

Bond Angle Determination at Metal Co-ordination Centres by E.X.A.F.S.

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Bromine and phosphorus ligand K-absorption edge E.X.A.F.S. have been used to derive co-ordination geometries at nickel centres.

E.X.A.F.S. (extended X-ray absorption spectroscopy) has attracted much attention as a technique to derive structural information about metal centres in a variety of disordered media, such as glasses, oxide surfaces, and solutions.¹ The technique provided good estimates of the atomic number(s) of the non-hydrogen atoms in the local environment of the absorbing atom, of their number, and of inter-atomic distances from the targeted element. What is generally absent is any angular information. Multiple scattering effects can yield some angular information about the atoms *adjacent* to the absorbing atom^{2,3} but the E.X.A.F.S. studies at a metal edge then will only provide a bond angle at a *ligand* atom, and normally only if the angle is $>ca. 130^\circ$. Orientational detail can be derived by exploiting the polarisation of synchrotron radiation, as has been utilised in surface science experiments,⁴ but such experiments are not applicable to isotropic and amorphous systems. An alternative approach to bond angle estimation would be to triangulate using distances derived from both metal and ligand absorption sites. Application to such approach has been widened in recent years with the extension of E.X.A.F.S. into the soft X-ray region (S.O.X.A.F.S.) so allowing access to common donor atoms such as phosphorus, sulphur, and chlorine.⁵ We report E.X.A.F.S. studies to estimate bond angles at nickel in phosphine complexes, some of which are precursors of alkene oligomerisation catalysts.⁶

X-Ray absorption spectra of these compounds were recorded using the Synchrotron Radiation Source at the Daresbury Laboratory. The P and Cl K-edge spectra were recorded *in vacuo* using fluorescence detection on Beam Line 3.⁵ The harder K-edges were recorded in transmission mode on Beam Lines 7 and 8.⁷ In general the S.O.X.A.F.S. data were of lower quality. Initially an electron-yield detection method was employed, but sample charging effects rendered the baseline unreliable; with the current low acceptance angle photon detector, the gain in having a reliable baseline with fluorescence detection was offset by a loss in signal/noise ratio.

The results of the E.X.A.F.S. analyses of compounds with reported crystal structure determinations are presented in Table 1. Analyses were carried out using *ab initio* phase shifts and back-scattering factors using spherical wave methods previously described.⁸ Over all determinations these unmodified parameters yielded a Ni-E bond length (sample of 21) with an average deviation of -0.023 \AA and a standard deviation of 0.060 \AA . These values are elevated by the rather large underestimates of the Ni-P distances from the phosphorus edge data. It is possible that as well as the lower data quality a contribution to this may be that the phase shifts for such a light element display a much larger chemical dependence than has been experienced for heavier elements. Excluding these data, the mean discrepancy and standard deviation are -0.005 and 0.047 \AA respectively. This sample contains a cross-section of structural problems, including high intershell correlations, as for the Ni-Cl and Ni-P distances in $\text{NiCl}_2(\text{PPh}_3)_2$ (4),⁹ and suggests that previous estimates of the precision in bond length determinations of $\pm 0.03 \text{ \AA}$ are not unreasonable.¹⁰ Absolute errors are obviously higher for the more distant non-bonded shells. The mean discrepancy and

standard deviation for the sample of 10 such estimations were -0.03 and 0.09 \AA respectively. So the most probable percentage errors on single determinations ($0.67 \times \sigma$) of bonded and non-bonded distances of an unknown compound can be estimated to be 1.4 and 1.6% respectively.

With this background, results for two examples of bond-angle estimation of two complexes for which there has not been a crystal structure determination are presented in Table 2. By comparison with bond lengths presented in Table 1, the Ni-P and Ni-Br distances have acceptable values. The experimental and computed Br K-edge E.X.A.F.S. of

Table 1. E.X.A.F.S. derived structural parameters: internuclear distances (\AA) and discrepancy from the mean X-ray diffraction distance (\AA).

Atom pair	Compound	Absorption edge	Inter-atomic distance	E.X.A.F.S. error
Ni-P	$\text{NiCl}_2(\text{PPh}_3)_2$, (4) ^a	Ni	2.22	-0.10
		P	2.21	-0.11
	$\text{NiBr}_2(\text{PPh}_3)_2$, (5) ^b	Ni	2.33	0.00
		P	2.17	-0.16
	$\text{NiBr}_2(\text{PEt}_3)_2$, (6) ^c	Ni	2.26	0.00
		P	2.22	-0.04
	$\text{NiCl}_2(\text{dppe})$, (7) ^d	Ni	2.16	0.01
		P	2.06	-0.09
Ni-Cl	NiCl_2 , (1) ^e	Ni	2.39	-0.04
		Cl	2.45	0.02
	$(\text{NEt}_4)_2[\text{NiCl}_4]$, (3) ^f	Ni	2.26	0.01
		Cl	2.22	-0.03
	(4)	Ni	2.26	0.05
		Cl	2.29	0.08
Ni-Br	(7)	Ni	2.21	0.01
		Ni	2.54	0.04
	NiBr_2 , (2) ^g	Br	2.47	-0.11
		Ni	2.34	0.00
	(5)	Br	2.32	-0.02
		Ni	2.29	-0.01
(6)	Br	2.31	0.01	
	P	3.07	0.00	
P ··· Cl	(7)	P	3.07	0.00
P ··· Br	(5)	Br	3.67	-0.03
		Br	3.14	-0.08
Cl ··· Cl	(1)	Cl	3.48	0.09
		Cl	3.78	0.11
	(3)	Cl	3.50	-0.16
		Cl	3.94	0.00
	(4)	Cl	3.50	-0.16
		Cl	3.94	0.00
Br ··· Br	(2)	Br	3.79	-0.14
		Br	4.06	-0.12
	(6)	Br	4.61	0.01

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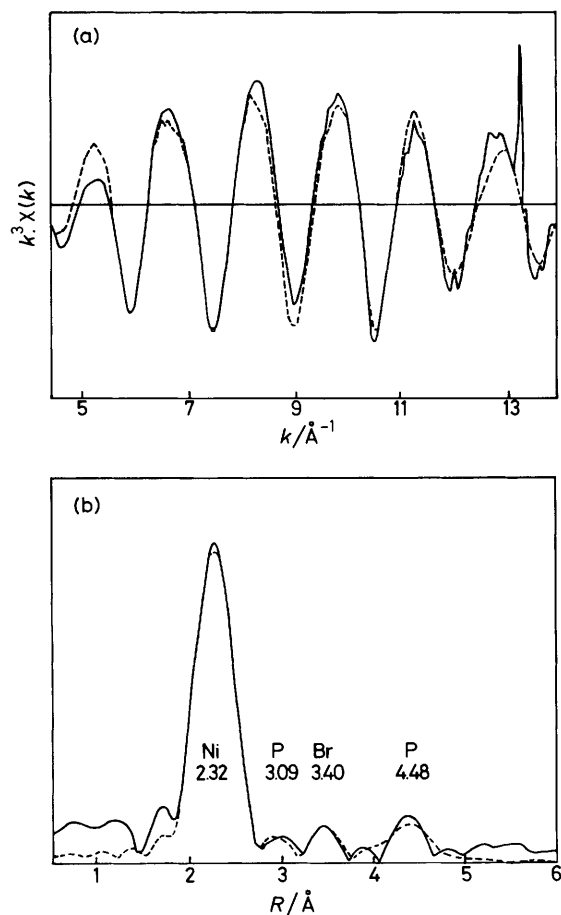


Figure 1. Experimental (—) and calculated (----) (a) k^3 weighted Br K-edge E.X.A.F.S. of $\text{NiBr}_2(\text{dppe})$ (**8**) and (b) their Fourier transforms, phase corrected for Ni.¹¹

Table 2. E.X.A.F.S. derived structural parameters: internuclear distances, R (Å), and Debye-Waller factors, α (Å²), where $\alpha = 2\sigma^2$ (σ = root mean square deviation in interatomic separation). The absorbing atom is listed first.

Compound	Shell	R	α
$\text{NiBr}_2(\text{dppe})$ (8)	Ni-P	2.16 (± 0.03)	0.0073(3)
	Ni-Br	2.33 (± 0.03)	0.0096(2)
	Br-Ni	2.32 (± 0.03)	0.0080(3)
	Br \cdots <i>cis</i> -P	3.09 (± 0.05)	0.015 ^a
	Br \cdots Br	3.40 (± 0.05)	0.010 ^a
	Br \cdots <i>trans</i> -P ^b	4.45 (± 0.07)	0.0234(8)
$[\text{NiCl}(\text{vppe})_2]\text{BPh}_4$ (9)	P-C	1.75 (± 0.02)	0.0005(5)
	Ni-P	2.20 (± 0.03)	0.0102(1)
	P-Ni	2.21 (± 0.03)	0.0173(12)
	Ni-Cl	2.29 (± 0.03)	0.0286(58)
	P \cdots <i>cis</i> -P	2.77 (± 0.04)	0.0216(16)
	P \cdots Cl	3.61 (± 0.06)	0.0147(35)
	P \cdots <i>trans</i> -P	4.34 (± 0.07)	-0.0100(12)

^a Value held constant. ^b Br-Ni-P angle set at 180° for calculation of multiple scattering. Errors in R are using the values of the most probable error derived from Table 1.

$\text{NiBr}_2(\text{dppe})$ ($\text{dppe} = \text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$) (**8**) and their Fourier transforms are presented in Figure 1. In addition to the large feature in the Fourier transforms due to the Ni atom, there are three smaller features, as expected for the *cis*-P, Br,

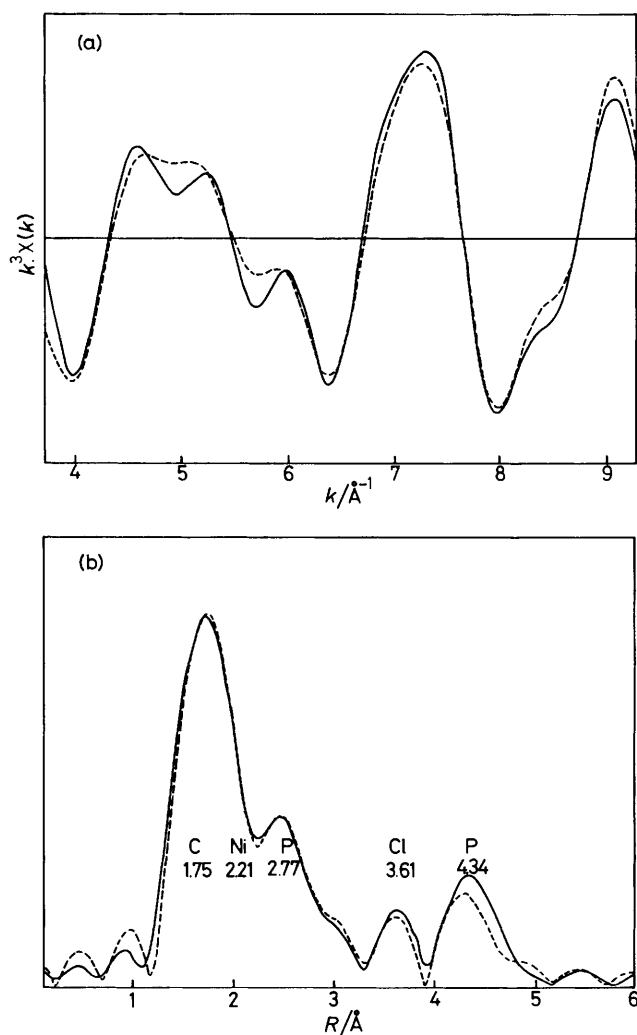


Figure 2. Fourier filtered² (1–4.5 Å) experimental (—) and calculated (----) (a) k^3 weighted P K-edge E.X.A.F.S. of $[\text{NiCl}(\text{vppe})_2]\text{BPh}_4$ (**9**) and (b) their Fourier transforms, phase corrected for Ni.¹¹

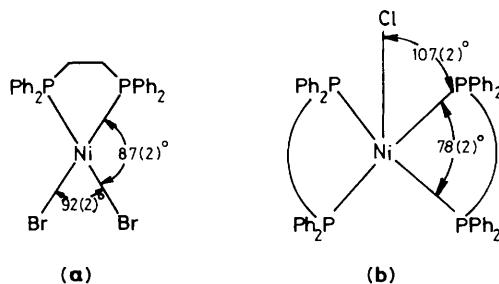


Figure 3. Estimated bond angles for (a) complex (**8**) and (b) (**9**).

and *trans*-P atoms in a *cis*-square planar complex (rather than a tetrahedral one). These non-bonded distances provide the bond angles in Figure 2a. The errors presented are estimated from the percentage distance errors cited above. These are larger estimates than is obtained from the least-squares analysis of the experimental spectra. The *trans*-Br-Ni-P angle is less well defined as 165(± 5)°. Corresponding values were calculated cross-referencing the Ni and P K-edge E.X.A.F.S.

for $[\text{NiCl}(\text{vppe})_2]\text{BPh}_4$ ($\text{vppe} = \text{cis-PPH}_2\text{CHCHPPH}_2$) (**9**) (Figure 2) (using the Ni edge-determined Ni-P distance) (Figure 3b). The Cl-Ni-P and *cis*-P-Ni-P angles are appropriate for a square-pyramidal complex. The *trans*-P-Ni-P angle estimate of $161(\pm 4)^\circ$ is close to the value calculated using a C_{4v} model at nickel (150°).

These results lay the foundations for using E.X.A.F.S. as a means of determining the bond angles at a co-ordination centre in many chemical systems. The apparently excellent results obtained for $\text{NiBr}_2(\text{dppe})$ (**8**) are assisted by the ease of obtaining X-ray spectra of high quality in the hard X-ray region encompassing Ni and Br K-edges. In part, the slightly less satisfactory evaluations from complex (**9**) can be ascribed to the poorer data quality of the P K-edge spectra and probably in part to some back-scattering from the non-adjacent carbon atoms in the phosphine.

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