



## Crystal and Molecular Structure of The Mixed-Metal Manganese(II) and Cobalt(II) Maleate Complex: $[\text{Co}_x\text{Mn}_{1-x}(\text{OOCCH}=\text{CHCOO})\cdot(\text{H}_2\text{O})_2]_n$

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**Abstract:** For the first time, by the interaction of cobalt maleate tetrahydrate with Mn(II) acetate, a polymeric polynuclear mixed-metal maleate complex of manganese(II) and cobalt(II) was obtained:  $[\text{Co}_x\text{Mn}_{1-x}(\text{OOCCH}=\text{CHCOO})\cdot(\text{H}_2\text{O})_2]_n$ . The composition and structure of the resulting complexes were studied by IR spectroscopy, UV-Vis spectroscopy, EPR, and elemental and thermogravimetric analysis. The crystal structure of the complex was established by X-ray diffraction. The results of X-ray diffraction analysis showed that maleic acid dianions coordinate with Mn(II) and Co(II) ions in the bidentate bridging form, forming seven-membered chelate rings with manganese and cobalt ions. Each metal ion achieves octahedral symmetry with coordination from two oxygen atoms of two water molecules and two bridging oxygen atoms of the maleate ligands of neighboring complex molecules. The electronic absorption spectra show the absorption band at 965 nm, which should be attributed to the Mn(II) complex. The band at 516 nm refers to the cobalt complex. In the EPR spectrum, a wide single band with  $g = 2.031$  is observed, indicating an electronic exchange interaction between Mn(II) and Co(II) ions. The presence of two metal ions in the complex was also confirmed by cyclic voltammetry. The voltammograms clearly show two reduction waves related to the two-electron reduction of  $\text{Co}^{2+}$  ( $E_c = -0.69$  V) and  $\text{Mn}^{2+}$  ( $E_c = -0.985$  V) ions.

**Keywords:** Mn(II), Co(II) maleate complex, crystal structure, coordination polymer.

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### 1. INTRODUCTION

Currently, synthetic and theoretical chemists in the field of "molecular magnetism" are drawn to polynuclear complexes featuring metal ions with intramolecular spin bonds (1-3).

The most important problem of molecular design of metal polyhedral complexes is the search for ligands and synthesis conditions for their creation. An effective method for solving this problem is the use of self-association techniques, by selecting appropriate ligands that have the ability to bind metal ions into polynuclear structures due to bridging fragments (atoms or groups). Another way to obtain polynuclear complexes is through the synthesis of mononuclear metal complexes with incomplete coordination saturation of the ligands in the complex.

Maleic acid derivatives are capable of forming bridging carboxylate poly(mono-, bi-, trival) polymer complexes with metal(Mn) ions (4-8). It is known that only the inclusion of the bidentate chelating ligand phenanthroline, bipyridyl, etc. is favorable for the formation of coordination polymers (9-11).

The synthesis of polynuclear complexes with purely maleate ligand has not been described in the literature (12-15), and there is only one work, in which the polymeric structure of Mn(II) complex with this ligand was shown by X-ray diffraction analysis (16). A polymeric maleate complex of Mn(II) was obtained by the interaction of manganese(II) carbonate with an aqueous solution of maleic acid. Along with this complex, a mononuclear manganese

maleate tetrahydrate complex was obtained in which maleic acid behaved as a monodentate monoanionic ligand. A similar structure was found for the maleates of a number of metals: Co(II) (17), Ni(II) (18), Zn(II) (19), etc.

In order to obtain a polymeric complex containing various metal ions, we reacted mononuclear cobalt maleate with manganese acetate. This very approach to the synthesis of polymeric structures using a complex with coordination-unsaturated ligands has not yet been published. As a result, a polymer polynuclear mixed-metal maleate complex of manganese(II) and cobalt(II) was obtained:  $[\text{Co}_x\text{Mn}_{1-x}(\text{OOCCH}=\text{CHCOO})\cdot(\text{H}_2\text{O})_2]_n$ . The polymer-polynuclear structure of the complex was confirmed by X-ray diffraction analysis.

## 2. EXPERIMENTAL

### 2.1. General and spectroscopic measurements

All chemicals in the synthesis were used without further purification. IR spectra of samples were recorded in vaseline in the 4000-400  $\text{cm}^{-1}$  range using a Nicolet IS10 spectrophotometer. Electronic absorption spectra were taken on a SPECORD 50 spectrophotometer in water solutions. EPR spectra were taken in solid state at room temperature on a Bruker BioSpin GmbH instrument. Thermogravimetric analysis was performed using a NETZSCH STA 449F3 derivatograph in an inert atmosphere; elemental analysis was performed in the analytical laboratory of TUBITAK, Ankara, on a LECO CHNS 932 analyzer. Energy-dispersive X-ray spectroscopy was performed on a SEM JEOL JSM 6610 LV electron microscope.

Polarization curves were taken in an IVIUMSTAT electrochemical interface potentiostat. To prepare the electrolyte, the complex was dissolved in bidistilled water (0.001 M). A glass three-electrode electrochemical cell was used. The working electrode was a Pt electrode with an area of  $0.3 \times 10^{-3} \text{ cm}^2$ , the reference electrode was a chlorosilver electrode, and the auxiliary electrode was a platinum plate with an area of  $4.0 \text{ cm}^2$ . The surface of the Pt electrode was cleaned with concentrated nitric acid.

#### 2.1.1. Synthesis of $[\text{Co}(\text{OOCCH}=\text{CHCOO})_2(\text{H}_2\text{O})_4]$

Cobalt maleate  $[\text{Co}(\text{OOCCH}=\text{CHCOO})_2(\text{H}_2\text{O})_4]$  was prepared by mixing cobalt chloride hexahydrate and maleic acid in water (at a molar ratio of 1:1). The mixture was brought to a boil and stirred for 30 minutes. Then it was filtered and left to crystallize. After cooling, bright red crystals precipitated out of it. The yield was 1.80 g (82%). FT-IR spectrum:

( $\nu$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{OH, coord. H}_2\text{O})$  3382  $\text{cm}^{-1}$ ,  $\nu_{\text{as}}(\text{COO}^-)$  1549  $\text{cm}^{-1}$ ,  $\nu_{\text{sym}}(\text{COO}^-)$  1482  $\text{cm}^{-1}$ .

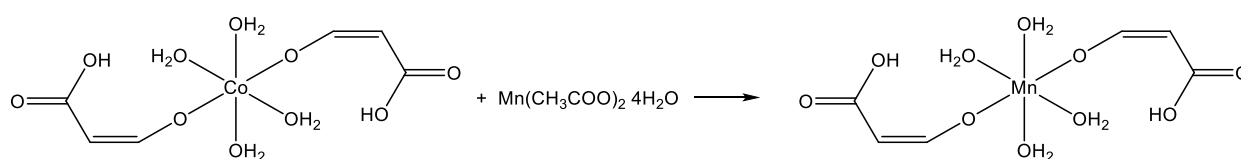
#### 2.1.2. Synthesis of $[\text{Co}_x\text{Mn}_{1-x}(\text{OOCCH}=\text{CHCOO})\cdot(\text{H}_2\text{O})_2]_n$

To 0.006 mol (1.00 g) of cobalt maleate tetrahydrate was added 0.005 mol (1.00 g) of manganese acetate. The mixture was brought to a boil and stirred for 1 h. Then the solution was filtered and left to crystallize. Upon cooling, crimson crystals of  $T_m > 250^\circ\text{C}$  precipitated from the solution. The obtained crystals were filtered and dried in the vacuum at room temperature. The yield was 0.80 g (85%). For  $\text{C}_8\text{H}_{16}\text{O}_{14}\text{MnCo}$ : Found: C 23.70, H 3.89, Mn 13.52, Co 14.51%. Calculated: C 23.61, H 3.93, Mn 13.56, and Co 14.54%. IR spectrum: ( $\nu$ ,  $\text{cm}^{-1}$ ):  $\nu(\text{OH, coord. H}_2\text{O})$  3440  $\text{cm}^{-1}$ ,  $\nu_{\text{as}}(\text{COO}^-)$  1590  $\text{cm}^{-1}$ ,  $\nu_{\text{sym}}(\text{COO}^-)$  1500  $\text{cm}^{-1}$ .

Single crystal X-ray diffraction experiments were performed on a Bruker APEX II CCD diffractometer using monochromatized Mo-K $\alpha$  X-radiation. Indexing, data collection, data reduction, and absorption correction were carried out using APEX2. The crystal structure was solved using SHELXT and then refined by full-matrix least-squares refinements on  $F^2$  using SHELXL in the Olex2 Software Package. The aromatic and aliphatic C-bound H atoms were positioned geometrically and refined using a riding mode. Crystal structure validations, geometrical calculations, and drawings were performed using Mercury software. The crystallographic data and details of the refinement of the structure of the complex are given in Table 1.

## 3. RESULTS AND DISCUSSION

Trimers of mixed and homovalent manganese complexes with different nucleation and oxidation degrees are known from the literature (20-22). However, the synthesis of mixed-metallic polymeric polynuclear manganese complexes by the interaction of cobalt maleate with manganese salts has not been described so far. It should be noted that during the interaction of cobalt maleate with sulfate and manganese nitrate the formation of a polymeric complex was not observed, and mononuclear compounds were formed. Polynuclear maleate manganese complexes are usually prepared by the interaction of maleic acid with a metal salt with the addition of a bidentate chelating ligand (23-31). We have found for the first time that the interaction of the mononuclear tetrahydrate complex of cobalt and manganese acetate produces a polymer-polymer mixed-metal maleate complex of manganese(II) and cobalt(II) (Scheme1).

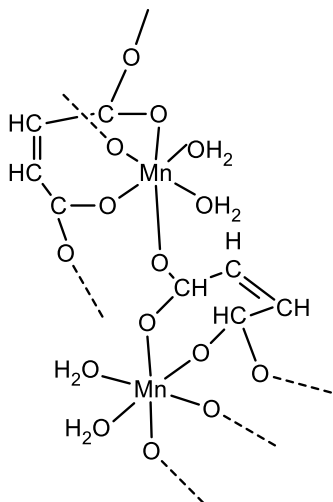


**Scheme 1:** Polymer-polymer mixed-metal maleate complex of manganese(II) and cobalt(II) structure.

**Table 1:** Crystal structure data and refinement parameters for  $[\text{Co}_x\text{Mn}_{1-x}(\text{OOCCH}=\text{CHCOO})\cdot(\text{H}_2\text{O})_2]_n$ .

Empirical formula	$\text{C}_8\text{H}_{16}\text{Mn}_2\text{O}_{14}$
Formula weight	406.52
Temperature/K	299.47
Crystal system	monoclinic
Space group	Cc
a/Å	8.2478(10)
b/Å	13.3183(17)
c/Å	7.7076(15)
$\alpha/^\circ$	90
$\beta/^\circ$	115.3800(10)
$\gamma/^\circ$	90
Volume/Å <sup>3</sup>	764.9(2)
Z	2
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.765
$\mu/\text{mm}^{-1}$	1.689
F(000)	397.0
Crystal size/mm <sup>3</sup>	0.324 × 0.263 × 0.194
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\theta$ range for data collection/ $^\circ$	6.118 to 54.966
Index ranges	$-10 \leq h \leq 10, -17 \leq k \leq 17, -9 \leq l \leq 7$
Reflections collected	2799
Independent reflections	1507 [ $R_{\text{int}} = 0.0221, R_{\text{sigma}} = 0.0365$ ]
Data/restraints/parameters	1507/2/115
Goodness-of-fit on $F^2$	0.944
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0171, wR_2 = 0.0438$
Final R indexes [all data]	$R_1 = 0.0174, wR_2 = 0.0439$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.19/-0.24
Flack parameter	0.027(10)

In the FT-IR spectra of the complex, the absorption bands near 1590 and 1500  $\text{cm}^{-1}$  refer to O–C–O asymmetric and symmetric stretching vibrations of maleate groups, respectively. The difference  $\Delta\nu$  between the wavenumbers of the absorption bands  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  is much less than the difference between the wave numbers of the absorption of similar vibrations of the free carboxylate and monodentate coordinated carboxylate groups and is 90  $\text{cm}^{-1}$ . It indicates the bidentate or bridging nature of the coordination of the carboxylate group (Scheme 2) (32).

**Scheme 2:** The fragment of polynuclear complex structure.

X-ray data do not allow us to distinguish between Mn(II) and Co(II) ions and their order in the crystal lattice because of the proximity of their scattering coefficients. According to the data of energy-dispersive X-ray spectroscopy, the content of manganese and cobalt was: Mn-49.49%; Co-28.39%.

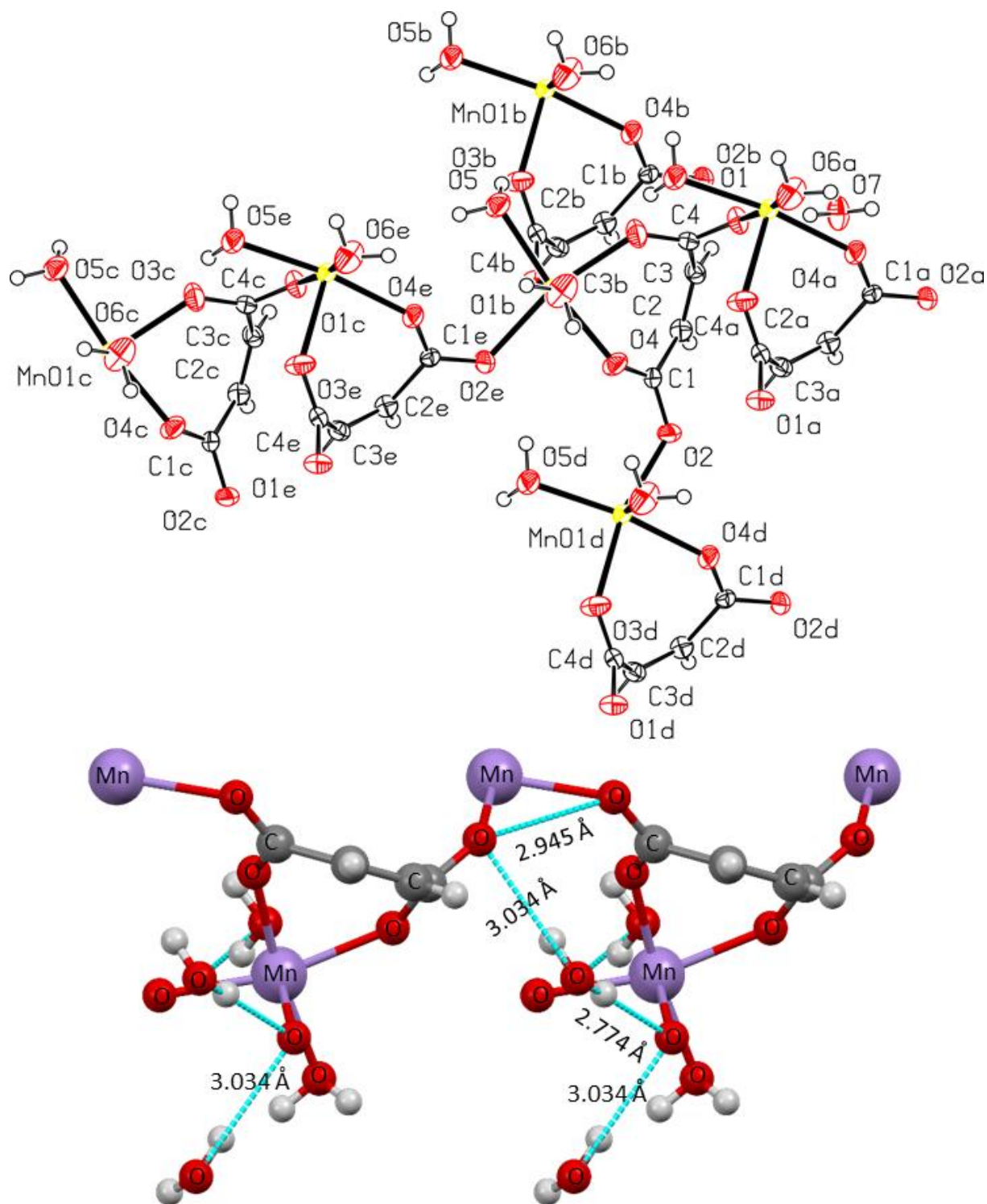
The results of X-ray analysis showed that two oxygen atoms, each with a carboxyl group of the maleate dianion, coordinate with Mn(II) and Co(II) ions to form seven-membered chelate cycles, and the remaining two oxygen atoms participate in the formation of bridges between neighboring complexes.

The polynuclear mixed-metal complex is three-dimensional, in which the metal ions have a distorted octahedral structure. The maleate ligand forms a seven-membered cycle with two oxygen atoms. The octahedral coordination in the equatorial plane is achieved by one oxygen atom of the maleate, two oxygen atoms of two water molecules, and one bridging oxygen atom from neighboring complexes. The axial positions are occupied by one oxygen atom of the maleate and one bridging oxygen atom from a neighboring molecule (Figure 1).

The distances between neighboring manganese metals are 5.138 Å. The distances between metal ions and oxygen atoms of water molecules in axial and equatorial positions do not differ significantly

(2.164 Å and 2.166 Å) (Table 2). The metal ion-oxygen distances are in the range of 2.1405-2.221 Å

and differ slightly from the distances in the polymeric Mn(II) complex of 2.154-2.23 Å (16).



**Figure 1:** A view of the structure of  $[\text{Co}_x\text{Mn}_{1-x}(\text{OOCCH}=\text{CHCOO})\cdot(\text{H}_2\text{O})_2]_n$ , showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (a)  $x, 1 - y, -1/2 + z$ ; (b)  $x, 1 - y, 1/2 + z$ ; (c)  $1/2 + x, -1/2 + y, 1 + z$ ; (d)  $-1/2 + x, 1/2 - y, -1/2 + z$ ; (e)  $1/2 + x, 1/2 - y, 1/2 + z$ .

**Table 2:** Bond lengths [Å] and angles [°] for  $[\text{Co}_x\text{Mn}_{1-x}(\text{OOCCH}=\text{CHCOO})\cdot(\text{H}_2\text{O})_2]_n$ 

Atom	Atom	Length/Å
Mn1	O1 <sup>1</sup>	2.221(2)
Mn1	O2 <sup>2</sup>	2.1573(18)
Mn1	O4	2.1407(18)
Mn1	O5	2.1644(19)
Mn1	O3	2.1717(18)
Mn1	O6	2.166(2)
O1	C4	1.261(3)
O2	C1	1.265(3)
O4	C1	1.236(3)
O3	C4	1.250(3)
C3	C4	1.494(3)
C3	C2	1.324(3)
C2	C1	1.499(3)

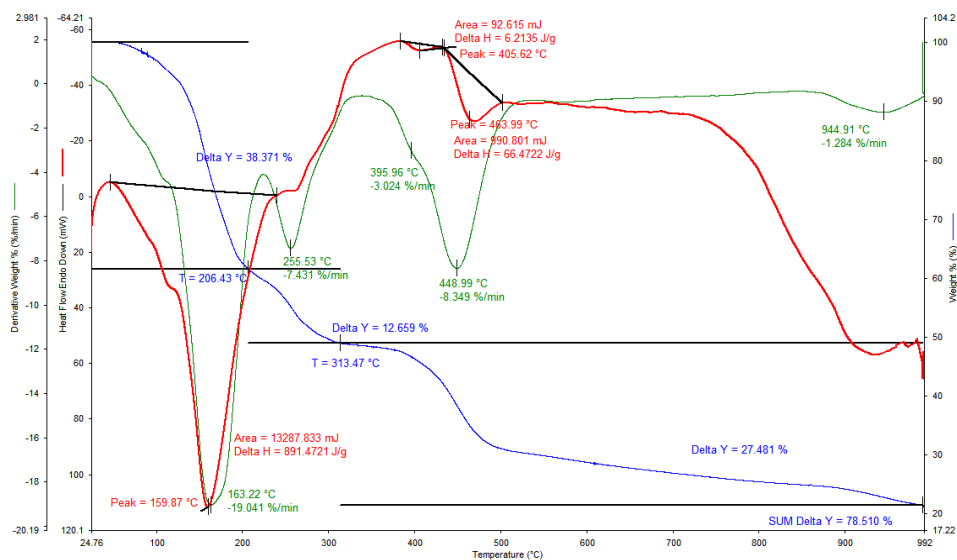
<sup>1</sup> $x, 1-y, 1/2+z$ ; <sup>2</sup> $1/2+x, 1/2-y, 1/2+z$

Atom	Atom	Atom	Angle/°
O2 <sup>1</sup>	Mn1	O1 <sup>2</sup>	84.53(7)
O2 <sup>1</sup>	Mn1	O5	104.09(7)
O2 <sup>1</sup>	Mn1	O3	166.08(7)
O2 <sup>1</sup>	Mn1	O6	95.64(9)
O4	Mn1	O1 <sup>2</sup>	90.68(8)
O4	Mn1	O2 <sup>1</sup>	82.25(7)
O4	Mn1	O5	171.94(7)
O4	Mn1	O3	83.86(8)
O4	Mn1	O6	94.25(9)
O5	Mn1	O1 <sup>2</sup>	85.04(8)
O5	Mn1	O3	89.83(8)
O5	Mn1	O6	90.12(9)
O3	Mn1	O1 <sup>2</sup>	96.61(8)
O6	Mn1	O1 <sup>2</sup>	175.04(10)
O6	Mn1	O3	84.41(10)
C4	O1	Mn1 <sup>3</sup>	131.57(17)
C1	O2	Mn1 <sup>4</sup>	124.42(15)
C1	O4	Mn1	135.02(17)
C4	O3	Mn1	131.66(15)
C2	C3	C4	128.0(2)
O1	C4	C3	115.0(2)
O3	C4	O1	123.3(2)
O3	C4	C3	121.6(2)
C3	C2	C1	126.6(2)
O2	C1	C2	114.8(2)
O4	C1	O2	123.0(2)
O4	C1	C2	122.2(2)

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

The thermogravimetric analysis of the mixed metal maleate complex  $[\text{Co}_x\text{Mn}_{1-x}(\text{OOCCH}=\text{CHCOO})\cdot(\text{H}_2\text{O})_2]_n$  (Figure 2) revealed that the complex decomposes in four stages within the temperature range of 25-990 °C. Up to 100 °C, hygroscopic water is lost. At 160 °C and 255 °C, both crystallization water and metal-coordinated water molecules are released. The theoretical percentage of water loss is 4.4%, which is in accordance with the

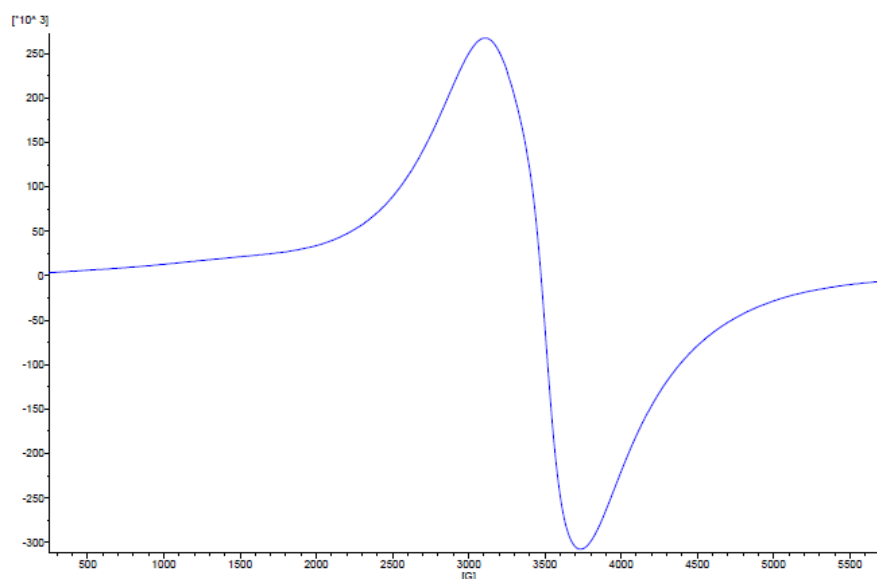
experimental results. Subsequently, the weight loss that commences at 395 °C can be attributed to the decarboxylation of the complex. Furthermore, the presence of 24.5% residue at 900 °C indicates that the organic ligand has completely decomposed, while cobalt or manganese metals remain as residues. In light of these results, it has been determined that the manganese maleate complex is resistant up to 400 °C, except for the loss of water molecules.



**Figure 2:** The thermogram of the  $[\text{Co}_x\text{Mn}_{1-x}(\text{OOCCH}=\text{CHCOO})\cdot(\text{H}_2\text{O})_2]_n$  complex.

In the EPR spectrum of the mixed-metal maleate complex, a single wide ( $\Delta H=600$  G) somewhat asymmetric signal with  $g=2.031$  is observed, which may indicate the electronic exchange interaction

between the Mn(II) and Co(II) ions in the octahedral environment (Figure 3). The  $g$ -factor is close to that of the Mn(II) compounds, which indicates the main contribution of these ions to the EPR spectrum.

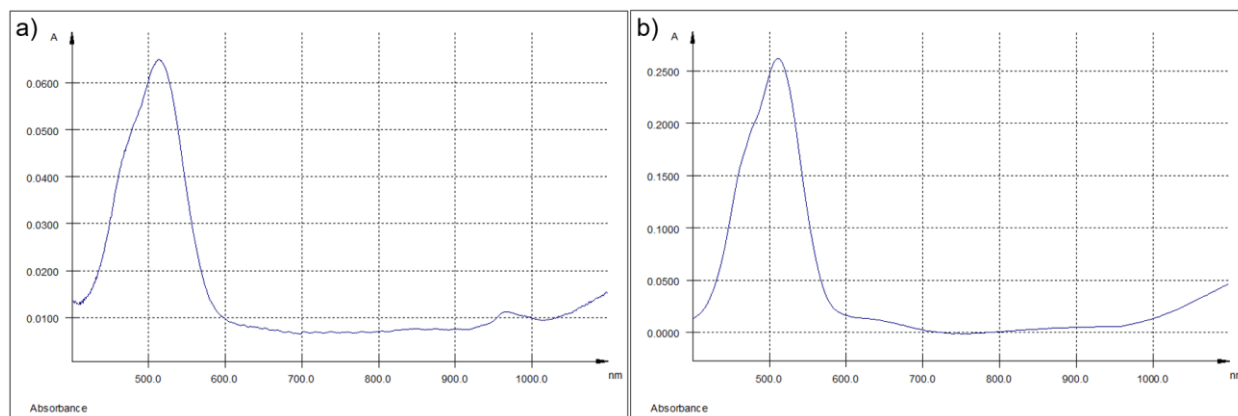


**Figure 3:** EPR of the  $[\text{Co}_x\text{Mn}_{1-x}(\text{OOCCH}=\text{CHCOO})\cdot(\text{H}_2\text{O})_2]_n$  complex.

In the electronic absorption spectra of the mixed metal maleate complex  $[\text{Co}_x\text{Mn}_{1-x}(\text{OOCCH}=\text{CHCOO})\cdot(\text{H}_2\text{O})_2]_n$  in the visible region, a peak at  $\lambda_{\text{max}}=516.4$  ( $\epsilon=2$ ) and very weak in intensity absorption bands at 641.8, 848, 965 nm corresponding to forbidden d-d transitions (with  $\epsilon<0.01$ ) are observed. There is also absorption above 1100 nm (see Figure 4). These absorption bands belong to cobalt(II) except for the absorption band at 965 nm, which is absent in the electronic absorption spectrum of Co(II) tetrahydrate maleate.

Therefore, the band at 965 nm should be attributed to the Mn(II) complex.

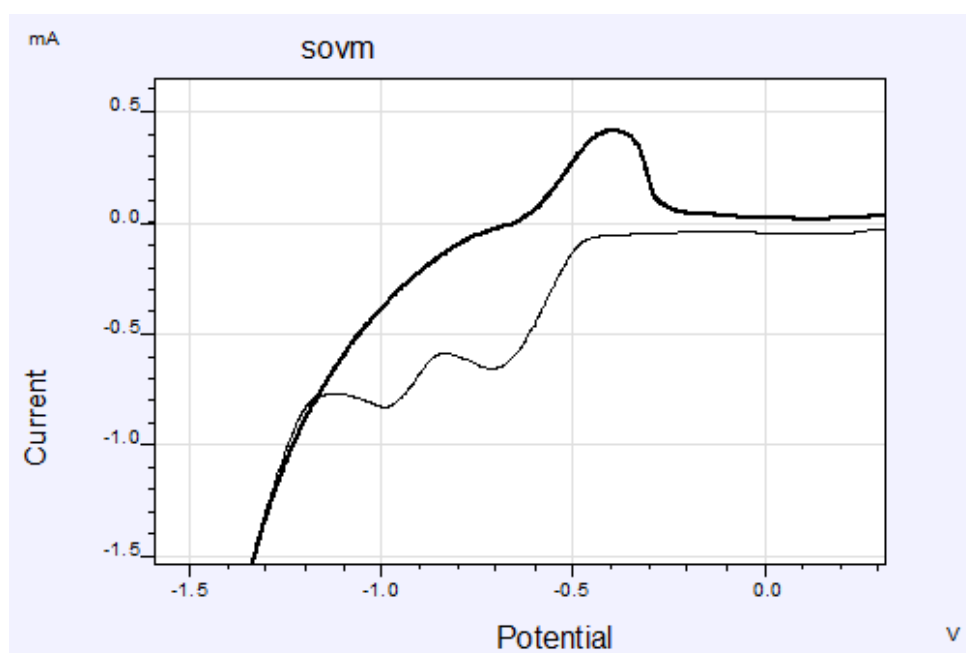
Note that the absorption at 510-520 nm usually refers to the  ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$  transition in octahedral Co(II) complexes. In our case, it is observed at 516.4 nm. Thus, the electron spectra also indicate the presence of both metal ions Co(II) and Mn(II) in the polymer complex.



**Figure 4:** Electronic absorption spectra in water: a)  $[\text{Co}_x\text{Mn}_{1-x}(\text{OOCCH}=\text{CHCOO})\cdot(\text{H}_2\text{O})_2]_n$  complex; b)  $[\text{Co}(\text{OOCCH}=\text{CHCOO})_2\cdot(\text{H}_2\text{O})_4]$

Cyclic voltammetry data indicate the presence of both metal ions Mn and Co in the complex (Figure 5). The voltammetry diagrams show two reduction

waves, corresponding to the two-electron reduction of  $\text{Co}^{2+}$  ions ( $E_c = -0.69$  V) and  $\text{Mn}^{2+}$  ( $E_c = -0.985$  V) (33).



**Figure 5:** Polarization curve on Pt electrode in electrolyte 0.001 M  $[\text{Co}_x\text{Mn}_{1-x}(\text{OOCCH}=\text{CHCOO})\cdot(\text{H}_2\text{O})_2]_n$ ,  $E_v=0.01$  V/s,  $T=298$  K.

#### 4. CONCLUSIONS

Thus, it is shown that the interaction of cobalt maleate tetrahydrate with manganese salts results in the formation of a polymer polynuclear mixed-metal manganese(II) and cobalt(II) maleate complex:  $[\text{Co}_x\text{Mn}_{1-x}(\text{OOCCH}=\text{CHCOO})\cdot(\text{H}_2\text{O})_2]_n$ . In this complex, Mn(II) and Co(II) ions are interconnected by oxygen bridges of maleate groups. The distances between neighboring manganese ions are 5.138 and 5.414 Å. However, this distance is sufficient for the electronic exchange of interactions between metal ions, as evidenced by the EPR spectrum. In the EPR spectrum, a broad single band  $g=2.031$  is observed, indicating an electronic exchange interaction between Mn(II) and Co(II) ions. The electronic absorption spectra show an absorption band at a wavelength of 965 nm, which should be attributed to the Mn(II) complex. The band at 516 nm refers to the cobalt complex.

Cyclic voltammetry data indicate the presence of both manganese and cobalt metal ions in the complex. Two waves of reduction related to the two-electron reduction of  $\text{Co}^{2+}$  ions ( $E_c = -0.69$  V) and  $\text{Mn}^{2+}$  ions ( $E_c = -0.985$  V) are clearly visible on the voltammetry diagrams.

CCDC- 2210011 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

#### 5. DISCLOSURE STATEMENT

No potential conflict of interest was reported by the authors.

## 6. ACKNOWLEDGEMENTS

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