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Synthesis and crystal structure of the salt $Na_6[(PhSiO_{1.5})_{22}Co_3O_6] \cdot 7H_2O$ containing a cobaltasiloxane anionic framework

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Abstract

The interaction of $[PhSiO(ONa)]_3 \cdot 3H_2O$ with $(PhSiO_{1.5})_8$, NaOH, and $CoCl_2$ gave a sodium heptahydrate of a new complex, a framework cobaltasiloxane anion whose crystal structure was determined by X-ray crystallography. The cobaltasiloxane framework of the $[(PhSiO_{1.5})_{22}Co_3O_6]^{6-}$ polyanion which has approximate C_3 symmetry is formed by three open-edged silsesquioxane cubes each of which one of its Si atoms is replaced by a Co atom, and has tetrahedral 4 × O coordination. Of the Na^+ cations three are positioned outside, and three are inside the anion framework, and are coordinated with its O atoms and water molecules. The bond lengths are: 1.92–2.01 Å for Co–O; 1.57 Å av. for Si–O(Co), and 1.63 Å av. for Si–O(Si). The bond angles at the O atoms of the anion are 121–158°, and for the Co-bonded O atoms these angles are consistent with their participation in the $O \ldots Na^+$ interactions.

Introduction

Up to now the organometallic siloxanes obtained from trifunctional organosilicon monomers and polyvalent metals are polymerics [1]. The details of structural features can only inferred since these polymers are amorphous. For the first time we have produced a comparatively low molecular mass organocobaltasiloxane (I) whose detailed structure has been established by an X-ray diffraction study. The trimeric structure of I can be regarded as the first real model of framework organometallic siloxanes. This work provides comprehensive data on the synthesis and X-ray crystal features of I. A short communication on this subject has appeared [2].

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Results and discussion

The crystal of $Na_6[(PhSiO_{1.5})_{22}Co_3O_6] \cdot 7H_2O$ (I) has a "molecular" structure: its individual "molecules" represent cobaltasiloxane hexaanions associated with the Na^+ cations which in turn are coordinated with the water molecules. The "molecules" of I, i.e. hydrated cationic-anionic associates (complexes) interact with one another by Van der Waals forces only, point of contact being the hydrophobic shells made up of the Ph substituents.

The structure of the cobaltasiloxane anion seems to be related to the molecular structure of the initial silsesquioxane cube $(PhSiO_{1.5})_8$. The anion (Figs. 1 and 2) is composed of three such cubes, each of which has had one of its Si atoms replaced by a Co atom, with one corner missing (the bridge O atom between the "upper" Si_4O_4 and "lower" Si_3CoO_4 faces). These open-edged cubes * are connected pairwise by three Co–O–Si bridges, by siloxane bonds via a central Si(22) atom. If the Ph substituents, are disregarded the anion can be said to have approximate C_3 symmetry. The extent of this symmetry depends on the regularity of the heavy-atom Co(1)Co(2)Co(3), Si(1)Si(8)Si(15), etc. triangles as well as on the closeness of their

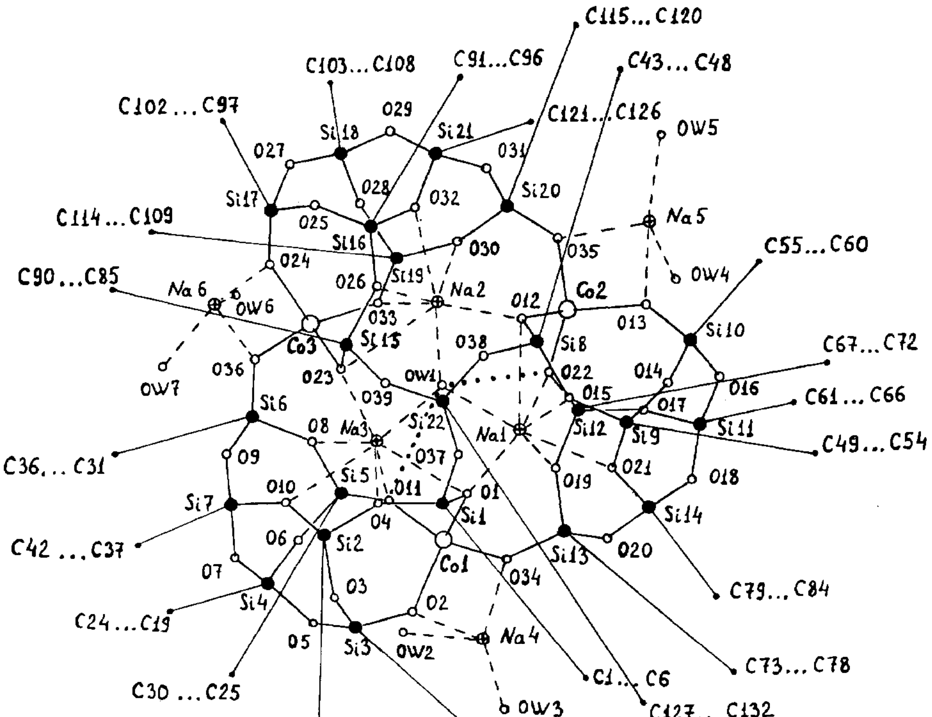

Fig. 1. General view of the hydrated cationic-anionic complex ("molecule") I with the atom numbering scheme. For Ph rings only positions in the anionic framework and atomic numbers are indicated. Broken lines show $Na^+ \ldots O$ interactions, dotted lines show H bonds.

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* Hereinafter referred to as "cubes".

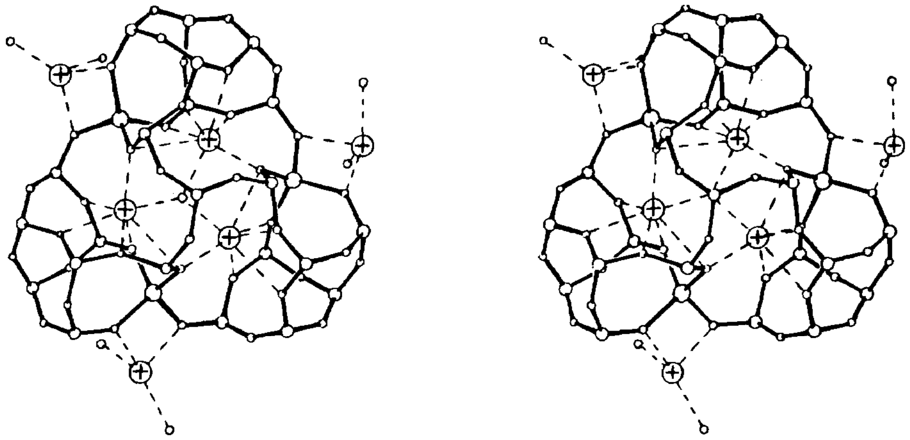

Fig. 2. Stereopair showing spatial structure of the anionic framework with associated cations and water molecules. Ph substituents at Si atoms are omitted. Atom numbering is the same as that for Fig. 1.

planes of orientation. The sides of these triangles differ by about 0.2 Å (for example, the Co... Co distances are 6.505–6.716(3) Å) whereas the dihedral angles between their planes do not exceed 1.5°. The corresponding Co... Si and Si... Si distances in the cobaltasiloxane cubes coincide within experimental error. However, the angles at the matching O atoms differ significantly by as much as 17°, and in addition to the differences can also be attributed to factors other than the coordination of some of these atoms with the cations. Nevertheless the conformations of the pseudosymmetry-related eight-membered siloxane and cobaltasiloxane cycles are fairly close to one another [3].

There are six Na^+ cations, the three outside the anion framework Na(4), Na(5), and Na(6), are coordinated to a pair of "cobalt" O atoms and a pair of water molecules each, whereas those inside the framework, Na(1), Na(2), and Na(3) are hepta-coordinated, to the central W(1) water molecule and to the six O atoms of the anion. The C_3 pseudosymmetry is fulfilled in the cation environment, too, although less accurately: the $Na^+ \dots Na^+$ separations inside the framework are 3.64–3.93 Å and the angle between the Na(1)Na(2)Na(3) and Co(1)Co(2)Co(3) planes is 4°.

The Ph substituents at the Si atoms together with the adjacent cations and water molecules enclose the anionic framework thus preventing the formation of "intermolecular" ionic and hydrogen bonds typical of other ionic siloxanes. Owing to the fact that the open cobaltasiloxane cubes are united by a single Si(22) atom only, the cavity inside the framework is like a deep open-mounted cup which, under the appropriate conditions, should enable the cations and water molecules to enter and to escape from the cup.

The presence of pseudosymmetry lends itself to the convenient use of mean values so as to compensate for a relatively small degree of accuracy in the determination of structure, although this is not true for all parameters. If the bond lengths largely depend on the valence environment of a given atom and because their differences in the fragments of "molecule" I related by C_3 pseudosymmetry are usually caused by experimental error, the bond angles and non-bonded distances are far less rigid so that their mean values should be used with caution.

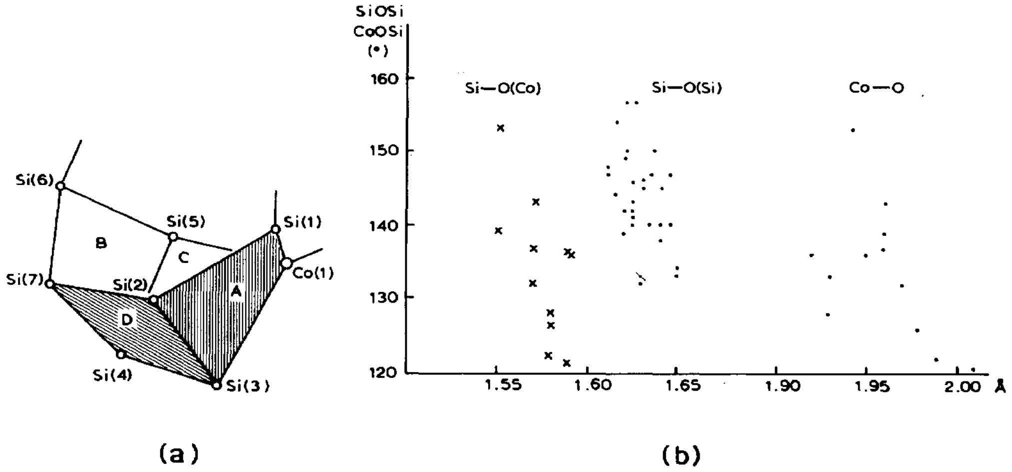

Fig. 3. (a) An opened Si_7Co-cube in structure I and the 8-membered cycles in it; (b) distribution of bond angles at O atoms of the anionic framework depending on Si–O and Co–O bond lengths. As the Si–O bond length in SiOSi moieties the mean value for each O atom is assumed.

Geometry of the cobaltasiloxane framework

The structure of the pseudosymmetry-bonded cobaltasiloxane cubes is governed on the one hand by their open nature and, on the other, by the replacement of one of the Si atoms by the Co atom. The largest rigid structural units in the cubes are eight-membered heterocycles. Considering the pseudosymmetry, it is possible to class such heterocycles into four types (A, B, C, and D) (Fig. 3) which differ in their composition and geometry. In Table 1 their relevant parameters are compared with those of the cycles in octaphenylsilsesquioxane $(PhSiO_{1.5})_8$ (II) [4] whose siloxane cube symmetry is the highest possible in the crystal and with the given substituents.

The mean Si–O bond length in I somewhat exceeds the corresponding value in II and the mean SiOSi angle is smaller than that in II. Generally, despite significant

Table 1

Mean geometrical parameters of 8-membered heterocycles in I and II

Cycle	Conformation [a]	Q (Å) [b]	SiOSi angle (°)	Si–O(Si) bond length (Å)	SiOCo angle (°) [c]	Si–O(Co) bond length (Å)
I A[d]	0.6BB+0.3C+0.1CR	1.11–1.13	146	1.63	123, 138	1.57
I B	0.7(B−BB)+0.2IC+0.1CR	0.96–1.11	146	1.63	–	–
I C	0.4(B−BB)+0.4(C−LC) +0.2CR	0.66–0.72	145	1.63	138, 142	1.57
I D	0.4(B−BB)+0.4LC+0.2CR	0.79–0.83	141	1.63	–	–
II	CR	0.4–0.5	149	1.614	–	–

[a] Calculated by use of the method in ref. 2. Coefficients of the symbols of the canonical forms display an approximate contribution by each form to an actual conformation. [b] General non-planarity of the cycle [2]. [c] Mean values for the O atoms in a given cycle only (first number), and common to cycles A and C (second number). [d] Types of cycles in I (see Fig. 3a).

variation of the Si–O(Si) bond lengths and SiOSi angles, they fit fairly well (with deviations of ca. 30 °) into the known [5] inverse dependence for siloxanes (Fig. 3b). A similar dependence is observed for the Si–O(Co) bonds, but the curve is displaced towards shorter lengths by ca. 0.06 Å. Such a correlation is not so pronounced for the Co–O bonds.

The conformations of the eight-membered heterocycles in I and II differ markedly. The heterocycles of the C and D types which are "clamped" by the polycyclic system of the cube (fused with three other heterocycles) have parameters which are close to these of the cycles in II although their nonplanarity is somewhat greater. The lateral (fused with two other heterocycles) heterocycles A and B bonded to the adjacent cubes are still more puckered so that the contribution of the canonical "crown" form of the eight-membered siloxane cycles in II to their conformation is negligible. Still more pronounced are the differences between the geometry of the heterocycles of the various types, on the Si_4 and Si_3Co quadrangles which have approximate *mm* symmetry (the mirror planes passing along the diagonals). For cycles C and D the deviations of the Co and Si atoms from the mean planes of the quadrangles do not exceed 0.12 Å, whereas for cycles A and B they are as large as 0.56 Å. In silsesquioxane II the Si_4 quadrangles are planar.

So, the conformational changes, on going from cube II to open-edged cube I, ignoring the replacement of Si by Co, can be described as follows (all the designations are given for one of the cubes). Upon breakage of the Si(1)...Si(6) edge the O(1)Si(1)O(4) and O(8)Si(6)O(9) triangles bend away from the centre of the cube in different directions so that the Si(1) and Si(6) atoms become separated by more than 6.5 Å. Just as this is taking place, cycles A and B assume a distorted "bath" conformation with a bend along the Si(1)...Si(3) and Si(4)...Si(6) lines, the angle between the mean planes of the C and D cycles decreases to 80 °, so that the Co(1) and Si(2), Si(5) and Si(7) atoms become closer by ca. 0.3 Å. It is evident that to some extent cube opening is controlled by the external conditions pertaining to framework closure. This is confirmed by (i) a large Si...Si distance which separates the ends of the broken cube edge and (ii) some tension in the cycles A and B: the average lengths of the Co(1)...Si(2), Si(5)...Si(7) diagonals and their counterparts are 4.123 and 4.013 Å respectively, which is smaller than the other diagonal distances by 0.2–0.4 Å and shorter than the sum of the Van der Waals radii for the Si...Si diagonals) (4.2 Å as given elsewhere [6]).

As can be seen from Table 1, the integral parameters of the cobaltasiloxane A and C cycles are very much the same as those for the siloxane B and D cycles. Comparison of the more planar C and D cycles indicates that in the former the Co...Si and Si...Si diagonal distances differ even less (Δ_m 0.15 Å) than in the latter (the two Si...Si distances, Δ_m 0.20 Å). The Co–O bond is longer than the Si–O bonds by ca. 0.35, and this difference for the shortest non-bonded Co...Si distances which, on the average, exceeds the corresponding Si...Si distances by no more than 0.15 Å (3.246 vs. 3.098 Å) is compensated for by decreasing the SiOCo as opposed to the SiOSi angles. It is not unlikely that the reason for the decrease in size of these angles as well as shortening of the Si–O(Co) bonds could be the excessive negative charge on the "cobalt" O atoms (see below).

Coordination of the cobalt atoms

The Co atoms in anion I have tetrahedral coordination with four O atoms and

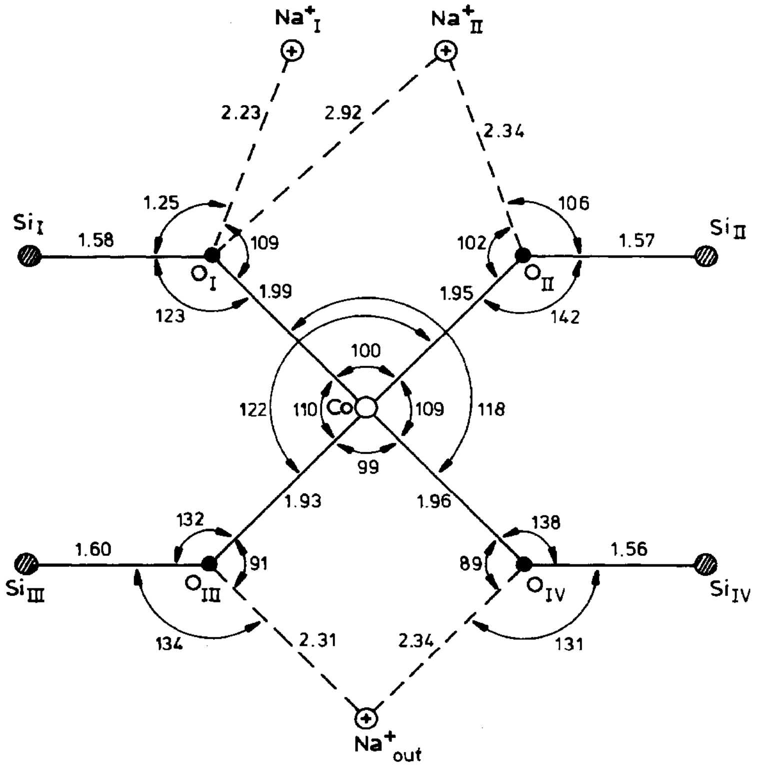

Fig. 4. Coordination of Co atoms and associated O atoms. All distances and angles are averaged over three corresponding parts of "molecule" I. Generalized designations: O_I = O(1), O(12), O(23); O_{II} = O(11), O(22), O(33); O_{III} = O(34), O(35), O(36); O_{IV} = O(2), O(13), O(24); Na_I^+ = Na(1), Na(2), Na(3); Na_{II}^+ = Na(3), Na(1), Na(2); Na_{out}^+ = Na(4), Na(5), Na(6).

the Co–O bond lengths being standard for the tetrahedral cobalt(II) compounds. Thus, in the structure of dibromobis(1-oxophosphabicyclo[3.3.1]nonane)cobalt(II) for example [7], the Co atom is coordinated with 2O and 2Br, and the Co–O distances are 1.927 and 1.973 Å, respectively. In compound I the Co–O bonds are also different which may be attributed to a dissimilar additional coordination of the Co-bonded O atoms (Fig. 4). In fact, the greatest average length (1.99 Å) is observed for the bond of the Co atom to O_I, whose contact with the Na_I^+ cation is the shortest (2.23 Å av.). The Si–O(Co) bond lengths are independent of the $Na^+ \ldots O(Co)$ distances so that the Co–O bonds are far less rigid, which is typical of the more ionic bonds. Note that the O_I atom is also coordinated, albeit weakly, with the second Na_{II}^+ cation, the shortest distance of this type, viz. Na(2)...O(23) of 2.75 Å, corresponds to the largest Co–O(23) distance of 2.01 Å.

Distortion of the coordination tetrahedrons about the Co atoms is greater than those about the Si atoms, which is a corollary to the reason given above. In the structure mentioned previously [7] the bond angles at the Co atoms vary between 103 and 117°. In the structure of a complicated Co complex [8] the NCoN bond angles are 105–119° although the environment of the Co atom is formed by four identical linear NCS ligands. A strong distortion of the O_ICoO_{II} and $O_{III}CoO_{IV}$ bond angles can be attributed to a contracting effect exerted by the "bridge"

Table 2

$Na^+\ldots O$ distances (Å)

Na(1)...O(W1)	2.57(1)	Na(3)...O(4)	2.55(1)
Na(1)...O(1)	2.22(1)	Na(3)...O(10)	2.57(1)
Na(1)...O(22)	2.39(1)	Na(3)...O(8)	2.73(1)
Na(1)...O(15)	2.45(1)	Na(3)...O(1)	2.98(1)
Na(1)...O(21)	2.58(1)		
Na(1)...O(19)	2.91(1)	Na(4)...O(2)	2.37(2)
Na(1)...O(12)	3.02(1)	Na(4)...O(34)	2.31(2)
		Na(4)...O(W2)	2.62(3)
Na(2)...O(W1)	2.41(1)	Na(4)...O(W3)	2.24(4)
Na(2)...O(12)	2.27(1)		
Na(2)...O(33)	2.29(1)	Na(5)...O(13)	2.35(2)
Na(2)...O(26)	2.60(1)	Na(5)...O(35)	2.27(2)
Na(2)...O(32)	2.95(1)	Na(5)...O(W4)	2.48(3)
Na(2)...O(30)	2.70(1)	Na(5)...O(W5)	2.70(4)
Na(2)...O(23)	2.75(1)		
		Na(6)...O(24)	2.29(2)
Na(3)...O(W1)	2.57(1)	Na(6)...O(36)	2.36(2)
Na(3)...O(23)	2.19(1)	Na(6)...O(W6)	2.20(3)
Na(3)...O(11)	2.36(1)	Na(6)...O(W7)	2.42(3)

cations. This is evident from the $O_{III}CoO_{IV}$ angles since the corresponding $Si_{III}CoSi_{IV}$ angles are on average 138°, so in order to obtain the observed values of $O_{III}CoO_{IV}$ an approximate coincidence of the orientations of the $CoO_{III}Si_{III}$ and $CoO_{IV}Si_{IV}$ planes is essential. This function probably fulfilled by the outside Na^+_{out} cations (see below).

Cation coordination

Each of the three intra-framework cations Na(1), Na(2), and Na(3) is coordinated with seven O atoms including the inside O(W1) atom of the water molecule (Figs. 1 and 2). The coordination polyhedron of these cations is irregular, five O atoms of each cobaltasiloxane cube are positioned on the same hemispherical surface relative to Na^+ whereas the other hemisphere contains only O(W1) and the O atom of the adjacent cube, the contact of this cation with the latter (Na(1)...O(1) and the corresponding ones) being the shortest.

The $Na^+\ldots O$ distances (Table 2) are normal, although contacts shorter than 2.30 Å seldom occur in such ionic structures. Figure 5 shows the distortion of the C_3 pseudosymmetry of the framework cationic-anionic associate I, this distortion is made up of the differences of the corresponding $Na^+\ldots O$ distances for Na(2), on

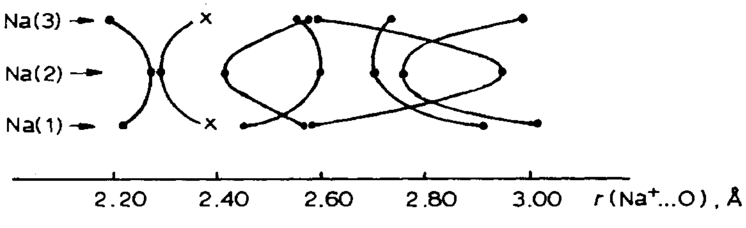

Fig. 5. Distribution of $Na^+\ldots O$ distances. Points for the O atoms connected by C_3 pseudosymmetry are joined by lines. Distances for the O atoms involved in H bonds with O(W1) are marked by crosses.

the one hand, and for Na(1) and Na(3), on the other. The distortion probably is due to the presence of the O(W1)...O(11) and O(W1)...O(22) H-bonds (see below) that weaken the Na(3)...O(11) and Na(1)...O(22) interactions, respectively. A similar situation is observed in the structure of the triphenylcyclotrisiloxanetriol sodium hydrate [9] in which the O atoms of the ionized Si–O^- silanole groups involved in the two H bonds are coordinated with the Na^+ cations at a distance of 2.30 Å and those in three other such bonds, at a distance of 2.69 Å. It is natural that the distribution of the remaining Na^+...O distances for Na(1) and Na(3) is also shifted with respect to that for Na(2). Generally, however, the bond energy of the intra-framework cations is approximately the same, the average distances being 2.59 Å for Na(1)...O, 2.57 Å for Na(2)...O, and 2.56 Å for Na(3)...O. The small values of the temperature parameters of these cations ($B_{aniso} < 6$ Å^2) indicate the rigidity of their arrangement, which is comparable to the fixed nature of the Co and Si atoms in the framework.

The outside Na(4), Na(5), and Na(6) cations are four coordinated (Figs 1 and 2), and the two water molecules in the environment of each of these cations having no other short contacts. This results in a strong thermal motion of these water molecules (very large temperature factors) and so low accuracy in determining their coordinates. Accordingly, the outside cations which interact with no more than two O atoms of the anion, are also subject to strong temperature oscillations. Owing to unreliable localization of the water molecules, which are possibly disordered, detailed discussion of the geometry of the outside cation coordination environment is not practicable. However, they are bonded to the "cobalt" O atoms of the framework, which points to the presence of a large negative charge on just these atoms.

Coordination of the oxygen atoms

These atoms have varied coordination with coordination numbers from $N = 1$ to 5. The O atoms of the extra-framework water molecules have $N = 1$. Those of the cobaltasiloxane framework have $N = 2$, some of them can be additionally coordinated with the cations up to $N = 3$ and $N = 4$. The internal water molecule interacts with the three cations and gives two H bonds to the anion O atoms, in this case $N = 5$. Here we consider the geometry of the O atom environments with $N > 2$.

The O atoms of the anion, bonded to the cations and have $N = 3$, show planar coordination. It can be seen from Fig. 6 that the directions of the Na^+...O strongest interactions (the smallest distances) concentrate at the planes of the O atom valence bonds ($\theta \to 0$). According to the classification system [10] proposed for the O atoms of water molecules in crystallohydrates, though, coordinations with $\theta < 25°$ relate to class 1 which is characterized by the strongest bonds to the cations (II) which is the case for I. A set of moderately strong bonds with $\theta \approx 50°$, which coincides approximately with the direction of the unshared electron pair of the sp^3-hybridized O atom (class 1′), is also clearly represented in Fig. 6. The O(1), O(12), and O(23) atoms which have the shortest contacts with Na(1), Na(2), and Na(3) are additionally coordinated with the "second" Na(3), Na(1), and Na(2) cations, respectively. These "second" interactions are much weaker and oriented nearly "axially" to the planes of the major bonds (− 76, 83, and 77°). Thus the O(1), O(12), and (23) atoms have a strongly distorted tetrahedral coordination, the weak bonds also being well described by the helical dependence $r(\theta)$.

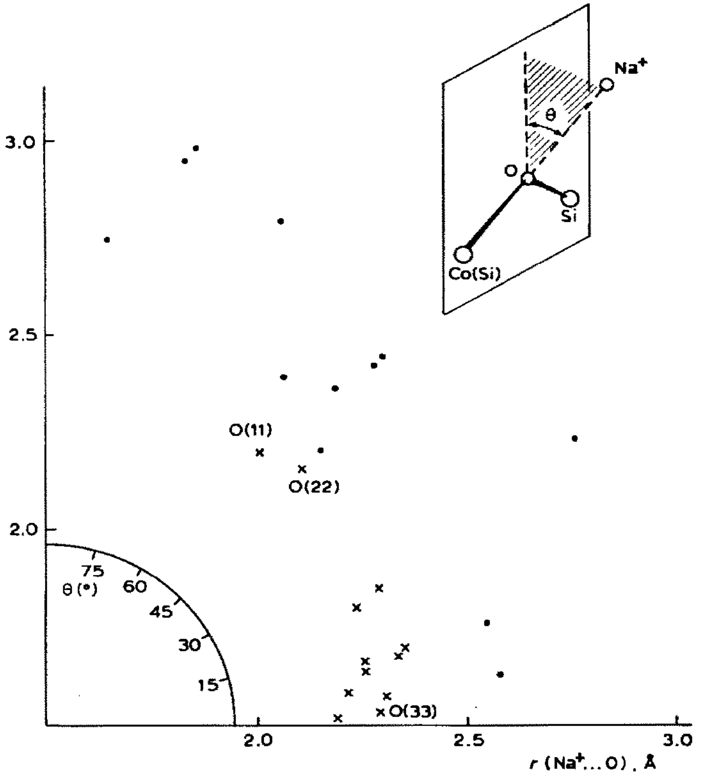

Fig. 6. Diagram showing a correlation between the length of the Na$^+$...O coordination bond and the angle Θ between this bond and the valence bonds plane of the O atom. Points for "cobalt" O atoms are marked by crosses.

Compared with the other atoms, the "cobalt" O atoms are more strongly bonded to the cations and, thus their environment is the most planar. Exceptions are the O(22) and O(11) atoms which participate in the H bonds to O(W1), and so their vectors of interaction with the cations rise sharply out of the CoOSi planes (θ 47 and 54°, class 2 [10], considering the H bonds to the water molecules, i.e. $N = 4$), whereas the O(22)...Na(1) and O(11)...Na(3) distances increase somewhat up to 2.39 and 2.36 Å, respectively, as opposed to 2.29 Å for the corresponding O(33)...Na(2) distance. But the feature of the planar coordination of the O atoms also strongly depend on the type of cation participating in the bonding, i.e. intra- or extra-framework. In the case of an intra-framework cation, the difference between the NaOCo and NaOSi angles for a given O atom is averaged at 14°, and for the extra-framework cations it can be as great as 43° (Fig. 4) with a minimum of 33°. A decrease of the NaOCo angles down to 90° on the average (coordination with the extra-framework cations) can be attributed to the $\mathrm{Na}^+_{\mathrm{out}}$...O distances tending to shorten as the $\mathrm{Si}_{\mathrm{III}}\mathrm{O}_{\mathrm{III}}\mathrm{CoO}_{\mathrm{IV}}\mathrm{Si}_{\mathrm{IV}}$ fragment becomes flatter. By contrast, for a given internal cation the distribution of the Na$^+$...O vector orientation relative to the shortest $\mathrm{Na}^+_{\mathrm{I}}$...$\mathrm{O}_{\mathrm{I}}$ vector is relatively symmetric, so that this cation can be positioned near the bisector of the corresponding $\mathrm{CoO}_{\mathrm{I}}\mathrm{Si}_{\mathrm{I}}$ angle.

The O(W1) atom of the internal water molecule is coordinated with three similarly positioned cations (Figs. 1 and 2). The O(W1)...Na$^+$ interaction distances

(Table 2) are moderately strong and unequal. That this molecule also participates in two H bonds is suggested by a sharp difference between the corresponding O(W1)...O(11) 2.77 Å, O(W1)...O(22) 2.69 Å, and O(W1)...O(33) 3.45 Å distances, the first two indicate moderately strong H bonds. Of the remaining O(W1)...O distances, the shortest one, to O(12), is equal to 3.22 Å. Intuitively, the intra-framework H bonds must be present although the positions af the H atoms were not located. This is supported by the nature of the coordination environment of the inside cations and O atoms and by the impracticability of a rigid O(W1) (a small value of B_{equiv} 3.9 Å^2) in the position observed. The O(W1)-bonded cations are positioned in the same hemisphere, i.e. the Na-coordination of O(W1) is pyramidal (the NaO(W1)Na angles are 94 -104°) with O(W1) deviating out of the Na-plane by as much as 1.20 Å and only the H bonds prevent the water molecule from shortening this distance. The plane of the angle O(22)O(W1)O(11) (equal to 119°) is expected to be close to that of the O(W1) covalent bonds so that the O(W1)...Na(2) bond of 2.41 Å, which is noticeably shorter than the other two O(W1)...Na^+ bonds (2.57 Å each), can be positioned in no plane but this one. Thus the O(W1) coordination is similar to that of the other cation-coordinated O atoms.

Siloxane O atoms are known for their coordination inertness, but in structure I they form part of the anion and seem to have an excessive negative charge localized mainly at the Co-bonded O atoms. This accounts for the coordination activity of the O(Co) atoms: the outside cations are bonded to these atoms and the internal Na^+ ... O(Co) interactions are the strongest. The assumption that the large negative charge of the anion is localized to the "cobalt" O atoms is consistent with the shortening of the Si–O(Co) bonds to 1.57 Å (av.). In the structure of the sodium siloxanolate, mentioned before [9], in which the valence environment of the Si atoms is close to that observed in I, the $Si–O^-$ distances are very much the same (1.581–1.591 Å), although they may be somewhat extended by the H bonds.

The effect of the cations on the geometry of the anionic framework appears to be limited to the comparatively small changes in the bond angles at the O atoms and, to a greater extent, to the changes in the orientation of the SiOSi and SiOCo triangles. The CoOSi and SiOSi bond angles are somewhat smaller for the O atoms which have the strongest bonds to the cations. This correlation, however, disappears for the angles that exceed 140°. On the other hand, flattening of the SiOCoOSi fragments, which have the outside cations located in the vicinity of their planes is observed. The fact that the internal Na(2) cation occurs in the planes of two triangles, viz. Co(2)O(12)Si(8) and Co(3)O(33)Si(19), is not accidental, either.

It is, however, hard to say by how much the framework symmetry distortions are induced by the "intermolecular" (inter-associate), and how much the "intramolecular" (intra-framework) interactions affect the symmetry. The distortion of the symmetry of the silsesquioxane cube II are characterized by the differences in the lengths of the spatial diagonals of ca. 0.07 Å, but the framework of I is far less rigid so that deviations from C_3 symmetry in it (by ca. 0.2 Å) can well be attributed to the packing conditions.

Experimental

Low-molecular cobaltaphenylsiloxane is formed when 6.66 mmol of $[PhSiO(ONa)]_3 \cdot 3H_2O$, 7.5 mmol of $(PhSiO_{1.5})_8$ and 20 mmol of NaOH, are added to a 10 mmol $CoCl_2$ in toluene/propanol (ca. 1/1) solution mixture for 16 h by a procedure similar to that described elsewhere [12]. In addition to the polymeric product, a crystalline substance I of intense-blue colour (yield 16%) is obtained. Compound I is soluble in acetone at room temperature, soluble in toluene and butanol (on heating), but is insoluble in aliphatics. After recrystallization from toluene, compound I has a composition as follows: C, 47.08; H, 3.96; Si, 18.71; Co, 5.11; Na, 3.9%. From the crystal data (see below) it was formulated as $C_{132}H_{124}Si_{22}O_{46}Co_3Na_6$, of composition: C, 46.92; H, 3.70; Si, 18.29; Co, 5.23; Na,

Table 3

Atomic coordinates ($\times 10^4$)[a]

Atom	x	y	z	Atom	x	y	z
Co(1)	8275(1)	3399(1)	1948(1)	O(1)	7255(5)	3726(5)	1801(4)
Co(2)	6479(1)	4911(1)	3662(1)	O(2)	8662(7)	2959(6)	1342(5)
Co(3)	8146(1)	6959(1)	2139(1)	O(3)	8252(5)	3743(6)	465(4)
Si(1)	6791(2)	3896(2)	1220(2)	O(4)	7253(5)	4440(5)	889(4)
Si(2)	7837(2)	4495(3)	484(2)	O(5)	9643(5)	3474(7)	777(4)
Si(3)	8817(3)	3153(3)	767(2)	O(6)	9917(5)	4334(7)	1657(4)
Si(4)	10054(2)	4201(3)	1036(2)	O(7)	9774(5)	4903(7)	672(4)
Si(5)	9520(2)	4651(3)	2144(2)	O(8)	9363(6)	5488(6)	2024(4)
Si(6)	9559(2)	6243(3)	1743(2)	O(9)	9375(5)	6108(6)	1093(4)
Si(7)	9136(2)	5486(3)	631(2)	O(10)	8393(4)	5117(5)	776(4)
Si(8)	5469(2)	4950(2)	2519(2)	O(11)	8762(5)	4301(6)	2164(4)
Si(9)	5349(2)	3309(2)	2754(2)	O(12)	6150(5)	5273(5)	2906(5)
Si(10)	5355(2)	3648(2)	3966(2)	O(13)	5793(6)	4362(6)	4010(5)
Si(11)	6640(2)	2628(2)	4251(2)	O(14)	5085(5)	3367(5)	3321(4)
Si(12)	7730(2)	3667(2)	3821(2)	O(15)	5558(5)	4063(5)	2512(4)
Si(13)	8056(2)	2445(2)	3007(2)	O(16)	5887(5)	3014(5)	4294(5)
Si(14)	6467(2)	2110(2)	3064(2)	O(17)	7264(5)	3187(5)	4180(4)
Si(15)	6699(2)	6419(2)	1423(2)	O(18)	6527(5)	2095(5)	3724(5)
Si(16)	6007(2)	7466(2)	2174(2)	O(19)	7965(5)	3167(6)	3342(4)
Si(17)	7344(2)	8473(3)	2210(2)	O(20)	7265(5)	2060(6)	2918(5)
Si(18)	7454(2)	8428(2)	3480(2)	O(21)	6124(5)	2879(5)	2840(4)
Si(19)	8113(2)	6928(2)	3504(2)	O(22)	7274(5)	4311(5)	3515(4)
Si(20)	6937(3)	6429(2)	4159(2)	O(23)	7501(5)	6223(5)	1716(4)
Si(21)	6052(2)	7577(3)	3419(2)	O(24)	7907(5)	7970(5)	2000(4)
Si(22)	5685(2)	5096(2)	1311(2)	O(25)	6514(5)	8163(5)	2109(4)
Na(1)	6876(3)	3941(3)	2587(3)	O(26)	6273(5)	6761(5)	1897(4)
Na(2)	7013(3)	6019(3)	2689(2)	O(27)	7543(5)	8662(5)	2865(4)
Na(3)	7939(3)	5142(3)	1698(2)	O(28)	7965(6)	7753(5)	3685(4)
Na(4)	9088(8)	2017(7)	1953(5)	O(29)	6607(5)	8248(5)	3487(4)
Na(5)	5971(7)	5108(5)	4782(5)	O(30)	7530(6)	6405(5)	3735(5)
Na(6)	9025(7)	8124(11)	1757(9)	O(31)	6291(5)	6993(5)	3880(4)
O(W1)	7777(4)	4986(5)	2700(4)	O(32)	6063(4)	7244(5)	2812(4)
O(W2)	10303(13)	2736(13)	2167(10)	O(33)	7965(5)	6799(5)	2877(4)
O(W3)	9403(11)	896(23)	1797(28)	O(34)	8335(6)	2610(6)	2449(4)
O(W4)	6939(17)	4256(13)	5167(10)	O(35)	6625(7)	5654(6)	4209(5)
O(W5)	5832(13)	6002(28)	5610(10)	O(36)	9100(5)	6893(6)	1948(5)
O(W6)	9773(14)	8084(16)	2547(12)	O(37)	6073(5)	4337(5)	1304(4)
O(W7)	9291(15)	7749(16)	877(12)	O(38)	5421(6)	5200(6)	1883(4)
				O(39)	6261(5)	5737(5)	1206(4)

[a] Atomic thermal parameters may be obtained from the authors.

Table 3a

Coordinates of C atoms ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
C(1)	6486(7)	3104(8)	799(6)	C(67)	8544(7)	3966(7)	4326(6)
C(2)	6417(10)	2466(9)	1030(7)	C(68)	8965(6)	3483(9)	4651(6)
C(3)	6195(10)	1851(10)	724(8)	C(69)	9528(10)	3670(10)	5023(8)
C(4)	5893(9)	1885(10)	197(7)	C(70)	9684(9)	4431(12)	5114(7)
C(5)	5924(8)	2568(12)	−52(7)	C(71)	9269(8)	4937(11)	4787(7)
C(6)	6195(8)	3163(10)	239(6)	C(72)	8681(10)	4680(9)	4370(7)
C(7)	7390(9)	4790(8)	−188(7)	C(73)	8745(8)	1837(10)	3405(6)
C(8)	7545(10)	4548(10)	−676(9)	C(74)	9424(9)	2147(13)	3607(9)
C(9)	7199(23)	4903(30)	−1266(15)	C(75)	10 077(18)	1818(16)	3828(14)
C(10)	6886(20)	5114(20)	−1257(8)	C(76)	9884(10)	1102(19)	3896(11)
C(11)	6562(14)	5505(12)	−837(12)	C(77)	9217(14)	635(13)	3623(12)
C(12)	6851(12)	5336(14)	−261(8)	C(78)	8613(12)	1118(13)	3427(13)
C(13)	8668(9)	2366(10)	312(6)	C(79)	5898(8)	1336(9)	2781(7)
C(14)	9341(22)	1955(19)	255(10)	C(80)	5688(9)	1282(10)	2229(9)
C(15)	9097(10)	1334(21)	29(13)	C(81)	5222(11)	625(12)	2037(10)
C(16)	8450(15)	1061(12)	−199(11)	C(82)	5051(9)	207(9)	2467(13)
C(17)	7759(15)	1443(15)	−163(9)	C(83)	5238(18)	243(21)	2974(13)
C(18)	7953(11)	2169(15)	100(9)	C(84)	5658(10)	832(9)	3137(8)
C(19)	11 012(10)	4061(16)	1052(8)	C(85)	6667(7)	7078(7)	850(5)
C(20)	11 387(19)	4252(53)	1360(15)	C(86)	6041(8)	7404(10)	625(7)
C(21)	12 076(38)	3656(14)	1542(14)	C(87)	6085(11)	7964(9)	241(8)
C(22)	12 519(10)	4127(20)	1182(8)	C(88)	6680(10)	8111(9)	60(8)
C(23)	12 182(12)	3816(25)	839(16)	C(89)	7332(10)	7785(11)	266(8)
C(24)	11 298(18)	4229(18)	633(12)	C(90)	7299(11)	7257(11)	653(7)
C(25)	11 199(8)	4511(10)	2810(6)	C(91)	5067(8)	7668(8)	1866(7)
C(26)	10 927(8)	4669(11)	2819(8)	C(92)	4535(9)	7207(10)	1900(10)
C(27)	11 410(8)	4574(11)	3336(8)	C(93)	3769(10)	7358(15)	1614(11)
C(28)	11 234(8)	4279(11)	3772(7)	C(94)	3583(10)	8003(12)	1396(10)
C(29)	10 485(9)	4071(12)	3745(7)	C(95)	4123(9)	8482(11)	1392(8)
C(30)	9950(9)	4236(9)	3269(6)	C(96)	4860(9)	8341(8)	1609(7)
C(31)	10 559(8)	6440(10)	1905(6)	C(97)	7367(8)	9340(9)	1855(6)
C(32)	10 833(9)	6730(13)	2415(8)	C(98)	7601(10)	9357(10)	1343(8)
C(33)	11 603(12)	6947(14)	2594(11)	C(99)	7776(15)	9949(12)	1047(10)
C(34)	11 978(12)	6863(17)	2260(10)	C(100)	7584(12)	10 623(15)	1334(11)
C(35)	11 770(13)	6418(29)	1856(15)	C(101)	7316(10)	10 711(9)	1874(9)
C(36)	11 001(10)	6215(23)	1591(10)	C(102)	7287(9)	10 014(11)	2131(9)
C(37)	8991(9)	5931(14)	−50(7)	C(103)	7703(7)	9187(8)	3962(6)
C(38)	8602(21)	6453(24)	−205(13)	C(104)	8257(8)	9164(10)	4402(7)
C(39)	8560(16)	6850(25)	−911(23)	C(105)	8397(8)	9778(7)	4755(6)
C(40)	8716(13)	6485(18)	−1003(13)	C(106)	7965(8)	10 380(8)	4651(6)
C(41)	9034(16)	5885(19)	−1091(9)	C(107)	7424(8)	10 392(8)	4206(7)
C(42)	9240(17)	5514(20)	−483(10)	C(108)	7297(8)	9797(8)	3848(7)
C(43)	4578(6)	5177(7)	2711(5)	C(109)	9045(8)	6709(8)	3834(7)
C(44)	3958(7)	4764(8)	2477(7)	C(110)	9437(8)	6269(9)	3562(8)
C(45)	3284(8)	4995(12)	2615(8)	C(111)	10 184(10)	6077(12)	3806(11)
C(46)	3221(9)	5574(10)	2947(7)	C(112)	10 476(13)	6339(17)	4319(12)
C(47)	3813(8)	5931(12)	3163(9)	C(113)	10 076(11)	6734(11)	4630(9)
C(48)	4514(9)	5743(10)	3036(8)	C(114)	9320(11)	6952(11)	4368(8)
C(49)	4665(8)	2889(8)	2248(8)	C(115)	7377(9)	6745(9)	4826(6)
C(50)	4736(11)	2900(11)	1692(9)	C(116)	7714(14)	6216(15)	5170(9)
C(51)	4188(13)	2573(13)	1275(9)	C(117)	8094(18)	6408(16)	5739(14)
C(52)	3688(10)	2246(11)	1427(24)	C(118)	8093(14)	7191(17)	5856(11)
C(53)	3542(11)	2209(12)	1951(11)	C(119)	7845(13)	7701(12)	5496(10)
C(54)	4067(9)	2523(10)	2404(11)	C(120)	7438(19)	7470(18)	5015(10)

Table 3a (continued)

Atom	x	y	z	Atom	x	y	z
C(55)	4582(7)	3726(7)	4327(6)	C(121)	5115(8)	7896(8)	3458(6)
C(56)	4662(9)	3641(10)	4884(7)	C(122)	4745(9)	7572(10)	3896(8)
C(57)	4065(9)	3877(10)	5160(7)	C(123)	4072(11)	7747(11)	3907(9)
C(58)	3412(9)	4135(10)	4866(7)	C(124)	3716(11)	8276(13)	3574(12)
C(59)	3342(8)	4248(11)	4300(8)	C(125)	4082(11)	8591(11)	3137(9)
C(60)	3942(9)	4010(11)	4015(8)	C(126)	4766(11)	8399(11)	3107(8)
C(61)	6961(8)	2146(8)	4902(6)	C(127)	4892(10)	5090(10)	745(9)
C(62)	6613(12)	1534(11)	5061(8)	C(128)	4250(9)	5106(16)	724(16)
C(63)	6896(15)	1164(10)	5561(8)	C(129)	3538(11)	5168(20)	213(15)
C(64)	7439(15)	1373(14)	5917(8)	C(130)	3907(9)	4942(14)	23(18)
C(65)	7831(12)	1996(15)	5773(8)	C(131)	4495(25)	4903(14)	−297(10)
C(66)	7579(9)	2406(12)	5266(8)	C(132)	5125(19)	4961(12)	207(12)

4.08%, which coincides better with the elemental analysis data than the ±0.5 atom for all the elements (excluding hydrogen).

Crystals of I are monoclinic; at −120 °C a 18.714(4), b 18.797(4), c 24.735(6) Å, β 99.98(2)°, V 8569(1) Å^3, $Z = 2$, d_{calc} 1.31 g/cm^3, space group $P2_1$.

The unit cell parameters and the intensities of 11840 reflections were measured with a Syntex $P2_1$ diffractometer (−120 °C, λ(Mo-K_α), graphite monochromator,

Table 4

Relevant bond lengths (Å) in cobaltasiloxane framework (e.s.d.'s 0.01 Å) [a]

Co(1)–O(1)	1.98	Si(5)–O(11)	1.57	Si(14)–O(20)	1.60
Co(1)–O(2)	1.96	Si(6)–O(8)	1.65	Si(14)–O(21)	1.64
Co(1)–O(11)	1.96	Si(6)–O(9)	1.61	Si(15)–O(23)	1.59
Co(1)–O(34)	1.92	Si(6)–O(36)	1.63	Si(15)–O(26)	1.66
Co(2)–O(12)	1.99	Si(7)–O(7)	1.61	Si(15)–O(39)	1.57
Co(2)–O(13)	1.96	Si(7)–O(9)	1.64	Si(16)–O(25)	1.64
Co(2)–O(22)	1.95	Si(7)–O(10)	1.65	Si(16)–O(26)	1.61
Co(2)–O(35)	1.93	Si(8)–O(12)	1.58	Si(16)–O(32)	1.62
Co(3)–O(23)	2.01	Si(8)–O(15)	1.68	Si(17)–O(24)	1.57
Co(3)–O(24)	1.97	Si(8)–O(38)	1.63	Si(17)–O(25)	1.64
Co(3)–O(33)	1.94	Si(9)–O(14)	1.57	Si(17)–O(27)	1.64
Co(3)–O(36)	1.93	Si(9)–O(15)	1.61	Si(18)–O(27)	1.62
Si(1)–O(1)	1.58	Si(9)–O(21)	1.64	Si(18)–O(28)	1.62
Si(1)–O(4)	1.65	Si(10)–O(13)	1.57	Si(18)–O(29)	1.63
Si(1)–O(37)	1.62	Si(10)–O(14)	1.67	Si(19)–O(28)	1.65
Si(2)–O(3)	1.62	Si(10)–O(16)	1.67	Si(19)–O(30)	1.64
Si(2)–O(4)	1.61	Si(11)–O(16)	1.61	Si(19)–O(33)	1.55
Si(2)–O(10)	1.65	Si(11)–O(17)	1.61	Si(20)–O(30)	1.65
Si(3)–O(2)	1.55	Si(11)–O(18)	1.63	Si(20)–O(31)	1.66
Si(3)–O(3)	1.62	Si(12)–O(17)	1.62	Si(20)–O(35)	1.58
Si(3)–O(5)	1.66	Si(12)–O(19)	1.63	Si(21)–O(29)	1.62
Si(4)–O(5)	1.64	Si(12)–O(22)	1.59	Si(21)–O(32)	1.59
Si(4)–O(6)	1.62	Si(13)–O(19)	1.61	Si(21)–O(32)	1.63
Si(4)–O(7)	1.63	Si(13)–O(20)	1.63	Si(22)–O(37)	1.60
Si(5)–O(6)	1.63	Si(13)–O(34)	1.59	Si(22)–O(38)	1.59
Si(5)–O(8)	1.62	Si(14)–O(18)	1.62	Si(22)–O(39)	1.67

[a] The Si–C bond lengths are 1.81–1.92 Å (av. 1.85 Å), e.s.d.'s 0.01–0.02 Å.

Table 5

Bond angles (°) at Co and O atoms in anionic framework (e.s.d.'s 0.4–0.5° and 0.6–0.8° respectively) [a]

O(1)Co(1)O(2)	117.7	Co(2)O(12)Si(8)	121.8
O(1)Co(1)O(11)	99.8	Co(2)O(13)Si(10)	142.8
O(1)Co(1)O(34)	107.7	Si(9)O(14)Si(10)	141.7
O(2)Co(1)O(11)	111.1	Si(8)O(15)Si(9)	147.1
O(2)Co(1)O(34)	100.3	Si(1)O(16)Si(11)	138.4
O(11)Co(1)O(34)	121.4	Si(11)O(17)Si(12)	153.6
O(12)Co(2)O(13)	118.3	Si(11)O(18)Si(14)	140.7
O(12)Co(2)O(22)	98.3	Si(12)O(19)Si(13)	157.4
O(12)Co(2)O(35)	113.3	Si(13)O(20)Si(14)	143.8
O(13)Co(2)O(22)	110.9	Si(9)O(21)Si(14)	139.7
O(13)Co(2)O(35)	95.6	Co(2)O(22)Si(12)	135.5
O(22)Co(2)O(35)	121.9	Co(3)O(23)Si(15)	120.8
O(23)Co(3)O(24)	118.5	Co(3)O(24)Si(17)	132.0
O(23)Co(3)O(33)	101.3	Si(16)O(25)Si(17)	145.0
O(23)Co(3)O(36)	109.1	Si(15)O(26)Si(16)	147.4
O(24)Co(3)O(33)	104.1	Si(17)O(27)Si(18)	145.9
O(24)Co(3)O(36)	102.2	Si(18)O(28)Si(19)	140.3
O(33)Co(3)O(36)	122.7	Si(18)O(29)Si(21)	140.2
Co(1)O(1)Si(1)	126.3	Si(19)O(30)Si(20)	139.7
Co(1)O(2)Si(3)	139.3	Si(20)O(31)Si(21)	146.2
Si(2)O(3)Si(3)	149.5	Si(16)O(32)Si(21)	142.2
Si(1)O(4)Si(2)	145.3	Co(3)O(33)Si(19)	152.9
Si(3)O(5)Si(4)	133.0	Co(1)O(34)Si(13)	136.0
Si(4)O(6)Si(5)	157.3	Co(2)O(35)Si(20)	128.4
Si(4)O(7)Si(7)	138.5	Co(3)O(36)Si(6)	133.4
Si(5)O(8)Si(6)	150.1	Si(1)O(37)Si(22)	147.4
Si(6)O(9)Si(7)	142.8	Si(8)O(38)Si(22)	148.2
Si(2)O(10)Si(7)	134.2	Si(15)O(39)Si(22)	148.6
Co(1)O(11)Si(5)	137.2		

[a] The OSiO bond angles are 102.4–114.2°, e.s.d.'s 0.6°.

$\theta/2\theta$ scan, $2\theta_{\max}$ 49°). 10107 reflections with $I > 2\sigma(I)$ were used for solving the structure and in the refinement. The structure contained 209 independent non-hydrogen atoms, and was solved by direct methods, with ca. 50 cobaltasiloxane framework atoms being localized in the *E*-synthesis. A subsequent series of electron-density syntheses revealed the positions of the remaining framework atoms, Na^+ cations, O atoms of the intra-framework water molecule, and ca. 100 carbon atoms of the Ph rings. The remaining non-hydrogen atoms were located by difference syntheses during refinement. The structure was refined by block-diagonal least squares, first isotropically to $R = 0.17$ and then anisotropically to $R = 0.14$. This stage indicated that the reflections with small θ's had been measured with a large degree of error. An appropriate restriction on the number of reflections ($\sin\theta/\lambda \geqslant 0.075$) made it possible to proceed with the refinement and so all the non-hydrogen atoms were revealed. Nevertheless, four of the 22 Ph rings retained their strong geometrical distortions and high temperature parameters of the C atoms. The study, which was aimed primarily at determining the structure of the cobaltasiloxane anion framework, and the arrangement of the cations and water molecules, was successful so that it was decided to terminate the procedure at this stage, because further procedures would require much computer time. Finally, $R = 0.075$, $R_w = 0.082$ for 9208 reflections with $I > 3\sigma(I)$.

Despite the absence of eight hydrogen atoms, as compared with the elemental analysis data, the observed structure of I is completely "saturated" with such atoms. Increasing their number is only possible at the expense of the undetected water molecules whose presence, however, is doubtful since the heights of the final zero synthesis peaks do not exceed 0.7 e/Å^3.

All calculations were performed with an Eclipse S/200 computer using INEXTL programs [13]. Atomic coordinates are given in Tables 3 and 3a, the relevant bond lengths and bond angles in the cobaltasiloxane framework are listed in Tables 4 and 5.

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