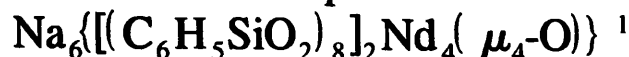


Cyclosiloxane sandwich complexes of a lanthanide metal:



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Received 21 April 1995; in revised form 16 October 1995

Abstract

The oligocyclosiloxane cluster ('sandwich') complex of Nd^{3+} , $\text{Na}_6\{[(\text{C}_6\text{H}_5\text{SiO}_2)_8]_2\text{Nd}_4(\mu_4\text{-O})\}$ has been prepared and characterized by analyses, infrared spectra, single crystal X-ray diffraction, magnetic susceptibility, conductivity and cyclic voltammetry. The $\mu_4\text{-O}^{2-}$ anion is in a square planar coordination environment. Electrochemical studies identify the cluster core as a moiety with a delocalized electron system.

Keywords: Neodymium; Lanthanide; Silicon; Siloxane; Cluster; Electrochemistry

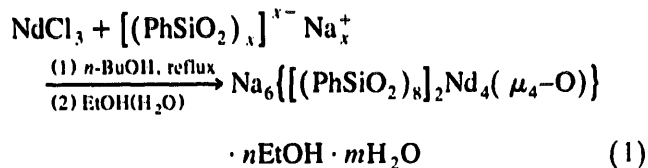
1. Introduction

Research concerning main-group oxide supported metal catalysts has produced spectacular achievements in the last two decades. Initially it was found that the main group oxides (SiO_2 , Al_2O_3 , MgO , etc.) were not inert at all but gave a great variety of surface reactions [1] with the supported metal species [2]. Since the exact structure of the surface complexes could not be determined directly on the molecular level, indirect methods [3] as well as molecular models [4] were applied to gain more information. These studies identified the surface as a large rigid ligand which decisively influences the reactivity of the supported metal. This recognition has recently led to an entirely new approach. The synthesis and characterization of metal complexes with surface-imitating oligomeric ligands have been studied initially. This has included mono- and bimetallic [5,6] as well as oligometallic [7] siloxanolate complexes of transition metals.

Some interesting catalytic applications of the lanthanide elements [8] prompted us to try synthesizing oligometallic cyclosiloxane derivatives of this group. Our studies within the rare earth metals were started with neodymium because of its particular catalytic applications [9]. Here we report on the synthesis and structure of the neodymium complex $\text{Na}_6\{[(\text{C}_6\text{H}_5\text{SiO}_2)_8]_2\text{Nd}_4(\mu_4\text{-O})\}$ (1).

2. Results and discussion

Complex 1 could be prepared smoothly from anhydrous NdCl_3 and sodium oligosiloxanolate [10] in *n*-butanolic solution according to Eq. (1):



where $n = 3\text{--}10$ and $m = 8\text{--}20$.

The preparation of the $\text{Na}_6\{[(\text{C}_6\text{H}_5\text{SiO}_2)_8]_2\text{Nd}_4(\mu_4\text{-O})\}$ complex unit was found to be reproducible; however, it is difficult to obtain the (crystalline) solvates with well-defined amounts and ratios of the solvate

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¹ Dedicated to Prof. Dr. hc. Karl-Heinz Thiele (Halle-Merseburg) on the occasion of his 65th birthday.

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molecules. Freshly prepared samples analysed by X-ray diffraction gave values near to $n = 10$, $m = 8$; samples stored in an exsiccator over anhydrous CaCl_2 for a few days gave values of $n = 6 \pm 1$ and $m = 8 \pm 1$; if EtOH with higher water content (10% v/v) was used for the recrystallization a crystalline product with $n = 5$, $m = 18$ was obtained. Sharp melting points of these products were not observed; the crystals turned opaque (through solvent loss) at 70–80 °C; decomposition of the remaining powder was observed at about 300 °C. This instability of the solvates is not uncommon in lanthanide chemistry; moreover, it has also been observed for non-lanthanide (transition metal) cyclosiloxanolate sandwich complexes [7].

The results of the X-ray diffraction structure determination are shown in Tables 1–3 and in Figs. 1–3. The main features of the structure are as follows.

- (i) The neodymium-siloxanolate core of the complex is composed of a planar $\text{Nd}_4(\mu_4\text{-O})$ unit and two octaphenyl-cyclooctasiloxanolate ligands coordinated to two opposite faces of the Nd_4O moiety, providing a sandwich-like structure.
- (ii) The cyclosiloxanolate ligands are of all-cis configuration. These ligands are arranged in a coaxial antiparallel manner around the Nd_4O unit. Each

Table 1
Structure determination summary of $1 \cdot 10\text{EtOH} \cdot 8\text{H}_2\text{O}$

Empirical formula	$\text{C}_{116}\text{H}_{136}\text{Na}_6\text{Nd}_4\text{O}_{31}\text{Si}_{16}$
Formula mass	3530.750
Unit cell dimensions:	
a (Å)	17.907(5)
b (Å)	22.910(7)
c (Å)	19.032(5)
β (deg)	105.54(2)
V (Å ³)	7522(7)
Z	2
d_{calc} (g cm ⁻³)	1.554
Crystal system	monoclinic
Space group	$P2_1/n$
Type of diffractometer	Siemens P3/PC
Radiation	Mo K α
Monochromator	graphite
Size of crystal (mm ³)	0.5 × 0.4 × 0.2
Temperature (K)	150
Data collection mode	$\theta/2\theta$
θ – maximum (deg)	25
Reciprocal space segment	$+h; +k; \pm l$
No. of symm. independent reflection	12630
$l > n\sigma(l)$ criterion	2
No. of observed reflections	10227
Linear absorption coefficient (cm ⁻¹)	15.8
Method of absorption correction	not applied
Method of solution	direct
Method of refinement	full matrix least squares
Parameters/data ratio	5.9
Final discrepancy factors	
R	0.065
R_w	0.065

Table 2
Atom coordinates ($\times 10^4$) and temperature factors $\text{Å}^2 \times 10^3$ of complex $1 \cdot 10\text{EtOH} \cdot 8\text{H}_2\text{O}$

Atom ^a	x	y	z	U^b
Nd(1)	5589(1)	-196(1)	-1051(1)	28(1)
Nd(2)	5731(1)	-916(1)	710(1)	28(1)
Si(1)	7357(2)	509(1)	-908(2)	35(1)
Si(2)	7464(2)	-321(1)	301(2)	35(1)
Si(3)	7571(2)	-567(1)	1845(2)	34(1)
Si(4)	6333(2)	29(1)	2333(2)	34(1)
Si(5)	5459(2)	1124(1)	2411(2)	33(1)
Si(6)	4924(2)	1746(1)	1003(2)	33(1)
Si(7)	5336(2)	2217(1)	-297(2)	35(1)
Si(8)	6096(2)	1366(1)	-1023(2)	33(1)
O(1)	7656(4)	297(3)	-59(4)	39(2)
O(2)	7816(4)	-229(3)	1175(4)	41(2)
O(3)	7225(3)	-58(3)	2262(4)	37(2)
O(4)	6243(4)	734(3)	2460(4)	34(2)
O(5)	5484(4)	1651(3)	1828(4)	36(2)
O(6)	5424(4)	2151(3)	576(4)	35(2)
O(7)	6104(4)	1819(3)	-438(4)	38(2)
O(8)	7010(4)	1155(3)	-860(4)	39(3)
O(11)	6713(4)	85(3)	-1377(4)	33(2)
O(21)	6551(4)	-426(4)	81(4)	54(3)
O(31)	6946(4)	-1062(3)	1534(4)	36(2)
O(41)	5703(4)	-181(3)	1614(4)	37(2)
O(51)	4701(4)	733(3)	2148(4)	35(2)
O(61)	4714(4)	1125(3)	584(4)	47(3)
O(71)	4565(4)	1902(3)	-764(4)	35(2)
O(81)	5556(3)	844(3)	-908(4)	34(2)
O(1x)	5000	0	0	70(6)
C(11)	8210(6)	587(6)	-1291(6)	45(4)
C(12)	8799(9)	165(8)	-1123(13)	121(11)
C(13)	9409(11)	187(10)	-1440(15)	148(14)
C(14)	9469(8)	609(9)	-1889(9)	88(7)
C(15)	8909(11)	976(11)	-2073(13)	149(13)
C(16)	8296(9)	957(8)	-1759(11)	112(9)
C(21)	8032(7)	-896(6)	-1(6)	50(4)
C(22)	8816(9)	-942(7)	351(10)	81(7)
C(23)	9296(12)	-1265(10)	55(13)	121(11)
C(24)	9036(18)	-1561(10)	-543(16)	145(15)
C(25)	8238(18)	-1536(9)	-926(13)	135(14)
C(26)	7763(10)	-1210(7)	-623(9)	82(7)
C(31)	8483(5)	-851(5)	2480(6)	38(4)
C(32)	8950(6)	-508(6)	3025(7)	51(4)
C(33)	9636(7)	-733(7)	3475(7)	66(5)
C(34)	9855(7)	-1293(6)	3381(8)	64(5)
C(35)	9408(8)	-1624(7)	2858(9)	75(6)
C(36)	8734(7)	-1413(6)	2406(8)	63(5)
C(41)	6281(7)	-333(5)	3184(7)	52(5)
C(42)	6929(9)	-581(8)	3687(8)	85(7)
C(43)	6908(12)	-803(9)	4344(10)	108(9)
C(44)	6249(14)	-790(9)	4556(11)	112(10)
C(45)	5613(12)	-569(11)	4103(12)	143(12)
C(46)	5629(10)	-335(9)	3437(11)	126(10)
C(51)	5573(6)	1476(5)	3312(6)	43(4)
C(52)	5342(9)	1217(7)	3861(7)	72(6)
C(53)	5463(10)	1475(9)	4547(8)	91(8)
C(54)	5799(10)	2015(8)	4678(8)	91(8)
C(55)	6038(11)	2276(8)	4129(9)	99(9)
C(56)	5932(9)	2020(6)	3468(7)	71(6)
C(61)	4080(6)	2183(5)	1097(7)	41(4)
C(62)	3939(7)	2275(6)	1757(8)	62(5)
C(63)	3319(9)	2628(8)	1821(12)	91(8)
C(64)	2855(11)	2864(8)	1246(13)	113(11)

Table 2 (continued)

Atom ^a	x	y	z	U ^b
C(65)	2947(10)	2782(10)	561(14)	135(12)
C(66)	3579(8)	2432(8)	499(10)	88(7)
C(71)	5413(7)	3000(5)	-510(7)	48(4)
C(72)	5736(9)	3408(6)	10(10)	75(7)
C(73)	5837(12)	3980(8)	-145(13)	105(10)
C(74)	5631(12)	4157(7)	-824(14)	111(11)
C(75)	5358(18)	3766(10)	-1371(13)	166(16)
C(76)	5240(16)	3189(9)	-1196(12)	146(13)
C(81)	5806(7)	1669(5)	-1962(6)	45(4)
C(82)	6305(10)	1982(9)	-2237(10)	110(9)
C(83)	6059(14)	2209(11)	-2958(12)	131(12)
C(84)	5379(14)	2165(9)	-3362(10)	105(10)
C(85)	4902(13)	1861(12)	-3086(10)	148(13)
C(86)	5106(10)	1595(10)	-2421(8)	107(9)
Na(1)	6432(3)	-454(3)	-2455(3)	86(3)
Na(2)	7299(4)	1178(3)	2085(3)	81(3)
Na(3)	7382(5)	1544(5)	422(5)	141(5)
O(1w)	6559(5)	920(4)	817(5)	57(2)
O(2w)	7063(11)	2180(9)	1429(10)	170(7)
O(3w)	8034(11)	3003(9)	1636(11)	179(7)
O(4w)	3275(9)	2214(7)	8203(8)	135(5)
O(1s)	5901(20)	-1128(16)	-2997(19)	152(12)
C(11s)	7682(24)	-1318(10)	-3278(22)	241(17)
C(12s)	8094(26)	-779(21)	-2698(25)	269(20)
O(2s)	6348(12)	458(9)	-3060(11)	80(6)
C(21s)	6585(23)	706(18)	-3613(22)	101(11)
C(22s)	6438(51)	190(39)	-4084(45)	158(29)
C(22a)	7089(41)	429(31)	-3927(36)	179(25)
O(3s)	7847(12)	1647(9)	3107(12)	74(5)
O(3sa)	7946(20)	1444(17)	3639(21)	157(12)
C(31s)	8229(34)	985(28)	3691(32)	178(20)
C(31a)	7847(22)	1015(18)	4030(21)	94(10)
C(32s)	8512(22)	796(17)	4617(21)	99(11)
O(4s)	8203(13)	2331(10)	426(12)	197(8)
C(41s)	8625(28)	2617(21)	-99(26)	114(14)
C(41a)	8001(35)	2683(26)	-393(32)	149(20)
C(42s)	8660(21)	2287(17)	-653(20)	206(14)
O(5s)	8291(9)	932(7)	1555(8)	119(4)
C(51s)	9045(19)	1071(15)	1716(17)	163(10)
C(52s)	9280(32)	1617(28)	1773(31)	155(20)
C(52a)	9193(30)	1159(24)	1067(30)	145(18)

^a The indexes w and s relate to atoms of the solvate water and ethanol molecules respectively. Atoms with index a belong to those solvate ethanol molecules which, together with the atoms corresponding to the numbers represent positions with $g = 0.5$ population.

^b Equivalent isotropic U defined as one third of the trace of the orthogonalised $U_{i,j}$ tensor.

second silanolate oxygen is in an identical coordination environment: (a) linked to only one Nd atom, or (b) bridging two of the metal atoms.

- (iii) The $\text{Nd}_4(\mu_4\text{-O})$ moiety is of square planar geometry. The $\text{Nd}-\mu_4\text{O}$ distances (2.539(1) and 2.645(1) Å) are in accordance with those observed in a Nd-alcoholate complex (2.38–2.51 Å for $\text{Nd}(\mu_3\text{-O})$) [11]. The large Nd–Nd distances (mean 3.66 Å) exclude substantial metal–metal bonding. This latter fact is in line with earlier observations [7] which showed that in clusters of higher valent

(transition) metals, significant direct metal–metal interactions are lacking. This is in sharp contrast with the behaviour of clusters of low-valent metals [12] and raises the question of whether these complexes can be regarded as clusters at all? (We shall return to this question later in this paper.)

- (iv) Quadruply bridging oxide anion is a rare phenomenon [13]: the geometry around the $\mu_4\text{-O}^{2-}$ ligand is normally tetrahedral or approximately tetrahedral. Square planar geometry of $\mu_4\text{-O}^{2-}$ is unprecedented, as far as we can ascertain.
- (v) Solvate molecules are not coordinated to the Nd ions (at least in that particular solvate which could be used for single-crystal X-ray diffraction), unlike similar compounds with transition metals [7]. Thus the coordination environment of each metal ion consists of six silanol-oxygens (four bridging, two terminal) plus the central O^{2-} ion. This corresponds approximately to a mono-face-capped trigonal prism, in contrast to the (distorted) tetragonal pyramidal array of ligands around each Nd atom in the alcoholate complex [11].
- (vi) The sodium cations fall into two groups. Four sodium ions are (pairwise) coordinated to ring-oxygens of the two (sila-crown-like) macrocyclic ligands (Fig. 3). The two remaining Na^+ ions are not in coordinative contact with the sandwich cluster, but are tetrahedrally coordinated by solvate molecules.

The neodymium complex can thus be regarded as a derivative of Nd^{3+} ions and more exactly formulated as $\text{Na}_2[[\text{Na}_2\text{cyclo}-(\text{PhSiO}_2)_8]_2\text{Nd}_4(\mu_4\text{-O})]$. This formulation is in perfect agreement with the relatively high conductivity of complex **1** in solution.

In fact, the molar conductivity value of about $93 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in DMF is of the same order as that for a uni-univalent electrolyte [14]. This result indicates that compound **1** in DMF is partially dissociated in solution. Taking into account the very different dimension of the Na^+ ion with respect to the dianionic skeleton and, consequently, its much higher mobility, the conductivity of a solution of compound **1** can mainly be attributed to the two Na^+ ions, resulting in a molar conductivity of compound **1** similar to that of a uni-univalent electrolyte.

IR spectra are in accordance with the X-ray structure determination, showing bands characteristic of the Ph groups, both solvates, Si–O and Si–C bonds together with far-IR bands which can be attributed to Nd–O and Na–O interactions.

We mentioned earlier that the absence of direct metal–metal bonds raises doubts as to whether this complex (and similar ones) can be regarded as a cluster, i.e. as a polymeric molecule with an electronic system which extends over the whole molecule (or at least to the metal containing fragment) [12,15]. We recently

found that cyclic voltammetry appears to be a useful tool for explore this aspect [16]. Thus a cyclic voltammetric study of complex **1** has also been performed. The

results identify complex **1** as a species which gives an almost completely reversible reduction–oxidation wave couple, whose anodic and cathodic peak potential val-

Table 3
Selected bond length (Å) and bond angle (deg) values of complex **1** · 10EtOH · 8H₂O

<i>Bond lengths</i>			
Nd(1)–Nd(2)	3.682(1)	Nd(2)–O(71a)	2.328(7)
Nd(1)–Nd(2a)	3.649(1)	Nd(1)–O(41a)	2.433(6)
Nd(1)–O(1x)	2.539(1)	Nd(1)–O(61a)	2.423(8)
Nd(2)–O(1x)	2.645(1)	Nd(2)–O(61a)	2.424(7)
O(1x)–Nd(1a)	2.539(1)	Nd(2)–O(81a)	2.438(7)
O(1x)–Nd(2a)	2.645(1)	Si(1)–O(1)	1.634(7)
Nd(1)–O(11)	2.350(7)	Si(1)–O(8)	1.619(8)
Nd(2)–O(31)	2.341(6)	Si(1)–O(11)	1.587(7)
Nd(1)–O(51a)	2.359(7)	Si(1)–C(11)	1.87(1)
Nd(1)–O(21)	2.429(6)	Si(2)–O(2)	1.628(7)
Nd(1)–O(81)	2.401(7)	Si(2)–O(1)	1.648(8)
Nd(2)–O(21)	2.406(8)	Si(2)–O(21)	1.593(7)
Nd(2)–O(41)	2.417(7)	Si(2)–C(21)	1.85(1)
<i>Bond angles</i>			
Nd(2)–Nd(1)–O(1x)	45.9	O(21)–Nd(1)–O(61a)	70.1(3)
Nd(1)–Nd(2)–O(1x)	43.6	Nd(2a)–Nd(1)–O(61a)	109.2(2)
O(1x)–Nd(1)–Nd(2a)	46.4	O(51a)–Nd(1)–O(61a)	81.3(2)
O(1x)–Nd(2)–Nd(1a)	44.1	Nd(1)–Nd(2)–O(31)	119.9(2)
O(21)–Nd(1)–O(1x)	71.6(2)	Nd(1)–Nd(2)–O(41)	109.1(2)
O(41)–Nd(2)–O(1x)	73.1(2)	O(31)–Nd(2)–O(41)	79.4(2)
O(81)–Nd(1)–O(1x)	72.9(2)	O(21)–Nd(2)–Nd(1a)	105.9(2)
O(1x)–Nd(1)–O(41a)	74.8(2)	O(41)–Nd(2)–Nd(1a)	41.4(1)
O(1x)–Nd(1)–O(61a)	71.7(2)	Nd(1)–Nd(2)–O(61a)	40.6(2)
O(1x)–Nd(2)–O(61a)	69.8(2)	O(31)–Nd(2)–O(61a)	130.2(3)
O(1x)–Nd(1)–O(51a)	138.7(2)	Nd(1)–Nd(2)–O(71a)	120.9(2)
O(11)–Nd(1)–O(1x)	136.5(2)	O(31)–Nd(2)–O(71a)	90.7(2)
O(21)–Nd(2)–O(1x)	70.1(2)	O(61a)–Nd(2)–O(71a)	80.6(2)
O(31)–Nd(2)–O(1x)	134.4(2)	O(21)–Nd(2)–O(81a)	140.6(2)
O(1x)–Nd(2)–O(71a)	134.8(1)	O(41)–Nd(2)–O(81a)	69.0(2)
Nd(1)–O(1x)–Nd(1a)	180.0	Nd(1)a–Nd(2)–O(81a)	40.7(2)
Nd(1a)–O(1x)–Nd(2a)	90.5	O(71a)–Nd(2)–O(81a)	79.8(2)
Nd(2)–O(1x)–Nd(1a)	89.5	Nd(2)–Nd(1)–O(21)	40.2(2)
Nd(2)–Nd(1)–O(11)	120.5(1)	Nd(2)–Nd(1)–O(81)	109.8(2)
O(11)–Nd(1)–O(21)	80.8(2)	O(21)–Nd(1)–O(81)	98.5(3)
O(11)–Nd(1)–O(81)	78.8(2)	Nd(2)–Nd(1)–Nd(2a)	92.3
O(11)–Nd(1)–Nd(2a)	119.8(2)	O(21)–Nd(1)–Nd(2a)	109.4(2)
O(81)–Nd(1)–Nd(2a)	41.4(2)	Nd(2)–Nd(1)–O(41a)	112.7(2)
O(11)–Nd(1)–O(41a)	124.5(2)	O(21)–Nd(1)–O(41a)	146.4(3)
O(81)–Nd(1)–O(41a)	69.4(2)	Nd(2a)–Nd(1)–O(41a)	41.0(2)
Nd(2)–Nd(1)–O(51a)	121.2(2)	O(110)–Nd(1)–O(51a)	84.8(2)
O(21)–Nd(1)–O(51a)	127.5(3)	O(81)–Nd(1)–O(51a)	127.7(2)
Nd(2a)–Nd(1)–O(51a)	121.5(2)	O(41a)–Nd(1)–O(51a)	80.6(2)
Nd(2)–Nd(1)–O(61a)	40.6(2)	O(11)–Nd(1)–O(61a)	129.0(3)
O(81)–Nd(1)–O(61a)	144.6(3)	O(1x)–Nd(2)–O(81a)	70.5(2)
O(41a)–Nd(1)–O(61a)	101.2(2)	O(61a)–Nd(2)–O(81a)	95.9(2)
Nd(1)–Nd(2)–O(21)	40.6(1)	O(1)–Si(1)–O(8)	104.1(4)
O(21)–Nd(2)–O(31)	79.5(2)	Nd(2)–O(41)–Si(4)	132.5(4)
O(21)–Nd(2)–O(41)	99.3(3)	Si(4)–O(41)–Nd(1)a	129.8(4)
Nd(1)–Nd(2)–Nd(1a)	87.7	Si(6)–O(61)–Nd(1)a	129.3(4)
O(31)–Nd(2)–Nd(1a)	120.7(2)	Nd(1a)–O(61)–Nd(2a)	98.9(3)
O(21)–Nd(2)–O(61a)	70.5(3)	Nd(1)–O(81)–Si(8)	134.2(4)
O(41)–Nd(2)–O(61a)	142.8(2)	Si(8)–O(81)–Nd(2a)	127.3(4)
Nd(1a)–Nd(2)–O(61a)	105.4(2)	Nd(2)–O(41)–Nd(1a)	97.6(2)
O(21)–Nd(2)–O(71a)	130.6(3)	Si(5)–O(51)–Nd(1a)	122.6(4)
O(41)–Nd(2)–O(71a)	126.6(3)	Si(6)–O(61)–Nd(2a)	130.0(4)
Nd(1a)–Nd(2)–O(71a)	120.3(2)	Si(7)–O(71)–Nd(2a)	125.9(3)
Nd(1)–Nd(2)–O(81a)	105.8(2)	Nd(1)–O(81)–Nd(2a)	97.9(2)
O(31)–Nd(2)–O(81a)	130.9(2)		

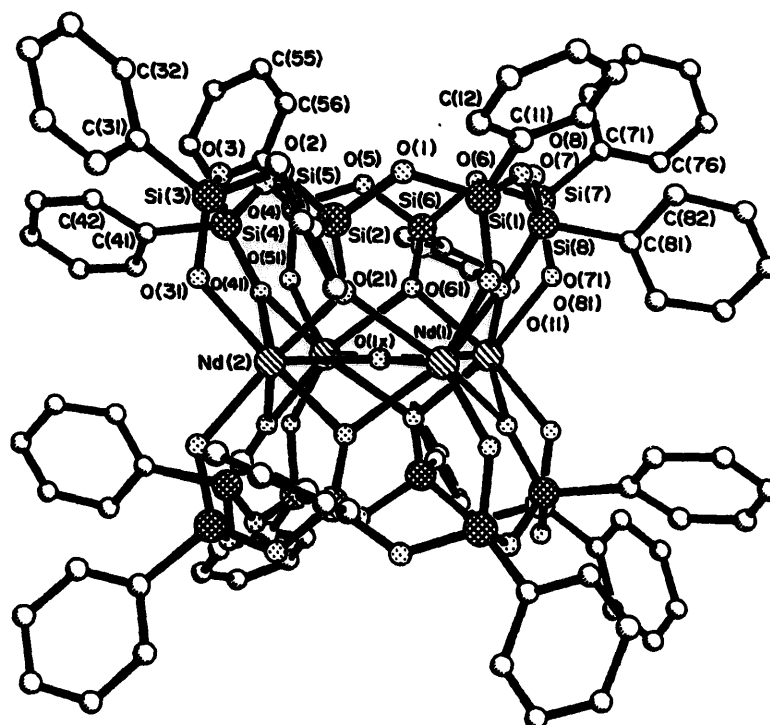


Fig. 1. Overall ORTEP view of the complex 1 (solvent omitted).

ues ($E_{pc} = -2.022$ V, $E_{pa} = -1.953$ V, $\Delta E = 0.069$ V) are very similar to those already observed for compounds of analogous structure with Ni^{2+} , Mn^{2+} or Cu^{2+} cations [16]. This indicates that the peak potential values of the oligometallic siloxane complexes are almost independent of the number of siloxane moieties in

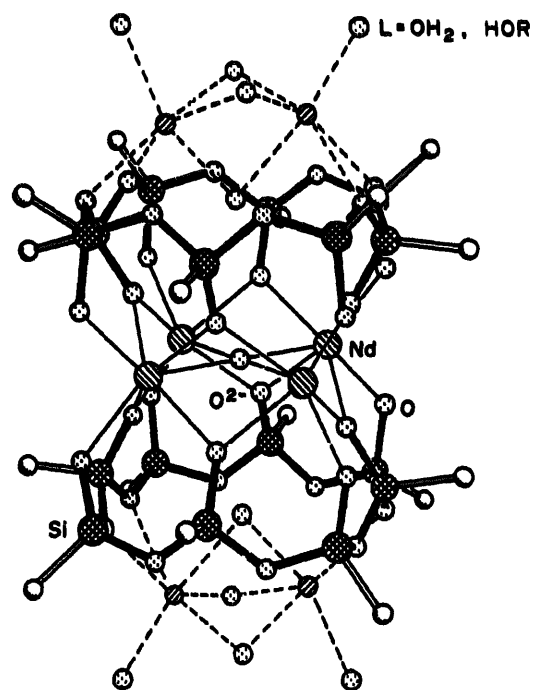
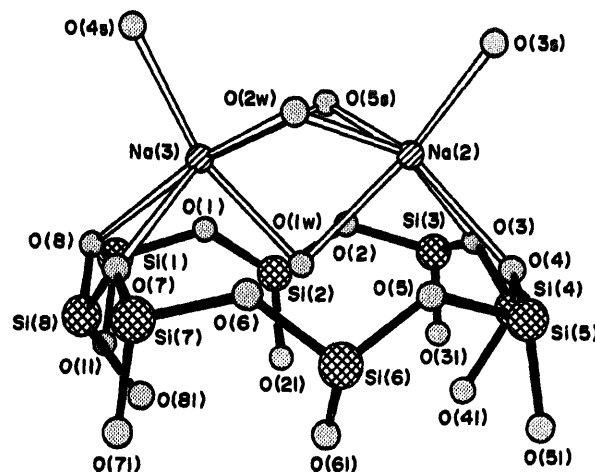
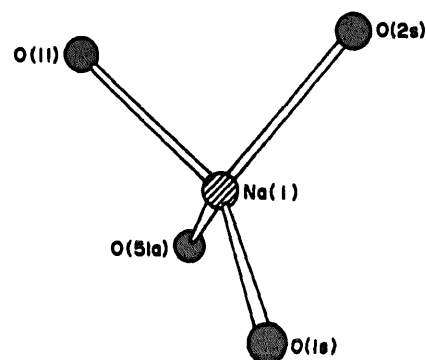


Fig. 2. The cluster core of complex 1.

Fig. 3. The coordination environment of the Na^+ ions in complex 1.

the cyclic oligomer and of the nature of the coordinated metal ion.

The reversibility of the waves can be interpreted as a sign of the resistance of the complex structure towards disintegration in the electrochemical process. The far negative potential³ of the wave, and the fact that only one wave is observed, indicates that complex 1 reacts as a unified electronic system [12,15,16], thus providing an important argument for regarding it as a metal cluster. However, whether the closed structure and some extent of electronic delocalization in the complex are enough to classify complex 1 (and similar compounds) as clusters in the absence of direct metal–metal interactions is open to discussion.

The reversibility at reduction–oxidation and the electronic ‘unity’ of the complex are factors which might demonstrate an important impact on the catalytic applications. This latter aspect is currently investigated in one of our laboratories.

A preliminary measurement of magnetic susceptibility shows $\mu_{\text{eff}} = 6.42$ BM. This can be regarded as a value near to six unpaired electrons ($\mu_{\text{eff, theor.}} = 6.93$ BM) for the whole molecule, or as a sign of about one unpaired electron per Nd atom ($6.42/1.73 = 3.71$). Both interpretations hint at the possibility of Nd–Nd (indirect) interactions. This aspect is now being studied by detailed temperature-dependent magnetic measurements in our laboratories.

3. Experimental

All materials were of commercial origin with the exception of the sodium oligo(phenylsiloxanolate) reagent which was prepared from PhSiCl_3 by published procedures [7,10].

IR spectra were obtained by Bruker FT-IR IFS 113V spectrophotometer, using KBr pellets for the 4000–500 cm^{-1} range, and PE pellets for the 500–50 cm^{-1} range; the spectra in the far-IR range were registered under reduced pressure.

Magnetic susceptibility was measured using a Gouy balance at room temperature.

The cyclic voltammetric measurements were performed by potentiostat/galvanostat PAR 273A instrument, using a hanging drop mercury electrode (HDME) under Ar atmosphere.

The conductivity was measured with Conductimeter Crison Mod. 525 (all constant 1.02).

The details of experimental conditions of the X-ray structure determination are summarized in Table 1.

Calculations were performed by IBM PC/AT using the SHELXTL PLUS program. Tables of hydrogen atom coordinates and anisotropic thermal parameters, and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

3.1. Preparation and characterization of complex 1

A 1 l four-neck reaction vessel was equipped with a KPG stirrer, reflux condenser and thermometer. In this reaction vessel (through the fourth neck) polyphenylsiloxane, 4.85 g (0.0376 mol PhSiO_2), sodium hydroxide, 0.84 g (0.021 mol) and 120 ml of *n*-butanol were charged. The reaction mixture was stirred and refluxed (oil bath) for 1.5 h. After this period the reaction mixture was left to cool to 50–60 °C and at this temperature to the solution sodium metal, 2.37 g (0.0094 mol) cut into small pieces, was added. After addition of the sodium pieces the reaction mixture was again warmed until it refluxed, continuously stirred for 1 h. Then the neodymium trichloride, NdCl_3 (anhydrous), 2.73 g (0.094 mol), was dissolved in 150 ml of *n*-butanol and this solution was added dropwise to the refluxing reaction mixture through the reflux condenser. After having finished the addition of the NdCl_3 solution the reaction mixture was refluxed for an additional 1 h. The solution was then left to cool to room temperature and filtered (to remove NaCl). Then the filtrate was drawn dry removing all *n*-BuOH at reduced pressure. The resulting white mass was recrystallized from toluene–96% EtOH (2:1). Yield of the recrystallized (white crystalline) product: 1.31 g (15.6%)

3.2. Characterization of complex 1

3.2.1. $\text{Na}_6\{[(\text{PhSiO}_2)_n]_2\text{Nd}_4(\mu_4\text{-O})\} \cdot 5\text{EtOH} \cdot 18\text{H}_2\text{O}$

Anal. Found: C, 36.7%; H, 4.3%; Na, 3.5%; Nd, 15.6%; Si, 13.8%. $\text{C}_{106}\text{H}_{141}\text{Na}_6\text{Nd}_4\text{O}_{56}\text{Si}_{16}$. Calc.: C, 36.63%; H, 4.09%; Na, 3.97%; Nd, 16.60%; Si, 12.92%

3.2.2. $\text{Na}_6\{[(\text{PhSiO}_2)_n]_2\text{Nd}_4(\mu_4\text{-O})\} \cdot 10\text{EtOH} \cdot 8\text{H}_2\text{O}$

Anal. Found: C, 39.2%; H, 4.6%. $\text{C}_{116}\text{H}_{156}\text{Na}_6\text{Nd}_4\text{O}_{51}\text{Si}_{16}$. Calc.: C, 39.46%; H, 4.45%

3.2.3. IR spectra

KBr pellet (cm^{-1}): 3700 sh; w (γ O–H, non assoc.); ~ 3400 m, br. (γ O–H, assoc.); 3100 vw, 3085 m, 3040 mw, 3002 vw, 2960 sh w (ν C–H); 1594 m, 1514 m, 1491 m, 1430 s, (ar. ring ν C–C); 1098 vs (ν Si–C(ar.)); 997 s, 963 s (ν Si–O); 741 ms, 698 ms (ar. γ C–H); 522 vw, 505 m, 429 mw (ν Si–O skeletal).

Polyethylene pellet (cm^{-1}): 463 vw, 428 w, (ν Si–O skeletal); 403 vw, 380 sh. w (ν Nd–O), 298 w, 260 w (δ NdO_6); 178 w, 121 vvw (ν Na–O).

³ Very different from that of the Nd^{3+} – Nd^0 couple (–1.45 V vs. SCE in CH_3CN) [17].

3.2.4. Conductivity

$$(\text{DMF}) \lambda_{eq} = 92.8 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}.$$

3.2.5. Cyclic voltammetry

Experimental conditions: solvent DMF, concentration of complex $1 \cdot 10^{-4}$ M, supporting electrolyte 0.1 M $(n\text{-Bu})_4\text{NClO}_4$, electrodes (HMDE)//Ag/AgCl/3 M NaCl//Pt: $T = 25 \pm 1$ °C, scanning rate 100 mV s⁻¹.

$$E_{pc} = 2.022 \text{ V}, E_{pa} = 1.953 \text{ V} (\Delta E = 69 \text{ mV}); i_{pc} = 1.6 \mu\text{A}, i'_{pc} = 1.87 \mu\text{A}, i_{pa} = 1.27 \mu\text{A}.$$

The trimethylsilylated free ligand does not provide any cyclic voltammetry signal under comparable conditions.

3.2.6. Magnetic susceptibility

The solvate $n = 10$, $m = 8$ showed $\chi_M^C = 17842.7 \times 10^{-6}$ c.g.s. units mol⁻¹ corrections were made according to Ref. [18].

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