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The reactions of silicon monoxide and aluminium monofluoride with 2,2′-bipyridyl

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Abstract

The high temperature species, SiO and AlF, have each been treated with 2,2′-bipyridyl in tetrahydrofuran solution at −105 °C and in an adamatane matrix at −196 °C to give products which have spectroscopic properties closely resembling the known compound $[SiCl_2(bipy)_2]$. When initially formed the products are highly coloured and paramagnetic in solution or in the adamantane matrix and their EPR spectra show the presence of singlet and triplet species. In the triplet species, two electrons are transferred from the silicon or aluminium centre to two bipyridyl ligands which must lie orthogonal to each other across the metal centres but it is uncertain whether the species are monomeric or oligomeric. Evaporation of the solutions causes irreversible precipitation of pyrophoric solids of composition SiO(bipy) or AlF(bipy).

Introduction

The low temperature chemistry of monovalent molecular species of boron and aluminium and of divalent species of silicon prepared at high temperatures, has been an active research area for many years [1–5]. We report here on new low temperature reactions of SiO and of AlF with 2,2′-bipyridyl (bipy) in solution and in solid matrices. The work appears to be the first reported example of adduct formation with AlF. The reaction of the bidentate ligand, bipy, with SiO and AlF is of interest because, surprisingly, its complexes with $SiCl_2$ and with alkaline earth metals, $[SiCl_2(bipy)_2]$ and $M(bipy)_2$, are paramagnetic and show transitions characteristic of triplet species, $S=1$ [6–10]. Analysis of the EPR spectrum suggests a structure having two bipyridyl radical anions coordinated to $SiCl_2^{2+}$ and M^{2+}; the electron spins on each bipyridyl anion adopt a parallel alignment and hence result in a triplet species because the two ligands are orthogonal to each other across the metal centre.

Experimental

Gaseous SiO was made by heating granular, solid silicon monoxide (Merck) to 1300 °C under vacuum; AlF was made by heating compressed pellets containing a mixture of powdered aluminium and aluminium trifluoride (each 99% pure) in a 6:1 mole ratio to 1100 °C under vacuum (the excess Al greatly reduced vaporization of molecular AlF_3 from the pellets).

Work in solution was carried out by evaporating the species under vacuum from heated alumina crucibles mounted inside an externally cooled, rotating Pyrex glass flask containing a solution of 2,2′-bipyridyl in tetrahydrofuran (for a description of the equipment, see refs. 11 and 12). In a typical run with silicon monoxide, 1 g (23 mmol) of solid SiO was evaporated over 1 h into a solution of 8 g (51 mmol) of bipy in 100 cm^3 of dry tetrahydrofuran cooled to about −105 °C. The pressure in the rotating reaction flask was kept below 10^{-1} Pa. The solution remained clear but became intensely purple coloured. When all the SiO had evaporated, the cold solution was removed from the reaction flask and stored at −80 °C. The solution was extremely oxygen and moisture sensitive and was immediately decolorized with precipitation of a brown solid on exposure to air. The solution remained purple at room temper-

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ature in the absence of air but some purple–brown solid precipitated irreversibly. Addition of pentane at low temperatures caused immediate, irreversible precipitation of a purple–brown, pyrophoric solid, which, after washing with tetrahydrofuran to remove free bipy, had a composition very close to SiO(bipy). *Anal.* found: Si, 13.80; C, 61.24; H, 4.48; N, 14.16. Calc. for $SiOC_{10}H_8N_2$: Si, 14.02; C, 59.97; H, 4.03; N, 13.99%. The same solid was obtained by evaporating the tetrahydrofuran at low temperatures and then washing the residue with fresh tetrahydrofuran to remove excess bipy. The washings were almost colourless showing precipitation of the solid was irreversible.

In a similar way, *c.* 1.2 g (26 mmol) of AlF was condensed into *c.* 150 cm^3 of tetrahydrofuran containing 6.0 g (38 mmol) of bipy at −105 °C during 1 h. The solution remained fairly clear but became intensely green–brown in colour. The resulting solution was filtered cold and stored at −80 °C. Part of the solution was evaporated to 1/3 its original volume at low temperatures and excess diethyl ether was added. A green–brown solid was precipitated irreversibly. This was washed with diethyl ether and tetrahydrofuran and vacuum dried. The solid was pyrophoric; analysis showed a composition close to AlF(bipy). *Anal.* Found: C, 59.25; H, 4.77; N, 13.84. Calc. for $AlFC_{10}H_8N_2$: C, 59.41; H, 3.99; N, 13.85%.

The rotating cryostat [13] was also used to study these reactions in a matrix of solid adamantane at 77 K. In each revolution of the cryostat, SiO or AlF vapours (generated continuously from a resistively heated molybdenum pouch) were condensed on a freshly deposited layer of bypridyl molecules and the combined layer was covered with adamantane molecules giving a matrix with a mole ratio of SiO/AlF:bipy:adamantane of about 1:5:300. Experiments lasted 30 min and typically 15 mg of SiO or AlF were condensed with 14 g of adamantane. The condensate was studied *in situ* by IR spectroscopy using a Mattson FTIR spectrometer with the beam directed by mirrors to reflect off the rotating cryostat drum. When condensation was complete, portions of the solid condensate were scraped off while still at −196 °C under high vacuum and transferred into quartz tubes for EPR spectrometry.

Results and discussion

Condensation of SiO and AlF vapours into solutions of bipy in tetrahydrofuran at low temperatures gave soluble, intensely coloured purple and green products, respectively. The colours persisted in solution at room temperature but attempts to change the solvent or to concentrate the solutions by evaporation resulted in irreversible precipitation of pyrophoric purple–brown and green–brown solids of composition SiO(bipy) and AlF(bipy), respectively. These solids were found to be insoluble in most inert solvents, although the AlF product was somewhat soluble in dimethyl sulfoxide. Reaction of the solids with water or with aqueous HCl in the absence of oxygen were slow and complex; almost no gas was evolved but mass spectrometry on the products show that some reduction and coupling of bipy molecules had occurred. With the SiO–bipy product, we obtained indications from mass spectrometry and from EPR that reaction with dry oxygen in solution gave a tetrapyridyl and formed traces of an anionic nitroxide.

The spectroscopic properties of both the SiO– and AlF–bipy products showed remarkable similarities to those exhibited by $[SiCl_2(bipy)_2]$ [6–8]. Thus, the UV–Vis spectra of tetrahydrofuran solutions of the SiO– and AlF–bipy products showed intense absorptions at 376 nm, close to a similar band at 383 nm for $[SiCl_2(bipy)_2]$, typical of solutions containing $(bipy)^-$ [14]. The SiO product showed an almost continuous series of absorptions from 400–580 nm, accounting for its permanganate-like colour, but the AlF product showed well defined maxima at 480 and 574 nm, and, as a result appeared green like MnO_4^{2-} and $[SiCl_2(bipy)_2]$. Strong absorptions were seen below 300 nm due to free bipy in the solutions.

The IR spectra of both the SiO– and AlF–bipy solid products at room temperature were quite complicated compared to free bipy, typical of complexes with charge transfer from the metal to the bipy ligand [15], and very similar to that reported for $[SiCl_2(bipy)_2]$ (see Table 1). We assigned the νSi–O band to a broad feature centered around 1006 cm^{-1} in the spectrum of the SiO–bipy product. This is at lower frequency than in many polysiloxane structures but we note that the Si–Cl stretching modes were assigned to bands at 508 and 485 cm^{-1} in $[SiCl_2(bipy)_2]$ [8, 16], also low compared to νSi–Cl bands in most compounds. We could not assign the νAl–F band with certainty although it may be a shoulder at 765 cm^{-1} on the side of C–H bending modes of free or coordinated bipy in this region; this is slightly lower in frequency than for free AlF isolated in noble gas matrices and much lower than for νAl–F in AlF_3 [17, 18]. The reflectance IR spectra obtained from the SiO– or AlF–bipy products in adamantane matrices showed similar bands due to coordinated bipy to those in the spectra of the solid products. However, for the SiO–bipy product there was no broad νSiO band, only a sharp, strong band at 990 cm^{-1} possibly due to a molecular species with a $(SiO)_2$ or $(SiO)_3$ ring. With the AlF–bipy product,

TABLE 1. The wavenumber of IR bands in the Nujol mull spectra of polymeric SiO(bipy) and AlF(bipy) and of molecular $[SiCl_2(bipy)_2]$[a]

SiO(bipy)	AlF(bipy)	$[SiCl_2(bipy)_2]$[a]	Assignment
1612 m	1614sh, 1606m	1610m	
1582m	1582s		
1570m		1573m	
1560m	1560ms	1560sh	νC=C and νC=N
1457vs	1456vs	(Nujol)	of rings
1448sh	1448vs	(Nujol)	
1420m	1421s		
1254m	1264m	1264m	ring stretch
1144, 1130ms	1156, 1147m	1153, 1145ms	
		1110m	
1066, 1060s	1065wm	1070w	
			δC–H in and out of plane
1038sh, 1027sh	1039m, 1032m	1035w, 1025w	
1023sh,	1025m, 1020sh		
1006vs, br		1006ms	νSi–O
996sh, 975sh	992ms, 977sh	965ms	$(bipy)^-$ring breathing
948s	967m		
	765sh		νAl–F?
756s	756vs	757s	πC–H
711ms	738s	735s	
668m	668ms	668m	ring bending
657mw	656m	655sh	modes
620mw	620m	628w	
		505sh, 493vs	νSi–Cl
450w		462w	
	415w		

[a]Values compiled from refs. 8 and 16.

a band at 762 cm^{-1}, perhaps assignable to νAlF, was better resolved from the neighbouring bipy πCH band at 753 cm^{-1} than in the spectrum of solid AlF–bipy. Exposing either the SiO–bipy or AlF–bipy solid products to air caused immediate loss of IR bands due to coordinated bipy.

The purple solution of SiO/bipy in tetrahydrofuran, when frozen at −196 °C, gave the EPR spectrum shown in Fig. 1. The spectrum, which is very similar to that of frozen solutions of $[SiCl_2(bipy)_2]$ [6–8], consists of a sharp central line (B) at $g=2.003$ with $\Delta H_{pp}=11$ G, and two sets of lines on either side of this central absorption ($A_\parallel$ and $A_\perp$). The latter are the parallel and perpendicular features for the $|-1>$ to $|0>$ and $|0>$ to $|+1>$ transitions of a randomly orientated axially symmetric triplet molecule. The separation between the inner lines is D and between the outer lines is $2D$ where D is the zero field splitting parameter. From the spectrum $g_\perp=g_\parallel=2.003$ and $D=158$ G. Confirmation of the assignment of these lines to a triplet molecule comes from the observation of a line at half field corresponding to the 'forbidden' $\Delta m_s=1$ transition, $|-1>$ to $|+1>$. On warming to room temperature, the triplet lines disappeared leaving a single resonance centered at 3490 G with $\Delta H_{pp}=12$ G and $g=2.0028$. The EPR spectrum of the SiO–bipy in the adamantane matrix at −196 °C showed the same basic features as that of the frozen tetrahydrofuran solution, but it was somewhat weaker. The half-field signal was too weak to observe and the parallel features of the triplet were not so well resolved. The main signal was centered at 3305 G and $g=2.002$ and the perpendicular lines gave $g_\perp=2.002$ and $D=176$ G.

The green AlF–bipy solution in tetrahydrofuran, when frozen in liquid nitrogen, showed an EPR spectrum which was similar to that observed with SiO–bipy with a center signal at 3420 G ($g=2.0031$, $\Delta H_{pp}=5$ G) and weaker triplet lines with parameters $g_{\perp \text{ and } \parallel}=2.0031$ and $D=157$ G. The ratio of intensities of the triplet signals to the intensity of the center signal was lower than for SiO–bipy and no half-field signal was detectable. The spectrum of the

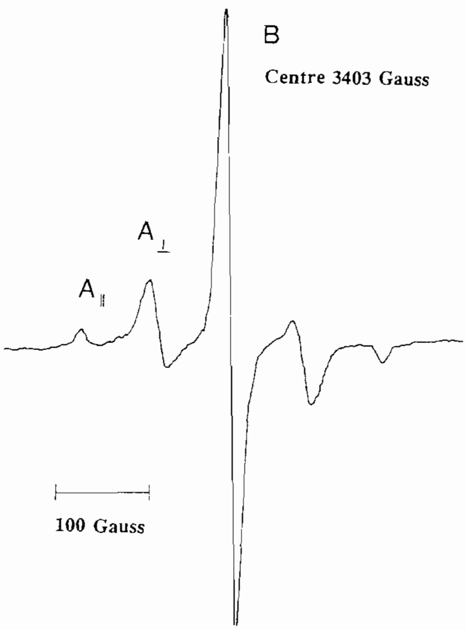


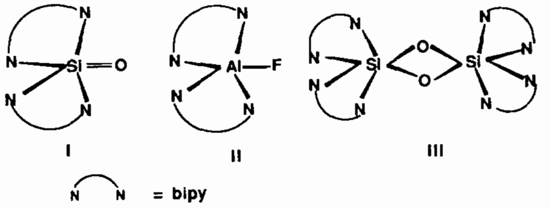
Fig. 1. EPR spectrum of the SiO–bipyridyl product in tetrahydrofuran solution frozen at −196 °C.

solution when warmed to room temperature showed a singlet at 3500 G ($g = 2.0028$, $\Delta H_{pp} = 18$ G) but the formation of a slight precipitate was evidence of some decomposition. The AlF–bipy in adamantane matrix gave a well resolved EPR spectrum, with the main singlet line at 3308 G, $g = 2.0016$, and triplet signals giving $g = 2.0016$ and $D = 173$ G.

The ^{19}F NMR spectrum of the AlF–bipy product in tetrahydrofuran showed one broad, weak resonance centred at 124.0 ppm relative to external $CFCl_3$. Attempts to obtain a ^{29}Si NMR spectrum of the SiO–bipy product were unsuccessful presumably due to broadening of any signal by paramagnetic species in solution.

Our intepretation of the EPR spectrum is similar to that of Broudy *et al.* [7] and Chu [8] for $[\mathrm{SiCl_2(bipy)_2}]$. The sharp central line (B) is assigned to a species such as $[\mathrm{SiO(bipy^-)}]^+(\mathrm{bipy}^-)]$ in which only there is weak coupling between the radical anions because of their large separation in the ion pairs. It is not unlikely that the species are polymeric $\{[-\mathrm{OSi}^{2+}(\mathrm{bipy}^-)]^+(\mathrm{bipy}^-)\}_n$ or $\{[-\mathrm{FAl}^{2+}(\mathrm{bipy}^-)]^+(\mathrm{bipy}^-)\}_m$ with some coordination to tetrahydrofuran, although the small differences between the adamantane matrix and tetrahydrofuran solution EPR spectra suggest that such coordination is only a minor influence on the structures of the complexes. EPR silent species such as oligomeric $[-\mathrm{OSi}^{2+}(\mathrm{bipy}^{2-})]_n$ and $[-\mathrm{FAl}^{2+}(\mathrm{bipy}^{2-})]_m$, stabilized in solution by weakly coordinated tetrahydrofuran, are also likely to be present. The observed ^{19}F NMR resonance of the AlF–bipy solution may be due to dissolved $[-\mathrm{FAl}^{2+}(\mathrm{bipy}^{2-})]_m$; the chemical shift of 124 ppm is to lower frequency than for aqueous AlF^{2+} or $AlF_2{}^+$ at about 157 ppm [19] or for $AlF(C_2H_5)_2$ at 160 ppm [20], although it is difficult to decide whether this is due to electronic rather than steric factors. The irreversible conversion of the soluble forms of the SiO– and AlF–bipy products to insoluble products, would appear to be due to loss of coordinated tetrahydrofuran as the change is brought about by the addition of other solvents (pentane or even diethyl ether) which lower the activity of the tetrahydrofuran. Loss of tetrahydrofuran may encourage further polymerization giving insoluble solids.

The species most likely to be responsible for the triplet transition features are monomeric $[\mathrm{OSi}^{2+}(\mathrm{bipy}^-)_2]$ (**I**) or $[\mathrm{FAl}^{2+}(\mathrm{bipy}^-)_2]$ (**II**) with structures similar to those of $[\mathrm{Cl_2Si}^{2+}(\mathrm{bipy}^-)_2]$ [7, 8] or $[\mathrm{Be}^{2+}(\mathrm{bipy}^-)_2]$ and $[\mathrm{Mg}^{2+}(\mathrm{bipy}^-)_2]$ [9]. Two electrons are transferred from the SiO or AlF groups to form two separate bipyridyl radical anions in close proximity and coordinated to the central group in which silicon and aluminium have formal oxidation states of +4 and +3, respectively. The triplet state is either the ground state or a low lying excited state with axial or pseudo-axial symmetry [9, 10]. Using the zero-field splitting of $D = 158$ G in frozen solution or 176 G in an adamantane matrix and applying Weissman's method [10] gives an average separation of the two unpaired electrons $\langle r \rangle$ of 5.4–5.6 Å. The corresponding value calculated for $[\mathrm{Cl_2Si}^{2+}(\mathrm{bipy}^-)_2]$ from the zero-field splitting of $D = 172$ G, was 5.45 Å in good agreement with the crystal structure data on octahedral $[\mathrm{SiCl_2(bipy)_2}]$ which showed a separation of the two centres of the two bipy groups of 5.5 Å. Brown *et al.* [9] calculated values of about 6.1 Å for the triplet species $[\mathrm{Be}^{2+}(\mathrm{bipy}^-)_2]$ and $[\mathrm{Mg}^{2+}(\mathrm{bipy}^-)_2]$ and concluded that those were consistent with a tetrahedral coordination of bipy to the metals.



One may infer from the similarities in the spectra, and from the calculated values of $\langle r \rangle$, that the SiO and AlF triplet species also adopt a configuration in which the two spins retain their parallel alignment because they reside in two bipyridyl π^* orbitals which are orthogonally disposed to each other. The monomeric structures **I** and **II** have terminal Si=O and Al–F groups, but it is to be expected that an Si=O group would polymerize more easily than an Al–F group so that more of the triplet species should be expected for the aluminium than for the silicon products; this is contrary to our observations although there are difficulties in reproducing experimental conditions from one system to the other. Alternative structures are dimers, trimers or higher oligomers of $[\text{–OSi}^{2+}(\text{bipy}^-)_2]$ and $[\text{–FAl}^{2+}(\text{bipy}^-)_2]$ and these would be direct analogues of $[\text{Cl}_2\text{Si}^{2+}(\text{bipy}^-)_2]$ since they would contain six coordinate silicon and aluminium and Si–O–Si or Al–F–>F linkages. We cannot rule out such structures, especially the dimer like III. However, models based on the dimensions found by X-ray for [*cis*-$\text{SiCl}_2(\text{bipy})_2$] [8] and for [*cis*-$\text{Si(OH)}_2(\text{bipy})_2]^{2+}$ [21] (a cation with little back donation of electron density from the silicon to bipy) indicate that there would be strong repulsive interactions between bipy units lying very close to each other on adjacent silicon or aluminium atoms which would lead to steric strain and should modify the EPR parameters to make them far less similar to those for $[\text{SiCl}_2(\text{bipy})_2]$.

Exploratory work we have carried on other reactions of AlF has shown that with oxygen containing ligands such as pentane-2,4-dione, disproportionation occurs giving AlF_3 and $[\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3]$. In contrast, there is no evidence from the reaction of AlF with bipy that $[\text{Al(bipy)}_3]$ [22] is formed.

Conclusions

Our results indicate that SiO and AlF each react with bipy to form very similar complexes in which there is extensive transfer of charge from the silicon or aluminum to the bipy. There is a strong tendency for tetrahydrofuran soluble complexes to convert irreversibly to intractable solids with a 1:1 SiO or AlF:bipy ratio. The spectroscopic properties of the products both in solution and in the solid state are very like those of molecular $[\text{SiCl}_2(\text{bipy})_2]$ suggesting similar structures in which the bipyridyl radical anions lie orthogonal to each other across the metal centres so as to produce a low energy triplet state.

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