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Structural analysis and self-absorption correction of 1.5 mM and 15 mM Ni (II) complexes: Probing the limit of dilute systems with identical coordination number, and conditions for subtle hypothesis testing

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A R T I C L E I N F O	A B S T R A C T	
A R T I C L E I N F O Keywords: Self-absorption XAFS XERT Nickel complex	We apply a novel correction for the self-absorption distortion in fluorescence X-ray Absorption Spectroscopy (XAS) data collected from both 15 mM and 1.5 mM Ni (II) complex solutions. Self-absorption is an inevitable systematic effect that distorts fluorescence XAS data and limits the available information content. This work builds on an earlier project (Trevorah et al., 2019) and demonstrates that this method is valid for dilute samples. Structural analysis of the corrected data yields significant new insights with tight constraints on the determined molecular structure and dynamic bond lengths. The samples considered are nickel (II) complexes, bis(N-n-propyl-salicylaldiminato) nickel(II), 'n-pr', and bis(N-i-propyl-salicylaldiminato) nickel(II), 'i-pr'. These complexes are notionally square-planar and tetrahedral, respectively, and have identical coordination numbers. In transmission detection XAFS, the geometry and distortion were well observed in 15 mM dilution for both high point density data sets and for high point accuracy but using more sparse data sets. In fluorescence the high point density data sets were just as insightful; however the sparse data sets provided insufficient data points in the region accessible with FEFF theory, and hence in this case were unable to distinguish between the distorted square planar and the distorted tetrahedral geometries, principally because of the increased difficulty in observing three-legged path contributions.	

1. Introduction

The backscattering and self-interference of a photoelectron ejected from the inner shell of an absorbing atom results in a phenomenon known as X-ray Absorption Fine Structure (XAFS). Careful analysis of this structure can reveal a great deal about the molecular geometry and interatomic bonding of the system of interest. XAFS experiments are most commonly conducted in 'fluorescence mode' which records the intensity of the fluorescence emanating from the absorbing atom of interest as a function of incident x-ray energy. Fluorescence XAFS has a number of advantages, particularly for dilute solutions or thick, metallic samples. However, fluorescence XAFS is more challenging to measure and quantify because of the number of systematic experimental effects, including harmonic contamination, scattering and bandwidth contributions to the spectra. Self-absorption is a key systematic effect, which is inevitable in fluorescence type measurements. Self-absorption is caused by the reabsorption of an emitted fluorescence photon by the sample itself, before the photon has a chance to reach and be registered by the detector. This systematic effect has a strong geometric dependence (as the emission angle affects the pathlength that the photon must travel along to escape the sample of interest) and so distorts the measurement information content beyond a simple (uniform) loss of statistic. In this way, careful propagation of experimental uncertainties is more important for analysis of fluorescence data and leads to a meaningful χ_r^2 goodness-of-fit comparison when determining the optimised structural model.

Our research group has an established interest in investigating the Ni (II) complexes analysed in this work (Islam et al., 2015; Chantler et al., 2015; Schalken and Chantler, 2018; Trevorah et al., 2020). Several data sets collected on these complexes have already been fully analysed and published yielding structural conclusions in excellent agreement, from transmission measurements and from fluorescence measurements. With this success in addressing self-absorption for 15 mM solutions, we now investigate more challenging data sets which include: more dilute 1.5 mM samples; and data collected much more sparsely across the energy range. These pose significant challenges for our self-absorption

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Received 9 March 2022; Received in revised form 28 April 2022; Accepted 1 May 2022 Available online 9 May 2022 0969-806X/Crown Copyright © 2022 Published by Elsevier Ltd. All rights reserved. correction methodology and also for subtle analysis; and probe unexplored regions of parameter space.

2. Experimental

Fluorescence and transmission XAS measurements were simultaneously taken of two closely-related organometallics: bis(N-n-propyl-salicyladiminato) nickel(II), 'n-pr' and bis(N-i-propyl-salicyladiminato) nickel (II) 'i-pr' at the Australian National Beamline Facility, Tsukuba, Japan. 15 mM solutions of each complex were prepared using 60% butyronitrile (BCN) + 40% acetonitrile (ACN) as the solvent to avoid microcrystallisation at cryostat temperatures, circa 80 K. The concentrations of the solute were 15.33 \pm 0.06 mM and 15.26 \pm 0.03 mM, respectively, corresponding to approximately 0.1% w/w or 1000 ppm (parts per million) nickel in the sample.

The sample is aligned in the experimental setup so that the beam is incident upon it at 45°. Sample (cell) thicknesses were 1.9577 \pm 0.0017 mm (i-pr) and 1.981 \pm 0.002 mm (n-pr) (Table 3, column 4 (Chantler et al., 2015),). The frozen solutions were contained in cells fashioned from a 25 \times 2 mm Teflon pellet, designed to allow a 1.5 \times 2 mm X-ray beam to pass through. Kapton adhesive tape and a light film of silicone grease were used to minimise the risk of the solution leaking between cells. The distance between the sample and the fluorescence detector elements is 107 \pm 2 mm. A detailed schematic of the transmission experiment with accurate distances can be found in Fig. 5, (Chantler et al., 2015).

A 36-element Ge planar detector (EURISYS EPIX 36-64-7-ER) was used to collect fluorescence. The 36-element detector contains 6 × 6 channels in a square array with each pixel having an area of 8 mm × 8 mm. The output file runs from channels 0 to 35, with 0 being the top downstream end and incrementing horizontally. The approximate gap between the active area of each channel is 0.4 mm. So, the separation of pixel centres at the detector surface is 8.4 mm. The central position of the detector is aligned to be ~45° to the solution cell or ~90° to the incident beam. Three pixels were unresponsive and are not discussed further.

Further experimental details including schematic and sample chamber in the 80 K cryostat can be found in (Chantler et al., 2015). The simultaneous data collection in both modes is important because previous XERT (Chantler et al., 2001) and Hybrid (Chantler et al., 2015) analyses have considered concentrated samples and this gives a critical comparison of fluorescence with transmission in a regime where both



Fig. 1. Raw *n*-*pr* 15 mM fluorescence spectra. Each spectrum corresponds to data collected from an individual fluorescence detector pixel. A wide dispersion is seen between individual pixel spectra and all spectra display an unphysical (rising) trend with energy due to self-absorption.



Fig. 2. Raw *n*-*p*r 1.5 mM fluorescence spectra. The lower absorption amplitude is to be expected due to factor of ten decrease in sample concentration.



Fig. 3. Raw *i-pr* 15 mM fluorescence spectra. Each spectrum corresponds to data collected from an individual fluorescence detector pixel.



Fig. 4. Raw *i*-pr 1.5 mM fluorescence spectra. It is clear that the raw spectra are not in good agreement with each other.



Fig. 5. Fluorescence XAS data of 15 mM *n-pr* now corrected for self-absorption. Black overlaid spectra is the simultaneously collected transmission data. Y-axis units indicate that this is a relative (as opposed to absolute) absorption measurement.

methods are, in fact, fully competitive.

3. Methods

Four fluorescence data sets were analysed in this work. These include samples of both 1.5 mM and 15 mM concentrations for both n-pr and i-pr samples. These measurements are distinct from those presented in previous publications by this group as they were measured using the High Point Accuracy (HPA) protocol which focusses on increased statistical precision per data point, as opposed to collecting the maximum number of data points per given time interval (further defined in (Schalken and Chantler, 2018)).

An example of the raw data is presented in Fig. 1 Clearly, there are several sources of distortion in the (raw) data, including uncalibrated detection efficiency of individual pixels, significant dispersion between spectra and an unphysical trend with energy due to self-absorption. The 'gaps' in the data seen around 10 keV are indeed areas of relatively large measurement step size. This was intended, since there is little useful XAFS data to extract this far beyond the edge, and it is more important to be able to model the overall absorption trend in this region (see Figs. 2–4).

The distortion due to self-absorption was corrected for using our established methodology and original software package, *SeAFFluX*. Experimental and geometric details were identical to those presented in our previous publications, as these measurements were taken as part of the same experiment (Trevorah et al., 2019). Examples of the corrected spectra can be seen in Figs. 5–9 and in terms of χ in Fig. 10.

The corrected spectra are found to be in excellent agreement with each other and with the simultaneously collected transmission type measurement, which was not affected by self-absorption. The corrected 15 mM spectra are found to agree practically 'within error' with the previously analysed transmission data. This is a strong proof-of-concept for our self-absorption methodology. A weaker agreement is found with our 1.5 mM data sets. This is to be expected as there is much poorer information content to begin with in these measurements, both in terms of weaker concentration of absorption material in the sample and in terms of satisfying the Nordfors criterion (Nordfors, 1960) for collecting high quality XAS data. A good agreement is found around the absorption edge and in the strong post-edge XAFS oscillations. The agreement in terms of trend with energy becomes increasingly worse \sim 300 eV beyond the edge. This disparity is very unlikely to be an error in experimental geometry alignment, as the 15 mM data is found to agree very well and all measurements were taken on the same beamline during the same



Fig. 6. Expansion of Fig. 5 illustrating the excellent agreement between transmission and fluorescence spectra after correction for self-absorption.



Fig. 7. Fluorescence XAS data of 1.5 mM n-pr that has been corrected for selfabsorption. Black overlaid spectra is the simultaneously collected transmission data.



Fig. 8. Fluorescence XAS data of 15 mM *i*-*pr* that has been corrected for self-absorption. Black overlaid spectra is the simultaneously collected transmission data.



Fig. 9. Fluorescence XAS data of 1.5 mM *i-pr* that has been corrected for self-absorption. Black overlaid spectra is the simultaneously collected transmission data.



Fig. 10. Illustration of *i-pr* 1.5 mM data converted to χ versus *k*. A vaguely respectable fit with $\chi_r^2 \sim 18$ is returned, yet the optimised model (red) is not able to find good agreement with the data. The data is too sparse beyond k = 6 and with poor statistics.

time-frame. We conclude that the 1.5 mM data is approaching the information content threshold required for self-absorption correction of this type (for fluorescence calibration and correction). (See Figs. 11 and 12)

Fig. 10 demonstrates that the extracted XAFS data from the (sparse) 1.5 mM samples is able to fit with FEFF modelling; but is too sparse and low in statistical quality to be able to accurately determine most key parameters, so are not included in further analysis herein. A solution of course is to collect more detailed spectra with high quality statistics e.g. at a high-flux beamline. Whilst this is an attractive question for the



Fig. 11. Optimised fit of 15 mM n-pr data with tetrahedral model (red).



Fig. 12. Optimised fit of 15 mM *n-pr* data with square planar model (red).

future, we pass on to the high point accuracy but sparse 15 mM data sets. The self-absorption correction of the 15 mM data looks quite promising. This is a significant achievement in itself, although further analysis is required to eke out the structural insight contained within these spectra. Structural modelling proceeds in the same way as in ().

3.1. Oscillation amplitude

A small scaling the overall amplitude of the XAFS oscillations was necessary when converting from $[\mu/\rho]$ to χ . This adjustment was guided by the richer data sets previously analysed (both fluorescence and transmission). A simple scaling factor was applied and the oscillation amplitude was reduced by 30%. This additional scaling is probably due to the sparser point density in this data set, which consequently led to difficulties in the spline and background subtraction process. This can also be related to the setting of the region of interest in the detector pixels, especially if the lower edge is slightly truncated. Part of this concern would be addressed by automatic collection of full-spectra from each channel. In this way, we are able to home in on the limit of solvent correction. However, we can correct this by directly comparing with simultaneously collected transmission data, which was excellent for structural analysis.

4. Results

In this study, we are testing whether it is possible to reliably tell the difference between the two isomers and geometries. These isomers have identical coordination number, by definition. In transmission detection, the hypothesis was clearly successful; and the fitted parameters could identify geometry and distorted square planar versus distorted tetrahedral bonding, even for the sparse but high accuracy data sets as we see here. This task is significantly more challenging than in our previous publications for fluorescence data, as the point density is approximately 25% of that relative to the data previously analysed. We begin by presenting the results of eFEFFIT structural analysis, with identical methodology as in our previous work.

4.1. eFEFFIT analysis

The optimised structural models for *n*-*p*r are overlaid with the χ versus *k* data in Figs. 11 and 12. A summary of the model parameters is presented in Table 1. A good qualitative agreement is found in both cases. Similarly, optimised structural models for *i*-*p*r are overlaid with the χ versus *k* data is Figs. 13 and 14, and a summary of the model parameters is presented in Table 2. A good qualitative agreement is found in both cases, with essentially no difference in the reported χ^2_r value.

However, the tetrahedral model is found to have a slightly better agreement for *n*-*pr* (a lower χ_r^2 value by 1.5). We fully believe the value and accuracy of the earlier published work with high point density from

Table 1

A summary of the optimised structural modelling of the 15 mM *n*-*pr* HPA data set. Both models find very good qualitative agreement with the data as seen in Figs. 11 and 12. The tetrahedral model finds slightly better agreement than the (expected) square planar model, although both models report an agreement within a χ_r^2 of 1.5.

Model Geometry:	Tetrahedral	Square Planar
Ni–N (Å)‡	1.976 ± 0.008	2.143 ± 0.005
Ni–O (Å)‡	2.116 ± 0.009	1.954 ± 0.003
N–Ni–O (°)	88 ± 1	88 ± 1
Ni–C1 (Å)	2.928 ± 0.023	2.895 ± 0.016
Ni–C ₂ (Å)	3.020 ± 0.010	2.982 ± 0.010
n-pr χ_r^2	3.58	5.08
ΔE_0 (eV)	6.70 f	4.00 f
S_{0}^{2}	0.98 f	1.00 f
α	1.020 ± 0.031	1.020 ± 0.003
$\sigma_N^2, \sigma_O^2 (\text{\AA}^2)^{\dagger}$	0.001 <i>f</i>	0.001 <i>f</i>
σ_{short}^2 (Å ²) [§]	0.002f	0.002f
σ^2 (Å ²)	0.005 ± 0.001	$\textbf{0.009} \pm \textbf{0.003}$

† σ_N^2 and σ_O^2 are for the two-legged Ni–N–Ni and Ni–O–Ni paths, set to 0.001 Å². *f* Fixed to a physical value. α is the bond and path-scaling parameter for all paths except the innermost 4 paths grid-searched in the table. ‡As always with XAS, the identification of N or O as the nearest neighbour is not well-determined, see text.

§ σ_{short}^2 is the thermal broadening parameter for the next shortest 15 photoelectron scattering *FEFF* paths, set to be 0.002 Å². σ^2 is the free parameter for all farther paths.



Fig. 13. Optimised fit of 15 mM i-pr data with tetrahedral model (red).



Fig. 14. Optimised fit of 15 mM *i-pr* data with square planar model (red).

transmission and fluorescence; that is, that the structure is (distorted) square planar. However, with the fluorescence data and the sparse point density the HPA (high point accuracy) a fairly poor agreement in found between data and theory beyond k = 7 as the point density is quite sparse from this point onwards. In this case, we conclude that we have identified the information content limit for iFEFFIT or eFEFFIT analysis.

Table 2

A summary of the optimised structural modelling of the 15 mM i-pr HPA data set. Both models find very good qualitative agreement with the data as seen in Figs. 13 and 14. The tetrahedral model finds slightly better agreement than the square planar model, although both models report essentially the same χ_r^2 value.

Model Geometry:	Tetrahedral	Square Planar
Ni–N (Å)‡	1.993 ± 0.017	2.014 ± 0.020
Ni–O (Å)‡	2.037 ± 0.013	2.018 ± 0.015
N–Ni–O (°)	92 ± 1	91 ± 1
Ni–C ₁ (Å)	2.978 ± 5.97	2.983 ± 0.016
Ni–C ₂ (Å)	$\textbf{2.978} \pm \textbf{2.99}$	2.950 ± 0.037
i-pr χ_r^2	4.562	4.608
ΔE_0 (eV)	5.32 ± 1.60	5.20 f
S_{0}^{2}	1.00 f	0.95 f
α	1.006 ± 0.006	1.007 ± 0.007
$\sigma_N^2, \sigma_O^2 (\text{\AA}^2)^{\dagger}$	0.001 <i>f</i>	0.001 <i>f</i>
$\sigma_{\rm short}^2$ (Å ²) [§]	0.002f	0.002f
σ^2 (Å ²)	0.005 ± 0.003	$\textbf{0.017} \pm \textbf{0.005}$

† σ_N^2 and σ_O^2 are for the two-legged Ni–N–Ni and Ni–O–Ni paths, set to 0.001 Å². *f* Fixed to a physical value. α is the bond and path-scaling parameter for all paths except the innermost 4 paths grid-searched in the table. ‡As always with XAS, the identification of N or O as the nearest neighbour is not well-determined, see text.

§ σ_{short}^2 is the thermal broadening parameter for the next shortest 15 photoelectron scattering *FEFF* paths, set to be 0.002 Å². σ^2 is the free parameter for all farther paths.

For *i-pr*, the point density of this data set is again quite poor beyond k = 6 and so we conclude that an iFEFFIT or eFEFFIT analysis is not able to reliably model our data at this concentration for such a subtle question. That is: we need a theory which can work for lower k where the data statistic is better; or we need (much) high point density; or we need better statistic for all points; or indeed all three. Roughly speaking, the distinction between square planar and tetrahedral (distorted or otherwise) depends upon being able to identify and distinguish three-legged paths in the data, and their strongest signatures are at low k.

Another structural modelling package, *FDMX* (Bourke et al., 2016), is known to have significant advantages over eFEFFIT or iFEFFIT, particularly in the low-*k* region. Hence this could allow a lower minimum *k* for the fit, and reveal better insight even with the current sparse data sets. Future work will utilise this package for structural analysis and contrast these results with the eFEFFIT results presented here.

5. Conclusions

SeAFFluX has been successfully applied to sparse and non-uniform fluorescence data sets, and to sparse and quite dilute 1.5 mM fluorescence data sets. The corrected spectra are in good agreement with corresponding transmission data sets. Our self-absorption correction methodology is able to be applied to fairly dilute and challenging fluorescence spectra. The eFEFFIT fitting is able to fit the data, but the parameter uncertainties and the differences in χ^2_r are not statistically meaningful. This process has revealed further insight both into the structural geometry of the Ni (II) complexes considered and also the practical limits of analysis of this type, with this point spacing and with this dilution and with this theoretical modelling. It is hoped that greater insight can be gleaned using the FDMX structural analysis package, and such results are to be presented in an upcoming manuscript. Future work aims to further explore these limits by investigating self-absorption corrections as applied to thick, metallic samples which are anticipated to prove to be a particular challenge.

Author statement

Christopher Chantler: Conceptualization, Methodology, Supervision, Writing, Reviewing and Editing. Ryan Trevorah: Software, Data

curation, Writing, Original draft preparation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.radphyschem.2022.110212.

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