Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Atwood, Jerry L. , Orr, G. William and Robinson, Kerry D.(1994) 'First structural authentication of third-sphere coordination: [p-sulfonatocalix[4]arene]$^{5-}$ as a third-sphere ligand for Eu^3 ', Supramolecular Chemistry, 3: 2, 89 — 91

To link to this Article: DOI: 10.1080/10610279408029846

URL: http://dx.doi.org/10.1080/10610279408029846

SUPRAMOLECULAR CHEMISTRY, Vol. 3, pp. 89–91
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COMMUNICATION

First structural authentication of third-sphere coordination: [p-sulfonatocalix[4]arene]$^{5-}$ as a third-sphere ligand for Eu^{3+}

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(Received September 16, 1993)

The central feature of the complicated structure of $Na[Eu_3$(p-sulfonatocalix[4]arene)$_2(OH_2)_{18}(ONC_5H_5)_3]\cdot14\ H_2O$ is the coordination sphere of one of the three independent europium atoms. Its first coordination sphere consists of seven water molecules, the oxygen atom of a pyridine N-oxide molecule, and a sulfonate oxygen atom from one of the two independent calix[4]arenes. The second-sphere coordination consists of the second calix[4]arene which is bound to the coordinated pyridine N-oxide via hydrophobic interactions, and a second pyridine N-oxide which is hydrogen bonded to a coordinated water molecule. The third-sphere coordination consists of the binding of the second-sphere coordinated pyridine N-oxide to the cavity of the first-sphere coordinated calix[4]arene. $Na[Eu_3$(p-sulfonatocalix[4]arene)$_2(OH_2)_{18}(ONC_5H_5)_3]\cdot14\ H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 20.973(2)$, $b = 18.678(2)$, $c = 29.502(4)$ Å, $\beta = 109.19(1)°$, and $D_c = 1.74\ g\ cm^{-3}$ for $Z = 4$. Refinement based on 10,043 observed reflections led to a final R value of 0.091.

INTRODUCTION

The concept of first- and second-sphere ligands for metal ions dates from the time of Werner. More recently, second-sphere coordination has been defined by Stoddart as the 'non-covalent bonding of chemical entities to the first coordination sphere of a transition metal complex.'[1] Crown ethers[2,3] cyclodextrins,[1,4–14] *and calix[4]arenes*[15–18] *have been used as second*-sphere ligands.[19] Indeed, second-sphere coordination holds promise as an organizational principle upon which larger supramolecular assemblies may be constructed. However, it is clear that the use of weak interactions for the construction of very large supramolecular aggregates with transition metals at the core will require third- and higher-sphere coordination. We report there the use of [p-sulfonatocalix[4]arene]$^{5-}$ as a third-sphere ligand to a Eu^{3+} ion in $Na[Eu_3$(p-sulfonatocalix[4]arene)$_2$ $(OH_2)_{18}(ONC_5H_5)_3]\cdot14\ H_2O$,[20] a complex which also exhibits first- and second-sphere coordination of p-sulfonatocalix[4]arene to the europium center.

The molecule possesses three different Eu^{3+} ions, but it is the environment of Eu2, shown in Fig 1, which is the most interesting.[21] The primary coordination sphere is made up of seven water molecules, the oxygen atom of a pyridine N-oxide molecule, and a sulfonate oxygen atom from one of the two independent calix[4]arenes. The second-sphere coordination consists of the second calix[4]arene which is bound to the coordinated pyridine N-oxide via hydrophobic interactions,[22] and a second pyridine N-oxide which is hydrogen bonded to a coordinated water molecule, W11. The third-sphere coordination consists of the binding of the second-sphere coordinated pyridine N-oxide to the cavity of the first-sphere coordinated calix[4]arene. The trail of coordination is Eu^{3+} to water (electrostatic interaction), water to pyridine N-oxide (hydrogen bonding), and pyridine N-oxide to calix[4]arene (van der Waals forces). Thus one calix[4]arene functions as both a first-sphere and a third-sphere ligand for Eu2, while the second calix[4]arene serves as a second-sphere ligand.

The complicated structure exhibits a bilayer packing arrangement of the calix[4]arenes.[23–25] As can be seen from Fig 2, Eu1 bridges three calixarenes together, two via sulfonate oxygen atoms and the third through a phenolic oxygen atom. The remainder of its coordination sphere is composed of four water

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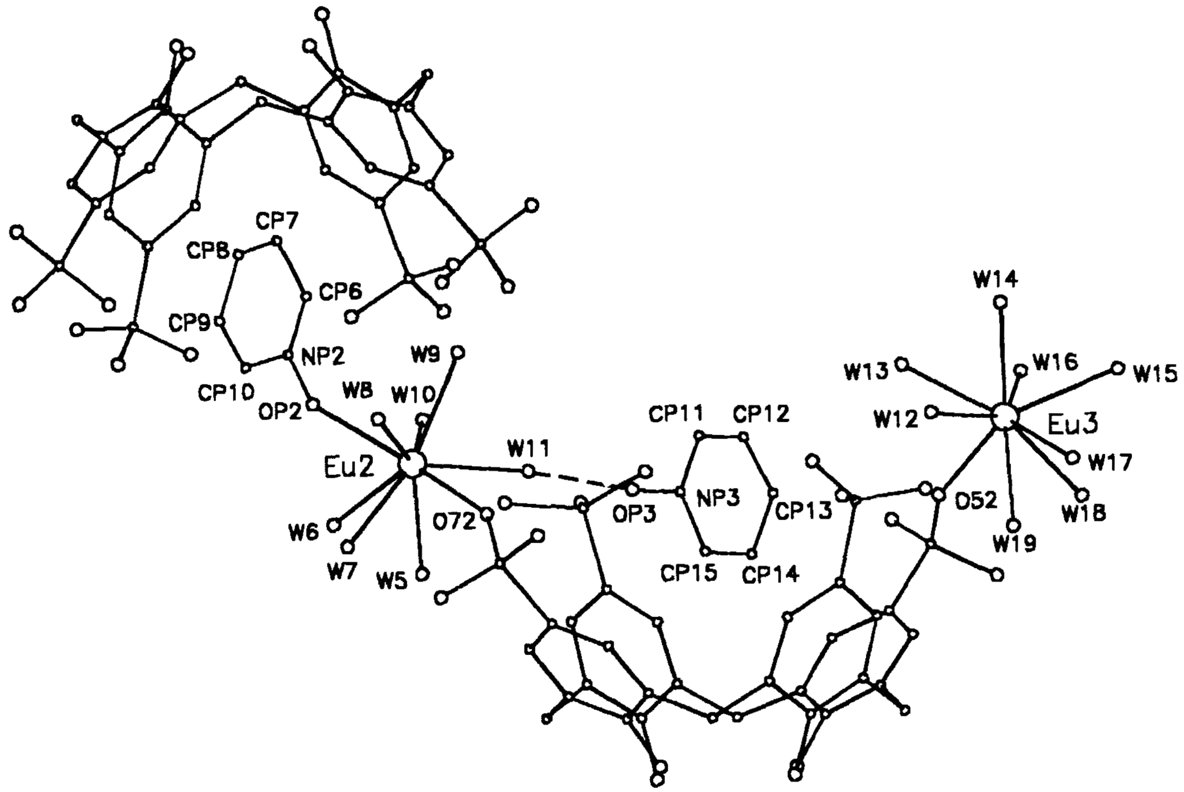

Figure 1 The coordination environment of Eu2 is emphasized. The third-sphere ligand, the calix[4]arene on the right, is bonded to the pyridine N-oxide via van der Waals forces; the pyridine N-oxide (second-sphere ligand) is hydrogen bonded to water molecule W11, and W11 (primary sphere ligand) is bonded to the Eu^{3+} ion.

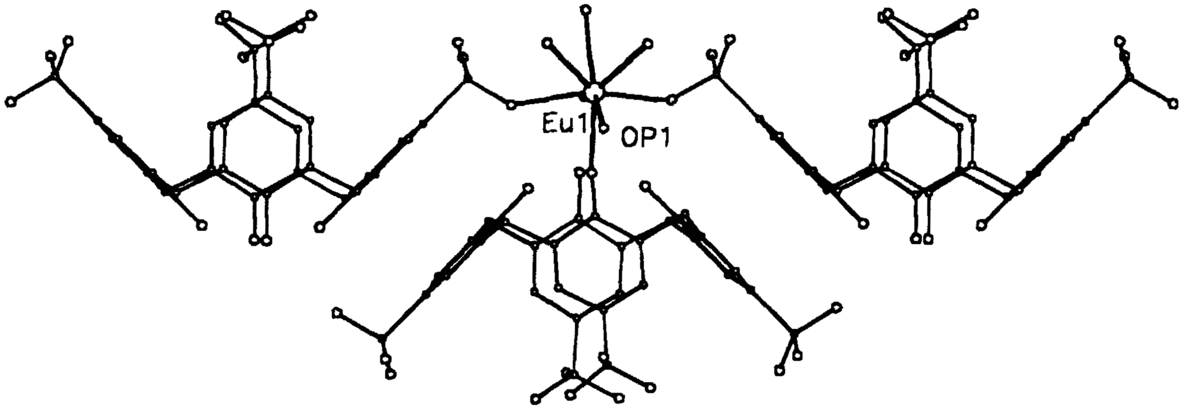

Figure 2 Eu1 bridges three calix[4]arenes together and this unit is a part of the bilayer packing of the calixarenes. Only the oxygen atom of a bonded pyridine N-oxide is shown for clarity.

molecules directed toward the hydrophilic layer and one pyridine N-oxide which is intercalated into the hydrophobic bilayer, Fig 3. The centroids of the two nearest calix[4]arenes are 3.36 and 3.45 Å from the plane of the pyridine N-oxide.

The third crystallographically independent Eu^{3+}, Eu3, is coordinated to eight water molecules and to the sulfonate oxygen atom of one of the calix[4]arenes, Fig 1.

ACKNOWLEDGMENTS

We are grateful to the National Science Foundation for support of this research.

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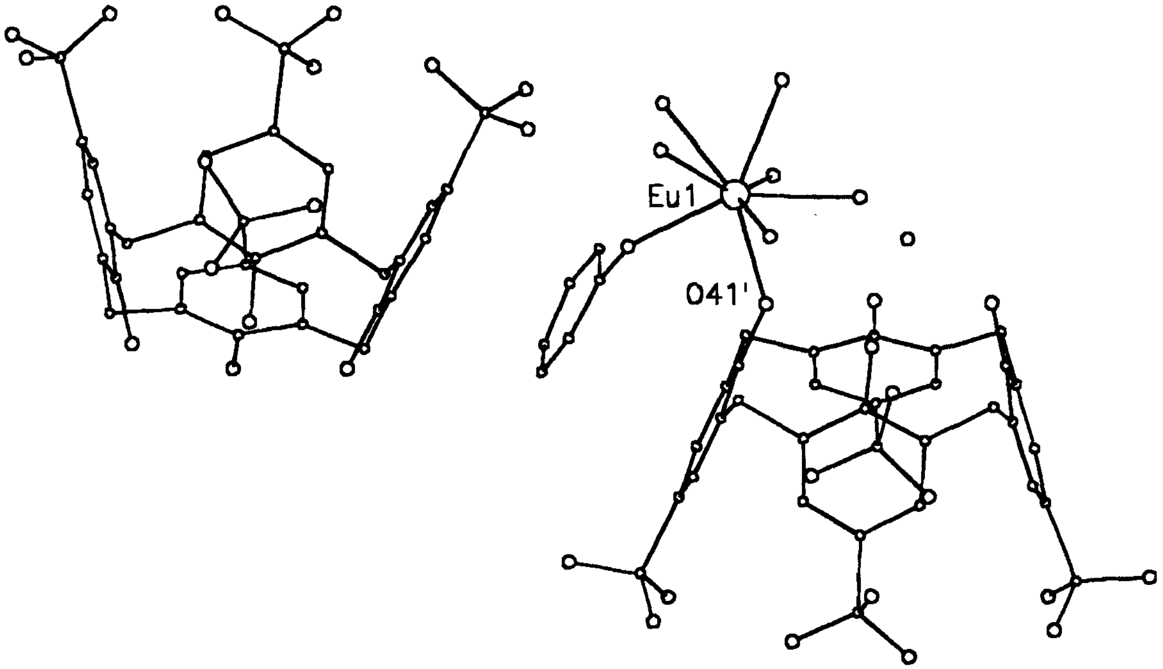

Figure 3 The pyridine N-oxide bound to Eu1 is intercalated into the bilayer packing arrangement. Only the oxygen atoms of two of the coordinated calix[4]arenes are shown for clarity.

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20 In a test tube, 200 mg (0.23 mmol) of Na_5[p-sulfonatocalix[4]arene], 99 mg (0.23 mmol) of $Eu(NO_3)_3 \cdot 6\ H_2O$, and 87 mg (0.92 mmol) of pyridine N-oxide were dissolved in 2.0 mL of distilled water. The resulting solution was transferred to a vacuum desiccator which was placed under a mild vacuum. Slow evaporation over a period of several days produced X-ray diffraction-quality crystals. Observation of these crystals with the aid of a microscope revealed the presence of only rhombohedral plates which were orange-pink in color.

21 $Na[Eu_3$(p-sulfonatocalix[4]arene$)_2(OH_2)_{18}(ONC_5H_5)_3] \cdot 14\ H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with a = 20.973(2), b = 18.678(2), c = 29.502(4) Å, $\beta = 109.19(1)°$, and $D_c = 1.74\ g\,cm^{-3}$ for Z = 4. Refinement based on 10,043 observed reflections led to a final R value of 0.091. Details of data collection, structure solution, and refinement have been previously given: Holton, J.; Lappert, M.F.; Ballard, D.G.H.; Pearce, R.; Atwood, J.L.; Hunter, W.E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

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