762. *Silicon Esters of Picolinic Acid.*

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Ultraviolet spectra of several silicon esters of picolinic acid show that intramolecular nitrogen–silicon co-ordination develops as the number of electronegative substituents on the silicon is increased.

There is evidence that the ability of a silicon atom to co-ordinate electron-donor molecules is influenced by its environment.[1] As an alternative means of gaining evidence on this behaviour several silicon esters of picolinic acid (whose structure is appropriate for chelation) have been prepared and examined spectrophotometrically. Just as the spectra of pyridine,[2] picolinic acid,[3] and methyl picolinate are modified by co-ordination, so any variation in the degree of development of intramolecular co-ordination between nitrogen and silicon in the silicon esters of this acid should lead to spectral differences.

Table 1. *Spectra and structures of silicon picolinates*

Compound †	Extinction coeff. (or optical density *) for max. at ~2190 Å	max. at 2640 Å	Ratio of $\varepsilon_{max.}$ values	Structural significance
Me_3SiPic	9000 (2185 Å)	3460	2·59	No N–Si bond
Me_2SiPic_2	15,400 (2185 Å)	7060	2·18	Weak N–Si bond
$MeClSiPic_2$	1·18 * (2175 Å)	0·62 *	1·90	Progressively stronger N–Si bond
Cl_2SiPic_2, isomer (i)	0·80 * (2200 Å)	0·59 *	1·36	
$SiPic_4$	1·56 * (2190 Å)	1·16 *	1·34	
MePic	8700 (2190 Å)	3540	2·46	Reference samples
,, (in H_2O)	7630 (2195 Å)	4380	1·74	
,, (in 0·01N-HCl)	5400 (2195 Å)	6900	0·78	

† Pic = Picolinate.

The ultraviolet spectrum of trimethylsilyl picolinate is found to be almost identical with that of methyl picolinate which was used as the reference compound. The spectra of the other esters (Table 1) in which the substituents provide a progressive increase in

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[1] (*a*) Burg, *J. Amer. Chem. Soc.*, 1954, **76**, 2674; (*b*) Fergusson, Grant, Hickford, and Wilkins, *J.*, 1959, 99; (*c*) West, *J. Amer. Chem. Soc.*, 1958, **80**, 3246.

[2] Eaborn, *J.*, 1955, 2047.

[3] Herington, *Discuss. Faraday Soc.*, 1950, **9**, 26; Evans, Herington, and Kynaston, *Trans. Faraday Soc.*, 1953, **49**, 1284.

electron withdrawal from the silicon show a corresponding change in the relative intensities of the two absorption peaks towards values characteristic of methyl picolinate in acid solution. It is concluded that the change arises from the development and strengthening of nitrogen–silicon bonding within the ester series. Such behaviour, which recalls structural differences amongst the silicon acetylacetonates,[1c] confirms the dependence of the co-ordination behaviour of the silicon atom on the character of the substituents.

Excepting methylchlorosilicon dipicolinate, which was prepared by the use of sodium picolinate, the esters were obtained by condensation of picolinic acid with the requisite chlorosilane. Two intermediate products of composition close to $SiCl_2(C_5H_4N{\cdot}CO_2)_2$ were obtained from silicon tetrachloride. These were found to recrystallise under identical conditions without interconversion. They are therefore isomers rather than dimorphs, which in itself is indicative of intramolecular co-ordination.

The ease with which di- rather than mono- or tri-picolinate derivatives are obtained from silicon tetrachloride and methyltrichlorosilane means that replacement can be carried most readily to a stage permitting six-fold co-ordination. Failure to obtain trichlorosilyl picolinate, a compound conditions should otherwise favour chelation, may be significant in view of other evidence against five-co-ordinated silicon.[1b, c]

There seems some correlation between the number of strong absorptions in the " ester region " of the infrared spectra of the compounds and the evidence on co-ordination. Methyl picolinate, trimethylsilyl picolinate, and dimethylsilicon dipicolinate each show two peaks (at 1743 and 1724 cm.$^{-1}$, 1717 and 1697 cm.$^{-1}$, and 1757 and 1682 cm.$^{-1}$, respectively). On the other hand, dichlorosilicon dipicolinate (1745) and methylchlorosilicon dipicolinate (1736 cm.$^{-1}$) each show one strong band. Silicon tetrapicolinate shows three bands (1723, 1706, and 1676 cm.$^{-1}$), which seems consistent with the presence of both co-ordinated and unco-ordinated nitrogen atoms as six-fold co-ordination around silicon would require.

EXPERIMENTAL

Reactions between chlorosilanes and picolinic acid (or sodium picolinate) were carried out in boiling benzene, with stirring. The crystalline esters were separated from the associated picolinic acid hydrochloride (or sodium chloride) by extraction with benzene.

Methyl picolinate [4] was purified by fractional distillation (93°/3 mm.). It melted at 19·0—19·5° and had n_D^{20} 1·5211 (Found: C, 61·5; H, 5·1; N, 9·8. Calc. for $C_6H_7NO_2$: C, 61·3; H, 5·15; N, 10·2%). This compound, as with the silicon esters, was handled in absence of moisture.

Ultraviolet spectra were recorded for cyclohexane solutions over the range 2000—3000 Å. For the least soluble compounds optical densities only are given (Table 1). Infrared spectra were determined for liquid films or (for the solids) Nujol mulls.

Preparation of Trimethylsilicon Picolinate and Dimethylsilicon Dipicolinate.—Trimethylchlorosilane (27·1 g.) and picolinic acid (48·6 g.) were allowed to react for 6 hr. The solution was fractionally distilled to give *trimethylsilyl picolinate* (33 g.), b. p. 91°/2 mm. (Found: C, 55·4; H, 6·2; H, 7·7%; *M*, cryoscopic in benzene, 191. $C_9H_{13}NO_2Si$ requires C, 55·3; H, 6·7; N, 7·2%; *M*, 195). The ester was hydrolysed quickly to picolinic acid and hexamethyldisiloxane.

Dimethyldichlorosilane (14·8 g.) and picolinic acid (57·0 g.), reacting for 24 hr., gave *dimethylsilicon dipicolinate*, sparingly soluble in benzene. The ester (33 g.) recovered by extraction was recrystallised (Found: C, 56·2; H, 4·3; N, 8·95; Cl, 0%; *M*, ebullioscopic in benzene, 291. $C_{14}H_{14}N_2O_4Si$ requires C, 55·6; H, 4·7; N, 9·3%; *M*, 302). A sample obtained by the use of silver picolinate gave: C, 55·2; H, 4·6; N, 9·3%.

Products from Silicon Tetrachloride and Picolinic Acid.—Reaction of the tetrachloride with more than four mol. of acid for 24—72 hr. gave only silicon tetrapicolinate, but reaction with less than 0·4 mol. of acid for 6 hr. gave the intermediate dichlorosilicon dipicolinates. Thus in a preparation where tetrachloride (12 g.) was treated with acid (52 g.) for 72 hr. the product of prolonged extraction gave the analysis: C, 55·5; H, 3·1; N, 10·8% ($C_{24}H_{16}N_4O_8Si$ requires

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[4] Levine and Sneed, *J. Amer. Chem. Soc.*, 1951, **73**, 5614.

C, 55·8; H, 3·1; N, 10·85%). The *tetra-ester*, m. p. 320° (decomp.), is decomposed by alkali but resistant to water.

Extraction of the crude product obtained under the alternative conditions gave (i) crystals adhering to the flask, and (ii) suspended powder having a different *X*-ray powder photograph [Found (i): C, 43·0; H, 3·0; Cl, 19·6; N, 7·6. Found (ii): C, 41·4; H, 2·7; Cl, 18·2; N, 7·7. $C_{10}H_8Cl_2N_2O_4Si$ requires C, 42·0; H, 2·8; Cl, 20·7; N, 8·2%]. It is possible that both *products* were slightly contaminated with silicon tetrapicolinate. Re-extraction of (ii) for 3 days caused some 10% to disproportionate to tetrapicolinate, as shown by analysis and by the appearance of the new *X*-ray powder lines.

Methylchlorosilicon Dipicolinate and Methylsilicon Tripicolinate.—Silane and finely powdered sodium picolinate (1 mol.) were allowed to react for 6 hr., giving a crystalline product (Found: C, 47·7; H, 3·25; Cl, 10·6; N, 8·1. Calc. for $C_{13}H_{11}ClN_2O_4Si$: C, 48·4; H, 3·4; Cl, 11·0; N, 8·7%).

Replacement of the remaining chlorine by use of an excess (4 mol.) of sodium picolinate occurred slowly, to give methylsilicon tripicolinate. A sample recovered after 72 hours' reaction was nearly pure (Found: C, 54·7; H, 3·5; N, 10·6; Cl, 0·2. Calc. for $C_{19}H_{15}N_3O_6Si$: C, 55·7; H, 3·7; N, 10·3%).

X-*Ray Powder Data.*—Values of *d*, for compounds for whose identification powder photography was useful, are listed.

Silicon tetrapicolinate: 8·14s, 6·26w, 5·97m, 5·62w, 5·25s, 4·75w, 4·39w, 3·99s, 3·78m, 3·37w, 3·16s.

Dichlorosilicon dipicolinate (i): 6·92s, 6·39s, 5·80w, 5·35m, 5·03s, 4·41m, 4·10s, 3·95s, 3·43s, 3·31s.

Dichlorosilicon dipicolinate (ii): 6·76m, 5·17s, 4·78m, 4·01m, 3·31s, 2·98w, 2·85m, 2·71w, 2·53m. 2·41w.

Methylchlorosilicon dipicolinate: 7·72m, 6·50s, 6·02w, 5·56m, 4·68w, 4·46w, 3·90m, 3·65w.

Methylsilicon tripicolinate: 8·05s, 7·03s, 5·84m, 5·34s, 4·77m, 4·13m, 3·94m, 3·83m, 3·46s.

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