

# Synthesis, structural and optical properties of novel borylated Cu(II) and Co(II) metal complexes of 4-benzylaminobiphenylglyoxime

Fatma Karipcin <sup>a</sup>, Saliha Ilican <sup>b,\*</sup>, Yasemin Caglar <sup>b</sup>, Mujdat Caglar <sup>b</sup>,  
Bülent Dede <sup>a</sup>, Yücel Şahin <sup>c</sup>

<sup>a</sup> Süleyman Demirel University, Faculty of Art and Sciences, Department of Chemistry, 32260 Isparta, Turkey

<sup>b</sup> Anadolu University, Faculty of Science, Department of Physics, 26470 Eskisehir, Turkey

<sup>c</sup> Anadolu University, Faculty of Science, Department of Chemistry, 26470 Eskisehir, Turkey

Received 4 January 2007; received in revised form 14 February 2007; accepted 15 February 2007

Available online 24 February 2007

## Abstract

4-Benzylaminobiphenylglyoxime ligand and its Cu(II) and Co(II) complexes were prepared. BF<sub>2</sub><sup>+</sup>-bridge containing 4-benzylaminobiphenylglyoxime complexes were obtained by replacing of the bridging protons of the dioxime complexes with BF<sub>2</sub> group. These compounds have been characterized by elemental analysis, spectroscopic (ICP-OES, infra-red) and magnetic susceptibility measurements. Thermal decomposition of the complexes is studied in nitrogen atmosphere. The final decomposition products are found to be the corresponding metal oxides. The optical constants such as optical conductivity, dielectric constant, refractive index were determined for the complexes. The analysis of the optical absorption data revealed that the band gap  $E_g$  was direct transitions. The optical dispersion parameters were determined according to Wemple and Didomenico method.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Borylated; Dioxime complexes; Magnetic properties; Optical constants; Dispersion parameters

## 1. Introduction

The chemistry of transition metal complexes with  $\alpha$ -dioxime ligands has been well studied and is the subject of several reviews and a lot of papers [1–7]. The presence of mildly acidic hydroxyl group and slightly basic nitrogen atoms causes *vic*-dioximes to be amphoteric ligands which form corrin type square-planar, square-pyramidal and octahedral complexes with transition metal cations such as cobalt(II) and copper(II) as central atoms. The lack of reactivity of the OH groups in the coordinated oximes was caused by the intramolecular hydrogen bonds O–H···O, existing in these compounds. Experiments on the reactivity of cobalt(II) and copper(II) dimethylglyoximates with boron, aluminium and zinc compounds have resulted in a new class of compounds corresponding to the formula given in

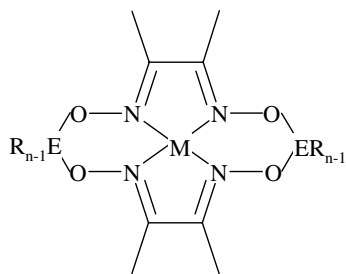
Fig. 1 [8,9]. The possibility of an apical modification of *vic*-dioximes is stipulated by the relative availability of functionalized boron-containing Lewis acids as efficient capping agents. Borylation significantly alters the character of the glyoxime complexes; solubility, color, reactivity, etc. [9,10].

Optical and electrical properties of the metal complexes have become an increasingly interesting area of semiconducting and optical materials because these materials possess great potential for device applications such as Schottky diode, light-emitted diode and optical sensor [11–13]. It is therefore important to investigate optical properties of them and obtain new optical materials based on metal complexes.

In the present study, we have prepared BF<sub>2</sub><sup>+</sup>-bridge containing 4-benzylaminobiphenylglyoximes by replace of the bridging protons of the cobalt(II) and copper(II) *vic*-dioxime complexes with BF<sub>2</sub> group. The structural characterizations of the complexes were investigated by elemental analysis, molar conductivities, magnetic moments, and IR

\* Corresponding author.

E-mail address: [silican@anadolu.edu.tr](mailto:silican@anadolu.edu.tr) (S. Ilican).



E=Al, B, Zn; n is the E metal valence

R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>, i-C<sub>4</sub>H<sub>9</sub>, Cl

Fig. 1. Formula for new class of compounds.

spectra. Furthermore, we also investigated the optical properties of these complexes to encourage the researchers for applying these materials in optical communication and optical devices.

## 2. Experimental details

### 2.1. Materials and methods

All solvents, benzyl amine and metal salts [CoCl<sub>2</sub> · 6H<sub>2</sub>O, Cu(AcO)<sub>2</sub> · H<sub>2</sub>O] used for the synthesis and physical measurements were purchased Aldrich, J.T. Baker and Merck were used without further purification. 4-(Chloroacetyl)biphenyl [14], 4-biphenylhydroximoyl chloride (HL) [14], 4-biphenylchloroglyoxime (H<sub>2</sub>L) [14,15], 4-benzylaminobiphenylglyoxime ligand (H<sub>2</sub>L<sup>1</sup>) and their Co(II) and Cu(II) complexes [3] were synthesized according to literature procedures. IR spectra (4000–400 cm<sup>-1</sup>) were recorded on a Shimadzu IRPrestige-21 FT-IR Spectrophotometer as KBr pellets. Carbon, hydrogen and nitrogen analysis were performed on a LECO 932 CHNS analyzer. B, Co and Cu contents were measured on Perkin–Elmer Optima 5300 DV ICP-OES Spectrometer. The conductance measurements were carried out using an Optic Ivymen System conductivity meter. Room temperature magnetic susceptibility measurements were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MX1). Melting points were measured on an IA 9100 Electrothermal apparatus. A Perkin–Elmer Diamond TGA thermal analyzer was used to record simultaneously TG and DTG curves. The experiments were carried out in dynamic nitrogen atmosphere (20 mL min<sup>-1</sup>) with a heating rate of 10 °C min<sup>-1</sup> in temperature range 20–1000 °C using platinum crucibles. The UV–Vis spectra of the films were recorded from 200 to 900 nm wavelength using Shimadzu UV-2450 UV–Vis Spectrophotometer at room temperature.

### 2.2. Preparation of the BF<sub>2</sub><sup>+</sup>-bridge containing Co(II) and Cu(II) vic-dioxime complexes [M(L<sup>1</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(BF<sub>2</sub>)<sub>2</sub>]

General procedure: The suspension of Co(II) and Cu(II) vic-dioxime complexes (0.5 mmol) in freshly distilled dry

acetonitrile (40 mL) was brought to the reflux temperature under an oxygen-free nitrogen atmosphere. Boron trifluoride diethyl ether complex (0.25 mL, 1 mmol) in acetonitrile (2 mL) was slowly added while the mixture was stirred. The resulting reaction mixture was completely dissolved within 30 min. After this changing, the mixture was refluxed 30 min further and the solvent was removed to dryness under reduced pressure. Then the residue was dissolved in acetonitrile (10 mL) and evaporated to dryness. The last step was repeated twice and the residue was dissolved in 10 mL of acetonitrile and then allowed to cool in refrigerator at overnight whereupon the product crystallized from the solution. The resulting products were filtered and then recrystallized from CHCl<sub>3</sub>–hexane (1:1). The last products were filtered, washed with diethyl ether and dried on P<sub>4</sub>O<sub>10</sub>.

[Co(L<sup>1</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(BF<sub>2</sub>)<sub>2</sub>]: Light brown complex, m.p. 172 °C, was isolated in 38% yield; IR (KBr disc.)/cm<sup>-1</sup> 3360(N–H); 1606(C=N); 1222(B–O); 1045(B–F); 942(N–O); molar conductivity (A<sub>m</sub>): 37 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>; μ<sub>eff</sub> = 3.12 B.M.; Elemental Anal. Calc. for C<sub>42</sub>H<sub>38</sub>N<sub>6</sub>O<sub>6</sub>CoB<sub>2</sub>F<sub>4</sub>: C, 57.37; H, 4.35; N, 9.56; Co, 6.70; B, 2.46. Found: C, 57.19; H, 3.96; N, 9.21; Co, 6.41; B, 2.34%.

[Co(HL<sup>1</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]: IR (KBr disc.)/cm<sup>-1</sup> 3443(H<sub>2</sub>O/OH); 3399(N–H); 1710(O–H–O); 1599(C=N); 1007(N–O) [3].

[Cu(L<sup>1</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(BF<sub>2</sub>)<sub>2</sub>]: Green complex, m.p. 140 °C, was isolated in 60% yield; IR (KBr disc.)/cm<sup>-1</sup> 3353(N–H); 1604(C=N); 1227(B–O); 1039(B–F); 937(N–O); molar conductivity (A<sub>m</sub>): 30 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>; μ<sub>eff</sub> = 1.65 B.M.; Elemental Anal. Calc. for C<sub>42</sub>H<sub>38</sub>N<sub>6</sub>O<sub>6</sub>CuB<sub>2</sub>F<sub>4</sub>: C, 57.07; H, 4.33; N, 9.51; Cu, 7.19; B, 2.45. Found: C, 56.86; H, 4.25; N, 9.15; Cu, 6.82; B, 2.27%.

[Cu(HL<sup>1</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]: IR (KBr disc.)/cm<sup>-1</sup> 3448(H<sub>2</sub>O/OH); 3401(N–H); 1710(O–H–O); 1602(C=N); 1007(N–O) [3].

The complex solutions were poured onto a glass substrate and then drying at 30 °C for 30 min was applied to obtain the thin film. The thicknesses of the films were determined as about 1 μm with Mettler Toledo MX5 microbalance by using weighing method.

## 3. Results and discussion

### 3.1. Synthesis of cobalt(II) and copper(II) vic-dioxime complexes with BF<sub>2</sub> group

4-(Chloroacetyl)biphenyl was prepared from chloroacetyl chloride and biphenyl in presence of aluminum chloride according to Friedel–Crafts acylation [14]. 4-Biphenylhydroximoyl chloride (HL) was obtained by reacting 4-(chloroacetyl)biphenyl with alkyl nitride in presence of dry HCl gas [14]. Subsequently, 4-biphenylchloroglyoxime (H<sub>2</sub>L) was prepared by the reaction of 4-biphenylhydroximoyl chloride and hydroxylamine hydrochloride [14,15]. Then, 4-benzylaminobiphenylglyoxime ligand (H<sub>2</sub>L<sup>1</sup>) has been synthesized from 4-biphenylchloroglyoxime and benzyl-

amine. M(II)-dioxime complexes of the type  $[M(HL^1)_2(H_2O)_2]$  [ $M(II) = Co(II)$  and  $Cu(II)$ ] have been synthesized using a standard procedure [3].  $BF_2^+$ -bridge containing 4-benzylaminobiphenylglyoxime complexes were synthesized by adding boron trifluoride diethyl ether complex to a refluxing acetonitrile solution containing the appropriate metal-dioxime complexes.

For the structural characterization of metal complexes, elemental analysis, ICP-OES, FT-IR and magnetic susceptibility measurements were used. The metal-to-ligand ratio of the complexes (1–2) was not change with replacing of the bridging protons of the dioxime complexes with  $BF_2$  group.

### 3.2. FT-IR Spectra

The FT-IR spectra of 4-benzylaminobiphenylglyoxime complexes (as KBr pellets) of the general formula  $[M(HL^1)_2(H_2O)_2]$ , exhibited  $C=N$  absorptions at  $1599$ – $1602\text{ cm}^{-1}$ . These facts suggest that the ligands is  $N,N'$  coordinated with  $M(II)$  ion to look like the proposed structure shown in Fig. 2 [3]. In the FT-IR spectra of the  $BF_2^+$ -capped  $M(II)$  complexes, a upward shift to for the  $C=N$  frequencies ( $1604$ – $1606\text{ cm}^{-1}$ ) indicated coordination through the N atoms. The upwards shift observed in the  $BF_2^+$ -bridged complexes were due to the strong electron-withdrawing effect of the boron linked groups incorporated into the dioxime complexes [6]. The broad band at  $1710\text{ cm}^{-1}$  assigned to the  $O-H-O$  bending vibrations, disappeared upon insertion of  $BF_2$  groups with the simultaneous appearance of peaks  $1222$ – $1227$  and  $1039$ – $1045\text{ cm}^{-1}$  for the  $B-O$  and  $B-F$  resonances, respectively. In the IR spectra of borlated metal complexes, bands at  $3353$ – $3360$  and  $942$ – $937\text{ cm}^{-1}$  belong to  $N-H$  and  $N-O$  stretching vibrations, respectively. In the complexes, broad bands in the  $3448$ – $3429\text{ cm}^{-1}$  range may be assigned to  $\nu(H_2O)$  of coordinated water molecules [16]. These vibration data are in agreement with those previously reported for borlated metal complexes [6–8,17,18].

According to the IR spectra, elemental analysis and magnetic susceptibility data, the complexes have a metal:ligand ratio of 1:2 and an octahedral structure (Fig. 3). The room temperature magnetic moment measurements show

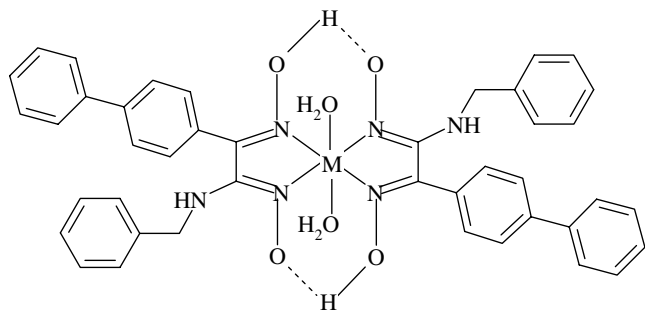


Fig. 2. The structure of 4-benzylaminobiphenylglyoxime complexes [ $M = Cu(II)$  and  $Co(II)$ ].

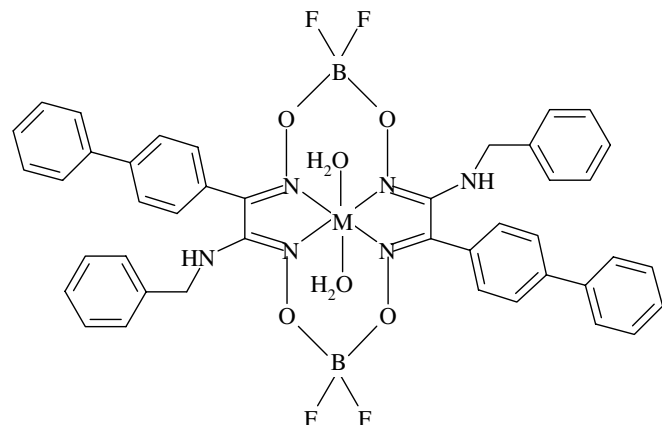


Fig. 3. The structure of borlated 4-benzylaminobiphenylglyoxime complexes [ $M = Cu(II)$  and  $Co(II)$ ].

that the  $Co(II)$  complex is paramagnetic with magnetic susceptibility 3.12. Magnetic susceptibility values of this  $Co(II)$  complex is within the range of high spin octahedral cobalt(II) complexes (the three-spin value is 3.87 B.M.). The  $Cu(II)$  complexes also was found to be paramagnetic with  $\mu_{\text{eff}} = 1.65$  B.M. This value fits the spin values 1.73 B.M. Though these are somewhat low values for the magnetic moments, there is likely some diamagnetism being contributed from the ligand ultimately decreasing the total paramagnetism of the complexes [19].

### 3.3. Thermogravimetric (TG) analysis

Thermal data of the complexes are given in Table 1. The correlations between the different decomposition steps of the complexes with the corresponding weight losses are discussed in terms of the proposed formulae of the complexes.

The  $Co(II)$  complex with the formula  $[C_{42}H_{38}N_6O_6CoB_2F_4]$  was thermally decomposed in three successive decomposition steps. The first estimated mass loss of 4.40% (calculated mass loss = 4.09%) within the temperature range  $160$ – $210\text{ }^\circ\text{C}$  may be attributed to the thermal dehydration of the complex. The last two decomposition steps occur within the temperature range  $200$ – $820\text{ }^\circ\text{C}$  with an estimated mass loss 86.90% (calculated mass loss = 87.39%), which is reasonably accounted for the loss of the ligand molecules leaving  $CoO$  as residue with total estimated mass loss 91.30% (total calculated mass loss = 91.48%). The theoretical and the experimental per cent mass losses obtained from these decomposition stages are in good agreement.

It is noted from the TG analysis that the  $Cu(II)$  complex with the general formula  $[C_{42}H_{38}N_6O_6CuB_2F_4]$ , loses 91.00% of its original mass between  $120$  and  $650\text{ }^\circ\text{C}$  and the 9% residue is a black coloured solid. The sample decomposes in three stages. Corresponding to loss of coordinated water molecules, the first decomposition occurs between  $120$  and  $200\text{ }^\circ\text{C}$  with estimated mass loss of 4.30% (calculated mass loss = 4.07%). The other two steps with estimated mass loss of 86.90%, which is due to loss of

Table 1  
Thermoanalytical results (TG, DTG) of metal complexes

Complex	TG range (°C)	DTG <sub>max</sub> (°C)	Estimated (%), calculated)		Assignment	Metallic residue
			Mass loss	Total mass loss		
Cu(II)	120–200	140	4.30 (4.07)		Loss of 2H <sub>2</sub> O (coord.)	CuO
	200–650	250, 310	86.90 (86.93)	91.20 (91.00)	Loss of ligand molecules	
Co(II)	160–210	170	4.40 (4.09)		Loss of 2H <sub>2</sub> O (coord.)	CoO
	210–820	280, 390	86.90 (87.39)	91.30 (91.48)	Loss of ligand molecules	

ligand molecules leaving CuO residue occurring within the temperature range 200–650 °C (calculated mass loss = 86.93%). The total estimated mass loss is 91.20% (total calculated mass loss = 91.00%). The mass losses found experimentally are very close to the theoretical values.

The TG studies on BF<sub>2</sub><sup>+</sup>-bridge containing chelates both Co(II) and Cu(II) showed that these two complexes have similar thermal decomposition mechanisms which is expected since they both have octahedral structure.

### 3.4. The dispersion parameters of the films

The transmittance and reflectance spectra of the films are shown in Fig. 4. The properties of the films changes with Cu(II) and Co(II) metals and this cause light loss on the films. Thus, the changes in the transmission take place. This suggests that the changes in the optical properties of the thin films are taking place and these changes affect the optical constants of the films. The optical properties of the films are characterized by the refractive index. The

refractive index is an important parameter for optical materials and applications. Optical properties were investigated for films by spectrophotometric measurement of transmittance, *T*, and reflectance, *R*, at normal incidence in the wavelength range of 190–900 nm. The refractive index of the films were calculated approximately from the following relation [20],

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

where *k* ( $k = \alpha\lambda/4\pi$ ) is the extinction coefficient. The *k* and *n* values dependence of wavelength are shown in Fig. 5a and b, respectively. The refractive index decreases with increasing wavelength. This result suggests that the films show a normal dispersion. The extinction coefficient of the Co(II) complex decreases with increasing wavelength, too. But it is not shown a considerable variation in the Cu(II) complex.

For photon energies less than the energy gap ( $E < E_g$ ), the refractive index of the film can be analyzed by Cauchy equation [21]

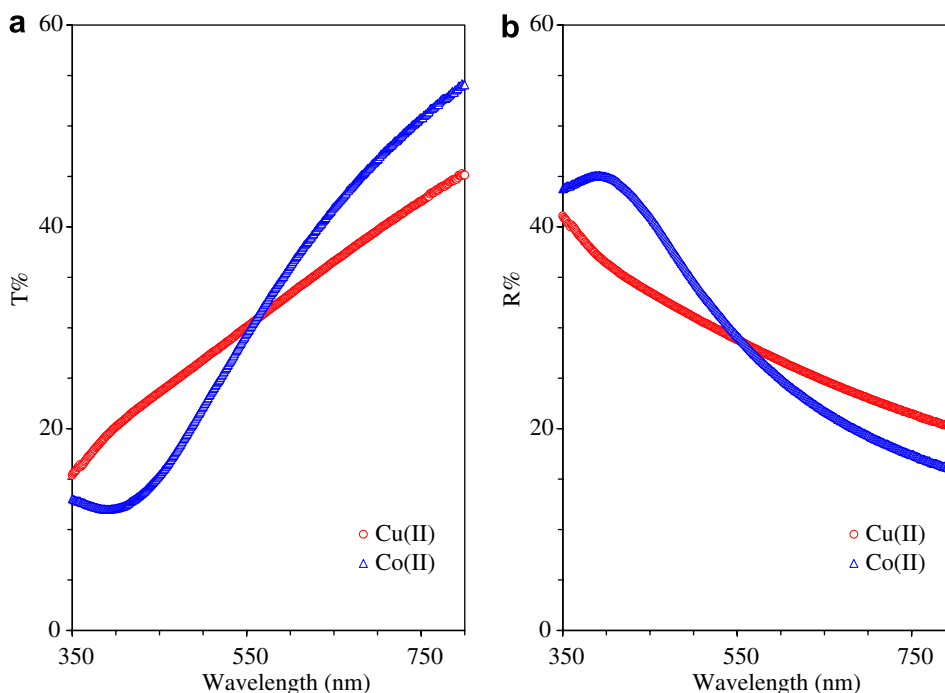


Fig. 4. (a) The transmittance and (b) reflectance spectra of the films.

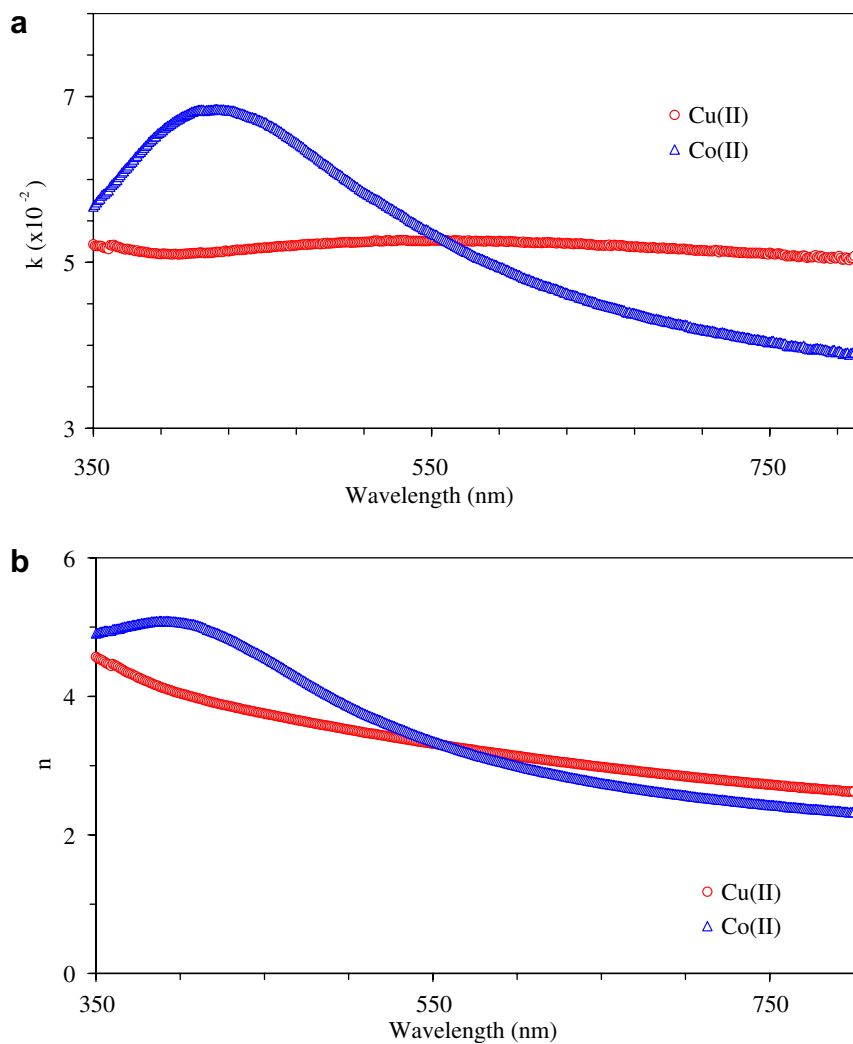


Fig. 5. The variation of (a) extinction coefficient and (b) refractive index of the films with wavelength.

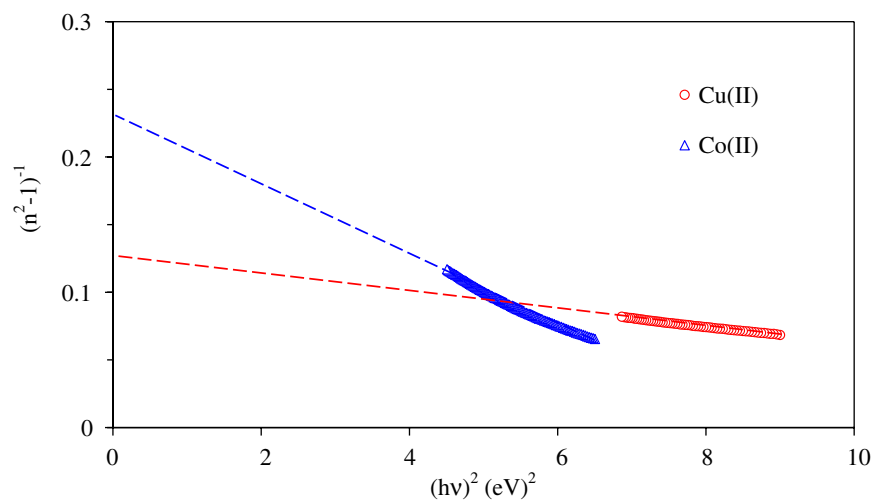


Fig. 6. Plots of  $(n^2 - 1)^{-1}$  vs.  $(h\nu)^2$  of the films.

Table 2  
The optical parameters of the films

Film	$E_g$ (eV)	$E_d$ (eV)	$E_o$ (eV)	$M_{-1}$	$M_{-3}$ (eV) <sup>-2</sup>	$\lambda_o$ (nm)	$S_o$ (m <sup>-2</sup> )	$n_\infty$	$\epsilon_\infty$
Cu(II)	2.81	36.12	4.47	8.09	0.41	278	$1.05 \times 10^{14}$	3.02	9.09
Co(II)	2.24	12.98	2.99	4.35	0.49	416	$2.51 \times 10^{13}$	2.31	5.35

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (2)$$

where  $A$ ,  $B$  and  $C$  are constants. The constants obtained from the fit are  $A = 2.497 \pm 0.005$ ,  $B = (2.548 \pm 0.01) \times 10^5 \text{ nm}^2$ ,  $C = (2.708 \pm 0.02) \times 10^{10} \text{ nm}^4$  and  $A = 1.402 \pm 0.004$ ,  $B = (5.764 \pm 0.02) \times 10^5 \text{ nm}^2$ ,  $C = (1.224 \pm 0.003) \times 10^{11} \text{ nm}^4$  for Cu(II) and Co(II) complexes, respectively. The parameter  $A$  in the Cauchy equation has the physical meaning of the electronic refractive index at infinite wavelength.

Wemple and DiDomenico [22,23] use a single-oscillator description of the frequency-dependent dielectric constant to define “dispersion energy” parameters  $E_d$  and  $E_o$ . The

Wemple and DiDomenico can fit the refractive index dispersion of the oxides studied. The dispersion plays an important role in the research for optical materials, because it is a significant factor in optical communication and in designing devices for spectral dispersion. Although these rules are quite different in detail, one common feature is the over-whelming evidence that both crystal structure and ionicity influence the refractive-index behaviour of solids in ways that can be simply described [22]. Wemple and DiDomenico have analyzed more than 100 widely different solids and liquids using a single-effective-oscillator fit of the form [22,23]. The model describes the dielectric response for transitions below the optical gap. The single-oscillator model below absorption edge is defined as [22]

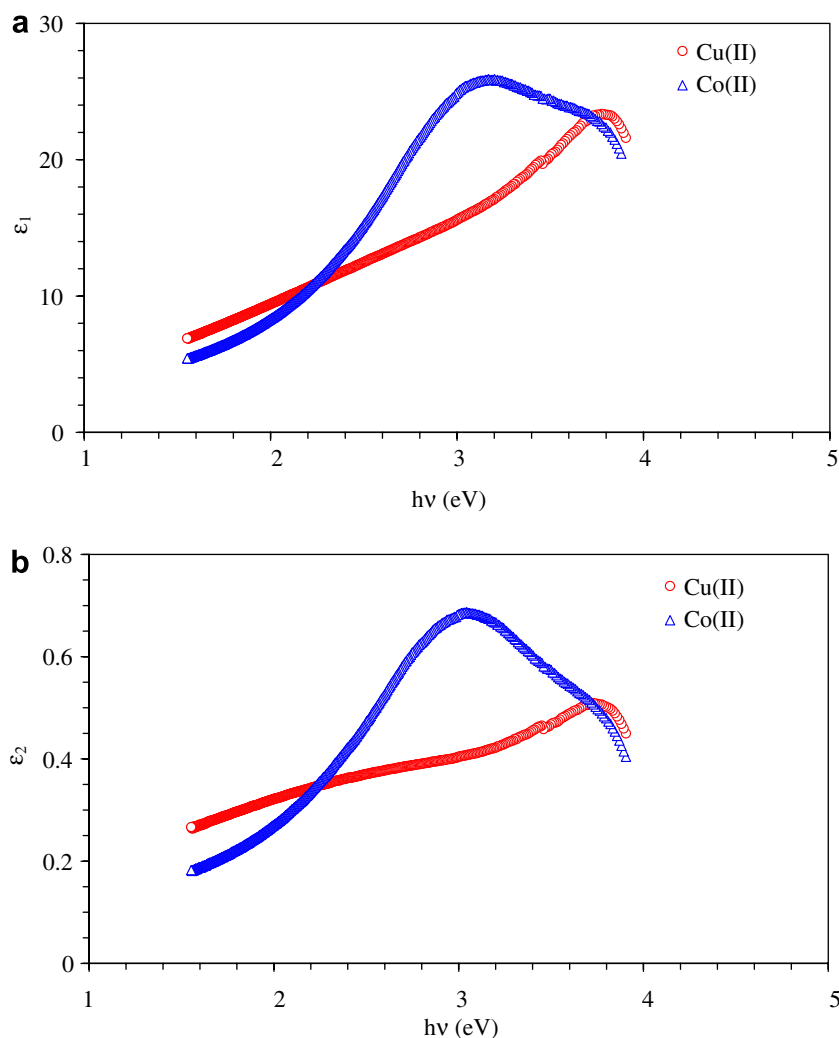


Fig. 7. The variation of real (a) and imaginary (b) parts of the dielectric constant of the films with photon energy.



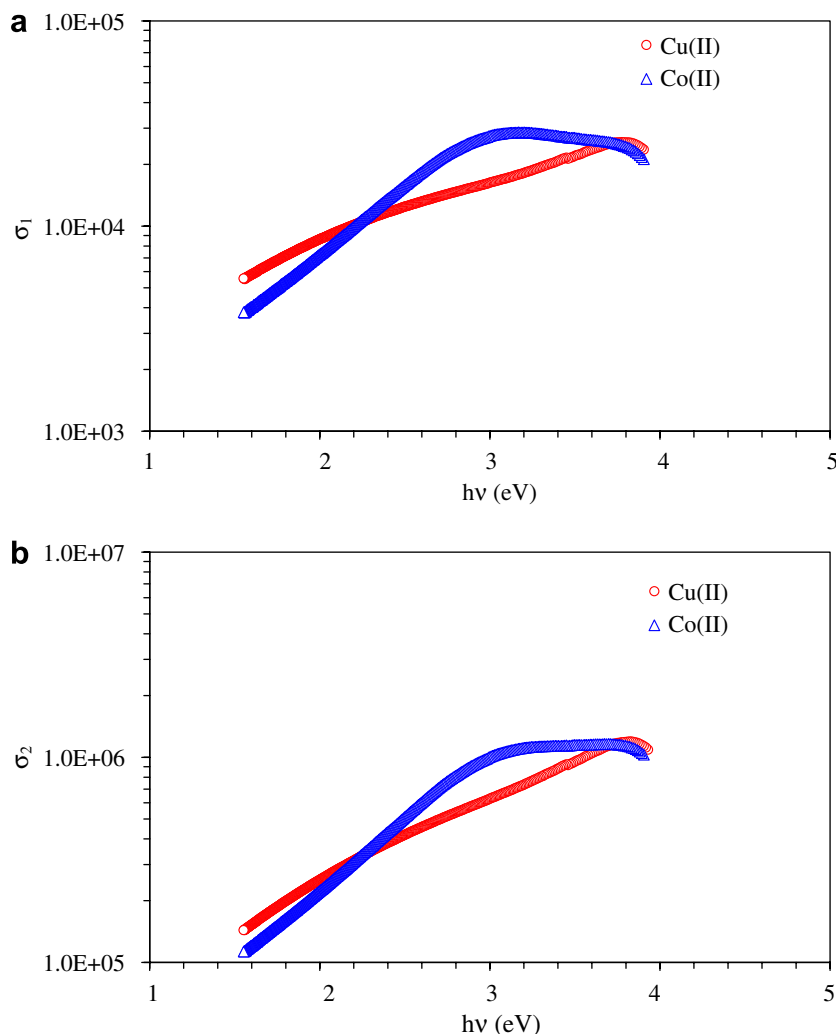


Fig. 8. The variation of real (a) and imaginary (b) parts of the optical conductivity of the films with photon energy.

$$n^2 - 1 = \frac{E_o E_d}{E^2 - E^2} \quad (3)$$

where  $E_d$  and  $E_o$  are single oscillator constants,  $E_o$  is the energy of the effective dispersion oscillator,  $E_d$  the so-called dispersion energy, which measures the average strength of interband optical transitions. The oscillator energy  $E_o$  is an average of the optical band gap,  $E_g$ , can be obtained from the Wemple–DiDomenico model [23] and this model have been widely studied in recent years [24–30].

Experimental verification of Eq. (3) can be obtained by plotting  $(n^2 - 1)^{-1}$  vs.  $(h\nu)^2$  as illustrated in Fig. 6.  $E_o$  and  $E_d$  values were determined from the slope,  $(E_o E_d)^{-1}$  and intercept  $(E_o/E_d)$ , on the vertical axis and are given in Table 2.  $E_o$  values change with the Cu(II) and Co(II) metals and follow order of  $E_{oCu(II)} > E_{oCo(II)}$ . We found that  $E_o$  value of the films is related empirically to the lowest direct band gap by  $E_o \approx 1.33E_g$  (for Cu(II)) and  $E_o \approx 1.59E_g$  (for Co(II)). This relation is in agreement with the obtained relation ( $E_o \approx 1.4E_g$ ) obtained from the single oscillator model [23].

The refractive index has been analyzed to yield the high-frequency dielectric constant ( $\epsilon_\infty = n_\infty^2$ ) [31,32]. Assuming the high-frequency properties could be treated as a single oscillator at wavelength  $\lambda_o$  at high frequency. The high frequency dielectric constant can be calculated by applying the following simple classical dispersion relation [31]:

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \quad (4)$$

where  $n_\infty$  is the refractive index at infinite wavelength  $\lambda_o$  (average interband oscillator wavelength)  $n$  is the refractive index and  $\lambda$  is the wavelength of the incident photon. The plots of  $(n^2 - 1)^{-1}$  vs.  $\lambda^{-2}$  were plotted to obtain  $n_\infty$  values. The intersection with  $(n^2 - 1)^{-1}$  axis is  $(n_\infty^2 - 1)^{-1}$  and hence,  $n_\infty^2$  at  $\lambda_o$  equal to  $\epsilon_\infty$  (high frequency dielectric constant). Values of  $\epsilon_\infty$  for the films are given in Table 2.

The dispersion data of refractive index was also fitted by the following relation

$$n^2 - 1 = \frac{S_o \lambda_o^2}{1 - (\lambda_o/\lambda)^2} \quad (5)$$

where  $\lambda$  is the wavelength of incident light.  $S_o$  is the average oscillator strength ( $S_o = (n_\infty^2 - 1)/\lambda_o^2$ ) and  $\lambda_o$  is an average oscillator wavelength. The  $S_o$  and  $\lambda_o$  values were obtained from the slope ( $1/S_o$ ) and intercept ( $S_o\lambda_o^2$ )<sup>-1</sup> of the curves plotted and are given in Table 2. The obtained  $S_o$  values change with Cu(II) and Co(II) metals.

### 3.5. Determination of the complex dielectric constants of the films

The fundamental electron excitation spectrum of the thin film was described by means of a frequency dependent of the complex electronic dielectric constant. The dielectric constant is defined as,  $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$  and real and imaginary parts of the dielectric constant are related to the  $n$  and  $k$  values. The  $\varepsilon_1$  and  $\varepsilon_2$  values were calculated using the formulas [33],

$$\varepsilon_1(\omega) = n^2(\omega) - k^2(\omega) \quad (6)$$

$$\varepsilon_2(\omega) = 2n(\omega)k(\omega) \quad (7)$$

The  $\varepsilon_1$  and  $\varepsilon_2$  values dependence of photon energy are respectively shown in Figs. 7a and b. Both  $\varepsilon_1$  and  $\varepsilon_2$  values increase up to certain value with increasing energy.

On the other hand, the parameters of the single-oscillator model  $E_o$  and  $E_d$  are connected to  $M_{-1}$  and  $M_{-3}$  moments of the optical spectra, through the two relations [23]

$$E_o^2 = \frac{M_{-1}}{M_{-3}}, \quad E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad (8)$$

The two moments  $M_{-1}$  and  $M_{-3}$  were calculated from the data on  $E_o$  and  $E_d$  are given in Table 2. The obtained  $M_{-1}$  and  $M_{-3}$  moments change with Cu(II) and Co(II) metals. These moments are measure of the average bond strength. Eq. (8) indicates a single oscillator approximation to the dielectric response of these materials. The optical moments are related to the macroscopic quantities like effective dielectric constant, effective number of valence electrons in material investigated [34].

### 3.6. Optical conductivity of the films

The real  $\sigma_1$  and imaginary  $\sigma_2$  parts of optical conductivity is described as [33]

$$\sigma_1 = \omega\varepsilon_2\varepsilon_o \quad \text{and} \quad \sigma_2 = \omega\varepsilon_1\varepsilon_o \quad (9)$$

where  $\omega$  is the angular frequency,  $\varepsilon_o$  is the free space dielectric constant. The real and imaginary parts of the optical conductivity dependence of energy are shown in Figs. 8a and b. From Figs. 8, it is seen that the optical conductivity increases with increasing energy and reaches a constant values. This suggests that the increase in optical conductivity is due to electrons excited by photon energy. The optical conductivity of the films changed due to the Cu(II) and Co(II) metals.

### 3.7. Absorption edge of the films

The measured transmittance ( $T$ ) was used to calculate approximately the absorption coefficient ( $\alpha$ ) using the relation

$$\alpha = \frac{1}{d} \ln \left( \frac{T}{(1-R)^2} \right) \quad (10)$$

where  $d$  is the thickness of the sample. The optical absorption edge was analyzed by the following relationship [35],

$$\alpha h\nu = B(h\nu - E_g)^m \quad (11)$$

where  $B$  is a constant and  $E_g$  is the optical band gap. The exponent  $m$  depends on the nature of the transition,  $m = 1/2, 2, 3/2$  or  $3$  for allowed direct, allowed non-direct, forbidden direct or forbidden non-direct transitions, respectively.

Fig. 9 shows the plots of  $(\alpha h\nu)^2$  vs.  $h\nu$  according to Eq. (11). The optical energy gap was determined by extrapolating the linear portions of these plots at  $(\alpha h\nu)^2 = 0$ . These plots give  $m = 1/2$ , which indicates that the direct transition dominates in the films. Thus, a more precise value was obtained from the linear part of the  $(\alpha h\nu)^2$  vs.  $h\nu$  (Fig. 9) and is given in Table 2. The  $E_g$  values of Cu(II) and Co(II) complexes are attributed to the charge carrier

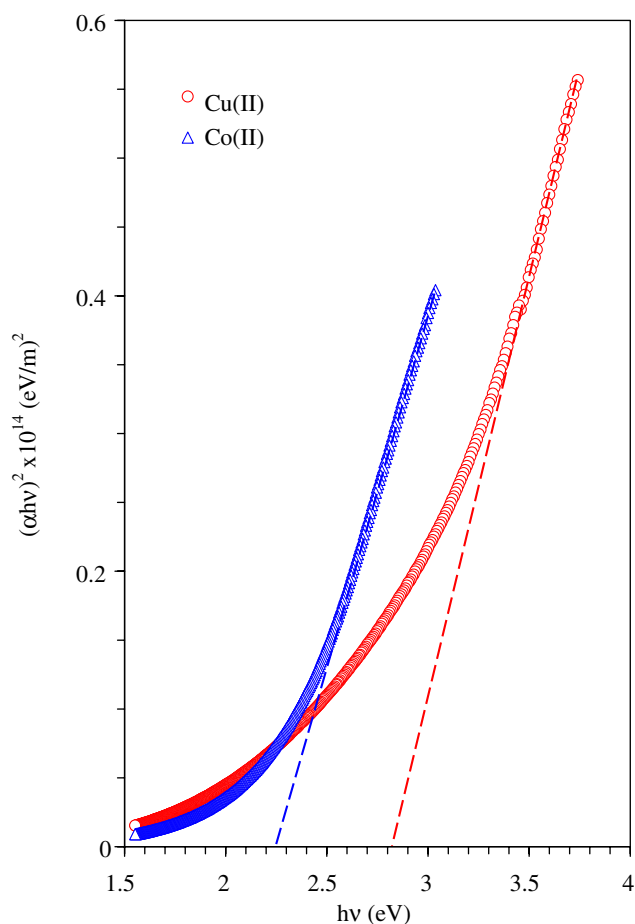


Fig. 9. The plots of  $(\alpha h\nu)^2$  vs. photon energy of the films.



transfer between metal and ligand. As seen from Table 2, the  $E_g$  value of Cu(II) complex are bigger than the Co(II). Due to completely filled d-orbital of copper atom according to cobalt atom, more energy will be required for the ejection of an electron from this orbital. So, that being larger of the energy gap of Cu complex is expected result. These results show that the dioxime complexes may be classed as organic semiconductors.

#### 4. Conclusions

$\text{BF}_2^+$ -bridge containing 4-benzylaminobiphenylglyoxime Cu(II) and Co(II) complexes were synthesized and characterized by elemental analysis, conductometric, magnetic, spectroscopic, thermal and optic measurements. It was found that these complexes have a metal:ligand ratio of 1:2 and an octahedral structure. Borylation does not alter metal:ligand ratio and geometry of these complexes. The elemental analysis and ICP-OES results of the complexes are in good agreement with the proposed formula. The IR data support the replacing of the bridging protons of the dioxime complexes with  $\text{BF}_2$  group and the proposed structure for the complexes. The optical band gaps of the films were determined. The refractive index dispersion curves obey the single-oscillator model. The dispersion parameters and optical constants of the films changed with Cu(II) and Co(II) metals. The novel metal complexes provide an alternative way for future designing of new optical devices.

#### References

- [1] A. Chakravorty, Chem. Rev. 3 (1974) 13.
- [2] F. Karipcin, İ. Karataş, Synth. React. Inorg. Met.-Org. Chem. 31 (2001) 1817.
- [3] F. Karipcin, F. Arabali, İ. Karatas, J. Chil. Chem. Soc. 51 (2006) 982.
- [4] İ. Karataş, H.İ. Uçan, Synth. React. Inorg. Met.-Org. Chem. 28 (1998) 383.
- [5] A. Coskun, İ. Karataş, Turk. J. Chem. 28 (2004) 173.
- [6] H. Kantekin, U. Ocak, Y. Gok, Z. Burakevich, Anorg. Allg. Chem. 627 (2001) 1095.
- [7] R. Dreos, G. Nardin, L. Randaccio, G. Tauzher, S. Vuano, Croatica Chem. Acta 72 (1999) 231.
- [8] N. Voiculescu, Appl. Organomet. Chem. 16 (2002) 569.
- [9] V.S. Stynes, I. Vernik, F. Zobi, Coord. Chem. Rev. 233 (2002) 273.
- [10] Y.Z. Voloshin, O.A. Varzatskii, A.I. Stash, V.K. Belsky, Y.N. Bubnov, I.I. Vorontsov, K.A. Potekhin, M.Y. Antipin, E.V. Polshin, Polyhedron 20 (2001) 2721.
- [11] Y. Wang, N. Herron, V.V. Grushin, D. LeCloux, V. Petrov, Appl. Phys. Lett. 79 (2001) 449.
- [12] Elianna Castillo, Mercè Granados, José Luis Cortina, J. Chromatogr. A 963 (2002) 205.
- [13] J. Spadavecchia, G. Ciccarella, P. Siciliano, S. Capone, R. Rella, Sensor Actuator B 100 (2004) 88.
- [14] N. Levin, W.H. Hartung, J. Org. Chem. 7 (1942) 408.
- [15] M.E.B. Jones, D.A. Thornton, R.F. Webb, Macromol. Chem. 49 (1961) 62.
- [16] M. Tumer, H. Koksall, M.K. Sener, S. Serin, Transition Met. Chem. 24 (1999) 414.
- [17] K. Burger, I. Ruff, F. Ruff, J. Inorg. Nucl. Chem. 27 (1965) 179.
- [18] A. Nakamura, A. Konishi, S. Otsuka, J. Chem. Soc., Dalton Trans. (1979) 488.
- [19] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, Wiley, New York, 1988.
- [20] F. Abeles (Ed.), Optical Properties of Solids, North-Holland Publishing Company, London, UK, 1972.
- [21] H.G. Tompkins, W.A. McGahan, Spectroscopic Ellipsometry and Reflectometry, John Wiley & Sons Inc., New York, 1999.
- [22] M. Didomenico, S.H. Wemple, J. Appl. Phys. 40 (1969) 720.
- [23] S.H. Wemple, M. Didomenico, Phys. Rev. B 3 (1971) 1338.
- [24] E. Marquez, J.B. Ramirez-Malo, P. Villares, R. Jimenez-Garay, R. Swanepoel, Thin Solid Films 254 (1995) 83.
- [25] S. Ilican, Y. Caglar, M. Caglar, F. Yakuphanoglu, Physica E 35 (2006) 131.
- [26] F. Yakuphanoglu, Opt. Mater. 29 (2006) 253.
- [27] F. Karipcin, B. Dede, Y. Caglar, D. Hür, S. Ilican, M. Caglar, Y. Şahin, Opt. Commun. 272 (2007) 131.
- [28] Y. Caglar, S. Ilican, M. Caglar, F. Yakuphanoglu, Spectrochim. Acta A (2007), in press.
- [29] M.M. El-Nahass, A.A.M. Farag, H.E.A. El-Sayed, Appl. Phys. A 77 (2003) 819.
- [30] J.M. González-Leal, E. Ma'rqez, A.M. Bernal-Oliva, J.J. Ruiz-Pérez, R. Jimenez-Garay, Thin Solid Films 317 (1998) 223.
- [31] J.N. Zemel, J.D. Jensen, R.B. Schoolar, Phys. Rev. A 140 (1965) 330.
- [32] T.S. Moss, Optical Properties of Semiconductors, Butter Worts Scientific publication Ltd., London, 1959.
- [33] J.N. Hodgson, Optical Absorption and Dispersion in Solids, Chapman and Hall LTD, 11 New fetter Lane, London EC4, 1970.
- [34] Mustafa Okutan, S. Eren San, Oğuz Köysal, Fahrettin Yakuphanoglu, Physica B 362 (2005) 180.
- [35] N.F. Mott, R.W. Gurney, Electronic Processes in Ionic Crystals, Oxford Univ. Press, London, 1940.