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# Binding and removal of octahedral, tetrahedral, square planar and linear anions in water by means of activated carbon functionalized with a pyrimidine-based anion receptor†

 Matteo Savastano,<sup>a</sup> Paloma Arranz-Mascarós,<sup>b</sup> Carla Bazzicalupi,<sup>a</sup> Antonio Bianchi,<sup>\*a</sup> Claudia Giorgi,<sup>a</sup> M. Luz Godino-Salido,<sup>b</sup> Maria Dolores Gutiérrez-Valero<sup>b</sup> and Rafael López-Garzón<sup>\*b</sup>

Binding of  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{Pt}(\text{CN})_4^{2-}$ ,  $\text{Co}(\text{CN})_6^{3-}$ ,  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  and  $\text{Fe}(\text{CN})_6^{4-}$  anions by the protonated (positively charged) forms of tren (tris(2-aminoethyl)amine) and of the tren-derivative (HL) containing a pyrimidine residue was studied by means of potentiometric measurements in 0.1 M  $\text{NMe}_4\text{Cl}$  solutions at  $298.1 \pm 0.1$  K. Both ligands form stable complexes with these anions which appear to be mostly stabilized by electrostatic forces. In the case of HL, an anion- $\pi$  interaction with the pyrimidine residue of the ligand also affords a significant contribution to complex stability. Some shape preference for tetrahedral and octahedral anions over square planar ones is observed. A hybrid AC/HL material obtained by adsorption of HL on commercial activated carbon (AC) was used to study the extraction of these anions from water. AC/HL shows enhanced adsorption capacity toward all the anions studied with respect to AC. This behavior is ascribed to the stronger interaction of anions with the HL function of AC/HL than with the  $\text{C}\pi\text{-H}_3\text{O}^+$  sites of unfunctionalized AC. Of special interest is the enhancement of the adsorption capacities found for  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  and  $\text{Pt}(\text{CN})_4^{2-}$ , two anions of great relevance for the extraction of platinum and gold from ores and from metallic wastes.

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## Introduction

Anion coordination chemistry, the binding of negatively charged species *via* non covalent interactions with Lewis acid receptors, is a dynamic research area attracting growing interest as a fertile source of applications.<sup>1–10</sup> We have recently shown, for instance, that functionalization of an activated carbon (AC) with the polyamine molecule HL gives rise to a hybrid material (AC/HL) with marked affinity for various anions, thus providing a promising tool for anion sequestration and the remediation of contaminated media.<sup>11</sup>

The method used for the functionalization of a commercially available AC was based on the irreversible  $\pi$ -stacking interaction between the pyrimidine anchor of HL and the arene centres of the graphite domains of AC (Fig. 1).<sup>11</sup> The characteristics of the AC/HL material mostly relies on the properties of the functionalities implanted on the carbon surface that are transferred to the

hybrid material.<sup>13</sup> HL contains a tren unit (L1) (Chart 1), whose protonated forms are efficient anion receptors,<sup>14</sup> and coherently also protonated forms of HL give rise to stable complexes with various anions, both inorganic and organic.<sup>11,15–17</sup> With the latter ligand, the participation of anion- $\pi$  interactions, involving the pyrimidine residue, can furnish further contributions to complex stability in addition to charge-charge attraction and hydrogen bonding. Indeed, crystal structures of HL complexes with anions

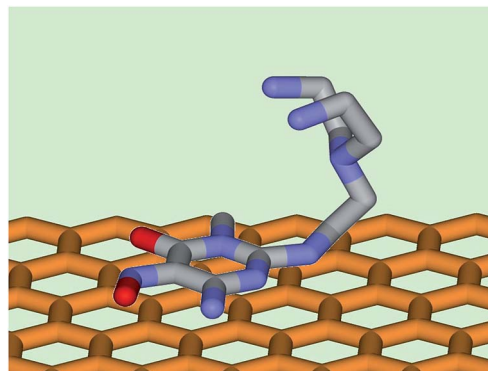


Fig. 1 Schematic representation of the interaction between the surface of activated carbon and the pyrimidine residue of HL.

<sup>a</sup>Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino, Italy. E-mail: antonio.bianchi@unifi.it

<sup>b</sup>Department of Inorganic and Organic Chemistry, University of Jaén 23071, Jaén, Spain. E-mail: rlopez@ujaen.es

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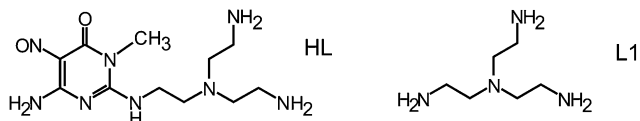


Chart 1 Tren (L1) and tren derivative (HL) studied in this work. The notation HL is used for the pyrimidine derivative since it can undergo deprotonation of the NH group linked to the pyrimidine ring.<sup>12</sup>

such as  $\text{HgCl}_4^{2-}$ ,  $\text{HgBr}_4^{2-}$ ,  $\text{CdI}_4^{2-}$  and  $\text{Co}(\text{CN})_6^{3-}$  showed very short (among the shortest ever reported) anion- $\pi$  interactions.<sup>11,17,18</sup> Accordingly, the AC/HL material is an efficient sorbent for anions such as  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{CrO}_4^{2-}$  and  $\text{HgCl}_4^{2-}$  in water over rather wide pH ranges.<sup>11</sup> More recently, we showed that HL forms stable to very stable complexes with other tetrahedral anions ( $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ) and with anions of different geometries such as  $\text{P}_2\text{O}_7^{4-}$ ,  $\text{P}_3\text{O}_{10}^{5-}$  and  $\text{Co}(\text{CN})_6^{3-}$ .<sup>16,17</sup>

In the present paper, we extend the study to metal complex anions such as  $\text{Pt}(\text{CN})_4^{2-}$ ,  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  and we relate the stability of  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{Pt}(\text{CN})_4^{2-}$ ,  $\text{Co}(\text{CN})_6^{3-}$ ,  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  complexes of HL with the stability of the analogous species formed by the parent ligand tren. Furthermore, we analyse the sorption ability of the hybrid AC/HL material towards  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{Pt}(\text{CN})_4^{2-}$ ,  $\text{Co}(\text{CN})_6^{3-}$ ,  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  to enlarge the base of data correlating the sorption properties of AC/HL with the binding ability of HL and of its constituents. Of particular interest was the study involving  $\text{Pt}(\text{CN})_4^{2-}$  and  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ , since a successful adsorption of these anions on the hybrid AC/HL material could have important technological applications. Cyanide leaching of platinum-group metals (PGM) and gold followed by activated carbon adsorption of the resulting cyanide complexes is a technique currently in use, in particular for gold, and receives continuous attention for improvements and extensions for the recovery of these precious metals from ores or from metallic wastes such as automobile exhaust catalysts.<sup>19–22</sup> Improvements of the activated carbon adsorption method is, of course, desirable, as well as replacement of the very toxic cyanide with safer ligands is desirable. Thiosulfate could be an alternative, at least in the case of gold.<sup>23</sup> The very stable  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  complex, for instance, is the main component obtained when thiosulfate is used as an alternative to cyanide for extraction of gold. Thiosulfate is essentially non-toxic and it is able to extract gold from ore types that are refractory to gold cyanidation, like carbonaceous or Carlin type ores. This alternative process, however, presents some drawbacks, the principal one being the lack of a suitable recovery technique, since  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  is not efficiently adsorbed by activated carbon, which is the standard technique used in gold cyanidation to separate the gold complex from the ore slurry. As we will show later on in this paper, functionalization with HL enhances the ability of activated carbon to adsorb both  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  and  $\text{Pt}(\text{CN})_4^{2-}$ .

## Experimental

### Materials

The HL ligand<sup>18</sup> and the hybrid AC/HL material<sup>11,24</sup> were prepared and characterized as previously described. The

commercial AC adsorbent supplied by Merck was also previously characterized.<sup>23</sup> The anions used for the potentiometric and the adsorption measurements were obtained as high purity  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{Na}_2\text{SeO}_4$ ,  $\text{Na}_3[\text{Au}(\text{S}_2\text{O}_3)_2]$ ,  $\text{K}_2[\text{Pt}(\text{CN})_4]$ ,  $\text{K}_3[\text{Co}(\text{CN})_6]$  and  $\text{K}_4[\text{Fe}(\text{CN})_6]$  salts from commercial sources and were used without further purification.

### Potentiometric measurements

pH-metric measurements ( $\text{pH} = -\log[\text{H}^+]$ ) employed for the determination of equilibrium constants were carried out in 0.1 M  $\text{NMe}_4\text{Cl}$  solutions at  $298.1 \pm 0.1$  K, by using the equipment and the methodology that has been already described.<sup>25</sup> The combined Hamilton glass electrode (LIQ-GLASS 238000/08) was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with  $\text{CO}_2$ -free  $\text{NMe}_4\text{OH}$  solutions and determining the equivalent point by Gran's method<sup>26</sup> which allows one to determine the standard potential  $E^0$  and the ionic product of water ( $\text{p}K_w = 13.83(1)$  at  $298.1 \pm 0.1$  K in 0.1 M  $\text{NMe}_4\text{Cl}$ ). At least three measurements were performed for each system in the pH ranges 2.5–10.5. The computer program Hyperquad<sup>27</sup> was used to calculate the equilibrium constants from e.m.f. data. The concentration of the ligand was  $1 \times 10^{-3}$  M, while the concentration of anions [A] was in the range  $[\text{L}] \leq [\text{A}] \leq 5[\text{L}]$ . Ligand protonation constants used in calculations were previously determined,<sup>11,14</sup> while anion protonation constants were taken from the literature.<sup>28</sup> Three measurements were performed for each anion and the titration curves were treated both separately or as a unique set without significant variations in the calculated stability constants. The final stability constants were obtained by processing the whole set of curves.

### Adsorption measurements

Equilibration times for anion adsorption measurements were preliminarily determined by means of independent experiments. For this purpose, different flasks containing 25 mL of  $10^{-3}$  M anion solution and 25 mg of adsorbent were prepared, kept under stirring, and the anion concentration was measured at different times by means of ICP mass measurements in all cases except for  $\text{Pt}(\text{CN})_4^{2-}$  whose concentration was measured by UV absorbance at 255 nm.

The anion adsorption isotherms were obtained at  $298.1 \pm 0.1$  K. Typically, 25 mg of adsorbent (AC or AC/HL) was added to a 100 mL plastic flask containing 25 mL of aqueous solution of the examined anion. Anion concentration was varied between  $5 \times 10^{-4}$  and  $1.1 \times 10^{-3}$  M, and the initial pH was adjusted to 6.0 by adding KOH or HCl solutions to the adsorbate solutions. The flasks were kept under stirring into a Selecta Unitronic-Orbital thermostated air-bath and the anion concentration in the equilibrium solutions was determined as indicated above. UV measurements were previously performed to ascertain that no desorption of HL occurred in the presence of the studied anions under the experimental conditions employed, and blank experiments were performed to verify that neither the ligand nor the anions were adsorbed by the plastic flasks.

To obtain the theoretical maximum adsorption capacities of the corresponding sorbents toward the anions ( $X_m$ ), the isotherm data  $X$  (mmols of anion adsorbed per gram of adsorbent) and  $C_{eq}$  (anion equilibrium concentrations) were fit to the linear form of the Langmuir equation<sup>29</sup>  $1/X = 1/B \times X_m \times C_{eq} + 1/X_m$ , where  $B$  is the Langmuir constant. This was done for all the adsorbent/adsorbate systems ( $R$  varying between 0.9661 and 0.9915) except for  $S_2O_3^{2-}$  due to high dispersion of the experimental data obtained in this case.

XPS spectra of  $AC/Pt(CN)_4^{2-}$  and  $AC/Au(S_2O_3)_2^{3-}$  samples, obtained from the adsorption experiments of  $Pt(CN)_4^{2-}$  and  $Au(S_2O_3)_2^{3-}$  on AC, were registered with a ESCA5701 instrument (Physical Electronics), by using the MgK $\alpha$  300 W 15 kV radiation of twin anode in the constant analyzer energy mode, with pass energy of 187.85 eV (for the survey spectrum) and 29.35 eV (for narrow atomic ranges). Pressure of the analysis chamber was maintained at  $4 \times 10^{-9}$  Torr. The binding energy and the Auger kinetic energy scale were regulated by setting the C1s transition at 284.6 eV. The accuracy of BE values was  $\pm 0.2$  eV.

## Results and discussion

### Anion complexation by HL and L1

The equilibrium constants for the interaction of  $S_2O_3^{2-}$ ,  $SeO_4^{2-}$ ,  $Pt(CN)_4^{2-}$ ,  $Co(CN)_6^{3-}$ ,  $Fe(CN)_6^{4-}$  and  $Au(S_2O_3)_2^{3-}$  with protonated forms of the pyrimidine derivative HL and the parent ligand tren (L1) were determined by means of computer analysis, performed by means of the Hyperquad<sup>27</sup> program, of potentiometric (pH-metric) titration data acquired in 0.1 M  $Me_4NCl$  aqueous solutions at 298.1 K. Their values are listed in Tables 1 and 2, respectively.

As can be seen from these tables, the stability constants of these complexes invariably increases as increasing positive charge accumulates on the ligands upon protonation. Only in the case of  $Pt(CN)_4^{2-}$ , the effect of ligand charge on complex stability is small or unappreciable within the experimental errors.

The two ligands display rather similar anion binding trends. For a given ligand charge, for instance, the tetrahedral anions  $S_2O_3^{2-}$  and  $SeO_4^{2-}$  show very similar binding constants, and similar behaviors were previously found for  $SO_4^{2-}$ ,  $HPO_4^{2-}$  and  $HAsO_4^{2-}$ .<sup>11,14</sup> Also the stability of complexes with the elongated  $Au(S_2O_3)_2^{3-}$  anion, having tetrahedral terminations, are comparable with the stability of complexes with the above tetrahedral anions, despite its greater charge. The more charged octahedral  $Co(CN)_6^{3-}$  and  $Fe(CN)_6^{4-}$  anions form complexes of greater stability, relative to the less charged anions,  $Fe(CN)_6^{4-}$  being the anion forming the most stable complexes. On the other hand, complexes of the square planar  $Pt(CN)_4^{2-}$  with HL are less stable than the analogous species formed by the other dicharged anions, and reduced stability is also observed for the complex with  $H_3L^{3+}$ .

Accordingly, anion binding by protonated forms of HL and L1 appears to be mostly regulated by electrostatic forces, and the ligands display some shape preference for tetrahedral and octahedral anions over square planar ones. Indeed, the crystal structures of the complexes formed by  $HgCl_4^{2-}$ ,  $HgBr_4^{2-}$  and

**Table 1** Equilibrium constants for the formation of anion complexes with HL determined by means of potentiometric measurements in 0.1 M  $Me_4NCl$  aqueous solution at 298.1 K

Equilibria	log $K$
$HL + S_2O_3^{2-} = [HL(S_2O_3)]^{2-}$	1.9(1) <sup>a,b,c</sup>
$H_2L^+ + S_2O_3^{2-} = [H_2L(S_2O_3)]^-$	2.83(7) <sup>b</sup>
$H_3L^{2+} + S_2O_3^{2-} = [H_3L(S_2O_3)]^0$	3.34(8) <sup>b</sup>
$H_4L^{3+} + S_2O_3^{2-} = [H_4L(S_2O_3)]^+$	3.95(9) <sup>b</sup>
$HL + SeO_4^{2-} = [HL(SeO_4)]^{2-}$	2.1(1) <sup>b,c</sup>
$H_2L^+ + SeO_4^{2-} = [H_2L(SeO_4)]^-$	2.68(6) <sup>b</sup>
$H_3L^{2+} + SeO_4^{2-} = [H_3L(SeO_4)]^0$	3.34(6) <sup>b</sup>
$H_4L^{3+} + SeO_4^{2-} = [H_4L(SeO_4)]^+$	3.96(8) <sup>b</sup>
$H_2L^+ + Pt(CN)_4^{2-} = [H_2L(Pt(CN)_4)]^-$	2.24(6) <sup>b</sup>
$H_3L^{2+} + Pt(CN)_4^{2-} = [H_3L(Pt(CN)_4)]^0$	2.62(6) <sup>b</sup>
$H_4L^{3+} + Pt(CN)_4^{2-} = [H_4L(Pt(CN)_4)]^+$	2.74(5) <sup>b</sup>
$HL + Co(CN)_6^{3-} = [HL(Co(CN)_6)]^{3-}$	2.0(1) <sup>b,c</sup>
$H_2L^+ + Co(CN)_6^{3-} = [H_2L(Co(CN)_6)]^{2-}$	2.72(6) <sup>b</sup>
$H_3L^{2+} + Co(CN)_6^{3-} = [H_3L(Co(CN)_6)]^-$	3.44(5) <sup>b</sup>
$H_4L^{3+} + Co(CN)_6^{3-} = [H_4L(Co(CN)_6)]^0$	4.24(6) <sup>b</sup>
$H_2L^+ + Fe(CN)_6^{4-} = [H_2L(Fe(CN)_6)]^{3-}$	2.91(8)
$H_3L^{2+} + Fe(CN)_6^{4-} = [H_3L(Fe(CN)_6)]^{2-}$	3.65(6)
$H_4L^{3+} + Fe(CN)_6^{4-} = [H_4L(Fe(CN)_6)]^-$	5.08(9)
$H_4L^{3+} + HFe(CN)_6^{3-} = [H_4L(HFe(CN)_6)]^0$	4.21(8)
$H_2L^+ + Au(S_2O_3)_2^{3-} = [H_2L(Au(S_2O_3)_2)]^{2-}$	2.33(7)
$H_3L^{2+} + Au(S_2O_3)_2^{3-} = [H_3L(Au(S_2O_3)_2)]^-$	3.31(5)
$H_4L^{3+} + Au(S_2O_3)_2^{3-} = [H_4L(Au(S_2O_3)_2)]^0$	3.86(6)

<sup>a</sup> Values in parentheses are standard deviations on the last significant figures. <sup>b</sup> Taken from ref. 17. <sup>c</sup> Determined by isothermal titration calorimetry.

**Table 2** Equilibrium constants for the formation of anion complexes with tren (L1) determined by means of potentiometric measurements in 0.1 M  $Me_4NCl$  aqueous solution at 298.1 K

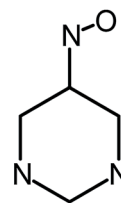
Equilibria	log $K$
$H_2L1^{2+} + S_2O_3^{2-} = [H_2L1(S_2O_3)]^0$	1.61(8) <sup>a</sup>
$H_3L1^{3+} + S_2O_3^{2-} = [H_3L1(S_2O_3)]^+$	2.08(7)
$H_4L1^{4+} + S_2O_3^{2-} = [H_4L1(S_2O_3)]^{2+}$	2.97(7)
$H_2L1^{2+} + SeO_4^{2-} = [H_2L1(SeO_4)]^0$	1.58(6)
$H_3L1^{3+} + SeO_4^{2-} = [H_3L1(SeO_4)]^+$	1.93(6)
$H_4L1^{4+} + SeO_4^{2-} = [H_4L1(SeO_4)]^{2+}$	3.28(4)
$HL1^+ + Pt(CN)_4^{2-} = [HL1(Pt(CN)_4)]^-$	2.03(8)
$H_2L1^{2+} + Pt(CN)_4^{2-} = [H_2L1(Pt(CN)_4)]^0$	2.26(7)
$H_3L1^{3+} + Pt(CN)_4^{2-} = [H_3L1(Pt(CN)_4)]^+$	2.18(7)
$HL1^+ + Co(CN)_6^{3-} = [HL1(Co(CN)_6)]^{2-}$	3.11(9)
$H_2L1^{2+} + Co(CN)_6^{3-} = [H_2L1(Co(CN)_6)]^-$	3.30(7)
$H_3L1^{3+} + Co(CN)_6^{3-} = [H_3L1(Co(CN)_6)]^0$	3.82(6)
$H_4L1^{4+} + Co(CN)_6^{3-} = [H_4L1(Co(CN)_6)]^+$	4.88(7)
$HL1^+ + Fe(CN)_6^{4-} = [HL1(Fe(CN)_6)]^{3-}$	3.24(6)
$H_2L1^{2+} + Fe(CN)_6^{4-} = [H_2L1(Fe(CN)_6)]^{2-}$	3.42(7)
$H_3L1^{3+} + Fe(CN)_6^{4-} = [H_3L1(Fe(CN)_6)]^-$	3.99(8)
$H_4L1^{4+} + Fe(CN)_6^{4-} = [H_4L1(Fe(CN)_6)]^0$	5.47(6)
$H_2L1^{2+} + Au(S_2O_3)_2^{3-} = [H_2L1(Au(S_2O_3)_2)]^-$	2.23(5)
$H_3L1^{3+} + Au(S_2O_3)_2^{3-} = [H_3L1(Au(S_2O_3)_2)]^0$	2.47(8)
$H_4L1^{4+} + Au(S_2O_3)_2^{3-} = [H_4L1(Au(S_2O_3)_2)]^+$	2.66(6)

<sup>a</sup> Values in parentheses are standard deviations on the last significant figures.

$CdI_4^{2-}$  with  $H_3L^{2+}$  and by  $Co(CN)_6^{3-}$  with  $H_4L^{3+}$  showed a good complementarity between the interacting partners, the anions being anchored to the ligand *via* salt-bridges with ligand

ammonium groups and very strong anion- $\pi$  interactions with the pyrimidine residue of HL acting as anion binding functionality (Fig. 2).<sup>11,17,18</sup> In particular, the  $\text{H}_4\text{L}[\text{Co}(\text{CN})_6]$  complex showed one of the strongest anion- $\pi$  interactions so far reported.<sup>17</sup>

While in  $\text{H}_3\text{L}^{2+}$  protonation involves the two primary amine groups of the tren moiety, in  $\text{H}_4\text{L}^{3+}$  also the pyrimidine nitroso group is protonated. Since protonation of the nitroso group modifies its  $\pi$ -electron cloud, we expect that it also produces a significant alteration of the  $\pi$ -density on the pyrimidine ring, thus affecting the anion- $\pi$  interactions occurring in these complexes. To get insight on this point, we performed a detailed analysis of the crystal structures deposited in the Cambridge Structural Database (CSD) for nitroso-pyrimidines containing nitroso groups in both neutral and protonated forms, by using the structure reported in Fig. 3a as a query for the database investigation and excluding metal coordinated NO groups. No limits to data quality were imposed. Visualization of these crystal structures evidences that protonation of the nitroso group determines, in addition to the expected lengthening of the N-O bonds and shortening of the adjacent N-C bonds, a significant elongation of the C-C distances of the pyrimidine ring. This is clearly shown in Fig. 3 by the correlations of N-C (Fig. 3b) and C-C (Fig. 3c) with N-O bond distances obtained from CSD. In this figure, data relative to the  $\{\text{H}_4\text{L}[\text{Co}(\text{CN})_6]\} \cdot 2\text{H}_2\text{O}$  complex<sup>17</sup> are displayed in red, while the yellow markers represent the mean value evaluated for the structures of complexes formed by  $\text{H}_3\text{L}^{2+}$  with  $\text{HgCl}_4^{2-}$ ,  $\text{HgBr}_4^{2-}$  and  $\text{CdI}_4^{2-}$ .<sup>11,18</sup> Accordingly, protonation of the nitroso group has an electron withdrawing effect on the pyrimidine  $\pi$ -electron density: the N-O bond acquires single bond character, the bond between the nitroso nitrogen and the linked carbon atom is shortened to a double bond distance, while the loss of  $\pi$ -



a

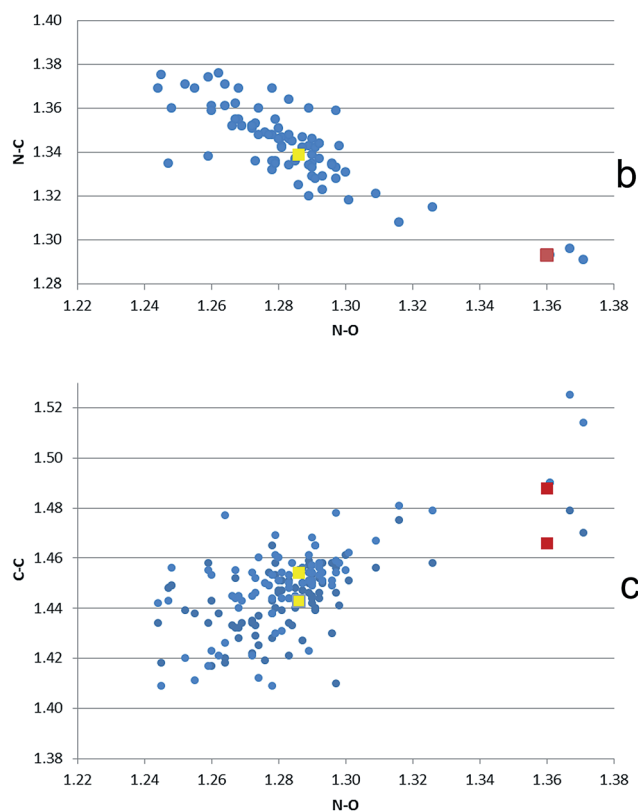


Fig. 3 (a) Basic structure used as a query for the database investigation; single, double, delocalized and aromatic bonds were considered. (b) N-C vs. N-O and (c) C-C vs. N-O bond lengths (blue markers: CSD data, red markers:  $\{\text{H}_4\text{L}[\text{Co}(\text{CN})_6]\} \cdot 2\text{H}_2\text{O}$  complex, yellow markers: mean values for the complexes formed by  $\text{H}_3\text{L}^{2+}$  with  $\text{HgCl}_4^{2-}$ ,  $\text{HgBr}_4^{2-}$  and  $\text{CdI}_4^{2-}$ ).

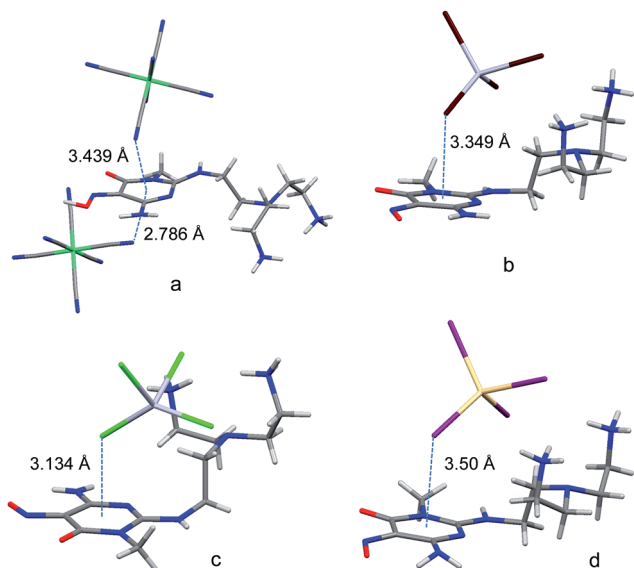


Fig. 2 Crystal structures of the complexes formed by  $\text{H}_4\text{L}^{3+}$  with  $\text{Co}(\text{CN})_6^{3-}$  (a)<sup>17</sup> and by  $\text{H}_3\text{L}^{2+}$  with  $\text{HgBr}_4^{2-}$  (b)  $\text{HgCl}_4^{2-}$  (c)<sup>11</sup> and  $\text{CdI}_4^{2-}$  (d)<sup>18</sup> (CSD refcodes IDIKAJ (a), AVISEE (b), AVISII (c), WASXAQ (d)).

electron density of the pyrimidine ring is particularly evident for the C-C bonds close to the nitroso group.

To verify whether the change in  $\pi$ -electron density brought about by protonation of the nitroso group affects the anion- $\pi$  interaction with our ligand in the solid state, we overlaid the nitroso-pyrimidine group in the crystal structures of the anion complexes with  $\text{H}_3\text{L}^{2+}$  and  $\text{H}_4\text{L}^{3+}$  and placed the anion atoms forming anion- $\pi$  interactions in their relative positions to obtain the picture shown in Fig. 4. It is clearly visible that the interacting  $\text{CN}^-$  group in the  $\{\text{H}_4\text{L}[\text{Co}(\text{CN})_6]\} \cdot 2\text{H}_2\text{O}$  complex is more displaced from the center of the pyrimidine ring than any other anion, and that it points towards the C-C bonds where a lower  $\pi$ -electron density is localized.

Evidences that also in aqueous solution anion- $\pi$  interactions contribute to stabilize these anion complexes were

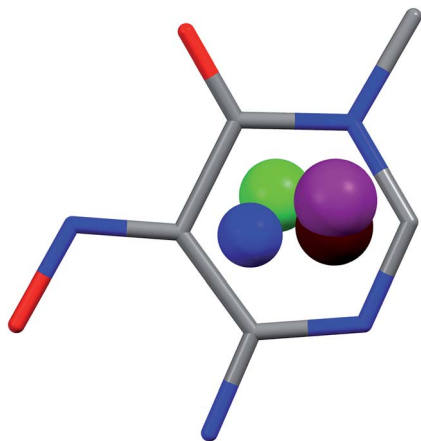


Fig. 4 Overlaid relative dispositions of the nitroso-pyrimidine group with the interacting anion atoms forming anion- $\pi$  interactions in the crystal structures of  $\text{H}_4\text{L}^{3+}$  with  $\text{Co}(\text{CN})_6^{3-}$  (blue) and of  $\text{H}_3\text{L}^{2+}$  with  $\text{HgCl}_4^{2-}$  (green),  $\text{HgBr}_4^{2-}$  (brown) and  $\text{CdI}_4^{2-}$  (purple).

obtained by means of isothermal titration measurements and by linear correlation of complex stability constants with ligand charge, which provided evaluations of the equilibrium constants for  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ , and  $\text{Co}(\text{CN})_6^{3-}$  association with the uncharged HL ligand to be in the range  $\log K = 1.6$ – $2.2$ .<sup>14,17</sup> Values for  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ , and  $\text{Co}(\text{CN})_6^{3-}$  complexes with HL are shown in Table 1.

As far as the anion binding abilities of the two ligands are compared, we observe that, for ligand species with the same positive charge, HL forms more stable complexes than L1, the complexes of  $\text{Co}(\text{CN})_6^{3-}$  and  $\text{Fe}(\text{CN})_6^{4-}$  with the monocharged  $\text{H}_2\text{L}^+$  and  $\text{HL}^+$  receptors representing the unique exceptions to this trend (Tables 1 and 2). Most likely, the anion- $\pi$  interactions and the less solvated environment provided by the pyrimidine residue of HL make the main contributions that enhance the ligand binding ability. Nevertheless, an interpretation of ligand binding ability in terms of binding selectivity cannot be performed by simply comparing the stability constants of analogous complexes, since the formation of these complexes is regulated by the protonation of ligands having different protonation properties. A useful method for the analysis of binding selectivity consists in considering a ternary system containing the anion and the two ligands, in equimolar amounts, and calculating the overall percentage of complexes formed by each ligand at different pH values.<sup>30,31</sup> The result of a similar analysis performed for the system HL/L1/ $\text{SeO}_4^{2-}$  (millimolar concentrations) is reported in the diagram of Fig. 5a, showing that the anion is preferentially bound by HL over the entire pH range in which complexation occurs. Conversely, the same analysis performed for the HL/L1/ $\text{Fe}(\text{CN})_6^{4-}$  system reveals that L1 is the preferred ligand by  $\text{Fe}(\text{CN})_6^{4-}$  (Fig. 5b). The results obtained for the other anions are displayed in Fig. S1† While the hexacyanometallate anions undergo preferential binding with HL, all the other anions prefer L1. Analogous results (see Fig. S2†) are obtained by comparison of the conditional stability constants calculated for the complexation equilibria  $\text{A}(\text{all forms}) + \text{L}(\text{all forms}) =$

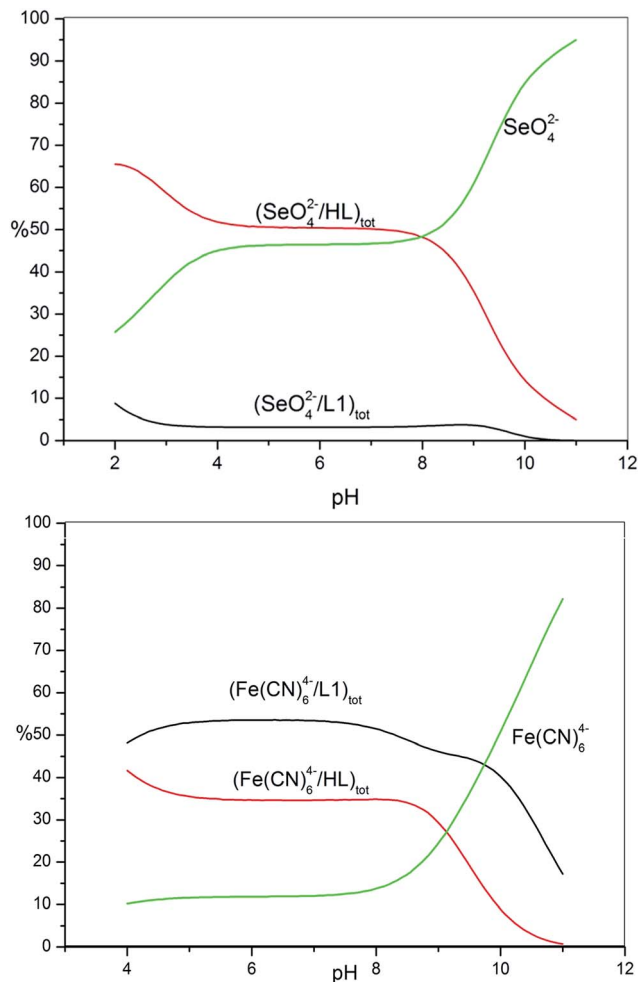


Fig. 5 Selectivity diagrams calculated for the systems (a) HL/L1/ $\text{SeO}_4^{2-}$ , (b) HL/L1/ $\text{Fe}(\text{CN})_6^{4-}$  showing the percentage of anion bound to each ligand as a function of pH. All reagents  $1 \times 10^{-3}$  M. Percentages are referred to total anion concentration.

$\text{AB}(\text{all forms})$  and expressed as  $K_{\text{AB}}^{\text{cond}} = [\text{AL}(\text{all forms})]/([\text{A}(\text{all forms})][\text{L}(\text{all forms})])$ , where A, L and AL are the anion, the ligand and the anion complex, respectively.<sup>31</sup>

In conclusion, the ligand tren (L1) maintains its anion binding properties upon functionalization to give its pyrimidine derivative HL. In some cases ( $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{Pt}(\text{CN})_4^{2-}$ ,  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ ), HL displays enhanced binding ability relative to tren, while in few case ( $\text{Co}(\text{CN})_6^{3-}$ ,  $\text{Fe}(\text{CN})_6^{4-}$ ) it is less efficient than the parent ligand. Nevertheless, in all cases HL is a promising candidate for the preparation of hybrid AC/HL materials for recovery of these anions from aqueous media.

#### Adsorption studies

The use of AC-based adsorbents is important compared to other sorbents because of its large surface area, high adsorption capacity, porous structure, negligible environmental toxicity, low cost, and high purity.<sup>21</sup> In previous works it was established that the hybrid AC/HL material behaves as an efficient adsorbent for  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{HgCl}_4^{2-}$  and  $\text{CrO}_4^{2-}$  anions<sup>11</sup> as

well as for some metal cations.<sup>18,24,32</sup> Therefore, having in mind the binding data shown in the previous section, it seemed interesting to extend the adsorption study to  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{Pt}(\text{CN})_4^{2-}$ ,  $\text{Co}(\text{CN})_6^{3-}$ ,  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  and  $\text{Fe}(\text{CN})_6^{4-}$  anions, especially to  $\text{Pt}(\text{CN})_4^{2-}$  and  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  because of the role they have, or might have, in precious metals extraction. To this purpose, we analyzed the adsorptivity toward the above set of anions of a commercial activated carbon (AC) and of the corresponding AC/HL hybrid material that was prepared as previously described.<sup>11,24</sup>

AC is a graphitized activated carbon with a surface area of  $1062 \text{ m}^2 \text{ g}^{-1}$  and containing oxygen as the only heteroatom component present in significant amount (3.9%).<sup>11,24</sup> Most of the surface area (*ca.*  $1000 \text{ m}^2 \text{ g}^{-1}$ ) is associated to narrow micropores (diameter  $< 2.5\text{--}3.0 \text{ nm}$ ) whereas the remaining area corresponds to mesopores ( $2.5\text{--}3 \text{ nm} < \text{diameter} < 50 \text{ nm}$ ) and macropores (diameter  $> 50 \text{ nm}$ ).<sup>33</sup> AC surface mainly exhibits weak Brönsted basic character,<sup>11</sup> which is reflected in its ability to bind protons from water giving rise to the accumulation of net positive charge in the 3.0–9.2 pH range. The low proton affinities of the (few) oxygen groups on the AC surface (carboxyl acids, carbonyl, quinone, lactone and phenol groups) exclude these functions from acting as binding sites for protons in the 2.5–10.0 pH range. Consequently, most of proton binding sites at AC surface are expected to be the arene centers of the graphite sheets ( $\text{C}\pi$ ), which interact with protons according to the  $\text{C}\pi + \text{H}_3\text{O}^+ \rightarrow \text{C}\pi\text{--H}_3\text{O}^+$  process.<sup>11,34</sup> The surface charge density,  $Q$  (mmol  $\text{H}^+$  per gram of AC), decreases steadily from *ca.*  $0.26 \text{ mmol H}^+$  per g, at pH 3.5, to  $0.15 \text{ mmol of H}^+$  per g at pH = 6.0.<sup>11</sup>

The textural and surface chemical properties of AC/HL have been described previously. The hybrid material AC/HL contains  $0.49 \text{ mmol of HL per gram of AC}$ , irreversibly adsorbed in water in the pH range 2.5–10. The specific surface area, pore distribution and surface chemical properties of AC/HL were also determined previously.<sup>11,33</sup>

Attachment of HL to the surface of AC, by  $\pi\text{--}\pi$  stacking interaction of the aromatic residue of HL with the  $\text{C}\pi$  sites AC,<sup>24</sup> has two effects on the physico-chemical properties of the latter: (i) transference of the Brönsted base properties of the amine residue of HL to the AC surface, determining a sharp increase of the positive surface charge of AC/HL, relative to AC, in the whole pH range,<sup>11</sup> and (ii) blocking of the entrance to the more inner pores of AC by HL molecules that reduces the accessible surface area of AC/HL to  $495 \text{ m}^2 \text{ g}^{-1}$ .<sup>33</sup>

For the studies of anion adsorption, pH 6.0 was chosen as the most suitable for comparative purposes, since at this pH all these anions form the same unique  $\text{H}_3\text{LA}^{n-}$  ( $n = 0\text{--}2$ ) complex (see Table 1). The adsorption isotherms on AC and AC/HL at pH 6.0 are shown in Fig. 6.

All the isotherms, except that of  $\text{S}_2\text{O}_3^{2-}$ , fit well to the Langmuir equation<sup>29</sup> (see Experimental section), which enabled to obtain the maximum adsorption capacities,  $X_{\text{mAC}}$  and  $X_{\text{mAC/HL}}$ , summarized in Table 3, although some deviation of experimental points from the calculated curves, that can be ascribed to the surface heterogeneity of the porous adsorbents, is observed. As can be seen in Fig. 6, the adsorption capacity of AC grows, in most of cases, when the anion charge increases. Since

the AC surface charge is the same for all systems, it is likely that anion adsorption on AC is due to electrostatic attraction with the positive charges of the protonated arene centers of AC, even if some dispersive contribution is also expected. The good fitting to Langmuir equation of the experimental isotherms (except for  $\text{S}_2\text{O}_3^{2-}$ ) is consistent with the existence of similar adsorbing sites on the adsorbent surface. The lowest adsorptivities are found for di-charged anions ( $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ), whereas intermediate adsorptivities correspond to the tri-charged  $\text{Co}(\text{CN})_6^{3-}$  and  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  and the highest adsorptivity corresponds to the tetra-charged  $\text{Fe}(\text{CN})_6^{4-}$ . In the last case, not only the higher negative charge, but also the possibility hydrogen bonding with  $\text{--OH}$  functions (from phenol groups) should be responsible for the higher adsorptivity observed for this anion.

It is worth commenting the adsorption of  $\text{Pt}(\text{CN})_4^{2-}$  and  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ . The adsorptivity on AC of the elongated tri-charged  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  is higher than that of  $\text{Co}(\text{CN})_6^{3-}$ , while adsorptivity of planar  $\text{Pt}(\text{CN})_4^{2-}$  is greater than that of all anions but  $\text{Fe}(\text{CN})_6^{4-}$ . The absence of reduced Pt(0) and Au(0) in the XPS spectra of samples of AC/ $\text{Pt}(\text{CN})_4^{2-}$  and AC/ $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ , respectively, rules out metal reduction as the cause of the high adsorptivities of these anions on AC. Three effects could contribute to the higher adsorptivities of this couple of anions: (i) their high hydrophobicity due to their high molecular sizes that determine lower water solubilities;<sup>35</sup> (ii) the existence of  $\text{C}\pi\text{--}d\pi$  interactions between the arene centers of AC and the metal center of linear  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  and planar  $\text{Pt}(\text{CN})_4^{2-}$  complexes,<sup>36</sup> although for  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  such interactions should be somewhat hindered by the non-planar structure of  $\text{S}_2\text{O}_3^{2-}$ ,<sup>37</sup> (iii)  $\text{C}\pi\text{--C}\equiv\text{N}\pi$  interactions between the arene centers of AC and the metal coordinated cyanide anions. Anyway, the influence of electrostatic components in anion interactions with the AC surface is clearly illustrated by the adsorptivity drop observed for  $\text{Pt}(\text{CN})_4^{2-}$  and  $\text{Co}(\text{CN})_6^{3-}$  from pH 2.5 to pH 6.0 (Fig. 6) as the positive net surface charge of AC decreases.

Also isotherms for anion adsorption at pH 6.0 on the hybrid AC/HL material (see Experimental section) are shown in Fig. 6, while the corresponding maximum adsorption capacities,  $X_{\text{mAC/HL}}$ , are summarized in Table 3. These data evidence that functionalization of AC with HL clearly improves its adsorption capacity. Assuming that most of HL molecules are anchored to AC through the pyrimidine moiety,<sup>24,38</sup> the enhanced adsorptivity of AC/HL can be ascribed to the high anion binding ability of the polyamine residue of HL.

In the cases of bi-anions  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{Pt}(\text{CN})_4^{2-}$ , the maximum adsorption capacities of AC/HL is about twice those of AC, which is consistent with the similar values of the stability constants of the  $\text{H}_3\text{LA}$  neutral complexes formed by these anions. In the cases of  $\text{Co}(\text{CN})_6^{3-}$  and  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ , we observed a lower enhancement. Although the stability constants of the  $\text{H}_3\text{LA}$  complexes formed by these tri-anions are similar to those of the bi-anions, the monoanionic character of  $[\text{H}_3\text{L}(\text{Co}(\text{CN})_6)]^-$  and  $[\text{H}_3\text{L}(\text{Au}(\text{S}_2\text{O}_3)_2)]^-$  determines higher water solubility, thus explaining their lower adsorptivities. Finally, the adsorptivity of AC/HL for  $\text{Fe}(\text{CN})_6^{4-}$  is enhanced by a factor of *ca.* 3, relative to AC, in agreement with the higher stability of the

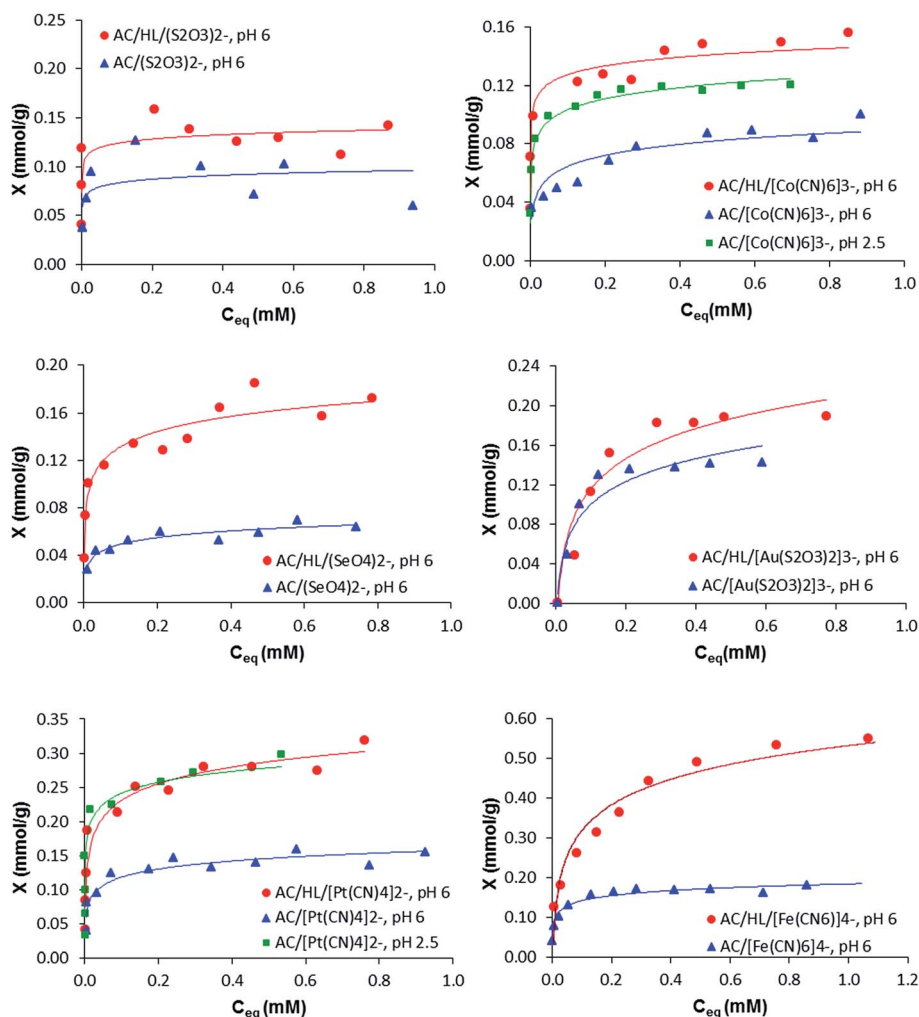


Fig. 6 Adsorption isotherms of the  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{Pt}(\text{CN})_4^{2-}$ ,  $\text{Co}(\text{CN})_6^{3-}$ ,  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  and  $\text{Fe}(\text{CN})_6^{4-}$  anions on AC and AC/HL.  $X$  = mmols of anion adsorbed per gram of adsorbent,  $C_{\text{eq}}$  = anion equilibrium concentration.

Table 3 Langmuir maximum anion adsorption capacities of AC,  $X_{\text{mAC}}$ , and of AC/HL,  $X_{\text{mAC/HL}}$  (in mmol of anion per gram of adsorbent), and corresponding normalized  $X_{\text{NmAC}}$  and  $X_{\text{NmAC/HL}}$  values

Anion species	$X_{\text{mAC}}$ (mmol g <sup>-1</sup> )	$X_{\text{mAC/HL}}$ (mmol g <sup>-1</sup> )	Improvement factor	$X_{\text{NmAC}}$ (mmol m <sup>-2</sup> )	$X_{\text{NmAC/HL}}$ (mmol m <sup>-2</sup> )	Normalized improvement factor
$\text{S}_2\text{O}_3^{2-}$	0.08 <sup>a</sup>	0.12 <sup>a</sup>	2	$4.85 \times 10^{-5}$	$2.02 \times 10^{-4}$	4.16
$\text{SeO}_4^{2-}$	0.060(2) [0.9690] <sup>b</sup>	0.138(8) [0.9840] <sup>b</sup>	2.30	$5.7 \times 10^{-5}$ (2) <sup>c</sup>	$2.8 \times 10^{-4}$ (2)	4.91
$\text{Pt}(\text{CN})_4^{2-}$	0.142(4) [0.9719] <sup>b</sup>	0.30(1) [0.9662] <sup>b</sup>	2.11	$1.34 \times 10^{-4}$ (3)	$6.1 \times 10^{-4}$ (2)	4.55
$\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$	0.157(6) [0.9664] <sup>b</sup>	0.209(6) [0.9661] <sup>b</sup>	1.33	$1.48 \times 10^{-4}$ (5)	$4.2 \times 10^{-4}$ (1)	2.84
$\text{Co}(\text{CN})_6^{3-}$	0.098(6) [0.9795] <sup>b</sup>	0.161(3) [0.9798] <sup>b</sup>	1.65	$9.2 \times 10^{-5}$ (5)	$3.26 \times 10^{-4}$ (6)	3.54
$\text{Fe}(\text{CN})_6^{4-}$	0.172(2) [0.9866] <sup>b</sup>	0.54(2) [0.9915] <sup>b</sup>	3.14	$1.62 \times 10^{-4}$ (2)	$1.10 \times 10^{-3}$ (4)	6.79

<sup>a</sup> Approximate values from the corresponding isotherms (Fig. 6). <sup>b</sup> Linear correlation coefficients ( $R$ ). <sup>c</sup> Values in parentheses are standard deviations on the last significant figure.

$[\text{H}_3\text{L}(\text{Fe}(\text{CN})_6)]^{2-}$  complex formed at pH 6.0. Worth mentioning is the enhancement of the adsorption capacity observed for  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  and  $\text{Pt}(\text{CN})_4^{2-}$  anions, since it may rise applicative interest for extraction and recovery of gold and platinum. The sequestering capacities of AC/HL toward these anions at pH 6.0

(39.4 and 58.7 mg g<sup>-1</sup> of adsorbent, respectively) are comparable with or better than those obtained with other functionalized activated carbons.<sup>39,40</sup>

In summary, this study points out that functionalization of AC with the polyamine HL provides a hybrid material which

significantly improves the ability of AC in the sequestration of the studied anions. This effect is a consequence of the anion binding ability of HL that is basically preserved after its adsorption onto the AC surface. These results enlarge a previous data base that correlates the metal ion and anion adsorbing properties of hybrid materials of AC/HL type with the ability of the HL ligand to bind the same species,<sup>11,18,24,32</sup> and encourage further thorough research on the factors that could improve the adsorption capacity, *i.e.* (i) the influence of the textural characteristics of AC and (ii) the design of the polyamine HL function.

Regarding the textural properties, adsorption of HL on AC surface results in blocking the entrance to the more inner (narrower) pores, giving rise to a decrease of surface area from 1062 m<sup>2</sup> g<sup>-1</sup> for AC to 495 m<sup>2</sup> g<sup>-1</sup> for AC/HL,<sup>33</sup> thus reducing the accessible surface area for larger functionalization with HL and interaction with other small molecular species (such as the anions here studied). Accordingly, a more suitable information on the improvement of adsorptivity derived from AC functionalization with HL is provided by the comparison of the adsorption capacities of both adsorbents normalized with respect to the accessible areas,  $X_{mN}$ . The values of  $X_{mN}$  for AC and AC/HL, that appear in Table 3, were obtained by dividing the maximum adsorption capacities,  $X_{mAC}$  and  $X_{mAC/HL}$ , by the accessible surface areas of the corresponding adsorbents. The improvement factors obtained by using such normalized values (see Table 3) increase greatly, thus showing that activated carbons having most of their surface areas accessible to the receptors (highly meso- and macroporous activated carbons) are the most suitable for ion recovery purposes.

With respect to the second point, the use of receptors containing a larger number of amine groups than HL should improve the anion binding ability of the hybrid material, since a greater positive charge would be achievable on the surface of the hybrid material. Furthermore, appropriate synthesis of tailored polyamine ligands, in particular of macrocyclic and cleft-like structures, would afford hybrid materials with enhanced anion extraction selectivity.

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