A Novel Thiophosphorylated Cavitand and its Complex with Silver Picrate. B. Tinant a, J.-P. Declercq a, B. Bibal b, and J.-P. Dutasta b, aUniversité Catholique de Louvain, Unité CPMC, I Place Pasteur, B-1348 Louvain-la-Neuve, b Ecole Normale Supérieure de Lyon, 46 Allée d’Italie, F-69364 Lyon Cedex 07, France.

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The phosphoryl and thiophosphoryl groups have been introduced into the preorganised structure of the calix-4-resorcinarene. We recently reported the synthesis of the phosphorylated cavitands, their high affinity for cationic species and the X-ray structures of the complexes with Cs⁺ and MeNH₃⁺ [1,2].

The amphiphilic thiophosphoryl derivative 1 was synthesised. The long R chain substituent at the lower rim was introduced in order to increase the lipophily of the ligand. The iii isomer with the four P=S groups pointing inward (i) the molecular cavity was obtained.

The complexing properties of these ligands for Mⁿ⁺ and ammonium cations have been characterized by liquid-liquid extraction experiments: cavitand 1 extracts Ag⁺ in a very selective way.

![Diagram](image)

1. X=S, R=C₁₁H₂₃
2. X=S, R=C₁₁H₂₃, M=Ag⁺

The ligand 1 and its complex with silver picrate 2 were crystallized and their structures refined using data collected with a MAR345 image plate at 100K. In the complex four Ag⁺ cations link two ligands by P=S...Ag...S=P bonds. The geometry of the free ligand and the complex will be discussed in details.