Oxidation of Silver Metal and Silver(I) Cations by Molybdenum, Tungsten, and Uranium Hexafluorides and by the Nitrosonium Cation in Acetonitrile. Preparation and Properties of Silver(III) Hexafluorometalates(V)

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Silver metal is oxidized by molybdenum, tungsten, or uranium hexafluorides or by the nitrosonium cation, all in acetonitrile, to give the solvated silver(I) cation from which silver(I) cations with ligated pyridine, py, or trimethyl phosphite are readily prepared. Oxidation of $[Ag(py)_4][MoF_6]$ and $[Ag(py)_2][UF_6]$ in MeCN by MoF_6 and UF_6 respectively leads to the silver(III) compounds $[Ag(py)_4(NCMe)][MoF_6]_3$ and $[Ag(py)_2(NCMe)_3][UF_6]_3$. The cations are strong oxidizing agents in MeCN. The solvated copper(I) cation and molecular iodine are oxidized to give copper(II) and the $[I(NCMe)_2]^+$ cation.

Room-temperature redox reactions between metals and molybdenum, tungsten, or uranium hexafluorides in acetonitrile are a convenient method of preparing many solvated metal cation hexafluorometalates(V). In an earlier paper the preparations of solvated silver(I) hexafluorotungstate(V) and solvated silver(II) hexafluoromolybdate(V) by the oxidation of silver metal using WF_6 and MoF_6 in MeCN were described, the silver(II) salt being identified by a partial microanalysis and its vibrational and e.s.r. spectra.[1] It was concluded that MoF_6 is the stronger oxidizing agent in MeCN, and this has been substantiated by later voltammetric[2] and synthetic work.[3,4] However attempts to repeat the preparation of silver(II) hexafluoromolybdate(V) were unsuccessful, only the silver(I) salt being isolated.

This failure prompted a more detailed investigation of reactions between silver(I) cations and transition-metal hexafluorides in MeCN. In particular we wished to determine the effect that ligands other than MeCN might have on the oxidation of Ag^I. By analogy with aqueous chemistry it was expected that the oxidation of Ag^I in the presence of pyridine, py, would yield the $[Ag(py)_4]^{2+}$ cation,[5] but oxidation in MeCN by MoF_6 or UF_6 leads to silver(III) cations.

Results and Discussion

Silver(I) *Complexes.*—The preparation of silver(I) hexafluorometalate(V) salts with acetonitrile, pyridine, or trimethyl phosphite co-ordinated to Ag^I is summarized in the Scheme. The reactions are straightforward, the ligand-replacement reactions being analogous to those used to prepare silver(I) cations with a variety of N, O, S, or Se donor ligands in sulphur dioxide starting from silver(I) hexafluoroarsenate.[6] The $[Ag\{P(OMe)_3\}_4]^+$ salts are analogous to the previously reported BF_4^- salt,[7] and they have similar low-temperature, 178 K, $^{31}P-\{^1H\}$ n.m.r. spectra; $\delta(^{31}P) = 134$ p.p.m. with respect to 85% H_3PO_4, $^1J(^{31}P-^{107/109}Ag) = 383$ (PF_6^-), 403 (MoF_6^-), and 367 Hz (UF_6^-). There is no evidence for the formation of cations with lower $P(OMe)_3:Ag^I$ molar ratios, but this is not surprising in view of the weakly basic nature of the anions.

The stoicheiometry of the pyridine complexes formed does depend on the counter anion. The salts isolated are of two types, $[Ag(py)_2][MF_6]$, M = P or U, and $[Ag(py)_4][MF_6]$, M = Mo or W. In the i.r. spectrum of $[Ag(py)_2][PF_6]$ the ν_3 mode of PF_6^- is split into two components, 882 and 840 cm^{-1} in the solid and 877 and 840 cm^{-1} in MeCN. This phenomenon is observed in other PF_6^- salts, however, and by itself does not constitute a proof of cation–anion interaction.

There is no spectroscopic evidence for interaction between $[Ag(py)_4]^+$ and $[MoF_6]^-$ either in the solid state or in MeCN. Both solid and solution Raman spectra contain a strong band at 680 cm^{-1} assigned to ν_1 of MoF_6^-. Bands in the i.r. spectrum at 635 (solid) and 645 cm^{-1} (MeCN) are assigned to ν_3 and a band at 252 cm^{-1} in the solid i.r. spectrum to ν_4 of MoF_6^-. The molybdenum extended *X*-ray absorption fine structure (EXAFS) spectrum[8] is consistent with the presence of a regular octahedral MoF_6^- anion, Mo–F 1.79 ± 0.01 Å compared with 1.74 ± 0.03 Å determined from an *X*-ray powder diffraction study of $NaMoF_6$.[9] The $[Ag(py)_4]^+$ cation is assumed to be tetrahedral as it is in the perchlorate salt.[10] The compound $[Ag(py)_4][MoF_6]$ is paramagnetic, Table 1, however no e.s.r. signal is observed from a frozen MeCN solution down to 77 K. This is also consistent with a negligible deviation from O_h symmetry for MoF_6^-. Despite the paramagnetism of the anion, the ^{13}C n.m.r. chemical shifts in $[Ag(py)_4]^+$ are identical to those in $[Ag(py)_2][PF_6]$, Table 2. The only difference in the spectra is the relatively broad signal observed for *meta* ^{13}C nuclei in the former cation.

The oxidation of silver metal by MoF_6 or UF_6 in MeCN is independent of the stoicheiometry used, at least up to the molar ratio $MF_6:Ag = 10:1$. When an excess of WF_6 is used, however, mixtures of solvated silver(I) hexafluorotungstate(V) and heptafluorotungstate(VI) are obtained as a consequence of the facile F^- ion-transfer reaction occurring between WF_6^- and WF_6. Similar behaviour was observed previously when copper[3] or iron[11] was oxidized by WF_6 in MeCN.

Silver(III) *Complexes.*—Oxidation of $[Ag(py)_4][MoF_6]$ by MoF_6 in MeCN and of $[Ag(py)_2][UF_6]$ by UF_6 in MeCN, in both cases below room temperature, leads to the isolation of orange solids which are identified from their analyses, spectra, and magnetic properties as the silver(III) salts $[Ag(py)_4(NCMe)][MoF_6]_3$ and $[Ag(py)_2(NCMe)_3][UF_6]_3$, Scheme. The compounds are moisture and light sensitive, and decompose slowly in MeCN at room temperature, this being evident after 0.5 h. The presence of co-ordinated MeCN and py is indicated by their vibrational spectra. Bands assigned to the MoF_6^- anion in the former compound are found at 679 and 681 cm^{-1} (Raman, solid and solution respectively, assigned to ν_1), 630 and 635 (i.r., solid and solution respectively, assigned to ν_3), and 252 cm^{-1} (i.r., solid, assigned to ν_4). The i.r. spectrum of the solid UF_6^- salt contains a band at 510 cm^{-1} assigned to the ν_3 vibration. The room-temperature magnetic properties of both salts are consistent with the silver(III) cations being diamagnetic.

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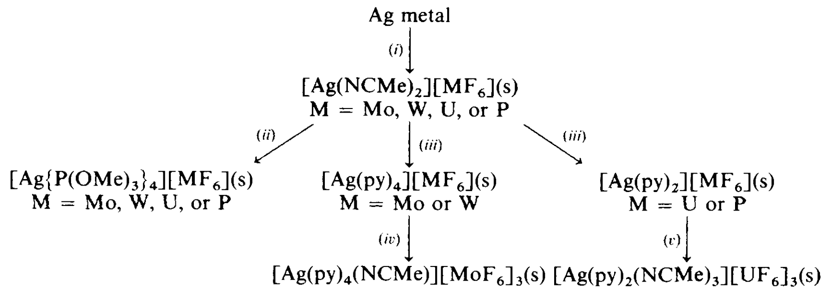
* *Non-S.I. units employed:* B.M. ≈ 9.273×10^{-24} A m^2; $\chi(S.I.) = \chi(c.g.s.) \times 4\pi \times 10^{-6}$.



Scheme. Silver(I) and silver(III) hexafluorometalates. (*i*) MoF_6, WF_6, UF_6, or $NO^+PF_6^-$ in MeCN; (*ii*) $P(OMe)_3$ in MeCN; (*iii*) py in MeCN; (*iv*) MoF_6 in MeCN at 258 K; (*v*) UF_6 in MeCN at 258 K

Table 1. Corrected molar magnetic susceptibilities, $\chi^{corr.}(M^V)$, and effective magnetic moments, $\mu_{eff.}$, per M^V atom in solid silver(III) and silver(I) hexafluorometalates(V) at 295 K

Complex	$10^6\chi^{corr.}(M^V)$/c.g.s.	$\mu_{eff.}$
$[Ag(py)_4(NCMe)][MoF_6]_3$	361 ± 58	0.93 ± 0.08
$[Ag(py)_4][MoF_6]$	394 ± 95	0.99 ± 0.11
$[Ag(NCMe)_2][MoF_6]$	421 ± 55	1.00 ± 0.06
$[Ag(py)_2(NCMe)_3][UF_6]_3$	1 080 ± 32	1.61 ± 0.02
$[Ag(py)_2][UF_6]$	991 ± 96	1.54 ± 0.08
$[Ag(NCMe)_2][UF_6]$	1 096 ± 89	1.61 ± 0.06
$[Ag(NCMe)_2][WF_6]$	178 ± 30	0.65 ± 0.08

Table 2. $^{13}C-\{^1H\}$ N.m.r. chemical shifts for ligated pyridine in silver(I) and silver(III) salts[a]

Complex	^{13}C Chemical shift, δ/p.p.m.		
	ortho	*para*	*meta*
$[Ag(py)_2][PF_6]$	151.6	138.8	125.8
$[Ag(py)_4][MoF_6]$	151.4	138.5	125.8
$[Ag(py)_4(NCMe)][MoF_6]_3$[b]	144.7	143.8	127.2
py in $CDCl_3$[c]	149.8	135.7	123.6

[a] In EtCN with respect to $SiMe_4$. [b] At 193 K; $\delta(^{13}C)$ = 121.1 p.p.m. assigned to CN of EtCN and MeCN. [c] L. F. Johnson and W. C. Jankowski, '^{13}C N.m.r. Spectra,' Wiley-Interscience, New York, 1972.

Magnetic susceptibilities, $\chi^{corr.}(M^V)$, M^V = Mo^V or U^V, determined for the solids are in good agreement with those determined for the corresponding silver(I) salts, Table 1. Values for $\chi^{corr.}(Mo^V)$ determined in MeCN solution are a little smaller in the case of the Ag^{III}, for example at 298 K $\chi^{corr.}(Mo^V)$ is 359 ± 60 c.g.s. from the silver(I) salt compared with 253 ± 46 c.g.s. determined from the silver(III) salt. The difference presumably arises from some decomposition of the former, however in both cases the relationship between temperature and $[\chi^{corr.}(Mo^V)]^{-1}$ is linear over the range 308—238 K. The value of $\chi^{corr.}(U^V)$ agrees well with that found previously for hydrazinium(2+) hexafluorouranate(V).[12] Values of $\chi^{corr.}(Mo^V)$ are smaller than those reported for alkali-metal hexafluoromolybdates(V), although the agreement in the hexafluorotungstate(V) case is good.[13] A possible reason for the differences found for the MoF_6^- salts is that those with alkali-metal cations were prepared from the reduction of MoF_6 by iodide ion in liquid SO_2. This could have led to contamination by the hexafluoromolybdate(IV) anion.[14]

The $^{13}C-\{^1H\}$ n.m.r. spectrum of $[Ag(py)_4(NCMe)][MoF_6]_3$ in EtCN is reversibly temperature dependent. The spectrum at 193 K consists of three sharp singlets assigned to co-ordinated pyridine, Table 2, and a relatively broad peak $\delta(^{13}C)$ = 121.1 p.p.m., due to cyano-^{13}C nuclei of MeCN and EtCN. All peaks broaden on warming and are barely discernible at 263 K. These observations, and the diamagnetic character of Ag^{III}, are consistent with a low-spin d^8 electronic configuration in which MeCN is co-ordinated weakly to square-planar $[Ag(py)_4]^{3+}$. In solution it is likely that two nitrile ligands are co-ordinated.

The $^{13}C-\{^1H\}$ n.m.r. spectrum of $[Ag(py)_2(NCMe)_3][UF_6]_3$ can be observed only at 189 K, since decomposition occurs too quickly at higher temperatures for the observations made to be meaningful. Signals due to two types of co-ordinated pyridine are present. The reaction of $[Ag(py)_2(NCMe)_3][UF_6]_3$ with py results in the replacement of co-ordinated MeCN by py, and two types of pyridine are observed in its low-temperature n.m.r. spectrum. It is apparent that these cations are substitutionally labile, and that several isomeric possibilities exist, although these have not been determined.

The stabilization of Ag^{III} by tetra-aza macrocyclic ligands is well known,[15] and the properties of these compounds have been widely studied.[16] Silver(III) complexes in the solid state with simple ligands such as fluoride and oxide, for example the compounds $MAgF_4$, M = Na or K,[17] and Ag_2O_3,[18] are also well known. The anion $[Ag(OH)_4]^-$ can be generated in basic aqueous solution.[19] In all cases square-planar stereochemistry about Ag^{III} has been demonstrated or can be reasonably inferred. The half-life of $[Ag(OH)_4]^-$ in 1.2 mol dm^{-3} aqueous NaOH is approximately 1.5 h,[19] therefore the ready decomposition of the silver(III) cations prepared here is not surprising.

The different behaviour observed in the present work compared with that found previously[1] can be ascribed to differences in the procedure used to purify the solvent. The acetonitrile used in this work was the more rigorously purified.[20] Disproportionation of Ag^I to Ag metal and Ag^{II} in reagent-grade or 'wet' MeCN can be induced by tetra-aza macrocyclic ligands,[21] and it is possible that the formation of Ag^{II} previously observed was the result of disproportionation of Ag^I induced by solvent impurities. What is now definitely established is that, in rigorously purified MeCN, oxidation of silver metal by MoF_6 or the stronger oxidizing agent UF_6[3] does not proceed beyond Ag^I unless pyridine is present.

Redox Reactions.—The solvated copper(I) cation and molecular iodine are both rapidly oxidized by the silver(III) cations in MeCN at room temperature, Ag^{III} being reduced to Ag^I. The reactions involving $[Cu(NCMe)_4]^+$ lead to copper(II) cations containing both ligated py and MeCN, but in the reactions of I_2 the oxidized product is $[I(NCMe)_2]^+$ (ref. 4) rather than $[I(py)_2]^+$. The reactions indicate that the oxidizing ability of these silver(III) cations in MeCN is comparable with that of the

Table 3. Analytical data* for silver(I) and silver(III) hexafluorometalates

		Analysis (%)					
Compound	Colour	C	H	Ag	F	M	N
$[Ag(NCMe)_2][MoF_6]$	Pale yellow			27.0 (27.0)		23.5 (24.0)	6.9 (7.0)
$[Ag(NCMe)_2][WF_6]$	Off-white			22.0 (22.1)			5.6 (5.9)
$[Ag(NCMe)_2][UF_6]$	Pale green	8.9 (8.9)	1.1 (1.1)	19.9 (19.9)	20.9 (21.0)	42.2 (43.9)	5.1 (5.2)
$[Ag(NCMe)_2][PF_6]$	Colourless			32.2 (32.2)			8.0 (8.4)
$[Ag\{P(OMe)_3\}_4][MoF_6]$	Pale yellow	17.6 (17.7)	4.4 (4.5)	13.2 (13.3)	14.0 (14.0)	12.2 (11.7)	
$[Ag\{P(OMe)_3\}_4][UF_6]$	Pale green			11.2 (11.3)			
$[Ag\{P(OMe)_3\}_4][PF_6]$	Colourless			14.6 (14.6)			
$[Ag(py)_4][MoF_6]$	Yellow			17.2 (17.0)		15.5 (15.1)	8.7 (8.8)
$[Ag(py)_4][WF_6]$	Pale yellow			15.0 (15.0)			
$[Ag(py)_2][UF_6]$	Pale green	19.4 (19.4)	1.6 (1.6)	17.2 (17.5)	20.7 (18.5)	40.9 (38.5)	4.5 (4.5)
$[Ag(py)_2][PF_6]$	Pale yellow			26.0 (26.3)			6.6 (6.8)
$[Ag(py)_4(NCMe)][MoF_6]_3$	Orange	24.3 (24.1)	2.1 (2.1)	10.0 (9.9)	31.4 (31.2)	26.0 (26.3)	6.3 (6.4)
$[Ag(py)_2(NCMe)_3][UF_6]_3$	Orange	13.7 (13.3)	1.4 (1.3)	7.3 (7.5)	23.6 (23.7)	49.8 (49.4)	4.5 (4.9)

* Required values are given in parentheses.

solvated thallium(III) cation,[3,4] and is exceeded only by those of the hexafluorides MoF_6 and UF_6.

A limited electrochemical study is in accord with this conclusion. The cyclic voltammogram of $[Ag(py)_4(NCMe)][MoF_6]_3$ in MeCN consists of quasi-reversible waves at $E_{\frac{1}{2}} = +1.65$ and -0.34 V *vs.* Ag^+–Ag^0 which are assigned to the couples MoF_6–MoF_6^- and MoF_6^-–MoF_6^{2-} by analogy with previous work.[2] Rather ill defined waves at +1.17 and +0.57 V are tentatively assigned to the couples Ag^{III}–Ag^{II} and Ag^{II}–Ag^{I} respectively. Waves due to redox processes involving MoF_6^- are observed in the cyclic voltammogram of $[Ag(py)_4][MoF_6]$ but those involving silver were not observed.

Experimental

All operations were carried out in a Pyrex vacuum line or an argon-atmosphere glove-box (<5 p.p.m. water) using previously described methods for reagent purification, carrying out reactions, and spectroscopic studies.[3,4,22] Magnetic susceptibilities of solids at room temperature were determined by the Gouy method using a microbalance (Cahn TA 450) and electromagnet (Newport 1.5″ type C). The compounds $Hg[Co(NCS)_4]$, $[Mn(acac)_3]$, and $[Ag(py)_4][NO_3]_2$ were used as calibrants and samples were contained in capped tubes. The usual diamagnetic corrections were made. Magnetic susceptibilities in MeCN solution were determined over the temperature range 308—238 K by the Evans method[23] at 90 MHz. Cyclic voltammograms were obtained using a P.A.R. model 175 universal programmer and model 173 potentiostat-galvanostat. Room-temperature measurements were made using a cell described previously,[3] and low-temperature measurements in an all-glass cell incorporating a cold-finger. Microanalyses were by Malissa and Reuter, Federal Republic of Germany. In some cases silver and nitrogen were determined also by atomic absorption spectroscopy and the Kjeldahl method respectively.

Oxidation of Silver Metal by Molybdenum, Tungsten, or Uranium Hexafluorides or by the Nitrosonium Cation.—Mixtures of silver foil (3.0 mmol), a hexafluoride or $NO^+PF_6^-$ (2.0 mmol), and MeCN (5 cm^3) were shaken for 15 min at room temperature. The solids isolated from solution by removal of volatile material were identified from their analysis, Table 3, and spectra as bis(acetonitrile)silver(I) hexafluorometalates. Oxidation of silver by UF_6 in MeCN was very exothermic and an impure product was obtained. Impurities were removed by washing with MeCN. Bands in the vibrational spectra of the products were assigned to the anions by comparison with known hexafluorometalates,[3,4,24] and the presence of the UF_6^- anion was confirmed by its electronic spectrum in MeCN.[25] Vibrational bands characteristic of co-ordinated MeCN[26] were at $\tilde{\nu}_{max.} = 2\,315$, 2 285, 1 030, and 945 cm^{-1}.

Oxidation of silver metal (1.2 mmol) by MoF_6 or UF_6 (12.0 mmol) in MeCN (5 cm^3) under similar conditions gave products identical to those described above.

Preparation of Silver(I) *Complexes.*—Mixtures of $[Ag(NCMe)_2][MF_6]$, M = P, Mo, W, or U, and pyridine or trimethyl phosphite (molar ratio Ag^I:ligand = 1:8) in MeCN (5 cm^3) were shaken at room temperature for 15 min. The solids isolated after removal of volatile material, MeCN, unchanged ligand, and a little dimethyl methylphosphonate from reactions with $P(OMe)_3$, were identified after recrystallization as (bis- or tetrakis-pyridine)silver(I) hexafluorometalates or tetrakis(trimethyl phosphite)silver(I) hexafluorometalates, Table 3. The presence of MF_6^- anions was shown by vibrational spectroscopy,[3,4,24] and for UF_6^- by electronic spectroscopy.[25] Other bands in the vibrational spectra were assigned to co-ordinated pyridine[27] or trimethyl phosphite,[28] but MeCN was absent.

Oxidation of Pyridinesilver(I) *Hexafluorometalates*.—Mixtures of $[Ag(py)_4][MoF_6]$ (1.1 mmol) and MoF_6 (3.8 mmol) or $[Ag(py)_2][UF_6]$ (1.1 mmol) and UF_6 (2.55 mmol), both in MeCN (5 cm^3), were shaken at 258 K for 3—5 min. In each case the solutions became dark orange, and orange solids were isolated on removal of volatile material below room temperature. The solids were identified from their analysis, Table 3, and their spectra as acetonitriletetrakis(pyridine)silver(III) hexafluoromolybdate(V) and tris(acetonitrile)bis(pyridine)silver(III) hexafluorouranate(V). Their vibrational spectra contained bands due to co-ordinated MeCN and py, and to the anions MoF_6^- or UF_6^-.

No reaction occurred between $[Ag(py)_2][PF_6]$ and NO^+-PF_6^- in MeCN at room temperature. A mixture of $[Ag(py)_4][WF_6]$ (0.7 mmol) and WF_6 (2.0 mmol) in MeCN (5 cm^3) led to the isolation of a cream solid containing Ag^I, co-ordinated MeCN and py, and the WF_7^- anion, identified by its vibrational spectrum.[3,11]

Redox Reactions.—(*a*) *With iodine*. Two series of reactions were performed. Portions of $[Ag(py)_4(NCMe)][MoF_6]_3$ or $[Ag(py)_2(NCMe)_3][UF_6]_3$ contained in frangible glass ampoules were added to solutions of I_2 in MeCN (5 cm^3, $[I_2] = 3 \times 10^{-3}$ or 2×10^{-3} mol dm^{-3}) contained in evacuable 10-mm Spectrosil cells. The mixtures were degassed and their electronic spectra, $\tilde{\nu}_{max.} = 21\,750$ cm^{-1}, $\varepsilon = 689 \pm 16$ dm^3 mol^{-1} cm^{-1}, recorded. The ampoules were broken, the solutions allowed to equilibrate, and their spectra redetermined in order to determine the concentration of I_2 that remained. Initial concentrations of Ag^{III} were in the ranges 5×10^{-4}—3.2×10^{-3} and 2×10^{-4}—2.3×10^{-3} mol dm^{-3}, and the combining ratio $[Ag^{III}]:[I_2]$ was 1 : 1. The $[I(NCMe)_2]^+$ cation was identified as a reaction product by means of its characteristic ν(CN) bands[4] in the i.r. spectrum of the product mixture.

(*b*) *With copper*(I). Three series of spectrophotometric experiments were carried out in a manner similar to that described above, to study reactions between tetrakis(acetonitrile)copper(I) hexafluorophosphate[29] and $[Ag(py)_4(NCMe)][MoF_6]_3$ or $[Ag(py)_2(NCMe)_3][UF_6]_3$ in MeCN. Initial concentrations were as follows: $[Cu^I]$ 1.0×10^{-2}, 0.265, and 0.181; $[Ag^{III}]$ 0.2×10^{-2}—1.8×10^{-2}, 0.3×10^{-2}—2.0×10^{-2} (MoF_6^- salt in both cases), and 0.6×10^{-2}—2.1×10^{-2} mol dm^{-3} (UF_6^- salt). The electronic spectra of the solution after reaction indicated that pyridine was co-ordinated to Cu^{II}, and in order to determine the concentrations of the latter it was necessary to make a spectroscopic study of the copper(II) cation in MeCN in the presence of various quantities of py.

Addition of py to a solution of copper(II) hexafluorophosphate[29] in MeCN resulted in an increase in $\tilde{\nu}_{max.}$ from 13 500 cm^{-1}, $\varepsilon = 28$ dm^3 mol^{-1} cm^{-1}, {characteristic of $[Cu(NCMe)_6]^{2+}$} to 17 250 cm^{-1}, $\varepsilon = 76$ dm^3 mol^{-1} cm^{-1}, when $[Cu^{II}]:[py] = 1:4$. The relationship between $\tilde{\nu}_{max.}$ and ε was linear. A further increase in [py] had no effect suggesting that the formation constants for pentakis- and hexakis-pyridine copper(II) complexes in MeCN were small. A similar situation has been found for complex formation between Cu^{II} and NH_3 in aqueous solution.[30] The electronic spectrum of hexakis(pyridine)copper(II) hexafluorophosphate (Found: C, 43.4; H, 3.7; Cu, 7.9; F, 27.4; N, 10.0. $C_{36}H_{30}CuF_{12}N_6P_2$ requires C, 43.5; H, 3.7; Cu, 7.7; F, 27.6; N, 10.2%) in MeCN also consisted of a broad band, $\tilde{\nu}_{max.} = 17\,200$ cm^{-1}, $\varepsilon = 76$ dm^3 mol^{-1} cm^{-1}. The linear relationship between $\tilde{\nu}_{max.}$ and ε for the Cu^{II}, py, MeCN system was used to determine $[Cu^{II}]$ from the reactions between solvated Cu^I and Ag^{III} in MeCN, and to estimate the average number of py ligands co-ordinated to Cu^{II} as a result of the reactions. The data obtained indicated that the combining ratio $[Ag^{III}]:[Cu^I]$ was 1 : 2 and that the average number of py ligands co-ordinated per Cu^{II} was between 1 and 2.

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