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Synthesis and structure of unusual skeletal cylindrical nickel cyclohexasiloxanolates

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ABSTRACT. Two unusual skeletal cylindrical nickel cyclohexasiloxanolates were synthesised as complexes with sodium chloride—$Na^+[(PhSiO_2)_6Ni_6(O_2SiPh)_6Cl]^-.14Bu^nOH$ and $Na^+.[(PhSiO_2)_6Ni_6(O_2SiPh)_6Cl]^-.9EtOH.4H_2O$, whose structures were determined by X-ray diffraction. The isostructural nickel siloxanolate molecules in these complexes have a sandwich structure: two "external" 12-membered cyclohexasiloxanolate ligands are coordinated to six Ni atoms distributed between them in a hexagonal arrangement, each silanolate O atom being linked to two Ni atoms and each Ni atom being coordinated to four silanolate O atoms (two atoms from each cyclic ligand). This Ni, Si, O skeleton has a non-crystallographic symmetry *6/mmm* and has the form of a cylinder in the centre of the inner cavity of which the Cl^- anion is encapsulated and is coordinated to six Ni atoms arranged in the form of a planar hexagon. The Na^+ counterion is outside the nickel siloxanolate molecule and is coordinated to the O atom of the siloxane rings and the solvating molecules. The coordination of the Ni atoms corresponds to a distorted tetragonal bipyramid: with four silanolate O atoms in the equatorial positions, an O atom of the solvating molecule in the proximal apical position, and the Cl^- ion in the distal apical position.

Polymetallosiloxanes have attracted attention in recent years as promising catalysts[1] and as models for the study of the structures and properties of the chemically modified surfaces of metals and semiconductors.[2] Nevertheless, the structure of polymetallosiloxanes and the dependence of their structural organisation on the initial compounds and the conditions of synthesis have been scarcely studied. One can only note the demonstration by X-ray diffraction of the trimeric structure of the anionic metallosiloxane skeleton made up of three incomplete cobaltasilsesquioxane cells within the $Na_6[(PhSiO_{1.5})_{22}Co_3O_6].7H_2O$ (I) crystal[3] and our recent X-ray diffraction study of the neutral octanuclear phenylsiloxanenickel oxide $[(PhSiO)_6(\mu\text{-}O)_6(Ni_8O_2)(\mu\text{-}O)_6(PhSiO)_6].14Bu^nOH.10H_2O.2Me_2CO$ (II).[4]

This communication describes an X-ray diffraction study of new hexanickel polymetallosiloxanes consisting of the solvates of complexes of nickel cyclohexasiloxanolates with sodium chloride: $Na^+[(PhSiO_2)_6Ni_6(O_2SiPh)_6Cl]^-.14Bu^nOH$ (III) and $Na^+[(PhSiO_2)_6.Ni_6(O_2SiPh)_6Cl]^-.9EtOH.4H_2O$ (IV). It was found that compounds (III) and (IV) have a completely unexpected non-trivial structure consisting of cylindrical skeletal hexanickel bis(cyclohexaphenylsiloxanolates) with an encapsulated Cl^- anion. In the synthesis of compounds (III) and (IV), a general method involving the exchange interaction of sodium organosilanolate with the metal chloride was used to introduce the metal atom (here, Ni) into the siloxane skeleton. This results in the formation of mainly amorphous polymeric mixtures of polymetallosiloxanes with different Si:M (M = Ni) ratios. However, it was possible to isolate pale-green crystals of compound (III) and yellow-green crystals of compound (IV), which were suitable for the X-ray diffraction experiment.

Table 1. The principal bond lengths in the structures of compounds (III) and (IV)*.

Bond	*d*, Å (III)	*d*, Å (IVA)	Bond	*d*, Å (IVB)
Ni(1)–O(1b)	2.057(6)	2.024(3)	Ni(4)–O(19b)	2.051(3)
Ni(1)–O(2b)	2.021(6)	2.081(3)	Ni(4)–O(20b)	2.023(3)
Ni(1)–O(3b)	2.030(6)	2.032(3)	Ni(4)–O(21b)	2.013(3)
Ni(1)–O(4b)	2.037(6)	2.001(3)	Ni(4)–O(22b)	2.021(3)
Ni(1)–O(7b) (in IVA–O(7d))	2.058(5)	2.043(4)	Ni(4)–O(25d)	2.070(4)
Ni(1)...Cl	2.898(1)	2.960(1)	Ni(4)...Cl(2)	2.831(1)
Ni(2)–O(3b)	2.038(6)	2.012(3)	Ni(5)–O(21b)	1.996(4)
Ni(2)–O(4b)	2.004(6)	2.033(3)	Ni(5)–O(22b)	2.031(3)
Ni(2)–O(5b)	2.053(6)	2.030(3)	Ni(5)–O(23b)	2.074(3)
Ni(2)–O(6b)	2.038(6)	2.009(4)	Ni(5)–O(24b)	2.002(3)
Ni(2)–O(8c) (in IVA–O(8d))	2.072(6)	2.033(3)	Ni(5)–O(26d)	2.046(4)
Ni(2)...Cl	2.884(1)	2.838(1)	Ni(5)–Cl(2)	2.907(1)
Ni(3)–O(1b)	2.059(6)	2.026(3)	Ni(6)–O(19b)	2.044(3)
Ni(3)–O(2b)	2.007(6)	2.064(3)	Ni(6)–O(24b)	2.013(3)
Ni(3)–O(5b)	2.093(6)	2.023(3)	Ni(6)–O(23b)	2.047(3)
Ni(3)–O(6b)	2.033(6)	2.020(3)	Ni(6)–O(24b)	1.998(3)
Ni(3)–O(9c) (in IV–O(9d))	2.069(5)	2.056(4)	Ni(6)–O(27d)	2.070(4)
Ni(3)...Cl	2.837(1)	2.824(1)	Ni(6)...Cl(2)	2.856(1)
Si(1)–O(1b)	1.586(8)	1.586(3)	Si(7)–O(19b)	1.610(3)
Si(1)–O(10a)	1.635(6)	1.635(4)	Si(7)–O(29a)	1.631(4)
Si(1)–O(15a)	1.626(6)	1.639(4)	Si(7)–O(33a)	1.627(3)
Si(2)–O(3b)	1.580(8)	1.585(3)	Si(8)–O(21b)	1.595(3)
Si(2)–O(10a)	1.627(6)	1.635(4)	Si(8)–O(28a)	1.637(4)
Si(2)–O(11a)	1.621(6)	1.636(4)	Si(8)–O(29a)	1.625(4)
Si(3)–O(5b)	1.602(8)	1.582(3)	Si(9)–O(23b)	1.616(3)
Si(3)–O(11a)	1.630(6)	1.644(4)	Si(9)–O(29a)	1.621(4)
Si(3)–O(12a)	1.612(6)	1.651(3)	Si(9)–O(30a)	1.625(3)
Si(4)–O(2b)	1.596(8)	1.597(3)	Si(10)–O(20b)	1.597(3)
Si(4)–O(12a)	1.663(7)	1.646(3)	Si(10)–O(30a)	1.620(3)
Si(4)–O(13a)	1.611(6)	1.635(4)	Si(10)–(31a)	1.635(4)
Si(5)–O(4b)	1.598(8)	1.590(3)	Si(11)–O(22b)	1.597(3)
Si(5)–O(13a)	1.655(6)	1.639(4)	Si(11)–O(31a)	1.635(3)
Si(5)–O(14a)	1.621(6)	1.640(4)	Si(11)–O(32a)	1.624(4)
Si(6)–O(6b)	1.576(8)	1.585(3)	Si(12)–O(24b)	1.599(3)
Si(6)–O(14a)	1.633(6)	1.628(4)	Si(12)–O(32a)	1.629(4)
Si(6)–O(15a)	1.643(6)	1.634(3)	Si(12)–O(32a)	1.625(3)
Ni(1)...Ni(2)	2.874(1)	2.866(1)	Ni(4)...Ni(5)	2.851(1)
Ni(1)...Ni(3)	2.879(1)	2.877(1)	Ni(4)...Ni(6)	2.861(1)
Ni(2)...Ni(3)	2.867(1)	2.883(1)	Ni(5)...Ni(6)	2.881(1)
Na...O(10a)	3.27(1)	2.512(5)		
Na...O(211a)	3.26(1)	2.696(5)		
Na...O(12a)	3.00(1)	2.606(5)		
Na...O(13a)	3.14(1)	3.481(5)		
Na...O(14a)	3.38(1)	2.981(5)		
Na...O(15a)	2.92(1)	2.624(5)		
Na...O(18c) [O(17g) in IV]	2.81(1)	2.360(5)		
Na...O(19c) [O(W1) in IV]	2.78(1)	2.305(5)		

* [a]siloxane O atoms; [b]silanolate O atoms; [c]O atoms of the BuOH molecules; [d]O atoms of the EtOH molecules.

Results and discussion

The X-ray diffraction study showed that the crystals of compounds (III) and (IV) are made up of structurally identical cylindrical centrosymmetrical nickel cyclohexasiloxanolate neutral skeletons with the non-crystallographic symmetry *6/mmm* surrounded by a framework of Ph groups linked to the silicon atoms of the solvating BuOH [in compound (III)] or EtOH [in compound (IV)] molecules linked to the Ni atoms (Figs. 1 and 2). The principal interatomic distances and bond angles in the structures of compound (III) and (IV) are listed in Tables 1 and 2.

Table 2. The bond angles at the Ni and Si atoms in the structures of compound (III) and (IV)*.

Angle	ω, deg		Angle	ω, deg
	(III)	(IVA)		(IVB)
O(1)Ni(1)O(2)	81.1(2)	80.2(1)	O(19)Ni(4)O(20)	80.7(1)
O(1)Ni(1)O(3)	97.0(2)	99.3(1)	O(19)Ni(4)O(21)	98.4(1)
O(1)Ni(1)O(4)	167.3(3)	165.2(1)	O(19)Ni(4)O(22)	169.5(1)
O(1)Ni(1)O(7)	96.6(2)	99.3(1)	O(19)Ni(4)O(25)	90.6(1)
O(2)Ni(1)O(3)	165.6(2)	165.5(1)	O(20)Ni(4)O(21)	167.7(1)
O(2)Ni(1)O(4)	99.0(2)	97.0(1)	O(20)Ni(4)O(22)	97.2(1)
O(2)Ni(1)O(7)	96.1(3)	98.5(1)	O(20)Ni(4)O(25)	94.9(1)
O(3)Ni(1)O(4)	79.7(2)	80.0(1)	O(21)Ni(4)O(22)	81.4(1)
O(3)Ni(1)O(7)	98.3(2)	95.0(1)	O(21)Ni(4)O(25)	97.4(1)
O(4)Ni(1)O(7)	96.0(2)	100.5(1)	O(22)Ni(4)O(25)	99.9(1)
ClNi(1)O(1)	83.6(2)	82.38(9)	Cl(2)Ni(4)O(19)	84.74(9)
ClNi(1)O(9)	81.5(2)	83.77(9)	Cl(2)Ni(4)O(20)	83.91(9)
ClNi(1)O(3)	84.1(2)	82.83(9)	Cl(2)Ni(4)O(21)	83.75(9)
ClNi(1)O(4)	83.8(2)	82.85(9)	Cl(2)Ni(4)O(22)	84.80(9)
ClNi(1)O(7)	177.5(2)	175.7(1)	Cl(2)Ni(4)O(25)	175.3(1)
O(1)Si(1)O(10)	112.0(3)	112.2(2)	O(19)Si(7)O(28)	111.3(2)
O(1)Si(1)O(15)	112.8(3)	113.5(2)	O(19)Si(7)O(33)	112.6(2)
O(1)Si(1)C(1)	111.8(4)	114.0(2)	O(19)Si(7)C(55)	111.3(2)
O(10)Si(1)O(15)	107.0(4)	102.3(2)	O(28)Si(7)O(33)	108.8(2)
O(10)Si(1)C(1)	106.7(4)	108.8(2)	O(28)Si(7)C(55)	106.4(2)
O(15)Si(1)C(1)	106.0(4)	105.3(2)	O(33)Si(7)C(55)	106.1(2)

*The bond angles at one of the Ni and Si atoms are quoted in view of the non-crystallographic symmetry *6/mmm* of the Ni, Si, O skeleton. For the types of O atoms, see Table 1.

The Cl^- anions are encapsulated at the centres of the cylindrical cavities of the skeletons, while the Na^+ counterions are located outside the skeletons and are coordinated to their siloxane O atoms and the solvating alcohol or water molecules (Figs. 3 and 4). In the crystal of compound (IV), made up of two crystallographically independent anionic complexes (IVA) and (IVB), the Na^+ cations are located in the vicinity of only one of them, namely (IVA).

As in the structure of compound (II), the Ni, Si, O skeletons in the structures of compounds (III) and (IV) are neutral and have a hybrid (internally heterodesmic) sandwich structure: the inner metallic fragment, made up of Ni atoms not linked to one another and located at the vertices of a planar hexagon, is incorporated between two outer cyclohexasilohexanolate "lids". The Ni_6 layer and the 12-membered siloxane rings are linked via the silanolate O atoms (Ni—O—Si bridges). However, the skeletons in compounds (III) and (IV) differ fundamentally from that of compound (II): the Ni_6 layer of $Ni_6(\mu\text{-}O)_{12/2}$ (the bridges consist of the silanolate O atoms) in compounds (III) and (IV) are obtained from the $Ni_8O_2(\mu\text{-}O)_{12/2}$ nickel oxide layer in compound (II) by the removal of two Ni atoms and two oxide O atoms. As a result, a cavity is generated within the Ni, Si, O skeleton in compound (III) and (IV), the coordination of all six Ni atoms to the siloxanolate rings ("lids") becomes identical, and the lids are in fact arranged exactly one on top of the other without any displacements (Figs. 1 and 2), so that the skeletons in compounds (III) and (IV) acquire an intrinsic approximate *6/mmm* symmetry.

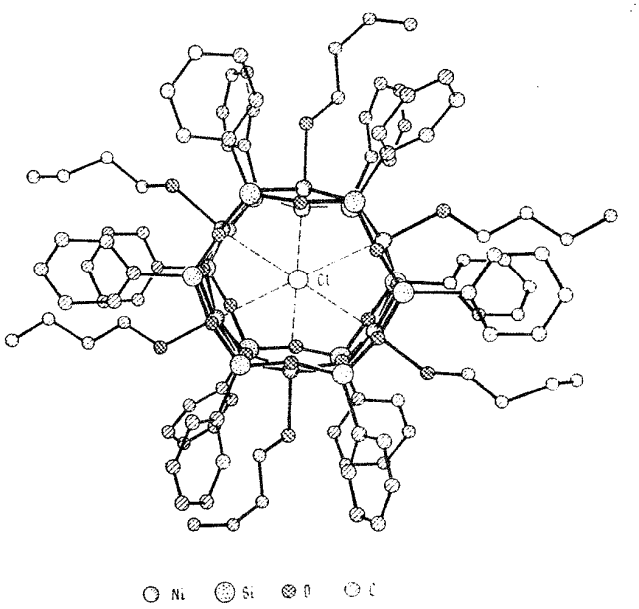
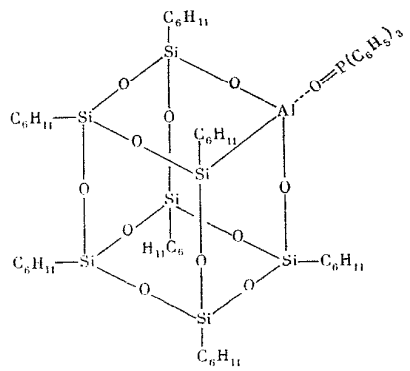


Figure 1. Projection of the anionic nickel cyclohexaphenylsilanolate complex with an encapsulated Cl^- anion onto the Ni(6) plane in the structure of compound (III).

We emphasise that the common feature of the polymetallosiloxanes (II), (III), and (IV) is the linking of the metal atoms to the organosilicon component of the molecules via bridging silanolate O atoms. This part (cyclohexasiloxanolate ligands) remains unchanged (with the exception of the deprotonation of the silanolate groups) on formation of complexes (II)—(IV).

This distinguishes the structure of complexes (II)—(IV) from the trimeric anionic cobaltasilsesquioxane (I) in which the Co atoms form part of the silsesquioxane skeleton, replacing some of the Si atoms in it. The aluminosilsesquioxane (V),[5] in the molecule of which the Al atom substitutes one of the vertices of the silsesquioxane cube, belongs to the same type of polymetallosiloxane as complex (I). The hydrolysis of compounds (I) and (V) should therefore lead, in contrast to complexes (II)—(IV), to a significant

change in the structure of the organosilicon components of their molecules.



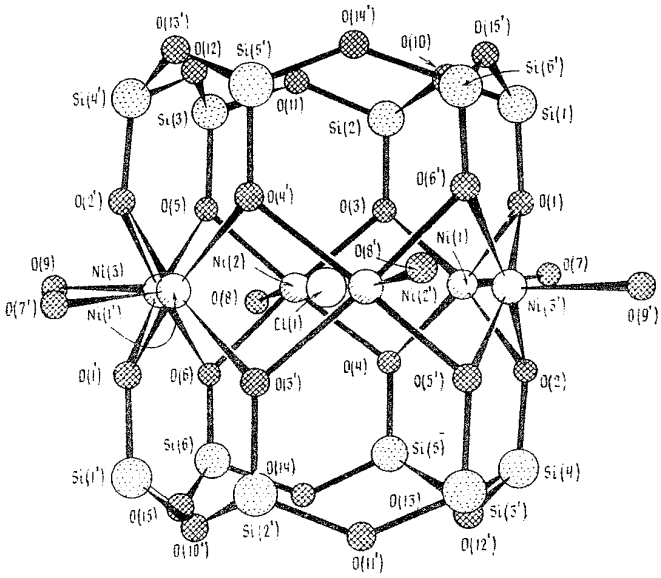


Figure 2. The Ni, Si, O skeleton with an encapsulated Cl^- anion in the structures of compounds (III) and (IV). The O atoms of the apical ligands are also shown. The O(13) atom is concealed under the Si(3′) atom. The atoms designated by primed numbers are linked to the "unprimed" numbers via the centre of symmetry.

Nickel siloxanolates (II) and (IV) differ fundamentally from phenylsiloxanenickel oxide (II) by the fact that the Ni atoms in the first two compounds form the $Ni_6O_{12/2}$ ring and not a fragment of the NiO crystal structure (a "lump" of the continuous NiO layer), which is observed in the crystal of compound (II). Furthermore, in contrast to the structure of compound (II), where Ni atoms of three types are present (although they are all involved in a relatively undistorted octahedral coordination with six O atoms, which are also of several different types), in the structures of compounds (III) and (IV) all the Ni atoms are in fact (albeit non-crystallographically) equivalent. Their coordination environment consists of a not entirely symmetrical tetragonal [4 + 1 + 1] bipyramid (Fig. 2).

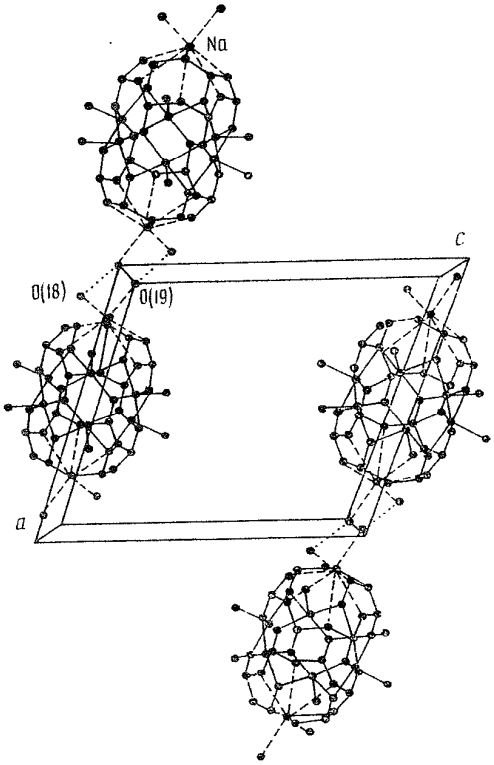


Figure 3. The *ac* projection of the structure of compound (III). The dashed lines indicate the coordination of the Na^+ cations and the dotted lines denote the hydrogen bonds. Only the Ni, Si, O skeletons and the O atoms of the butanol molecules (ethanol and water molecules in Fig. 4), coordinated to the Ni atom and the Na^+ ions, are shown.

The equatorial positions of the bipyramid contain the μ_3-silanolate† O(1)...O(6) and O(1′)...O(6′) atoms and the external (relative to the skeleton) apical positions contain almost as strongly bound O(7)...O(9) and O(7′)...O(9) atoms of the butanol molecules in compound (III) and ethanol molecules in compound (IV). In the apical positions of the second type ("internal") all six Ni atoms are occupied by one (!) encapsulated Cl^- anion (Figs. 1 and 2). The six bipyramids, joined together via opposite equatorial edges, form an annular Ni_6O_{12} belt in the middle part of the cylindrical skeleton.

The apical and equatorial Ni–O distances differ little [2.058(5)–2.072(6) Å and 2.004(6)–2.093(6) Å in compound (III) and 2.033(4)–2.070(4) Å and 1.996(4)–2.081(4) Å in compound (IV)] and are close to the values observed, for example, in compound (II) [2.006–2.176(9) Å] or in NiO [2.097(1) Å [6]]. On the other hand, the "second" apical distances to the encapsulated Cl^- anions [2.837(1)–2.898(1) Å in compound (III) and 2.824(1)–2.960(1) Å in compound (IV)] greatly exceed the Ni–Cl bond length (2.47 Å) in the $NiCl_2$ structure (the $CoCl_2$ structural type)[7] and are closer to the sum of the ionic radii of Cl^- and Ni^{2+} (3.19 Å).[7] Naturally the Ni

† The atoms with the numbers *n* and *n′* are linked via the centres of symmetry of the Ni, Si, O skeletons.

atoms deviate from the planes of the equatorial O atoms towards the apical O atoms of the solvating molecules on average by 0.25 Å in compound (III) and by 0.22 and 0.21 Å in compounds (IVA) and (IVB).

The difference between the ways in which the Ni polyhedra are combined in compounds (III) and (IV), on the one hand, and in compound (II), on the other, leads, in particular, to a difference between the Ni...Ni distances in compounds (II) and (IV) [2.851–2.879(1) Å] and those in compound (II) [3.073–3.156(2) Å[. All these distances are significantly greater than in metallic nickel (2.70 Å [7]).

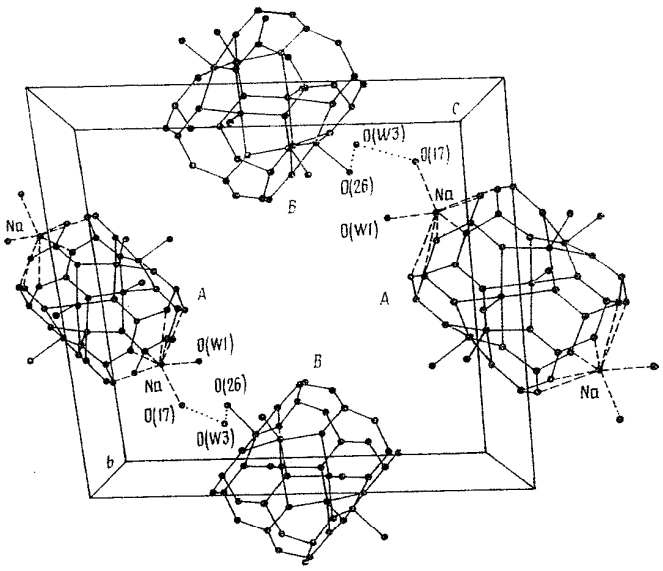


Figure 4. The *bc* projection of the structure of compound (IV) (for explanation, see Fig. 3).

The planar (!) hexenary coordination to the metal atoms of the Cl^- anions located in the centres of the cavities of the cylindrical skeletons, observed in the crystals of compound (II) and (III), is unusual and, so far as we are aware, this is the first observation. The formally neutral Ni atoms in reality have a fairly significant positive charge and the electrostatic interaction of the encapsulated Cl^- anions with the Na^+ counterions located outside the Ni, Si, O skeletons is greatly weakened as a consequence of the large distance between them [$Cl^-...Na^+$ = 5.28(1) Å in compound (III) and 4.64(1) Å in compound (IV), while the sum of the ionic radii is 3.43 Å.[7]].

It is remarkable that, despite the unusual planar coordination of the Cl^- anions, an increase as well as a marked anisotropy of the thermal parameters are not observed [for example the values of B_{eq}^{iso} for the Ni atoms in compound (IV) are 1.38(2), 1.32(2), and 1.35(2) Å^2, while the value for the Cl^- anion is 2.21(2) Å^2]. Apart from the $Cl^-...6Ni^{\delta+}$ attractive interactions already mentioned, an additional cause of the rigid fixation of the Cl^- anions in the plane of the Ni(6) skeletons in compounds (III) and (IV) is probably $Cl^-...O^{\delta-}$ electrostatic repulsion between the Cl^- anions and the 12 negatively charged silanolate O atoms surrounding them and disposed above and below the Ni(6)Cl^- layer (Fig. 2).

We shall consider in greater detail the geometry of certain structural fragments of the skeletons of compounds (III) and (IV) (Fig. 2). The Ni(6) layers in compounds (III) and (IV) are in fact planar, the maximum deviations of the Ni atoms from their average planes amounting to 0.009 Å in compound (III) and 0.01 and 0.009 Å in compounds (IVA) and (IVB). All the six-membered nickel–siloxane rings NiOSiOSiO in the structure of compounds (III) (6 rings) and (IV) (12 rings) have a virtually planar conformation: the maximum deviation from the mean square plane of the ring is 0.13 Å for the O(10) atom in compound (III), 0.18 Å for the Si(4) atom in compound (IVA), and 0.14 Å for the Si(12) atom in compound (IVB). In contrast to compound (II), the four-membered $(NiO)_2$ rings in compounds (III) and (IV) are non-planar; the angle of bend along the Ni...Ni line is 132(3°).

The hexasiloxane rings in the structures of compounds (III) and (IV) have a somewhat distorted crown conformation, as in the structure of compound (II) (Table 3). A shortening of the exocyclic Si–O(Ni) silanolate bonds is observed compared with the Si–O(Si) siloxane linkages in the siloxane rings [the average Si–O(Ni) distances are 1.590(9) Å in compound (III), 1.595(8) Å in compound (IVA), and 1.602(7) Å in compound (IVB)], which is also characteristic of the structures of compounds (II) and (I) [as regards the Si–O(Co) and Si–O(Si) distances].

Table 3. The torsional angles in the $(SiO)_6$ rings in the structures of compounds (III) and (IV).

Angle	ω, deg (III)	ω, deg (IVA)	Angle	ω, deg (IVB)
Si(1)O(10)Si(2)O(11)	114.4	127.7	Si(7)O(28)Si(8)O(29)	145.2
O(10)Si(2)O(11)Si(3)	−119.3	−107.4	O(28)Si(8)O(29)Si(9)	−109.2
Si(2)O(11)Si(3)O(12)	110.7	105.1	Si(8)O(29)Si(9)O(30)	110.3
O(11)Si(3)O(12)Si(4′)	−106.9	−155.8	O(29)Si(9)O(30)Si(10′)	−113.0
Si(3)O(12)Si(4′)O(13′)	148.7	156.3	Si(9)O(30)Si(10′)O(31′)	112.1
O(12)Si(4′)O(13′)Si(5′)	−148.1	−94.7	O(30)Si(10′)O(31′)O(11′)	−146.0
Si(4′)O(13′)Si(5′)O(14′)	101.6	99.2	Si(10′)O(31′)Si(11′)O(32′)	145.7
O(13′)Si(5′)O(14′)Si(6′)	−104.1	−137.6	O(31′)Si(11′)O(32′)Si(12′)	−104.8
Si(5′)O(14′)Si(6′)O(15′)	128.1	135.8	Si(11′)O(32′)Si(12′)O(33′)	110.1
O(14′)Si(6′)O(15′)Si(1)	−125.6	−128.9	O(32′)Si(12′)O(33′)Si(7)	−112.6
Si(6′)O(15′)Si(1)O(10)	134.1	127.2	Si(12′)O(33′)Si(7)O(28)	106.8
O(15′)Si(1)O(10)Si(2)	−133.3	−126.6	O(33′)Si(7)O(28)Si(8)	−144.6

Comparison of the 12-membered cyclohexasiloxanolate ligands in compounds (III) and (IV) with the cyclosiloxanes whose structures have been investigated[8] shows that the Si–O bond lengths in the rings of these ligands (1.628–1.633 Å) have in general the usual values for cyclosiloxanes (1.62–1.65 Å). The OSiO bond angles in the rings of compounds (III) [104.4–108.6(4)°, mean 106.7°], (IVA)

[102.3–105.7(2)°, mean 103.8°], and (IVB) [105.5–110.0(2)°, mean 107.8°] are in general less than the tetrahedral value characteristic of cyclosiloxanes. The SiOSi angles in the rings of compounds (III) [135.0–138.8(5)°, mean 137.0°], (IVA) [132.8–138.3(2)°, mean 135.1°], and (IVB) [134.2–139.0(2), mean 137.1°] are close to the values observed in the somewhat strained six-membered cyclotrisiloxanes (131–134°) and are significantly smaller than the values found in the larger SiO rings (for example, 142–149° in the eight-membered cyclotetrasiloxanes). Apparently this feature of the SiOSi angles in compounds (III) and (IV) is due to the coordination of the siloxanolate rings of the Ni atoms, which may lead to some strain in these rings and to an increase in their puckering (a decrease in the endocyclic angles).

We shall now consider other features of the crystal structures of compounds (III) and (IV). The weakness of the $Na^+...Cl^-$ ionic interactions in the crystals of compounds (III) and (IV), caused by the large interionic distances (see above), is also manifested by the completely different disposition of the Na^+ cations. In the structure of compound (III), the Na^+ ion occupies two half-populated positions linked to the centre of symmetry. In the crystal of compound (III) (Fig. 3), the "halves" of the Na^+ cation are located near the two siloxane "lids" of the anionic complex. The Na^+ cation is coordinated to all six O atoms of the nearest lid and "on the outside" it is coordinated to a further two atoms, O(18) and O(19), of the solvating butanol molecules [the Na...O distances are 2.78–3.38(1) Å, while the sum of the ionic radii is 2.58 Å [7]].

In the crystal of compound (IV) (Fig. 4) the two Na^+ cations linked to the centre of symmetry are located at the opposite "lids" of only one of the two symmetrically independent anionic complexes and all six O atoms of the hexasiloxane lid are also involved in the coordination of each Na^+ cation. However, on the outer side the coordination involves a further one O atom from each water and ethanol molecule [the Na...O distances are 2.305(5)–3.481(5) Å]. Thus, despite the differences in the coordination of the Na^+ cations, their coordination numbers in the structures of compounds (III) and (IV) are the same and equal to eight.

In the structure of compound (III) both symmetrically independent solvating butanol molecules [O(16) and O(17) atoms], which are not coordinated to the Ni atoms or Na^+ ions, are linked to the O(7) and O(9) atoms of the terminal BuOH ligands of the Ni, Si, O skeleton by O–H...O hydrogen bonds with the distances O(16)...O(7) = 2.68(2) Å and O(17)...O(9) $(1-x, 1-y, 1-z)$ = 2.76(1) Å. The two butanol molecules coordinated to the Na^+ cations form a O(19)...O(18) $(-x, 1-y, 1-z)$ hydrogen bond with one another whose length is 2.67(2) Å. They combine the Na^+ cations (and hence the anionic complexes coordinated to them) into a chain along the [100] direction.

Four O–H...O hydrogen bonds involving three out of the four molecules of the water of crystallisation [the fourth O(W1) molecule is coordinated to the Na^+ cation in the complex (IVA)] are formed in the crystal of compound (IV). The O(W2)...O(W4) = 2.67(1) Å hydrogen bond links two water molecules, the O(W2)...O(21) = 2.79(1) Å bond joins a water molecule to the O(21) silanolate oxygen atom of the (IVB) skeleton, while the $O(W3)...O(17)_A$ = 2.79(1) Å and $O(W3)...O(26)_B$ = 2.71(1) Å bonds join the O(W3) atom of a water molecule to the EtOH molecule coordinated to the Na^+ cation of complex (IVA) and to the EtOH molecule coordinated to one of the nickel atoms—Ni(5) in complex (IVB). One of the ethanol molecules [with O(16)] is not involved in coordination to either Ni or Na^+.

Thus chains arranged in the [011] direction and made up of complexes (IVA) and (IVB), joined by a system of hydrogen bonds involving the O[W(3)] water molecules, are formed in the crystal of compound (IV). This may be one of the reasons for the disposition of the Na^+ cations at only one of the crystallographically independent complexes [complex (IVA)]. On the other hand, the difference in the packing and coordination of the Na^+ cations of the anionic complexes in the crystals of compounds (III) and (IV) is apparently caused by the different sizes of the butanol [in complex (III)] and ethanol [in complex (IV)] ligands.

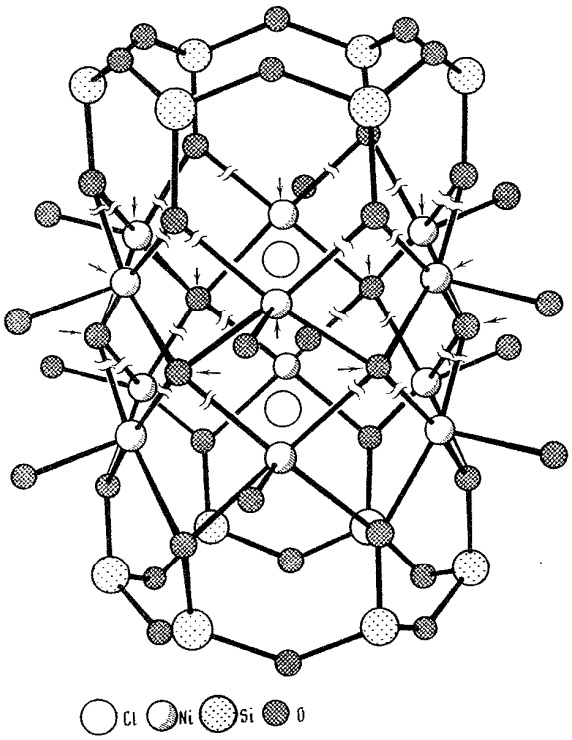


Figure 5. Hypothetical scheme for the growth of the nickel siloxanolate skeleton as a result of the inclusion of $Ni(6)(\mu\text{-}O)_6$ nickel oxide rings. One such additional ring (its Ni and O atoms are indicated by arrows), and the Ni–O bonds, with breaks in which the additional rings are inserted, are shown.

The characteristic features of the structure of the Ni, Si, O skeletons in compounds (III) and (IV) suggest a hypothetical model of the further growth of the nickel siloxanolate skeleton along its long axis as a result of the inclusion of the $Ni_6(\mu\text{-}O)_6$ nickel oxide rings, whilst retaining the cyclohexasiloxanolate ligands at the end-faces of the skeleton (Fig. 5). The mobility of the Cl^- anions within the tubular intraskeletal cavity (channel) arising under these conditions is greater than in complexes (III) and (IV) (there is some analogy with solid ionic electrolytes but having anionic and not the more traditional cationic conductivity).

Experimental

Synthesis of complexes (III) and (IV). Sodium phenylsilanolate $[PhSi(O)ONa]_3$ (11.53 g or 0.24 mmol), obtained by the method of Zhdanov et al.,[9] was dissolved with heating in 200 cm^3 of butanol and the resulting solution was treated with 4.67 g (0.036 mmol) of $NiCl_2$. The reaction mass was refluxed for 1 h whilst stirring. The whole solution was separated from the precipitated NaCl by filtration. From the resulting filtrate, 100 cm^3 of butanol was distilled away and the residue was kept at 0 °C for 10 h. The yellow-green crystals precipitated on cooling were filtered off, washed with butanol, and dried *in vacuo* (100 °C/20 torr). The yield of the crystalline product (III) was 1.9 g (16%). A portion (0.5 g) of the crystals obtained was additionally recrystallised from butanol and the crystals obtained were used for the X-ray diffraction study of complex (III). The remaining crystals were dried *in vacuo*. The composition of the product was as follows (%): C 45.15; H 4.99; Si 13.27; Ni 11.12; Cl 1.28; Na 0.74.

The solvent was completely distilled away from the filtrate remaining after separating the crystalline product. Part of the resinous product (3 g) was dissolved in 200 cm^3 of a 4:1 toluene–ethanol mixture. On standing, the yellow-green crystalline product (IV) separated from the solution in a form suitable for X-ray diffraction study. After drying *in vacuo* (100 °C/20 torr), 1 g (33.3%) of crystals having the following composition was obtained (%): C 37.20; H 4.56; Si 13.84; Ni 13.03; Cl 1.26; Na 1.26.

The results of elemental analysis of both products are not fully consistent with the composition obtained in the X-ray diffraction study. This is due both to the partial loss of the solvent of crystallisation during the drying of the products before elemental analysis and to the traces of water in the reagents employed.

X-Ray diffraction study of complexes (III) and (IV). The X-ray diffraction experiment was carried out for both compounds on an automatic four-circle Syntex $P2_1$ diffractometer at −120 °C (MoK_α radiation, graphite monochromator). The crystallographic data for compounds (III) and (IV) and their experimental X-ray diffraction characteristics are given below:

Compound	(III)	(IV)
a, Å	16.10(10)	17.644(9)
b, Å	17.40(1)	18.088(9)
c, Å	18.13(1)	18.867(9)
α, deg	66.12(4)	84.18(4)
β, deg	64.27(5)	86.43(9)
γ, deg	62.35(5)	69.87(4)
V, $Å^3$	3919.0(2)	5622(5)
Z	1	2
d_{calc}, g cm^{-3}	1.32	1.51
Space group	$P\bar{1}$	$P\bar{1}$
$2\theta_{max}$, deg	θ/2θ *, 50	θ/2θ *, 45
R	0.081	0.042

*Scanning.

The structures of compounds (III) and (IV) were solved by direct methods in accordance with the MULTAN program; the refinement was carried out by the block-diagonal least squares method, isotropically for non-hydrogen atoms. The numbers of measured reflections were 9761 in compound (III) and 13 590 in compound (IV); the number of reflections with $I > 2\sigma$, used in the calculations was 7892 for (III) and 11 859 for (IV). In compound (IV), the positions of all the hydrogen atoms were found on difference synthesis and were included in the isotropic refinement [in compound (III) the positions of the hydrogen atoms could not be located because of the intense thermal vibrations of the solvating molecules). In the structure of compound (III), the Na^+ cation occupies two positions, with populations of 1/2, linked to the centre of symmetry. In the structure of compound (IV), there are two symmetrically independent anionic complexes [(IVA) and (IVB)]. The high temperature parameters of the majority of the atoms of solvating molecules indicate their possible disorder; for some of these atoms, it was indeed possible to find two positions for each. The atomic coordinates are deposited at the Cambridge Crystallographic Data Centre‡. All the calculations were performed on an Eclipse S/200 computer using INEXTL programs.[10]

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