Cobalt(II) and nickel(II) complexes with a tetraanionic ligand of \(p\)-tert-butylsulfonylcalix[4]arene were synthesized and their X-ray structures show that the calixarene acts as a bis-tridentate dinucleating ligand with the 1,2-alternate conformation.

In recent years, polynuclear complexes were widely investigated because of the interests from their structural complexity and diversity, and chemical and physical behaviors arising from cooperative effects of multi metal ions. In syntheses of such compounds, use of well-organized multidentate ligands is effective to construct and to control multi-metal centered structures. Ligands with several coordination sites and with moderately rigid structures are often employed for such purposes. This study aims to search a novel building-unit for multi-metal centered complexes and to find out its coordination ability.

Calix[4]arenes are well investigated in supramolecular and molecular recognition chemistry. The introduction of hetero atoms vests them with the remarkable coordination abilities to metal ions. In most cases, ligating groups such as alcohols and amines are introduced at the upper and lower rim positions. Recently we reported the synthesis of \(p\)-tert-butylthiacalix[4]arene (X = S; \(H_4L'\)), which contains hetero groups at the skeleton, and was derived by oxidation of \(p\)-tert-butylthiacalix[4]arene (X = S; \(H_4L'\)).

\(H_4L\) possesses four phenol groups together with eight sulfonyl oxygens which potentially coordinate to transition metal ions in multidentate fashions. We have already reported that \(H_4L'\), a precursor of \(H_4L\), forms a tetrarnuclear complex with zinc(II) ions, \([Zn_4(L')(H_2L')]_2\), which contains two dianionic \(H_2L'\) and tetraanionic \(L'\), acting as tetra- and octadentate ligands. \(H_4L\) may also act as a multidentate ligand for transition metal ions and can be used as a building unit for polynuclear complexes. Here we report cobalt(II) and nickel(II) complexes with \(L'\), \([M_2(L)(H_2O)_2(dmf)_4]\) (M = Co(II) (1), Ni(II) (2); dmf = dimethylformamide) in which the calixarene acts as a bis-tridentate facial ligand.

A novel dinuclear complex of Co(II) was synthesized as in Scheme 1. An excess of cobalt(II) acetate in ethanol and \(H_4L\) in ethanol were mixed and the resulting pink solution was refluxed for 1 h. Then the resulting pink solution was evaporated to dryness and the residue was recrystallized from dmf.

For Ni(II) complex, an excess of acetylacetonatonickel(II) dihydrate and \(H_4L\) were mixed and refluxed in chloroform, and then the resulting pale green solution was evaporated to dryness. The residue was purified by chromatography (Bio-Beads S-X3 / CHCl3), and from the main component, desired product 2 was isolated by recrystallization from dmf.

\(H_4L\) has low extraction ability for transition metal ions, however, we succeeded in the syntheses of transition metal complexes with sulfonylcalix[4]arene in non-aqueous media in the presence of a base (acetate or acetylacetonate anion).

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**Sulfonylcalix[4]arene as a Bis-Tridentate Facial Ligand:**

**Syntheses and Structures of Dinuclear Complexes, \([M_2(L)(H_2O)_2(dmf)_4]\) (M = Co(II), Ni(II); \(H_4L = p\)-tert-Butylsulfonylcalix[4]arene)**

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**Figure 1.** Ortep drawing of \([Co_2L(H_2O)(dmf)]_4\) with thermal ellipsoids at 30% probability. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Co-O(1) 2.0116(12), Co-O(2) 2.1911(13), Co-O(4) 2.0220(12), Co-O(7) 2.0992(16), Co-O(8) 2.1009(13), Co-O(9) 2.1209(13), S(1)-O(2) 1.4625(12), S(1)-O(3) 1.4351(13), S(2)-O(5) 1.4469(14), S(2)-O(6) 1.4487(14), O(1)-Co-O(2) 84.79(5), O(1)-Co-O(4) 101.18(5), O(1)-Co-O(7) 88.38(6), O(1)-Co-O(8) 170.02(5), O(1)-Co-O(9) 87.78(5), O(2)-Co-O(4) 84.23(5), O(2)-Co-O(7) 169.92(6), O(2)-Co-O(8) 97.28(5), O(2)-Co-O(9) 96.32(5), O(4)-Co-O(7) 89.86(6), O(4)-Co-O(8) 88.75(5), O(4)-Co-O(9) 171.03(5), O(7)-Co-O(8) 90.73(6), O(7)-Co-O(9) 90.80(6), O(9)-Co-O(9) 82.29(5).
Structures of the complexes are shown in Figures 1 and 2, respectively. They have very similar structures. Both two complexes crystallized in triclinic, each has crystallographic inversion center at the midpoint of the complex, and a half of each molecule is crystallographically independent. Each complex consists of two metal(II) ions, L\(^\text{2+}\) in the 1,2-alternate conformation, two aqua ligands, and four coordinating dmf molecules. In the complexes, the calix[4]arene coordinates to metal ion in a tridentate facial fashion via two phenoxy oxygen (O1 and O4) and a sulfonyl oxygen (O2). A very few complexes with sulfonyl oxygen–metal bondings are structurally characterized, and cobalt(II) and nickel(II) complexes with such bonds have not been reported thus far. To our knowledge, the present two complexes are the first example where such bond formations were revealed by X-ray crystallography. Hexacoordination of each metal ion in 1 and 2 is completed by additional three oxygen atoms from coordinating water (O7) and dmf molecules (O8 and O9). The shortest M–O bonds are formed with phenoxy oxygen atoms as expected, whereas the longest separations are found in metal-sulfonyl oxygen bonds, and other coordination distances are almost the same. The differences between M–O\(_{\text{sulfonyl}}\) (2.1911(13) Å (1) and 2.1052(2) Å (2)) and M–O\(_{\text{phenox}}\) and M–O\(_{\text{dmf}}\) (2.0992(16)–2.1209(13) Å and 2.054(2)–2.076(2) Å, respectively) are less than 0.1 Å. These results indicate that the sulfonyl oxygens have reasonably strong coordination ability, and \(\text{L}^{2-}\) commonly acts as a bis-tridentate facial ligand via phenoxy and sulfonyl oxygen atoms. Coordination bond formation affects only slightly on the S=O bondings. The ligating S=O groups (1.4625(12) Å (1) and 1.465(2) Å (2)) are slightly elongated upon coordination, whereas other S=O bonds which are not involved in coordination are in the range of 1.4351(13)–1.447(2) Å.

In the complexes reported here, the calixarene ligand takes the 1,2-alternate form and two metal ions occupy anti position to each other. The ligand can take also the cone conformation which makes two metal ions arranged at syn position.