

### Preparation of complexes 1-5

The preparation of complexes **1-4** was carried out following literature methods (see references 6 (**1**), 7 (**2**), 9 (**3**) and 11 (**4**) in paper) with only slight modifications in some cases (see below). The purity of the samples was assessed by  $^1\text{H}$  and  $^{31}\text{P}$  NMR. In all cases the data obtained corresponded well with the published data.

$^{31}\text{P}\{^1\text{H}\}$ -NMR (referenced to external 85%  $\text{H}_3\text{PO}_4$ ), and  $^1\text{H}$ -NMR (standard  $\text{SiMe}_4$ ) spectra were recorded on a Bruker Advance DPX 300, at *r.t.* using  $\text{CDCl}_3$  as solvent. The conductivity of complex **1** was measured on a Jenway Conductivity Meter 4320.

$[\text{Au}_2(\text{dppm})_2\text{Cl}_2]$  (**1**) was prepared by addition of bis(diphenylphosphino)methane (dppm) to an equimolar amount of  $[\text{AuCl}(\text{tht})]$  (0.1 g) dissolved in dichloromethane (30 mL) and the resulting mixture stirred under nitrogen for 2 hours. Diethyl ether (*ca.* 20 mL) was added to form **1** as a colourless solid (yield = 78 %). The sample was later recrystallised by dissolving it in a mixture of dichloromethane:acetonitrile and subsequently adding diethyl ether to encourage precipitation of **1**. NMR:  $d_{\text{H}}$ (300 MHz) 7.87 and 7.37 (20 H, br singlets, Ph), 4.88 (2 H, br s,  $\text{CH}_2$ );  $d_{\text{P}}$ (121.5 MHz) 33.2 (s).  $\Lambda_{\text{M}} = 2.1 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$  ( $0.8 \times 10^{-3}$  M in chloroform).

$[\text{Au}_2(\text{dppm})_2][\text{BF}_4]$  (**2**) was prepared by addition of excess  $\text{Ag}[\text{BF}_4]$  to a dichloromethane solution of **1**. The mixture was stirred in the dark under nitrogen for 1 hour, and then filtered over celite. By addition of diethyl ether, the desired product precipitated, and was filtered and dried in air (yield = 70 %). NMR:  $d_{\text{H}}$ (300 MHz) 7.1-8.0 (20 H, m, Ph), 4.5 (2 H, br s,  $\text{CH}_2$ );  $d_{\text{P}}$ (121.5 MHz) 35.7 (s).

$[\text{Au}(\text{SPh})(\text{PPh}_3)]$  (**3**) was prepared by addition of thiophenol into a dichloromethane (30 mL) solution of an equimolar amount of  $[\text{AuCl}(\text{PPh}_3)]$  (0.100 g). The reaction mixture was stirred for 3 hours under nitrogen. Then, 20 mL of hexane were added to obtain a colourless solid, which was filtered and dried in air (yield = 70 %). NMR:  $d_{\text{H}}$ (300 MHz) 6.9-7.8 (m, Ph);  $d_{\text{P}}$ (121.5 MHz) 39.1 (s).

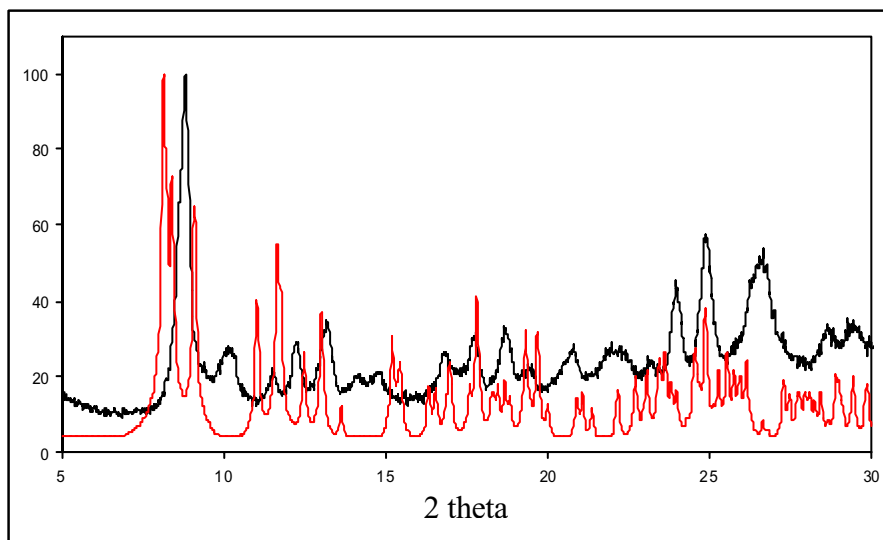
$[(\text{AuCl})_2(\mu\text{-xantphos})]$  (**4**). NMR:  $d_{\text{H}}$ (300 MHz) 7.62 [2 H, dd,  $^3J(\text{HH}) = 7.7$  Hz,  $^4J(\text{HH}) = 1.2$  Hz, H(1,8)], 7.44-7.25 (20 H, m, Ph), 7.06 [2 H, apparent t,  $^3J(\text{HH}) = 7.7$  Hz, H(2,7)], 6.44 [2 H, ddd,  $^3J(\text{HH}) = 7.7$  Hz,  $^4J(\text{HH}) = 1.3$  Hz,  $^3J(\text{HP}) = 12.7$  Hz, H(3,6)], 1.69 (6 H, s, 2  $\text{CH}_3$ );  $d_{\text{P}}$ (121.5 MHz) 24.0 (s).

[{Au(SC<sub>6</sub>H<sub>4</sub>Me-3)}<sub>2</sub>(μ-dpephos)] (**5**): To a solution of [(AuCl)<sub>2</sub>(μ-dpephos)]<sup>11</sup> (100 mg, 0.092 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (*ca.* 15 mL) was added triethylamine (33 μL, 0.24 mmol) and a solution of 3-methylbenzenethiol (25 μL, 0.21 mmol) in ethanol (*ca.* 1 mL). After 1 h, the solvent was removed under vacuum and the resulting white residue washed with ethanol/hexane (1:1, *ca.* 30 mL) and dried in air (83.0 mg, 77 %) (Found: C, 51.10; H, 3.88. C<sub>50</sub>H<sub>42</sub>Au<sub>2</sub>P<sub>2</sub>OS<sub>2</sub> requires C, 50.94; H, 3.59 %); d<sub>H</sub>(300 MHz) 7.47-6.67 (36 H, m, Ph), 2.19 (6 H, s, Me); d<sub>P</sub>(121.5 MHz) 29.4 (s).

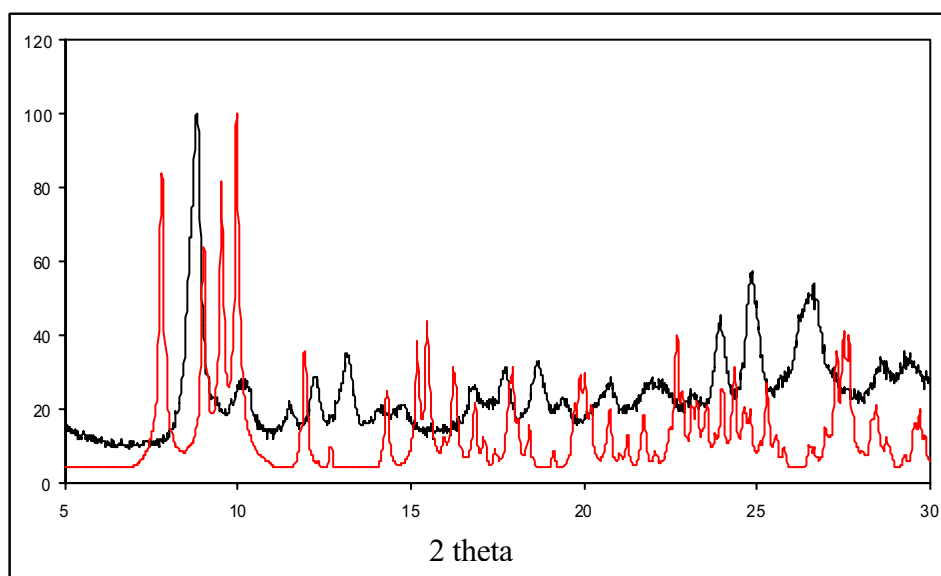
A crystal of **5** was mounted on to the diffractometer at low temperature under nitrogen at *ca.* 120K. The structure was solved using direct methods and refined with the SHELXTL version 5 and the non-hydrogen atoms were refined with anisotropic thermal parameters except carbon atoms C16c, c24c and c25c, which are isotropic. The atomic displacement parameters of the rings show evidence of probable disorder however this could not be modelled. The weighting scheme has been fixed at 0.1000, as this did not converge on refinement. Hydrogen-atom positions were added at idealised positions with a riding model and fixed thermal parameters ( $U_{ij} = 1.2U_{eq}$  for the atom to which they are bonded). The function minimised was  $\Sigma[w(|F_o|^2 - |F_c|^2)]$  with reflection weights  $w^1 = [\sigma^2 |F_o|^2 + (g_1P)^2 + (g_2P)]$  where  $P = [\max |F_o|^2 + 2|F_c|^2]/3$ . Additional material available from the Cambridge Crystallographic Data Centre comprises relevant tables of atomic coordinates, bond lengths and angles, and thermal parameters.

### X-ray Powder Diffraction studies

Comparison between the experimental XRPD patterns of complex **1** (precipitated from  $\text{CH}_2\text{Cl}_2$ /diethyl ether; pure by  $^1\text{H}$  and  $^{31}\text{P}$  NMR) and the calculated ones for the crystals containing acetone (a) or acetonitrile (b).



(a)



(b)

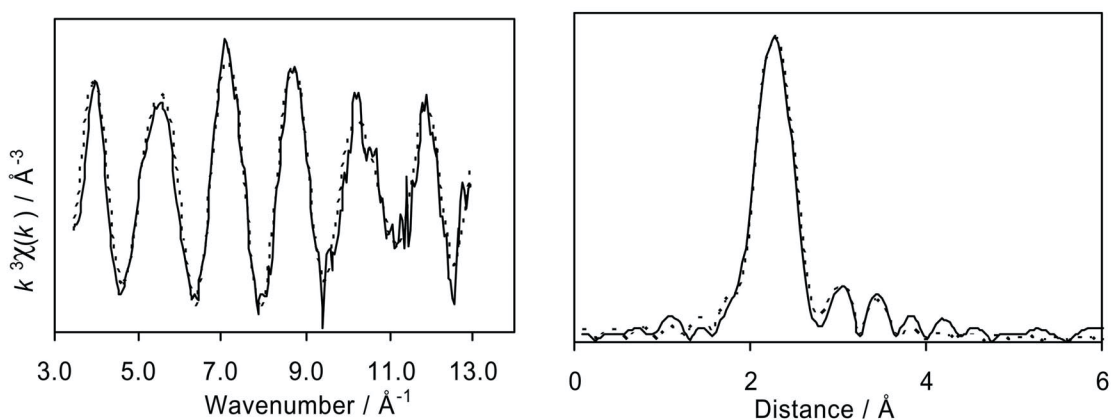
**Experimental (solid line) and fitted (broken line) EXAFS (left) and pseudo-radial distribution functions (right) for complexes 1-5**

Solid samples were collected in transmission as self supporting pellets diluted (*ca.* 30% w/w) in boron nitride or polyvinylpyrrolidone. The samples dissolved in acetonitrile (**2**: *ca.*  $10^{-2}$  M) or chloroform (**1**, **3**, **4**: *ca.*  $2\text{--}3 \times 10^{-3}$  M; **5**: *ca.*  $3 \times 10^{-2}$  M) were supported between polyethylene windows and sealed to limit evaporative losses. Due to the difference in solubility the solution of **2** was collected in transmission and those of **1**, **3**, **4** and **5** in fluorescence using a 13 element solid state Canberra fluorescence detector. Typically 5-10 (transmission) or 15-30 (fluorescence) scans were collected over  $k = 3$  to  $14 \text{ \AA}^{-1}$ . To evaluate the extent of any beam induced reduction of the gold, the EXAFS scans were examined individually and only those which did not change with time used in the fitting.

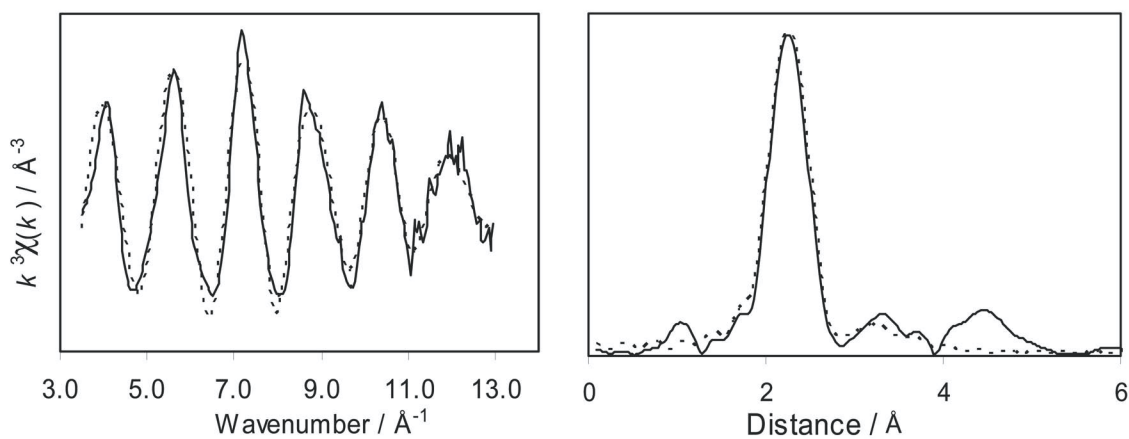
The best statistical fits were determined using the reduced  $\chi^2$  test. The number of independent data points ( $N_{\text{ind}}$ ) was calculated as  $N_{\text{ind}} \sim (2\Delta k \Delta r)/\pi$ , where  $\Delta k$  and  $\Delta r$  are the ranges in  $k$  and  $r$  space over which the data are fitted. In our case,  $\Delta k = 8\text{--}12 \text{ \AA}^{-1}$  (*i.e.*,  $k_{\text{min}} = 3 \text{ \AA}^{-1}$ ,  $k_{\text{max}} = 11\text{--}15 \text{ \AA}^{-1}$ ) and  $\Delta r = 10 \text{ \AA}$  ( $r_{\text{min}} = 0$ ,  $r_{\text{max}} = 10 \text{ \AA}$ ).

**Complex 1** (crystallised from dichloromethane/diethyl ether)

Solid (measured as pellet in BN)

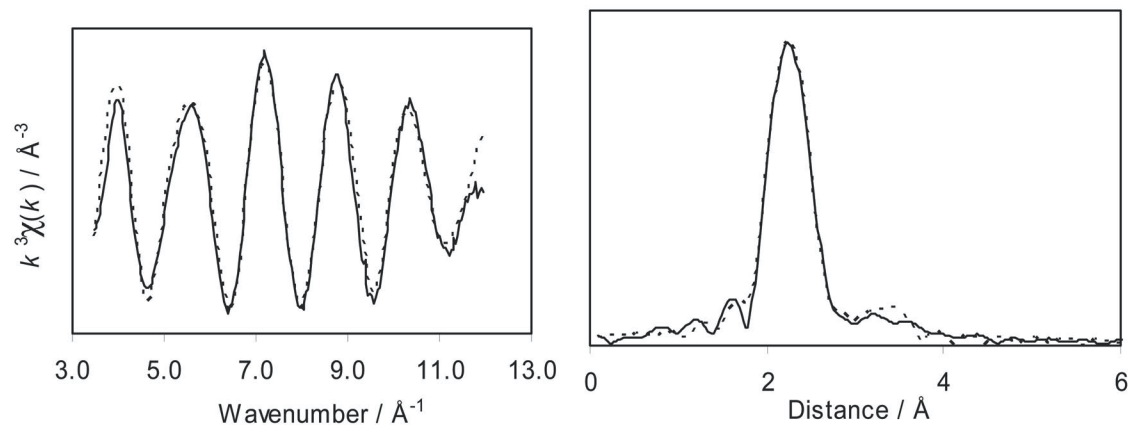


Solution



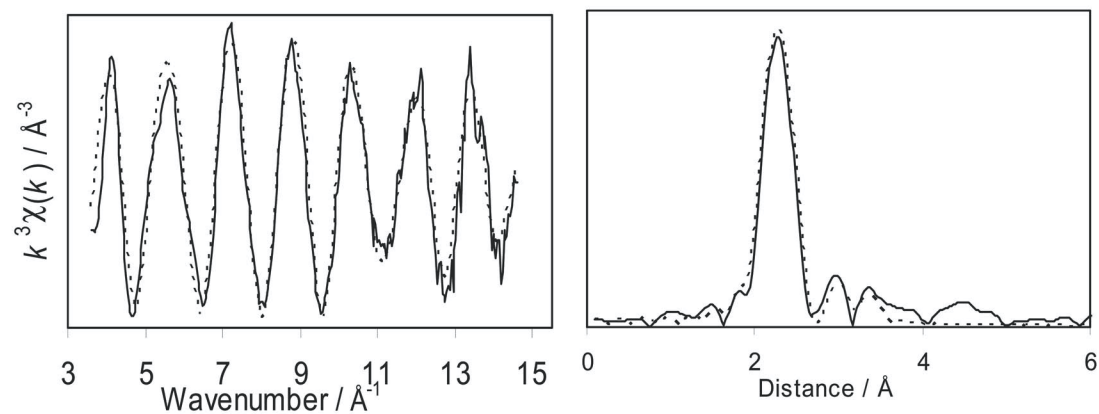
**Complex 1** (recrystallised from acetonitrile)

Solid (measured as pellet in polyvinylpyrrolidone)

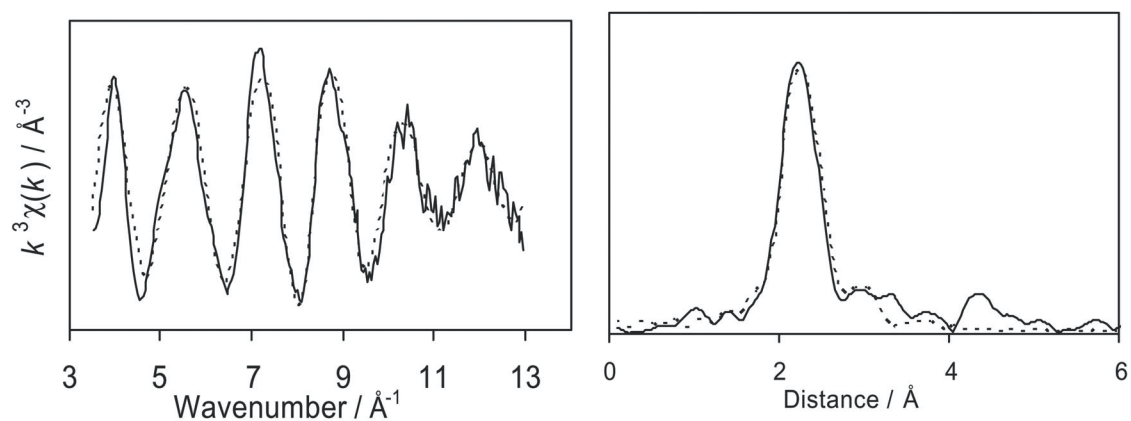


**Complex 2**

Solid

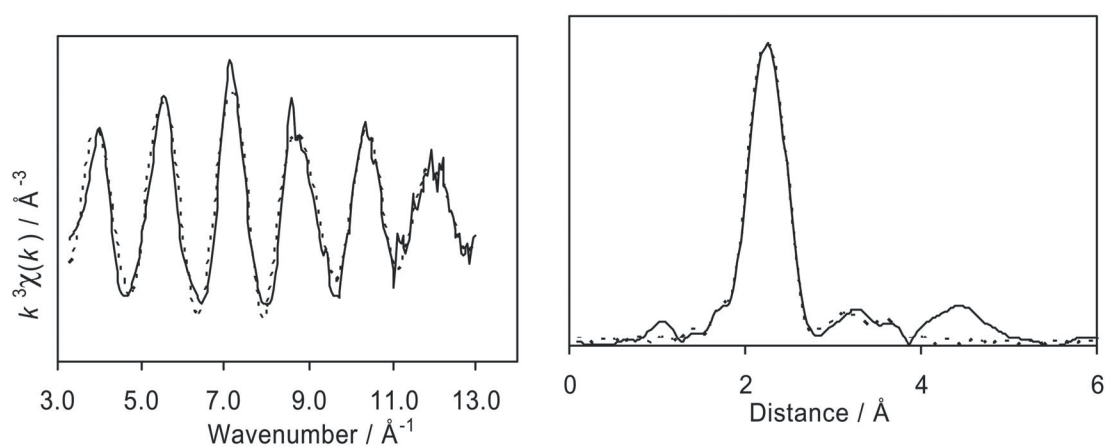


Solution

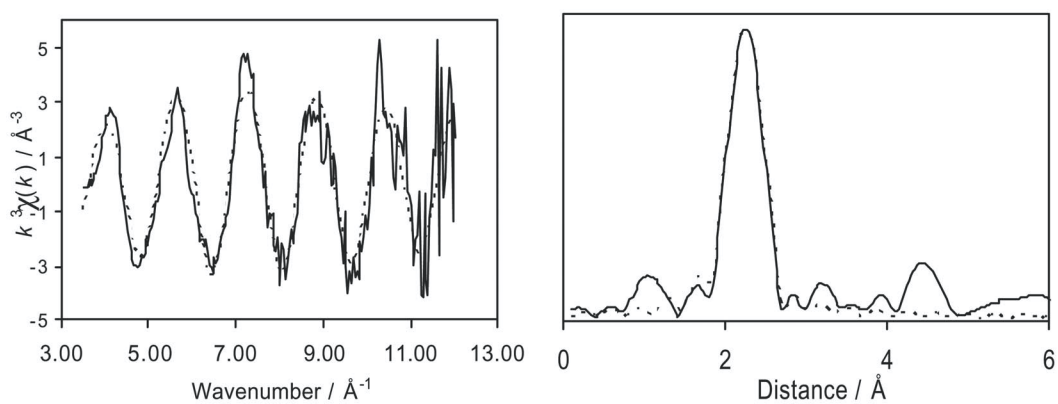


### Complex 3

Solid

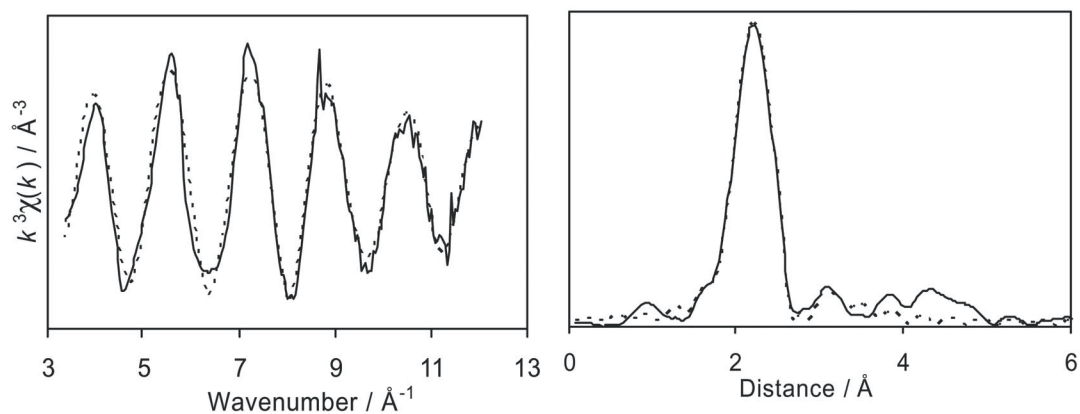


Solution

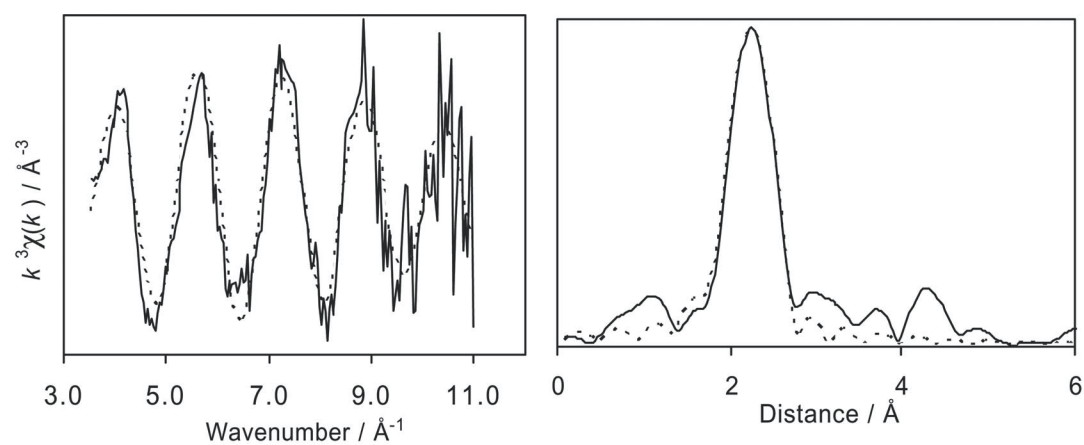


### Complex 4

Solid

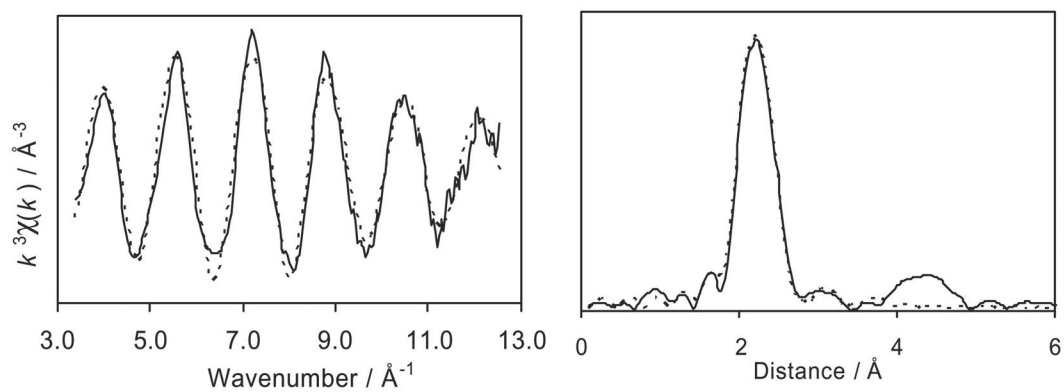


Solution



### Complex 5

Solid



Solution

