distinct than that obtained at 21 °C. Figure 2b shows the periodic peaks, but the peak separation for positive sample bias changes from ~150 to ~70 mV and that for negative sample bias changes from ~200 to ~100 mV. When the sample temperature was increased to 100 °C, the current was more than that at 21 °C and 42.8 °C (Fig. 3a). This is probably due to the greater motion of LC molecules at higher temperature. As a result, the current through a molecule increases. At this temperature the staircase disappears (Fig. 3b). This suggests that the motion of the LC molecules in the isotropic phase hinders the staircase behaviour.

Peaks of the kind shown in Fig. 1 have been interpreted as evidence of the incremental charging effect by considering the capacitance of the system[3-5]. When a metal droplet of diameter 100 Å is used, the peaks are separated by ~10-50 mV, which corresponds to the charging energy. As the size of molecule used in my experiment is about one-tenth that of a conventional metal droplet, it seems that the peaks separated by ~100-200 mV in our experiment can also be interpreted on the basis of capacitance. But this is not the case, as I will discuss below.

First, I shall argue why the staircase cannot be attributed to the quantization of the energy levels of the LC molecule due to its finite size. A calculation of the energy levels for an isolated LC molecule[8] (that is, where the interaction between molecule and substrate is ignored) shows that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are separated by ~10 eV. This indicates that the HOMO-LUMO gap is too large to produce the staircase observed here.

Next, I consider to what extent the $I-V$ curves can be interpreted as proof of the incremental charging effect. The structure of the staircase expected theoretically would be perfectly periodic. The difference of the charging energy corresponding to the change from ne to $(n+1)e$ is given by $\delta e^{\pm} = (n \pm 1)^2 e^2/2C - n^2 e^2/2C$ (refs 2, 6). The difference in the periodicity of the steps for positive and negative bias in my $I-V$ curves shows that these results should be understood in terms of a new theory which is different from the capacitive charging energy treatment, the latter being applicable only to fairly large (100 Å) particles. The question is, what is the definition of the capacitance in the case of molecules? When the particle size is as little as 10 Å, the charging energy $n^2 e^2/2C$ could be replaced

by the total energy difference between the ionized state and the neutral state. The terrace widths of the staircase would then be different for ionized states, as the energies of the different ionized states will not in general be the same. According to this interpretation, one can gain insight into the different ionized states from the staircase behaviour.

A self-consistent-field calculation for an isolated cyanobenzene molecule shows that the total energy difference between the neutral state and the −1 ionized state is 1.96 eV, and that between the +1 and neutral state is 8.96 eV. Clearly these total energy differences are too large to explain the observed peak separation, although qualitatively the difference between negative and positive ionized states is in the same direction as that observed. But again, this calculation ignores electron correlations, whereas the peaks observed show that the total energy of a molecule is changed considerably when the molecule interacts with the substrate surface. This suggests that there might be strong electron correlation, which might therefore have to be included for a complete understanding of the experimental results (including the changes in peak separation with temperature).

These observations of incremental charging suggest the possibility of molecular devices based on single-electron tunnelling[9] at room temperature. □

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FIG. 3 a, The $I-V$ curve at a sample temperature of 100 °C. The staircase cannot be seen, and the current is higher than for results obtained at lower temperatures. b, Current derivative dI/dV against V for a.

Synthesis of pentacoordinate silicon complexes from SiO₂

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THE potential role of inorganic and organometallic silicon compounds in the development of new chemical reagents, polymers, glasses and ceramics[1] is limited at present by the paucity of simple silicon-containing starting materials. Whereas industrial carbon-based chemistry can draw on the diversity of compounds produced from crude oil, coal or other natural sources, silicon chemistry[2] relies almost exclusively on the carbothermal reduction of SiO₂ to silicon. This is then transformed into feedstock chemicals by reaction with HCl, or by routes such as the 'direct process' for making methylchlorosilanes[2], in which silicon is reacted with methyl chloride at 200–350 °C over a copper/tin catalyst. Organosilicon compounds are in demand in fields ranging from organic synthesis to ceramics to the electronics industry. New synthetic routes to these materials are therefore highly desirable, especially if they rely on low-cost SiO₂ and on processing methods that avoid the energy-intensive and equipment-intensive carbothermal reduction step which currently precedes almost all silicon
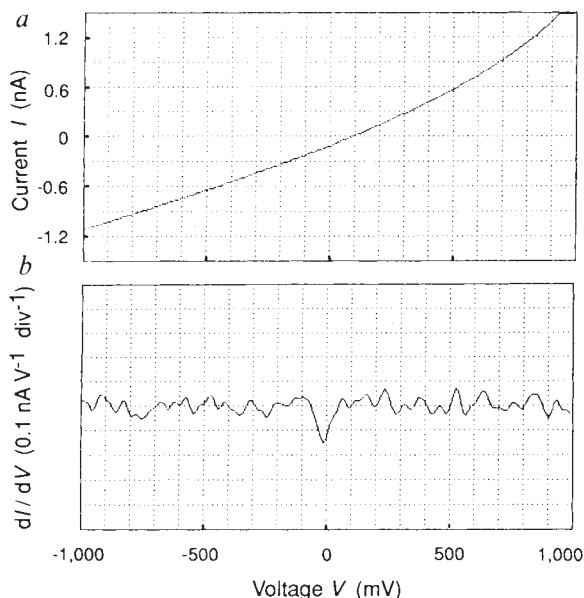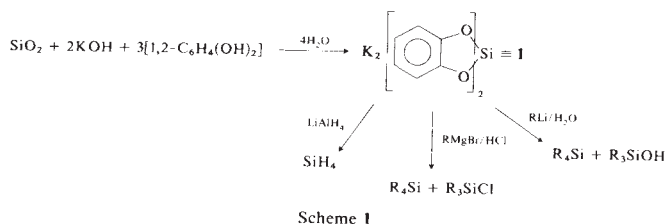
chemistry. Here we describe a direct process in which SiO_2 is reacted with ethylene glycol and an alkali base to produce highly reactive, pentacoordinate silicates which provide access to a wide variety of new silicon compounds.

Earlier investigations[3-5] have explored the chemical reactivity of the hexacoordinate silicon compound tris(catecholato) silicate, **1**, readily made by reaction of silica, sand or even quartz with catechol (1,2-dihydroxobenzene) in basic media (see scheme 1)[6-8]. Unfortunately, **1** is quite stable and can only be modified usefully by reaction with strong nucleophiles:

$$SiO_2 + 2KOH + 3[1,2\text{-}C_6H_4(OH)_2] \xrightarrow{-4H_2O} K_2 \left[\text{(benzene ring)}\begin{array}{c}O\\O\end{array}Si \right]_2 \equiv 1$$

LiAlH₄ / SiH₄ ; RMgBr/HCl ; RLi/H₂O → R₄Si + R₃SiOH

R₄Si + R₃SiCl

Scheme 1

The work of Kenney and Goodwin[9], which is complementary to the work in refs 3–5, demonstrates that protonation of mineral silicates followed by careful azeotropic removal of water provides up to 70% yields of the tetracoordinate silicon compound, $Si(OCH_2CH_3)_4$:

$$CaSiO_3 + 2HCl \xrightarrow[\text{(toluene/}CH_3CH_2OH \text{ azeotrope)}]{-3H_2O} Si(OCH_2CH_3)_4$$
$$+ CaCl_2 \qquad (1)$$
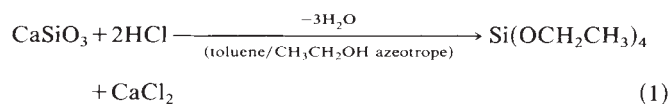
We describe here a general method of synthesizing pentacoordinate, rather than hexa- or tetra-coordinate silicates, directly from SiO_2, ethylene glycol and base. The resulting glycolato silicates are very reactive, inexpensive and offer unique opportunities for the synthesis of a wide variety of silicon containing chemicals and polymers. Furthermore, they offer the opportunity to develop new routes to silicon-containing glasses, ceramics and zeolites.

A mixture of 60 g silica gel ($>600 \, m^2 \, g^{-1}$), fused silica (325 mesh, 0.5–0.8 $m^2 \, g^{-1}$) or sand ($<0.2 \, m^2 \, g^{-1}$), 1.1 equivalents of a group 1 metal hydroxide (for example 44 g KOH) and an excess (2 l) of ethylene glycol (or other -1,2-diol, such as propane-1,2-diol) was heated under N_2 in a magnetically stirred, standard pyrex distillation setup so that the ethylene glycol was distilled off slowly (with removal of water), to result in the dissolution of the silica gel (1–2 h), fused silica (3–6 h) or sand (>200 h).

The products were isolated by cooling the much-reduced volume of the reaction solution to effect crystallization, or by precipitation with CH_3CN. Further washing with CH_3CN, followed by drying under vacuum (130 °C), provided white powders in $>80\%$ isolated yields (350 g where KOH was used). The reaction can be run using Li, Na, K or Cs hydroxide.

The products are essentially insoluble in all polar solvents except CH_3OH (but not in CH_3CH_2OH). Recrystallization is readily effected using CH_3OH/CH_3CN. The following results are from a typical elemental analysis for M = K (analysis carried out by Galbraith Laboratories, Inc., Knoxville) calc. (found) 27.53 (27.63)% C; 4.98 (4.64)% H; 13.60 (12.92)% Si; 17.84 (17.99)% K; 37.01 (36.81)% O (by difference). These results indicate a dimeric pentacoordinate species, labelled **2** in reaction (2) (refs 10, 11). In this scheme M is Li, Na or K. The Cs salt can be isolated as a monomer. Analysis gave typical values calculated (found) as 20.72 (21.06)% C; 3.63 (3.83)% H; 8.58 (8.21)% Si; 39.38 (38.84)% Cs; 27.32 (27.06)% O by difference. This indicates that a monomeric species, such as **3** in scheme 2 (below) was formed as
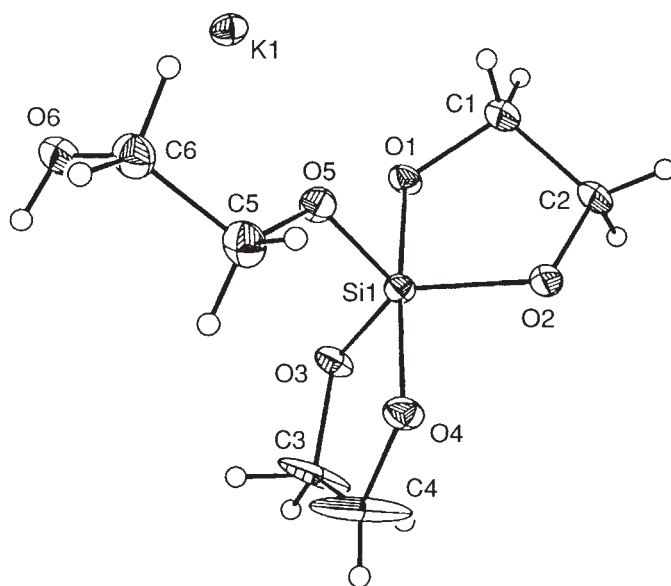

FIG. 1 X-ray single crystal structure of $KSi(OCH_2CH_2O)_2OCH_2CH_2OH$. Crystal grown from ethylene glycol/acetonitrile.

supported by the infrared (nujol) peak found for O–H at $3,300 \, cm^{-1}$ and the solubility in dimethylsulphoxide (DMSO).

NMR studies suggest that the products dissolve in CD_3OD through an exchange reaction. The ^{13}C spectra for all of the salts (Li, Na, K and Cs) show two peaks at 61.3 ± 0.3 and 64.3 ± 0.3 p.p.m. Similarly, a single peak appears in the ^{29}Si NMR at $\sim -103.1 \pm 0.3$ p.p.m. The ^{1}H spectra all contain one broad singlet at ~ 3.4 p.p.m. The ^{13}C peak at 64.3 p.p.m. and the ^{1}H peak at 3.4 p.p.m. are consistent with free ethylene glycol, despite analytical results that indicate the materials are pure. The ^{29}Si NMR peaks are consistent with those previously reported for aliphatic, pentacoordinate silicates[11-14].

A plot of the ratio of the ^{13}C peak heights for free ethylene glycol to those for bound glycol, as a function of temperature for the dry K salt dissolved CD_3OD, shows a first-order increase in free ethylene glycol as the temperature is lowered to -50 °C. At -50 °C, the ratio of free to bound glycol is $0.85 \, (\pm 0.05)$. Therefore, it appears that exchange proceeds beyond replacement of a bridging or monodentate glycol (in the Cs salt) with more than one $CD_3O\text{-}$ group. The likely exchanges are shown in scheme 2.

The extent of the exchanges and the exact mechanism(s) whereby they occur must await more detailed kinetic studies.

Further support for the alcohol exchange process and for an intermediate monomeric species comes from the recrystallization of the dimer from ethylene glycol/acetonitrile which provides X-ray-quality crystals. The structure shown in Fig. 1 was refined to $R_w = 0.0492$. The structure is typical of an ionic solid in that the potassium contact distances between nearest neighbours are essentially identical. As is common for pentacoordinate, aliphatic silicate complexes, the ligand oxygens

Scheme 2

643
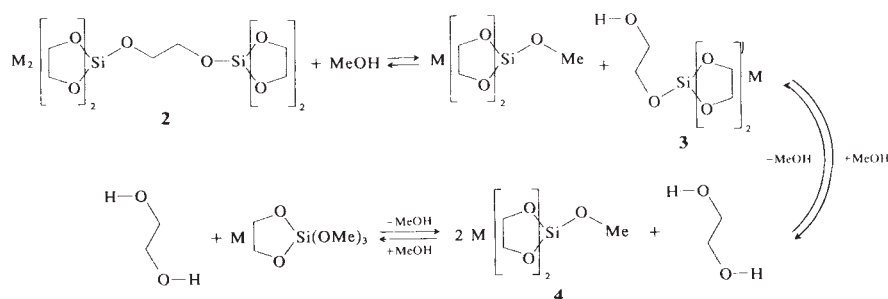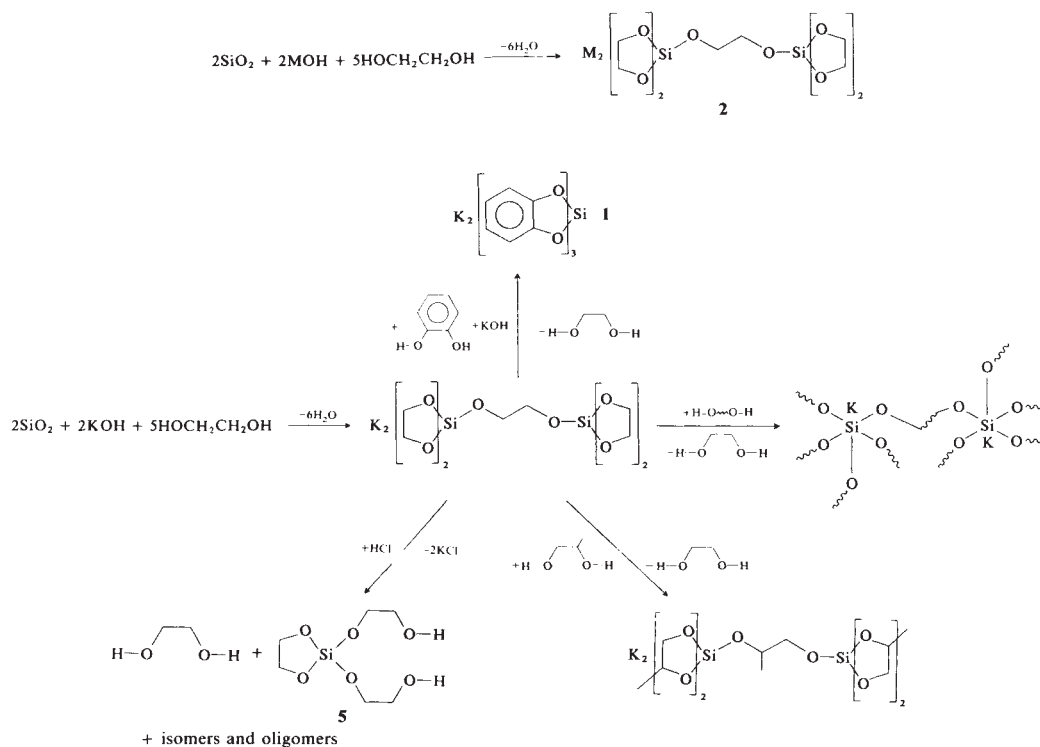
Scheme 3

occupy a trigonal bipyramidal geometry about the silicon[12-14].

The ready exchange of alkoxy ligands permits the synthesis of a wide variety of derivatives. Refluxing $M_2[Si_2(OCH_2CH_2O)_5]$ in an excess of a different 1,2-diol (for example, 1,2-propanediol or pinacol (2,3-dimethyl-2,3-butanediol)) followed by a removal by distillation of excess diol and free ethylene glycol (0.5-2 h at the reaction temperature) results in complete ligand exchange and the formation of new dimeric materials (following drying under vacuum at 130 °C), as illustrated in scheme 3. Pinacolate derivatives have been prepared previously[12-14]. Reaction of **2** with 6 equivalents of catechol and an additional equivalent of base provides the tris(catecholato)Si^{2-} species of scheme 1, in quantitative yield. With 4-5 equivalents and no additional base, the tris species is also isolated, but novel polymers are produced simultaneously (ref. 15, and R.M.L. and N. Budrys, unpublished results).

Exchange with other diols including 1,3-propanediol, $H(OCH_2CH_2)_4OH$ and hydroquinone produces polymer products with anionic silicon moieties in the polymer backbone (scheme 3). Detailed characterization of the polymers will be reported elsewhere, but the following example illustrates the simplicity of the process.

Heating a mixture of 9.9 g (24 mmol) of $Li_2[Si_2(OCH_2CH_2O)_5]$ and 30 g (124 mmol) of $H(OCH_2CH_2)_4OH$ under vacuum ($\sim$0.1 mm Hg) for $\sim$3 h at 130 °C results in dissolution of the lithium salt and recovery of 8-12 ml of a clear liquid distillate (depending on total heating time) that consists of roughly equal molar amounts of $H(OCH_2CH_2)_4OH$ and $HOCH_2CH_2OH$ (determined by gas chromatography). The material remaining in the flask becomes increasingly viscous with time as bidentate glycol groups are replaced by monodentate, crosslinking $H(OCH_2CH_2)_4OH$. The new polymer is soluble in CH_3OH, CH_3CH_2OH and 1:1 $CH_3CH_2OH:CH_3CN$ and may be useful as an ion conductor for battery applications[16,17].

Finally, pyrolysis of the glycolato silicates leads directly to silicate glasses or glass ceramics[19]. The alkali complexes, when pyrolysed in air at 10 °C min^{-1} to temperatures above 300 °C for at least 2 h, provide the line compounds $M_2Si_2O_5$ (ref. 18). If excess base is used, then partially crystallized alkali-rich silicate glasses are formed preferentially.

The four-coordinate alkoxy silane complex, **5**, obtained by neutralization of **2** with HCl gas, can be used as a substitute for $Si(OCH_2CH_3)_4$ in sol-gel reactions. Unlike $Si(OCH_2CH_3)_4$, **5** is miscible with H_2O, offers rheologically useful properties for coating and fibre applications and can be used directly to form glass-polymer composites, 'ceramers'. It can also be mixed with the various alkali derivatives of **2** and heated to form alkali-poor silicate glasses (unpublished results, R.M.L. *et al.*). □

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