Preparation and Properties of Bis(acetonitrile)iodine(I) Hexafluoromolybdate(V) and Hexafluorouranate(V)

Gerard M. Anderson and John M. Winfield *
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

Elemental iodine is oxidized by molybdenum or uranium hexafluoride in acetonitrile at ambient temperature to give bis(acetonitrile)iodine(I) hexafluoromolybdate(V) or hexafluorouranate(V). The solids' vibrational spectra are consistent with linear co-ordination of MeCN to I^+. Co-ordinated MeCN is readily displaced by pyridine (py) to give an $[I(py)_2]^+$ salt. In MeCN solution the solvated I^+ decomposes to give I_2 as one product, it iodinates benzene and its derivatives, and oxidizes the solvated copper(I) cation, NO, and thallium metal to give the solvated copper(II) cation, NO^+, and a mixture of solvated cations of Tl^{I} and Tl^{III} respectively. The solvated thallium(III) cation oxidizes iodine ion in MeCN at room temperature giving I_2 or solvated I^+ depending on the concentration ratio. Oxidation states of solvated thallium cations are conveniently identified by ^{205}Tl n.m.r. spectroscopy.

Hexafluoromolybdates(V) of alkali metals are readily prepared by iodide reduction of molybdenum hexafluoride in liquid SO_2,[1] and if excess of I^- is used further reduction to give hexafluoromolybdates(IV) occurs.[2] When we attempted to carry out this reduction in acetonitrile, further oxidation of I_2, initially produced, was observed, and this prompted an examination of the redox behaviour of MoF_6 and UF_6 towards I_2 in MeCN. The results of this study are now described. A preliminary report of the preparation of bis(acetonitrile)iodine(I) hexafluoromolybdate(V) has already appeared.[3]

Results and Discussion

Bis(acetonitrile)iodine(I) *Hexafluorometalates*(V).—*Preparation.* Addition of MoF_6 to a frozen solution of I_2 in MeCN, mol ratio $MoF_6:I_2 \gg 2:1$, results in a rapid change in colour, from dark red through yellow-green to pale yellow, as the mixture is allowed to warm to room temperature. A colourless solid, identified as bis(acetonitrile)iodine(I) hexafluoromolybdate(V), $[I(NCMe)_2][MoF_6]$, crystallizes from solution as volatile material is removed at room temperature. The corresponding hexafluorouranate(V), $[I(NCMe)_2][UF_6]$, is prepared in a similar manner using UF_6, and is isolated as a pale green solid. Although the existence of the I^+ cation solvated by MeCN has often been postulated, most recently as one component of an electrical energy storage cycle,[4] the compounds described here appear to be the first examples of its isolated salts. Both solids decompose slowly *in vacuo* at room temperature to give I_2 as one product, but can be stored for long periods at 233 K.

Prior dissolution of I_2 in MeCN and a large excess of the hexafluoride over the 2:1 mol ratio required for a stoicheiometric reaction are both required to ensure pure products, otherwise the solids are contaminated by unreacted I_2. Polynuclear cations, for example I_3^+, which are characteristically formed when I_2 is oxidized in strongly acidic solvents,[5] are apparently not formed in the basic solvent MeCN.

The reactions described above are consistent with previously reported voltammetric studies. Both hexafluorides are strong one-electron oxidizing agents in MeCN, the half-wave potential, $E_{\frac{1}{2}}$, *vs.* Ag^+–Ag^0 determined by cyclic voltammetry for the couple MoF_6–MoF_6^- being +1.60 V.[6,7] An irreversible anodic wave at *ca.* 1.1 V *vs.* Ag^+–Ag^0 observed at a rotating platinum electrode from solutions of NaI or NMe_4I_3 in MeCN has been assigned to the oxidation $I \longrightarrow I^+$.[8] An analogous wave from I_2 in MeCN was not observed, but was found in a later study[9] by cyclic voltammetry using a pyrolytic graphite electrode.

The cyclic voltammogram of $[I(NCMe)_2][MoF_6]$ in MeCN, obtained after several scans, contains a quasi-reversible wave, $E_{\frac{1}{2}} = +1.60$ V *vs.* Ag^+–Ag^0, due to MoF_6–MoF_6^- and a complex set of anodic and cathodic waves at lower applied potential. Part of this arises from the quasi-reversible MoF_6^-–MoF_6^{2-} couple, $E_{\frac{1}{2}} = -0.40$ V,[6,7] and the remainder is identical with the cyclic voltammogram of I_2 in MeCN.

A further illustration of the importance of the solvent in redox reactions between I_2 and these hexafluorides is provided by the behaviour of I_2 towards UF_6 and MoF_6 in iodine pentafluoride. Iodine is oxidized by UF_6 to form the I_2^+ cation which undergoes further oxidation, whereas I_2 and MoF_6 do not react.[10]

Spectroscopic characterization. The vibrational spectrum of solid $[I(NCMe)_2][MoF_6]$ is consistent with the presence of octahedral MoF_6^- and co-ordinated MeCN. Band assignments, Table 1, are made by comparison with the vibrational spectra of hexafluoromolybdates(V) of NO^+[11] and Tl^{III},[7] salts of metal cations containing co-ordinated MeCN,[12] $BF_3 \cdot NCMe$ and $SbF_5 \cdot NCMe$.[13] Satisfactory Raman spectra were obtained only below 50 K. Above this temperature the spectrum is dominated by the resonance-Raman spectrum of I_2 vapour. Medium-intensity bands at 174 (Raman) and 220 cm^{-1} (i.r.) are assigned to symmetric and asymmetric N–I–N stretching modes respectively, their positions being reasonable in comparison with the spectra of ICl_2^- and IBr_2^- anions.[14] The data imply that $[I(NCMe)_2]^+$ is centrosymmetric analogous to the well known bis(pyridine)iodine(I), $[I(py)_2]^+$, cation.[15] Orange $[I(py)_2][MoF_6]$ is formed readily from pyridine and $[I(NCMe)_2][MoF_6]$ in MeCN at room temperature. Its vibrational spectrum contains bands attributable to MoF_6^- and to co-ordinated pyridine,[16] but no definitive band assignments in the 200-cm^{-1} region were possible.

The Raman spectrum of $[I(NCMe)_2][UF_6]$ contains a band at 613 cm^{-1} assigned to ν_1 of UF_6^- by analogy with the spectrum of $[Tl(NCMe)_5][UF_6]_3$,[17] and a band at 178 cm^{-1} is tentatively assigned to the symmetric N–I–N stretch. In its i.r. spectrum, Table 1, ν_3 of UF_6^- is assigned at 520 cm^{-1} by analogy with the thallium(III) salt.[17]

The i.r. spectra of both $[I(NCMe)_2]^+$ salts contain more bands in the C≡N stretching region than can be accounted for on the basis of a single type of co-ordinated MeCN, therefore individual band assignments in this region are not given. However, the spectra are very characteristic, and they enable the $[I(NCMe)_2]^+$ cation to be identified in solid mixtures, for example in the presence of $[Tl(NCMe)_5]^{3+}$, Figure. It is

Table 1. Vibrational spectra (cm^{-1}) of $[I(NCMe)_2][MF_6]$, M = Mo or U

$[I(NCMe)_2][MoF_6]$			
Raman, solid[a]	I.r., solid[b]	$[I(NCMe)_2][UF_6]$ I.r., solid[b]	Assignment
	2 311s 2 299m 2 280m	2 312m 2 298m 2 295m 2 282m	CH_3 def. + CC str. (A_1) CN str. (A_1)
	2 248w	2 246w	2 × CC str. + CCN def. (A_1)
	2 045w		
	1 355m	1 355m	CH_3 def. (A_1)
		1 080w	
	1 028m	1 030m	CH_3 rock (E)
		965w	
949w	936m	941 (sh) 934m	CC str. (A_1)
	786w	790w	2 × CCN def. (A_1)
675s[c]			ν_1 MF_6^- (A_{1g})
	635s	560 (sh) 520s	ν_3 MF_6^- (T_{1u})
425vw			ν_2 MF_6^- (E_g)
383w	405m	406m	CCN def. (E)
	253s		ν_4 MF_6^- (T_{1u})
232w			ν_5 MF_6^- (T_{2g})
	220m		NIN asym. str.
174m			NIN sym. str.

[a] At 10 K; s = strong, m = medium, w = weak, and sh = shoulder. [b] At room temperature, Nujol mull between AgCl or Si. [c] Polarized in MeCN at room temperature.

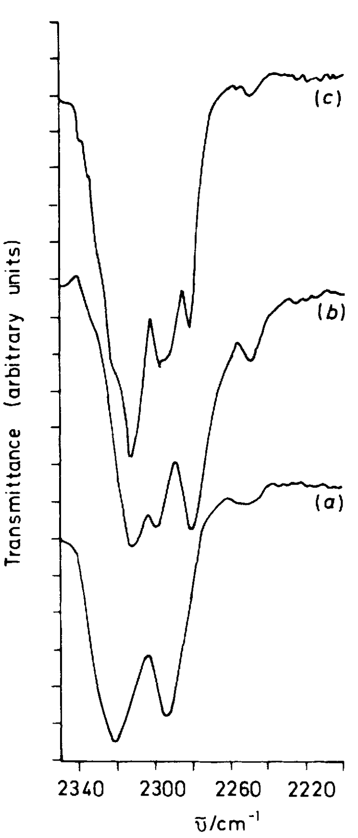

Figure. I.r. spectra, Nujol mulls, in the C≡N stretching region of (*a*) $[Tl(NCMe)_5][MoF_6]_3$, (*b*) $[I(NCMe)_2][MoF_6]$, and (*c*) a product mixture from thallium(III) hexafluoromolybdate(V) and $NBu^n{}_4I$ in MeCN

considered that the extra bands reflect site-symmetry effects in the solids and do not indicate that $[I(NCMe)_2]^+$ is non-centrosymmetric.

The electronic spectrum of $[I(NCMe)_2][MoF_6]$ in MeCN has a strong band, $\lambda_{max.}$ *ca.* 230 nm, but contains no significant absorption at longer wavelength. The spectrum of the UF_6^- salt is similar with the addition of bands in the visible and near-i.r. regions due to UF_6^-.[17] Iodine, formed by slow decomposition in solution, or present as a trace impurity in the solid, is therefore readily detected spectroscopically at 460 nm, for example 1.7×10^{-4} mol dm^{-3} I_2 was detected in 2.7×10^{-2} mol dm^{-3} $[I(NCMe)_2][MoF_6]$ solution. The rate of formation of I_2 in solution is highly dependent on the sample's history.

Reactions of $[I(NCMe)_2][MoF_6]$.—(*a*) *Iodination of benzene and its derivatives.* Benzene reacts rapidly with $[I(NCMe)_2][MoF_6]$ in MeCN at room temperature to give iodobenzene. Similar reactions of toluene, anisole, aniline, and salicylic acid give respectively a mixture of $2\text{-}IC_6H_4CH_3$, $4\text{-}IC_6H_4CH_3$, and $2,4\text{-}I_2C_6H_3CH_3$, a mixture of $4\text{-}IC_6H_4(OCH_3)$ and $2,4\text{-}I_2C_6H_3(OCH_3)$, $4\text{-}IC_6H_4(NH_2)$, and $3,5\text{-}I_2C_6H_2(CO_2H)(OH)$. For the iodination of anisole, which was examined in greatest detail, there appears to be no simple relationship between reaction stoicheiometry and the degree of iodination; $2,4\text{-}I_2C_6H_3(OCH_3)$ is a major product in nearly every case. The nature of the products suggests strongly that the reactions proceed *via* an electrophilic substitution mechanism, presumed to involve solvated I^+.

These reactions occur under conditions comparable to those used for iodination with thallium(III) trifluoroacetate and I^- anion.[18] For example, $C_6H_5(NH_2)$ can be iodinated in MeCN to give $4\text{-}IC_6H_4(NH_2)$ using $Tl[OC(O)CF_3]_3$ followed by aqueous I^-.[19] The presumed intermediate is an arylthallium(III) species, but it occurred to us that, in MeCN, oxidation of I^- to solvated I^+ by Tl^{III} was also a possibility. This reaction was investigated as part of a study of the redox reactions of $[I(NCMe)_2][MoF_6]$ described below.

(*b*) *Redox reactions.* On the basis of published half-wave potentials for the couples solvated NO^+–NO and solvated Cu^{2+}–solvated Cu^+ in MeCN ($E_{\frac{1}{2}}$ = +0.87[7] and +0.75 V[20] *vs.* Ag^+–Ag^0), solvated I^+ should be capable of oxidizing both NO and $[Cu(NCMe)_4]^+$. This proves to be the case, the products from the rapid, room-temperature reactions being MoF_6^- salts of NO^+ and $[Cu(NCMe)_6]^{2+}$. Solvated Tl^{3+} is a stronger oxidizing agent in MeCN than solvated Cu^{2+}, although $E_{\frac{1}{2}}$ for the Tl^{III}–Tl^{I} couple could not be determined.[7] In order to obtain further chemical information relating to the oxidizing ability of Tl^{III} in MeCN, redox reactions between various thallium and iodine species have been performed, using ^{205}Tl n.m.r. spectroscopy to identify thallium oxidation states.

Solvated Tl^{3+} and Tl^+ cations in MeCN are readily differentiated by their ^{205}Tl chemical shifts, Table 2. Resonance from Tl^{3+} occurs at higher frequency than that from Tl^+, consistent with previous studies of compounds of Tl^{III} and Tl^{I} in various solvents.[21] Signals due to solvated Tl^+ are very sensitive to the presence of paramagnetic MoF_6^-, for example the ^{205}Tl resonance from $TlPF_6$ in MeCN occurs at 92 p.p.m. to higher applied field than that from $TlMoF_6$, Table 2, the peak widths at half-height being 18 and 2 800 Hz respectively. A similar trend, decreased shielding and increased signal broadening with increase in $[MoF_6^-]$, is observed in solutions prepared from $TlPF_6$ and $[Tl(NCMe)_5][MoF_6]_3$ (Table 2). The range of ^{205}Tl chemical shifts observed from Tl^{3+} samples is smaller, 43 p.p.m., than for Tl^+ and the peak widths at half-height are in the range 140—250 Hz. Despite the breadth of the signals, relative

Table 2. ^{205}Tl N.m.r. chemical shifts[a] in MeCN

Solute	δ(Tl$^{\text{I}}$)	δ(Tl$^{\text{III}}$)	[Tl$^{\text{I}}$]	[Tl$^{\text{III}}$]	[MoF$_6^-$]
	p.p.m.		mol dm^{-3}		
TlPF$_6$	−268		0.30		
TlMoF$_6$	−176		0.12		0.12
[Tl(NCMe)$_5$][MoF$_6$]$_3$		+2 067		0.20	0.60
'Tl(MoF$_6$)$_2$'	−45	+2 078	1:0.8[b]		*ca.* 1.4
TlPF$_6$ + [Tl(NCMe)$_5$][MoF$_6$]$_3$	−234	*c*	0.050	0.019	0.056
	−213	+2 035	0.050	0.025	0.075
	−179	+2 053	0.050	0.111	0.333
	−146	+2 063	0.050	0.162	0.485

[a] With respect to TlNO$_3$ (aq) at Ξ = 57.683 833 MHz. [b] Determined from the n.m.r. integral. [c] Not observed.

Table 3. I.r. spectra (cm^{-1}) in the C≡N stretching region of some compounds of I$^{\text{I}}$ and Tl$^{\text{III}}$

Sample*					
[I(NCMe)$_2$]-[MoF$_6$]		2 311s	2 299m		2 280m
[Tl(NCMe)$_5$]-[MoF$_6$]$_3$	2 321s			2 294m	
Thallium(I,III) hexafluoromolybdate(V)	2 322s			2 293m	
Product from Tl^0 + [I(NCMe)$_2$]-[MoF$_6$]	2 322m	2 312 (sh)	2 297s		2 280 (sh)
Product from NBu$^n{}_4$I + [Tl(NCMe)$_5$]-[MoF$_6$]$_3$	2 322 (sh)	2 312s	2 297m	2 292 (sh)	2 281m

* Nujol mull between AgCl.

intensities determined from n.m.r. spectra agreed reasonably well with solution stoicheiometries.

Colourless [Tl(NCMe)$_5$][MoF$_6$]$_3$ is formed from the oxidation of Tl metal by MoF$_6$ in MeCN only if the concentration of MoF$_6$ is high, otherwise the product is a yellow solid in which the Tl:Mo atomic ratio is approximately 1:2.[7] The ^{205}Tl n.m.r. spectrum of the latter product, Table 2, is consistent with its formulation as a mixture of thallium-(I) and -(III) hexafluoromolybdates(V). Its i.r. spectrum, Table 3, is also consistent with this view, but is not definitive since MeCN is not co-ordinated to Tl$^+$ in the solid state. Oxidation of Tl metal by [I(NCMe)$_2$][MoF$_6$] in MeCN at room temperature leads to I$_2$ and a yellow solid, whose ^{205}Tl n.m.r. spectrum in MeCN consists of peaks, δ −157 and +2 053 p.p.m., assigned to Tl$^+$ and Tl^{3+} in the ratio *ca.* 20:1. The solid's i.r. spectrum, Table 3, contains bands attributable to [Tl(NCMe)$_5$]$^{3+}$ and [I(NCMe)$_2$]$^+$. Oxidation of a mixture of Tl metal and I$_2$ by MoF$_6$ in MeCN leads to a mixture of products in which the Tl$^{\text{I}}$:Tl$^{\text{III}}$ ratio is 1:5.

Iodide anion is oxidized by Tl^{3+} in MeCN at room temperature to give I$_3^-$, I$_2$ mixtures or solvated I$^+$ depending on the ratio [Tl^{3+}]:[I$^-$]. With [Tl^{3+}] < [I$^-$], mixtures of I$_2$ and I$_3^-$, identified by electronic spectroscopy, are formed, but when [Tl^{3+}] is > [I$^-$], iodine, which is the initial oxidation product, undergoes further reaction to give solvated I$^+$, identified in the solid state as [I(NCMe)$_2$]$^+$ by its i.r. spectrum, Table 3 and the Figure. In all cases the reduction product is Tl$^+$, identified in solution by ^{205}Tl n.m.r. spectroscopy.

The work described in this paper indicates that although MeCN is sufficiently basic to stabilize the I$^+$ cation, its interaction is relatively weak, and thus the cation is chemically reactive. It is a stronger oxidizing agent in MeCN than NO$^+$ and is comparable to solvated Tl^{3+}. This suggests that iodination of aromatic molecules by the Tl^{3+}, I$^-$ reagent in MeCN could proceed *via* solvated I$^+$ as the intermediate.

Experimental

All operations were carried out in a Pyrex vacuum line or an argon-atmosphere glove-box (< 5 p.p.m. water). Volatile fluorides, MoF$_6$ (Fluorochem) and UF$_6$ (B.N.F. plc), were purified by low-temperature trap-to-trap distillation over predried NaF. Iodine (B.D.H., AnalaR) was resublimed in a greaseless vessel. Acetonitrile (Rathburn HPLC grade S) was purified and dried using a published procedure,[22] and pyridine (B.D.H. AnalaR) was distilled *in vacuo* and stored over activated 3A molecular sieves. Tetra-n-butylammonium iodide (B.D.H., AnalaR) was pumped at room temperature before use, and stored in the glove-box. Nitric oxide (Air Products) was used as received; no impurities were detected in its i.r. spectrum. The salt NOMoF$_6$ was prepared from MoF$_6$ and NO;[23] its Raman spectrum was identical with that reported previously.[11] Thallium metal (B.D.H., 99.99%) was stored in a glove-box and freshly cut pieces were used in reactions. The aromatic compounds (all AnalaR) were used as received.

The salts [Cu(NCMe)$_4$][MoF$_6$], TlPF$_6$, [Tl(NCMe)$_5$][MoF$_6$]$_3$, and the mixed thallium(I, III) hexafluoromolybdate(V) were prepared as previously described.[7] Thallium metal dissolved rapidly in a solution of NOMoF$_6$ in MeCN at room temperature. The products were NO and a mustard-coloured solid identified as *thallium*(I) *hexafluoromolybdate*(V) (Found: F, 27.5; Mo, 23.25; Tl, 49.1. F$_6$MoTl requires F, 27.5; Mo, 23.2; Tl, 49.3%). I.r.: 620 and 240 cm^{-1} (ν_3 and ν_4 of MoF$_6^-$). For ^{205}Tl n.m.r. spectrum see Table 2.

Reaction vessels, fitted with Pyrex polytetrafluoroethylene stopcocks, had two limbs enabling solutions to be decanted under vacuum. Similar vessels, with one limb replaced by an n.m.r. tube, 10-mm Spectrosil cell, or Pyrex capillary tube, were used to prepare solutions for spectroscopic examination. I.r. spectra of solids were obtained as Nujol mulls between AgCl or silicon plates. Solid samples for Raman spectroscopy were contained in Pyrex capillaries which could be mounted in a helium cryostat (Air Products Displex).

Instrumention was as follows: Raman, Spex Ramalog with 520.8- or 647.1-nm excitation; i.r., PE 983 with 3 600 data station; electronic, Beckman 5270; n.m.r., PE R32 for ^{1}H at 90 MHz, JEOL FX90 for ^{205}Tl at 51.62(Tl$^{\text{I}}$) and 51.74 MHz (Tl$^{\text{III}}$). Cyclic voltammetry was carried out as previously described.[7] Microanalyses were by Malissa and Reuter.

Preparation of Bis(*acetonitrile*)*iodine*(I) *Hexafluorometalates*(V).—(*a*) *Bis*(*acetonitrile*)*iodine*(I) *hexafluoromolybdate*(V). A solution of iodine (0.2 mmol) in MeCN (5 cm^3) was prepared *in vacuo* and MoF$_6$ (*ca.* 5 mmol) added to the frozen solution. On warming the mixture to room temperature a rapid colour change, red to green to yellow, was observed. Removal of volatile material left a colourless *solid* (Found: C, 11.35; H, 1.5; F, 27.4; I, 30.5; Mo, 22.75; N, 6.6. C$_4$H$_6$F$_6$IMoN$_2$ requires C, 11.5; H, 1.45; F, 27.2; I, 30.3; Mo, 22.9; N, 6.7%). The solid hydrolysed in water to give I$_2$ as one product; addition of KI gave further I$_2$. Its spectra have been described above.

A mixture of NBu$^n{}_4$I (0.30 g) and MoF$_6$ (1 g) in MeCN (4 cm^3) gave a red solution on warming to room temperature, but the colour faded rapidly to pale yellow. A cream solid was isolated whose i.r. spectrum contained bands due to the NBu$^n{}_4{}^+$ cation and bands identical to those of [I(NCMe)$_2$][MoF$_6$], Table 1.

(*b*) *Bis*(*acetonitrile*)*iodine*(I) *hexafluorouranate*(V). Uranium hexafluoride reacted with a frozen solution of I$_2$ in MeCN under similar conditions to those described above to give a pale green solid (Found: C, 8.5; H, 1.1; F, 20.5; I, 22.5; N, 4.85; U, 42.35.

$C_4H_6F_6IN_2U$ requires C, 8.6; H, 1.1; F, 20.3; I, 22.6; N, 5.0; U, 42.4%). Its spectra have been described above.

Reactions of $[I(NCMe)_2][MoF_6]$ *in* MeCN.—(*a*) *With pyridine.* A mixture of $[I(NCMe)_2][MoF_6]$ (0.7 mmol), pyridine (5.0 mmol), and MeCN (5 cm^3) gave an orange solution at room temperature. An orange solid isolated was identified as *bis(pyridine)iodine*(I) *hexafluoromolybdate*(V) (Found: C, 24.4; H, 2.1; F, 23.2; I, 25.5; Mo, 19.3; N, 5.7. $C_{10}H_{10}F_6IMoN_2$ requires C, 24.3; H, 2.0; F, 23.0; I, 25.6; Mo, 19.4; N, 5.7%).

(*b*) *With benzene and substituted benzenes.* Aliquots (2 cm^3) of a standard $[I(NCMe)_2][MoF_6]$ solution (0.24 mol dm^{-3}) in MeCN were added to benzene, aniline, anisole, salicylic acid, and toluene (3.5—5.5 mmol) at room temperature in a glove-box. Iodine was immediately produced together with solid material. The mixtures were extracted with light petroleum (b.p. 40—60 °C), the solutions concentrated, and the organic product identified by ^1H n.m.r. spectroscopy using ^1H-{^1H} experiments and making comparisons with authentic spectra[24] where possible. Iodination of anisole was studied in more detail by injecting various quantities (0.18—1.80 mmol) of anisole from a microsyringe into aliquots (2 cm^3) of $[I(NCMe)_2][MoF_6]$ solution (0.06 mol dm^{-3}) at room temperature. The identified products were 4-iodo- and 2,4-di-iodo-anisole. The latter was usually predominant, and in one case was the sole product; its identity was confirmed by the mass spectrum. No attempt was made to optimize the yields.

(*c*) *With nitric oxide.* A mixture of $[I(NCMe)_2][MoF_6]$ (0.80 mmol) and NO (3.0 mmol) in MeCN (5 cm^3) was shaken at room temperature for 10 min. Iodine, identified by its electronic spectrum in MeCN, $\lambda_{max.}$ = 460 nm, was immediately liberated. The other product was an orange solid whose Raman spectrum was identical with that of $NOMoF_6$.[11]

(*d*) *With tetrakis(acetonitrile)copper*(I) *hexafluoromolybdate*(V). The salt $[I(NCMe)_2][MoF_6]$ (0.70 mmol), contained in a frangible ampoule, was added to $[Cu(NCMe)_4][MoF_6]$ (0.69 mmol) and MeCN (4 cm^3) in an evacuable Spectrosil cell. The ampoule was broken, I_2 was immediately released, and the solution's electronic spectrum also contained a broad, asymmetric band, $\lambda_{max.}$ = 740 nm, due to $[Cu(NCMe)_6]^{2+}$ (ref. 7).

(*e*) *With thallium metal.* A mixture of thallium metal (0.30 mmol) and $[I(NCMe)_2][MoF_6]$ (0.80 mmol) in MeCN (5 cm^3) was allowed to react at room temperature for 1 h. It was necessary to wash the metal during reaction with fresh MeCN to remove adsorbed I_2, formed as one product. The other product was a yellow solid whose ^{205}Tl n.m.r. spectrum in MeCN contained signals due to Tl^I and Tl^{III}, ratio *ca.* 20:1. Its i.r. spectrum was characteristic of the hexafluoromolybdates(V) of $[I(NCMe)_2]^+$ and $[Tl(NCMe)_5]^{3+}$ (Table 3). On one occasion a thallium(III) product was not observed.

The reaction between Tl metal (0.24 mmol), I_2 (0.20 mmol), and MoF_6 (4.76 mmol) in MeCN (5 cm^3) was rapid, 10 min, at room temperature. The product was a yellow solid whose ^{205}Tl n.m.r. spectrum in MeCN indicated a mol ratio Tl^I:Tl^{III} = *ca.* 1:5. The i.r. spectrum of the solid showed that hexafluoromolybdates(V) of $[I(NCMe)_2]^+$ and $[Tl(NCMe)_5]^{3+}$ were present.

(*f*) *With thallium*(I) *hexafluorophosphate.* A mixture of $[I(NCMe)_2][MoF_6]$ (0.70 mmol) and $TlPF_6$ (0.69 mmol) in MeCN (4 cm^3) reacted rapidly at room temperature, I_2 being immediately liberated. The i.r. spectrum of the yellow solid produced contained bands attributable to $[I(NCMe)_2]^+$, $[Tl(NCMe)_5]^{3+}$, PF_6^-, and MoF_6^-, however a thallium(III) signal was not detected in its ^{205}Tl n.m.r. spectrum.

Oxidation of Iodide Anion by Solvated Thallium(III).—Aliquots (4.00 cm^3) of a standard thallium(III) hexafluoromolybdate(V) solution (0.040 mol dm^{-3}) were transferred in a glove-box by means of a microburette to previously dried, evacuable Spectrosil cells. The ^{205}Tl n.m.r. spectrum of the reagent indicated that some Tl^+ was present, and this was allowed for in calculating $[Tl^{III}]$. Weighed portions of $NBu^n{}_4I$, contained in frangible ampoules, were added, the solutions degassed *in vacuo*, and spectral baselines obtained. After breaking the ampoules the spectra of the mixtures were obtained. When $[Tl^{III}]$:$[I^-]$ was 1:1.2 or 1:2.4 the spectra were characteristic of I_2,I_3^- mixtures. When $[Tl^{III}]$:$[I^-]$ was 1:0.6 or 1:0.4 the spectra were virtually unchanged after reaction, but the i.r. spectra of the isolated solids indicated that $[I(NCMe)_2]^+$ and $[Tl(NCMe)_5]^{3+}$ were present. Identical behaviour was observed using $[Tl^{III}]$ = 0.031 mol dm^{-3} and $[Tl^{III}]$:$[I^-]$ = 1:0.8, 1:1.1, 1:1.6, 1:3.1, and 1:4.4.

Oxidation of I^- was also studied using a mixture of thallium(I, III) hexafluoromolybdate(V) (1.7 g) and $NBu^n{}_4I$ (0.16 mmol) in MeCN (2.5 cm^3) at room temperature. Iodine was immediately produced and the other product was a yellow solid. The ^{205}Tl n.m.r. spectra of solutions in MeCN before and after reaction were obtained with the following results: before reaction, $\delta(Tl^I)$ − 126, $\delta(Tl^{III})$ + 2 063 p.p.m., $\nu_{\frac{1}{2}}(Tl^I)$ 650, $\nu_{\frac{1}{2}}(Tl^{III})$ 250 Hz, $[Tl^{III}]$:$[Tl^I]$ = 8.5:1; after reaction, $\delta(Tl^I)$ −134, $\delta(Tl^{III})$ + 2 059 p.p.m., $\nu_{\frac{1}{2}}(Tl^I)$ 750, $\nu_{\frac{1}{2}}(Tl^{III})$ 350 Hz, $[Tl^{III}]$:$[Tl^I]$ = 1:2.5. The solid's i.r. spectrum, Table 3, indicated that hexafluoromolybdates(V) of $[I(NCMe)_2]^+$ and $[Tl(NCMe)_5]^{3+}$ were present.

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