COMPLEXES WITH SCHIFF BASES[1]
II. COMPLEX COMPOUNDS OF Mn(II), Fe(II), Ni(II) AND Cu(II) WITH N,N'-BIS(3-FORMYL-5, 6-DIHYDROXY-BENZILIDEN) ETHYLENEDIAMINE

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abstract: Four new complexes of M(II) (M: Mn, Fe, Ni, Cu) with a Schiff bases derived from 5-formyl-protocatehaldehide 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), Ni(II) and Cu(II)) and trinuclear (for Fe(II)) species.

Introduction

By continuing our research on complexes with the Schiff bases [1÷4], we have studied the systems which contain the Schiff base derived from 5-formyl-protocatehaldehide and ethylenediamine and M(II) acetates (M: Mn, Ni, Cu) or Fe(II) sulfate.

There were obtained four new complexes, three formulated as mononuclear species: $[MnL(OH)]$, $[NiL]$ and $[CuL]\cdot 2H_2O$ and a trinuclear compound $[Fe_3L_2(H_2O)_6]SO_4$ where L is the dianion of N,N'-bis(3-formyl-5, 6-dihydroxy-benziliden) ethylenediamine.

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/H_2O (1:1 v/v) solution which contains 2.45 g $Mn(CH_3COO)_2\cdot 4H_2O$ (1 mmole) and 3.84 g (1 mmole) (H_2L) (KOH solution was added stoichiometrically to deprotonate the OH groups) was refluxed on a steam bath during 30 min. The sparingly soluble, yellowish brown coloured product was filtered off and

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washed with MeOH/H_2O (1:1 v/v). *Chemical analysis. Found*: Mn 12.41; N 6.76; C 50.56%. $MnC_{18}H_{15}N_2O_7$ *requires*: Mn 12.90; N 6.57; C 50.70%.

2. $[Fe_3L_2(H_2O)_6]SO_4$ (**II**). Working as above, and using 2.78 g $FeSO_4 \cdot 7H_2O$ (1 mmole) and 3.84 g (1 mmole) (H_2L), it was obtained a black, sparingly soluble compound. *Chemical analysis. Found*: Fe 15.41; N 5.38; C 40.25; S 2.76%. $Fe_3C_{36}H_{40}N_4O_{22}S$ *requires*: Fe 15.54; N 5.19; C 40.00, S 2.96%.

3. [*NiL*] (**III**). To a solution in MeOH/H_2O (1:1 v/v) which contains 1.99 g $Ni(CH_3COO)_2 \cdot 4H_2O$ (1 mmole) it were added 3.84 g (1 mmole) H_2L. After 30 min refluxing on the steam bath, the sparingly soluble, green product was separated and washed with MeOH/H_2O. *Chemical analysis. Found*: Ni 14.17; N 6.95; C 52.61%. $NiC_{18}H_{14}N_2O_6$ *requires*: Ni 14.06; N 6.80; C 52.42%.

4. [*CuL*] $\cdot 2H_2O$ (**IV**). Working as above, by using 2.19 g (1 mmole) $Cu(CH_3COO)_2 \cdot H_2O$, it was obtained a yellow colored, sparingly soluble product. *Chemical analysis. Found*: Cu 13.72; N 6.29; C 47.84%. $CuC_{18}H_{18}N_2O_8$ *requires*: Cu 13.89; N 6.18; C 47.68%.

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.

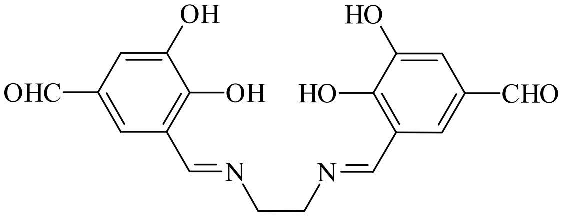
Results and Discussion

In the systems:

$M(CH_3COO)_2$ – H_2L M: Mn, Ni, Cu

$FeSO_4$ – H_2L

where H_2L is:



the syntheses have been developed in MeOH/H_2O (1:1 v/v) using the reactants in the 1:1 molar ratio. There were isolated four new compounds as sparingly soluble products with different colours.

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

(I)	[MnL(OH)]	yellowish brown
(II)	$[Fe_3L_2(H_2O)_6]SO_4$	black
(III)	[NiL]	red
(IV)	$[CuL]\cdot 2H_2O$	redish brown

Infrared spectra

The infrared spectrum of the ligand H_2L was recorded within the 400÷4000 cm^{-1} range and compared with those of the new four complexes (Table 1).

Table 1. IR spectra (cm^{-1}).

H_2L	**(I)**	**(II)**	**(III)**	**(IV)**	Assignments
–	415 w	430 w	435 w	440 w	ν(M–O)
–	–	590 w	–	–	$\rho_w(H_2O)$
–	–	615 m	–	–	$\nu_4(SO_4)$
856 m	850 w	845 w	849 m	850 w	γ(CH)
967 m	988 m	980 m	985 m	997 m	δ(CH)
–	1078 m	–	–	–	δ(OH)
–	–	1135 s	–	–	$\nu_3(SO_4)$
1147 s	1150 s	1148 m	1155 s	1154 s	ν(C–O)
1266 m	1275 vs	1275 vs	1275 vs	1277vs	ν(C–N)
1453 m	1460 m	1440 m	1460 m	1459 s	$\delta(CH_2)$
1557 s	1538 m	1545 m	1545 m	1550 m	ν(C=C)
1618 vs	1588 s	1592 vs	1595 vs	1600 vs	ν(C=N)
1633 s	1636 vs	1646 s	1645 s	1640 vs	ν(C=O)
–	3406 s	3393 m	–	3447 m	ν(OH)

(**I**) [MnL(OH)]; (**II**) $[Fe_3L(H_2O)_6]SO_4$; (**III**) [NiL]; (**IV**) $[CuL]\cdot 2H_2O$.

According to the literature data [5, 6] the most important remarks are the following:

– the spectra of all complexes are alike with that of the free Schiff base H_2L, containing the absorption bands which are assigned to the vibrations: $\rho(CH_2)$, $\delta(CH_2)$, $\nu(CH_2)$, ν(C=C), ν(C=N) and ν(C=O); that suggests the presence of a generally unaltered structure of this ligand;

– the band assigned to the ν(C=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 (IV); in addition, in the spectrum of the iron complex appears a band assigned to the coordinated water molecules ($\rho_w(H_2O)$);

- 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 ν(M-O).

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

- all the complexes contain the deprotonated Schiff base L^{2-} as ligand;
- the complex (II) contains water molecules as ligands; the manganese compound contains hydroxyl groups coordinated.

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.

Table 2. Electronic spectra.

Compound	$\bar{\nu}_{max}$ (cm^{-1})	Assignments
H_2L	20410	$\pi \rightarrow \pi^*$
	27470	CT
[MnL(OH)]	19920	$\pi \rightarrow \pi^*$
	18420	$^5E \rightarrow {}^5T_2$
	20200	$\pi \rightarrow \pi^*$
$[Fe_3L_2(H_2O)_6]SO_4$	$\begin{cases}16390\\12820\end{cases}$	$^5T_2 \rightarrow {}^5E$
[NiL]	21700	$\pi \rightarrow \pi^*$
	17640	$^1A_1 \rightarrow {}^1A_2$
	26315	CT
$[CuL]\cdot 2H_2O$	23475	$\pi \rightarrow \pi^*$
	17860	$d_{z^2} \rightarrow d_{x^2-y^2}$

The examination of these spectra offers the following information, according to the literature data [7]:

- 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 $[Fe_3L_2(H_2O)_6]SO_4$ is characteristic for Fe(II) $3d^6$ ion in an octahedral environment;
- the electronic spectrum of complex $[CuL]\cdot 2H_2O$ suggests a square-planar stereochemistry of Cu(II) ion, fact confirmed by EPR-spectrum.

The EPR spectrum of $[CuL]\cdot 2H_2O$ complex is intense and anisotropic (Fig. 1), with parameters: $g_{II} = 2.1798$ and $g_{\perp} = 2.0658$. A such spectrum ($g_{II} < g_{\perp} \cong 2.0$) is consistent with a square-planar stereochemistry [8, 9].

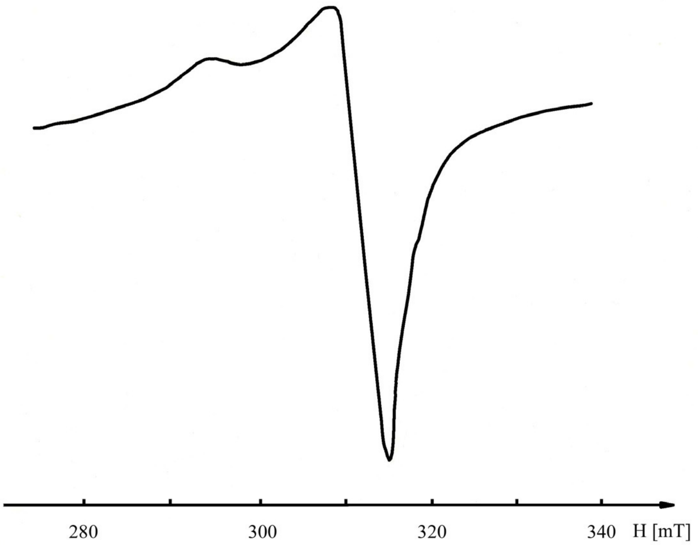
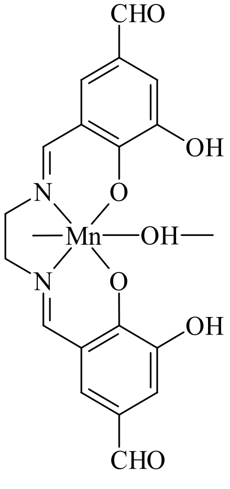
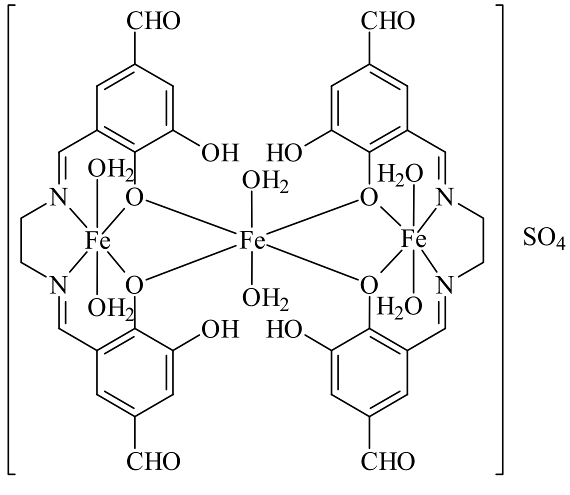


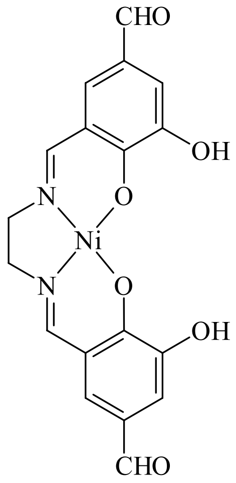
Fig. 1: *EPR spectrum for the cooper complex.*

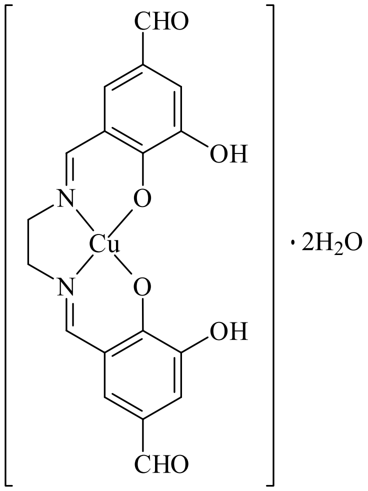
Conclusions

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









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