

# Synthesis of saturated Curtis-type Ni derivatives as dithioxalate–perchlorate Thin film by vacuum thermal evaporation and electrical and optical evaluation

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## Abstract

The bridge  $[\text{Ni}(\text{racMe}_6[14]\text{aneN}_4)(\text{C}_2\text{S}_2\text{O}_2)\cdot 2(\text{ClO}_4)]$  has been synthesized by coupling reactions of monomers  $[\text{Ni}(\text{racMe}_6[14]\text{aneN}_4)(\text{ClO}_4)_2]$  containing the central metals in the oxidation state  $\text{II}^+$ , with molecules of dithioloxalic acid dipotassium salt  $(\text{C}_2\text{S}_2\text{O}_2)\text{K}_2$ , to obtain a stacked arrangement that exhibits electrical properties. The synthesized powder and thin films of this material, deposited by vacuum thermal evaporation, show the same intra-molecular bonds as is shown by IR spectroscopy studies, which indicates that thermal evaporation does not alter these bonds, but thin films are amorphous. The effect of temperature on the conductivity has been measured in thin films ( $\sim 419$  nm in thickness) deposited by vacuum thermal evaporation. They show a typical semiconductor behavior with an activation energy of 0.22 eV. The optical band gap was determined and found to be 2.2 eV and arose from indirect transitions.

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## 1. Introduction

With the increasing complexity of new materials for novel technologies, recently organometallic compounds have been the subject of study since they show some advantages over organic compounds because they possess a metal atom in the structural unit which yields large molecular hyperpolarizability due to the transfer of electron density between the metal atom and the ligands [1]. Metallomacrocyclic coordination derivatives have been the subject of studies mainly because of potential application in different areas of nonlinear optics [2], and gas and pollution sensing [3–5]. Recently, electrical conductivity has been demonstrated to exist in a new class of metallomacrocyclic based on tetraaza macrocycles [6].

In this work, we present the synthesis of a new semi-conducting material based on tetraaza macrocycles. We assembled the perchlorate anion, present as a counterion in unsaturated Curtis macrocycles, with dithioloxalic acid

dipotassium salt  $(\text{C}_2\text{S}_2\text{O}_2)\text{K}_2$ . Thermal evaporation of this material to produce thin films and the optical band gap calculation are presented as well. Solid metallorganic molecules are formed by condensation and organization of molecular units.

As observed in amorphous inorganic semiconductors, loss of periodicity and subsequently their crystalline structure, results in the localization of electronic wave functions with a turn of a tail in the function of density of states. In the edges of valence and conduction, bands extend into the forbidden gap. As a result, electrical conduction is explained by the band theory and hopping model, establishing a mobility edge for the charge carriers [7].

## 2. Experimental procedure

### 2.1. Synthesis

#### 2.1.1. General information

Elemental analyses were performed by Galbraith Laboratories.  $[\text{Ni}(\text{racMe}_6[14]\text{aneN}_4)(\text{ClO}_4)_2]$  was prepared

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according to reported procedures [8] and purified by recrystallization from water. The dithioloallic acid dipotassium salt ( $C_2S_2O_2$ ) $K_2$  purchased from Kodak Chemical Co. was used as obtained. The reactions were performed under normal laboratory conditions, all solvents were purified by distillation just before reaction.

Routine infrared spectra of the obtained powders were recorded on a Nicolet–Magna-IR 750 spectrophotometer as KBr pellets, and infrared spectra for the deposited thin film were measured with a FT-IR Nicolet 5X spectrophotometer, with a uncertainty of  $4\text{ cm}^{-1}$ , X-ray spectra of the deposited films were obtained by means of a Siemens D-500 system. The ellipsometric measurements were made using a Gaertner Model L117 ellipsometer using the 630 nm wavelength from a He–Ne laser. The current–voltage ( $I$ – $V$ ) characteristics were obtained at room temperature and the dependence of the electrical conductivity of the sample as a function of temperature in the range (123–47 K) were measured with a Keithley 230 programmable voltage source and a Keithley 485 auto-ranging pico-ammeter both PC controlled. The temperature of the sample was measured with

a chromel–alumel thermocouple attached to a HP 3421 data acquisition unit.

The synthesized compound was  $[Ni(\text{racMe}_6[14]\text{aneN}_4)(C_2S_2O_2)\cdot 2(ClO_4)]$ . In this case  $Ni(\text{rac-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane})$  perchlorate (0.1 g,  $1.852 \times 10^{-4}$  mol) dissolved in 25 ml of ethanol was mixed with dithioloallic acid dipotassium salt ( $C_2S_2O_2$ ) $K_2$  (0.37 g,  $1.2 \times 10^{-3}$  mol) dissolved in 25 ml of ethanol. The pH of the solution was set at  $7.5 \pm 0.2$  with dilute ethanolic KOH solution. The mixture was warmed to 338 K while stirring, the solution gradually changes from light green color to mauve color after the mixture was allowed to cool to 277 K for 12 h. Afterwards, the mixture was filtered and the powder obtained was suspended in 50 ml of 1:1(v/v) ethyl acetate and THF. The suspension was heated to 308 K and filtered hot, and the residual purple solution was warmed and stirred for 12 h at 308 K evaporating its volume by half. After being cooled to room temperature, a red dark powder was filtered and washed with ethanol and water. Yield: 36% elem. anal. for  $C_{20}H_{34}S_4O_{12}N_4Cl_2Ni$  calculated (found) %: C, 30.78 (26.71); H, 4.39 (4.67); N, 7.1 (7.20). Decomposi-

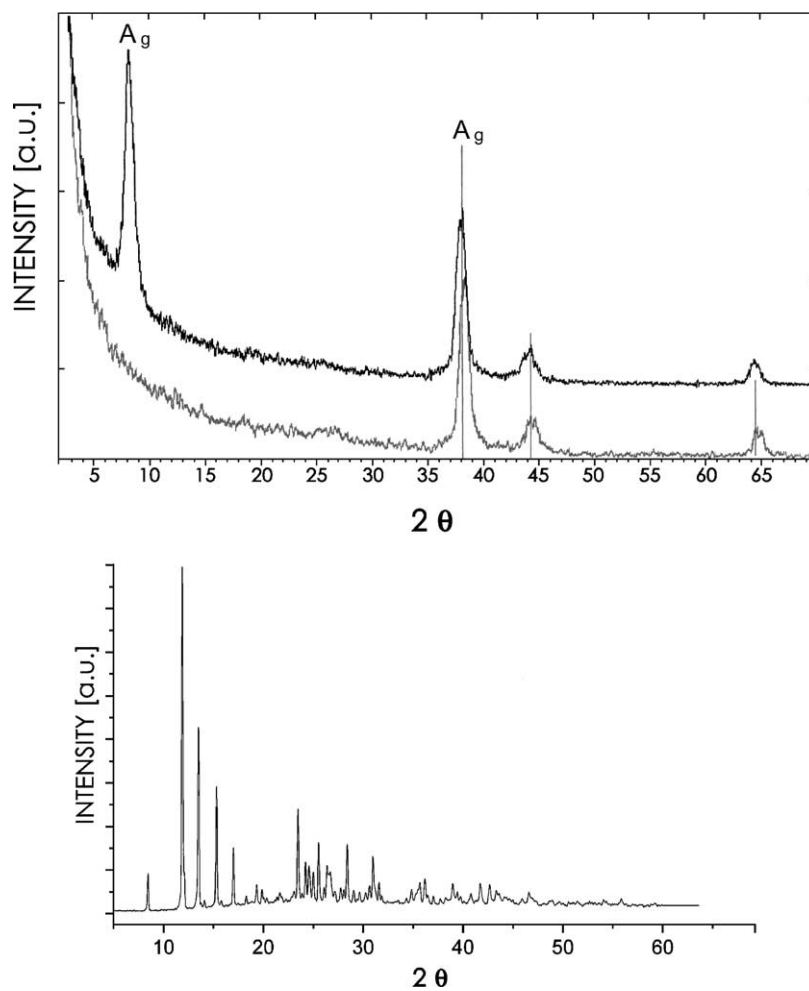


Fig. 1. X-ray diffraction patterns of  $[Ni(\text{racMe}_6[14]\text{aneN}_4)(C_2S_2O_2)\cdot 2(ClO_4)]$  films deposited at 453 K on 7059 Corning glass (top) and the powders (bottom).

tion temperature 538 K. IR (KBr,  $\text{cm}^{-1}$ )  $\nu$  max: 3270–3190 (N–H); 3423 (O–H); 2967–2876 ( $\text{CH}_3$ ); 1647–1577 (C–O); 1310 (C=S); 1089–626 ( $\text{ClO}_4^-$ ). MS (FAB)  $m/e$ : [ $M^+ + \text{H}$ ] 460, [ $M^+ - 119$ ] 341, [ $M^+ - 153$ ] 307, [ $M^+ - 220$ ] 240, [ $M^+ - 261$ ] 199, [ $M^+ - 340$ ] 120 and [ $M^+ - 372$ ] 88.

Mass spectra ion mode  $\text{FAB}^+$  of the mass spectrometry was employed to research the relative abundances of important ions, to verify the molecular weight of the complex and to assign structure [12]. It was also used to study the comparative effects of different metal ions on the fragmentation reactions of the ligand [13]. In this study the spectra of the macrocyclic compound showed fragments containing the Ni atom which was confirmed by the corresponding isotopic distributions. The molecular ion peak of fragmentation [ $M^+ + \text{H}$ ] 460 is the fragment due to the loss of ion ( $\text{ClO}_4^-$ ). The FT-IR data account and the identified structures from their mass spectra ion mode  $\text{FAB}^+$  revealed the formation of  $[\text{Ni}(\text{racMe}_6[14]\text{janeN}_4)(\text{C}_2\text{S}_2\text{O}_2) \cdot 2(\text{ClO}_4)]$ .

## 2.2. Thin films

Thin-film deposition was carried out by vacuum thermal evaporation onto 7059 Corning glass slices and single-crystalline silicon wafers, ultrasonically degreased in warm ethanol and dried under a nitrogen atmosphere. To prevent the powder products from arriving on the surface of the substrate, the evaporation source was a molybdenum boat with two grids. The temperature of evaporation in the boat was 473 K during evaporation, measured by means of a chromel–alumel thermocouple. It should be remarked that the synthesized compound sublimates. The electrical current through the molybdenum boat was slowly increased up to 293 K, below the first change observed by the TGA thermogram to prevent thermal decomposition of the compound. For infrared and ellipsometric measurements the substrates used were (1 0 0) oriented and  $200 \Omega \text{ cm}$  C–Si slices. For optical transmission measurements, the substrates were 7059 Corning glass slices. The electrical conductivity of the films were studied by means of four-probe; the substrates were 7059 Corning glass coated with four metallic strips; these metallic strips acting as electrodes for electrical measurements. To get an ohmic behavior between the deposited films and the metallic electrodes, four gold or silver strips were deposited by vacuum thermal evaporation onto 7059 Corning glass slices.

## 3. Results and discussion

The X-ray diffraction patterns for the obtained powders and for films deposited onto the bare 7059 Corning glass slices and onto the metal-coated 7059 Corning glass, shown in Fig. 1. The X-ray diffraction spectrum for the synthesized powders shows a number of intense peaks suggesting that the produced material has crystalline microstructure. However, it was not possible to obtain single

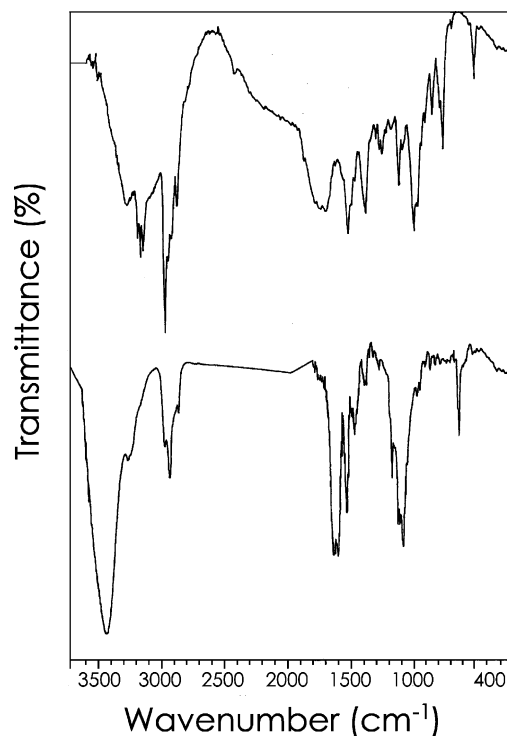


Fig. 2. Comparison of FT-IR spectrum of a 419 nm thick film deposited from  $[\text{Ni}(\text{racMe}_6[14]\text{janeN}_4)(\text{C}_2\text{S}_2\text{O}_2) \cdot 2(\text{ClO}_4)]$  on a p-type C–Si slices to 453 K (top) with IR spectra of powder (bottom).

crystalline samples that permit us to determine the crystalline structure of this material. On the other hand, in the spectrum in Fig. 1 no diffraction peaks are observed; so  $[\text{Ni}(\text{racMe}_6[14]\text{janeN}_4)(\text{C}_2\text{S}_2\text{O}_2) \cdot 2(\text{ClO}_4)]$  films are thought to be amorphous although the thickness of the deposited films 350–400 nm is large enough to observe peaks indicating crystalline structure in polycrystalline films, even for small grain size. If it is considered that the substrate was kept at room temperature during evaporation, the macro-ions arriving on the surface of the substrate do not have enough energy, and hence surface mobility, to achieve a crystalline assembly.

In Fig. 2, the IR spectra of the powder is reported with the Fourier transformed infrared (FT-IR) absorption spectrum of a deposited film. The film spectrum, taken directly after deposition, exhibits a strong absorption band at  $2800 \text{ cm}^{-1}$ , and a distinct band at  $1440 \text{ cm}^{-1}$ , both bands characteristic of  $\text{CH}_3$  groups [9]. Absorption bands are also located at 1100 and  $640 \text{ cm}^{-1}$ , both characteristic of the ( $\text{ClO}_4^-$ ) [10]. The bands at 1100 and  $640 \text{ cm}^{-1}$  can be used to identify the presence of the monomer  $[\text{Ni}(\text{racMe}_6[14]\text{janeN}_4)(\text{ClO}_4)_2]$  in the films, and bands which might arise from (C=S) at  $1290 \text{ cm}^{-1}$  [11], (NH) at  $3250 \text{ cm}^{-1}$  [10]. The FT-IR data is a proof of the formation of  $[\text{Ni}(\text{racMe}_6[14]\text{janeN}_4)(\text{C}_2\text{S}_2\text{O}_2) \cdot 2(\text{ClO}_4)]$  network structure in the films.

More specifically, the comparison between the localization of the absorption bands in the spectra of the synthesized

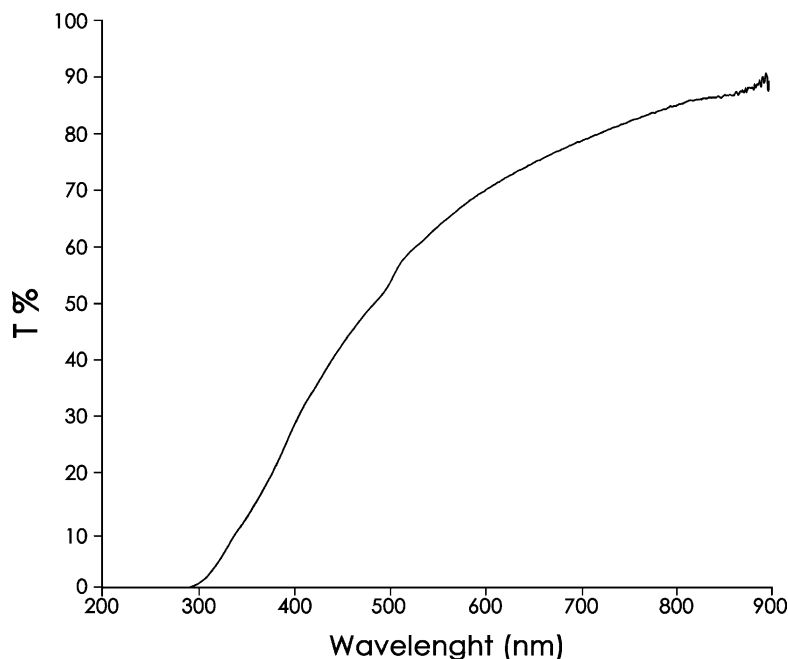


Fig. 3. The experimental data of transmittance for a  $[\text{Ni}(\text{racMe}_6[14]\text{aneN}_4)(\text{C}_2\text{S}_2\text{O}_2)\cdot 2(\text{ClO}_4)]$  film in the wavelength range 200–900 nm.

powders and those of the deposited films show as expected some presents a strong absorption features which confirm that the deposited films are formed by the same macro-ions as those of the original synthesized powder. These results appear to indicate that in the film growth process the deposited compound is not affected by the thermal evaporation and deposition process.

From ellipsometry measurements, the thickness of the deposited films studied  $t_h = 419$  nm and the refractive index  $2.323 \pm 0.005$  are obtained for a wavelength of 630 nm. Taking into account the refractive index values, the optical reflectance  $R=16\%$  was obtained for the deposited films [14]. The UV-Vis optical transmission spectra results were analyzed in the strong absorption edge region.

In Fig. 3, the spectral transmittance curve for deposited  $[\text{Ni}(\text{racMe}_6[14]\text{aneN}_4)(\text{C}_2\text{S}_2\text{O}_2)\cdot 2(\text{ClO}_4)]$  films are shown in the wavelength range from 200 to 900 nm. The film has an absorption edge at a wavelength of around 300 nm moreover. In the NIR spectral region, the transmission increases with increasing  $\lambda$  which shows the high transparency of the present film in the NIR. It can be concluded from Fig. 3 that spectral variation in  $\alpha$  can be interpreted as an optical transition in the visible and near-infrared range [17]. The width of optical band gap  $E_g$  can be determined from fitted by straight line in an  $(\alpha h\nu)^{1/2}$  against  $(h\nu)$  plot. The absorption coefficient  $\alpha$  near the band edge in many amorphous semiconductors shows an exponential dependence on photon energy usually obeying Urbach's empirical relation [18]:

$$\alpha h\nu = \beta(h\nu - E_g)^n \quad (1)$$

where  $\beta^{-1}$  is the band edge parameter,  $n$  a number that characterizes the transition process, which takes values 1/2, 1, 2,

or 3/2 depending on the nature of the electronic transitions responsible for the absorption,  $n$  is usually equal to 2 and  $E_g$  is the optical band-gap energy [15]. In amorphous semiconductors the optical transitions are described, to a first approximation, by the called non-direct transitions. In these electronic transitions from states of valence band to states of the conduction band there is no conservation of the electronic momentum [16].

Using a least-squares fit, was determined from the intercepts of extrapolated linear of plot of  $(\alpha h\nu)^{1/2}$  versus  $(h\nu)$  or the  $[\text{Ni}(\text{racMe}_6[14]\text{aneN}_4)(\text{C}_2\text{S}_2\text{O}_2)\cdot 2(\text{ClO}_4)]$  thin films. The value of the width of band tails is calculated and as shown in Fig. 4. The obtained value of  $E_g$  is 2.2 eV. It is seen that exponential absorption tails characterizes amorphous materials and appear in the plots [19].

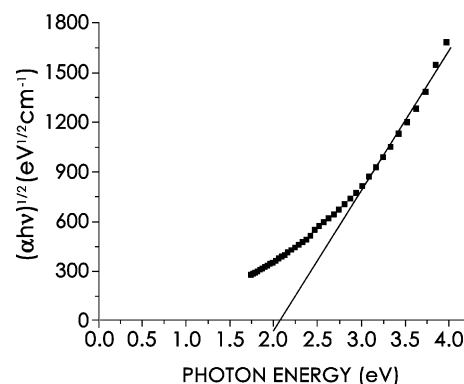


Fig. 4. Dependence of  $(\alpha h\nu)^{1/2}$  as function of the photon energy  $h\nu$ , for a  $[\text{Ni}(\text{racMe}_6[14]\text{aneN}_4)(\text{C}_2\text{S}_2\text{O}_2)\cdot 2(\text{ClO}_4)]$  thin film.

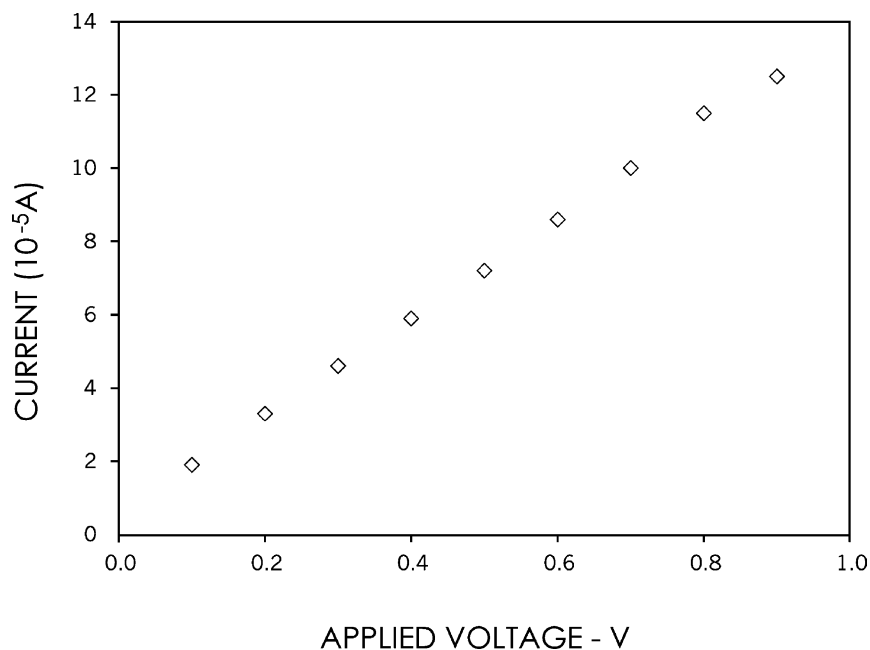


Fig. 5. Typical forward bias current–voltage ( $I$ – $V$ ) characteristics for films of  $[\text{Ni}(\text{racMe}_6[14]\text{aneN}_4)(\text{C}_2\text{S}_2\text{O}_2)\cdot 2(\text{ClO}_4)]$  deposited onto gold electrodes coated glass slices.

In order to establish if the electric contact between the deposited films and the evaporated gold electrodes shows ohmic behavior, the current–voltage characteristics were obtained at room temperature. Fig. 5 shows typical forward current–voltage characteristics, for applied voltages lower than 1 V. The value obtained for dark electrical conductivity for the films was  $8.5 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ . In this applied voltage range, the slope of a graph  $\log I$  versus  $\log V$ , is approximately equal to 1. This behavior indicates that the electrical contact between the gold electrode and the deposited film

is an ohmic one. A similar behavior is observed with silver electrodes.

Fig. 6 shows the dependence of the electrical conductivity on temperature, during measurements, for a constant applied voltage with magnitude in the ohmic regime. This curve shows the typical dependence associated with a semiconductor material, with the electrical conductivity increasing as the temperature increases.

In this curve two regions are defined, one corresponding to low temperature where the electrical conductivity is almost

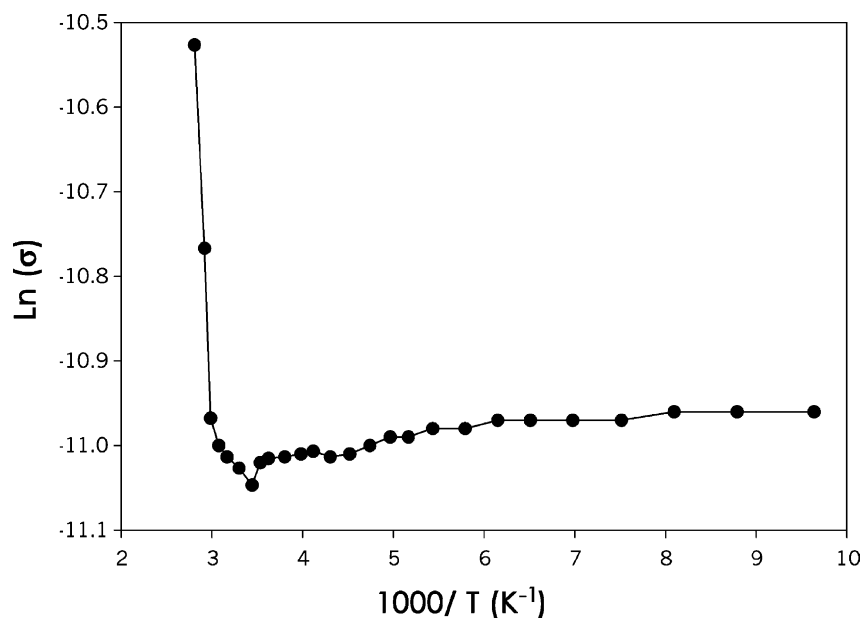


Fig. 6. Electrical current as a function of the temperature during the measurement of  $[\text{Ni}(\text{racMe}_6[14]\text{aneN}_4)(\text{C}_2\text{S}_2\text{O}_2)\cdot 2(\text{ClO}_4)]$  thin films deposited on glass.

constant, and other one corresponding to high temperature where a sudden increase in  $\ln \sigma$  is observed. This behavior indicates that the electrical conductivity  $\sigma(T)$  is thermally activated and it is assumed to arise from the contribution due to conduction between extended states. This behavior is described by the Arrhenius law of the form:

$$\sigma = \sigma_m \exp\left(-\frac{\Delta E_m}{KT}\right) \quad (2)$$

where  $\sigma_m$  is the pre-exponential factor and  $\Delta E_m$  is an activation energy for electrical conductivity. The  $\Delta E_m$  calculated values 0.22 eV. These calculated  $\Delta E_m$  values are much lower than the value obtained for the optical band gap, this fact indicates that  $\Delta E_m$  is an activation energy involving both the energy necessary to excite electrons from the localized states toward extended states through the mobility edge and the electrical conduction by means of the hopping mechanism between localized states.

Taking into account the optical and electrical properties of the deposited films, it appears to be possible to apply this material to the preparation of electronic devices.

#### 4. Conclusions

A summary of the identified structure by IR and Ion Mode FAB<sup>+</sup> revealed in the structure of the complex dithioloalate ion  $(C_2S_2O_2)^{2-}$  acting as a bridge between Ni(II<sup>+</sup>) complexes is present. The coordination number increases from 4 to 6, giving the characteristic color of that coordination and the remaining perchlorate ion  $(ClO_4)^-$  neutralizes the charges remaining on the dithioloalate ion  $(C_2S_2O_2)^{2-}$ . The IR percentage transmittance for the synthesized powders exhibits a strong absorption band at maximum  $773\text{ cm}^{-1}$ , attributed to perchlorate ion  $(ClO_4)^-$ . There is another band with a maximum at  $1310\text{ cm}^{-1}$ , also attributed to the presence of C=S bonds.

The molecular weight of the complex, determined from its mass spectra was  $m/z = 802$  and its pattern makes clear that the complex studied is well defined and have stable species.

Thin films of this material deposited by vacuum thermal evaporation have been shown to be feasible. Although the deposited material is amorphous in nature, it is formed by the same chemical unit as those of the synthesized powder. The thermal evaporation process does not change the intra-molecular bonds, suggesting that the deposition process can be considered as a molecular process and the substrate temperature is not high enough to give surface mobility to the molecular units to produce crystalline films. The value of the calculated optical band gap, the order of

magnitude of the electrical conductivity and the possibility to prepare it in thin films appears to make it possible to apply this material in the preparation of electronic devices. Although more work is necessary to get crystalline films. New semiconductor compound has been synthesized, as it is showed by the dependence of the electrical conductivity on temperature. The  $[Ni(\text{racMe}_6[14]\text{aneN}_4)] \cdot 2(ClO_4)$  systems have been stacked and organized into a condensed phase by a covalent overlap between the Ni(II<sup>+</sup>) metal ion coordinating atoms of the ligand  $(C_2S_2O_2)^{2-}$ .

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