

COMPLEXES WITH SCHIFF BASES

I. COMPLEX COMPOUNDS OF Mn(II), Fe(II), Cu(II), AND Zn(II) WITH N,N'-BIS(3-FORMYL-5-METHOXY-6-HYDROXY-BENZILIDEN) ETHYLENEDIAMINE

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The new four complexes of M(II) (M: Mn, Fe, Cu, Zn) with a Schiff bases derived from 5-formyl-vanillin and ethylenediamine were prepared. These compounds were characterized on the basis of elemental chemical analysis, electronic, infrared and EPR spectra and formulated as mononuclear (for Mn(II), Cu(II) and Zn(II)) and trinuclear (for Fe(II)) species.

Introduction

By continuing our research on complexes with the Schiff bases [1÷3], we have studied the systems which contain the Schiff base derived from 5-formyl-vanillin and ethylenediamine and M(II) acetates (M: Mn, Cu, Zn) or Fe(II) sulfate.

There were obtained four new complexes, three formulated as mononuclear species: [MnL(OH)], [CuL(H₂O)₂] and [ZnL] and a trinuclear compound [Fe₃L₂(H₂O)₆]SO₄ where L is the dianion of N,N'-bis(3-formyl-5-methoxy-6-hydroxy-benziliden) ethylenediamine (L).

The compounds were formulated according to the chemical analysis, electronic, infrared and EPR spectra.

Experimental

All reagents used were p.a. grade.

The syntheses of the complexes

1. [MnL(OH)] (**I**). The MeOH/H₂O (1:1 v/v) solution which contains 2.45 g Mn(CH₃COO)₂·4H₂O (1 mmole) and 3.84 g (1 mmole) (H₂L) (KOH solution was added stoichiometrically to deprotonate the OH groups) was refluxed on a steam bath during 30 min. The sparingly soluble, yellowish brown colored product was filtered off and washed with MeOH/H₂O (1:1 v/v). *Chemical analysis. Found:* Mn 12.21; N 6.46; C 52.56%. *MnC₂₀H₁₉N₂O₇ requires:* Mn 12.09; N 6.17; C 52.87%.

2. [Fe₃L₂(H₂O)₆]SO₄ (**II**). Working as above, and using 2.78 g FeSO₄·7H₂O (1 mmole) and 3.84 g (1 mmole) (H₂L), it was obtained a black, sparingly soluble compound. *Chemical*

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analysis. Found: Fe 14.21; N 7.48; C 41.45%. *Fe₃C₄₀H₄₈N₆O₂₂S requires:* Fe 14.39; N 7.22; C 41.26, S %.

3. [CuL(H₂O)₂] (III). To a solution in MeOH/H₂O (1:1 v/v) which contains 1.99 g Cu(CH₃COO)₂·H₂O (1 mmole) it were added 3.84 g (1 mmole) H₂L. After 30 min refluxing on the steam bath, the sparingly soluble, green product was separated and washed with MeOH/H₂O. *Chemical analysis. Found:* Cu 13.27; N 5.45; C 49.61%. *CuC₂₀H₂₂N₂O₈ requires:* Cu 13.19; N 5.18; C 49.84%.

4. [ZnL] (IV). Working as above, by using 2.19 g (1 mmole) Zn(CH₃COO)₂·2H₂O, it was obtained a yellow colored, sparingly soluble product. *Chemical analysis. Found:* Zn 14.51; N 6.59; C 53.74%. *ZnC₂₀H₁₈N₂O₆ requires:* Zn 14.60; N 6.26; C 53.65%.

The elemental chemical analyses were performed by usual micromethods.

The diffuse reflectance spectra were recorded in the 24-14 kK (380-1200 nm) range, on a VSU2-P Zeiss-Jena spectrophotometer, using MgO as standard.

The IR spectra were recorded on an IR, BIORAD FTS 135 spectrophotometer in the 400-4000 cm⁻¹ range using KBr pellets.

The EPR - spectra were recorded in polycrystalline powder, with an ART - 5 - IFIN (Bucharest) spectrometer in X - band (9060 MHz frequency), magnetic field modulation 100 kc/s and Mn(II) as standard.

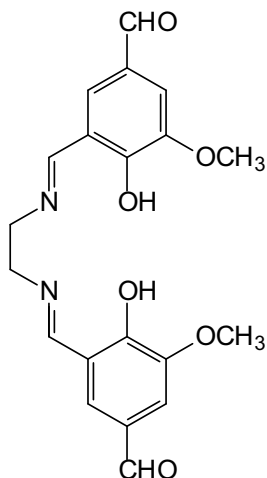
Results and Discussion

In the systems:

M(CH₃COO)₂ – H₂L M: Mn, Cu, Zn

FeSO₄ – H₂L

where H₂L is:



the syntheses have been developed in MeOH/H₂O (1:1 v/v) using the reactants in the 1:1 molar ratio. There were isolated four new compounds as sparingly soluble products with a different colors.

The complexes were formulated according to the chemical analyses as it follows:

(I)	[MnL(OH)]	yellowish brown
(II)	[Fe ₃ L ₂ (H ₂ O) ₆]SO ₄	black
(III)	[CuL(H ₂ O) ₂]	green
(IV)	[ZnL]	yellow

Infrared spectra

The infrared spectrum of the ligand H₂L was recorded within the 400÷4000 cm⁻¹ range and compared with those of the new four complexes (Table 1).

According to the literature data [4,5] the most important remarks are the following:

- the spectra of all complexes are alike with that of the free Schiff base H₂L, containing the absorption bands which are assigned to the vibrations: $\rho(\text{CH}_2)$, $\delta(\text{CH}_2)$, $\delta(\text{CH}_3)$, $\nu(\text{CH}_2)$ and $\nu(\text{C}=\text{O})$; that suggests the presence of a generally unaltered structure of this ligand;
- the band assigned to the $\nu(\text{C}=\text{N})$ vibration mode is shifted to the lower energy in the spectra of complexes; that fact is in accord with a coordination of nitrogen atom at the metallic ion;
- the presence of a broad and intense band at about 3400 cm⁻¹ is an evidence for the presence of water molecules in complexes (II) and (III); in addition, in the spectra of these complexes appear bands assigned to the coordinated water molecules ($\rho_w(\text{H}_2\text{O})$);
- for the manganese complex the IR spectrum contains a band which was assigned to the OH coordinated groups;
- in the spectrum of the complex (II) appears the two bands infrared active for the free sulfate ion;
- the bands that occur in the low wavenumbers range were assigned to the stretching vibrations $\nu(\text{M}-\text{O})$.

Thus, the infrared spectra suggests the following information about structure of complexes:

- all the complexes contain the deprotonated Schiff base L²⁻ as ligand;
- the complexes (II) and (III) contain water molecules as ligands; the manganese and iron compounds contain hydroxyl groups coordinated at metal ions.

Table 1. IR spectra (cm⁻¹)

H ₂ L	(I)	(II)	(III)	(IV)	Assignments
-	420 w	476 w	472 w	430 w	$\nu(\text{M}-\text{O})$
-	-	577 w	535 w	-	$\rho_w(\text{H}_2\text{O})$

Table 1. Continued

H ₂ L	(I)	(II)	(III)	(IV)	Assignments
-	-	615 m	-	-	$\nu_4(\text{SO}_4)$
864 m	879 m	848 m	835 m	869 m	$\gamma(\text{CH})$
979 m	991 m	989 m	989 m	985 m	$\delta(\text{CH})$
1015 m	1020 w	1020 w	1015 w	1020 w	$\nu_s(\text{C}_{\text{arom}}-\text{O}-\text{C}_{\text{alif}})$
-	1085 m	-	-	-	$\delta(\text{OH})$
-	-	1135 s	-	-	$\nu_3(\text{SO}_4)$
1150 vs	1153 s	1149 s	1152 s	1155 s	$\nu(\text{C}-\text{O})$
1186 m	1191 w	1190 w	1191 w	1190 w	$\nu_{\text{as}}(\text{C}_{\text{arom}}-\text{O}-\text{C}_{\text{alif}})$
1288 m	1272 vs	1275 vs	1276 vs	1275 vs	$\nu(\text{C}-\text{N})$
1386 m	1390 m	1383 fi	1386 m	1385 m	$\delta_s(\text{CH}_3)$
1458 m	1451 m	1453 m	1460 m	1460 m	$\delta(\text{CH}_2)$
1605 vs	1600 vs	1598 vs	1600 vs	1600 vs	$\nu(\text{C}=\text{C})$
1642 s	1625 vs	1627 s	1628 s	1625 s	$\nu(\text{C}=\text{N})$
1676 m	1678 m	1672 s	1684 s	1675 s	$\nu(\text{C}=\text{O})$
-	-	3391 m	3447 m	-	$\nu(\text{OH})$

(I)	[MnL(OH)]
(II)	[Fe ₃ L(H ₂ O) ₆]SO ₄
(III)	[CuL(H ₂ O) ₂]
(IV)	[ZnL]

Electronic spectra

In order to obtain informations about the stereochemistry, the oxidation state and the coordination number for the complexes, the diffuse reflectance spectra were recorded within the 380-1200 nm (24-14 kK) range (Table 2).

Also, it was recorded the spectrum of the Schiff base.

The examination of these spectra offers the following informations, according to the literature data [6]:

- for the complex (I) the electronic spectrum is characteristic for Mn(III) ions in an octahedral stereochemistry;
- the electronic spectrum of iron (II) trinuclear complex [Fe₃L₂(H₂O)₆]SO₄ is characteristic for Fe(II) 3d⁶ ion in an octahedral environment;
- the electronic spectrum of complex [CuL(H₂O)₂] suggests a tetragonal distorted octahedral stereochemistry (*via z*-elongation, „z-out”) of Cu(II) ion; the z-elongation is confirmed by EPR-spectrum. This fact has been interpreted in terms of Jahn-Teller effect.

Table 2. Electronic spectra

Compound	$\bar{\nu}_{\max}$ (cm ⁻¹)	Assignments
H ₂ L	21785	$\pi \rightarrow \pi^*$
	25640	CT
[MnL(OH)]	20965	$\pi \rightarrow \pi^*$
	14285	${}^5E \rightarrow {}^5T_2$
	26315	CT
[Fe ₃ L ₂ (H ₂ O) ₆]SO ₄	19840	$\pi \rightarrow \pi^*$
	$\left\{ \begin{array}{l} 16210 \\ 13385 \end{array} \right.$	${}^5T_2 \rightarrow {}^5E$
	26315	CT
	22075	$\pi \rightarrow \pi^*$
[CuL(H ₂ O) ₂]	17120	$d_{z^2} \rightarrow d_{x^2-y^2}$
	16890	$d_{xy} \rightarrow d_{x^2-y^2}$
	16370	$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$
[ZnL]	26300	CT
	20930	$\pi \rightarrow \pi^*$

The EPR spectrum of [CuL(H₂O)₂] complex is intense and anisotropic (Fig. 1), with parameters: $g_{\parallel} = 2.1865$ and $g_{\perp} = 2.0761$; this spectrum can be assigned to an axial elongated octahedron ($g_{\parallel} < g_{\perp} \cong 2.0$) [7,8].

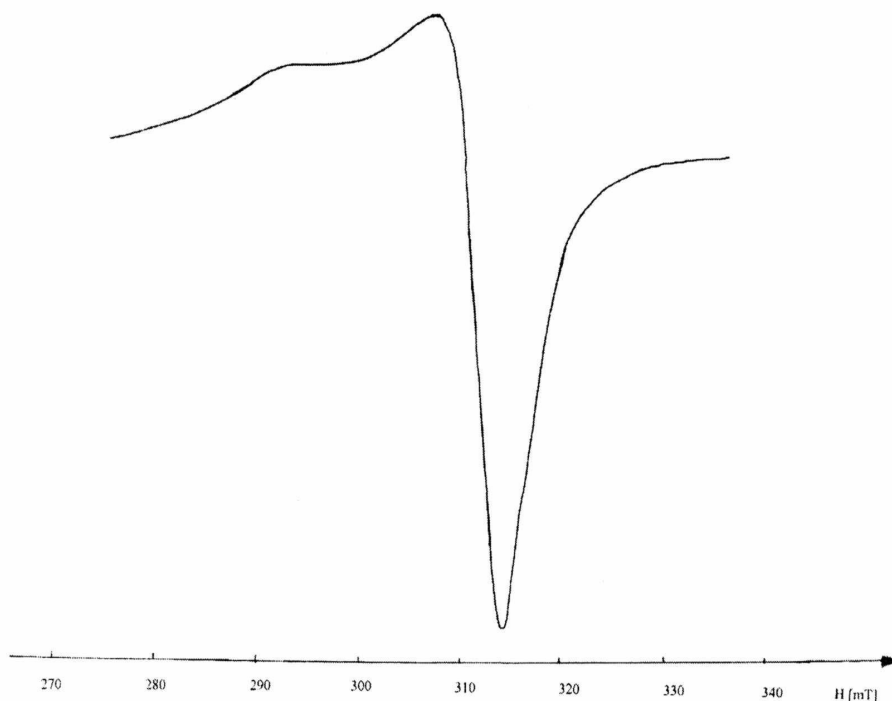
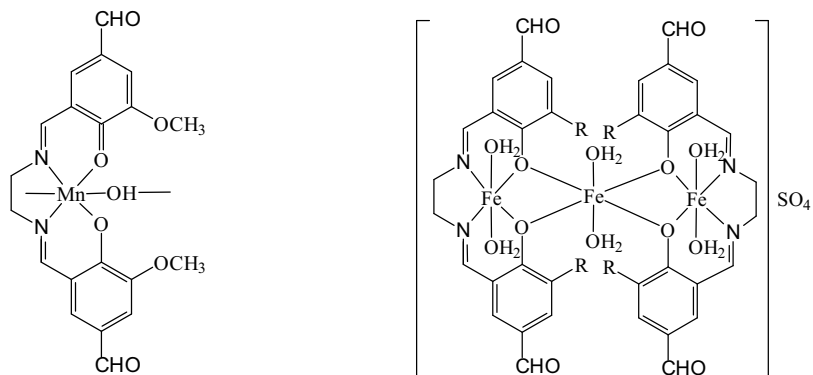
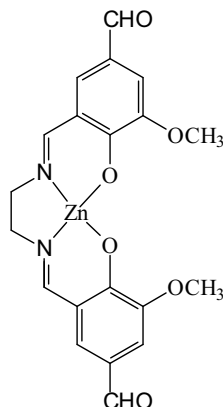
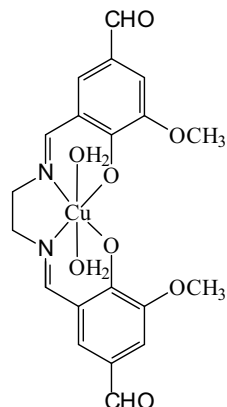


Fig. 1: EPR spectrum for the copper complex

Conclusions

1. There were obtained four new complex compounds with a Schiff base derived from 5-formyl-vanillin and ethylenediamine.
2. By correlating the data of chemical analysis, IR, electronic and EPR spectra, the proposed formula for the new complexes are the following:





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