Crystal Structure Determination of $Rh_6(CO)_{14}(dppm)$ using Intensity Data from Synchrotron Radiation Laue Diffraction Photographs

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Laue diffraction patterns, using the full white beam from a synchrotron source, can be recorded on film with exposure times of 1 s or less; a comparatively small number of photographs taken with the crystal in different orientations can record a large proportion of the unique reflections, allowing a crystal structure to be determined fully from a set of films recorded within a period of 1—10 minutes.

The synchrotron radiation source (SRS) at Daresbury laboratory provides a very intense (10^{14} photons s^{-1} mm^{-2}) beam of *X*-rays, with a continuous range of wavelengths from 0.25 to >2 Å.[1] Laue diffraction patterns such as that shown in Figure 1 have been recorded using components of an Arndt–Wonacott camera,[2] the essentials being a collimator (0.2 mm used here), a spindle with goniometer head, and a film cassette, in this case a flat cassette 6 cm behind the crystal and beamstop. Packs of at least six films, interleaved with metal foils or additional films, are used to cover the full range of intensities.

As a pilot project we studied a crystal of $Rh_6(CO)_{14}$ (dppm) (dppm = $Ph_2PCH_2PPh_2$) synthesized in this laboratory.[3] The unit cell and space group were established from previous oscillation and Weissenberg photographs (Cu-K_α) and diffractometer measurements (Mo-K_α). Nine film packs were recorded, at 20° intervals around the spindle, for a crystal of dimensions 0.3 × 0.3 × 0.3 mm in an arbitrary orientation.[†] The films were densitometered on a 50 × 50 μm raster and the digitised images retained on magnetic tape.

Software has been developed at Daresbury Laboratory to convert these digitised film images into reflection intensities.[4,5] The crystal orientation is found using a program LGEN; the orientation and unit cell parameters are refined (GENLAUE) for each film until the predicted and observed spot positions are in agreement (root-mean-square difference 0.05—0.075 mm on the film). The minimum and maximum wavelengths contributing to the pattern and the effective d_{min} ($\lambda/2 \sin \theta_{max}$) for the crystal must also be judged by comparison of the observed and simulated patterns. Integration of film density in an appropriately chosen box around each predicted spot position is followed by film pack scaling and merging (using empirical wavelength dependent interfilm scale factors) and Lorentz–polarisation correction. Finally, a wavelength normalisation curve must be established and applied, and the film packs scaled together and merged. This wavelength normalisation procedure, probably the most critical stage in the derivation of intensities, is necessary because different reflections have been measured at different wavelengths for which incident intensity, sample absorption, and film response are different.

In this study each film pack yielded 2000—2400 reflections in the wavelength range 0.25—2 Å, with merging *R* factors, indicating agreement between intensity measurements on successive films in the pack, of 0.09—0.13. Normalisation, scaling, and merging of the intensity measurements for wavelengths between 0.54 and 0.91 Å gave 3958 unique reflections with a merging *R* value of 0.12; attempts to use the measurements over the whole wavelength range have so far not given a merging *R* value better than 0.16 [$R_{merg} = \Sigma_i(I_i - I_m)/\Sigma_i I_m$ where I_i are wavelength normalised intensities and I_m is the mean of two or more measurements of the same or symmetry equivalent reflections]. The structure was solved using SHELX86[6] to find the Rh_6 octahedron (giving, at this stage, $R = 0.24$ for 1467 selected stronger reflections); SHELX76[7] was used to find the remaining non-hydrogen atoms and to refine all the atom parameters (Rh vibrations anisotropic, others isotropic, carbonyl and phenyl group dimensions fixed). At present $R = 0.16$ for 2800 reflections with $F > 6\sigma(F)$. We attribute the high *R* factor to errors in F_{obs}, and anticipate that improvements in the processing

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[†] *Crystal data:* $C_{39}H_{22}O_{14}P_2Rh_6$, $M = 1393.4$, monoclinic, $a = 16.643(15)$, $b = 19.018(20)$, $c = 13.821(11)$ Å, $\beta = 87.382(16)°$, $U = 4370$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 2.117$ g cm^{-3}, $\mu = 11.1$ ($\lambda = 0.55$ Å) to 45.0 cm^{-1} ($\lambda = 0.90$ Å). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

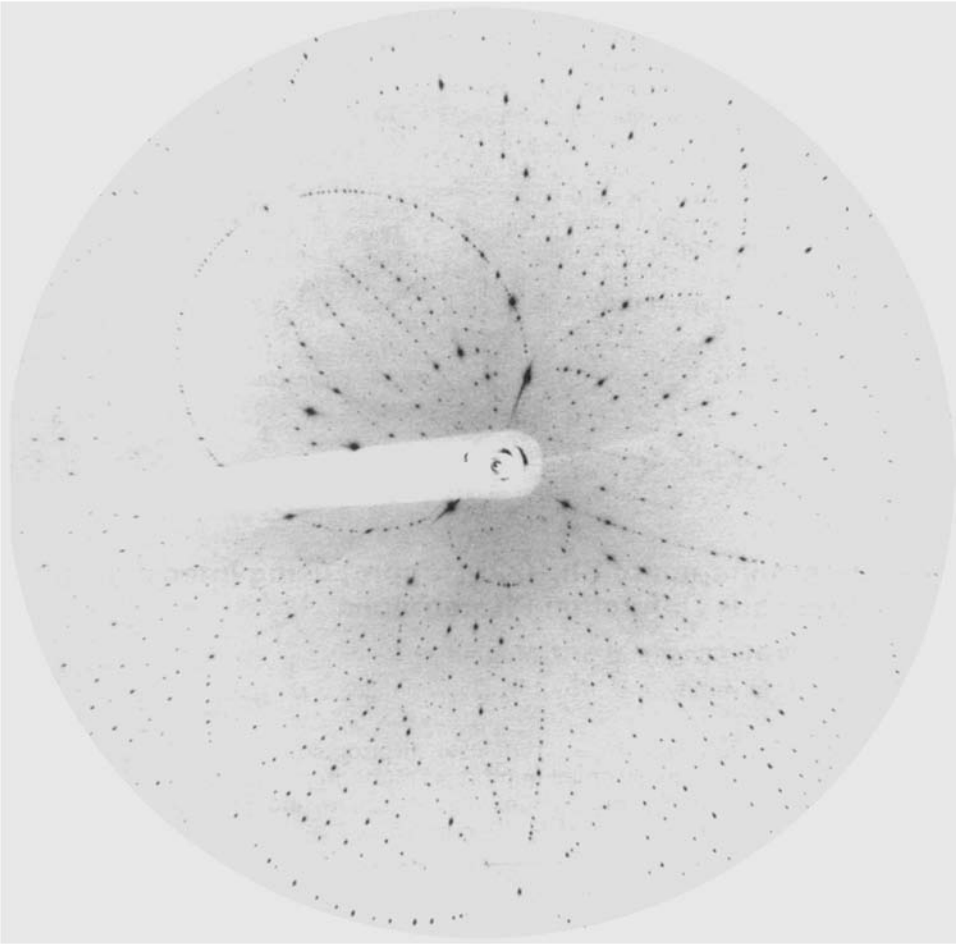

Figure 1. Laue diffraction photograph of $Rh_6(CO)_{14}$ (dppm), exposure time 10 s with SRS at 15 mA (single bunch mode).

procedures, in particular the introduction of an absorption correction, will reduce these significantly.

The structure is illustrated in Figure 2. An octahedron of rhodium atoms has four face-capping carbonyl groups, ten terminal carbonyl groups, and the diphosphine ligand bridging two rhodium atoms. Bond lengths and stereochemistry are normal for this type of compound [*e.g.* $Rh_6(CO)_{10}(dppm)_3$, ref. 8], and the structure is consistent with n.m.r. spectral data and expectations from its chemistry.[3]

The potential applications of SR Laue diffraction are in two areas; the study of small crystals and the study of time dependent changes in crystals. For small crystals the exposure times are very reasonable. The structure of a crystal of another organometallic compound, $FeRh(CO)_5$(dppee) [dppee = $Ph_2PCH(=CH_2)PPh_2$], has recently been determined, and refined to $R = 0.14$ for 553 reflections,[10] although unfortunately in this case the crystal was disordered, with two molecular orientations present; this crystal was fairly small, 0.32 × 0.06 × 0.05 mm, and the exposure time was 6 s per film pack (with the SRS beam intensity ten times that used in the experiment described here). Laue diffraction could well have advantages over conventional diffractometers and sources for similar and smaller crystals, although monochromatised SR and an area detector diffractometer are probably even better.[11] (It should be possible to combine the information

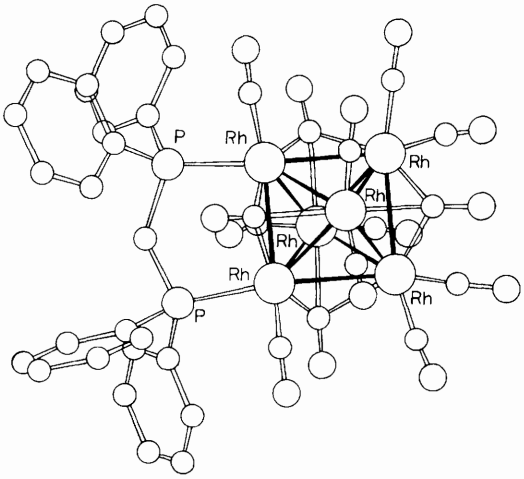

Figure 2. Structure determined for $Rh_6(CO)_{14}$ (dppm). The Rh–Rh bond lengths are in the range 2.720(6)—2.796(5) Å; Rh–P bond lengths are 2.30(1) and 2.33(1) Å; terminal Rh–C bond lengths are in the range 1.72(5)—1.93(6) Å, and face-capping Rh–C, 2.13(3)—2.37(4) Å. (Diagram prepared with program PLUTO.)[9]

from Laue diffraction, which gives axial ratios, and from powder diffraction, to obtain the unit cell if this is otherwise unknown.)

Laue diffraction also opens the way to studies of time dependent changes in crystals; such studies have hitherto used powder diffraction data,[12] but with single crystal data a structural change can be followed in much greater detail in a more complex crystal. The method has already been beautifully exploited by Hajdu *et al.* in the study of the enzyme phosphorylase[13] where substrate is diffused into the crystal and can be seen (from the electron density difference maps from the Laue intensity data) to become bound to protein within minutes. Other changes which take place within a crystal could be similarly followed, for example, crystal to crystal phase transformations and radiation induced changes.

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