STUDIA UBB CHEMIA, LVI, 1, 2011

ASYMMETRIC Co(III)-COMPLEXES OF ETHYL-METHYL-DIOXIME

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ABSTRACT. There is abundant literature regarding the symmetric α-dioximes, R'–C(=NOH)–C(=NOH)–R", (R'=R") and their derivatives. However, this is not the case for asymmetric α-dioximes, and the goal of this research was to increase knowledge in this domain. The thermal stability of the asymmetric α-dioximes and their Co-complexes is lower than that of the similar symmetric derivatives. This difference has also been observed in spectroscopical analysis.

In this study, the synthesis of a series of Co-complexes of the type $[Co(Et\text{-}Me\text{-}DioxH)_2L_2]^+$, (L=amine) was described and characterized with thermoanalytical and spectroscopical methods.

Keywords: *α-dioxime, heterocyclic amines, Co-complexes, thermal decomposition, spectroscopic measurements*

INTRODUCTION

Coordination compounds of α-dioximes, R^1–C(=NOH)–C(=NOH)–R^2, (R^1=R^2, $R^1 \neq R^2$) along with mainly transition metals, were the subject of a great number of preparative, physico-chemical and analytical studies. Various physico-chemical properties (e. g., electrochemical relations, dipole-moments, polarizability, the variation of the energy level of these molecules) constitute the basis of the modern quantum-chemical examination.

The nature of the R^1 and R^2 groups influences the substitution reactions, spectral properties, and thermal stability of the above mentioned metal complexes. Among these derivatives the greatest stability have the symmetric compounds with $R^1 = R^2$ values.

There is scant research regarding the chemical properties of the asymmetric α-dioximes ($R^1 \neq R^2$, R^1, R^2 = H, alkyl-, aryl-, alicyclic-, heterocyclic groups). It was observed that the thermal stability of the asymmetric complexes is lower than that of the analogous symmetric ones, and their hydrolysis in solutions also takes place with higher rates [1–24].

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Some Co-dioximine complexes present antibacterial activity. The skeleton of the B_{12}-vitamine molecule, which is used in the treatment of pernicious anemia, is also a Co(III)-dioximine group. It is noteworthy that such substances can be useful in the field of medicine.

In this study a new synthesis of the ethyl-methyl-dioxime and some new Co(III)-complexes of this chelating agent were described and characterized by chemical and biochemical methods.

RESULTS AND DISCUSSION

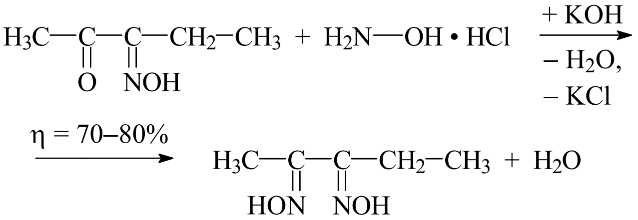
Four Co(III)-complexes, type $[Co(DioxH)_2(amine)_2]X$ were obtained by oxidizing Co(II)-salts in water–alcohol solution, in the presence of dioximes, aromatic or heterocyclic amines with an oxidation reagent (O_2, H_2O_2).

$$2\ CoX_2 + 4\ DioxH_2 + 6\ Amine + \tfrac{1}{2}\ O_2 = 2\ [Co(DioxH)_2(Amine)_2]^+X^- + H_2O +$$
$$+\ 2\ AmineH^+X^-,\ X^- = CH_3–CH_2–COO^-,\ NO_3^-,\ ClO_4^-$$

The used dioxime was ethyl-methyl-dioxime, also prepared. In the first step was prepared the Me-Et-dione-monoxime from methyl-n-propyl-ketone acidified with HCl, with isonitroso method, bubbling gaseous ethyl-nitrite, in a cooling mixture.

$$CH_3–CO–CH_2–CH_2–CH_3 + Et–ONO \rightarrow CH_3–CO–C(=NOH)–CH_2–CH_3 + EtOH$$

The intermediary product, methyl-ethyl-2,3-dion-monoxime, was transformed with hydroxyl-amine in the corresponding α-dioxime.



$$H_3C-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{NOH}}{C}-CH_2-CH_3 + H_2N-OH \cdot HCl \xrightarrow[-\,H_2O,\ -\,KCl]{+\,KOH}$$
$$\xrightarrow{\eta\,=\,70–80\%} H_3C-\underset{\overset{\|}{HON}}{C}-\underset{\overset{\|}{NOH}}{C}-CH_2-CH_3 + H_2O$$

The behaviour of the asymmetric α-dioximes, including Et-Me-dioxime, with transition metal ions is similar to behaviour of the symmetric α-dioximes. In some cases were obtained colored, water-insoluble products: [Me-Et-$(DioxH)_2$M(II)] (M = Ni, Pd, Pt), and in other cases specific colored solutions. For example, orange-brown with Ni(II), Pd(II), Co(III), red with Fe(II), Re(IV), etc. [25].

Electronic spectra (UV–VIS)

The electronic-spectra were recorded for a few $[Co(Me\text{-}Et\text{-}DioxH)_2(amine)_2]X$ type complexes. Here we found the internal absorption bands for the oxime- and pyridine-derivative ligands. In the case of aromatic and heterocyclic amines, the observed band is shifted to higher wavelengths. The *d–d* very weak bands were also observed. We are planning to make more studies for the UV–VIS bands in the future.

IR-spectral measurements

We recorded the middle- and far-IR spectra for our compounds, and the most important results are summarized in the experimental part.

If we compare our IR-spectra with the spectrum of symmetric [Co(DMG)$_2$(β-picoline)$_2$]I compound, we can observe the following: The $\delta_{O-H\cdots O}$ weak, large band (1733–1750 cm^{-1}), which stabilizes the compound, appears in the same wave number region, in both cases, which indicates a very similar structure.

The bands $\nu_{C=N}$ appear close to each other in our studied compounds (1547–1551 cm^{-1}). Also we can observe a small difference between the ν_{NOH} and ν_{N-O} bands (1228–1230 cm^{-1} and 1104–1109 cm^{-1}). In the far IR the ν_{Co-N} band is just similar in the studied compounds (512–514 cm^{-1}).

In the range of 400–100 cm^{-1} several deformation vibrations appeared, mostly for the heterocyclic amines and for the N–Co–N groups (δ_{N-Co-N}: 379–383 cm^{-1}) [26].

Thermoanalytical study

The TG, DTG, DTA curves were recorded for the studied complexes. The thermal decomposition curves of [Co(Me-Et-DioxH)$_2$(3,4-lutidine)$_2$]Br are presented in Fig. 1, and the results for all studied complexes are included in Table 1.

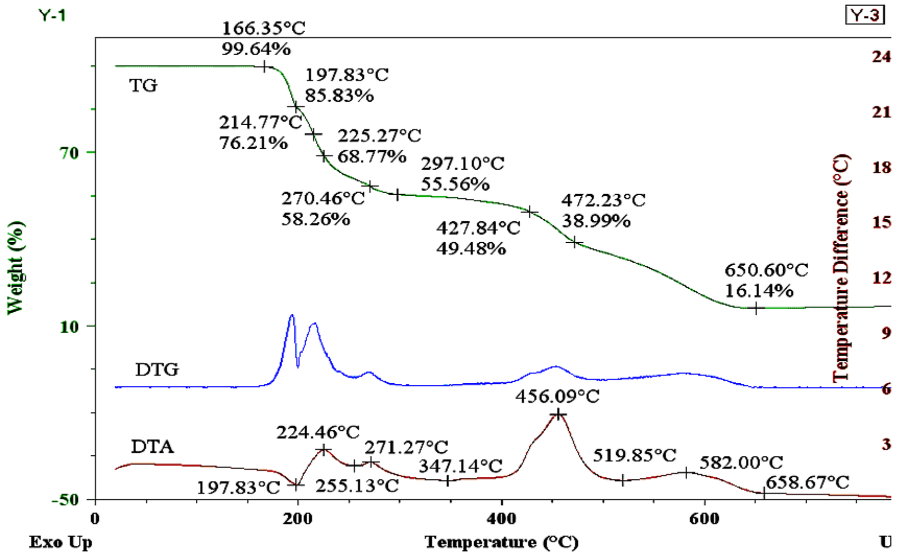


Figure 1. Thermal decomposition curves of *[Co(Me-Et-DioxH)$_2$(3,4-lutidine)$_2$]Br.*

Table 1. Thermoanalytical data of [Co(Me-Et-DioxH)$_2$(amine)$_2$]X-complexes

[A(3,4-lut)$_2$]Br		[A(3,4-lut)$_2$]I		[A(3-Me-Py)$_2$]Br		[A(3-Me-Py)$_2$]I	
t(°C)	**m; $-\Delta$m**	**t(°C)**	**m; $-\Delta$m**	**t(°C)**	**m; $-\Delta$m**	**t(°C)**	**m; $-\Delta$m**
166.35	99.64; 0.36	149.40	98.87; 1.13	102.59	98.71; 1.29	110.66	99.4; 0.6
197.83	85.83; 14.17	171.19	91.85; 8.15	113.08	91.06; 8.94	137.29	89.12; 10.8
214.77	76.21; 23.79	187.33	86.87; 13.13	138.91	84.53; 15.47	163.12	85.91; 14.09
225.27	68.77; 31.23	227.69	79.12; 20.88	192.18	82.11; 17.89	180.88	82.78; 17.22
270.46	58.26; 41.74	278.53	66.10; 33.90	209.13	76.03; 23.97	222.85	77.7; 22.3
297.10	55.56; 44.44	362.47	61.69; 38.31	234.14	64.22; 35.78	273.69	62.15; 37.85
427.84	49.48; 50.52	416.55	41.89; 58.11	264.81	59.17; 40.83	364.89	58.20; 41.80
650.60	16.14; 83.84	471.43	20.84; 79.16	410.90	51.05; 48.95	406.05	39.29; 60.71
				447.21	42.09; 57.91	463.36	12.25; 87.75
				690.95	15.55; 84.45		

[A(3,4-lut)$_2$]Br		[A(3,4-lut)$_2$]I		[A(3-Me-Py)$_2$]Br		[A(3-Me-Py)$_2$]I	
DTG	**DTA**	**DTG**	**DTA**	**DTG**	**DTA**	**DTG**	**DTA**
214, 225, 270, 456, 582	197.83 (endo), 224.46 (exo), 255.13 (endo), 271.27 (exo), 347.14 (endo), 456.09 (exo), 519.85 (endo), 582 (exo), 658.67 (endo)	171, 187, 228, 240, 270, 418	171.19 (endo), 241.41 (exo), 256.74 (endo), 310.82 (endo), 418.16 (exo), 484.3 (exo)	113, 192, 209, 265, 410, 690	113 (endo), 192.98 (endo), 222 (exo), 251.9 (endo), 268.85 (exo), 339.87 (endo), 423.3 (exo), 657 (exo)	163, 137, 238, 406	134.87 (endo), 238 (exo), 311 (endo), 405.25 (exo)

A = Co(Me-Et-DioxH)$_2$

The mechanism of the thermal decomposition of the [Co(Me-Et-DioxH)$_2$ (amine)$_2$]X type complexes was established from the TG steps. In the first step a redox process takes place:

$$Co^{3+} + e^{-} \rightarrow Co^{2+}$$

and the X^- anion is oxidized:

$$2\,Br^- - 2\,e^- \rightarrow Br_2$$
$$2\,I^- - 2\,e^- \rightarrow I_2$$

(For example, in the presented figure the Br^- elimination takes place until 198°C)

This is then followed by the amine and dioxime elimination:

$$[Co(Me\text{-}Et\text{-}DioxH)_2(amin)_2]^0 \rightarrow [Co(Me\text{-}Et\text{-}DioxH)_2(amin)]^0 \rightarrow$$
$$\rightarrow [Co(Me\text{-}Et\text{-}DioxH)_2]^0 \rightarrow [Co(Me\text{-}Et\text{-}DioxH)]^+ \rightarrow 1/3\ Co_3O_4$$

(In figure 1, the two amine elimination can be observed until 225°C, respectively 297°C. The two dioxime elimination takes place between 297 – 651°C)

Mass spectrometric measurements

In the mass spectra abundant positive ions corresponding to $[Co(Me\text{-}Et\text{-}DioxH)_2(amine)_2]$ species were observed (m/z 531 and 503 for lutidine and β-picoline containing compounds, respectively). Further fragment ions in the spectra correspond to loss of amine groups (table 2) [27].

Table 2. Electrospray mass spectrometric data for $[Co(Me\text{-}Et\text{-}DioxH)_2(amine)_2]X$

Nr.	Compound	Fragments (m/z)
1.	$[Co(Me\text{-}Et\text{-}DioxH)_2(3,4\text{-}lutidine)_2]Br$	227 (2%) $[Co(Me\text{-}Et\text{-}furazane)_2]^+$, 317 (30%) $[Co(Me\text{-}Et\text{-}DioxH)_2]^+$, 424.2 (35%) $[Co(Me\text{-}Et\text{-}DioxH)_2(3,4\text{-}lutidine)]^+$, 531.2 (100%) $[Co(Me\text{-}Et\text{-}DioxH)_2(3,4\text{-}lutidine)_2]^+$
2.	$[Co(Me\text{-}Et\text{-}DioxH)_2(3,4\text{-}lutidine)_2]I$	317 (25%) $[Co(Me\text{-}Et\text{-}DioxH)_2]^+$, 424.4 (40%) $[Co(Me\text{-}Et\text{-}DioxH)_2(3,4\text{-}lutidine)]^+$, 531.2 (100%) $[Co(Me\text{-}Et\text{-}DioxH)_2(3,4\text{-}lutidine)_2]^+$
3.	$[Co(Me\text{-}Et\text{-}DioxH)_2(\beta\text{-}picoline)_2]Br$	317.2 (28%) $[Co(Me\text{-}Et\text{-}DioxH)_2]^+$, 410.2 (29%) $[Co(Me\text{-}Et\text{-}DioxH)_2(\beta\text{-}picoline)]^+$, 503.2 (100%) $[Co(Me\text{-}Et\text{-}DioxH)_2(\beta\text{-}picoline)_2]^+$
4.	$[Co(Me\text{-}Et\text{-}DioxH)_2(\beta\text{-}picoline)_2]I$	317.0 (17%) $[Co(Me\text{-}Et\text{-}DioxH)_2]^+$, 410.2 (19%) $[Co(Me\text{-}Et\text{-}DioxH)_2(\beta\text{-}picoline)]^+$, 503.4 (100%) $[Co(Me\text{-}Et\text{-}DioxH)_2(\beta\text{-}picoline)_2]^+$

Biological probes

The antimicrobial effects of our complexes were studied for Gram-negative and Gram-positive germs. The Gram staining [28, 29] is an empirical solution for dividing the germs in two parts (Gram-negative and Gram-positive), in accordance with their physical and chemical properties of the cell-wall.

Our results are included in table 3. When the studied compound blocked the growing of germs, is marked with “+” [30–38].

Table 3. Antimicrobial studies

Nr.	Compound	Escherichia coli (Gram-negative)	B. Subtilis (Gram-positive)
1.	$[Co(Me\text{-}Et\text{-}DioxH)_2(3,4\text{-}lutidine)_2]Br$	–	+
2.	$[Co(Me\text{-}Et\text{-}DioxH)_2(3,4\text{-}lutidine)_2]I$	–	+
3.	$[Co(Me\text{-}Et\text{-}DioxH)_2(\beta\text{-}picoline)_2]Br$	–	+
4.	$[Co(Me\text{-}Et\text{-}DioxH)_2(\beta\text{-}picoline)_2]I$	–	–

CONCLUSIONS

The literature data and our XRD single crystal measurements for similar compounds [39] shows that the $[Co^{III}(DioxH)_2L_2]X$ type derivatives have octahedral structure. The equatorial plain of the octahedron is occupied by two dioxime ligands, and two O–H···O hydrogen-bridge stabilize the molecule. The two peak-points are occupied by two neutral or negative charged atomic groups, as shown in the figure 2.

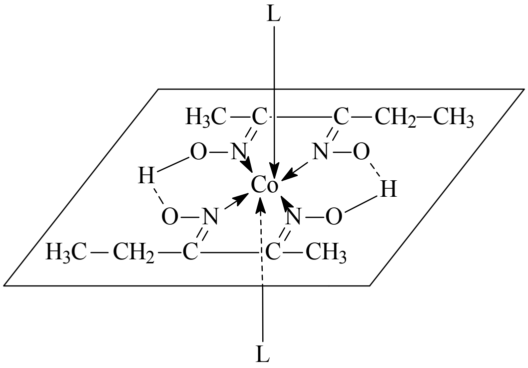


Figure 2. General structure of $[Co(Et\text{-}Me\text{-}DioxH)_2L_2]$ type complexes.

In our biological studies were used Gram positive and Gram negative germs. The results prove that the prepared complexes inhibit the growth of B. Subtilis germ.

EXPERIMENTAL SECTION

The electronic-spectra were recorded in ethyl-alcohol solution of 10^{-5} mol/l concentration with Jasco V-670 Spectrophotometer.

The IR spectra of the complexes were obtained in KBr and polyethylene pellets in the mid-IR (4000–450 cm^{-1}) and far-IR (650–150 cm^{-1}) range, respectively, on a Perkin–Elmer System 2000 FTIR spectrometer, operating with a resolution of 4 cm^{-1}.

Thermal measurements were performed with a 951 TG and 910 DSC calorimeter (DuPont Instruments), in air atmosphere, at a heating rate of 10 $K{\cdot}min^{-1}$ (sample mass 4–10 mg).

Mass spectrometric (MS) measurements were carried out by a PE Sciex API 2000 triple quadruple mass spectrometer, using electrospray ionization (ESI) in the 200–1200 m/z region. By ESI-MS, ionization takes place at milder conditions as compared with classical mass spectrometry, therefore it is more sensible for the detection of single and associated dimmer molecule ions and their fragment ions.

Synthesis of ethyl-methyl-dioxime

Me-Et-dione-monoxime was prepared with isonitroso method: in 0.5 mol methyl-n-propyl-ketone acidified with 2.5 ml HCl was bubbled gaseous ethyl-nitrite, in a cooling mixture (ice + NaCl + H_2O), (–5 ÷ 5°C) for 80–90 minutes.

The intermediary product, methyl-ethyl-2,3-dion-monoxime, was transformed with hydroxyl-amine (0.6 mol $NH_2OH{\bullet}HCl$ by neutralization with 0.6 mol NaOH at 60–70°C, solved in EtOH) in the corresponding α-dioxime.

The white Me-Et-dioxime crystallized after standing.

The crude product was re-crystallized from ethyl alcohol. Yield: 70–80%.

The preparation of Co(III)-complexes

If are oxidize Co(II)-salts (CoX_2, where X = acetate, NO_3, ClO_4) in water–alcohol solution, in the presence of ethyl-methyl-dioxime, aromatic or heterocyclic amines (mol-rate: 1:2:3) with an oxidation reagent (O_2, H_2O_2), it results in binary complex salts.

Table 4. Preparation data for $[Co(DioxH)_2(amine)_2]X$ type derivatives

Nr.	Starting materials (g; mol)				Product	Yield (g; %)
	$Co(Ac)_2$	Me-Et-$DioxH_2$	Amine	KX		
1.	10.65; 0.05	13.2; 0.1	3,4-lutidine 16; 0.15	KBr 10; 0.08	$[Co(Me\text{-}Et\text{-}DioxH)_2(3,4\text{-}lutidine)_2]Br$	19; 62
2.	10.65; 0.05	13.2; 0.1	3,4-lutidine 16; 0.15	KI 10; 0.06	$[Co(Me\text{-}Et\text{-}DioxH)_2(3,4\text{-}lutidine)_2]I$	20.7;63
3.	10.65; 0.05	13.2; 0.1	β-picoline 14; 0.15	KBr 10; 0.08	$[Co(Me\text{-}Et\text{-}DioxH)_2(\beta\text{-}picoline)_2]Br$	18.3; 68
4.	10.65; 0.05	13.2; 0.1	β-picoline 14; 0.15	KI 10; 0.06	$[Co(Me\text{-}Et\text{-}DioxH)_2(\beta\text{-}picoline)_2]I$	22.3; 70.8

It was bubbled 2–3 hours air through the solution of 0.05 mol $Co(acetate)_2{\cdot}2\,H_2O$, 0.10 mol Me-Et-$DioxH_2$ in 200 ml 50 % EtOH, then added 0.15 mol β-picoline or 3,4-lutidine dissolved in 15–20 ml EtOH. The oxidation was continued for 1 more hour. The resulted dark brown solution was filtered, and added to 100–100 ml filtered solution of 10–10 g KBr or KI, dissolved in a small quantity of water. The dried crystallized brown product was filtered, washed with diluted alcoholic solution, and dried it on air. Details of the preparations, yields are given in Table 4.

Analysis

The studied complexes were characterized by N, X, H-microanalysis and their Co content was determined volumetrically with 0.01 m EDTA, using murexide indicator, after destruction of the samples (H_2SO_4 + KNO_3). The microscopic aspect, chemical analysis and IR-spectral measurement results for the studied compounds are given in tables 5, 6.

Table 5. Chemical analysis and microscopic aspect for $[Co(DioxH)_2(amine)_2]X$ type derivatives

Nr.	Compound	Mol-weigh	Chem. analysis		Color	Microscopic aspect
			Calc.	Found		
1.	$[Co(Me\text{-}Et\text{-}DioxH)_2$ $(3,4\text{-lutidine})_2]Br$	611.08	Co: 9.6 N: 13.7 Br: 49.3 H: 5.9	9.4 13.5 48.7 6.1	light brown	Rectangular, long, plates
2.	$[Co(Me\text{-}Et\text{-}DioxH)_2$ $(3,4\text{-lutidine})_2]I$	657.95	Co: 8.9 N: 12.8 I: 43.9 H: 5.4	9.1 13.1 44.2 5.0	light brown	Irregular crops
3.	$[Co(Me\text{-}Et\text{-}DioxH)_2$ $(\beta\text{-picoline})_2]Br$	538.38	Co: 10.1 N: 14.4 Br: 45.4 H: 5.4	9.8 14.7 44.9 5.7	reddish brown	Long, triangular based prisms
4.	$[Co(Me\text{-}Et\text{-}DioxH)_2$ $(\beta\text{-picoline})_2]I$	630.38	Co: 9.3 N: 13.3 I: 42.0 H: 5.0	9.7 12.9 43.2 4.7	light brown	Irregular, small plates

(β-picoline = 3-methyl-pyridine; 3,4-lutidine = 3,4-dimethyl-pyridine)

Table 6. FTIR-spectroscopic dates

Vibration (cm^{-1})	$[Co(Me\text{-}Et\text{-}DioxH)_2$ $(3,4\text{-lutidine})_2]Br$	$[Co(Me\text{-}Et\text{-}DioxH)_2$ $(3,4\text{-lutidine})_2]I$	$[Co(Me\text{-}Et\text{-}DioxH)_2$ $(\beta\text{-picoline})_2]Br$	$[Co(Me\text{-}Et\text{-}DioxH)_2$ $(\beta\text{-picoline})_2]I$
ν_{O-H}	3436 s	3437 s	3409 vs	3435 m
ν_{C-H}	3014 w 2983 s 2932 s 2871 m	3015 w 2982 m 2936 m	3115 m 2975 m 2932 m 2872 m	3116 m 3018 m 2973; 2935 2832 m
$\delta_{O-H\cdots O}$	1750 w	1740 w	1740 w	1733 w
ν_{C-C}	1616 s	1616 s	1611 m	1607 m
$\nu_{C=N}$	1547 vs	1547 vs	1551 vs	1547 vs
δ_{CH3}	1454 vs	1453 vs	1453 vs	1457 vs
δ_{CH2}	1384 m	1384 m	1384 m	1383 m

Vibration (cm^{-1})	**[Co(Me-Et-DioxH)$_2$ (3,4-lutidine)$_2$]Br**	**[Co(Me-Et-DioxH)$_2$ (3,4-lutidine)$_2$]I**	**[Co(Me-Et-DioxH)$_2$ (β-picoline)$_2$]Br**	**[Co(Me-Et-DioxH)$_2$ (β-picoline)$_2$]I**
ν_{NOH}	1280 vs	1229 vs	1229 vs	1228 vs
$\nu_{N–O}$	1104 vs	1109 s	1108 vs	1109 vs
γ_{CH2}	722 s	721 s	701 vs	701 vs
$\nu_{Co–N}$	512 vs	513 vs	514 vs	514 vs
$\delta_{N–Co–N}$	379 m	380 m	383 m	383 m

s = strong; vs = very strong; m = medium; w = weak

Electronic spectra (UV–VIS)

The electronic-spectra were recorded for a few [Co(Me-Et-DioxH)$_2$ (amine)$_2$]X type complexes, and the observed absorption bands are summarized in table 7.

Table 7. Electronic spectra date

Compound	Absorption band (nm)	Observation
[Co(Me-Et-DioxH)$_2$(3,4-lutidine)$_2$]Br	201.5 vs 246.5 m	Internal absorption bands for the oxime- and pyridine-derivative ligands
[Co(Me-Et-DioxH)$_2$(β-picoline)$_2$]Br	204.0 vs 246.5 m	

vs = very strong; m = medium

Biological probes

The antimicrobial effects of our complexes were studied for Gram-negative and Gram-positive germs. The observation was made with the disk method. Filtering paper disks were impregnate with a concentrate probe solution, sterilized (with UV-radiation or in autoclave), then putted it on the germ substrate. After 24 hour incubation were observed whether the studied compound blocked the growth of the germ substrate. The case, when there was no growth of germ substrate around the disks, was called inhibition zone.

ACKNOWLEDGEMENT

The authors wish to express their thankfulness to the “Domus Hungarica Foundation” of Hungary for the several fellowships provided to Csaba Várhelyi jr.

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