CHELATES OF Cu(II) AND Ni(II) WITH THE OXIME AND *o*-METHYLOXIME DERIVED FROM 4-HYDROXY-5-ETHOXY-ISOPHTALALDEHYDE

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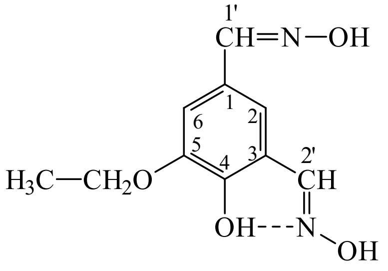
abstract: Metal chelates of 4-hydroxy-5-ethoxy-isophtalaldehyde dioxime (A) and 4-hydroxy-5-ethoxy-isophtalaldehyde-bis (O-methyloxime) (B) were prepared and characterized by elemental analysis, electronic, IR, EPR spectra and thermodifferential analysis.

Introduction

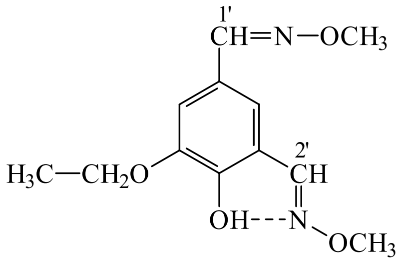
The interest in the study of the ability of some oxime to form coordination compounds with metal ions may be explained by the applications of these compounds and in understanding the increased biological activity of some drugs when they are administrated as metal complexes [1÷3].

Our previous paper [4] has reported the synthesis and characterization of the coordination compounds of some oxime derivatives of 5-formylvaniline with Ni(II) and Cu(II) ions.

The present paper deals with coordination of the some metal ions with others oxime derived from 4-hydroxy-5-ethoxy isophtalaldehyde for purpose of comparison Two new ligands able to generate complexes have been synthesized [5] and characterized by ^{1}H- and ^{13}C-NMR spectra. These compounds are: 4-hydroxy-5-ethoxyisophtalaldehyde dioxime (a); 4-hydroxy-5-ethoxyisophtalaldehyde-bis (O-methyloxime) (b).



(a)



(b)

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Analele Universității din Bucureşti – Chimie, Anul XII (serie nouă), vol. I-II, pag. 117–122

Experimental

The ligands were prepared according to a literature method [5] and $Cu(CH_3COO)_2.H_2O$ and $Ni(CH_3COO)_2.6H_2O$ p.a. Merck were used.

The chelates, $ML_2(CH_3OH)_2$ have been obtained following the same general procedure. In a typical experiment to a methanolic solution of ligand (2 mmol) was added a methanolic solution of the metal acetate (1 mmol). The precipitate obtained was filtered off, washed with methanol and air dried at room temperature.

Chemical analysis:

1) $CuA_2(CH_3COO)_2$ – Found: Cu 11.32; C 45.70; H 5.10; CuO 14.52; Calcd. for $CuC_{22}H_{32}O_{10}N_4$: Cu 11.04; C 45.86; H 5.55; CuO 13.82.
2) $NiA2(CH_3COO)_2$ – Found: Ni 10.37; C 45.69; H 5.13; NiO 13.67; Calcd. for $NiC_{22}H_{32}O_{10}N_4$: Ni 10.28; C 46.26; H 5.61; NiO 13.09.
3) $CuB_2(CH_3COO)_2$ – Found: Cu 9.95; C 50.02; H 5.91; CuO 13.15; Calcd. for $CuC_{26}H_{40}O_{10}N_4$: Cu 10.06; C 49.40; H 6.33; CuO 12.59.

^{1}H-NMR and ^{13}C-NMR data:

4-hydroxy-5-ethoxyisophtalaldehyde-dioxime (A):

^{1}H-NMR ($CDCl_3$, δ_{ppm}): 10.96 (HO-oxime 1'); 11.41 (HO-oxime 2'); 9.85 - HO; 8.00 (H-oxime 1'); 8.30 (H-oxime 2'); 7.27 (H-2); 7.18 (H-6).

^{13}C-NMR ($CDCl_3$, δ_{ppm}): 147.69 (CH=N, -1'); 147.20 (CH=N, -2'); 124.42 (C-1); 118.43 (C-2); 118.57 (C-3); 146.82 (C-4); 146.95 (C-5); 110.36 (C-6); 64.04 (CH_2); 14.62 (CH_3);

4-hydroxy-5-ethoxyisophtalaldehyde-bis (O-methyloxime) (B):

^{1}H-NMR ($CDCl_3$, δ_{ppm}): 9.68 - HO; 8.11 (H-1'); 8.36 (H-2'); 7.34 (H-2); 4.19 (H-6); 4.06 (CH_2); 1.34 (CH_3); 3.82 (CH_3O-1'); 3.90 (CH_3O-2').

^{13}C-NMR ($CDCl_3$, δ_{ppm}): 148.40 (CH=N, -1'); 147.40 (CH=N, -2'); 123.24 (C-1); 117.82 (C-2); 118.10 (C-3); 146.82 (C-4); 145.30 (C-5); 110.36 (C-6); 61.12 (CH_3O, -1'); 61.41 (CH_3O, -2'); 64.25 (CH_2); 14.55 (CH_3).

The carbon and hydrogen contents were determined by microcombustion. The metal content was determined gravimtrically using the standard method. The methanol content and residue MO) were calculated from the TG curve.

All melting points were recorded with a Boetius microapparatus and are uncorrected.

Electronic spectra within 400÷900 nm range were obtained with a JASCO 570 V spectrophotometer by the diffuse reflectance technique with MgO as the standard.

NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300 MHz (^{1}H-NMR) and 75 MHz (^{13}C-NMR) respectively, in $CDCl_3$. The chemical shifts were referred to a tetramethylsilane (TMS) as an internal standard.

EPR spectra were recorded at room temperature in polycrystalline powders on ART-5-IFA spectrograph. The clystron frequency was 9060 MHz. The EPR spectral parameters were calculated against Mn(II) standard.

Thermodifferential analysis was carried out with a Paulik-Paulik-Erdey Derivatograph Q-1500 D MOM. Conditions of measurements: temperature range at 1000°C; heating program: 10 degree/min; sensitivity DTA 1/10; $m_2 = 0.0418$ g; S = 50 mg; $m_3 = 0.0434$ g; S = 50 mg; atmosphere over sample air, α-alumine was used as a reference material.

IR spectra within 400÷4000 cm^{-1} range were performed on KBr pellet by means of a FT-IR-RAMAN JASCO 620 spectrophotometer.

Results and Discussion

By treating the methanolic solution of the Ni(II) and Cu(II) acetate with methanolic solution of the ligand A or B at a metal:ligand molar ratio of 1:2 or 1:4, the compounds of the $CuL_2(CH_3OH)_2$ type are obtained (where L = A or B), but $NiA_2(CH_3OH)_2$ compound only has obtained. In the same conditions (reaction medium, molar ratio, temperature), the ligand B did not generate any compound with Ni(II) acetate (Table 1).

Table 1. Analytical data and some physical data of the compounds.

No.	Compound	Empirical formula*	Melting point, °C	Colour
1	$CuA_2(CH_3OH)_2$	$CuC_{22}H_{32}O_{10}N_4$	245-246	Brown-red
2	$NiA_2(CH_3OH)_2$	$NiC_{22}H_{32}O_{10}N_4$	280-282	Green
3	$CuB_2(CH_3OH)_2$	$CuC_{26}H_{40}O_{10}N_4$	187-188	Brown-red

* The elemental analysis data were in good agreement with the calculated percentages of Cu, Ni, C, H for all the synthesized compounds

All compounds were microcrystalline materials, stable in air. The complex compounds contain also two molecules of methanol which can be either as coordinated methanol or as crystalline solvent.

Thermodifferential analysis curves for the complex compounds are similar. In Fig. 1 is shown in detail differential curve for $CuB_2(CH_3OH)_2$ compound. The results indicate that the compound is stable up to 150°C when it begins to lose weight. Weight loss at 190°C: found = 10.13% calcd for $2CH_3OH$ = 10.93%. Hence the two molecules of methanol are present as coordinated ones, in this chelates.

Diffuse reflectance spectra of Cu(II) complex compounds (1 and 3) present a broad band with a maximum at 696 nm and 764 nm respectively and another band (540 nm) or a shoulder (522 nm) respectively. These spectra are consistent with a distorted octahedron axially up to a square planar [6, 7].

The spectrum of Ni(II) compound presents the three spin-allowed bands: ν_1, ν_2 and ν_3 characteristic of the Ni(II) octahedral compounds. Their assignments are in agreement with data in the literature [8, 9] (Table 2).

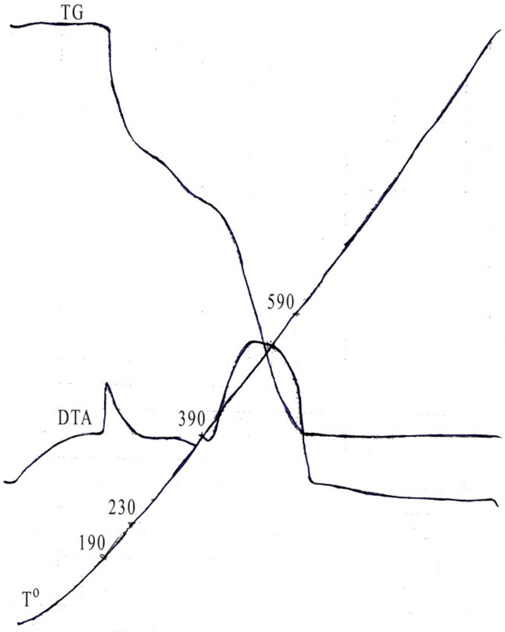


Fig. 1: *Thermodifferential curve of* $CuB_2(CH_3OH)_2$ *compound*

Table 2. Electronic spectral data and EPR spectral parameters.

No.	Compound	λ_{max}, nm	Assignments	$g_{\|\|}$	$g_{\perp}$
1	$CuA_2(CH_3OH)_2$	540, 696	d-d	2.0706	2.1694
2	$NiA_2(CH_3OH)_2$	870 652, 500 404	$\nu_1\ {}^3T_{1g}\leftarrow{}^3A_{2g}$ $\nu_2\ {}^3T_{2g}(F)\leftarrow{}^3A_{2g};\ {}^1E_g\leftarrow{}^3A_{2g}$ $\nu_3\ {}^3T_{2g}(P)\leftarrow{}^3A_{2g}$		
3	$CuB_2(CH_3OH)_2$	522sh, 764	d-d	2.0736	2.2056

sh = shoulder

The band ν_2 appears as well-formed doublet. The structure of this band was interpreted either as a spin-orbit coupling or as a spin-forbidden transition at the ${}^1E_g$ level [8,9].

The EPR spectra recorded at room temperature on polycristalline sample present EPR signals characteristic of a monomeric species of Cu(II) with various degrees of axial distortion for compounds noted 1, 3 (Fig. 2). The shape of the line is in agreement with the geometry axial compressed octahedron with $g_{||} < g_{\perp}$ supporting the electronic spectra of the complex compounds 1, 3.

The main bands and their assignments in IR spectra of free ligands and complex compounds are shown in Table 3. A comparison of the position of bands in complex compounds spectra with their positions in the spectra of the free ligands shown changes of the bands due to ν_{OH}, $\nu_{C=N}$. The presence of the OH and –CH=N-OH groups with lying in vicinal position with respect to each other favours intramolecular hydrogen bond (-OH…N).

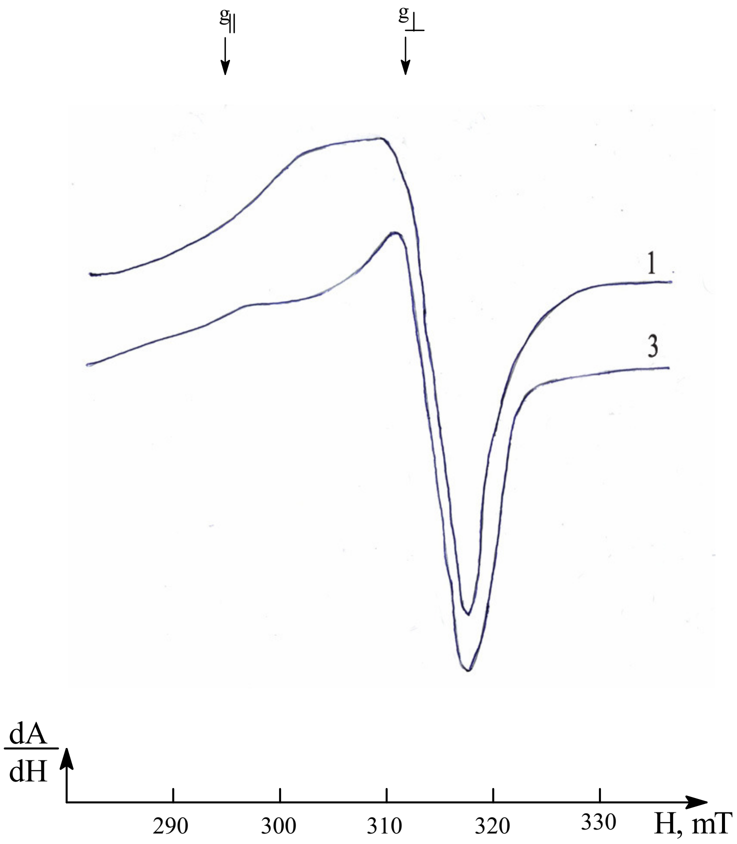


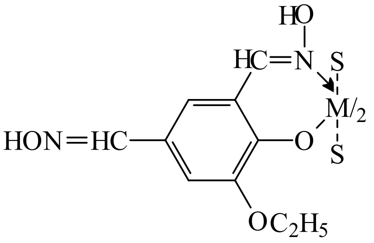
Fig. 2: *EPR spectra of the compounds 1 and 3*

Table 3. The main absorption bands in the IR spectra (cm^{-1}) and their assignments.

No.	Ligand / Compound	ν_{OH} nonassociated	ν_{OH} associated	$\nu_{C=N}$
	A	3516br.vs	3337br.m	1624m
1	$CuA_2(CH_3OH)_2$	3399m	-	1640m
2	$NiA_2(CH_3OH)_2$	3388m	-	1670m
	B	-	3331br	1609m
3	$CuB_2(CH_3OH)_2$	-	-	1616vs

vs – very strong, m – medium, br - broad

In the spectra of the ligands the band due to ν_{OH} appears as a broad one with two peaks: 3516, 3337 cm^{-1} (ligand A) and one peak at 3331 cm^{-1} (ligand B). The bands at 3337 and 3031 cm^{-1} are characteristic of the hydrogen bond that occurs between the atom of oxime nitrogen and the proton of the hydroxyl group from the position 4 in the isophtalaldehyde fragment. These bands have disappeared in the spectra of the complex compounds. This could be indicate that on metal chelate formation the chelate structure (-OH…N) disappears whereas the metal chelate structure (-OM...N) appears. The band due to $\nu_{C=N}$ (which occurs in the ligand spectra at 1624 cm^{-1} and 1609 cm^{-1} respectively) is shifted to higher values suggesting the coordination of the ligands through oxime nitrogen. Thus, the ligands act bidentately forming chelates of the $ML_2(CH_3OH)_2$ type. The six-coordinated surrounding of the metalic ion is due to coordinatively bond methanol molecules. Based on the previous discussion of spectral data, elemental and thermal analysis, the structures of the synthesized complexes were suggested in Fig. 3.



S = the two methanol molecules axially bonded
through donor atom oxygen

Fig. 3: *Structural formula proposed for the $ML_2(CH_3OH)_2$ compounds.*

Conclusions

In the new obtained complexes, the metal ion is hexacoordinated.

The ligands A and B act bidentately forming chelates.

The two methanol molecules are axially bonded.

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