

# Siloxane clusters of higher valence transition metals: redox properties

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## Abstract

Cyclic voltammetric behaviour of polymetallic complexes of hexaphenylcyclohexasiloxane–hexaol with Ni, Mn and dodecaphenylcyclododecasiloxane–dodecaol with Cu was studied. The complexes react electrochemically as a unit assembly of the complexed metals.

*Key words:* Siloxane; Manganese; Nickel; Copper; Sodium

## 1. Introduction

The exploration of the true structure and nature of the surface species formed on oxide supports from transition metal complexes is one of the most important goals in present catalysis research [1]. One of the most efficient methods of exploration of this problem is the preparation of model compounds which, in some cases, could be isolated and structurally characterized. Early examples include silanolate osmium [2] and rhodium [3] complexes. Very recently monometallic and dimetallic [4] as well as polymetallic [5] complexes of oligosiloxane ligands were reported. These compounds can be regarded as models of metals on the silica surface. The latter type is of particular interest since these compounds contain assemblies of four to six transition metal atoms in higher oxidation state (*e.g.* Ni<sup>II</sup>). Structural studies reveal no direct metal–metal bonding in these complexes. On the contrary it

would be important to know whether these compounds react as assemblies of individual (independent) metal atoms or collectively as interacting groups, *i.e.* a novel kind of (higher valence) metal “cluster”. The answer to this question could be important from the viewpoint of catalytic [6], bioinorganic [7] or materials [8] chemistry.

## 2. Results and discussion

Electrochemical study of the redox properties of low valence transition metal clusters has provided useful structural information about the number of skeletal electrons [9] or even about the reactivity of a given fragment of the molecule [10]. This prompted us to start a systematic electrochemical study of the oligosiloxane complexes, which were obtained by exchange reaction of sodium phenylsiloxanolate with transition metal chlorides and reported recently by one of our teams [5]. The preliminary results of this work are described in the present paper. The oligo-cyclo-siloxane derivatives investigated in the course of this work were sandwich-type complexes of four to six transition metal atoms between two hexaphenyl-cyclo-

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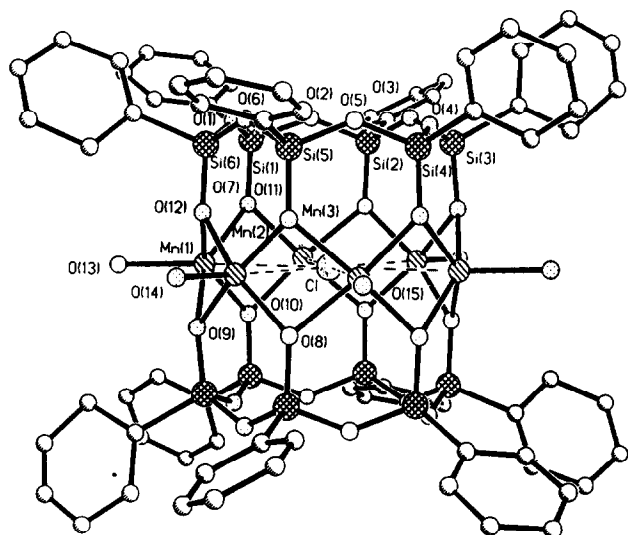
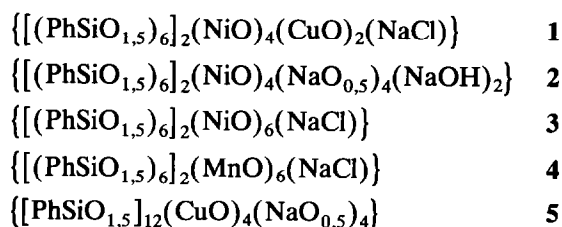


Fig. 1. Structure of 1-4 [5a].

siloxane rings (Fig. 1, 1-4) [5a], except for 5 (Fig. 2), which had one large dodecaphenyl-dodecacyclosiloxane ring [5b]:



All complexes were studied in dimethylformamide (DMF) by cyclic voltammetry. Compounds 1-5 show a very similar electrochemical behaviour; a cathodic peak and a corresponding anodic wave of closely similar

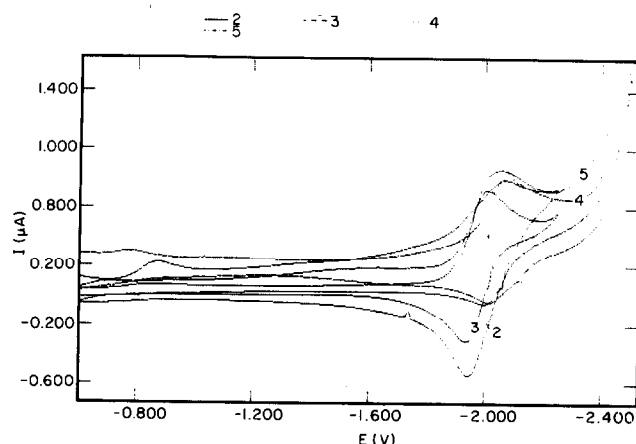


Fig. 3. C-V curves of 2-5 in DMF (0.1 M tetrabutylammonium perchlorate (TBAP)) at 25°C on HDME (scan rate, 50 mV s<sup>-1</sup>; depolarizer concentration, 1 × 10<sup>-4</sup> M; in an Ar atmosphere).

height (Fig. 3) can be observed. The slope and the characteristics of the voltammetric curve suggest a quasi-reversible electron transfer process, while the dependence of the peak current on the scan rate indicates that the process is diffusion controlled (Fig. 4). For all compounds the peak potential values fall in a narrow range, very different from those of the free metal ions in the same solvent (Ni<sup>2+</sup>, -1.06 V; Mn<sup>2+</sup>, -1.12 V; Cu<sup>2+</sup>, 0.02 V (all with respect to Ag/AgCl in DMF)) [11]. The reversibility of the electrochemical reduction is almost independent of the nature and number of the metal ions in the complexes. These features can be interpreted by assuming that the (cyclosiloxane)<sub>2</sub>M<sub>n</sub> complexes undergo reduction without considerable structural changes and most probably

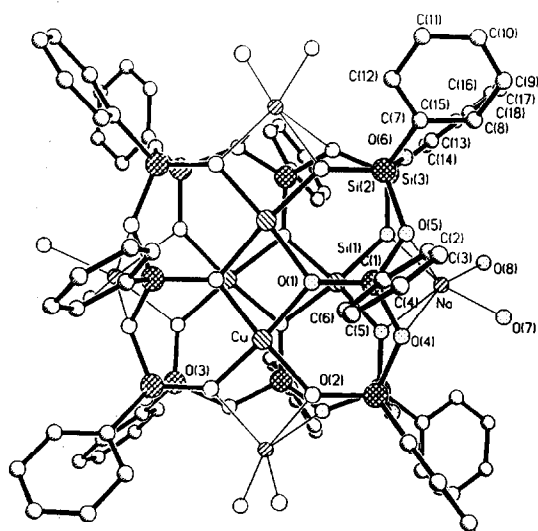


Fig. 2. Structure of 5 [5b].

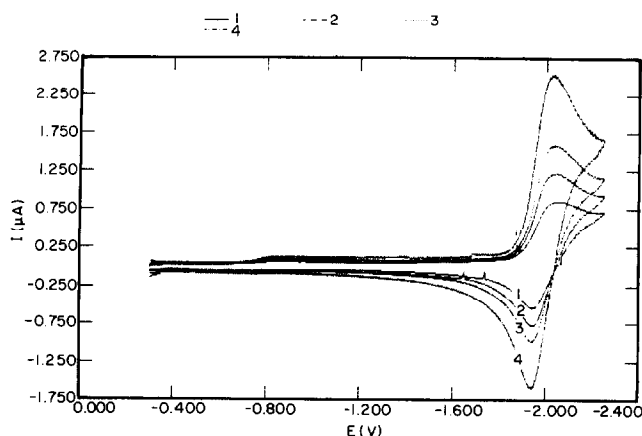


Fig. 4. C-V curves of 2 in DMF (0.1 M TBAP) at 25°C on HDME at different scan rates: curve 1, 50 mV s<sup>-1</sup>; curve 2, 100 mV s<sup>-1</sup>; curve 3, 200 mV s<sup>-1</sup>; curve 4, 500 mV s<sup>-1</sup> (depolarizer concentration, 1 × 10<sup>-4</sup> M; in an Ar atmosphere).

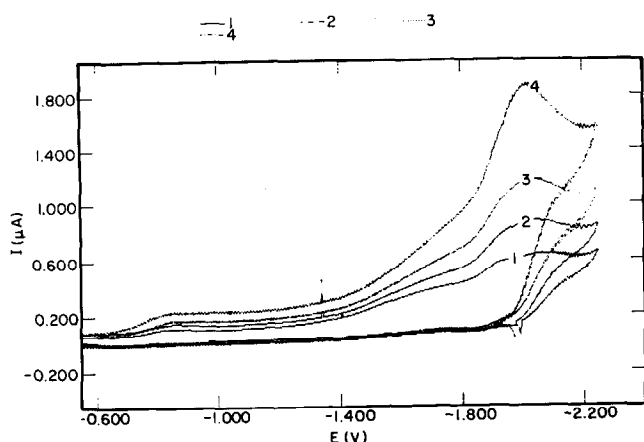


Fig. 5.  $C-V$  curves of **1** in DMF (0.1 M TBAP) at 25°C on HDME at different scan rates: curve 1, 50  $\text{mV s}^{-1}$ ; curve 2, 100  $\text{mV s}^{-1}$ ; curve 3, 200  $\text{mV s}^{-1}$ ; curve 4, 500  $\text{mV s}^{-1}$  (depolarizer concentration,  $1 \times 10^{-4}$  M; in an Ar atmosphere).

delocalize the electron(s) taken up on the whole complex core. The large shift in the reduction potentials towards negative values with respect to the uncomplexed metal ions indicates that the complexation is very strong, in line with the considerable stability of the complexes towards thermal decomposition and chemical oxidation. Compound **1** reveals a somewhat different electrochemical behaviour: (i) the two cathodic peaks of **2-5** become three peaks on decrease in the scan rate; (ii) no anodic counterpart can be observed (Fig. 5). The electron transfer is therefore irreversible but still diffusion controlled. The peak current is similar to those observed for the other complexes.

The similar peak currents of the cathodic waves observed for the different compounds (Fig. 1) suggest that the same numbers of the electrons are involved in the reduction process. These observations shed new light on the structure of **1-5**. The supposed bond delocalization, leading to "collective" reactivity of the complexed metals, is now under investigation by other physical and chemical methods in our laboratories.

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