



Dedicated to Dr. Maria Zaharescu  
on the occasion of her 80th anniversary

## NEW MONONUCLEAR COBALT(III) AND MANGANESE(III) COMPLEXES CONTAINING A HEXADENTATE SCHIFF BASE LIGAND<sup>\*\*</sup>

Ildiko BUTA,<sup>a</sup> Anamaria ARDELEAN,<sup>a</sup> Liliana CSEH,<sup>a</sup> Valentin BADEA<sup>b</sup>, Florica MANEA,<sup>b</sup>  
Emese GAL,<sup>c</sup> Peter LÖNNECKE,<sup>d</sup> Evamarie HEY-HAWKINS<sup>d</sup> and Otilia COSTISOR<sup>a\*</sup>

<sup>a</sup>Institute of Chemistry of Roumanian Academy, 24 Mihai Viteazu Bvd. 300223-Timișoara, Roumania, [ocostisor@acad-icht.tm.edu.ro](mailto:ocostisor@acad-icht.tm.edu.ro)

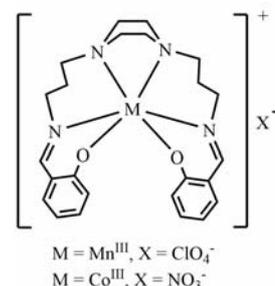
<sup>b</sup>University Politehnica Timișoara, Faculty of Industrial Chemistry and Environmental Engineering,  
6 Vasile Parvan Bvd. 300223-Timișoara, Roumania

<sup>c</sup>University Babes-Bolyai, Faculty of Chemistry and Chemical Engineering, 1 Arany Janos Str. 400028-Cluj-Napoca, Roumania

<sup>d</sup>Institute of Inorganic Chemistry, Universität Leipzig, Faculty of Chemistry and Mineralogy, Johannisallee 29, 04103-Leipzig, Germany

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Two new mononuclear complexes [MnL](ClO<sub>4</sub>) (**1**) and [CoL](NO<sub>3</sub>)·2CH<sub>3</sub>OH (**2**) containing N,N'-bis[(2-hydroxybenzylideneamino)propyl]-piperazine (H<sub>2</sub>L) have been synthesized and structurally characterized. Complex **1** crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c*, with cell dimensions *a* = 11.5180(6), *b* = 15.7885(8), *c* = 13.2207(7) Å, β = 90.162(4)°, complex **2** in the trigonal space group, with cell dimensions *a* = 17.4723(3), *b* = 17.4723(3), *c* = 47.655(1) Å, γ = 120°. X-ray structure determinations of **1** and **2** revealed that both compounds consist of mononuclear complex cations containing trivalent metal centers, Mn<sup>III</sup> or Co<sup>III</sup>. The metal ions are coordinated in a distorted octahedral fashion by the N<sub>4</sub> donor set of the ligand in basal and the two phenoxo oxygen atoms in apical positions. Spectral properties are consistent with the crystallographic results. The electrochemical properties of the complexes have been investigated by cyclic voltammetry. The reversible behavior of the Mn<sup>III</sup>/Mn<sup>II</sup> system was slightly affected by the changes in the coordination environment during the overall redox process, while the Co<sup>III</sup>/Co<sup>II</sup> system exhibited an irreversible behavior.



### INTRODUCTION

Manganese and cobalt complexes in high oxidation state play an important role in a diverse range of enzymatic and electron-transfer processes in biological systems<sup>1</sup> and as antibacterial or antiviral agents.<sup>2</sup> The ability to act as an electron carrier between biochemical redox centers is explained by the property of metal ions to exist in relative stable oxidation states that differ by one unit.<sup>3</sup> The preferred oxidation state is dependent on the type of ligand present in the coordination

sphere. Ligands with donor atoms less electronegative than oxygen stabilize the oxidation state next higher than that of the stable aqua complexes.<sup>4</sup>

Kuma *et al.*<sup>5</sup> reported earlier the synthesis of cobalt(III) and manganese(III) with N,N'-bis[(2-hydroxybenzylideneamino)-propyl]-piperazine (H<sub>2</sub>L) using as starting materials metal(II) acetates in the presence of sodium perchlorate. Their nature has been established by elemental analyses, spectral and magnetic studies. In previous work, we reported the synthesis and structure of

\* Corresponding author: [ocostisor@acad-icht.tm.edu.ro](mailto:ocostisor@acad-icht.tm.edu.ro)

\*\* Supplementary Information on <http://web.icf.ro/rrch/> or <http://revroum.lew.ro/>

[Co(L)]<sub>3</sub>(ClO<sub>4</sub>)<sub>3</sub>·4H<sub>2</sub>O starting from cobalt(II) perchlorate.<sup>6</sup> As a continuous work in our lab, in order to understand the role of the ligand and the counter ion on the nature of the complexes, including the oxidation state of the metal ion, we report here the synthesis and crystal structures of N,N'-bis[(2-hydroxybenzilideneamino)propyl]-piperazinemanganese(III) perchlorate [MnL](ClO<sub>4</sub>) (**1**) and N,N'-bis[(2-hydroxybenzilideneamino)propyl]-piperazinecobalt(III) nitrate [CoL](NO<sub>3</sub>)·2CH<sub>3</sub>OH (**2**).

## RESULTS AND DISCUSSION

Mononuclear complexes [MnL](ClO<sub>4</sub>) (**1**) and [CoL](NO<sub>3</sub>)·2CH<sub>3</sub>OH (**2**) containing the dianion of the ligand N,N'-bis[(2-hydroxybenzilideneamino)propyl]-piperazine (L<sup>2-</sup>) were synthesized in a methanol-chloroform (1:1) mixture and in the presence of Et<sub>3</sub>N as a deprotonating agent for H<sub>2</sub>L. The oxidation of the metal ions M<sup>II</sup> to M<sup>III</sup> (M: Mn, Co), occurs and the coordination of L<sup>2-</sup> stabilizes the high oxidation state. The general synthetic route to **1** and **2** is presented in Scheme 1. The complexes are stable in air and soluble in most organic solvents such as alcohols, DMSO and DMF. The molar conductance values of a 10<sup>-4</sup> molar DMF solution are in the range from 90 - 100 Ω·cm·mol<sup>-1</sup> indicating that the metal complexes **1** and **2** are 1:1 electrolytes.

### 1. X-ray crystal structures

Crystallographic data for complexes **1** and **2** are summarized in Table S1 and selected bond lengths and angles of the complexes can be found in Table S2.

#### *Crystal structure of [MnL](ClO<sub>4</sub>) (**1**)*

Compound **1** crystallizes in the monoclinic system, space group *P*2<sub>1</sub>/*c*, with four molecules in the unit cell (Figure 1). The compound consists of a mononuclear complex unit [MnL]<sup>+</sup> and a perchlorate ion.

The cation contains the hexadentate ligand L<sup>2-</sup> wrapped around the manganese(III) ion, thus describing a distorted octahedral environment with the median plane formed by four nitrogen atoms arising from two imino and two piperazine nitrogen atoms with Mn-N<sub>imino</sub> distance of 2.069(2) Å and Mn-N<sub>pip</sub> of 2.339(2) and 2.359(2) Å, respectively. The apical positions of the

octahedron are occupied by the two phenoxo oxygen atoms with the Mn-O<sub>phenoxo</sub> distances of 1.870(2) and 1.871(2) Å. The *trans* O1-Mn1-O2 and *cis* N1-Mn1-N4 angles of 170.69(9)° and 134.12°, respectively denotes a highly distorted octahedral environment of the Mn<sup>III</sup> ion. The two -CH<sub>2</sub>-CH<sub>2</sub>- piperazine straps with a “bite” angle N2-Mn1-N3 of 63.74(8)°, form two connected five-membered chelate rings. The torsion angles C12-C11-N2-C10<sub>propyl</sub> and C13-C14-N3-C15<sub>propyl</sub> of -177.8(2) and -177.5(2)°, respectively, indicate the *boat* conformation of the piperazine moiety. Small contact distances for C1...C5\* (3.34 Å) and C3...C6\* (3.62 Å) indicates the presence of parallel π...π stacking interactions between the phenyl rings belonging to two adjacent [MnL]<sup>+</sup> units, forming a supramolecular chain along (101) (Figure S1).<sup>7</sup> The architecture is held together through van der Waals forces and hydrogen bonds established between perchlorate oxygen atoms and carbon atoms from the ligand (C-H...O distance is in the range between 3.160(4) and 3.366(1) Å).

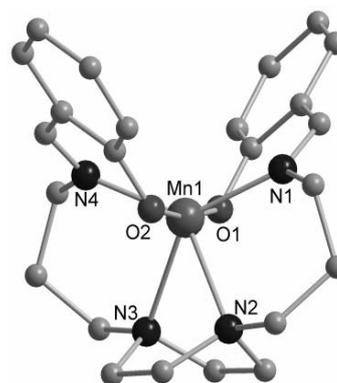


Fig. 1 – Molecular structure and atom labelling scheme of **1** (hydrogen atoms and perchlorate anion are omitted for clarity).

#### *Crystal structure of [CoL](NO<sub>3</sub>)·2CH<sub>3</sub>OH (**2**)*

X-ray diffraction reveals that **2** crystallizes in the trigonal system, space group *R*3̄*c*. The molecular structure with the numbering scheme is shown in Figure 2. The crystal lattice of **2** shows the presence of the cation [CoL]<sup>+</sup>, a nitrate anion and solvent molecules.

However, the nitrate anion and all solvent molecules could not be localized with a reasonable accuracy. They are found to be highly disordered in channels along (001). The electron density for these highly disordered moieties has been removed from the experimental data with the SQUEEZE routine implemented in PLATON.<sup>8</sup> Similar to **1**,

the cobalt(III) ion is hexacoordinated by the doubly deprotonated ligand  $L^{2-}$ , thus generating a slightly distorted octahedral geometry (*trans* angle O1-Co1-O1' of 176.71(9)°). The four nitrogen atoms of the Schiff base are situated in the basal plane of the octahedron. The complex cation  $[CoL]^+$  is located on a twofold axis [symmetry code: (') =  $-x+4/3, -x+y+2/3, -z+7/6$ ]. The interatomic distances are similar to **1**, Co1-N<sub>imino</sub> and Co1-N<sub>pip</sub> of 1.927(2) and 1.986(2) Å, respectively. The apical positions are occupied by phenoxo oxygen with Co1-O<sub>phenoxo</sub> distance of 1.899(1) Å. The "bite" angle formed by the atoms N2 and N2' with the Co<sup>III</sup> ion (N2-Co1-N2' 73.65(7)°) support the *boat* conformation of the piperazine moiety. Molecular packing along *c* axis shows a circular arrangement of  $[CoL]^+$  units with solvent molecules and nitrate anions in the formed channels (Figure S2). The stability of the system is assured by van der Waals forces and hydrogen bonds.

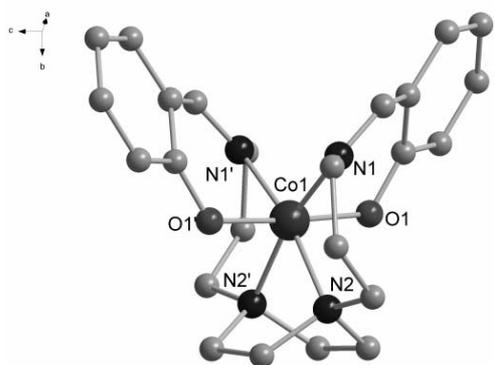


Fig. 2 – Molecular structure and atom labelling scheme of **2** (hydrogen atoms and nitrate groups are omitted for clarity) [symmetry code: (') =  $-x+4/3, -x+y+2/3, -z+7/6$ ].

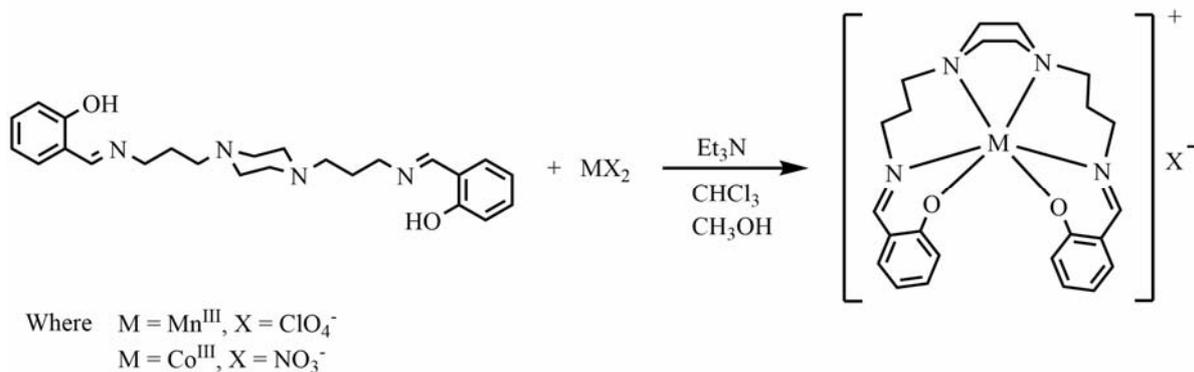
## 2. Spectral and magnetic properties

The FT-IR spectra of **1** and **2** show characteristic bands of the ligand  $L^{2-}$  affected by its coordination to  $M^{III}$  ( $M = Mn, Co$ )<sup>6</sup>. Thus, the  $\nu_{C=N}$

stretching vibration at 1621 in **1** and 1625  $cm^{-1}$  in **2**, respectively, appears shifted to lower wavenumbers compared to the  $H_2L$  (1631  $cm^{-1}$ ). The absorption band in the region 1290 - 1311  $cm^{-1}$  is assigned to the  $\nu_{C-O_{phenoxo}}$  vibration. The band assigned to the piperazine skeleton appears in the region of 850 - 860  $cm^{-1}$  compared with 846  $cm^{-1}$  in  $H_2L$ . In the spectrum of **1**, the stretching modes  $\nu_3$  (1095  $cm^{-1}$ ) and  $\nu_4$  (622  $cm^{-1}$ ) are assigned to the uncoordinated perchlorate ion of  $T_d$  symmetry. A strong vibration band at 1384  $cm^{-1}$  in the spectrum of **2** is attributed to the ionic nitrate group.<sup>9</sup>

The electronic spectrum of **1** shows two intense bands at 319 and 358 nm which can be attributed to  $\pi-\pi^*$  transitions and to  $n-\pi^*$  transitions, respectively. A broad band situated at 468 nm may be assigned to the  ${}^5T_{2g} \leftarrow {}^5E_g$  transition of a six-coordinate  $Mn^{III}$  in a high-spin configuration.<sup>10</sup> In the spectrum of **2**, the intense band situated at 399 nm is assigned to a charge transfer transition. A large band centered at 505 nm with a shoulder situated at 563 nm can be attributed to  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1E_g$  transitions characteristic of octahedral  $Co^{III}$ .<sup>11</sup>

The room-temperature magnetic moment of complex **1** is 4.486 BM, characteristic for a high-spin ( $d^4$ ) octahedral complex of manganese(III), which is in agreement with the observations of Kuma.<sup>5</sup> The cobalt(III) complex **2** is diamagnetic. The  ${}^1H$  NMR spectrum of **2** shows a shift of proton resonance signals to lower values compared to its position in the spectrum of  $H_2L$ . Moreover, the signal at 13.55 ppm assigned to the -OH proton in  $H_2L$  is absent in the spectrum of the complex, supporting the presence of the ligand  $L^{2-}$ . The signals in the aliphatic region of the complex suggest a distorted molecule because the signals of mirror plane protons of propylene chains are at different values as was observed previously in our work<sup>6</sup>. (Fig. S3).



Scheme 1 – Synthetic route to complexes **1** and **2**.

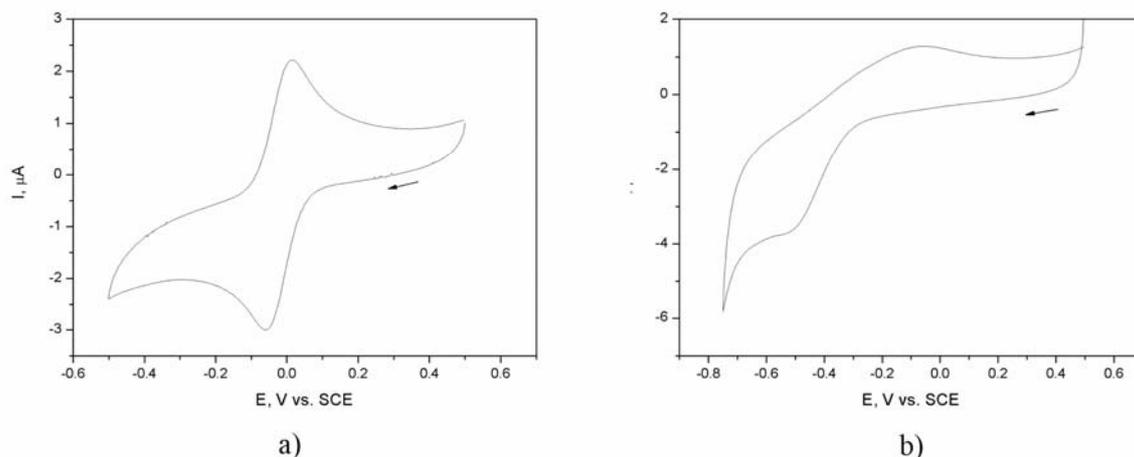


Fig. 3 – Cyclic voltammograms for a)  $10^{-3}$  M  $[\text{MnL}]^+$  and b)  $10^{-3}$  M  $[\text{CoL}]^+$  in 0.1 M TBAC in DMSO at a scan rate of  $0.02 \text{ V s}^{-1}$  (arrow shows the scanning direction indicating the starting point).

### 3. Cyclic Voltammetry

The electrochemical behavior of **1** and **2** was studied by cyclic voltammetry (CV) in DMSO. The cyclic voltammograms recorded at glassy carbon (GC) electrode in  $10^{-3}$  M solution of **1** and **2** in DMSO and 0.1 M tetrabutylammonium perchlorate (TBAC) are presented in Figure 3. In order to identify the presence of  $\text{Mn}^{\text{III}}$  the potential value was scanned within the potential range of  $-0.5 \text{ V/SCE} \div 0.5 \text{ V/SCE}$ , where SCE is saturated calomel electrode. The reduction process occurred at the potential value of  $-0.056 \text{ V/SCE}$  and the corresponding oxidation peak appeared at  $0.016 \text{ V/SCE}$  during anodic scanning, which is assigned to the redox couple of  $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ .<sup>12</sup> Based on the cyclic voltammetry characteristics of an ideal reversible system assuming and  $\Delta E_p = 56.5 \text{ mV}$  for the one-electron transfer, the results from Figure 3a exhibited a quasi-reversible one-electron reduction-oxidation system (and  $\Delta E_p = 70 \text{ mV}$ ). The deviation from the ideal reversible system occurs due to the modification in coordination environment as a result of the electroreduction process. A different electrochemical behavior was found for the  $[\text{CoL}]^+$  complex **2** (Figure 3b). The potential range was enlarged towards the negative direction because the cathodic peak corresponding to the reduction process of  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  was observed at  $-0.513 \text{ V vs. SCE}$ , similarly to the potential range reported in the literature.<sup>13</sup> In the reverse potential scan, a smaller anodic peak is noticed at  $-0.08 \text{ V vs. SCE}$ , which denotes the electrochemical irreversibility of the system ( $\Delta E_p = 433 \text{ mV}$  for the one-electron transfer process). This suggests that the mechanism of the overall process has a strong influence on coordination environment of the metal ion.

### EXPERIMENTAL

$N,N'$ -bis[(2-hydroxybenzylideneamino)-propyl]-piperazine ( $\text{H}_2\text{L}$ ) was obtained according to the procedure described earlier.<sup>6</sup>

#### Synthesis of $[\text{MnL}](\text{ClO}_4)$ (**1**)

0.25 g, (0.6 mmol)  $\text{H}_2\text{L}$  dissolved in  $\text{CHCl}_3\text{-MeOH}$  (1:1 v/v, 30 mL) was treated with  $\text{Et}_3\text{N}$  (0.25 mL, 1.85 mmol) and  $\text{Mn}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  (0.3 g, 1.22 mmol) dissolved in MeOH (20 mL). The mixture was stirred for 1 h at room temperature and slow evaporation of the resulting mixture yielded after a few days green crystals of **1**. Yield: 0.26 g (77 %). *Anal. Calc.* for  $\text{C}_{24}\text{H}_{30}\text{ClMnN}_4\text{O}_6$  (560.91): C, 51.39; H, 5.39; N, 9.99. Found: C, 51.67; H, 5.65; N, 10.09 %. IR [ $\text{KBr}, \text{cm}^{-1}$ ]: 3440(m), 3024(w), 2926(w), 2862(w), 1621(s), 1540(s), 1471(m), 1448(m), 1398(m), 1347(w), 1324(m), 1290(m), 1200(w), 1152(m), 1092(vs), 972(w), 918(w), 857(w), 802(w), 762(m), 622(m), 571(w), 464(w), 444(w), 416(w). Molar conductivity  $\Lambda_m, \Omega^{-1}\text{mol}^{-1}\text{cm}^2$  (DMF,  $10^{-5} \text{ M}$ ): 94.1. UV-Vis (DMF,  $10^{-4} \text{ M}$ )  $\lambda_{\text{max}}$  [nm] ( $\epsilon/\text{Lmol}^{-1}\text{cm}^{-1}$ ): 319 (1760), 358 (1978), 468 (288).

#### Synthesis of $[\text{CoL}](\text{NO}_3) \cdot 2\text{CH}_3\text{OH}$ (**2**)

$\text{H}_2\text{L}$  (0.50 g, 1.22 mmol) in  $\text{CHCl}_3\text{-MeOH}$  (1:1 v/v, 30 mL) was treated with  $\text{Et}_3\text{N}$  (0.51 mL, 3.7 mmol) and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.70 g, 2.44 mmol) dissolved in MeOH (20 mL). The mixture was stirred for 1 h at room temperature and the derived brown solid was filtered off. Brown single crystals suitable for X-ray analysis were obtained by slow evaporation of the mother liquor. Yield 0.45 g (61 %). *Anal. Calc.* for  $\text{C}_{26}\text{H}_{38}\text{CoN}_5\text{O}_7$  (591.55): C, 52.79; H, 6.48; N, 11.84. Found: C, 52.34; H, 6.15; N, 12.39 %. IR [ $\text{KBr}, \text{cm}^{-1}$ ]: 3403(w), 3046(w), 2942(w), 2885(w), 1625(vs), 1595(m), 1542(s), 1471(m), 1455(m), 1384(m), 1337(m), 1311(m), 1236(w), 1214(m), 1169(w), 1152(w), 1121(w), 1083(w), 1028(w), 904(w), 848(w), 766(m), 739(w), 627(w), 596(m), 567(w), 469(w).  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ),  $\delta$  (ppm): 7.77 (s, 2H), 7.28 (dd, 2H), 7.20 (t, 2H), 7.02 (d, 2H), 6.63 (t, 2H), 4.10 (m, 2H), 3.19-3.55 (m, 22H), 2.90-3.16 (m, 2H), 2.56-2.77 (m, 4H), 2.27-2.44 (m, 6H), 1.80-1.98 (m, 2H). Molar conductivity  $\Lambda_m, \Omega^{-1}\text{mol}^{-1}\text{cm}^2$  (DMF,  $10^{-4} \text{ M}$ ): 103.2. UV-Vis (DMF,  $10^{-4} \text{ M}$ )  $\lambda_{\text{max}}$  [nm] ( $\epsilon/\text{Lmol}^{-1}\text{cm}^{-1}$ ): 399 (5400), 506 (630), 563 (348).

## CONCLUSIONS

Mononuclear complexes [MnL](ClO<sub>4</sub>) (**1**) and [CoL](NO<sub>3</sub>)·2CH<sub>3</sub>OH (**2**) were obtained and structurally characterized. Single crystal X-ray analysis revealed that the hexadentate ligand L<sup>2-</sup> is wrapped around the metal ions thus generating a distorted octahedral environment around the metal ions. The strong field of the Schiff base stabilizes the high oxidation state of the two metal ions. The electrochemical studies show a quasi-reversible one-electron reduction-oxidation process for [MnL]<sup>+</sup>, while the Co<sup>III</sup>/Co<sup>II</sup> system exhibited an irreversible behavior.

## Supplementary material

Full experimental details and CCDC 1588642 (**1**), 1588643 (**2**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via <https://summary.ccdc.cam.ac.uk/structure-summary-form> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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