Chemoselectivity in Cyclosiloxanolate Cluster Formation: An Alkali Cation Effect?

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Dedicated to Prof. Dr. Karl-Heinz Thiele (Halle-Merseburg) on the occasion of his 70th birthday

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The Cu_4 derivatives of $[EtSiO_2]Na$ have been synthesised and their cyclic voltammetry, spectroscopic behaviour and X-ray structure determination described. The changes in the alkali cation, Na^+ in place of K^+, might have a "tuning" effect in the organisation on the siloxanolate clusters resulting in a macrocyclic ($[EtSiO_2]_{12}$) ligand instead of two cyclic ($[EtSiO_2]_6$) ligands.

Introduction

Efforts at modelling[1] silica-supported transition metal catalysts[2] resulted in the discovery of reactions leading to cyclosiloxanolate clusters of higher valent transition metals.[3] This new class of metal clusters showed redox,[4] catalytic[5] and magnetic[6] features, which are interesting in their own right.

One of the most remarkable features of this chemistry is the high chemoselectivity of the organisation of these complexes.[3c,7] However, almost nothing is known about the factors which influence the architecture of the cyclosiloxanolate clusters. In this paper we report an observation which might be the first step in this direction.

Results and Discussion

It has been observed by one of our groups that the reaction of potassium ethylsiloxanolate with copper(II) chloride gives the sandwich-type complex **1** [Equation (1)].[8]

$$12\ \text{“}EtSiO_2K\text{”} + 4\ CuCl_2 \rightarrow K_2\{[\text{cyclo-}(EtSiO_2)_6]_2Cu_4K_2\}\cdot 4n\text{BuOH}\ (\mathbf{1}) + 8\ KCl \qquad (1)$$

Since copper(II) in earlier studies showed a tendency to also give tetrahedrally arranged Cu_4 derivatives with *only one* macrocyclic ($[RSiO_2]_{12}$) ligand, we tested whether changes in the experimental conditions would also result in tetrahedral moieties from ethylsiloxanolate anions. We therefore decided to try to change the alkali cation, which might be a "tuning" factor in the organisation of the siloxanolate clusters. In fact we observed that using sodium ethylsiloxanolate, we obtained the new complex **2** according to Equation (2)

$$12\ \text{“}EtSiO_2Na\text{”} + 4\ CuCl_2 \rightarrow Na_4[\text{cyclo-}(EtSiO_2)_{12}Cu_4]\cdot L_x\ (\mathbf{2}) + 8\ NaCl \qquad (2)$$

where L_x = (**a**) 2 *n*BuOH·4NaCl; (**b**) 4 *n*BuOH. The yields observed from Equation (2) were comparable with the yields obtained with other cyclosiloxanolate clusters,[3c,7] which shows that the chemoselectivity observed in Equation (1) could *de facto* be changed by changing the alkali cation.

The new complex **2** has been characterised by elemental analysis and physical methods. Conductivity measurements showed the presence of a nondissociated cluster and relatively easy dissociation of the externally coordinated sodium ions, with λ_{eq} similar to that of other tetrahedral Cu_4 complexes.[9] Cyclic voltammetry showed a nearly reversible redox process at very negative potentials, more than 1.5 V more negative than the peak potential reported for the noncomplexed Cu^{II}/Cu^0 couple.[10] This indicates a considerable stability of the complex core of **2** in solution towards dissociation, as well as survival of the reduction/oxidation process involved in the CV cycles. This behaviour seems to be

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a general feature of the transition metal cyclosiloxanolate complexes.[4,9]

The medium (4000−400 cm^{-1}) and far (500−50 cm^{-1}) infrared spectra confirmed the presence of the structural elements proposed for the structure of complex **2** (C−H, Si−C, Si−O, Cu−O, Na−O interactions) indicating fairly weak Na−O interactions.

The single crystal X-ray structure determination gives a final proof for the structure of complex **2b** which, lying about the *a* Wickoff position, has a crystallographically imposed S_4 (−4) symmetry (Figure 1). The complex consists of a dodecahapto 36-membered macrocyclic ligand of formula $[(EtSiO_2)_{12}]^{12-}$ (Figure 2) binding four Cu^{2+} cations spatially arranged in a flattened tetrahedral unit. Four Na^+ cations are also loosely connected to the surface of the macrocycle leading to an overall neutral 44-membered cage. The twelve silicon and the four sodium atoms carry one exo ligand each (twelve ethyl radicals and four *n*-butyl alcohols, respectively) and the resulting "flattened spherical" moiety has a substantial lipophilic surface.

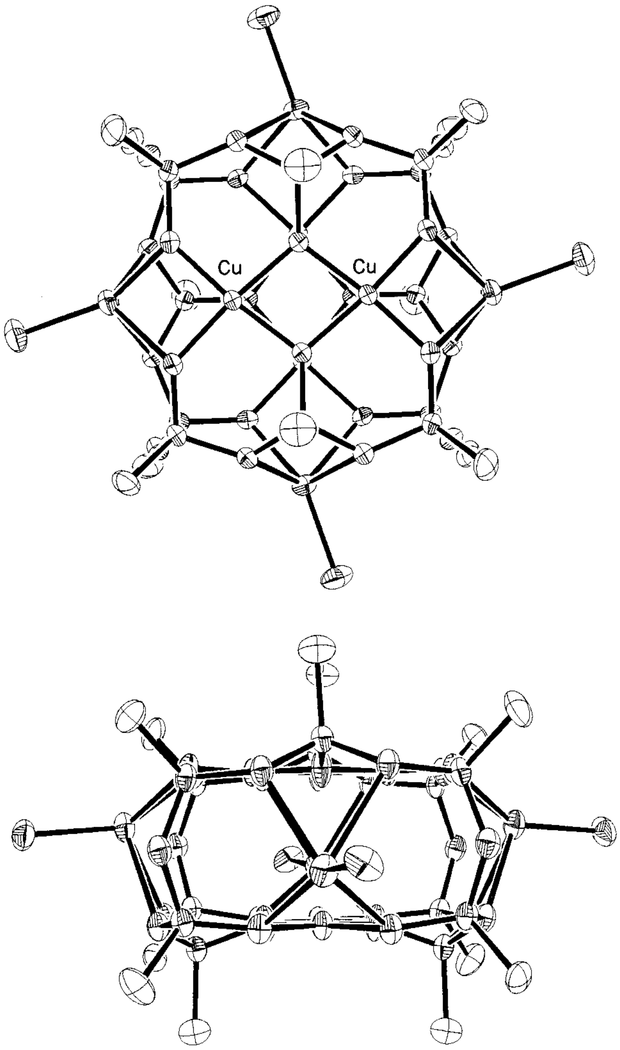

Figure 1. Two ORTEP drawings of $[(EtSiO_2)_{12}Cu_4Na_4]\cdot4n$BuOH **(2b)**; the four disordered *n*-butyl alcohol ligands and the terminal methyl groups of the ethyl radicals are omitted for clarity; top: view down the S_4 axis; bottom: normal to the first view

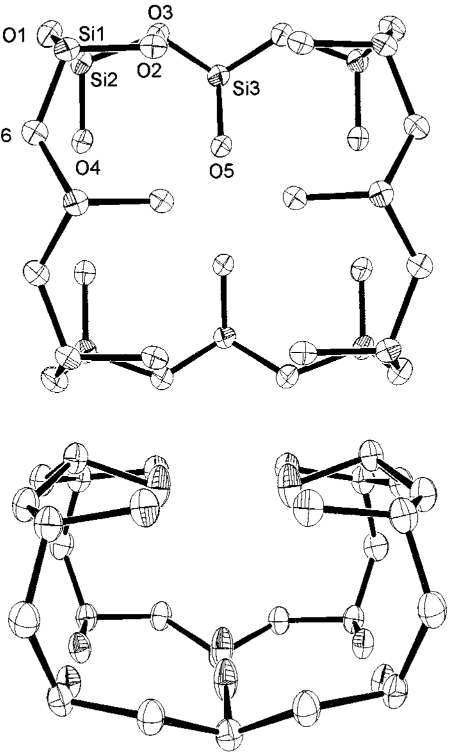

Figure 2. ORTEP drawing of the 36-membered macrocyclic cyclododeca(ethyl-siloxandodecanolate) ligand; top: view down the S_4 axis (the silicon atoms have shaded octants); bottom: almost normal to the first view (the silanolate oxygen atoms have shaded octants)

The Cu···Cu distances (≈ 3 Å) are too large to allow considerable metal−metal interactions. The coordination environment of the Cu^{2+} ions (four silanolate oxygens) is distorted square planar (as far as is allowed by the flexibility of the large ring). The Na^+ ions are coordinated to both silanolate (2) and siloxane (2) oxygens as well as to an "external" solvate butyl alcohol oxygen, thus reaching an approximately tetragonal pyramidal coordination environment.

Selected bond lengths and angles for the macrocyclic ligand are reported in Table 1; their average values ($Si-O_{silanol}$ 1.608 Å; $Si-O_{siloxane}$ 1.643 Å; Si−C 1.861 Å; $O_{siloxane}-Si-O_{siloxane}$ 106.7°; $O_{siloxane}-Si-O_{silanol}$ 109.46°; $O_{siloxane}-Si-C$ 109.2°; $O_{silanol}-Si-C$ 112.5°; Si−O−Si 128.9°) are close to those observed previously.[7,8]

The regiochemistry of the cyclododecasiloxandodecaolate ligand shows a peculiar distribution of the organic and silanol substituents with respect to each other (Figure 2). The stereospecificity of the cyclooligomerisation leading to the macrocyclic ligand is a clear indication that the metal "core" is organised first in the formation of the cyclosiloxanolate clusters, perhaps using also solvent (butyl alcohol) ligands, and this is followed by the building up of the siloxane chain from *suitably oriented* monomeric units. In the initial phase of the organisation we can thus identify the weak, but geometrically different,[11] orienting role ("template" effect) of the alkali cations. The stereochemistry of the Si_{12}-macrocycle in the present study is especially informative, especially when contrasted with the all-*cis* stereo-

Table 1. Selected bond lengths (Å) and angles (deg) for $[(EtSiO_2)_{12}Cu_4Na_4]\cdot 4n$BuOH

Cu−O(2)	1.900(2)	Cu−O(5)#1[a]	1.937(3)
Cu−O(4)#1[a]	1.939(2)	Cu−O(5)#2[b]	1.949(2)
Si(1)−O(2)	1.597(3)	Si(1)−O(1)	1.638(3)
Si(1)−O(6)	1.663(3)	Si(1)−C(1)	1.858(4)
Si(2)−O(4)	1.611(3)	Si(2)−O(1)	1.635(3)
Si(2)−O(3)	1.660(3)	Si(2)−C(2)	1.865(4)
Si(3)−O(5)	1.617(3)	Si(3)−O(6)#1[a]	1.628(3)
Si(3)−O(3)	1.635(2)	Si(3)−C(3)	1.860(5)
Na−O(7)	2.251(3)	Na−O(2)	2.322(3)
Na−O(4)#1[a]	2.402(3)	Na−O(3)	2.520(3)
Na−O(6)#1[a]	2.670(3)	C(1)−C(11A)	1.429(10)
C(1)−C(11B)	1.449(10)	C(2)−C(21)	1.558(6)
C(3)−C(31)	1.533(7)	O(7)−C(5)	1.440(5)
C(5)−C(6B)	1.508(6)	C(5)−C(6A)	1.508(6)
C(6A)−C(7A)	1.508(6)	C(6B)−C(7B)	1.508(6)
C(7A)−C(8A)	1.508(6)	C(7B)−C(8B)	1.508(6)
O(2)−Cu−O(5)#1[a]	174.11(10)	O(2)−Cu−O(4)#1[a]	90.39(10)
O(5)#1−Cu−O(4)#1[a]	95.46(10)	O(2)−Cu−O(5)#2[b]	95.55(10)
O(5)#1−Cu−O(5)#2[a][b]	78.58(11)	O(4)#1−Cu−O(5)#2[a][b]	173.88(10)
O(2)−Si(1)−O(1)	110.43(14)	O(2)−Si(1)−O(6)	110.59(13)
O(1)−Si(1)−O(6)	105.97(13)	O(2)−Si(1)−C(1)	113.46(19)
O(1)−Si(1)−C(1)	107.36(19)	O(6)−Si(1)−C(1)	108.71(17)
O(4)−Si(2)−O(1)	111.94(14)	O(4)−Si(2)−O(3)	109.54(13)
O(1)−Si(2)−O(3)	106.62(14)	O(4)−Si(2)−C(2)	112.52(16)
O(1)−Si(2)−C(2)	107.20(17)	O(3)−Si(2)−C(2)	108.80(16)
O(5)−Si(3)−O(6)#1[a]	108.53(14)	O(5)−Si(3)−O(3)	108.62(14)
O(6)#1−Si(3)−O(3)[a]	104.61(14)	O(5)−Si(3)−C(3)	111.45(19)
O(6)#1−Si(3)−C(3)[a]	112.43(19)	O(3)−Si(3)−C(3)	110.91(19)
O(7)−Na−O(2)	145.09(12)	O(7)−Na−O(4)#1[a]	116.23(12)
O(2)−Na−O(4)#1[a]	70.39(9)	O(7)−Na−O(3)	113.35(11)
O(2)−Na−O(3)	86.56(10)	O(4)#1−Na−O(3)[a]	120.90(10)
O(7)−Na−O(6)#1[a]	94.70(10)	O(2)−Na−O(6)#1[a]	120.21(10)
O(4)#1−Na−O(6)#1[a]	86.04(9)	O(3)−Na−O(6)#1[a]	59.61(8)
Si(2)−O(1)−Si(1)	132.59(16)	Si(1)−O(2)−Cu	134.61(14)
Si(1)−O(2)−Na	120.71(14)	Cu−O(2)−Na	93.48(10)
Si(3)−O(3)−Si(2)	126.20(16)	Si(3)−O(3)−Na	96.45(12)
Si(2)−O(3)−Na	121.08(14)	Si(2)−O(4)−Cu#2[b]	133.60(14)
Si(2)−O(4)−Na#2[b]	120.73(14)	Cu#2−O(4)−Na#2[b]	90.06(10)
Si(3)−O(5)−Cu#2	125.92(15)	Si(3)−O(5)−Cu#1[a]	127.63(15)
Cu#2−O(5)−Cu#1[a]	101.41(11)	Si(3)#2−O(6)−Si(1)[b]	127.83(16)
Si(3)#2−O(6)−Na#2[b]	91.12(11)	Si(1)−O(6)−Na#2[b]	120.30(13)
C(11A)−C(1)−Si(1)	119.4(5)	C(11B)−C(1)−Si(1)	120.8(5)
C(21)−C(2)−Si(2)	112.3(3)	C(31)−C(3)−Si(3)	114.8(4)
C(5)−O(7)−Na	120.4(2)	O(7)−C(5)−C(6B)	114.5(8)
O(7)−C(5)−C(6A)	111.6(5)	C(7A)−C(6A)−C(5)	113.5(8)
C(7B)−C(6B)−C(5)	106.6(11)	C(6A)−C(7A)−C(8A)	118.2(12)
C(6B)−C(7B)−C(8B)	119.5(18)		

[a] Symmetry transformations used to generate equivalent atoms: #1: $y - 1/4$, $-x + 1/4$, $-z + 1/4$. − [b] Symmetry transformations used to generate equivalent atoms: #2: $-y + 1/4$, $x + 1/4$, $-z + 1/4$.

chemistry of the Si_6[6,7,9] and Si_8[3c,12] ligands obtained in earlier studies.

Experimental Section

Starting materials were of commercial origin with the exception of the sodium ethylsilanolate, which was prepared in situ as described for the corresponding Ph derivative.[3c] − Conductivity measurements were obtained with a Conductimeter Crison mod 525 (all constant 1.02) instrument. − Cyclic voltammetric (CV) measurements were performed by Potentiostat-Galvanostat PAR 273A instrument under Ar atmosphere. − Infrared spectra were obtained by Bruker FT-IR IFS 113V spectrophotometer, using KBr pellets for the 4000−400 cm^{-1} range, and PE pellets for the 500−50 cm^{-1} range.

Preparation of the "$EtSiO_2Na$" Reagent: In a 100-mL two-necked round-bottom reaction vessel, equipped with a reflux condenser (closed with a $CaCl_2$ desiccator tube) and an Ar inlet poly(ethylsiloxane) "resin"[3c] (2.56 g, 0.03 mol) was suspended in 50 mL of dry *n*BuOH. To this suspension, under a dry, deoxygenated Ar atmosphere was added sodium hydroxide (0.60 g, 0.015 mol) in one portion while the suspension was (magnetically) stirred. Then, the reaction mixture was heated and refluxed (≈ 30 min) until it turned clear, indicating that the "resin" was completely dissolved. After the solution had cooled to room temp. metallic sodium (0.345 g, 0.015 mol), cut into small pieces, was added. After the Na had completely dissolved, the reaction mixture was again heated to reflux for an additional 30 min. This solution was used for the subsequent reaction.

Preparation of $Na_4[(EtSiO_2)_{12}Cu_4]$: The "$EtSiO_2Na$" reagent, prepared as described above, was used for the following preparation in the same reaction vessel, substituting the Ar inlet tube for a dropping funnel. A solution of anhydrous $CuCl_2$ (1.35 g, 0.01 mol), in 15 mL of dry *n*BuOH was poured into the dropping funnel and this (green) solution was then added dropwise to the solution of the "$EtSiO_2Na$" reagent during 30 min. After the first drops, the (blue) reaction mixture became turbid as a consequence of the formation of a fine white precipitate (NaCl). After the addition was complete the dropping funnel was removed and the reaction mixture was heated to reflux under a dry Ar atmosphere for an additional 5 h. After this period the NaCl precipitate was centrifuged off while the solution was still warm, then the reaction mixture was left to cool to room temp. and the solvent was evaporated at reduced pressure and room temp. The residue was extracted with 20 mL of *n*BuOH. This extract was chilled to −30 °C. Blue crystals were obtained. Recrystallisation from *n*BuOH was repeated 2−3 times. The yield of the crude product was 2.633 g (62.4%), and that of the re-crystallised product 0.672 g (15.7%).

Crude Product: $C_{32}H_{80}Cl_4Cu_4Na_8O_{26}Si_{12}$ {$[(EtSiO_2)_{12}Cu_4Na_4]\cdot 2n$BuOH$\cdot 4$NaCl}: calcd. C 21.38, H 4.49, Cu 14.13, Na 10.22; found C 21.3, H 4.6, Cu 12.7, Na 15.5.

Recrystallised Product: $C_{40}H_{100}Cu_4Na_4O_{28}Si_{12}$ {$[(EtSiO_2)_{12}Cu_4Na_4]\cdot 4n$BuOH}: calcd. C 28.06, H 5.89, Cu 14.84, Na 5.37; found C 27.9, H 5.6, Cu 14.3, Na 6.2.

The deviations of the measured elemental composition from the calculated formulae are attributed to minor amounts of co-crystallised NaCl and to instability of the crystal solvates. The re-crystallised product was characterised by conductivity, cyclic voltammetry, infrared spectroscopy and X-ray single crystal diffraction.

Conductivity: Solvent: *n*BuOH, concentration 1×10^{-4} M, $\lambda_{eq} = 10.4\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Cyclic Voltammetry: Solvent: *n*BuOH, supporting electrolyte: 0.05 M nBu_4NClO_4 (TBAP), redox system: HMDE//Ag/AgCl//Pt, scan speed: 100 mV/s, $E_{pc} = -1.78$V, $E_{pa} = -1.68$ V, $E^0 = (E_{pc} + E_{pa})/2 = 1.73$ V.

Table 2. Crystal data and structure refinement for $[(EtSiO_2)_{12}Cu_4Na_4]\cdot 4n$BuOH

Empirical formula	$C_{20}H_5Cu_2Na_2O_{14}Si_6$
Formula weight	856.20
Temperature	173(2) K
Wavelength	0.71069 Å
Crystal system, space group	Tetragonal, *I*41/*a* (No 88)
Unit cell dimensions	$a = 22.814(5)$ Å $b = 22.814(5)$ Å $c = 14.767(3)$ Å
Volume	7686(3) Å^3
Z, Calculated density	8, 1.480 Mg/m^3
Absorption coefficient	1.371 mm^{-1}
F(000)	3568
Crystal size	0.1 × 0.1 × 0.1 mm
Theta range for data collection	1.64−27.03°
Limiting indices	$-22 \leq h \leq 29$ $-28 \leq k \leq 27$ $-17 \leq l \leq 18$
Reflections collected/unique	20814/3894 [*R*(int) = 0.0339]
Completeness to φ = 27.03	92.5%
Absorption correction	SADABS
Max. and min. transmission	1.000 and 0.904
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3894/6/227
Goodness-of-fit on F^2	1.097
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0413$, $wR2 = 0.1227$
R indices (all data)	$R1 = 0.0585$, $wR2 = 0.1309$
Largest diff. peak and hole	0.623 and −0.380 e·Å^{-3}

Medium-Infrared Spectroscopy: (4000−400 cm^{-1}) (KBr pellet): $\tilde{\nu}$ = 3664 w (νO−H, assoc.); 2960 m, 2939 w, 2912 w, 2876 w, 2848 w (νC−H); 1644 m (νC−O); 1592 m, 1462 m, 1416 m, 1247 m (νC−C); 1126 s (νSi−C); 1033 s, 991 s, 954 m (νSi−O), 771 m (δC−H); 695 m (δC−C + νCu−O); 488 m, 470 w, 462 w (νSi−O skeletal + νCu−O?).

Far-Infrared Spectroscopy: (500−50 cm^{-1}) (polyethylene pellet): $\tilde{\nu}$ = 440 w (δSi−O skeletal); 364 w (νCu−O); 274 vw (δCu−O + Si−O−Si skeletal); 181 vw, 154 vw, 102 w (νNa−O).

X-ray Structure Determination of [*n*BuOH Na]$_4$[cyclo(EtSiO$_2$)$_{12}$-Cu$_4$]·[2b]: A suitable crystal of **2b** was chosen and mounted, in air, on a glass fiber onto a goniometer head. Data were collected at 170 K on a Siemens SMART CCD area-detector diffractometer equipped with a Siemens LT3 cooling device. Crystal data are reported in Table 2.

Graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation was used with the generator working at 45 kV and 40 mA. Cell parameters and orientation matrix were obtained from least-squares refinement on reflections measured in three different sets of 15 frames each, in the range $0 < \varphi < 23°$. The data collection was performed by measuring 1400 frames (20 s per frame; ω scan method, $\Delta\omega = 0.3°$; sample-detector distance fixed at 5 cm) which, upon data reduction, afforded almost all reflections belonging to the sphere with $2\varphi < 54°$. The first 100 frames were recollected at the end to monitor crystal decay, which was not observed; an absorption correction was applied (SADABS).[13]

A total of 20814 reflections were collected (3894 unique, R_{int} = 0.0339; R_σ = 0.0283[14]). The structure was solved by direct methods (SIR97[15]) and refined with full-matrix-block least-squares (SHELX97[16]); anisotropic temperature factors were assigned to all non-hydrogen atoms except for the disordered C8A/C8B. Due to the disorder of some of the aliphatic residues hydrogen atoms were omitted from the structural model. A summary of crystal data and refinement details are reported in Table 2.

Crystallographic data (excluding structure factors) for the structure included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142093. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[14] $R_{\mathrm{int}} = \Sigma|F_o^2 - F_{\mathrm{mean}}^2|/\Sigma F_o^2$; $R_\sigma = \Sigma\sigma(F_o^2)/\Sigma F_o^2$; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma(F_o^2 - F_c^2)^2/\Sigma \mathrm{w} F_o^4]^{1/2}$

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