

# Redox reactions between molybdenum or tungsten hexafluorides and p, f or d block elements in acetonitrile: comparisons with reactions involving nitrosonium fluorometallates, the effect of fluoride ligand transfer and redox inhibition due to surface oxide

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## Abstract

The outcome of reactions between antimony, bismuth, lanthanum, neodymium, europium, thulium, gold or nickel and the one-electron oxidizing agents, molybdenum hexa-fluoride, tungsten hexa-fluoride or the nitrosonium cation in the presence of acetonitrile, cannot always be predicted on the basis of the relative oxidizing abilities of the reagents. Fluoride ligand transfer from hexafluorometallate(V) anions to the solvated cation is a major factor in reactions that involve oxidation of antimony and bismuth, although the solvated bismuth(III) cation can be stabilized by the macrocycle, 1,4,8,11-tetraazacyclotetradecane. Passivation of the metal surface by an oxide layer appears to be important in lanthanum and nickel oxidations, resulting in an apparent inversion of reactivity between molybdenum and tungsten hexafluorides.  
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## 1. Introduction

The use of molybdenum and tungsten hexafluorides as conventional one-electron oxidants in acetonitrile is well established [1–3]. Acetonitrile-solvated cations of a variety of d block and post-transition metals can be synthesized by this route and have provided a convenient starting point for investigation of the coordination chemistry of, for example, iron(II) [4–6], copper(II) and thallium(III) [7,8] in this solvent. Similarly, the coordination chemistry of iodine(I) in MeCN is accessible by this route [9–11]. Cyclic voltammetry has established that MoF<sub>6</sub> is thermodynamically a stronger oxidizing agent than WF<sub>6</sub> [2,3] and that the nitrosonium cation, used as a one-electron oxidant for several d block metals [12,13] including gold [14] and palladium [15] and for the f block metal, europium [16], has an oxidizing power intermediate between MoF<sub>6</sub> and WF<sub>6</sub> [3]. The outcomes of such reactions can be rationalized on a simple thermodynamic basis, providing the cations are well-solvated

by MeCN or are complexed by suitable ligands; for example Tl<sup>III</sup> and I<sup>I</sup> are accessible using the stronger oxidant MoF<sub>6</sub> [7,9] and oxidation of [Ag(py<sub>4</sub>)<sub>4</sub>]<sup>+</sup> to Ag<sup>III</sup> is observed only with MoF<sub>6</sub>, or with the strongest oxidant UF<sub>6</sub> [17]. In practice, the behaviour of MoF<sub>6</sub> and UF<sub>6</sub> is similar, use of the latter being restricted to rapid reactions because of its slow reduction to uranium(V) in MeCN [18].

Complications can arise from additional reactions, particularly when p block elements are oxidized, for example between [Br(NCMe)<sub>x</sub>]<sup>+</sup> and MeCN leading to the [Br(C<sub>6</sub>H<sub>9</sub>N<sub>3</sub>)<sub>3</sub>]<sup>+</sup> cation [19] or from a fluoride ion transfer reaction between the anion, [MF<sub>6</sub>]<sup>-</sup>, and a solvated cation. The latter reaction has been postulated to occur following the oxidation of tellurium by MoF<sub>6</sub> or UF<sub>6</sub>, leading to products formulated as [Te<sup>IV</sup>F<sub>3</sub>(NCMe)<sub>2</sub>][M<sup>V</sup>F<sub>6</sub>][M<sup>V</sup>F<sub>5</sub>(NCMe)<sub>3</sub>], M=Mo or U, [20]. The first objective of the work reported here was to determine whether this type of reaction occurs for the oxidation of other p block elements of comparable electronegativity, for example, antimony and bismuth, and if so, whether fluoride ion transfer could be prevented by the presence of ligands other than MeCN. The second objective was to examine the applicability of hexa-

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fluoride oxidations to f block elements. In this part of the study it became apparent that thermodynamic oxidizing ability was not the sole factor determining the outcome of a reaction and that metal surface passivation was important in some cases. This observation prompted a re-examination of the oxidation of nickel.

## 2. Results and discussion

### 2.1. Survey of reactions

The reactivity of molybdenum and tungsten hexafluorides and the nitrosonium cation, counter-anion  $[\text{PF}_6]^-$  unless stated otherwise, towards the elements antimony, bismuth, gold, nickel, lanthanum, neodymium, europium and thulium in the presence of acetonitrile at ambient temperatures is summarized in Table 1. Oxidation reactions were observed between antimony or bismuth and all reagents, in each case the expected tri-positive oxidation state being formed. The pattern for lanthanide metal oxidations was however rather different and would not have been predicted a priori. Gold was oxidized by the stronger oxidants  $\text{MoF}_6$  and  $[\text{NO}]^+$  but  $\text{WF}_6$  appeared not to react. Nickel metal presented the most puzzling situation, where the strongest oxidizing agent,  $\text{MoF}_6$ , reacted only when exposed to an oxide-free metal surface, whereas the weakest oxidizing agent  $\text{WF}_6$ , reacted only when an oxide film is present on the nickel surface.

### 2.2. Oxidation of Sb and Bi

Attention was concentrated on reactions between Sb and  $\text{MoF}_6$  or  $\text{WF}_6$  and between Sb or Bi and  $[\text{NO}][\text{PF}_6]$ . The behaviour of Sb appeared to be similar to that observed between tellurium and  $\text{MoF}_6$  or  $\text{UF}_6$  [20], in that oxidation of Sb and extensive fluoride transfer from tungsten or molybdenum to antimony occurred. On the basis of partial analysis and their IR spectra, the products were tentatively formulated as  $[\text{SbF}_2(\text{NCMe})_3][\text{M}^{\text{V}}\text{F}_6][\text{M}^{\text{V}}\text{F}_5(\text{NCMe})_2]$ , M = Mo or W. Fluoride transfer from phosphorus to antimony or bismuth was facile also in reactions of  $[\text{NO}][\text{PF}_6]$  with these elements. In many reactions antimony or bismuth trifluoride was a substantial component of the product mixtures and if trace hydrolysis occurred during the bismuth reaction, the sole product was bismuth(III) phosphate. The labile nature of fluorine in the  $[\text{PF}_6]^-$  anion has been the subject of comment elsewhere [21] and fluoride abstraction from  $[\text{PF}_6]^-$  and subsequent hydrolysis reactions are well documented in transition metal complex chemistry (e.g., Refs. [22–24]). However, evidence for the solvated cation salt  $[\text{Bi}(\text{NCMe})_x][\text{PF}_6]_3$  was obtained. The colourless solid decomposed rapidly during its isolation from MeCN solution, even below room temperature, but fluoride-free  $\text{Bi}^{\text{III}}$  could be stabilized by the addition of the macrocycle 1,4,8,11-tetraazacyclotetradecane, [14]ane $\text{N}_4$ , the product isolated being  $[\text{Bi}([14]\text{aneN}_4)(\text{NCMe})_6][\text{PF}_6]_3$ . A  $\text{Bi}^{\text{III}}$  cation,  $[\text{BiCl}_2-$

$(\text{NCMe})_4]^+$ , is obtained from the reaction of  $\text{BiCl}_3$  with  $\text{SbCl}_5$  in MeCN [25] and several examples of  $\text{Sb}^{\text{III}}$  [26,27] or  $\text{Bi}^{\text{III}}$  [28,29] chloride derivatives coordinated by macrocyclic O- or S-donor molecules are known. Combining the observations made in the present work with those reported previously for the oxidation of Pb [1], Tl [3,7], Te [20] and I [9–11], enables a unified, albeit speculative in some respects, picture for the oxidations of heavier p block elements in MeCN to be presented, Scheme 1. The balance determining the ligation of MeCN or  $\text{F}^-$  to the positive p block species will be the result of several factors and no attempt has been made to quantify these. The role of the macrocyclic ligand in inhibiting  $\text{F}^-$  transfer to  $\text{Bi}^{\text{III}}$  is appar-

Table 1  
Reactivity of some p, f and d block elements towards  $\text{MoF}_6$ ,  $\text{WF}_6$  or the  $[\text{NO}]^+$  cation in the presence of MeCN at ambient temperature

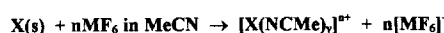
Element	Oxidant		
	$\text{MoF}_6$	$[\text{NO}][\text{MF}_6]^a$	$\text{WF}_6$
Sb	yes	yes	yes
Bi	yes	yes	yes
La	no	yes	yes
Nd	yes	yes	no
Eu	yes	yes	yes
Tm	no	yes	no
Au	yes <sup>b</sup>	yes	no
Ni (untreated)	no <sup>c</sup>	yes	yes
Ni (film)	yes	not studied	no

<sup>a</sup> Counter-anion  $[\text{PF}_6]^-$  or, with Au,  $[\text{MoF}_6]^-$ .

<sup>b</sup> Reaction very exothermic.

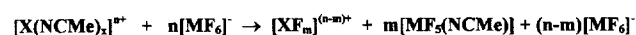
<sup>c</sup> Ni foil that had been cleaned by pretreatment with  $[\text{NO}][\text{PF}_6]$  in MeCN, did react.

#### (A) Redox



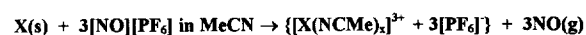
X	M	n
Tl	Mo	3
Tl	W	1
Pb	W	2
I	Mo	1

#### (B) Fluoride transfer anion $\rightarrow$ cation

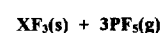


X	M	n	m
Te	Mo	4	3
Sb	Mo, W	3	2

#### (C) Redox and fluoride transfer using $[\text{NO}][\text{PF}_6]$



↓



X = Bi or Sb

Scheme 1.

ent, consistent with the previous report of the stabilization of  $I^1$  by this means [11].

### 2.3. Oxidation of lanthanides

It is now well established that differences in redox chemistry across the lanthanide series are to be expected, being accounted for by variations in, for example, the elements' metallic radii and third ionization energies [30]. Four lanthanide metals were chosen to reflect this situation. Lanthanum and europium were expected to be the most reactive, with the possibility of forming  $Eu^{II}$  rather than  $Eu^{III}$ , thulium least reactive and neodymium occupying an intermediate position. However, this order was not reflected in all respects by their behaviour towards  $MoF_6$ ,  $WF_6$  and  $[NO][PF_6]$  (Table 1). In all cases reactions were slow, yields of products isolated were small and, unexpectedly, in some cases, no reaction was observed. As expected Eu reacted with all three oxidants, and also with  $[NO][BF_4]$  [16] but La reacted with  $[NO][PF_6]$  and  $WF_6$  but not with  $MoF_6$ . The element Tm was the most difficult to oxidize, reacting only with  $[NO][PF_6]$ , while Nd reacted with  $[NO][PF_6]$  and with  $MoF_6$ , providing a freshly cut metal surface was exposed, but not with  $WF_6$ . Although  $[NO][PF_6]$  appears to be the reagent of choice (Table 1), the products could not be obtained free of the oxidant. Interestingly,  $[NO][BF_4]$  reacted only with Eu, suggesting that the outcome of oxidations using  $[NO]^+$  depends on the exact nature of the salt produced. The  $[BF_4]^-$  anion is believed to interact strongly with  $Eu^{III}$  leading to the formation of a polymeric compound  $[Eu(NCMe)_3(BF_4)_3]_n$  [16]. Displacement of ligated MeCN by fluorometallate(V) anions in the products isolated from reactions between Nd or Eu and  $MoF_6$  is possible, although there was no evidence for this from their vibrational spectra, since the stoichiometry of the pale yellow solids was  $Ln(NCMe)_3(MoF_6)_3$   $Ln = Nd$  or  $Eu$ , implying a very low coordination number which would be unusual for  $Ln^{III}$ . In both cases, reaction with pyridine yielded pink or deep yellow  $[Ln(NCMe)(py)_7][MoF_6]_3$  and trimethylamine reacted to give  $[Ln(NCMe)_2(NCMe)_4][MoF_6]_3$ . Similar behaviour was found in reactions between La or Eu and  $WF_6$ , although the IR spectra of the products indicated that  $[WF_7]^-$  was present in addition to  $[WF_6]^-$ , a situation commonly found in oxidations that involve  $WF_6$  (e.g., Ref. [4]) due to the solution equilibrium  $[WF_6]^- + WF_6 + MeCN \rightleftharpoons [WF_7]^- + WF_5(NCMe)$ . It seems unlikely that the lack of observed reaction between La metal and  $MoF_6$  has a thermodynamic origin and a tentative explanation is that the metal surface is passivated by an oxide layer which is removable by  $WF_6$  or  $[NO][PF_6]$  treatments but not by  $MoF_6$ . This is discussed below in the context of nickel oxidations.

### 2.4. Oxidations involving gold or nickel

Oxidation of gold to  $Au^I$  in MeCN can be achieved either using  $[NO][ClO_4]$  [14] or by anodic oxidation in the pres-

ence of complexing ligands [31]. Reactions between massive gold and  $[NO][PF_6]$  or  $[NO][MoF_6]$  in MeCN were very slow at room temperature but the reaction between freshly-prepared gold powder and  $[NO][MoF_6]$  was rapid, leading to pale yellow  $[Au(NCMe)_2][MoF_6]$  from which red  $[Au(py)_2][MoF_6]$  was formed by ligand replacement. Oxidation of  $Cu^I$  to  $Cu^{II}$  in MeCN by  $[Au(NCMe)_2]^+$  was quantitative but oxidation of  $I_2$  to  $I^1$  did not occur. Comparison with previously reported electrochemical data [2,3,9] suggests that the lack of observable reaction between Au and  $WF_6$  (Table 1) has a thermodynamic origin but that  $MoF_6$  should be capable of oxidizing Au to  $Au^I$ . This was observed but the reaction was very exothermic and even below room temperature, produced an impure  $Au^I$  salt. In contrast to  $Ag^I$  chemistry [17], there was no definitive evidence for oxidation to  $Au^{III}$  even starting from  $[Au(py)_2]^+$ .

In our original study of d- and post-d element oxidation by  $MoF_6$  or  $WF_6$  in MeCN, it was observed that little or no reaction occurred between  $MoF_6$  and Mn, Ni and Pb whereas solvated cation hexafluorotungstates(V) could be isolated from analogous reactions with  $WF_6$  [1]. Nickel was chosen for re-examination since the octahedral cation  $[Ni(NCMe)_6]^{2+}$  is well known, being accessible either by oxidation of Ni metal with  $[NO][BF_4]$  [13] or by dehydration of aquated  $Ni^{II}$  salts in MeCN [32]. Its X-ray structure has been reported [33], its behaviour in solution has been studied (from Ref. [34] and data quoted in Ref. [35]) and it has a characteristic electronic spectrum [13,32,34] by which its presence in solution can be easily detected.

Previous work was confirmed in that Ni was oxidized to  $[Ni(NCMe)_6]^{2+}$  by  $WF_6$  or  $[NO][PF_6]$  in the presence of MeCN. In the former reaction, samples free of  $[WF_7]^-$  could be obtained by exposing Ni foil to a mixture of  $WF_6$  and MeCN vapors, a technique that has also been employed for iron oxidation [4]. However, no reaction was observed between Ni foil and  $MoF_6$  in MeCN. Addition of pyridine to a reaction mixture whose components had been in contact for several hours, produced yellow  $[MoF_5(py)_2]$  which was formed also in the absence of Ni. Reaction between  $MoF_6$  in MeCN and Ni foil that had previously been 'cleaned' by reaction with  $[NO][PF_6]$  in MeCN did produce some  $[Ni(NCMe)_6]^{2+}$  however, and reaction between a Ni film, freshly evaporated onto Pyrex, and  $MoF_6$  also resulted in  $[Ni(NCMe)_6]^{2+}$ . In contrast, no reaction occurred between  $WF_6$  in MeCN and an evaporated Ni film unless the film was first exposed to air, when  $[Ni(NCMe)_6]^{2+}$  was formed. Exposure of  $WF_6$  labelled with the fluorine-18 isotope ( $t_{1/2} = 110$  min,  $\beta^+$  emitter) led to the detection of a small count from the metal surface, corresponding to 0.2% of the total  $[^{18}F]$  activity present in the system. Evidently  $WF_6$  was adsorbed at the Ni surface but no reaction ensued.

The obvious explanation for the behaviour is that the oxide layer, inevitably present on the metal surface unless rigorous procedures are adopted for its removal, inhibits the electron transfer process and that this passivating layer can be removed efficiently by  $WF_6$  and by  $[NO]^+$ . In this situation,  $WF_6$  and

Table 2

Compounds isolated from redox reactions between selected p, f or d block elements and MoF<sub>6</sub>, WF<sub>6</sub> or [NO]<sup>+</sup> salts

Compound	Colour	Analysis % found (required)					
		C	H	F	N	Cation element	Mo or P
[Bi([14]-aneN <sub>4</sub> )(NCMe) <sub>6</sub> ][PF <sub>6</sub> ] <sub>3</sub>	off-white	24.3(24.2)	4.15(3.85)	31.0(31.4)	12.6(12.85)	19.2(19.1)	8.4(8.5)
[Nd(NCMe) <sub>3</sub> ][MoF <sub>6</sub> ] <sub>3</sub>	pale yellow	8.0(8.0)	1.0(1.0)		4.8(4.7)	15.9(16.1)	31.6(32.1)
[Nd(py) <sub>7</sub> (NCMe)][MoF <sub>6</sub> ] <sub>3</sub>	pink	32.8(32.5)	2.7(2.8)		7.8(8.1)		
[Nd(NMe <sub>3</sub> ) <sub>4</sub> (NCMe) <sub>2</sub> ][MoF <sub>6</sub> ] <sub>3</sub>	pink	17.3(17.6)	3.3(3.9)		7.6(7.7)		
[Eu(NCMe) <sub>3</sub> ][MoF <sub>6</sub> ] <sub>3</sub>	pale yellow	8.1(7.9)	1.1(1.0)		4.55(4.65)	17.0(16.8)	32.35(31.8)
[Eu(py) <sub>7</sub> (NCMe)][MoF <sub>6</sub> ] <sub>3</sub>	deep yellow	32.1(32.3)	2.8(2.8)		7.9(8.1)		
[Eu(NMe <sub>3</sub> ) <sub>4</sub> (NCMe) <sub>2</sub> ][MoF <sub>6</sub> ] <sub>3</sub>	deep yellow	17.5(17.5)	3.8(3.85)		7.7(7.6)		
[Au(NCMe) <sub>2</sub> ][MoF <sub>6</sub> ]	pale yellow	9.6(9.8)	1.1(1.2)	23.5(23.3)	5.6(5.7)	39.9(40.3)	19.8(19.6)
[Au(py) <sub>2</sub> ][MoF <sub>6</sub> ]	red					34.4(34.8)	16.7(16.8)

[NO]<sup>+</sup> salts are effective oxidants but MoF<sub>6</sub> is not. The behaviour encountered for La appears to be identical to that of Ni and possibly a similar explanation applies.

### 3. Conclusions

Although the outcome of redox reactions between metallic or non-metal elements and MoF<sub>6</sub> or WF<sub>6</sub> in the presence of MeCN can be rationalized in many cases by the application of simple thermodynamic principles, this work demonstrates the importance of other factors that are kinetic in origin, two important examples being the lability of the fluoro-ligand in hexafluorometallate(V) anions and inhibiting effects of a surface oxide layer.

### 4. Experimental

All operations were carried out using standard Pyrex vacuum line and glove box techniques and, except where noted below, using procedures and instrumentation described earlier [6,11,17,20,21]. The elements whose oxidation behaviour was studied were commercial samples whose stated purities were >99.9%. Hexafluorides (Fluorochem) were purified by repeated trap-to-trap distillation in vacuo and were stored over activated NaF. The nitrosonium salts, [PF<sub>6</sub>]<sup>-</sup> or [BF<sub>4</sub>]<sup>-</sup> counter-anions (Fluorochem), were used as received and NOMoF<sub>6</sub> was prepared by a standard method [36]. Acetonitrile (Rathburn HPLC grade) was purified as previously described [37]. The elements Mo, Ni and Sb were determined by AAS, lanthanides by EDTA titration, and other microanalyses were performed either at Glasgow (C,H,N) or by Malissa and Reuter, Germany. Details of pure products isolated are given in Table 2; in these and in other solids isolated, the presence of coordinated MeCN [38] pyridine (py) [39], NMe<sub>3</sub> [40] and the appropriate hexafluorometallate(V) anion [1,4,6,20] was established by IR and Raman spectroscopy. Representative reactions are described below.

#### 4.1. Oxidation of antimony and bismuth

Bismuth shot (3.2 mmol) was allowed to react with [NO][PF<sub>6</sub>] (2.3 mmol) in MeCN (5 cm<sup>3</sup>) for 12 h at room temperature in a double limb Pyrex vessel during which time NO was evolved. A colourless solid was isolated from solution below room temperature; its IR spectrum consisted of bands attributable to coordinated MeCN and [PF<sub>6</sub>]<sup>-</sup>. Attempts to redissolve the solid in MeCN led to the precipitation of insoluble colourless material, presumed to be BiF<sub>3</sub> (see also below).

The reaction was repeated in a three limbed vessel that incorporated a glass frit, [14]-aneN<sub>4</sub> (1.0 mmol), prepared by the modified Richman–Atkins method [41], being added to the second limb of the vessel. The colourless solid isolated from solution after 12 h was redissolved in fresh MeCN and the solution poured through the frit onto [14]-aneN<sub>4</sub>, some of which dissolved to give a pale green solution. This was filtered and solvent removed at low temperature to give an off-white solid identified from its analysis (Table 2), IR spectrum that contained bands attributable to [14]-aneN<sub>4</sub> [11], MeCN and [PF<sub>6</sub>]<sup>-</sup> and its <sup>13</sup>C{<sup>1</sup>H} NMR spectrum that contained signals at δ<sub>13C</sub> 27.5, 47.6 and 50.4 ppm w.r.t. Me<sub>4</sub>Si characteristic of [14]-aneN<sub>4</sub> complexes [11], as [Bi][PF<sub>6</sub>]<sub>3</sub>.

An analogous reaction between lump Sb and [NO][PF<sub>6</sub>] yielded a colourless product that precipitated from solution on isolation and appeared to be predominantly SbF<sub>3</sub> (Found: C, 0.6; H, 0.1; N, 0.4; F, 31.8; P, 2.0; Sb, 64.25. SbF<sub>3</sub> req. F, 31.9; Sb 68.1%). Similar behaviour was found in products from Bi and [NO][PF<sub>6</sub>] in MeCN and in this case the colourless solid, only partially soluble in MeCN, was formulated as a mixture of [Bi(NCMe)<sub>6</sub>][PF<sub>6</sub>]<sub>3</sub> + BiF<sub>3</sub> (Found: C, 17.8; H, 2.2; Bi, 25.1; F, 36.7; N, 10.4; P, 7.3. C<sub>12</sub>H<sub>18</sub>BiF<sub>8</sub>N<sub>6</sub>P<sub>3</sub> req. C, 16.2; H, 2.0; Br, 23.5; F, 38.4; N, 9.4; P, 10.4%). If the reaction between Bi and [NO][PF<sub>6</sub>] was not carried out under rigidly anhydrous conditions, the product isolated was bismuth(III) phosphate, identified from its XRD powder pattern and vibrational spectrum [42].

The colourless solids isolated from pale yellow solutions resulting from reactions between Sb and MoF<sub>6</sub> or WF<sub>6</sub> in MeCN under similar conditions were formulated from their IR spectra as [SbF<sub>2</sub>(NCMe)<sub>3</sub>][MF<sub>6</sub>][MF<sub>5</sub>(NCMe)]<sub>2</sub>, M = Mo or W, by analogy with the reaction products from Te + MoF<sub>6</sub> or UF<sub>6</sub> in MeCN [20] since bands attributable to [MoF<sub>5</sub>(NCMe)] [43] or [WF<sub>5</sub>(NCMe)] [44] were observed. Partial analyses were consistent (Found: Mo, 32.4; Sb, 13.2; req. Mo, 30.1; Sb, 12.7% and found: Sb, 9.9; req. Sb, 10.0%) with this view and because simple solvated Sb<sup>III</sup> cations were not obtained, the reactions were not investigated further.

#### 4.2. Oxidation of lanthanides

Pieces of Nd ingot (1.0 mmol), freshly cut to expose new surface, were allowed to react with MoF<sub>6</sub> (10.0 mmol) and MeCN (5 cm<sup>3</sup>) at room temperature over 3 days, shaking the mixture and subjecting it to a freeze–pump–thaw cycle at regular intervals. Removal of volatile material at ambient temperatures from the pale yellow solution, gave a small quantity of yellow [Nd(NCMe)<sub>3</sub>][MoF<sub>6</sub>]<sub>3</sub> (Table 2). Neodymium powder did not react under identical conditions. Similarly prepared, was pale yellow [Eu(NCMe)<sub>3</sub>][MoF<sub>6</sub>]<sub>3</sub> (Table 2) from Eu powder. Both compounds contained bands in their IR spectra due to coordinated MeCN and [MoF<sub>6</sub>]<sup>−</sup>; their electronic spectra contained bands, λ<sub>max</sub> = 37,300 (ε = 91) (Nd<sup>III</sup>) and 29,100 cm<sup>−1</sup> (ε = 77) (Eu<sup>III</sup>) and μ<sub>eff</sub> values, determined at room temperature, were 5.13 and 4.97 B.M., respectively. Addition of pyridine or NMe<sub>3</sub> to solutions of the salts led to precipitation of mixed py–MeCN or NMe<sub>3</sub>–MeCN complexes (Table 2).

Analogous reactions between La or Eu powders and WF<sub>6</sub> in MeCN resulted in pale yellow solids whose partial analyses corresponded to [Ln(NCMe)<sub>3</sub>][WF<sub>6</sub>]<sub>3</sub>, Ln = La or Eu (Found: C, 6.2; H, 0.8; La, 11.95; N, 3.6; C<sub>6</sub>H<sub>9</sub>F<sub>18</sub>LaN<sub>3</sub>W<sub>3</sub> req. C, 6.2; H, 0.8; La, 12.0; N, 3.6. Found: C, 6.25; H, 0.85; Eu, 12.9; N, 3.8; C<sub>6</sub>H<sub>9</sub>EuF<sub>18</sub>N<sub>3</sub>W<sub>3</sub> req. C, 6.2; H, 0.8; Eu, 13.0; N, 3.6%), however, their IR spectra indicated that both [WF<sub>6</sub>]<sup>−</sup> and [WF<sub>7</sub>]<sup>−</sup> anions were present. Their electronic spectra contained bands λ<sub>max</sub> = 32,800 (ε = 84) and 29,200 cm<sup>−1</sup> (ε = 80), respectively; both compounds reacted with py and NMe<sub>3</sub> in an analogous manner to the [MoF<sub>6</sub>]<sup>−</sup> salts described above.

Although [NO][PF<sub>6</sub>] in MeCN reacted with all four lanthanide metals investigated, as indicated by the appearance of new bands in the electronic spectra of reaction mixtures, reactions were slow and the solids isolated were always contaminated with unchanged [NO][PF<sub>6</sub>] as indicated by Ln<sup>III</sup> analyses.

#### 4.3. Oxidation of Au and Ni

Reactions between Au foil or wire and [NO]<sup>+</sup> salts in MeCN were very slow and it was necessary to prepare Au powder by treatment with aqua regia then oxalic acid. The

resulting powder was washed with dilute aqueous HNO<sub>3</sub> then deionized H<sub>2</sub>O, before drying in vacuo. Reaction between Au powder (0.4 mmol) and [NO][MoF<sub>6</sub>] (0.07 mmol) in MeCN (5 cm<sup>3</sup>) yielded pale yellow [Au(NCMe)<sub>2</sub>][MoF<sub>6</sub>] after 1.5 h, identified from its analysis (Table 2) and IR spectrum. Reaction between the salt and py in MeCN yielded red [Au(py)<sub>2</sub>][MoF<sub>6</sub>] (Table 2). Longer reaction times, using either [NO][MoF<sub>6</sub>] or [NO][PF<sub>6</sub>], resulted in yellow solids in which the mole ratios Au:Mo or Au:P were, respectively, 1:2.5 or 1:1.4 suggesting that Au<sup>III</sup> may have been formed either by further oxidation or disproportionation.

No reaction was observed between Au and WF<sub>6</sub> in MeCN even after 12 h; in contrast, the reaction between Au and MoF<sub>6</sub> was difficult to control even below room temperature and resulted in an impure product.

A mixture of Ni foil, [NO][PF<sub>6</sub>] (2.0 mmol) and MeCN (5 cm<sup>3</sup>), allowed to react at room temperature overnight, gave a purple solution from which purple [Ni(NCMe)<sub>6</sub>][PF<sub>6</sub>]<sub>2</sub>, identified from its electronic and IR spectra (Found: Ni, 9.8; C<sub>12</sub>H<sub>18</sub>F<sub>12</sub>N<sub>6</sub>NiP<sub>2</sub> req. Ni, 9.8%), was isolated. Similarly prepared was the corresponding [WF<sub>6</sub>]<sup>−</sup> salt which could be obtained free of [WF<sub>7</sub>]<sup>−</sup> by allowing the Ni wire to contact WF<sub>6</sub> and MeCN vapors rather than liquid, the purple solid which coated the surface of the wire being removed by washing with MeCN.

No reaction was observed when Ni powder, wire or foil were exposed to MoF<sub>6</sub> in MeCN even when the Ni:MoF<sub>6</sub> mole ratio was 1:20. Addition of py to a mixture of Ni and MoF<sub>6</sub> in MeCN however led to an immediate exothermic reaction and the precipitation of yellow [MoF<sub>5</sub>(py)<sub>2</sub>] (Found: C 34.1; H, 2.8; F, 27.4; Mo, 27.45; N, 7.8. C<sub>10</sub>H<sub>10</sub>F<sub>5</sub>MoN<sub>2</sub> req. C, 34.4; H, 2.9; F, 27.2; Mo, 27.5; N, 8.0%). In addition to bands assignable to coordinated py, its vibrational spectrum contained strong bands ν<sub>max</sub> 625 and 570 cm<sup>−1</sup> (IR) and 679 cm<sup>−1</sup> (Raman). An identical solid was obtained from a reaction where Ni was absent.

A piece of Ni foil, contained in one limb of a three-limbed flask, was allowed to react with [NO][PF<sub>6</sub>] in MeCN overnight. The Ni<sup>II</sup> solution formed was removed by decanting and the foil washed with four portions of MeCN. The limb containing the Ni<sup>II</sup> salt and washings was then sealed off. A mixture of MoF<sub>6</sub> and MeCN was added and allowed to react with the cleaned Ni foil overnight. The presence of [Ni(NCMe)<sub>6</sub>]<sup>2+</sup> in solution was identified by electronic spectroscopy.

One limb of a two-limb flask was equipped with a Ni filament (0.5 mm diameter) spot-welded to tungsten electrodes that were sealed through the glass. The assembly was pumped (< 10<sup>−3</sup> Torr) for 2 days during which time the filament was heated electrically up to 1450°C, a temperature sufficient to remove surface oxide without loss of Ni by evaporation. Raising the filament temperature while cooling the outer surface (−196°C) led to evaporation of Ni and film formation. Addition of MoF<sub>6</sub> and MeCN resulted in an immediate reaction at room temperature to give a purple

solution from which a solid containing purple  $[\text{Ni}(\text{NCMe})_6]^{2+}$  and  $[\text{MoF}_6]^-$  was isolated.

Treatment of an evaporated Ni film with  $\text{WF}_6$  in MeCN produced no effect after 2 h, although reaction did occur on those parts of the Ni filament near the spot welds where the temperature had been insufficient to allow evaporation. The evaporation procedure was repeated with spot welds sheathed in glass and the film was exposed to moist air briefly before  $\text{WF}_6$  and MeCN were added. Reaction occurred to give a product spectroscopically identical to that described earlier. Vapor from a solution of  $[\text{}^{18}\text{F}]$ -labelled  $\text{WF}_6$  in MeCN [45], contained in one limb of a Pyrex counting cell, was exposed to an evaporated Ni film prepared in the other limb.  $[\text{}^{18}\text{F}]$  activity was immediately detected from the film, counts (corrected for decay) being constant over 1 h, and was unaffected by removal of volatile  $\text{WF}_5^{18}\text{F}$ . There was no evidence for a chemical reaction.

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### References

- [1] A. Prescott, D.W.A. Sharp, J.M. Winfield, *J. Chem. Soc., Dalton Trans.* (1975) 936.
- [2] S. Brownstein, G.A. Heath, A. Sengupta, D.W.A. Sharp, *J. Chem. Soc., Chem. Commun.* (1983) 669.
- [3] G.M. Anderson, J. Iqbal, D.W.A. Sharp, J.M. Winfield, J.H. Cameron, A.G. McLeod, *J. Fluor. Chem.* 24 (1984) 303.
- [4] C.J. Barbour, J.H. Cameron, J.M. Winfield, *J. Chem. Soc., Dalton Trans.* (1980) 2001.
- [5] J.H. Cameron, A.G. Lappin, J.M. Winfield, A. McAuley, *J. Chem. Soc., Dalton Trans.* (1981) 2172.
- [6] L. McGhee, R.M. Siddique, J.M. Winfield, *J. Chem. Soc., Dalton Trans.* (1988) 1309.
- [7] R.M. Siddique, J.M. Winfield, *J. Fluor. Chem.* 40 (1988) 71.
- [8] R.M. Siddique, J.M. Winfield, *Can. J. Chem.* 67 (1989) 1780.
- [9] G.M. Anderson, J.M. Winfield, *J. Chem. Soc., Dalton Trans.* (1986) 337.
- [10] C.D. Garner, L. McGhee, A. Steel, J.M. Winfield, *J. Fluor. Chem.* 69 (1994) 73.
- [11] S.H. Wang, S.I. Ajiboye, G. Haining, L. McGhee, R.D. Peacock, G. Peattie, R.M. Siddique, J.M. Winfield, *J. Chem. Soc., Dalton Trans.* (1995) 3837.
- [12] B.J. Hathaway, D.G. Holah, J.D. Postlethwaite, *J. Chem. Soc.* (1961) 3215.
- [13] B.J. Hathaway, D.G. Holah, A.E. Underhill, *J. Chem. Soc.* (1962) 2444.
- [14] G. Bergerhoff, *Z. Anorg. Allg. Chem.* 327 (1964) 139.
- [15] B.B. Wayland, R.F. Schramm, *Inorg. Chem.* 8 (1969) 971.
- [16] R.R. Thomas, V. Chebolu, A. Sen, *J. Am. Chem. Soc.* 108 (1986) 4096.
- [17] J. Iqbal, D.W.A. Sharp, J.M. Winfield, *J. Chem. Soc., Dalton Trans.* (1989) 461.
- [18] J.A. Berry, R.T. Poole, A. Prescott, D.W.A. Sharp, *J. Chem. Soc., Dalton Trans.* (1976) 272.
- [19] L. McGhee, D.S. Rycroft, J.M. Winfield, *J. Fluor. Chem.* 36 (1987) 351.
- [20] L. McGhee, J.M. Winfield, *J. Fluor. Chem.* 57 (1992) 147.
- [21] M.F. Ghorab, J.M. Winfield, *J. Fluor. Chem.* 49 (1990) 367.
- [22] S.J. Thompson, P.M. Bailey, C. White, P.M. Maitlis, *Angew. Chem., Int. Ed. Engl.* 15 (1976) 490.
- [23] D.W. Bruce, R.F. Jones, D.J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.* (1984) 2249.
- [24] B.J. Thomas, J.F. Mitchell, K.H. Theopold, J.A. Leary, *J. Organomet. Chem.* 348 (1988) 333.
- [25] G.R. Willey, H. Collins, M.G.B. Drew, *J. Chem. Soc., Dalton Trans.* (1991) 961.
- [26] G.R. Willey, M.T. Lakin, M. Ravindran, N.W. Alcock, *J. Chem. Soc., Chem. Commun.* (1991) 271.
- [27] M. Schäfer, G. Frenzen, B. Neumüller, K. Dehnicke, *Angew. Chem., Int. Ed. Engl.* 31 (1992) 334.
- [28] N.W. Alcock, M. Ravindran, G.R. Willey, *J. Chem. Soc., Chem. Commun.* (1989) 1063.
- [29] G.R. Willey, M.T. Lakin, N.W. Alcock, *J. Chem. Soc., Dalton Trans.* (1992) 1339.
- [30] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984, p. 1429ff.
- [31] A.D. Goolsby, D.T. Sawyer, *Anal. Chem.* 40 (1968) 1978.
- [32] A.E. Wickenden, R.A. Krause, *Inorg. Chem.* 4 (1965) 404.
- [33] I. Sjötofte, R.G. Hazell, S.E. Rasmussen, *Acta. Crystallogr., Sect. B.* 32 (1976) 1692.
- [34] M. Munakata, S. Kitagawa, M. Miyazima, *Inorg. Chem.* 24 (1985) 1638.
- [35] L. Fielding, P. Moore, *J. Chem. Soc., Chem. Commun.* (1988) 49.
- [36] J.R. Geichman, E.A. Smith, S.S. Trond, P.R. Ogle, *Inorg. Chem.* 1 (1962) 661.
- [37] J.M. Winfield, *J. Fluor. Chem.* 25 (1984) 91.
- [38] D.M. Byler, D.F. Shriver, *Inorg. Chem.* 12 (1973) 1412.
- [39] N.S. Gill, R.H. Nuttall, D.E. Scaife, D.W.A. Sharp, *J. Inorg. Nucl. Chem.* 18 (1961) 79.
- [40] J.N. Gayles, *Spectrochim. Acta, Part A* 23 (1967) 1521.
- [41] E.K. Barefield, F. Wagner, A.W. Herlinger, A.R. Dahl, *Inorg. Synth.* 16 (1976) 220.
- [42] B. Romero, S. Bruque, M.A.G. Aranda, J.E. Iglesias, *Inorg. Chem.* 33 (1994) 1869.
- [43] J.C. Fuggle, D.W.A. Sharp, J.M. Winfield, *J. Fluor. Chem.* 1 (1971/1972) 427.
- [44] N. Bao, J.M. Winfield, *J. Fluor. Chem.* 50 (1990) 339.
- [45] M.F. Ghorab, J.M. Winfield, *J. Fluor. Chem.* 62 (1993) 101.