Propagation of uncertainty in experiment: structures of Ni (II) coordination complexes

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Introduction

Accurate experimental XAFS (X-ray Absorption Fine Structure) data including uncertainties is required during analysis for valid comparison of results and conclusions of hypothesis testing on structural determinations. Here we develop an approach to investigate data without standard interpolation of experimental data and with minimal loss of information content in the raw data. We investigate nickel coordination complexes bis(i-n-propyl-salicylaldiminato) nickel(II), (i-pr), and bis(N-n-propyl-salicylaldiminato) nickel(II), (n-pr). We use the additional physical insight afforded by the correct propagation of experimental uncertainty to determine newly refined structures for the innermost co-ordination shell. This work is presented in [1].

[1] Schalken, M. J. and Chantler, C. T. Journal of Synchrotron Radiation, 2017. (*Under review)*

Method

New computer software has been developed which enables fitting of experimental spectra with those obtained via theoretical models without any distortion of experimetnal uncertainties, by using non-interpolated data throughout the analysis. We investigate two sets of data for each complex [2]; one optimised for high point accuracy and one optimised for high point density. Clearly both are important and in this investigation the quality of the physical insight from each is directly represented by measured and propagated uncertainties to fairly represent the relevant accuracies. The analysis of Islam et al. [3] has been extended through this new approach.

[2] Chantler, C. T. *et al.* (2015). Journal of Synchrotron Radiation, 22(4), 1008–1021.
[3] Islam, M. T. *et al.* (2015). Journal of Synchrotron Radiation, 22(6), 1475–1491.

Results

Our results provide evidence for an approximate tetrahedral geometry for the i-pr Ni complex that is more symmetric than previously concluded, with our high point accuracy (HPA) data yielding ligand lengths of 2.021 ±0.006Å and 2.018±0.006 Å for Ni-N and Ni-O bonds respectively, and an even more skewed square planar (i.e. rhombohedral) arrangement for the n-pr complex with corresponding bond lengths of 2.133±0.004 Å and 1.960±0.003Å.

Discussion

The ability to distinguish using hypothesis testing between the subtle differences in XAFS spectra arising from the approximate local tetrahedral and square planar geometries of the complexes is highlighted. We have investigated the effect of standard interpolation on experimental XAFS spectra prior to fitting with theoretical model structures. While often done as a necessary step for Fourier transformation into position space, this will nonetheless skew the fit away from actual data taken, and fails to preserve the information content within the data uncertainty. The artificial effects interpolation imposes on χ^2_r are demonstrated, and a method to circumvent this is presented which uses an interval-wise scaling of uncertainties to conserve the local contribution to the final χ^2_r and thus information content, when a regular grid is required, eg, for further analysis in r-space.

Conclusion

We have illustrated the effect interpolation has on the resulting χ^2_r, and the magnitude of some consequent errors. Correct propagation of information content gained from a high accuracy experimental techniques throughout the analysis procedure has been demonstrated, and by doing so we have been able to determine new information on the local structures of Ni complexes.