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## Structure Determination with Laue Diffraction Data – Including Refinement when Anomalous Scatterers are Present

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### Abstract

The structure of a small single crystal of the organometallic compound  $[\text{AuOs}_3\text{H}(\text{CO})_8(\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4)(\text{PPh}_3)]\text{PF}_6 \cdot 0.5\text{C}_6\text{H}_5\text{Cl}$ , whose chemical constitution was only partially known, has been determined and refined. Synchrotron radiation with wavelengths in the range 0.24–0.65 Å was used for recording the Laue diffraction patterns from which the reflection intensities were measured. Data processing and initial structure determination followed established procedures. Over this wavelength range, the scattering factors of Au and Os change significantly on account of the anomalous scattering contributions,  $f'$  and  $f''$ ; the program *SHELXL92* [Sheldrick (1992). *Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany] can allow for this variation and with it the structure refinement was completed, giving  $R1 = 0.078$ ,  $wR2 = 0.192$  for 10 625 (unmerged) reflection intensities in the space group  $C2/c$ . Metallation of one phenyl group of the dppm ligand has occurred and the chemical aspects are further discussed by Harding, Kariuki, Mathews, Smith & Braunstein [(1993), *J. Chem. Soc. Dalton Trans.* pp. 33–36]. Synchrotron radiation Laue diffraction data for another organometallic compound,  $\text{Ru}(\text{C}_{12}\text{H}_{10}\text{O}_4)(\text{C}_8\text{H}_{11}\text{P})_2(\text{CO})_2$ , have also been recorded and used for structure refinement. This crystal of already known structure is non-centrosymmetric, space group  $P2_12_12_1$ , and provided a further test of the use of wavelength-dependent structure factors in *SHELXL92*.

Refinement converged to  $R1 = 0.075$ ,  $wR2 = 0.201$  for 7241 reflection intensities and the enantiomorph was unambiguously determined.

### Introduction

It is our aim to show that the Laue method for recording diffraction data, with synchrotron radiation, can be used for the complete structure determination of compounds of moderate complexity. The Laue method was, of course, used to establish the structures of many very simple compounds such as sodium chloride (Bragg, 1913; Glusker, 1981). Interest in the application of the Laue method has been revived with the advent of synchrotron radiation, with its continuous range of wavelengths and very high intensity. Helliwell, Habash *et al.* (1989) developed software for deriving reliable reflection intensities from Laue diffraction patterns and such intensity measurements are now being used for protein and virus crystals and for the study of structural changes on a time scale of seconds or less (Helliwell, 1992; Moffat, Chen, Kingman, McRee & Getzoff, 1992). They have also been shown to be sufficient for the structure determination of an organic compound,  $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_2$  (Helliwell, Gomez de Anderez, Habash, Helliwell & Vernon, 1989); structure refinement to  $R = 0.053$  for 1914 reflection intensities indicates the quality of data possible. Laue intensity measurements have also been used for the determination of the otherwise unknown structures of three metal

Table 1. *Crystal data*

|  | AuOs   | RuP   |
|--|--|---|
| Formula                                    | C <sub>51</sub> H <sub>37</sub> AuO <sub>8</sub> Os <sub>3</sub> P <sub>3</sub> PF <sub>6</sub> ·0.5C <sub>6</sub> H <sub>5</sub> Cl | C <sub>30</sub> H <sub>12</sub> P <sub>2</sub> O <sub>6</sub> Ru                    |
| Formula weight                             | 1839.6   | 651.6   |
| System                                     | Monoclinic   | Orthorhombic  |
| Space group                                | C2/c   | P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>                                       |
| Unit cell                                  |  |   |
| <i>a</i> (Å)                               | 37.46 (4)  | 9.367 (10)  |
| <i>b</i> (Å)                               | 9.645 (10)   | 13.689 (20)   |
| <i>c</i> (Å)                               | 34.86 (4)  | 23.042 (30)   |
| <i>β</i> (°)                               | 104.6 (1)  |   |
| Volume                                     | 12 188   | 2955  |
| <i>Z</i>                                   | 8  | 4   |
| <i>F</i> (000)                             | 6856   | 1336  |
| <i>D<sub>c</sub></i> (Mg m <sup>-3</sup> ) | 2.00   | 1.46  |
| <i>μ</i> (mm <sup>-1</sup> )               | 0.46 at <i>λ</i> = 0.24 Å<br>to 8.12 at <i>λ</i> = 0.70 Å  | 0.30 at <i>λ</i> = 0.30 Å<br>1.63 at <i>λ</i> = 0.56 Å<br>1.54 at <i>λ</i> = 1.00 Å |

procedure similar to *DIFABS* (Walker & Stuart, 1983) was developed and used for the molybdenum complex quoted above and is described by Maginn, Harding & Campbell (1993). The other requirement when *complete* structure determination is the objective is the determination of the unit cell. The derivation of the unit cell from the Laue diffraction pattern of a crystal in an arbitrary orientation is described by Carr, Cruickshank & Harding (1992) and Carr, Dodd & Harding (1993), and the determination of the unit cell of AuOs is given as an example (of an unknown crystal) in the second paper.

Crystal data for both compounds are given in Table 1.

complexes, FeRhCl(CO)<sub>5</sub>dpppe (Harding, Maginn, Campbell, Clifton & Machin, 1988), (Mo<sub>5</sub>O<sub>23</sub>S<sub>2</sub>)-(NEt<sub>4</sub>)<sub>4</sub>.C<sub>6</sub>H<sub>5</sub>CN (Maginn, Harding & Campbell, 1993) and Rh<sub>6</sub>(CO)<sub>14</sub>dppm (Clucas, Harding & Maginn, 1988), the first two of which were very small crystals, too small for conventional diffractometer data collection. All these crystals contain heavier atoms, for which, on account of anomalous dispersion, there is some variation of the scattering factors with wavelength; no allowance was made for this in the refinements, even though in the Laue method different reflections are measured at different wavelengths; consequently the formal *R* factors were poor (0.14, 0.10 and 0.16). The present paper shows how, with Sheldrick's new program *SHELXL92* (Sheldrick, 1992), this wavelength dependence can be satisfactorily included in the calculation (of *F<sub>c</sub>*) and that its inclusion may indeed be necessary for the establishment of structural detail, as well as for achieving a reasonable *R* factor.

Laue diffraction data on two compounds are described here. [AuOs<sub>3</sub>H(CO)<sub>8</sub>{Ph<sub>2</sub>PCH<sub>2</sub>P(Ph)-C<sub>6</sub>H<sub>4</sub>}(PPh<sub>3</sub>)]PF<sub>6</sub>·0.5C<sub>6</sub>H<sub>5</sub>Cl (henceforth AuOs) was a newly synthesized compound (Harding, Kariuki, Mathews, Smith & Braunstein, 1993) of unknown structure, for which the crystals were too small for satisfactory data collection on our Rigaku AFC6S diffractometer. For this crystal we have shown that complete structure determination from the Laue diffraction data alone is possible. The AuOs crystal was found to have the space group *C2/c*. Ru(C<sub>12</sub>H<sub>10</sub>O<sub>4</sub>)-(C<sub>8</sub>H<sub>11</sub>P)<sub>2</sub>(CO)<sub>2</sub> (henceforth RuP), whose structure in space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* is already known (Blake, Crook, Mawby, Reid & Reynolds, 1992), was selected as an example of a non-centrosymmetric crystal; for this crystal we have shown that satisfactory structure refinement and enantiomorph determination is possible with the Laue diffraction data.

Laue intensity measurements for crystals containing heavier atoms may also require absorption correction, even if the crystal is fairly small. A

## Experimental

### *X-ray photographs, derivation of spot intensities*

Laue diffraction patterns for AuOs were recorded on workstation 9.7 of the SRS at SERC Daresbury Laboratory. The incident beam was attenuated by 0.2 mm Al and 0.114 mm Cu in order to reduce possible radiation damage and to shift the useful intensity distribution to shorter wavelengths. Five film packs were recorded, each of composition *FFspFspFCuFCuF*, where *F* represents film, *sp* represents an additional film used as a spacer, but not for measurements, and *Cu* represents 0.038 mm Cu foil. The exposure time was 14 s with the SRS running at *ca* 200 mA. For RuP, the beam was attenuated by 0.2 mm Al only and the film packs were of composition *FFspFspFCuF*; exposure time was 0.2 s with the SRS at 130 mA.

Films were scanned, crystal orientation found and refined, spot intensities integrated and the intensities from films within each film pack merged by established procedures (Helliwell, Habash *et al.*, 1989). This yielded *L<sub>p</sub>*-corrected un-normalized intensities, in the form *hkl I sig(I) λ* for the single reflections in each film pack; multiple Laue spots were not used. Examples of Laue diffraction photographs are shown in Fig. 1. Other details of the experiments and the processing are collected in Table 2. Soft limits were initially estimated by comparison of observed and predicted patterns in the regions around the nodal spots; *d<sub>min</sub>* was subsequently checked by analysis of the measured intensities as a function of *1/d*. For AuOs, the *proportion* of good reflection intensity measurements [*I* > 5σ(*I*)] in a shell of reciprocal space is approximately constant to *d* = 0.85 Å; it then drops by a factor of four between 0.85 and 0.70 Å, the cut-off point used. Similarly for RuP, the *proportion* of good intensity measurements is approximately constant to *d* = 0.89 Å and then drops rapidly.

*Preliminary wavelength normalization and structure determination*

**AuOs:** Using the program *LAUENORM* and reflections with  $I > 4\sigma(I)$ , from the five film packs a wavelength normalization function was derived and applied.

All the data were merged and inspected for symmetry in the reciprocal lattice and for systematic absences; space group *C2/c* (or *Cc*) was deduced. Repetition of *LAUENORM* with merging and with

Table 2. *Experimental details*

|   | AuOs               |       |       | RuP             |       |       |       |       |
|---|--------------------|-------|-------|-----------------|-------|-------|-------|-------|
| Crystal size (mm)                       | 0.27 × 0.06 × 0.04 |       |       | 0.9 × 1.3 × 0.4 |       |       |       |       |
| Crystal-film distance (mm)              | 61                 |       |       | 53              |       |       |       |       |
| $\lambda_{\min}$ (Å)                    | 0.24               |       |       | 0.28            |       |       |       |       |
| $\lambda_{\max}$ (Å)                    | 1.80               |       |       | 1.50            |       |       |       |       |
| $d_{\min}$ (Å)                          | 0.70               |       |       | 0.70            |       |       |       |       |
|   | in processing      |       |       |                 |       |       |       |       |
| AuOs film packs $\varphi$ (°)           | 20                 | 80    | -60   | 0               | 60    |       |       |       |
| Genlaue prediction,                     | 0.02-              | 0.04- | 0.04- | 0.05-           | 0.04- |       |       |       |
| r.m.s. deviation (mm)                   | 0.05               | 0.07  | 0.08  | 0.08            | 0.06  |       |       |       |
| Intlaue, spots measured                 | 4083               | 3773  | 4133  | 3972            | 3714  |       |       |       |
| Merging within film packs               | 0.072              | 0.082 | 0.063 | 0.072           | 0.061 |       |       |       |
| $R_{\text{merg}}$                       |                    |       |       |                 |       |       |       |       |
| No. single reflns.                      | 3542               | 3268  | 3592  | 3435            | 3277  |       |       |       |
| No. with $I > 3\sigma(I)$               | 2163               | 2231  | 2572  | 2325            | 2230  |       |       |       |
| RuP film packs $\varphi$ (°)            | 0                  | 60    | 120   | 20              | 80    | 140   | 40    | 100   |
| Genlaue prediction                      | 0.13               | 0.13  | 0.16  | 0.25            | 0.17  | 0.17  | 0.18  | 0.18  |
| r.m.s. deviation (mm)*                  |                    |       |       |                 |       |       |       |       |
| Intlaue, spots measured                 | 3058               | 3026  | 3076  | 2979            | 3108  | 2783  | 3115  | 3096  |
| Merging of film packs                   | 0.037              | 0.038 | 0.050 | 0.044           | 0.068 | 0.046 | 0.044 | 0.040 |
| $R_{\text{merg}}$                       |                    |       |       |                 |       |       |       |       |
| No. of singles                          | 2674               | 2580  | 2651  | 2555            | 2676  | 2496  | 2697  | 2683  |
| No. with $I > 3\sigma(I)$               | 1528               | 1468  | 1499  | 997             | 1375  | 1487  | 1354  | 1422  |
| Final refinement                        | AuOs               |       |       | RuP             |       |       |       |       |
| No. of reflections used                 | 10 625             |       |       | 7241            |       |       |       |       |
| Wavelength range (Å)                    | 0.29-0.65†         |       |       | 0.42-1.04‡      |       |       |       |       |
| Refinement on                           | $F^2$              |       |       | $F^2$           |       |       |       |       |
| No. of restraints                       | 237                |       |       | 0               |       |       |       |       |
| No. of parameters                       | 345§               |       |       | 380§            |       |       |       |       |
| Goodness-of-fit on $F^2$                | 1.24               |       |       | 1.53            |       |       |       |       |
| Final $R_1$                             | 0.078              |       |       | 0.075           |       |       |       |       |
| Final $R_1^{\dagger\dagger}$            | 0.074              |       |       | 0.086           |       |       |       |       |
| Final $wR_2$                            | 0.192              |       |       | 0.203           |       |       |       |       |
| Extinction coefficient                  | 0.058 (2)          |       |       | 0.21 (2)        |       |       |       |       |
| Maximum, minimum                        | 1.19,              |       |       | 0.45,           |       |       |       |       |
| electron density in final               | -1.52              |       |       | -0.54           |       |       |       |       |
| difference map ( $e \text{ \AA}^{-3}$ ) |                    |       |       |                 |       |       |       |       |

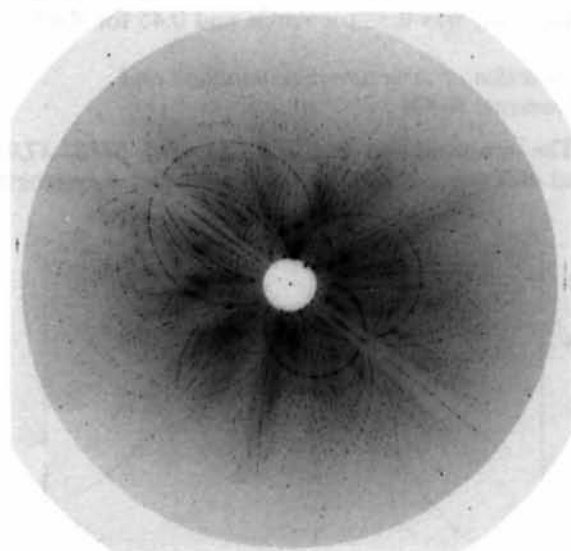
\* These r.m.s. deviations are much higher than is usually regarded as desirable. They were calculated from *ca* 400 spots per film, probably including many weak ones, instead of the more usual 100-200.

† Omitting the Ag edge 0.48-0.49 Å.

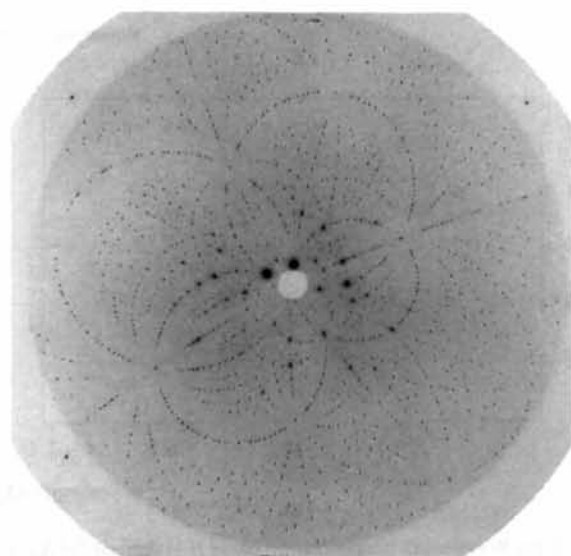
‡ Omitting the Ag edge 0.48-0.49 Å, Ru edge 0.55-0.57 Å and Br edge 0.90-0.92 Å.

§ Including those used for the absorption surface and wavelength normalization function, 175 for AuOs and 280 for RuP.

¶ For data merged after the contribution of  $f''$  had been removed from  $F_{\text{obs}}$ .



(a)



(b)

Fig. 1. Examples of Laue diffraction photographs used for intensity measurement, (a) AuOs and (b) RuP. Experimental details are given in Table 2.

the assumption of monoclinic symmetry yielded 7174 independent reflections,  $R_{\text{merg}} = 0.10$  (Helliwell, Habash *et al.*, 1989). These reflection intensities were used in *SHELXS86* (Sheldrick, 1985) to derive the Au, Os and P positions and then in *SHELX76* (Sheldrick, 1976) to derive and refine most of the structure by conventional methods. This yielded  $R = 0.128$ , but one phenyl group could not be located and the structure at this stage also lacked the solvent molecule found later.

**RuP:** using the program *LAUENORM* and reflections with  $I > 4\sigma(I)$ , the wavelength normalization function was derived and applied, giving 1897 independent reflection intensities,  $R_{\text{merg}} = 0.163$ . These reflection intensities were used in *SHELX*, together with the published coordinates (Blake, Crook, Mawby, Reid & Reynolds, 1992); refinement

of the scale factor gave  $R = 0.157$ , clearly not very satisfactory.

*Absorption correction and improved normalization* was possible using the program *LAUESCALE* (Maginn, Harding & Campbell, 1993). For each film pack, un-normalized  $I(hkl)$  values were compared with  $F(hkl)^2$  calculated by *SHELXL92* (Sheldrick, 1992) at the correct wavelength. The  $f'$  and  $f''$  values at wavelengths throughout the range were calculated with the program *FPRIME* (Cromer & Lieberman, 1970) and input to *SHELXL* as a table. Fig. 2 shows the variation of these anomalous scattering contributions, and Fig. 3 the final wavelength normalization functions which were derived and applied, for AuOs and RuP. The absorption surface, fitted to a polynomial, was derived and applied at the same time. The ratio of maximum-to-minimum transmission, for any one angle of incidence to the crystal (*i.e.* within one film pack), gives an indication of the

magnitude of absorption correction required.  $T_{\max}/T_{\min}$  ranged from 2.2 to 3.9 for AuOs and from 2.0 to 2.9 for six of the eight RuP film packs ( $T_{\max}/T_{\min}$  appeared to be much larger on the other two RuP film packs, 5.5 and 9.5, but the number of spots affected by these extreme values was very small).

In *LAUESCALE*,  $R_{\text{scale}}$  indicates the agreement of  $I(hkl)$  after normalization with  $F(hkl)^2$ ; for AuOs,  $R_{\text{scale}}$  values were in the range 0.080–0.113 and for RuP, 0.074–0.118. The fraction of theoretically accessible reflections which had  $I > 3\sigma(I)$  on output from *LAUESCALE*, and were actually used in refinement, was 0.38 for AuOs and 0.45 for RuP.

#### Completion of structure determination and refinement: AuOs

The renormalized  $F(hkl)^2$  values, in *SHELXL92* (and still using  $f'$  and  $f''$  at the correct wavelength

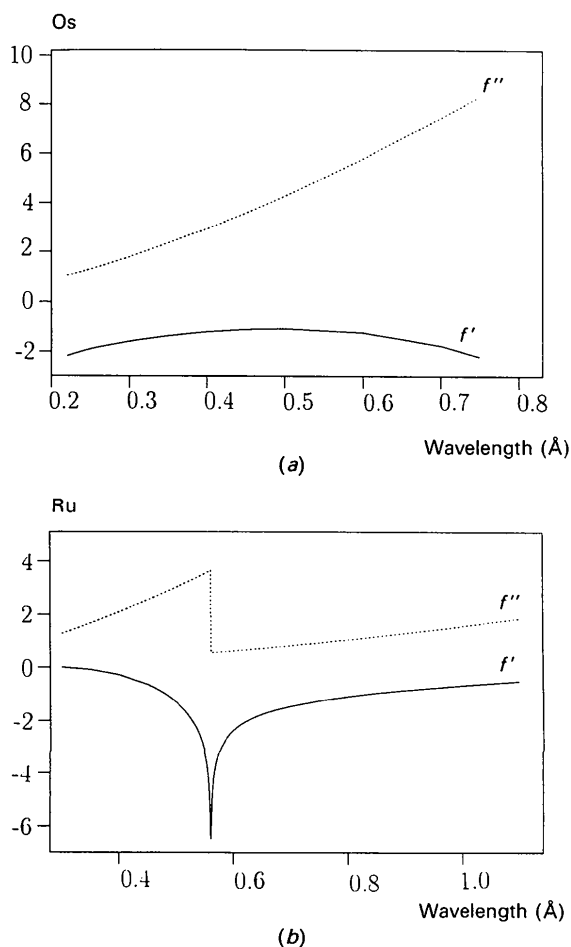


Fig. 2. (a) Anomalous scattering contributions  $f'$  (full line) and  $f''$  (dotted line) calculated with the program *FPRIME* (Cromer & Lieberman, 1970) for Os as a function of wavelength; Au is very similar. (b) Anomalous scattering contributions  $f'$  and  $f''$  for Ru.

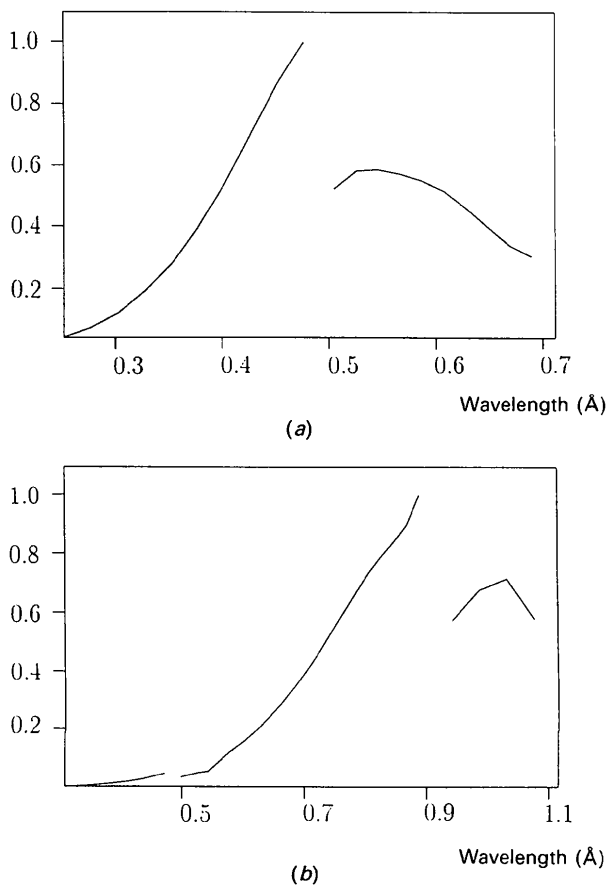


Fig. 3. (a) Wavelength normalization curve  $f(\lambda)$  derived for AuOs; the experimental points were fitted to a polynomial of the order 5 in each of the wavelength ranges 0.24–0.48 and 0.49–0.70 Å; the discontinuity corresponds to the absorption edge of Ag in the film. (b) Similar wavelength normalization curve for RuP;  $f(\lambda)$  is  $I_{\text{Laue}}/I_{\text{mono}}$ .

for each reflection), now allowed the remaining phenyl group and solvent molecule to be located in an electron-density difference map. Refinement then proceeded, with H atoms included at calculated positions, and anisotropic displacement parameters for Os, Au, Cl, P and F; restraints were applied to make the phenyl groups regular hexagons, the  $\text{PF}_6^-$  group a regular octahedron, all the C—O distances the same, chemically equivalent P—C distances the same, and also to make many atomic displacement parameters of adjacent atoms similar. After some refinement, it was evident that data at the extremes of the wavelength range were giving the poorest agreement with  $F_{\text{calc}}$ ; the wavelength range used for the final refinement was reduced to 0.29–0.65 Å. At short wavelengths the reflections omitted may have quite large errors because of the uncertainties in the  $f(\lambda)$  curve; at long wavelengths the errors are more likely to be due to absorption. Other details are given in Table 2 and the  $R$  factor as a function of wavelength is given in Table 3. [In the formula given, the H atom attached to Os was included on chemical grounds [Harding, Kariuki, Mathews, Smith & Braunstein, (1993); it was not found crystallographically and was not included in the structure-factor calculations.]

#### Structure refinement: RuP

Similarly, *SHELXL92* allowed structure refinement and in the case of this non-centrosymmetric crystal, the Flack parameter  $x$  was refined to establish the enantiomorph. The result was very clear,  $x = 0.04$  (3) for the published coordinates (and  $x = 0.895$ ,  $R = 0.081$  for inverted coordinates). H atoms were included and anisotropic atomic displacement parameters were used for all non-H atoms. Details are given in Table 2.\*

### Results and Discussion

The structure of AuOs has been successfully determined for Laue diffraction patterns alone, and for a rather small crystal; structure refinement has been achieved to an accuracy which is as good or better than that often obtained with monochromatic diffractometer data and normal sized crystals. The atom parameters are given in Table 4 and the ion illustrated in Fig. 4. Metallation of one phenyl group of dppm has occurred. Between the time when these experiments were started and their conclusion, an opportunity arose to collect monochromatic data on

Table 3. Analysis of agreement between  $F_{\text{obs}}$  and  $F_{\text{calc}}$  as a function of wavelength

| Wavelength (Å) | No. of reflections | $R1$  | Mean $\sigma(F^2)/F^2$ |
|----------------|--------------------|-------|------------------------|
| <b>AuOs</b>    |                    |       |                        |
| 0.290–0.329    | 907                | 0.110 | 0.100                  |
| 0.329–0.368    | 1190               | 0.087 | 0.091                  |
| 0.368–0.407    | 1415               | 0.074 | 0.084                  |
| 0.407–0.446    | 1570               | 0.065 | 0.078                  |
| 0.446–0.485    | 1592               | 0.070 | 0.076                  |
| 0.495–0.526    | 993                | 0.064 | 0.092                  |
| 0.526–0.557    | 931                | 0.074 | 0.097                  |
| 0.557–0.588    | 803                | 0.074 | 0.095                  |
| 0.588–0.619    | 683                | 0.074 | 0.090                  |
| 0.619–0.650    | 541                | 0.102 | 0.090                  |
| All            | 10 625             | 0.078 | 0.088                  |
| <b>RuP</b>     |                    |       |                        |
| 0.42–0.45      | 487                | 0.107 | 0.113                  |
| 0.45–0.48      | 608                | 0.099 | 0.120                  |
| 0.49–0.52      | 545                | 0.117 | 0.090                  |
| 0.52–0.55      | 551                | 0.112 | 0.095                  |
| 0.55–0.58      | 215                | 0.102 | 0.095                  |
| 0.58–0.61      | 676                | 0.073 | 0.090                  |
| 0.61–0.64      | 649                | 0.065 | 0.080                  |
| 0.64–0.67      | 602                | 0.059 | 0.069                  |
| 0.67–0.70      | 527                | 0.050 | 0.063                  |
| 0.70–0.73      | 471                | 0.049 | 0.056                  |
| 0.73–0.76      | 383                | 0.047 | 0.057                  |
| 0.76–0.79      | 369                | 0.051 | 0.051                  |
| 0.79–0.82      | 277                | 0.053 | 0.046                  |
| 0.82–0.85      | 268                | 0.052 | 0.044                  |
| 0.85–0.88      | 201                | 0.051 | 0.044                  |
| 0.88–0.91      | 101                | 0.045 | 0.035                  |
| 0.92–0.95      | 116                | 0.099 | 0.064                  |
| 0.95–0.98      | 84                 | 0.067 | 0.060                  |
| 0.98–1.01      | 70                 | 0.068 | 0.054                  |
| 1.01–1.04      | 41                 | 0.083 | 0.042                  |
| All            | 7241               | 0.075 | 0.075                  |

the FAST diffractometer on the SRS at SERC Daresbury Laboratory; the structure was (with some difficulty) determined from this data too and refined to  $R = 0.056$  for 2212 unique reflections with  $F > 3\sigma(F)$  (Harding, Kariuki, Mathews, Smith & Braunstein, 1993). The atom positions derived from the monochromatic and Laue data agree within a few e.s.d.'s and the e.s.d.'s suggest that the Laue data has given the more accurate positions. There are small systematic differences in the  $U$  values (and  $U_{ij}$  values) derived from the Laue data and the monochromatic data.  $U_{\text{eq(Laue)}}$  is equal to  $0.9U_{\text{eq(mono)}}$  within  $3\sigma$  and the e.s.d.'s from the Laue data are smaller than those from the monochromatic data by a factor of 3–6.

The structure of RuP has been successfully refined from Laue intensity data and the enantiomorph unambiguously established. The results are in agreement with the previously determined structure (in this case from a crystal of good size and quality; 4792 observed reflection intensities were used to refine 373 parameters, giving  $R = 0.040$ .) The r.m.s. difference between atom coordinates of all non-H atoms derived from Laue and monochromatic data is

\* Lists of structure factors, anisotropic atomic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: LI0165. Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. AuOs: Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

|        | x        | y          | z        | $U_{eq}$ |
|--------|----------|------------|----------|----------|
| Os(1)  | 1770 (1) | 1794 (1)   | 1945 (1) | 40 (1)   |
| Os(2)  | 1631 (1) | 290 (1)    | 1173 (1) | 37 (1)   |
| Os(3)  | 1920 (1) | -1071 (1)  | 1872 (1) | 45 (1)   |
| Au(1)  | 2345 (1) | -710 (1)   | 1328 (1) | 45 (1)   |
| Cl(1)* | 3136 (4) | 4684 (10)  | 118 (4)  | 85 (9)   |
| P(1)   | 1151 (1) | 1139 (3)   | 1828 (1) | 43 (1)   |
| P(2)   | 2885 (1) | -1241 (4)  | 1159 (1) | 48 (2)   |
| P(3)   | 1047 (1) | 1289 (3)   | 933 (1)  | 41 (1)   |
| O(1)   | 1551 (6) | -1794 (15) | 524 (5)  | 77 (11)  |
| O(2)   | 2044 (5) | 2156 (14)  | 731 (5)  | 75 (12)  |
| O(3)   | 2675 (3) | -462 (18)  | 2388 (5) | 74 (6)   |
| O(4)   | 2108 (5) | -4002 (12) | 1679 (8) | 95 (11)  |
| O(5)   | 1660 (5) | -1905 (24) | 2591 (5) | 94 (10)  |
| O(6)   | 1521 (4) | 4758 (12)  | 1992 (5) | 72 (9)   |
| O(7)   | 1984 (7) | 1497 (27)  | 2839 (4) | 103 (15) |
| O(8)   | 2559 (4) | 2506 (16)  | 1924 (6) | 76 (7)   |
| C(1)   | 1581 (4) | -1044 (15) | 772 (5)  | 52 (3)   |
| C(2)   | 1898 (4) | 1489 (13)  | 897 (4)  | 46 (3)   |
| C(3)   | 2397 (4) | -642 (17)  | 2192 (5) | 56 (3)   |
| C(4)   | 2042 (5) | -2943 (16) | 1738 (6) | 61 (4)   |
| C(5)   | 1754 (6) | -1496 (21) | 2332 (6) | 69 (4)   |
| C(6)   | 1614 (4) | -3710 (14) | 1965 (5) | 51 (3)   |
| C(7)   | 1889 (4) | 1587 (16)  | 2506 (4) | 53 (3)   |
| C(8)   | 2265 (4) | 2216 (18)  | 1923 (5) | 55 (3)   |
| C(9)   | 882 (4)  | 1902 (14)  | 1358 (3) | 46 (3)   |
| P(4)   | 126 (2)  | 4118 (7)   | 3919 (2) | 93 (4)   |
| F(1)   | 184 (7)  | 4256 (28)  | 3505 (5) | 180 (16) |
| F(2)   | 192 (5)  | 5655 (14)  | 3984 (7) | 186 (17) |
| F(3)   | -283 (4) | 4396 (17)  | 3750 (7) | 141 (8)  |
| F(4)   | 57 (5)   | 2585 (14)  | 3852 (7) | 176 (15) |
| F(5)   | 75 (8)   | 3974 (29)  | 4335 (5) | 185 (19) |
| F(6)   | 535 (4)  | 3850 (20)  | 4079 (7) | 172 (8)  |
| C(11)  | 3297 (3) | -428 (14)  | 1450 (4) | 63 (4)   |
| C(12)  | 3579 (4) | -48 (18)   | 1277 (3) | 103 (8)  |
| C(13)  | 3894 (4) | 599 (19)   | 1504 (5) | 88 (6)   |
| C(14)  | 3926 (3) | 865 (18)   | 1903 (5) | 95 (7)   |
| C(15)  | 3644 (4) | 485 (16)   | 2076 (3) | 79 (5)   |
| C(16)  | 3330 (3) | -162 (14)  | 1849 (4) | 64 (4)   |
| C(21)  | 2978 (3) | -3072 (8)  | 1210 (5) | 57 (3)   |
| C(22)  | 3334 (3) | -3609 (11) | 1318 (5) | 68 (4)   |
| C(23)  | 3387 (3) | -5033 (12) | 1358 (6) | 71 (5)   |
| C(24)  | 3085 (4) | -5920 (8)  | 1290 (6) | 89 (6)   |
| C(25)  | 2730 (3) | -5382 (12) | 1182 (7) | 84 (6)   |
| C(26)  | 2676 (3) | -3958 (13) | 1143 (6) | 84 (6)   |
| C(31)  | 2867 (4) | -795 (13)  | 653 (3)  | 59 (3)   |
| C(32)  | 2828 (5) | 591 (12)   | 541 (4)  | 79 (5)   |
| C(33)  | 2826 (7) | 972 (13)   | 156 (5)  | 99 (8)   |
| C(34)  | 2862 (7) | -33 (19)   | -117 (4) | 92 (7)   |
| C(35)  | 2901 (7) | -1419 (17) | -6 (4)   | 111 (9)  |
| C(36)  | 2903 (5) | -1800 (11) | 380 (4)  | 81 (5)   |
| C(41)  | 1092 (3) | -638 (8)   | 1711 (3) | 53 (3)   |
| C(42)  | 804 (3)  | -1411 (11) | 1788 (4) | 63 (4)   |
| C(43)  | 732 (3)  | -2735 (11) | 1630 (4) | 73 (5)   |
| C(44)  | 947 (3)  | -3287 (8)  | 1396 (4) | 63 (4)   |
| C(45)  | 1235 (3) | -2514 (9)  | 1319 (3) | 53 (3)   |
| C(46)  | 1307 (2) | -1189 (8)  | 1477 (3) | 45 (2)   |
| C(51)  | 697 (3)  | 144 (11)   | 645 (4)  | 52 (3)   |
| C(52)  | 737 (4)  | -229 (15)  | 273 (4)  | 76 (5)   |
| C(53)  | 506 (5)  | -1223 (17) | 51 (4)   | 91 (6)   |
| C(54)  | 234 (4)  | -1844 (16) | 200 (5)  | 90 (6)   |
| C(55)  | 194 (4)  | -1471 (16) | 572 (5)  | 91 (7)   |
| C(56)  | 425 (4)  | -477 (15)  | 794 (4)  | 76 (5)   |
| C(61)  | 1008 (3) | 2811 (10)  | 634 (4)  | 46 (2)   |
| C(62)  | 1287 (3) | 3798 (12)  | 719 (4)  | 63 (4)   |
| C(63)  | 1257 (5) | 4995 (13)  | 491 (6)  | 79 (5)   |
| C(64)  | 949 (7)  | 5205 (19)  | 178 (7)  | 138 (14) |
| C(65)  | 669 (6)  | 4218 (23)  | 93 (7)   | 116 (10) |
| C(66)  | 699 (4)  | 3021 (17)  | 321 (6)  | 103 (8)  |
| C(71)  | 902 (4)  | 1612 (14)  | 2187 (4) | 63 (4)   |
| C(72)  | 1008 (4) | 1007 (14)  | 2560 (4) | 79 (5)   |

Table 4 (cont.)

|        | x         | y         | z        | $U_{eq}$ |
|--------|-----------|-----------|----------|----------|
| C(73)  | 853 (5)   | 1457 (18) | 2861 (4) | 90 (6)   |
| C(74)  | 592 (6)   | 2512 (20) | 2788 (5) | 109 (10) |
| C(75)  | 486 (5)   | 3117 (16) | 2415 (5) | 97 (7)   |
| C(76)  | 641 (4)   | 2667 (14) | 2114 (4) | 70 (4)   |
| C(81)* | 3589 (11) | 4445 (40) | 331 (15) | 89 (12)  |
| C(82)* | 3814 (18) | 5496 (35) | 532 (23) | 131 (21) |
| C(83)* | 4147 (20) | 5171 (57) | 798 (28) | 170 (30) |
| C(84)* | 4255 (18) | 3795 (66) | 862 (28) | 144 (25) |
| C(85)* | 4031 (16) | 2743 (45) | 661 (23) | 146 (24) |
| C(86)* | 3697 (13) | 3068 (35) | 395 (16) | 86 (11)  |

\* Site occupancy 0.5.

0.033 Å. E.s.d.'s of atom positions from the Laue data are not more than twice those from the monochromatic data.  $U_{eq(Laue)}$  is equal to 1.2  $U_{eq(mono)}$  within  $3\sigma$  for all atoms except Ru; for Ru,  $U_{eq(Laue)}$  is equal to 1.4  $U_{eq(mono)}$ ; these differences are remarkably small and are probably due to some inadequacy of the absorption correction in one of the data sets.

The wavelength normalization curves derived experimentally are illustrated in Fig. 3. The factors which determine these curves in any one experiment are the intensity distribution in the incident synchrotron radiation, modified by attenuators (Cu and Al for AuOs, Al only for RuP), the film response and the absorption by the crystal. These account for the big differences between the curves for the two compounds. The Al attenuation used for RuP followed our previous normal practice; the additional Cu attenuation was devised for AuOs in order to make more use of shorter wavelengths and to avoid wavelengths near the Au and Os absorption edges (*ca*

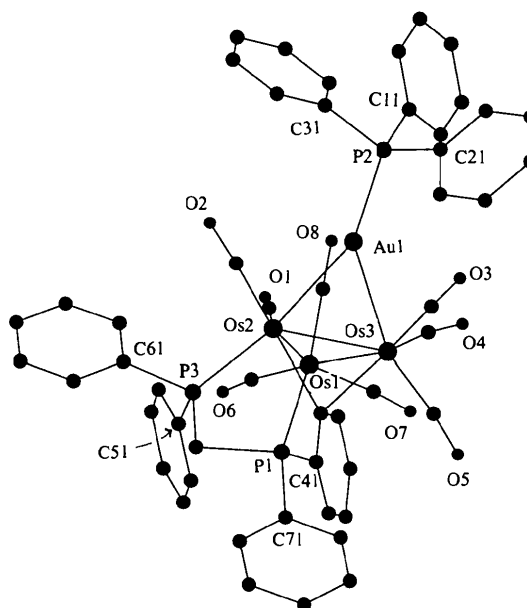


Fig. 4. The structure of the AuOs<sub>3</sub> cluster cation, with atomic numbering indicated. H atoms omitted for clarity.

0.9 Å) and thus reduce the possibility of radiation damage.

The effect of an attenuator in modifying the useful range of wavelengths can be shown by an example. Table 5 shows the wavelength normalization function,  $f(\lambda)$ , determined experimentally from Laue films for a crystal of a simple organic compound recorded in a different experiment on workstation 9.7 with no attenuation. It also shows the calculated effect of attenuators like those we have used in the incident beam. The measured intensities from the Laue films must be divided by  $f(\lambda)$ ; consequently, for the experiment with no attenuation, reflections measured at  $\lambda = ca$  0.30 Å will, after normalization, be much less accurate than those of similar magnitude measured at  $\lambda ca$  0.9 Å, because they are weak initially and then multiplied by a large relative  $1/f(\lambda)$ , which itself is not very well determined. However, in the third case, with Al and Cu attenuators, the relative magnitudes of the normalization factors at  $\lambda = 0.3$  and 0.9 Å are not nearly so different and this experimental arrangement allows much better use to be made of the many reflections recorded at shorter wavelengths. The second case is intermediate. Even with no attenuation, there are, for a simple compound, very very few reflections that can be recorded as singles with  $\lambda > 1.2$  Å. This use of shorter wavelengths has the additional advantage of reducing radiation damage and air scattering. There is, of course, the disadvantage that the exposure time is increased, but except for time-resolved experiments, an increase from 0.1 to 14 s is not a great inconvenience! We, therefore, strongly recommend the use of suitable attenuators when recording Laue diffraction data.

The two data collections and structure refinements thus show that the Laue method could be satisfactorily used for further unknown compounds of this complexity, including anomalous scatterers. For straightforward structure determination of normal-sized crystals, a conventional X-ray source and diffractometer give somewhat better results much more conveniently, but for small crystals a synchrotron source and the Laue method are much more effective. The total exposure time was 2 min for AuOs; time at the workstation was 1–2 h. The data processing time is still considerable, but will be reduced by the introduction of image plates and by automation planned in the Laue programs. Time-resolved studies or microcrystal studies of compounds of this nature could therefore be undertaken by the Laue method, with a reasonable expectation that useful data would be obtained. These are areas where the Laue method has real potential.

Table 5. Wavelength normalization functions,  $f(\lambda)$ , at a small selection of wavelengths, to illustrate the effects of attenuators

The first function was derived experimentally, on an SRS workstation 9.7, for a crystal of an organic compound. The second and third are calculated from it, using the absorption coefficients of Al and Cu. (There are discontinuities at 0.49 and 0.92 Å, due to absorption edges in silver bromide of the film.)

| Attenuator/wavelength (Å) | 0.24 | 0.30 | 0.60 | 0.90 | 1.20 | 1.50 |
|---------------------------|------|------|------|------|------|------|
| None                      | 2.39 | 6.25 | 226  | 1960 | 1458 | 1936 |
| 0.2 mm Al                 | 2.36 | 6.07 | 190  | 1130 | 410  | 172  |
| 0.2 mm Al + 0.076 mm Cu   | 2.05 | 4.47 | 21.8 | 1.61 | 0    | 6.21 |

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