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Bimetallic siloxane cluster of higher valent transition metals: $Na\{[\eta^6\text{-cyclo-}(PhSiO_2)_6]_2Co_2Ni_4(\mu_6\text{-}Cl)\}$

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Abstract

The bimetallic siloxane cluster/cage compound $Na\{[\eta^6\text{-cyclo-}(PhSiO_2)_6]_2Co_2Ni_4(\mu_6\text{-}Cl)\}$ was prepared and characterized by single crystal X-ray diffraction, spectroscopic, magnetic and electrochemical methods.

Keywords: Nickel; Cobalt; Cyclosiloxane; Cluster; Cage; Heterobimetallics

1. Introduction

In catalysis research one of the most urgent challenges is certainly to explore the two dimensional chemistry of transition metals "supported" on the surface of (main group metal) oxides [1]. It became evident in the 80s that catalyst/support interactions can be described in terms of well-defined surface complexes, which give a variety of chemical transformations in this "supported" state [1,2]. However only a very limited number of methods (e.g. reflection spectra, EXAFS) give direct information about the actual nature of these surface species. One of the most efficient indirect methods is the synthesis and characterization of transition metal complexes with surface model ligands. Early, well-characterized examples include silanolate osmium [3] and rhodium [4] complexes. More recently the degree of approximation to actual surface conditions was brought one step closer by the syntheses of mono- and di- [5] as well as polymetallic [6] derivatives of oligosiloxane ligands. These compounds can be regarded not only as conceptual models but also as physical prototypes of the surface conditions.

Now we report the synthesis and characterization of a new hexametallic derivative of a cyclic oligosiloxane ligand with *two different* transition metals in the same molecule.

2. Experimental section

Starting materials were of commercial origin with the exception of the poly-(phenylsilsesquioxane) ligand precursor, which was prepared as described earlier [6,7].

UV-Vis spectra were obtained with a Cecil CE 6606 instrument. The conductivity was obtained with a Conductimeter Crison mod 525 (all constant 1.02) instrument and the cyclic voltammetric measurements were performed by a Potentiostat-Galvanostat PAR 273A instrument using hanging-drop mercury (HDME) electrode, under Ar atmosphere in DMF. Attempt at obtaining ^{1}H-NMR spectra was made using Bruker AMX 400 (FT, 400 MHz) instrument.

Infrared spectra were obtained by a Bruker FT-IR IFS 113V instrument, using KBr pellets for the 4000–500 cm^{-1} and polyethylene pellets for the 500–50 cm^{-1} range, the far infrared spectra were registered under reduced pressure. X-ray diffraction measurements were made at 153 K using an automatic four-circle Siemens P3/PC diffractometer.

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2.1. Preparation of $Na\{[\eta^6\text{-cyclo-}(PhSiO_2)_6]_2Co_2Ni_4(\mu_6\text{-}Cl)\}$

Poly-(phenylsilsesquioxane) (**1**) $[PhSiO_{1.5}]_n$, 10 g (77 mmol) and sodium hydroxide, 1.78 g (44.5 mmol) were suspended in 200 ml of n-butanol in a reaction vessel equipped with a KPG stirrer and a reflux condenser. The reaction mixture, stirred, was heated by oil bath (120 ± 5°C) under reflux for 30 min and when the solution was obtained metallic sodium (1.02 g, 44.5 mmol) cut into small pieces was added at once. Then the solution was stirred and refluxed for 30 min. After this period, still under reflux and stirring, hexammine nickel (II) dichloride, $[Ni(NH_3)_6]Cl_2$, 5.90 g (25.5 mmol) was added at once, the colour of the solution in the reaction mixture turning to orange. Then the reaction mixture was stirred and refluxed for an additional 30 min. To the reaction mixture, while under stirring and reflux, was then added the solution of cobalt chloride, $CoCl_2$ (anhydrous), 2.48 g (19.1 mmol) in 40 ml of n-butanol dropwise. The resultant dark green slurry was stirred under reflux for 40 min. Then the oil bath was removed, the precipitate (NaCl) was filtered off from the warm reaction mixture and the solvent was drawn dry at low pressure. The green residue (15.35 g) was extracted by 100 ml of dimethylformamide (DMF) and the extracted material was recrystallized from DMF. The product was proved to be a solvate of the title compound **3**. Yield: 6.34 g (36.5%).

2.2. Characterization of complex $\mathbf{3} \cdot 7\ DMF \cdot 8\ H_2O$

Analyses found: C 42.7, H 4.3, Cl 1.6 N 3.4, Na 1.0, Si 12.7, ratio of Co/Ni (molar) = 1 : 2.03. $Na\{[(C_6H_5SiO_2)_6]_2Co_2Ni_4Cl\}[HC(O)N(CH_3)_2]_7(H_2O)_8$: $C_{93}H_{125}ClCo_2N_7NaNi_4O_{39}Si_{12}$ Calcd.: C 41.17, H 4.64, Cl 1.31, N 3.61, Na 0.85, Si 12.76, Co/Ni ratio (molar) = 1 : 2.00.

Solubility: n-butanol, ethanol/toluene (1 : 4 v/v), DMF, DMSO, THF. ^{1}H-NMR: attempted with a solution in THF-d_8. Supposedly the paramagnetism of the complex **3** (see later) prevents observation of the Ph-signals. Signals corresponding to (dissociated ?) DMF were obtained. Cyclic voltammetry results are in Fig. 1, experimental conditions: solvent DMF, concentration of **3** 10^{-4} M, supporting electrolyte 0.1 M $n\text{-}Bu_4NClO_4$, electrodes: hanging mercury drop (HMDE)//Ag/AgCl/3M NaCl//Pt. Conductivity: $\lambda = 33.2$ μS cm^{-1} (DMF).

Magnetic susceptibility (27.2°C, Gouy method): $\chi_M{}^c = 45062.45 \times 10^{-6}$ unit × mol; $\mu_{eff} = 10.4455$ BM; $n_{eff}(= \mu_{eff}/\mu_{Si}$ calc.) = 6.04. UV-VIS (DMF): $\lambda_1 = 266$ nm ($\epsilon_1 = 3552$ M^{-1} cm^{-1}), $\lambda_2 = 419$ nm ($\epsilon_2 = 202$ M^{-1} cm^{-1}), $\lambda_3 = 577$ nm ($\epsilon_3 = 79$ M^{-1} cm^{-1}). MIR (KBr pellet): 3710w (ν O–H, non assoc.), ~ 3400mw br (ν O–H, assoc.), 3120mw, 3080mw, 3008w, 2910w (ν C–H), 1650s (ν C–O), 1600w, 1490w, 1410m, 1350m (ar. ring ν C–C), 1123ms (ν Si–C(ar.)), 1045vs (ν Si–O, with more ionic O), 1028vs, doublet, (ν Si–O, with more covalent O), 732mw, 723m, 702m (ar. C–H), 510mw, 498s, 463m (ν Si–O skeletal). FIR (polyethylene pellet): 463w (ν Si–O skeletal), 374vw, 360sh, vw, 326vvw (ν Ni–O and Co–O) 247m (δ CoO_4 or δ CoO_5), 240sh, w (Si–O–Si skeletal and/or δ CoO_5), 187vvw, 162vvw, 121w (ν Na–O). X-ray diffraction: light-green crystal of **3** are triclinic, at −120°C: $a = 18.47(2)$, $b = 18.67(1)$, $c = 20.75(2)$ Å, $\alpha = 81.93(2)$, $\beta = 82.44(2)$, $\gamma = 62.52(2)°$, $V = 6265(9)$ Å^3, space group $P\text{-}1$, $Z = 2$. ($C_{90}H_{102}ClN_6(Co/Ni)_6O_{30}Si_{12} \cdot 0.5Na \cdot 3C_3H_7NO \cdot 2CH_4O \cdot 1.5H_2O$), $\mu = 11.0$ cm^{-1}, $d_{calc} = 1.46$ g/cm^3.

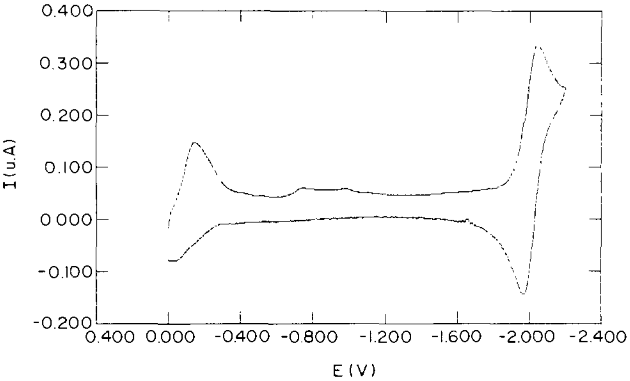

Fig. 1. Cyclic voltammogram of **3**. Conditions are given in the Experimental section.

Unit cell parameters and intensities of 15560 reflections were measured with a Siemens P3/PC diffractiometer at −120°C (λ Mo Kα, graphite monochromator, $\theta/2\theta$-scan, $\theta_{max} = 22°$). The structure was solved by direct method and refined anisotropically by a full-matrix least-squares technique. Hydrogen atoms were not located (for phenyl and methyne hydrogens their positions were calculated geometrically and were included in the refinement in the rigid model approximation with $U_{ISO} = 0.05$ Å^2). Disordering of two phenyl groups (at Si4 and Si11), two coordinated DMF molecules (at Ni1 and Ni5) and three solvate DMF molecules over two positions was resolved in difference Fourier maps. One Na$^+$ counter-ion, two solvate MeOH molecules and three solvate water molecules were objectively located and refined isotropically (excluding Na) with occupancy factors g = 0.5. All atomic positions of disordered groups and molecules were also refined isotropically with g = 0.5, excluding the O8sa (g = 0.67) and O8sb (g = 0.33) atoms of the one of the DMF solvate molecules.

All calculations were carried out on IBM-PC/AT computers using the SHELXTL-Plus program package (PC-Version) [8]. A full set of the tables containing all geometric parameters and structure factors is available from the authors on request. Atomic coordinates are

Table 1
Atomic coordinates (×10^4) of the crystal of Na{[η^6-c-(PhSiO$_2$)$_6$]$_2$ Co$_2$Ni$_4$(μ_6-Cl)}·3(C$_3$H$_7$NO)·2(CH$_3$OH)·1.5(H$_2$O)

Atom	x	y	z	U (eq)
Ni(1)	391(1)	1263(1)	−591(1)	27(1)
Ni(2)	−1037(1)	1198(1)	−929(1)	23(1)
Ni(3)	1436(1)	77(1)	341(1)	27(1)
Cl(1)	0	0	0	38(2)
Si(1)	154(2)	1843(2)	878(2)	20(2)
Si(2)	−1359(2)	2488(2)	131(2)	22(2)
Si(3)	−2472(2)	1679(2)	276(2)	23(2)
Si(4)	−2105(2)	167(2)	1205(2)	21(2)
Si(5)	−597(2)	−477(2)	1960(2)	21(2)
Si(6)	518(2)	327(2)	1813(2)	20(2)
O(1)	−796(5)	2387(5)	720(4)	23(4)
O(2)	−2085(5)	2255(5)	444(4)	28(4)
O(3)	−2522(5)	1122(5)	952(4)	27(4)
O(4)	−1552(5)	31(5)	1810(4)	25(4)
O(5)	−279(5)	177(5)	2077(4)	24(4)
O(6)	190(5)	1292(5)	1567(4)	26(4)
O(1M)	690(4)	1293(5)	310(4)	21(4)
O(2M)	−834(5)	1961(4)	−451(4)	20(4)
O(3M)	−1970(5)	1142(5)	−296(4)	24(4)
O(4M)	1579(5)	382(5)	−636(4)	22(4)
O(5M)	51(5)	1042(4)	−1396(4)	22(4)
O(6M)	−1063(5)	235(5)	−1255(4)	22(4)
O(1S)	636(6)	2174(6)	−1064(6)	53(6)
N(1SA)	313(31)	2953(29)	−2048(24)	139(17)
N(1SB)	−5(29)	3374(30)	−1723(24)	129(17)
C(1S1)	258(22)	2545(20)	−1407(16)	23(8)
C(1S2)	−797(32)	3771(31)	−2272(25)	106(17)
C(1S3)	1199(42)	2846(39)	−2238(32)	175(26)
C(1S4)	−78(22)	2670(20)	−1530(16)	42(10)
C(1S5)	−363(32)	3463(30)	−2499(24)	98(16)
C(1S6)	350(63)	3877(62)	−1185(50)	314(50)
O(2S)	−1749(5)	2075(5)	−1597(4)	35(5)
N(2S)	−2568(8)	2499(8)	−2428(6)	57(7)
C(2S1)	−2120(8)	1960(9)	−1970(7)	36(7)
C(2S2)	−2660(13)	3365(11)	−2469(10)	94(12)
C(2S3)	−2949(14)	2319(14)	−2922(11)	125(15)
O(3S)	2436(6)	131(7)	612(5)	47(6)
N(3S)	3579(9)	−499(12)	1196(8)	97(11)
C(3S1)	2944(10)	−455(12)	877(9)	61(10)
C(3S2)	3584(13)	261(14)	1296(12)	113(16)
C(3S3)	4196(14)	−1307(16)	1472(16)	173(19)
Na(1)	1847(7)	1380(7)	−284(5)	44(6)
O(7SA)	2736(27)	1765(24)	−357(19)	120(14)
O(7SB)	4532(18)	523(16)	−128(14)	100(9)
N(7SA)	3843(19)	1858(18)	5(14)	60(8)
N(7SB)	3178(22)	1499(18)	−154(14)	44(8)
C(7S1)	3629(35)	1416(34)	−256(25)	94(17)
C(7S2)	4734(26)	1522(25)	17(20)	91(13)
C(7S3)	3286(24)	2565(26)	229(19)	78(12)
C(7S4)	3865(27)	826(27)	−316(19)	77(12)
C(7S5)	3347(27)	2013(28)	287(21)	80(13)
C(7S6)	2364(33)	1711(31)	−196(25)	95(17)
C(11)	554(8)	2567(8)	1003(7)	30(7)
C(12)	1116(11)	2411(10)	1443(9)	75(11)
C(13)	1428(12)	2919(12)	1500(9)	78(13)
C(14)	1254(12)	3577(12)	1117(12)	91(13)
C(15)	794(17)	3726(15)	611(17)	198(25)
C(16)	460(14)	3205(12)	556(12)	122(17)
C(21)	−1863(8)	3589(8)	−157(6)	30(6)
C(22)	−2298(9)	3848(9)	−709(7)	44(8)
C(23)	−2703(10)	4672(9)	−907(7)	53(9)
C(24)	−2683(10)	5246(9)	−605(8)	52(9)
C(25)	−2244(12)	5000(9)	−75(10)	87(12)
C(26)	−1826(11)	4183(9)	161(8)	65(10)
C(31)	−3544(7)	2351(8)	59(7)	28(6)
C(32)	−3692(9)	2734(9)	−550(8)	46(8)
C(33)	−4470(12)	3243(12)	−743(9)	82(11)
C(34)	−5126(13)	3430(18)	−339(12)	146(18)
C(35)	−4995(11)	3018(17)	291(12)	141(17)
C(36)	−4213(9)	2495(10)	478(9)	64(10)
C(41)	−2950(8)	−76(9)	1548(6)	34(7)
C(42)	−2645(19)	−941(19)	1810(15)	44(8)
C(42′)	−2985(16)	−525(16)	2066(13)	26(7)
C(43)	−3209(26)	−1201(25)	2094(20)	83(12)
C(43′)	−3675(26)	−630(23)	2325(18)	62(11)
C(44)	−4227(15)	−443(19)	2035(12)	106(18)
C(45)	−4402(24)	207(23)	1890(21)	56(11)
C(45′)	−4394(25)	227(25)	1435(22)	81(13)
C(46)	−3758(20)	433(19)	1594(17)	48(9)
C(46′)	−3676(22)	326(21)	1161(18)	60(10)
C(51)	−562(9)	−1103(8)	2754(6)	32(7)
C(52)	−1216(10)	−1074(10)	3139(7)	51(9)
C(53)	−1153(14)	−1552(11)	3724(9)	77(12)
C(54)	−403(15)	−2077(11)	3930(9)	80(12)
C(55)	251(14)	−2103(12)	3571(9)	104(13)
C(56)	194(10)	−1632(10)	2977(8)	66(9)
C(61)	1118(8)	115(8)	2528(6)	29(7)
C(62)	948(9)	−191(8)	3134(6)	36(7)
C(63)	1428(10)	−394(9)	3645(6)	48(8)
C(64)	2144(10)	−311(10)	3548(7)	59(10)
C(65)	2329(10)	14(10)	2954(8)	56(9)
C(66)	1846(9)	210(8)	2449(7)	42(8)
Ni(4)	3618(1)	5630(1)	−4032(1)	25(1)
Ni(5)	3957(1)	4257(1)	−4730(1)	23(1)
Ni(6)	4679(1)	6407(1)	−4316(1)	26(1)
Cl(2)	5000	5000	−5000	52(3)
Si(7)	2951(2)	7301(2)	−5042(2)	22(2)
Si(8)	2524(2)	5989(2)	−5286(2)	23(2)
Si(9)	3524(2)	4771(2)	−6266(2)	22(2)
Si(10)	4997(2)	4864(2)	−7013(2)	22(2)
Si(11)	5434(2)	6172(2)	−6758(2)	23(2)
Si(12)	4451(2)	7388(2)	−5779(2)	22(2)
O(7)	2467(5)	6892(5)	−5350(4)	26(4)
O(8)	2884(5)	5632(5)	−5997(4)	23(4)
O(9)	4074(5)	4950(5)	−6881(3)	23(4)
O(10)	4915(5)	5771(5)	−7026(4)	22(4)
O(11)	4780(5)	7042(5)	−6481(4)	27(4)
O(12)	3503(5)	7532(5)	−5628(4)	24(4)
O(7M)	3487(5)	6732(4)	−4466(4)	22(4)
O(8M)	3079(5)	5405(5)	−4713(4)	24(4)
O(9M)	4080(5)	4154(5)	−5711(3)	23(4)
O(10M)	4428(5)	5753(4)	−3519(3)	19(4)
O(11M)	3975(5)	4433(5)	−3786(4)	21(4)
O(12M)	4996(5)	3193(5)	−4790(4)	26(4)
O(4S)	2593(6)	6104(6)	−3365(4)	38(5)
N(4S)	1675(9)	7193(10)	−2835(7)	75(9)
C(4S1)	2253(10)	6831(10)	−3290(7)	44(9)
C(4S2)	1280(13)	8089(12)	−2787(10)	110(13)
C(4S3)	1415(14)	6693(17)	−2303(10)	128(17)
O(5S)	3122(6)	3785(7)	−4501(5)	45(6)
N(5SA)	2906(25)	2655(24)	−4413(19)	110(12)
N(5SB)	1996(24)	3979(22)	−3860(18)	101(11)
C(5S1)	3394(24)	3035(26)	−4527(19)	78(12)
C(5S2)	3396(47)	1506(49)	−4516(44)	201(32)
C(5S3)	2167(43)	3085(42)	−4061(32)	148(23)
C(5S4)	2608(26)	4089(24)	−4090(20)	73(11)

Table 1 (*Continued*)

Atom	*x*	*y*	*z*	*U* (eq)
C(5S5)	1383(36)	4369(35)	−3389(29)	144(20)
C(5S6)	1781(50)	3524(52)	−4286(41)	198(36)
O(1W)	1607(19)	4684(19)	−3029(16)	117(11)
O(2W)	2527(15)	4820(15)	−3731(12)	87(8)
O(6S)	4354(6)	7440(5)	−3861(5)	41(5)
N(6S)	3571(10)	8212(8)	−3046(7)	75(9)
C(6S1)	3930(10)	7541(10)	−3341(8)	52(9)
C(6S2)	3649(17)	8934(11)	−3328(10)	134(17)
C(6S3)	3095(17)	8253(15)	−2410(11)	148(18)
C(71)	2141(8)	8272(8)	−4753(6)	26(6)
C(72)	1292(9)	8484(9)	−4675(7)	41(8)
C(73)	722(9)	9208(10)	−4462(7)	48(8)
C(74)	953(11)	9757(9)	−4307(7)	50(8)
C(75)	1755(12)	9583(9)	−4386(8)	64(10)
C(76)	2338(10)	8839(9)	−4595(7)	51(8)
C(81)	1490(8)	6062(8)	−5117(7)	31(7)
C(82)	1146(8)	5847(9)	−5578(8)	44(8)
C(83)	418(11)	5807(10)	−5429(10)	61(10)
C(84)	−8(12)	6023(11)	−4863(13)	81(13)
C(85)	292(12)	6242(12)	−4390(10)	86(12)
C(86)	1051(10)	6253(10)	−4533(9)	58(10)
C(91)	2880(8)	4377(9)	−6588(7)	35(7)
C(92)	2510(9)	3986(10)	−6179(8)	50(9)
C(94)	1834(12)	3879(11)	−7039(9)	73(12)
C(95)	2228(12)	4256(12)	−7465(9)	79(13)
C(95)	2002(10)	3725(11)	−6423(10)	70(12)
C(96)	2711(10)	4519(10)	−7236(8)	65(11)
C(101)	5373(8)	4558(8)	−7842(7)	33(7)
C(102)	6176(10)	4108(10)	−8019(6)	54(9)
C(103)	6479(11)	3889(11)	−8661(8)	64(10)
C(104)	5973(14)	4155(12)	−9130(9)	80(13)
C(105)	5151(11)	4584(12)	−8968(8)	79(12)
C(106)	4858(11)	4792(10)	−8350(7)	65(10)
C(111)	6029(8)	6408(9)	−7470(7)	33(7)
C(112)	5895(17)	7094(17)	−7801(14)	31(7)
C(117)	6167(20)	7081(20)	−7456(17)	55(9)
C(113)	6327(22)	7248(21)	−8372(18)	50(9)
C(118)	6591(23)	7306(22)	−8021(19)	64(10)
C(114)	6970(16)	6731(18)	−8535(10)	108(17)
C(115)	7224(27)	5871(27)	−8261(21)	90(13)
C(119)	6587(35)	6330(34)	−8604(26)	124(18)
C(116)	6681(26)	5775(24)	−7740(19)	76(12)
C(120)	6124(26)	6164(26)	−8025(22)	86(13)
C(121)	4448(8)	8382(8)	−5845(6)	30(7)
C(122)	4368(9)	8898(9)	−6418(7)	43(8)
C(123)	4319(10)	9648(10)	−6436(8)	54(9)
C(124)	4336(15)	9948(12)	−5896(11)	103(16)
C(125)	4348(16)	9520(14)	−5323(10)	122(19)
C(126)	4438(13)	8722(11)	−5301(8)	80(13)
O(1E)	3597(25)	1902(25)	−4907(20)	160(15)
C(1E)	3487(48)	1565(48)	−3991(41)	216(34)
O(2E)	218(34)	5492(33)	−2469(26)	249(23)
C(2E)	993(53)	4875(53)	−2021(42)	266(38)
O(8SA)	4164(16)	2290(16)	−6509(13)	112(9)
O(8SB)	3558(51)	1786(48)	−7546(40)	180(34)
N(8S)	4148(22)	2349(22)	−7529(14)	147(20)
C(8S1)	4028(23)	2103(25)	−6962(32)	216(35)
C(8S2)	4537(19)	2886(26)	−7769(17)	191(28)
C(8S3)	3625(23)	2109(32)	−7999(18)	219(33)
O(9SA)	630(32)	2058(30)	−6660(26)	226(22)
O(9SB)	960(24)	1562(22)	−5659(19)	150(13)
N(9S)	1528(22)	1696(19)	−6156(17)	60(10)
C(9S1)	1106(29)	1851(24)	−6237(21)	62(12)
C(9S2)	2289(36)	1684(34)	−5766(31)	134(20)
C(9S3)	2154(31)	1928(28)	−6961(25)	107(15)
C(9S4)	1853(42)	1412(38)	−5530(32)	157(23)
C(9S5)	1585(27)	1973(24)	−6613(22)	71(12)
C(9S6)	2323(27)	1712(25)	−6359(24)	90(13)
O(3W)	4194(11)	2786(11)	4533(9)	42(5)

Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

given in Table 1, the main geometrical parameters in Tables 2 and 3.

3. Results and discussion

The preparative approach to a bimetallic cluster can proceed by three principal paths: (i) reaction of the oligosiloxane ligand with a mixture of the transition metal ions to be built into the cluster, (ii) preparation of a cluster of one metal and step-by-step exchange of the ions of this "first" metal and (iii) preparation of a cluster with two metals of very different character (*i.e.* transition *and* main group metal) and to change only one of these (the more mobile). Some preliminary experiments and considerations based on earlier structural studies [6] convinced us that path (iii) is the most appropriate. It was convenient to choose as intermediate the known complex $Na_2\{[(PhSiO_2)_6]_2Na_4Ni_4(OH)_2\} \cdot 16$ (n-BuOH) (**2**) [6c] in which a transition metal is combined with an alkali metal; moreover X-ray molecular structure determination revealed that the cluster-Na^+ ions occupy very exposed positions in the somewhat twisted cluster framework. These considerations proved to be useful and the title complex **3** could be obtained with medium to good overall yields by the following reactions:

$$12/n[PhSiO_{1.5}]_n + 7\ NaOH + 7\ Na + 4[Ni(NH_3)_6]Cl_2 \longrightarrow \underset{\mathbf{2}}{Na_2\{[(PhSiO_2)_6]_2Na_4Ni_4(OH)_2\}} \quad (1)$$

$$\mathbf{2} + 3\ CoCl_2 \xrightarrow[-Co(OH)_2,\ -5NaCl]{} \underset{\mathbf{3}}{Na\{[(PhSiO_2)_6]_2Co_2Ni_4Cl\}} \quad (2)$$

The product **3** was isolated as crystalline solvates and characterized by elemental analyses, UV-Vis and IR spectra, magnetic susceptibility, cyclic voltammetry and X-ray diffraction (cf. Experimental section). Some of these results need to be commented upon.

The UV-Vis spectra are not well resolved but the position and intensity of the bands at > 250 nm are compatible with approximately square planar Ni^{II} and Co^{II} bound to ligands with high ligand field [9].

Table 2
Bond lengths(d, pm) in complex **3**

Ni(1)-O(1M)	2.033(9)	Ni(1)-O(2M)	2.029(7)
Ni(1)-O(4M)	2.046(7)	nI(1)-O(5M)	2.014(10)
Ni(1)-O(1S)	2.045(13)	Ni(2)-O(2M)	2.034(10)
Ni(2)-O(3M)	2.058(9)	Ni(2)-O(5M)	2.023(9)
Ni(2)-O(6M)	2.031(10)	Ni(2)-O(2S)	2.046(8)
Ni(3)-O(1M)	2.037(8)	Ni(3)-O(4M)	2.043(8)
Ni(3)-O(3S)	2.049(14)	Ni(3)-O(3MA)	2.030(8)
Ni(3)-O(6MA)	2.032(8)	Si(1)-O(1)	1.623(8)
Si(1)-O(6)	1.629(8)	Si(1)-O(1M)	1.587(8)
Si(1)-C(11)	1.873(18)	Si(2)-O(1)	1.642(10)
Si(2)-O(2)	1.625(11)	Si(2)-O(2M)	1.584(8)
Si(2)-C(21)	1.866(13)	Si(3)-O(2)	1.633(12)
Si(3)-O(3)	1.643(9)	Si(3)-O(3M)	1.569(8)
Si(3)-C(31)	1.864(12)	Si(4)-O(3)	1.621(8)
Si(4)-O(4)	1.640(10)	Si(4)-C(41)	1.848(18)
Si(4)-O(4MA)	1.584(8)	Si(5)-O(4)	1.619(9)
Si(5)-O(5)	1.638(12)	Si(5)-C(51)	1.872(13)
Si(5)-O(5MA)	1.598(8)	Si(6)-O(5)	1.635(11)
Si(6)-O(6)	1.638(9)	Si(6)-C(61)	1.857(15)
Si(6)-O(6MA)	1.585(8)	O(1M)-Na(1)	2.385(16)
O(3M)-Ni(3A)	2.030(8)	O(4M)-Na(1)	2.361(18)
O(4M)-Si(4A)	1.584(8)	O(5M)-Si(5A)	1.598(8)
O(6M)-Ni(3A)	2.032(8)	O(6M)-Si(6A)	1.585(8)
O(1S)-C(1S1)	1.009(33)	O(1S)-C(1S4)	1.578(36)
O(1S)-Na(1)	2.654(16)	N(1SA)-C(1S1)	1.453(59)
N(1SA)-C(1S2)	1.979(136)	N(1SA)-C(1S3)	1.557(98)
N(1SB)-C(1S4)	1.381(73)	N(1SB)-C(1S5)	1.777(77)
N(1SB)-C(1S6)	1.902(148)	O(2S)-C(2S1)	1.198(21)
N(2S)-C(2S1)	1.332(17)	N(2S)-C(2S2)	1.535(27)
N(2S)-C(2S3)	1.470(33)	O(3S)-C(3S1)	1.182(18)
O(3S)-Na(1)	2.655(14)	N(3S)-C(3S1)	1.384(30)
N(3S)-C(3S2)	1.467(39)	N(3S)-C(3S3)	1.499(28)
Na(1)-O(7SA)	2.055(59)	O(7SA)-C(7S1)	1.500(77)
O(7SB)-C(7S4)	1.187(55)	N(7SA)-C(7S1)	1.271(85)
N(7SA)-C(7S2)	1.468(55)	N(7SA)-C(7S3)	1.344(46)
N(7SB)-C(7S4)	1.355(47)	N(7SB)-C(7S5)	1.567(70)
N(7SB)-C(7S6)	1.379(73)	C(11)-C(12)	1.376(26)
C(11)-C(16)	1.360(26)	C(12)-C(13)	1.341(36)
C(13)-C(14)	1.293(29)	C(14)-C(15)	1.354(44)
C(15)-C(16)	1.394(47)	C(21)-C(22)	1.385(20)
C(21)-C(26)	1.399(26)	C(22)-C(23)	1.390(20)
C(23)-C(24)	1.332(28)	C(24)-C(25)	1.350(28)
C(25)-C(26)	1.402(21)	C(31)-C(32)	1.357(20)
C(31)-C(36)	1.353(21)	C(32)-C(33)	1.383(23)
C(33)-C(34)	1.311(30)	C(34)-C(35)	1.409(34)
C(35)-C(36)	1.389(23)	C(41)-C(42)	1.489(35)
C(41)-C(42′)	1.280(30)	C(41)-C(46)	1.349(32)
C(41)-C(46′)	1.480(40)	C(42)-C(43)	1.377(65)
C(42′)-C(43′)	1.406(59)	C(43)-C(44)	1.763(43)
C(43′)-C(44)	1.139(53)	C(44)-C(45)	1.109(54)
C(44)-C(45′)	1.588(51)	C(45)-C(46)	1.472(63)
C(45′)-C(46′)	1.454(66)	C(51)-C(52)	1.340(23)
C(51)-C(56)	1.381(20)	C(52)-C(53)	1.386(23)
C(53)-C(54)	1.359(30)	C(54)-C(55)	1.317(35)
C(55)-C(56)	1.396(25)	C(61)-C(62)	1.366(18)
C(61)-C(66)	1.421(25)	C(62)-C(63)	1.369(21)
C(63)-C(64)	1.388(29)	C(64)-C(65)	1.369(23)
C(65)-C(66)	1.366(24)	Ni(4)-O(7M)	2.045(8)
Ni(4)-O(8M)	2.022(10)	Ni(4)-O(10M)	2.055(10)
Ni(4)-O(11M)	2.025(8)	Ni(4)-O(4S)	2.096(9)
Ni(5)-O(8M)	2.006(7)	Ni(5)-O(9M)	2.045(8)
Ni(5)-O(11M)	2.038(8)	Ni(5)-O(12M)	2.032(7)
Ni(5)-O(5S)	2.079(14)	Ni(6)-O(7M)	2.051(9)
Ni(6)-O(10M)	2.047(8)	Ni(6)-O(6S)	2.066(11)

Table 2 (*Continued*)

Ni(6)-O(9MA)	2.038(8)	Ni(6)-O(12A)	2.022(8)
Si(7)-O(7)	1.644(12)	Si(7)-O(12)	1.624(9)
Si(7)-O(7M)	1.588(8)	Si(7)-C(71)	1.856(12)
Si(8)-O(7)	1.627(10)	Si(8)-O(8)	1.635(8)
Si(8)-O(8M)	1.605(8)	Si(8)-C(81)	1.841(16)
Si(9)-O(8)	1.618(8)	Si(9)-O(9)	1.620(9)
Si(9)-O(9M)	1.599(8)	Si(9)-C(91)	1.883(19)
Si(10)-O(9)	1.625(10)	Si(10)-O(10)	1.626(10)
Si(10)-C(101)	1.834(14)	Si(10)-O(10A)	1.581(8)
Si(11)-O(10)	1.644(12)	Si(11)-O(11)	1.643(8)
Si(11)-C(111)	1.849(15)	Si(11)-O(11A)	1.603(8)
Si(12)-O(11)	1.603(8)	Si(12)-O(12)	1.638(10)
Si(12)-C(121)	1.840(17)	Si(12)-O(12A)	1.598(8)
O(9M)-Ni(6A)	2.038(8)	O(10M)-Si(1A)	1.581(8)
O(11M)-Si(1B)	1.603(8)	O(12M)-Ni(6A)	2.022(8)
O(12M)-Si(1C)	1.598(8)	O(4S)-C(4S1)	1.228(20)
N(4S)-C(4S1)	1.317(20)	N(4S)-C(4S2)	1.497(27)
N(4S)-C(4S3)	1.518(33)	O(5S)-C(5S1)	1.258(48)
O(5S)-C(5S4)	1.174(40)	N(5SA)-C(5S1)	1.363(78)
N(5SA)-C(5S2)	1.937(95)	N(5SA)-C(5S3)	1.389(72)
N(5SB)-C(5S4)	1.261(70)	N(5SB)-C(5S5)	1.384(65)
N(5SB)-C(5S6)	1.508(123)	O(6S)-C(6S1)	1.228(19)
N(6S)-C(6S1)	1.314(22)	N(6S)-C(6S2)	1.454(30)
N(6S)-C(6S3)	1.478(28)	C(71)-C(72)	1.421(22)
C(71)-C(76)	1.359(27)	C(72)-C(73)	1.365(19)
C(73)-C(74)	1.365(30)	C(74)-C(75)	1.354(29)
C(75)-C(76)	1.394(20)	C(81)-C(82)	1.408(26)
C(81)-C(86)	1.360(21)	C(82)-C(83)	1.374(28)
C(83)-C(84)	1.326(30)	C(84)-C(85)	1.378(38)
C(85)-C(86)	1.404(31)	C(91)-C(92)	1.362(25)
C(91)-C(96)	1.381(22)	C(92)-C(95)	1.411(32)
C(94)-C(95)	1.390(32)	C(94)-C(95)	1.316(29)
C(95)-C(96)	1.359(35)	C(101)-C(102)	1.353(20)
C(101)-C(106)	1.399(23)	C(102)-C(103)	1.414(21)
C(103)-C(104)	1.320(28)	C(104)-C(105)	1.370(28)
C(105)-C(106)	1.361(22)	C(111)-C(112)	1.294(32)
C(111)-C(117)	1.398(47)	C(111)-C(116)	1.362(38)
C(111)-C(120)	1.258(52)	C(112)-C(113)	1.411(47)
C(117)-C(118)	1.444(54)	C(113)-C(114)	1.177(38)
C(118)-C(114)	1.488(46)	C(114)-C(115)	1.497(55)
C(114)-C(119)	1.277(87)	C(115)-C(116)	1.426(64)
C(119)-C(120)	1.463(75)	C(121)-C(122)	1.400(19)
C(121)-C(126)	1.364(26)	C(122)-C(123)	1.355(27)
C(123)-C(124)	1.331(31)	C(124)-C(125)	1.334(30)
C(125)-C(126)	1.416(36)		

The IR spectra confirm elements of the structure, indicating relatively strong Co–O and Ni–O coordination and permitting the detection of even weak Na–O interaction in the low-energy range of the far-IR spectra.

The magnetic susceptibility measurement should be regarded as orientative. In the case of such a complicated molecule the diamagnetic corrections can be made (or interpreted) in a variety of ways. However the $\chi_{\mathrm{molar}} = 45062.45 \cdot 10^{-6}$ (unit × mol) and $\mu_{\mathrm{eff}} = 10.4455$ BM values correspond fairly well to 6 (6.04) unpaired electrons, most probably: 1 e/metal. This again indicates the oligosiloxane ligand as a high-field one. This result seems to complement well the more thorough magnetic studies of Fehér et al. [5c], done however with early transition metals. Whether in the present (and similar) cases magnetic metal–metal coupling could be suspected or even proved is the goal of further studies which are in course in our laboratories.

The cyclic voltammetry (Fig. 1) showed two important results. The voltammogram shows a high-intensity wave at $E_{pc} = 2.044$ mV. This wave appears to correspond roughly to 1 e^- uptake by each metal atom in

Table 3
Bond angles(°) in complex **3**

O(1M)–Ni(1)–O(2M)	97.6(3)	O(1M)–Ni(1)–O(4M)	80.5(3)
O(2M)–Ni(1)–O(4M)	168.8(4)	O(1M)–Ni(1)–O(5M)	168.2(4)
O(2M)–Ni(1)–O(5M)	81.5(3)	O(4M)–Ni(1)–O(5M)	98.0(3)
O(1M)–Ni(1)–O(1S)	97.8(5)	O(2M)–Ni(1)–O(1S)	95.5(4)
O(4M)–Ni(1)–O(1S)	95.8(4)	O(5M)–Ni(1)–O(1S)	94.0(5)
O(2M)–Ni(2)–O(3M)	97.6(4)	O(2M)–Ni(2)–O(5M)	81.2(4)
O(3M)–Ni(2)–O(5M)	166.2(3)	O(2M)–Ni(2)–O(6M)	166.5(3)
O(3M)–Ni(2)–O(6M)	81.2(4)	O(5M)–Ni(2)–O(6M)	96.7(4)
O(2M)–Ni(2)–O(2S)	95.6(4)	O(3M)–Ni(2)–O(2S)	97.6(3)
O(5M)–Ni(2)–O(2S)	96.2(3)	O(6M)–Ni(2)–O(2S)	97.9(4)
O(1M)–Ni(3)–O(4M)	80.5(3)	O(1M)–Ni(3)–O(3S)	98.8(4)
O(4M)–Ni(3)–O(3S)	97.6(4)	O(1M)–Ni(3)–O(3MA)	167.5(4)
O(4M)–Ni(3)–O(3MA)	96.8(3)	O(3S)–Ni(3)–O(3MA)	96.7(4)
O(1M)–Ni(3)–O(6MA)	97.9(3)	O(4M)–Ni(3)–O(6MA)	166.9(4)
O(3S)–Ni(3)–O(6MA)	95.5(4)	O(3MA)–Ni(3)–O(6MA)	81.9(3)
O(1)–Si(1)–O(6)	108.7(5)	O(1)–Si(1)–O(1M)	112.5(5)
O(6)–Si(1)–O(1M)	110.9(4)	O(1)–Si(1)–C(11)	106.7(5)
O(6)–Si(1)–C(11)	107.3(6)	O(1M)–Si(1)–C(11)	110.4(6)
O(1)–Si(2)–O(2)	108.1(5)	O(1)–Si(2)–O(2M)	112.3(4)
O(2)–Si(2)–O(2M)	111.9(6)	O(1)–Si(2)–C(21)	106.7(6)
O(2)–Si(2)–C(21)	106.6(5)	O(2M)–Si(2)–C(21)	110.9(5)
O(2)–Si(3)–O(3)	107.3(5)	O(2)–Si(3)–O(3M)	112.9(5)
O(3)–Si(3)–O(3M)	111.6(4)	O(2)–Si(3)–C(31)	107.8(6)
O(3)–Si(3)–C(31)	107.1(6)	O(3M)–Si(3)–C(31)	109.9(6)
O(3)–Si(4)–O(4)	108.3(5)	O(3)–Si(4)–C(41)	106.6(5)
O(4)–Si(4)–C(41)	107.0(6)	O(3)–Si(4)–O(4MA)	111.9(4)
O(4)–Si(4)–O(4MA)	111.8(4)	C(41)–Si(4)–O(4MA)	111.0(7)
O(4)–Si(5)–O(5)	107.4(5)	O(4)–Si(5)–C(51)	106.7(6)
O(5)–Si(5)–C(51)	107.0(6)	O(4)–Si(5)–O(5MA)	112.6(5)
O(5)–Si(5)–O(5MA)	112.3(5)	C(51)–Si(5)–O(5MA)	110.5(5)
O(5)–Si(6)–O(6)	107.9(4)	O(5)–Si(6)–C(61)	106.7(6)
O(6)–Si(6)–C(61)	107.2(6)	O(5)–Si(6)–O(6MA)	112.2(6)
O(6)–Si(6)–O(6MA)	112.0(4)	C(61)–Si(6)–O(6MA)	110.6(5)
Si(1)–O(1)–Si(2)	136.1(5)	Si(2)–O(2)–Si(3)	136.8(6)
Si(3)–O(3)–Si(4)	136.6(5)	Si(4)–O(4)–Si(5)	136.7(5)
Si(5)–O(5)–Si(6)	135.2(5)	Si(1)–O(6)–Si(6)	137.3(5)
Ni(1)–O(1M)–Ni(3)	89.4(4)	Ni(1)–O(1M)–Si(1)	130.0(4)
Ni(3)–O(1M)–Si(1)	130.3(4)	Ni(1)–O(1M)–Na(1)	83.5(4)
Ni(3)–O(1M)–Na(1)	83.5(4)	Si(1)–O(1M)–Na(1)	124.0(7)
Ni(1)–O(2M)–Ni(2)	90.1(3)	Ni(1)–O(2M)–Si(2)	130.4(6)
Ni(2)–O(2M)–Si(2)	130.2(6)	Ni(2)–O(3M)–Si(3)	129.1(7)
Ni(2)–O(3M)–Ni(3A)	89.4(3)	Si(3)–O(3M)–Ni(3A)	131.3(5)
Ni(1)–O(4M)–Ni(3)	88.9(3)	Ni(1)–O(4M)–Na(1)	83.8(4)
Ni(3)–O(4M)–Na(1)	84.0(4)	Ni(1)–O(4M)–Si(4A)	130.0(5)
Ni(3)–O(4M)–Si(4A)	130.4(4)	Na(1)–O(4M)–Si(4A)	123.9(6)
Ni(1)–O(5M)–Ni(2)	90.8(3)	Ni(1)–O(5M)–Si(5A)	129.7(5)
Ni(2)–O(5M)–Si(5A)	130.7(6)	Ni(2)–O(6M)–Ni(3A)	90.1(3)
Ni(2)–O(6M)–Si(6A)	131.2(6)	Ni(3A)–O(6M)–Si(6A)	129.3(5)
Ni(1)–O(1S)–C(1S1)	117.1(28)	Ni(1)–O(1S)–C(1S4)	105.1(18)
Ni(1)–O(1S)–Na(1)	76.7(4)	C(1S1)–O(1S)–Na(1)	166.0(27)
C(1S4)–O(1S)–Na(1)	178.1(17)	C(1S1)–N(1SA)–C(1S2)	109.1(49)
C(1S1)–O(1SA)–C(1S3)	110.9(42)	C(1S2)–N(1SA)–C(1S3)	135.6(52)
C(1S4)–N(1SB)–C(1S5)	91.9(43)	C(1S4)–N(1SB)–C(1S6)	124.0(47)
C(1S5)–N(1SB)–C(1S6)	144.0(50)	O(1S)–C(1S1)–N(1SA)	138.5(42)
O(1S)–C(1S4)–N(1SB)	103.5(36)	Ni(2)–O(2S)–C(2S1)	123.5(9)
C(2S1)–N(2S)–C(2S2)	117.9(16)	C(2S1)–N(2S)–C(2S3)	124.9(16)

the cluster and it is reasonable to suppose that it corresponds to spin/spin pairing of the unpaired electrons indicated by the magnetic measurement (this hypothesis should be tested by preparative electrolysis and subsequent magnetic measurement). The other interesting feature of the voltammogram is that the

Table 3 (*Continued*)

C(2S2)-N(2S)-C(2S3)	117.2(14)	O(2S)-C(2S1)-N(2S)	126.0(16)
Ni(3)-O(3S)-C(3S1)	118.9(15)	Ni(3)-O(3S)-Na(1)	76.6(5)
C(3S1)-O(3S)-Na(1)	156.4(12)	C(3S1)-N(3S)-C(3S2)	118.2(16)
C(3S1)-N(3S)-C(3S3)	119.6(23)	C(3S2)-N(3S)-C(3S3)	112.1(21)
O(3S)-C(3S1)-N(3S)	127.1(23)	O(1M)-Na(1)-O(4M)	67.5(5)
O(1M)-Na(1)-O(1S)	75.0(5)	O(4M)-Na(1)-O(1S)	74.2(5)
O(1M)-Na(1)-O(3S)	73.7(4)	O(4M)-Na(1)-O(3S)	75.5(5)
O(1S)-Na(1)-O(3S)	142.7(7)	O(1M)-Na(1)-O(7SA)	149.2(13)
O(4M)-Na(1)-O(7SA)	141.4(12)	O(1S)-Na(1)-O(7SA)	117.0(12)
O(3S)-Na(1)-O(7SA)	100.2(12)	Na(1)-O(7SA)-C(7S1)	138.5(36)
C(7S1)-N(7SA)-C(7S2)	113.0(35)	C(7S1)-N(7SA)-C(7S3)	121.3(41)
C(7S2)-N(7SA)-c(7S3)	125.7(42)	C(7S4)-N(7SB)-C(7S5)	112.3(39)
C(7S4)-N(7SB)-C(7S6)	130.9(47)	C(7S5)-N(7SB)-C(7S6)	115.3(33)
O(7SA)-C(7S1)-N(7SA)	116.1(41)	O(7SB)-C(7S4)-N(7SB)	131.4(50)
Si(1)-C(11)-C(12)	124.1(12)	Si(1)-C(11)-C(16)	120.9(16)
C(12)-C(11)-C(16)	113.2(20)	C(11)-C(12)-C(13)	123.1(16)
C(12)-C(13)-C(14)	122.0(22)	C(13)-C(14)-C(15)	119.0(27)
C(14)-C(15)-C(16)	118.9(25)	C(11)-C(16)-C(15)	122.6(24)
Si(2)-C(21)-C(22)	120.0(12)	Si(2)-C(21)-C(26)	123.0(10)
C(22)-C(21)-C(26)	117.1(13)	C(21)-C(22)-C(23)	119.9(16)
C(22)-C(23)-C(24)	123.7(16)	C(23)-C(24)-C(25)	117.0(14)
C(24)-C(25)-C(26)	122.9(20)	C(21)-C(26)-C(25)	119.4(17)
Si(3)-C(31)-C(32)	120.3(10)	Si(3)-C(31)-C(36)	124.1(11)
C(32)-C(31)-C(36)	115.6(12)	C(31)-C(32)-C(33)	123.4(15)
C(32)-C(33)-C(34)	122.3(18)	C(33)-C(34)-C(35)	115.6(18)
C(34)-C(35)-C(36)	121.5(19)	C(31)-C(36)-C(35)	121.4(17)
Si(4)-C(41)-C(42)	112.0(15)	Si(4)-C(41)-C(42′)	128.8(17)
C(42)-C(41)-C(42′)	38.1(17)	Si(4)-C(41)-C(46)	127.7(20)
C(42)-C(41)-C(46)	120.3(24)	Si(4)-C(41)-C(46′)	113.4(18)
C(42′)-C(41)-C(46′)	117.8(24)	C(41)-C(42)-C(43)	118.1(25)
C(41)-C(42′)-C(43′)	125.6(26)	C(42)-C(43)-C(44)	112.7(30)
C(42′)-C(43′)-C(44)	122.8(35)	C(43)-C(44)-C(45)	124.1(38)
C(43′)-C(44)-C(45′)	119.3(41)	C(44)-C(45)-C(46)	118.3(32)
C(44)-C(45′)-C(46′)	114.1(31)	C(41)-C(46)-C(45)	125.1(28)
C(41)-C(46′)-C(45′)	116.5(29)	Si(5)-C(51)-C(52)	125.4(10)
Si(5)-C(51)-C(56)	118.3(12)	C(52)-C(51)-C(56)	116.2(13)
C(51)-C(52)-C(53)	123.0(16)	C(52)-C(53)-C(54)	119.8(21)
C(53)-C(54)-C(55)	118.7(18)	C(54)-C(55)-C(56)	121.8(19)
C(51)-C(56)-C(55)	120.4(17)	Si(6)-C(61)-C(62)	124.7(13)
Si(6)-C(61)-C(66)	119.7(10)	C(62)-C(61)-C(66)	115.5(13)
C(61)-C(62)-C(63)	123.9(17)	C(62)-C(63)-C(64)	119.2(14)
C(63)-C(64)-C(65)	118.9(16)	C(64)-C(65)-C(66)	121.0(19)
C(61)-C(66)-C(65)	121.3(14)	O(7M)-Ni(4)-O(8M)	96.1(4)
O(7M)-Ni(4)-O(10M)	81.6(4)	O(8M)-Ni(4)-O(10M)	164.8(3)
O(7M)-Ni(4)-O(11M)	165.4(3)	O(8M)-Ni(4)-O(11M)	80.4(3)
O(10M)-Ni(4)-O(11M)	98.1(3)	O(7M)-Ni(4)-O(4S)	95.3(4)
O(8M)-Ni(4)-O(4S)	97.7(4)	O(10M)-Ni(4)-O(4S)	97.5(4)
O(11M)-Ni(4)-O(4S)	99.2(4)	O(8M)-Ni(5)-O(9M)	99.3(3)
O(8M)-Ni(5)-O(11M)	80.5(3)	O(9M)-Ni(5)-O(11M)	170.5(4)
O(8M)-Ni(5)-O(12M)	169.0(4)	O(9M)-Ni(5)-O(12M)	79.6(3)
O(11M)-Ni(5)-O(12M)	98.8(3)	O(8M)-Ni(5)-O(5S)	92.8(4)
O(9M)-Ni(5)-O(5S)	95.9(4)	O(11M)-Ni(5)-O(5S)	93.7(4)
O(12M)-Ni(5)-O(5S)	98.2(4)	O(7M)-Ni(6)-O(10M)	81.7(3)
O(7M)-Ni(6)-O(6S)	92.4(4)	O(10M)-Ni(6)-O(6S)	97.7(4)
O(7M)-Ni(6)-O(9MA)	165.8(4)	O(10M)-Ni(6)-O(9MA)	97.1(3)
O(6S)-Ni(6)-O(9MA)	101.7(4)	O(7M)-Ni(6)-O(12A)	97.7(3)
O(10M)-Ni(6)-O(12A)	166.1(4)	O(6S)-Ni(6)-O(12A)	97.2(4)
O(9MA)-Ni(6)-O(12A)	80.0(3)	O(7)-Si(7)-O(12)	108.6(5)
O(7)-Si(7)-O(7M)	112.6(5)	O(12)-Si(7)-O(7M)	111.6(5)

high intensity wave appears at a very high negative potential [10] as a single signal. This is in accordance with our earlier finding [6d] that homometallic oligosiloxane clusters are reduced as integrated electronic systems and not as an assembly of higher valent transition metals. This now receives additional support

Table 3 (*Continued*)

O(7)–Si(7)–C(71)	105.6(6)	O(12)–Si(7)–C(71)	106.8(6)
O(7M)–Si(7)–C(71)	111.3(5)	O(7)–Si(8)–O(8)	107.0(5)
O(7)–Si(8)–O(8M)	112.2(6)	O(8)–Si(8)–O(8M)	111.8(4)
O(7)–Si(8)–C(81)	109.5(5)	O(8)–Si(8)–C(81)	107.5(6)
O(8M)–Si(8)–C(81)	108.7(6)	O(8)–Si(9)–O(9)	107.6(5)
O(8)–Si(9)–O(9M)	111.9(4)	O(9)–Si(9)–O(9M)	111.5(4)
O(8)–Si(9)–C(91)	105.6(5)	O(9)–Si(9)–C(91)	107.6(6)
O(9M)–Si(9)–C(91)	112.3(6)	O(9)–Si(10)–O(10)	106.6(4)
O(9)–Si(10)–C(101)	107.5(7)	O(10)–Si(10)–C(101)	106.0(6)
O(9)–Si(10)–O(10A)	111.3(5)	O(10)–Si(10)–O(10A)	112.6(5)
C(101)–Si(10)–O(10A)	112.4(5)	O(10)–Si(11)–O(11)	108.3(5)
O(10)–Si(11)–C(111)	107.4(6)	O(11)–Si(11)–C(111)	106.6(6)
O(10)–Si(11)–O(11A)	111.3(5)	O(11)–Si(11)–O(11A)	112.0(4)
C(111)–Si(11)–O(11A)	111.0(5)	O(11)–Si(12)–O(12)	108.2(5)
O(11)–Si(12)–C(121)	106.9(6)	O(12)–Si(12)–C(121)	107.9(5)
O(11)–Si(12)–O(12A)	112.8(4)	O(12)–Si(12)–O(12A)	111.1(5)
C(121)–Si(12)–O(12A)	109.7(6)	Si(7)–O(7)–Si(8)	134.6(5)
Si(8)–O(8)–Si(9)	136.9(5)	Si(9)–O(9)–Si(10)	136.5(5)
Si(10)–O(10)–Si(11)	135.9(5)	Si(11)–O(11)–Si(12)	136.5(5)
Si(7)–O(12)–Si(12)	138.0(5)	Ni(4)–O(7M)–Ni(6)	89.9(3)
Ni(4)–O(7M)–Si(7)	130.8(6)	Ni(6)–O(7M)–Si(7)	129.7(5)
Ni(4)–O(8M)–Ni(5)	91.9(3)	Ni(4)–O(8M)–Si(8)	131.3(6)
Ni(5)–O(8M)–Si(8)	128.9(5)	Ni(5)–O(9M)–Si(9)	128.7(4)
Ni(5)–O(9M)–Ni(6A)	89.7(3)	Si(9)–O(9M)–Ni(6A)	129.8(5)
Ni(4)–O(10M)–Ni(6)	89.7(3)	Ni(4)–O(10M)–Si(1A)	129.0(6)
Ni(6)–O(10M)–Si(1A)	130.4(5)	Ni(4)–O(11M)–Ni(5)	90.9(3)
Ni(4)–O(11M)–Si(1B)	130.0(6)	Ni(5)–O(11M)–Si(1B)	129.0(4)
Ni(5)–O(12M)–Ni(6A)	90.5(3)	Ni(5)–O(12M)–Si(1C)	128.9(5)
Ni(6A)–O(12M)–Si(1C)	130.2(5)	Ni(4)–O(4S)–C(4S1)	120.1(11)
C(4S1)–N(4S)–C(4S2)	123.1(18)	C(4S1)–N(4S)–C(4S3)	120.1(17)
C(4S2)–N(4S)–C(4S3)	116.7(15)	O(4S)–C(4S1)–N(4S)	126.5(18)
Ni(5)–O(5S)–C(5S1)	116.9(22)	Ni(5)–O(5S)–C(5S4)	115.6(29)
C(5S1)–N(5SA)–C(5S2)	118.3(39)	C(5S1)–N(5SA)–C(5S3)	114.1(52)
C(5S2)–N(5SA)–C(5S3)	125.0(55)	C(5S4)–N(5SB)–C(5S5)	130.3(55)
C(5S4)–N(5SB)–C(5S6)	113.4(46)	C(5S5)–N(5SB)–C(5S6)	114.0(56)
O(5S)–C(5S1)–N(5SA)	122.7(32)	O(5S)–C(5S4)–N(5SB)	131.8(49)
Ni(6)–O(6S)–C(6S1)	119.2(12)	C(6S1)–N(6S)–C(6S2)	120.9(16)
C(6S1)–N(6S)–C(6S3)	121.3(18)	C(6S2)–N(6S)–C(6S3)	117.8(17)
O(6S)–C(6S1)–N(6S)	126.2(18)	Si(7)–C(71)–C(72)	124.5(13)
Si(7)–C(71)–C(76)	120.5(11)	C(72)–C(71)–C(76)	115.0(12)
C(71)–C(72)–C(73)	122.0(18)	C(72)–C(73)–C(74)	120.7(16)
C(73)–C(74)–C(75)	119.0(14)	C(74)–C(75)–C(76)	120.2(20)
C(71)–C(76)–C(75)	123.0(17)	Si(8)–C(81)–C(82)	120.4(10)
Si(8)–C(81)–C(86)	122.7(14)	C(82)–C(81)–C(86)	116.7(16)
C(81)–C(82)–C(83)	120.9(15)	C(82)–C(83)–C(84)	120.8(22)
C(83)–C(84)–C(85)	121.0(22)	C(84)–C(85)–C(86)	118.1(19)
C(81)–C(86)–C(85)	122.3(20)	Si(9)–C(91)–C(92)	121.1(12)
Si(9)–C(91)–C(96)	122.2(14)	C(92)–C(91)–C(96)	116.6(18)
C(91)–C(92)–C(95)	120.5(16)	C(95)–C(94)–C(95)	117.9(23)
C(94)–C(95)–C(96)	120.5(18)	C(92)–C(95)–C(94)	122.1(20)
C(91)–C(96)–C(95)	122.2(18)	Si(10)–C(101)–C(102)	122.8(12)
Si(10)–C(101)–C(106)	122.8(10)	C(102)–C(101)–C(106)	114.4(13)
C(101)–C(102)–C(103)	123.5(15)	C(102)–C(103)–C(104)	119.8(16)
C(103)–C(104)–C(105)	118.6(16)	C(104)–C(105)–C(106)	121.4(18)
C(101)–C(106)–C(105)	122.0(15)	Si(11)–C(111)–C(112)	130.2(14)
Si(11)–C(111)–C(117)	117.0(16)	Si(11)–C(111)–C(116)	117.7(21)
C(112)–C(111)–C(116)	111.9(24)	Si(11)–C(111)–C(120)	124.6(28)
C(117)–C(111)–C(120)	115.5(30)	C(111)–C(112)–C(113)	128.9(23)
C(111)–C(117)–C(118)	118.2(31)	C(112)–C(113)–C(114)	118.8(30)

Table 3 (*Continued*)

C(117)..C(118)..C(114)	117.5(37)	C(113)..C(114)..C(115)	120.4(34)
C(118)..C(114)..C(119)	114.5(35)	C(114)..C(115)..C(116)	114.1(30)
C(114)..C(119)..C(120)	117.0(50)	C(111)..C(116)..C(115)	123.6(37)
C(111)..C(120)..C(119)	126.9(54)	Si(12)..C(121)..C(122)	125.6(13)
Si(12)..C(121)..C(126)	120.8(12)	C(122)..C(121)..C(126)	113.3(16)
C(121)..C(122)..C(123)	123.5(16)	C(122)..C(123)..C(124)	121.4(16)
C(123)..C(124)..C(125)	118.9(24)	C(124)..C(125)..C(126)	120.0(22)
C(121)..C(126)..C(125)	122.7(16)		

from the fact that the cluster containing two *different* transition metals is reduced by a unique potential, which appears to be characteristic for the whole cluster.

The conductivity measurements (corrected for dissociation) show complex **3** to be 1 : 1 electrolyte proving that the interstitial chloride ion remains in the "cage" and is also in solution.

The most important proof for the molecular structure of complex **3** was provided by the X-ray diffraction measurement. The results of the molecular structure determination are shown in Tables 1–3. The molecular model of the complex is shown in Fig. 2 and the structure of the complex core is shown in Fig. 3.

According to the diffraction measurement the $Si_{12}O_{24}M_6$ core shows a symmetric hexagonal box with the Cl^-ion in the centre of the cage. The six transition metals cannot be distinguished. The conformation of the Ph groups outside the cage generates two crystallographically independent centrosymmetrically related anions (Fig. 3).

The two all-*cis*-hexaphenylcyclohexasiloxanolate hexaanionic ligands display the "ideal" symmetric "crown" conformation, the central "sheet" of six metal atoms form the vertices of an almost regular hexagon and is sandwiched in between the hexaanions. Their silanolate O^- groups have a μ_2-bridging function (M ··· O distances 2.01–2.00(1), av. 2.035 Å) forming a distorted square planar environment around the M^{2+} ions, which are displaced from the plane of the surrounding O towards the exterior of the framework by ca. 0.23 Å. The octahedral coordination of M^{2+} is completed by the "outer" terminal neutral DMF molecules (M ··· O 2.05–2.10(1), av. 2.064 Å) and "inner" μ_6-bridging Cl^--ligand, occupying a special position in the crystallographic inversion centre in the M_6 plane (M ··· Cl 2.812–2.941(2), av. 2.880 Å).

The negative charge of the Cl^- ion is compensated by the Na^+ cation. It is disordered over two equally occupied positions in the plane of the M^{2+} ions of the complex anion **3a** being coordinated by two -olate O^- groups of the two top and bottom organosiloxanolate ligands (Na ··· O 2.39 and 2.36(2) Å), as well as by two carbonyls of M-coordinated DMF molecules (Na ··· O 2.65 and 2.66(2) Å) and one carbonyl oxygen of the "outer" DMF molecule (Na ··· O7a 2.06(6) Å). The position of the latter is also only half-populated (just like the corresponding Na^+-ion). The same cavity in the absence of Na^+ ion is occupied by differently oriented DMF molecule in a clathrate-like manner (in

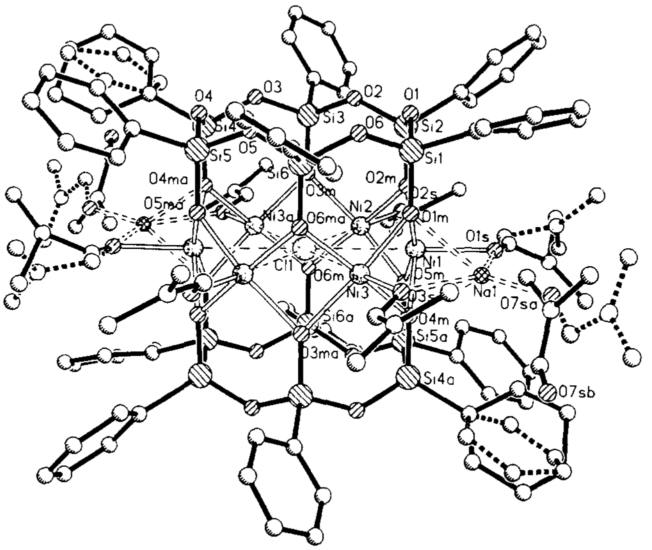

Fig. 2. General view of the molecule $3 \cdot 3(C_3H_7NO)$ (Na^+ omitted).

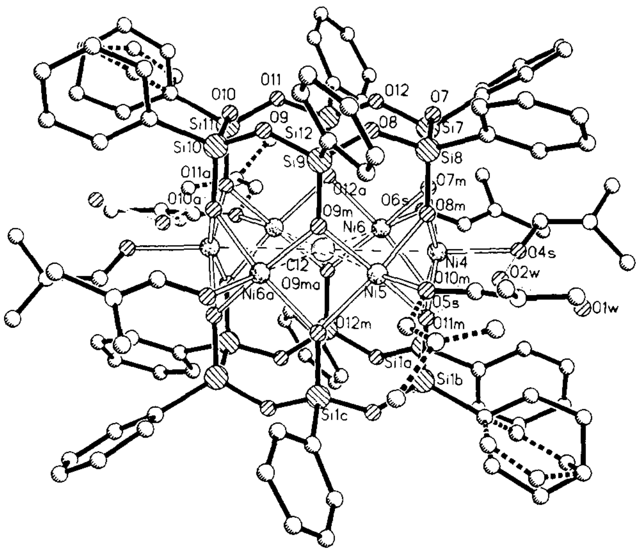

Fig. 3. General view of the central cage of $3 \cdot 3(C_3H_7NO)$.

this case the position of the carbonyl group is occupied by an N-methyl group of the DMF solvate molecule). The electron density peak in the position, corresponding to that occupied by the Na^+ ion in **3a**, was also observed in **3b**. However, our attempts to refine it as a Na^+ ion with the 0.5 occupancy factor yielded a very high temperature factor value.

The formation and structure of complex **3** represents a new step in the exploration of the coordination behaviour of cyclic oligosiloxanes, as well-characterized surface imitating ligands. Some characteristics of this complex, as magnetic and electrochemical behaviour may indicate new application perspectives, which are currently being explored in our laboratories.

Complex **3** and eventual similar compounds may find imminent catalytic applications [11] and represent a new class of bimetallic (cluster) complexes (cf. [12]). They may also contribute to the understanding of the chemical environment of interstitial metal assemblies in oxide supports [11b,13]. We are currently testing the possibility of preparation of similar complexes with early/late transition metal combinations [14].

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