Encapsulation of Copper(II) Complexes with Pentadentate N_3O_2 Schiff Base Ligands in a Pillared Layered Clay

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Keywords: Clays / Microporous materials / Copper / Schiff bases

Two copper(II) complexes with five-coordinate Schiff-base ligands derived from acetylacetone and with a N_3O_2 coordination sphere, namely bis(acetylacetonate)-3-amino-bis(propyldiimine) and bis(acetylacetonate)-3-methylamino-bis(propyldiimine), were entrapped in the interlayers of a pillared layered clay (PILC). A two-step process in the liquid phase was used: (i) adsorption of copper(II) acetylacetonate in the porous structure of the PILC, and (ii) in situ Schiff condensation of the copper(II) precursor complex with the corresponding triamine. The new materials were characterised by chemical analysis, surface techniques (SEM and XPS), X-ray powder diffraction, nitrogen adsorption isotherms and spectroscopic methods (FTIR, UV/Vis). These data indicate conclusively that the Cu^{II} complexes are encapsulated in the PILC, and that the entrapped complexes exhibit structural and electronic properties that are different from those of the free complexes. These differences can arise from distortions caused either by steric effects imposed by the structure of pillared clay, or by strong interactions with the matrix.

Introduction

Transition metal complexes have been proven to be efficient catalysts in several industrial chemical reactions.[1−3] A particularly strong area of research in catalysis is the immobilization of metal complexes used in homogeneous catalysis onto solid supports such as zeolites,[4,5] polymers,[6,7] carbons,[8−10] and other porous-structured materials.[11−13] This heterogenization often combines the homogeneous catalytic properties of metal complexes with some characteristics of the heterogeneous catalysts, such as shape selectivity, ease of separation from reaction media, and reusability without appreciable loss of catalytic activity.

Pillared layered clays (PILCs) are a recently developed family of porous materials obtained by exchanging the interlayered cations of swelling clays with bulky inorganic polyoxo and polyhydroxy cations.[14,15] Upon calcination they are converted into metal oxide clusters creating an interlayer space of molecular dimensions and a well-defined pore system.[14−17] Introduction of pillars between layers is an attractive route for the preparation of porous materials in which pore size and thermal stability can be tailored by the appropriate choice of the polyoxo and polyhydroxy cations.[17]

The most widely used polycation is $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, usually denoted as Al_{13}, mainly because its polymerisation is better understood than that of other cations. Consequently, the alumina-pillared clays (Al-pillared clays) are by far the best documented pillared clays.[15] Although metallic polyoxo or polyhydroxo cations of Al^{3+} and also of other ions, namely Zr^{4+}, Ti^{4+}, Cr^{3+}, Fe^{3+}, or Ga^{3+}, are the most widely used intercalating species, several coordination and organometallic compounds have recently been considered for this purpose.[19−21]

The catalytic properties of PILCs are mainly related to their acid character,[15,18] as seen by their uses in hydrogenation, hydrotreating and isomerisation reactions. The incorporation of transition metal elements to the composition of Al PILCs not only increases their Brönsted acidity, but also allows them to be used in catalytic redox reactions.[15,18]

In recent years, pillared clays have also been used as supports for transition metal compounds, typically their salts, which are deposited on pillared clays by ionic exchange, incipient wetness, or dry impregnation of calcined samples. Copper, vanadium, and platinum have been the preferred active phases, and, to a lesser extent, molybdenum, cobalt, and other elements.[15] Nevertheless, the use of pillared clays to act as hosts for coordination and organometallic compounds is poorly documented,[22] in contrast with what is found for other aluminosilicates, such as zeolites[4,5] and swelled clays.[23]

We have been interested in the heterogenisation of transition metal complexes in zeolites[24,25] and activated carbons[8−10] and have shown that the methodologies used

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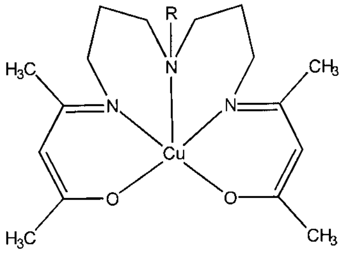
for immobilisation/anchorage of the metal complexes are largely determined by the supports. The analogy between PILCs and zeolites NaX and NaY prompted us to explore the properties of the former as supports for the encapsulation of transition metal complexes. Here we use a pillared clay, denoted as BENAVILA (named after the region in Portugal from where the clay was obtained), which has been extensively characterised previously.[26] We have chosen to encapsulate two copper Schiff-base complexes, since their in situ preparation has been worked out for their immobilisation in FAU zeolites.[24,25]

The two copper(II) complexes with pentadentate N_3O_2 Schiff-base ligands derived from acetylacetone − bis(acetylacetonate)-3-amino-bis(propyldiimine) and bis(acetylacetonate)-3-methylamino-bis(propyldiimine) (Scheme 1) − were encapsulated in the pores of BENAVILA using a procedure similar to that used in the encapsulation of the same complexes in NaX and NaY zeolites.[24,25] This methodology involves in situ Schiff condensation between a Cu^{II} precursor complex, $[Cu(acac)_2]$, and the corresponding triamine.



Scheme 1. $[Cu(acac_2trien)]$, R = H; $[Cu(acac_2Metrien)]$, R = CH_3

The BENAVILA with entrapped complexes was characterised by chemical analysis, surface techniques (SEM and XPS), X-ray powder diffraction, nitrogen adsorption isotherms and spectroscopic methods (FTIR and UV/Vis). Our data indicate that copper complexes in the PILC exhibit structural and electronic properties that are different from those of the free complexes, caused either by steric effects imposed by the structure of the pillared clay, or by strong interactions with the matrix.

Results and Discussion

Morphology and Cu Content of the Modified BENAVILA

The modified PILC with $[Cu(acac)_2]$, denoted as $[Cu(acac)_2]$@BEN, was not purified by Soxhlet extraction, as the precursor square-planar complex $[Cu(acac)_2]$, due to its dimensions, can diffuse out of the supporting material. Soxhlet extraction was performed only for the modified BENAVILA with the complexes $[Cu(acac_2trien)]$ and $[Cu(acac_2Metrien)]$; these materials {denoted as $[Cu(acac_2trien)]$@BEN and $[Cu(acac_2Metrien)$@BEN} did not change colour after extensive extraction, and after the last extraction no bands due to copper species could be detected in the extracting solvent. These results indicate that the resulting metal complexes are too large to diffuse out of the PILC layers, and that encapsulation of metal complexes after in situ Schiff condensation has taken place.

Analysis of the SEM micrographs of the parent and modified BENAVILA indicates that there is no change in the BENAVILA morphology and structure upon complex encapsulation. In the SEM micrograph of all samples, exemplified in Figure 1 for $[Cu(acac_2Metrien)]$@BEN, two types of particles with different morphology and dimen-

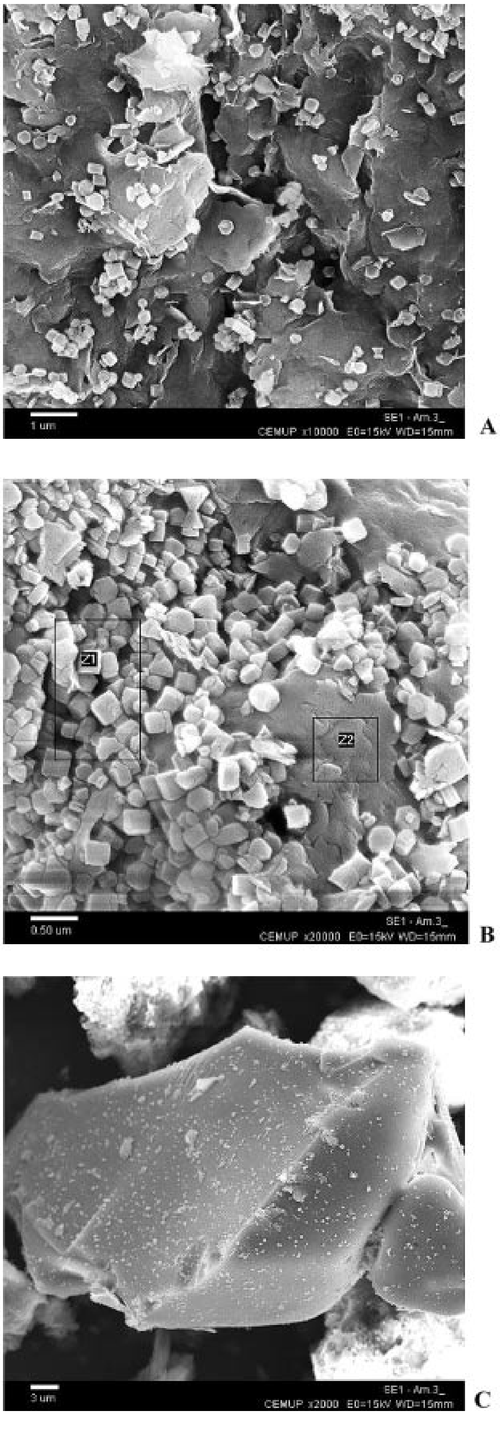


Figure 1. SEM photographs of $[Cu(acac_2Metrien)]$@BEN with different resolutions: × 10000 (A); × 20000 (B) and × 2000 (C)

sions can be observed: (i) small crystalline particles with dimensions of roughly 0.2 µm, and (ii) particles with lamellar morphology and larger dimensions (Figure 1A). By semi-quantitative EDS analysis of the different particles (Figure 1B) it is possible to assign the latter particles to the pillared clay (Figure 1C). As the small crystalline particles have high aluminium and oxygen content relative to the general composition of BENAVILA particles, we propose them to be probably aluminium oxides originating in the pillaring process. Furthermore, no crystals due to adsorbed metal complexes could be detected in any of the modified pillared clays, suggesting that the metal complexes are evenly distributed throughout the PILC.

A comparison of the X-ray diffractograms of the parent BENAVILA with those of modified PILCs (Figure 2) indicates that the structure of the PILC is retained upon metal complex immobilisation, as revealed by the proximity of the basal spacing, which is 1.8 nm for the nonencapsulated material and 1.73 nm for the encapsulated samples. As can be seen from this figure no appreciable changes are seen in the characteristic diffraction peak after encapsulation.

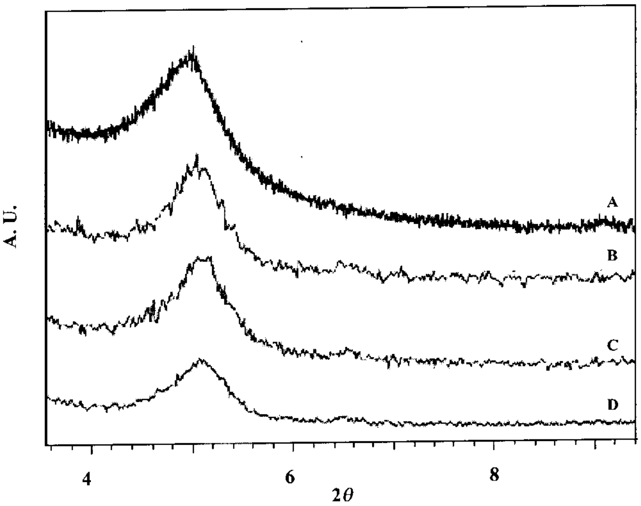


Figure 2. X-ray diffractograms for the BEN PILC: before encapsulation (A) and after encapsulation with [Cu(acac)$_2$] (B); [Cu(acac)$_2$trien] (C) and [Cu(acac)$_2$Metrien] (D)

The Si/Al, Cu/Si and Cu/Al molar ratios obtained by bulk chemical analysis and by XPS are presented in Table 1. A comparison of the Si/Al ratios obtained by chemical analysis and XPS reveals that the surface of the clay is, in general, enriched in silicon upon immobilisation of the complexes, as has been observed in several zeolites with occluded metal complexes.[27,28]

A comparison between the copper content determined by chemical analysis (Table 1) in [Cu(acac)$_2$]@BEN with that in the samples resulting from the Schiff condensation suggests that practically all adsorbed [Cu(acac)$_2$] complexes have reacted with the triamines and have became trapped inside the PILC. The Cu/Si and Cu/Al ratios obtained by chemical analysis and XPS do not differ markedly, although the values of XPS for [Cu(acac$_2$trien)]@BEN and [Cu(acac$_2$Metrien)]@BEN are slightly lower than those obtained by CA. This result suggests that upon reaction with triamines the copper complexes are located preferentially in inner pores.

Table 1. Si/Al, Cu/Si and Cu/Al ratios determined by chemical analysis (CA) and XPS in BENAVILA

Samples	Si/Al		Cu/Si		Cu/Al	
	CA	XPS	CA	XPS	CA	XPS
BENAVILA	1.16	1.17	–	–	–	–
[Cu(acac)$_2$]@BEN	1.17	1.22	0.017	0.017	0.020	0.014
[Cu(acac$_2$trien)]@BEN	1.18	1.19	0.017	0.014	0.020	0.012
[Cu(acac$_2$Metrien)]@BEN	1.22	1.21	0.020	0.016	0.024	0.013

A comparison between Cu content in BENAVILA with that in NaX[25] and in NaY[24] zeolites indicates that the loading of metal complexes occurs to a larger extent in the PILC. Despite its lower micropore volume, the PILC has a more open structure than the faujasite zeolites. Two factors can account for this behaviour: on the one hand the heights of the galleries, which have been estimated as 8.4 Å, are larger than the supercage entrances of Y and X zeolites (7.3 Å). On the other hand, the nature of the network of PILCs microporosity, in which the spacing between the pillars is not absolutely regular, can lead to the existence of regions of lower pillar density that can favour the accommodation of large molecules. Moreover, few studies have been made on the cross-linking between the pillars and the clay sheets, which leaves as an open question the possibility of the pillars also being distorted to some degree.[29]

The N_2 adsorption isotherms for parent and modified BENAVILA (Figure 3) are typical of solids which are mainly microporous, although the existence of hysteresis loops suggests some degree of mesoporosity, which is a consequence of the secondary structure of the clay particles. It is interesting to note that the loops are similar in all samples, which means that the encapsulation process does not modify the original mesoporosity of the PILC.

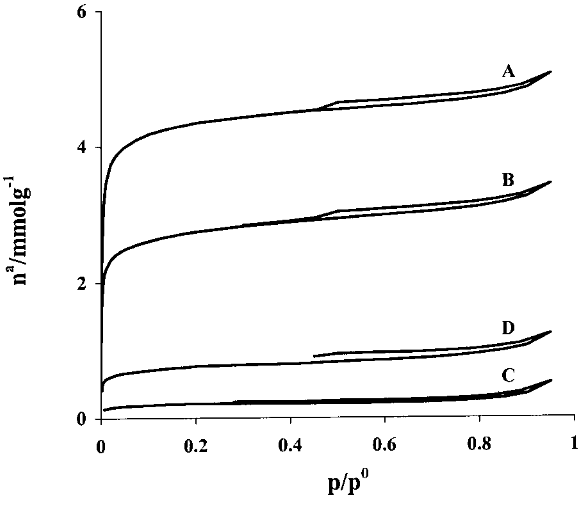


Figure 3. Nitrogen adsorption-desorption isotherms at 77 K of the samples BENAVILA (A), [Cu(acac)$_2$]@BEN (B), [Cu(acac$_2$trien)]@BEN (C), and [Cu(acac$_2$Metrien)]@BEN (D)

As expected, a decrease in adsorption capacity of the PILC was observed after immobilisation of [Cu(acac)$_2$] (to around 53% of the initial value), and a much more drastic decrease (up to 3−12% of the initial value) after Schiff-base condensation. The micropore volumes (obtained by the t-method) and the BET surface are presented in Table 2. The large reduction in micropore volume observed in the Cu-encapsulated BENAVILA is interpreted as arising from the presence of the copper compounds in the interlayers. As the copper content in all samples is roughly the same (Table 1), the observed lowering of micropore volume on going from [Cu(acac)$_2$] to [Cu(acac$_2$Metrien)] and [Cu(acac$_2$trien)] must be attributed to the larger volume of the latter complexes, thus providing indirect confirmation that Schiff condensation took place within the PILC.

Table 2. Textural properties for parent and copper-modified BENAVILA

Samples	A_{BET} (m^2/g)	V_{micro}[a] (cm^3/g)
BENAVILA	350	0.115
[Cu(acac)$_2$]@BEN	221	0.066
[Cu(acac)$_2$trien]@BEN	17	0.003
[Cu(acac)$_2$Metrien]@BEN	61	0.014

[a] Estimated using the t-method.

FTIR Spectra

Vibrational spectroscopy can provide information on both the encapsulated metal complexes and on the crystallinity of the host material. The FTIR spectra of the parent and modified BENAVILA are shown in Figure 4. The spectra of all samples are dominated by the very intense bands of BENAVILA in the range 3700−3300 cm^{-1}, due to surface hydroxyl groups, and in the range 1300−450 cm^{-1} which are assigned to lattice vibrations (Figure 4, I).[30] The bands due to the complexes are much weaker, as they are diluted in the PILC, and can only be observed in the region 1620−1200 cm^{-1}, where the BENAVILA matrix does not absorb (Figure 4, II).

No shift or broadening of the PILC structure-sensitive vibrations was observed upon inclusion of the complexes, which provides evidence, at the molecular level, that the matrix remains unchanged upon encapsulation of the copper complexes.

The IR bands of adsorbed [Cu(acac)$_2$] in the range 1620−1200 cm^{-1}, which are assigned to the coupled C=O and C=C stretching vibrations and to bending vibrations of methyl groups, occur at frequencies which are shifted by between 5 and 9 cm^{-1} from those shown by the free complex (Figure 4, II-B, E).[31] Furthermore, some changes in relative band intensities can also be observed in these bands. These observations confirm the presence of [Cu(acac)$_2$] in the PILC, and suggest that the structure of the adsorbed complex is distorted when compared with that of the square-planar free complex. This is a consequence of host-guest interactions with the PILC, eventually to the extent of the formation of a chemical bond to the framework, as the PILC can act as a ligand to copper through its matrix oxygen atoms.

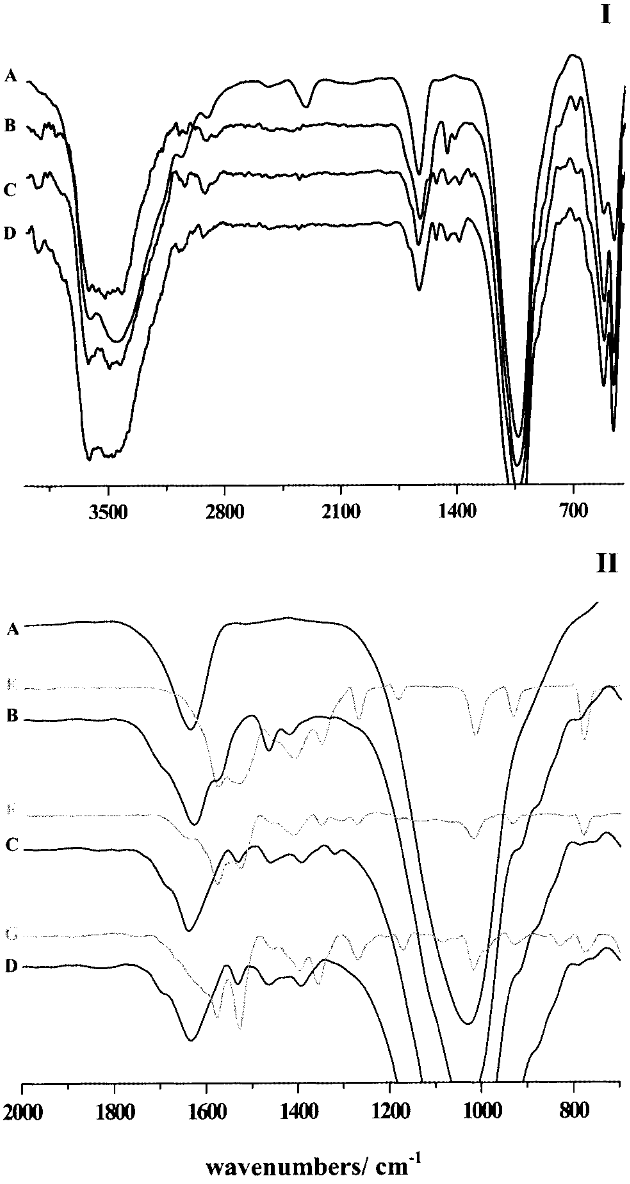


Figure 4. FTIR spectra: (I) in the range 4000−400 cm^{-1}: BENAVILA (A), [Cu(acac)$_2$]@BEN (B), [Cu(acac$_2$trien)]@BEN (C), and [Cu(acac$_2$Metrien)]@BEN (D); (II) in the region 2000−700 cm^{-1}: BENAVILA (A), [Cu(acac)$_2$]@BEN (B), [Cu(acac$_2$trien)]@BEN (C), [Cu(acac$_2$Metrien)]@BEN (D), and the free complexes [Cu(acac)$_2$] (E), [Cu(acac$_2$trien)] (F), and [Cu(acac$_2$Metrien)] (G)

The IR spectra of [Cu(acac$_2$trien)]@BEN and [Cu(acac$_2$Metrien)]@BEN (Figure 4, II-C, D) clearly show the absence of the characteristic coupled ν(C=O) + ν(C=C) vibration of [Cu(acac)$_2$], as expected after Schiff condensation with the triamines within the PILC. The trapped complexes exhibit IR bands at 1527−1533, 1466−1464 and 1394 cm^{-1} which are similarly shifted by between 5 and 10 cm^{-1} relative to those of the free complexes (Figure 4, II-F, G). These variations in band frequency can also be attributed to distortion of the complexes induced by the PILC porous structure, or to coordination of the complexes to the oxygen matrix through the sixth (free) coordination position.

UV/Vis Spectroscopy

The parent pillared layered clay exhibits, in the range 1300−200 nm, several medium-intensity broad bands at λ_{max} =265, 482 and 630 nm. These bands occur in the same range as some of the expected d-d bands for the copper complexes, which prevents a direct observation of their electronic spectra due not only to their low concentration but also to their small extinction coefficients (Figure 5).

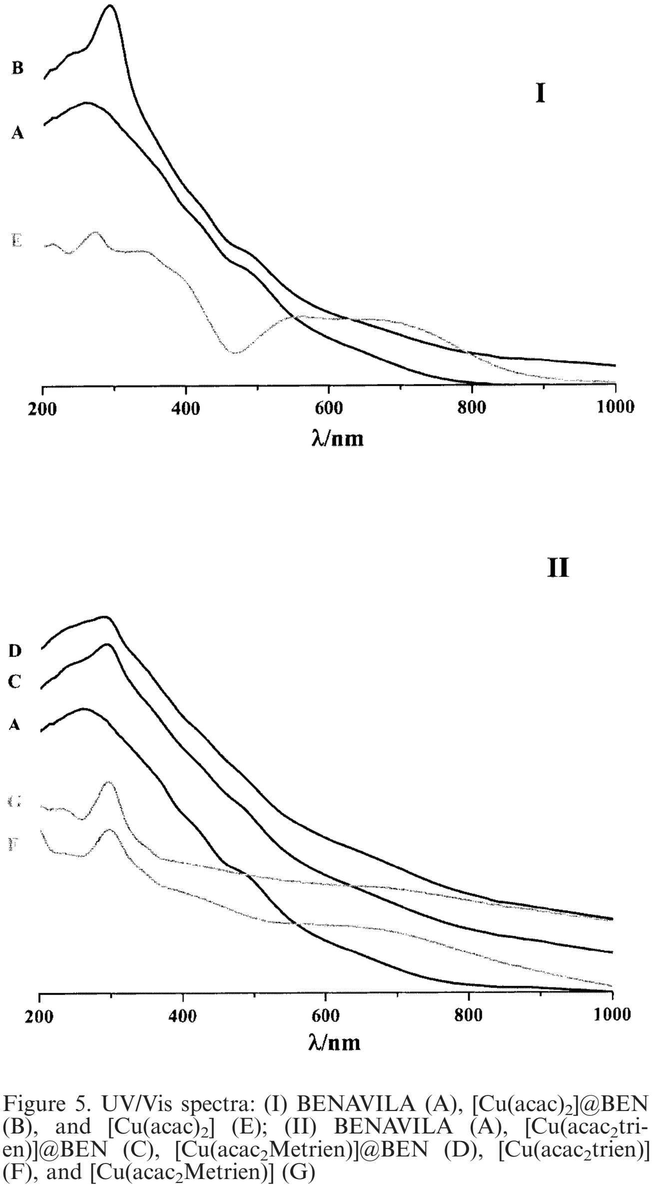


Figure 5. UV/Vis spectra: (I) BENAVILA (A), [Cu(acac)$_2$]@BEN (B), and [Cu(acac)$_2$] (E); (II) BENAVILA (A), [Cu(acac$_2$trien)]@BEN (C), [Cu(acac$_2$Metrien)]@BEN (D), [Cu(acac$_2$trien)] (F), and [Cu(acac$_2$Metrien)] (G)

The visible electronic spectrum of [Cu(acac)$_2$]@BEN is similar to that of parent BENAVILA as the d-d bands at 450−600 nm, typical of the square-planar free complex,[33] are completely masked by the PILC electronic bands, (Figure 5, I). However, a charge-transfer band due to the complex can be detected at λ_{max} = 294 nm and can be taken as a proof of the presence of the complex inside the PILC. Similarly, the visible-region spectra of [Cu(acac$_2$trien)]@BEN and [Cu(acac$_2$Metrien)]@BEN are dominated by the same features as parent BENAVILA (Figure 5, II): no d-d bands typical of pentacoordinate complexes could be observed at $\lambda \approx 450$ and 650 nm.[33] However, as the latter band usually tails into the near-IR region, and BENAVILA does not absorb in this region, the increase in absorbance observed in the range 800−1000 nm for [Cu(acac$_2$trien)]@BEN and [Cu(acac$_2$Metrien)]@BEN, can be taken as an indication of the presence of the complexes inside the BENAVILA. Similarly to the spectrum of [Cu(acac)$_2$]@BEN, it is possible to observe one charge-transfer band at $\lambda_{max} \approx 290$ nm in the spectra of [Cu(acac$_2$trien)]@BEN and [Cu(acac$_2$Metrien)]@BEN due to the trapped complexes, again providing a proof of the presence of the complexes inside the PILC. Due to the lack of resolution of the electronic spectra of the resulting materials, no information on the structure of the entrapped complexes could be derived from this technique.

Conclusions

By combining surface analysis and spectroscopic data it was possible to conclude that [Cu(acac$_2$trien)] and [Cu(acac$_2$Metrien)] can be encapsulated in the interlayers of BENAVILA by in situ Schiff condensation between pre-adsorbed [Cu(acac)$_2$] and the corresponding triamine, without damage of the main matrix or loss of its crystallinity. It was shown that the complex loading in the PILC is larger (approximately 0.12 mmol·g^{-1}) than for the faujasite zeolites NaX and NaY.

FTIR data suggest that copper(II) complexes entrapped in BENAVILA exhibit structural properties that are different from those of the complexes encapsulated in FAU zeolites (NaX and NaY), which have been shown to be mainly physically entrapped in the FAU supercages and with no significant interaction with the zeolite matrix. In the case of PILCs the occluded complexes exhibit distortion induced either by the porous structure or by strong interactions with the oxygen atoms of the host matrix.

The strategy used for the encapsulation of copper complexes can be extended to other metals with known catalytic properties. These novel materials may thus be used as heterogeneous catalysts, indicating that is possible to extend the potential applications of pillared clays in the field of catalysis.

Experimental Section

Reagents and Solvents: All solvents were obtained from Merck (grade *pro analysi*); copper(II) acetylacetonate was obtained from Aldrich and used as received, bis(3-aminopropyl)amine (trien) and bis(3-aminopropyl)methylamine (Metrien) were obtained from Aldrich and were distilled prior to use. The complexes [Cu-

(acac$_2$trien)] and [Cu(acac$_2$Metrien)] were prepared by published procedures.[32]

The BENAVILA PILC was prepared following the procedure described by Pires et al.[26] The parent material was collected from a soil in Benavila, Portugal, and purified according to published methods, with the difference that the clay was not purified by sedimentation, but only by sieving. The pillaring was achieved as described elsewhere.[26] Briefly, an oligomer solution was prepared from $AlCl_3$ and NaOH (both 0.2 M), with an OH/Al ratio of two. After mixing and aging for 2 hours the pH was increased to 6. This oligomer solution was added dropwise to the clay dispersion (2.5 g of clay in 500 mL of water) at 80 °C, whilst stirring, refluxed for 3 h and kept overnight at 25 °C. After centrifugation the solid was washed in a dialysis tube until a conductivity of less than 1 mS·m^{-1}. After being freeze dried and calcined at 350 °C the PILC BENAVILA, with alumina pillars, was obtained. Physical properties: specific surface area of 350 m^2/g and a microporous volume of 0.115 cm^3/g. From the d_{001} reflections, which indicated a basal spacing of 1.8 nm, and subtracting the height of the sheets from the basal spacing, the heights of the galleries of this PILC were estimated to be 0.84 nm.[26]

Sample Preparation

Preparation of [Cu(acac)$_2$]@BEN: [Cu(acac)$_2$] (0.2 mmol) was dissolved in 40 cm^3 of dichloromethane and added to 1.2 g of the PILC BENAVILA (the amount of copper corresponds to about 10^{20} Cu^{2+} ions per gram of PILC). After 7 hours refluxing, the blue colour of the [Cu(acac)$_2$] solution had disappeared indicating that the complex was adsorbed by the clay, although no significant alteration of the original brown-orange colour of BENAVILA was observed. The solid material, denoted as [Cu(acac)$_2$]@BEN, was collected by filtration and dried under vacuum at 90 °C for 1 hour.

Preparation of [Cu(acac$_2$trien)]@BEN and [Cu(acac$_2$Metrien)]@BEN: [Cu(acac)$_2$]@BEN (0.4 g) in 40 cm^3 of dichloromethane, was refluxed for 3 h with a twofold excess of bis(3-aminopropyl)amine (trien) or bis(3-aminopropyl)methylamine (Metrien). The pillared clays changed their colour to a brownish green, providing a first indication that the Schiff condensation had taken place and the complexes [Cu(acac$_2$trien)] and [Cu(acac$_2$Metrien)] formed. After filtration, the solid materials, denoted as [Cu(acac$_2$trien)]@BEN and [Cu(acac$_2$Metrien)]@BEN, were dried under vacuum at 90 °C for 1 hour. To remove any excess triamine, unchanged [Cu(acac)$_2$] and residual Cu^{II} complexes physically adsorbed on the external surface, the solids were Soxhlet extracted with dichloromethane (4 hours) and then with acetone (4 hours). The solids were dried at 90 °C, under vacuum, for 8 hours.

Characterisation Procedures: The elemental chemical analyses (Si, Al, and Cu) were performed by Kingston Analytical Services, UK, using inductively coupled plasma atomic emission spectroscopy. X-ray photoelectron spectroscopy and scanning electron microscopy were obtained at the Centro de Materiais da Universidade do Porto (CEMUP), Porto, Portugal, on a VG Scientific ESCALAB 200A spectrometer using a non-monochromatized Mg-K_α radiation (1253.6 eV), and on a JSM-6301F Scanning Microscope with EDS (NORAN Voyager), respectively

Nitrogen adsorption measurements were performed at 77 K, using an automated apparatus (ASAP 2010). Prior to the adsorption measurements, the samples were outgassed (under vacuum) at 125 °C for 2.5 hours.

FTIR spectra were obtained at room temperature using a Shimadzu Mattson spectrometer in the 4000−400 cm^{-1} range. The transmission spectra of the samples were recorded using KBr (Merck spectroscopic grade) pellets with 32 scans and 4 cm^{-1} resolution. Diffuse reflectance electronic spectra were registered on a Shimadzu UV/3101PC spectrophotometer in the range 1500−200 nm.

X-ray diffractograms were obtained with oriented mounts, on a Philips PX 1820 instrument. To prepare the oriented films, the solids were dispersed in distilled water by ultrasound and then deposited on glass slides.

Acknowledgments

Dr. Carlos Sá performed the SEM and XPS measurements at Centro de Materiais da Universidade do Porto (CEMUP), Porto, Portugal. This work was supported by the Fundação para a Ciência e a Tecnologia (FCT, Lisboa) through Project no. POCTI/42931/QUI/2001. R. F. thanks FCT for a fellowship.

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Received April 27, 2002
[I02221]