

# Systematic Structural Coordination Chemistry of p-tertButyltetrathiacalix[4]arene: Further Complexes of Transition-Metal Ions

## Abstract

In extension of earlier work on complexes of p-tert-butyltetrathiacalix[4]arene, LH<sub>4</sub>, with late transition-metal MII species, we report studies of complexes modelled on the basis of single-crystal X-ray studies as derivatives of VV, WVI, MnII, Fe III, Ni II, Cu II and PdII, the last as a trio of heteronuclear species also involving CaII. In complexes [VO(OH)(LH<sub>2</sub>)· 2.5dmf·2H<sub>2</sub>O] (x2) (1), Cl<sub>2</sub>W(L)·3.5C<sub>6</sub>H<sub>6</sub> (2) and [Mn(LH<sub>2</sub>)· 3.5CH<sub>2</sub>Cl<sub>2</sub>](x2) (3) included dmf is found only in the partially deprotonated calixarene cavities of 1 and 3. In oligonuclear OFe<sub>3</sub>(HCO<sub>2</sub>)(LH)<sub>2</sub>·2H<sub>2</sub>O·6dmf (4) and 2Cuac<sub>2</sub>·Cu<sub>2</sub>(L)· dmf·4.5CH<sub>2</sub>Cl<sub>2</sub> (6) (ac = acetate) included dmf is found in both. NiII provides several species, including 5a, binuclear (Et<sub>3</sub>NH)Ni<sub>2</sub>(LH)(LH<sub>2</sub>)·2dmf·2Me<sub>2</sub>CO·H<sub>2</sub>O, 5b, a remarkable hexanuclear (binuclear+tetranuclear) aggregate, Ni<sub>6</sub>(L)(LH)<sub>2</sub>·(LH<sub>2</sub>)·4MeCN·6H<sub>2</sub>O, and 5c, an even more remarkable Ni<sub>32</sub> aggregate modelled as (centrosymmetric) Ni<sub>32</sub>(OH)<sub>40</sub>(L)<sub>6</sub>· 8dmsO·10dmf, in which there are two sets of nickel atoms, one disposed at the corners of a cube (Ni<sub>8</sub>), the other (Ni<sub>24</sub>) at the vertices of a cuboctahedron (the Ni<sub>8</sub> vertices at the centres of the hexagonal faces); the hydroxy groups comprise two sets: one, (OH)<sub>24</sub>, disposed outside the spheroidal shell of nickel atoms, the other, (OH)<sub>16</sub>, disordered within, the thiacalixarene ligands L<sub>6</sub> being disposed about the axes of the octahedron. Heteronuclear species have been found as CaII/ PdII combinations CaPd<sub>2</sub>(LH)<sub>2</sub>·1.5CH<sub>2</sub>Cl<sub>2</sub> (7a), CaPd(LH<sub>2</sub>)· 3dmsO·H<sub>2</sub>O·4.5MeCN (7b), Ca<sub>2</sub>Pd(LH)<sub>2</sub>·3.5dmsO·1.5H<sub>2</sub>O· 4MeCN (7c), all with included solvent.

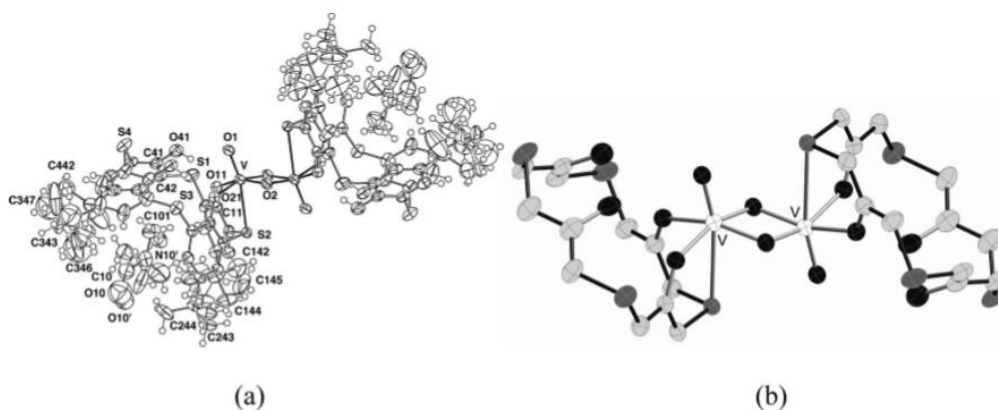


Figure 1. (a) Projection of the centrosymmetric binuclear array of  $[(\text{dmf}\cdot\text{LH}_2)_2\text{OV}(\mu\text{-OH})]_2(\cdot 3\text{dmf}\cdot 4\text{H}_2\text{O})$  (1) showing the included dmf. V–O (terminal; bridging) are 1.607(2); 1.806(2), 1.846(2) Å. Within the OSO tripods, V–S; O are 2.7602(8); 1.983(2), 1.978(2) Å. Within the V<sub>2</sub>O<sub>2</sub> central rhomb, V···V is 2.7486(10), O···O 2.44(2) Å, O–V–O 82.37(10), V–O–V 97.6(1)°. (b) Simplified, perspective view of the coordination core of the dimer, showing only the macrocyclic ring atoms (and their oxygen substituents) of the calixarene.