

Synthesis and immobilization of molybdenum complexes in a pillared layered clay

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Abstract

New molecular systems based on donor/acceptor groups connected by π -conjugated bridge, *trans*-[MoF(NNC₇H₆SO₂)-(Ph₂PCH₂CH₂PPh₂)₂][BF₄], have been synthesized. This complex with nonlinear optical (NLO) applications was immobilized by an adsorption process from liquid phase, in the interlayer of a pillared clay (PILC). The metal complex and the new materials were characterized by thermal analysis (DSC), chemical analysis, surface techniques (XPS), X-ray powder diffraction (XRD), nitrogen adsorption isotherms, spectroscopic methods (NMR, FT-IR and UV/Vis) and electrochemical measurements. The studies of the electrochemical and the spectroscopic properties of the complex show interactions between donor and acceptor groups across the conjugated bridge. The results obtained from the studies using different techniques of analysis confirm that the molybdenum complex was effectively immobilized in the host matrix and this process does not modify the morphology or structure of the PILC upon metal complex loading.

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1. Introduction

Molecular materials with nonlinear optical (NLO) properties are of great interest for applications in optoelectronic and photonic devices emerging in the 21st century. Organotransition metal complexes form an important subclass of NLO materials which are under intense investigation. Such compounds show promising potential resulting from the electronic properties where the existence of polarizable *d* electrons can contribute to enhanced NLO responses, and redox activity providing extensive opportunities for modulation of NLO properties [1].

The great majority of NLO materials involve highly polarizable complexes usually described by the hyperpolarizabilities β parameter [2]. The main molecular

feature of these complexes are π -conjugated ligands with electron-donor (D) and acceptor (A) groups (D- π -A) [3]. Most NLO chromophores have generally not been found to be good photonic media due to thermal relaxation, large absorption and high optical losses. Therefore combining adequate solid supports and NLO molecules is probably one of the best ways to obtain active materials with large optical nonlinearity and low losses [4].

The systems of metal complexes encapsulated into solid supports hosts has attracted much interest, due to the possibility of obtaining stable structures with potential applications in different fields. Indeed encapsulation of metal complexes in porous solids like pillared clays (PILCs) might combine some characteristics of the support—pore diameter and interlayer space—with the electronic and stereochemical properties of the complex and could lead to the highly selective formation of certain products with a precise structure [5]. Nevertheless, the use of pillared clays to act as hosts for organometallic compounds is poorly documented [6,7], in contrast

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with what is found for other aluminosilicates, such as zeolites [8]. In addition to this, the use of pillared clay matrices can probably reduce the thermal relaxation of the molecular dipoles. The same behavior is observed with NLO chromophores in organic–inorganic hybrid materials [9].

The preparation methods and the textural and surface chemistry of PILCs were reviewed by different authors [10]. These are predominantly microporous materials (pore width <2 nm) although some mesoporosity (pore width between 2 and 50 nm) can also be present in some cases due to the aggregation of the clay platelets [11].

The aim of the present work is to describe the synthesis and characterization, and the immobilization of a molybdenum complex, *trans*-[MoF(NNCHC₆H₅SO₂)-(Ph₂PCH₂CH₂PPh₂)₂][BF₄], with potential NLO properties, in the pores of a pillared clay by an adsorption process using a liquid phase as a mediator in this process. The host matrix, designated WYO is an aluminium oxide pillared clay prepared by the intercalation of a montmorillonite from Wyoming (USA) by a previously optimized procedure [12]. Using the same nomenclature, the prepared material containing the metal complex is denominated as [MoL][BF₄]WYO, where Mo = FMO-(Ph₂PCH₂CH₂PPh₂)₂ and L is a diazo(3,4-ethylenedioxythiophene) ligand. A second objective of this work consists in establishing a correlation between the data collected from all different characterization techniques in order to provide more detailed information on the immobilization process.

2. Experimental section

2.1. Reagents and solvents

All the reaction syntheses of the complex were carried out under nitrogen or argon atmosphere with the use of standard Schlenk techniques unless otherwise stated. THF and Et₂O were dried by distilling over sodium/benzophenone and dichloromethane was dried by distilling over CaH₂ and stored over 4 Å molecular sieves. All other chemicals were supplied by Aldrich and used without further purification. The complexes, *trans*-[Mo(N₂)(dppe)₂] and *trans*-[MoF(NNH₂)(dppe)₂][BF₄] were prepared by published methods [13].

2.2. Sample preparation

2.2.1. Preparation of host matrix PILC

A Na, Ca montmorillonite from Wyoming “Volcay SPV-200” was obtained from the American Colloid Company (Arlington Heights, Illinois). The pillared clay (WYO) was obtained as follows [12]. An oligomer solution, was prepared from AlCl₃ (0.2 M) and NaOH

(0.5 M) with a ratio OH/Al = 2, aged 2 h at 60 °C after which the pH was increased to 6. This solution was then added dropwise to an aqueous suspension of clay (2.5 g in 500 cm³) at 80 °C under stirring, refluxed (for 3 h) and kept overnight at 25 °C. After centrifugation and washing in a dialysis tube until the conductivity was less than 1 mS m⁻¹ the solid was freeze-dried and calcinated at 350 °C, under dried air, with a ramp of 1 °C min⁻¹, the final temperature being kept for 2 h.

2.2.2. Preparation of metal complex

Step 1. Synthesis of ligand 2-formyl-3,4-ethylenedioxythiophene

POCl₃ (4.2 mmol) was added to DMF (4.2 mmol) at 0 °C and the mixture was stirred during 15 min at 0 °C. Then the 3,4-ethylenedioxythiophene (3.5 mmol) dissolved in DMF (1.5 mL) was added dropwise with stirring and the reaction mixture was heated for 2 h at 60 °C. The solution was then poured slowly into 65 mL saturated sodium acetate aqueous solution and stirred for 2 h 30 min. The organic layer was diluted with ether, washed with saturated NaHCO₃ aqueous solution, and dried with anhydrous MgSO₄. Evaporation of the organic extract under reduced pressure gave the 2-formyl-3,4-ethylenedioxythiophene in the form of a beige solid (66%). Recrystallization from ether gave the 2-formyl-3,4-ethylenedioxythiophene as a colourless solid Mp: 135–137 °C. FTIR (ν/cm⁻¹): 3108, 2954, 2923, 2853, 1648 (CHO), 1520, 1493, 1460, 1439, 1375, 1268, 1259, 1235, 1125, 1064, 1011, 987, 960, 910, 848, 760, 695, 666. ¹H NMR (CDCl₃), δ, 4.26–4.31 (m, 2H, CH₂), 4.35–4.40 (m, 2H, CH₂), 6.79 (s, 1H, 5-H), 9.89 (s, 1H, CHO). C₇H₆O₃S: Calcd. C, 49.36; H, 3.52; S, 18.84. Found: C, 49.38; H, 3.70; S, 18.49.

Step 2. Synthesis of complex *trans*-[MoF(NNCHC₆H₅SO₂)(dppe)₂][BF₄]

The complex *trans*-[MoF(NNH₂)(dppe)₂][BF₄] (0.2 g, 0.19 mmol) was dissolved in THF (20 mL) at room temperature. An excess of 2-formyl-3,4-ethylenedioxythiophene (0.06 g, 0.40 mmol) was added to the solution stirred for 24 h. During this time the solution colour changed from brown to pink. The solution was reduced in volume to ≈5 mL and the pink solid filtered off. The solid was extracted with CH₂Cl₂ and filtered through celite. The solution was evaporated to dryness and the solid washed with cold THF (3 × 5 mL) then Et₂O (2 × 3 mL) and dried in vacuo giving *trans*-[MoF(NNCHC₆H₅SO₂)(dppe)₂][BF₄]. The yield of pink *trans*-[MoF(NNCHC₆H₅SO₂)(dppe)₂][BF₄] was 0.12 g, 52%. FAB mass spectrum: *m/z* 1093 (M⁺). NMR (CDCl₃): ¹H (relative to SiMe₄, 300 MHz), δ, 2.7–3.0 (2xbrm 8H, PCH₂CH₂P), 3.6–3.9 (m, 4H, OCH₂CH₂O), 4.4 (s, 1H, NNCH), 6.6 (s, 1H, 5-H), and 7.0–7.6 (m, 48H, PPh); ³¹P-¹H (relative to P(OMe)₃, 121.7 MHz), δ, -98.0 (s, MoP). MoC₅₉H₅₄O₂SN₂P₄F₅B (1180.79): Calcd. C, 60.01; H, 4.61; N, 2.37; S, 2.72. Found: C,

60.30; H, 4.72; N, 2.51; S, 2.85. FTIR (ν/cm^{-1}): 1561 [$\nu(\text{C}=\text{N})$], 691, 742, 1435 and 1484 [$\nu(\text{PC}_6\text{H}_5)$], and 1052 [$\nu(\text{BF}_4)$]; UV–Vis (λ/cm): 509.

2.2.3. Immobilization of the metal complex in the host matrix

An amount of 0.006 mmol (7 mg) of metal complex was dissolved in 30 mL of THF, in a ultrasound bath for 10 min. After complete dissolution, this mixture was added to 0.5 g of the WYO PILC (the amount of molybdenum corresponds to about 10^{17} Mo^{IV} ions per gram of PILC). The final material was washed with Et₂O followed by filtration and dried in an oven at 60 °C for 8 h. The samples were purified with acetone (4 h) using Soxhlet extraction to remove the residual metal complex physically adsorbed on the external surface. Finally, the materials were dried in an oven at 90 °C, under vacuum, for 12 h.

2.3. Characterization procedures

Voltammetric measurements were performed using a potentiostat/galvanostat AUTOLAB/PSTAT 12 with the low current module ECD from ECO-CHEMIE and the data analysis processed by the General Purpose Electrochemical System software package also from ECO-CHEMIE. Three electrode-two compartment cells equipped with vitreous carbon-disc working electrodes, a platinum-wire secondary electrode and a silver-wire pseudo-reference electrode were employed for cyclic voltammetric measurements. The concentrations of the compounds were typically 1–2 mmol dm⁻³ and 0.2 mol dm⁻³ [NBu₄][BF₄] was used as the supporting electrolyte in acetonitrile solvent. The UV–Vis absorption spectra of ligand and complex were obtained using a Shimadzu UV/2501PC spectrophotometer using quartz cells, extinction coefficients (ϵ) are quoted in M⁻¹ cm⁻¹. ¹H spectra were recorded using a Varian Unity Plus spectrometer at 300 MHz, chemical shifts being given in ppm. Mass spectra (FAB) were obtained using an Analytical Fison Instruments Auto Spec VG spectrometer, using 3-nitrobenzyl alcohol as the matrix. Elemental chemical analysis were performed using a Leco CHNS-932. Room temperature FTIR spectra of the free complex and PILCs materials were recorded on a Bomem MB104 spectrometer. The transmission spectra of the powdered samples were obtained using KBr pellets over the range 4000–600 cm⁻¹ by averaging 20 scans

at a maximum resolution of 4 cm⁻¹. X-ray diffraction patterns were recorded using a Philips Analytical X-ray model PW1710 BASED diffractometer system. The solids samples were dispersed in distilled water by ultrasound and then deposited on glass slides and exposed to the Cu K α radiation at room temperature in a 2 θ range between 2° and 8°. X-ray photoelectron spectroscopy were obtained at the C.A.C.T.I. from Vigo University, Spain, on a VG Scientific ESCALAB 250iXL spectrometer using a Alka monochromatized radiation (1486.92 eV). Thermal analyses were carried out with a Mettler TC11 controller and a DSC20 Mettler oven equipped with a cooling accessory under high purity argon supplied at a constant 50 mL min⁻¹ flow rate. All samples were placed in 20 μ L aluminium pans, were subjected to a 10 °C min⁻¹ heating rate and were characterized between 25 and 300 °C. Nitrogen adsorption measurements were performed at -196 °C, using an automated apparatus (ASAP 2010). Prior to the adsorption measurements, the samples were out gassed (under vacuum) at 150 °C for 2.5 h.

3. Results and discussion

3.1. Synthesis and characterization of the diazo(3,4-ethylenedioxythiophene) complex of molybdenum

This particular work constitutes the starting point of previous studies in which it was found that the molybdenum complex [MoL][BF₄] exhibits a rich spectroscopic and electrochemical behavior, showing intramolecular charge delocalization. This charge-transfer process between metal and ligand may be beneficial for the construction of nonlinear optical materials [14].

The complex of molybdenum, [MoL][BF₄], was obtained by condensation of hydrazido complex, *trans*-[MoF(NNH₂)(dppe)₂][BF₄], with carbonyl compound, 2-formyl-3,4-ethylenedioxythiophene (Fig. 1). This complex is of particular interest because the conjugated structure includes the central metal atom, the diazothiophene linker and the ethylenedioxy group.

3.2. Electrochemical studies

To get a deeper insight into the ground state properties and more specifically the mutual donor–acceptor

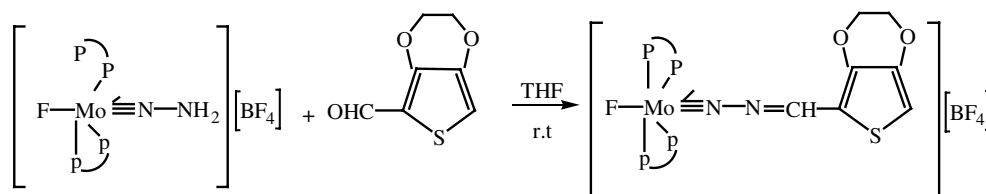


Fig. 1. Synthesis of *trans*-[MoF(NNCHC₆H₅SO₂)(dppe)₂][BF₄] complex.

electronic behavior, the redox properties of the ligand 2-formyl-3,4-ethylenedioxythiophene and the complex $[\text{MoL}][\text{BF}_4]$ were studied by cyclic voltammetry in acetonitrile solvent at carbon electrode.

The ligand is electrochemically active, displaying an irreversible one-electron reduction at -1.91 V vs. fc^+/fc producing a radical anion species, which is the normal behavior of substituted thiophenes [15]. On the oxidation side, the voltammograms show the presence of two reversible one-electron oxidation waves at 0.28 and 0.56 V vs. fc^+/fc corresponding to the formation of the cation radical and dication.

The complex exhibits two electrochemically reversible one-electron oxidations with a half wave potential at 0.46 and 0.81 V vs. fc^+/fc , and which is positively shifted with respect to *trans*- $[\text{MoF}(\text{NNCH}_2)(\text{dppe})_2]^+$ [16]. The dependency of the electron transfer processes involving donating and accepting terminal groups can be evaluated by comparing the $E_{1/2}$ values. A more positive half wave potential, suggests that the molybdenum unit is more difficult to oxidize. In contrast, the reduction of the complex ($\text{Mo}^{\text{IV}}/\text{Mo}^{\text{III}}$) occurs in an irreversible one-electron transfer at -1.34 V vs. fc^+/fc . These data illustrate an increased shift of the reduction potential towards more positive values in comparison with that observed on diazoalkane complexes [16].

3.3. UV/Vis spectroscopic studies

The electronic absorption spectrum of the 2-formyl-3,4-ethylenedioxythiophene shows a strong relatively low-energy $\pi-\pi^*$ transition at $\lambda_{\text{max}} = 335$ nm and with $\varepsilon = 2.6 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The shift from 231 nm in parent thiophene [17] to 335 nm is provided by donor/acceptor groups. The electronic spectrum of the complex is dominated by the $\pi-\pi^*$ transition assigned to of the bridging ligand observed at 362 nm and a shoulder metal-to-ligand charger transfer band at 505 nm. A decrease to lower transition energies of the ligand, after coordination, is observed with a shift from 335 to 362 nm. Also, low-energy metal–ligand charger transfer bands, observed at 505 nm, arise from promotion of an electron from molybdenum d_π orbital to the π^* orbital of the pyridyl group [18]. This typical behavior occurs in the $450\text{--}600$ nm region of the spectrum depending on the substituent attached to the ligand. As a result they are partly obscured by the low-energy tail of very strong $\pi-\pi^*$ transitions of the bridge and are generally only visible as shoulders.

3.4. Immobilization of molybdenum complex

The approach for the preparation of modified clay with entrapped metal complex used in this work was the adsorption of the complex within the interlayer of the host matrix. This approach required that the metal

complex diffused inwards the space available of the PILC interlayer. For this matrix, the galleries height is estimated in 9.3 \AA and the spacing between the pillars is not absolutely regular, which can lead to existence of regions of lower pillar density that can favor the accommodation of large molecules [19].

In order to get the maximum information about immobilization procedure, the material characterization was performed at different stages during the preparation procedure. The residual solvents obtained in the process of metal complex encapsulation, before and after Soxhlet extraction were analyzed by FTIR.

3.4.1. $[\text{MoL}][\text{BF}_4]\text{WYO}$ before Soxhlet extraction

After 6 h of reflux, the characteristic pink colour of the metal complex in THF solution disappeared indicating that the clay had adsorbed the complex, although no significant alteration of the original brown–gray colour of WYO was observed. IR spectra measurements performed in the residual solvent confirmed the absence of the bands due to the metal complex.

3.4.2. $[\text{MoL}][\text{BF}_4]\text{WYO}$ after Soxhlet extraction

The PILC with the hosted complex was extracted with acetone and further studies were performed on the material. The purpose of this extraction procedure is thus not only to remove the excess of free metal complex but also to study the eventual influence of the solvent in the mobility of the immobilized metal complex. The final material with metal complex kept its colour (brown–gray) after extraction, and no bands due to metal species were detected in the IR spectra of the extracting solvent.

4. Characterization studies

4.1. Morphology and composition of the modified PILC

Powder diffraction patterns were obtained for host matrix and $[\text{MoL}][\text{BF}_4]\text{WYO}$ samples (Fig. 2). No significant variations were observed in the diffraction pat-

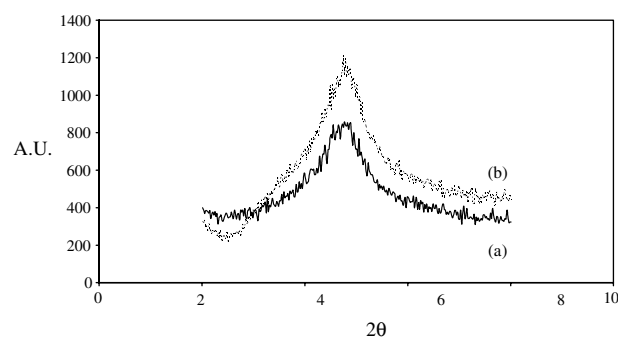


Fig. 2. X-ray diffractograms of the solids samples: (a) WYO and (b) $[\text{MoL}][\text{BF}_4]\text{WYO}$.

tern due to the structure of the PILC before and after the immobilization procedure. In fact, as revealed by the proximity of the basal spacing, which is 18.9 Å for the host matrix and 18.4 Å for the immobilized sample, it appears that the structure of the PILC is retained upon metal complex encapsulation.

The XPS analysis detected the presence of molybdenum in the $[\text{MoL}][\text{BF}_4]\text{WYO}$ sample. Fig. 3 shows the XPS measurement profiles recorded using different emission angles of core-level binding for the sample. The analysis of the obtained data provides information about the distribution of molybdenum content through the surface layer of PILC and the oxidation state of the metal.

The increase in intensity of Mo 3d peak from $\theta = 30^\circ$ to 90° is indicative of an asymmetric distribution of the metal across the sample depth. The low Mo/Si ratio observed in the region close to the surface seems to indicate that the outermost surface is less enriched in Mo. However, the maximum Mo is observed by increasing up to $\theta = 75^\circ$, indicating an Mo-rich region at a subsurface layer (Table 1). These results suggest that the metal complex diffuses through the PILC layers but due to its size the limits of the immobilization sites are restricted to a narrow region across the surface. These localization probably increase the noncentrosymmetry of molybdenum complex [9].

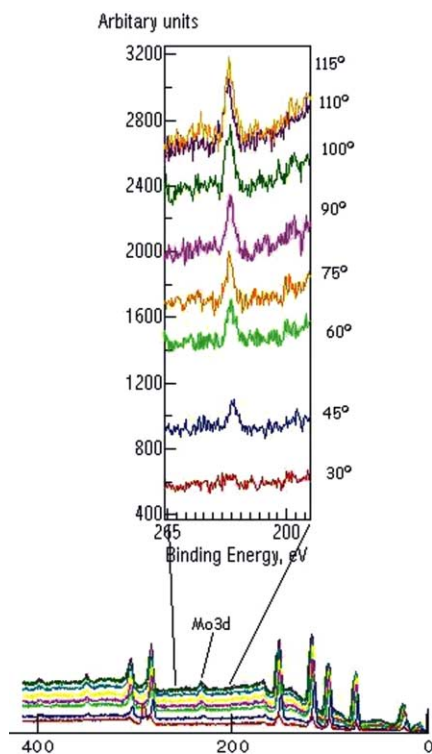


Fig. 3. High resolution XPS spectra of the Mo 3d region taken on the surface of the $[\text{MoL}][\text{BF}_4]\text{WYO}$.

Table 1
Si/Al, Mo/Si and Mo/Al ratios determined by XPS analysis of $[\text{MoL}][\text{BF}_4]\text{WYO}$

θ	Si/Al	Mo/Si	Mo/Al
30	0.83	0.0013	0.0011
45	0.66	0.0029	0.0020
60	0.69	0.0042	0.0030
75	0.68	0.0057	0.0039
90	0.59	0.0039	0.0023

By this technique the medium binding energy values for the Mo $3d_{5/2}$ was found to be equal to 230.7 eV. This value confirms that the metal present is in an oxidation state of four [20]. This result also suggested that the clay environment does not affect the valence state of the metal atom of the complex and neither covalent or ionic interaction between complex guest and PILC host are involved.

The nitrogen isotherms at -196°C in PILC samples obtained before and after the immobilization of the complex, are presented in Fig. 4. The curve for the initial PILC is very steep in the region of the low relative pressures, as a consequence of the microporous nature of these materials. In addition, a slight hysteresis loop, related with the mesoporosity developed due to the aggregation of the clay platelets, is also observed. After encapsulation, the general shape of the isotherm is maintained, but the adsorbed amounts are lower. Besides, no relevant changes in the isotherm of the immobilized PILC were noticed before and after the Soxhlet extraction. The specific surface areas (A_{BET}) and

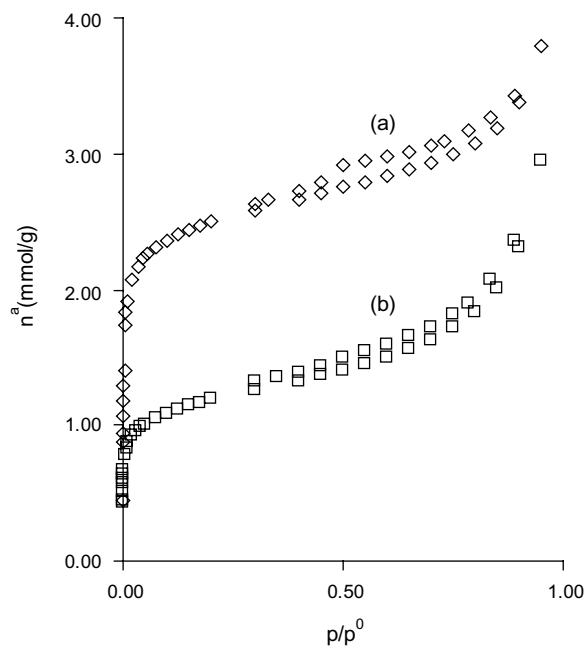


Fig. 4. Nitrogen adsorption–desorption isotherms at -196°C of the solids samples: (a) WYO, (b) $[\text{MoL}][\text{BF}_4]\text{WYO}$.

the microporous volumes (from *t*-method), for the initial and the immobilized PILC, are 200 and 95 m² g⁻¹, and 0.070 and 0.025 mL g⁻¹, respectively. These observations are compatible with the reduction of the microporosity as a consequence of the immobilization of the studied complex.

4.2. Infrared studies

The data obtained by IR analysis were used to provide structural information of the PILC framework and the immobilized complex. The infrared spectra of host matrix, [MoL][BF₄]*WYO* and a free complex are shown in Fig. 5(a).

The spectrum of free complex is dominated by the bands characteristic of diphenylphosphine ligands (1484, 1435, 742 and 691 cm⁻¹) and the BF₄ anion (1052, 744 and 720 cm⁻¹) [13]. The band of the diazo(3,4-ethylenedioxythiophene) which is assigned to $\nu(\text{C}=\text{N})$ group was observed at 1565 cm⁻¹.

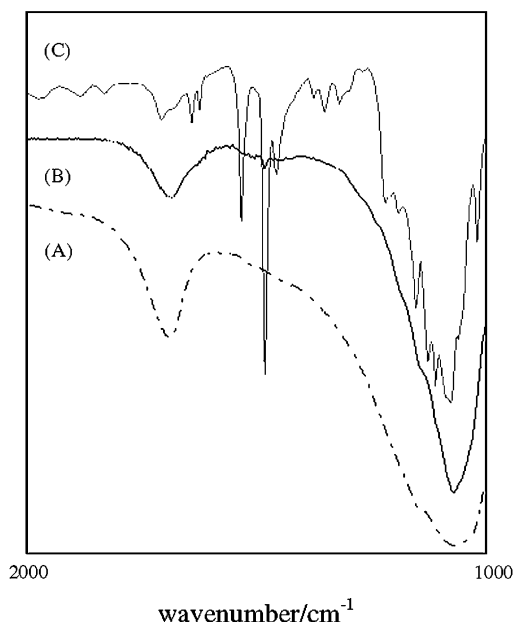
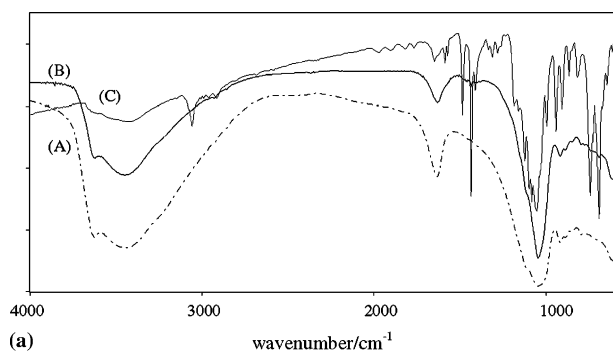


Fig. 5. Infrared spectra of the solids samples; (A) WYO, (B) [MoL][BF₄]*WYO* and (C) [MoL][BF₄]; (a) in the range 4000–600 cm⁻¹, (b) in the range 2000–1000 cm⁻¹.

The spectra of the PILC with metal complex, [MoL][BF₄]*WYO*, is dominated by bands due to the host matrix WYO: the strong bands in the range 3700–3300 cm⁻¹ are attributed to surface hydroxyl groups, and bands corresponding to the lattice vibrations associated with the matrix are observed in the spectral region between 1300 and 450 cm⁻¹ [21]. The bands due to the complex are much weaker, as the complex is diluted in the PILC, and can only be observed in the region 1600–1200 cm⁻¹, where the matrix is not observed (Fig. 5(b)). In this region, the IR spectra of [MoL][BF₄]*WYO* exhibits two bands characteristic of diphenylphosphine ligands (1484 and 1435 cm⁻¹) and does not show any shift or broadening of the PILC structure-sensitive vibrations bands assigned to matrix. The presence of these bands indicates that the metal complex has been immobilized in the PILC host and primarily has kept its integrity.

4.3. Thermal studies

Complementary studies using a differential scanning calorimetry (DSC) technique contributed to a better understanding of the effect of the molybdenum complex on the thermal properties of PILC framework. The DSC thermograms of molybdenum complex shown in Fig. 6 indicates that this complex exhibits a sharp exothermic peak around 230 °C assigned to partial degradation (oxidative) or decomposition of the complex.

The DSC traces obtained for pure matrix WYO and [MoL][BF₄]*WYO* samples collected before and after Soxhlet extraction are also presented in Fig. 6, using a

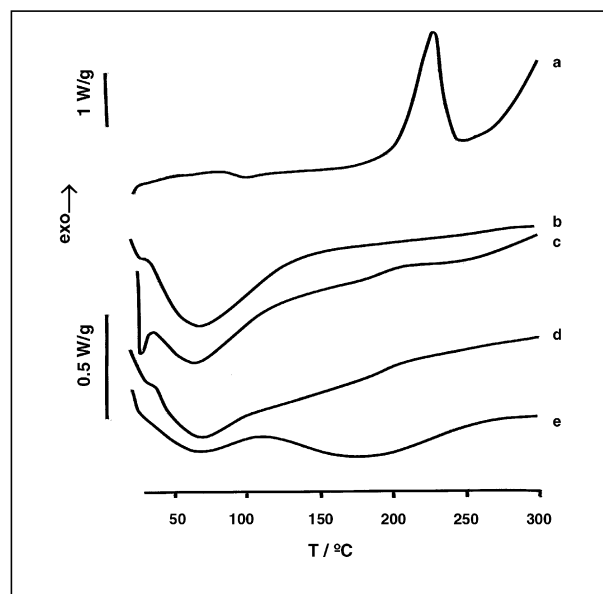


Fig. 6. DSC traces of solids samples: (a) [MoL][BF₄] complex, (b) WYO, (c) WYO after Soxhlet extraction, (d) [MoL][BF₄]*WYO* before Soxhlet extraction and (e) [MoL][BF₄]*WYO* after Soxhlet extraction.

more sensitive heat flux scale. The obtained results show that the material has an high thermal stability within the studied temperature interval, confirming the expected mechanical and thermal properties for this material. For all the studied samples, the obtained thermograms have in common a broad endothermic peak with a maximum around 60 °C which can be assigned to the evaporation or desorption of solvent molecules retained at PILC structure. The form of the peak suggests that it could result from processes involving either occluded or adsorbed solvent molecules (THF, Et₂O, acetone) which were involved in the complex insertion procedures during sample preparation.

The DSC thermograms obtained for WYO host matrix subjected to a Soxhlet extraction with acetone, shows a new sharp endothermic peak which could be associated with the release of acetone molecules occluded at PILC structure.

The sample [MoL][BF₄]WYO, subjected to a Soxhlet extraction process, shows a broad endothermic process, between 120 and 250 °C, which is not observed with such intensity on similar sample not subjected to the same extraction process. This difference in behavior, compared with the WYO matrix, suggests that it could be related to the Soxhlet extraction process, although further studies are necessary for a better understanding.

5. Conclusion

In conclusion, we synthesized and immobilized a new molybdenum complex, *trans*-[MoF(NNC₇H₆SO₂)-(Ph₂PCH₂CH₂PPh₂)₂][BF₄], which has a significant delocalization between donor/acceptor groups yielding an influence in the electronic properties of the complex.

Concerning the immobilization process, the results obtained confirm that the metal complex can be immobilized in the interlayer of a Wyoming pillared clay by adsorption process, without damage to the original matrix or loss of its crystallinity, although as expected, the microporous volume of the PILC is reduced as a consequence of the immobilization.

To take advantage of the present results in clay-based materials for nonlinear optical applications, future work must develop ways to control the organization of dye molecules on clay surfaces. However, the present studies are very encouraging and warrant further research on clay-based nonlinear optical applications.

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References

- [1] (a) D.M. Burland, R.D. Miller, C.A. Walsh, *Chem. Rev.* 94 (1994) 31;
(b) T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays, A. Persoons, *J. Mater. Chem.* 7 (1997) 2175;
(c) S.R. Marder, B. Kippelen, A.K.V. Jen, N. Peyghambarian, *Nature* 388 (1997) 845.
- [2] B.J. Coe, J.A. Harris, I. Asselberghs, A. Persoons, J.C. Jeffery, L.H. Rees, T. Gelbrich, M.B. Hursthouse, *Chem. Soc. Dalton Trans.* (1999) 3617.
- [3] F. Meyers, S.R. Marder, J.W. Perry, in: L.V. Interrante, M.J. Hampden-Smith (Eds.), *Chemistry of Advanced Materials*, Wiley-VCH, New York, 1998, p. 207.
- [4] Y.H. Min, K.S. Lee, C.S. Yoon, *J. Mater. Chem.* 8 (1998) 1225.
- [5] R.A. Schoonheydt, in: H. van Bekkum, E.M. Flanigen, J.C. Jansen (Eds.), *Introduction to Zeolite Science and Practice, Studies in Surface Science and Catalysis*, vol. 58, Elsevier, Amsterdam, 1991, p. 201.
- [6] V. Ramaswamy, M.S. Krishnan, A.V. Ramaswamy, *J. Mol. Catal.* 181 (2002) 81.
- [7] R. Ferreira, C. Freire, B. de Castro, A.P. Carvalho, J. Pires, M. Brotas de Carvalho, *Eur. J. Inorg. Chem.* (2002) 3032.
- [8] (a) P.P. Knops-Gerrits, D.E. DeVos, F. Thibault-Starzyk, P.A. Jacobs, *Nature* 369 (1994) 543;
(b) D.E. DeVos, P.P. Knops-Gerrits, R.F. Parton, B.M. Weckhuysen, P.A. Jacobs, R.A. Schoonheydt, *J. Inclusion Phenom. Mol. Recognit. Chem.* 21 (1995) 159;
(c) I. Neves, C. Freire, A.N. Zakharov, B. de Castro, J.L. Figueiredo, *Colloids Surf. A. Physicochem. Eng. Aspects* 115 (1996) 249.
- [9] (a) K.S. Lee, T.D. Kim, Y.H. Min, C.S. Yoon, *Synth. Met.* 117 (2001) 311;
(b) C. Boutton, M. Kauranen, A. Persoons, M.P. Keung, K.Y. Jacobs, R.A. Schoonheydt, *Clays Clay Miner.* 45 (3) (1997) 483.
- [10] (a) D.E.W. Vaughan, in: R. Burch (Ed.), *Pillared Clays: Catalysis Today*, Elsevier, Amsterdam, 1988, p. 187;
(b) A. Gil, L.M. Gandía, M.A. Vicente, *Catal. Rev.—Sci. Eng.* 42 (1 & 2) (2000) 145–212.
- [11] IUPAC K.S. Sing, D.H. Everett, R.A.W. Haul, L. Mouscou, R. Pierotti, J. Rouquérol, T. Siemieniowska, *Pure Appl. Chem.* 57 (1985) 603.
- [12] (a) J. Pires, M.B. Carvalho, A.P. Carvalho, *Zeolites* 19 (1997) 107;
(b) M.B. Carvalho, J. Pires, A.P. Carvalho, *Micropor. Mater.* 6 (1996) 65.
- [13] (a) M. Hidai, K. Tominari, Y. Uchida, *J. Am. Chem. Soc.* 94 (1972) 110;
(b) M. Hidai, Y. Mizobe, M. Sato, T. Kodama, Y. Uchida, *J. Am. Chem. Soc.* 100 (1978) 5740;
(c) M. Hidai, T. Kodama, M. Sato, M. Harakawa, Y. Uchida, *Inorg. Chem.* 15 (1976) 2694;
(d) P.C. Bevan, J. Chatt, M. Hidai, G.J. Leigh, *J. Organomet. Chem.* 160 (1978) 165.
- [14] (a) S. Houbrechts, K. Clays, A. Persoons, Z. Pikramenou, J.M. Lehn, *Chem. Phys. Lett.* 258 (1996) 485;
(b) M. Stahelin, D.M. Burland, J.E. Rice, *Chem. Phys. Lett.* 191 (1992) 245.
- [15] K. Takahashi, T. Nihira, *Bull. Chem. Soc. Jpn.* 65 (1992) 1855.

- [16] D.L. Hughes, M.Y. Mohammed, C.J. Pickett, *J. Chem. Soc. Chem. Commun.* (1989) 1399.
- [17] J.W. Sease, L. Zechmeister, *J. Am. Chem. Soc.* 69 (1947) 270.
- [18] A.J. Amorosa, A.M.W. Cargill Thompson, J.P. Maher, J.A. McCleverty, M.D. Ward, *Inorg. Chem.* 34 (1995) 4828.
- [19] T.J. Pinnavaia, S.D. Landau, M.S. Tzou, I.D. Johnson, *J. Am. Chem. Soc.* 107 (1985) 7222.
- [20] (a) A. Cimino, B.A. Angelis, *J. Catal.* 36 (1975) 11;
(b) K.S. Kim, W.E. Baitinger, J.W. Amy, N. Winograd, *J. Electron Spectrosc. Relat. Phenom.* 5 (1974) 351.
- [21] J.D. Russel, A.R. Fraser, in: M.J. Wilson (Ed.), *Clay Mineralogy: Spectroscopic and Chemical Determinative Methods*, Chapman & Hall, London, 1996, p. 11.