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LETTER

The importance of multiple scattering pathways involving the absorbing atom in the interpretation and analysis of metal K-edge XAFS data of co-ordination compounds

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The presence of peaks at twice the metal–ligand distance (*2R*) in the Fourier transform of the Ni K-edge XAFS data of *trans*-[$NiBr_2(PEt_3)_2$], and the absence of such peaks in the data of *tetrahedral*-[$NiBr_2(PPh_3)_2$] confirm unambiguously that these *2R* features are due to multiple scattering pathways involving the central metal atom in linear (or near linear) L–M–L units. Attention is drawn to the dangers of mis-interpreting these *2R* features as due to solvation shells or lattice packing.

We have previously observed peaks in the Fourier transforms (FT) of metal K-edge XAFS data at approximately twice the metal–ligand distance (*2R*) that could not be interpreted other than as arising from multiple scattering pathways involving the central, absorbing atom,[1,2] but were unable to confirm these observations at the time due to the limitations of EXCURV92.[10] Other workers had identified these type of multiple scattering pathways in the spectra of some solid state oxides and hydroxides,[3] and then subsequently in the spectra of uranyl complexes,[4] yttrium thiocyanates,[5] and in hexa-aqua complexes.[6,7] However, in all the cases to date, the *2R* features were masked and overlapped to varying degrees by other scattering interactions. Therefore, to confirm unambiguously whether *2R* features in the FT's are due to such multiple scattering pathways, we studied a pair of homoleptic compounds, *tetrahedral*-[$NiBr_2(PPh_3)_2$] and *trans*-[$NiBr_2(PEt_3)_2$],[8] where only the co-ordination geometry at the metal centre was varied, with the number and type of ligand donor atoms remaining constant and where the *2R* features (if present) would not be overlapped with any other significant shell(s).

The FT's of the Ni K-edge XAFS data for *tetrahedral*-[$NiBr_2(PPh_3)_2$] and *trans*-[$NiBr_2(PEt_3)_2$] are shown in Fig. 1, and from these it is immediately obvious that there is a feature at *ca.* *2R* in the FT of the *trans*-[$NiBr_2(PEt_3)_2$] data which is absent in the FT of the *tetrahedral*-[$NiBr_2(PPh_3)_2$] data and therefore must be due to the linear arrangement of atoms in the square planar complex as there are no other significant structural differences between the complexes. (Although the data in Fig. 1 were recorded at 10 K, we have also observed *2R* features in the Ni K-edge data of *cis*-[$NiBr_2$(dppe)] at both 77 and 300 K.) Full cluster multiple scattering calculations using EXCURV98[11] are shown in Fig. 1 and confirm this assignment of the *2R features*, and the different scattering pathways and their relative contributions to the *2R* peaks in the Ni K-edge data are shown in Scheme 1. The detailed calculations[8] showed (i) that the intensity of the *2R* features is dominated by the multiple scattering pathway involving both Br atoms and the central Ni atom, (ii) that the relative intensity of the *R* and *2R* features remains approximately constant when the Debye–Waller factor is varied from 0.001 to 0.015 Å^2 for any given absorber–scatterer interaction, (iii) that the relative importance of the Ni–P pathways compared to the Ni–Br pathways increases with an increase in their Debye–Waller factors, (iv) the intensity of the *2R* peaks is very sensitive to bond angle at the absorbing atom and falls off rapidly below 165°, and (v) although in principle, multiple scattering contributions should also give rise to peaks at *3R* (and *4R*), they are calculated to have about 1/30th the importance of the contributions to the *2R* peaks, and only to be observable with very low Debye–Waller factors of <0.002 Å^2.

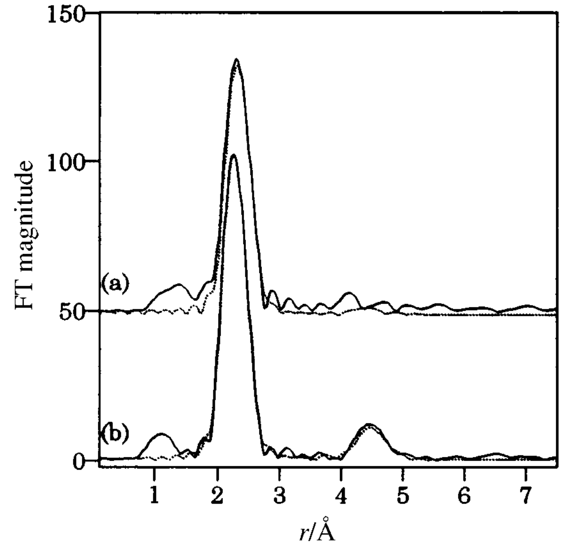
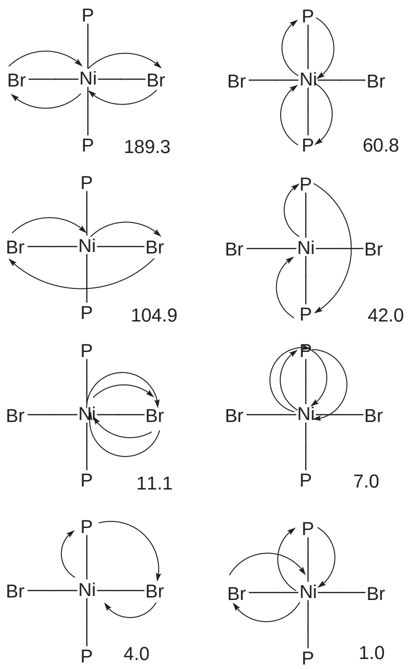


Fig. 1 Fourier transforms of Ni K-edge XAFS data at 10 K of (a) *tetrahedral*-[$NiBr_2(PPh_3)_2$] and (b) *trans*-[$NiBr_2(PEt_3)_2$]. Experimental data, solid line; calculated data, dotted line.



Scheme 1 Diagrammatic representation of the multiple scattering pathways (and their relative importance) that contribute to the *2R* features in Ni K-edge XAFS data of *trans*-[$NiBr_2(PEt_3)_2$].

In conclusion, we have shown unambiguously that multiple scattering pathways involving the central atom which give rise to *2R* features in the FT's are readily observable in the metal K-edge spectra of co-ordination compounds with linear (or very near linear) ligand–metal–ligand geometries. Therefore, extreme caution should be taken in interpreting data that contain such *2R* features, as otherwise they could be mis-assigned to solid state packing or solvent interactions. For example, it has recently been shown[6,7] that features at approximately *2R* in the metal K-edge spectra of hexa-aqua complexes are made up of contributions from both the second hydration shells *and 2R* multiple scattering pathways, and that in our previous analysis of the Zn K-edge data of $ZnCl_2$ isolated in an N_2 matrix,[9] features at *2R* were mistakenly fitted to $Zn \cdots N_2$ interactions, but re-analysis shows that a considerable portion of the intensity is due to *2R* multiple scattering pathways.

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