Linear Molecular Aggregation in Solution: EXAFS studies of ML_4 Complexes

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Analysis of Pt or Ir L_{III}-edge EXAFS spectra for $K_2[Pt(CN)_4]0.3Br\cdot3H_2O$ (**1**), $K_2[Pt(CN)_4]\cdot3H_2O$ (**2**), $[Pt(CNMe)_3Et]PF_6$ (**3**), and $[Ir(CNMe)_4]Cl$ (**4**) in solid and solution phases shows evidence for metal···metal interactions in solid (**1**), (**3**), and (**4**) and in solutions of (**4**).

The aggregation of molecules is fundamental to the growth of solid molecular materials from solution. In certain well known cases unusual, highly anisotropic, solid-state properties arise when molecular metal complexes of general formula ML_4 (M = Pt^{II}, Ir^{I} *etc.*, L = CN, CO, CNR *etc.*) interact strongly with one another through linear-chain metal···metal (M···M) contacts.[1] It is clearly of interest to characterize the processes by which the monomeric complexes form into chain polymer species. Spectroscopic studies on solutions of these complexes have shown evidence for chain formation, especially at high concentrations.[1—4] We report EXAFS studies on representative examples of such metal complexes which provide, for the first time, geometric information on intermolecular association of this sort in both solution and solid states.

The complexes studied were $K_2[Pt(CN)_4]0.3Br\cdot3H_2O$ (**1**), $K_2[Pt(CN)_4]\cdot3H_2O$ (**2**), $[Pt(CNMe)_3Et]PF_6$ (**3**), and $[Ir(CNMe)_4]Cl$ (**4**) in solid and solution phases.† The solid state structures of (**1**),[8] (**2**),[6] and (**3**)[3] are known from crystallographic studies. Compound (**1**) shows strong Pt···Pt interac-

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† Compound (**1**) was prepared as the crystalline hydrate $K_2[Pt(CN)_4]0.3Br\cdot3H_2O$ by literature methods.[5] Compound (**2**) was purchased from Aldrich and recrystallised from water immediately prior to measurement of EXAFS spectra; solid samples were prepared under air saturated with water vapour to minimise water loss from crystals which are very prone to dehydration.[6] Compounds (**3**) and (**4**) were prepared by literature methods[2,7] and characterised by uv/visible spectroscopy.

tions in the solid [Pt···Pt av. 2.895(2) Å at 300 K, 2.846(3) Å at 8 K][8] which are responsible for its remarkable quasi-one-dimensional conductivity.[1] Compounds (**2**) and (**3**) show weaker Pt···Pt contacts [*ca.* 3.48 Å in (**2**),[6] and *ca.* 3.58 Å in (**3**)[3]]. Iridium complex (**4**) has been studied by UV spectroscopy[2] in dilute (*ca.* 10^{-3} mol dm^{-3}) methanol solution and its structure assigned as oligomeric, with monomer units linked by Ir···Ir interactions. We have collected EXAFS spectra‡ on solid and solution samples of each of (**1**)—(**4**), and analysed these by model fitting.[9] Table 1 gives details of important geometric results. Figure 1a shows a typical observed *vs.* theoretical EXAFS and Figure 2 a typical Fourier transform (quasi-radial distribution function) plot. The ligand geometries in these species are well determined by the EXAFS results, *e.g.*, for the room temperature determinations of (**1**) the average Pt–C and Pt···N distances are 2.000(3) and 3.162(5) Å by EXAFS model fitting; *cf.* 2.007(7) and 3.175(10) Å by *X*-ray crystallography.[8]

The metal–metal interactions in solid (**1**) are clearly observed by EXAFS spectroscopy [see Table 1, Pt···Pt 2.874(6) and 2.832(3) Å at room and low temperatures; *cf.* crystallographic values[8] 2.895(2) and 2.846(3) Å respectively]. In contrast, in aqueous solution these contacts are clearly absent at the lower concentrations (290 and 120 mmol dm^{-3}) for which there is evidence for bromine co-ordination to platinum (at *ca.* 2.4 Å), as would be expected for disproportionation of (**1**) to give solvated Pt^{II} and Pt^{IV} monomer units. At the highest concentration (500 mmol dm^{-3}), there is ambiguity about the secondary (solute···solute, solute···solvent) structural features, but it is not clear that Pt···Pt interactions are present.

For (**2**) only Pt···ligand features may be unambiguously assigned in both solid and solution EXAFS spectra, good fits to spectra being obtained with two-shell models (Pt–C, Pt···N). In crystals of the fully hydrated solid, linear chains are known[6] to form with Pt···Pt contacts of length 3.478(1) Å. These contacts are not identifiable in the EXAFS data for solid (**2**), presumably because of partial dehydration in the finely ground samples studied and consequent disorder. Concentrated (*ca.* 1 mol dm^{-3}) aqueous solutions of (**2**) have recently[4] been reported to contain oligomers of the anions [[{Pt(CN)$_4$}$_n$]$^{2n-}$, n = 3, 5 *etc.*], although in amounts which are highly dependent on temperature and monomer concentration. The EXAFS data are evidently insensitive to the Pt···Pt contacts in such oligomers even at the highest concentration, presumably as a consequence of considerable disorder in the Pt···Pt distances involved and the consequent reduction of their influence on the EXAFS for k >10 Å^{-1}.[11]

Table 1. EXAFS analyses for ML$_4$ species in solid and solution[a] (distances in Å).

Compound		M–C	M···N	M···M
$K_2[Pt(CN)_4]0.3Br\cdot3H_2O$ (**1**)				
Solid RT		1.994(3)[b]	3.162(6)	2.874(6)
LT		2.000(3)	3.185(5)	2.832(3)
Solution (H_2O)	500[d]	1.984(3)	3.160(5)	—
	290	1.997(2)	3.166(3)	—
	120	1.998(2)	3.169(3)	—
$K_2[Pt(CN)_4]\cdot3H_2O$ (**2**)				
Solid RT		1.989(2)	3.162(3)	—
LT		1.988(3)	3.164(4)	—
Solution (H_2O)	1040[d]	1.989(3)	3.159(4)	—
	760	1.992(3)	3.162(5)	—
	260	1.990(3)	3.159(4)	—
	31	1.990(3)	3.157(4)	—
$[Pt(CNMe)_3Et]PF_6$ (**3**)				
Solid RT		1.952(3)	3.125(5)	3.62(2)
LT		1.990(3)	3.152(5)	3.64(1)
Solution (Me_2CO)	1200[d]	1.967(3)	3.137(3)	—
$[Ir(CNMe)_4]Cl$ (**4**)				
Solid RT		1.973(7)	3.162(14)	2.871(6)
LT		1.996(3)	3.142(5)	2.827(3)
Solution (MeOH)	200[d]	1.964(4)	3.124(5)	2.842(4)
	131	1.961(3)	3.146(7)	2.836(3)
	29[c]	1.963(4)	3.146(7)	2.844(3)
	2.9[c]	1.964(9)	3.16(2)	2.852(3)

[a] All solution and RT spectra were measured at ambient temperature (298 K); LT spectra were measured at liquid nitrogen temperature (78 K); $k_{\text{max.}}$ for transmission data was in the range 15.6—20.1 Å^{-1}, and in the range 13—15 Å^{-1} for fluorescence data. [b] The estimated standard deviation in the least significant digit as calculated by EXCURV88 model fitting is given in parentheses, here and throughout this paper. We note that such estimates of precision are likely to be underestimates of accuracy. Residual indices R and R' were calculated as below:

$$R = \sum_i \{k^3(\chi^{\text{obs}}_i - \chi^{\text{calc}}_i)\}^2 / \sum_i \{k^3\chi^{\text{obs}}_i\}^2.$$

R' was calculated as for R, with final model parameters, but with data Fourier filtered with $r_{\text{max.}}$ = 6 Å to remove noise. For transmission data R values lie in the range 0.04—0.30 (av. 0.12), and R' in the range 0.06—0.16 (av. 0.10). R and R' lie in the ranges 0.12—0.52 and 0.10—0.22 for fluorescence data. [c] Fluorescence data. [d] Conc./mmol dm^{-3}.

For (**3**) the crystal structure[3] shows linear aggregation of the cations, with Pt···Pt distances of 3.579(2) Å. These contacts and the ligand geometries are satisfactorily assigned and fitted in the solid state EXAFS spectra of (**3**). The acetone solution spectra show only equivocal evidence for the Pt···Pt contacts which have been postulated[3,7] for such solutions on the basis of their non-Beer's law behaviour, Pt···Pt and Pt···O (solvent) contacts at distances of *ca.* 3.2—3.6 Å were

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‡ Platinum and iridium L$_{III}$ absorption edge EXAFS data were collected at the Daresbury SRS on station 7.1 in transmission mode, except where noted in Table 1. Solid samples were typically of *ca.* 1 mm thickness and were diluted in boron nitride in order to achieve changes in log(I_0/I) in the range 1—2 at the absorption edge. Solution samples were measured in cells of thicknesses between 0.3 and 6 mm in order to achieve changes in log(I_0/I) in the range 1—2 at the absorption edge. Raw data were corrected for dark currents and converted to k-space (with EXCALIB[9]), and backgrounds subtracted (with EXBACK[9]) to yield EXAFS functions $\chi^{\text{obs}}_i(k)$. These were Fourier filtered to remove features at distances below *ca.* 1.2 Å but *not* to remove long-distance features of the quasi-radial distribution function (*i.e.* no noise removal was attempted). Model fitting was carried out with EXCURV88, using curved wave theory allowing for multiple scattering to third order for the nitrogen (and methyl carbon) atom shells of the cyanide (and isocyanide) ligands. Only shells significant at the 1% level[10] were included in final models. Full details of the final models employed for the samples listed in Table 1 are available from the authors on request. *Ab initio* phase shifts and back-scattering factors using spherical wave theory with 25 l values were used throughout, except for carbon and nitrogen phases in (**1**)—(**3**) for which calculated phases were modified [$\phi'(k) = (1.0 + bk)\,\phi(k)$; $b = -0.014$ for C and -0.013 for N]. These corrections, the values used for the proportion of absorption leading to EXAFS ('AFAC' = 0.8), and the magnitude of inelastic effects modelled by an imaginary potential ('VPI' = −4.0 eV), were derived from fits to compound (**2**) in the solid state. We note that to achieve good quality fits with the linear ligands present adequate treatment of multiple scattering effects is essential. Furthermore, in order to distinguish between ligand and metal atoms in the environment of the absorbing atom, good quality data for 10 < k < 15—20 Å^{-1} is necessary, since it is in this region that light and heavy atom back-scattering is best differentiated.

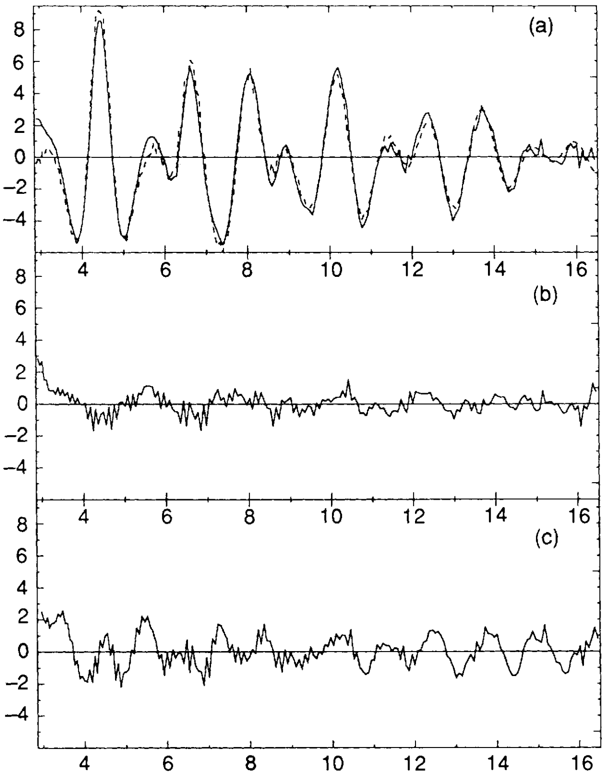

Figure 1. (a) Observed (——) and calculated (----) k^3-weighted Ir $\mathrm{L_{III}}$-edge EXAFS spectrum for (4) in 200 mmol dm^{-3} methanol solution. (b) Difference (observed − calculated final model contributions) k^3-weighted Ir $\mathrm{L_{III}}$-edge EXAFS spectrum for (4) in 200 mmol dm^{-3} methanol solution. (c) Difference (observed − calculated Ir–C, Ir···N, and Ir···Me shell contributions) k^3-weighted Ir $\mathrm{L_{III}}$-edge EXAFS spectrum for (4) in 200 mmol dm^{-3} methanol solution. The main features are due to Ir···Ir contacts at *ca.* 2.8 Å.

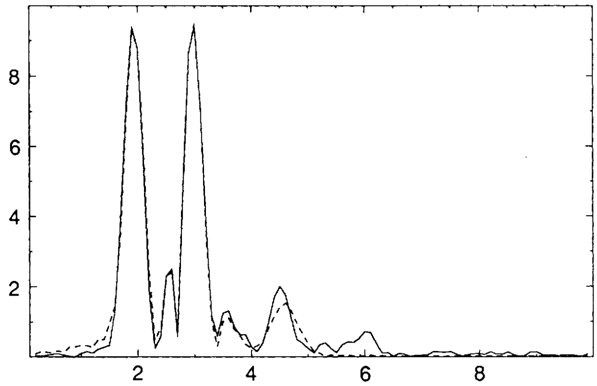

Figure 2. Observed (——) and calculated (----) Fourier transform (quasi-radial distribution function) of k^3-weighted Ir $\mathrm{L_{III}}$-edge EXAFS spectrum for (4) in 200 mmol dm^{-3} methanol solution.

modelled, the Pt···O assignment providing marginally better fits.

Analysis of the EXAFS data confirms that both in the solid and in methanolic solution [Ir(CNMe)$_4$]Cl (4) is oligomeric§ with Ir···Ir distances of *ca.* 2.85 Å, even at *ca.* 3 mmol dm^{-3} concentration. The presence of the Ir···Ir contacts in the solution (and solid) was clearly demonstrated by the excellent fits achieved [see Figure 1(a) and (b)], and by inspection of the difference EXAFS [$k^3(\chi^{\text{obs}} - \chi^{\text{calc}})$] after fitting the Ir–C, Ir···N, and Ir···methyl carbon shells [see Figure 1(c)]. The difference EXAFS features in the low k region are rather poorly resolved, since the Ir···N shell can compensate for the missing Ir···Ir contribution in the model, but beyond k *ca.* 10 Å^{-1} the different back-scattering properties of nitrogen and iridium allow clear identification of the EXAFS due to the latter. The frequency of these EXAFS features corresponds to an Ir···Ir separation of *ca.* 2.7 Å [refined value 2.842(4) Å]. The fitted Ir···Ir distances in (4) are similar to those in the unbridged linear chain species Ir(CO)$_3$X [X = Cl, Br; Ir···Ir 2.844(1) and 2.898(2) Å respectively, see ch. 5 of ref. 1]. They are considerably shorter than the crystallographically determined metal···metal separation in the d^8 ML$_4$ dimer [Ir$_2$(μ-tmb)$_4$](BPh$_4$)$_2$ [tmb = CNCMe$_2$(CH$_2$)$_2$CMe$_2$NC; Ir···Ir = 3.199(1) Å][12] perhaps because of the constraints imposed by the bridging tmb ligand (N···N 3.68 Å).

We therefore conclude that EXAFS data may be collected for solid or solution samples to sufficient accuracy to allow identification of intramolecular geometries and intermolecular M···M contacts in well ordered linear chain species. In cases where the M···M interactions are highly disordered, and presumably rather weak [as in (2)] they may be difficult or even impossible to detect by EXAFS methods,[11] especially if the distances involved are >3 Å. Other techniques are required for such systems. It is clear that d^8 ML$_4$ complexes show a range of associative behaviour in solutions, varying from complete disruption of the linear chains observed in the solid [as in dilute solutions of (1)], to formation of weakly [as in (2)] or strongly bound oligomeric species [as in (4)].

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§ The number of metal···metal contacts (N) per metal atom in compounds (1)—(4) may, in principle, be determined from the EXAFS data and therefore the extent of oligomerisation may be assigned. Thus N = 2.0 implies infinite chain length (polymer), N = 1.5 tetramer formation, N = 1.0 dimer, and N = 0.0 the presence of monomer species only. In practice N is rather imprecisely determined and was fixed at 2.0 for cases in Table 1.