Crystal Structure of $[HFeCo_3(CO)_9\{P(OMe)_3\}_3]$

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Summary The crystal structure of the title compound has been determined at −139 °C including location of the hydrogen atom triply bridging the three cobalt atoms and in a position 0·75 Å out of the plane of the three atoms on the side away from the iron atom.

The question of the placement of the hydrogen atom in the tetranuclear complex $[HFeCo_3(CO)_{12}]$[1] (**1**) has been the subject of a number of studies leading to the suggestion that it is located in the centre of the metal atom cage.[2,3] A recent publication[4] on the synthesis of various phosphine and phosphite derivatives of the complex (**1**) prompted us to report our own observations.

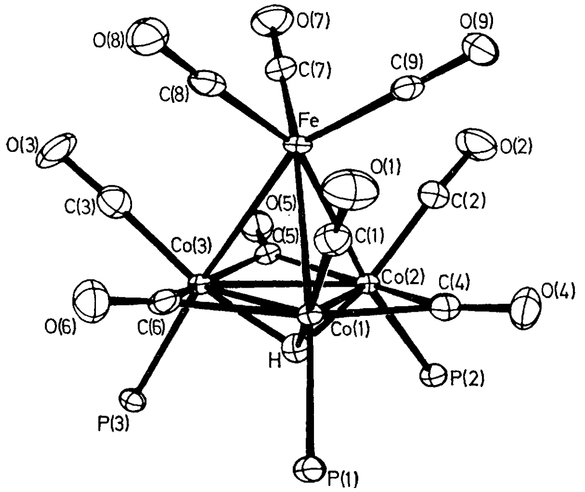

FIGURE. Molecular structure of $[HFeCo_3(CO)_9\{P(OMe)_3\}_3]$ (OMe groups removed for clarity). Some important molecular parameters averaged assuming C_{3v} symmetry are: Fe–Co, 2·560 ± 0·002; Co–Co 2·488 ± 0·012; Co–P, 2·173 ± 0·002; Co–H, 1·63 ± 0·15; ∠ Co–H–Co, 100 ± 6; Fe–Co–H, 84 ± 3°. Estimated standard deviations are calculated using the formula $[\Sigma_{i=1}^{n}(X_i^2 - \bar{X}^2)/(n-1)]^{\frac{1}{2}}$, where X_i and $\bar{X}$ are values and mean values, respectively.

Treatment of the complex (**1**) with $P(OMe)_3$, in the ratio 1:3·6 (mmol/200 ml solvent), in refluxing hexane afforded a mixture of the substituted derivatives $[HFeCo_3(CO)_{12-x}\{P(OMe)_3\}_x]$, x = 1—4, which were separated by column chromatography [silica; C_6H_{14}, followed by CH_2Cl_2–C_6H_{14} (4:1)] to give the title compound (69%) which was recrystallised from hexane. Satisfactory mass spectral data, and C and H analyses were obtained for all the derivatives.

Crystal data: $C_{18}H_{25}Co_3FeO_{18}P_3$, *M* 858, monoclinic space group $P2_1/c$; cell dimensions (at 25 °C), a = 16·336(3), b = 10·896(2), c = 18·583(2) Å; β = 97·259(12)°; Z = 4; U = 3281(1) Å,[3] D_m (by flotation in $C_2H_4Br_2$–CCl_4) = 1·72-(1) g cm^{-3}, D_c = 1·737 g cm^{-3}.

Mo-K_α data were collected at −139 °C† in order to minimize thermal motion and were corrected for the effects of absorption. The structure was solved by direct methods, and all atoms other than hydrogen on the metal cluster, but including hydrogen atoms refined as part of rigid Me groups on the $P(OMe)_3$ ligands were located by standard Fourier techniques. At this point, molecular bond lengths and angles show nearly perfect C_{3v} symmetry, a condition not imposed by space-group symmetry. This observation requires the hydrogen atom on the metal cluster to lie on the three-fold axis of the molecule, as was earlier proposed for $[HFeCo_3(CO)_{12}]$ based on its C_{3v} symmetry deduced from spectroscopic studies.[2,3]

A difference map calculated at this stage shows many peaks in the range 1·5—2·0 e/Å^3 all within 1·2 Å of a metal atom except for one which is located within 0·2 Å of the three-fold axis off the tri-cobalt face away from the iron atom. The method of La Placa and Ibers[5] was then applied using only low-angle reflections to locate and refine the hydrogen atom on the metal cluster. A difference Fourier map based on reflections $\sin\theta/\lambda \leqslant 0·33$ Å^{-1} (834 in number) reveals six maxima > 0·5 e/Å^3. The highest of these at 0·83 e/Å^3 lies near the three-fold axis corresponding to the aforementioned peak triply bridging the tri-cobalt face. No other peak was observed along or near the three-fold axis either within the metal atom cluster or outside it near the iron atom. The other five peaks in the intensity range 0·5—0·7 e/Å^3 all lie within 1·1 Å of a metal atom and within 1·4 Å of a ligand atom attached to that metal and could not reasonably represent a hydrogen atom. The 0·83 e/Å^3 peak was refined using the low-angle data set; a Hamilton[6] significance test of R factors with and without this peak indicates a significance level (with this peak as hydrogen) > 99·5%, for both the small and the complete data sets.

The final R factor is 0·061 for 6057 observed reflections. The structure and some relevant distances and angles are given in the Figure. Around the basal Co_3 plane, we may define three of the non-bridging ligands as *axial* and three as *equatorial*. A phosphite ligand is thus on each of the three cobalt atoms, each in an *axial* position. In contrast, in the structure of $[Ir_4(CO)_9(PPh_3)_3]$,[7] two of the phosphorus ligands are *equatorial* while the third is *axial*. The hydride in the title compound is located bridging the Co_3 face [Co–H distances are 1·46(11), 1·68(11), and 1·74(11) Å, average 1·63 ± 0·15 Å], 0·75 Å out of the Co_3 plane in the direction away from the iron atom. This supports recent spectroscopic analysis in which considerable negative charge on the iron atom is deduced from extremely low stretching force constants calculated for the carbonyl groups on that atom.[8] No information is available yet on the n.m.r. spectrum of the hydrogen atom on the cluster despite satisfactory solubility of the derivatives isolated, owing to quadrupole broadening by the three cobalt nuclei and effort is being made to overcome this obstacle.

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† Cell dimensions at −139 °C: a = 15·992(6), b = 10·638(3), c = 18·403(4) Å; β = 98·515(25)°; Z = 4, U = 3093(3) Å^3.

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