

Observation of the Adsorption of $\text{K}^+\text{Au}(\text{CN})_2^-$ Ion Pairs on the Surface of Nanoporous Carbon by XANES

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The adsorption of dicyanoaurate(I) complexes on nanoporous carbon is widely used for the recovery of gold in the extractive metallurgy industry. However, there is no agreement on the adsorption mechanism concerning the nature of the adsorbed species on carbon surface. A novel experiment was designed in this study by treating the adsorbed dicyanoaurate(I) with 18-crown-6, which has a strong affinity for the K^+ ion, followed by nitrogen K-edge XANES measurement, which is sensitive to the chemical environment of the absorbing atom. The results showed that there was a red shift of the lowest energy transition ($\text{K} \rightarrow \pi^*$ resonance) of the nitrogen atom from 401.0 to 399.7 eV after the adsorbed dicyanoaurate(I) was treated with 18-crown-6 because of increased electron densities on N atoms, indicating that the K^+ ions were coadsorbed with dicyanoaurate(I) complexes as $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs. The nitrogen $\text{K} \rightarrow \pi^*$ resonance energy of dicyanoaurate(I) decreased upon adsorption as $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs compared with $\text{KAu}(\text{CN})_2$ solid (401.3 eV to 401.0 eV). This is probably due to decreased Au–Au association, which increases π -back-donation from metal centers to CN ligands thereby increasing electron densities on the nitrogen atoms accordingly. A minority of the dicyanoaurate(I) was adsorbed as unpaired $\text{Au}(\text{CN})_2^-$ ions species. The unpaired adsorption was partly suppressed by the presence of Ca^{2+} ions. The novelty of the approach used in this work is applicable to the research of other adsorption systems.

Introduction

The structure and adsorption of dicyanoaurate(I) have long been of considerable interest due to its remarkable importance in both theoretical coordination chemistry and industrial applications. The adsorption of dicyanoaurate(I) complexes on nanoporous carbon has been widely and successfully used for the extraction of gold with the carbon-in-pulp (CIP) process in industry. There has been extensive research on the adsorption mechanism of dicyanoaurate(I) on nanoporous carbon and a better understanding of various factors influencing the adsorption/desorption process has been achieved, which in turn has improved the CIP operations in the extractive metallurgy industry.¹ However, the mechanism regarding the nature of the adsorbed dicyanoaurate(I) species and the adsorption sites in carbon is not fully understood and there is no agreement reached yet on these issues. The controversy on these two aspects of the adsorption mechanism is concerned with ion pair $\text{M}^{n+}[\text{Au}(\text{CN})_2^-]_n$ vs unpaired $\text{Au}(\text{CN})_2^-$ adsorption and the adsorption on the hydrophilic functional groups vs hydrophobic graphene layers.

The ion-pair mechanism involves the adsorption of dicyanoaurate(I) complexes on the surface of nanoporous carbon as $\text{M}^{n+}[\text{Au}(\text{CN})_2^-]_n$ ion pairs, where M^{n+} can be common cations in an aqueous processing solution such as Ca^{2+} , Mg^{2+} , Na^+ , K^+ , etc. It was proposed² after the observation that the presence of these cations enhanced the adsorption of gold and has been accepted by many researchers.^{3–8} It was suggested recently from an in situ scanning tunneling microscopy (STM) study⁹ that $\text{Au}(\text{CN})_2^-$ ions adsorbed along the step edges of the highly oriented pyrolytic graphite (HOPG) following the intercalation of Ca^{2+} ions. In contrast to the ion-pair adsorption mechanism,

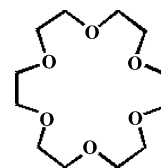


Figure 1. Molecular structure of 18-crown-6 ether.

it was pointed out^{10–12} that the formation of an intimate ion-pair association $\text{M}^{n+}[\text{Au}(\text{CN})_2^-]_n$ during adsorption possibly was not necessary because of the highly conductive nature of the graphitic substrate. A dual adsorption mechanism has been proposed¹³ that the adsorption of dicyanoaurate(I) complexes under high ionic strength involved an ion-pair mechanism whereas under low ionic strength, a portion of the gold was adsorbed by electrostatic interaction with ion exchange sites. In more recent studies^{14,15} which employed flow microcalorimetry and quantitative analysis of adsorbed $\text{Au}(\text{CN})_2^-$ and K^+ on carbon surface under various conditions, it was found that at very low equilibrium concentration, dicyanoaurate(I) complexes were adsorbed irreversibly probably involving an anionic exchange mechanism between $\text{Au}(\text{CN})_2^-$ ions and some anions initially present on the surface of nanoporous carbon. At relatively high concentration, the adsorption of dicyanoaurate(I) complexes was partly reversible, which may involve physical adsorption of neutral molecular species, i.e., $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs, onto less active parts of the surface through van der Waals interactions.

Despite the ion-pair mechanism being favored by many researchers, no direct evidence has been observed yet. In this study, attempts have been made to obtain direct evidence for the ion-pair adsorption mechanism by combining X-ray absorption near edge structure (XANES) measurements with a novel sample preparation method—complexing K^+ ions using the crown ether 18-crown-6. The structure of 18-crown-6 ether is shown in Figure 1. It has an estimated cavity diameter of 2.6–

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3.2 Å and is most suitable for complexing with K^+ (ionic diameter 2.66 Å) etc.^{16–23} In this paper the nanoporous carbon with adsorbed dicyanoaurate(I) species from $\text{KAu}(\text{CN})_2$ solution was treated with 18-crown-6. The crown ether treated dicyanoaurate(I) species adsorbed on carbon together with samples prepared by adsorption at various pH values and in the presence of calcium ions were subjected to XANES spectroscopy study. The speciation of the adsorbed dicyanoaurate(I) complexes has been determined based on nitrogen $\text{K} \rightarrow \pi^*$ transition energy from XANES measurements. The aurophilic Au–Au interaction has also been addressed since it plays a very important role in the processes involving the solid state and aqueous solutions of the dicyanoaurate(I) complex.^{24–27}

Experimental Section

FTIR was used to study the $\nu_{\text{C-N}}$ of $\text{KAu}(\text{CN})_2$ in the following forms: crystal, aqueous solution, and 18-crown-6/methanol treated solid. The infrared spectra were recorded on a Nicolet 20-PCIR Fourier Transformed Infrared Spectrometer with a CsI optics DTGS detector. The measurement resolution was set at 4 cm^{-1} . The KBr/sample disks were prepared by mixing 0.5% of finely ground samples in KBr. The aqueous solution sample was placed between two CaF_2 windows as a thin film.

The nitrogen X-ray absorption near edge (K edge) structure (XANES) spectroscopy measurements were performed by using beam line Station 1.1 of the Synchrotron Radiation Source (SRS) at Daresbury Laboratory. The SRS storage ring was operated at 2 GeV with the ring currents 100–300 mA. The monochromator was a high-energy spherical grating monochromator with an Au grating and a slit width of 0.1 mm. Detection was by total electron yield. The sample was ground finely and pressed mechanically on an indium foil to form a thin layer. The measurements were carried out at ambient temperature under high vacuum (10^{-6} – 10^{-8} bar). The spectra were calibrated by using acridine as a reference, which has a strong absorption at 399.7 eV.

The nanoporous carbon used in this study was a coconut shell based carbon with the following characteristics: ultimate analysis (wt % daf) C 97.8, H 0.2, N 0.0, O 2.0 (by difference); CO_2 surface area ($\text{m}^2\text{ g}^{-1}$, 273 K, D–R) 445; micropore volume ($\text{cm}^3\text{ g}^{-1}$, from extrapolation of the D–R equation for CO_2 adsorption at 273 K) 0.30; total pore volume ($\text{cm}^3\text{ g}^{-1}$, from N_2 adsorption at 77 K at $p/p^0 = 1$) 0.43.

The carbon samples with adsorbed dicyanoaurate(I) species were prepared by mixing 0.1 g of carbon (≤ 300 mesh) with 50 mL of 1.5 mM $\text{KAu}(\text{CN})_2$ aqueous solutions at various pH values. The effect of Ca^{2+} ions on the adsorption of gold was studied by addition of CaCl_2 to the $\text{KAu}(\text{CN})_2$ solution at a molar ratio of $\text{Ca}/\text{Au} = 30$. The mixtures were held in a water bath at 20°C for 72 h. The solids were washed 3 times with 50 mL of distilled water after filtration and air-dried at room temperature. The quantitative analysis showed that about 0.38 mmol g^{-1} of dicyanoaurate(I) was adsorbed on carbon at an equilibrium concentration of 0.74 mM, which is approximately 1200 times that of the trapped residual solution in pores estimated according to the total pore volume. Thus the XANES spectra were obtained predominantly from the adsorbed species rather than the entrained residual $\text{KAu}(\text{CN})_2$. The carbon sample with adsorbed dicyanoaurate(I) species prepared from $\text{KAu}(\text{CN})_2$ solution at pH 10 was treated with 18-crown-6 by grinding the carbon in 0.18 M crown ether/methanol solution. A few drops of the resultant slurry was applied on the indium plate and allowed to dry before the XANES measurement.

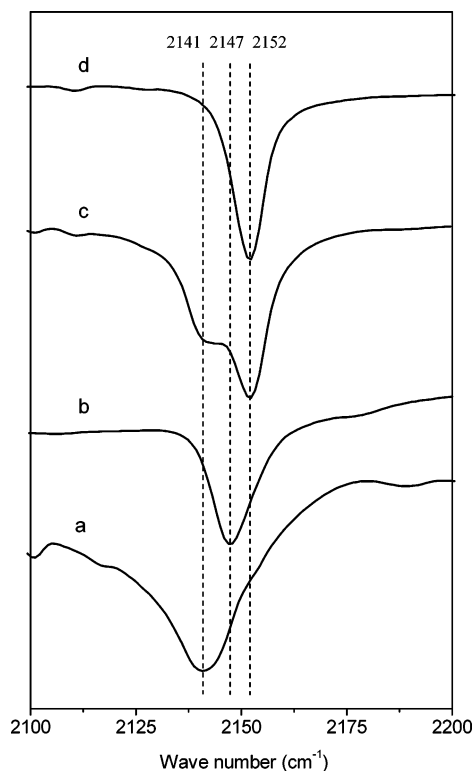


Figure 2. Infrared spectra of $\text{KAu}(\text{CN})_2$ in various forms: (a) solid $\text{KAu}(\text{CN})_2$; (b) aqueous $\text{KAu}(\text{CN})_2$ solution; (c) 18-crown-6 treated $\text{KAu}(\text{CN})_2$; and (d) water-insoluble part of the 18-crown-6 treated $\text{KAu}(\text{CN})_2$.

Results and Discussion

Figure 2 shows the FTIR spectra of $\text{KAu}(\text{CN})_2$ in various forms: solid, aqueous solution, 18-crown-6 treated, and the water-insoluble part of the resultant solid. A detailed study of $\text{KAu}(\text{CN})_2$ with FTIR has been reported in the literature,²⁸ which showed that solid and aqueous $\text{KAu}(\text{CN})_2$ have a well-resolved cyanide stretching vibration band at 2141 and 2147 cm^{-1} respectively. In this study, IR spectra were recorded to examine the effect of 18-crown-6 treatment on the structure of $\text{KAu}(\text{CN})_2$. It can be seen that after dissolution and dissociation of K^+ with $\text{Au}(\text{CN})_2^-$ in water, the $\nu_{\text{C-N}}$ shifts to higher frequency. The FTIR spectrum of the $\text{KAu}(\text{CN})_2$ treated with crown ether by grinding the crystals in 18-crown-6 methanol solution shows a strong band at 2152 cm^{-1} followed by a shoulder at 2141 cm^{-1} . The latter band is due to $\nu_{\text{C-N}}$ in solid $\text{KAu}(\text{CN})_2$ remaining intact after crown ether treatment. The strong band at 2152 cm^{-1} is attributed to the cyanide stretching vibration $\nu_{\text{C-N}}$ in $\text{Au}(\text{CN})_2^-$ after the counter K^+ ions are complexed. No dissociation of $\text{Au}(\text{CN})_2^-$ complex occurs after treatment by 18-crown-6. The crown ether treated $\text{KAu}(\text{CN})_2$ was agitated in water to remove the residual $\text{KAu}(\text{CN})_2$. The resultant water-insoluble substance shows a strong and well-resolved band at 2152 cm^{-1} in the IR spectrum, which is attributed to the $\text{Au}(\text{CN})_2^-$ complex after K^+ being trapped by 18-crown-6. The crystal structure of $\text{KAu}(\text{CN})_2$ consists of layers of linear $\text{Au}(\text{CN})_2^-$ ions alternating with layers of K^+ ions,²⁹ which are strongly coordinated to the N atoms of the cyanide groups. Complexation of K^+ ions by 18-crown-6 results in a water-insoluble species that is tentatively expressed as $[(18\text{-crown-6})\text{K}^+]\text{Au}(\text{CN})_2^-$ in this study. Apparently from the IR spectrum of this species where there is a red shift of $\nu_{\text{C-N}}$ compared with solid $\text{KAu}(\text{CN})_2$, the effect of trapping K^+ ions by 18-crown-6 is similar to the dissolution of $\text{KAu}(\text{CN})_2$ in water, which also increases the IR frequency of the CN. In both cases the K^+

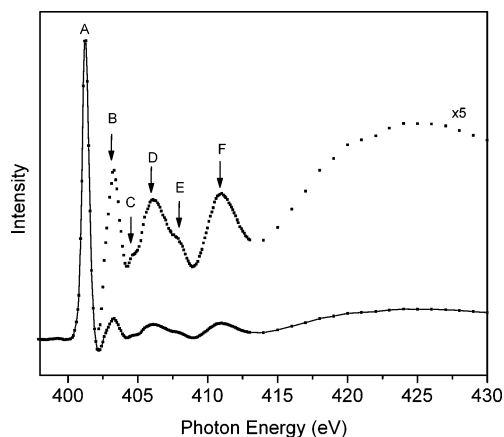


Figure 3. Nitrogen K-shell XANES spectrum of potassium dicyanoaurate(I) $\text{KAu}(\text{CN})_2$ solid.

ions are removed from around the $\text{Au}(\text{CN})_2^-$ ions. Another factor that influences the $\nu_{\text{C-N}}$ is the Au–Au interactions. The solvation by water and encapsulation by crown ether should lead to the reduction in the extent of Au–Au interactions hence increasing the back-donation to the cyanide π^* and leading to lower $\nu_{\text{C-N}}$. However, the overall effect is that the $\nu_{\text{C-N}}$ shifts to higher frequency.

The nitrogen K-edge XANES spectrum of $\text{KAu}(\text{CN})_2$ solid is illustrated in Figure 3. The assignment of nitrogen K-shell excitation bands has been described elsewhere.³⁰ Briefly the sharp lowest energy resonance A is attributed to the transition to CN-based π^* molecular orbital $2\pi_u$ ($\text{K} \rightarrow \pi^*$), which is the lowest unoccupied molecular orbital (LUMO) in the linear dicyanoaurate(I) complex $[\text{Au}(\text{CN})_2^-]_n$, whereas the second lowest energy feature B is assigned to the transition to the $3\pi_g$ molecular orbital ($\text{K} \rightarrow \pi^*$), another unoccupied π orbital in $[\text{Au}(\text{CN})_2^-]_n$. The formula $[\text{Au}(\text{CN})_2^-]_n$ is used to represent the dicyanoaurate(I) complex due to Au–Au association in $\text{KAu}(\text{CN})_2$. The features C, D, and E are probably due to transitions to Rydberg states whereas feature F is considered to arise from double excitation, which likely involves simultaneous $\text{N } 1s \rightarrow 2\pi_u$ or possibly $3\pi_g$ molecular orbital ($\text{K} \rightarrow \pi^*$) transition together with the excitation of an electron of CN^- 1π based orbitals ($1\pi_u, 1\pi_g$) to the lowest unoccupied molecular orbital (LUMO) $2\pi_u$ or $3\pi_g$. The broad features at above 420 eV are attributed to shape resonances which involve transitions to the σ^* orbitals located in the continuum.

Figures 4 and 5 show the nitrogen K-edge XANES spectra of the dicyanoaurate(I) complexes adsorbed on the carbon surface at pH 10 before and after treatment with 18-crown-6, respectively. From these figures it can be seen that these nitrogen K-shell near edge absorption spectra are similar to that of the $\text{KAu}(\text{CN})_2$ solid. Both are dominated by the sharp lowest energy resonances followed by a number of weak features at higher energies. However, a new band A1 arises at the lowest energy region after dicyanoaurate(I) is adsorbed on the carbon surface from the $\text{KAu}(\text{CN})_2$ aqueous solution at pH 10 (see Figure 4). The intensity of band A1 increases after 18-crown-6 treatment whereas the relative intensity of band A decreases (see Figure 5). From the FTIR study we learned that the treatment of $\text{KAu}(\text{CN})_2$ with 18-crown-6 has a similar effect to the dissolution in water both dissociating K^+ with $\text{Au}(\text{CN})_2^-$ with the latter being freed from the system. Therefore, band A in Figure 4 is due to the $\text{K} \rightarrow \pi^*$ transition in the $\text{KAu}(\text{CN})_2$ neutral molecules which have been adsorbed as ion pairs, whereas band A1 is the same transition but due to the unpaired dicyanoaurate(I) complex $\text{Au}(\text{CN})_2^-$. This indicates that dicyanoaurate(I) complexes are

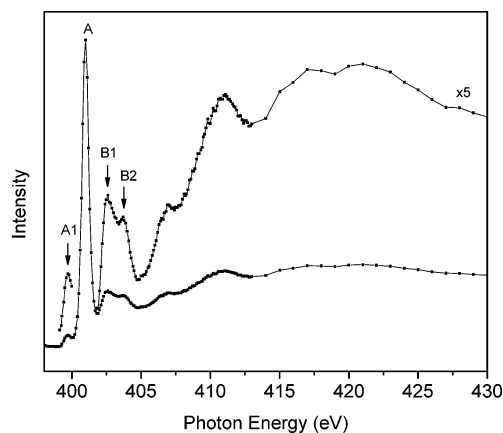


Figure 4. Nitrogen K-shell XANES spectrum of dicyanoaurate(I) adsorbed on the carbon surface from the $\text{KAu}(\text{CN})_2$ aqueous solution at pH 10.

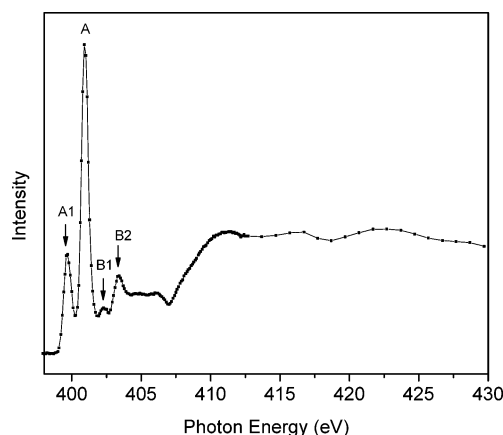


Figure 5. Nitrogen K-shell XANES spectrum of 18-crown-6 treated dicyanoaurate(I) after adsorption from the $\text{KAu}(\text{CN})_2$ aqueous solution at pH 10.

adsorbed predominantly as $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs from $\text{KAu}(\text{CN})_2$ solution at pH 10. There is also a small amount of gold adsorbed as unpaired $\text{Au}(\text{CN})_2^-$ ions. The treatment and complexation of K^+ ions with 18-crown-6 convert some of the adsorbed $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs to the pseudo-unpaired $\text{Au}(\text{CN})_2^-$ as shown by the change of the relative peak intensities of bands A and A1 in Figures 4 and 5. The splitting of band B into B1 and B2 is also observed after adsorption on carbon surface. It is likely that they are attributed to the second lowest $\text{K} \rightarrow \pi^*$ transition ($\text{K} \rightarrow 3\pi_g$) of the adsorbed $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs and unpaired $\text{Au}(\text{CN})_2^-$ ions.

A comparison of the lowest nitrogen $\text{K} \rightarrow \pi^*$ transition energy of $\text{KAu}(\text{CN})_2$ solid with that of $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs adsorbed on the carbon surface reveals that there is a red shift upon adsorption. The edge jump (band A) of the $\text{KAu}(\text{CN})_2$ solid is located at 401.3 eV whereas this energy shifts to a lower position (401.0 eV) after adsorption as $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs. It has been well established that the core level binding energy of an atom in a molecule obtained by XPS is sensitive to its oxidation state and chemical environment, which are reflected directly by the effective atomic charge. There is a good linear relationship between the atomic charge in a molecule and the $1s$ electron orbital energy for C, N, O, F, and Cl.³¹ Similar information can be extracted from the X-ray absorption near edge structure. The energy of the first bound excited state in the near edge structure ($\text{K} \rightarrow \pi^*$) has been found to be closely related to the effective atomic charge of the absorbing atom.^{30,32} Thus it is proposed that the red shift of the $\text{K} \rightarrow \pi^*$ transition

energy of the adsorbed $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs compared with the $\text{KAu}(\text{CN})_2$ solid is due to the lowering of the atomic charge on the N atoms in dicyanoaurate(I) complexes after adsorption. This may be caused by the decreased Au–Au association after $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs are adsorbed on the carbon surface. Oligomerization of $\text{Au}(\text{CN})_2^-$ and $\text{Ag}(\text{CN})_2^-$ ions due to aurophilic Au–Au and argentophilic Ag–Ag interactions has been proposed^{24–27} to play an important role in many processes involving the solid state and aqueous solutions. It was observed^{24,27,33,34} that doping alkali halide crystals and A-zeolite with dicyanoaurate(I) and dicyanoargentate(I) led to higher stretching frequencies $\nu(\text{C}\equiv\text{N})$ due to Au–Au and Ag–Ag associations. This is because increased Au–Au and Ag–Ag interactions reduce the back-donation from the central metal ion to the empty π^* molecular orbital of CN^- . However, when other substrates such as high surface area, nonporous silica, and alumina were impregnated with dicyanoargentate, no increased Ag–Ag association was observed.²⁷ In this study, it is likely that there is a decreased Au–Au association compared with the $\text{KAu}(\text{CN})_2$ solid after $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs are adsorbed on the carbon surface (rather than impregnation). It was reported³⁰ that Au–Au and Ag–Ag association in $\text{KAu}(\text{CN})_2$ and $\text{KAg}(\text{CN})_2$ solids led to reduced electron densities on the metal centers that would otherwise be used for π -back-donation and as a result the atomic charge on the N atom is increased. In contrast, the decreased Au–Au interaction increases the back-donation from the central metal ion to CN thereby increasing the electron density on the N atom. As a result, the nitrogen K $\rightarrow \pi^*$ transition energy shifts to a lower position.

The adsorption of $\text{K}^+\text{Au}(\text{CN})_2^-$ may also involve electronic interaction between the ion pairs and the substrate surface. It was proposed, based on a XPS study,¹⁰ that dicyanoaurate(I) is adsorbed on the graphene layers via a weak π donation from the basal plane surfaces, which are enriched in π electrons,³⁵ to the central gold atom. This weak donation that increases the electron densities on the nitrogen atoms may also play a role in the observed red shift of the nitrogen K $\rightarrow \pi^*$ transition energy.

The nitrogen K $\rightarrow \pi^*$ transition energy was observed to shift from 401.0 eV to 399.7 eV after the $\text{K}^+\text{Au}(\text{CN})_2^-$ adsorbed sample was treated with 18-crown-6. Complexation of the K^+ ion by 18-crown-6 means a positive ion is removed from around the $\text{Au}(\text{CN})_2^-$ ion. The increased steric factor caused by the distancing of the K^+ from the N atoms of cyanide also leads to a reduction of Au–Au interactions hence increasing back-donations. Both effects increase the electron densities around the nitrogen atoms thereby reducing the K $\rightarrow \pi^*$ transition energy of the pseudo-unpaired dicyanoaurate(I) created by crown ether treatment, which is located at the same position as that of adsorbed unpaired $\text{Au}(\text{CN})_2^-$.

The nitrogen K-edge XANES spectrum of dicyanoaurate(I) complexes adsorbed on the carbon surface from $\text{KAu}(\text{CN})_2$ solution at pH 7 is shown in Figure 6. Obviously it looks almost identical with that of pH 10, indicating that $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs are the dominant adsorbed gold species with a small amount of gold adsorbed as unpaired $\text{Au}(\text{CN})_2^-$. The adsorption of unpaired $\text{Au}(\text{CN})_2^-$ is significantly reduced at pH 2 as indicated by the much weaker shoulder before band A (see Figure 7). By analogy to the above assignment, band A is attributed to the adsorption of ion pairs that probably include both $\text{K}^+\text{Au}(\text{CN})_2^-$ and $\text{H}^+\text{Au}(\text{CN})_2^-$. A new feature arises after band A as a strong shoulder S, which is probably due to AuCN because adsorbed dicyanoaurate(I) is partly converted to an oligomer form of AuCN at pH < 4 as revealed by a Mössbauer study.³⁶

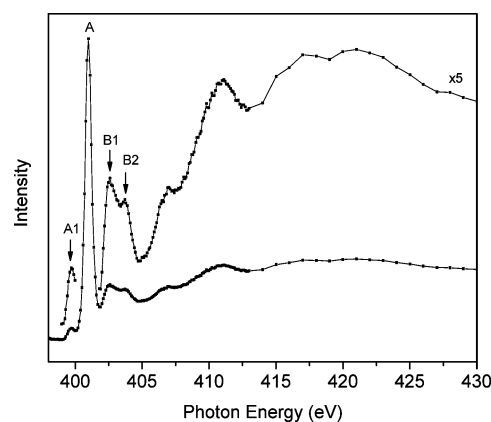


Figure 6. Nitrogen K-shell XANES spectrum of dicyanoaurate(I) adsorbed on the carbon surface from the $\text{KAu}(\text{CN})_2$ aqueous solution at pH 7.

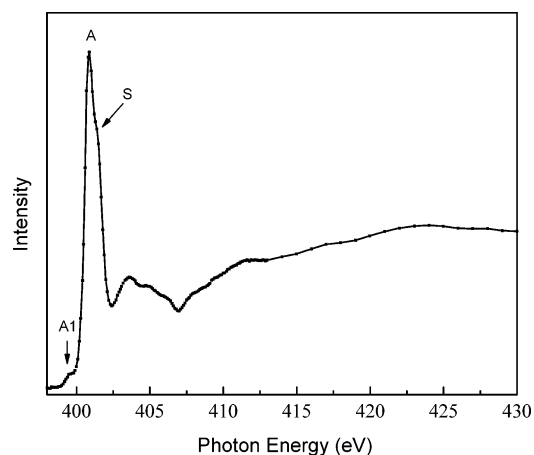


Figure 7. Nitrogen K-shell XANES spectrum of dicyanoaurate(I) adsorbed on the carbon surface from the $\text{KAu}(\text{CN})_2$ aqueous solution at pH 2.

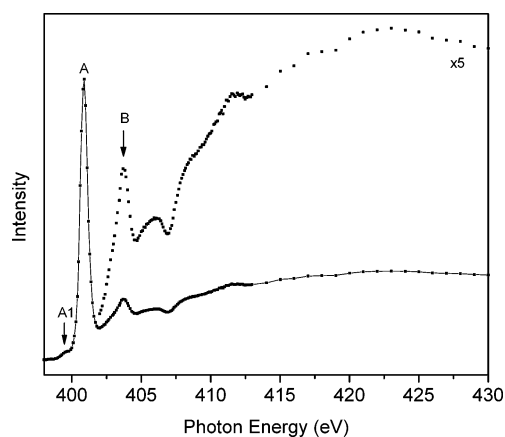


Figure 8. Nitrogen K-shell XANES spectrum of dicyanoaurate(I) adsorbed on the carbon surface from the $\text{KAu}(\text{CN})_2\text{--CaCl}_2$ ($\text{Ca}/\text{Au} = 30$) aqueous solution at pH 10.

Figure 8 shows the nitrogen K-shell XANES spectrum of the dicyanoaurate(I) complex adsorbed on the carbon surface from the $\text{KAu}(\text{CN})_2\text{--CaCl}_2$ ($\text{Ca}/\text{Au} = 30$) aqueous solution at pH 10. By comparing with the adsorption in the absence of CaCl_2 (see Figure 4), it can be seen that the addition of Ca^{2+} ions has changed the nitrogen K-shell excitation features. The sharp lowest energy band A at 401 eV is attributed to the adsorbed $\text{M}^{n+}[\text{Au}(\text{CN})_2^-]_n$ ion pairs (where M^{n+} is Ca^{2+} and K^+). The relative intensity of band A1 due to the adsorbed

unpaired $\text{Au}(\text{CN})_2^-$ decreases so significantly that the band nearly disappears from the spectrum. This indicates that the presence of Ca^{2+} ions has partly suppressed the adsorption of unpaired $\text{Au}(\text{CN})_2^-$. Simple electrostatic effects are very likely to be responsible for the higher affinity of the $\text{Au}(\text{CN})_2^-$ complex to Ca^{2+} ions than K^+ ions due to stronger attraction to a $2+$ ion. It has long been known² that the presence of Ca^{2+} ions in the medium can enhance the adsorption of gold cyanide species. The Ca^{2+} ions may be involved in the adsorption of dicyanoaurate(I) complexes as $\text{Ca}^{2+}[\text{Au}(\text{CN})_2^-]_2$ ion pairs, which in turn reduced the concentration of unpaired $\text{Au}(\text{CN})_2^-$.

The nature of the adsorbed dicyanoaurate(I) species on carbon depends on the pH and the coverage. The above discussion has shown that at alkaline and neutral pH regions, dicyanoaurate(I) is adsorbed mainly as $\text{M}^{n+}[\text{Au}(\text{CN})_2^-]_n$ ion pairs. A small amount of gold is also adsorbed as unpaired $\text{Au}(\text{CN})_2^-$ ions. Under acidic condition, the adsorbed species partly exists as AuCN . The current findings are in good agreement with previous studies^{14,15} which showed that at neutral and alkaline pH dicyanoaurate(I) is adsorbed as unpaired $\text{Au}(\text{CN})_2^-$ ions at low coverage and mainly as ion pairs at high coverage. It was also reported³⁶ that at neutral and alkaline pH both $\text{Au}(\text{CN})_2^-$ ions and $\text{M}^{n+}[\text{Au}(\text{CN})_2^-]_n$ ion pairs are adsorbed, whereas at acidic pH the oligomer form of AuCN is the dominant species on the carbon surface.

Concluding Remarks

This study provides for the first time direct evidence for the adsorption of $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs on the carbon surface, which has puzzled researchers for many years. A novel approach was employed by treating the adsorbed dicyanoaurate(I) with crown ether 18-crown-6, which has a strong affinity for K^+ ions, followed by analysis with nitrogen K-edge XANES spectroscopy. The experiment was designed based on the finding that if K^+ ions are coadsorbed as $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs, their complexation by 18-crown-6 will result in a perturbation of the nitrogen K-shell excitations which are sensitive to the chemical environment and can be detected by XANES. The adsorbed dicyanoaurate(I) shows similar nitrogen K-edge excitation features to those in solid $\text{KAu}(\text{CN})_2$. In this study, nitrogen $\text{K} \rightarrow \pi^*$ transition energy is used to identify the adsorbed species. The results show that dicyanoaurate(I) complexes are adsorbed predominantly as $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs with the remaining small amount as unpaired $\text{Au}(\text{CN})_2^-$ ions from $\text{KAu}(\text{CN})_2$ aqueous solution under neutral and alkaline conditions. The adsorption of unpaired $\text{Au}(\text{CN})_2^-$ ions is partly suppressed in the presence of Ca^{2+} ions or in acidic medium. The nitrogen $\text{K} \rightarrow \pi^*$ transition energy of dicyanoaurate(I) decreases from 401.3 eV ($\text{KAu}(\text{CN})_2$ solids) to 401.0 eV upon adsorption as $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs and further to 399.7 eV for unpaired $\text{Au}(\text{CN})_2^-$ ion adsorption. The red shifts of the nitrogen $\text{K} \rightarrow \pi^*$ transition energies are due to the increased electron densities on nitrogen atoms of the dicyanoaurate(I) complexes. The adsorption of $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs probably results in decreased Au–Au association compared with the $\text{KAu}(\text{CN})_2$ solid, which increases π -back-donation from metal centers to the cyanide ligands and the electron densities on the nitrogen atoms as a result. The treatment of adsorbed $\text{K}^+\text{Au}(\text{CN})_2^-$ ion pairs with 18-crown-6, which complexes the K^+ ions, creates

some pseudo-unpaired $\text{Au}(\text{CN})_2^-$ ions whose lowest nitrogen $\text{K} \rightarrow \pi^*$ transition energy is located at the same position (399.7 eV) as that of the adsorbed unpaired $\text{Au}(\text{CN})_2^-$ ions. The significant red shift of the nitrogen $\text{K} \rightarrow \pi^*$ transition energy upon complexation of K^+ by 18-crown-6 is due to the increased electron densities of nitrogen atoms in $\text{Au}(\text{CN})_2^-$ ions.

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