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Nickel β–diketonato Compounds Studies using Extended X-ray Absorption of Fine Structure (EXAFS) and Energy Dispersive EXAFS (EDE)

M. B. Abdul Rahman[1], J. Evans[2] and A. J. Dent[3]

[1] *Department of Chemistry, Universiti Putra Malaysia, 43400 UPM Serdang, Malaysia.*
[2] *Department of Chemistry, University of Southampton, SO17 3AS Highfield, England.*
[3] *Daresbury Laboratory, Synchrotron Radiation Source, Warrington, England.*
Tel : 03-8946 6798, Fax: 03-8943 2508, E-mail: basya@fsas.upm.edu.my

Abstract : Extended X-ray Absorption Fine Structure (EXAFS) and Energy Dispersive EXAFS (EDE) data have been analysed for the nickel β–diketonato complexes, Ni(dpm)$_2$ and Ni(dpm)$_2$(PPh$_3$)$_2$, using the curved wave theory with *ab initio* phaseshifts. The derived parameters for the metal compounds were in good agreement between both methods, within experimental error of 0.02-0.05 Å for the bond distances. The derived structural parameters from EXAFS and EDE gave averaged distances of Ni-O 1.86 Å, Ni-C 2.00 Å and Ni-P 2.20 Å. EDE measurements using a new rectangular Si(111) monochromator and a Hamamatsu S4874 photodiode array at a Station 9.3 of Daresbury Laboratory have yielded consecutive spectra data taken at 1-1000 accumulations with 2-30 ms integration time to follow the changes during initiation of the catalytic reaction. The Ni(dpm)$_2$ spectra were acquired within 16 s, and Ni(dpm)$_2$(PPh$_3$)$_2$ spectra were acquired within 0.24 s for each spectrum.

Abstrak : Penjerapan sinar-X diperpanjangkan untuk struktur halus (EXAFS) dan Penyebaran Tenaga EXAFS (EDE) telah digunakan untuk menganalisis mangkin nikel β–diketonata, Ni(dpm)$_2$ dan Ni(dpm)$_2$(PPh$_3$)$_2$, menggunakan teori keluk gelombang dengan anjakan fasa *ab initio*. Nilai terbitan parameter bagi sebatian logam adalah bersesuaian dengan kaedah tersebut, di dalam julat ralat ujikaji sebanyak 0.02-0.05 Å bagi jarak ikatan. Purata jarak ikatan bagi struktur dari kaedah EXAFS dan EDE adalah Ni-O 1.86 Å, Ni-C 2.00 Å dan Ni-P 2.20 Å. Kaedah EDE menggunakan monokromator segiempat tepat Si(111) yang baru dan fotodiod Hamamatsu S4874 di Station 9.3, Daresbury Laboratory. Kaedah ini dapat merakamkan 1-1000 akumulasi dengan 2-30 ms masa integrasi untuk mengikuti perubahan semasa berlakunya proses pemangkinnan. Spektra Ni(dpm)$_2$ dirakamkan pada kadar 16 s, manakala spektra Ni(dpm)$_2$(PPh$_3$)$_2$ dirakamkan pada kadar 0.24 s bagi setiap spektrum.

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Introduction

Ni(dpm)$_2$ is used in this research for comparison with previous studies of Ni(acac)$_2$, since the bulky tertiary-butyl groups prevent polymerisation of the complex giving a monomeric structure [1-4]. Furthermore, we are interested in using the adducts of Ni(dpm)$_2$(PPh$_3$)$_2$, which is pseudo-octahedral, in order to study the selectivity of phosphines as co-catalysts. The catalytic activity of β–diketonato nickel complexes towards alkene oligomerisation on addition of co-catalysts is strongly affected by the nature of β–diketonato substituents. Previously, numerous workers have investigated the mechanism of nickel oligomerisation, e.g. Ni(acac)$_2$, Ni(sacsac)$_2$ and Ni(cod)$_2$ with alkyl-aluminium, AlEt$_2$(OEt) and AlEt$_3$ using XAS, EXAFS and QuEXAFS spectroscopic techniques [1-12]. The high solubility of Ni(dpm)$_2$ and of its adducts has been noted, and it was thought that use of this β–diketonato nickel complexes might produce products more soluble than acetylacetonato adducts. As EDE requires homogeneous and concentrated solutions for transmission detection, it is very important to study the solutions required for the *in situ* experiments with different acquisition parameters. This will help us to further understand the structure analysis including the effectiveness of the theoretical phase shifts by comparison between results from EXAFS, EDE and X-ray crystallography.

Experimental Procedures

Synthesis of bis (2,2,6,6-tetramethyl-3,5-heptanedionato) nickel(II)

A complex of Ni(dpm)$_2$ was prepared by the Collins' method [13]. The ligand, 2,2,6,6,-tetramethyl-3,5-heptanedionato (hdpm) (40 mmol) was dissolved in ethanol (95 %, 20 ml) and added to a solution of Ni(NO$_3$)$_2$.6H$_2$O (20 mmol) in a mixture of ethanol-water (50/50). To this was added slowly a solution of NaOH (40 mmol) in a mixture of ethanol-water (50/50) while stirring at room temperature. The precipitate formed was filtered and air-dried overnight with further drying at 110°C, changing from a green to a purple powder. The crude solid was purified either by sublimation at 0.1 mm/Hg at 120°C or recrystallisation from dry toluene.

Synthesis of bis (2,2,6,6-tetramethyl-3,5-heptanedionato) bistriphenylphosphine nickel(II)

The Fackler [14] method was employed for the preparation of this compound. Ni(dpm)$_2$ (1 mmol) was dissolved in dried and degassed toluene (5 ml). A solution of PPh_3 (2 mmol) in toluene (5 ml) was added to give a ratio of Ni:P of 1:2. On addition of the PPh_3 the colour changed from purple to dark green (as an indication, a brown solution appeared in excess dilution). After removing the solvent under vacuum a light-lime green, air stable powder was isolated. Evaporation produced a green solid.

EXAFS analysis of Ni compounds in the solid state

The $Ni(dpm)_2$ was grounded with boron nitride [ratio 4:3 (w/w)] to give a homogeneous solid sample. The $Ni(dpm)_2(PPh_3)_2$ complex was grounded with boron nitride (mass ratio of 2:1 of Ni:BN). The Ni K-edge EXAFS spectroscopic data were recorded in the transmission mode on Station 7.1, Daresbury Laboratory using a single crystal Si(111) monochromator at room temperature. The coordination numbers were initially set at the known crystal structure values [15] calculated from the STCALC option in the PAXAS programme.

EDE analysis of the 80 mM solution of nickel complexes in toluene

The EDE transmission data was set for a 80mM solution of $Ni(dpm)_2$ in toluene at room temperature. The EDE spectra were acquired at Station 9.3 (using a single crystal Si(111) monochromator, Hamamatsu S3094 detector [16]) in 1000 scans with an integration time of 30 ms. The EDE spectrum of a 80 mM solution of $Ni(dpm)_2(PPh_3)_2$ was recorded in 1000 scans and 18 ms integration time.

Results and Discussion

Bis(2,2,6,6-tetramethyl-3,5-heptanedionato) nickel(II)

The chelating dpm ligands, with their tertiary-butyl groups, enhance the solubility of the complex in non-polar organic solvents [14]. The ligands also shield the coordination sites around the metal center [17]. Compared to $Ni(acac)_2$ and other nickel octahedral Ni(II) complexes, $Ni(dpm)_2$ was found to be diamagnetic [18], in common with other square planar complexes.

EXAFS analysis of $Ni(dpm)_2$ in the solid state

The background subtracted k^3-weighted EXAFS and Fourier transform, phaseshift corrected for oxygen, of solid $Ni(dpm)_2$ are shown in Figure 1.

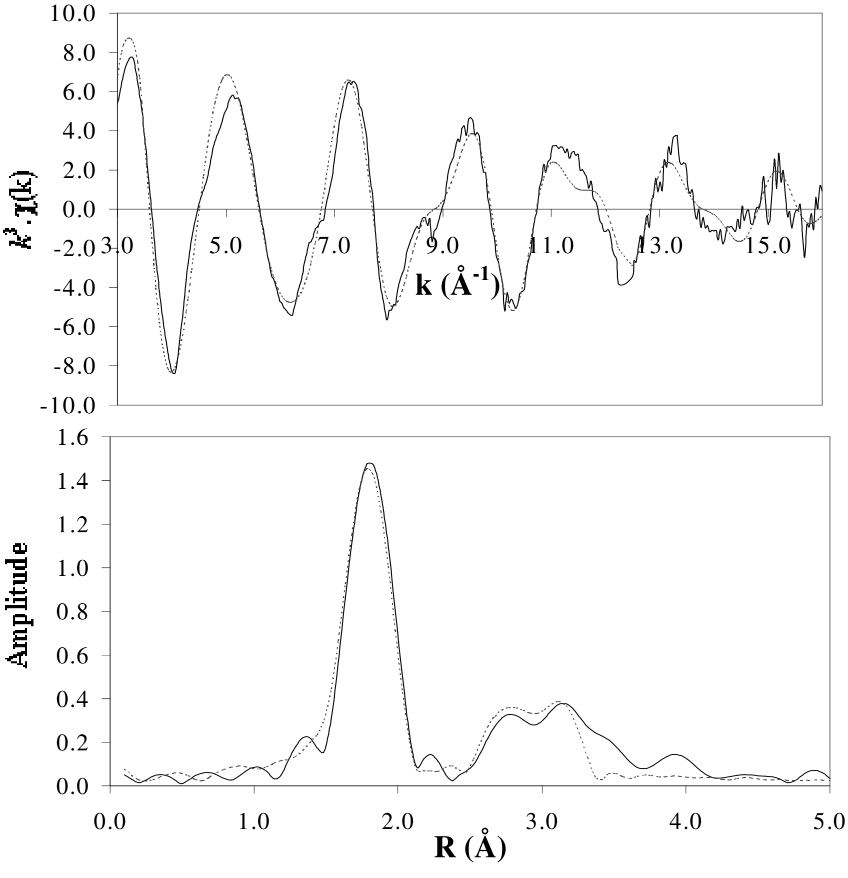

Figure 1 : The Ni K-edge k^3-weighted EXAFS and Fourier transform, phaseshift corrected for oxygen, of $Ni(dpm)_2$:BN of ratio 4:3. (——) Experimental and (----) spherical wave theory. *R*-factors, R = 26.90 % and E_0 values, E_0 = 5.47 eV.

Table 1 : EXAFS derived structural parameters of Ni(dpm)$_2$, compared to the x-ray crystal structure derived distances.

Shell	CN	R_{EXAFS} (Å)	a (Å^2)	$R_{crystal\ structure}$(Å)
O	4.0 (2)	1.818 (1)	0.007 (0)	1.836
C	4.0 (4)	2.782 (5)	0.008 (1)	2.829
C	2.3 (3)	3.104 (5)	0.002 (0)	3.212

statistical errors are given in parentheses

CN	**Coordination number**
R_{EXAFS} (Å)	**EXAFS derived distance from central atom**
$R_{crystal\ structure}$ (Å)	**Crystal structure derived distance from central atom**
a (Å^2)	**Debye-Waller factor A = 2σ^2, σ = mean square internuclear separation**

It was found both *t*-butyl groups have similar orientation with respect to the chelate ring. The 4.0 (2) oxygen atoms at 1.818 (1) Å for the first shell best fit the EXAFS spectrum. The 4.0 (4) carbon atoms at 2.782 (5) Å were then fitted as the second shell, followed by another 2.3 (3) carbon atoms at 3.104 (5) Å. The distances obtained are consistent with the crystal structure for a square planar Ni(dpm)$_2$ complex. The EXAFS derived for Ni-O distance compares well with the X-ray crystal structure (Table 1).

The Ni-O distance was shorter *ca.* 0.02 Å in Ni(dpm)$_2$ when compared to [Ni(acac)$_2$]$_3$ due to two possible reasons [13] : dpm is a better donor ligand due to greater electron donating effect from tertiary-butyl group compared to the methyl group in acac and the absence of electrons from the $d_{x^2-y^2}$ orbital which is σ-antibonding with respect to the Ni-O interactions. The Debye-Waller factor for carbons in the third coordination shell was very low, most likely due to more distant carbons from the tertiary-butyl group giving some contribution to the shell. Further discussions will be restricted to intermolecular parameters up to 4.0 Å [20].

No significant correlations were observed between the distances and Debye-Waller factors for the two shells. The fit index ratio for the parameters lower than the 0.96 is accepted, according to Joyner [21]. Correlation coefficients [22] were found to be in the range -0.630 to 0.683, indicating an acceptable fit. As further support to the significance tests a contour map of the fit index as a function of two parameters was plotted. A fit index contour map of Ni-C$_3$ (R2) versus Ni-C$_6$ (R3) is as shown in Figure 2. The contours are approximately circular in shape indicating a well fitted data.

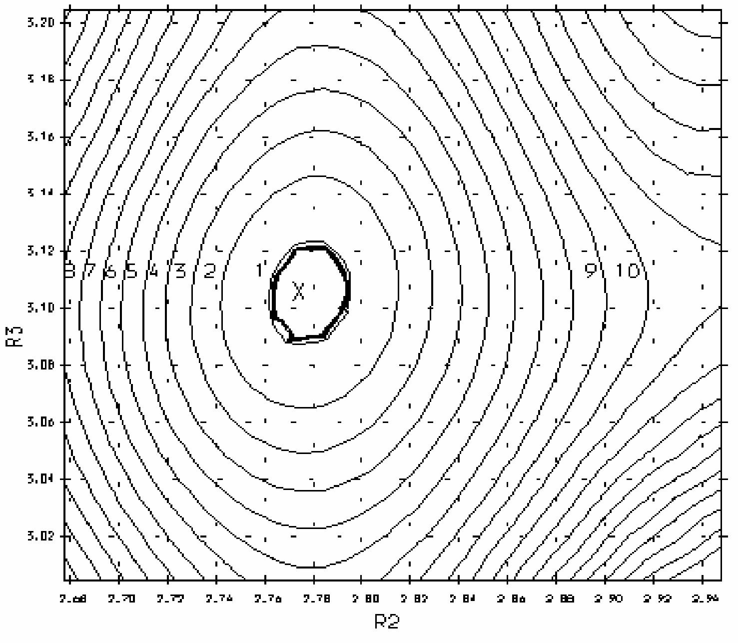

Figure 2 : Fit index contour map of the correlations between Ni-C$_3$ (R2) and Ni-C$_6$ (R3) distances from the nickel centre for of Ni(dpm)$_2$.
Lower contour : 0.442 Upper contour : 1.398 Increment : 0.050
Approximate minimum : 0.429 at 2.786, 3.114

EDE analysis of the 80 mM solution of Ni(dpm)$_2$ in toluene

The refinement of EDE transmission data for a 80mM solution of Ni(dpm)$_2$ in toluene at room temperature gave comparable bond distances to the dpm groups and was also used to verify the accuracy of the fast EDE measurement to both the conventional EXAFS and crystal structure. The EDE spectra were acquired at Station 9.3 (using a single crystal Si(111) monochromator, Hamamatsu S3094 detector) in 1000 scans with an integration time of 30 ms, to give a complete spectra within 30 seconds as shown in Figure 3.

The 80 mM solution of Ni(dpm)$_2$ spectrum acquired was best analysed up to $k = 9.0$ Å^{-1}, as high noise levels are noted above that k limit. The Ni-O$_1$ bond distance was fitted at 1.832 (2) Å consisting 4.0 (1) oxygen atoms in the first coordination shell. The Ni-C$_3$ bond distances (4.0 carbon (3) atoms in the second shell) is fitted at 2.743 (4) Å. Comparing the solution Ni-O$_1$ bond distance with solid state EXAFS and EDE, the distance is slightly longer in the latter at 1.832 Å. However, it is comparable to 1.836 Å of the crystal structure [15] data as summarised in Table 2. Attempts to fit the third coordination shell with 2.0 (2) adjacent carbon atoms at 3.014 (5) Å gave difficulties as the data acquired was short but gave a decrease in the fit index according to the Joyner [21] test and an acceptable R value, R = 28.98 %. The data were recorded in 30 seconds, which is fast compared to the conventional EXAFS determination method that usually takes about 45-50 minutes, thus achieving the goal of improved time resolution [23].

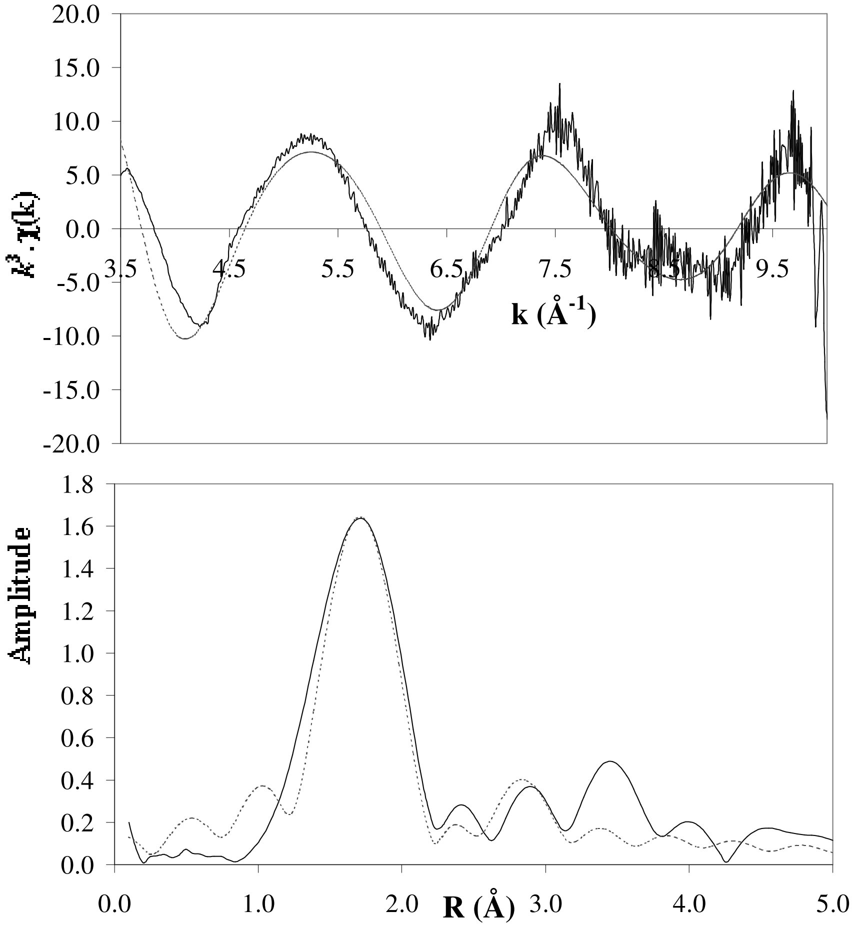

Figure 3 : The Ni K-edge k^3-weighted EDE and Fourier transform, phaseshift corrected for oxygen, of Ni(dpm)$_2$ in 80 mM solution at room temperature with acquisition time of 1000 scans × 30 ms. (——) Experimental and (----) spherical wave theory. *R*-factors, $R = 28.98$ % and E_0 values, $E_0 = 5.423$ eV.

Table 2 : EDE derived structural parameters of Ni(dpm)$_2$, compared to the EXAFS parameters structure derived distances.

Shell	CN	R_{EDE} (Å)	a (Å^2)	R_{EXAFS}
O	4.0 (1)	1.832 (2)	0.010 (0)	1.818 (1)
C	4.0 (3)	2.743 (4)	0.004 (1)	2.782 (5)
C	2.0 (2)	3.014 (5)	0.015 (2)	3.104 (5)

statistical errors are given in parentheses

CN	**Coordination number**
R_{EDE} (Å)	**EDE derived distance from central atom**
R_{EXAFS} (Å)	**EXAFS derived distance from central atom**
a (Å^2)	**Debye-Waller factor A = 2σ^2, σ = mean square internuclear separation**

Bis(2,2,6,6-tetramethyl-3,5-heptanedionato) bistriphenylphosphine nickel(II)

Comparing to Ni(dpm)$_2$, this paramagnetic [24] Ni(dpm)$_2$(PPh$_3$)$_2$ formed a *pseudo*-octahedral complex as shown in Figure 4.

EXAFS characterisation of Ni(dpm)$_2$(PPh$_3$)$_2$ in the solid state

The Ni K-edge k^3-weighted EXAFS and Fourier transform is shown in Figure 6 and the structural parameters derived are summarised in Table 3. For the first coordination shell, 4.0 (5) oxygen atoms is fitted at 1.968 (1) Å. The second coordination shell is best fitted at 2.305 (8) Å by 2.0 (1) phosphorus atoms. Inclusion of 4.0 (4) carbon atoms at 2.851 (5) Å in the third coordination shell and 2.0 carbon atoms at 3.521 (11) Å in the fourth coordination shell appeared to be valid accordingly to Joyner [21].

On addition of the phosphorus ligands, the Ni-O distance becomes elongated to 1.968 Å from 1.836 Å due to the steric hindrance and the occupancy of the antibonding $d_{x}2_{-y}2$ orbital. The 4.0 (5) oxygen atoms are maintained in the first coordination shell indicating that no dpm group is lost. The *pseudo*-octahedral structure in Figure 4 can be proposed from the EXAFS results. No crystal structure data is available for comparison, but the parameters derived for Ni-P are within 0.02 Å of Ni(PPh$_3$)$_2$(CO)$_2$ [25]. The high Debye-Waller factor observed for the phosphorus shell can be explained by the presence of inequivalent triphenylphosphine ligand, causing high static disorder. Changes in XANES (see Figure 6) are also apparent on addition of PPh$_3$, lending further support to the EXAFS analysis [26].

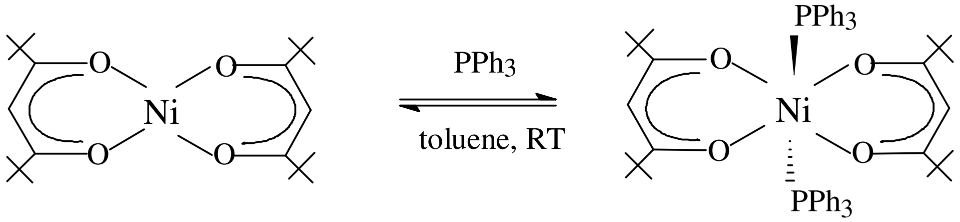

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Figure 4 : Ni(dpm)$_2$ forming octahedral complex of Ni(dpm)$_2$(PPh$_3$)$_2$.

Table 3: EXAFS derived structural parameters for Ni(dpm)$_2$(PPh$_3$)$_2$, solid sample at room temperature.

Shell	CN	R_{EXAFS} (Å)	a (Å^2)
O	4.0 (5)	1.968 (1)	0.007 (0)
P	2.0 (1)	2.305 (8)	0.032 (2)
C	4.0 (4)	2.851 (5)	0.011 (5)

statistical errors are given in parentheses

CN	**Coordination number**
R_{EXAFS} (Å)	**EXAFS derived distance from central atom**
a (Å^2)	**Debye-Waller factor A = 2σ^2, σ = mean square internuclear separation**

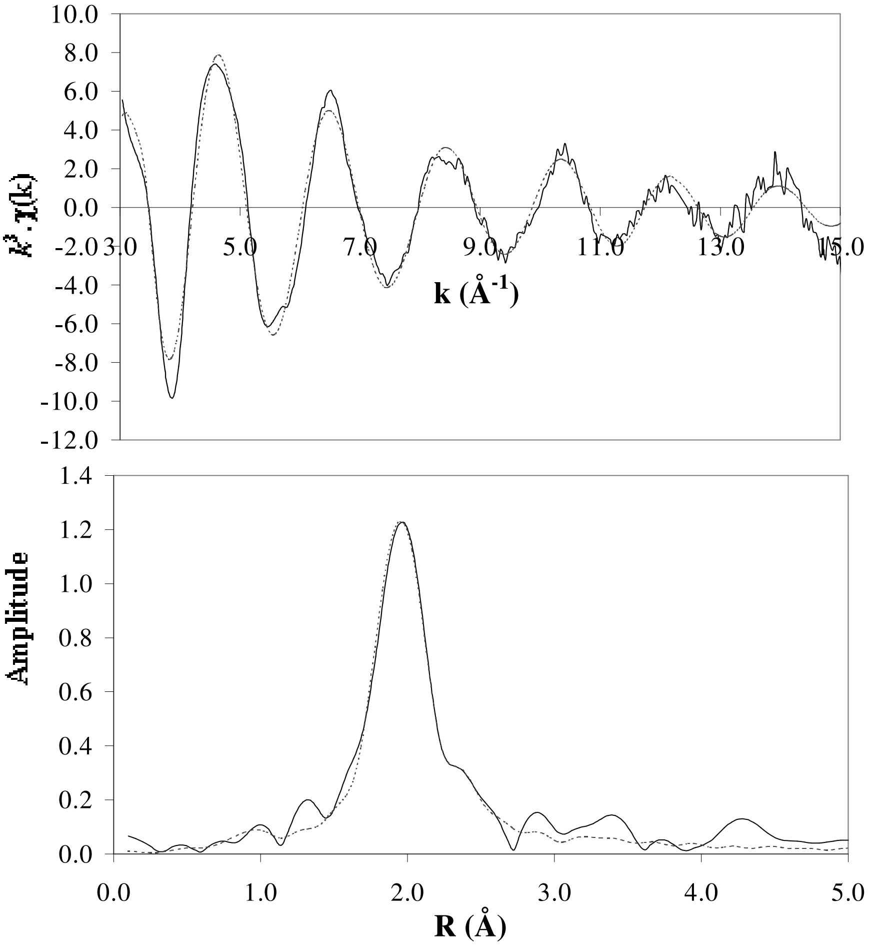

Figure 5 : The Ni K-edge k^3-weighted EXAFS and Fourier transform, phaseshift corrected for oxygen, of $Ni(dpm)_2(PPh_3)_2$. (——) Experimental and (----) spherical wave theory. *R*-factors, R = 20.78 % and E_0 values, E_0 = 3.97 eV.

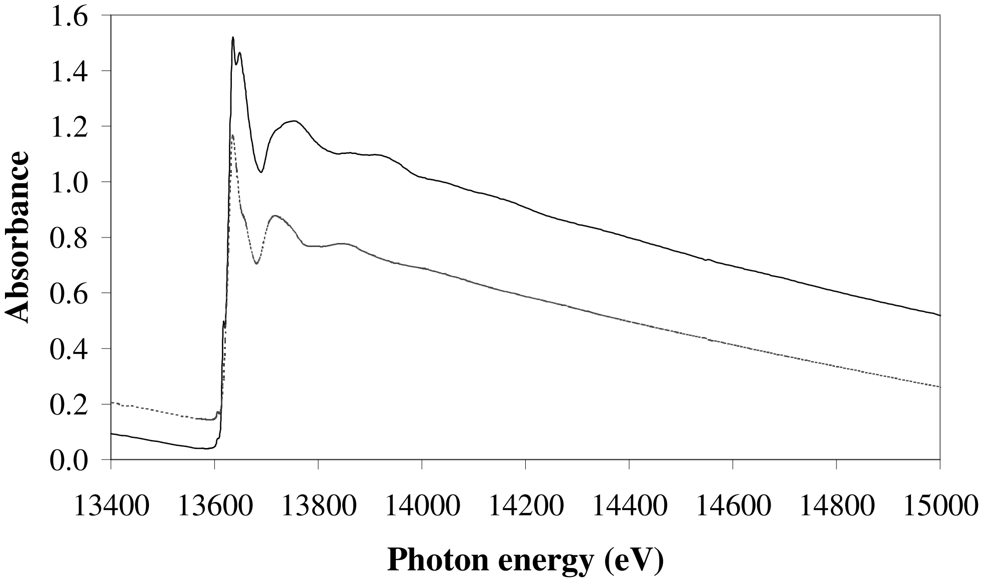

Figure 6 : X-ray absorption spectra of solid $Ni(dpm)_2$ and $Ni(dpm)_2(PPh_3)_2$.

Table 4 : EDE derived structural parameters of a 80mM solution $Ni(dpm)_2(PPh_3)_2$, compared to the EXAFS derived structural distances.

Shell	CN	R_{EDE} (Å)	a (Å^2)	R_{EXAFS} (Å)
O	4.2 (2)	1.902 (4)	0.012 (1)	1.968 (1)
P	2.3 (5)	2.278 (3)	0.019 (0)	2.305 (8)

statistical errors are given in parentheses

CN	**Coordination number**
R_{EDE} (Å)	**EDE derived distance from central atom**
R_{EXAFS} (Å)	**EXAFS derived distance from central atom**
a (Å^2)	**Debye-Waller factor A = $2\sigma^2$, σ = mean square internuclear separation**

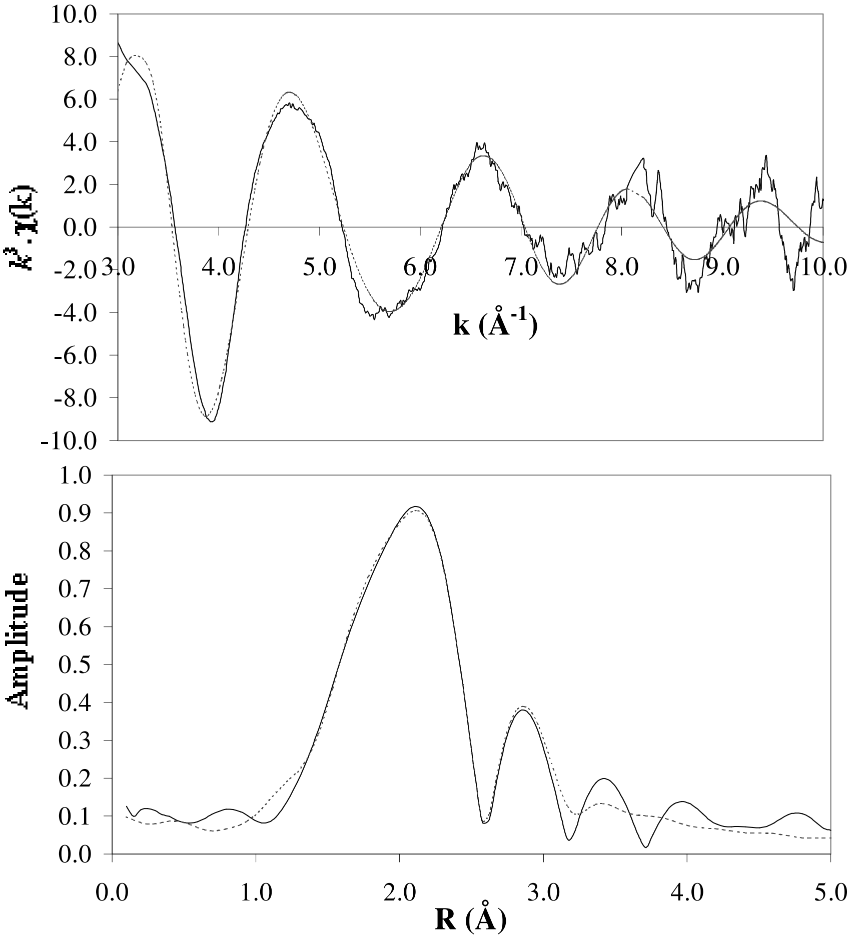

Figure 7 : The EDE Ni K-edge k^3-weighted EXAFS and Fourier transform, phaseshift corrected for oxygen, of $Ni(dpm)_2(PPh_3)_2$ in toluene (80 mM) at room temperature (scan times of 1000 scans × 18 ms). (——) Experimental and (----) spherical wave theory. R-factors, R = 32.30 % and E_0 values, E_0 = 4.09 eV.

EDE characterisation of a 80 mM solution of $Ni(dpm)_2(PPh_3)_2$ in toluene

The EDE spectrum of a 80 mM solution of $Ni(dpm)_2(PPh_3)_2$ was recorded in 1000 scans and 18 ms integration time. Analysis in curve fitting of Ni K-edge EDE is displayed in Figure 7 with its Fourier transform. Noise levels started to increase at 9.0 k Å^{-1}, restricting the derived parameters only up to two or three coordination spheres. The major peak in the Fourier transform consists of the first and second coordination shells of oxygen and phosphorus atoms. The first coordination shell is fitted at 1.902 (4) Å with 4.2 (2) oxygen atoms from the bidentate ligands. The second coordination shell with 2.3 (5) phosphorus atoms is fitted at 2.278 (3) Å. The broadening of the first peak in the Fourier transform was affected by the shorter data length, and leads to poorer resolution between shell parameters. A contour map of the fit indices for the Ni-O (R1) versus Ni-P (R2) bond distance (Figure 8) shows that the parameters are well defined with a slightly steeper gradient for the phosphorus shell, as expected for the larger backscatterer. Refining the fit with the phenyl groups gave an unreasonable, negative Debye-Waller factor and increasing in the fit index, failing the Joyner test [21].

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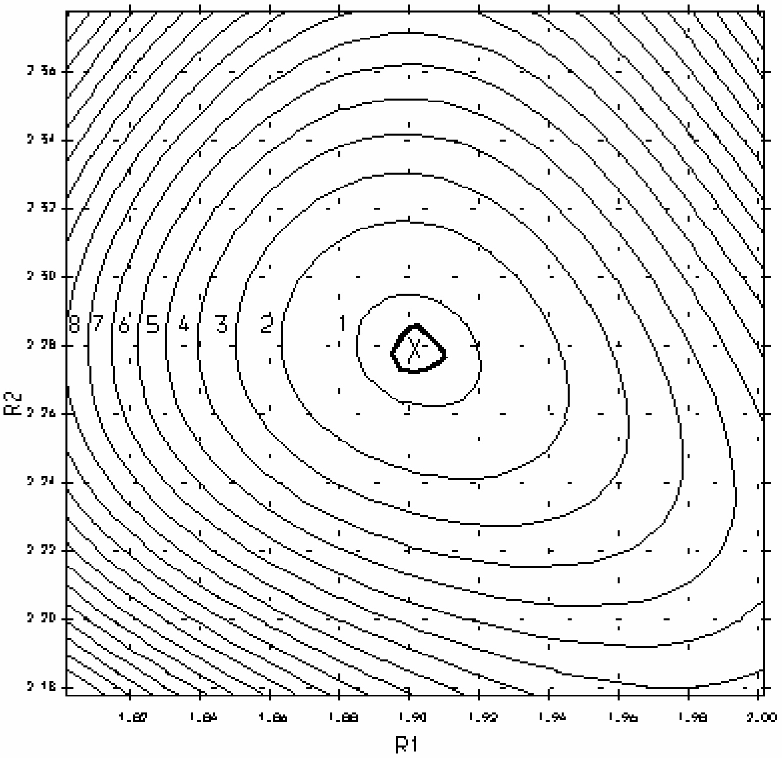

Figure 8 : Fit index contour map of the correlations between Ni-O (R1) and Ni-P (R2) distances from the nickel centre for the EDE data of $Ni(dpm)_2(PPh_3)_2$.

Conclusions

The studies of model compounds, $Ni(dpm)_2$ and $Ni(dpm)_2(PPh_3)_2$, with different methods of X-ray absorption spectroscopy, standard EXAFS and energy dispersive EXAFS gave reliable data. Structural parameters derived from EXAFS and EDE were in good agreement within experimental errors. The EDE spectra achieved the goal of the research with a time scale less than 30 s using a triangular Si(111) crystal at Station 9.3. Thus, the determination of intermediates in catalytic reaction can be monitored in future spectroscopic studies.

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