X-Ray Crystal Structure of Bis[(propylthio)acetato]cobalt(II) Hexamer

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Summary Bis[(propylthio)acetato]cobalt(II) hexamer has been found, by *X*-ray crystal structure analysis, to have a structure in which the six cobalt(II) atoms form a ring in a boat configuration which is bridged by the ligands which bond in two different ways; there is no metal–metal interaction.

BIS[(PROPYLTHIO)ACETATO]COBALT(II) DIHYDRATE, a pink complex, has been obtained by the direct reaction of the free ligand with a cobalt(II) salt in weakly alkaline aqueous solution. The amorphous anhydrous salt was obtained by repeated drying with benzene in a rotary evaporator at 80 °C.[1,2] It is readily soluble in organic solvents. When a solution in *p*-xylene was kept under a light petroleum atmosphere at ambient temperature for several days, deep red crystals separated out. These crystals were air stable at room temperature for several weeks, while crystals obtained from benzene solution in the same way soon lost their solvent molecules and effloresced. Its magnetic moment in the solid state is $4{\cdot}9_5$ B.M. at 30 °C (calculated as the monomer complex). The absorption maxima in its solid-state reflection spectra appeared at 465, 499, 519, and 563 nm, while the absorption maxima in benzene solution were at 465 nm (logϵ 1·3), 499 (1·3), 518 (1·2), and 564 (1·4), respectively. These facts suggest that the cobalt(II) atoms in the crystal are in a slightly deformed octahedral environment.[3]

The (alkylthio)acetato ligand can act, at most, as a bidentate ligand in a monomer chelate, and a kind of the polymeric structure would be expected in the anhydrate. Therefore we have carried out an *X*-ray crystal structure analysis.‡

Crystal data: $[\mathrm{Co(Pr^n{\cdot}S{\cdot}CH_2{\cdot}CO_2)_2}]_6{\cdot}\mathrm{C_8H_{10}}$, M^+ 2058·0, triclinic, space group: $P\bar{1}$, a = 14·19(2), b = 14·35(2), c = 13·94(2) Å, α = 102·2(3), β = 105·3(2), γ = 62·0(1)°,

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‡ Satisfactory analytical data were obtained for this compound.

$U = 2404{\cdot}6$ Å^3, $D_c = 1{\cdot}420$, $D_m = 1{\cdot}418$ g cm^{-3}, $Z = 1$, $\mu = 13{\cdot}8$ cm^{-1} (Mo-K_α).

Intensity data were collected by the θ—2θ scan technique ($2\theta < 50°$) on a Philips PW 1100 automated four-circle diffractometer using Mo-K_α radiation (0·7107 Å). The crystal used was a parallelepiped (0·3 × 0·3 × 0·3 mm), and was coated with quick-drying adhesive to prevent the loss of xylene from the crystal. 3624 independent [$I > 3\sigma(I)$] reflections were used for the calculation. The positions of the cobalt and sulphur atoms were deduced from a three-dimensional Patterson map, and the remaining non-hydrogen atoms and their thermal parameters were refined, at first by repeated block-diagonal least squares, and then by a full-matrix procedure. Using anisotropic thermal parameters, the convergence reached $R = 0{\cdot}049$. The central part of the complex was clearly ascertained, and the positions of eight hydrogen atoms, in addition to all non-hydrogen atoms, were determined. However, owing to the large amplitude of the thermal vibrations, some of the non-co-ordinated sulphur atoms, and the carbon atoms at the end of the propyl group of the ligand, as well as those of xylene, show small deviations in their inter-atomic distances and in their bond angles from their normally expected values. The positions of the two non-co-ordinated sulphur atoms, as well as those of two carbon atoms at the end of the propyl groups were divided into two. The probability of occupancy of each position was 83·3 and 16·7% for S(4), 69·0 and 31·0% for S(6), and 63·7 and 36·3% for both C(24) and C(25).§

A perspective view of the centrosymmetric complex is shown in Figure 1. For simplicity, only the predominant position is given for the atoms of mixed occupancy. As the average Co–Co distance is 3·53 Å, and ∠Co–Co–Co is 99·4°, the thick lines between the cobalt atoms in Figure 1 do not represent bonds; they merely show the relative positions clearly. The ligands in the complex co-ordinate in one of two ways (Figure 2). Firstly there are those which form a bridge between two adjacent cobalt atoms by co-ordinating to each of them through an oxygen atom of a carboxy group. The other ones co-ordinate to three cobalt atoms in the following way. The sulphido sulphur atom co-ordinates to Co(n), one of the carboxy oxygen atom bonds to both Co(n) and Co($n + 1$) while the other oxygen atom of the same carboxy group bonds with Co($n + 2$). Thus, one cobalt atom bonds with one sulphur and five oxygen atoms. The Co–O and Co–S bond lengths are in the range 2·02—2·56 Å, and the S–Co–O and O–Co–O bond angles in the range 78·5—99·7°. Therefore, the configuration around cobalt is distorted octahedral. The centre of the p-xylene molecule coincides with the centre of symmetry of the unit cell. No bonding between the xylene and any atoms of the complex occurs.

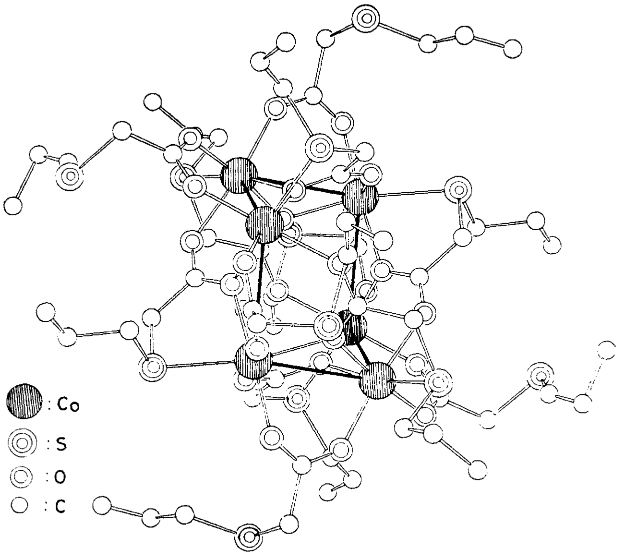

FIGURE 1. Perspective view of the hexamer.

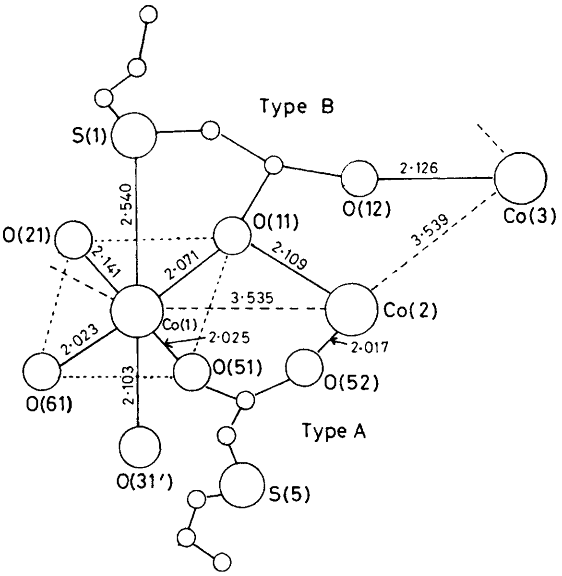

FIGURE 2. Arrangement of atoms around Co$^{\text{I}}$ showing both types of co-ordination.

Until now, no cluster of this type has been reported with (alkylthio)acetato complexes; the only example of this type of compound observed is bis(phenoxyacetato)-copper(II) hexamer.[4]

The average molecular weight of the solute in benzene of these crystals, from the freezing point depression method, was 910 ± 90; about a half of its molecular weight. This fact seems to show that, although xylene is liberated, the compound itself does not dissociate easily even in benzene.

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§ 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 the communication. The structure factor table and tables of interatomic distances and angles (including non bonded contacts) are available as Supplementary Publication No SUP. 22716 (21 pp) from the British Library. For details of obtaining this material, see Notice to Authors No. 7, *J.C.S. Dalton* or *Perkin I* or *II*, Index Issues.

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