

3.146 Å). Eightfold coordination is completed by two nitrogen atoms (ordered thiocyanate anions) at 3.30 and 3.32 Å.

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References

- DALE, J. & KRISTIANSEN, P. O. (1972). *Acta Chem. Scand.* **26**, 1471–1478.
 DOBLER, M. & PHIZACKERLEY, R. P. (1974). *Acta Cryst.* **B30**, 2746–2748.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Acta Cryst. (1974). **B30**, 2750

Calcium Thiocyanate Complex of 1,4,7,10,13,16-Hexaoxacyclooctadecane

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Abstract. $C_{12}H_{24}O_6 \cdot Ca(NCS)_2$, monoclinic, $C2/c$, $a = 13.34$, $b = 10.69$, $c = 15.39$ Å, $\beta = 106.2^\circ$, $U = 2108$ Å³, $Z = 4$. Crystallized from chloroform/hexane. The structure is disordered.

Introduction. Intensity measurements (1700 reflexions) were carried out as for the sodium complex (Dobler, Dunitz & Seiler, 1974).^{*} The structure was solved by direct methods. The first E maps showed the calcium atoms (at symmetry centres) and linear thiocyanate groups, and subsequent F_o syntheses showed that the electron density in the mean plane of the hexaether was incompatible with a single orientation. The distribution of peaks was roughly similar to that found in the disordered potassium toluene-*p*-sulphonate complex (Groth, 1971).

Discussion. Each Ca^{2+} ion is surrounded by a nearly planar hexagon of oxygen atoms in at least two orientations related by rotation in the mean plane.

^{*} A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30561 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The $Ca^{+} \cdots O$ distances are 2.56–2.74 Å. Hexagonal bipyramidal coordination is completed by the nitrogen atoms of the thiocyanate anions ($Ca^{+} \cdots N$ 2.35 Å) which point approximately along the virtual threefold axis of the hexagon. Pairs of anions, belonging to different calcium ions, are related by the screw axes. The structure is fairly open.

A second crystal modification containing solvent of crystallization is obtained by cooling an aqueous acetone solution: monoclinic, $P2_1/c$, $a = 7.74$, $b = 14.09$, $c = 21.27$ Å, $\beta = 98.9^\circ$, $U = 2292$ Å³. The unit-cell volume points to a dihydrate, $C_{12}H_{24}O_6 \cdot Ca(NCS)_2 \cdot 2H_2O$ ($Z = 4$). These crystals disintegrate rapidly under X-radiation, even when enclosed in capillaries with mother liquor. They were not studied further.

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References

- DOBLER, M., DUNITZ, J. D. & SEILER, P. (1974). *Acta Cryst.* **B30**, 2741–2743.
 GROTH, P. (1971). *Acta Chem. Scand.* **25**, 3189–3191.