The Use of Differential EXAFS Analysis for the determination of Small Structural Differences between two closely-related Ruthenium Complexes

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Abstract. X-ray Absorption Spectroscopy (XAS) is a sensitive and powerful technique in revealing the structure of a material, providing as well high accuracy on interatomic distances. Nevertheless, when dealing with systems that differ only by small structural features, a standard data analysis might be unable of discriminating between such differences. A differential approach was proposed by Bressler, Chergui, and co-workers [2003, Phys. Rev. Lett. 90, 047403][2006, J. Phys. Chem B, 110, 14035][2009 Angew. Chem., Int. Ed. 48 2711] to solve this problem and differentiate between excited and unexcited state structures during pump-and-probe transient XAS experiments. In this contribution, we apply the differential data analysis procedure to the study of two closely-related molecular complexes, namely cis-[Ru(bpy)_2(py)_2]^2+ and cis-[Ru(bpy)_2(py)(H_2O)]^2+, characterized under static conditions. It is herein demonstrated that the method, based on a direct fit of differential curves, is able to reveal the small differences present between the two structures which, conversely, could not be resolved by standard EXAFS fitting of full spectra.

1. Introduction

A major challenge for X-ray spectroscopy is to improve sensitivity and accuracy in order to increase the capability to discriminate minimal differences between similar structures. In the case of EXAFS spectroscopy, the quality of the experimental data reached nowadays allows to obtain structural parameters with accuracy up to 0.01 Å (if the experimental energy range, number of points and acquisition time are properly selected to obtain the best signal to noise ratio). Nevertheless, when dealing with complex structures (where the distribution of atoms around the absorbing atom is very heterogeneous, both for the variety of elements and their bond lengths), the accuracy that can be reached is limited also by the fitting procedure. In fact, the mathematical correlations between fit variables can increase the errors on the optimized parameters. Research for the highest accuracy is not crucial when the aim of an EXAFS study is to reveal the structure of an unknown system, but it becomes essential if the goal is comparing similar systems. When structural differences are close to the technique limits, there is a high risk of losing such information. This problem is common in pump-and-probe experiments, where the aim is to appreciate small time-dependent changes between the ground state geometry and the structural features of photo-generated transient species and
photoproducts. For this kind of time resolved studies, Bressler, Chergui and co-workers[1-2] specifically developed the so-called X-ray transient absorption spectroscopy (XTA) which is based on a differential approach for both data acquisition and analysis. The technique directly records differential spectra, measuring for each point of the spectrum the value of excited and unexcited system. The differential approach was adopted successfully for light-responsive molecules but also in case of systems sensitive to magnetic fields[3] and changes of temperature[4-5], pressure[6-7], and pH[8-10]. A recently proposed strategy to obtain quantitative structural refinement from XTA data is based on a direct fitting of the differential signal, in energy or wavevector (k) space, by means of systematic variations of structural parameters. It was shown that this method, besides emphasizing the variations between the spectra, can increase the sensitivity of the experiment and reduce possible systematic errors during the fitting procedure[11-16].

In our contribution we present an alternative application for this differential data analysis approach by studying two distinct systems measured under static conditions and highlighting their small structural differences.

In particular, we performed a study of the two closely-related molecular complexes cis-[Ru(bpy)_2(py)_2]^2+ (1) and cis-[Ru(bpy)_2(py)(H_2O)]^2+ (2) (where bpy = bipyridine and py = pyridine).

Complex 1 upon UV and visible light excitation in water solution releases one of the py ligand with high yield (ca. 20%)[17]; the subsequent coordination of a water molecule results in the stable aqua photoproduct 2. Such kind of photoactivatable complexes has shown unique properties that have been successfully exploited for several applications. They are promising cage compounds for their ability to release bioactive ligands[18-20], and the high reactivity of the aqua photoproducts formed under light irradiation can be exploited to design photocontrollable anticancer agents [21-24]. Aiming at a thorough structural characterization of these systems and understanding their photoreactivity is fundamental for further developments. We recently have undertaken a comprehensive investigation on 1 and 2 and their light-driven dynamics by means of a multi-technique characterization, based on TR-WAXS (Wide Angle X-ray Scattering)[25], XTA (X-ray Transient Absorption) and OTA (Optical Transient Absorption) experiments supported by DFT (density functional theory) calculations[26]. The results presented in this work set the bases for a full comprehension of the system in static conditions by revealing small structural differences otherwise not appreciable. Moreover the data analysis here described gives an important contribution to the correct interpretation of the time-resolved EXAFS studies.

2. Experimental Section

Sample Preparation

The complexes cis-[Ru(bpy)_2(py)_2](ClO_4)_2[27] and cis-[Ru(bpy)_2(py)(H_2O)](ClO_4)_2[28] were synthesized as described in the literature and characterized accordingly. To increase the water solubility of cis-[Ru(bpy)_2(py)_2]^2+, the chloride derivative cis-[Ru(bpy)_2(py)_2]Cl_2 was prepared by anion exchange of a methanol solution of cis-[Ru(bpy)_2(py)_2](ClO_4)_2 on a Dowex weakly basic anion exchanger resin (purchased from Aldrich).

EXAFS data acquisition

The EXAFS spectrum for 1 was measured during an XTA experiment performed at the 11-ID-D beamline (APS, Chicago). The data were acquired in fluorescence mode; the sample was a 1 mM water solution flowing in a properly designed cell[29-30]. The EXAFS spectrum of 2 was collected in transmission mode at BM26A (ESRF, Grenoble). The sample (aqueous solution) was measured in a specific liquid cell with a thickness optimized to obtain an edge jump close to unit. Both the experiments were performed at the Ru K-edge (22117 eV) and the spectra were calibrated in energy thanks to the simultaneous collection of a reference metal foil.
Computational details

The geometry optimization of 1 and 2 was performed with the DFT method, employing the Gaussian 09 (G09) program package[31]. The geometries were fully optimized with the PBE0[32-33] functional at the LanL2DZ/6-311G** level[34-35], using the CPCM method[36-38] to include the solvent effect (water).

3. Results and Discussions

3.1. Comparison of X-ray absorption spectra and results of the standard EXAFS fitting procedure

Observing the data reported in Figure 1a, it is evident that the spectra of 1 and 2 are almost identical both in the XANES and EXAFS regions. This is not surprising since, from and EXAFS perspective, the two structures are very similar. The major difference between 1 and 2 is the change of one of the ligands from a py ring to a water molecule (see inset in Figure 1a). In terms of EXAFS signal contributions, the first shell signal is expected to be only minimally perturbed since the N atom of the py and the O of the water molecule are almost iso-electronic. The higher shells suffer of signal loss due to lacking scattering paths related to the py ring, however the cumulative contribution of such paths can be estimated to be only 1/6 of the global signal (loss of 1 over 6 rings, 2 py rings and 4 rings associated in 2 bpy units).

Despite these considerations, we performed a test to check if it was possible or not to discriminate the two systems by a standard EXAFS analysis. Initially we tried to obtain a high quality fit on the spectrum of 1. It was found that the best reproduction of the experimental curve, considering both fit goodness and physical meaningfulness of the parameters, was obtained fitting in R-space (range AR = 1.0 – 5.0 Å) the k-weighted FT function, transformed in the 2.5 – 10.8 Å⁻¹ k-range (2ΔkΔR/π ~ 21). Phase and amplitude functions of each path were calculated by the FEFF code[39] using the DFT optimized structure as input. All the EXAFS paths up to R = 5.0 Å were included in the fitting model. To limit the number of optimized variables, a common amplitude factor (S₀²) and an energy shift (ΔE) were adopted. Both py and bpy ligands were considered as rigid objects, thereby all path lengths were calculated according to geometrical constraints as a consequence of a radial translation along the corresponding Ru–N axis. In this way only other four parameters were optimized during the fit: R_Ru-N(py) and R_Ru-N(bpy) and their associated Debye-Waller (DW) factors σ breaches and σ breaches. Once performed the fit, we obtained an outstanding agreement between experimental and simulated curve as visible in Figure 1b and confirmed by the R-factor close to 1%. The results (Table 1) show a slight general contraction with respect to the distances predicted by DFT but mainly validated the calculated structure, in agreement with what obtained from previous studies on other similar complexes.[20,24-25,40]

Figure 1. (a) Normalized μx(E) spectra for GS (black line) and for PHP (orange line), in the inset χ(k) EXAFS curves for GS and PHP (same colors). Schemes of GS and PHP structures are also reported (Ru purple, N blue, C grey, O red). (b) Upper part: experimental χ(k) spectrum (black diamond) and its best fit (dark gray line) for GS; lower part: experimental χ(k) spectrum (orange circles) of PHP and its simulated curve (red line) obtained by a test fit using the same conditions and the same theoretical structure adopted for GS.
For the fit of 2, close attention was paid to maintain exactly the same conditions adopted in the case of 1, in terms of fitting-space, number of parameters and geometrical constraints. In order to obtain the best fit of experimental data, the normal procedure would have required calculating the EXAFS paths from the structure of 2 to generate the simulated curve. However, our aim was firstly to test if it was possible to discriminate the two systems, so we adopted the same paths previously calculated from the structure of 1. In this way it was possible to establish if the differences between the two structures were negligible controlling if they could be compensated on a pure mathematical plane (small variations of the parameter values leading to an overall good fit). The simulated curve ensued from the best fit showed an outstanding agreement with experimental spectrum of 2 (Figure 1b) and the R-factor obtained was of 1%, as in the case of the best fit for the spectrum of 1. Moreover, all the refined parameters values were comparable with the ones previously found for the fit of 1 within their experimental error. The loss of a py unit in 2 was well compensated by a slight increase of the associated DW factor $\sigma^2_{\text{py}}$, from (0.0032 ± 0.0008) Å$^2$ to (0.0041 ± 0.0009) Å$^2$. In view of these results, it was demonstrated that the sensitivity of the standard EXAFS analysis was not sufficient to disclose the differences between the two structures.

| Parameters | 1 standard fit [DFT] | 2 test fit (with 1 structure) |
|------------|----------------------|-------------------------------|
| R-factor   | 0.011                | 0.010                         |
| $S_0^2$    | 0.95 ± 0.06          | 0.94 ± 0.06                   |
| $\Delta E$ (eV) | 0.8 ± 0.5   | −0.4 ± 0.6                    |
| $R_{\text{N(py)}}$ (Å) | 2.05 ± 0.02 [2.08] | 2.04 ± 0.01                  |
| $\sigma^2_{\text{N(py)}}$ (Å$^2$) | 0.0026 ± 0.0008 | 0.0023 ± 0.0008               |
| $R_{\text{N(py)}}$ (Å) | 2.09 ± 0.03 [2.14] | 2.12 ± 0.03                  |
| $\sigma^2_{\text{N(py)}}$ (Å$^2$) | 0.0032 ± 0.0008 | 0.0041 ± 0.0009               |

### 3.2. The differential analysis: method and results

Once established that the standard EXAFS analysis method is not suitable for our systems, we tried to apply the differential analysis. First of all, we calculated the experimental differential curve (Figure 2a) by the subtraction of the two spectra $\chi(k_2) - \chi(k_1)$, were $\chi(k_2)$ and $\chi(k_1)$ indicate the EXAFS spectra of 1 and 2. Afterward, for a direct fitting of this curve, it was necessary to generate simulated differential signals starting from hypothetic structures of 2. Hence, the following procedure was adopted. Most of the paths previously included in the simulation of the EXAFS spectrum of 1 were kept, and only the ones involving C atoms of the py ring missing in 2 were removed. The paths involving the N atom of the py unit were maintained, since this atom is substituted by the almost isoelectronic oxygen of the water molecule; however they were described with two additional parameters, namely $R_{\text{Nh2o}}$ and $\sigma^2_{\text{O}}$. Fixing the amplitude $S_0^2$ at the value obtained during the fit of 1, only 7 parameters remained to be refined: the energy shift ($\Delta E$), 3 bond length variations ($\Delta R_{\text{ppy}}$, $\Delta R_{\text{py}}$, $\Delta R_{\text{o}}$) referred to the DFT optimized structure of 1 and their corresponding 3 DWs ($\sigma^2_{\text{ppy}}$, $\sigma^2_{\text{py}}$, $\sigma^2_{\text{O}}$). All these parameters were initially set at values obtained during the fit of 1, or derived by the structural changes predicted by DFT calculations (the new $\Delta R_{\text{o}}$, $\sigma^2_{\text{O}}$ refer to the values of the N$_{\text{py}}$).

Then, a systematical variation was planned as explained in more details hereinafter. For each combination of parameter values (correlated to a structural variation), the sum of all EXAFS contributions was calculated, obtaining a series of simulated curve for 2. After subtracting the simulated curve for 1 (best fit), a series of simulated differential curves was created with the purpose to be compared with the differential experimental data.

The simultaneous exploration of the whole 7-dimensional parameter space, adopting a sampling step fine enough to appreciate small structural differences, would be highly time-consuming. For this reason, a proper selected consecutive series of 2D or 3D sub-spaces was initially explored with a
gross sampling step trying to approach the global minimum. During all these partial minimization cycles, it was observed that variations in the DW factors were negligible in terms of influence on the differential curves with respect to the variation of the other parameters. Therefore, for the subsequent steps of the analysis, $\sigma^2_{\text{bpy}}$ and $\sigma^2_{\text{py}}$ were fixed to the values of the best fit for 1, while $\sigma^2_{\text{O}}$ was set to 0.005 Å$^2$, a local minimum of one minimization cycle. In this way the working dimensions were reduced to 4, including the energy shift and the three distortions along the Ru–N(bpy), Ru–N(py) and Ru–O(H$_2$O) bonds axes. Relying on the structural variations predicted by DFT and on the minima found in the sub-spaces previously explored, a refined analysis with restricted ranges and finer steps for each parameter was performed next. Among the grid of hundreds of simulated and tested curves, the lower R-factor value (0.147) was obtained in correspondence of the following combination of parameter values: \{ΔE = −1.0 eV; ΔR$_{\text{N(bpy)}}$ = −0.03 Å; ΔR$_{\text{N(py)}}$ = −0.07 Å; ΔR$_{\text{O(H2O)}}$ = −0.02 Å\} which represent the results of the fit. Starting from the DFT structure of 1 and applying the bond length variations (ΔR$_L$) obtained it is then possible to calculate the structure of 2 optimized by means of the differential fit (Table 2).

| Parameters | DFT | EXAFS |
|------------|-----|-------|
| R-factor   | 0.011 | 0.147 $^a$ |
| $S_0^2$    | 0.95 ± 0.06 | 0.95 |
| ΔE (eV)    | 0.8 ± 0.5 | −1.0 ± 0.5 |
| $R_{\text{N(bpy)}}$(Å) | 2.08 | 2.07 |
| $\Delta R_{\text{N(bpy)}}$(Å) $^*$ | −0.01 | 0.00 |
| $\sigma^2_{\text{N(bpy)}}$(Å$^2$) | 0.0026 ± 0.0008 | 0.0026 |
| $R_{\text{N(py)}}$(Å) | 2.14 | 2.13 |
| $\Delta R_{\text{N(py)}}$(Å) $^*$ | −0.01 | −0.02 |
| $\sigma^2_{\text{N(py)}}$(Å$^2$) | 0.0032 ± 0.0008 | 0.0032 |
| $R_{\text{O(H2O)}}$(Å) | --- | 2.21 |
| $\Delta R_{\text{O(H2O)}}$(Å) $^*$ | +0.07 | +0.03 |
| $\sigma^2_{\text{O(H2O)}}$(Å$^2$) | --- | 0.005 ± 0.001 |

Table 2. Results from standard EXAFS analysis of 1 and from differential analysis of 2. The results are compared to DFT predicted distances averaged per type of ligand. The errors on the refined parameters for 2 correspond to the step adopted for the differential parameter variation. $^a$ΔR$_L = R_{L(2)} - R_{L(1)}$ reported in the table do not correspond with AR$_L$, the fit parameters. $^b$The two R-factors are not directly comparable because calculated differently.

The simulated differential curve, corresponding to the minimum found, correctly reproduces all the features of the experimental differential curve (see Figure 2a), providing a further validation of the robustness of the method and of the results obtained. Observing the differences ΔR$_L = R_{L(2)} - R_{L(1)}$ between the refined structures of 2 and 1 resulted by the fits, it is worth noting that the differential analysis could detect the expected structural changes. The refined Ru–O bond length for the water molecule in 2 was found to be noticeably higher (+0.03 Å) than the corresponding Ru–N(py) bond length for py ring in 1. Also the corresponding DWs were relevantly different: the value of 0.005 Å$^2$ relative to the H$_2$O ligand is higher with respect to 0.0032 Å$^2$ found for the py, as expected substituting a pyridine ring with a smaller water molecule. A remarkable achievement obtained by means of the differential analysis is the possibility to capture the small rearrangements in the other ligands around the Ru centre induced by the presence of either py or water. In particular, the bpy average distances remained unvaried, while the bond length for the remaining py ring appeared to be contracted of −0.02 Å in 2.
Figure 2. (a) Differential EXAFS curve calculated by subtraction of 2 – 1 spectra. Experimental data (black diamonds) and best fit (red line). (b) 2D cut of the 4D R-factor surface, obtained by fixing the other parameters to the values found in correspondence of the minimum.

Furthermore, the results of the differential refinement can be compared with the dR_L calculated from the DFT optimized structures (see Table2). The fit results and the theoretical predictions agree in indicating a longer Ru–O(H2O) bond in 2 with respect to the Ru–N(py) bond in 1. It is difficult to comment upon the values related to bpy and py because the parameterization adopted for the data analysis still contains many approximations necessary to reduce the number of variables. In this regard, it is worth noting that EXAFS analysis could afford only information averaged on all atoms of the same element belonging to the same unit (bpy or py). On the contrary, DFT calculations provided the single atomic positions for every atom of the complex. Examining the single Ru–N distances optimized by DFT for complexes 1 and 2, four of them are predicted to be mainly unchanged, while the Ru–N(bpy) of the bpy ring in trans to the Ru–O bond is expected to be shortened of 0.04 Å.

Hence, it is possible that the differential analysis was able to reveal this shortening predicted by the DFT. However, such contraction was incorrectly related to a variation of the Ru–N(py) bond. Many causes could have contributed to this misinterpretation. Firstly it is not straightforward, in terms of EXAFS signal, to distinguish between a py ring or one of the rings of a bpy. On top of that, the rigidity imposed during the parameterization to the bpy units would not allow the fit to move a single Ru–N(bpy) bond (EXAFS paths 4-times degenerated) while the Ru–N(py) bond length was the only parameter which could be changed independently. For these reasons, it was hypothesized that the detected shortening of a Ru–N bond should be assigned to the Ru–N(bpy) in trans positions with respect to the water molecule. This hypothesis was also supported by the strong anti-correlation found between ΔR_{py} and ΔR_{O} variables. This anti-correlation appears as a diagonal line of minima in a 2D cut of the 4D R-factor surface (Figure 2b), where the other two parameters have been fixed to the optimized values of the best fit.

4. Conclusions

Differential EXAFS analysis is a powerful method with applicability that ranges from the study of spectra measured in static conditions to excited-state systems. In particular, the application of this method can be really useful when studying systems characterized by small differences, close to the state-of-art sensitivity limit of the XAS technique, as in the case of cis-[Ru(bpy)2(py)2]2+ and cis-[Ru(bpy)2(py)(H2O)]2+. It is worth pointing out that such approach could require a remarkably higher amount of time compared to a standard analysis. However, the direct fitting on differential curves provides a superior accuracy for the derived structural parameters when compared to conventional EXAFS fits of the individual (not differential) spectra, where the absolute measure of the distances is affected by errors which do not allow distinguishing slight structural modifications. In order to adopt
such a complex analysis for static EXAFS spectra, it is necessary to deal with experimental data correctly calibrated in energy and normalized so that they could be safely compared and subtracted.

With respect to the specific case proposed, the differential fit allowed the discrimination between the longer Ru–O bond and higher DW associated to the water molecule in cis-[Ru(bpy)$_2$(py)(H$_2$O)]$_2^+$ with respect to Ru–N and DW related to the py ring in cis-[Ru(bpy)$_2$(py)$_2$]$_2^+$. In addition, it was possible to appreciate also a small structural rearrangement of one of the other ligands around the Ru atom; the measure of a shorter Ru-N bond in cis-[Ru(bpy)$_2$(py)(H$_2$O)]$_2^+$ was finally assigned to the nitrogen of a bpy unit in trans position with respect to the water molecule with the help of considerations based on the results of DFT optimized structures. DFT calculations played a key role when the complexity of the case of study required approximations in the parameterization. Moreover, the computational study assisted the selection of guessed values and their variation ranges during the exploration of the n-dimensional space of variables, when looking for the best fit. DFT calculations were relevant both in providing structures used as input model for the simulation of EXAFS contributions, and in testing the reliability of the data interpretation by means of a synergic cross-comparison.

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