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## Structures of complexes of copper with macrocyclic organosiloxanolate ligands

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**ABSTRACT.** Two new complexes of  $\text{Cu}^{2+}$  with macrocyclic organosiloxanolate ligands,  $\text{Na}_4\{[\text{PhSiO}_2]_{12}\text{Cu}_4\} \cdot 8\text{Bu}^n\text{OH}$  and  $\text{K}_4\{[\text{ViSiO}_2]_{12}\text{Cu}_4\} \cdot 6\text{Bu}^n\text{OH}$ , have been synthesised and studied by X-ray crystallography. The basic structural units in these complexes are the cyclododecasiloxanolate ligands,  $\text{L} = -[-\text{PhSiO}_2-]_{12}-$  and  $-[-\text{ViSiO}_2-]_{12}-$ , with tris(*cis*)-*trans*-tris(*cis*) configuration and "horse saddle" conformation (the symmetries of the complexes are 4 and 222 respectively). The Cu atoms in both complexes have square planar coordination by the olate oxygens,  $\text{O}_m$ . Electron neutrality of the complexes is achieved via four external Na and K cations each of which are coordinated by two olate  $\text{O}_m$  atoms, two siloxane  $\text{O}_c$  oxygen atoms of the ligand (or four  $\text{O}_c$  atoms) and two ( $\text{Na}^+$ ) or three ( $\text{K}^+$ )  $\text{O}_s$  atoms of  $\text{Bu}^n\text{OH}$  solvent molecules.

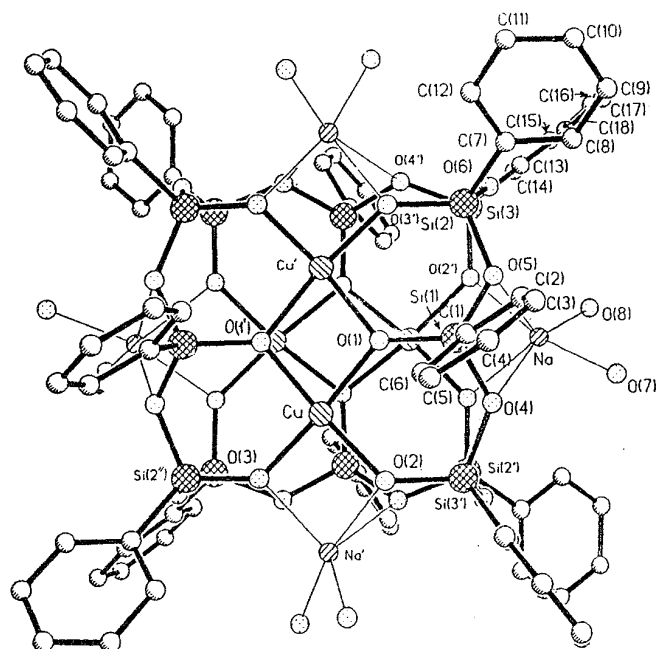
In a continuation of an investigation of polymetalloorganosiloxanates, the products of the reaction of sodium or potassium siloxanates with transition metal salts, we have carried out X-ray crystallographic investigations of two copper-containing polymetallo-organosiloxanates with a qualitatively new structure:  $\text{Na}_4\{[\text{PhSiO}_2]_{12}\text{Cu}_4\} \cdot 8\text{Bu}^n\text{OH}$  (I) and  $\text{K}_4\{[\text{ViSiO}_2]_{12}\text{Cu}_4\} \cdot 6\text{Bu}^n\text{OH}$  (II). We previously reported the synthesis and structure of the neutral Cu(II) complex  $\{[\text{PhSiO}_2]_6\text{Cu}_4[\text{O}_2\text{SiPh}]_6\} \cdot 6\text{EtOH}$  (III).<sup>1</sup>

## Results and discussion

The structures of complexes I and II, which have crystallographic symmetry 4 and 222 respectively, are shown in Fig. 1 and 2. The two complexes have practically the same central metallo-organosiloxanolate nucleus, the structure of which is presented in Fig. 3. The basic geometric parameters of the molecules are given in Tables 1–4.

The basic structural units in complexes I and II are the cyclododecasiloxanolate ligands,  $\text{L} = -[-\text{PhSiO}_2-]_{12}-$  and  $-[-\text{ViSiO}_2-]_{12}-$ . In both complexes these 24-membered cyclic ligands have the same tris(*cis*)-*trans*-tris(*cis*)-*trans*-tris(*cis*)-*trans*-tris(*cis*) configuration (*cis* and *trans* are the mutual orientations of the exocyclic substituents Ph and  $\text{O}_m$  on neighbouring Si atoms) and "horse saddle" conformation (Fig. 3). These dodecadentate ligands coordinate four Cu atoms, which are placed at the vertices of a tetrahedron inside the ligand, via the olate atoms  $\text{O}_m$ .

It is interesting that the "sandwich" complex III, which we studied earlier, has two cyclohexasiloxanolate ligands  $-[-\text{PhSiO}_2-]_6-$  of half the size which are characterised by an all-*cis* configuration and a "crown" conformation (Fig. 4).



**Figure 1.** Structure of complex I. Only the oxygen atoms O(7) and O(8) of the butanol solvate molecules are shown. The  $\bar{4}$  axis lies between atoms O(1) and O(1'), Cu and Cu' and is approximately perpendicular to the plane of the figure.

**Table 1.** Principal bond lengths in structure I\*.

Bond	d, Å	Bond	d, Å	Bond	d, Å
Cu–O(1)	1.944(7)	Si(2)–C(7)	1.84(1)	Na–O(2')	2.420(9)
Cu–O(2)	1.892(7)	Si(2)–O(3')	1.587(8)	Na–O(3')	2.293(9)
Cu–O(3)	1.887(7)	Si(3)–O(6)	1.645(7)	O(1)–Cu'	1.941(7)
Cu–O(4')	1.941(7)	Si(3)–C(13)	1.86(1)	O(2)–Si(3')	1.607(8)
Si(1)–O(1)	1.610(8)	Si(3)–O(2')	1.607(8)	O(2)–Na'	2.420(9)
Si(1)–O(4)	1.629(7)	Si(3)–O(4')	1.641(7)	O(3)–Si(2')	1.587(8)
Si(1)–O(5)	1.634(7)	Na–O(4)	2.882(8)	O(3)–Na'	2.293(9)
Si(1)–C(4)	1.87(1)	Na–O(5)	2.717(8)	O(4)–Si(3')	1.641(7)
Si(2)–O(5)	1.663(8)	Na–O(7)	2.24(1)	Si(2)–O(6)	1.633(7)
Na–O(8)	2.36(1)				

\*Dashed and undashed atoms with the same number are related by the inversion axis  $\bar{4}$ .

The siloxanolate ligand in structures I and II chelate the  $\text{Cu}^{2+}$  ions with the exocyclic olate atoms,  $\text{O}_m$ . A notable shortening of the Si– $\text{O}_m$  bonds (1.587–1.610(8) Å, average 1.60 Å in I, 1.59–1.61(1) Å, average 1.60 Å in II, and 1.59–1.66(2) Å, average 1.62 Å in III) is observed relative to the endocyclic Si– $\text{O}_c$  bonds (1.629–1.663(8) Å, average 1.64 Å in I, 1.61–1.66(1) Å, average 1.63 Å in II, and 1.57–1.73(2) Å, average 1.63 Å in III). On the other hand the Cu– $\text{O}_m$  distances in structures I (1.887–1.944(7) Å, average 1.92 Å), II (1.881–1.980(9) Å, average 1.94 Å) and III [1.92(2)–2.34(4) Å, average 2.03 Å] are close to the sum of the ionic radii of  $\text{O}^{2-}$  and  $\text{Cu}^{2+}$  (1.93 Å for 4-coordinate and 2.01 Å for

5-coordinate  $\text{Cu}^{2+}$  2,3). This indicates that the interaction between the metal and the siloxanolate ligand is primarily ionic in the polymetallo-organosiloxanates I–III studied. The Si–O and O–M bond lengths have similar characteristics in the nickel-containing polymetallo-organosiloxanates we have studied:  $\text{Na}\{[\text{PhSiO}_2]_6\text{Ni}_6(\mu_6\text{-Cl})[\text{O}_2\text{SiPh}]_6\}$ ,<sup>4</sup>  $[\text{PhSiO}_2]_6\text{Ni}_8(\mu_3\text{-O})_2[\text{O}_2\text{SiPh}]_6$ ,<sup>5</sup>  $\text{Na}_2\{[\text{PhSiO}_2]_6\text{Na}_4\text{Ni}_4(\mu_3\text{-OH})_2-[\text{O}_2\text{SiPh}]_6\}$ <sup>6</sup> and also in the known ionic structure of sodium triphenylcyclotrisiloxanolate.<sup>7</sup> The OSiO bond angles ( $105.5\text{--}112.4(5)^\circ$  in I,  $105.9\text{--}107.0(4)^\circ$  in II, and  $107\text{--}110(1)^\circ$  in III) are close to the ideal tetrahedral value, while the endocyclic  $\text{SiO}_c\text{Si}$  bond angles in I and II vary over wide ranges [ $126.8\text{--}135.5(8)^\circ$  in I and  $126.1\text{--}140.5(8)^\circ$  in II] just as in complex III [ $132\text{--}141(1)^\circ$ ]. The values of the angles  $\text{O}_c\text{SiO}_c$  and  $\text{SiO}_c\text{Si}$  are typical for cyclic siloxanes (e.g., the  $\text{SiO}_c\text{Si}$  angles in trisiloxanes range from  $131\text{--}135^\circ$  8).

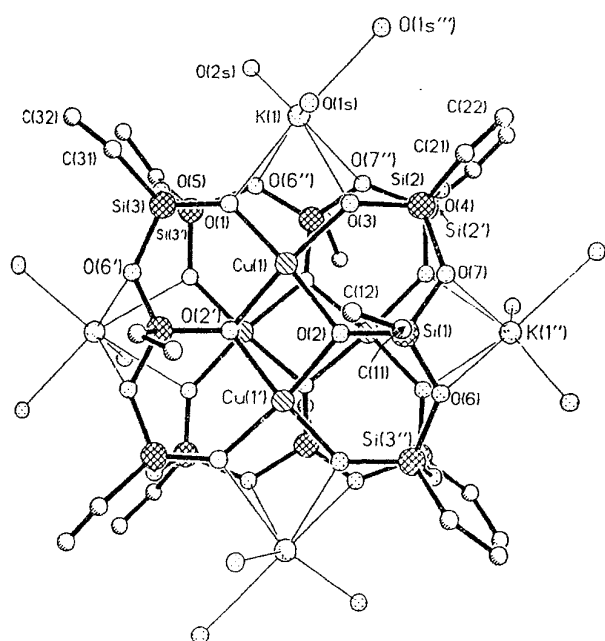


Figure 2. Structure of complex II. Only the oxygen atoms O(1s), O(1s'') and O(2s) of the butanol solvent molecules are shown. Two of the 2-fold axes parallel the Cu(1)–Cu(1') and O(2)–O(2') vectors, while the third is perpendicular to the other two and intersects them at the centre of the molecule.

The Cu atoms in I and II have clear square-planar coordination ( $4O_m$ ) in contrast to the tetragonal-pyramidal coordination ( $4O_m + O_c$  from a solvent molecule) in III, although two almost parallel  $\text{Cu}_2\text{O}_6$  units (maximum deviation from the mean plane is  $0.284 \text{ \AA}$  in I and  $0.092 \text{ \AA}$  in II) are placed cross-wise (effect of the 4 axis) with interplanar distances of  $3.899(3) \text{ \AA}$  in I and  $3.386(3) \text{ \AA}$  in II, i.e., the metallo-organosiloxanolate nucleus in II is noticeably more compressed than in I. However in both cases the distance between  $\text{Cu}_2\text{O}_6$  units is such as to exclude apical coordination of a Cu atom by an  $O_m$  atom in the neighbouring  $\text{Cu}_2\text{O}_6$  unit. All 12  $O_m$

atoms of a ligand take part in coordination to Cu atoms, four of them having a bridging chelating  $\mu_2$  function, while the other eight are terminal.

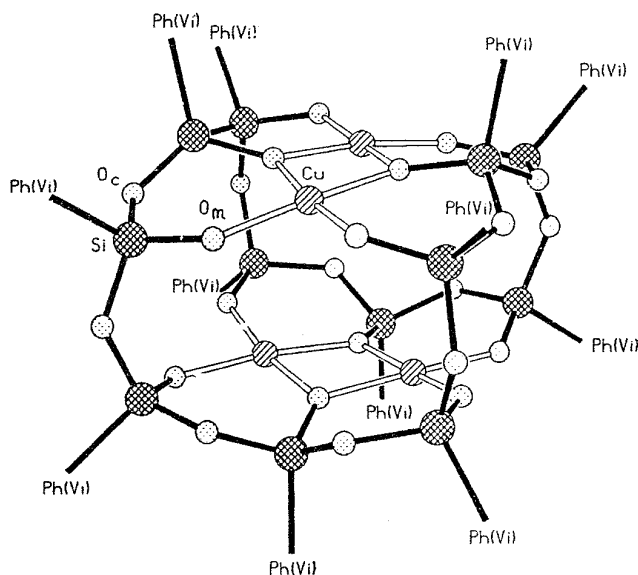


Figure 3. The copper siloxanolate nucleus of complexes I and II. The black lines are covalent bonds, the white lines are coordinate bonds. The  $\bar{4}$  axis is approximately vertical.

Table 2. Principal bond angles in structure I.

Angle	$\alpha$ , deg	Angle	$\alpha$ , deg
O(1)CuO(2)	96.3(3)	O(4)NaO(8)	165.7(4)
O(1)CuO(3)	171.5(3)	O(4)NaO(5)	55.2(2)
O(2)CuO(3)	90.3(3)	O(5)NaO(8)	136.3(4)
O(1)CuO(1')	77.7(3)	O(5)NaO(7)	86.0(4)
O(2)CuO(1')	172.4(3)	O(7)NaO(8)	103.5(4)
O(3)CuO(1')	96.2(3)	O(4)NaO(2')	120.2(3)
O(1)Si(1)O(4)	110.0(4)	O(5)NaO(2')	89.1(3)
O(1)Si(1)O(5)	110.8(4)	O(7)NaO(2')	167.2(4)
O(4)Si(1)O(5)	105.5(4)	O(8)NaO(2')	72.2(3)
O(1)Si(1)C(1)	110.8(4)	CuO(1)Si(1)	130.0(4)
O(4)Si(1)C(1)	108.9(4)	CuO(1)Cu'	101.7(3)
O(5)Si(1)C(1)	110.7(4)	Si(1)O(1)Cu'	128.1(4)
O(5)Si(2)O(6)	104.5(4)	CuO(2)Si(3')	132.5(4)
O(5)Si(2)C(7)	108.5(4)	CuO(2)Na'	93.7(3)
O(6)Si(2)C(7)	105.5(4)	Si(3')O(2)Na'	115.7(4)
O(5)Si(2)O(3')	110.6(4)	CuO(3)Si(2'')	136.0(5)
O(6)Si(2)O(3')	112.4(4)	CuO(3)Na'	98.1(3)
C(7)Si(2)O(3')	114.6(4)	Si(2'')O(3)Na'	122.0(4)
O(6)Si(3)C(13)	105.2(4)	Si(1)O(4)Na	93.6(3)
O(6)Si(3)O(2')	112.4(4)	Si(1)O(4)Si(3')	129.3(5)
C(13)Si(3)O(2')	112.6(5)	NaO(4)Si(3')	117.7(3)
O(6)Si(3)O(4')	107.5(4)	Si(1)O(5)Si(2)	126.8(4)
C(13)Si(3)O(4')	108.0(5)	Si(1)O(5)Na	99.7(3)
O(2'')Si(3)O(4')	110.8(4)	Si(2)O(5)Na	116.9(3)
O(4)NaO(7)	65.9(4)	Si(2)O(6)Si(3)	135.5(5)

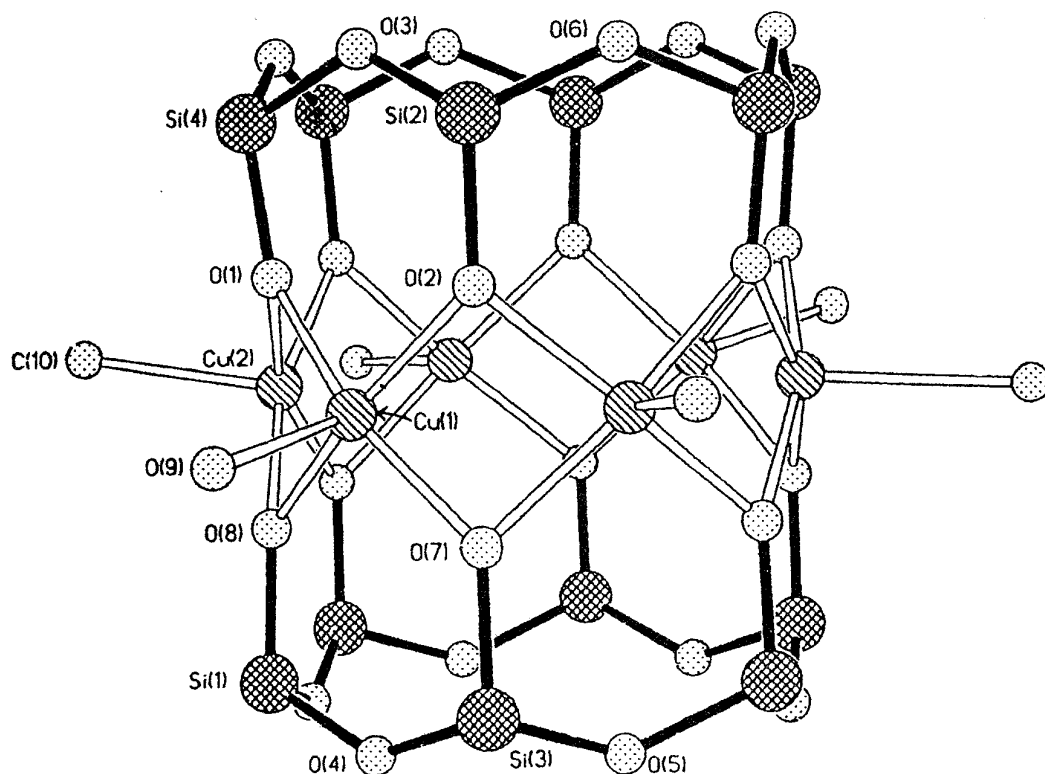


Figure 4. Structure of complex III. The Ph substituents on Si are not shown and only the oxygen atoms O(9) and O(10) of the ethanol solvate molecules are included.

Table 3. Principal bond lengths in structure II\*.

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Cu(1)-O(1)	1.881(9)	K(1)-O(1s)	3.06(1)	Si(2)-O(4)	1.608(6)
Cu(1)-O(2)	1.980(9)	K(1)-O(6 <sup>''</sup> )	3.04(1)	Si(2)-O(7)	1.64(1)
Cu(1)-O(3)	1.941(8)	K(1)-O(7 <sup>''</sup> )	2.91(1)	Si(2)-C(21)	1.84(2)
Cu(1)-O(2)	1.949(8)	Si(1)-O(2)	1.61(1)	Si(3)-O(1)	1.61(1)
K(1)-O(1)	2.75(1)	Si(1)-O(6)	1.61(1)	Si(3)-O(5)	1.605(6)
K(1)-O(1s <sup>'''</sup> )	2.688(9)	Si(1)-O(7)	1.65(1)	Si(3)-O(6 <sup>''</sup> )	1.66(1)
K(1)-O(2s)	3.02(3)	Si(1)-C(11)	1.85(2)	Si(3)-C(31)	1.87(2)
K(1)-O(3)	2.80(1)	Si(2)-O(3)	1.59(1)	O(2)-Cu(1)	1.949(8)

\*Undashed and dashed atoms with the same number are connected by the two-fold axis [ $x, \frac{5}{8}, \frac{1}{8}$ ], with two dashes by the two-fold axis [ $\frac{1}{8}, \frac{5}{8}, z$ ], and with three dashes by the centre of inversion [ $0, \frac{1}{2}, 0$ ].

The electroneutrality of the tetranegative anions of complexes I and II is achieved with "external" Na<sup>+</sup> and K<sup>+</sup> counter-ions respectively. In both cases pairs of O<sub>m</sub> and O<sub>e</sub> atoms plus solvent atoms O<sub>s</sub> from the *n*-BuOH solvent molecules take part in the coordination of Na<sup>+</sup> and K<sup>+</sup>. In I, the coordination sphere of the Na<sup>+</sup> ion includes two O<sub>s</sub> atoms, while in II the K<sup>+</sup> cation has three O<sub>s</sub> atoms (coordination numbers 6 and 7 respectively). This is explained by its larger ionic radius (1.02 Å for Na<sup>+</sup> and 1.38 Å for K<sup>+</sup> 2,3). The coordination polyhedron of the Na<sup>+</sup> ion is a distorted bicapped tetrahedron [Na<sup>+</sup>-O 2.24-2.88(1) Å, Table 1] while that of K<sup>+</sup> is a distorted trigonal dodecahedron (7 K<sup>+</sup>-O 2.80-3.06(1) Å, Table 3; K<sup>+</sup>...C(22<sup>'''</sup>) 3.35(1) Å, see experimental).

The crystal structure of I is composed of isolated complexes surrounded by a "shell" of phenyl groups attached to silicon and alkyl groups of the solvate molecules. In contrast, the structure of II consists of a three-dimensional network constructed of complexes connected by bridging solvate molecules via the K<sup>+</sup> ions (Fig. 5).

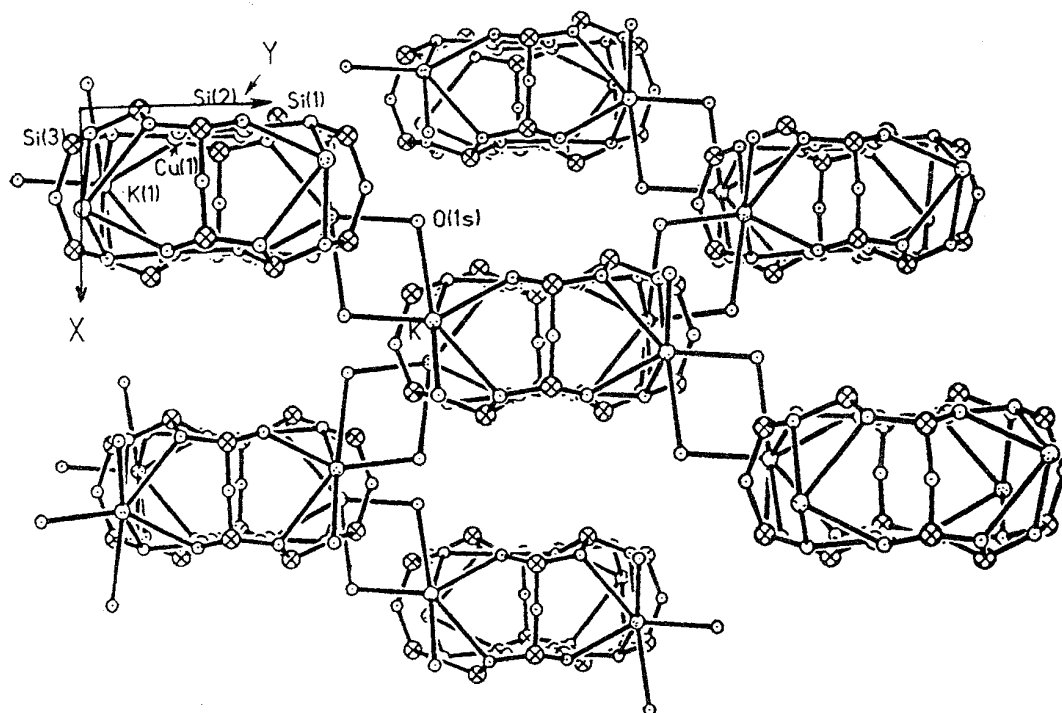


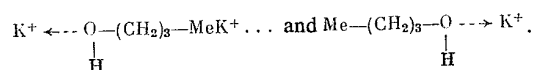
Figure 5. Crystal structure of complex II projected on the *ab* plane. The molecules of the complex form a three-dimensional infinite motive connected via K—O—K bridges.

The basic conclusion from his study is that, despite the different counter-ions and the different substituents on Si (Ph in I, Vi (vinyl) in II), these copper-containing polymetallo-organosiloxanolates have the same molecular structure (apart from the unimportant differences in coordination of the counter-ions and the packing of the complexes mentioned above), which is markedly different from that of complex III, studied previously.

## Experimental

**X-Ray crystallographic study of I and II.** Diffraction data were collected with a Siemens P3/PC automatic four-circle diffractometer (MoK $\alpha$  radiation, graphite monochromator,  $2\theta_{\max} = 60$  and  $50^\circ$  respectively) at temperatures of 150 and 213 K respectively.† Crystals of I are tetragonal,  $a = 31.280(4)$ ,  $c = 12.645(3)$  Å;  $V = 12372$  Å<sup>3</sup>, space group  $I4_1/a$ ,  $Z = 4$  (molecule in a special position with symmetry  $4$ ),  $d_{\text{calc}} = 1.396$  g cm<sup>-3</sup>. Crystals of II are rhombic,  $a = 17.441(3)$ ,  $b = 25.764(5)$ ,  $c = 40.365(8)$  Å;  $V = 18138(10)$  Å<sup>3</sup>, space group  $Fddd$ ,  $Z = 8$  (molecule in a special position with symmetry  $222$ ),  $d_{\text{calc}} = 1.400$  g cm<sup>-3</sup>. Structures I and II were solved by direct methods and refined by block diagonal least squares in the anisotropic approximation. In structure II the end carbon atoms of two of the vinyl groups, C(12) and C(22), of

symmetry independent parts of the complex are disordered over two positions with approximately equal occupancy. In addition, one of the butanol solvate molecules [including atom O(2s)] is also disordered over two positions close to a two-fold axis [ $3/8, 3/8, z$ ] between two K<sup>+</sup> ions belonging to neighbouring complexes, which means that statistically one of the two K<sup>+</sup> ions is coordinated by O(2s) while the corresponding position in the coordination sphere of its neighbour (symmetrically connected by the two-fold axis) is screened by the terminal Me group of the same butanol molecule and *vice versa*:



H atoms in calculated positions (except for the disordered groups) were included in the refinement with fixed positional parameters and  $B_{\text{iso}} = 8.0$  Å<sup>2</sup>. Finally  $R = 0.095$ ,  $R_w = 0.093$  based on 3742 reflections with  $I \geq 3\sigma(I)$  for I and  $R = 0.093$ ,  $R_w = 0.084$  based on 1645 reflections with  $I \geq 2\sigma(I)$ . All programmes were carried out with an IBM PC/AT using the SHELXTL PLUS suite of programmes. Atomic coordinates for structures I and II are deposited in the Cambridge Structural Data bank.‡

**Synthesis of I.** Polyphenylsilsesquioxane (15.48 g, 0.12 mol), prepared by a known method,<sup>9</sup> NaOH (2.40 g, 0.06 mol), and Na

† Single crystals of II decompose below 203 K, probably as a result of a phase change.

‡ Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

(1.38 g, 0.06 mol) were boiled in n-butanol (240 cm<sup>3</sup>) for 1 h, a solution of CuCl<sub>2</sub> (5.38 g, 0.04 mol) in butanol (160 cm<sup>3</sup>) was then added, and the mixture boiled for a further 30 min, after which the NaCl was filtered off. Blue crystals, which deposited from the filtrate after partial removal of the butanol, were recrystallised from butanol (120 cm<sup>3</sup>) and dried at 80–85 °C (1 Torr) to give I (12.71 g, 63.8%).

Found (%): C 43.00; H 4.02; Cu 11.24; Na 4.72; Si 14.84.  
Calculated for C<sub>10.4</sub>H<sub>14.0</sub>Cu<sub>4</sub>Na<sub>4</sub>O<sub>32</sub>Si<sub>12</sub> (based on X-ray crystallography) (%): C 48.31; H 5.45; Cu 9.83; Na 3.56; O 19.80; Si 13.04.

Table 4. Principal bond angles in structure II.

Angle	$\omega$ , deg	Angle	$\omega$ , deg
O(1)Cu(1)O(2)	174.2(4)	O(7)Si(1)C(11)	108.1(9)
O(1)Cu(1)O(3)	91.2(4)	O(3)Si(2)O(4)	112.7(5)
O(2)Cu(1)O(3)	94.5(4)	O(3)Si(2)O(7)	110.3(5)
O(1)Cu(1)O(2)	95.5(4)	O(4)Si(2)O(7)	106.5(5)
O(2)Cu(1)O(2)	78.7(4)	O(3)Si(2)C(21)	112.1(7)
O(3)Cu(1)O(2)	172.8(4)	O(4)Si(2)C(21)	109.3(8)
O(1)K(1)O(3)	58.9(3)	O(7)Si(2)C(21)	105.5(7)
O(1)K(1)O(1s)	70.0(3)	O(1)Si(3)O(5)	112.5(5)
O(3)K(1)O(1s)	55.5(3)	O(1)Si(3)C(31)	111.8(8)
O(1)K(1)O(2s)	115.2(5)	O(5)Si(3)C(31)	107.5(8)
O(3)K(1)O(2s)	157.3(5)	O(1)Si(3)O(6')	110.3(5)
O(1s)K(1)O(2s)	146.3(5)	O(5)Si(3)O(6')	107.0(4)
O(1)K(1)O(6'')	76.4(3)	C(31)Si(3)O(6')	107.5(8)
O(3)K(1)O(6'')	102.8(3)	Cu(1)O(1)K(1)	100.2(4)
O(1s)K(1)O(6'')	146.1(3)	Cu(1)O(1)Si(3)	132.9(6)
O(2s)K(1)O(6'')	55.5(5)	K(1)O(1)Si(3)	114.5(5)
O(1)K(1)O(7'')	101.4(3)	Cu(1)O(2)Si(1)	124.5(6)
O(3)K(1)O(7'')	77.9(3)	Cu(1)O(2)Cu(1')	101.2(4)
O(1s)K(1)O(7'')	130.6(3)	Si(1)O(2)Cu(1')	126.6(6)
O(2s)K(1)O(7'')	82.4(5)	Cu(1)O(3)K(1)	96.9(4)
O(6'')K(1)O(7'')	52.2(3)	Cu(1)O(3)Si(2)	133.0(6)
O(1)K(1)O(1s''')	146.9(3)	K(1)O(3)Si(2)	113.3(5)
O(3)K(1)O(1s''')	98.0(3)	Si(2)O(4)Si(2)	140.5(8)
O(1s)K(1)O(1s''')	77.4(3)	Si(3)O(5)Si(3')	138.6(9)
O(2s)K(1)O(1s''')	94.9(5)	Si(1)O(6)K(1')	97.2(4)
O(2)Si(1)O(6)	108.3(6)	Si(1)O(6)Si(3'')	127.8(6)
O(2)Si(1)O(7)	109.4(6)	K(1')O(6)Si(3'')	118.5(5)
O(6)Si(1)O(7)	105.9(5)	Si(1)O(7)Si(2)	126.1(6)
O(2)Si(1)C(11)	114.4(10)	Si(1)O(7)K(1')	99.9(4)
O(6)Si(1)C(11)	110.4(9)	Si(2)O(7)K(1')	119.8(5)

**Synthesis of II.** Bluish crystals of compound II (9.02 g, 47.42% after crystallisation) were obtained analogously from vinylsilsequioxane (12.51 g, 0.158 mol),<sup>9</sup> KOH (8.86 g, 0.158 mol) and CuCl<sub>2</sub> (7.08 g, 0.053 mol) in butanol (400 cm<sup>3</sup>).

Found (%): C 24.48; H 4.04; Cu 13.46; K 10.42; Si 19.87.  
Calculated for C<sub>48</sub>H<sub>96</sub>Cu<sub>4</sub>K<sub>4</sub>O<sub>30</sub>Si<sub>12</sub> (%): C 30.33; H 5.09; Cu 13.37; K 8.23; O 25.25; Si 17.73.

The results of the elemental analyses do not agree completely with those calculated on the basis of the X-ray crystallographic study which is explained by partial loss of the solvent of crystallisation when the sample was dried before analysis. In addition the percentage of K was determined by titration which led to some difference from the calculated value.

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## The synthesis of surface compounds of cobalt with titanium and molybdenum disulphides and their catalytic properties in the hydrogenation of butadiene

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**ABSTRACT.** The interaction of Co<sub>2</sub>(CO)<sub>8</sub> with crystalline layered disulphides MS<sub>2</sub> (M = Ti, Mo) affords surface compounds containing cobalt atoms or cobalt carbonyl fragments on the lateral and/or basal faces of the crystals. The catalytic properties of the cobalt compounds with MS<sub>2</sub> in the hydrogenation of butadiene were investigated.

One promising way of synthesising catalysts involves the conversion of transition metal complexes, or atoms, into a heterogeneous form on the surfaces of different carriers containing atoms capable of playing the role of ligands. In this connection, the use of layered metal disulphides MS<sub>2</sub> (M = Ti, Mo) as carriers is of considerable interest. The S–M–S layers in these compounds can be regarded as polysulphide acceptor macroligands capable of accepting electrons in the unoccupied *d* band, and of donating