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Synthesis and structural characterization of the anionic chelates of hypercoordinate silicon, the derivatives of glycolic and tartaric acids

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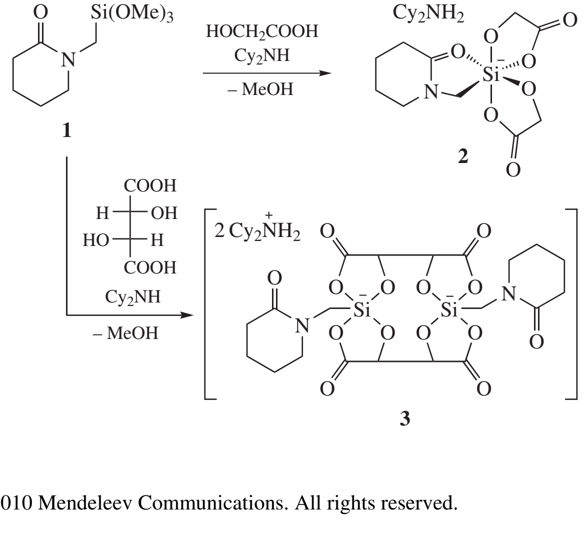
Reactions of 1-(trimethoxysilylmethyl)-2-piperidone with glycolic and (*R*,*R*)-tartaric acids in the presence of dicyclohexylamine afford cation–anionic complexes with different coordination states of the Si atoms.

More than 45 anionic chelates of penta- and hexacoordinate silicon containing fragments of 2-hydroxy acids have been reported,[1(a)] mainly by Tacke and co-workers.[1(b),(c)] The majority (about 40) of these compounds are zwitterionic spirocyclic bischelates with $SiCO_4$ or SiO_5 central coordination sets. Our studies of neutral,[2(a),(b)] cationic[2(b)] and anionic[2(c)] derivatives of 2-hydroxy acids have been focused on the influence of the Si environment on the possibility and strength of the O→Si coordination involving the amide oxygen. To complement these studies, two new types of anionic complexes of hypercoordinate silicon are reported here. Both bis(glycolato-*O*,*O*′)[(2-oxopiperidin-1-yl)methyl-*C*,*O*]silicate **2** and bis{[μ²-(*R*,*R*)-tartrato-*O*,*O*′,*O*″,*O*‴][(2-oxopiperidin-1-yl)methyl]}disilicate **3** contain two fragments of 2-hydroxy acids as dianionic O,O′-chelating ligands and one amidomethyl or lactamomethyl fragment that can act either as a C,O-chelate ligand or as a monodentate carbon substituent at the Si atom.

The dicyclohexylammonium salts of **2** and **3** were prepared by the reaction of compound **1** with two equivalents of glycolic acid or one equivalent of (*R*,*R*)-tartaric acid in the presence of dicyclohexylamine (Cy_2NH) using the technique developed for the anionic complexes of pyrocathechol.[†,2(c)] In the case of glycolic acid, the reaction led to anionic hexacoordinate complex **2** with a $SiCO_5$ central coordination set, a rare example of trischelates with different bidentate ligands.

In contrast, the reaction with (*R*,*R*)-tartaric acid afforded binuclear anionic complex **3** with pentacoordinate silicon atoms.



The structures of **2** and **3** were confirmed by elemental analysis, IR and ^{1}H, ^{13}C and ^{29}Si NMR spectra and X-ray analysis. The ^{29}Si NMR signals were observed at –91.4 and –95.8 ppm, respectively. In our opinion, the above chemical shifts indicate the presence of pentacoordinate silicon atoms in both complexes. Possibly, the Si(1)–O(1′) bond in **2** is dissociated in solution. Note that, for similar pentacoordinate bis(cathecholates) and hexacoordinate tris(cathecholates), the ^{29}Si NMR signals were observed at –84 and –135 ppm, respectively.[2(c),3]

The peculiarities of crystal and molecular structures of **2** and **3** were revealed by single crystal X-ray studies.[‡] General views of their molecules are shown in Figures 1 and 2. Additional

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[†] ^{1}H, ^{13}C and ^{29}Si NMR spectra in $CDCl_3$ were recorded on a Bruker Avance II 600 spectrometer at 600, 150.9 and 119.2 MHz, respectively. Chemical shifts were measured in solutions using TMS as an internal reference.

Compound **1** was prepared by a published procedure.[6]

*Synthesis of dicyclohexylammonium bis(glycolato-*O,O′*)[(2-oxopiperidin-1-yl)methyl-*C,O*]silicate* **2**. A mixture of compound **1** (1 g, 4.3 mmol), glycolic acid (0.65 g, 8.6 mmol) and dicyclohexylamine (0.78 g, 4.3 mmol) in 10 ml of *o*-xylene was heated for 30 min until MeOH was distilled off. The mixture was cooled down to room temperature; the crystals formed were filtered off and washed with hexane to afford 1.88 g (94%) of complex **2**, mp 190–192 °C (MeCN). ^{1}H NMR ($CDCl_3$) δ: 1.01–2.19 (m, 20H, $2C_6H_{10}$), 1.81 (m, 2H, H-4), 2.09 (m, 2H, H-5), 2.55 (m, 2H, H-3), 3.00 (m, 2H, H-6), 3.41 (s, 2H, NCH_2), 4.05, 4.10 (2s, 4H, $2OCH_2$), 8.7 (br. s, 2H, NH_2). ^{13}C NMR ($CDCl_3$) δ: 21.24 (C-4), 22.45 (C-5), 47.13 (NCH_2Si), 51.30 (C-6), 53.59 ($2OCH_2$), 163.27 [2OC(O)], 178.64 [NC(O)]. ^{29}Si NMR ($CDCl_3$) δ: –91.4. Found (%): C, 56.24; H, 8.21; N, 5.91. Calc. for $C_{22}H_{38}N_2SiO_7$ (%): C, 56.15; H, 8.14; N, 5.95.

*Synthesis of dicyclohexylammonium bis{[μ₂-(*R,R*)-tartrato-*O,O′,O″,O‴*]-[(2-oxopiperidin-1-yl)methyl]}disilicate* **3**. An equimolar mixture of compound **1** (2.33 g, 0.01 mol), (*R*,*R*)-tartaric acid [1.50 g, 0.01 mol, $[\alpha]_D^{20}$ +13.9° (*c* 3.6, H_2O)] and dicyclohexylamine (1.8 g, 0.01 mol) in 20 ml of *o*-xylene was heated for 30 min until MeOH was distilled off. The mixture was cooled down to room temperature and poured into hexane. The crystals formed were filtered off and washed with diethyl ether to afford 3.77 g (38%) of complex **3**, mp 219–221 °C (MeCN), $[\alpha]_D^{25}$ –4.8° (*c* 2.18, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 1.12–3.21 (m, 38H, $2C_6H_{11}$ + 2 lactam fragments), 3.22 (m, 4H, 4CH), 4.38 (s, 4H, $2NCH_2$), 7.4 (br. s, 4H, NH_2). ^{13}C NMR ($CDCl_3$) δ: 22.68 (C-4), 25.05 (C-5), 45.22 (NCH_2Si), 49.98 (C-6), 75.22 (OCH), 169.70 [NC(O)], 175.15 [CHC(O)]. ^{29}Si NMR ($CDCl_3$) δ: –95.8. Found (%): C, 56.43; H, 7.72; N, 7.09. Calc. for $C_{46}H_{75}N_5Si_2O_{14}$ (**3**·MeCN) (%): C, 56.48; H, 7.73; N, 7.16.

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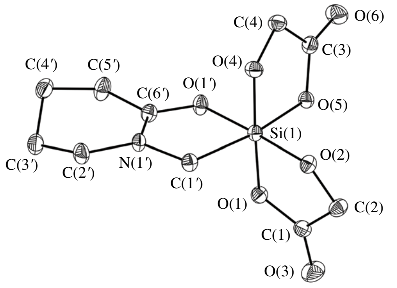

Figure 1 Molecular structure of anion **2** (probability level of displacement ellipsoids is 50%). Selected bond lengths (Å) and angles (°): Si(1)–O(1) 1.8078(12), Si(1)–O(1′) 1.8953(12), Si(1)–O(2) 1.7419(12), Si(1)–O(4) 1.7317(12), Si(1)–O(5) 1.8317(12), Si(1)–C(1′) 1.9314(16); O(1)–Si(1)–O(1′) 85.83(5), O(1)–Si(1)–O(2) 87.77(5), O(1)–Si(1)–O(4) 173.16(6), O(1)–Si(1)–O(5) 85.98(5), O(1)–Si(1)–C(1′) 93.19(6), O(1′)–Si(1)–O(2) 173.07(6), O(1′)–Si(1)–O(4) 91.11(6), O(1′)–Si(1)–O(5) 83.67(5), O(1′)–Si(1)–C(1′) 84.57(6), O(2)–Si(1)–O(4) 94.97(6), O(2)–Si(1)–O(5) 93.24(5), O(2)–Si(1)–C(1′) 98.45(6), O(4)–Si(1)–O(5) 87.60(5), O(4)–Si(1)–C(1′) 92.61(6), O(5)–Si(1)–C(1′) 168.24(6).

information on the crystal structures of **2** and **3** is given in the Online Supplementary Materials.

The coordination polyhedron of the Si(1) atom in anionic complex **2** corresponds to a distorted octahedron (Figure 1). The Si(1) atom deviates from the C(1′)O(1)O(5)O(4) and C(1′)O(1′)O(5)O(2) planes by 0.1197(4) and 0.0543(5) Å, respectively. The distortion of the chelate rings formed by the two glycolate moieties in **2**, probably, results from the formation of two strong H-bonds with dicyclohexylammonium cations. The five-membered rings O(1)C(1)C(2)O(2)Si(1) and O(4)C(4)C(5)O(5)Si(1) adopt an envelope conformation.

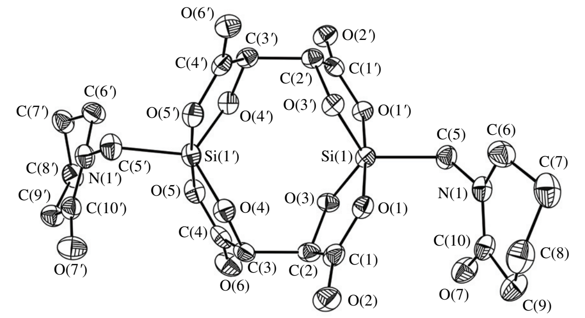

Figure 2 Molecular structure of dianion **3** (the probability level of the displacement ellipsoids is 50%). Selected bond lengths (Å) and angles (°): Si(1)–O(1) 1.8067(13), Si(1)–O(1′) 1.8260(13), Si(1)–O(3) 1.6713(15), Si(1)–O(3′) 1.6691(14), Si(1)–C(5) 1.895(2), Si(1′)–O(4) 1.6714(15), Si(1′)–O(4′) 1.6731(15), Si(1′)–O(5) 1.7860(15), Si(1′)–O(5′) 1.8426(15), Si(1′)–C(5′) 1.883(2); O(1)–Si(1)–O(1′) 175.96(7), O(1)–Si(1)–O(3) 89.65(7), O(1)–Si(1)–O(3′) 89.85(7), O(1)–Si(1)–C(5) 94.80(8), O(1′)–Si(1)–O(3) 88.16(7), O(1′)–Si(1)–O(3′) 88.38(6), O(1′)–Si(1)–C(5) 89.24(8), O(3)–Si(1)–O(3′) 121.10(7), O(3)–Si(1)–C(5) 120.16(9), O(3′)–Si(1)–C(5) 118.56(9), O(4)–Si(1′)–O(4′) 120.84(7), O(4)–Si(1′)–O(5) 89.61(7), O(4)–Si(1′)–O(5′) 87.76(7), O(4)–Si(1′)–C(5′) 121.13(9), O(4′)–Si(1′)–O(5) 90.24(7), O(4′)–Si(1′)–O(5′) 88.45(7), O(4′)–Si(1′)–C(5′) 117.62(9), O(5)–Si(1′)–O(5′) 175.94(7), O(5)–Si(1′)–C(5′) 96.60(8), O(5′)–Si(1′)–C(5′) 87.41(8).

In contrast to the above compound, the hexacoordinated state of Si atoms in compound **3** is not achieved. Two tetradentate (*R*,*R*)-tartrato(4–) ligands form a globular structure of λ^5Si,λ^5Si′-disilicate anion due to the coordination with two Si atoms (Figure 2). The coordination polyhedra of Si(1) and Si(1′) atoms can be described as distorted trigonal bipyramids (TBP) with the deviation of the latter atom from the equatorial planes towards the O(1) and O(5) atoms by 0.0430(6) and 0.0645(6) Å, respectively. The Si(1) atom forms an intramolecular contact with the oxygen atom of the piperidone moiety [the O(7)···Si(1) distance is 3.525(2) Å]. The average TBP degree in coordination polyhedra of Si(1) and Si(1′) atoms calculated from the formula proposed by Kost *et al.*[4] is 91.6%. In terms of the dihedral angle method,[5] complex **3** is close to a Berry reaction pathway, but some deviation is still noticeable. The closest point to a Berry reaction pathway is approximately 6.1%, which is similar to the value given by the Kost method.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2010.09.011.

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‡ *Crystallographic data for* **2**: crystals of $C_{22}H_{38}N_2O_7Si$ are monoclinic, space group $P2_1/c$, $a = 10.4868(8)$, $b = 13.6505(11)$ and $c = 16.8505(14)$ Å, $\beta = 100.988(2)°$, $V = 2367.9(3)$ Å^3, $Z = 4$, $M = 470.63$, $d_{calc} = 1.320$ g cm^{-3}, μ(MoKα) = 0.14 mm^{-1}, $F(000) = 1016$. Intensities of 30817 reflections were measured with a Bruker Smart APEX II diffractometer at 100 K [λ(MoKα) = 0.71073 Å], and 7258 independent reflections ($R_{int} = 0.0723$) were used in a further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. All hydrogen atoms were calculated from geometrical point of view with exception of H(1AB) and H(1AC), which were located from difference Fourier maps. Hydrogen atoms were refined in the rigid body approximation with the U_{iso}(H) parameters equal to $1.2U_{eq}$(C,N), where U_{eq}(C,N) are the equivalent thermal parameters of the carbon and nitrogen atoms, respectively, to which corresponding H atoms are bonded. The refinement converged to $wR_2 = 0.1333$ and GOF = 1.025 for all independent reflections [$R_1 = 0.0488$ was calculated against F for 5041 observed reflections with $I > 2\sigma(I)$].

Crystallographic data for **3**·MeCN: crystals of $C_{46}H_{75}N_5O_{14}Si_2$ are monoclinic, space group $P2_1$, $a = 10.5988(6)$, $b = 21.4406(12)$ and $c = 11.6179(6)$ Å, $\beta = 105.6652(11)°$, $V = 2542.0(2)$ Å^3, $Z = 2$, $M = 978.29$, $d_{calc} = 1.278$ g cm^{-3}, μ(MoKα) = 0.14 mm^{-1}, $F(000) = 1052$. Intensities of 29630 reflections were measured with a Bruker Smart 1000 diffractometer at 100 K [λ(MoKα) = 0.71073 Å]; 14340 independent reflections ($R_{int} = 0.0248$) were used in a further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. All hydrogen atoms were calculated from geometrical point of view with exception of H(2B), H(2C), H(2′B) and H(2′C), which were located from difference Fourier maps. Hydrogen atoms were refined in the rigid body approximation with the U_{iso}(H) parameters equal to $1.2U_{eq}$(C,N), where U_{eq}(C,N) are the equivalent thermal parameters of the carbon and nitrogen atoms, respectively, to which corresponding H atoms are bonded. The refinement converged to $wR_2 = 0.0994$ and GOF = 1.001 for all independent reflections [$R_1 = 0.0457$ was calculated against F for 11472 observed reflections with $I > 2\sigma(I)$].

CCDC 766901 and 766902 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2010.

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