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# Heterogenization of a Functionalized Copper(II) Schiff Base Complex by Direct Immobilization onto an Oxidized Activated Carbon

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A copper(II) Schiff base complex bearing hydroxyl groups [bis(4-hydroxysalicylaldehyde)ethylenediamine] copper(II), [Cu(4-HOsalen)], was directly anchored onto an air-oxidized activated carbon. Oxidation of the activated carbon was done with a mixture of air and N<sub>2</sub> (with 5% O<sub>2</sub>) to increase the oxygenated surface functional groups, and complex immobilization was made by attachment of the metal complex hydroxyl groups to carbon surface groups. The adsorption/desorption of the metal complexes onto the oxidized activated carbon was monitored by UV–vis spectroscopy. Carbon-based materials were characterized by elemental analysis, surface techniques (scanning electron microscopy and X-ray photoelectron microscopy), nitrogen adsorption isotherms, and thermal analysis (temperature-programmed desorption and thermogravimetry). EPR spectra of both free and carbon-supported [Cu(4-HOsalen)] complexes were recorded. A comparative study with the unfunctionalized copper complex, [Cu(salen)], was also performed to assess the role of the hydroxyl groups in copper complex anchorage. Data from all the techniques have provided evidence that copper complexes with the hydroxyl functionalized Schiff base are chemically bound to carbon surface groups through the ligand substituent, whereas the unfunctionalized complex, [Cu(salen)], was only physically adsorbed onto the activated carbon and was leached during Soxhlet extraction.

## Introduction

Schiff base transition metal complexes have been extensively studied because of their potential use as catalysts in a wide range of oxidation reactions.<sup>1–4</sup> Particularly, copper(II) Schiff base complexes have been used as catalysts in the aziridination<sup>5</sup> and cyclopropanation of olefins<sup>6</sup> and also in the peroxidative oxidation of phenol to dihydroxy benzynes,<sup>7</sup> in which they act as models for catalase enzymes.

The heterogenization of transition metal complexes is an area of growing interest, with zeolites and polymers being the most widely used supports in the heterogenization of Schiff base complexes. However, activated carbons are materials that have good potential characteristics for being used as supports, because they are very porous and possess high surface areas.<sup>8</sup> Furthermore, when compared to silicas and zeolites, they exhibit a richer surface composition with several functional groups—such

as hydroxyls, carbonyls, lactones, and carboxylic acids—that can also be selectively increased by thermal or chemical processes.<sup>9</sup> The variety of surface groups allows for a wider range of strategies to attach covalently catalytic active transition metal complexes to activated carbons, which will reduce catalyst leaching and will improve catalyst reuse.

Despite being used mainly as supports for catalytic active metals in gas-phase oxidation reactions,<sup>10</sup> there are some recent reports on the heterogenization of noble metal complexes onto activated carbons (direct support attachment) and their application as catalysts in hydrogenation<sup>11,12</sup> and hydroformylation reactions of alkenes.<sup>13</sup> In the former example,<sup>11,12</sup> there is no mention of catalyst leaching or reuse, albeit the Pt(II) metal complexes are only physically adsorbed onto the activated carbon surface. In the latter report, catalyst leaching was observed and was found to depend on the polarity of the solvent used to carry out the catalytic reactions.<sup>13</sup> In the oxidation of alkanes by iron–phthalocyanin complexes supported on activated carbon<sup>14</sup> and activated carbon black,<sup>15</sup> no refer-

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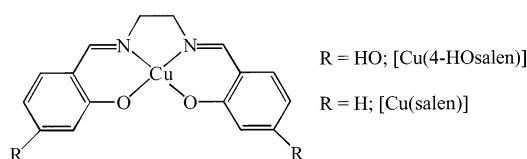
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Scheme 1



ence to leaching or reuse has been made, despite the fact that the catalysts have been prepared by impregnation. Copper(II) and cobalt(II) acetylacetonates have been immobilized onto modified activated carbons using the oxygen functional groups of the supports and have been successfully used in liquid-phase oxidations of pinane with no leaching.<sup>16</sup>

We have been interested in the preparation of heterogeneous catalysts based on Schiff base transition metal complexes using activated carbons as support, namely, we have been concerned with the development of novel strategies to effectively anchor this type of complex. We have reported the successful immobilization of a square planar nickel(II) Schiff base complex functionalized with hydroxyl groups using cyanuric chloride as the linking agent<sup>17,18</sup> and the immobilization of a six-coordinate nickel(II) Schiff base complex functionalized with amine groups, which covalently bonds to acyl chloride functionalities (via amide ligation) created on the surface of the activated carbon upon treatment with thionyl chloride.<sup>18</sup>

In this paper we report a novel methodology for the direct anchoring of a four-coordinate copper(II) Schiff base complex bearing hydroxyl groups in the aldehyde moiety, [Cu(4-HOsalen)], onto the surface of an air-oxidized activated carbon (Scheme 1). The effectiveness of the methodology was confirmed by monitoring the adsorption/desorption of the copper complex onto the activated carbon by UV-vis spectroscopy and by the characterization of the resulting carbon-based materials with proximate and elemental analysis, surface techniques (scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS)), nitrogen adsorption isotherms, thermal methods (thermogravimetry and temperature-programmed desorption (TPD)), and electron paramagnetic resonance. By combining data from all techniques and by comparing with those of the unfunctionalized Schiff base complex, [Cu(salen)], it was possible to conclude that [Cu(4-HOsalen)] is covalently bound to activated carbon functionalities through the hydroxyl groups of the aldehyde moieties, whereas [Cu(salen)] is only physically adsorbed onto the activated carbon.

## Experimental Section

**Materials.** The starting carbon material was a NORIT ROX 0.8 activated carbon (rodlike pellets with 0.8 mm diameter and 5 mm length). The activated carbon was purified by Soxhlet extraction with HCl 2 mol dm<sup>-3</sup> for 6 h, washed with deionized water until pH 6–7, and then dried in an oven at 150 °C for 13 h (carbon A1).

The reagents and solvents used in the synthesis of the Schiff base complex, in the modification of the activated carbon surface and in the anchoring of metal complexes, were used as received. Copper(II) acetate monohydrate, ethylenediamine, *N,N*-dimethylformamide, 1,4-dioxane, dichloromethane, and acetone were from Merck (pro analysi), and 4-hydroxysalicylaldehyde was from Aldrich.

ethylformamide, 1,4-dioxane, dichloromethane, and acetone were from Merck (pro analysi), and 4-hydroxysalicylaldehyde was from Aldrich.

**Preparation of the Schiff Base Complexes.** The ligand bis(4-hydroxysalicylaldehyde)ethylenediamine, H<sub>2</sub>(4-HOsalen), was prepared following standard methods by refluxing methanol solutions of ethylenediamine and 4-hydroxysalicylaldehyde.<sup>19</sup> The respective copper(II) complex, [Cu(4-HOsalen)], was also prepared as described in the literature by refluxing ethanolic solutions of equimolar quantities of copper(II) acetate monohydrate and ligand.<sup>19</sup> The copper complex was recrystallized from 1,4-dioxane. The complex [Cu(salen)] was prepared following standard methods.<sup>19</sup>

[H<sub>2</sub>(4-HOsalen)], bis(4-hydroxysalicylaldehyde)ethylenediamine: C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>. Anal. Calcd: C, 64.0; H, 9.3; N, 5.4. Found: C, 64.5; H, 9.3; N, 5.4. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 200 MHz, 297 K),  $\delta$  (ppm): 13.7 (s, 2H, OH), 9.9 (s, 2H, OH), 8.3 (s, 2H, N=CH), 7.2–7.1 (d, 2H, aromatic), 6.3–6.1 (m, 4H, aromatic), 3.8 (s, 4H, CH<sub>2</sub>); UV-vis,  $\lambda_{\text{max}}$  (nm): 253, 278, 357,  $\approx$ 440 (i); FTIR,  $\nu$  (cm<sup>-1</sup>): 3385 (m), 3122 (w), 1640 (vs), 1586 (s), 1505 (m), 1474 (s), 1416 (m), 1397 (i), 1358 (s), 1285 (m), 1235 (s), 1212 (s), 1181 (m), 1166 (s), 1112 (m), 1000 (m), 976 (m), 942 (m), 895 (m), 838 (s), 834 (i), 803 (s), 791 (i), 749 (m), 733 (w), 672 (m), 610 (s), 591 (m), 560 (m), 521 (w), 455 (i), 452 (m), 432 (m).

[Cu(4-HOsalen)], [bis(4-hydroxysalicylaldehyde)ethylenediamine] copper(II): C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>Cu. Anal. Calcd: C, 53.1; H, 7.7; N, 3.9. Found: C, 52.4; H, 7.2; N, 3.8. UV-vis,  $\lambda_{\text{max}}$  (nm): 234, 277, 323, 368,  $\approx$ 405 (i), 547; FTIR,  $\nu$  (cm<sup>-1</sup>): 1626 (vs), 1593 (vs), 1537 (vs), 1487 (w), 1448 (s), 1400 (w), 1388 (w), 1363 (w), 1333 (m), 1275 (w), 1252 (m), 1223 (vs), 1173 (s), 1123 (s), 1084 (w), 1051 (w), 1014 (m), 985 (m), 876 (w), 850 (m), 802 (m), 750 (w), 661 (w), 644 (m), 590 (w), 563 (m), 803 (w), 472 (w), 447 (w), 403 (w); XPS spectrum (eV): O1s, 532.0 and 533.9; N1s, 399.8; Cu2p 3/2, 936.1; C1s, 285.0 and 286.6.

[H<sub>2</sub>(salen)], bis(salicylaldehyde)ethylenediamine: C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 200 MHz, 297 K),  $\delta$  (ppm): 13.6 (s, 2H, OH), 8.6 (s, 2H, N=CH), 7.4–7.3 (d, 4H, aromatic), 6.9–6.8 (m, 4H, aromatic), 3.9 (s, 4H, CH<sub>2</sub>); UV-vis,  $\lambda_{\text{max}}$  (nm): 253, 296, 348, 412; FTIR,  $\nu$  (cm<sup>-1</sup>): 1635 (vs), 1610 (m), 1577 (s), 1498 (s), 1460 (m), 1417 (m), 1371 (w), 1317 (vw), 1282 (s), 1248 (w), 1219 (w), 1200 (w), 1149 (m), 1113 (w), 1041 (m), 1020 (m), 980 (w), 972 (w), 937 (vw), 899 (w), 858 (s), 775 (m), 750 (s), 742 (s), 648 (w), 561 (w), 472 (w), 432 (w).

[Cu(salen)], [bis(salicylaldehyde)ethylenediamine] copper(II): C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>Cu. Anal. Calcd: C, 61.2; H, 5.1; N, 7.9. Found: C, 61.6; H, 5.2; N, 7.8. UV-vis,  $\lambda_{\text{max}}$  (nm): 278 (i), 337, 400 (i), 480 (i), 587; FTIR,  $\nu$  (cm<sup>-1</sup>): 3076 (w), 3049 (w), 3020 (w), 2953 (w), 2925 (w), 2913 (w), 2850 (vw), 1650 (vs), 1630 (vs), 1599 (m), 1539 (m), 1530 (s), 1468 (m), 1449 (vs), 1427 (m), 1388 (m), 1350 (m), 1335 (s), 1304 (m), 1238 (w), 1217 (vw), 1191 (s), 1142 (s), 1126 (s), 1087 (m), 1052 (m), 1027 (m), 979 (m), 955 (m), 933 (w), 906 (w), 856 (m), 850 (m), 789 (w), 751 (s), 743 (m), 734 (s), 648 (w), 637 (vw), 617 (m), 600 (vw), 578 (w), 571 (m), 499 (w), 467 (m), 461 (w); XPS spectrum (eV): O1s, 531.7; N1s, 399.9; Cu2p 3/2, 935.2; C1s, 285.2 and 286.7(i).

**Functionalization of Activated Carbon. Carbon Oxidation.** The purified NORIT ROX 0.8 activated carbon, denoted A1, was oxidized with a mixture of air and N<sub>2</sub> (with 5% O<sub>2</sub>) at 698 K for 10 h; burnoff = 6%.<sup>9</sup> The oxidized carbon will be designated by A2.

**Adsorption of [Cu(4-HOsalen)].** Two materials were prepared by varying the time of adsorption; in the first case, 1.2 g of oxidized activated carbon (A2) was added to 150.0 cm<sup>3</sup> of a 1.073 mmol dm<sup>-3</sup> solution of [Cu(4-HOsalen)] (160.9  $\mu$ mol) in *N,N*-dimethylformamide, and the mixture was heated and kept at 100 °C for 16 h; in the second case, 1.2 g of oxidized activated carbon (A2) was added to 400.0 cm<sup>3</sup> of a 0.7985 mmol dm<sup>-3</sup> solution of [Cu(4-HOsalen)] (319.4  $\mu$ mol) in *N,N*-dimethylformamide, and the mixture was heated and kept at 100 °C for 30 h. The dark blue color of the copper(II) solutions progressively disappeared and was periodically monitored by UV-vis. The resulting materials, A3 (16 h adsorption) and A4 (30 h adsorption), were purified by Soxhlet extraction with *N,N*-dimethylformamide for 16 h and

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with acetone for 8 h, during which any eventual desorption of the metal complex was also monitored by UV-vis. Finally, both materials were dried in an oven for 13 h at 120 °C under vacuum.

**Adsorption of [Cu(salen)].** A total of 1.5 g of air-oxidized activated carbon (A2) was added to 400.0 cm<sup>3</sup> of a 1.026 mmol dm<sup>-3</sup> solution of [Cu(salen)] (410.4 μmol) in dichloromethane. The mixture was refluxed for 30 h, and the progressive disappearance of the dark blue color of the copper(II) solution was monitored by UV-vis. The resulting material was purified by Soxhlet extraction with dichloromethane for 16 h, and desorption of the metal complex was monitored by UV-vis. Finally, it was dried in an oven for 13 h at 120 °C under vacuum. The resulting material is denoted as A5.

**Physical Measurements.** <sup>1</sup>H NMR spectra were recorded with a Bruker AC 200 at 25 °C, using SiMe<sub>4</sub> as an internal reference. FTIR spectra were obtained as potassium bromide pellets in the range of 400–4000 cm<sup>-1</sup> with a Biorad FTS 155, and diffuse reflectance electronic spectra were obtained on a Shimadzu UV-3101 PC in the range of 1600–200 nm, using barium sulfate as a reference.

EPR spectra were recorded with a X-band Bruker ESP 300E, both at room temperature and at 120 K. The spectra were calibrated with diphenylpicrylhydrazyl (dpph) with  $g = 2.0037$ , and the magnetic field was calibrated using Mn(II) in MgO. Typical experimental conditions were as follows: modulation frequency 100 kHz, modulation amplitude 0.5–1 mT, and microwave power 5–15 mW. The reported EPR parameters were obtained by simulation using the program Win EPR Simfonia (Bruker) assuming rhombic spin Hamiltonians. The values of  $g_x$  and  $g_y$  and  $A_x$  and  $A_y$  are less accurate because of their dependence on the line widths (20–40 G) used in the simulations.

Adsorption/desorption of the copper(II) metal complexes was monitored by UV-vis spectroscopy using aliquots of 1.00 cm<sup>3</sup> from the reaction mixture and diluting to 10.00 cm<sup>3</sup>. The charge-transfer bands at 348 nm ([Cu(4-HOsalen)]) and at 367 nm ([Cu(salen)]) were used to quantify the copper solution content; calibration curves:  $\epsilon_{348} = 15\,246\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$  ( $R^2 = 0.9989$ ) and  $\epsilon_{367} = 11\,538\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$  ( $R^2 = 0.9998$ ). Spectra were recorded using quartz cells in the range of 250–800 nm using a UNICAM UV300 spectrometer.

XPS and SEM were obtained at Centro de Materiais da Universidade do Porto (Portugal) in a VG Scientific ESCALAB 200A spectrometer, using nonmonochromatized Mg K $\alpha$  radiation (1253.6 eV), and in a JSM-6301F scanning microscope with EDS (NORAN Voyager), respectively. XPS spectra of metal complexes were obtained in pellets. To correct for possible deviations caused by electric charge of the samples, the C1s line at 285.0 eV was taken as an internal standard.<sup>20,21</sup>

Elemental analysis (C, H, and N) was performed with a Carlo Erba EA 1108 elemental analyzer. Kingston Analytical Services, U.K., performed the metal analysis.

Textural characterization of carbon-based materials was based on N<sub>2</sub> adsorption isotherms, which were determined at 77 K with a Coulter Ominisorp 100 CX apparatus. The samples were degassed at 350 °C (A1 and A2) or at 120 °C (other samples) until a final vacuum of 10<sup>-6</sup> Torr was reached. The micropore volume ( $V_{\text{micro}}$ ) and mesopore surface area ( $S_{\text{me}}$ ) were determined by the  $t$ -method, using the standard isotherm for carbon materials proposed by Rodríguez-Reinoso et al.<sup>22</sup> The total pore volume ( $V_{\text{p}}$ ) at  $p/p_0 = 0.95$  was estimated from N<sub>2</sub> uptake, using 0.8081 g cm<sup>-3</sup> for the density of N<sub>2</sub> in its normal liquid state. The porosity volume other than that because of micropores (mainly mesopores;  $V_{\text{me}}$ ) was calculated by subtracting the micropore volume ( $V_{\text{micro}}$ ) obtained by the  $t$ -method from the total pore volume ( $V_{\text{p}}$ ).<sup>23</sup>

The thermograms were recorded with a Mettler TA 4000 thermal analyzer, using a heating rate of 5 K min<sup>-1</sup> and a N<sub>2</sub> carrier gas flow rate of 200 cm<sup>3</sup> min<sup>-1</sup>. The TPD profiles were obtained with a custom-built setup consisting of a U-shaped

tubular microreactor placed inside an electrical furnace. The flow rate of the helium carrier gas (25 cm<sup>3</sup> min<sup>-1</sup>) and the heating rate of the furnace (5 K min<sup>-1</sup>) were controlled with appropriate units. The masses at  $m/z = 28$  and 44 were monitored with a Spectramass Dataquad quadrupole mass spectrometer.

## Results and Discussion

**Characterization of Free Metal Complexes.** EPR spectra of [Cu(4-HOsalen)] in frozen methanol and DMF solutions are similar to those of other copper(II) complexes with similar Schiff base ligands;<sup>24–26</sup> the spectrum shows rhombic symmetry and exhibits in all magnetic regions well-resolved hyperfine couplings with copper (<sup>63</sup>Cu/<sup>65</sup>-Cu,  $I = 3/2$ ) and superhyperfine splittings in the higher magnetic regions (see EPR section). The similarity between the spectrum and those observed for similar Schiff bases allows the same orientation scheme for the tensor axes:  $g_1 = g_z$ ,  $g_2 = g_x$ ,  $g_3 = g_y$ , where  $g_1$  and  $g_3$  refer to the lowest and highest magnetic field  $g$  values (obviously,  $|A_1| = |A_z|$ ,  $|A_2| = |A_x|$ , and  $|A_3| = |A_y|$ ).<sup>24–26</sup> Furthermore, as  $g_z > g_x$ ,  $g_y$ , the complex [Cu(4-HOsalen)] has a  $d_{xy}$  ground state.<sup>24–26</sup> Values of the copper hyperfine coupling in the  $z$  region are typical of almost square planar complexes (or with incipient axial coordination).<sup>24–26</sup> The UV-vis reflectance spectrum is also typical of square planar copper complexes, as it exhibits only a shoulder at  $\lambda_{\text{max}} = 547\text{ nm}$  in an intense charge-transfer band, which corresponds to the low-energy part of the three unresolved d–d transitions  $d_{xy} \leftarrow (d_{yz}, d_{xz}, d_{z^2})$ .<sup>27</sup>

A high-resolution XPS spectrum of [Cu(4-HOsalen)] in the O1s region shows two peaks at 532.0 and 533.9 eV that are assigned to the two different types of oxygen atoms present in the complex: those coordinated to the metal and those of the uncoordinated hydroxylic groups of the aldehyde moiety, respectively.<sup>17</sup> There is a single peak, at 399.8 eV in the N1s region, that is assigned to the nitrogen atom of the C=N bond.<sup>17,20,28</sup> In the C1s region two peaks are also observed, one at 285.0 eV, which corresponds to aromatic and aliphatic carbon atoms, and the other at 286.6 eV, which is associated with carbon atoms bound to oxygen and nitrogen.<sup>29–31</sup>

**Characterization of Modified Carbons.** The carbon NORIT ROX 0.8 (A1) and the air-oxidized activated carbon (A2) have been extensively characterized by us in a previous paper,<sup>17</sup> and consequently their characterization will be omitted, whereby the discussion will be focused on the new materials, A3–A5.

**Adsorption/Desorption of Copper(II) Complexes.** UV-vis spectra of the solution were taken during adsorption of metal complexes and are presented in Figures 1a and 2a. Both complexes are progressively adsorbed onto the oxidized activated carbon, since the intensity of the bands because of copper(II) in solution decreases with time. From the amount of copper(II) depleted from solution, it is possible to estimate the amount of complex adsorbed per gram of activated carbon (Figures 1b and 2b). Under the experimental conditions used, the following results were obtained for complex adsorption (μmol/g of carbon): 125

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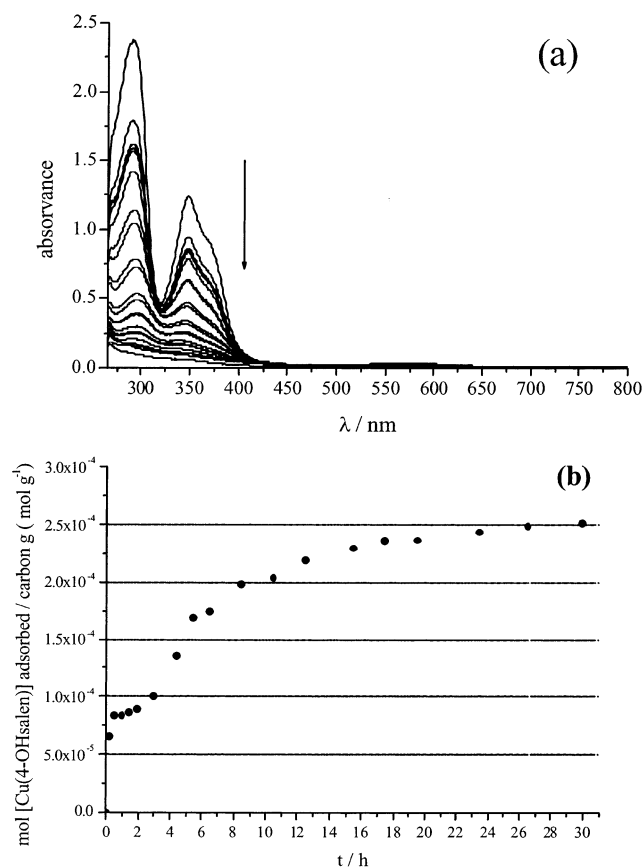
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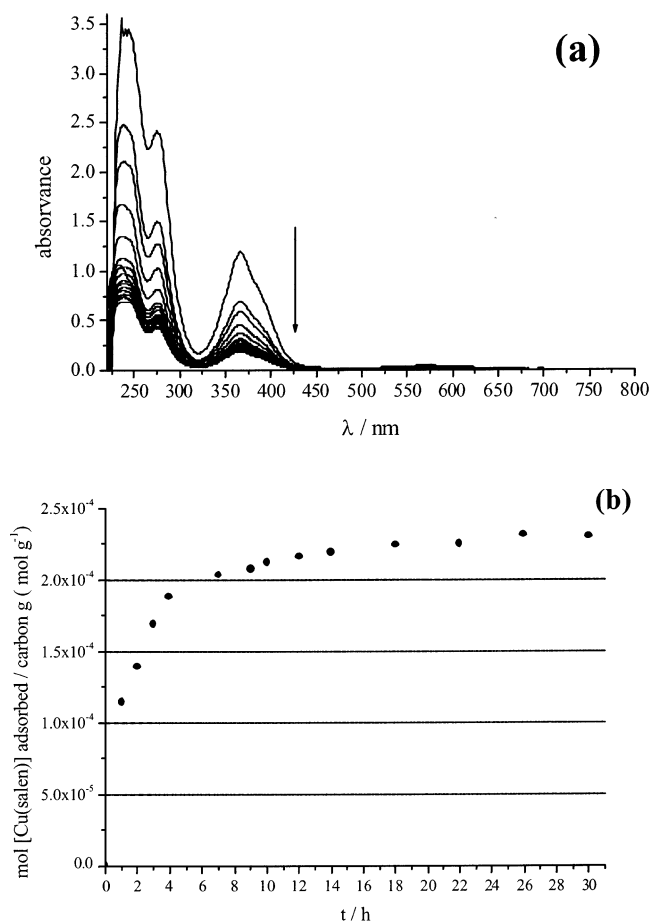


**Figure 1.** Adsorption of [Cu(4-HOsalen)]: (a) solution UV-vis spectra recorded during 30 h of complex adsorption onto the oxidized activated carbon and (b) plot of moles of complex adsorbed per gram of activated carbon vs time of adsorption.

for A3, 259 for A4, and 230 for A5 that correspond to a copper loading (mass of copper/mass of carbon  $\times$  100) of 0.80, 1.64, and 1.46%, respectively (Table 1). These results correspond to an efficiency of adsorption for the complexes (amount of adsorbed copper/initial amount of copper in solution  $\times$  100) of the following: 93.4 (A3), 97.1 (A4), and 84.0% (A5).

The modified activated carbons A3 and A4 were subjected to a 16 h Soxhlet extraction with DMF followed by one with acetone, whereas for A5 only dichloromethane was used. For A3 and A4, no bands characteristic of [Cu(4-HOsalen)] were present in the UV-vis spectra of the extracting solvents, and thus it is possible to conclude that no leaching took place during Soxhlet extraction. Moreover, no features due to copper(II) could be found in the EPR spectra of the extracting solvents. In contrast, 15.8% of the adsorbed [Cu(salen)] was leached after a 16 h Soxhlet extraction with dichloromethane. The resulting activated carbon (A5) has only 194  $\mu$ mol of [Cu(salen)] per gram of carbon, which corresponds to a copper loading of 1.23%.

Both complexes can interact with oxygen surface carbon groups through the copper center or through the aromatic ligand system. Nevertheless, our results suggest that these interactions are not effective in the immobilization of metal complexes and that the uncoordinated hydroxyl groups in the aldehyde moiety of the Schiff base must play a decisive role in the irreversible immobilization of [Cu(4-HOsalen)]. In this perspective, we propose that [Cu(salen)] must be physically adsorbed onto the oxidized activated carbon since leaching takes place during solvent extraction, whereas its hydroxyl analogue, [Cu(4-HOsalen)], must be covalently bound to carbon surface groups through



**Figure 2.** Adsorption of [Cu(salen)]: (a) solution spectra recorded during 30 h of complex adsorption onto the oxidized activated carbon and (b) plot of moles of complex adsorbed per gram of activated carbon vs time of adsorption.

**Table 1. Proximate and Elemental Analysis of Carbon-Based Materials**

| sample | proximate analysis (wt %) |                    |      | elemental analysis (wt %) |      |       |      |
|--------|---------------------------|--------------------|------|---------------------------|------|-------|------|
|        | volatiles                 | C <sub>fixed</sub> | ash  | Cu <sup>a</sup>           | N    | C     | H    |
| A1     | 8.81                      | 89.44              | 1.74 |                           | 0.45 | 86.99 | 0.55 |
| A2     | 17.91                     | 80.99              | 1.09 |                           | 0.47 | 81.78 | 0.56 |
| A3     | 16.48                     | 75.35              | 8.17 | 0.802                     | 1.86 | 84.25 | 0.95 |
| A4     | 22.37                     | 73.84              | 3.79 | 1.64                      | 1.87 | 82.07 | 1.30 |
| A5     | 18.48                     | 78.95              | 2.57 | 1.23                      | 0.89 | 84.59 | 0.54 |

<sup>a</sup> Determined by UV-vis spectrophotometry, as described in text. For A5, the value refers to final loading after Soxhlet extraction.

the ligand hydroxyl substituents. Extensive characterization of the modified carbons has been done in order to get insights into the irreversible immobilization of [Cu(4-HOsalen)] onto the air-oxidized activated carbon.

**Composition and Morphology.** The proximate and elemental analyses of A1–A5 are included in Table 1, and from them it is possible to detect a significant increase in nitrogen content with adsorption of metal complexes onto the oxidized activated carbon, which corresponds to the nitrogen atoms of the adsorbed complexes.

By semiquantitative EDS analysis of both A3 and A4, it is possible to observe the presence of copper(II) in the exterior of the pellets and in cross sections. The metal complexes are heterogeneously distributed throughout the pellet, reaching much smaller concentrations in the center than in the external surface. In A5, the observed concentration profile is reversed, with the smaller concentrations occurring in the external surface (a probable

**Table 2. Textural Properties of Carbon-Based Materials**

| sample | $V_{\text{micro}}^a$<br>( $\text{cm}^3 \text{g}^{-1}$ ) | $S_{\text{me}}^a$<br>( $\text{m}^2 \text{g}^{-1}$ ) | $V_t^b$<br>( $\text{cm}^3 \text{g}^{-1}$ ) | $V_{\text{meso}}^c$<br>( $\text{cm}^3 \text{g}^{-1}$ ) |
|--------|---|---|--|--|
| A1     | 0.359   | 122   | 0.527                                      | 0.168  |
| A2     | 0.418   | 127   | 0.634                                      | 0.216  |
| A3     | 0.285   | 100   | 0.423                                      | 0.138  |
| A4     | 0.236   | 94  | 0.373                                      | 0.137  |
| A5     | 0.370   | 94  | 0.509                                      | 0.139  |

<sup>a</sup> Calculated by the *t*-method. <sup>b</sup> Total pore volume at  $p/p_0 = 0.95$ .

<sup>c</sup> Obtained by subtracting the micropore volume from the total pore volume at  $p/p_0 = 0.95$ .

consequence of [Cu(salen)] leaching during Soxhlet purification), since the superficially adsorbed complexes are easier to remove.

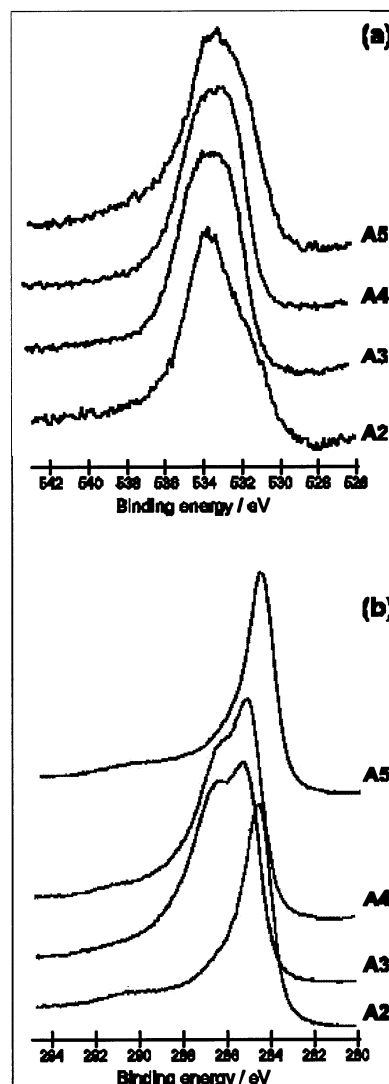
The textural properties of A1–A5 are collected in Table 2. Upon adsorption of metal complexes onto the activated carbons there is a significant decrease in micropore volume and in other types of porosity present. Relative to A2, sample A3 shows a decrease of 32% in the micropore volume and of 36% in the wider pores volume, whereas for A4 (the sample was prepared with a longer adsorption time) the corresponding decreases are 44 and 37%. These results seem to indicate that both metal complexes preferentially adsorb in the wider pores (mesopores and macropores), as for shorter adsorption time the percentage of decrease in the micropore volume is smaller than that of the larger pores, whereas for the longer adsorption time the percentage of decrease in the latter volume remains practically constant and that of the micropore increases significantly.

**X-ray Photoelectron Spectroscopy.** In Figure 3, panels a and b, are represented the high-resolution spectra of samples A2–A5 in the O1s and C1s regions, respectively. The areas under the O1s, N1s, C1s, and Cu2p 3/2 peaks in the high-resolution spectra are collected in Table 3. It becomes evident that the profiles for samples A3 and A4 are very similar in all regions. In the O1s region a large and symmetric peak can be observed that is different from that of A2; the low-energy region has increased in intensity, which may correspond to both types of complex oxygen atoms. Both materials show in the C1s region two peaks at  $\approx 285.0$  and  $\approx 286.6$  eV, the former being due to the graphitic structure.<sup>9,29,30</sup> As the free complex has also two peaks in this region (exactly at 285.0 and 286.6 eV), the high-energy peak in the spectra of A3 and A4 must be attributed to adsorbed complex molecules.

New intense spectra are observed in the Cu2p 3/2 region with a peak at 936.1 eV, which is practically identical to that of free complexes, suggesting that their immobilization is not accompanied by further coordination to the metal and that it retains the same four-coordinate structure. In the N1s region, the almost symmetric peak at 400.0 eV corresponds to the nitrogen atoms of the complexes.

The profiles of the O1s and C1s regions for A5 are markedly different from those of A3 and A4 but similar to those of A2; furthermore, the peaks due to nitrogen and copper are very weak. These results suggest that the salen complexes have been extensively leached from the most external surface during Soxhlet extraction.

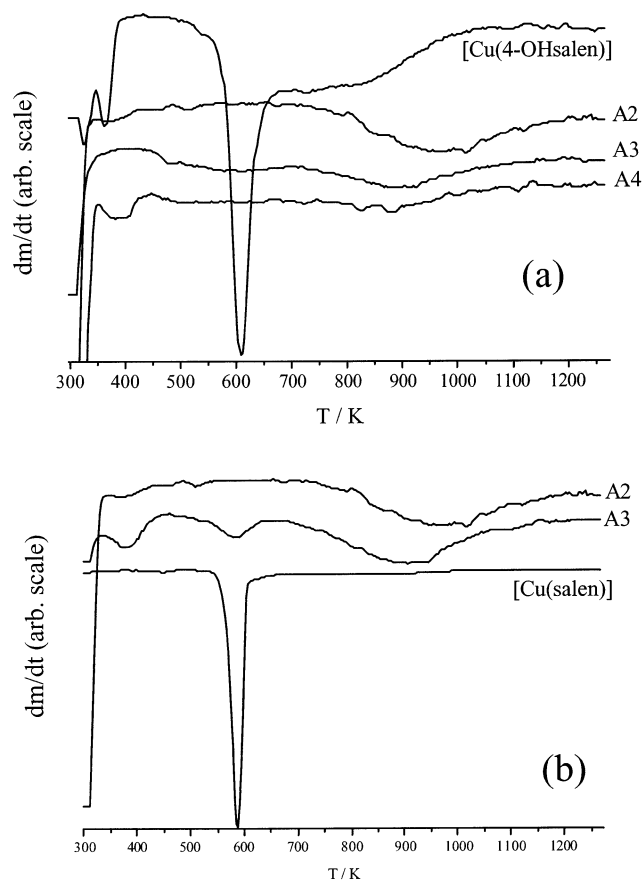
**Thermal Analysis.** The derivative thermograms of samples A3, A4, and [Cu(4-HOsalen)] are depicted in Figure 4a, and the derivative thermograms of A5 and [Cu(salen)] are presented in Figure 4b; in both figures the parent carbon A2 is also shown. Both complexes exhibit an intense peak at 587 K for salen and at 607 K for the hydroxyl derivative, with the latter exhibiting also a broad peak in the range of 700–1000 K.

**Figure 3.** XPS spectra for A2–A5 carbon-based materials: (a) O1s region and (b) C1s region.**Table 3. Area under the Peaks of the O1s, N1s, C1s, and Cu2p 3/2 Regions in the XPS Spectra**

| sample | atomic % |      |       |      |
|--------|----------|------|-------|------|
|        | O        | N    | C     | Cu   |
| A1     | 7.66     | 0.58 | 90.41 |      |
| A2     | 12.58    | 0.70 | 86.15 |      |
| A3     | 22.61    | 9.52 | 64.94 | 2.71 |
| A4     | 26.02    | 9.28 | 59.83 | 3.67 |
| A5     | 9.68     | 0.85 | 88.71 | 0.17 |

For A2 the broad peak in the range of 800–1250 K is assigned to the decomposition of carbon surface groups. Upon the anchoring of [Cu(4-HOsalen)], no peak due to decomposition of free complex can be observed in A3 and A4, contrasting to what is observed in A5, for which a small peak at 587 K (temperature of free complex decomposition) is observed. Regarding carbon surface groups, there is a shift of the peak to lower temperatures for all modified carbons, suggesting changes in the carbon surface groups upon immobilization of both metal complexes. However, for A3 and A4, the peak shift is also associated with a decrease in peak intensity or with peak broadening, implying a decrease in the quantity or a change in the type of surface groups, probably a consequence of the reaction with the complex. These results



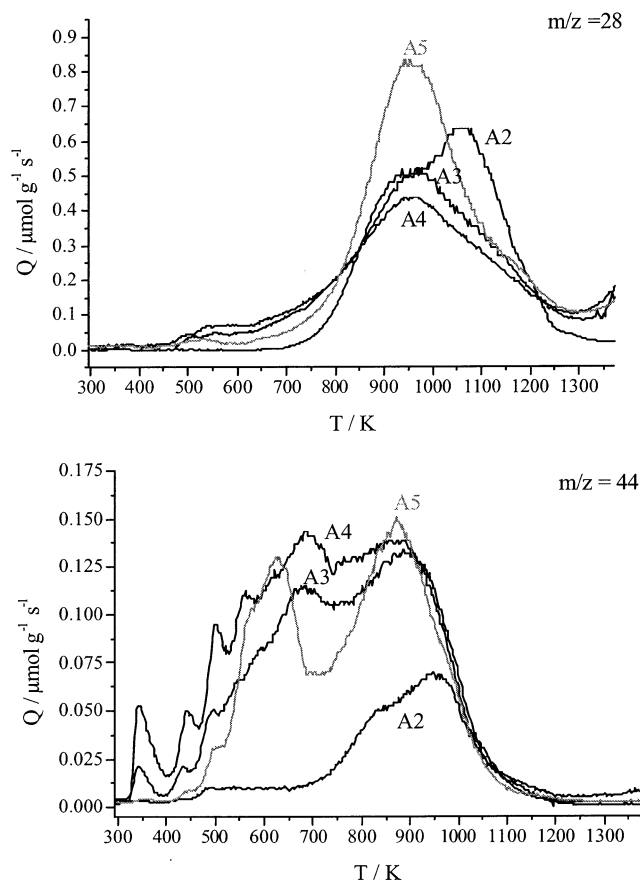


**Figure 4.** Derivative thermogravimetry curves of (a) [Cu(4-OHsalen)] complex and A2–A4 samples and (b) [Cu(salen)] complex and A2 and A5 samples.

indicate that [Cu(4-HOsalen)] and [Cu(salen)] interact in a different way with carbon surface groups.

The TPD  $m/z = 28$  and 44 profiles for the A2–A5 samples are included in Figure 5, and the areas under the peaks are collected in Table 4. A considerable difference in TPD  $m/z = 28$  and 44 profiles between carbons with adsorbed materials and A2 is observed, which is quantitatively shown by an increase in the total quantity evolved as  $m/z = 28$  and 44 (Table 4), a consequence of the presence of the complexes within the activated carbon. However, it must be recognized that for these samples the fragments with  $m/z = 28$  and 44 cannot be unambiguously assigned to CO and CO<sub>2</sub>, as the complexes can produce (upon decomposition) other products with these  $m/z$  values.

When compared to the parent oxidized carbon, the anchorage of [Cu(4-HOsalen)] (A3 and A4) produces a decrease in the total fragment quantity evolved at  $m/z = 28$  that corresponds to decreases in the peaks at (i) 1060 K, usually assigned to carbonyl and quinone carbon surface groups, (ii) 900 K, usually assigned to phenol groups, and (iii) eventually 820 K (because of carboxylic anhydrides) that is partially masked by the peak due to phenol groups.<sup>9</sup> The decrease in the quantity evolved at  $m/z = 28$  can be taken as an indication of bond formation between [Cu(4-HOsalen)] and the surface groups via the ligand hydroxyl substituents, for which the fragments will have different  $m/z$  values. Carbonyl and carboxylic anhydrides are the two groups that can potentially react with hydroxyl groups originating bonds between the carbon surface and the complex. For the carbonyl group a direct nucleophilic attack of the hydroxyl can originate an ether bond to the complex, as depicted in Scheme 2a. Carboxylic anhydrides may also be subject to a nucleophilic attack from the



**Figure 5.** TPD profiles at  $m/z = 28$  and 44 for the A2–A5 samples.

**Table 4.** Amounts of Fragments with  $m/z = 28$  and 44 Released during the TPD Experiments for the Carbon-Based Materials<sup>a</sup>

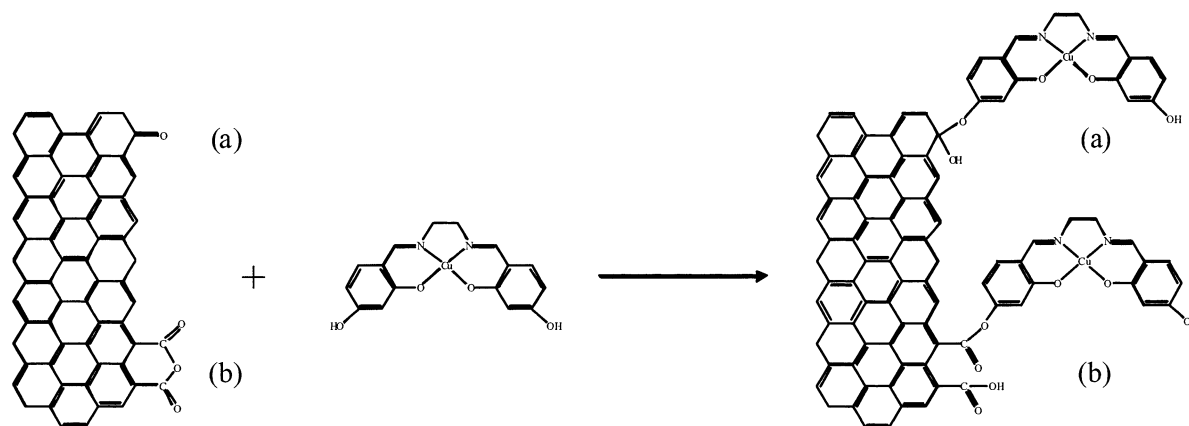
| sample | $m/z = 28$<br>( $\mu\text{mol g}^{-1}$ ) | $m/z = 44$<br>( $\mu\text{mol g}^{-1}$ ) | total<br>( $\mu\text{mol g}^{-1}$ ) |
|--------|--|--|-------------------------------------|
| A1     | 497                                      | 114                                      | 611                                 |
| A2     | 2323                                     | 225                                      | 2548                                |
| A3     | 2223                                     | 671                                      | 2894                                |
| A4     | 2065                                     | 807                                      | 2872                                |
| A5     | 2758                                     | 614                                      | 3372                                |

<sup>a</sup> Obtained from the areas under the peaks.

hydroxyl groups, originating new carboxylic groups and an ester group as depicted in Scheme 2b.

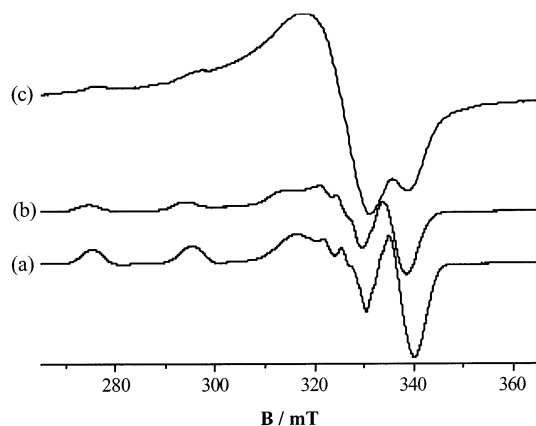
Additionally, for these samples there is an increase in the quantity of fragments evolved at  $m/z = 44$  that corresponds to the appearance of several low-temperature decomposition groups and of two intense peaks at 685 and 890 K. In this case, no unambiguous conclusions can be taken as these fragments can result from the new surface groups that result from the reaction between the complex and the carbon surface or from the decomposition of complexes. With the increase in adsorption time (going from A3 to A4), there is a further decrease in fragments at  $m/z = 28$  and an increase in fragments at  $m/z = 44$ , which is a result of the higher metal complex loading in A4.

When compared to A3 and A4, sample A5 shows different  $m/z = 28$  and 44 profiles, and when compared to A2, it shows a significant increase in the quantities evolved at both  $m/z$  values. In the  $m/z = 28$  profile of A5 (when compared to that of A2) there is a small decrease in the peak at 1060 K, but the peak at  $\approx 960$  K exhibits a large increase; whereas in the  $m/z = 44$  profile two large

**Scheme 2. Putative Reactions between Hydroxyl Groups of the Metal Complex and Carbon Surface Groups****Table 5. EPR Data for the Copper(II) Complexes**

| sample               | <i>T</i> (K) | <i>g<sub>z</sub></i> | <i>g<sub>y</sub></i> | <i>g<sub>x</sub></i> | <i>g<sub>av</sub></i> <sup>a</sup> | <i>A<sub>z</sub></i>   <sup>b</sup> | <i>A<sub>y</sub></i>   <sup>b</sup> | <i>A<sub>x</sub></i>   <sup>b</sup> |
|----------------------|--------------|----------------------|----------------------|----------------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| [Cu(4-OHsalen)]/MeHO | 120          | 2.215                | 2.062                | 2.055                | 2.111                              | 192.2                               | 16.8                                | 36.5                                |
| [Cu(4-OHsalen)]/DMF  | 130          | 2.203                | 2.050                | 2.059                | 2.104                              | 197.4                               | 16.7                                | 36.3                                |
| A4                   | rt           | 2.194                | 2.058                | 2.055                | 2.102                              | 196.3                               | 16.7                                | 36.3                                |

<sup>a</sup>  $g_{av} = 1/3(g_x + g_y + g_z)$ . <sup>b</sup> Values are expressed in  $10^{-4} \text{ cm}^{-1}$ .

**Figure 6.** EPR spectra of [Cu(4-HOsalen)] in (a) frozen DMF solution, (b) frozen methanol solution, and (c) immobilized onto the activated carbon.

peaks with maxima at 626 and 873 K are observed. The increase in the quantity evolved at both  $m/z$  values can include complex and carbon surface group fragments; in this context an alteration in the carbon surface groups cannot be excluded too, but it must be different from those that take place in A3 and A4.

The TPD data corroborate that both complexes adsorb differently on the activated carbon. For A3 and A4 the observed decrease in the total fragment quantity evolved at  $m/z = 28$  can be taken as an indication that some of these groups (as represented in Scheme 2) have reacted with [Cu(4-HOsalen)] and become inaccessible to decomposition as fragments with  $m/z = 28$ , contrasting to what happens in the parent material. For A5, although the data point toward physical adsorption of [Cu(salen)], they also suggest a non-negligible change in the surface groups of the activated carbon.

**Electron Paramagnetic Resonance.** Powder EPR spectra of A4 and EPR spectra of free metal complex [Cu(4-HOsalen)] in frozen methanol and *N,N*-dimethylformamide solutions are collected in Figure 6, and the EPR parameters obtained after simulation of experimental data are summarized in Table 5. It must be pointed out that

the spectra of A3 are practically identical to those of A4, albeit with less intensity.

The supported [Cu(4-HOsalen)] complexes show an EPR spectrum typical of magnetically diluted copper(II) species, indicating that the complex is distributed within the carbon matrix. The spectrum is very similar to that of a free complex in solutions of methanol and DMF, and thus the same orientation scheme for the tensor axes and the same  $d_{xy}$  ground state can be proposed for the anchored complex (see above).<sup>24–26</sup> In the  $g_z$  region two of the four peaks due to coupling between the unpaired electron spin and the copper nuclear spin are observed, and in the  $g_{xy}$  regions two peaks are observed, albeit with lower resolution than those in the free complex solution spectra, as expected for solid-state EPR spectra. The similarity between the  $g$  and  $A$  values for the anchored complex and those of free complexes in solution (Table 5) suggests that in the anchored complex the metal center has a four-coordinate environment and thus implies that chemical ligation to surface groups through the metal center can be excluded. In fact, EPR spectra of copper square planar complexes are very sensitive to effective axial coordination, and an increase in  $g_z$  and a decrease in  $A_z$  relative to four-coordinate species are expected upon axial coordination, and these changes constitute a reliable test for axial coordination.<sup>24–26,32</sup> In this context, the similarity between the  $g$  and the  $A$  values of free and immobilized complexes can be taken as an indication that irreversible immobilization of [Cu(4-HOsalen)] has been obtained through the binding of carbon surface groups to the ligand substituents and not to the metal center.

### Concluding Remarks

Adsorption and desorption studies by UV-vis of [Cu(4-HOsalen)] and [Cu(salen)] onto an air-oxidized activated carbon show that [Cu(4-HOsalen)] is irreversibly immobilized in the activated carbon, whereas [Cu(salen)] is leached during the purification process. Nitrogen isotherms at 77 K show that both metal complexes tend to adsorb preferentially in the wider pores (mesopores and macropores).



Although both complexes can interact with oxygen surface carbon groups through the copper center or through the aromatic ligand system, the comparative study between [Cu(4-HOsalen)] and [Cu(salen)] conclusively shows that such interactions are not strong enough to anchor the complexes and that the hydroxyl groups in the aldehyde moiety of the ligand are responsible for the irreversible immobilization of [Cu(4-HOsalen)] onto the activated carbon through covalent bonding to carbon surface groups (see Scheme 2).

This type of anchoring of Schiff base transition metal complexes onto oxidized activated carbons provides a route for the preparation of new heterogeneous materials with

catalytic properties, in which metal loading can be easily controlled. Moreover, since these types of complexes seem to anchor first onto the mesopores and macropores, diffusion limitations of the reactants to the active sites can be minimized.

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