Structure and adsorption properties of a porous cooper hexacyanoferrate polymorph

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ABSTRACT

The key questions addressed here were: the structure elucidation and the investigation of the adsorption space and framework expansion effect of a Cu(II) hexacyanoferrate (III) polymorph (labelled Cu-PBA-I). The structural analysis was performed with a broad set of characterization methods. Additionally, a low and high pressure carbon dioxide adsorption investigation was performed, assuming, to comprehend the adsorption experiments, that the adsorbent plus the adsorbed phase were a solid solution. We concluded: that the Cu-PBA-I presented the following composition, $K_{1/4}Cu(II)[Fe(III)(CN)_6]_{3/4}\cdot nH_2O$, exhibited an antiferromagnetic behavior and displayed a thermally stable $\bar{I}4m2$ space group lattice in the degassed state. Moreover, the low pressure adsorption study allowed the calculation of the micropore volume, $W = 0.09 \text{ cm}^3/\text{g}$ and the isosteric heat of adsorption, $q_{iso} = 19 \text{ kJ/mol}$; further, the high pressure adsorption data revealed an extremely high adsorption capacity owing to a framework expansion effect. Finally, the DRIFTS spectrum of adsorbed CO_2 displayed peaks corresponding to carbon dioxide physically adsorbed and interacting with electron accepting Lewis acid sites. Hence, was produced an excellent adsorbent which combine porosity and anti-ferromagnetism, antagonist properties rarely found together.

Keywords: carbon dioxide, adsorption, Prussian blue analog, antiferromagnetism, gas storage.

1. INTRODUCTION

One essential characteristic of the sustainable development of the present and future Human society involve the economically and environmentally advantageous storage, separation and removal of small gas molecules, as for example: carbon dioxide, methane, ammonia and hydrogen, between others [1]. Particularly, for these purposes CO₂ occupies a special position; since their emissions cause global warming; because it influence the balance of received and emitted energy leading to the increase of the earth temperature, stimulating: sea level elevation, the increase in the oceans acidity and the strengthening of tropical storms, between other harmful effects [2].

One of the carbon dioxide emission sources is the burning of fossil fuels for industrial, transportation and other uses, since these processes releases large amounts of CO₂ into the atmosphere perturbing carbon steadiness in the earth that has been stable over hundreds of millions of years [3]. Hence, undoubtedly some approaches to reduce CO₂ emissions are urgently required to minimize climate change. In this regard, to reduce these emissions hydrogen as a clean fuel for transportation and industrial uses and methane as a car fuel, since it is considerably cleaner than petroleum, has been used [4,5]. In addition, the elimination of CO₂ from the chimney of power plants, presently a key source of emissions, is normally achieved by cooling and pressing the exhaust or by contacting the fumes across a fluidized bed of aqueous amine solution, however, both methods are expensive and ineffective [6]. Other methods based on chemisorption of CO₂ on oxide surfaces or adsorption within porous silicates, carbons, metal organic frameworks and other adsorbents have been pursued as means for CO₂ uptake [3-6].

However, the attainment of new adsorbents for carbon dioxide storage is still a vigorous research topic [5]. In this regard, transition metal cyanides [8-21] exhibiting structures assembled with transition metals, attached through the linear cyanide ion, as a consequence of their magnetism [14], physical adsorption [15-19] and other attributes [9-14], are a significant class of materials. In particular, metal hexacyanometalates isostructural to Prussian blue, namely Prussian blue analogs (PBAs), exhibit developed adsorption and magnetic properties between other characteristics [9,19,20,21].

The backbone of the structure of PBAs is the $-M'-C \equiv N-M-N \equiv C-M'-$ chain. This atomic sequence is straight hence PBAs typically crystallize in the cubic system, specifically, in the $Fm\bar{3}m$ space group and in less extent in the $Pm\bar{3}m$ [19]. Even though, some PBAs crystalizes in the tetrahedral, $I\bar{4}m2$ [10] and $I4mm$ [18] space groups. Moreover, if $M' = Fe(III)$, and $M = M(II)$, the following, $A_xM(II)[Fe(III)(CN)_6]_z \diamond_{1-z} nH_2O$, generalized formula has been proposed to describe the stoichiometry of these materials [9], where the symbol, $\diamond$, indicates $[Fe(III)(CN)_6]^\mu$ vacancies, generated together with the interstitial cations to produce charge balance in the framework. In this regard, some possible representatives compositions for these materials are [13], $AM(II)[Fe(III)(CN)_6]$ ($M/Fe=1$), $M(II)[Fe(III)(CN)_6]_{2/3} \diamond_{1/3} nH_2O$ ($M/Fe=3/2$) and $A_{1/4}M(II)[Fe(III)(CN)_6]_{3/4} \diamond_{1/4} nH_2O$ ($M/Fe=4/3$), where the voids results to microporous frameworks.

The investigation of carbon dioxide physical adsorption [22] and the analysis of the infrared spectra of adsorbed CO_2 [23-25] are outstanding methods for the characterization of the porosity and surface chemistry of porous materials. Hence, the adsorption of this gas is an excellent tool for the investigation of the adsorption space of PBAs and other materials [26-31].

For the last years the investigation of PBAs became an expanding research field, specially, when materials with high thermal stability and porosity are produced [32-36]. Thereafter, the main questions investigated here were: the structural elucidation and the study of the adsorption properties and thermal stability of a porous Cu(II) hexacyanoferrate (III) polymorph (labelled Cu-PBA-I) and the synthesis and characterization of the standard Cu(II) hexacyanoferrate (III) (labelled Cu-PBA) for comparison.

2. EXPERIMENTAL SECTION

The consumable chemicals were analytical grade. Water was bi-distilled.

Firstly, the synthesis of the standard Cu(II) hexacyanoferrate(III) was carried out following the recipes reported in literature [19] to get the sample labelled Cu-PBA. Secondly, the synthesis of the Cu(II) hexacyanoferrate(III), different to the standard one, took place by mixing 0.025 moles of solid potassium hexacyanoferrate (III) and solutions containing 0.025 moles of $\text{Cu}(\text{NO}_3)_2$ in 250 mL of water, at 70 °C, under constant stirring, next, the formed precipitate was filtered, washed with distilled water and dried at 343 K for 24 h to get the sample labelled Cu-PBA-I.

Next, X-Ray diffraction (XRD) profiles were collected (Bruker D8 Advance) using a Bragg-Brentano vertical goniometer configuration. The angular measurements were made using steps of 0.01 degree. The X-ray radiation source was a ceramic X-ray diffraction Cu anode tube type KFL C 2K. In addition, a Soller slit was included and a Ni filter was placed prior to the detector. Also, a LynxEye™ one-dimensional detector was used for X-ray detection.

Afterwards, the scanning electron microscopy (SEM) images were obtained at 20 kV (JEOL, JSM-6360) for sample grains placed on a carbon tape. At the same time as, elemental chemical analysis was performed using the energy dispersive x-ray analysis (EDAX) included in the SEM. Subsequently, the thermo-gravimetric analysis (TGA) testing process was carried out (TA, Q-500). The sample and holder were heated according to a predetermined thermal cycle from 25 to 700 °C at a heating rate of 5 °C/min while flowing 100 ml/min of pure N₂ (Praxair, 99.99 %). The TGA profiles were collected as a *Wt. %* versus *T* (°C) graphic, where $Wt.\% = (M_t / M_0) \times 100$ is the percent -ratio of the sample mass for the thermal treatment M_t and the initial mass of the sample M_0 .

Afterward, diffuse reflectance Fourier transform infrared spectrometry (DRIFTS) spectra were gathered (Nicolet iS10). The spectra were collected at a resolution of 4 cm⁻¹ employing 200 scans per sample in a high temperature infrared cell. The hydrated samples spectra were obtained at room temperature under N₂ flow at 50 ml/min rate. To get the spectra of the dehydrated samples it were heated at 473 under a flow of N₂ at 50 ml/min rate for 2 hours. Then, the spectra of the degassed materials were obtained at room temperature, under N₂ flow. Similarly, a Raman spectrum was taken with a Renishaw Raman microspectrometer RM2000 system equipped with a Leica microscope using a 20x objective and a charge-coupled device (CCD) detector. Then, the spectrum was obtained with a laser line at 532 nm, generated by a Spectra Physics EXCELSIOR solid state diode laser, in the range of 100-3500 Raman Shift (cm⁻¹) with an integration time of 15s per scan, averaging fifteen scans.

Later, the magnetization curve (M versus H) was collected at room temperature (300 K) in the vibrating sample magnetometer (VSM) (Lakeshore 7400). To perform the test, the powder

sample was weighted, located on the sample holder and subsequently was generated the ramp from -2.2 to 2.2 T and backward.

Lastly, carbon dioxide (Praxair, 99.99 %) adsorption was investigated at 300 K and pressure up to 1 bar (LP) (Quantachrome AS-1) and at 300 K and pressure up to 30 bar (HP) (Quantachrome iSorbHP-100), on samples degassed at 423 K for three hours in high vacuum (10^{-6} Torr). The backfilling process was performed using helium (Praxair, 99.99 %). Furthermore, the DRIFTS spectrum of carbon dioxide adsorbed in the Cu-PBA-I was collected utilizing as background the dehydrated sample at room temperature. After that, a CO_2 flow at a rate of 50 ml/min for three minutes was passed through the dehydrated samples, next, the sample was purged under N_2 flow at a rate of 50 ml/min for one minute, and then a spectrum of the carbon dioxide molecule adsorbed on the Cu-PBA-I adsorption space was obtained at room temperature under N_2 flow.

Finally, the curve fitting processes were performed with the analysis and peak separation software PeakFit[®] (Seasolve Software Inc., Framingham, Massachusetts) based on a least square procedure [37]. The program made possible the calculation of the best fitting parameters in the case of curve fitting. For peak separation the software made possible the calculation of the band parameters, i.e., intensity, peak position and half-band-width using for the spectrum fitting Lorentzian functions.

3. RESULTS AND DISCUSSION

3.1. Structural characterization of the synthesized Cu-PBA-I

First of all, the powder XRD profiles of the as-synthesized Cu-PBA and Cu-PBA-I were collected and resolved into separate Bragg components using the Pawley powder pattern

decomposition method, by means of the Bruker AXS TOPAS[®] powder X-ray diffraction analysis software. The profiles were fitted assuming the $Pm\bar{3}m$ space group (SG) for the Cu-PBA (Fig. 1a) [23] and the tetragonal $I\bar{4}m2$ SG for the Cu-PBA-I (Fig. 1b) respectively. Likewise, in Table 1 are reported the refined parameters. The profile of the Cu-PBA and the refined cell parameters (Table 1) agreed with the XRD data previously published [19]; meanwhile, the crystallographic information reported for the Cu-PBA-I, indicated that was produced a different polymorph.

Secondly, three SEM images corresponding to the Cu-PBA-I material were collected (Fig. 1a, 1b and 1c). These images exhibited the formation of particles of 60 μm shaped by aggregates of 0.5-1 μm formed by the 25 nm Cu-PBA-I crystallites. In addition, EDAX elemental chemical analysis of the Cu-PBA-I was performed (see Fig. 1d). In this regard, the elemental composition was calculated as the average of ten tests similar to those reported in Fig 1d. Thereafter, the average concentration plus the calculated standard deviation (σ) expressed in molar per-cent was calculated and reported in Table 2.

Subsequently, to further understand the properties of both synthesized materials, the thermogravimetric analysis (TGA) method was used (Fig. 3). The TGA results made possible the following inferences: water was released up to 200 $^{\circ}\text{C}$, for both materials; in this sense, the derivative of the TG profiles evidenced, for the Cu-PBA, demonstrated that the liberation of adsorbed water took place, in two steps, the first at 60 $^{\circ}\text{C}$ and the second at 150 $^{\circ}\text{C}$, meanwhile, for the PBA-I a broad peak that was resolved in two components, i.e., one at 80 $^{\circ}\text{C}$ and the other at 110 $^{\circ}\text{C}$ was observed (see Fig. 3e). Finally, at 300 $^{\circ}\text{C}$ for the Cu-PBA and 210 $^{\circ}\text{C}$ for the Cu-PBA-I the decomposition of both materials was evidenced [18]. Hence, the TGA profiles demonstrated the release of “zeolitic” water from the Cu-PBA-I in the course of heating, a behavior similar to those exhibited by the Cu-PBA [19].

Next, in Fig. 4 are shown the DRIFTS spectra of the as-synthesized (Fig. 4a and 4b) and dehydrated (Fig. 4c and 4d) Cu-PBA-I. The main IR active vibrations observed in the 1500-2500 cm^{-1} range are the absorption bands corresponding to the OH bending at 1610 cm^{-1} and the CN stretching modes [33]. Since, CN bands are the main vibrations in Prussian blue analogues; then, a curve fitting processes, to analyze the band components was made (Fig. 4b). In this regard, in Table 3 are reported the calculated peak position (x_i), half-band-width (σ) and intensity (A) of the peaks related to the CN vibration modes. The peaks located ca. 2174 cm^{-1} and ca. 2103 cm^{-1} in the hydrated (Fig. 4b) and dehydrated (Fig. 4d) Cu-PBA-I were associated to the CN stretching vibration, $\text{Cu(II)}-\text{N}\equiv\text{C}-\text{Fe(III)}$ [32]. Since, Cu-PBA-I is a rather pure material, as is evidenced in the XRD pattern (Fig. 1b); hence, the existence of two peaks; could be only related to the PBA structure; for the reason that, the $\text{Cu(II)}-\text{N}\equiv\text{C}-\text{Fe(III)}$ chains are located on two different sub-lattices, α and β in the tetragonal $I\bar{4}m2$ SG body centered cubic framework, (Fig. 5a). For example, Fe (III) is located in the vertices (α sub-lattice) and the center (β sub-lattice) of the tetragonal cell [9]. Furthermore, the peak located on 2010 cm^{-1} was assigned to the CN group ($-\text{N}\equiv\text{C}-\text{Fe(III)}-\text{C}\equiv\text{N}-\text{Cu(II)}-$) not bonded at the N termination, while the band located on ca. 1945 cm^{-1} for the dehydrated Cu-PBA-II, can be accredited to a minute new phase formed in the course heating [34]. Moreover, the bands present in the 3000-3800 cm^{-1} range were related to the hydroxyl functionalities, in this regard, the narrow peak 3660 cm^{-1} , was assigned to the stretching vibrations of the OH groups corresponding to linked water, while the vibrations related to the hydrogen bonded water molecules were evidenced in the broad peak located in the range between 3000-3600 cm^{-1} [35]. Both bands almost disappeared after dehydration (Fig. 4b). Thereafter, in Fig. 5 and Table 4 are reported the position and the assignment of the Raman bands in the low frequency region. In this frequency span, the typical bands related to iron and

cooper coordinated to carbon and nitrogen, are, two stretching modes, i.e., $\nu(FeC)$ and $\nu(CuN)$ together with four bending ones, namely, $\delta(FeCN)$, $\delta(NFeN)$, $\delta(CuCN)$ and $\delta(NCuN)$ [8]. In the case of cubic PBAs six bands must be observed, even though, for tetragonal PBAs two additional bands are detected, because of their lower symmetry [36]. In this regard, since we observed eight peaks (Table 4), hence the Raman data confirmed the assumed the tetragonal $I\bar{4}m2$ SG for the Cu-PBA-f.

Afterwards, the magnetization curve of the Cu-PBA-I is reported in Fig. 6. This curve indicated an antiferromagnetic behavior; because, it shows saturation, hysteresis and a very small magnetization. We could explain this antiferromagnetic effect as related to the existence of two different $Cu(II) - N \equiv C - Fe(III)$ chains located on two different sub-lattices, α and β (Fig. 7a). Each chain is ferromagnetic since Cu(II) has six electrons in t_{2g} orbitals and three electrons in the e_g orbitals, where the unpaired electron is placed in a e_g orbital; meanwhile, Fe(III) has five electrons in t_{2g} orbitals; therefore, the unpaired electron is placed in a t_{2g} orbital; hence, since each chain is ferromagnetic; but in the present; based on the obtained results (Fig. 6) their magnetization are oppositely-directed.

Now, the elemental composition (Table 2), the TGA profiles (Fig, 3) and the PBAs compositions reported in literature [13], i.e., $AM(II)[Fe(III)(CN)_6](M/Fe=1)$, $M(II)[Fe(III)(CN)_6]_{2/3}\cdot\frac{1}{3}nH_2O$ ($M/Fe=3/2$) and $A_{1/4}M(II)[Fe(III)(CN)_6]_{3/4}\cdot\frac{1}{4}nH_2O$ ($M/Fe=4/3$), allowed us to propose the following chemical formula: $K_{1/4}Cu(II)[Fe(III)(CN)_6]_{3/4}\cdot\frac{1}{4}nH_2O$, for the produced Cu-PBA-I. Subsequently, using the experimentally obtained crystallographic information (Table 1), the proposed chemical formula, the atomic positions reported in Table 5, Wyckoff sites and occupancy factors reported in the International Tables for Crystallography

[40] and crystallographic data found in literature [41], was produced with the software PowderCell-2.4 [42] the unit cell representation for the framework of the Cu-PBA-I (see Fig. 7). Finally, the XRD diffraction pattern of the Cu-PBA-I was fitted with the Rietveld method by means of the Bruker AXS TOPAS[®] software package using the atomic positions, Wyckoff sites and occupancy factors previously applied to generate the Cu-PBA-I framework (Fig. 78). The fitting process was performed while the atomic position, occupancy factors and isotropic thermal factors for the cations and anisotropic thermal factors for the oxygen ions were kept fixed, and the cell parameters refined. The calculated cell parameters were, within the experimental error, the same reported in Table 1. These results validated the proposed framework.

3.3. Carbon dioxide adsorption on Cu-PBA-I

To get the CO₂ adsorption isotherm, the tested material was degassed in vacuum at 423 K for 3 hours. Subsequently, adsorption data at 300 K was collected, for, P , the adsorption equilibrium pressure up to 1 Bar (low pressure range), that is, $0.00002 < P/P_0 < 0.015$, where, P_0 , is the vapor pressure of carbon dioxide at 300 K. Next, to characterize the adsorption space of the Cu-PBA-I was used the Dubinin-Radushkevitch (D-R) adsorption isotherm equation:

$$\ln(n_a) = \ln(N_a^0) - \left(\frac{RT}{E} \right)^2 \ln \left(\frac{P_0}{P} \right)^2 \quad (1)$$

Wherein, n_a , is the amount adsorbed, P/P_0 , is the relative pressure, E , is the characteristic energy of adsorption, and, N_a^0 , is the maximum amount adsorbed in the micropore volume at low pressure (LP). Subsequently, the fitting of the adsorption isotherm of carbon dioxide at 300 K, up to 1 bar, on the Cu-PBA-I and the Cu-PBA, for comparisson, to the D-R equation (Fig. 8) allowed the calculation (see Table 6) of, N_a^0 and, E , plus, W_0 , the micropore volume, calculated using the

Gurtvich rule, $W_0 = N_a^0 V_{CO_2}$ (where, $V_{CO_2} = 48.3 \text{ cm}^3/\text{mol}$ is the carbon dioxide molar volume)

and, q_{iso} , the isosteric heat of adsorption, computed using the following methodology [42]:

$$q_{iso}(\theta) = -\Delta G(\theta) + EF(T, \theta), \quad \Delta G(\theta) = RT \ln(P/P_0) \quad \text{and} \quad F(T, \theta) = (\alpha T/2) (\ln[1/\theta])^{-\frac{1}{2}},$$

where, $\theta = n_a/N_a$; $\alpha = -d \ln N_a/dT$, $E = \Delta G(1/e)$, for $\theta = 1/e$, for, $e \approx 2.71828183$. Hence, for

$\theta = 1/e \approx 0.37$ was possible to get the following equation,

$$q_{iso}(0.37) = -\Delta G(0.37) + EF(T, 0.37) = E[F(T, 0.37) - 1], \text{ where, } F(T, 0.37) \approx 2.16, \text{ consequently,}$$

on this ground, was obtained the relation: $q_{iso}(0.37) = 1.16E$ [43].

The magnitude of the micropore volume (W_0) implied that the Cu-PBA-I PBA is a microporous crystalline material. Furthermore, the value measured for the isosteric heat of adsorption was sufficiently small to infer the absence of strong acid sites in the adsorption space [44].

Similarly, in Fig. 9 are exhibited the high pressure carbon dioxide adsorption-desorption isotherms in terms of the surface excess amount carbon dioxide adsorption isotherm, n_a (mmol/g)

(Fig. 9a) and the pore volume (cm^3/g) (Fig. 9b). Where, the excess adsorption amount was

measured with the volumetric method using the following equation: $n_a = n_t - \rho_g V_g$, in which, n_t ,

was the total amount adsorbed, ρ_g , the adsorbate density and, V_g , the dead volume that include

the pore volume of the adsorbent [45]. To measure, V_g , was used a reference gas, specifically,

He, for which the amount adsorbed, n_a , is considered zero i.e., $n_a = n_t - \rho_g V_g = 0$, accordingly,

$V_g = n_t/\rho_g$, where, ρ_g , is the density of He [46]. Meanwhile the pore volume was calculated

with the expression, $W = n_t V_{CO_2}$, where, $V_{CO_2} \text{ cm}^3/\text{mol}$ was the carbon dioxide molar volume.

Subsequently, the adsorption isotherms reported in Fig. 9 indicated that as a consequence of the process the adsorption space was not saturated, conversely, the amount adsorbed continuously

increased. This fact is possible because an adsorbent in the course of the adsorption processes could experience deformation, that is, adsorption can produce the expansion of the adsorbent structure [47, 48].

Now, to work out the adsorption process an important assumption was made, specifically, the adsorbent plus the adsorbed phase was considered as a solid solution, i.e., the adsorbate-adsorbent system (aA); thereafter, the fundamental thermodynamic equation, within the frame of the solution thermodynamic approach; for this system is given by [49]:

$$dU_{aA} = TdS_{aA} - PdV_{aA} + \mu_a dn^a + \mu_A dm \quad (2)$$

Where, U_{aA} , S_{aA} and V_{aA} are the internal energy, entropy and volume of the system aA , while μ_a (in J/mol) and μ_A (in J/Kg) are the chemical potentials of the adsorbed and solid phases in the solution and, n^a , and m the amount of moles of adsorbate and the adsorbent mass in the system aA . Hence:

$$U_{aA} = TS_{aA} - PV_{aA} + \mu_a n^a + \mu_A m \quad (3)$$

On this ground, is possible to write the internal energy per unit mass of adsorbent as follows:

$$\bar{U}_{aA} = T\bar{S}_{aA} - P\bar{V}_{aA} + \mu_a n_a + \mu_A$$

Where, $n_a = n^a/m$. Now the internal energy for the unit mass of empty adsorbent is given by:

$$\bar{U}_A = T\bar{S}_A - P\bar{V}_A + \mu_A^0$$

Therefore:

$$U_a = \bar{U}_{aA} - \bar{U}_A = TS_a - PV_a + \mu_a n_a + \Phi \quad (4)$$

Where, $S_a = \bar{S}_{aA} - \bar{S}_A$, $V_a = \bar{V}_{aA} - \bar{V}_A$ and $\Phi = \mu_a - \mu_A^0$. Likewise, the fundamental thermodynamic equation for the adsorbed phase is given by:

$$dU_a = TdS_a - PdV_a + \mu_a dn_a + d\Phi \quad (5)$$

Therefore, since the Grand potential is defined as: $\Omega = U - TS - \mu n$, hence:

$$\begin{aligned} \Omega_a &= U_a - TS_a - \mu_a n_a - \Phi \\ d\Omega_a &= dU_a - TdS_a - S_a dT - d\mu_a n_a - \mu_a dn_a - d\Phi \end{aligned} \quad (6)$$

Consequently, substituting equation “5” in equation “6” we get:

$$d\Omega_a = -PdV_a - S_a dT - n_a d\mu_a$$

Now, in equilibrium: $d\mu_a = d\mu_g = RT \ln f$, where f , is the fugacity of the adsorbate, thereafter:

$$d\Omega_a = -PdV_a - S_a dT - n_a RT \ln f = d\Phi \quad (7)$$

But since, $\Omega_a = \Phi$, then, for $T = \text{const}$:

$$\Phi = RT \int_0^f n_a d(\ln f) - V_a P \quad (8)$$

In the frame of the osmotic theory of adsorption [50], $\Phi = \Pi W$, hence:

$$\Pi W = RT \int_0^f n_a d(\ln f) - V_a P \quad (9)$$

Where, W , is the micropore volume of the adsorbent and, $\Pi = P^0 - P$, is the osmotic pressure where P^0 , is a pressure that can compress the adsorbate and produce the same effect created by an adsorption field, i.e., an amount, n_a , of molecules [22]. Subsequently, in order to operate with equation “9”, the fugacity of carbon dioxide must be calculated. In this regard, this parameter was computed by using the following expression [51]:

$$\ln f = \ln P + \left[b - \frac{a}{RT} \right] \left(\frac{P}{RT} \right) \quad (10)$$

Where, a and b are the van der Waals parameters for carbon dioxide, specifically,

$$a = 36.58 \left[(m^3/mol)^2 Pa \right] \text{ and } b = 42.9 \left[m^3/mol \right].$$

Accordingly, in Fig. 10 is shown the Π versus P plot, calculated with equations “9” and “10”. This figure shows a maximum in the osmotic pressure versus pressure plot, fact indicating that a pressure-responsive framework opening sorption event, took place due to a structural transformation in the adsorbent framework induced by the guest molecules [52, 53].

3.4. DRIFTS study of carbon dioxide adsorption on Cu-PBA-I

In Figs. 11 are reported the DRIFTS spectra of the dehydrated Cu-PBA-I (Fig 11a) and the same sample during CO₂ adsorption (Fig. 11b). Subsequently, this spectrum was fitted with Gaussian-Lorentzian functions (Fig. 12c). Next, the fitting parameters, namely, the peak positions, x_i , peak full width at half maximum, Δx_i , and the peak area, A_i , were calculated with the peak separation software PeakFit[®], in the course of the fitting with Gaussian-Lorentzian functions of the carbon dioxide DRIFTS spectrum (see Table 7).

Since the free carbon dioxide molecule belongs to the $D_{\infty h}$ point group symmetry, four primary vibration modes [13], namely, the symmetric stretching, ν_1 , at 1338 cm⁻¹ the doubly degenerate bending vibration, ν_{2a} and ν_{2b} at 667 cm⁻¹, and the asymmetric stretching vibration ν_3 at 2349 cm⁻¹ can be observed.

The study of adsorbed CO₂ with IR spectroscopy [23] is normally focused on the range from, 2250 to 2400 cm⁻¹, that is, the range where is observed the asymmetric stretching vibration, ν_3 ; given that, this vibrational mode of the carbon dioxide molecule is to some extent disturbed from the equivalent position for the gas phase during adsorption [24]. In this regard, in the spectrum reported in Fig. 7c, the band detected at 2338 cm⁻¹ (Table 7), was the result of the physical adsorption of the carbon dioxide molecule [25]. Further, the bands located on 2321 cm⁻¹ was assigned to a combination band [23]. Moreover, there is another band observed at 2348 cm⁻¹, that

should correspond to the adsorption of carbon dioxide on an electron accepting Lewis acid site forming the following adducts: $Cu^{2+} \cdots O=C=O$ [54].

4. Conclusions

A polymorph of Cu(II) hexacyanoferrate (III) (Cu-PBA-I) and the standard Cu(II) hexacyanoferrate (III) (Cu-PBA), were synthesized. The key questions addressed in the reported research were the: structure elucidation, investigation of the adsorption space, framework expansion effect in the course of adsorption and magnetic properties of the produced Cu(II) hexacyanoferrate (III) polymorph (labelled Cu-PBA-I). To answer these questions, these materials were thoroughly investigated with a group of characterization methods, specifically, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDAX), thermo-gravimetric analysis (TGA), diffuse reflectance Fourier transform infrared spectrometry (DRIFTS), Raman spectrometry (RS), and magnetic measurements. Additionally, low and high pressure carbon dioxide adsorption isotherms were collected, supposing, to understand the adsorption experiment, that the adsorbent plus the adsorbed phase were a solid solution. The inferences made were, the Cu-PBA-I exhibited the following composition, $K_{1/4}Cu(II)[Fe(III)(CN)_6]_{3/4} \cdot nH_2O$; showed an antiferromagnetic behavior at room temperature and displayed a thermally stable $I\bar{4}m2$ space group lattice in the degassed at 423 K state. Moreover, the low pressure adsorption study made possible the calculation of the micropore volume, $W = 0.09 \text{ cm}^3/\text{g}$ and isosteric heat of adsorption, $q_{iso} = 19 \text{ kJ/mol}$; further, the high pressure adsorption isotherms revealed that a pressure-responsive framework opening sorption event, took place due to a structural transformation in the adsorbent framework induced by the

guest molecules, producing an extremely high adsorption capacity owing to the framework expansion effect. Additionally, the DRIFTS spectrum of adsorbed CO₂ displayed peaks corresponding to CO₂ physically adsorbed and forming the following adducts, $Cu^{2+} \cdots O=C=O$, that is carbon dioxide adsorbed on an electron accepting Lewis acid site.

Hence is possible to conclude that the produced Cu-PBA-I is an excellent adsorbent for carbon dioxide storage and other small molecules which amalgamate porosity and anti-ferromagnetism, antagonist properties rarely found concurrently.

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Figure

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Table 1. Refined cell parameters and crystallite sizes

<i>Sample</i>	<i>a</i> (<i>Å</i>)	<i>c</i> (<i>Å</i>)	<i>V</i> (<i>Å</i> ³)	<i>Φ</i> (<i>nm</i>)	<i>S.G.</i>
Cu-PBA	10.078(2)		1024.1 (2)	30 (1)	<i>Pm</i> $\bar{3}$ <i>m</i>
Cu-PBA-I	9.87 (1)	10.52 (1)	926.8 (3)	25 (1)	<i>I</i> $\bar{4}$ <i>m</i> 2

Table 2. Average elemental composition (standard deviation) for the Cu-PBA-II

Sample	C_K (σ)	C_{Fe} (σ)	C_{Cu} (σ)
Cu-PBA-I	0.2 (1)	1.2 (5)	1.5 (5)

Table 3. Low pressure micropore volume (W_0), characteristic energy of adsorption (E) and isosteric heat of adsorption (q_{iso} at $\theta = 0.37$).

<i>Sample</i>	N_a^0 (mmol / g)	E (kJ / mol)	W_0 (cm ³ / g)	q_{iso} (0.37) kJ/mol
Cu-PBA	1.62 (1)	17 (2)	0.078 (5)	20 (2)
Cu-PBA-I	1.84 (1)	16 (2)	0.089 (5)	19 (2)

Table 4. Parameters of the IR peaks related to adsorbed carbon dioxide on Cu-PBA-I.

Sample	$x_1[\Delta x_1](cm^{-1})$	$A_1(\%)$	$x_2[\Delta x_2](cm^{-1})$	$A_2(\%)$
Adsorbed CO₂	2339 [17]	60	2306 [64]	40