# Investigation of the Optical Properties of the Solutions of the Tetraaquabis(saccharinato)metal(II)dihydrate [Metal: Co(II) and Ni(II)] Complexes at Different Molarity and Volume of Stock Solutions

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*We investigated the optical properties and the transmittance characterizations of the stock solutions of the Co(II) and Ni(II) complexes of Saccharin and determined the molar extinction coefficients at different molarity. The molar extinction coefficients (ε) values of the Co(II) and Ni(II) complexes in the first region decrease with increasing molarity, and the ε values of the Co(II) and Ni(II) complexes at lower wavelength are higher than that of the values at higher wavelength. The absorption band edge values of the Co(II) complex shift from 3.584 to 3.139 eV with the increasing molarity, while the absorption band edge values of the Ni(II) complex shift from 3.574 to 3.493 eV with the increasing molarity. The plots of refractive index of the Co(II) and Ni(II) complexes consist of two anomalous (abnormal) dispersion regions and one normal dispersion region. The direct energy-gap of the Co(II) complex can be more decreased with molarity. The absorbance, molar extinction coefficients, refractive index values of the Co(II) and Ni(II) complexes decrease, while the average transmittance in the visible region, direct optical band-gap values of the Co(II) and Ni(II) complexes increase with increasing volume of DMF solvent or decreasing volume of the solutions of the Co(II) and Ni(II) complexes.*

*Keywords: Tetraaquabissaccharinato complexes of Co(II) and Ni(II), molar extinction coefficient, molarity, absorption band edge, refractive index, anomalous (abnormal) and normal dispersion.*

Saccharin (*o*-sulfobenzimide; 1,2-benzothiazole-3(2H)-one 1,1-dioxide) is one of the best known and most widely used artificial sweetening agents [1]. The first systematic syntheses and structural studies of aqua complexes of metal saccharin were reported by the groups of Haider and Cotton [2,3].

During the last 20 years different research groups have performed systematic studies on these types of systems, obtaining a great number of new and often fascinating saccharin–metal complexes. Replacement of the acidic hydrogen from a saccharin molecule produces a negative centre on the nitrogen atom, which could then coordinate with a suitable metal(II) atom [4,5].

Saccharin, its derivatives and some metal saccharin are found to be enzymatic inhibitors and are also used as food additives and electroplating brighteners [6]. Saccharin has a very low solubility, but the sodium salt with its deprotonated form saccharin (sac) is very soluble. [7]. Studying the coordination nature of saccharin and determining the binding site(s) to metal ions are perhaps key to understand the bioinorganic chemistry of saccharin [8].

There are use of space with lots of features such as using in salt form in pharmaceutical chemistry and disposal of the body. Biological effects of saccharin have increased on its complexes more than saccharin ligand in the literature.

We synthesized and characterized metal complexes of saccharin before. However, we didn't encounter such a study about the optical properties of complexes of saccharin with interesting features at literature. In this study, the optical properties of the stock solutions of the Co(II) and Ni(II) complexes of ligand and the transmittance characterizations and the molar extinction coefficients at different molarities were determined. To examine optical properties, homogeneously dissolved ligand and its complexes were prepared with DMF. Then, the optical band gap properties of the Co(II) and Ni(II) complexes of the ligand at different molarities were investigated. Finally, we determined the effect on the optical properties of the volume of working stock of the Co(II) and Ni(II) complexes of the ligand for 50 mM. The aim of this study was to investigate the optical properties of nickel and cobalt complexes in $d^7$, $d^8$ configurations respectively.

## Experimental part

### *Materials and methods*

All solvents were analytical grade materials used as purchased. The metal salts $Co(SO_4).6H_2O$ and $Ni(SO_4).6H_2O$ (Merck products) were used as starting materials for the preparation of ligands.

The optical measurements were conducted on a Shimadzu model UV-1800 Spectrophotometer in the wavelength 1100-190 nm. All complexes were weighed an AND Model HRZ250-AZ (precision-0,1 mg) analytical balance.

### *Synthesis of Co(II), Ni(II) complexes*

Aqueous Co(II) and Ni(II) complexes of saccharine were synthesized, by activating $MSO_4$ or $M(NO_3)_2$ salts with Na(Sac) in the water and the obtained dust solid complexes were dissolved in water by heating at 70°C, and

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$$MSO_4 + 2NaSac + 6H_2O \rightarrow [M(sac)_2(H_2O)_4].2H_2O + Na_2SO_4$$

*Tetraquabis(saccharin)metal(II)dihidrat*

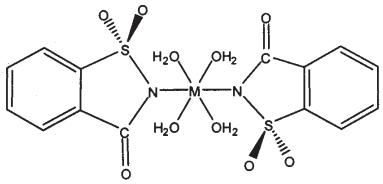

Fig. 1. Structure of complexes

M:Co, Ni, Cu

recrystalised again, according with studies in the literature [9].

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*Preparation of the stock solutions of the Co(II) and Ni(II)complexes of ligand at different molarity*

The molecular weight and formula of the Co(II) and Ni(II) complexes of the ligand were found to be 531.38 g/mol and $C_{14}H_{20}N_2O_{12}S_2Co$, 531.14 g/mol and $C_{14}H_{20}N_2O_{12}S_2Ni$, respectively. To prepare the stock solutions, both Co(II) and Ni(II) complexes of the ligand were weighed and dissolved homogeneously in N,N-dimethylformamide for 1, 10 and 50 mM using 10 ml and for 100 mM using 5mM. 1, 10, 50 and 100 mM. Ultimately, all prepared stock solutions were filtered through PTFE membrane filter before optical measurements. The real pictures of the filtered solutions of the Co(II) and Ni(II) complexes of ligand for 1, 10, 50 and 100 mM are shown in figure 2(a,b), respectively. As seen in figure 2(a,b), the colors of the solutions of the Co(II) and Ni(II) complexes of the ligand are becoming naturally more darker with increasing their molarity.

*The optical measurements of the stock solutions of the Co(II)and Ni(II) complexes of the ligand*

We used the cylindrical cuvettes (Hellma QS-100) of 3.5 mL volume and 10 mm optical path length for all the solutions of the Co(II) and Ni(II) complexes. The optical measurements of all the solutions were recorded by a Shimadzu model UV-1800 Spectrophotometer in the wavelength of 1100-190 nm. Then, the solutions of the Co(II) and Ni(II) complexes of the ligand were prepared for four different DMF Solutions (v/v) ratios. So, the optical measurements of the last solutions were again taken by the same spectrophotometer for the same wavelengths.

a

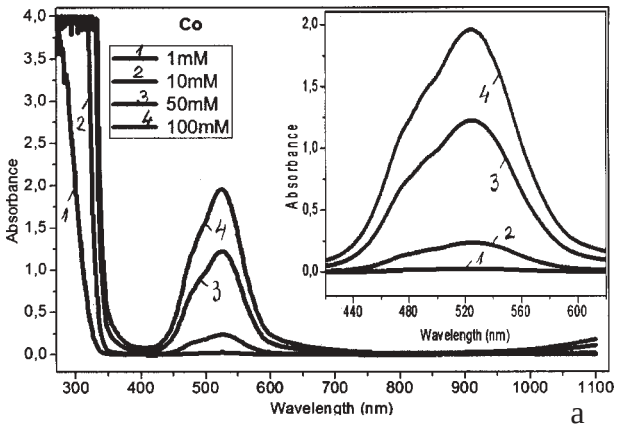
b

Fig. 2. The real pictures of the filtered solutions of the (a) Co(II) and (b) Ni(II) complexes of ligand for 1, 10, 50 and 100 mM.

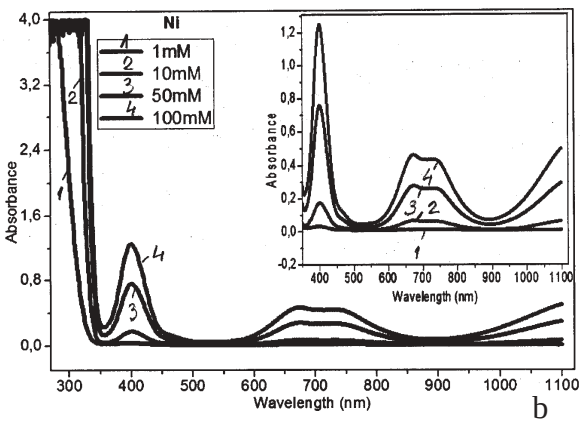
## Results and discussions

*Determination of the molar extinction coefficients at different molarity*

The absorbance spectra of the Co(II) and Ni(II) complexes of the ligand were taken to investigate their optical properties for 1, 10, 50 and 100 mM and the plots of the absorbance against wavelength are shown in figure 3(a,b), respectively. As seen in figure 3a, the curves of the plots consist of three regions: the absorbance values of the Co(II) complex sharply decrease until about 400 nm, then a peak occurs in the range of 420 and 630 nm and in the last region the absorbance values of the Co(II) complex remain almost constant after 630 nm. Also, the absorbance values of the Co(II) complex increase with increasing molarity and as seen in inset of figure 3a, the peaks of the Co(II) complex increase with increasing molarity. Similarly, as seen in inset of figure 3b, the curves of the plots occurs four region: the absorbance values of the Ni(II) complex sharply decrease until about 350 nm in the first region, a peak occurs in the range of about 350 and 480 nm in the second region, an another peak occurs in the range of about 570 and 880 nm in the third region, and the absorbance values of the Ni(II) increase after 900 nm in the last region. The absorbance values of the Ni(II) complex increase with increasing molarity and as seen in inset of figure 3b, the both peaks of the Ni(II) complex increase with increasing molarity.




a




b

Fig. 3. The plots of the absorbance vs. wavelength of the (a) Co(II) and (b) Ni(II) complexes of the ligand for 1, 10, 50 and 100 mM.

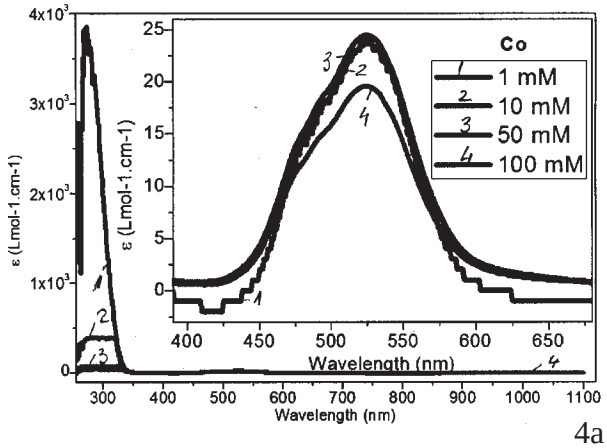
The molar extinction coefficient (ε) values of the Co(II) and Ni(II) complexes of the ligand can be determined with an equation known as the Beer–Lambert law,

$$\varepsilon = \frac{Abs}{cl} \qquad (1)$$

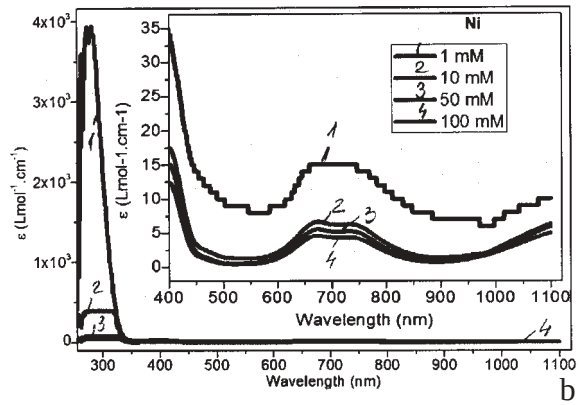
where Abs is an actual absorption, ε is an optical path length, and c is the molar concentration of the used cuvettes. The ε values of the Co(II) and Ni(II) complexes of the ligand were calculated from eq. (1). The ε plots of the Co(II) and Ni(II) complexes of the ligand for 1, 10, 50 and 100 mM are shown in figure 4(a,b), respectively. As seen in figure 4a, the curves of the plots consist of two region: the ε values of the Co(II) complex sharply decrease until about 365 nm, and in the other region the ε values of the Co(II) complex remain almost constant according to more higher ε values after 365 nm, but a peak occurs in the range of 420 and 630 nm of these constant region. Also, the ε values of the Co(II) complex in the first region decrease with increasing molarity, and the ε values of the Co(II) complex at lower wavelength are higher than that of the values at higher wavelength. As seen in figure 4b, the curves of the plots consist of two region: the ε values of the Ni(II) complex sharply decrease until about 350 nm, and in the second region the ε values of the Ni(II) complex remain almost constant according to more higher εvalues after 350 nm, but a peak occurs in the range of 550 and 900 nm of these constant region. The values of the Ni(II) complex in the first region decrease with increasing molarity, and the ε values of the Ni(II) complex at lower wavelength are higher than that of the values at higher wavelength. Also, as seen in inset of figure 4b, the peak of the Ni(II) complex decreases with increasing molarity.

*The transmittance characterizations at different molarity*

The transmittance spectra of the Co(II) and Ni(II) complexes of the ligand were taken to investigate their optical properties for 1, 10, 50 and 100 mM and they are shown in figure 5(a,b), respectively. In the visible region, the average transmittance ($T_{avg}$) values of the Co(II) and Ni(II) complexes of the ligand were calculated and given

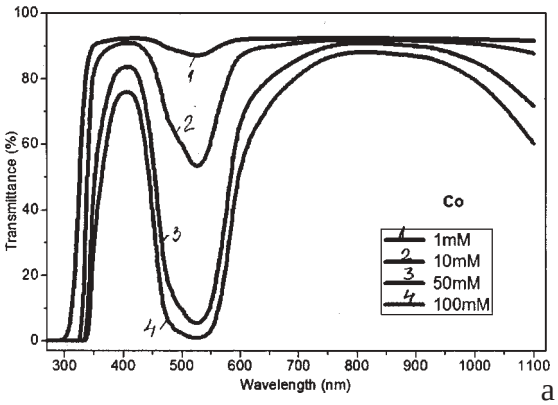



4a




b

Fig. 4. The molar extinction coefficient (ε) plots of the (a) Co(II) and (b) Ni(II) complexes of the ligand for 1, 10, 50 and 100 mM

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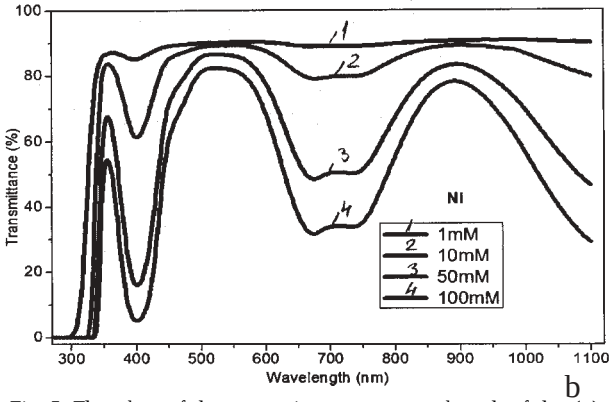



b

Fig. 5. The plots of the transmittance vs. wavelength of the (a) Co(II) and (b) Ni(II) complexes of the ligand for 1, 10, 50 and 100 mM.

in table 1. As seen in table 1, the $T_{avg}$ values (91.178% and 89.246%) of the Co(II) and Ni(II) complexes of the ligand for 1 mM are the highest values, while the $T_{avg}$ values (52.187% and 52.578%) of the Co(II) and Ni(II) complexes of the ligand for 100 mM are the lowest values. It is observed that the average transmittance values of the Co(II) and Ni(II) complexes of the ligand in the visible region decrease with increasing molarity. Also, as seen in table 1, the $T_{avg}$ value (91.178%) of the Co(II) complex of the ligand for 1

| | Co(II) | | | | Ni(II) | | | |
|---|---|---|---|---|---|---|---|---|
| Molarity (mM) | $T_{avg}$(%) | $\lambda_{max.\ peak}$ (nm) | Absorption band edge (eV) | $E_{gd}$ (eV) | $T_{avg}$(%) | $\lambda_{max.\ peak}$ (nm) | Absorption band edge (eV) | $E_{gd}$ (eV) |
| 1 | 91.178 | 346 | 3.584 | 3.971 | 89.246 | 347 | 3.574 | 3.954 |
| 10 | 81.916 | 360 | 3.445 | 3.757 | 82.937 | 353 | 3.513 | 3.745 |
| 50 | 60.605 | 390 | 3.180 | 3.645 | 64.105 | 355 | 3.493 | 3.662 |
| 100 | 52.187 | 395 | 3.139 | 3.618 | 52.578 | 355 | 3.493 | 3.632 |

**Table 1**
THE $T_{avg}$, $\lambda_{max.\ peak}$, ABSORPTION BAND EDGE, $E_{gd}$ VALUES OF THE Co(II) AND Ni(II) COMPLEXES OF THE LIGAND AT DIFFERENT MOLARITY.

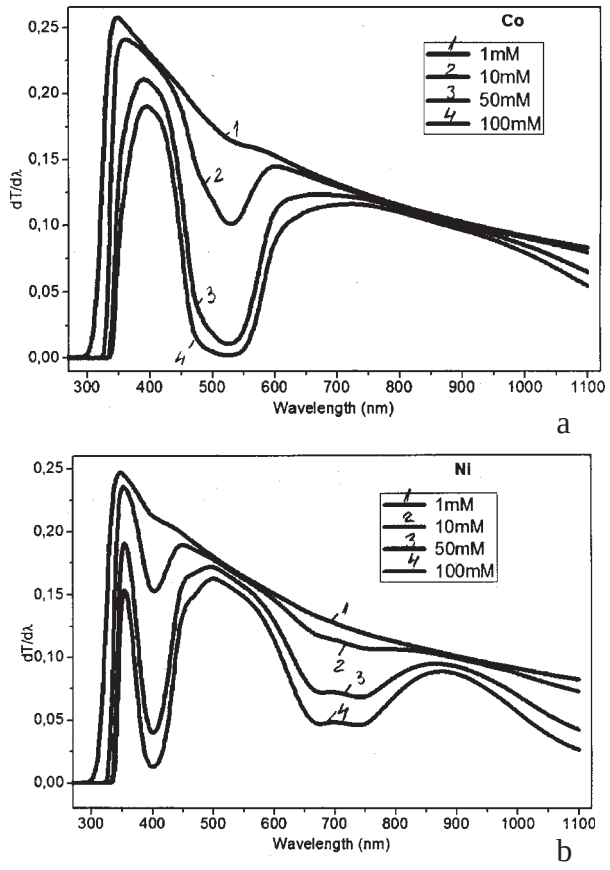



Fig. 6. The curves of dT/dλ vs. wavelength of the (a) Co(II) and (b) Ni(II) complexes of the ligand for 1, 10, 50 and 100 mM.

mM is higher than the $T_{avg}$ value (89.246%) of the Ni(II) complex of the ligand for 1 mM, while the $T_{avg}$ value (52.187%) of the Co(II) complex of the ligand for 100 mM is lower than the $T_{avg}$ value (52.578%) of the Ni(II) complex of the ligand for 100 mM. This result demonstrates that the transmittance values of the Co(II) and Ni(II) complexes of the ligand can be changed with molarity. To estimate the absorption band edge of the solutions of the Co(II) and Ni(II) complexes, the first derivative of the optical transmittance can be computed. For this purpose, we plotted the curves of dT/dë versus wavelength of the Co(II) and Ni(II) complexes for 1, 10, 50 and 100 mM, as shown in figure 6(a,b), respectively. As seen in figure 6a, the maximum peak position corresponds to the absorption band edge and there is a shift in the direction of the higher wavelengths with increasing molarity. The absorption band edge values of the Co(II) and Ni(II) complexes were calculated from the maximum peak position and given in table 1. As seen in table 1, the maximum peak values of the Co(II) complex vary from 346 to 395 nm, while the maximum peak values of the Ni(II) complex vary from 347 to 355 nm. These results suggest that the absorption band edge values of the Co(II) complex shift from 3.584 to 3.139 eV with the increasing molarity, while the absorption band edge values of the Ni(II) complex shift from 3.574 to 3.493 eV with the increasing molarity. It is observed that the rate of change in the absorption band edge of the Co(II) complex is higher than the rate of change in the absorption band edge of the Ni(II) complex with changing molarity.

*Determination of the refractive index at different molarity*

The reflectance spectra plots of the Co(II) and Ni(II) complexes of the ligand for 1, 10, 50 and 100 mM are shown in gihure 7(a,b). As seen in figure 7(a,b), reflectance spectra of the Co(II) and Ni(II) complexes change with increasing wavelength and increase with increasing molarity.

The refractive index is a significant parameter for optical applications. Thus, it is important to determine optical constants of the Co(II) and Ni(II) complexes. The complex optical refractive index of the films is expressed as,

$$n = n(\omega) + ik(\omega) \quad (2)$$

where n is the real part and k is the imaginary part of complex refractive index. The reflectance R(λ) as a function of the refractive index n and the absorption index k is given by the Fresnel Formula as [10];

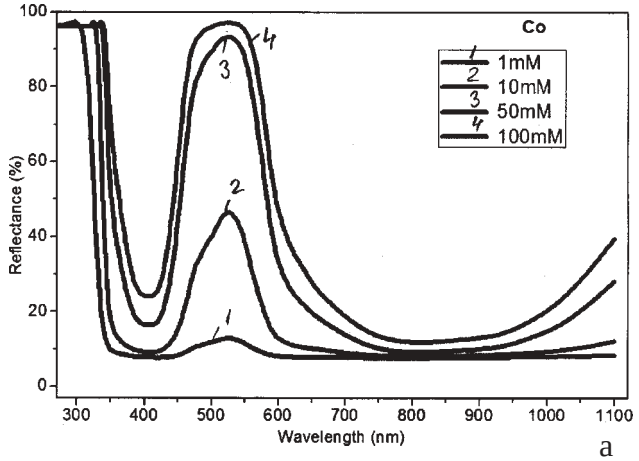
$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (3)$$

where $k = \alpha\lambda/4\pi$. When the eq. (3) is solved via elementary algebraic manipulation, then the refractive index can be obtained from the following equation,

$$n = \left\{ \left( \frac{1+R}{1-R} \right) \left[ \frac{4R}{(1-R)^2} - k^2 \right]^{1/2} \right\} \quad (4)$$

The refractive index n values of the Co(II) and Ni(II) complexes of the ligand for 1, 10, 50 and 100 mM were calculated from eq. (4). Figure 8(a,b) shows the n plot vs. wavelength of the Co(II) and Ni(II) complexes. As seen in figure 8(a,b), the refractive index values of the Co(II) and Ni(II) complexes increase with increasing molarity and show anomalous or abnormal dispersion and normal dispersion behavior. As seen in figure 8a and its inset, the n values of the Co(II) complex increase with increasing wavelength in the spectral range of about 450-525 nm and 850-1100 nm. The regions in these ranges of wavelength are anomalous or abnormal dispersion regions. As seen in figure 8a and its inset, the n values of the Co(II) complex decrease with increasing wavelength in the spectral range of about 525-1100 nm. The region in this range of wavelength is normal dispersion region. As seen in figure 8b, the n values of the Ni(II) complex increase with increasing wavelength in the spectral range of about 550-680 nm and 900-1100 nm. The regions in these ranges of wavelength are anomalous or abnormal dispersion regions. As seen in figure 8b, the n values of the Ni(II) complex decrease with increasing wavelength in the spectral range of about 680-900 nm. The region in this range of wavelength is normal dispersion region. These results show that the plots of refractive index of the Co(II) and Ni(II) complexes consist of two anomalous (abnormal) dispersion region and one normal dispersion region. In our study, the normal dispersion region can be used for determination of the main dispersion parameters of the Co(II) and Ni(II) complexes [11]. The abnormal (anomalous) behaviors of the Co(II) and Ni(II) complexes are owing to the resonance effect between the electrons polarization and the incident electromagnetic radiation, which leads to the coupling of electrons in solutions of the Co(II) and Ni(II) complexes to the oscillating electric field [12]. As seen in figure 8c, the n values of the Co(II) complex in lower wavelength (about $\lambda < 570$ nm) are higher than that of the values of the Ni(II) complex, while the n values of the Co(II) complex in higher wavelength (about $\lambda > 570$ nm) are lower than that of the values of the Ni(II) complex.

*Optical band gap properties of the Co(II) and Ni(II) complexes of the ligand at different molarity*



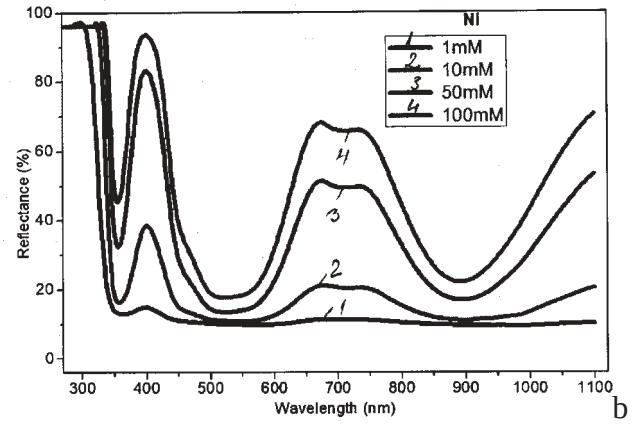
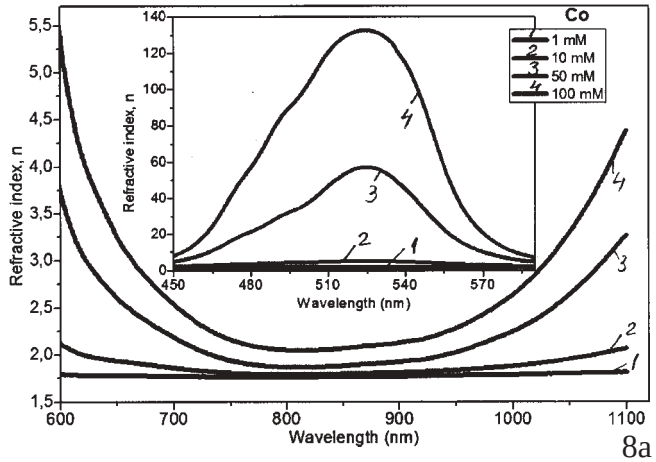
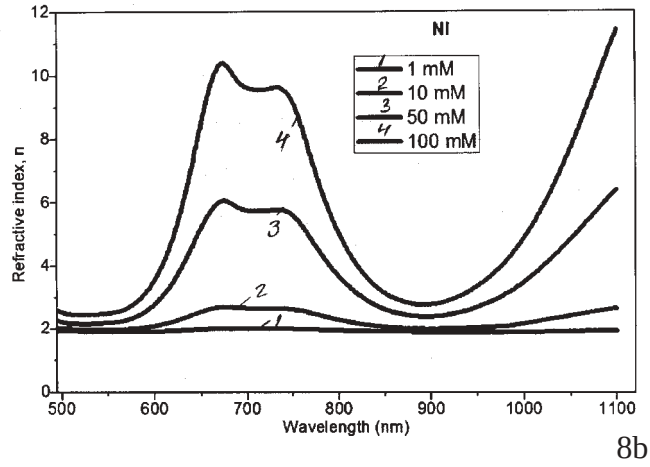




Fig. 7. The plots of the reflectance spectra vs. wavelength of the (a) Co(II) and (b) Ni(II) complexes of the ligand for 1, 10, 50 and 100 mM.



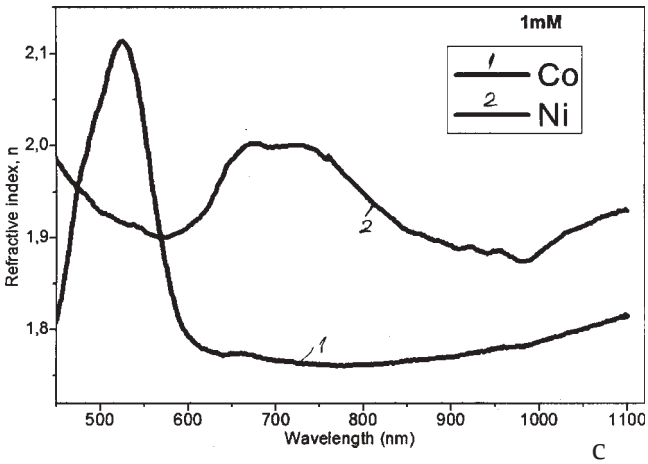




Fig. 8. The n plots vs. wavelength of the (a) Co(II) and (b) Ni(II) complexes of the ligand for 1, 10, 50 and 100 mM, (c) both Co(II) and Ni(II) complexes of the ligand for 1 mM.

The optical band gap of optical transitions can be obtained dependence of absorption coefficient on photon energy. It is evaluated that the band structure of the film obeys the rule of direct transition and in a direct band gap material; the absorption coefficient dependence on photon energy is analyzed by the following relation [13, 14],

$$\alpha = A(h\nu - E_g)^m \quad (5)$$

where A is a constant, $h\nu$ is the photon energy, $E_g$ is the optical band and m is the parameter measuring type of band gaps. To determine the optical band gap of the Co(II) and Ni(II) complexes, the $(\alpha h\nu)^2$ plots vs. the photon energy E of the Co(II) and Ni(II) complexes are shown in figure 9(a,b). As seen in inset of figure 9(a,b), there is a linear region for the direct band gap the $E_{gd}$ of the Co(II) and Ni(II) complexes. By extrapolating the linear plot to $(\alpha h\nu)^2=0$, the $E_{gd}$ values of the Co(II) and Ni(II) complexes were obtained and given in table 1. As seen in table 1, the $E_{gd}$ values of the Co(II) and Ni(II) complexes decrease with increasing molarity. The $E_{gd}$ value (3.971 eV) of the Co(II) complex for 1 mM is the highest value of all the solutions, while the $E_{gd}$ value (3.618 eV) of the Co(II) complex for 100 mM is the lowest value of all the solutions. This suggests that the direct energy-gap of the Co(II) complex can be more decreased with increasing molarity. The $E_{gd}$ value (3.954 eV) of the Ni(II) complex for 1 mM is lower than the $E_{gd}$ value (3.971 eV) of the Co(II) complex for 1 mM, while the $E_{gd}$ value (3.632 eV) of the Ni(II) complex for 100 mM is higher than the $E_{gd}$ value (3.618 eV) of the Co(II) complex for 100 mM.

*The effect on the optical properties of the volume of working stock of the Co(II) and Ni(II) complexes of the ligand for 50 mM*

In this section, we used the solutions of the Co(II) and Ni(II) complexes prepared for 50 mM. Here, the 3.0 mL solutions of the Co(II) and Ni(II) complexes are used to measure the optical properties of them. Firstly, we measured 3.0 mL solutions of both complexes, then we performed the optical measurements for 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni (II) solutions (v/v), respectively.

The plots of the absorbance vs. wavelength of the solutions of the Co(II) and Ni(II) complexes for 0.0/3.0, 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni(II) solutions (v/v) are shown in Fig. 10(a,b), respectively. As seen in figure 10(a,b) and their insets, the absorbance

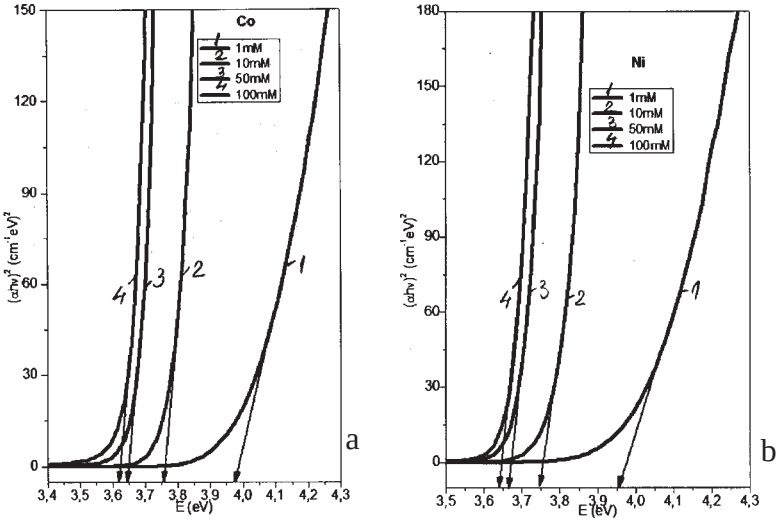



Fig. 9. The $(\alpha h\nu)^2$ plots vs. the photon energy E of the (a) Co(II) and (b) Ni(II) complexes of the ligand for 1, 10, 50 and 100 mM.

| DMF:CoS or NiS (v/v) | Co(II) $T_{avg}$(%) | Co(II) $\lambda_{max.\ peak}$ (nm) | Co(II) Absorption band edge (eV) | Co(II) $E_{gd}$ (eV) | Ni(II) $T_{avg}$(%) | Ni(II) $\lambda_{max.\ peak}$ (nm) | Ni(II) Absorption band edge (eV) | Ni(II) $E_{gd}$ (eV) |
|---|---|---|---|---|---|---|---|---|
| **0.0:3.0** | 60.605 | 390 | 3.180 | 3.645 | 64.105 | 355 | 3.493 | 3.662 |
| **0.5:2.5** | 60.639 | 390 | 3.180 | 3.665 | 63.634 | 354 | 3.503 | 3.667 |
| **1.0:2.0** | 64.077 | 389 | 3.188 | 3.674 | 70.605 | 354 | 3.503 | 3.683 |
| **1.5:1.5** | 72.150 | 380 | 3.263 | 3.703 | 78.662 | 354 | 3.503 | 3.705 |
| **2.0:1.0** | 75.670 | 377 | 3.289 | 3.723 | 79.661 | 354 | 3.503 | 3.714 |

**Table 2**
THE $T_{avg}$,$\lambda_{max.\ peak}$, ABSORPTION BAND EDGE, $E_{gd}$ VALUES OF THE Co(II) AND Ni(II) COMPLEXES OF THE LIGAND FOR DIFFERENT DMF/CO(II) AND NI(II) SOLUTIONS (v/v)

values of the Co(II) and Ni(II) complexes decrease with increasing volume of DMF solvent or decreasing volume of the solutions of the Co(II) and Ni(II) complexes.

The molar extinction coefficient (ε) values of the solutions of the Co(II) and Ni(II) complexes for 0.0/3.0, 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni (II) solutions (v/v) were calculated from eq. (1). The å values of the Co(II) and Ni(II) complexes of the ligand are shown in figure 11(a,b), respectively. As seen in inset of figure 11a, the ε value (24.46 $Lmol^{-1}cm^{-1}$) of the Co(II) complex at 525 nm for 0.0 mL/3.0 mL DMF/Co(II) solution (v/v) is 3.088 times higher than the ε value (7.92 $Lmol^{-1}cm^{-1}$) of the Co(II) complex at 525 nm for 2.0 mL/1.0 mL DMF/Co(II) solution (v/v). As seen in inset of figure 11b, the ε value (15.14 $Lmol^{-1}cm^{-1}$) of the Ni(II) complex at 400 nm for 0.0 mL/3.0 mL DMF/Ni(II) solution (v/v) is 2.713 times higher than the ε value (5.58 $Lmol^{-1}cm^{-1}$) of the Ni(II) complex at 400 nm for 2.0 mL/1.0 mL DMF/Ni(II) solution (v/v). As seen in figure 11(a,b) and their insets, the molar extinction coefficients of the Co(II) and Ni(II) complexes decrease with increasing volume of DMF solvent or decreasing volume of the solutions of the Co(II) and Ni(II) complexes.

The transmittance spectra plots of the Co(II) and Ni(II) complexes of the ligand for 0.0/3.0, 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni(II) solutions (v/v) are shown in figure 12(a,b), respectively. In the visible region, the average transmittance ($T_{avg}$) values of the Co(II) and Ni(II) complexes of the ligand were calculated and given in table 2. As seen in table 2, the $T_{avg}$ values (60.605% and 64.105%) of the Co(II) and Ni(II) complexes of the ligand for 0.0 mL/3.0 mL DMF/Co(II) and Ni(II) solutions (v/v) are the lowest values, while the $T_{avg}$ values (75.670% and 79.661%) of the Co(II) and Ni(II) complexes of the ligand for 2.0 mL/1.0 mL DMF/Co(II) and Ni(II) solutions (v/v) are the highest. These results show that the average transmittance values of the Co(II) and Ni(II) complexes in the visible region increase with increasing volume of DMF solvent or decreasing volume of the solutions of the Co(II) and Ni(II) complexes.

The curves of $dT/d\lambda$ versus wavelength of the Co(II) and Ni(II) complexes for 0.0/3.0, 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni(II) solutions (v/v) are displayed in figure 13(a,b), respectively. The absorption band edge values of the Co(II) and Ni(II) complexes were calculated from the maximum peak position and given in table 2. As seen in table 2, the maximum peak values of the Co(II) complex vary from 390 to 377 nm, while the maximum peak values of the Ni(II) complex vary very little from 355 to 354 nm. These results suggest that the absorption band edge values of the Co(II) complex shift from 3.180 to 3.289 eV, while the absorption band edge values of the Ni(II) complex shift only from 3.493 to 3.503 eV with increasing volume of DMF solvent or decreasing volume of the solutions of the Co(II) and Ni(II) complexes.

The reflectance spectra plots of the Co(II) and Ni(II) complexes of the ligand for 0.0/3.0, 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni(II) solutions (v/v) are shown in figure 14(a,b). As seen in figure 14(a,b), reflectance spectra of the Co(II) and Ni(II) complexes change with increasing wavelength and decrease with increasing volume of DMF solvent or decreasing volume of the solutions of the Co(II) and Ni(II) complexes.

The refractive index n values of the Co(II) and Ni(II) complexes of the ligand for 0.0/3.0, 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni (II) solutions (v/v) were calculated from eq. (4). Figure 15(a,b) shows the n plot vs. wavelength of the Co(II) and Ni(II) complexes. As seen in figure 15(a,b), the refractive index values of the Co(II) and Ni(II) complexes change with increasing wavelength and decrease with increasing volume of DMF

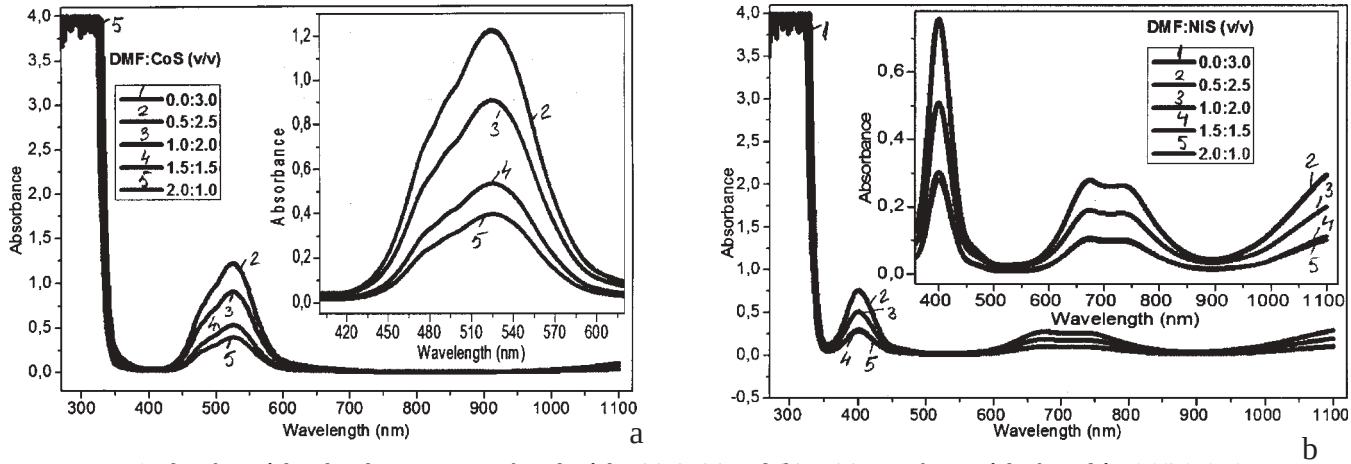



Fig. 10. The plots of the absorbance vs. wavelength of the (a) Co(II) and (b) Ni(II) complexes of the ligand for 0.0/3.0, 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni (II) solutions (v/v)

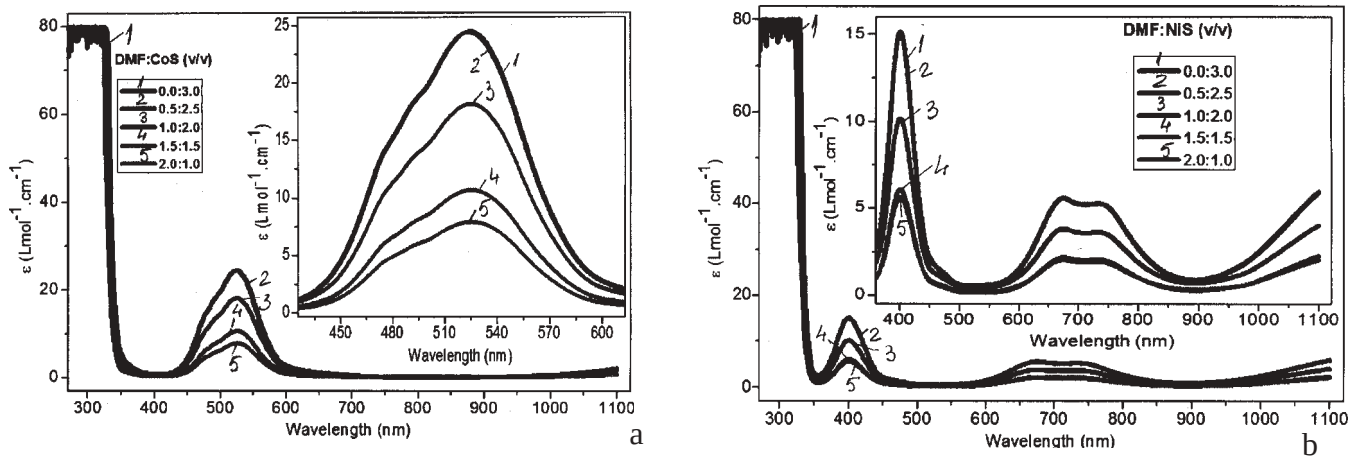



Fig. 11. The molar extinction coefficient (ε) plots of the (a) Co(II) and (b) Ni(II) complexes of the ligand for 0.0/3.0, 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni (II) solutions (v/v)

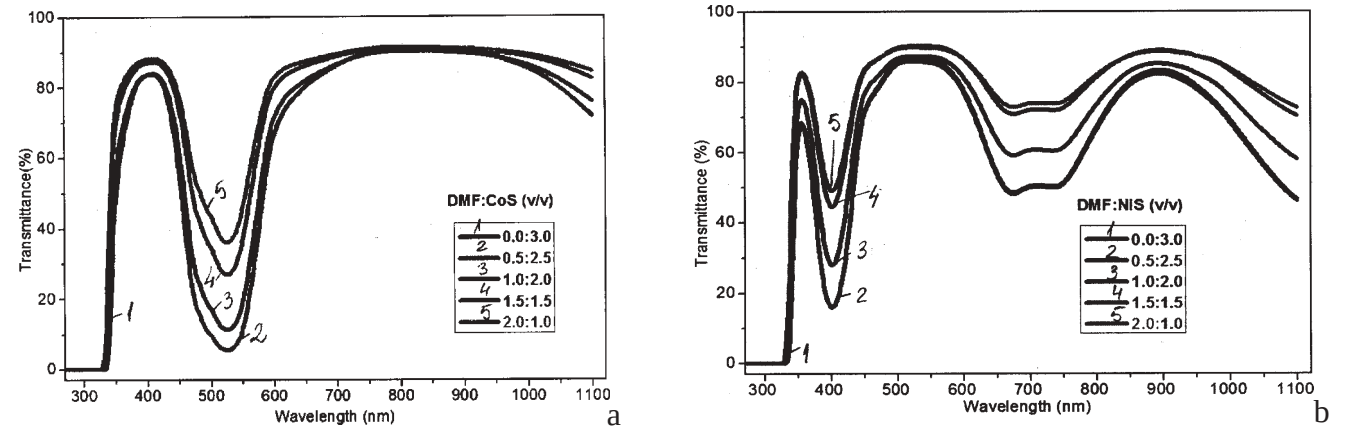



Fig. 12. The plots of the transmittance vs. wavelength of the (a) Co(II) and (b) Ni(II) complexes of the ligand for 0.0/3.0, 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni (II) solutions (v/v)

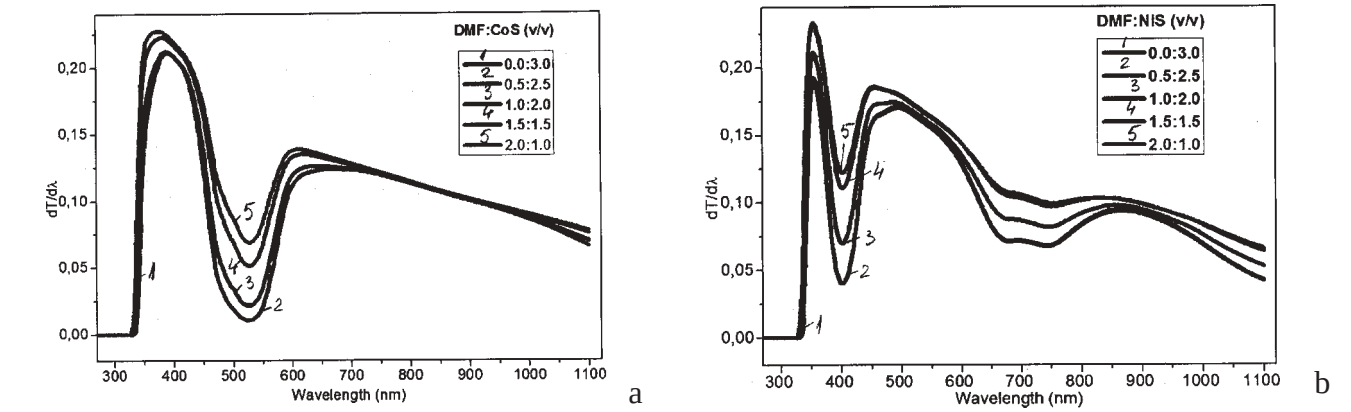



Fig. 13. The curves of dT/dλ vs. wavelength of the (a) Co(II) and (b) Ni(II) complexes of the ligand for 0.0/3.0, 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni (II) solutions (v/v).

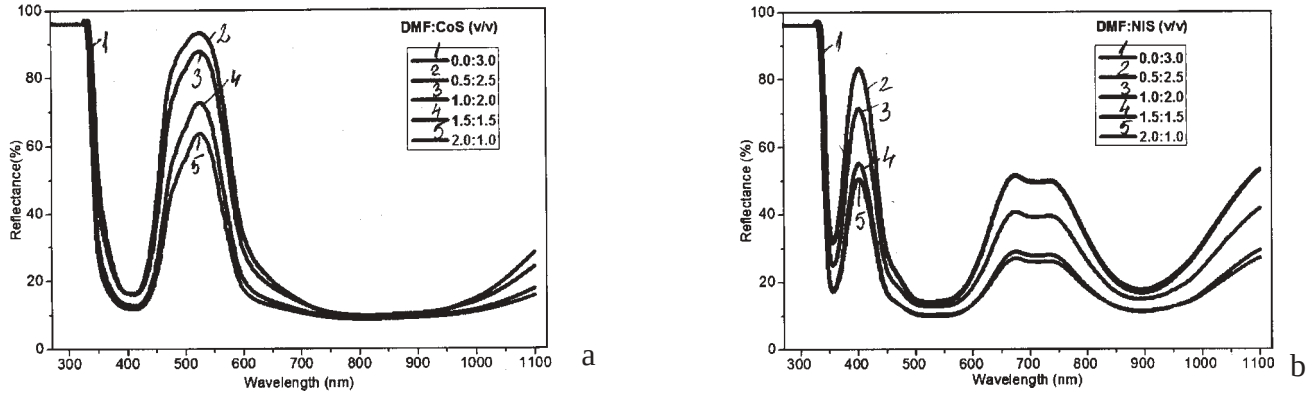



Fig. 14. The plots of the reflectance spectra vs. wavelength of the (a) Co(II) and (b) Ni(II) complexes of the ligand for 0.0/3.0, 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni (II) solutions (v/v)

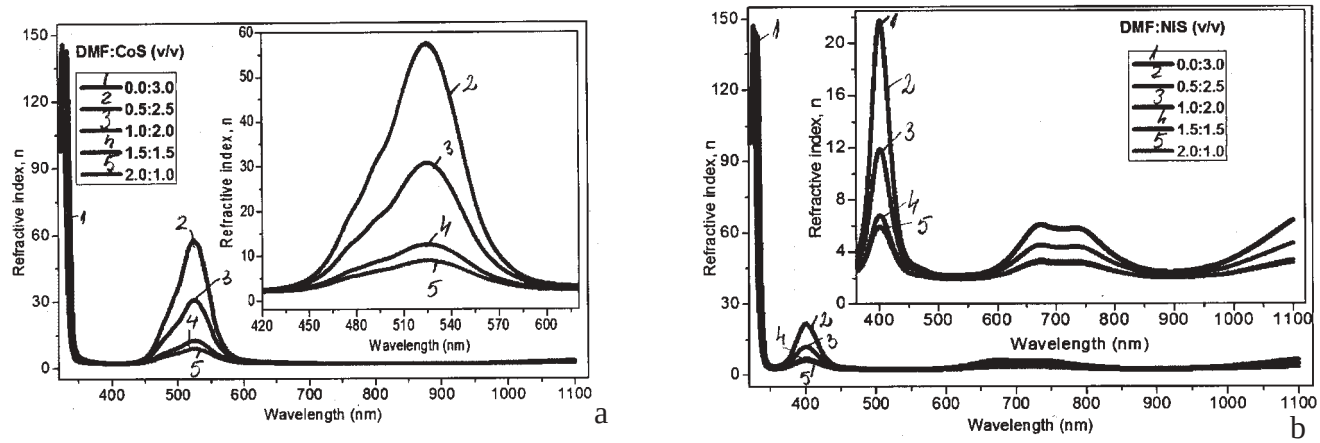



Fig. 15. The n plots vs. wavelength of the (a) Co(II) and (b) Ni(II) complexes of the ligand for 0.0/3.0, 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni (II) solutions (v/v)

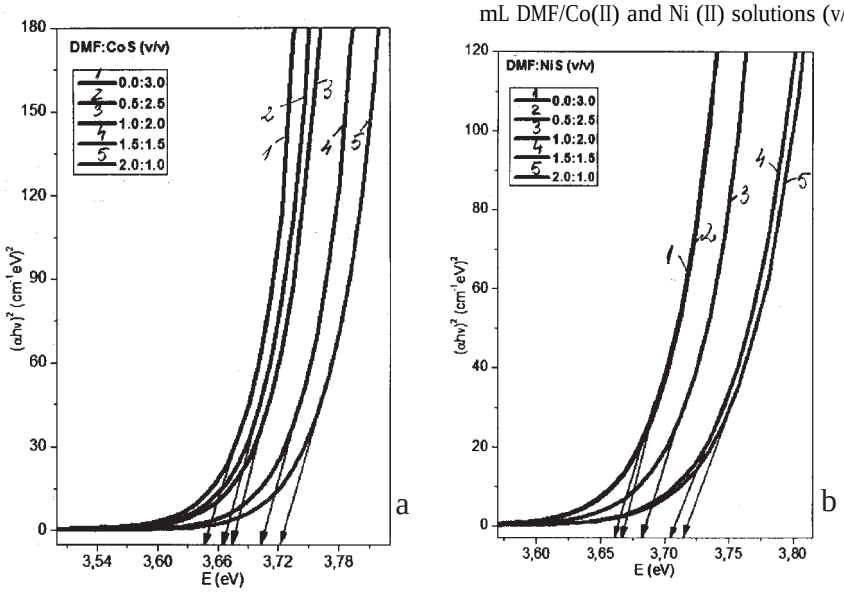



Fig. 16. The $(\alpha h\nu)^2$ plots vs. the photon energy E of the (a) Co(II) and (b) Ni(II) complexes of the ligand for 0.0/3.0, 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni (II) solutions (v/v).

solvent or decreasing volume of the solutions of the Co(II) and Ni(II) complexes.

To determine the optical band gap of the Co(II) and Ni(II) complexes, the $(\alpha h\nu)^2$ plots vs. the E of the Co(II) and Ni(II) complexes for 0.0/3.0, 0.5/2.5, 1.0/2.0, 1.5/1.5 and 2.0 mL/1.0 mL DMF/Co(II) and Ni(II) solutions (v/v) are shown in figure 16(a,b). By extrapolating the linear plot to $(\alpha h\nu)^2=0$, the $E_{gd}$ values of the Co(II) and Ni(II) complexes were obtained and given in table 2. As seen in table 2, the $E_{gd}$ values of the Co(II) and Ni(II) complexes increase with increasing volume of DMF solvent or decreasing volume of the solutions of the Co(II) and Ni(II) complexes.

## Conclusions

The molar extinction coefficients (ε) values of the Co(II) and Ni(II) complexes in the first region decrease with increasing molarity, and the ε values of the Co(II) and Ni(II) complexes at lower wavelength are higher than that of the values at higher wavelength. The $T_{avg}$ values (91.178% and 89.246%) of the Co(II) and Ni(II) complexes of the ligand for 1 mM are the highest values, while the $T_{avg}$ values (52.187% and 52.578%) of the Co(II) and Ni(II) complexes of the ligand for 100 mM are the lowest values. The $T_{avg}$ value (91.178%) of the Co(II) complex of the ligand for 1 mM is higher than the $T_{avg}$ value (81.916%) of the Ni(II) complex of the ligand for 1 mM, while the $T_{avg}$ value (52.187%) of the Co(II) complex of the ligand for 100 mM is lower than the $T_{avg}$ value (52.578%) of the Ni(II) complex

of the ligand for 100 mM. The absorption band edge values of the Co(II) complex shift from 3.584 to 3.139 eV with the increasing molarity, while the absorption band edge values of the Ni(II) complex shift from 3.574 to 3.493 eV with the increasing molarity. The plots of refractive index of the Co(II) and Ni(II) complexes consist of two anomalous (abnormal) dispersion region and one normal dispersion region. The $E_{gd}$ values of the Co(II) and Ni(II) complexes decrease with increasing molarity. The $E_{gd}$ value (3.971 eV) of the Co(II) complex for 1 mM is the highest value of all the solutions, while the $E_{gd}$ value (3.618 eV) of the Co(II) complex for 100 mM is the lowest value of all the solutions. This suggests that the direct energy-gap of the Co(II) complex can be more decreased with molarity. The $E_{gd}$ value (3.954 eV) of the Ni(II) complex for 1 mM is lower than the $E_{gd}$ value (3.971 eV) of the Co(II) complex for 1 mM, while the $E_{gd}$ value (3.632 eV) of the Ni(II) complex for 100 mM is higher than the $E_{gd}$ value (3.618 eV) of the Co(II) complex for 100 mM. The absorbance, molar extinction coefficients, refractive index values of the Co(II) and Ni(II) complexes decrease, while the average transmittance in the visible region, direct optical band-gap values of the Co(II) and Ni(II) complexes increase with increasing volume of DMF solvent or decreasing volume of the solutions of the Co(II) and Ni(II) complexes [15]. In our next study we will synthesis mixed ligand copmlexes of saccharin and will investigated their optical properties. We will use as reference these data at the next study.

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