

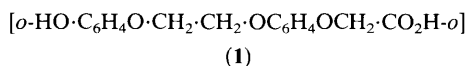
X-Ray Analysis of the [1-(*o*-carboxymethoxyphenoxy)-2-(*o*-hydroxyphenoxy)ethanato-sodium] Tetramer, a Sodium–Oxygen Cubane Structure

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The crystal structure of the title compound shows a tetrameric association, with alternating sodium and oxygen atoms at the corners of a cube, pentagonal bipyramidal co-ordination round each sodium, and each ligand in the tetramer co-ordinating to all four sodium ions; the hydroxy acid polyether ligands, L, are arranged in hydrogen-bonded dimer pairs, as found in other L complexes.

[1-(*o*-Carboxymethoxyphenoxy)-2-(*o*-hydroxyphenoxy)ethane], HL (**1**),¹ when co-ordinated to cobalt(II) has shown remarkable selectivity for potassium ions.^{2–4} The acid salt, KHL₂, has been synthesised and characterised by X-ray crystallography, and is postulated⁴ as the possible intermediate for the cobalt complex Co(KL₂)₂.² The corresponding cobalt–sodium complex or the sodium acid salt has not been isolated, and so the structure of NaL was undertaken as the only available sodium ion comparison.



HL (0.756 g) dissolved in hot ethanol (25 ml) was treated with sodium hydroxide (0.1 g) in hot ethanol (15 ml); concentration and cooling to room temperature produced small colourless crystals (0.7 g), m.p. 252–255 °C; satisfactory elemental analyses were obtained.

Crystal data—Na₄(C₁₆H₁₅O₆)₄·C₂H₅OH, *i.e.* C₆₆H₆₆Na₄O₂₅, *M* = 1351.2, monoclinic, *a* = 19.908(4), *b* = 15.728(2), *c* = 21.869(4) Å, β = 111.92(2)°, *U* = 6352 Å³, space group C2/c (No. 15), *Z* = 4, *D*_c = 1.413 g cm⁻³, μ(Mo-*K*_α) = 1.2 cm⁻¹, λ(Mo-*K*_α) = 0.71069 Å. Crystal size 0.14 × 0.10 × 0.05 mm.

The crystals do not diffract well. Intensities were measured twice, slowly, by diffractometer, for 2952 independent reflections in the θ range 1.5–20°. Measurements were corrected for Lorentz–polarisation effects, merged, and corrected by Bayesian statistics (to remove negative intensities).⁵

The structure was eventually solved by MULTAN,⁶ and refined by full-matrix least-squares methods (in SHELX)⁷ to convergence with *R* 0.209 and *R'* 0.128 for all reflections. A structure factor calculation for the 728 'observed' reflections

with *I* > 2σ(*I*) gives *R* 0.057 and *R'* 0.042, confirming that the high *R* factor from refinement results from weak diffraction data, not from any gross error in the model.†

In addition to the NaL units, a molecule of ethanol solvate was located, statistically disordered in one of two sites close to an inversion centre; the solvate molecule is hydrogen-bonded to the carbonyl O-atom of one of the L ligands.

The X-ray crystal structure shows alternating oxygen and sodium atoms at the corners of a fairly regular cube which is at the centre of an Na₄L₄ tetramer. The O–Na–O angles fall in a narrow range (83.2–86.5°) just less than 90°, and the Na–O–Na angles (93.8–96.1°) are correspondingly just greater than 90°. In the cube, there are two crystallographically independent sodium ions which have similar pentagonal bipyramidal co-ordination spheres (Figure 1). Each sodium ion is co-ordinated by oxygen atoms from all four L ligands within the tetramer. The carboxylate oxygen atoms from each of the four L ligands form the oxygen corners of the cube. Each sodium ion is therefore co-ordinated by the carboxylate oxygens of three ligands, and also by three ether oxygens from one of these ligands. The seventh co-ordination position involves the phenolic oxygen of the fourth L ligand. For each sodium ion, one equatorial Na–O distance is significantly longer [Na(1)–O(8) 2.85(1) Å, and, correspondingly, Na(2)–O(38) 2.70(1) Å] than the others [2.32(1)–2.51(1) Å].

The L ligands are further held in position in cyclic dimer

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

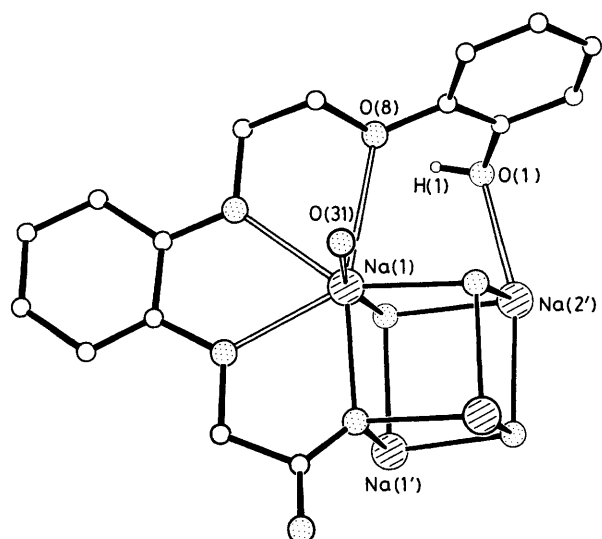


Figure 1. One L ligand and its co-ordination to the sodium–oxygen cube. O(31) is the phenolic oxygen atom of the second, independent ligand. (') denotes relation by a two-fold symmetry axis (approximately horizontal in the plane of the paper).

pairs by hydrogen bonding between the phenolic OH of one ligand and the carbonyl oxygen of the other; this is the arrangement already described for the ligands in $\text{Co}(\text{KL}_2)_2$,² $\text{Co}(\text{RbL}_2)_2$,³ and KHL_2 .⁴ The ligands in each dimer pair are related by a two-fold symmetry axis, and the two dimer pairs (related by pseudo $\bar{4}$ symmetry), together with the four Na ions, form the discrete molecular tetramer.

The conformations of the two independent ligands are very similar, but quite different from those in which potassium or rubidium is co-ordinated: there, five O atoms of each ligand are held in an almost planar arrangement, and the rest of the molecule is restrained towards coplanarity. The sodium ion is too small to co-ordinate in this way, and in making alternative interactions, the ligand adopts a buckled conformation (so that the dimer pair folds back on itself and has a saddle shape), whilst maintaining the strong hydrogen bonds within the dimer unit (Figure 2).

The distortions of the angles from 90° in the cubane structure are as expected for the required short Na–O distances [2.32(1)–2.42(1) Å] and the normal bridged Na ··· Na contacts [3.446(6)–3.570(9) Å]. Although a very distorted sodium–hydrogen cubane structure has been reported,⁸ to our knowledge the present structure is the first sodium–oxygen cube. Similar discrete molecular units have been found in the structure of sodium t-butoxide,⁹ where the

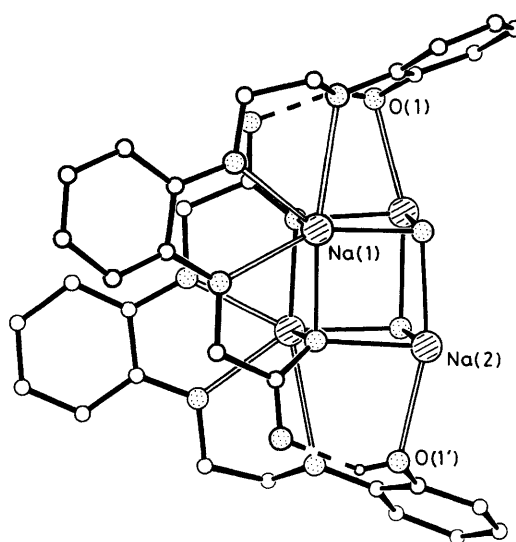


Figure 2. The sodium–oxygen cube and two L ligands, related by two-fold symmetry, showing the saddle shape of the hydrogen-bonded dimer unit.

units are hexamers and nonamers. In the present structure, since each sodium ion is co-ordinated by oxygens from all four ligands, and each ligand co-ordinates all four sodium ions, a tight, co-ordinatively saturated tetramer is generated with a compact lipophilic exterior able to exclude external donation. These factors help to explain the presence of the cubane tetramer, rather than the infinite chain structures often found in sodium salts.

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