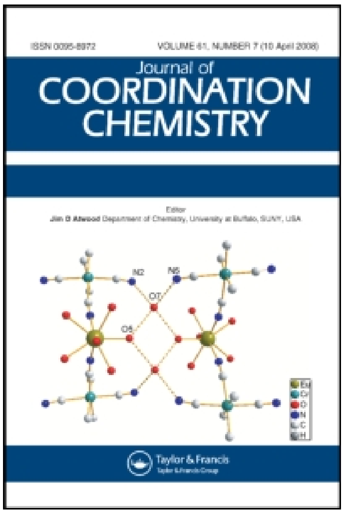

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SEMICONDUCTOR COPPER(II) MACROCYCLIC COMPLEXES. SYNTHESIS, CHARACTERIZATION AND ELECTRICAL PROPERTIES OF COPPER(II) COMPLEXES OF THE TYPE [Cu(TAABL)](NO_3) · nH_2O WITH L = $NH(CH_2)_2NH_2$, $NH(CH_2)_4NH_2$, $NH(CH_2)_{12}NH_2$, AND THE COMPLEX [Cu(TAAB($C_{14}H_9N_2O_2)_2$)] · $4H_2O$

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SEMICONDUCTOR COPPER(II) MACROCYCLIC COMPLEXES. SYNTHESIS, CHARACTERIZATION AND ELECTRICAL PROPERTIES OF COPPER(II) COMPLEXES OF THE TYPE $[Cu(TAABL)](NO_3)\cdot nH_2O$ WITH $L = NH(CH_2)_2NH_2$, $NH(CH_2)_4NH_2$, $NH(CH_2)_{12}NH_2$, AND THE COMPLEX $[Cu(TAAB(C_{14}H_9N_2O_2)_2)]\cdot 4H_2O$

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The complexes $[Cu(TAABNH(CH_2)_2NH_2)](NO_3)\cdot 2H_2O$, (1) $[Cu(TAABNH(CH_2)_4NH_2)](NO_3)\cdot 4H_2O$, (2), $[Cu(TAABNH(CH_2)_{12}NH_2](NO_3)\cdot 4H_2O$, (3) and $[Cu(TAAB(C_{14}H_{10}N_2O_2)_2]\cdot 4H_2O$, (4) have been synthesized and characterized by IR, mass spectroscopy, electronic spectroscopy, thermogravimetric analysis and elemental analysis. Electrical conductivity and activation energy evaluation were obtained from study of the temperature dependence of the electrical current (in tablet and thin film). Refraction and reflectance indices, absorption coefficient and optical activation energy were established through ellipsometry and UV-Vis spectroscopy. The electrical conductivity values at room temperature were within the range of semiconducting molecular solids ($10^{-6} - 10^{1} \Omega^{-1} cm^{-1}$).

Keywords: Copper(II); Macrocycles; Semiconductors

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INTRODUCTION

Increasing interest in molecular materials arose in the last 50 years, since many exhibit important electrical, magnetic or optical properties [1]. Traditionally coordination chemistry has been concerned with studying the changes of the properties of metal ions by modifying the ligand arrangement around single centers. However, the properties of order infinite aggregates of metal ions has emerged as a subject of synthetic study [2]. Thus, the connectivity of the lattice and the nature of the bridging groups tuning the intermetallic interactions are very important in determining the properties of the bulk material [2, 3]. Several polymeric metallic macrocycles may be examples of this kind of molecular material that show novel properties [2–4].

We chose the copper(II) macrocyclic complex tetrabenzo[b,f,j,n] [1, 5, 9, 13] tetrazacyclohexdecine(2, 3; 6, 7; 10, 11;1 4, 15-Bzo$_4$[16]octane-1, 5, 9, 13-N$_4$), hereafter referred as Cu(TAAB)$^{2+}$, as starting material because this cyclotetrameric Schiff-base-copper(II) complex and its nickel(II) analog yield partially solvolyzed neutral material containing α-amino ether linkages. The attacking nucleophiles in documented examples include alkoxide [5] and hydroxide ions [6] or amine and diamine [7, 8], and all the resulting complexes exhibit nucleophilic addition of two groups to the macroligand around the metal center. In order to generate new partially solvolyzed products from Cu(TAAB)$^{2+}$ employing diamines, we synthesized compounds of the type [Cu(TAABL)](NO$_3$)$\cdot$4H$_2$O with L = 1,2-ethylenediamine, 1,4-diaminobutane, 1,12-diaminododecane and [Cu(TAABL$_2$)]$\cdot$nH$_2$O with L = 2,6-diaminoanthraquinone. These complexes have been characterized by IR, mass spectroscopy, electronic spectroscopy, thermogravimetric analysis and elemental microanalyses. The conductivity and the temperature dependence of the electrical current were determined in tablets and thin films.

EXPERIMENTAL

Chemicals of commercial grade were purchased from Aldrich and used as supplied. The [Cu(TAAB)](NO$_3$)$_2$ was prepared as described previously [9]. The FAB mass spectra were measured on a 3-nitrobenzyl alcohol support in the positive ion mode on a Jeol JMS-SX102A instrument. Infrared spectra, as KBr discs and thin films, were recorded on 282-B IR Perkin Elmer and Nicolet 5-Mx FT-IR spectrophotometers, respectively. Electronic spectra of solid samples were measured by diffuse reflectance on a Cary 5E UV-Vis, while the UV-Vis spectra using films were obtained on a Shimadzu 260 spectrophotometer. Refraction index and the thickness of films were determined by ellipsometry with a Gaetner L117 variable angle manual ellipsometer. Magnetic susceptibility of powder samples was recorded at room temperature on a Johnson Matthey Gouy balance using Evan's method for solid samples. Thermogravimetrical analyses were obtained on a V_41C Du Pont 2100 device under N_2 (velocity 20°C/min). Powder diffraction was performed in a SIEMENS D5000 powder diffractometer, with copper radiation Kα and graphite monochromator at 1° (2θ/min). The electrical current measurements were recorded on a Keithley 230 voltage source and a Keithley 485 peak amperimeter coupled to a HP3421 data collector (tablets and thin films). Galbraith Laboratories (Knoxville, TN) performed C, H and N microanalyses.

PREPARATIONS

$[Cu(TAABNH(CH_2)_2NH_2](NO_3)\cdot 2H_2O$, **1**: 5 mL of ethylenediamine in 15 mL of water was dropped into a solution prepared by dissolving 0.5g (0.8 mmol) of $[Cu(TAAB)](NO_3)_2$ in 50 mL of water. The color of the solution changed to a deep green and precipitate appeared. After 3 hours of stirring the mixture, the precipitate was filtered, washed with water and dried *in vacuo*. Product was recrystallized from methanol. Yields 0.38 g (98%), m. p. (d) 197°C. Anal. Calcd. for $Cu_1C_{30}H_{31}N_7O_5$ (%): C, 56.91; H, 4.93; N, 15.49. Found: C, 56.87; H, 4.58; N, 15.41. μ_{eff} (BM), 2.25. ν(cm^{-1}): 14600, 20000, 27800.

$[CU(TAABNH(CH_2)_4NH_2](NO_3)\cdot 4H_2O$, *2*: It was prepared similarly.to **1** from 5 mL of 1,4-diaminebutane and $[Cu(TAAB)](NO_3)_2$ (0.5g, 0.8 mmol). Yield 0.38 g (85.2%), m. p. (d) 121°C. Anal. Calcd. for $Cu_1C_{32}H_{39}N_7O_7$ (%): C, 55.12; H, 5.64; N, 14.06. Found: C, 55.02; H, 5.78; N, 13.74. μ_{eff} (BM), 2.61. ν(cm^{-1}): 14600, 19900, 25000.

$[Cu(TAABNH(CH_2)_{12}NH_2](NO_3)\cdot 4H_2O$, *3*: A solution of 0.32 g (2 mol) of 1,12-diaminododecane dissolved in 32 mL of water was dropped into a solution prepared by dissolving 0.5g (0.8 mmol) of $[Cu(TAAB)](NO_3)_2$ in 50 mL of water. The color of the solution changed to light green and precipitate appeared. The mixture was stirred seven hours, then the precipitate was filtered, washed with water and dried *in vacuo*. Product was recrystallized from dichloromethane. Yield 0.39 g (72.5%), m. p. (d)

116°C. Anal. Calcd. for $Cu_1C_{40}H_{55}N_7O_7$(%): C, 59.35; H, 6.85; N, 12.11. Found: C, 59.18; H, 6.39; N, 11.66. μ_{eff} (BM), 2.03. ν(cm^{-1}): 14300, 19300, 26100.

[Cu(TAAB($C_{14}H_{10}N_2O_2$)$_2$]·4H_2O, 4: A solution of 0.38 g (2 mmol) of 2,6-diaminoanthraquinone dissolved in 38 mL was added to a solution of 0.5g (0.8 mmol) of [Cu(TAAB)]$(NO_3)_2$ in 50 mL of absolute methanol. The color of the solution changed to greenish red. The mixture was stirred for 72 hours and precipitate appeared. It was filtered and washed with methanol. Product was recrystallized from dimethylformamide. Yields 0.5 g (65.5%), m. p. (d) 305°C. Anal. Calcd. for $Cu_1C_{52}H_{46}N_8O_8$ (%): C, 64.09; H, 4.76; N, 11.50. Found: C, 64.35; H, 4.21; N, 11.19. μ_{eff} (BM), 2.02. ν(cm^{-1}): 14400, 20600, 25400.

RESULTS AND DISCUSSION

New copper(II) complexes were obtained from the partial nucleophilic addition of only one diamine group (ethylenediamine, 1,4-diaminobutane and 1,12-diaminododecane) to the macroligand in Cu(TAAB)$^{2+}$. Therefore, these complexes may be viewed as containing three azomethine donors and only one ionized *gem*-diamine donor. Similar nucleophilic addition reactions involving Ni(TAAB)$^{2+}$ and Cu(TAAB)$^{2+}$ have been performed with alkoxide [5], hydroxide [6] and some amine and diamine ions [7, 8]. Those reported complexes contain two azomethine donors and either two ionized α-amino ether donor or two ionized *gem*-diamine donors. Thus, disubstitution was carried out on the TAAB ligand. This disubstitution was observed by using 2,6-diaminoanthraquinone in the case of compound **4**.

Compounds (**1** to **4**) have greenish color and are air stable. Compounds **1**, **2** and **3** are slightly soluble in dichloromethane, acetone, chloroform and methanol, while compound **4**, containing 2,6-diaminoanthraquinone, is completely insoluble in polar and non-polar solvents.

The IR spectra of these complexes exhibit some common features (Tab. I): (1) A band corresponding to the C = N vibration is present between 1567 – 1574, which also occurs in the starting material ([Cu(TAAB)]$(NO_3)_2$). This contrasts with the absence of this band in the vibrational spectra of the disubstituted copper(II) complexes reported by Kummar *et al.* [7, 8]. (2) A new band appears for ν(CN) within the range of 1525 to 1530, which was also observed by Kummar *et al.* [7, 8] for the related copper(II) complexes. (3) Two bands are present at 3020 and 3325 to

TABLE I IR data (cm^{-1}) for $[Cu(TAABL)](NO_3)\cdot nH_2O$ (**1** to **3**) and $[Cu(TAAB(C_{14}H_{10}N_2O_2)_2]\cdot 4H_2O$ (**4**)[a]

Complex	$\nu(C=N)$	$\nu(C=N)$	$\nu(NO_3)^{-1}$	$\nu(NH)$	$\nu(NH)$	$\nu(OH)$
1	1567 (1567)	1528 (1533)	825, 1360, 1383 (825, 1384)	3324 (3324)	3058 (3058)	3406
2	1568 (1568)	1530 (1533)	830, 1359, 1384 (1394)	[b] (3320)	3028 (3032)	3408
3	1567 (1564)	1527 (1529)	830, 1350, 1389 (1375)	3327 (3325)	3013 (3004)	3435
4	1574 (1579)	1525 (1539)	–	3337 (3325)	3070 (3071)	3422

[a] Numbers in parentheses are the IR data for samples in thin films.
[b] Over by ν(OH).

3350 cm^{-1} assigned to the symmetric and asymmetric primary NH and secondary NH stretching modes. (4) A band assigned to ν(OH) vibration around 3400, indicates the presence of water molecules in the complexes. This was confirmed by thermogravimetric analysis. (5) Three bands around 832, 1360 and 1387 cm^{-1} are assigned to the NO_3^- ion for derivatives **1** to **3**, but not for compound **4**. These bands disappear in the related complexes containing the disubstituted macroligand [7, 8]. According to these results, when $[Cu(TAAB)](NO_3)_2$ was treated with alkyldiamines, a simple substitution was carried out; and by using 2,6-diaminoanthraquinone, a double nucleophilic substitution was performed as observed for analogous reported complexes [7, 8]. This proposal was confirmed by the elemental analyses and the thermogravimetric data.

The positive ion FAB mass spectra show signals for the corresponding molecular ions of **1** (535 m/z $[Cu(TAABNH(CH_2)_2NH)]^+$), **2** (563 m/z $[Cu(TAABNH(CH_2)_4NH)]^+$), and **3** (675 m/z $[Cu(TAABNH(CH_2)_{12}NH)]^+$). Some other important fragments were observed for the three compounds, *i.e.*, $[Cu(TAAB)]^+$ (476 m/z) and $[Cu(TAABNH]^+$ (491 m/z). All of the observed signals exhibit the expected, characteristic, isotopic distribution patterns. At this point, the most remarkable feature is, that heavier fragments than those corresponding to the nucleophilic addition of only one ionized *gem*-diamine donor to the ligand, were not observed. The FAB mass spectrum for **4** was not recorded due to solubility problems.

Thermogravimetric analyses were performed to learn the proper range of temperature to prepare thin films of the complexes for testing their electrical properties. The compounds **1**, **2**, **3** and **4** show the loss of two water molecules at 189.7, 300, 140 and 475°C, respectively. The water molecules could be coordinated as in $[Cu(TAAB(OH)_2)(H_2O)_2]$ [4], at least for complexes **2** and **4**. In addition, complexes **2**, **3** and **4** exhibit the loss of two more water molecules at lower temperature (at 225, 120 and 175°C, respectively), probably crystallization molecules. The complexes exhibit a 50% decomposition near 800°C, complex **4** is the most thermally stable with only 6% decompositlon at 801°C. Derivative **3** is much more unstable, decomposing in 90% at 779°C. Thermal stability is required for complexes, which are expected to be semiconducting compounds.

The reflectance spectra of these compounds exhibit three bands in the regions 14,300–14600, 19,300–20,600 and 25,400–27,800. A tetragonal six-coordinate environment may be suggested for the copper(II) center, according to the observed spectra of related compounds [4, 7, 9–11]. This arrangement can be achieved by water axial ligation to the expected square-planar $Cu(TAABL)^{2+}$ ($L = NH(CH_2)_2NH_2$, $NH(CH_2)_4NH_2$, $NH(CH_2)_{12}$ NH_2, and $(C_{14}H_9N_2O_2)_2$) as suggested for $[Cu(TAAB(OH)_2)(H_2O)_2]$ [4]. The thermogravimetric data support this proposal. The highest energy bands are not due solely to *d–d* transitions but rather to allowed charge transfer ligand-copper, copper-ligand or ligand–ligand transitions, which occur in the visible-UV region and are more intense than *d–d* transitions [11, 12].

The four copper(II) complexes exhibit magnetic moments within the range of 2.02 to 2.61 BM. The anomalous high values of 2.25 and 2.61 BM (for **1** and **2**, respectively) may not be only ascribed to temperature-independent paramagnetism and/or insufficient correction for diamagnetism employing Pascal's constants. A further investigation by recording the variation of the molar magnetic susceptibility with the absolute temperature, is necessary to identify important magnetic interactions as the antiferromagnetic or, the less common, ferromagnetic interaction present in dinuclear or polynuclear structures [11].

Electrical Properties

Figure 1 shows the temperature dependence of the electrical current of the complexes **1** to **4** and the starting material, $[Cu(TAAB)](NO_3)_2$. We tried to establish the behavior of these material as semiconducting, conducting or insulating complexes, and their resistance to the electrical current. However, the conductivity values obtained for compounds are not absolute because the tablet thickness (~1 mm) is gross, and the real trajectory of the conductivity along the material is unknown. It is observed that compounds treated with alkyl amines show semiconducting behavior, while complex **4**, containing 2,6-diaminoanthraquinone, behaves as a semiconductor within the range of −80°C to −40°C. Over 40°C the latter compound has metallic

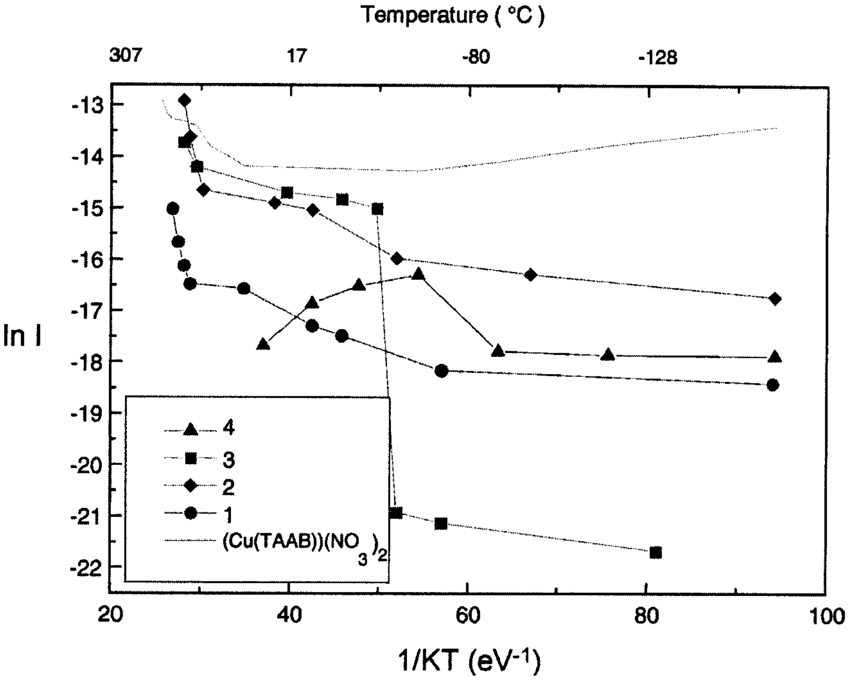

FIGURE 1 Plots of the ln(electrical current) *vs.* 1/K(temperature) for [Cu(TAAB)]$(NO_3)_2$ (the starting material), [Cu(TAABL)]$(NO_3)\cdot nH_2O$ (compounds **1** to **3**) and [Cu(TAAB $(C_{14}H_{10}N_2O_2)_2$] $\cdot 4H_2O$ (**4**) in tablets with constant applied voltage of 100 V in the ohmic regime.

behavior because the amount of current decreases as temperature increases. On the other hand, with the exception of **4**, the other curves present a significant change in slope for temperatures near 160°C where, according to thermogravimetry data, the compounds lose water molecules.

The conductivity at room temperature for each tablet of molecular solid and the starting material were measured. The results of the electrical conductivity are shown in Table II. None of them are within the expected range of electrical conductivity for molecular semiconductors (10^{-6}–$10^{-1}\,\mathrm{cm}^{-1}\Omega^{-1}$). This may be due to the fact that the measurements of the electrical current variation with temperature were performed on tablets, where the conductivity is different by 3 to 6 orders of magnitude in comparison to the conductivity obtained on films. The use of films is more reliable way to measure electrical conductivity [13].

Figure 2 shows the temperature dependence of the electrical current through thin films of compounds **1** to **4** and [Cu(TAAB)]$(NO_3)_2$. The starting material generates higher electrical current flux, similar to the behavior of a

TABLE II Tablets dimension and conductivity for the starting material, [Cu(TAABL)]$(NO_3)\cdot nH_2O$ (**1** to **3**) and [Cu(TAAB$(C_{14}H_{10}N_2O_2)_2$]$\cdot 4H_2O$ (**4**) at 20°C (samples in tablets, Ohmic voltage of 100 V)

Complex	*Thickness t (mm)*	*Distance between electrodes w (mm)*	*Diameter (mm)*	*Electrical current I (A)*	*Resistance R* (Ω)	*Conductivity* σ ($\Omega^{-1}cm^{-1}$)
[Cu(TAAB)]$(NO_3)_2$	1.50	3.0	12.9	4.901E-7	204.0E6	7.6E-9
1	1.95	3.2	12.6	2.191E-8	4.560E9	2.9E-10
2	0.45	3.0	12.8	3.364E-7	297.3E6	1.8E-8
3	1.35	5.1	12.8	9.83E-10	1.02E11	2.9 − 11
4	1.10	6.0	12.9	2.098E-8	4.766E9	8.9E-9

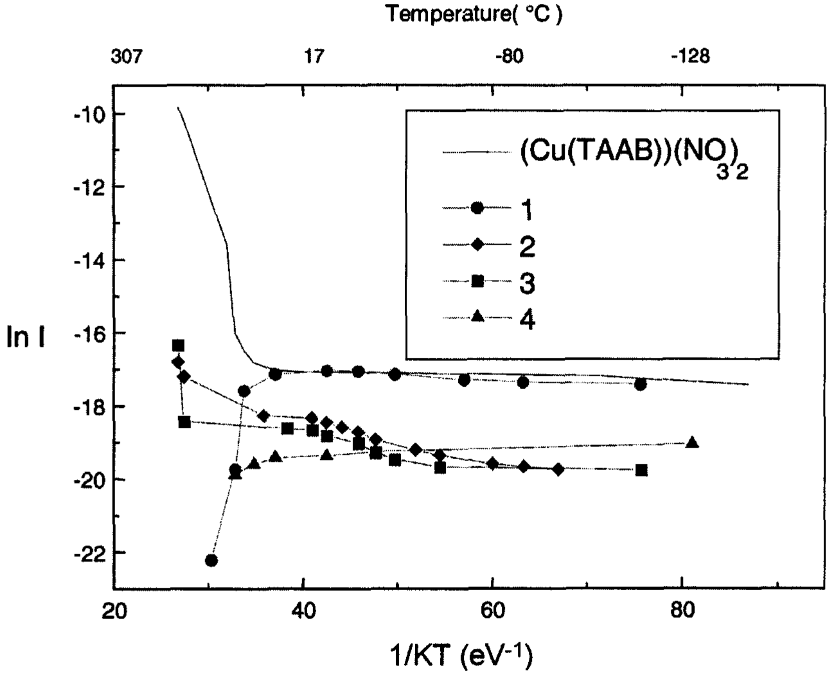

FIGURE 2 Plots of the ln(electrical current) *vs.* 1/K(temperature) for $[Cu(TAAB)](NO_3)_2$ (the starting material), $[Cu(TAABL)](NO_3)\cdot nH_2O$ (compounds 1 to 3) and [Cu(TAAB $(C_{14}H_{10}N_2O_2)_2]\cdot 4H_2O$ (4) in thin films with constant applied voltage of 100 V in the ohmic regime.

semiconducting compound since the temperature and current flux increase. Compounds **2** and **3** also show this behavior although their current values are not as high as those obtained for the starting material. On the other hand, the current transport in compounds **1** and **4** is almost constant until 12°C. However, at higher values the materials behave as conducting species. The reason for these variations may be the different substituent bonded to the macroligand. Apparently, the current is bigger if there is no substituent on the TAAB ligand or if it is a small one, as for $[Cu(TAAB)](NO_3)_2$ and **1**, respectively.

Table III shows the results of the electrical conductivity on thin films for each complex and $[Cu(TAAB)](NO_3)_2$. All compounds show an electrical conductivity value within the range reported for molecular semiconducting compounds ($106^{-6} - 10^{1}\,\Omega^{-1}\mathrm{cm}^{-1}$). This is important, because a semiconductor is generally defined in terms of its conductivity at room temperature and the temperature dependence of conductivity, besides its contents and kind of impurity, structure, stacking way and orbital overlap.

TABLE III Films dimension and conductivity for the starting material, $[Cu(TAABL)](NO_3)\cdot nH_2O$ (**1** to **3**) and $[Cu(TAAB(C_{14}H_{10}N_2O_2)_2\cdot 4H_2O$ (**4**) at 20°C (samples in films, Ohmic voltage of 100 V)

Complex	*Thickness t (mm)*	*Distance between electrodes w (cm)*	*Electrode Lengths L (cm)*	*Electrical current I (A)*	*Resistance R (Ω)*	*Conductivity* σ $(\Omega^{-1}cm^{-1})$
$[Cu(TAAB)](NO_3)_2$	680E-8	1.1	1.65	3.918E-8	2.552E9	3.8E-5
1	1412E-8	0.85	1.95	3.946E-8	2.534E9	1.2E-5
2	160E-8	1.5	2.00	1.098E-8	9.107E9	5.2E-5
3	1912E-8	1.25	1.80	8.480E-9	1.18E10	3.1E-6
4	175E-8	0.5	2.10	3.815E-9	2.62E10	5.2E-6

Although the electrical conductivity values of **1** and **4** are within the established range for molecular semiconductors, their behavior is not of a semiconducting material. Current flux remains constant, with change in temperature. The remaining compounds only exhibit semiconducting behavior at high temperature and this may be due to the supplied thermal energy, which is high enough to allow electrons to jump into the conduction band.

The purpose of IR spectra on thin films was to determine if there were significant changes on the materials during preparation of the films (Tab. I). Substrate adsorption was corrected by subtracting the monocrystalline silicon spectrum. Amorphous films were obtained and therefore, the atom positions are not as regular as in crystals, yet they were not random. These systems still possess a well-defined short range order similar to that is observed in the crystalline phase. Thus, the atomic separation and the number and distribution of the nearest neighbors will be on average the same in any part of the sample [14].

Refraction index and reflectance of films for the compounds are shown in Table IV. The films can be analyzed according to the Tauc model [15] for optical properties. This model was developed for studying optical properties of amorphous semiconducting materials due to the following features: (1) The estimated reflectance for thin films shows values 15% or lower; (2) the IR spectroscopic results indicate that chemical composition of films is fundamentally the same as the original compounds, and (3) X-ray powder diffraction results indicate the amorphous nature of the films.

Adsorption coefficient (α) values and photon energy (E_{photon}) for molecular solids [16], were obtained from UV-vis spectra. The following graphics show the adsorption coefficient dependence of the photon energy (Fig. 3). It was observed that compound **4** presents the highest absorption coefficient, followed by $[Cu(TAAB)](NO_3)_2$ and complex **2**.

Table IV also shows the optical activation energies obtained from measurements of the temperature variation with the electrical current transport and the electrical conductivity in films. The optical activation energy, calculated with the Tauc model, did not present any similarity to the activation energies obtained from measurements of the variation of electrical current with temperature. Therefore, the Tauc model does not explain completely the behavior of our compounds. For these amorphous materials, "the bands model" may be appropriate, since the short scope order is the most influential factor. The absence of long scope order has the effect of diffusing band edges and forming tails [14]. The electronic states of these tails are located and are not the same for the bands. In these states, electrons have lower mobility compared to those of the bands. The Fermi

TABLE IV Optical parameters for the starting material, [Cu(TAABL)](NO_3)·nH_2O (1 to 3) and [Cu(TAAB($C_{14}H_{10}N_2O_2$)$_2$]·$4H_2O$ (4) in thin films.

Complex	*Refraction index*	*Reflectance* (%)	*Optical activation energy* E_g (*eV*)	*Activation energy* E_{ac} (*eV*)
[Cu(TAAB)](NO_3)$_2$	1.672	6.3	2.3	0.0112
1	1.771	7.7	2.0	0.005
2	1.698	6.7	2.2	0.086
3	1.609	5.5	1.5	0.097
4	1.570	4.9	2.2	0.034

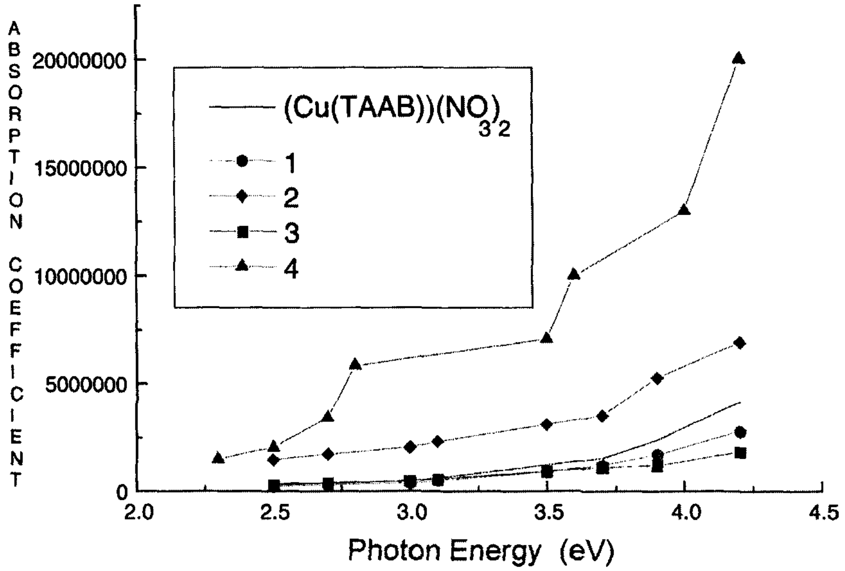

FIGURE 3 Plots of the absorption coefficients *vs.* photon energies for [Cu(TAAB)](NO_3)$_2$ (the starting material), [Cu(TAABL)](NO_3)·nH_2O (compounds 1 to 3) and [Cu(TAAB($C_{14}H_{10}N_2O_2$)$_2$]·$4H_2O$ (4)

energy (E_F) is then, similar to the energy bands in crystalline materials [14]. However, it was not possible to establish the region where charge transfer occurs for our compounds.

References

[1] J. A. Schlueter, U. Geiser, A. M. Kini, H. H. Wang, J. M. Williams, D. Naumann, T. Roy, B. Hoge and R. Eujen, *Coord. Chem. Rev.* **190–192**, 781 (1999); (b) H. Tanaka, T. Adachi, E. Ojima, H. Fujiwara, K. Kato and H. Kobayashi, *J. Am. Chem. Soc.* **121**, 11243 (1999); (c) J. Simon and F. Tournillac, *New J. Chem.* **11**, 383 (1987).

[2] P. Day, *Coord. Chem. Rev.* **190–192**, 827 (1999).

[3] (a) A. J. Epstein and Y. Yang, *MRS Bulletin* June 13–15, 1997, (b) A. J. Jircitano, M. C. Colton and K. Bowman, *Inorg. Chem.* **20**, 890 (1981).
[4] (a) O. Schneider and M. Hanack, *Angew. Chem. Int. Ed. Engl.* **19**, 392 (1980); (b) A. J. Jircitano, M. C. Colton and K. Bowman, *Inorg. Chem.* **20**, 890 (1981).
[5] L. T. Taylor, F. L. Urbach and D. H. Busch, *J. Am. Chem. Soc.* **91**, 1072 (1969).
[6] J. Labuda and V. Plaskoň, *Inorg. Chim. Acta.* **146**, 13 (1988).
[7] L. Katovic, T. Taylor and D. H. Busch, *Inorg. Chem.* **3**, 458 (1971).
[8] S. Kumar, R. Malhotra and K. S. Dhindsa, *Polyhedron* **11**, 1383 (1992).
[9] G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.* **86**, 4834 (1964).
[10] B. K. Coltrains and S. Jackels, *Inorg. Chem.* **20**, 2032 (1981).
[11] Wilkinson, G. (Ed.) "*Comprehensive Coordination Chemistry*" Volume 5, Late Transition Elements, 1^a edn. Pergamon Press, NY, 1987
[12] A. B. Lever "Inorganic Electronic Spectroscopy" 2^a edn., Elsevier 33 Science Publishers, NY, 1984.
[13] A. J. Jircitano, M. D. Timken, K. Bowman and J. R. Ferrano, *J. Am. Chem. Soc.* **101**, 7761 (1979).
[14] R. W. Cahn, P. Haasenm and E. J. Kramer "*Material Science and Technology*, A comprehensive Treatment" **4**, Ed. W. Schroeter, 1^a edn., VCH Publisher Inc., NY, 1991.
[15] (a) J. Metz and M. Hanack, *J. Am. Chem. Soc.* **105**, 828 (1983); (b) D.H. Busch, *J. Chem. Educ.* **41**, 77 (1964).
[16] B. O. Seraphin "*Optical Properties of Solids. New Developments*" 1^a edn., North-Holland Publishing Company, NY, 1976.