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Novel class of transition metal coordination compounds with macrocyclic organosiloxanolate ligands; their synthesis and crystal structure

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Abstract

Interaction of sodium organosiloxanolates with transition metal chlorides leads to the formation of a novel class of coordination compounds, polymetallaorganosiloxanolates (PMOS) $\{SiPh(O)O\}_n^{n-}M_{(1/2n-x)}^{2+}Na_x$ (M = Mn, Co, Ni, Cu), whose structure is elucidated by an X-ray diffraction study.

Introduction

At present much interest is paid to catalytic systems based on siloxane matrices containing transition metal atoms. In particular such systems are used in reactions of oxidation [1], halogenation and cracking [2] of hydrocarbon and polymerization of olefins [3]. Individual, relatively low molecular polymetallaorganosiloxanolates (PMOS), prepared by us recently, may be considered as appropriate models of the above mentioned catalysts. Moreover, investigations of PMOS reactivity and structure allow us to regard these compounds with a unique structural organization as a new class of ionic sorbents [4] and as a prototype of organosilicon monolayers on the surfaces of metals and metal oxides.

We have already reported the preparation and structure of the following PMOS: $Na\{[PhSiO_2]_6Ni_6(\mu_6\text{-}Cl)[O_2SiPh]_6\} \cdot nL$ ($nL = 14^nBuOH$ (Ia) [5]; $9EtOH \cdot 4H_2O$ (Ib) [5]), $\{[PhSiO_2]_6Ni_8(\mu_3\text{-}O)_2[O_2SiPh]_6\} \cdot 14^nBuOH \cdot 10H_2O \cdot 2Me_2CO$ (II) [6] and $Na_2\{[PhSiO_2]_6Na_4Ni_4(\mu_3\text{-}OH)_2[O_2SiPh]_6\} \cdot 16^nBuOH$ (III) [7]. In the present communication the structures of three new PMOS with other transition metals are discussed: $Na\{[PhSiO_2]_6Mn_6(\mu_6\text{-}Cl)[O_2SiPh]_6\} \cdot 10^nBuOH$ (IV), $Na\{[PhSiO_2]_6Co_6(\mu_6\text{-}Cl)[O_2SiPh]_6\} \cdot 7Me_2CO \cdot 1.5^nBuOH \cdot 0.5EtOH \cdot 0.5CHCl_3$ (V), $\{[PhSiO_2]_6Cu_6[O_2SiPh]_6\} \cdot 6EtOH$ (VI).

Discussion

The main structure forming unit of PMOS I–VI is the hexaphenylcyclohexasiloxanolate macrocyclic ligand $\{SiPh(O)O^-\}_6$ with a completely *cis*-configuration. Two such antiparallel ligands form sandwich-like complexes by coordination (with siloxanolate O_M atoms) of the planar cationic layer involving 4–8 transition metal ions. In the PMOS studied the ligands are either coaxial (in I, IV–VI; Fig. 1) or mutually shifted by *ca.* 1.5 Å parallel to the cationic layer plane (in II and III; Figs. 2 and 3). In most cases the sandwich-like PMOS molecules are additionally stabilized by encapsulation of bridging anionic ligands in the cationic layer: μ_6-Cl^- in I, IV and V, $2\mu_3$-O^2 in II, $2\mu_3$-OH^- in III. An exception is the copper complex VI, wherein the "inner" bridging anion is absent (evidently, due to the Cu^{2+} tendency to form a five-fold tetragonal-pyramidal coordination) and thus the molecule VI has a vacant inner cavity.

Electroneutrality of the anionic complexes I and III–V is ensured by the Na^+ counterions situated in an outer sphere of the complex. The two main types of Na^+ ions coordination are realized: either by the O_M atoms (when Na^+ ions adjoin the cationic layer as in III) or by the siloxane (endomacrocylic) O_C atoms, i.e. like coordination in the crown-ether complexes. In both cases the Na^+ ions are also coordinated by the O_S atoms of solvating molecules (including the O_W atoms of water molecules in Ib and II). Solvating molecules coordinate (with the O_S atoms) also transition metal ions in the complexes I–VI expanding the coordina-

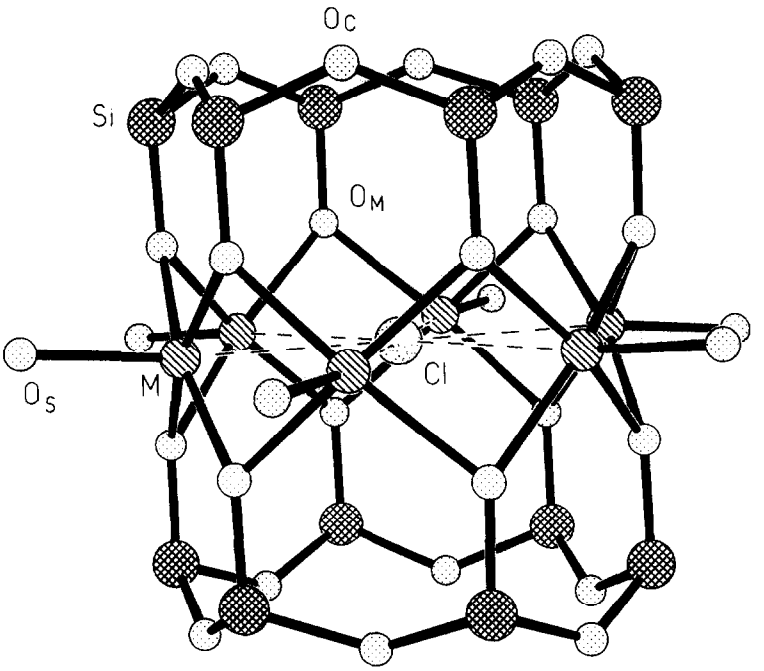

Fig. 1. The structure of the metallasiloxanolate framework of PMOS I, IV–VI (Ph substituents of siloxanolate ligands and alkyl groups of coordinated solvating molecules are not shown). M = Ni (I), Mn (IV), Co (V), Cu (VI). In structure VI the encapsulated Cl^- ion is absent.

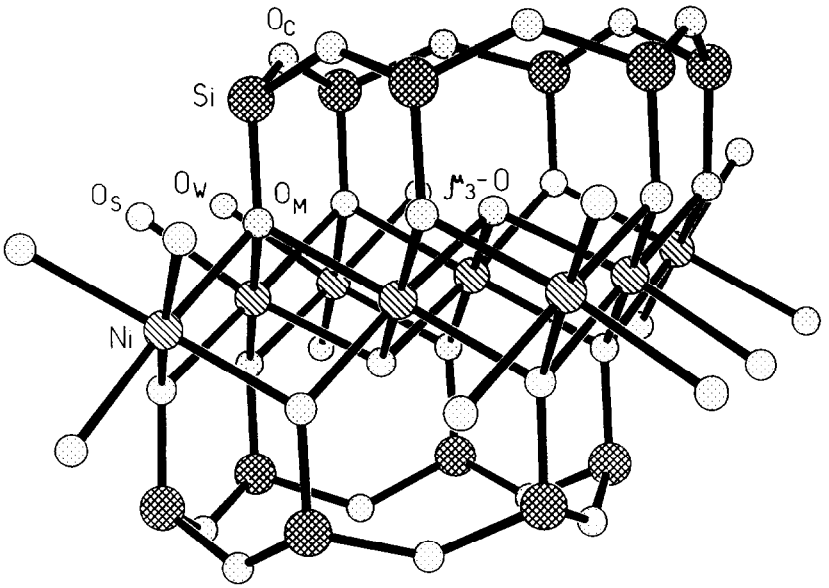

Fig. 2. The metallasiloxanolate framework in structure II.

tion of Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions to octahedral and tetragonal-pyramidal respectively.

Due to the coordination of metal atoms, the hexasiloxanolate macrocycle has a rigid crown conformation with a central hole comparable in size with holes

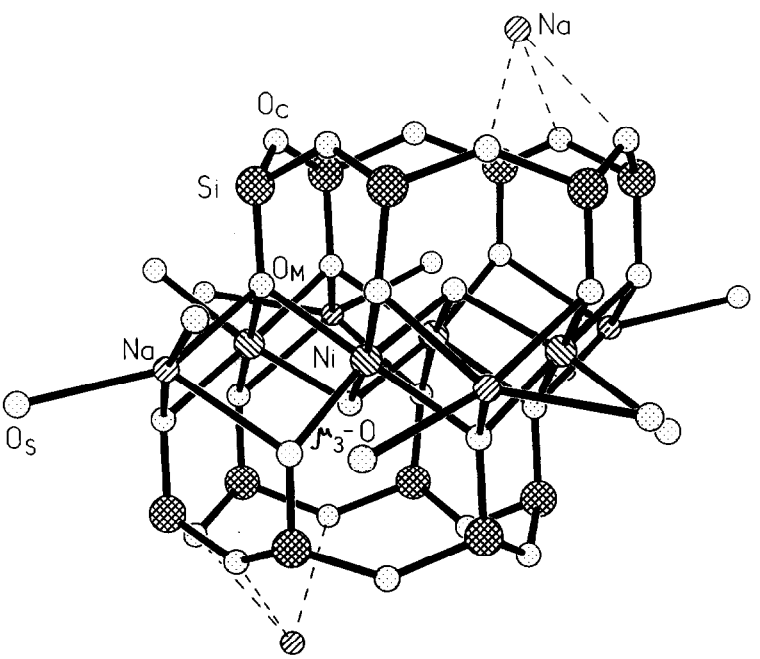

Fig. 3. The metallasiloxanolate framework in structure III.

observed in crown-ether complexes (the diametral O · · · O distances are 4.2–6.0 Å in I–VI and 5.3–5.6 Å in 18-crown-6 [8]). However, contrary to the crown-ether complexes, in PMOS the lone electron pairs of the endocyclic O_C atoms are oriented "outwards" and thereby ensure a possibility for penetration of small anions (Cl^- and OH^-) through a macrocycle hole into the cationic moiety of a complex. Thus the exchange of encapsulated anionic ligands in PMOS may be considered quite probable. Changing of such a ligand gives rise to a profound rearrangement of a complex, accompanied by exchange of one μ_6-ligand (Cl^- in I) for two μ_3-ligands (OH^- in II or O^{2-} in III) by a parallel shift of hexacyclosiloxanolate ligands.

Shortening of the exocyclic Si–O_M bonds (1.56–1.62 Å) in comparison with the endocyclic Si–O_C bonds (1.62–1.65 Å) and a closeness of the M–O_M distances to the same of ionic radii testify to a predominantly ionic type of metal–ligand interaction in PMOS. A similar shortening of the Si–O_M (1.586 Å) relative to the Si–O_C (1.647 Å) bonds has been observed earlier [9] in sodium triphenylcyclotrisiloxanolate, $[PhSi(O)O]_3Na_3$, with a definite ionic structure and the analogous but 6-membered cyclic anion. The Si–O_C bond lengths in I–VI (1.62–1.65 Å) are usual for siloxanes [10]. The O_C–Si–O_C bond angles (107–111°) are close to the tetrahedral value and the greatly increased Si–O_C–Si bond angles (131–140°) are close to those observed in 6-membered cyclosiloxanes (131–135°) [10], but somewhat smaller than in 8-membered SiO cycles (142–149°) [10].

At present, by variation of the synthetic conditions and employment of rare earth halides as metal salts we have qualitatively prepared and structurally studied new PMOS, differing by composition and structure from those described in refs. 5–7 and the present communication. These results will be published separately [11].

Experimental

Crystal data

IV: $C_{72}H_{60}ClMn_6NaO_{24}Si_{12} \cdot 10^nBuOH$, $M = 2774.4$, monoclinic, $a = 18.450(4)$, $b = 17.710(4)$, $c = 20.510(4)$ Å, $\beta = 104.44(3)°$, $U = 6490(2)$ Å^3, $Z = 2$, $D_c = 1.428$ g cm^{-3}. Space group $P2_1/n$ (nonstandard setting of no. 14), μ(Mo-K_α) = 0.737 mm^{-1}, R (R_w) = 0.106 (0.109) for 4403 reflections with $I \geqslant 2\sigma(I)$.

V: $C_{72}H_{60}ClCo_6NaO_{24}Si_{12} \cdot 7Me_2CO \cdot 0.5EtOH \cdot 1.5^nBuOH \cdot 0.5CHCl_3$, $M =$ 2657.8, triclinic, $a = 19.510(4)$, $b = 22.330(4)$, $c = 28.300(6)$ Å, $\alpha = 88.37(3)$, $\beta =$ 89.92(3), $\gamma = 79.88(3)°$, $U = 12132(4)$ Å^3, $Z = 4$, $D_c = 1.463$ g cm^{-3}. Space group $P\bar{1}$, μ(Mo-K_α) = 1.04 mm^{-1}, R (R_w) = 0.091 (0.102) for 12628 reflections with $I \geqslant 2.5\sigma(I)$.

VI: $C_{72}H_{60}Cu_6O_{24}Si_{12} \cdot 6EtOH$, $M = 2303.1$, rombohedral, $a = 14.725(1)$ Å, $\alpha = 65.836(4)°$, $U = 2542.9$ Å^3, $Z = 1$, $D_c = 1.513$ g cm^{-3}. Space group $R3$, μ(Mo-K_α) = 0.208 mm^{-1}, R (R_w) = 0.051 (0.047) for 3336 reflections with $I \leqslant 2\sigma(I)$.

The X-ray diffraction study of IV–VI was carried out with an automated Siemens P3/PC diffractometer at $T = 153$ K, Mo-K_α radiation ($\bar{\lambda} = 0.71073$ Å), $\theta/2\theta$ scan, $\theta_{max} = 28$, 20 and 31° respectively. The structures were solved by direct methods and refined by block-diagonal least-squares in anisotropic approximation. No attempts to locate H atoms were made. Atomic coordinates of IV–VI are given in Tables 1–3.

Table 1

Atomic coordinates ($\times 10^4$) in structure IV

Atom	x	y	z	Atom	x	y	z
Mn(1)	3928(2)	801(2)	5833(2)	C(34)a	8240(47)	1586(46)	2813(43)
Mn(2)	5081(1)	−430(1)	6389(1)	C(3.5)	8319(26)	720(27)	3143(23)
Mn(3)	3934(1)	1173(2)	4399(1)	C(35)a	8697(45)	1336(50)	3439(41)
Cl	5000	0	5000	C(3.6)	7636(29)	526(30)	3349(26)
Si(1)	4933(3)	2315(3)	5529(2)	C(36)a	8008(33)	1010(32)	3784(27)
Si(2)	5426(3)	2124(3)	4231(2)	C(4.1)	8313(9)	−262(9)	5452(8)
Si(3)	6645(3)	1010(3)	4166(2)	C(4.2)	8456(11)	−750(13)	4946(11)
Si(4)	7341(3)	21(3)	5408(2)	C(4.3)	9229(13)	−969(13)	4997(13)
Si(5)	6830(3)	182(3)	6688(2)	C(4.4)	9800(11)	−694(14)	5493(13)
Si(6)	5619(3)	1315(3)	6753(2)	C(4.5)	9652(11)	−235(14)	5961(11)
Na	6581(13)	−2019(13)	7501(9)	C(4.6)	8918(11)	−21(13)	5926(9)
O(1)	5503(5)	1986(6)	6206(5)	C(5.1)	7479(10)	−153(10)	7489(8)
O(2)	5394(6)	2448(6)	4950(5)	C(5.2)	8097(11)	−576(11)	7512(11)
O(3)	6253(5)	1823(6)	4279(5)	C(5.3)	8557(13)	−835(14)	8103(16)
O(4)	7120(6)	721(7)	4907(6)	C(5.4)	8409(14)	−628(15)	8722(13)
O(5)	7331(6)	313(6)	6151(5)	C(5.5)	7858(18)	−234(20)	8719(11)
O(6)	6453(5)	986(6)	6836(5)	C(5.6)	7365(14)	77(17)	8121(13)
O(7)	4257(6)	1735(6)	5263(5)	C(6.1)	5554(9)	1754(10)	7557(8)
O(8)	5181(5)	−1462(5)	5979(5)	C(6.2)	5774(16)	2475(13)	7740(10)
O(9)	3967(6)	−399(7)	6179(5)	C(6.3)	5684(20)	2807(15)	8345(13)
O(10)	3216(6)	640(6)	4830(5)	C(6.4)	5383(13)	2443(17)	8763(15)
O(11)	6181(5)	−424(6)	6402(5)	C(6.5)	5172(15)	1734(21)	8621(13)
O(12)	5021(6)	660(6)	6553(5)	C(6.6)	5225(15)	1348(14)	7964(11)
O(13)	3272(11)	1213(12)	6511(11)	C(1)	3326(59)	1744(62)	6758(52)
O(14)	5403(7)	−918(8)	7400(6)	C(2)	2841(45)	2120(44)	6432(36)
O(15)	6793(6)	−1982(7)	6243(6)	C(3)	2095(43)	2004(42)	6623(36)
O(16)	7451(14)	−2694(13)	8266(15)	C(4)	1334(58)	2810(58)	6480(51)
O(17)	6318(21)	−199(21)	2565(17)	C(5)	5086(46)	−921(46)	7893(41)
O(17)a	6768(72)	−1098(74)	2258(63)	C(6)	5357(34)	−799(36)	8615(33)
C(1.1)	4618(9)	3239(9)	5729(9)	C(7)	5784(60)	−462(64)	8616(55)
C(1.2)	4433(16)	3382(14)	6350(11)	C(7)a	5388(35)	−540(39)	9392(33)
C(1.3)	4182(20)	4107(16)	6497(14)	C(8)	6038(18)	−176(20)	9422(17)
C(1.4)	4141(14)	4705(14)	6063(14)	C(8)a	5274(18)	−1190(20)	9807(17)
C(1.5)	4318(12)	4581(11)	5421(13)	C(9)	7051(25)	−2682(26)	6014(22)
C(1.6)	4582(11)	3830(11)	5299(10)	C(9)a	7494(30)	−2205(31)	6310(26)
C(2.1)	5229(10)	2886(9)	3636(8)	C(10)	7486(21)	−2499(23)	5437(19)
C(2.2)	4600(12)	3305(12)	3537(11)	C(10)a	7460(47)	−2913(50)	5699(43)
C(2.3)	4370(14)	3894(16)	3028(16)	C(11)	7636(23)	−3554(24)	5203(21)
C(2.4)	4855(16)	4049(16)	2607(14)	C(12)	8063(40)	−3274(41)	4701(36)
C(2.5)	5503(18)	3686(21)	2712(15)	C(13)	7647(23)	−2554(23)	8968(20)
C(2.6)	5690(15)	3058(15)	3203(15)	C(14)	7159(36)	−2388(36)	9212(29)
C(3.1)	7319(13)	1218(12)	3647(11)	C(15)	6692(42)	−2828(41)	9216(34)
C(3.2)	7719(18)	1905(20)	3703(16)	C(16)	6187(52)	−2843(52)	9546(46)
C(3.2)a	6905(44)	1523(45)	2917(42)	C(17)	6693(49)	160(52)	2092(44)
C(3.3)	8356(20)	1985(22)	3452(19)	C(17)a	6785(45)	−742(51)	1682(40)
C(3.3)a	7319(101)	1418(98)	2437(86)	C(18)	6980(67)	−345(75)	1761(67)
C(3.4)	8557(38)	1378(38)	3184(39)	C(19)	7053(54)	−235(60)	1250(56)
				C(20)	7245(49)	−719(53)	941(43)

In a typical experiment, phenylsesquioxane of $[PhSiO_{1.5}]_n$ composition was treated with an equimolar amount of NaOH in ^{n}BuOH on heating and stirring to complete dissolution. The solution of metal chloride ($CoCl_2$, $MnCl_2$, $CuCl_2$) in

Table 2

Atomic coordinates ($\times 10^4$) in structure V

Atom	x	y	z	Atom	x	y	z
Co(1)	−2518(2)	−2074(1)	7602(1)	Si(23)	2938(3)	5214(3)	−3517(2)
Co(2)	−2146(1)	−1723(1)	6665(1)	Si(24)	3519(3)	4046(3)	−4016(2)
Co(3)	−1157(2)	−896(1)	6521(1)	Na(1)	2053(5)	2669(4)	−1549(3)
Co(4)	−526(2)	−444(1)	7320(1)	Na(2)	4796(4)	4710(4)	−3572(3)
Co(5)	−923(2)	−816(1)	8257(1)	O(31)	2348(7)	2040(6)	−2648(4)
Co(6)	−1914(1)	−1613(1)	8418(1)	O(32)	3286(7)	1936(7)	−1978(5)
Cl(1)	−1508(3)	−1275(3)	7481(2)	O(33)	3294(7)	2706(6)	−1320(5)
Si(1)	−1347(3)	−3074(3)	7057(2)	O(34)	2544(7)	3723(6)	−1078(5)
Si(2)	−548(3)	−2360(3)	6389(2)	O(35)	1595(7)	3815(6)	−1718(5)
Si(3)	441(3)	−1597(3)	6790(2)	O(36)	1604(8)	3053(6)	−2363(5)
Si(4)	571(3)	−1557(3)	7857(2)	O(37)	3625(7)	2218(6)	−2848(4)
Si(5)	−255(3)	−2243(3)	8535(2)	O(38)	4372(7)	2517(5)	−1927(4)
Si(6)	−1233(3)	−3018(3)	8126(2)	O(39)	3813(7)	3726(6)	−1437(5)
Si(7)	−3647(3)	−991(3)	7044(2)	O(40)	2470(7)	4588(6)	−1753(5)
Si(8)	−2802(3)	−267(3)	6429(2)	O(41)	1718(6)	4194(5)	−2633(3)
Si(9)	−1834(3)	507(3)	6828(2)	O(42)	2271(7)	3053(6)	−3191(5)
Si(10)	−1666(3)	562(3)	7887(2)	O(43)	4346(6)	3810(6)	−3931(5)
Si(11)	−2522(3)	−151(3)	8518(2)	O(44)	5424(7)	3451(6)	−3391(4)
Si(12)	−3507(3)	−915(3)	8107(2)	O(45)	5349(6)	4274(5)	−2756(4)
O(1)	−1054(7)	−3250(6)	7599(5)	O(46)	4511(7)	5277(6)	−2601(5)
O(2)	−710(7)	−2933(6)	6723(5)	O(47)	3491(9)	5488(8)	−3200(6)
O(3)	177(7)	−2188(7)	6559(6)	O(48)	3414(7)	4761(6)	−3874(5)
O(4)	737(7)	−1794(6)	7324(5)	O(49)	4428(7)	2801(6)	−3390(5)
O(5)	364(7)	−2112(6)	8175(5)	O(50)	5140(6)	3149(6)	−2496(4)
O(6)	−526(7)	−2858(6)	8369(5)	O(51)	4568(7)	4347(6)	−1983(4)
O(7)	−1983(7)	−2537(5)	7055(4)	O(52)	3229(6)	5199(6)	−2321(4)
O(8)	−1166(7)	−1795(6)	6421(4)	O(53)	2453(6)	4868(6)	−3203(4)
O(9)	−179(7)	−1027(6)	6791(5)	O(54)	3064(6)	3681(6)	−3707(4)
O(10)	−36(7)	−973(6)	7860(5)	O(55)	5168(8)	1696(7)	−2601(5)
O(11)	−865(7)	−1674(5)	8559(4)	O(56)	1558(9)	5590(8)	−2478(6)
O(12)	−1854(6)	−2466(5)	8142(4)	O(57)	1465(8)	4143(7)	−3734(6)
O(13)	−3817(6)	−748(6)	7574(4)	O(58)	1093(20)	2880(17)	−958(14)
O(14)	−3483(6)	−428(6)	6717(5)	O(59)	2126(15)	1718(13)	−1238(11)
O(15)	−2575(7)	333(6)	6672(4)	O(60)	4802(15)	5709(13)	−3786(10)
O(16)	−1947(7)	785(6)	7362(5)	O(61)	5803(19)	4511(17)	−4080(14)
O(17)	−2321(7)	420(6)	8196(5)	O(62)	3212(8)	2316(7)	−3926(5)
O(18)	−3255(7)	−306(6)	8318(4)	O(63)	5400(8)	3232(7)	−1441(5)
O(19)	−3021(6)	−1553(5)	7056(4)	O(64)	3684(9)	5115(8)	−1253(6)
O(20)	−2184(7)	−833(6)	6412(4)	C(131)	3374(11)	1014(10)	−2683(8)
O(21)	−1208(7)	−52(5)	6801(4)	C(132)	4072(23)	697(20)	−2651(16)
O(22)	−1048(7)	−12(5)	7865(4)	C(1A2)	3611(27)	565(24)	−2375(19)
O(23)	−1897(7)	−711(6)	8525(5)	C(133)	4245(36)	54(31)	−2769(24)
O(24)	−2882(6)	−1482(6)	8114(5)	C(1A3)	3743(31)	−35(28)	−2449(22)
O(25)	−3325(8)	−2604(7)	7631(6)	C(134)	3764(20)	−168(16)	−2911(13)
O(26)	−2664(7)	−1969(7)	6041(5)	C(135)	3011(73)	56(64)	−2950(50)
O(27)	−853(8)	−645(7)	5816(5)	C(1A5)	3284(31)	238(28)	−3302(23)
O(28)	311(9)	74(8)	7252(6)	C(136)	2956(41)	673(38)	−2757(29)
O(29)	−489(9)	−454(8)	8874(7)	C(1A6)	3131(28)	862(25)	−3133(21)
O(30)	−2297(8)	−1830(7)	9099(6)	C(141)	4206(11)	1564(10)	−1252(8)
C(1.1)	−1583(11)	−3776(10)	6821(8)	C(142)	4643(15)	1065(13)	−1459(10)
C(1.2)	−2151(12)	−4013(11)	7026(9)	C(143)	4872(17)	534(15)	−1197(12)
C(1.3)	−2361(13)	−4577(12)	6864(9)	C(144)	4773(17)	476(15)	−711(12)
C(1.4)	−1958(14)	−4857(12)	6482(10)	C(145)	4350(15)	975(13)	−503(10)

Table 2 (continued)

Atom	x	y	z	Atom	x	y	z
C(1.5)	−1432(13)	−4656(12)	6279(9)	C(146)	4085(13)	1519(12)	−772(9)
C(1.6)	−1218(12)	−4100(10)	6459(8)	C(151)	3681(11)	3271(9)	−491(7)
C(2.1)	−472(12)	−2593(10)	5765(8)	C(152)	4380(15)	3025(13)	−408(11)
C(2.2)	−1013(13)	−2858(11)	5562(9)	C(153)	4652(17)	2935(15)	63(12)
C(2.3)	−1050(13)	−2939(11)	5065(9)	C(154)	4237(17)	3097(14)	448(11)
C(2.4)	−549(16)	−2754(14)	4791(11)	C(155)	3523(21)	3327(18)	361(15)
C(2.5)	−1(15)	−2483(13)	4960(10)	C(156)	3255(16)	3388(14)	−111(12)
C(2.6)	40(13)	−2413(12)	5463(10)	C(161)	1412(10)	4706(9)	−1032(7)
C(3.1)	1209(11)	−1442(10)	6447(8)	C(162)	1559(16)	4800(14)	−574(11)
C(3.2)	1152(13)	−1239(11)	5984(9)	C(163)	1036(20)	5176(17)	−290(14)
C(3.3)	1750(14)	−1131(12)	5732(10)	C(164)	408(16)	5388(14)	−495(11)
C(3.4)	2408(17)	−1179(15)	5982(13)	C(165)	269(14)	5381(14)	−966(12)
C(3.5)	2455(22)	−1387(19)	6441(16)	C(166)	780(15)	4992(13)	−1219(10)
C(3.6)	1849(17)	−1492(14)	6686(12)	C(171)	388(10)	3977(9)	−2322(7)
C(4.1)	1373(12)	−1375(11)	8117(9)	C(172)	74(12)	4512(10)	−2550(8)
C(4.2)	1750(15)	−984(13)	7895(11)	C(173)	−685(14)	4639(12)	−2588(10)
C(4.3)	2329(16)	−763(14)	8104(11)	C(174)	−1058(15)	4267(13)	−2413(10)
C(4.4)	2537(16)	−1002(14)	8546(12)	C(175)	−745(18)	3720(16)	−2162(12)
C(4.5)	2217(17)	−1421(15)	8791(12)	C(176)	−4(12)	3564(11)	−2114(9)
C(4.6)	1611(16)	−1626(14)	8563(11)	C(181)	1090(12)	2445(11)	−3096(8)
C(5.1)	188(11)	−2419(10)	9120(8)	C(182)	607(26)	2969(21)	−3339(17)
C(5.2)	522(13)	−2997(11)	9236(9)	C(183)	−117(33)	2808(30)	−3510(22)
C(5.3)	937(16)	−3092(14)	9649(12)	C(184)	−171(24)	2142(24)	−3422(18)
C(5.4)	977(16)	−2619(15)	9955(11)	C(185)	115(29)	1888(24)	−3172(20)
C(5.5)	650(16)	−2043(14)	9848(11)	C(186)	820(30)	1998(26)	−2968(20)
C(5.6)	247(14)	−1934(12)	9415(10)	C(191)	5334(10)	2800(8)	−4215(7)
C(6.1)	−1429(12)	−3691(10)	8482(8)	C(192)	4959(11)	2657(10)	−4597(8)
C(6.2)	−1292(13)	−4277(12)	8298(9)	C(193)	5324(14)	2398(12)	−5013(10)
C(6.3)	−1391(13)	−4779(12)	8596(10)	C(194)	6040(12)	2290(10)	−5007(8)
C(6.4)	−1629(15)	−4701(13)	9030(11)	C(195)	6432(13)	2413(12)	−4619(9)
C(6.5)	−1743(13)	−4118(12)	9239(9)	C(196)	6051(12)	2671(10)	−4215(8)
C(6.6)	−1647(12)	−3606(11)	8952(9)	C(201)	6508(12)	3306(10)	−2723(8)
C(7.1)	−4446(11)	−1201(9)	6773(7)	C(202)	6789(12)	2841(10)	−2404(8)
C(7.2)	−4808(13)	−1604(11)	7010(9)	C(203)	7529(14)	2672(12)	−2363(10)
C(7.3)	−5379(13)	−1844(12)	6815(9)	C(204)	7971(16)	2943(14)	−2614(11)
C(7.4)	−5536(14)	−1640(12)	6349(10)	C(205)	7725(17)	3418(15)	−2961(12)
C(7.5)	−5217(13)	−1239(11)	6089(9)	C(206)	6965(13)	3598(11)	−3018(9)
C(7.6)	−4651(12)	−1040(11)	6318(9)	C(211)	5672(12)	5013(11)	−2016(9)
C(8.1)	−3070(11)	−38(9)	5793(7)	C(212)	6372(12)	4981(11)	−2197(9)
C(8.2)	−3261(12)	−481(10)	5501(8)	C(213)	6884(14)	5233(12)	−1951(10)
C(8.3)	−3401(13)	−368(11)	5031(9)	C(214)	6695(15)	5522(13)	−1517(10)
C(8.4)	−3346(12)	229(11)	4836(9)	C(215)	6048(14)	5567(12)	−1339(10)
C(8.5)	−3155(14)	662(12)	5136(10)	C(216)	5526(12)	5301(11)	−1593(9)
C(8.6)	−3058(12)	564(11)	5612(9)	C(221)	3546(13)	6382(11)	−2514(9)
C(9.1)	−1711(11)	1149(10)	6395(8)	C(222)	3997(18)	6585(16)	−2216(12)
C(9.2)	−1994(12)	1763(10)	6511(8)	C(223)	3768(22)	7252(19)	−2094(15)
C(9.3)	−1983(15)	2223(13)	6154(11)	C(224)	3223(21)	7590(17)	−2291(14)
C(9.4)	−1635(14)	2054(12)	5717(10)	C(225)	2760(29)	7378(26)	−2516(20)
C(9.5)	−1369(15)	1473(14)	5624(11)	C(226)	2891(28)	6700(26)	−2697(19)
C(9.6)	−1393(12)	1006(11)	5969(9)	C(231)	2473(12)	5852(10)	−3865(8)
C(101)	−1328(12)	1214(10)	8163(8)	C(232)	2782(30)	6149(28)	−4156(21)
C(102)	−828(15)	1444(13)	7932(10)	C(234)	1918(29)	7023(23)	−4207(20)
C(103)	−521(18)	1921(16)	8153(13)	C(233)	2487(34)	6789(30)	−4396(22)
C(104)	−806(19)	2136(16)	8593(13)	C(235)	1577(22)	6848(19)	−3846(16)

Table 2 (continued)

Atom	x	y	z	Atom	x	y	z
C(105)	−1317(19)	1932(16)	8814(13)	C(236)	1901(17)	6245(16)	−3668(12)
C(106)	−1604(13)	1440(12)	8571(9)	C(241)	3322(11)	4009(10)	−4654(8)
C(111)	−2692(12)	104(10)	9144(8)	C(242)	2661(14)	3908(12)	−4802(10)
C(112)	−2162(13)	269(12)	9404(10)	C(243)	2508(15)	3927(13)	−5293(10)
C(113)	−2291(16)	459(14)	9884(11)	C(244)	2998(14)	3998(12)	−5629(10)
C(114)	−2901(16)	419(13)	10084(11)	C(245)	3610(14)	4112(12)	−5492(10)
C(115)	−3453(15)	258(13)	9832(11)	C(246)	3823(14)	4099(12)	−5005(10)
C(116)	−3353(14)	106(13)	9344(10)	C(19)	5751(12)	1450(10)	−2708(8)
C(121)	−4247(12)	−1077(10)	8478(8)	C(20)	6206(13)	1704(12)	−3046(9)
C(122)	−4174(14)	−1286(12)	8943(10)	C(21)	6031(16)	793(14)	−2512(11)
C(123)	−4730(17)	−1422(14)	9211(12)	C(22)	1246(17)	6036(15)	−2357(12)
C(124)	−5367(18)	−1383(15)	9020(13)	C(23)	1721(30)	6159(27)	−1820(22)
C(125)	−5481(18)	−1202(15)	8550(13)	C(24)	763(19)	6516(17)	−2509(13)
C(126)	−4906(16)	−1090(14)	8256(11)	C(25)	953(22)	4512(19)	−3800(16)
C(1)	−3638(15)	−2772(13)	7955(11)	C(26)	403(23)	4328(20)	−4195(16)
C(2)	−3361(15)	−2775(13)	8468(11)	C(27)	861(19)	5220(17)	−3547(13)
C(3)	−4301(19)	−3032(17)	7864(14)	C(28)	685(24)	3249(21)	−680(17)
C(4)	−3115(13)	−2262(11)	5969(9)	C(29)	−6(20)	3621(17)	−773(13)
C(5)	−3373(13)	−2634(11)	6361(9)	C(30)	1005(19)	3218(17)	−134(14)
C(6)	−3467(14)	−2224(12)	5492(10)	C(31)	2082(23)	1200(20)	−1405(16)
C(7)	−1060(13)	−789(12)	5436(9)	C(32)	2567(22)	723(20)	−1121(15)
C(8)	−1543(13)	−1197(12)	5338(9)	C(33)	1739(22)	1104(19)	−1816(16)
C(9)	−659(24)	−521(21)	4979(17)	C(34)	4756(29)	6372(25)	−3660(19)
C(10)	615(14)	222(12)	6880(10)	C(35)	4126(23)	6737(19)	−3785(15)
C(11)	1375(20)	349(18)	6911(14)	C(36)	5287(13)	6192(11)	−3328(9)
C(12)	349(16)	234(14)	6371(11)	C(37)	5929(23)	4355(20)	−4503(17)
C(13)	−49(20)	−133(18)	8888(15)	C(38)	6831(19)	4166(16)	−4344(13)
C(14)	57(37)	223(33)	9433(27)	C(39)	5793(29)	4232(26)	−4929(22)
C(15)	318(18)	117(16)	8476(13)	C(40)	2605(16)	2428(14)	−4236(11)
C(16)	−2182(13)	−1678(11)	9497(9)	C(41)	2334(34)	1702(31)	−4135(24)
C(17)	−2691(17)	−1784(15)	9893(12)	C(42)	5836(35)	3638(29)	−1384(23)
C(18)	−1596(15)	−1354(13)	9627(11)	C(43)	6634(24)	3501(19)	−1213(15)
Co(7)	3330(1)	2862(1)	−3360(1)	C(44)	7196(29)	3759(23)	−1306(19)
Co(8)	4493(1)	2559(1)	−2677(1)	C(45)	7855(27)	3691(22)	−1006(18)
Co(9)	4549(1)	3417(1)	−1915(1)	C(46)	3222(31)	5589(30)	−1113(22)
Co(10)	3532(1)	4539(1)	−1805(1)	C(47)	3306(31)	6252(30)	−932(21)
Co(11)	2360(1)	4821(1)	−2469(1)	C(48)	2652(32)	6860(28)	−896(21)
Co(12)	2284(1)	3969(1)	−3233(1)	Cl(3)	1278(9)	6284(8)	−5478(7)
Cl(2)	3441(3)	3698(3)	−2571(2)	Cl(4)	1709(9)	5190(9)	−4908(7)
Si(13)	3174(3)	1834(3)	−2543(2)	Cl(5)	405(9)	5968(7)	−4705(6)
Si(14)	3814(3)	2215(3)	−1645(2)	C(49)	1554(29)	6045(26)	−4740(21)
Si(15)	3344(3)	3378(3)	−1107(2)	O(65)	4088(9)	1432(8)	−4351(6)
Si(16)	2034(3)	4222(3)	−1420(2)	C(50)	4629(14)	1106(12)	−4189(10)
Si(17)	1361(3)	3785(3)	−2279(2)	C(51)	5049(18)	649(16)	−4512(13)
Si(18)	1853(3)	2669(3)	−2843(2)	C(52)	4917(21)	1201(19)	−3706(15)
Si(19)	4852(3)	3197(3)	−3704(2)	O(66)	5842(11)	2077(10)	8400(8)
Si(20)	5573(3)	3535(3)	−2826(2)	C(53)	6218(16)	1578(15)	8688(12)
Si(21)	4994(3)	4697(3)	−2330(2)	C(54)	6588(22)	1781(19)	9070(16)
Si(22)	3672(3)	5548(3)	−2647(2)	C(55)	6047(31)	1987(26)	9464(22)
				C(56)	6783(39)	2197(35)	9860(27)

Table 3

Atomic coordinates ($\times 10^4$) in structure VI

Atom	x	y	z	Atom	x	y	z
Cu(1)	7928(4)	8945(4)	1347(4)	C(7)	5094(21)	9352(20)	881(23)
Cu(2)	9876(4)	7464(4)	872(4)	C(8)	4286(21)	9982(25)	285(25)
Si(1)	9618(6)	8750(7)	2353(6)	C(9)	3215(21)	10087(23)	858(22)
Si(2)	6437(6)	9189(6)	70(6)	C(10)	2996(19)	9488(26)	2060(29)
Si(3)	8145(7)	10879(7)	1729(7)	C(11)	3734(24)	8920(27)	2510(23)
Si(4)	7960(6)	7060(6)	715(6)	C(12)	4806(22)	8885(24)	1867(23)
O(1)	8438(14)	7638(13)	1033(14)	C(13)	7045(19)	11371(19)	2739(19)
O(2)	7013(14)	9627(13)	485(13)	C(14)	5977(24)	11881(24)	2508(23)
O(3)	6983(15)	7968(14)	167(15)	C(15)	5204(22)	12405(25)	3258(21)
O(4)	9005(14)	9982(14)	2226(15)	C(16)	5428(28)	12283(23)	4378(20)
O(5)	8601(14)	11725(14)	873(12)	C(17)	6367(27)	11866(26)	4497(24)
O(6)	6484(14)	9812(13)	−1139(13)	C(18)	7234(20)	11384(22)	3624(20)
O(7)	7681(13)	10384(12)	1238(12)	C(19)	7331(20)	6035(19)	1769(21)
O(8)	9165(14)	8330(14)	1836(14)	C(20)	7359(22)	5152(22)	1680(20)
O(9)	6532(31)	8937(28)	2911(24)	C(21)	6951(20)	4457(16)	2477(18)
O(10)	356(18)	5721(18)	1855(24)	C(22)	6449(18)	4666(16)	3494(15)
C(1)	9471(22)	8064(24)	3792(21)	C(23)	6549(26)	5347(25)	3612(23)
C(2)	10079(21)	6936(20)	3971(22)	C(24)	6934(17)	6158(16)	2783(17)
C(3)	9930(27)	6308(26)	4975(27)	C(25)	5924(19)	9160(25)	3611(25)
C(4)	9208(30)	6741(27)	5870(26)	C(26)	5293(35)	8438(45)	4484(30)
C(5)	8755(25)	7695(20)	5644(23)	C(27)	70(33)	4913(21)	2299(25)
C(6)	8868(20)	8381(18)	4572(20)	C(28)	2819(41)	765(49)	3986(40)

^{n}BuOH in the amount corresponding to $Na^+/Cl^- = 1:1$ was added to a prepared solution of sodium phenylsiloxanolate. The reaction mixture was then refluxed under stirring for 1 h. The hot solution was filtered from the NaCl precipitate, concentrated by distillation of the solvent and allowed to stand for 2–3 days at room or lower (0 °C) temperature. The precipitate formed was separated and recrystallized. Crystals suitable for an X-ray diffraction study were usually obtained only from the mixed solvents. Yields of crystalline products were 8–75%. All compounds prepared were characterized by an elemental analysis whose results were in satisfactory agreement with the compositions calculated from X-ray structural data.

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