{ cm}^{-1}$  is attributed to the free nitrate group. The three absorption bands occurring at  $1455\text{ cm}^{-1}$ ,  $1294\text{ cm}^{-1}$  and  $1026\text{ cm}^{-1}$  respectively attributable to  $\nu_1$  ( $\nu_{\text{N=O}}$ ),  $\nu_5$  ( $\nu_{\text{asNO}_2}$ ) and  $\nu_2$  ( $\nu_{\text{sNO}_2}$ ) clearly identify a nitrate group coordinated in bidentate fashion [37]. In fact the separation  $\Delta\nu = \nu_1 - \nu_5$  is used as criterion of differentiation of the different modes of coordination of the nitrate moiety. The  $\Delta\nu$  value of  $161\text{ cm}^{-1}$  is in accordance with the presence of bidentate nitrate group [45]. In the UV-vis spectra of the monohydrazone ligands two bands are observed at 233 and 318 nm for  $\text{H}_4\text{L}^1$  and at 235 and 315 nm for  $\text{H}_4\text{L}^2$ . For both spectra the first band is attributable to the  $n \rightarrow \pi^*$  transitions in aromatic rings while the second band is assignable to the  $n \rightarrow \pi^*$  transition. The electronic spectra of the manganese complex in DMF shows three main bands at 219, 357 and 421 nm and the cobalt (II) complex in DMF exhibits three main bands around 225, 321 and 421 nm and a shoulder around 530 nm. By comparing these bands to the absorption in the spectra of the free ligand, bathochromic shifts is observed for the maxima bands of the free ligand. The band observed at 357 nm for Mn(II) complex and the band pointed at 321 nm for Co(II) complex are assigned to the aromatic ring transition  $\pi \rightarrow \pi^*$  and the other bands are attributed to the  $n \rightarrow \pi^*$  transitions of C=N chromophore. The values of the conductance of the two complexes in DMF are  $192\text{ }\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  for the manganese (II) complex which is 2:1 electrolyte and  $83.1\text{ }\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  for the cobalt (II) complex which is 1:1 electrolyte in nature [46]. The magnetic susceptibility measurements of the complexes were performed at room temperature. The value of  $7.72\text{ }\mu_{\text{B}}$  for the manganese complex is less than the expected value of  $ca.10\text{ }\mu_{\text{B}}$  for two Mn(II) ions, indicating the presence of two metal atoms per molecule which are in weak antiferromagnetic coupling interaction. For the complex of cobalt (II) the magnetic moment value of  $4.99\text{ }\mu_{\text{B}}$  is in the range expected for a mononuclear hepta coordinated cobalt (II) complex [28].

### 3.2. Description of the Structures

Suitable single-crystals for X-ray diffraction of the Mn(II) and Co(II) complexes were obtained by slow solvent evaporation at room temperature. Crystal data, collection and refinement parameters are listed in Table 1. Selected bond lengths and angles are summarized in Table 2. Hydrogen bond data for complexes 1 and 2 are gathered in Table 3. Figures 1-4 displays the asymmetric unit and the packing diagrams of the two compounds.

**Table 2.** Selected bond lengths (Å) and angles (°) for the complexes (1) and (2).

Mn1-O3W	2.1454 (11)	Co1-O1	2.267 (2)
Mn1-O2W	2.1606 (11)	Co1-O3	2.104 (2)
Mn1-O1	2.2135 (10)	Co1-O4	2.092 (2)
Mn1-O1 <sup>i</sup>	2.3219 (9)	Co1-O5	2.212 (2)
Mn1-N4 <sup>z</sup>	2.3247 (11)	Co1-O6	2.298 (3)
Mn1-N1	2.5223 (13)	Co1-N1	2.192 (2)
Mn1-N5i	2.2968 (12)	Co1-N0aa	2.119 (2)
O3W-Mn1-O2W	169.82 (5)	O3-Co1-O1	89.79 (8)
O3W-Mn1-O1	87.86 (4)	O4-Co1-O1	87.90 (8)
O2W-Mn1-O1	89.17 (5)	O4-Co1-O3	175.31 (8)
O3W-Mn1-N5i	90.22 (4)	O5-Co1-O1	75.71 (8)
O2W-Mn1-N5 <sup>i</sup>	89.22 (5)	O5-Co1-O3	88.23 (9)
O1-Mn1-N5 <sup>i</sup>	159.89 (4)	O5-Co1-O4	87.24 (9)
O3W-Mn1-O1 <sup>i</sup>	98.61 (5)	O6-Co1-O1	131.55 (8)
O2W-Mn1-O1 <sup>i</sup>	89.04 (4)	O6-Co1-O3	91.92 (10)
O1-Mn1-O1 <sup>i</sup>	65.78 (4)	O6-Co1-O4	86.56 (9)
N5 <sup>i</sup> -Mn1-O1 <sup>i</sup>	134.22 (4)	O6-Co1-O5	55.96 (8)
O3W-Mn1-N4 <sup>i</sup>	89.02 (5)	N1-Co1-O1	145.80 (8)
O2W-Mn1-N4 <sup>i</sup>	100.24 (5)	O1-C7	1.214 (3)
O1-Mn1-N4 <sup>i</sup>	131.13 (4)	N1-Co1-O3	89.45 (8)
N5 <sup>i</sup> -Mn1-N4 <sup>i</sup>	68.80 (4)	N1-Co1-O4	94.75 (8)
O1 <sup>i</sup> -Mn1-N4 <sup>i</sup>	66.56 (4)	N1-Co1-O5	138.42 (8)
O3W-Mn1-N1	87.18 (5)	N1-Co1-O6	82.65 (8)
O2W-Mn1-N1	82.68 (5)	N0aa-Co1-O1	71.50 (8)
O1-Mn1-N1	67.72 (4)	N0aa-Co1-O3	89.51 (9)
N5 <sup>i</sup> -Mn1-N1	92.20 (4)	N0aa-Co1-O4	93.63 (8)
O1 <sup>i</sup> -Mn1-N1	132.81 (4)	N0aa-Co1-O5	147.14 (8)
N4 <sup>i</sup> -Mn1-N1	160.62 (4)	N0aa-Co1-O6	156.90 (9)
N2-N1-Mn1	107.78 (8)	N0aa-Co1-N1	74.30 (8)

Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .**Table 3.** Hydrogen bonds for the complexes (1) and (2).

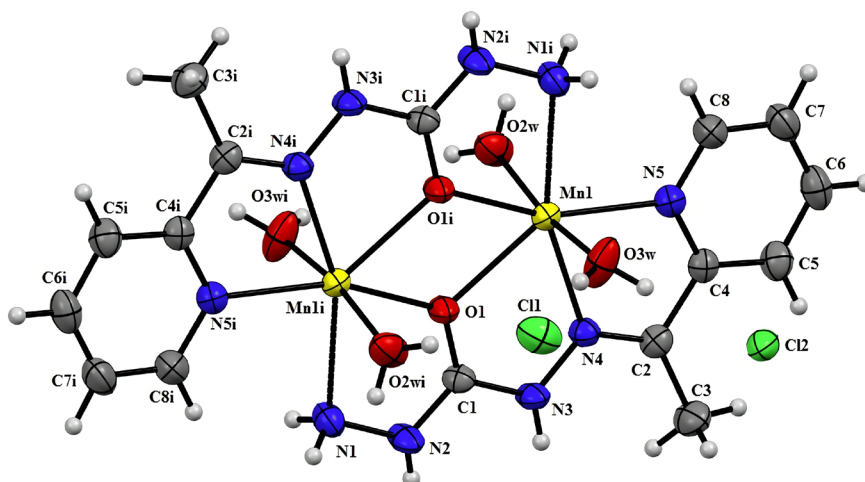
Complex 1				
<i>D-H...A</i>	<i>D-H</i>	<i>H...A</i>	<i>D...A</i>	<i>D-H...A</i>
N1-H1A...Cl1 <sup>i</sup>	0.89	2.68	3.4728(14)	149.7
N2-H2N...Cl2 <sup>ii</sup>	0.81(2)	2.689(19)	3.2518(14)	128.3(16)
N2-H2N...Cl2 <sup>iii</sup>	0.81(2)	2.71(2)	3.3574(14)	138.2(16)
N3-H3N...Cl2 <sup>iii</sup>	0.812(19)	2.324(19)	3.1125(13)	163.9(17)
C3-H32...Cl2 <sup>iii</sup>	0.96	2.91	3.7900(17)	153.4
C3-H34...N3 <sup>iii</sup>	0.96	2.67	3.633(2)	175.9
C8-H8...Cl1 <sup>iv</sup>	0.93	2.91	3.5245(17)	124.5
O2W-H2W1...Cl1 <sup>i</sup>	0.811(15)	2.286(15)	3.0939(12)	175(2)
O2W-H2W2...Cl1	0.798(15)	2.323(16)	3.1133(12)	171(2)



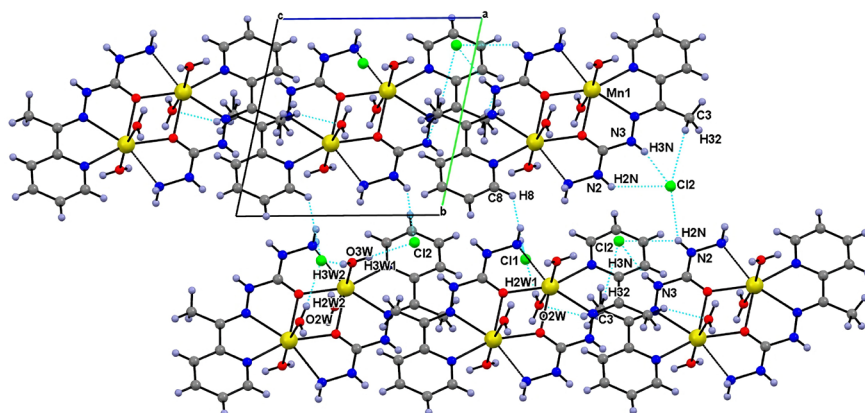
## Continued

O3W-H3W1...Cl2 <sup>v</sup>	0.824(15)	2.204(16)	3.0255(12)	175(2)
O3W-H3W2...Cl1 <sup>v</sup>	0.800(16)	2.352(17)	3.1424 (13)	169(2)
Complex 2				
<i>D</i> -H... <i>A</i>	<i>D</i> -H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> -H... <i>A</i>
O4-H4a...O7 <sup>vi</sup>	0.851(9)	2.053	2.902	174.24
O4-H4a...O6 <sup>vi</sup>	0.851(9)	2.687	3.220	122.02
O4 <sup>vi</sup> -H4a...O7	0.851(9)	2.053	2.902	174.24
O4 <sup>vi</sup> -H4a...O6	0.851(9)	2.687	3.220	122.02
O4-H4b...O8	0.851(9)	2.381	3.194	160.27
O4-H4b...O9	0.851(9)	2.173	2.911	145.53
N3 <sup>vii</sup> -H3...O10	0.860(3)	2.088	2.846	146.61
C6 <sup>vii</sup> -H6...O10	0.929(3)	2.286	3.045	138.49

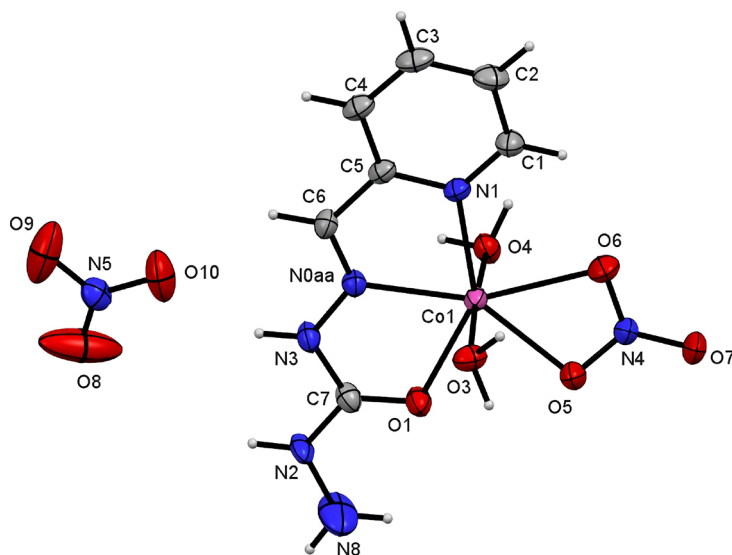
Symmetry codes: (i)  $-x, -y + 1, -z + 1$ ; (ii)  $x, y + 1, z$ ; (iii)  $-x + 1, -y + 1, -z$ ; (iv)  $-x + 1, -y, -z + 1$ ; (v)  $-x + 1, -y + 1, -z + 1$ ; (vi)  $-x, 1-y, 1-z$ ; (vii)  $1 - x, -y, 2 - z$ .



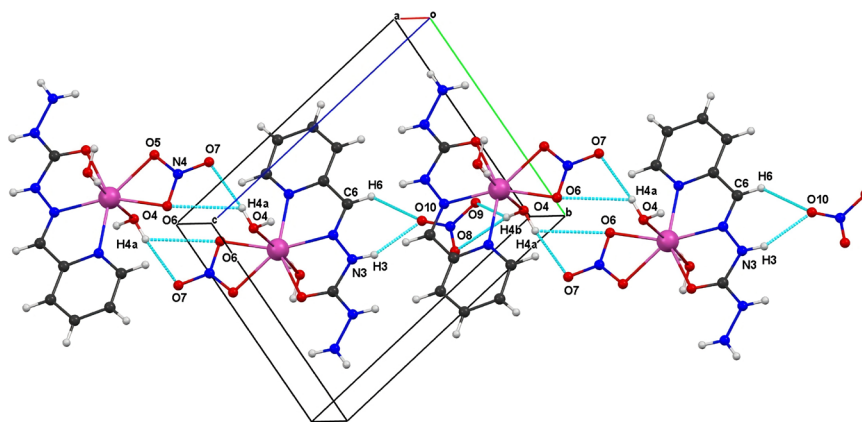
**Figure 1.** ORTEP plot (30% probability ellipsoids) showing the molecule structure of the complex 1.



**Figure 2.** Hydrogen bonds in complex 1.



**Figure 3.** ORTEP plot (30% probability ellipsoids) showing the molecule structure of the complex **2**.



**Figure 4.** Hydrogen bonds in complex **2**.

### 3.2.1. Complex 1

The  $[\text{Mn}_2(\text{H}_4\text{L}^1)_2(\text{H}_2\text{O})_4] \cdot 4\text{Cl}$  complex crystallizes in the triclinic system with the space group P-1. The view of the structure of the complex **1** is depicted in **Figure 1**. The asymmetric unit contains two manganese (II) atoms, two organic ligand molecules, four coordinated water molecules and four free chloride anions. Each of the ligand molecules acts in tetradentate fashion through one nitrogen atom from the pyridine, one imino nitrogen atom, one nitrogen atom amino and one carbonyl oxygen atom which acts as bridge between the two manganese (II) atoms. Each of the two metal ions Mn(II) is heptacoordinated and the coordination polyhedron of the Mn(II) center is best described as a distorted pentagonal bipyramid with a  $\text{MnN}_5\text{O}_4$  chromophore. Each equatorial planes around each Mn(II) atom is occupied by a pyridine nitrogen atom, an imino nitrogen atom, one oxygen atom from the same ligand, one carbonyl bridged oxygen atom and one amino nitrogen atom from another ligand molecule. The apical positions are

occupied by two oxygen atoms of the coordinated water molecules. The angles formed between the metal center and the ligand donor atoms in equatorial position are different from the ideal angle for a regular pentagon ( $72^\circ$ ) [ $N5^i-Mn1-N4^i = 68.80(4)^\circ$ ,  $O1^i-Mn1-N4^i = 66.56(4)^\circ$ ,  $N5^i-Mn1-N1 = 92.20(4)^\circ$ ,  $O1-Mn1-N1 = 67.72(4)^\circ$ ,  $O1-Mn1-O1^i = 65.78(4)^\circ$ ] with a sum of  $361.1^\circ$  [47]. The apical angle formed by the water oxygen atoms in axial positions around the manganese (II) atom [ $O2w-Mn1-O3w = 169.82(5)^\circ$ ] significantly deviate from the ideal value of  $180^\circ$  (Table 2). The angles  $Mn1-O1-Mn1^i$  and  $O1-Mn-O1^i$  are respectively  $114.22(4)^\circ$  and  $65.78(4)^\circ$ . For the Mn atom the apical position is occupied by the water oxygen atoms Ow2 and OW3 with  $2.1606(11) \text{ \AA}$  and  $2.1454(11) \text{ \AA}$  distance. These distances are shorter than those of the equatorial bonds [ $Mn1-O1 = 2.2135(10) \text{ \AA}$ ,  $Mn1-N5^i = 2.2968(12) \text{ \AA}$ ,  $Mn1-O1^i = 2.3219(9) \text{ \AA}$ ,  $Mn1-N4^i = 2.3247(11) \text{ \AA}$  and  $Mn1-N1 = 2.5223(13) \text{ \AA}$ ] (Table 2) and are comparable to those found in similar complex [27]. The interatomic distance O1-C1 of  $1.2433(16) \text{ \AA}$  is close proximity to that observed in the structure of the free ligand which is of the order of  $1.231(3) \text{ \AA}$ . This fact is indicative of double character bond upon complexation with the Mn(II) ion. Each mononuclear Mn(II) molecule complex is connected to another complex molecule by hydrogen bonding interactions leading to the formation of a supramolecular chain structure propagating along the *a* axis. The chains are connected by hydrogen bonding interaction of type N-H...Cl, C-H...Cl, Ow-H...Cl, and C-H...N. The uncoordinated chloride anion acts via hydrogen bonds as bridge between the chains leading to the formation of a 3D supramolecular structure (Figure 2, Table 3).

### 3.2.2. Complex 2

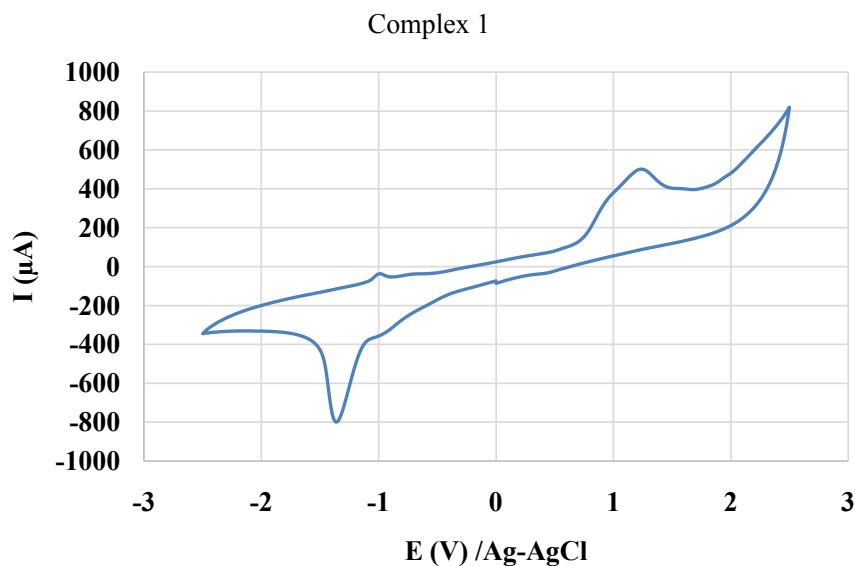
The compound  $[Co(H_4L_D)(H_2O)_2(NO_3)] \cdot NO_3$  crystallizes in the triclinic system with a P-1 space group. The view of the structure of the complex 2 is depicted in Figure 3. The asymmetric unit is composed by a cobalt (II) atom coordinated to one organic ligand molecule, one bidentated coordinated nitrate anion, two coordinated water molecules and one uncoordinated nitrate ion. The ligand acts in tridentate manner through the oxygen atom of the carbonyl moiety, the imino nitrogen atom and the pyridine nitrogen atom. The cobalt ion is situated in a  $N_2O_5$  core and the environment is best described as pentagonal bipyramid geometry (Figure 3). The equatorial plane around the Co(II) ion is occupied by the three donor atoms from the organic ligand molecule and the two oxygen atoms of the coordinated nitrate group while the apical positions are occupied by the two oxygen atoms of the coordinated water molecules. The angles formed between the equatorial atoms and the Co(II) ion are:  $N0aa-Co1-O1 = 71.50(8)^\circ$ ,  $N0aa-Co1-N1 = 74.30(8)^\circ$ ,  $N1-Co1-O6 = 55.96(8)^\circ$ ,  $O5-Co1-O1 = 75.71(8)^\circ$  and are different from the ideal angle value of  $72^\circ$  for a pentagonal basal plan [48]. The angle  $O4-Co1-O3$  formed between the apical atoms and the Co(II) ion deviated from the ideal value of  $180^\circ$  with a value of  $175.31(8)^\circ$ . The sum of the angles around Co(II) is  $360.12^\circ$  and is very close to the ideal sum of  $360^\circ$ . These

deviations are indicative of a distortion of geometry around the cobalt center which is best described as a distorted pentagonal bipyramid. The equatorial distances [Co1-O1 = 2.267 (2) Å, Co1-O5 = 2.212 (2) Å, Co1-O6 = 2.298 (3) Å, Co1-N1 = 2.192 (2) Å and Co1-N0aa = 2.119 (2) Å] are longer than that of the axial distances [Co1-O3 = 2.104 (2) Å, Co1-O4 = 2.092 (2) Å] (**Table 2**) and are comparable to the values reported for a seven coordinated cobalt(II) complex [29].

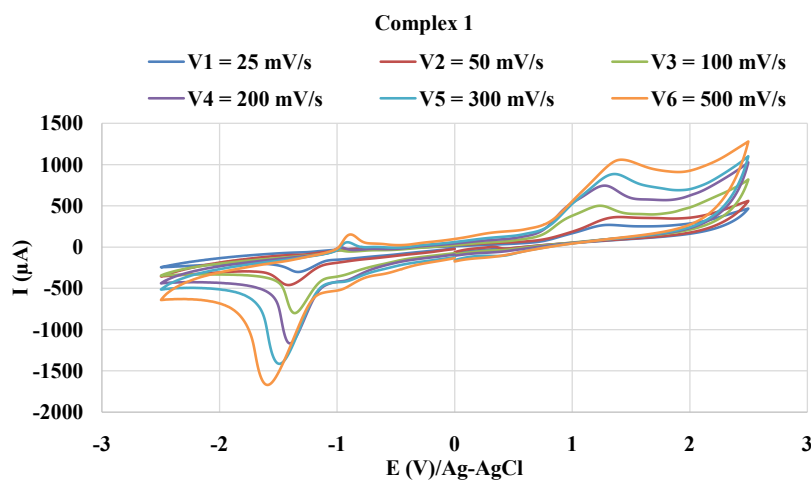
In the crystal, the complex molecules are linked by hydrogen bonds, giving rise to a three-dimensional network (**Figure 4**, **Table 3**). The structure is built up from pentagonal bipyramids around the Co(II) atom, which are assembled in layers parallel to the *bc* plane. These layers are interconnected by hydrogen bonds. The coordinating axial water molecule points into the interlayer space and acts as a hydrogen-bond donor towards oxygen atom O-NO<sub>2</sub> of the coordinated nitrate (**Figure 4**) O1W-H1WB...ONO<sub>2</sub>. Within a layer, the molecules are not interconnected by hydrogen bonds.

### 3.2.3. Electrochemistry Study [Mn<sub>2</sub>(H<sub>4</sub>L)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]-4Cl

The electrochemical properties of the Mn(II) complex were studied by cyclic voltammeter using a graphite carbon working electrode and a Pt-wire auxiliary electrode in acetonitrile using LiClO<sub>4</sub> as the supporting electrolyte. The voltammetric parameters were studied in the scan rate interval 100 - 200 mV s<sup>-1</sup>. In **Figure 5** describes the electrochemical behavior of the complex in acetonitrile medium. The cyclic voltammogram of the complex [Mn<sub>2</sub>(H<sub>4</sub>L)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]-4Cl was recorded at -3.00 to +3.00 V (*vs* Ag/AgCl) with a scan rate of 100 mV/s in DMF solution at room temperature. We note one oxidation and two reduction peaks and two oxidation (**Figure 5**). The cathodic wave shows two distinct reductive peaks at *ca.* -0.9 V and -1.3 V ( $\Delta E = 0.4$  V) which correspond to two electrons charge



**Figure 5.** Cyclic Voltammograms of the complex in CH<sub>3</sub>CN containing 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>]. Working electrode: a 5 mm diameter of graphitecarbon electrode, scan rate: 100 m·Vs<sup>-1</sup>.



**Figure 6.** Cyclic Voltammograms of the complex in  $\text{CH}_3\text{CN}$  containing 0.1 M  $[\text{NBu}_4][\text{PF}_6]$  Scan rate: 25, 150, 100, 200, 300 and 500  $\text{mVs}^{-1}$ . Working electrode: a 2 mm diameter of graphite carbon electrode.

transfer process  $\text{Mn(II)Mn(II)} \rightarrow \text{Mn(II)Mn(I)}$  and  $\text{Mn(II)Mn(I)} \rightarrow \text{Mn(I)Mn(I)}$ . The anodic wave shows two oxidative peaks  $-1.00$  and  $+1.2$  V corresponding to the reversible process  $\text{Mn(I)Mn(I)} \rightarrow \text{Mn(II)Mn(I)}$  and  $\text{Mn(II)Mn(I)} \rightarrow \text{Mn(II)Mn(II)}$ . A reversible transition  $\text{Mn(II)} \rightarrow \text{Mn(I)}$  had already been observed for a  $\text{Mn(II)}$  complex in acetonitrile media [49]. By varying the scans speed the intensities of all the peaks increase with the scanning speed (Figure 6).

#### 4. Conclusion

We describe here one seven coordinated manganese (II) complexes of the tetradentate ligand 1-(1-(pyridin-2-yl)ethylidene)carbonohydrazide and one seven coordinated cobalt(II) of the tridentate 1-(pyridin-2-ylmethylene)carbonohydrazide. The single crystal structure of the  $\text{Mn(II)}$  complex **1** as well as of the  $\text{Co(II)}$  complex **2** has revealed a distorted pentagonal-bipyramidal geometry. The equatorial plane in complex **1** is occupied by  $\text{N}_2\text{O}$  and  $\text{NO}$  from two tetradentate ligand molecules acting as bridges between two  $\text{Mn(II)}$  ions. The axial positions are occupied by two coordinated water molecules. In the complex **2**, the equatorial plane of the bipyramid is occupied by the tridentate  $\text{N}_2\text{O}$  ligand and two oxygen atoms from the coordinated nitrate anion which acts in bidentate chelating fashion, the two apical positions being occupied by two coordinated water molecules. The cyclic voltammetry studies in  $\text{CH}_3\text{CN}$  show that the manganese (II) complex **2** shows two electrons charge transfer process.

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#### Supporting Information

CCDC-1944387 and 1944386 contains the supplementary crystallographic data

for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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