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CIS-TRIOXA-TRIS-σ-HOMOBENZENE AS TRIDENTATE LIGAND

X-RAY CRYSTAL STRUCTURE ANALYSES OF $[Li(C_6H_6O_3)_2PF_6]$ AND $[Ca(C_6H_6O_3)_3H_2O(ClO_4)_2]$

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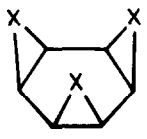
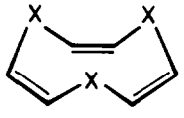
In the title complexes the cis-benzenetrioxide acts as tridentate ligand, allowing for octahedral and unusual tetracapped trigonal prismatic coordination (TECTP).

The propensity of the trishetero-tris-σ-homobenzenes **1 - 3** to complex metal ions was originally studied with analytical/preparative-synthetic purposes. Severe limitations to this end were caused, however, by the instability of most of these complexes in solution [1]. Nevertheless, interest for their crystal structures was raised by the expectation (based on model calculations), that the specific geometrical/electronic properties of the rigid and



X = O(NH,S) : **1** (**2**,**3**)



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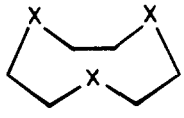

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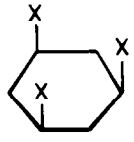

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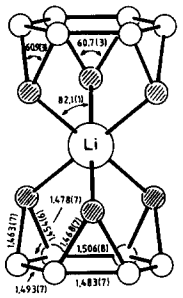
potentially tridentate ligands **1 - 3** - as compared e.g. with the topologically related ligands **4 - 6** [2] - should allow for rather unusual (high) coordination. In the case of trioxide **1** complexes of types $M(L\text{-}L\text{-}L)_2$ (minimal ionic radius R=0.584 Å), $M(L\text{-}L\text{-}L)_3$ (R=1.211 Å) and $M(L\text{-}L\text{-}L)_4$ (R=1.271 Å) were predicted and isolated in great number (1:2 : Li,Na,K,Ru,Cs; 1:3 : Ca; 1:4 : Sr,Ba). For the 1:4 $Ba(ClO_4)_2$-complex a (distorted) icosahedral BaO_{12}-coordination-sphere with four tridentate **1** -ligands has been already elucidated by x-ray diffraction analysis [1,3]. Having collected suitable single crystals the structures of the 1:2/1:3 $Li(PF_6)/Ca(ClO_4)_2$-complexes (**7** / **8**) could also be solved now.

Structure of $[Li(C_6H_6O_3)_2PF_6]$ (**7**) (Fig 1/2): The complex crystallised from acetone-solution in the monoclinic space group C2/m No. 12 (a= 7.9243(7), b= 9.8425(8), c= 9.4235(2)Å,

β= 100.22°, Z= 2, $d_{calc.}$= 1.89, $d_{obs.}$= 1.86 g/cm^3, 1111 reflections in least squares refinement, final R-factor = 0.085). The central lithium ion is six-coordinated with the oxygen atoms of two molecules **1** , which lie at the corners of an octahedron. The Li-O-distances are somewhat shorter than expected (av. 2.102 Å, ionic radius for LiL_6 = 0.76 Å according to Shannon [6]) but longer than those for ideal octahedral geometry. The intra-/inter- **1** O-O-distances are consequently quite different (av. 2.755 vs. 3.144 Å). Compared with the isolated



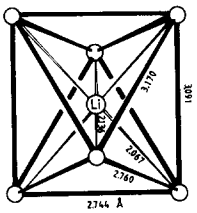
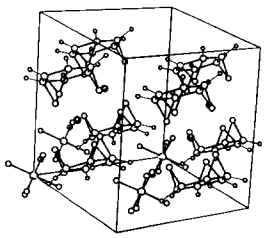


Fig. 1
Structure and LiO_6-coordination-polyhedron of **7**

trioxide (2.823 Å, 106.9°) [7] the intra- **1** O-O-distances in **7** are shorter, the interplanary angles between the epoxide rings and the six-membered ring smaller (av. 103.7°). The relative arrangement of the Li/P-atoms corresponds nicely to the cubic space centered lattice (CsCl type) [8].



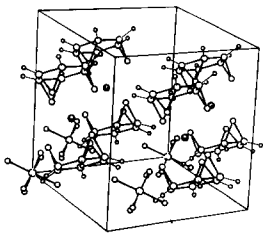


Fig. 2
Stereoview of the packing in the lattice of **7**

Structure of $[Ca(C_6H_6O_3)_3H_2O(ClO_4)_2]$ (**8**) (Fig. 3/4) : After many unsuccessful attempts to recrystallise the microcrystalline material of composition $[Ca(C_6H_6O_3)_3(ClO_4)_2]$ from various solvents single crystals could be obtained from glyme solution (slow evaporation in an air-open system). Elemental analysis and density measurements indicate the incorporation of one equivalent of water (monoclinic space group $P2_1/c$, No. 14; a= 2.1792 (4), b= 1.9040 (5), c= 1.1763 (3) Å; β= 98.50°, Z= 8, $d_{calc.}$= 1.75, $d_{obs.}$= 1.77 g/cm^3, 5320 reflections in least squares refinement, final R-factor = 0.072). The asymmetric unit consists of two molecules (the structure has pseudo-symmetry [9]), the central calcium ions are ten-coordinated by the nine oxygen atoms of three ligands **1** and the O-atom of water. The Ca-O(epoxide) distances [10] in the two molecules range from 2.444 to 2.480 Å, the Ca-O(water) distances from 2.399 to

2.423 Å, the O-O-edges from 2.682 to 3.860 Å. The CaO_{10}-polyhedron is unusual; it is best fitted with the geometry of a tetracapped trigonal prism (TECTP; C_{3v}) [11,12]. This hexadecahedron consists of 10 corners, 24 edges and 16 triangles. The approximated threefold-axis

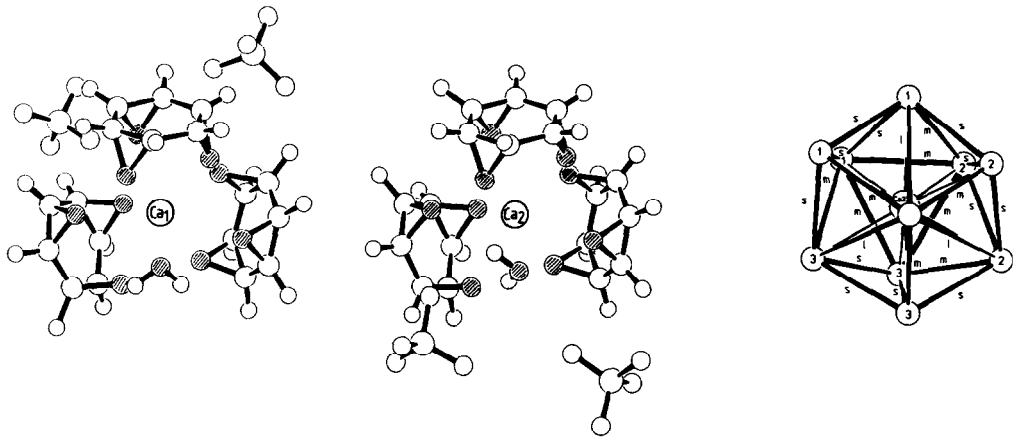


Fig. 3 Structures and CaO_{10}-coordination polyhedron of **8**

lies in the direction of the Ca-O(water) bond. The average intra- **1** O-O-distance (2.735 Å) is similar to that in **7** . In accord with the geometry of the C_{3v}-polyhedron the peripheral inter-**1** O-O-distances are similarly short (av. 2.746 Å (s)), all others being more or less released (by 0.1 - 0.2 Å (m), 0.9 Å (l)). Remarkably [13], in the molecule 2 the water-hydrogen-atoms are placed within the coordination sphere (Ca-H : 2.213/2.313 Å). That the Ca-complex accommodates an additional H_2O-ligand is unterstood in view of the small difference in the minimal ionic radius for nine- and ten- coordination (1.211 vs. 1.217 Å) [1]; according to

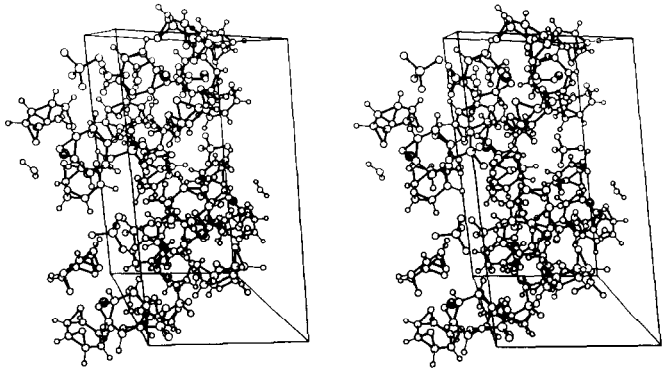


Fig. 4
Stereoview of the packing in the lattice of **8**

Shannon [6] 1.18 (1.23) Å for nine(ten)-coordinated Ca, 1.44 (1.61) Å for twelve-coordinated Sr (Ba).

The x-ray crystal structure analyses for the $Li(L\text{-}L\text{-}L)_2$-, $Ca(L\text{-}L\text{-}L)_3L$- and Sr/Ba $(L\text{-}L\text{-}L)_4$-

complexes confirm the expectation, that with the cis-trioxide **1** as uncharged rigid, organic ligand unusually high coordinations become possible. In the recently solved structure of $[La(C_6H_9N_3)_4CH_3CN(ClO_4)_3]$ with four tridentate trisimine (**2**) ligands the LaN_{12}-icosahedron closely resembles the SrO_{12}-sphere [3, 14].

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