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The importance of multiple scattering pathways through the central atom in the analysis of metal K-edge XAFS data of coordination complexes

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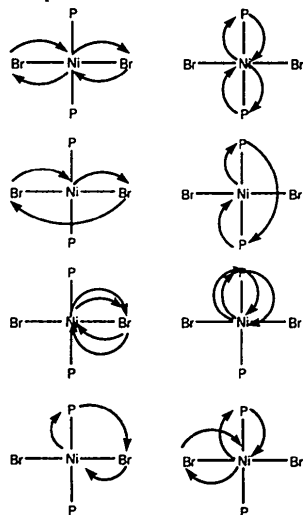
Features at twice the metal-ligand distance in the Fourier transforms of metal K-edge XAFS data are demonstrated to be due to multiple scattering pathways involving the central metal atom, and to be very sensitive to bond angle.

Keywords: XAFS; multiple scattering; Ni K-edge, bond angle determinations.

1. Introduction

Whilst the presence of multiple scattering in compounds containing linear ligands (such as CO or CN⁻) and/or ring systems (such as imidazole or histidine) has long been recognised and used to obtain important structural data, the multiple scattering pathways through the central atom such as those shown below have not received so much attention. We have previously observed, and cautiously identified peaks at twice the metal-ligand distance (2R) in the FT's of metal K-edge XAFS to be due to such pathways (Young, 1996a, 1996b), but have not been able to fit them using EXCURV92. These type of multiple scattering paths are implemented within the FEFF codes and subsequent versions of EXCURVE. Whilst a number of workers have identified such features in their data (O'Day *et al.*, 1994; Hudson *et al.*, 1996; Díaz-Moreno *et al.*, 1998; Sakane *et al.*, 1998), our belief is that the majority of XAFS users are not sufficiently aware of these important pathways, or how they can be used to obtain geometric information from the central metal K-edge data alone. There is also the danger that they may be mis-interpreted as due to inter-molecular interactions such as stacking in solid phase systems, or solvent interactions in solution.

Therefore, in order to confirm the identity of these 2R features in the FT's we decided to study a pair of homoleptic compounds, where only the co-ordination geometry at the metal was changed, with the number and type of ligands remaining constant. To our mind the best examples for this work were the nickel phosphine halide complexes, *tetrahedral*-[NiBr₂(PPh₃)₂] and *trans*-[NiBr₂(PEt₃)₂] as any multiple scattering features would not be



masked by other scattering events. In order to maximise the intensity of the long scattering pathways the spectra were recorded at *ca.* 10 K.

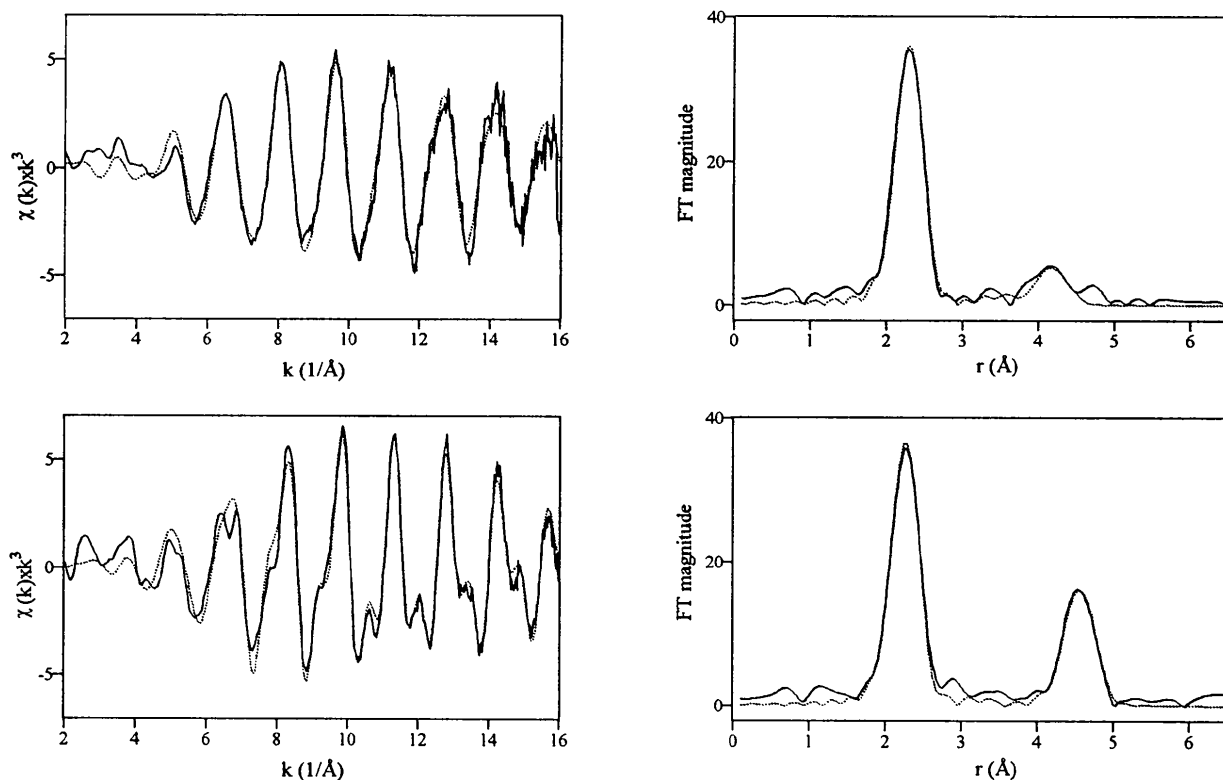
2. Experimental

The samples were prepared by the addition of stoichiometric quantities of the ligand, either neat (PEt₃) or in EtOH (PPh₃) to a dry EtOH solution of NiBr₂. The precipitates were filtered, washed with EtOH, ether and petrol and dried under vacuum. The purity was confirmed by elemental (CHN) analysis. For the XAFS measurements the samples were ground with graphite and pressed into 13 mm pellets *ca.* 1 mm thick, and mounted on the sample stage of an APD DE204SL closed cycle He cryostat with a base temperature of *ca.* 10 K. The Ni K-edge and Br K-edge data (with edge steps of 0.7 to 1.3) were recorded on the same samples in transmission mode on station 9.2 of the Daresbury SRS using a Si(220) double crystal monochromator operating at 50% harmonic rejection. Background subtraction was carried out using PAXAS (Binsted, 1988), and the XAFS data were simulated using a cluster multiple scattering approach with the Rehr-Albers formalism (Rehr & Albers, 1990,1992) within EXCURV98 (Binsted, 1998). To reduce the computation time, the spectra were initially fitted using single scattering for the first shell to identify the Ni-P and Ni-Br distances. Once these were obtained, a full cluster multiple scattering calculation was then carried out.

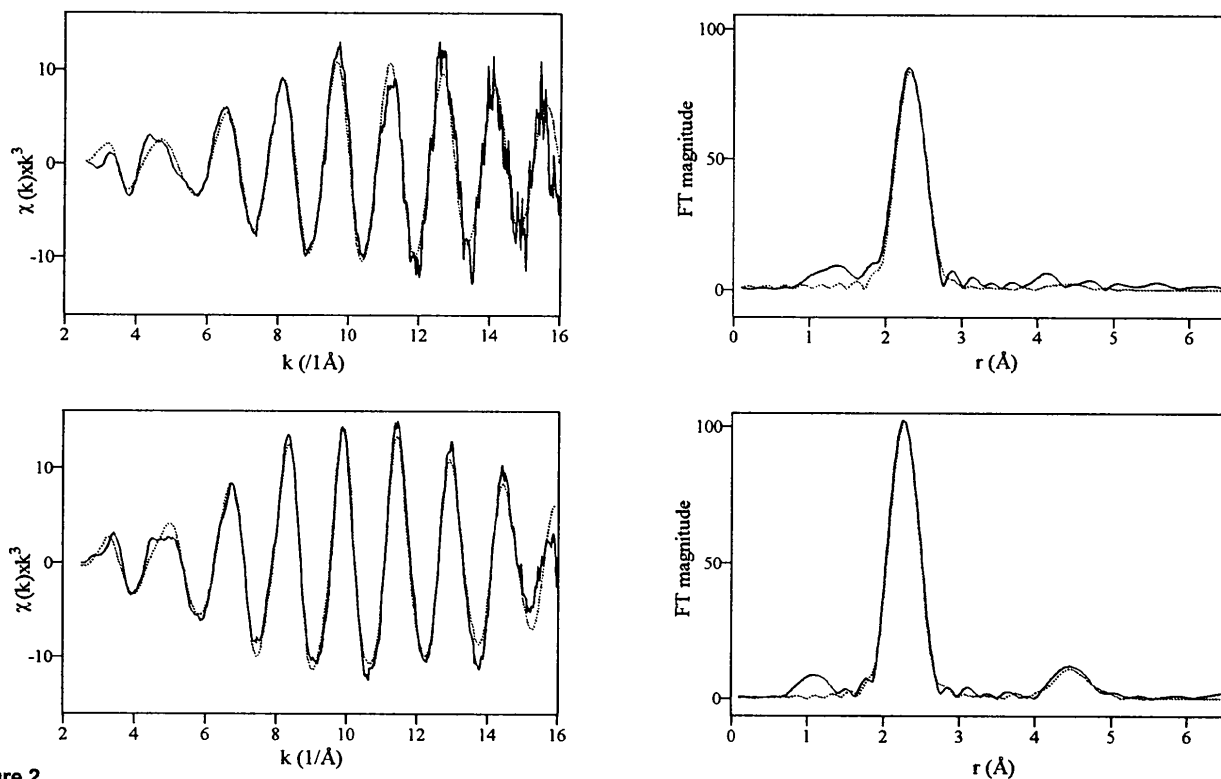
3. Results and Discussion

The Br K-edge XAFS and FT's for the two compounds are shown in Figure 1, together with the best fit refined data. As to be expected, the intensity of the Br...Br shell in the FT of the *trans*-[NiBr₂(PEt₃)₂] data is much enhanced compared to that in the FT of the *tetrahedral*-[NiBr₂(PPh₃)₂] data due to the well known multiple scattering through the central Ni atom. The intensity of the Br...Br feature in the FT of the *trans*-[NiBr₂(PEt₃)₂] data is very dependent on bond angle, with the multiple scattering causing (compared to single scattering) an intensity enhancement at 180°, an intensity reduction at about 155°, and very little effect at bond angles below 140°. Therefore, the intensity of the Br...Br shell is a very sensitive measure of bond angle close to linearity.

The Ni K-edge XAFS and FT's for the two compounds are shown in Figure 2. It is immediately clear that there is a significant difference between the FT of *tetrahedral*-[NiBr₂(PPh₃)₂] and that of *trans*-[NiBr₂(PEt₃)₂], where the latter contains a clear feature in the FT at approximately twice the first shell distance, which is absent in the FT of *tetrahedral*-[NiBr₂(PPh₃)₂]. Even without further calculation it is clear that these 2R features must be due to the linear arrangement of the atoms in the square planar complex as the position of this peak in the FT of the *trans*-[NiBr₂(PEt₃)₂] Ni K-edge data is in virtually the same position as the Br...Br feature in the FT of the *trans*-[NiBr₂(PEt₃)₂] Br K-edge data. Therefore, the 2R features can be used diagnostically for the presence of linear units, a fact that we have identified earlier (Young, 1996a) and are currently using to great effect in the study of small triatomic species isolated in cryogenic matrices. The intensity of the 2R feature is very sensitive to bond angle at the metal centre, and therefore provides an accurate means of bond angle determination where the trigonometric functions are at their least sensitive.

**Figure 1**

Br K-edge XAFS and Fourier Transforms for *tetrahedral*-[NiBr₂(PPh₃)₂] (top) and *trans*-[NiBr₂(PEt₃)₂] (bottom) at 10 K. Solid line, experimental data; dotted line, theoretical data.

**Figure 2**

Ni K-edge XAFS and Fourier Transforms for *tetrahedral*-[NiBr₂(PPh₃)₂] (top) and *trans*-[NiBr₂(PEt₃)₂] (bottom) at 10 K. Solid line, experimental data; dotted line, theoretical data.

Whilst the data in the figures were collected at 10 K, we have also observed the 2R features in the 77 K and 300 K FT of the Ni K-edge data of *cis*-[NiBr₂(dppe)].

Using EXCURV98 it is now possible to fit such multiple scattering pathways using the cluster approach, and the best fit refinements are also shown in the Figures and the data are given in the table, together with previously published X-ray data. Even though the data for *tetrahedral*-[NiBr₂(PPh₃)₂] was also fitted using a full cluster multiple scattering approach it is clear that there are no significant features in the data beyond the first shell. One of the problems of fitting data with two overlapping shells in the first co-ordination environment has always been deciding which refined distance belongs to which atom type. However, in the case of data containing features at 2R, it is much easier to arrive at the correct answer, as in the case of these NiBr₂P₂ complexes, the pathways involving the Br atoms are much more significant than those containing the P atoms. It should also be possible in principle, to identify *cis* and *trans* isomers as in the former there will be two equal paths through the central atom, but in the latter case there will be two different pathways through the central atom. We have also noticed that the Debye-Waller factor for the Ni-P shells is much better defined once the full multiple scattering calculations have been carried out.

It is clear from Table 1 that the refined XAFS data gave values in good agreement with single crystal X-ray data (and the previous XAFS data (Corker *et al.*, 1989) for both *tetrahedral*-[NiBr₂(PPh₃)₂] (Jarvis *et al.*, 1968) and for *trans*-[NiBr₂(PET₃)₂] (Scatturin *et al.*, 1958). Whilst, the quality of the original X-ray data for *trans*-[NiBr₂(PET₃)₂] was very poor, our inter-atomic distances are also in good agreement with those from related *trans* square planar complexes. For example, Stalick and Ibers, (1970) and Godfrey *et al.*, (1993) have reported Ni-Br distances of 2.297 and 2.291 Å and Ni-P distances of 2.251 and 2.232 Å.

Table 1

Refined Ni and Br K-edge XAFS data at 10 K for [NiBr₂(PET₃)₂] and [NiBr₂(PPh₃)₂].

[NiBr ₂ (PET ₃) ₂]	XAFS		X-ray ^(Jarvis, 1968)
	r/Å	2σ ² /Å ²	r/Å
Ni-P	2.252(7)	0.0065(20)	2.26
Ni-Br	2.298(2)	0.0052(6)	2.30
	R = 17.97	E _r = -7.77	
Br-Ni	2.306(2)	0.0044(2)	2.30
Br...P	3.218(56)	0.038(19)	3.22
Br...Br	4.603(4)	0.0063(4)	4.60
	R = 25.90	E _r = -7.23	

[NiBr ₂ (PPh ₃) ₂]	XAFS		X-ray ^(Scatturin, 1958)
	r/Å	2σ ² /Å ²	r/Å
Ni-P	2.344(12)	0.0124(56)	2.323(5), 2.343(5)
Ni-Br	2.348(3)	0.0043(3)	2.346(3), 2.329(3)
	R = 27.59	E _r = -8.54	
Br-Ni	2.340(2)	0.0041(2)	2.346(3), 2.329(3)
Br...P	3.740(48)	0.0439(155)	3.737, 3.805, 3.607, 3.656
Br...Br	4.198(9)	0.0094(15)	4.182
	R = 28.83	E _r = -7.71	

Standard deviations in parentheses; 2σ² is the Debye-Waller factor; inter-atomic distance errors arising from data collection and analysis are estimated to be ±1.5% for well defined co-ordination shells (Corker *et al.*, 1989); in all cases the Br...P shells were poorly defined, with relatively large Debye-Waller factors; E_r is a refined parameter to account for the difference in experimental and theoretical Fermi levels;

$$R = \left[\int |\chi^T - \chi^E| k^3 dk / \int |\chi^E| k^3 dk \right] \times 100\% .$$

4. Conclusions

This work has shown that multiple scattering pathways through the central atom are readily observable in the metal K-edge XAFS spectra of co-ordination compounds. These 2R features can be used to identify the presence of linear or near-linear units and therefore aid in the assignment of molecular geometry. Care should be taken in interpreting data both in the solid and solution that contain features at approximately twice the metal ligand distances, as these may be mis-assigned to packing or solvent interactions. We have also shown that the use of multiple scattering results in a more accurate determination of bond angles

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