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PREPARATION AND CHARACTERIZATION OF ADDUCTS OF SILICON TETRAFLUORIDE WITH THIAZOLES

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SUMMARY

Stable solid adducts of silicon tetrafluoride with the following thiazoles have been prepared: 2-aminothiazole, 2-amino-5-methylthiazole, 2-amino-6-methylbenzothiazole, 2-amino-7-nitrobenzothiazole and 2,4-dimethylthiazole. These adducts have been characterised by chemical and infrared spectral analysis. In all the cases except that of 2,4-dimethylthiazole ($SiF_4.2L$) the composition is 1:1. Both exocyclic and endocyclic nitrogen atoms are the coordinating centres in all the four cases while only endocyclic participates in coordination in the case of 2,4-dimethylthiazole. No indication has been found for the involvement of sulphur in coordination. Probable structures of these adducts have been proposed in which silicon is hexacoordinate.

INTRODUCTION

Silicon tetrafluoride, a Lewis acid, is known to form stable adducts with donor groups such as amines [1], during which the coordination number of silicon increases from four to five or six. Most of the adducts studied so far [1] have been with nitrogen donor ligands. Only a few stable adducts with oxygen-containing ligands such as triphenylphosphine oxide [2] dimethylsulfoxide [3] and dimethylformamide [4] have been synthesized. Silicon tetrafluoride

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forms only unstable adducts with phosphorus-containing ligands; e.g., with trimethylphosphine [5] both 1 : 1 and 1:2 adducts are formed which are stable only at low temperature. However, the attempts to prepare triphenylphosphine adducts [6] were unsuccessful even when the reaction was done at -96°C. Reports concerning the adducts with donor groups containing sulphur are completely lacking.

Thus, it was of interest to study the nature of interaction of silicon tetrafluoride with sulphur containing ligands such as thiazoles. Thiazoles, particularly 2-aminothiazoles, behave as very good ligands and form complexes with transition metal ions as well as molecular complexes with metal halides [7,8,9,10]. The preparation and characterization of adducts of silicon tetrafluoride with thiazoles are described and the type of bonding involved is discussed.

EXPERIMENTAL

Reagents

The ligands used for the preparation of the adducts are : I, 2-aminothiazole; II, 2-amino-5-methylthiazole; III, 2-amino-6-methylbenzothiazole; IV, 2-amino-7-nitrobenzothiazole; V 2,4-dimethylthiazole. Ligand I (98% pure) was procured from Fluka and was purified by repeated recrystallization from ethylene dichloride. All the other ligands (II-V) were prepared by standard methods [11,12,13]. Silicon tetrafluoride (SiF_4) was prepared by the fluorination of silicon tetrachloride with lead fluoride in acetonitrile [14]. The purity of SiF_4 was checked by infrared and chemical analysis (99.8%). Diethyl ether (solvent) was washed with cold water, dried over calcium chloride and distilled over lithium aluminium hydride.

Synthesis of adducts

The standard techniques used for the handling of air and moisture sensitive compounds were followed for synthesizing the adducts. A known amount of the ligand was dissolved in a suitable solvent such as diethyl ether (100 ml) and placed in a evacuated reaction vessel (250 ml RB flask fitted with appropriate GG joints and vacuum stopcocks). The liquid was allowed to react at room temperature with a known excess (1:2) of SiF_4 held in a glass globe connected to the reaction vessels. In all the cases, there was an immediate formation of a precipitate. The reaction mixture was stirred for 6 hours. The unreacted SiF_4 was recovered and measured [14]. The precipitate was filtered, washed with dry solvent several times and dried in vacuum. Table 1 incorporates preparative details and some physical properties of the adducts.

Characterization of adducts

The composition of the adducts were determined by elemental analysis (C,H and S) (Table 2).

The adducts were further characterized by infrared spectroscopy (IR). The IR spectra (400-4000 cm^{-1}) of the solids were recorded in Nujol mulls using a Perkin Elmer 599 spectrophotometer. Due to H-bonding in the solid state, ν(N-H) and $\delta(NH_2)$ vibrations come at lower and higher frequencies respectively as compared to the solution spectra. Hence, this effect was eliminated by recording the spectra of pure ligands in a dilute chloroform solution [9,10]. The values of important absorption bands are given in Table 3.

Table 1. Preparation of adducts of silicon tetrafluoride with thiazoles

Ligand	No. of m.moles of			Combining ratios Ligand: SiF_4	Adduct	Solubility of the adduct in $CHCl_3$ and CH_3Cl	Nature of the adduct
	Ligand	SiF_4	Reacted SiF_4				
I	18.78	31.93	19.95	1:1	I_A	Insoluble	Slightly yellowish powdery non-hygroscopic solid
II	15.56	32.35	16.35	1:1	II_A	Insoluble	White powdery non-hygroscopic solid
III	14.59	30.79	13.50	1:1	III_A	Insoluble	White, powdery non-hygroscopic solid
IV	12.50	30.75	13.45	1:1	IV_A	Insoluble	Yellowish powdery non-hygroscopic solid
V	15.45	32.67	7.31	2:1	V_A	Soluble	White, powdery hygroscopic solid

Table 2. Analytical data of the adducts of silicon tetrafluoride with thiazoles

Adduct	Elemental Analysis						Composition of the adduct Ligand:SiF_4	Melting point of pure ligand °C	Melting point of adduct °C
	Calculated			Observed					
	C	H	S	C	H	S			
I_A	17.63	1.96	15.67	17.5	1.89	16.05	1:1	90.0	225-227 with decomposition
II_A	22.02	2.75	14.68	21.50	2.55	14.15	1:1	43.8	235-240
III_A	35.8	2.98	11.96	35.5	3.00	11.99	1:1	135.5	227-230
IV_A	28.09	1.67	10.7	27.85	1.45	10.10	1:1	254.5	222-224
V_A	36.36	4.24	19.39	37.1	4.5	20.1	2:1	142.5(b.p.)	148-152

Table 3. Infrared spectral data of thiazole adducts of silicon tetrafluoride and the free ligands

Compound		ν(N-H)	δ(NH_2)	ν(C=N)	$\nu(C-N)_{exo-cyclic}$	ν(C-S)	ν(Si-F)	δ(Si-F)
I	Solution	3495 m 3400 m 3290 w	1600 s	1580 m	1325 s			
	Solid	3420 m 3290 m	1630 s	1580 m	1330 m	690 m		
I_A	Solid	3380 m 3190 m	1650 s	1570 m	1350 m	700 s	700 s 730 s	475 m
II	Solution	3490 m 3400 m 3290 w	1600 s	1615 m	1320 s			
	Solid	3440 m 3280 m	1615 m	1615 m	1330 m	690 m		
II_A	Solid	3380 m 3200 m	1650 s	1600 m	1350 m	730 s	730 s 760 s	480 m
III	Solution	3500 m 3400 m	1615 s	1600 m	1320 m			
	Solid	3400 m 3370 m	1640 s	1610 m	1320 m	670 m		
III_A	Solid	3480 m 3370 m	1630 s	1580 m	1370 s	670 m	730 s 740 m	480 m

IV	Solution	3495 m 3400 m	1600 s	1590 s	1340 m			
	Solid	3470 m 3380 m 3340 w	1610 m	1590 s	1340 m	690 m		
IV_A	Solid	3400 m 3200 m	1620 m	1580 m	1360 s	730 s	730 s 740 s	470 m
V	Neat liquid			1610 m		700 w		
V_A	Solid			1600 m		700 w	740 vs	480 m

RESULTS AND DISCUSSION

The experimental observations show that SiF_4 forms stable solid adducts with thiazoles, the composition of which varies depending on the nature ofthe ligand. With all the thiazoles containing a 2-amino group, 1:1 adducts are formed while with 2,4-dimethylthiazole a 1:2 adduct is formed.

2-Aminothiazoles are potential chelating agents, the possible coordination sites being the ring nitrogen, ring sulphur and exocyclic nitrogen (in the case of 2-aminothiazoles) atoms. The presence of an amino group in the 2-position of the thiazole ring introduces a large negative charge on the ring nitrogen atom, which is in agreement with protonation studies although the exocyclic nitrogen can be protonated in strongly acidic media [15].

2-Aminothiazole has been found to be more basic than thiazole [15]. Thus the exocyclic and ring nitrogen atoms are the most probable sites of coordination, the ring nitrogen atom being more probable than the amino nitrogen. However some workers have claimed alternative coordination sites in the metal complexes of thiazoles. Singh and coworkers [9,10] came to the conclusion that the amino nitrogen rather than the ring nitrogen is coordinating in the complexes of 2-aminothiazole with transition metal ions and metal tetraalides on the basis of infrared spectroscopic data. These authors have explained this preferential coordination on the basis of relative ease of availability of electrons at this site, the amino nitrogen being in sp^3 hybridization, loosely holds its electron pair, as compared with the ring nitrogen which is present in sp^2-hybridization. The lone pair of electrons on the ring sulphur are involved in the aromaticity of the ring and hence comparatively less available. The authors have also taken into consideration steric factors. The amino group in the 2-position sterically hinders the attack of a Lewis acid on either the ring nitrogen or sulphur, thus making these sites less favourable for coordination. On the other hand, Campbell and coworkers [16,17] are of the opinion that the ring nitrogen rather than the amino nitrogen in the transition metal complexes of 2-amino-benzothiazole is the coordinating site. Participation of ring sulphur in coordination cannot be ruled out, as Duff and coworkers [18] have proposed structures involving both ring nitrogen and sulphur in coordination in the complexes of benzothiazole with transition metals.

On comparing the spectra of (IA-IVA) with those of the pure ligands (I-IV) (Table 3) it is found that the ν(N-H) absorption frequencies are lowered by 20-200 cm^{-1}, whereas the δ (NH_2) absorption bands have increased in frequency by about 20-30 cm^{-1}. These observations are taken to indicate that the exocyclic amino nitrogen atoms are involved in coordination. The observation that ν(C-N) exocyclic frequency has increased after adduct formation supports this suggestion. However the ν(C-S) absorption band has not undergone any shift to lower frequency on adduct formation, but it has either remained at the same position (in IIIA) as in the pure ligand or has moved slightly to higher frequency and has merged with ν(Si-F) absorption bands (IA, IIA, IVA). Because of this overlap it is difficult to identify separately the ν(C-S) absorption bands. These changes are taken to indicate that ring sulphur is not involved in coordination, as the ν(C-S) vibration should go to lower frequencies if the sulphur atom were coordinated. Similar changes have been observed in the metal complexes of 2-aminothiazole [9,10] where the coordination takes place via the amino nitrogen. In all the adducts, (IA-IVA), there is a small but definite lowering of the ν (C=N) frequency which suggests that the ring nitrogen is also coordinating. Similar observations have been made in the case of the complexes of thioacetamidothiazole [19] with transition metals wherein the coordination sites have been proposed to be the thioamide sulphur and oxygen respectively along with the ring nitrogen.

All the adducts (IA-IVA) exhibit two strong absorption bands in the region 700-800 cm^{-1} assigned to ν(Si-F) vibration and a medium intensity band around 475 cm^{-1} assigned to δ (Si-F) vibration. Appearance of ν (Si-F) vibrations in 700-800 cm^{-1} region only indicates that silicon is hexacoordinate [3,4,21]. Only one ν (Si-F) band is expected for trans-octahedral adducts [22]. More than one absorption band for ν(Si-F) suggests that the adducts are cis-octahedral in structure [22]. Although a minimum of three ν(Si-F) bands are expected for cis-isomers [22], only two are observed in the present system possibly because of overlap of absorption bands.

The above discussion indicates that both exocyclic amino nitrogen and ring nitrogen are involved in coordination (IA-IVA). There is no spectroscopic evidence for the participation of ring sulphurs in adduct formation. Silicon is hexacoordinate and probably cis in structure.

There is not much change in the spectrum of the V_A adduct as compared to that of the pure ligand as far as the ligand vibrations are concerned. The only notable features are that there is a decrease in frequencies of about 10 cm^{-1} in the ν(C=N) ring absorption frequency and the ν(C-S) band has remained at the same position after adduct formation. These indicate that ring nitrogen and not ring sulphur is participating in coordination. The other absorption bands of significance in the spectrum of V_A are a strong single band at 740 cm^{-1} and a medium intensity band at 480 cm^{-1} assigned to ν(Si-F) and δ (Si-F) vibrations respectively. The appearance of a single ν(Si-F) band suggests that silicon is hexacoordinate and trans-octahedral. Estes and coworkers [23] have prepared complexes of thiazole with Cu(II) chloride and bromide and found that they are similar to the known pyridine analogues; they are of the opinion that the ring nitrogen is the coordinating site. Also it is known that SiF_4 forms 2:1 adduct with pyridine [1] which has been found to have trans-octahedral structure.

CONCLUSIONS

The above discussions lead to the opinion that in adduct V_A silicon is hexacoordinate and the structure is <u>trans</u>-octahedral, the bonding site being nitrogen.

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