PREPARATION AND CHARACTERIZATION OF MOLECULAR-MATERIAL CONTAINING DIAQUA TETRABENZO (b,f,j,n) {1,5,9,13} TETRAAZACYCLOHEXADECINE COPPER (II) BISANTHRAFLAVATES

M. E. Sánchez Vergara[a*], J.R.Álvarez Bada[b] B. Frontana Uribe[c]

[a] Coordinación de Ingeniería Mecatrónica. Escuela de Ingeniería, Universidad Anahuac del Norte. México.
[b] Instituto Tecnológico y de Estudios Superiores de Monterrey, Campus Ciudad de México, México.
[c] Instituto de Química, Universidad Nacional Autónoma de México, México D. F.

elena.sanchez@anahuac.mx, rbada@itesm.mx

Received on October 5th, 2007. Accepted on November 15th, 2007.

ABSTRACT

For the recent years, molecular materials have been subject of considerable interest due to their characteristic electrical properties, which confer them conducting, semiconducting and superconducting behaviour. This work concerns the preparation of molecular materials by chemical synthesis and electrosynthesis. New materials were synthesized using both methods from tetrabenzo (b, f, j, n) {1,5,9,13} tetraazacyclohexadecine copper (II). These compounds were characterized through IR and mass spectroscopy as well as by SEM and EDS analyses.

RESUMEN

En años recientes, el estudio de los materiales moleculares ha estado sujeto a un considerable interés, debido a sus propiedades eléctricas características, que les confieren un comportamiento conductor, semiconductor y superconductor. El presente trabajo se refiere a la preparación de materiales moleculares, utilizando como vías alternas la síntesis química y la electrosíntesis. Nuevos materiales fueron sintetizados a partir del tetrabenzo (b, f, j, n) {1,5,9,13} tetraazacyclohexadecino de cobre (II). Estos compuestos fueron caracterizados a partir de espectroscopia IR, espectrometría de masas, Microscopía Electrónica de Barrido (MEB) y Espectroscopia de energía dispersa (EDS).

Key words: Chemical synthesis; Electrosynthesis; Molecular Materials; Cyclic voltammetry; Macrocycle

INTRODUCTION

Over the last 25 years, there have been considerable efforts in order to find new materials for electronic and optoelectronic applications. Most research has dealt with inorganic materials, while the organic and organometallic derivatives have been relatively neglected. Nevertheless, the potential usefulness of organic and organometallic compounds became clear when it was reported that the tetrathiofulvalene chloride (TTF) salt is conductive at relatively low temperatures between 50 and 60 K [1] and the application of (organo-) aluminium compounds as thin films for microelectronics was investigated [2]. Organometallic devices may be considered for electronics applications requiring large area coverage, structural flexibility and low-temperature processing [3]. Compounds combining different organometallic moieties and their electron transfer processes have attracted considerable attention [4-6].

It has been observed, that a regular stacking of molecules, such as those found in molecular materials, allows the formation of semiconducting, conducting or superconducting compounds. These molecular materials generally exhibit preferential directions for electrical conductivity. Their highly anisotropic conductivities almost reach metallic values along a preferred direction defined by their structural configuration. This arises from a great number of long and parallel chains or molecular stacks along which conduction seems to occur [7]. Tetrabenzo (b,f,j,n) {1,5,9,13} tetraazacyclohexadecine metal (II) complexes, for example, have been extensively studied due to their electrical properties [8].

16 varieties of $M(TAAB)^{2+}$ macrocyclic complexes have a delocalized electronic structure. Around the macrocyclic cation, the coordination sphere surrounding the metallic ion is almost flat. However the general geometry of the macrocyclic complex shows a saddle form, or S_4 symmetry, mathematically described as a hyperbolic paraboloid. This kind of complexes are formed by the self-condensations of o-aminobenzaldehide in the presence of transition metallic ions such as Ni (II), Co (II) and Cu (II), which have the ability to act as a template, so as to isolate macrocyclic ligands. These compounds are highly stable at room temperature, but the magnetic and spectral properties that they show depend on the anion they bind with [8]. For example, the $Ni(TAAB)X^2$ compounds show tetragonal geometry. The study of the incorporation of substituent groups at the macrocyclic ligand is quite interesting because of the possibility of using such systems in nanoelectronics systems.

These compounds are of particular interest in the study of low-dimensional metals and semiconductors as one may bridge macrocycle nuclei with linear bidentate axial ligands, which suggests a model for low-dimensional polymeric conduction in macrocycles [8]. In these ligand-bridged systems, the central metal-axial ligand spine is expected to be a reasonable pathway for conduction [9]. Special attention must be given to ligand-bridged materials with a highly delocalized electronic structure such as macrocycle complexes that have been used as models for the construction of conductive materials [10,11]. The tetrabenzo (b,f,j,n) {1,5,9,12,13} tetraazacyclohexadecine copper (II) complex is one of the macrocycles employed for that purpose in this work [12]. These materials may show interesting changes in their electric conductivity when incorporating substitute groups to their macrocyclic ligands.

In this paper, we report the preparation by chemical synthesis and electrosynthesis of molecular-materials containing diaqua tetrabenzo (b,f,j,n) {1,5,9,13} tetraazacyclohexadecine copper (II) bisanthraflavates and base molecules L like pyridine, 2-methylpyrazine, piperidine and *n*-butylamine. Electrosynthesis is a convenient technique for the synthesis of molecular conductors [12-14] involving the formation of radical ions through chemical reduction or oxidation and simultaneous salt crystallization derived with the inorganic counter-ion of the support electrolite. The advantages of this technique include precise control of the structure at high temperatures.

EXPERIMENTAL SECTION

Reagent-grade commercial products were used without further purification. Nitrate of [tetrabenzo (b,f,j,n) {1,5,9,13} tetraazacyclohexadecine] copper (II): $[Cu(TAAB)(H_2O)_2](NO_3)_2$ macrocycles were prepared according to literature [15].

Electrosynthesis procedure

Electrosynthesis is carried out using platinum as the anode and the cathode. The cleaning of the electrodes is performed by treatment with *aqua regia*, followed by successive anodic and cathodic polarisation of the electrode in dilute sulphuric acid. Solutions of tetrabenzo (b,f,j,n) {1,5,9,13} tetraazacyclohexadecine copper (II) (12 mg) in ethanol or methanol (20 mL) are introduced into the cathodic compartment of an H-shaped electrochemical cell. The pure ligand L (L = butylamine (5 mL), pyridine (5 mL), 2-methylpyrazine (100 mg), piperidine (5 mL)) as supporting electrolyte in ethanol or methanol (15 mL) is introduced into the anodic compartment. Galvanostatic electrolysis was conducted at a constant current density of 5 μAcm^{-2} and 298 K. Within 25-30 days, a black compound grows on the electrode.

Chemical synthesis procedure

The molecular materials M(TAAB)L were prepared by stirring tetrabenzo (b,f,j,n) {1,5,9,13} tetraazacyclohexadecine copper (II) in the pure ligand L (L = pyridine, 2-methylpyrazine, piperidine, n-butylamine) for 2 days. The brown solution was cooled and filtered. The resulting powder was dried under vacuum, yielding the products M(TAAB)L.

Synthesis of $[Cu(TAAB)(H_2O)_2](bu)_2$ *(compound 1a)*: A 0.1 g (0.169 mmol) sample of tetrabenzo (b,f,j,n) {1,5,9,13} tetraazacyclohexadecine copper (II) in 10mL of absolute methanol was treated later with 20 mL of 1,4 butylamine (in excess) between 2 days. The brown solution is concentrated and refrigerated to crystallize the product. The solid was filtered off, washed with absolute methanol and vacuum-dried. The product was recrystallized in 1:1 acetonitryl-methanol. Yield 83% (0.89 g).

Synthesis of $[Cu(TAAB)(H_2O)_2](py)_2$ *(compound **1b**)*: A 0.1 g (0.169 mmol) sample of tetrabenzo (b,f,j,n) {1,5,9,13} tetraazacyclohexadecine copper (II) in 10mL of absolute methanol was treated later with 10 mL pyridine (in excess) for 2 days. The black solution is concentrated and refrigerated to crystallize the product. The solid was filtered off, washed with absolute methanol and vacuum-dried. The product was recrystallized in 1:1 acetonitryl-methanol. Yield 88% (0.89 g).

Synthesis of $[Cu(TAAB)(H_2O)_2](mepyz)_2$ *(compound **1c**)*: 0.2 g (0.64 mmol) of methylpyrazine previously dissolved in 10 mL of absolute ethanol was added to a 0.1 g (0.169 mmol) sample of tetrabenzo (b,f,j,n) {1,5,9,13} tetraazacyclohexadecine copper (II) in 10mL of absolute ethanol The resulting solution was refluxed for two days until an olive-green precipitate appeared. The red solution is concentrated and refrigerated to crystallize the product. The solid was filtered off, washed with absolute ethanol and vacuum-dried. The product was recrystallized in a 1:1 ethanol-water. Yield 89% (0.89 g).

Synthesis of $[Cu(TAAB)(H_2O)_2](pip)_2$ *(compound 1d)*: A 0.1 g (0.169 mmol) sample of tetrabenzo (b,f,j,n) {1,5,9,13} tetraazacyclohexadecine copper (II) in 10ml of absolute methanol was treated later with 10 mL piperidine (in excess) for 2 days. The black solution is concentrated and refrigerated to crystallize the product. The solid was filtered off, washed with absolute methanol and vacuum-dried. The product was recrystallized in 1:1 acetonitryl-methanol. Yield 78% (0.89 g).

Characterization methods

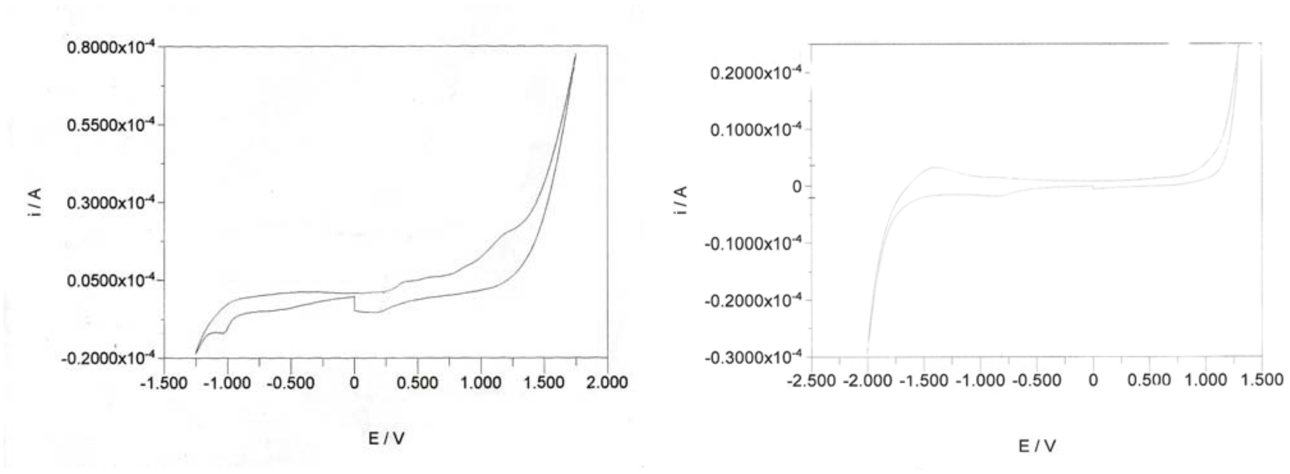
Electrochemical experiments were conducted with an Autolab PGSTAT30 system in a conventional three-electrode mode. Elemental analysis of the electrodeposited films was performed with a scanning electron microscope (SEM) Jeol JSM5900 coupled to an energy-dispersive spectrophotometer (EDS) working at 20 keV. The acquisition of the EDS data was stopped when it reached 5000 counts. The infrared spectra were obtained by using an IR spectrophotometer Perkin Elmer

282-B. The spectra were recorded by the KBr-pellet technique.

RESULTS AND DISCUSSION

Cyclic voltammetry was performed on the starting compounds to investigate their redox properties individually. From this information, it was possible to investigate their ability to electrodeposit material by themselves as well as to infer a possible molecular-material formation from the mixtures. The cyclic-voltammetry responses of the tetrabenzo (b,f,j,n) {1,5,9,13} tetraazacyclohexadecine copper (II) and the pyridine system are shown in figs. 1a and 1b, respectively. The voltamperagram of Fig. 1a shows an interesting behaviour; because of the molecule containing Cu(II), there are several changes which are related to reduction and oxidation processes. We analyzed the negative or left side of the graph to look for the reduction peaks. Starting at -1.021V, it goes up until it reaches one peak at 0.250 V and a continuous cathodic current with reductive behaviour. It stops at a 1.75 V potential with an approximated intensity of 0.8000x10^{-4} μA. The inverse scanning was changed and we found an oxidation peak at 1.173 V with cathodic intensities. Further on, there is another peak at 0.380 V and cathodic intensity of 0.0500 x 10^{-4} μA. Oxidation continues until reaching the -1.250V point and an anodic current intensity of -0.2 x 10^{-3} μA. This compound may reduce as well as oxidize. At the voltamperegram of Fig. 1b, one observes two almost imperceptible peaks. Towards the positive side of the reaction, there is an oxidative behaviour at a potential of 1.335V; then it descends abruptly until it shows a passivity range from 0.75 V until -0.500 V and a current practically equal to zero. After that point, there is an oxidation peak at -1.400 V and an intensity of cathodic current of 0.3636x10^{-4} μA. Oxidation continues and descends quickly until -2.000 V, where there is an anodic current intensity of -0.3000 x 10^{-4} μA.

The compound showed a well-defined electroactivity with one redox pair of peaks. The potential of the anodic current peak nonlinearly increased with the scan rate. Anodic and cathodic peak currents are observed in both cyclic-voltammetry plots. From the redox peak values of both compounds, it was possible to find the appropriate potential difference for the formation of molecular materials in the electrosynthesis cells as suggested by the Saito and Ferraris criterion [16]. This analysis was performed on each of the starting compounds and similar results were found for both.



(a) (b)

Fig. 1. Cyclic voltammetry of the (a) tetrabenzo (b,f,j,n) {1,5,9,13} Tetraazacyclohexadecine copper (II) and (b) pyridine species

The purpose of IR spectroscopy on thin films was to determine the presence of functional groups and the most important and representative bonds of different synthesized compounds. Table 1 shows the IR band spectra for the newly synthesized compounds in their different forms (chemical synthesis and electrosynthesis). The IR spectra show that compounds obtained by chemical synthesis have the same absorption bands as the compounds obtained by electrosynthesis. Studies realized by Kumar and Katovic [17, 18], confirm the fact that the nucleophilic addition of two ligands to the azometine bonds corresponding to the macrocycle occurs during the synthesis. If the reaction takes place in a proper way, four absorption bonds assigned to the vibration of the orto-disubstituted benzenes must be present [15]. The absence of the band attributed to the imine-group vibration is also necessary [17, 18], as the binding between the macrocycle and the substituent is shown in this zone; on the other hand, the presence of the band related to the stretching vibration of the two remaining azomethine bonds in the 2910-3372 cm^{-1} region [17,18] is a consequence of the absence of the imine-group vibration band. Furthermore, those bands related to vibrations of the nitrate anion must disappear as a result of the double nucleofilic addition. It is known that highly-ordered anisotropic molecules forming long symmetrical chains are a distinctive feature of molecular materials. Such formations can take place only by substituting the nitrate groups in the acceptor by the group of the donor compound. The IR spectrum of the powder compound shows four absorption bands located around 1610, 1588, 1493 and 1444 cm^{-1} related to the stretching vibration of the ortho-disubstituted benzene radicals in the macrocycle. On the other hand, the bands at the 823, 1355 and 1387 cm^{-1} regions of the NO_3^{-1} ion do not appear in the synthesized materials, which suggests that, for this compound, a double nucleofilic substitution by two molecules of ligand takes place in the macrocycle.

Table 1. IR data for the reported compounds obtained by chemical synthesis and electrosynthesis. All units cm^{-1}.

Compound	ν (C_6 ring)	ν (C_6 ring)	ν (C_6 ring)	ν (C_6 ring)
$[Cu(TAAB)(H_2O)_2](bu)_2$ *chemical synthesis*	1610	1585	1493	1444
$[Cu(TAAB)(H_2O)_2](bu)_2$ *electrosynthesis*	1609	1581	1497	1440
$[Cu(TAAB)(H_2O)_2](py)_2$ *chemical synthesis*	1610	1585	1493	1444
$[Cu(TAAB)(H_2O)_2](py)_2$ *electrosynthesis*	1607	1586	1496	1446
$[Cu(TAAB)(H_2O)_2](mepyz)_2$ *chemical synthesis*	1614	1588	1496	1435
$[Cu(TAAB)(H_2O)_2](mepyz)_2$ *electrosynthesis*	1615	1588	1497	1431
$[Cu(TAAB)(H_2O)_2](pip)_2$ *chemical synthesis*	1607	1589	1493	1444
$[Cu(TAAB)(H_2O)_2](pip)_2$ *electrosynthesis*	1609	1588	1496	1443

The SEM micrographs of the chemically and electrochemically synthesized *$[Cu(TAAB)(H_2O)_2](bu)_2$*, compounds are shown in Fig. 2. In all cases, the compounds showed a granular appearance. The surface of the deposited films was composed of elongated granules.

The SEM micrographs of the chemically and electrochemically synthesized $[Cu(TAAB)(H_2O)_2](py)_2$ compounds are shown in Fig. 3. In all cases, the compounds showed an irregular appearance. Nevertheless, the compound prepared by electrosynthesis, shows small, randomly-deposited granules.

The SEM micrographs of the chemically and electrochemically synthesized $[Cu(TAAB)(H_2O)_2](mepyz)_2$ compounds are shown in Fig. 4. Both micrographs show materials with an irregular morphology and wrinkled appearance.

Finally, the SEM micrographs of the chemically and electrochemically synthesized $[Cu(TAAB)(H_2O)_2](pip)_2$ compounds are shown in Fig. 5. These micrographs show piles of irregular material in randomly distributed agglomerations, with the electrochemically-synthesized material showing a more uniform and smooth appearance.

The EDS results presented in Fig. 6 show the presence of nitrogen and carbon due to n-butilamine, copper and oxygen from the Cu(II) TAAB nitrate. Similar results were found for the remaining synthesized materials.

The most important types of molecular fragments obtained by mass spectrometry with the FAB^+ technique are summarized in table 2, where the mass/charge (m/e) relation values corresponding to the most abundant isotopes are also listed.

The spectra provide the molecular fragment which corresponds to tetrabenzo (b,f,j,n) {1,5,9,13} tetraazacyclohexadecine copper (II) $[C_{28}H_{20}N_4Cu]^+$ m/e = 537, and the fragment corresponding to the pure ligand L (L = pyridine $[C_5H_5N]^+$ m/e = 79, 2-methylpyrazine $[C_4H_3N_2]^+$ m/e = 94, piperidine $[C_5H_{10}N]^+$ m/e = 84, n-butylamine $[C_4H_9]^+$ m/e = 57).

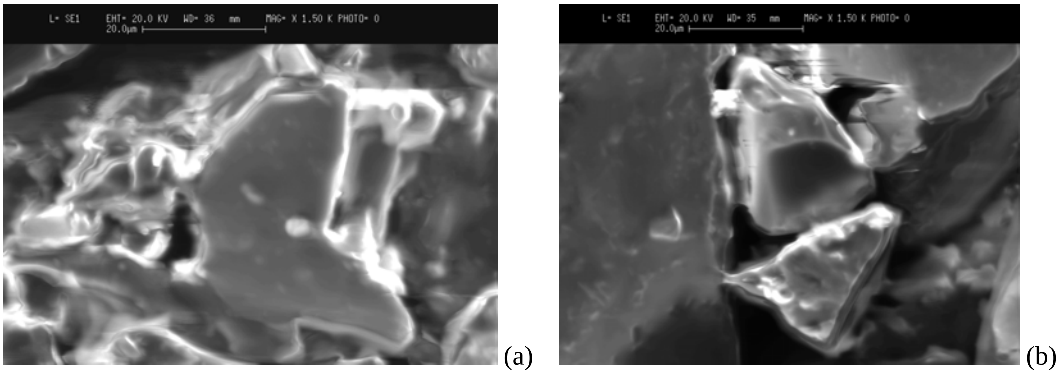


Fig. 2. SEM micrograph of the $[Cu(TAAB)(H_2O)_2](bu)_2$, chemically (a) and electrochemically synthesized (b) at 1500x.

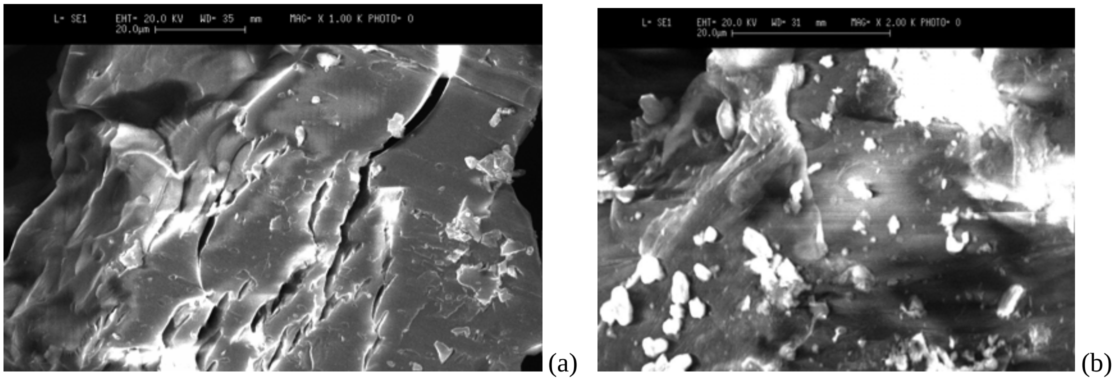


Fig. 3. SEM micrograph of the (b) $[Cu(TAAB)(H_2O)_2](py)_2$, chemically (a) and electrochemically synthesized (b) at 1000 and 2000x, respectively.

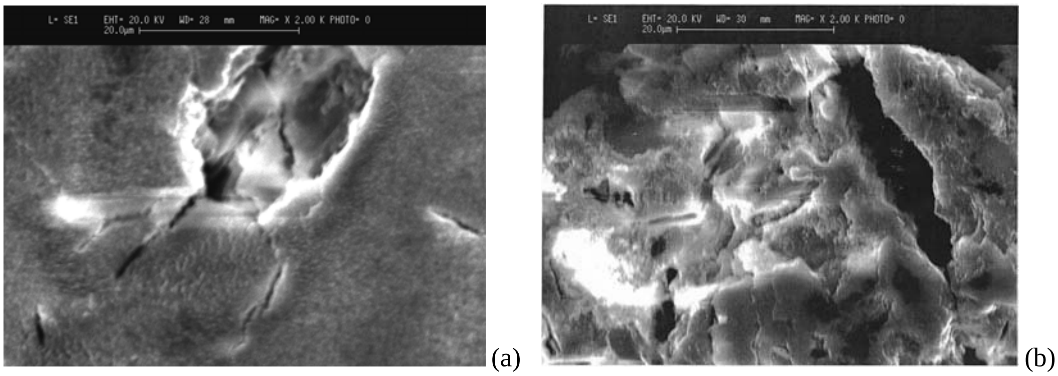
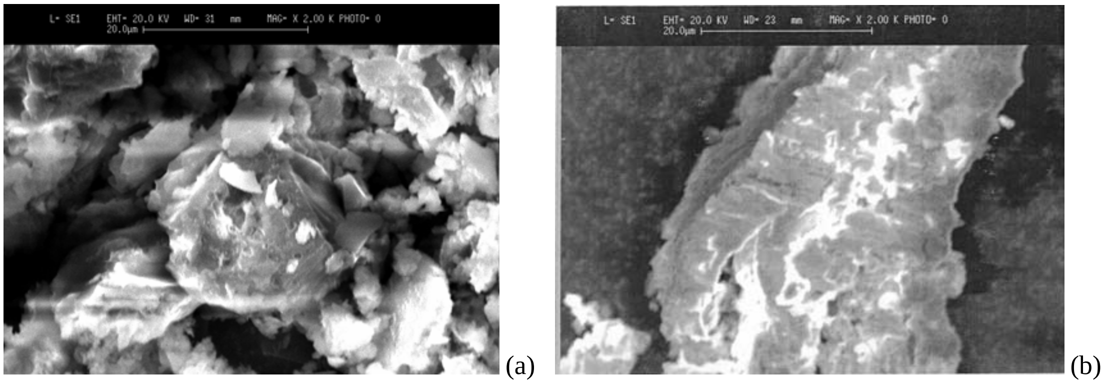


Fig. 4. SEM micrograph of the $[Cu(TAAB)(H_2O)_2](mepyz)_2$ chemically
(a) and electrochemically synthesized (b) at 2000x.



Fi. 5. SEM micrograph of the $[Cu(TAAB)(H_2O)_2](pip)_2$ chemically
(a) and electrochemically synthesized (b) at 2000x.

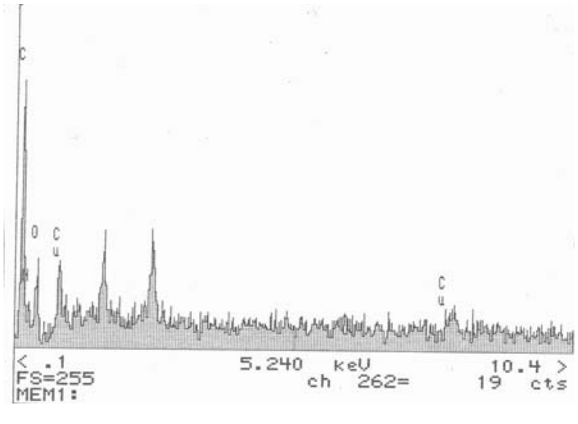


Fig. 6. EDS for $[Cu(TAAB)(H_2O)_2](pip)_2$

The fragments corresponding to $[Cu(TAAB)(H_2O)_2](bu)_2$, $[Cu(TAAB)(H_2O)_2](py)_2$, $[Cu(TAAB)(H_2O)_2](mepyz)_2$ and $[Cu(TAAB)(H_2O)_2](pip)_2$ and fragments with two added ligands as in chemically synthesized materials, as well as those obtained through electrocrystallization. Higher-molecular-weight fragments do not appear in the mass spectrum, partly because of the limited solubility of the materials.

Table 2. Characteristic molecular fragments for the reported compounds obtained bychemical synthesis and electrosynthesis.

COMPOUND	FRAGMENT	M/E
$[Cu(TAAB)(H_2O)_2](bu)_2$ *chemical synthesis*	$[C_{36}H_{38}N_4Cu]^+$	589
$[Cu(TAAB)(H_2O)_2](bu)_2$ *electrosynthesis*	$[C_{36}H_{38}N_4Cu]^+$	590
$[Cu(TAAB)(H_2O)_2](py)_2$ *chemical synthesis*	$[C_{38}H_{30}N_6Cu]^+$	633
$[Cu(TAAB)(H_2O)_2](py)_2$ *electrosynthesis*	$[C_{38}H_{30}N_6Cu]^+$	633
$[Cu(TAAB)(H_2O)_2](mepyz)_2$ *chemical synthesis*	$[C_{36}H_{26}N_8Cu]^+$	634
$[Cu(TAAB)(H_2O)_2](mepyz)_2$ *electrosynthesis*	$[C_{36}H_{26}N_8Cu]^+$	633
$[Cu(TAAB)(H_2O)_2](pip)_2$ *chemical synthesis*	$[C_{38}H_{40}N_6Cu]^+$	644
$[Cu(TAAB)(H_2O)_2](pip)_2$ *electrosynthesis*	$[C_{38}H_{40}N_6Cu]^+$	644

CONCLUSIONS

The electrosynthesis of new molecular materials constituted of diaqua tetrabenzo (b,f,j,n) {1,5,9,13} tetraazacyclohexadecine copper (II) bisanthraflavates and base molecules L like pyridine, 2-methylpyrazine, piperidine and *n*-butylamine has been presented. These synthesized molecular materials were prepared in two forms: chemical synthesis and electrosynthesis in electrocrystallization cells. In both cases, molecular materials were synthesized from donor and acceptor species. In general, these materials show amorphous and irregular morphologies and some wrinkles. It is important to note that the electrosynthesis is a slower process that generates smaller amounts of molecular materials than the chemical method. This complicates the subsequent evaluation of the optical and electrical properties of materials, since they are measured from thin films whose preparation requires considerable amount of material that will be evaporated and deposited at low pressures over several substrates. The chemical method provides enough material to prepare the corresponding thin films. Nevertheless, the purity of those materials obtained by electrosynthesis is superior to the purity of the chemically-obtained materials, which need additional processes of purification and crystallization.

REFERENCES

[1] M.R. Bryce, J. Mater. Chem. 5 (1995)148.

[2] G.B. Stringfellow, Organometallics Chemical Vapor Epitaxy. Academic Press, New York, 1989.

[3] R.A. Laudise, Ch. Kloc, P.G. Simpking, T. Siegrist, J. Crystal Growth 187 (1998) 449.

[4] S. Rigaut, J. Massue, D. Touchard, J. L. Fillaut, S. Golhen, P. H. Dixneuf, Angew. Chem. Int. Edit. Engl. 41 (2002) 4513.

[5] J. C. Roeder, F. Meyer, E. Kaifer, Angew. Chem. Int. Edit. Engl. 41 (2002) 2304

[6] D. Astruc, Acc. Chem. Res. 30 (1997) 383.

[7] M. Rivera, C. Alvarez-Toledano, A. Moreno, J.D. Sepúlveda-Sánchez, T. Hernández-Pérez, M.E. Sánchez-Vergara, J. Braz. Chem. Soc. 16, No.3A (2005) 316.

[8] M. E. Sánchez-Vergara , A. Ortiz, Cecilio Álvarez-Toledano and J.R. Álvarez. Thin Solid Films.488, (2005), 34.

[9]K. Soo-Jong, M. Michiko, S. Kiyotaka, Journal of Porphyrins and Phthalocyanines 4 (2000) 136.

[10] B.N. Duncan, L. Inabe, N.K. Jaggi, J.W. Lyding, O. Schender, M. Hanack, C.R. Kanneworf, T.J. Marks and L.H. Schwatz, J. Am. Chem. Soc. 106 (1984) 3207.

[11] H. Kobayashi, A. Kobayashi and P. Cassoux, Chem. Soc. Rev. 29 (2000) 325.

[12] J. Labuda and V. Plaskoñ, Inorg. Chim. Acta 13 (1988) 146.

[13] M. D. Ward, *Inorg. Chem.*, 25 (1986) 4444.

[14] J. Puigdollers, C. Voz, A. Orpella, I. Martin, M. Vetter, R. Alcubilla, *Thin solid films*, 427 (2003) 367.

[15] B. Douglas, Wiley Interscience, (1968), Vol. XVIII, 1-52.

[16] G. Saito, J. Ferraris, *Bull. Chem. Soc. Jpn.*, 53 (8) (1980) 2141.

[17] S. Kumar, R. Malhotra, K.S., Dhindsa, *Polyhedron*, 11 (1992) 1383.

[18] L. Katovic, T. Taylor, D. Busch, *Inorganic Chemistry*, 3 (1971) 458.