

Solubilization of silica: Synthesis, characterization and study of penta-coordinated pyridine N-oxide silicon complexes[#]

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Abstract. In an effort to design agents that could solubilize silica in water, under ambient conditions and pH, as takes place in nature, novel zwitterionic, penta-oxo-coordinated silicon compounds with silicate cores have been prepared from 4-substituted pyridine N-oxides (H, OMe, morpholino, NO₂) as donor ligands, their structures established by ¹H, ¹³C and MS, and the coordination number of silicon, by ²⁹Si NMR. The formation of complexes from pyridine N-oxides is noteworthy since they arise from interaction with a weakly nucleophilic oxygen centre. The ability of the pyridine N-oxides to enhance the solubilization of silica in water has been experimentally demonstrated. Possible rationalization of this observation on the basis of O → Si coordination via the oxygen atom of pyridine N-oxide is suggested.

Keywords. Solubilization of silica in water; step-wise design; penta-oxo coordinated silicon compounds.

1. Introduction

Effective methods for the solubilization of silica in water could be of use in the development of broader, safer and environmentally friendly procedures for silica utilization^{1–6} and for the delineation of possible pathways in biosilicification.^{7,8}

In most of earth's minerals silicon is tetra-coordinated. The hypervalent states of silicon – penta and hexa – are generally made accessible by synthetic procedures.⁹ In recent years, penta-oxygen-coordinated silicon compounds have been explored for the solubilization and utilization of silica. The conditions used, by reaction of silica with ethylene glycol in the presence of strong bases, are harsh.^{3,4,6} The present study is directed at possible solubilization of silica in water at ambient pH, as takes place in Nature, where extra-cellular matter – cell membranes, biofluids, soil solutions – are generally rich in ligands that bind to silicon, whose coordination deviates from the usual tetra coordination.¹

The origin of the present work is related to the empirical observation that the uptake of silica from the soil by the rice plant is enhanced on addition of polyvinylpyridine N-oxide,¹⁰ an agent that is known to dissolve fine silica deposited in the lungs.¹¹ We rationalized this process on the basis of formation of zwitterionic penta-coordinated silicon (figure 1), although the weakly nucleophilic oxygen centre in these compounds (pKa of pyridine N-oxide = 0.79¹²) is reported to ligand only to metal centres.¹³

In order to confirm the possibility of the existence of such compounds, we have prepared zwitterionic penta-coordinated silicon compounds from 4-substituted pyridine N-oxides (H, OMe, morpholino, NO₂)

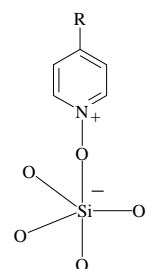


Figure 1. Structure of a typical zwitterionic penta-coordinated silicon–pyridine N-oxide complex.

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[#]Dedicated to Professor S Swaminathan on the occasion of his 80th birthday

as donor ligands, their structures established by ^1H , ^{13}C , MS, and the pentacoordination of silicon by ^{29}Si NMR. We have also demonstrated the ability of pyridine N-oxides to enhance the solubility of silica in water, which in turn suggests additional $\text{O} \rightarrow \text{Si}$ coordination, making the silica residue ionic and hence increasing its solubility in water.

2. Experimental

2.1 General

The syntheses were carried out under dry nitrogen atmosphere. The organic solvents used were dried and purified according to standard procedures, stored under nitrogen and distilled prior to reaction. Melting points were recorded on a Buchi melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1600-FT spectrometer either as neat liquids or as KBr pellets and prominent peaks are expressed in cm^{-1} . ^1H , ^{13}C and ^{29}Si NMR spectra were recorded on GEMINI-200 MHz or Varian UNITY-400 MHz instruments. The chemical shifts are expressed in δ (ppm) with TMS at 0.000 as internal reference. FAB, and ES mass spectra were done on VG Autospec, micromass Quattro LC and Voyager-DE, STR biospectrometry instruments. UV spectra of the complexes were recorded as acetonitrile solutions in a GBC CINTRA 10e UV-Vis-DRS spectrophotometer in the range 190–400 nm. Elemental analysis were carried out in automatic analysers. Structural assignment for all stable compounds reported here is supported by, FT-IR, ^1H NMR, ^{13}C NMR, ^{29}Si NMR, FAB/ES MS, UV and satisfactory analytical data.

2.2 Materials

2.2a Bis(tetramethylethylenedioxy) silane (1) (improved procedure): Under nitrogen and rigorously dry conditions, a solution of SiCl_4 (17 g, 100 mmol) in dry toluene (30 ml) was gradually added to a stirred solution of water free pinacol (24 g, 200 mmol) in dry toluene (100 ml), carefully controlling the evolution of HCl and maintaining the temperature at 35–40°C. The mixture was refluxed for 4 h, solvents evaporated *in vacuo* and the residue sublimed at 115–118°C/5 Torr to afford 8.76 g (34%) of **1**, m.p. 112–113°C (lit¹⁴ 112°C).

^1H NMR (200 MHz, CDCl_3): δ 1.2 (*m*, 24H); ^{13}C NMR: (300 MHz, CDCl_3): δ 24.7 (aliphatic),

81.3 (*t*-C–O); ^{29}Si NMR (400 MHz, solid state): δ –44.0.

Analysis calculated for $\text{C}_{12}\text{H}_{24}\text{O}_4\text{Si}$: C, 55.39; H, 9.23. Found: C, 55.71; H, 9.14.

2.2b N-Oxypyridinium bis(tetramethylethylenedioxy) siliconates, 2 (4-H), 3 (4-OMe), 4 (4-morpholino) and 5 (4-nitro): An acetonitrile solution of **1** (0.390 g, 1.5 mmol; 5 mL) was admixed with an acetonitrile solution of the 4-substituted pyridine N-oxide (1.5 mmol, 5 mL) left aside overnight, solvents evaporated and the residue triturated with hexane (2×5 ml) to remove **1** and dried.

2: Yield: 0.370 g (70%); m.p. 42°C. ^1H NMR (200 MHz, CDCl_3): δ 1.1 (*s*, 18H), 1.3 (*s*, 6H) (pinacol CH_3), 7.3 (*m*, 1H, **g**), 7.3 (*m*, 2H, **b**), 8.3 (*m*, 2H, **a**); ^{13}C NMR (200 MHz, CDCl_3): δ 24.5 (aliphatic), 74.0 (*t*-C–O), 125.5 (**g**), 126.0 (**b**), 138.8 (**a**); ^{29}Si NMR (400 MHz, solid): δ –108.6; ES-MS (*m/z*) (%): 356 ($\text{M} + \text{H}^+$) (10), 191 ($2 \times \text{pyridine-N-oxide} + \text{H}^+$) (75); $\text{UV}_{\text{I}_{\text{max}}}$ (CH_3CN): 275 nm (**e** 40562); Analysis calculated for $\text{C}_{17}\text{H}_{29}\text{NO}_5\text{Si}$: C, 57.46; H, 8.17; N, 3.94%. Found: C, 57.01; H, 7.82; N, 3.88%.

3: Yield: 0.530 g (92%); semi solid, which becomes hard at 0°C. ^1H NMR (200 MHz, $\text{DMSO}-d_6$): δ 1.1 (*s*, 18H), 1.3 (*s*, 6H) (pinacol CH_3), 3.8 (*s*, 3H, $-\text{OCH}_3$), 7.0 (*d*, $J = 8.7$ Hz, 2H, **b**), 8.1 (*d*, $J = 8.7$ Hz, 2H, **a**); ^{13}C NMR (200 MHz, $\text{DMSO}-d_6$): δ 24.3 (aliphatic), 55.6 ($-\text{OCH}_3$), 73.0 (*t*-C–O), 111.6 (**b**), 138.8 (**a**), 156.1 (**g**); ^{29}Si NMR (400 MHz, solid): δ –108.4; FABMS (*m/z*) (%) (Gly): 402 (10) ($\text{M} + \text{O}^+$), 126 (100) ($4\text{-methoxy py-N-oxide} + \text{H}^+$); $\text{UV}_{\text{I}_{\text{max}}}$ (CH_3CN): 282 nm (**e** 19000); Analysis calculated for $\text{C}_{18}\text{H}_{31}\text{O}_6\text{NSi}$: C, 56.10; H, 8.05; N, 3.64%. Found: C, 55.91; H, 7.95; N, 3.61%.

4: Yield: 0.495 g (75%); m.p.: 254°C (dec.). ^1H NMR (200 MHz, $\text{DMSO}-d_6$): δ 1.0 (*s*, 18H), 1.3 (*s*, 6H) (pinacol CH_3), 3.2 (*br*, 4H, $-\text{CH}_2\text{-N}$), 3.7 (*s*, 4H, $-\text{CH}_2\text{-O}$), 6.8 (*d*, $J = 8.0$ Hz, 2H, **b**), 7.9 (*d*, $J = 8.0$ Hz, 2H, **a**); ^{13}C NMR (200 MHz, $\text{DMSO}-d_6$): δ 25.2 (aliphatic), 46.2 ($-\text{CH}_2\text{-N}$), 65.6 ($-\text{CH}_2\text{-O}$), 73.5 (*t*-C–O), 110.2 (**b**), 138.4 (**a**), 148.0 (**g**); ^{29}Si NMR (400 MHz, solid): δ –110.5; FAB MS (*m/z*) (%) (MNBA): 441 (10) ($\text{M} + \text{H}^+$), 181 (40) ($4\text{-morpholinopyridine-N-oxide} + \text{H}^+$); $\text{UV}_{\text{I}_{\text{max}}}$ (CH_3CN): 255, 300 nm (**e** 22125, 17313); Analysis calculated for $\text{C}_{21}\text{H}_{36}\text{N}_2\text{O}_6\text{Si}$: C, 57.27; H, 8.18; N, 6.36%. Found: C, 56.89; H, 8.41; N, 5.98%.

5: Yield: 0.210 g (36%); unstable solid that rapidly reverses to **1** and 4-nitropyridine-N-oxide. ^{29}Si NMR (400 MHz, solid): **d** –108.9.

2.3 Methods – Silica transport studies to water by pyridine N-oxides, **I** (4-H), **II** (4-OMe), **III** (4-OH) and **IV** (4-morpholino)

2.3a Preparation of the standard plot: All operations were carried out in polycarbonate vessels and deionised water was used for all dilutions. From a standard solution of sodium meta silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$), aliquots were withdrawn, transferred to 25 ml volumetric flasks, and water was added (15 ml) followed by 5% ammonium molybdate (2 ml) in 1 N sulphuric acid. After 10 min, 10N sulphuric acid (0.5 ml) and 0.5 ml of the reducing solution, whose composition was, 0.2% 1-aminonaphthol 4-sulphonic acid, 2.4% sodium sulphite and 12% sodium metabisulphate. The volume was made up to 25 ml and, after 10 min standing, the absorbance at 820 nm recorded. A straight-line plot, where silicon present in the range of 0.00–50 μg can be read out from the observed absorbance, was obtained.¹⁵

In all runs, silica gel (ACME, 200 mesh) was used and each set comprised plots with and without added pyridine N-oxide, enabling the estimation of silicon uptake on addition of the agent.

2.3b Blank runs: For each example, a 100-ml volumetric flask was charged with 2.00 g of silica, made up to 100 ml with deionised water and vigorously shaken for 1 h (several blank runs have shown that one hour shaking is adequate to reach equilibrium). Through a filter (polycarbonate funnel fitted with cotton plug), 1, 2, 3, 4, 5 ml from the stock were pipetted into five 25 ml volumetric flasks, and processed as described above to secure concentration vs absorbance plots.

2.3c Transport to water by pyridine N-oxides: For each example, after the blank run, without delay, 0.010 g of pyridine N-oxides were added to the stock solution, the volume made up to 100 ml, shaken for 1 h, and through a filter as described above, 1, 2, 3, 4, 5 ml were pipetted into five 25 ml volumetric flasks, and processed as described above to secure concentration vs absorbance plots.

2.3d Quantitative estimation of the enhancement of silica solubility in water with 4-morpholino pyri-

dine N-oxide (IV): A solution of **IV** (0.050 g) in water (10 ml) was admixed with silica gel (0.500 g), left stirred overnight, centrifuged, passed through a filter and the clear solution left aside for **1d**, to re-establish the equilibrium between bulk and solubilized silica,¹⁵ centrifuged and dried to afford 0.0035 g of granular silica. A parallel run without **IV** deposited <0.001 g silica gel.

3. Results and discussion

^{29}Si Silicon NMR is a reliable tool for the determination of the coordination state of the silicon connected to oxygen atoms. The tetra-oxo, penta-oxo and hexa-oxo silicon are characterized by peaks in the neighbourhood of, respectively, –80, –110 and –140 ppm with respect to TMS standard.¹

Initial efforts to prepare penta-coordinated silicon compounds with the commercially available tetraethoxysilane and pyridine N-oxides gave poor results. In the event, the suggestion¹⁶ that *bis*(tetramethylethylenedioxy) silane (**1**) exhibiting strong distortion of bond at silicon and carbon centres may well be suited for the preparation of penta-coordinated silicon compounds proved helpful. The suggested activity difference between **1**, and those having normal tetra-coordination is further reflected in the ^{29}Si NMR. Thus, whereas tetraethoxysilane exhibited a peak at –81.8 ppm that for **1** was –44.0 ppm. Penta-oxygen coordinated compounds prepared from **1**, uniformly exhibiting solid state ^{29}Si NMR peaks in the normal range of ~ -110 ppm^{9a} were stable and amenable to adequate characterization. Compounds **2–5** from the core unit **1** and 4-substituted (H, OMe, morpholino, NO_2) pyridine N-oxides with the experimentally found ^{29}Si NMR values and yields are presented in figure 2.¹⁷ The penta-coordinated silicon representation is based on AM1 optimised geometries.¹⁸

In the ^1H NMR spectrum of **1** the 24 protons appear as a single peak at 1.2 ppm. On complexation with pyridine N-oxides they fall into two distinct sets at 1.1 ppm (18H) and 1.3 ppm (6H). This may arise from the field effects of the pyridine ring on the proximate six protons (figure 2 arrows). Compared to the parent pyridine N-oxide, the electron-donating substituents 4-OMe and 4-morpholino show a shift of respectively, 0.2 and 0.4 ppm for the **a** protons and 0.3 and 0.5 ppm for the **b** protons. The ligated pyridine N-oxides show little change compared to the corresponding precursor.

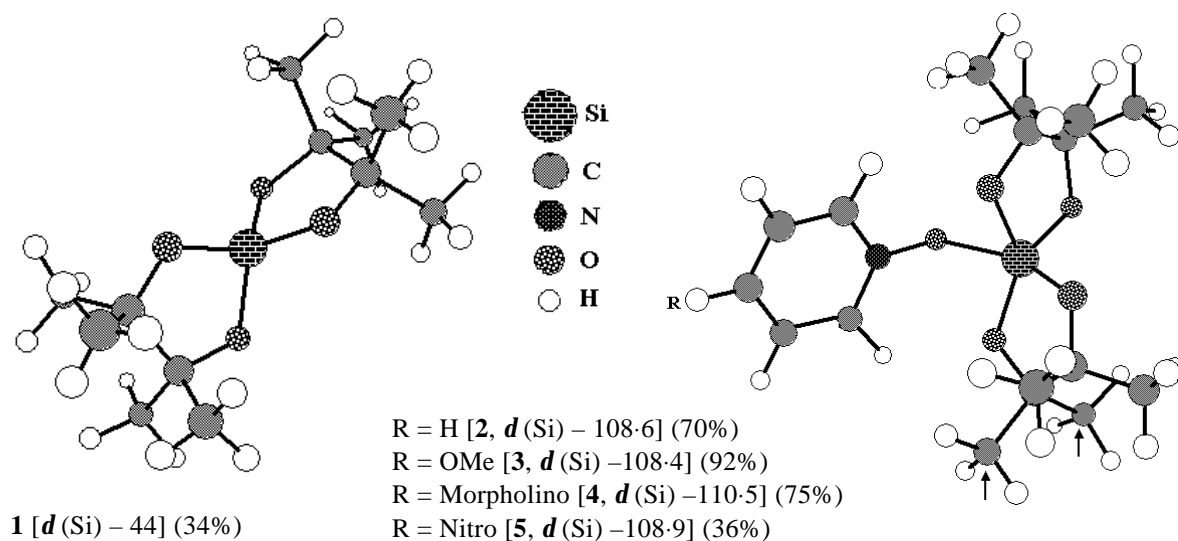


Figure 2. Penta-coordinated silicon complexes from silicon pinacolate.

The ^{13}C NMR peak of the tertiary carbon of **1** (81.3 ppm) is shifted to 74 ppm on penta-coordination. On the basis of literature information^{16,9a} this may be attributed to the change of the O–C–C angles from 104° to 109° .

Since the ^{13}C shifts are known to be sensitive to the electronic charge at the carbon centre,¹⁹ it was considered useful to analyse such effects on the pyridine ring on complexation (table 1a).

The overwhelming effects of substitution of the electron donating groups at the *g*-position is equally reflected both in the parents and the complexes. In the parent system, the *b* carbons are shifted by 17.2 ppm and 19.2 ppm in the case of respectively, the 4-OMe and 4-morpholino. In sharp contrast the *g* carbons are shifted by 30.3 ppm and 24.3 ppm. The substitutions show little effect on the *a* carbon. Table 1a also shows that complexation with Si has little effect on this profile. The effect of similar substitution is seen in the *pKa* values of pyridine-N oxides.¹² The estimated *pKa*¹² for the 4-OMe and 4-morpholino pyridine N-oxides would be ~ 2.5 and ~ 3.7 compared to 0.79 for the parent denoting considerable enhancement of charge at the oxygen centre. This aspect has a bearing on the complexation with **1**. The ^{29}Si NMR of **2** (4-H) and **5** (4-nitro) showed in addition to peaks at -108.6 and -108.9 , corresponding to penta coordination, peak at -44 ppm, assigned to pinacol silicate, which was completely absent in the case of **3** (4-OMe) and **4** (4-morpholino). We do believe that the OMe and the morpholino group enhances the stability of the silicon complexes.

The outcome of a comparative UV spectral study of the 4-substituted pyridine N-oxides (4-H, 4-OMe, 4-morpholino) on complexation with silicon pinacolate (**1**) is presented in table 1b. The complexation does not affect the I_{max} values. The 11% and 18% enhancement of the ϵ values on complexation with 4-methoxy (I_{max} 282 nm) and 4-morpholino (I_{max} 300 nm) pyridine N-oxides is perhaps indicative of strong association, in spite of drop in the mole fractions of these chromophores. Compound (**1**) showed no absorption in the range studied.

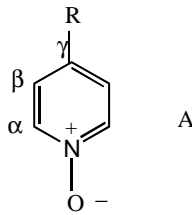
The ^{29}Si NMR peaks however lie in the narrow region of -108.4 to -110.5 ppm.

The present work has shown that formation of penta-coordinated silicon compounds is possible via oxygen coordination from pyridine-N oxide ligands. In case such intermediates are involved in the enhancement of the uptake of silica by poly vinyl pyridine N-oxide from the soil in the rice plant,¹⁰ the pyridine N-oxides, **I–IV**, related to **2–5** could be expected to increase the solubility of silica in water. This has been examined.

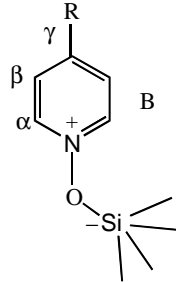
The uptake of silica was monitored colorimetrically, by a procedure standardized in the present study, full details of which are presented in the experimental. The outcome presented in table 2 represents mean values from five runs, for the blank and that for pyridine N-oxides studied.

From table 2, it can be computed that the enhancement of solubilization of silica in water for 1000 *m* moles per litre of the carrier would be respectively, 84 (4-H), 183 (4-OMe), 121 (4-OH) and 335 (4-morpholino) *m* moles per litre.

Table 1. (a) A comparison of the ^{13}C NMR of 4 substituted pyridine N-oxides (CDCl_3) and their penta-coordinated silicon complexes with silicon pinacolate (CDCl_3 , $\text{DMSO}-d_6$). (b) A comparison of the UV spectra of 4 substituted pyridine N-oxides (CH_3CN) and their penta-coordinated silicon complexes with silicon pinacolate (CH_3CN).



A



B

1a					B			
R	H	OMe	Morph	Nitro	H	OMe	Morph	Nitro
a	139.4	138.0	139.1	139.5	138.8	138.8	138.4	–
b	127.2	110.0	108.0	120.3	126.0	111.6	110.2	–
g	125.7	156.0	150.0	120.3	125.5	156.1	148.0	–

1b				B		
R	H	OMe	Morph	H	OMe	Morph
I_{\max}^*	275	282	255, 300	275	282	255, 300
e_{\max}^{**}	43125	17071	20875, 14687	40562	19000	22125, 17313

*nm; ** mol^{-1} litre. cm^{-1}

Table 2. Demonstration of the enhancement of solubility of silica in water mediated by pyridine N-oxides.

Agent 0-100 g/l (m moles/l)	Solubilized silica (m moles/l) \pm SD (N)
None	204 \pm 2.61 (20)
I Pyridine N-oxide (1052)	292 \pm 3.03 (5)
II 4-methoxypyridine N-oxide (800)	350 \pm 3.79 (5)
III 4-hydroxypyridine N-oxide (900)	313 \pm 3.41 (5)
IV 4-morpholinopyridine N-oxide (555)	390 \pm 4.29 (5)

Whilst all the pyridine N-oxides enhance the solubility of silica, the finding that 4-morpholinopyridine N-oxide, at a concentration of ~ 500 m moles/l, can nearly double the solubility of silica in water is noteworthy. This may arise from a combination of factors that permit resonance stabilization of the pyridine nitrogen and possible further coordination of the ether oxygen to silicon.

The solubility of silica in a 0.028 molar solution of 4-morpholinopyridine N-oxide (**IV**) was found to be 0.0058 molar compared to 0.0017 molar in a blank

run. In this experiment granular silica was slowly precipitated, suggesting release of the agent, which is highly soluble in water. This result tends to suggest that **IV** promotes the transport of silica to the aqueous phase and the intermediates involved are hydrolysed to **IV** and silica. The latter precipitates as granular silica on standing.²⁰ The nature of silicon in the aqueous phase, in the presence of the agent needs to be ascertained by detailed NMR studies, in order to provide a rational explanation for the observed solubility enhancement. It is likely that the $\text{O} \rightarrow \text{Si}$ coordination from pyridine N-oxides partly transfers the negative charge to make the silica end charged. This would consequently increase the solubility of silica in the polar water.

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