

# X-ray Absorption Spectroscopy Study of the In-Solution Structure of $\text{Ni}^{2+}$ , $\text{Co}^{2+}$ , and $\text{Ag}^+$ Solvates in Acetonitrile Including Multiple Scattering Contributions

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An X-ray absorption spectroscopy study of the in-solution structures of the acetonitrile solvates of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ag}^+$  cations has been performed. For the first two cations an octahedral arrangement of the acetonitrile molecules around the central metal atom has been found, while in the case of the  $\text{Ag}^+$  a tetrahedral arrangement has been found. In all cases the acetonitrile molecules were bonded to the central cation through the nitrogen atom at distances  $R(\text{Co}^{2+}-\text{N}) = 2.11 \text{ \AA}$ ,  $R(\text{Ni}^{2+}-\text{N}) 2.07 \text{ \AA}$ ,  $R(\text{Ag}^+-\text{N}) = 2.27 \text{ \AA}$ . The unusual high amplitude of the second peak in the radial distribution function, corresponding to the carbon atom of the cyanide group, for the three studied solvates, indicated that the angle formed by  $\text{M}-\text{N}-\text{C}$  was very close to  $180^\circ$ . The quantitative analysis of the most intense multiple scattering contributions among those involving N atoms, C atoms from the cyanide group and C atoms from the methyl group provided values of  $\text{M}^{n+}-\text{C}_1$  and  $\text{M}^{n+}-\text{C}_2$  coordination distances as well as an estimate of coordination angles.

## Introduction

Acetonitrile is one of the organic solvents most widely used in chemical synthesis where it is normally used as the solvent media. Nevertheless, in some cases it forms stable solvates that are often used as precursors for coordination and organometallic compounds. For this reason, a large amount of acetonitrile solvates have been synthesized following their first report by Henke<sup>1</sup> in 1851. For some of them, the solid-state structure has been solved by X-ray diffraction, but since most of the reactions involving these solvates take place in the liquid state, it is important to have some knowledge about the structure of these solvates in solution to assist in the understanding of their behavior and reactivity.

X-ray absorption spectroscopy (XAS) has been shown to be a suitable technique for the study of the structure of ions dissolved in aqueous and nonaqueous solvents, since it enables us to probe the local coordination of ions in solution.<sup>2</sup> In the nonaqueous solvents, the number of correlation functions can be restricted to those involving a given atom (the absorbing one). Moreover, whereas pair correlation functions can be obtained as well by X-ray and neutron diffraction, information about higher order correlation functions, related with multiple scattering phenomena, can only be extracted from the XAS data. Although the amplitude of the high order correlation functions is often much smaller than that of the pair correlation functions, the multiple scattering processes responsible for them might appear enhanced in some cases. For instance, if a linear arrangement is adopted by the scattering atoms around the absorbing center,<sup>3,4</sup> as is the case in some nonaqueous solvates. The obvious interest of the analysis of these functions is that it

provides not only radial distribution functions of the coordinating atoms with respect to the absorbing one but also the polyhedral arrangement of the solvent molecules with respect to the metal.

Given the capabilities of the technique and the complexity of the acetonitrile solvates, in this paper we address the study of the solvation structure of two divalent cations in acetonitrile solution,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ , and one monovalent cation,  $\text{Ag}^+$ , by Extended X-ray Absorption Fine Structure spectroscopy, EXAFS.

Previous UV-vis<sup>5,6</sup> studies performed for the divalent cations pointed to the existence of octahedral complexes, a coordination geometry also confirmed by means of a proton NMR<sup>7</sup> study of a solution of  $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{ClO}_4)_2$  in acetonitrile. This geometry was also found in an X-ray absorption study of a solution of  $\text{Ni}^{2+}$  cations in acetonitrile, which provided a value for the  $\text{Ni}^{2+}-\text{N}$  distance of  $2.07 \text{ \AA}$ .<sup>8</sup> Similarly, in a X-ray diffraction study of the crystalline compound  $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{SbF}_6)_2$ , the basic units were octahedral arrangements of solvent molecules around the nickel cation being the  $\text{Ni}^{2+}-\text{N}$  distances  $2.075(3) \text{ \AA}$ .<sup>9</sup> NMR studies of  $\text{Co}^{2+}$  acetonitrile solutions pointed as well to octahedral coordination,<sup>10</sup> this geometry was confirmed by an X-ray absorption study in acetonitrile solution which provided a value of  $2.11 \text{ \AA}$  for the  $\text{C}-\text{N}$  distance.<sup>11</sup>

The solvation structure of silver cations has been studied by XRD, X-ray absorption spectroscopy, and ab initio theoretical calculations.<sup>12,13</sup> These studies pointed to a tetrahedral arrangement of the acetonitrile molecules around the silver cation. In studies of crystalline  $[\text{Ag}(\text{CH}_3\text{CN})_4]\text{ClO}_4$  by XRD, a tetrahedral environment around the cation site was identified, with distances  $\text{Ag}^+-\text{N}$  ranging from  $2.18$  to  $2.33 \text{ \AA}$ , the average distance being  $2.26 \text{ \AA}$ .<sup>13</sup> In the absorption studies the  $\text{Ag}^+-\text{N}$  distances found varied from  $2.24$  to  $2.33 \text{ \AA}$ .<sup>12</sup>

However, other studies pointed to different coordination numbers (two or even three) coordination polyhedron (square planar or linear) or even different ways of bonding (in a lateral

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way, through the triple bond  $\text{C}\equiv\text{N}$ ).<sup>14–16</sup> Thus, a electron-spin echo modulation study of a  $\text{AgClO}_4$  solution in acetonitrile indicated that the solvation structure was formed by four acetonitrile molecules bonded to  $\text{Ag}^+$  ion in a square-planar configuration in a side-on fashion, with their molecular dipoles oriented perpendicular to the plane, being the estimated distance from the silver cation to the center of the  $\text{C}\equiv\text{N}$  bond 2.3 Å.<sup>16</sup>

In none of the absorption works above-mentioned the analysis of the EXAFS signals goes beyond the first shell formed by nitrogen atoms. The lack of information about higher coordination shells for these acetonitrile solvates, as well as the controversy concerning coordination distance and geometry for the silver cation, compelled us to measure and analyze the EXAFS spectra of these three systems, taking into account the single scattering contributions and the multiple scattering ones originated by the linear or quasi-linear arrangement of the atoms from the acetonitrile molecule with respect to the central cation. Results obtained from the analysis of the first coordination shell of nitrogen atoms are consistent with those previously obtained for related systems. Moreover, the analysis of the higher shells which correspond to carbon atoms has allowed for the determination of the polyhedral environment of the acetonitrile molecules around the central cations, as well as the manner in which solvent molecules are bonded to the metal, information not available until now.

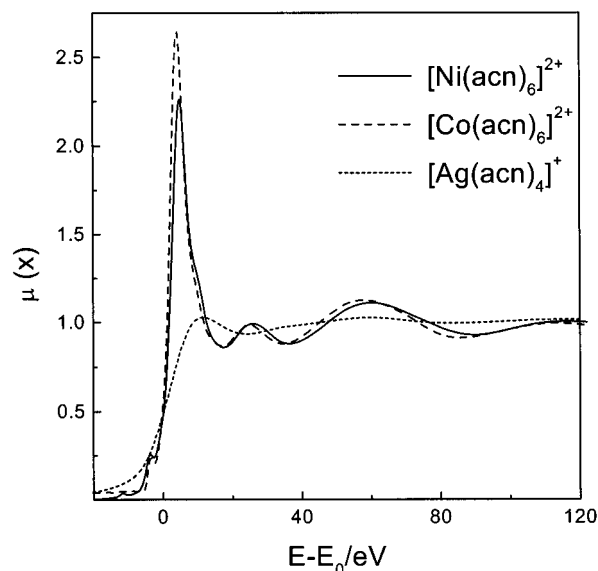
## Experimental Section

**(a) Sample Preparation.** To prepare the nickel solvate,  $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{Br}_3)_2$ , 2 g of Ni powder (Aldrich Chem Co.) was reacted with 2 mL of bromine (Aldrich Chem Co.) in 15 mL of dry acetonitrile (Aldrich Chem Co.) under an inert atmosphere. The hot solution was filtered, and on cooling, crystals of the acetonitrile solvate precipitated. These were then filtered, washed with acetonitrile and dried under vacuum.<sup>5</sup> The compound was identified by IR spectroscopy. A 0.2 M solution was prepared by dissolving the required amount of the synthesized solid compound in dry acetonitrile.

In the case of the preparation of  $[\text{Co}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ , 1 g of Co powder (Aldrich Chem Co.) was reacted with 4 g of nitrosyl tetrafluoroborate (Aldrich Chem Co.) in 40 mL of dry acetonitrile (Aldrich Chem Co.) for several hours under an inert atmosphere. The orange-red solution was filtered and then evaporated to dryness under vacuum. The solid powder obtained was dissolved in a minimum quantity of hot acetonitrile, and hot ethyl acetate was added until the solution became cloudy. On cooling to  $-20^\circ\text{C}$ , orange crystals of the acetonitrile solvate settled, and then were filtered and dried under vacuum.<sup>6</sup> The compound was identified with the aid of the IR spectroscopy. A 1.0 M solution was prepared by dissolving the required amount of the synthesized solid compound in dry acetonitrile.

The 1.0 M acetonitrile solution of  $[\text{Ag}(\text{CH}_3\text{CN})_4]^+$  was prepared from  $\text{AgNO}_3$  salt (Aldrich Chem Co.), by dissolving the required amount in dry acetonitrile.<sup>12c</sup>

**(b) EXAFS Measurements and Data Analysis.** The K-edge X-ray absorption spectra of the  $\text{Ag}^+$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  acetonitrile solutions were measured at Daresbury Laboratory Synchrotron Light Source (U.K.), which was operating with a ring current of 250 mA and energy of 2.0 GeV. The Co and Ni K edges (at 7705 and 8333 eV) were measured at Station 8.1, using double crystal Si(111) and Si(220) monochromators, respectively, and higher harmonic rejection was carried out by detuning both crystals. Energy calibration was carried out using a cobalt foil. The Ag K edge (25514 eV) was measured at beamline 9.2, using a channel cut Si(220) monochromator. In this case, higher



**Figure 1.** Normalized XANES region of the K edge absorption spectra of the solvates of  $\text{Ni}^{2+}$  0.2 M (solid line),  $\text{Co}^{2+}$  1.0 M (dashed line) and  $\text{Ag}^+$  1.0 M (dotted line) in acetonitrile solution.

harmonics contamination was not significant. Energy calibration was achieved with a silver foil. The estimated energy resolution was 1.5 eV for Ni and Co K edges (as determined by the width of the small preedge peak) and 3 eV for Ag K edge (as determined by the sharper white line of the aqueous solution spectra).

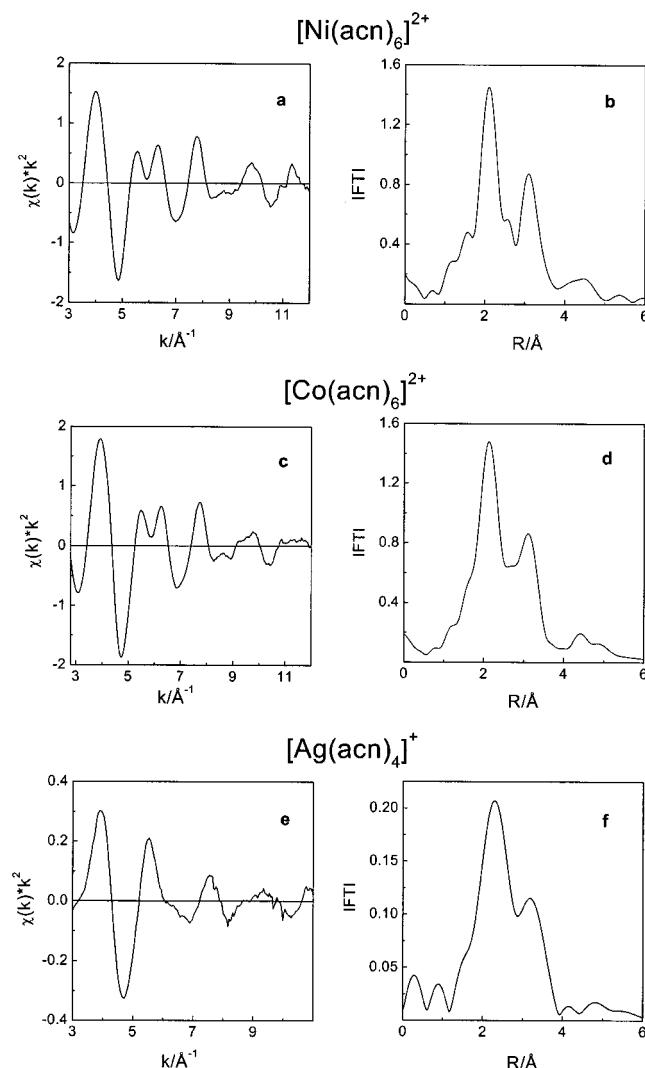
All data were collected at room temperature, in transmission mode in specially designed cell allowing for variable X-ray path lengths.<sup>17</sup> This was necessary for optimization of the absorption edge jump for each solution. Ion chambers, filled with a He/Ar gas mixture and optimized to absorb 20% of the beam intensity in  $I_0$  and 80% in  $I_t$ , were used as detectors. Counting time was evenly increased through the recording of each scan, starting with 1 s at the beginning of the EXAFS region, and finishing with 8 s at  $k = 14 \text{ \AA}^{-1}$ . Several scans were averaged to improve the signal-to-noise ratio.

The EXAFS functions  $\chi(k)$  were obtained from the X-ray absorption spectra by subtracting a Victoreen curve followed by a cubic spline background removal using the program XDAP,<sup>18</sup> and normalizing to the height of the measured absorption edge.  $E_0$  was defined as the maximum of the first derivative of the absorption edge.

To analyze the EXAFS spectra of the three solvates, in a first step an ab initio calculation of the contributions to the EXAFS signal of each scattering path, either single or multiple, were made using the FEFF 7.00 code.<sup>19</sup> The mean square displacement value,  $\sigma^2$ , was set equal to zero for all the paths in the three systems studied, while the amplitude reduction factor,  $S_0^2$ , was set equal to 1.0. A plane wave amplitude filter was used, according to which only paths with amplitude equal to or higher than 4% of the most intense path were taken into account. The EXAFS signals calculated for the paths thus obtained were used to fit the experimental spectra using FEFFIT program (version 2.54), from the University of Washington.<sup>20</sup>

## Results

Figure 1 includes the normalized X-ray absorption near edge spectra (XANES) of the  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ag}^+$  solvates in acetonitrile solution, with concentrations 0.2 M for the nickel solution and 1.0 M for the other two cations. As can be seen,



**Figure 2.** (a, c, e)  $k^2$ -weighted EXAFS spectra of the solvates of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ag}^+$  in acetonitrile solution. (b, d, f) Magnitude of the Fourier transform,  $M$ - $N$  phase corrected, of the spectra included in the previous Figures.

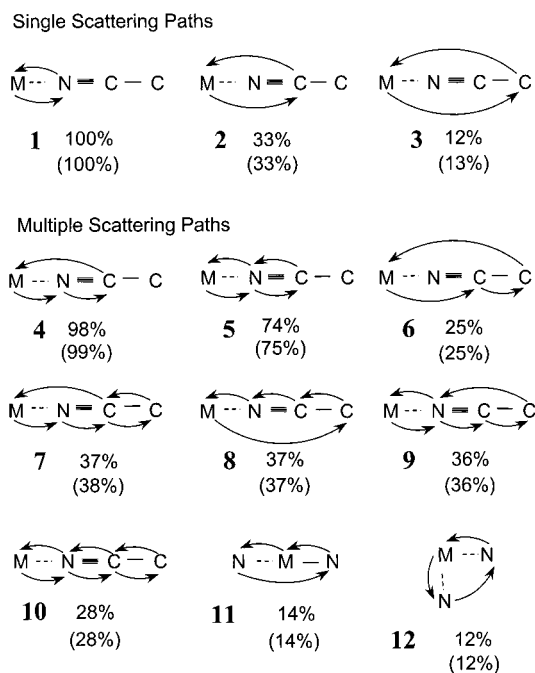
the spectra corresponding to  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  solvates are quite similar. The small differences between these two spectra can be attributed to the smaller ionic radius of  $\text{Ni}^{2+}$  cations, which cause different interatomic distances, rather than to a different chemical environment. This similarity between both spectra leads to the expected result that the chemical environment for  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  cations is very close, in parallel to the similar chemical behavior in acetonitrile solution.<sup>21</sup> In contrast, the XANES spectrum of the silver solvate differs largely from the other two. The considerable differences cannot be accounted for by the smaller energy resolution of the silver spectrum. This region of the absorption spectrum being very sensitive to the coordination environment, this cation must have a solvation structure different from that of the divalent cations.

Parts a, c, and e of Figure 2 show the EXAFS functions for the three cations studied. As in the XANES spectrum, the functions corresponding to  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  solvates are quite similar, whereas that corresponding to the  $\text{Ag}^+$  solvate differs significantly in features and amplitude of the signal (note the different scales used in Figure 2a–d and 2e–f). The complexity of the measured spectra indicates the presence of several frequency components, corresponding to a wide range of interatomic distances.

Parts b, d, and f of Figure 2 show the magnitude of the phase corrected  $k^2$ -Fourier transforms of the EXAFS waves. The intense first peak, observed at around 2.0 Å for  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  solvates and at around 2.3 Å for the  $\text{Ag}^+$  solvate, is attributable to the nitrogen atom of the acetonitrile molecule. A second peak, appearing at about 3.0 Å in the case of the  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  systems and at 3.2 Å for the  $\text{Ag}^+$  solution, can be assigned to the carbon atom of the cyanide group of the acetonitrile molecule. The amplitude of this peak is rather large in all cases, which is surprising taking into account that it is a contribution of the same number of atoms as for the first peak, the backscatter is a light atom, carbon, and the distance at which the maximum appears is approximately 1 Å larger than that of the first peak. This unusually high amplitude can be due to the enhancement of the multiple scattering contributions observed when two or more backscatter atoms are aligned with the absorbing one.<sup>3,4</sup> Subsequently in the analysis of the EXAFS spectra of these systems, a linear arrangement of the acetonitrile molecules with the central cation was considered in a first approach. An additional smaller contribution between 4.0 and 5.0 Å observed in the  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  spectra (Figure 2b,d) could tentatively be assigned to the carbon atom belonging to the methyl group of the acetonitrile molecule.

**(a)  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  Acetonitrile Solvates Analysis.** Taking into account previous results of related systems,<sup>5–11</sup> an octahedral configuration of the acetonitrile molecules around the central cation was considered to calculate the significant contributions to the absorption spectra. Likewise, considering the high amplitude of the second peak in the FT, a linear arrangement of the nitrogen and carbon atoms was assumed and, in a first approach, only N and C atoms from the cyanide group were taken into account. Since no good reproduction of the experimental data was obtained, C atoms from the methyl group were included as well. The model structures used were built considering a perfect symmetric octahedral distribution of acetonitrile molecules around  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  cations, with the Ni–N distance equal to 2.08 Å, Co–N 2.09 Å, N–C<sub>1</sub> 1.15 Å, and C<sub>1</sub>–C<sub>2</sub> 1.46 Å.<sup>21</sup> (See Table 1S in Supporting Information as a model FEFF input file for the  $\text{Co}^{2+}$ –acetonitrile solvate). For this structure and using the amplitude filter described above (equal to or higher than 4% of the most intense path) and considering those paths whose maximum effective distance is equal to or minor than 4.8 Å, 24 paths were obtained: three of them corresponded to the single scattering contributions and the rest to multiple scattering contributions. Figure 3 includes a scheme of the single scattering paths and some of the multiple scattering paths used in the analysis of the spectra, showing their respective intensities for zero mean square displacements,  $\sigma^2 = 0.0$ , for the  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  (in brackets) solvates. Among the multiple scattering paths included in the figure, the first three (paths 4–6) correspond to the classical focusing effect due to the forward scattering of two neighbor atoms aligned with the absorbing one, described in several studies.<sup>3,4,22</sup> Other paths (7–10) showing high amplitude are those corresponding to the forward scattering processes involving three scatterer atoms aligned with the absorbing one. This arrangement, not as frequent as the previous one, neither in solid compounds nor in dissolved molecular species, has been observed by some authors,<sup>4,23</sup> causing the so-called “superfocusing” effect.<sup>24</sup> The contribution from the first coordination shell involving N–M–N chains (path 11) does not have negligible amplitude. It is similar to that found in tetrahalides<sup>25</sup> and aquo complexes,<sup>26</sup> where an additional contribution from the second hydration shell<sup>27,28</sup> overimposes to it, enhancing the appearance of a second peak





**Figure 3.** Single scattering paths and most significant multiple scattering paths for the Ni<sup>2+</sup> and Co<sup>2+</sup> acetonitrile solvates in an octahedral configuration. The number and type of legs are indicated, as well as the amplitudes compared to that of the first shell for zero Debye–Waller factors (values for the Co<sup>2+</sup> solvate in brackets).

at high  $R$  in the FT spectrum. Five of the considered paths include nonaligned atoms, e.g., path 12, with significant amplitudes as well.

Because of the high number paths, 24, that had to be included in the fit, the number of free parameters in the analysis of the spectra was rather high. To reduce them, an *independent vibration approximation model*<sup>29,30</sup> was considered. This model has shown to be useful in related systems.<sup>4b,27b</sup> According to it, the Debye–Waller factors for some of these multiple scattering paths were not treated as free parameters. Rather they were defined as functions of the Debye–Waller factors found for the single scattering paths to the nitrogen atom,  $\sigma_1^2$ , and the carbon atoms of the cyanide and the methyl groups,  $\sigma_2^2$  and  $\sigma_3^2$ , respectively. Then the Debye–Waller factor for the paths 4 and 5 are the same as for the single scattering path 2. In the same way, the Debye–Waller factors for paths 6–10 is the one found for path number 3. In the case of path number 11, there is not a simple relationship between the Debye–Waller factor corresponding to this path and the Debye–Waller factor of the paths of single scattering, but in the range of medium to high temperature its value is approximately twice that of the single scattering path number 1.<sup>29</sup> When this *noncorrelated motion model* is taken into account, only 16 paths show a Debye–Waller factor small enough to yield significant EXAFS contributions. The other paths have got large DW values, and their contribution to the EXAFS signal is thus negligible.<sup>30,31</sup>

In this way, only *seven free parameters* need to be considered in the fitting procedure. The inner potential correction,  $\Delta E_0$ , the Debye–Waller factors for paths 1, 2 and 3,  $\sigma_1^2$ ,  $\sigma_2^2$  and  $\sigma_3^2$ , respectively, and the respective interatomic distances M–N, M–C<sub>1</sub> and M–C<sub>2</sub>, C<sub>1</sub> being the carbon of the cyanide group and C<sub>2</sub> that of the methyl group. Once the relevant scattering paths were selected, the experimental spectra were fit using FEFFIT program.<sup>20</sup> Fitting was carried out in  $R$  space between 1.0 and 4.8 Å, with a  $k^2$ -weighting.

**TABLE 1: Best Fit Parameters Obtained from the Analysis of the EXAFS Spectra of the Acetonitrile Solvates of Indicated Concentration<sup>a</sup>**

	0.2 M [Ni(acn) <sub>6</sub> ] <sup>2+</sup>	1.0 M [Co(acn) <sub>6</sub> ] <sup>2+</sup>	1.0 M [Ag(acn) <sub>4</sub> ] <sup>+</sup>
$\Delta E_0$ (eV)	$5.5 \pm 0.9$	$3.9 \pm 1.1$	$4.7 \pm 0.7$
$\sigma_1^2$ (M–N) (Å <sup>2</sup> )	$0.0051 \pm 0.0005$	$0.0053 \pm 0.0008$	$0.0136 \pm 0.0007$
$\sigma_2^2$ (M–C <sub>1</sub> ) (Å <sup>2</sup> )	$0.009 \pm 0.001$	$0.009 \pm 0.001$	$0.022 \pm 0.002$
$\sigma_3^2$ (M–C <sub>2</sub> ) (Å <sup>2</sup> )	$0.011 \pm 0.003$	$0.011 \pm 0.004$	
$R$ (M–N) (Å)	$2.07 \pm 0.007$	$2.11 \pm 0.009$	$2.27 \pm 0.006$
$R$ (M–C <sub>1</sub> ) (Å)	$3.21 \pm 0.01$	$3.24 \pm 0.02$	$3.36 \pm 0.02$
$R$ (M–C <sub>2</sub> ) (Å)	$4.68 \pm 0.03$	$4.71 \pm 0.03$	
$r$	0.018	0.035	0.007
$\chi^2_{\text{red}}$	561.82	1489.28	91.56

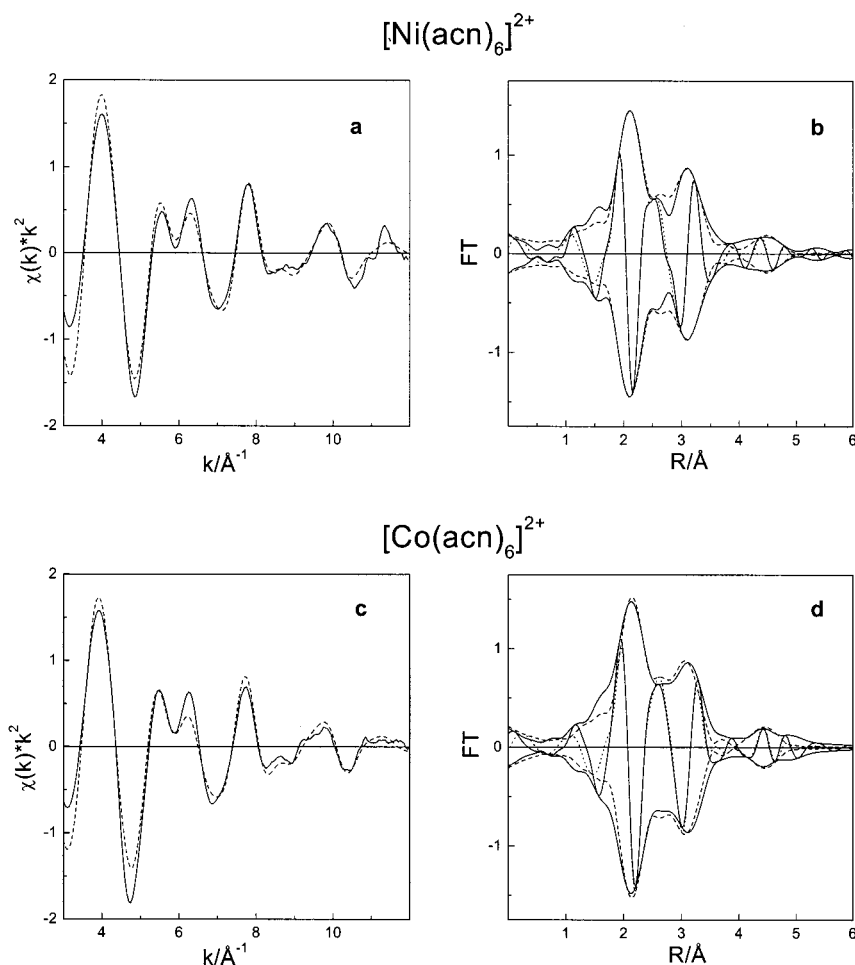
<sup>a</sup>  $\Delta E_0$ : inner potential correction.  $\sigma_n^2$ : Debye–Waller factors.  $R$ : coordination distances.  $r$  and  $\chi^2_{\text{red}}$ : goodness of fit parameters (see ref 20). Ni, Co K edge:  $\Delta k = 3\text{--}12 \text{ Å}^{-1}$ ;  $\Delta R = 1.0\text{--}4.8 \text{ Å}$ ;  $k^2$ . Ag K-edge:  $\Delta k = 3\text{--}11 \text{ Å}^{-1}$ ;  $\Delta R = 1.0\text{--}4.0 \text{ Å}$ ;  $k^2$ .

In the course of the data analysis procedure, the sensitivity of the refined model structures to the angle formed by the acetonitrile ligands and the central cation were tested. The distances M–N, M–C<sub>1</sub> and M–C<sub>2</sub>, as well as the angle between the vectors M–N and N–C<sub>1</sub>–C<sub>2</sub> were taken as fitting parameters. The acetonitrile molecule was modeled as a linear molecule, i.e., with N–C<sub>1</sub>–C<sub>2</sub> collinear, and the distances N–C<sub>1</sub> and C<sub>1</sub>–C<sub>2</sub> were taken as the average distances determined from the crystallographic measurements, 1.15 and 1.46 Å, respectively.<sup>21</sup> In all the tested cases the results indicate that there are insufficient constraints provided by the data to determine the angular value accurately. Satisfactory values were found to range from 160° to 180°.

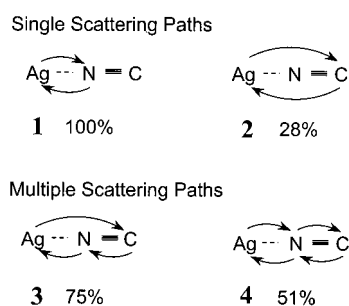
The parameters obtained for the best fits for the Ni<sup>2+</sup> and Co<sup>2+</sup> solvates in acetonitrile are given in Table 1. As seen there, good fits are obtained with closely similar sets of structural parameters, the main difference being the slightly higher values of the distances found for the Co<sup>2+</sup> solvate, which is expected taking into account the higher ionic radius of the Co<sup>2+</sup> cation as compared with the Ni<sup>2+</sup> one. Comparative plots of the calculated and the experimental EXAFS spectra for Ni<sup>2+</sup> solvate, in  $k$  and  $R$  space, are shown in Figure 4a,b, while those corresponding to Co<sup>2+</sup> solvate spectra are included in Figure 4c,d. As can be seen in the figure, in both cases the fits reproduce reasonably the experimental spectra with the exception of the small sharp feature appearing in the experimental spectrum of Ni<sup>2+</sup> solvate at 11.5 Å, probably an experimental artifact, since it appears at the same energy in the spectra of other nickel-containing systems.

There are additional slight disagreements throughout the spectra of both cations, the most visible being that of the cobalt spectrum at around 6.5 Å. The main reason for these small disagreements are the constraints imposed to the system to reduce the number of free parameters to a minimum: only seven free parameters for a systems including 19 atoms, which initially yielded 24 potentially significant paths, from which the 8 paths showing the smaller amplitude were discarded. Moreover, the *independent vibration approximation model* gives the values of the Debye–Waller factors of several MS paths from those of the SS ones. Alternatively, the disagreements could be due to small deviations from the assumed value of 180° for the M–N–C angle.

**(b) Ag<sup>+</sup> Acetonitrile Solvate Analysis.** The studies concerning Ag<sup>+</sup> solution chemistry have long pointed out the lower coordination number for this cation.<sup>12–16</sup> Thus, in a first approach, the structure used was a tetrahedral distribution of acetonitrile molecules surrounding the silver cation through the nitrogen atom in a linear arrangement. In this case only N and C atoms from the cyanide group were required. The value of



**Figure 4.** (a, c) Raw EXAFS data,  $k^2$ -weighted, of the  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  acetonitrile solvates: experimental function (solid line) and fit obtained by using the parameters included in Table 1 (dashed line). (b, d) M-N phase corrected Fourier transform of the EXAFS spectra included in Figure 4a and 4c. Magnitude: experimental (solid line); best fit (dashed line). Imaginary part: experimental (solid line); best fit (dotted line).



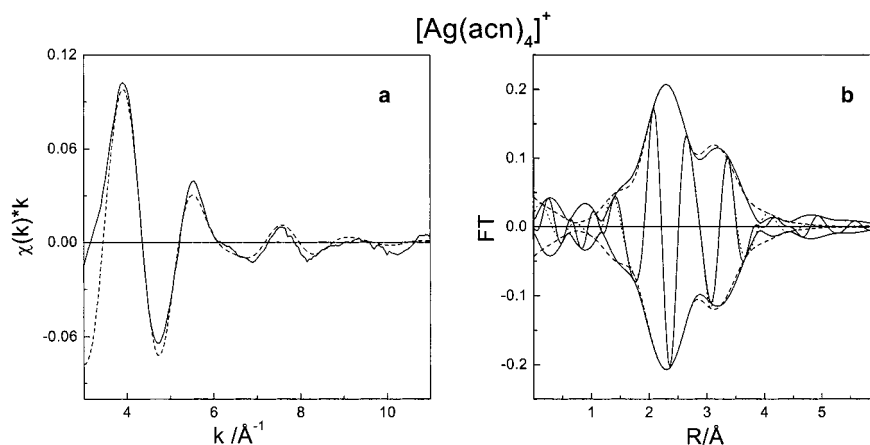
**Figure 5.** Scattering paths calculated for the  $\text{Ag}^+$  acetonitrile solvate in a tetrahedral configuration. The number and type of legs are indicated, as well as the amplitudes compared to that of the first shell for zero Debye-Waller factors.

Ag-N distance used in the FEFF input file was 2.35  $\text{\AA}$ , while as in the  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  solvate analysis, the value of N-C<sub>1</sub> was 1.15  $\text{\AA}$ . Using the amplitude filter above-mentioned and considering those paths whose maximum effective distance is equal to or minor than 3.5  $\text{\AA}$ , the four paths included in Figure 5 were obtained, two corresponding to single scattering paths and the other two to multiple scattering ones. A smaller number of paths is obtained for this cation when compared to  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  solvates because the carbon atom corresponding to the methyl group was not included and, moreover, the tetrahedral environment considered in this system rendered the angle N-Ag-N much smaller than 180°, and consequently, the

amplitude of the paths involving this string of atoms was in fact negligible.

As in the previous cases, the *independent vibration approximation* model was considered to estimate DW factors of the multiple scattering paths. Thus, the Debye-Waller factor used for paths 3 and 4 was the same that used for path 2. According to this approximation, *five variables* were used in the analysis. The internal potential correction,  $\Delta E_0$ , the Debye-Waller factors for paths 1 and 2,  $\sigma_1^2$  and  $\sigma_2^2$ , and the coordination distances Ag-N and Ag-C. As in the case of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ , the fitting procedure was carried out in  $R$  space between 1.0 and 4.0  $\text{\AA}$  with  $k^2$ -weighting. The parameters obtained for the best fit are included in Table 1. As can be seen in Figure 6, which includes comparative plots of the calculated and the experimental EXAFS spectrum for  $\text{Ag}^+$  acetonitrile solvate in  $k$  and  $R$  spaces, the fitted spectrum reproduces the experimental one fairly well.

Because of the controversy found in the literature concerning the coordination environment of silver cations, additional structures were used to calculate the contributions to the spectrum of this solvate. Thus, calculations considering a linear arrangement of two acetonitrile molecules, or a square planar geometry of four acetonitrile molecules around the central cation were carried out, but none of them yielded good fits. The lateral coordination of the acetonitrile molecule was rejected due to the high amplitude of the second peak in the Fourier transform of the spectrum.



**Figure 6.** (a) Raw EXAFS data,  $k$ -weighted, of the  $\text{Ag}^{+}$  acetonitrile solvate: experimental function (solid line) and fit obtained by using the parameters included in Table 1 (dashed line). (b) Ag–N phase corrected Fourier transform of the EXAFS spectra included in Figure 6a. Magnitude: experimental (solid line); best fit (dashed line). Imaginary part: experimental (solid line); best fit (dotted line).

## Discussion

Concerning the first coordination shell and given the quality of the fits obtained by using the octahedral structure for the  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  acetonitrile solvates, we conclude that the solvation structure of these two cations is formed by six acetonitrile molecules in an octahedral arrangement, thus confirming previous results from UV–vis<sup>5,6</sup> and NMR<sup>7,10</sup> spectroscopies. For the  $\text{Ni}^{2+}$  solvate, N atoms from acetonitrile molecules are located at 2.07 Å from the central cation whereas for the  $\text{Co}^{2+}$  solvate, acetonitrile molecules are located at 2.11 Å from the central cation. The same values were found by Inada and Funahashi in two XAS studies<sup>8,11</sup> of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  cations in acetonitrile solution. Similarly, in a XRD study of the crystalline compound  $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{SbF}_6)_2$  the reported value for  $\text{Ni}^{2+}$ –N coordination distance was 2.07 Å.

The differences here found between the values of  $\text{M}^{2+}$ –N coordination distances, run parallel to the differences between their effective ionic radius, 0.69 and 0.75 Å for  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ , respectively.<sup>32</sup> It is worth noting that the distance  $\text{M}^{2+}$ –N found in a XAS study for the bulkier  $\text{Mn}^{2+}$  (effective ionic radius = 0.83 Å) in acetonitrile solution, is 2.21 Å,<sup>33</sup> larger than the values obtained for the cations here studied. Debye–Waller factors for  $\text{M}^{2+}$ –N contributions found for these three cations follow a similar trend, the smallest one is that of  $\text{Ni}^{2+}$ –N, 0.0051 Å<sup>2</sup> (see Table 1) and the largest is that of  $\text{Mn}^{2+}$ –N, 0.0067 Å<sup>2</sup>.<sup>33</sup> Similar differences in coordination distances have been found between these cations in a XAS study of the solvation structure in several oxygen-coordinating solvents,<sup>34</sup> and by XAS, ND, and XRD in their hydration structures.<sup>35</sup>

For the  $\text{Ag}^{+}$  cation the analysis performed shows that the first shell solvation structure in acetonitrile solution is formed by four solvent molecules located in a tetrahedral arrangement, thus discarding alternative coordination.<sup>14–16</sup> These acetonitrile molecules are placed in a linear manner with respect to the central cation, as deduced from the good fit obtained for the studied spectrum, the  $\text{Ag}^{+}$ –N distance found is 2.27 Å, a value within the range of previous reports (2.24–2.33 Å), whereas the DW factor for this interaction, much weaker than those found in the divalent cations solvates, is twice as big as the previous ones, 0.013 Å<sup>2</sup>.

The high intensity of the second peak found in the Fourier transform of the spectra of these solvated cations pointed to a linear arrangement of acetonitrile molecules, which would emphasize MS effects, thus allowing the accurate analysis of the higher order correlation functions. This assumption was

confirmed by the quality of the fit assuming the aligned arrangement, and it has provided structural information not easily available for dissolved systems of nonaqueous solvents, i.e., coordination distances for the second and third coordination shells and rough estimates of coordinating angles. Thus, the distance from the  $\text{Ni}^{2+}$  cation to the carbon atom of the cyanide group is 3.21 Å whereas the distance to the carbon atom in the methyl group is 4.68 Å. Similarly, the  $\text{Co}^{2+}$ –C distance to the carbon atom of the cyanide group is 3.24 Å, and the distance to the carbon atom of the methyl group is 4.71 Å. The difference between the coordination distances of the two higher shells for both solvates,  $\Delta R = 0.03$  Å, is very similar to the difference between  $\text{M}^{2+}$ –N first shell coordination distance,  $\Delta R = 0.04$  Å, what confirms again the close similarity between the structure of both solvates, the main difference being the effective ionic radius of both cations.

Concerning the coordination angle formed by the solvent molecules and the central cation, as stated before, there are insufficient constraints provided by the data to determine its value accurately, and satisfactory values were found to range from 160° to 180°. Thus, the slight disagreements found between the experimental spectra and the fit in  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  spectra (see Figure 4) could be due to small deviations from the assumed value of 180°, such as that found in the crystalline compound  $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{SbF}_6)_2$ , where the Ni–N–C angle determined by means of XRD is 175.5(3)°.<sup>9</sup>

Within the series, the silver solvate shows a nonnegligible shortening in the N–C<sub>1</sub> distance of 0.04 Å with respect to the other two cations, calculated as the difference between metal–carbon and metal–nitrogen distances [ $\Delta R = R(\text{M}–\text{C}_1) - R(\text{M}–\text{N})$ ]. Two reasons may be envisaged for this trend. The first one is that the N–C<sub>1</sub> distance within acetonitrile molecules could be shorter in the  $\text{Ag}^{+}$  solvate. According to the donor–acceptor model of Gutman,<sup>36</sup> the stronger the intermolecular interaction, the larger the lengthening of the closest intramolecular bond is. In our case, it is clear that the interaction of acetonitrile molecules with divalent cations is stronger than that with the monovalent one, then the N–C<sub>1</sub> distance will become larger in the  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  acetonitrilated than in the  $\text{Ag}^{+}$  one. The second reason could be the nonlinear arrangement of acetonitrile molecules around  $\text{Ag}^{+}$  cations, a value of approximately 15° for the angle M–N–C<sub>1</sub> is compatible with the shortening in the M–C<sub>1</sub> distance. Ab initio calculations of the bonding properties of nitriles support this bending although no solvent effects were considered.<sup>37</sup> All these structural parameters

are compatible with the obtained values within the crystal structure of  $[\text{Ag}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ . A useful approach to identify the reason for the observed shortening is to obtain the pair and three body distributions functions of the investigated system from molecular dynamics calculations, as already done in the study of the solvation structure of  $\text{Sr}^{2+}$  cations in acetonitrile solutions, what allowed the accurate determination of the  $\text{M}^{2+}-\text{N}-\text{C}$  angle, which was equal to  $163^\circ$ .<sup>38</sup>

Once reasonable structures have been obtained from EXAFS analysis, a step beyond is to compute the XANES spectra to help in the refined analysis of the relative orientation of acetonitrile molecules, as well as to complete the electronic description of the solvated cations. Nevertheless, as shown in previous works,<sup>4b,39</sup> the importance of multiple scattering contributions in this type of structure makes particularly delicate this modeling; in addition, the cluster size to be considered could exceed the information on few shells and would compel to carry out computer simulations to give structural information beyond the first shell.

## Conclusions

The analysis of the EXAFS spectra for solvates of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ag}^+$  in acetonitrile solution shows the importance of multiple scattering contributions in the determination of the second and higher shell structure in nonaqueous solvents. These MS contributions are emphasized in paths that involve chain of aligned atoms, causing the focusing and superfocusing effects.

For  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  acetonitrile solvates, the octahedral environment previously proposed as well as the  $\text{Ni}^{2+}-\text{N}$  and  $\text{Co}^{2+}-\text{N}$  distances of 2.07 and 2.11 Å, have been confirmed. From the analysis of the MS contributions we can conclude that the acetonitrile ligands are bound forming an angle close to  $180^\circ$  with respect to the metal ion. The  $\text{Ag}^+$  acetonitrile solvate is formed by four solvent molecules at 2.27 Å in a tetrahedral environment with a linear arrangement as well, although a slightly bent arrangement is compatible with the obtained results.

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**Supporting Information Available:** Input file for FEFF code (Table 1S). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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