Cyclooligosiloxanolate cluster complexes of transition metals and lanthanides

C. Zucchi [a], O.I. Shchegolikhina [b], M. Borsari [a], A. Cornia [a], G. Gavioli [a],
A.C. Fabretti [a], E. Rentschler [c], D. Gatteschi [c], R. Ugo [d], R. Psaro [d],
Yu.A. Pozdniakova [b], S.V. Lindeman [b], A.A. Zhdanov [b], G. Pályi [a,*]

[a] *Department of Chemistry, University of Modena, Via Campi 183, I-41100 Modena, Italy*
[b] *A.N. Nesmeyanov Institute of Organoelement Compounds, 28 Vavilov Str., Moscow 117813, Russian Federation*
[c] *Department of Chemistry, University of Firenze, Via Maragliano 77, I-50144 Firenze, Italy*
[d] *Department of Inorganic and Organometallic Chemistry and CNR Center, University of Milano, Via Venezian 21, I-20133 Milano, Italy*

Abstract

Cyclooligosiloxanolate complexes of higher valent transition metals and lanthanides were synthesized and characterized by single-crystal X-ray diffraction experiments, spectra, cyclic voltammetry, conductivity and magnetic behaviour. These complexes are sandwich-type clusters containing assemblies of 4 to 8 metals between siloxanolate ligand 'layers'. A high degree of electron delocalization in the metal containing fragment of these complexes is detected by electrochemical and magnetic measurements. The synthesis, crystal and molecular structure determined by X-ray diffraction of $Na_6\{[C_6H_5SiO_2)_8]_2Gd_4(\mu_4\text{-}O)\}$ is reported.

Keywords: Cluster complexes; Cyclooligosiloxanolate clusters; Lanthanides; Siloxanolate; Transition metals

1. Introduction

Synthesis and structural characterization of surface imitating transition metal complexes emerged as one of the most important approaches [1] in the exploration of the molecular events and bonding conditions in the substrate/catalyst interphase [2] of supported transition metal catalysts. The first generation of such complexes contains ligands with single surface imitating groups (prominently silanol complexes of Os, Ru [3] and Rh [4]). More recently a second generation of surface model complexes has been developed, with polydentate ligands imitating entire fragments of the support surface. Mono- and di- [5] as well as oligometallic [6,7] complexes of this latter type have been reported.

This paper presents a summary of the preparation, solid state and solution structure as well as magnetic behaviour of the polymetallic complexes of cyclosiloxanolate ligands together with details of the preparation of the precursor reagent

* Corresponding author.

of the cyclosiloxanolate ligands and one lanthanoide (Gd) derivative.

2. Experimental

The preparation of the complexes discussed as well as the physical methods of characterization are described in the publications listed under Refs. [6,7].

The preparation of the ligand precursor reagent has been reported only very briefly [8], the details of the procedure are reported here.

2.1. Preparation of polysiloxane resin

A solution of 100 ml ($d = 1.321$, 0.624 mol) of phenyltrichlorosilane in 100 ml of anhydrous toluene is prepared in a dropping funnel. This solution is added dropwise under vigorous stirring into a 1-l two-neck round-bottom flask that contains 300 g of ice, 50 ml of water and 150 ml of toluene. The stirring is continued for 30 min after the addition of the PhSiCl$_3$ solution.

The organic phase is washed with water in a separatory funnel till neutral reaction then the solvent is evaporated and the residue is dried at 130–150°C for 2 to 4 h.

The solid resin (PhSiO$_{1.5}$)$_n$ so obtained may contain the rest of the solvent, so a Si determination is required.

2.2. Preparation of a solution of 'PhSiO$_2$Na' reagent

In a two-neck round-bottom flask with cooler and CaCl$_2$ desiccator 10 mmol of resin is suspended in 50 ml of nBuOH and then NaOH 0.20 g (5 mmol) is added at once under stirring (the reaction mixture has to remain anhydrous). The suspension is heated under reflux until the reaction mixture turns colourless. The solution is left to cool to r.t. then metallic sodium 0.115 g (5 mmol) is added and subsequently the reaction mixture is refluxed for an additional 30

min. The solution is used as such for the preparation of complexes.

2.3. General procedure for the reaction with MX$_2$

In a dropping funnel 5 mmol of anhydrous MX$_2$ (M = metal, X = halogen) is dissolved in 10 ml of nBuOH and added dropwise to the boiling solution of the sodium siloxanolate described above. A fine precipitate (NaCl) is formed immediately and the solution gets turbid. Then the reaction mixture is left stirred and heated for an additional 30–40 min. The NaCl precipitate is then centrifuged or filtered off from the warm solution and subsequently the solvent is evaporated. The residue is extracted by nBuOH and the product is obtained in crystalline form by recrystallization either from nBuOH or its mixtures with other solvents.

If the MX$_2$ is not or not fully soluble in nBuOH a suspension is prepared with a minimum amount of solvent and 1 drop of indicator (such as phenolphthaleine) is added. The suspension is refluxed till acid or neutral reaction.

Some representative yields are as follows: **1** (Mn$_6$) 40.5% [6](c); **4** (Cu$_6$) 73% [6](c); **5** (Cu$_2$Ni$_4$) 36.5% [6](d); **10** (Na$_4$Ni$_4$) 68% [7](b); **18** (Cu$_4$) 64% [7](c).

2.4. Preparation of Na$_6${[C$_6$H$_5$SiO$_2$)$_8$]$_2$Gd$_4$(μ_4-O)} · 10EtOH · 8H$_2$O

Polyphenylsiloxane (4 g, 31 mmol 'PhSiO$_2$'), sodium hydroxide (0.69 g, 17 mmol) and 100 ml of n-butanol were charged into a 1-l, four-neck reaction vessel, equipped with a KPG stirrer, reflux condenser and thermometer, through its fourth neck. The reaction mixture was initially (1.5 h) stirred and refluxed (oil bath), then it was left to cool to 50–60°C; when sodium metal (1.96 g, 9.4 mmol, cut into small pieces) was added at once the mixture was stirred and refluxed for an additional 1 h. After this period gadolinium trichloride, GdCl$_3$ (anhydrous) (2.05 g, 7.8 mmol), dissolved in 120 ml of n-butanol

was added dropwise, through the reflux condenser, while stirring and reflux was continued. After having finished the addition of the $GdCl_3$ solution, the reaction mixture was refluxed for an additional 1 h, then it was left to cool to r.t. and was filtered (to remove the insoluble NaCl). The filtrate was drawn dry by removing the solvent at reduced pressure. The resulting white mass was recrystallized from toluene/96% EtOH (2:1). Yield of the recrystallized, white product was 1.81 g (26%).

Analysed: C 39.2%; H 4.4%; Gd 17.4%; Na 3.9%; Si 12.8%. Calculated, $C_{116}H_{156}Gd_4Na_6O_{51}Si_{16}$: C 39.00%; H 4.12%; Gd 17.61%; Na 3.86%; Si 12.58%.

The crystalline product was characterized by single-crystal X-ray diffraction. The conditions of the measurement are shown in Table 1, some selected interatomic distances and bond angles are tabulated in Table 2, a schematic view of the structure is shown in Fig. 1.

3. Results and discussion

The cyclosiloxanolate complexes of transition metals and lanthanides were prepared utilizing an in situ prepared solution of siloxanolate fragments. This reagent can be conveniently and reproducibly prepared from monoorganyl-poly(sesquisiloxane) by treatment with alcoholic (preferentially nBuOH) sodium hydroxide. It

Table 1
Crystal structure determination summary of $16 \cdot 10\text{EtOH} \cdot 8H_2O$

Empirical formula		$C_{116}H_{156}Gd_4Na_6O_{51}Si_{16}$
Formula mass		3572.71
Unit cell dimensions	a (Å)	17.68(1)
	b (Å)	23.00(1)
	c (Å)	19.03(1)
	alpha (deg.)	90
	beta (deg.)	105.53(4)
	gamma (deg.)	90
	V (Å^3)	7455(12)
	Z	2
d (calc, g/cm^3)		1.591
Crystal system		monoclinic
Space group		P2$_1$/n
Diffractometer		Siemens P3/PC
Radiation		MoK α
Monochromator		graphite
Size of the crystal (mm)		0.3 × 0.3 × 0.15
Temperature (K)		150
Data collection mode		$\Theta/2\Theta$
Θ-Range		20
Reciprocal space segment		$+h; +k; \pm l$
No. of symmetry independent reflections		7352
$I > n\sigma$ (I) criterion		3.5
No. of observed reflections		4923
Linear absorption coefficient (cm^{-1})		19.8
method of absorption correction		not applied
Method of solution		direct
Method of refinement		full-matrix least squares
Parameters/date ratio		3.2
R		0.079
R_w		0.081
Programs used		SHELXTL PLUS (PCVersion)

Table 2
Selected interatomic distance (Å) and bond angle (deg.) values of complex **16 · 10EtOH · 8H$_2$O**

Interatomic distance and bond angle ranges and averages of selected bonds	
Si–O$_{Gd}$ (Å)	1.55–1.64(2)
av.	1.60
Si–O (Å)	1.58–1.67(2)
av.	1.65
Gd–O$_{Gd}$ (terminal) (Å)	2.26–2.33(2)
av.	2.29
Gd–O$_{Gd}$ (μ_2) (Å)	2.32–2.42(1)
av.	2.37
Gd–O$_{Gd}$ (μ_4) (Å)	2.48–2.58(1)
av.	2.53
Si–O–Si (deg.)	125–131(1)
av.	127.5
O–Si–O (deg.)	103–113(1)
av.	105.5

Bond lengths

Gd(1)–Gd(2)	3.589(2)	Gd(1)–O(11)	2.29(2)
Gd(1)–O(21)	2.35(2)	Gd(1)–O(81)	2.40(2)
Gd(1)–O(1)x	2.481(2)	Gd(1)–Si(5)a	3.453(8)
Gd(1)–Gd(2)a	3.567(2)	Gd(1)–O(51)a	2.31(2)
Gd(1)–O(41)a	2.36(2)	Gd(2)–O(21)	2.33(2)
Gd(1)–O(61)a	2.42(2)	Gd(2)–O(41)	2.32(2)
Gd(2)–O(31)	2.31(2)	Gd(2)–Gd(1)a	3.567(2)
Gd(2)–O(1)x	2.579(1)	Gd(2)–O(71)a	2.26(2)
Gd(2)–O(61)a	2.37(2)	Si(1)–O(1)	1.64(2)
Gd(2)–O(81)a	2.41(2)	Si(1)–O(11)	1.63(2)
Si(1)–O(8)	1.58(2)	Si(2)–O(2)	1.67(2)
Si(1)–C(11)	1.87(3)	Si(2)–C(21)	1.82(3)
Si(2)–O(1)	1.64(2)	Si(3)–O(3)	1.62(2)
Si(2)–O(21)	1.64(2)	Si(3)–C(31)	1.88(3)
Si(3)–O(2)	1.67(2)	Si(4)–O(4)	1.69(2)
Si(3)–O(31)	1.60(2)	Si(4)–C(41)	1.83(4)
Si(4)–O(3)	1.64(2)	Si(5)–O(4)	1.64(2)
Si(4)–O(41)	1.63(2)	Si(5)–O(51)	1.58(2)
Si(5)–O(5)	1.66(2)	Si(5)–Gd(1)a	3.453(2)
Si(5)–C(51)	1.85(3)	Si(6)–O(6)	1.67(2)
Si(6)–O(5)	1.62(2)	Si(6)–O(61)	1.89(3)
Si(6)–O(61)	1.61(2)	Si(7)–O(7)	1.63(2)
Si(7)–O(6)	1.62(2)	Si(7)–C(71)	1.86(3)
Si(7)–O(71)	1.62(2)	Si(8)–O(8)	1.63(2)
Si(8)–O(7)	1.65(2)	Si(8)–C(81)	1.84(3)
Si(8)–O(81)	1.55(2)	O(51)–Gd(1)a	2.31(2)
O(41)–Gd(1)a	2.36(2)	O(61)–Gd(1)a	2.42(2)
O(61)–Gd(2)a	2.37(2)	O(71)–Gd(2)a	2.26(2)
O(81)–Gd(2)a	2.41(2)	O(1)x–Gd(1)a	2.481(2)
O(1)x–Gd(2)a	2.579(1)		

Bond angles

Gd(2)–Gd(1)–O(11)	120.8(4)	O(2)–Si(3)–C(31)	107.8(11)
O(11)–Gd(1)–O(21)	81.9(6)	O(31)–Si(3)–C(31)	113.2(10)
O(11)–Gd(1)–O(81)	80.5(6)	Gd(2)–Gd(1)–O(21)	39.6(5)
Gd(2)–Gd(1)–O(1)x	45.9	Gd(2)–Gd(1)–O(81)	110.2(4)
O(21)–Gd(1)–O(1)x	71.2(5)	O(21)–Gd(1)–O(81)	98.5(6)
O(11)–Gd(1)–Gd(2)a	122.1(4)	O(11)–Gd(1)–O(1)x	138.8(4)
O(81)–Gd(1)–O(2)a	42.2(5)	O(81)–Gd(1)–O(1)x	73.6(5)
O(11)–Gd(1)–Si(5)a	104.0(4)	Gd(2)–Gd(1)–Gd(2)a	92.2
O(81)–Gd(1)–Si(5)a	131.9(4)	O(21)–Gd(1)–Gd(2)a	109.0(5)
Gd(2)–Gd(1)–O(41)a	111.1(5)	O(1)x–Gd(1)–Gd(2)a	46.3
O(21)–Gd(1)–O(41)a	144.3(7)	Gd(2)–Gd(1)–Si(5)a	107.8(1)

Table 2 (continued)

Bond angles

O(1)x–Gd(1)–O(41)a	73.1(5)	O(21)–Gd(1)–Si(5)a	129.6(5)
Gd(2)a–Gd(1)–O(41)a	40.0(4)	O(1)x–Gd(1)–Si(5)a	117.2(2)
Gd(2)–Gd(1)–O(51)a	121.9(4)	Gd(2)a–Gd(1)–Si(5)a	109.1(1)
O(21)–Gd(1)–O(51)a	127.7(6)	O(11)–Gd(1)–O(41)a	126.5(6)
O(1)x–Gd(1)–O(51)a	139.4(5)	O(81)–Gd(1)–O(41)a	69.8(6)
Gd(2)a–Gd(1)–O(51)a	121.7(4)	Si(5)a–Gd(1)–O(41)a	81.8(6)
O(41)a–Gd(1)–O(51)a	82.1(6)	O(11)–Gd(1)–O(51)a	81.8(6)
O(11)–Gd(1)–O(61)a	127.0(6)	O(81)–Gd(1)–O(51)a	126.9(5)
O(81)–Gd(1)–O(61)a	145.6(6)	Si(5)a–Gd(1)–O(51)a	22.2(5)
Si(5)a–Gd(1)–O(61)a	67.3(4)	Gd(2)–Gd(1)–O(61)a	40.8(4)
O(51)a–Gd(1)–O(61)a	81.8(6)	O(21)–Gd(1)–O(61)a	69.8(6)
Gd(1)–Gd(2)–O(31)	121.1(5)	O(1)x–Gd(1)–O(61)a	72.0(4)
Gd(1)–Gd(2)–O(41)	107.8(4)	Gd(2)a–Gd(1)–O(61)a	109.4(5)
O(31)–Gd(2)–O(41)	80.2(6)	O(41)a–Gd(1)–O(61)a	100.4(6)
O(21)–Gd(2)–O(1)x	69.7(4)	Gd(1)–Gd(2)–O(21)	40.1(4)
O(41)–Gd(2)–O(1)x	71.9(4)	O(21)–Gd(2)–O(31)	81.3(6)
O(21)–Gd(2)–Gd(1)a	105.6(5)	O(21)–Gd(2)–O(41)	98.3(7)
O(41)–Gd(2)–Gd(1)a	40.8(4)	Gd(1)–Gd(2)–O(1)x	43.7
Gd(1)–Gd(2)–O(61)a	41.9(4)	O(31)–Gd(2)–O(1)x	135.6(4)
O(31)–Gd(2)–O(61)a	130.2(7)	Gd(1)–Gd(2)–Gd(1)a	87.8
O(1)x–Gd(2)–O(61)a	71.1(4)	O(31)–Gd(2)–Gd(1)a	120.9(4)
Gd(1)–Gd(2)–O(71)a	122.3(5)	O(1)x–Gd(2)–Gd(1)a	44.1
O(31)–Gd(2)–O(71)a	87.7(6)	O(21)–Gd(2)–O(61)a	71.0(6)
O(1)x–Gd(2)–O(71)a	136.7(4)	O(41)–Gd(2)–O(61)a	142.9(6)
O(61)a–Gd(2)–O(71)a	80.7(6)	Gd(1)a–Gd(2)–O(61)a	106.3(4)
O(21)–Gd(2)–O(81)a	141.4(6)	O(21)–Gd(2)–O(71)a	130.7(7)
O(41)–Gd(2)–O(81)a	70.3(6)	O(41)–Gd(2)–O(71)a	127.0(7)
Gd(1)a–Gd(2)–O(81)a	42.0(4)	Gd(1)a–Gd(2)–O(71)a	120.9(5)
O(71)a–Gd(2)–O(81)a	79.3(6)	Gd(1)–Gd(2)–O(81)a	106.7(3)
O(1)–Si(1)–O(11)	109.9(9)	O(31)–Gd(2)–O(81)a	129.6(6)
O(1)–Si(1)–C(11)	107.4(10)	O(1)x–Gd(2)–O(81)a	71.7(3)
O(11)–Si(1)–C(11)	113.4(11)	O(61)a–Gd(2)–O(81)a	95.6(6)
O(1)–Si(2)–O(21)	111.5(10)	O(1)–Si(1)–O(8)	104.7(10)
O(1)–Si(2)–C(21)	108.9(14)	O(8)–Si(1)–O(11)	112.0(9)
O(21)–Si(2)–O(21)	116.8(12)	O(8)–Si(1)–C(11)	109.0(12)
O(2)–Si(3)–O(31)	113.3(10)	O(1)–Si(2)–O(2)	102.7(10)
O(2)–Si(2)–O(21)	110.8(11)	Gd(1)–O(1)x–Gd(1)a	180.0
O(2)–Si(2)–C(21)	105.2(13)	Gd(1)–O(1)x–Gd(2)a	89.7
O(2)–Si(3)–O(3)	103.0(10)	Gd(1)a–O(1)x–Gd(2)a	90.3
O(3)–Si(3)–O(31)	110.2(10)	O(4)–Si(4)–O(41)	110.4(9)
O(3)–Si(3)–C(31)	108.6(10)	O(4)–Si(4)–C(41)	105.3(13)
O(3)–Si(4)–C(4)	105.2(10)	O(4)–Si(5)–O(5)	103.0(11)
O(3)–Si(4)–O(41)	110.5(10)	O(5)–Si(5)–O(51)	112.4(9)
O(3)–Si(4)–C(41)	109.8(15)	O(5)–Si(5)–C(51)	108.7(12)
O(41)–Si(4)–C(41)	115.2(14)	O(4)–Si(5)–Gd(1)a	90.6(7)
O(4)–Si(5)–O(51)	110.8(10)	O(51)–Si(5)–Gd(1)a	33.5(8)
O(4)–Si(5)–C(51)	105.7(11)	O(5)–Si(6)–O(6)	106.0(9)
O(51)–Si(5)–C(51)	115.3(13)	O(6)–Si(6)–O(61)	108.4(10)
O(5)–Si(5)–Gd(1)a	92.7(6)	O(6)–Si(6)–C(61)	106.9(12)
C(51)–Si(5)–Gd(1)a	148.7(10)	O(6)–Si(7)–O(7)	104.0(9)
O(5)–Si(6)–O(61)	111.2(9)	O(7)–Si(7)–C(71)	109.6(10)
O(5)–Si(6)–C(61)	109.2(13)	O(7)–Si(7)–C(71)	106.9(14)
O(61)–Si(6)–C(61)	114.7(12)	O(7)–Si(8)–O(8)	106.2(9)
O(6)–Si(7)–O(71)	111.6(10)	O(8)–Si(8)–O(81)	109.9(10)
O(6)–Si(7)–C(61)	110.3(13)	O(8)–Si(8)–C(81)	109.5(13)
O(71)–Si(7)–C(71)	113.9(12)	Si(1)–O(1)–Si(2)	125.8(10)
O(7)–Si(8)–O(81)	108.3(10)	Si(3)–O(3)–Si(4)	128.8(11)
O(7)–Si(8)–C(81)	108.3(11)	Si(5)–O(5)–Si(6)	127.8(11)
O(81)–Si(8)–C(81)	114.4(12)	Si(7)–O(7)–Si(8)	125.5(10)
Si(2)–O(2)–Si(3)	125.4(11)	Gd(1)–O(11)–Si(1)	123.6(10)
Si(4)–O(4)–Si(5)	127.5(11)	Gd(1)–O(21)–Si(2)	126.9(11)
Si(6)–O(6)–Si(7)	127.7(10)	Gd(2)–O(31)–Si(3)	125.4(9)

Table 2 (continued)

Bond angles			
Si(1)–O(8)–Si(8)	131.3(12)	Gd(2)–O(41)–Gd(1)a	99.1(6)
Gd(1)–O(21)–Gd(2)	100.3(6)	Si(5)–O(51)–Gd(1)a	124.2(12)
Gd(2)–O(21)–Si(2)	132.4(10)	Si(6)–O(61)–Gd(2)a	131.9(9)
Gd(2)–O(41)–Si(4)	132.0(10)	Si(7)–O(71)–Gd(2)a	126.3(9)
Si(4)–O(41)–Gd(1)a	128.8(10)	Gd(1)–O(81)–Gd(2)a	95.8(7)
Si(6)–O(61)–Gd(1)a	128.8(10)	Gd(1)–O(1)x–Gd(2)	90.3
Gd(1)a–O(61)–Gd(2)a	97.3(6)	Gd(2)–O(1)x–Gd(1)a	89.7
Gd(1)–O(81)–Si(8)	133.6(12)	Gd(2)–O(1)x–Gd(2)a	180.0
Si(8)–O(81)–Gd(2)a	129.3(10)		

can reasonably be supposed that the monomeric organylsilanolate fragments undergo oligocyclizations [9] which are controlled by the template effects of the transition metal cations (similarly to the cyclooligomerization of epoxides [10]), thus resulting in different sizes of the siloxanolate cyclooligomers. This picture is supported (beyond analogies) by the X-ray struc-
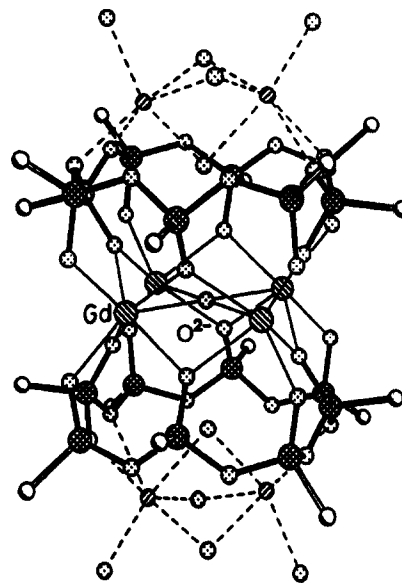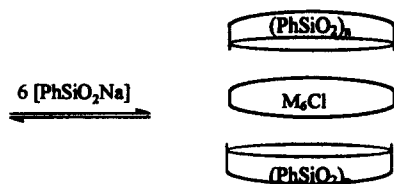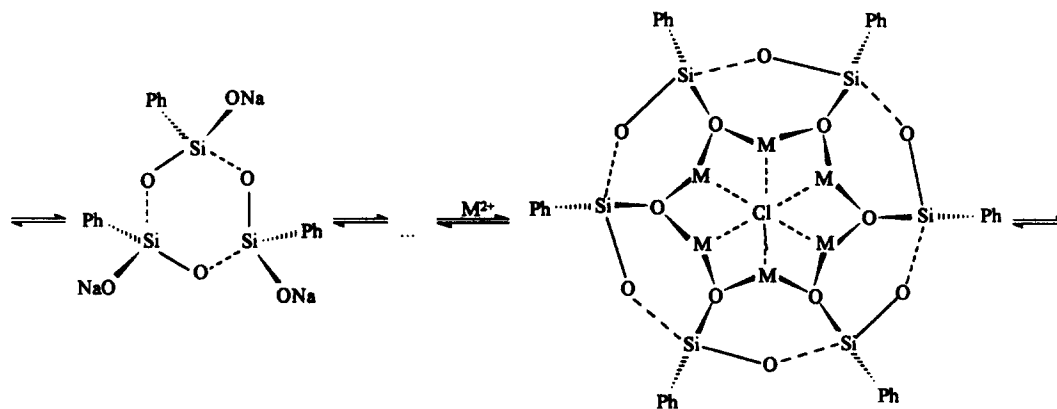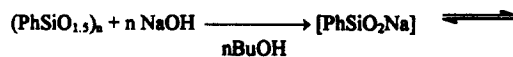

Fig. 1. The molecular structure of the complex core of $Na_6\{[(C_6H_5SiO_2)_8]_2Gd_4(\mu_4\text{-}O)\} \cdot 10EtOH \cdot 8H_2O$.

$$n\ PhSiCl_3 + 1.5\ n\ H_2O \rightarrow (PhSiO_{1.5})_n + 3n\ HCl$$

$$(PhSiO_{1.5})_n + n\ NaOH \xrightarrow{nBuOH} [PhSiO_2Na]$$
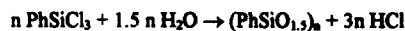
Scheme 1. Supposed reaction course in the formation of the cyclosiloxanolate/metal complexes, exemplified through type A.

tural results on the bis-cyclosiloxanolate sandwich complexes and of the decomplexed ligands [11]. The supposed main steps are shown in Scheme 1.

The details of preparation of the monomeric 'PhSiO$_2$Na' reagent together with one specific example, the gadolinium complex **16**, are reported in this paper.

The preparation of Na$_6${[C$_6$H$_5$SiO$_2$)$_8$]$_2$Gd$_4$(μ_4-O)} (**16**) proceeds similarly to that of the Nd (**14**) [12] derivative. The most important features of the structure are as follows:

1. The overall structure is composed of three 'sheets': the planar Gd$_4$(μ_4-O) moiety is situated between the two cyclooctasiloxanolate ligand 'layers', providing a sandwich-type structure.

2. The siloxanolate ligands are of all-*cis* configuration. Each second siloxanolate oxygen is in the equivalent coordination environment linked to only one Gd atom or bridging two Gd atoms.

3. The planar Gd$_4$(μ_4-O) moiety merits attention. The long Gd–Gd distances (Table 2) exclude substantial metal–metal interaction. The square planar coordination of an O^{2-} ligand was observed only in complexes **12** to **17** [11,12] according to the best of our knowledge.

4. The coordination environment of the Gd atoms corresponds approximately to a mono-face-capped trigonal prism, consisted of 6 silanol oxygens (4 bridging, 2 terminal) and the μ_4-O^{2-} ion.

5. The sodium ions are situated outside the sandwich-like cluster core, falling into two sets: 4 Na$^+$ ions are coordinated (pairwise) to ring-oxygens of the two cyclosiloxanolate ligands, while 2 Na$^+$ ions are not in direct contact with the cluster core, these are tetrahedrally coordinated by solvate molecules.

All cyclosiloxanolate complexes (Fig. 1, Fig. 2; Scheme 2) obtained in course of our studies contain a group of 4 to 6 transition metal ions in a 'coverage' of the oligocyclic ligands. The
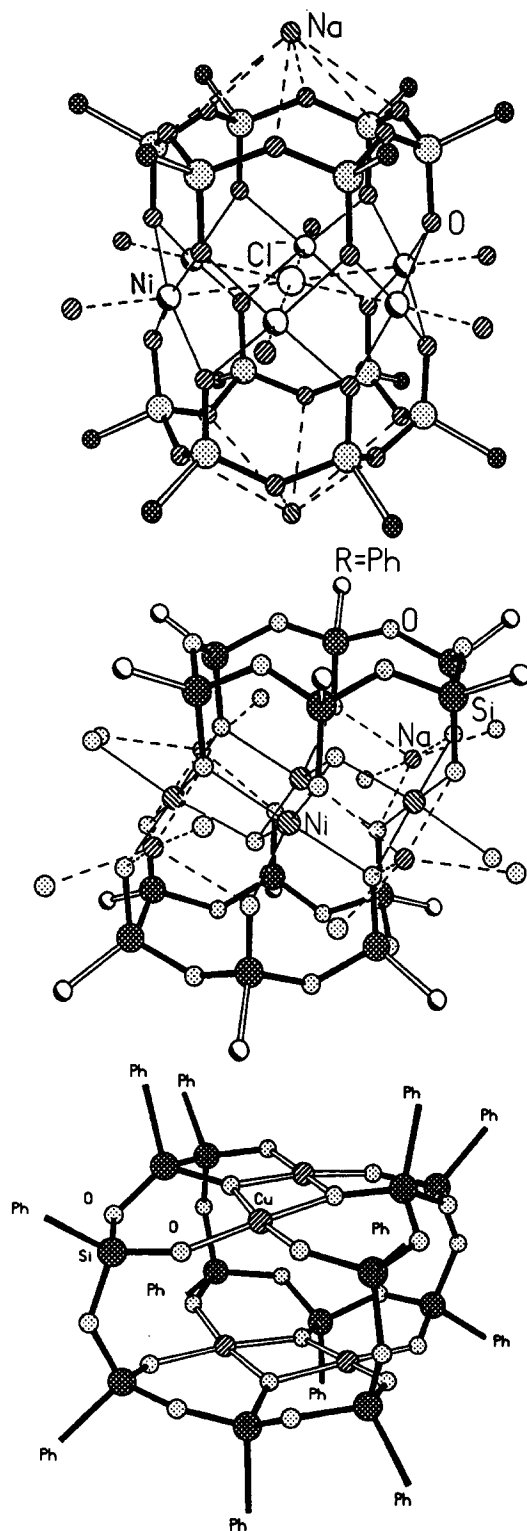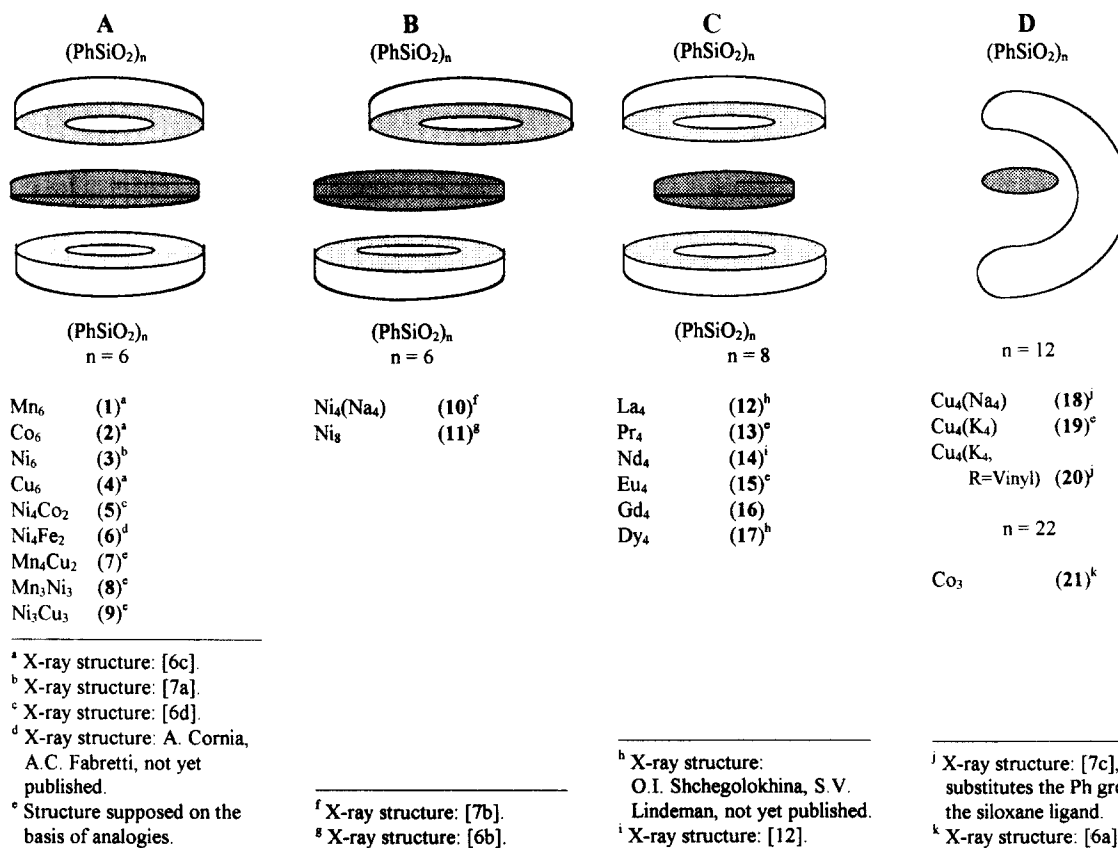

Fig. 2. Typical structures of the cyclosiloxanolate complexes. Top: type A, **3** [7]; center: type B, **10** [7], bottom: type D: **18** [7].

organization of the internal structure of these complexes falls in two principal types: (i) the metal ions are layered between two layers of the cyclic ligand ('sandwich'-type **A**, **B** and **C**) or (ii) the metal ion assemblies are 'folded' into one cyclosiloxanolate ligand envelop (type **D**). The complexes, due to the relatively high oxidation degree of the metal ions, do not contain direct metal–metal interactions (as clearly shown by the X-ray structural data). The metal ions are connected by siloxanolate bridges (all) and in the majority of the cases by encapsulated anions (μ_6-Cl$^-$: type **A**, μ_4-O^{2-}: type **C** and **11**) or by bridging hydroxide ligands (μ_3-OH: **10**).

It is a challenging question whether these complexes can be called metal ion clusters. If metal clusters are defined as assemblies of metal atoms with direct metal–metal bonds [13] then the answer is obviously not. On the other hand several oligometallic compounds had been described where non-metallic atoms are participating in the molecular architecture [14], as for example (μ_4-S)$_2$(μ_2-CO)Fe$_2$Co$_2$(CO)$_{10}$ [15] which is held together by 4 Fe–S, 4 Co–S, 2 Co–C and only 2 Fe–Co, 1 Fe–Fe and 1 Co–Co bonds or even (μ_2-P$_2$) Co$_2$(CO)$_6$ with its 1 P=P (double), 4 Co–P and 1 Co–Co bonds [16] are regarded as 'heteronuclear' metal clusters. We believe that instead of this formal approach it would be more coherent to define clusters as assemblies of metal atoms with significant direct or indirect metal–metal interactions. In this broader sense the present complex type and several so-called cage [17] compounds could be discussed together with metal–metal bounded

A (PhSiO$_2$)$_n$	**B** (PhSiO$_2$)$_n$	**C** (PhSiO$_2$)$_n$	**D** (PhSiO$_2$)$_n$
(PhSiO$_2$)$_n$ n = 6	(PhSiO$_2$)$_n$ n = 6	(PhSiO$_2$)$_n$ n = 8	n = 12

Mn$_6$	(1)[a]	Ni$_4$(Na$_4$)	(10)[f]	La$_4$	(12)[h]	Cu$_4$(Na$_4$)	(18)[j]
Co$_6$	(2)[a]	Ni$_8$	(11)[g]	Pr$_4$	(13)[e]	Cu$_4$(K$_4$)	(19)[e]
Ni$_6$	(3)[b]			Nd$_4$	(14)[i]	Cu$_4$(K$_4$,	
Cu$_6$	(4)[a]			Eu$_4$	(15)[e]	R=Vinyl)	(20)[j]
Ni$_4$Co$_2$	(5)[c]			Gd$_4$	(16)		
Ni$_4$Fe$_2$	(6)[d]			Dy$_4$	(17)[h]	n = 22	
Mn$_4$Cu$_2$	(7)[e]						
Mn$_3$Ni$_3$	(8)[e]					Co$_3$	(21)[k]
Ni$_3$Cu$_3$	(9)[e]						

[a] X-ray structure: [6c].
[b] X-ray structure: [7a].
[c] X-ray structure: [6d].
[d] X-ray structure: A. Cornia, A.C. Fabretti, not yet published.
[e] Structure supposed on the basis of analogies.
[f] X-ray structure: [7b].
[g] X-ray structure: [6b].
[h] X-ray structure: O.I. Shchegolokhina, S.V. Lindeman, not yet published.
[i] X-ray structure: [12].
[j] X-ray structure: [7c], R substitutes the Ph group in the siloxane ligand.
[k] X-ray structure: [6a].

Scheme 2. Structural types of the cyclosiloxanolate/transition metal complexes.
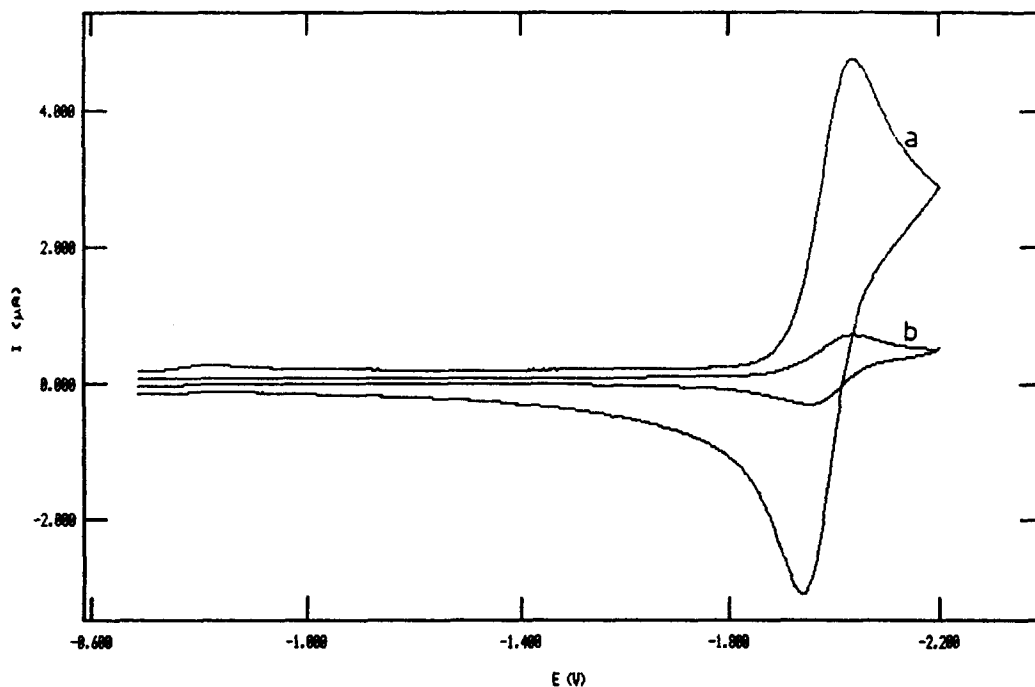
Fig. 3. Cyclic voltammogram of complex 13 (DMF, 0.1 M (nBu)$_4$NClO$_4$, HMDE, ref. Ag/AgCl/3 M NaCl/Pt).

compounds. In the forthcoming part of this paper we shall discuss this aspect on the basis of recent experimental experience.

The cyclic voltammetric study of several cyclosiloxanolate complexes [18] revealed that these compounds give rise to one diffusion controlled reduction wave with a high degree of reversibility (Fig. 3). The redox potential of the complexes is very far from (more negative than) those of the free metals ions. These features were observed also for complexes with two different metals.

Conductometric studies showed [18](b) that the cyclosiloxanolate complexes are very resistant to dissociation in solution.

Magnetic susceptibility measurements at room temperature [6](d),[12,19] identified complexes 3, 5, 6, 10 and 14 as paramagnetic substances. The temperature dependence of the magnetic susceptibility of complexes 3 and 10 [19] revealed that the silanolate oxygen bridges mediate ferromagnetic interactions between the metal atoms. The μ_6-Cl atom in 3 mediates

antiferromagnetic coupling between the Ni(II) ions in this complex.

It can be concluded that the electrochemical and magnetic studies indicate a high degree of indirect metal–metal interaction in the cyclosiloxanolate complexes, which might be interpreted in terms of extensive electronic delocalization over the complex core, providing thus a basis for regarding these compounds as being metal cluster complexes in that broader sense which was suggested earlier in this paper. The stable molecular structure and the reversibility of the reduction/oxidation processes are important factors in the catalytic [20] applications of the cyclosiloxanolate complexes.

Acknowledgements

References

[1] (a) R. Psaro and R. Ugo, in B.C. Gates, L. Guczi and H. Knözinger (Eds.), Metal Clusters in Catalysis, Elsevier, Amsterdam, 1986, p. 427; (b) H.H. Lamb, B.C. Gates and H. Knözinger, Angew. Chem., Int. Ed. Engl., 27 (1988) 1127; (c) J.M. Basset, B.C. Gates, J.P. Candy, A. Choplin, M. Leconte, F. Quignard and C. Santini, Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis, Kluwer, Dordrecht, 1988.

[2] G.A. Somorjai, Chemistry in Two Dimensions: Surfaces, Cornell University Press, Ithaca, NY, 1981.

[3] (a) A.K. Smith, B. Besson, J.M. Basset, R. Psaro, A. Fusi and R. Ugo, J. Organomet. Chem., 192 (1980) C31; (b) L. D'Ornales, A. Chopin, J.M. Basset and S. Shore, Nouv. J. Chimie, 9 (1985) 155; (c) J. Puga, T.P. Fehler, B.C. Gates, D. Braga and F. Grepin, Inorg. Chem., 29 (1990) 2376.

[4] (a) A. Theolier, A.K. Smith, M. Leconte, J.M. Basset, G.M. Zanderighi, R. Psaro and R. Ugo, J. Organomet. Chem., 191 (1980) 415; (b) A. Vizi-Orosz and L. Markó, Transition Met. Chem., 7 (1982) 216; (c) G. Pályi, C. Zucchi, R. Ugo, R. Psaro, A. Sironi and A. Vizi-Orosz, J. Mol. Catal., 74 (1992) 51; (d) A. Vizi-Orosz, R. Ugo, A. Sironi, M. Moret, C. Zucchi, F. Ghelfi and G. Pályi, Inorg. Chem., 33 (1994) 4600.

[5] (a) F.J. Fehér, J. Am. Chem. Soc., 108 (1986) 3850; (b) F.J. Fehér, S.L. Gonzales and J.W. Ziller, Inorg. Chem., 27 (1988) 3440; (c) F.J. Fehér and J.F. Walzer, Inorg. Chem., 29 (1990) 1604; (d) F.T. Edelmann, Angew. Chem., Int. Ed. Engl., 31 (1992) 600; (e) M. Montevalli, D. Shah, S.A.A. Shah and A.C. Sullivan, J. Chem. Soc., Chem. Commun., (1994) 2427; (f) W.A. Herrmann, R.A. Anwander and V. Dufand, Angew. Chem., Int. Ed. Engl., 33 (1994) 1285.

[6] (a) Yu.E. Ovchinnikov, V.E. Shklover, Yu.T. Struchkov, M.M. Levitsky and A.A. Zhdanov, J. Organomet. Chem., 347 (1988) 253; (b) M.M. Levitskky, O.I. Shchegolikhina, A.A. Zhdaniv, V.A. Igonin, Yu.E. Ovchinnikov, V.E. Shklover and Yu.T. Struchkov, J. Organomet. Chem., 401 (1991) 199; (c) V.A. Igonin, O.I. Shchegolikhina, S.V. Lindeman, M.M. Levitsky, Yu.T. Struchkov and A.A. Zhdanov, J. Organomet. Chem., 423 (1992) 351; (d) G. Gavioli, R. Battistuzzi, P. Santi, C. Zucchi, G. Pályi, R. Ugo, A. Vizi-Orosz, O.I. Shchegolikhina, Yu.A. Pozdniakova, S.V. Lindeman and A.A. Zhdanov, J. Organomet. Chem., 485 (1995) 257.

[7] (a) O.I. Shchegolikhina, A.A. Zhdaniv, V.A. Igonin, Yu.E. Ovchinnikov, V.E. Shklover and Yu.T. Struchkov, Metal-loorg Khim., 4 (1991) 74; Engl. Transl., 4 (1991) 39; (b) V.A. Igonin, S.V. Lindeman, K.A. Potekhin, V.E. Shklover, Yu.T. Struchkov, O.I. Shchegolikhina, A.A. Zhdanov and I.V. Razumovskaya, Metalloorg Khim., 4 (1991) 790; Engl. Transl., 4 (1991) 383; (c) V.A. Igonin, S.V. Lindeman, Yu.T. Struchkov, O.I. Shchegolikhina, A.A. Zhdanov, Yu.A. Molodtsova and I.V. Razumovskaya, Metalloorg Khim., 4 (1991) 1355; Engl. Transl., 4 (1991) 672.

[8] A.A. Zhdanov, A.A. Andrianov and M.M. Levitsky, Izv. Akad. Nauk, SSSR, Ser. Khim., (1974) 653.

[9] (a) J.A. Semlyen, Makromol. Chem., Macromol. Symp., 6 (1986) 155; (b) T.C. Kendrich, B. Parbhoo, J.W. White, in S. Patai (Ed.), Silicon–Heteroatomic Bond, Wiley, New York, 1991, p. 67.

[10] (a) C.J. Pedersen, Aldrichim. Acta, 4 (1971) 1; (b) C.J. Pedersen and H.K. Fensdorff, Angew. Chem., Int. Ed. Engl., 11 (1972) 16; (c) D.S.C. Black and A.J. Hartshorn, Coord. Chem. Rev., 9 (1972) 219; (d) G.R. Newkome, J.D. Saner, J.M. Roper and D.C. Hager, Chem. Rev., 77 (1977) 513; (e) N.S. Poonia and A.V. Bajaj, Coord. Chem. Rev., 79 (1979) 389; (f) W. Saenger, I.H. Suh and G. Weber, Isr. J. Chem., 18 (1979) 253.

[11] O.I. Shchegolikhina, S.V. Lindeman and A.A. Zhdanov, unpublished results.

[12] O.I. Shchegolikhina, Yu.A. Pozdniakova, S.V. Lindeman, A.A. Zhdanov, R. Psaro, R. Ugo, G. Gavioli, R. Battistuzzi, M. Borsari, T. Rüffer, C. Zucchi and G. Pályi, submitted for publication.

[13] F.A Cotton, Quart. Rev. (London), 20 (1966) 389.

[14] (a) G. Pályi, F. Piacenti and L. Markó, Inorg. Chim. Acta, Rev., 4 (1970) 109; (b) L. Markó, Gazz. Chim. Ital., 109 (1979) 247; (c) D.F. Shriver, H.D. Kaesz and R.D. Adams (Eds.), The Chemistry of Metal Cluster Complexes, VCH Publishers, New York, 1990, pp. 59, 62, 73, 140, 146, 157, 342.

[15] H. Vahrenkamp and E. Wucherer, Angew. Chem., Int. Ed. Engl., 20 (1981) 680.

[16] C.F. Campana, A. Vizi-Orosz, G. Pályi, L. Markó and L. Dahl, Inorg. Chem., 18 (1979) 3054.

[17] see e.g. (a) J.E. Huheey, Inorganic Chemistry, Harper, Cambridge, 1983, p. 723; (b) D. Gatteschi, A. Caneschi, L. Pardi and R. Sessoli, Science, 265 (1994) 1054; (c) T. Vossmeyer, G. Reck, L. Katsikas, E.T.K. Haupt, B. Schulz and H. Weller, Science, 267 (1995) 1476.

[18] G. Gavioli, M. Borsari, C. Zucchi, G. Pályi, R. Psaro, R. Ugo, O.I. Shchegolikhina and A.A. Zhdanov, J. Organomet. Chem., 467 (1994) 165; (b) idem, submitted for publication.

[19] A. Cornia, A.C. Fabretti, D. Gatteschi, G. Pályi, E. Rentschler, O.I. Shchegolikhina and A.A. Zhdanov, Inorg. Chem., 34 (1995) 5383.

[20] V.L. Kuznetsov, G.L. Elizarova, L.G. Matrienko, I.G. Latyunkhova, V.N. Kolominchuk, A.A. Zhdanov and O.I. Shchegolikhina, J. Organomet. Chem., 475 (1994) 65.