Crystal and Molecular Structure of a Trimeric Cobalt(II) Complex: Trisdimethoxyethane-tri-μ-trifluoroacetato-μ_3-chloro-μ_3-sulphato-tricobalt(II)

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Summary The crystal structure of a new polynuclear cobalt(II) complex with three different anions acting as bridging groups is reported.

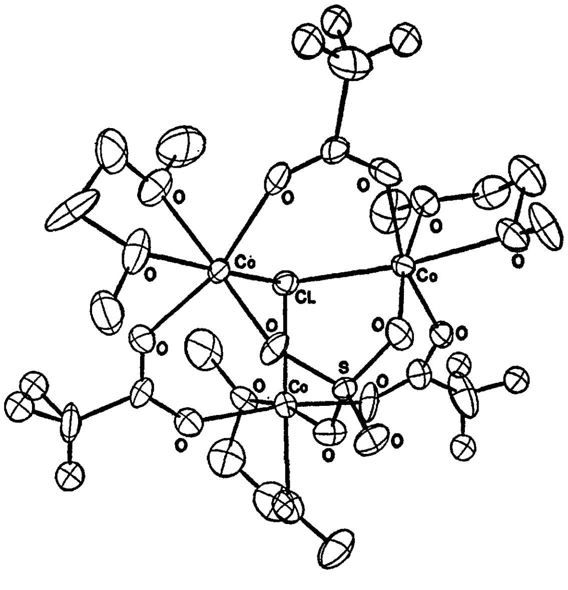
In the course of an investigation by X-ray methods of the structures of the trifluoroacetates of nickel and cobalt halides,[1] various synthetic conditions were tried in order to obtain suitable crystals. Although such crystals have not been acquired, a new cobalt complex was isolated and its structure is reported here.

Addition, under nitrogen, of thionyl chloride to a ten fold excess of cobalt trifluoroacetate in purified dimethoxyethane (dme) yields red crystals, $(CF_3CO_2)_3Co_3ClSO_4(dme)_3$ (I).

(I) crystallizes in the triclinic system with one trimeric molecule in a unit cell of dimensions: $a = 9{\cdot}656(2)$, $b = 9{\cdot}653(2)$, $c = 12{\cdot}925(4)$ Å, $\alpha = 132{\cdot}03(3)$, $\beta = 90{\cdot}02(3)$, $\gamma = 95{\cdot}92(3)$°, $U = 886$ Å^3, $D_c = 1{\cdot}70$ g cm^{-3}, space group P_1.

3957 independent non-zero reflections were recorded on a four-circle automatic diffractometer, using Mo-K_α radiation. The structure was solved by the heavy-atom method and a full-matrix least-squares refinement[2] led to the discrepancy factors $R_1 = 0{\cdot}064$, $R_2 = 0{\cdot}073$.

Crystals of (I) contain discrete molecules composed of trinuclear units of cobalt(II) atoms (Figure).[3] The approx-



Figure

imate molecular symmetry is C_{3v}. The three cobalt atoms are located at the corners of an equilateral triangle of side 3·786(2) Å. These atoms are held together by three bridging systems: (i) The chlorine atom located at 2·48(1) from the three cobalt atoms and at 1·15 Å from the plane passing through these atoms. (ii) The sulphate group, located on the other side of the metal plane, acting as a tripod bridge, bonded to the three metals by three of its oxygen atoms. The mean value of the three sulphate oxygen-cobalt distances is 2·00(1) Å. (iii) The three trifluoroacetate groups acting as bidendate cobalt–cobalt bridging groups. The carboxylic group of these anions are located approximately in the plane of the metal atoms. The mean value of the distances between the trifluoroacetate oxygen atoms and the metal atoms is 2·05(1) Å.

The co-ordination polyhedron (distorted octahedron) is completed by the oxygen atoms of a dme molecule acting as a bidendate chelating group. The mean value of the Co–O–(dme) distances is 2·14(1) Å.

An analogous tripod arrangement of the sulphate ligand with three metal atoms has recently been found in a trinuclear copper complex.[4]

(I) is paramagnetic; the effective magnetic moment is 4·68 B.M. The susceptibility, investigated in the range 160—360 K, follows a Curie–Weiss law.

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[1] F. X. de Charentenay, G. Codet, and J. Otton, unpublished results.

[2] C. T. Prewitt, SFLS-5, ORNL-TM 305, 1966.

[3] C. K. Johnson, Program ORTEP, ORNL-TM, 1965, 3794.

[4] R. Belkett and B. F. Moskins, *J.C.S. Dalton*, 1972, 291.