Five-co-ordinate, Bis(catecholato) Complexes of Silicon(IV) †

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The synthesis of a series of five-co-ordinate bis(catecholato) complexes of silicon(IV) of the type $[SiRL_2]^-$ is reported, where R = Ph, Me, Et, or Pr^n and H_2L = catechol and its derivatives. The complexes have been characterised by ^1H, ^{13}C and ^{29}Si NMR spectroscopy in Me_2SO, elemental analysis and fast atom bombardment mass spectroscopy. Complexes derived from asymmetric catechols which give rise to non-statistical, geometrical isomerism in the distorted trigonal-bipyramidal conformation have been investigated by multinuclear NMR spectroscopy. The crystal structure of the bis(3,5-dinitrocatecholato)methylsilicate anion is reported. It exhibits a slightly distorted trigonal-bipyramidal geometry. Aryl–aryl and nitro–nitro interactions play a dominant role in the solid-state packing. Mixed-ligand complexes containing different catecholato derivatives have also been studied.

Recently, there has been a resurgence in the synthesis of five-co-ordinate silicon complexes,[1–3] reflecting developments in the inorganic and organosilicon chemistry of new solid-state materials. The existence of stable five-co-ordinate silicon complexes is also of considerable interest because they are the basis of a fundamental postulate in the theory of organosilicon displacement reactions.[4] The formation of five-co-ordinate arylbis(catecholato) complexes of silicon(IV) was first reported by Frye.[5] The crystal and molecular structure of a bis(catecholato)phenylsilicate anion was later reported by Boer *et al.*,[6] who confirmed the proposed distorted trigonal-bipyramidal conformation. In contrast, the corresponding bis(catecholato)fluorosilicate anion was found to have a distorted square-pyramidal geometry.[7] However, solution studies of these complexes have been largely neglected, although Cella *et al.*[8] have used ^{29}Si NMR spectroscopy to distinguish between five- and six-co-ordinate silicon(IV) complexes in solution. We have previously reported the synthesis and isomerism of tris(bidentate ligand) six-co-ordinate silicon(IV) complexes in solution.[9,10] Here we describe the synthesis and study of a series of five-co-ordinate bis(catecholate) complexes of silicon(IV). The complexes have been characterised by ^1H, ^{13}C and ^{29}Si NMR spectroscopy in Me_2SO, elemental analysis and fast atom bombardment (FAB) mass spectroscopy. Complexes derived from asymmetric catechols give rise to novel isomerism and these are analysed by multinuclear NMR spectroscopy in order to gain more detailed information about the species present in solution. The crystal structure of $[NEt_3H][SiMe(3,5\text{-dncat})_2]$ is reported, where $H_2(3,5\text{-dncat})$ is 3,5-dinitrocatechol.

Experimental

Materials.—Triethoxyphenylsilane, triethoxymethylsilane, catechol (H_2cat), 3,5-di-*tert*-butylcatechol (H_2dbcat), 4-*tert*-butylcatechol (H_2bcat), tetrachlorocatechol (H_2tccat), tetrabromocatechol ($H_2tbrcat$), 2,3-dihydroxybenzaldehyde [3-formylcatechol, $H_2(3\text{-fcat})$], 3,4-dihydroxybenzaldehyde [4-formylcatechol, $H_2(4\text{-fcat})$] and 4-nitrocatechol (H_2ncat) were obtained commercially from Aldrich and used without further purification. Triethoxyethylsilane, trimethoxypropylsilane and 2,3-dihydroxynaphthalene (H_2napdo) were obtained from Fluka. 4,5-Dichlorocatechol[11] (H_2dccat), 3,5-dinitrocatechol[12] [$H_2(3,5\text{-dncat})$] and 4,5-dinitrocatechol[13] [$H_2(4,5\text{-dncat})$] were prepared by literature methods.

Physical Measurements.—Proton, ^{13}C-$\{^1H\}$ and ^{29}Si-$\{^1H\}$ NMR spectra were recorded on a JEOL EX270 (270 MHz) spectrometer. Chemical shifts are quoted relative to internal tetramethylsilane for all three nuclei. The relaxation reagent, $[Cr(acac)_3]$ (acac = acetylacetonate), was added (0.08 mol dm^{-3}) to overcome the problem associated with the long relaxation times and negative magnetic moment of the ^{29}Si nucleus. Mass spectra were recorded on a Micromass VG7070E (Imperial College) and a VG 2AB-SE (School of Pharmacy) spectrometer in the negative-ion FAB mode, with the sample suspended in a *m*-nitrobenzyl alcohol matrix.

Preparation of Solid Pentadentate Silicon(IV) *Complexes.*—$[NEt_3H][SiPh(cat)_2]$. The compound $SiPh(OEt)_3$ (0.55 cm^3, 2.27 mmol) and NEt_3 (0.32 cm^3, 2.27 mmol) were sequentially added to H_2cat (0.50 g, 4.54 mmol) in ethanol (5 cm^3) under nitrogen. The mixture was refluxed for 18 h and diethyl ether (5 cm^3) then added. The white solid precipitated was filtered off, washed with ether (10 cm^3) and dried *in vacuo* at 60 °C for 2 d. Yield: 0.48 g, 50%. NMR $[(CD_3)_2SO]$: ^1H (270 MHz), δ 1.16 (9 H, t, J = 7.3, CH_3), 3.08 (6 H, q, J = 7.3 Hz, CH_2), 6.52 (8 H, m, cat), 7.12 (3 H, m, Ph, H^3, H^4 and H^5), 7.49 (2 H, m, Ph, H^2 and H^6), and *ca.* 8.8 (1 H, br, NH); ^{13}C-$\{^1H\}$ (67.8 MHz), δ 8.5 (CH_3), 45.6 (CH_2), 109.6 (cat, C^4 and C^5), 117.4 (cat, C^3 and C^6), 126.6 (Ph, C^3 and C^5), 127.7 (Ph, C^4), 134.6 (Ph, C^2 and C^6), 141.7 (Ph, C^1) and 150.2 (cat, C^1 and C^2).

The complexes $[NEt_3H][SiPh(napdo)_2]$ (yield 80%) and $[NEt_3H][SiPh(ncat)_2]$ (44%) were prepared using an analogous method. Two isomers were observed in the NMR spectra of $[NEt_3H][SiPh(ncat)_2]^-$ in the ratio of *ca.* 5:4. The complexes $[NEt_3H][SiMe(napdo)_2]$ (49%), $[NEt_3H][SiMe(4,5\text{-dncat})_2]$ (33%) and $[NEt_3H][SiMe(3,5\text{-dncat})_2]$ (56%) were prepared using $SiMe(OEt)_3$ as the starting material.

$K[SiPh(cat)_2]$. Potassium metal (0.17 g, 4.35 mmol) was dissolved in ethanol (20 cm^3) under nitrogen. The solution was stirred for 10 min followed by the addition of H_2cat (0.96 g, 8.72 mmol) and $SiPh(OEt)_3$ (1.05 cm^3, 4.35 mmol). The mixture was refluxed for 18 h and the complex was further precipitated with

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Results of ^{29}Si NMR spectroscopy, elemental analysis and FAB mass spectrometry

Complex X[SiRL$_2$]				Analysis[b] (%)			Mass spectrometry[c]	
R	L^{2-}	X$^+$	^{29}Si NMR,[a] δ	C	H	N	[SiRL$_2$]$^-$ [d]	[SiRL(OH) − H]$^-$
Ph	dbcat	K	−88.06, −87.31	69.45 (69.70)	7.60 (7.75)		545	341 (14)
Ph	cat	NEt$_3$H	−87.53	67.70 (68.05)	6.75 (6.90)	3.20 (3.30)	321	229 (18)
Ph	cat	K	−87.51	60.30 (59.95)	3.50 (3.65)		321	229 (11)
Ph	napdo	NBu$_4$	−87.14	75.75 (76.00)	8.20 (8.05)	2.05 (2.10)	421	279 (9)
Ph	napdo	NEt$_3$H	−87.11	72.10 (73.40)	6.15 (6.35)	2.55 (2.65)	421	279 (9)
Ph	bcat	K	−87.07	67.05 (66.05)	6.10 (6.20)		433	285 (32)
Ph	tbrcat	K	−86.03	21.20 (21.80)	0.75 (0.50)		953	545 (5)
Ph	4-fcat	K	−85.12	59.95 (57.70)	2.95 (3.15)		377	257 (8)
Ph	3-fcat	K	−85.12, −84.90	57.85 (57.70)	3.15 (3.15)		377	257 (15)
Ph	dccat	K	−84.23	43.10 (43.40)	2.00 (1.80)		459	299 (10)
Ph	tccat	K	−83.94	31.30 (34.00)	0.85 (0.80)		597	367 (5)
Ph	ncat	NEt$_3$H	−83.41	55.80 (56.15)	5.10 (5.30)	8.00 (8.20)	411	274 (8)
Pr^n	napdo	K	−74.83	63.15 (64.75)	4.30 (4.50)		387	245 (13)
Et	cat	K	−74.77	54.05 (53.80)	4.00 (4.20)		273	181 (28)
Me	cat	K	−74.32	52.25 (52.30)	3.70 (3.70)		259	167 (33)
Et	napdo	K	−74.13	62.60 (64.05)	4.30 (4.15)		373	231 (9)
Me	napdo	NEt$_3$H	−73.68	70.60 (70.25)	6.80 (6.75)	3.75 (3.05)	359	217 (26)
Me	4-fcat	K	−71.45, −71.33	51.20 (50.85)	3.40 (3.15)		315	195 (7)
Me	ncat	K	−69.41, −69.27	40.35 (40.20)	2.30 (2.35)	7.10 (7.20)	349	212 (0)
Et	ncat	K	−68.88, −68.77	41.90 (41.80)	2.50 (2.75)	7.05 (6.95)	363	226 (6)
Me	3,5-dncat	NEt$_3$H	−67.19, −65.33	42.25 (42.15)	4.30 (4.30)	12.70 (12.95)	439	257 (15)
Me	4,5-dncat	NEt$_3$H	−66.81	43.10 (42.15)	4.50 (4.30)	13.10 (12.95)	439	257 (57)

[a] Chemical shifts are quoted relative to tetramethylsilane. [b] Figures in parentheses represent calculated values. [c] Figures in parentheses represent relative peak intensities. Matrix used is *m*-nitrobenzyl alcohol. [d] Relative intensity 100%.

diethyl ether (10 cm^3). The white solid was filtered off, washed with diethyl ether (20 cm^3) and dried *in vacuo* at 60 °C for 2 d. Yield: 1.06 g, 65%. NMR [(CD$_3$)$_2$SO]: ^{1}H (270 MHz), δ 6.53 (8 H, m, cat), 7.12 (3 H, m, Ph, H^3, H^4 and H^5) and 7.49 (2 H, m, Ph, H^2 and H^6); ^{13}C-{^{1}H} (67.8 MHz), δ 109.8 (cat, C^4 and C^5), 117.5 (cat, C^3 and C^6), 126.7 (Ph, C^3 and C^5), 127.8 (Ph, C^4), 134.6 (Ph, C^2 and C^6), 141.6 (Ph, C^1) and 150.2 (cat, C^1 and C^2).

The complexes K[SiPh(bcat)$_2$] (yield 43%), K[SiPh(dbcat)$_2$] (42%, isomer ratio *ca.* 2:1), K[SiPh(tbrcat)$_2$] (76%), K[SiPh(tccat)$_2$] (74%), K[SiPh(4-fcat)$_2$] (62%, isomer ratio *ca.* 2:1), K[SiPh(3-fcat)$_2$] (92%, isomer ratio *ca.* 2:1) and K[SiPh(dccat)$_2$] (37%) were prepared using an analogous method; K[SiPr^n(napdo)$_2$] (94%) was prepared using SiPr^n(OMe)$_3$ as the starting material. The complexes K[SiEt(cat)$_2$] (29%), K[SiEt(napdo)$_2$] (93%) and K[SiEt(ncat)$_2$] (74%, isomer ratio *ca.* 5:4) were prepared using SiEt(OEt)$_3$ as the starting material, K[SiMe(cat)$_2$] (96%), K[SiMe(ncat)$_2$] (88%, isomer ratio *ca.* 4:3) and K[SiMe(4-fcat)$_2$] using SiMe(OEt)$_3$.

[NBu$^n_4$][SiPh(napdo)$_2$]. The compounds SiPh(OEt)$_3$ (0.75 cm^3, 3.12 mmol) and NBu$^n_4$OH (2.02 cm^3, 40% aqueous solution, 3.12 mmol) were sequentially added to H$_2$napdo (1.00 g, 6.24 mmol) in ethanol (10 cm^3) under nitrogen. The mixture was refluxed for 18 h, reduced to half volume, followed by addition of diethyl ether (30 cm^3). The white solid was filtered off and washed with ether (10 cm^3). The complex was purified by recrystallisation from hot methanol (30 cm^3) and dried *in vacuo* at 60 °C for 2 d. Yield: 1.41 g, 68%. NMR [(CD$_3$)$_2$SO]: ^{1}H (270 MHz), δ 0.91 (12 H, t, J = 7.3, C^{4}H$_3$), 1.29 (8 H, q, J = 7.3 Hz, C^{3}H$_2$), 1.54 (8 H, br, C^{2}H$_2$), 3.13 (8 H, m, C^{1}H$_2$), 6.98 (4 H, s, napdo, H^1 and H^4), *ca.* 7.1 (4 H, m, napdo, H^5 and H^8), 7.12 (3 H, m, Ph, H^3, H^4 and H^5), *ca.* 7.5 (2 H, m, Ph, H^2 and H^6) and 7.53 (4 H, m, napdo, H^6 and H^7); ^{13}C-{^{1}H} (67.8 MHz), δ 13.4 (C^{4}H$_3$), 19.1 (C^{3}H$_2$), 22.9 (C^{2}H$_2$), 57.3 (C^{1}H$_2$), 104.0 (napdo, C^6 and C^7), 121.9 (napdo, C^5 and C^8), 125.7 (napdo, C^1 and C^4), 126.8 (Ph, C^3 and C^5), 128.1 (Ph, C^4), 129.1 (napdo, C^9 and C^{10}), 134.5 (Ph, C^2 and C^6), 140.6 (Ph, C^1) and 150.9 (napdo, C^2 and C^3).

X-Ray Crystallography.—Crystals of [NEt$_3$H][SiMe(3,5-dncat)$_2$] suitable for X-ray diffraction measurements crystallised directly on cooling from ethanolic solution.

Crystal data. C$_{19}$H$_{23}$N$_5$O$_{12}$Si, M = 541.5, monoclinic, a = 10.122(5), b = 13.393(6), c = 17.454(6) Å, β = 93.36(2)°, U = 2362(2) Å^3, space group $P2_1/c$, Z = 4, D_c = 1.523 Mg m^{-3}. Clear prisms, dimensions 0.3 × 0.4 × 0.2 mm, μ(Mo-Kα) = 0.175 mm^{-1}, λ = 0.710 73 Å, $F(000)$ = 1128.

Data collection and processing. Siemens *P*4 diffractometer, room temperature, ω-scan method, (2θ range 3.0–45.0°), graphite-monochromated Mo-Kα radiation; 3260 independent measured reflections, 1701 observed [$|F_o| > 3\sigma(|F_o|)$], corrected for Lorentz and polarisation factors.

Structure analysis and refinement. The structure was solved by direct methods and all the non-hydrogen atoms refined anisotropically. The hydrogen atoms were idealised (C–H 0.96 Å), assigned isotropic thermal parameters U(H) = 1.2 U_{eq}(C) and allowed to ride on their parent carbons. The methyl group was refined as a rigid body. Refinement was by full-matrix least squares to $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o| = 0.059$, $R' = 0.059$ [$w^{-1} = \sigma^2(F) + 0.0020F^2$]. The mean and maximum shift/error in the final refinement cycles were 0.000 for both structures. The maximum and minimum residual electron densities were 0.24 and −0.32 e Å^{-3} respectively. Computations were carried out on an IBM 386/70 computer using SHELXTL PC.[14]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Table 1 shows the ^{29}Si NMR spectroscopy, FAB mass spectroscopy and elemental analysis data obtained for the complexes studied. The elemental analysis results correlate well with calculated values, thus confirming the empirical formulations. The monomolecular nature of the complexes is suggested by the results of the FAB mass spectra which show, in all cases, the parent [SiRL$_2$]$^-$ anion. The [SiRL(OH) − H]$^-$ species are presumably formed by hydrolysis due to traces of water in the matrix.

It was shown by Cella *et al.*[8] that six co-ordinate complexes of

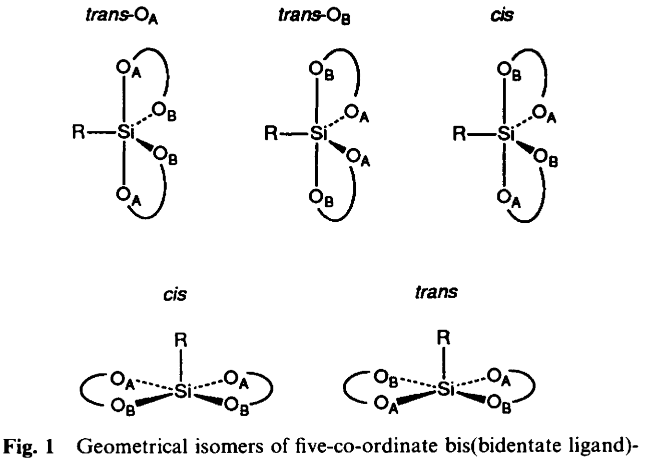

Fig. 1 Geometrical isomers of five-co-ordinate bis(bidentate ligand)-silicon(IV) complexes

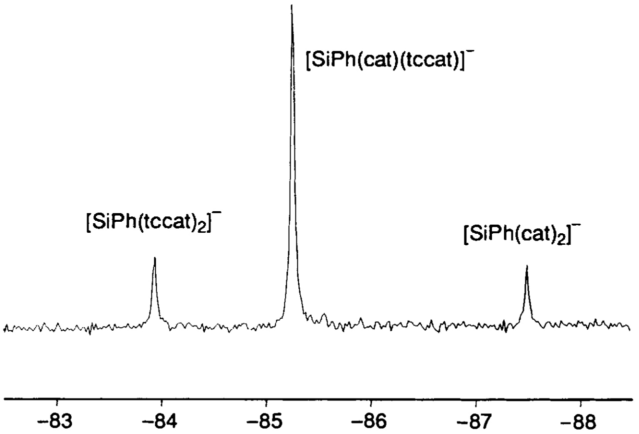

Fig. 2 The ^{29}Si NMR spectrum of a mixture of K[SiPh(cat)$_2$] and K[SiPh(tccat)$_2$] [53.7 MHz, Me$_2$SO, internal SiMe$_4$, 0.08 mol dm^{-3} Cr(acac)$_3$ relaxant]

silicon give much more negative values of δ(^{29}Si) than do complexes in which the silicon is bound to only four oxygen atoms. We have previously described factors affecting δ within the six-co-ordinate complexes of silicon(IV).[9,10] The reduced symmetry of the five-co-ordinate nucleus gives rise to a dipole moment and is therefore more sensitive to the electronic effects of the surrounding ligands. This is supported by the substantial ^{29}Si chemical shift differences observed for five-co-ordinate complexes with different types of ligands.[8,15]

Since the R group is bound directly to the ^{29}Si nucleus it is not surprising that the value of δ depends primarily on the nature of this R group. When R = phenyl the complexes give much more negative values of δ than when R = alkyl. Although the alkyl moiety has a greater electron 'pushing' capacity (σ donation) than the aryl, the delocalised π system in the phenyl ligand allows for d_π–p_π interaction to dominate the overall shielding of the ^{29}Si nucleus.

Different substituents on the catechol cause small but, nevertheless, significant changes in δ which parallel the electronegativities of the substituents. This phenomena has been correlated quantitatively (for *meta-* and *para-*substituents only) by a plot of δ *versus* the sum of the Hammett factors for tris(catecholato) complexes of silicon(IV) and tin(IV).[9,16] Within the same R group, the five-co-ordinate complexes described give an analogous relationship. That is, for the 4- and 4,5-substituted catechols there is a reasonably linear relationship between δ and Σσ, where Σσ is the sum of the Hammett σ_m and σ_p values for the substituent, calculated with respect to the oxygens.

There are two commonly idealised co-ordination geometries for five-co-ordinate complexes, trigonal bipyramidal (*TBPY*) and square pyramidal (*SPY*). Asymmetric catechols can form at least five different geometrical isomers, three with the *TBPY* conformation and two with the *SPY* conformation (Fig. 1). For only these five isomers to occur, two assumptions have been made. First, in the *TBPY* conformation the R group remains in the equatorial position because an axial R group would force one of the chelates to 'bite' at the much larger angle of 120°. Secondly, in the *SPY* conformation, the R group remains in the axial position to utilise the lowest molecular-orbital-energy configuration.

The multinuclear (^1H, ^{13}C and ^{29}Si) NMR spectra of the five-co-ordinate complexes derived from asymmetric catechols exhibit two sets of peaks which we attribute to two geometrical isomers. The only exceptions are the ^{29}Si NMR spectra of K[SiPh(bcat)$_2$], K[SiPh(4-fcat)$_2$] and [NEt$_3$H][SiPh(ncat)$_2$] which show only a single resonance; this is probably due to overlap of the resonances. The last two complexes showed two isomers in both the ^1H and ^{13}C NMR spectra. The absence of isomerism with all the symmetrical catechols rules out the possibility that the two species derive from the separation of *TBPY* and *SPY* conformations.

If we first consider the possibility of isomerism within the idealised conformations, then on a statistical basis we would expect three peaks of equal intensity for the *TBPY* conformation and two for the *SPY* conformation. The observed results may be explained on the basis of the *TBPY* conformation if one of the three isomers is thermodynamically unfavourable. This is unlikely since the differences in energy between *TBPY* isomers are usually very small. The possibility of the third isomer's signal overlapping that of one of the other isomers, in all cases, requires that two different geometrical isomers give rise to the same shielding effects upon different nuclei.

If we consider the solution structure based on the *SPY* conformation with varying degrees of distortion towards *TBPY* depending on the nature of the substituents then the two distinct isomers can be separated as simple *cis* and *trans* isomers. It is interesting that the isomer distributions vary from a ratio of *ca.* 1:1 to 2:1 in solution. This may reflect the degree of distortion in the complex such that a 1:1 isomer ratio complex will be predominantly *SPY*, and a 2:1 isomer ratio complex will be predominantly *TBPY*. Based on the above surmise we can deduce that the isomer with the higher intensity ratio is formally the *trans-TBPY* or the *cis-SPY* isomer, since there are two *trans-TBPY* isomers which can easily distort towards the *cis-SPY* isomer.

Further analysis of the NMR data reveals that the 'stronger', *i.e.* more electronegative, catechols give rise to complexes with more *SPY* character. Conversely, the effect of the R group may be steric, *i.e.* the phenyl moiety twists the catechols out of the square plane, thus increasing the *TBPY* character.

Two mixtures were prepared by dissolution of equivalents of each of two complexes in Me$_2$SO for ^{29}Si NMR analysis. Mixture A {K[SiPh(cat)$_2$] and K[SiPh(tccat)$_2$]} contained two complexes with symmetric catechols and each complex gave its own characteristic ^{29}Si NMR (δ −87.5 and −83.9 respectively). The equilibrated mixture contained a high, non-statistical proportion of the [SiPh(cat)(tccat)]$^-$ species. This was characterised by a ^{29}Si NMR resonance between the individual complexes at δ −85.3 (Fig. 2). Equilibrium was achieved at ambient temperature over a period of *ca.* 24 h. Mixture B {K[SiPh(3-fcat)$_2$ and K[SiPh(dbcat)$_2$]} contained two complexes with asymmetric catechols. Each complex showed the presence of two resonances due to the isomerism described above. The equilibrated mixture showed the presence of two further species (Fig. 3). These are attributed to the isomers of the [SiPh(3-fcat)(dbcat)]$^-$ anion. Equilibrium was not established after 8 weeks, whereupon decomposition prevented a more quantitative kinetic analysis. However, it is apparent from the two mixtures described that the kinetics of redistribution of ligands between complexes varies dramatically according to the catecholate

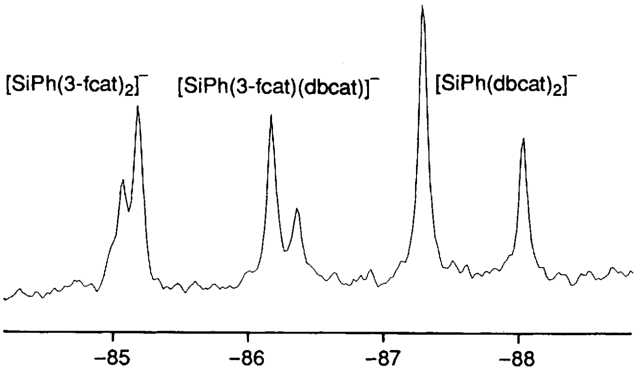

Fig. 3 The ^{29}Si NMR spectrum of a mixture of K[SiPh(3-fcat)$_2$] and K[SiPh(dbcat)$_2$]. Details as in Fig. 2

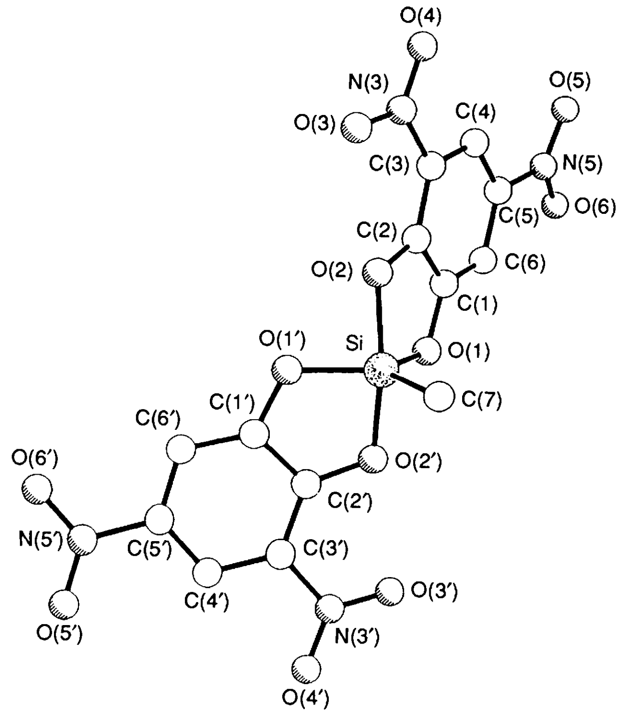

Fig. 4 The crystal structure of the anion in [NEt$_3$H][SiMe(3,5-dncat)$_2$]

involved. It is reasonable to conclude that the rate of redistribution decreases as the strength of the catecholate derivative increases. The non-statistical distribution of complexes in a mixture (*e.g.* A) indicates thermodynamic stability of a mixed complex in Me$_2$SO. The likely explanation lies in the electronic rather than the steric effects in the complex, since the five-co-ordination imposes little steric constraint.

The crystal structure of [NEt$_3$H][SiMe(dncat)$_2$] shows the anion (Fig. 4) to have a slightly distorted trigonal-bipyramidal geometry with the two ligands being *trans* as depicted in Fig. 1. Fractional atomic coordinates are listed in Table 2, with bond lengths and angles in Table 3. The equatorial atoms are coplanar to within 0.01 Å. There is a slight enlargement of the O(1)–Si–O(1′) angle [126.3(3)°], whilst the two Me–Si–O angles are the same (117°). The axial O(2)–Si–O(2′) angle [167.5(3)°] is significantly reduced from linear and there is an accompanying enlargement of both the O(2)–Si–Me and O(2′)–Si–Me angles [97.5(3) and 95.0(3)° respectively]. The pattern of Si–O bond lengths is compatible with both the valence forms of the ligands and the axial/equatorial co-ordination at silicon. As expected the *trans* axial Si–O(2) and Si–O(2′) bond distances [1.805(5) and 1.813(5) Å respectively] are both significantly longer than the equatorial Si–O(1) and Si–O(1′) bond distances [1.701(5) and 1.702(5) Å respectively]. Furthermore, the C(2)–O(2) and C(2′)–O(2′) bonds [average 1.311(11) Å] which are *ortho* and *para* to the nitro groups are noticeably shorter than C(1)–O(1) and C(1′)–O(1′) [average 1.355(11) Å] reflecting the preferential conjugation of the nitro groups.

Table 2 Atomic coordinates (× 10^4) of [NEt$_3$H][SiMe(3,5-dncat)$_2$]

Atom	*x*	*y*	*z*
Si	283(2)	1 927(2)	6 702(1)
O(1)	1 577(4)	1 294(4)	6 356(2)
C(1)	1 463(7)	1 117(5)	5 593(4)
C(2)	215(6)	1 416(5)	5 264(4)
O(2)	−557(4)	1 815(4)	5 765(2)
C(3)	−31(6)	1 266(5)	4 483(3)
N(3)	−1 310(6)	1 529(4)	4 098(4)
O(3)	−2 197(5)	1 808(5)	4 476(3)
O(4)	−1 421(5)	1 464(5)	3 398(3)
C(4)	948(7)	891(5)	4 028(4)
C(5)	2 130(7)	621(5)	4 379(4)
N(5)	3 170(7)	285(5)	3 890(4)
O(5)	2 996(5)	362(5)	3 198(3)
O(6)	4 165(6)	−77(5)	4 207(3)
C(6)	2 421(7)	705(5)	5 171(4)
O(1′)	−1 099(4)	1 415(4)	7 050(2)
C(1′)	−1 016(7)	1 239(6)	7 818(4)
C(2′)	277(7)	1 428(6)	8 145(4)
O(2′)	1 090(4)	1 747(4)	7 647(2)
C(3′)	475(7)	1 317(5)	8 935(4)
N(3′)	1 757(6)	1 548(5)	9 321(3)
O(3′)	2 694(5)	1 702(5)	8 941(3)
O(4′)	1 826(5)	1 583(4)	10 022(3)
C(4′)	−539(7)	1 014(5)	9 377(4)
C(5′)	−1 755(6)	808(5)	9 023(4)
N(5′)	−2 837(7)	516(4)	9 492(3)
O(5′)	−2 648(5)	534(4)	10 194(3)
O(6′)	−3 886(6)	263(5)	9 164(3)
C(6′)	−2 025(7)	925(5)	8 237(4)
C(7)	414(7)	3 298(5)	6 722(4)
N(10)	−5 587(5)	−1 556(5)	8 602(3)
C(11)	−4 329(7)	−1 758(7)	8 206(4)
C(12)	−4 491(10)	−2 537(8)	7 592(6)
C(13)	−6 697(7)	−1 173(7)	8 084(4)
C(14)	−6 364(8)	−236(7)	7 682(5)
C(15)	−6 033(7)	−2 408(6)	9 077(4)
C(16)	−5 129(8)	−2 561(7)	9 775(5)

Table 3 Selected bond lengths (Å) and angles (°)

Si–O(1)	1.701(5)	Si–O(2)	1.805(5)
Si–O(1′)	1.702(5)	Si–O(2′)	1.813(5)
Si–C(7)	1.842(7)	O(1)–C(1)	1.351(8)
C(2)–O(2)	1.319(8)	O(1′)–C(1′)	1.358(8)
C(2′)–O(2′)	1.303(8)		
O(1)–Si–O(2)	88.2(2)	O(1)–Si–O(1′)	126.3(3)
O(2)–Si–O(1′)	86.4(2)	O(1)–Si–O(2′)	86.6(2)
O(2)–Si–O(2′)	167.5(3)	O(1′)–Si–O(2′)	87.6(2)
O(1)–Si–C(7)	116.6(3)	O(2)–Si–C(7)	97.5(3)
O(1′)–Si–C(7)	117.1(3)	O(2′)–Si–C(7)	95.0(3)
Si–O(1)–C(1)	114.5(4)	O(1)–C(1)–C(2)	111.9(6)
C(1)–C(2)–O(2)	113.3(5)	O(2)–C(2)–C(3)	129.1(6)
Si–O(2)–C(2)	111.6(4)	Si–O(1′)–C(1′)	114.7(4)
O(1′)–C(1′)–C(2′)	111.6(6)	O(1′)–C(1′)–C(6′)	125.5(6)
C(1′)–C(2′)–O(2′)	113.2(6)	Si–O(2′)–C(2′)	112.4(4)

In the crystal the anions and cations form discrete layers, the NH groups of the cations being hydrogen bonded to one of the nitro groups [N(10) ··· O(6′) 3.11, H(10) ··· O(6′) 2.22 Å; N–H ··· O 147°]. Within each layer of anions there are two major interanion interactions: first, aromatic face-to-face π–π interactions [Fig. 5(*a*)] between the rings attached to O(1) and O(2) of adjacent parallel aryl rings (mean interplanar

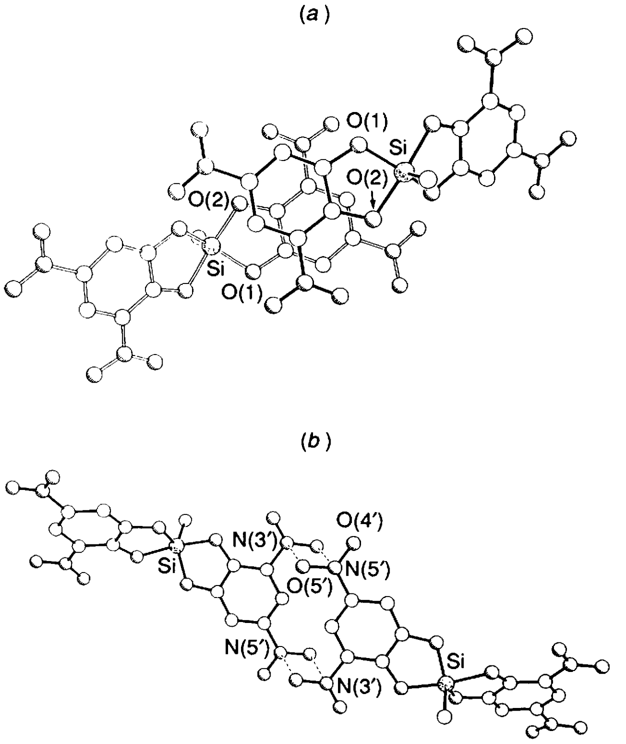

Fig. 5 Ring–ring overlap (*a*) and $NO_2 \cdots NO_2$ interactions (*b*) between symmetry-related anions in the structure of $[NEt_3H][SiMe(3,5\text{-dncat})_2]$

separation 3.45 Å); secondly, pairs of electrostatic N–O ··· N–O interactions [Fig. 5(*b*)] between N(5′)–O(5′) and N(3′)–O(4′). The N(3′) ··· O(5′) and N(5′) ··· O(4′) distances are 3.04 and 3.11 Å respectively. The angle subtended by the O(5′) ··· N(3′) vector and the C(3′)N(3′)O(3′)O(4′) plane is 75°; that subtended by the O(4′) ··· N(5′) vector and the C(5′)N(5′)O(5′)O(6′) plane is 73°. These two types of interaction together with additional weaker $NO_2 \cdots$ aryl interaction (*ca.* 3.3 Å) result in infinite stacks of anions in the crystallographic *b* direction.

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