Iodine and molybdenum K-edge extended X-ray absorption fine structure of some iodine(I) hexafluoromolybdates(V) in the solid state and in acetonitrile solution

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Abstract

Iodine and molybdenum K-edge extended X-ray absorption fine structure of the compounds [I(NCMe)$_2$][MoF$_6$], [I(py)$_2$][MoF$_6$], [I(py)$_2$][NO$_3$] and [Ag(py)$_4$][MoF$_6$] provide good evidence for the discrete ions [IL$_2$]$^+$, L = MeCN or py, having linear N–I–N skeletons with I–N distances in the range 2.16–2.22 Å, and octahedral [MoF$_6$]$^-$ with an Mo–F distance of 1.78 ± 0.02 Å, both in the solid state and in acetonitrile solution.

1. Introduction

The behaviour of the [I(NCMe)$_2$]$^+$ cation in acetonitrile solution is very different from that of its pyridine analogue. This cation has been isolated as its hexafluoromolybdate(V) or hexafluorouranate(V) salt, and in MeCN is a relatively strong, one-electron oxidizing agent, for example oxidizing NO to [NO]$^+$ and solvated Cu^{I} to Cu^{II}. The reactions of these salts with benzene and activated benzene derivatives are consistent with the presence of the electrophilic I$^+$ cation [1]. No crystals of an [I(NCMe)$_2$]$^+$ salt suitable for X-ray structural determination have been obtained to date. For this reason, we have undertaken an extended X-ray absorption fine structure (EXAFS) study whose principal objective was to determine the structure of [I(NCMe)$_2$]$^+$ in MeCN.

The EXAFS associated with the absorption edge of an element contains information concerning the nature of the immediate chemical environment of that element [2,3]. Specifically, EXAFS provides details concerning the distance, nature, number and degree of disorder of the shells of neighbouring atoms (usually within c. 3.5 Å of the element of interest). The technique is versatile, in that it can be applied to the majority of elements and has no requirement for crystalline materials. Thus, structural information can be obtained for solution species and one particular attraction is the

ability to investigate chemically unstable or highly reactive species.

This approach has been used for Br$_2$O, BrOBrO$_3$ and for the solution species [BrO$_x$]$^-$, x = 1–4 [4]. Several transition metal fluorides and related fluorometallates have also been studied [5,6]. When using EXAFS to undertake structural determinations, it is highly desirable to make comparisons with related species whose structures have been established by other means. For this reason, the compounds [I(py)$_2$][NO$_3$], [I(py)$_2$]-[MoF$_6$] and [Ag(py)$_4$][MoF$_6$] were used as spectroscopic calibrants. An X-ray crystallographic study of [I(py)$_2$][I$_3$]·2I$_2$ has shown that the [I(py)$_2$]$^+$ cation is linear and centrosymmetric [7]. Iodine Mössbauer spectra of [I(py)$_2$][NO$_3$] have been interpreted on a similar basis, the I–N bonding being largely of p character [8]. Although the structure of [Ag(py)$_4$][MoF$_6$] has not been determined, the [Ag(py)$_4$]$^+$ cation is likely to be tetrahedral as it is in the perchlorate salt [9], and the spectra and properties of the hexafluoromolybdate(V) salt in the solid state and in MeCN solution are consistent with the presence of discrete [Ag(py)$_4$]$^+$ and [MoF$_6$]$^-$ ions [10].

2. Experimental details

The compounds [I(NCMe)$_2$][MoF$_6$], [I(py)$_2$][MoF$_6$], [I(py)$_2$][NO$_3$] and [Ag(py)$_4$][MoF$_6$] were prepared using published procedures [1, 10, 11]. Acetonitrile (Rathburn HPLC grade) was purified and dried as previously

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described [12]. All operations, apart from those involving [I(py)$_2$][NO$_3$], were carried out in vacuo or in an inert atmosphere glove box (water, <5 ppm). The solids were mixed with boron nitride (Fluka), 50% by volume, and pressed between pieces of Mylar film (thickness 0.07 mm) within an aluminium spacer (thickness, 1 mm). Mylar/aluminium seals were made with quick setting Araldite adhesive. Solutions were contained in home-made cylindrical, Pyrex cells (19 mm diameter, 3 mm path length) or aluminium cells (30 mm square, 3 mm path length) with glass windows (0.15 mm) sealed with silicone cement. The windows were too fragile to permit reliable evacuation, hence the solutions, [I(NCMe)$_2$][MoF$_6$], c. 0.18 mol dm^{-3}, [I(py)$_2$][MoF$_6$], c. 0.2 mol dm^{-3}, were prepared in vacuo and loaded into the cells in the glove box. Argon was bled from the cells by expansion into a vacuum, the cells were stored at 195 K while being transported to Daresbury and were stored at c. 230 K between EXAFS experiments.

EXAFS measurements were performed on station 9.2 of the Daresbury SRS operating at an energy of 2 GeV and an average current of 140 mA. Iodine and molybdenum K-edge X-ray absorption spectra were recorded in the transmission mode using a Si 220 channel-cut monochromator. Data for solid [I(py)$_2$][NO$_3$] were recorded at 133 K and all other measurements were performed for samples between 273 K and room temperature. Data analyses employed phase shifts calculated by ab initio methods using the MUFPOT (Daresbury) program. To obtain satisfactory final fits of the iodine EXAFS, it was necessary to include multiple scattering contributions.

3. Results

3.1. Iodine K-edge EXAFS

The iodine K-edge EXAFS is broadened due to the short core-hole lifetime. The phase shifts used for data interpretation were checked by analysis of the data obtained for solid [I(py)$_2$][NO$_3$] (Fig. 1). A satisfactory treatment of the back scattering from the four shells of the pyridine ring, notably that from the C$_3$ and C$_5$ carbon atoms, required the inclusion of multiple scattering. In addition, use was made of Fourier filtering to allow the backscattering contribution of the nitrogen shell to be refined separately. The value of the I—N distance obtained for solid [I(py)$_2$][NO$_3$], 2.22 ± 0.03 Å (Table 1) is in agreement with the value of 2.16 ± 0.1 Å reported for [I(py)$_2$][I$_3$]·2I$_2$ [7]. The profiles of the iodine K-edge EXAFS recorded for [I(py)$_2$][NO$_3$] in MeCN solution and [I(py)$_2$][MoF$_6$] as a solid and in MeCN solution were virtually indistinguishable from that of [I(py)$_2$][NO$_3$] over the common data range

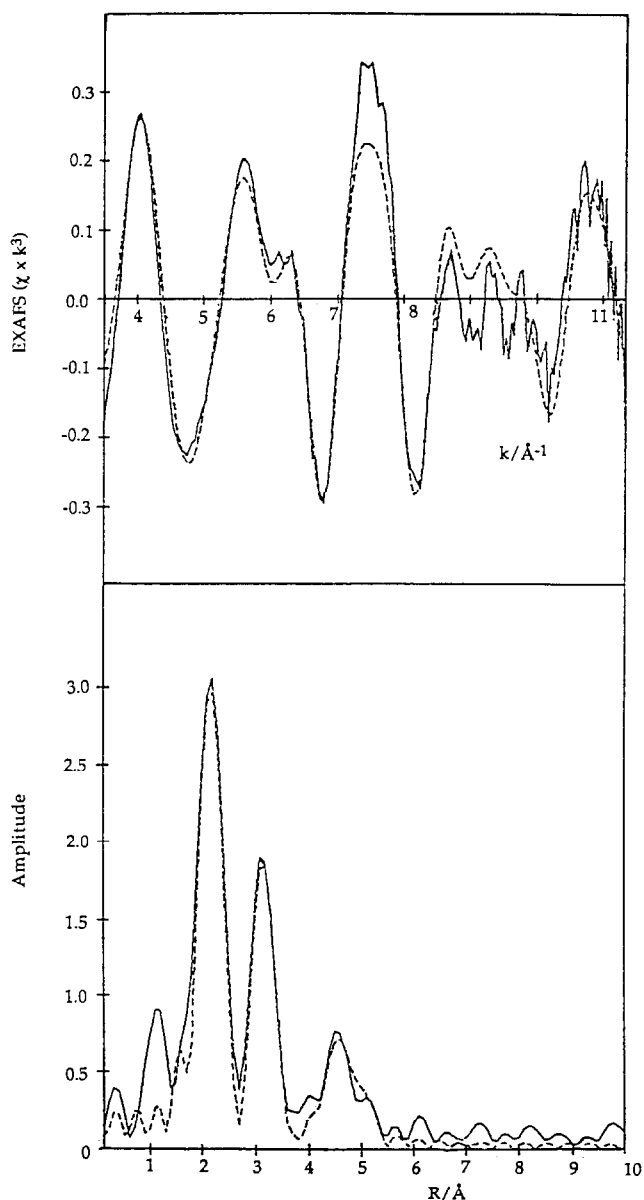Fig. 1. Iodine K-edge EXAFS (χk^3) of [I(py)$_2$][NO$_3$] solid at 133 K and Fourier transform: (———) experimental data; (— — —) simulated data for 2 N at 2.22 Å ($\sigma^2 = 0.011$ Å^2), 2 C at 3.09 Å ($\sigma^2 = 0.010$ Å^2), 2 C at 3.12 Å ($\sigma^2 = 0.011$ Å^2), 2 C at 4.36 Å ($\sigma^2 = 0.011$ Å^2), 2 C at 4.45 Å ($\sigma^2 = 0.014$ Å^2), 2 N at 4.98 Å ($\sigma^2 = 0.001$ Å^2).

TABLE 1. Iodine–nitrogen distances[a] (Å) obtained from the analysis of iodine K-edge EXAFS data

Compound	Solid	MeCN solution
[I(py)$_2$][NO$_3$]	2.22	2.16
[I(py)$_2$][MoF$_6$]	2.21	2.21
[I(NCMe)$_2$][MoF$_6$]	2.17	2.17

[a]Estimated error, ± 0.03 Å.

$(k = 3.5–9.0$ Å$^{-1})$. All these EXAFS data were analyzed as described above and the I−N distance obtained ranged from 2.16 to 2.22 Å (Table 1). Thus, the [I(py)$_2$]$^+$ cation retains essentially the same structure in the solid and solution phases investigated herein.

The iodine K-edge EXAFS obtained for [I(NCMe)$_2$][MoF$_6$] solid and in MeCN solution (Fig. 2) were virtually identical over the common data range $(k = 3.5–9.0$ Å$^{-1})$. The inclusion of multiple scattering was important for the data analysis, especially to obtain the correct amplitudes and distances for the carbon of the nitrile. Also, Fourier filtering was employed to assess the individual back-scattering contribution made by the nitrogen shell. The I−N distances obtained for the solid $(2.17 \pm 0.03$ Å$)$ and MeCN solution $(2.17 \pm 0.03$ Å$)$ phases of [I(NCMe)$_2$][MoF$_6$] are compared with the I−N distance obtained for [I(py)$_2$]$^+$ in Table 1.

3.2. Molybdenum K-edge EXAFS

The EXAFS recorded for [Ag(py)$_4$][MoF$_6$] as a solid and [I(py)$_2$][MoF$_6$] and [I(NCMe)$_2$][MoF$_6$] in MeCN solution (Fig. 3) were all consistent with the back-
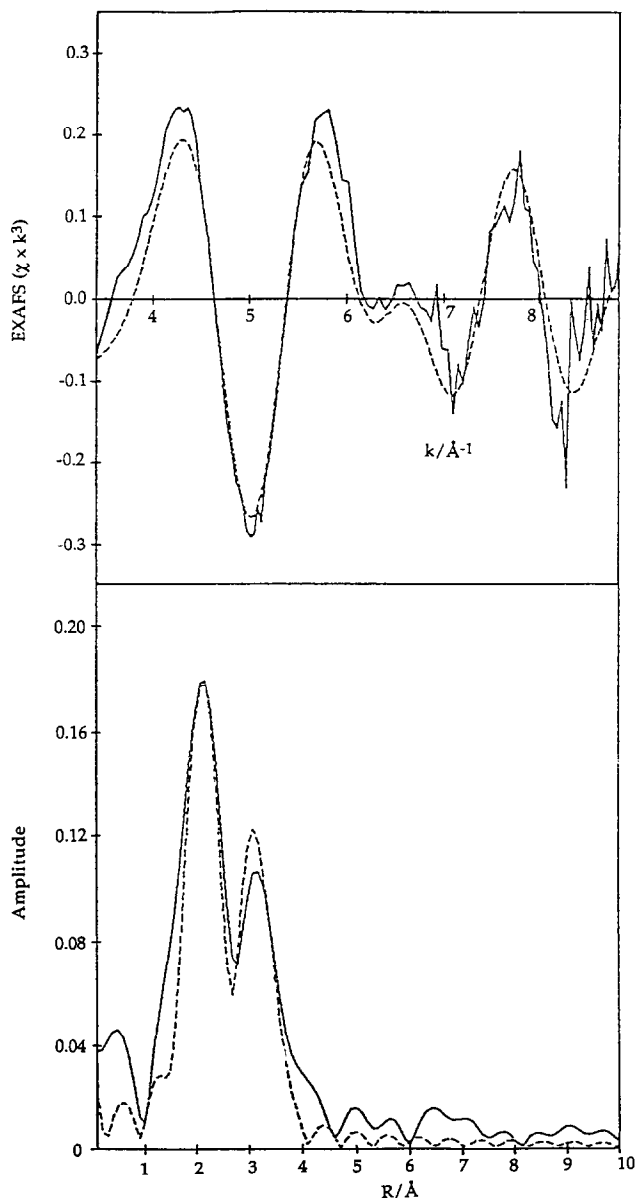

Fig. 2. Iodine K-edge EXAFS (χk^3) of [I(NCMe)$_2$][MoF$_6$] in MeCN solution at ambient temperature and Fourier transform: (——) experimental data; (— — —) simulated data for 2 N at 2.17 Å $(\sigma^2 = 0.023$ Å$^2)$ and 2 C at 3.32 Å $(\sigma^2 = 0.027$ Å$^2)$.
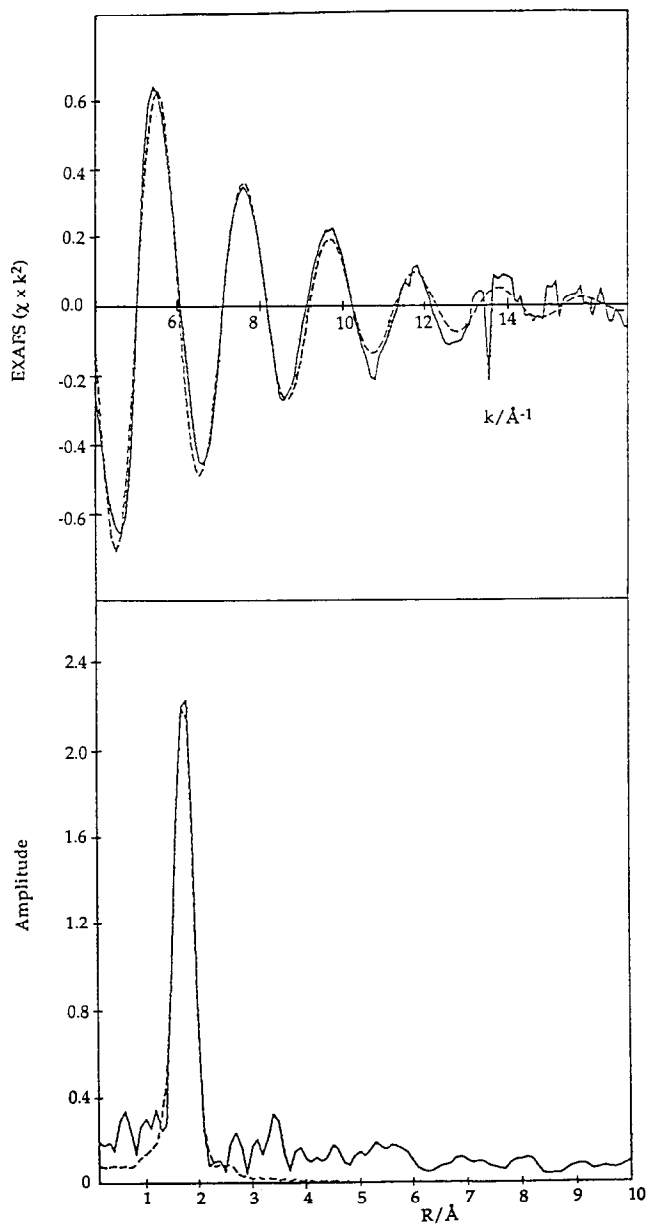

Fig. 3. Molybdenum K-edge EXAFS (χk^2) of [I(NCMe)$_2$][MoF$_6$] in MeCN solution at ambient temperature and Fourier transform: (——) experimental data; (— — —) simulated data for 6 F at 1.77 Å $(\sigma^2 = 0.009$ Å$^2)$.

TABLE 2. Molybdenum–fluorine distances[a] (Å) obtained from the analysis of molybdenum K-edge EXAFS data

Compound	Solid	MeCN solution
[I(py)$_2$][MoF$_6$]	–	1.77
[I(NCMe)$_2$][MoF$_6$]	–	1.77
[Ag(py)$_4$][MoF$_6$]	1.79	–

[a]Estimated error, ±0.02 Å.

scattering arising from a single shell of fluorine atoms at 1.78 ± 0.02 Å (Table 2). Salts of [MoF$_6$]$^-$ do not appear to have been characterized by single crystal X-ray crystallography; an X-ray powder study of NaMoF$_6$ reported some time ago gave Mo$-$F$=1.74 \pm 0.03$ Å [13]. Other comparisons may be made with molybdenum penta- and hexa-fluorides. The average Mo$-$F-(terminal) distance in solid (MoF$_5$)$_4$, determined by X-ray diffraction some years ago, is 1.78 Å [14]. A more recent gas-phase electron diffraction study determined the average Mo$-$F(terminal) distance in [MoF$_5$]$_3$ as 1.814(6) Å [15]. The Mo$-$F distances in solid, orthorhombic MoF$_6$ at 193 K are in the range 1.766–1.861 Å (average value 1.812 Å), and at 77 K the average distance is 1.824 Å [16]. In the cubic, plastic phase of MoF$_6$ at 266 K, the Mo$-$F distance is 1.802(14) Å [17] and for MoF$_6$ in the gas phase it is 1.820(3) Å [18]. The Mo$-$F distance determined from an EXAFS study of MoF$_6$ at 10 K is 1.81 Å [5]. The EXAFS data for [MoF$_6$]$^-$ provide no indication for a Jahn–Teller distortion being manifest in the radial distribution of the Mo$-$F bonds; this is not surprising since any such distortion would be expected to be very small.

The molybdenum K-edge EXAFS of solid [I(py)$_2$][MoF$_6$] indicated back-scattering contributions from two shells of light atoms, one at c. 1.8 Å and one at c. 1.6 Å. The latter is assigned to an Mo$=$O group arising from partial hydrolysis of the sample, by comparison with Mo$=$O(terminal) distances of 1.62(1) and 1.65(1) Å in solid [MoF$_4$O]$_\infty$ [19] and of 1.650(7) Å in gaseous MoOF$_4$ [20]. The absence of this feature in the other molybdenum K-edge EXAFS was taken to indicate that significant hydrolysis has not occured in those cases.

4. Discussion

This EXAFS study has provided good evidence for the presence of discrete ions in the compounds [IL$_2$][MoF$_6$], L = MeCN or py, both in the solid state and in MeCN solutions. Anion–cation interaction in MeCN appears to be minimal, a situation similar to that inferred from the NMR spectra of solvated metal

TABLE 3. Structural data for some corresponding MeCN and py complexes

Compound	M$-$L distance (Å)	Ref.
[Cu(NCMe)$_4$][ClO$_4$]	1.95(1)–2.02(1)	[24]
[Cu(NCMe)$_4$]$^+$ in MeCN	1.99(2)	[25][a]
[Cu(py)$_4$][ClO$_4$]	2.05(1) 2.046(4)	[26] [9]
cis-[Pt(NCMe)$_2$Cl$_2$]	1.977(12)–1.981(11), 1.95(2), 1.99(2)	[27]
cis-[Pt(py)$_2$Cl$_2$]	2.04(1), 2.01(1)	[28]
BF$_3$(NCMe)	1.630(4)	[29]
BF$_3$(py)	1.602(4), 1.604(4)	[30]

[a]Determined by EXAFS.

cation, fluoroanion salts in MeCN, for example MeCN-solvated Cu^{2+} vis-à-vis [PF$_6$]$^-$ [21] or [Ag(py)$_4$-(NCMe)$_2$]$^{3+}$ vis-à-vis [MoF$_6$]$^-$ [10]. The only exception encountered so far is solvated Tl$^+$, which from ^{205}Tl NMR studies appears to show some degree of ion pairing with the anions [PF$_6$]$^-$, [WF$_7$]$^-$, [MoF$_6$]$^-$ and [UF$_6$]$^-$ in MeCN. However, the interaction between solvated Tl^{3+} and [UF$_6$]$^-$ in the same solvent appears to be minimal, probably because of the effective solvation of Tl^{3+} by MeCN [22].

Linear N$-$I$-$N skeletons in [I(NCMe)$_2$]$^+$ salts have been suggested previously on the basis of their vibrational spectra [1]. Interestingly, mono-ligated I^I cations, [IL]$^+$, L = MeCN or py, synthesized from [I$_3$]$^+$ salts, have been described recently [23]. The linear geometry for [IL$_2$]$^+$ cations is unexceptional as it would be predicted by VSEPR. What is unusual at first sight, however, is the equality of the I$-$N distances (within the precision of the EXAFS data) in view of the very different properties of MeCN and py as ligands to I^I. However, this situation is also found in Cu^I, Pt^{II} and BF$_3$ complexes involving these ligands (Table 3). Bonds involving MeCN are marginally shorter than those involving py in the Cu^I and Pt^{II} cases, but the reverse is found when BF$_3$ is the Lewis acid. Pyridine would be regarded as the stronger donor; this would appear to apply to I$^+$ since the ability of py to stabilize the I($+1$) oxidation state would account for the different chemical behaviour of the two [IL$_2$]$^+$ cations.

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