

- DRITS, V. A., GONCHAROV, Y. I., ALEKSANDROVA, V. A., KHADZHI, I. P. & DMITRIK, A. L. (1974). *Kristallografiya*, **19**, 1186–1193.
- FEJES, P. L. (1977). *Acta Cryst.* **A33**, 109–113.
- GOODMAN, P. & MOODIE, A. F. (1974). *Acta Cryst.* **A30**, 280–290.
- HUTCHISON, J. L., IRUSTETA, M. C. & WHITTAKER, E. J. W. (1975). *Acta Cryst.* **A31**, 794–801.
- JEFFERSON, D. A., MALLINSON, L. G., HUTCHISON, J. L. & THOMAS, J. M. (1978). *Contrib. Mineral. Petrol.* **66**, 1–4.
- TATEYAMA, H., SHIMODA, S. & SUDO, T. (1978). *Contrib. Mineral. Petrol.* **66**, 149–159.
- VEBLEN, D. R. & BURNHAM, C. W. (1977). *Science*, **198**, 359–365.
- VEBLEN, D. R. & BURNHAM, C. W. (1978). *Am. Mineral.* **63**, 1053–1073.
- VEBLEN, D. R. & BUSECK, P. R. (1979). *Am. Mineral.* **64**, 687–700.
- VEBLEN, D. R. & BUSECK, P. R. (1980). *Am. Mineral.* **65**, 599–623.
- VEBLEN, D. R. & BUSECK, P. R. (1981). *Am. Mineral.* **66**, 1107–1134.
- ZAKHAROV, N. D., KHADZHI, I. P. & ROZHANSKI, V. N. (1979). *Dokl. Akad. Nauk SSSR*, **249**, 359–362.

Acta Cryst. (1988). **B44**, 142–146

Crystal Structure Determination of an Organometallic Compound from Synchrotron Radiation Laue Diffraction Photographs

BY MARJORIE M. HARDING AND S. J. MAGINN

Department of Inorganic, Physical and Industrial Chemistry, Liverpool University, PO Box 147, Liverpool L69 3BX, England

AND J. W. CAMPBELL, I. CLIFTON AND PELLA MACHIN

SERC Daresbury Laboratory, Warrington WA4 4AD, England

(Received 5 August 1987; accepted 23 November 1987)

Abstract

Laue diffraction patterns for a small single crystal of the organometallic compound [FeRhCl(CO)₅dppee] [dppee is Ph₂PCH(=CH₂)PPh₂] were recorded with the SRS wiggler beam at SERC Daresbury Laboratory. The intensities were measured from these photographs and the structure determined by Patterson and Fourier methods. The crystal had previously given weak Cu K α Weissenberg photographs from which the unit-cell dimensions and space group were determined. The diffraction data did not extend to plane spacings much less than 1.2 Å and the crystals were found to be disordered; refinement with stereochemical restraints gave $R = 0.14$. This is a pilot study; the technique could have uses for very small crystals or for 'kinetic crystallography'. The crystals of [FeRhCl(C₂₆H₂₂P₂)(CO)₅], $M_r = 730.7$, are monoclinic, $a = 8.26$, $b = 19.81$, $c = 9.77$ Å, $\beta = 111.3$ (2)° (e.s.d. of ratio of cell edges ca 0.1% from Laue diffraction pattern fitting, e.s.d. of absolute values ca 1% from weak, low-resolution Weissenberg photograph), $U = 1489.5$ Å³, $F(000) = 732$, space group $P2_1$ or $P2_1/m$ from systematic absences (in Weissenberg photograph, not accessible from Laue), $Z = 2$, D_m (floatation) = 1.62, $D_x = 1.63$ g cm⁻³. The molecule has an Fe–Rh bond, 2.7 Å, and a bridging diphosphine group.

Introduction

Laue diffraction patterns can be recorded with the full 'white' beam of the SRS wiggler at SERC Daresbury

Laboratory. Recently programs and procedures have been developed at Daresbury for the measurement of intensities in these Laue photographs, both for proteins and for simpler compounds (Campbell *et al.*, 1988; Helliwell, Machin & Papiz, 1987). The exposure times are remarkably short, 1 s or less for a normal-sized crystal, and a large proportion of reciprocal space can be recorded in a few photographs. Our interest has been to use these procedures for single-crystal structure determination for very small crystals, e.g. 5–50 μ m dimensions, too small for study with conventional sources, and for which before the development of synchrotron radiation (SR) sources, the only available approach was powder diffraction. Wood, Thompson & Matthewman (1983) have also reported a smaller pilot study in which SR Laue photographs were measured and an attempt was made to refine the parameters of an already known structure (of a normal-sized crystal). Recently the use of the Enraf–Nonius FAST area-detector diffractometer on the wiggler beamline, workstation 9.6 at Daresbury has allowed single-crystal monochromatic intensity data collection and structure determination for a very small crystal of an organic silicate (dimensions $18 \times 8 \times 175$ μ m³) (Andrews *et al.*, 1988). It is apparent from this and other studies that many very small crystals have a large mosaic spread (Andrews, Hails, Harding & Cruickshank, 1987) or other evidence of poor ordering; this makes the measurement of reflection intensities even more difficult than would be predicted on the basis of the size and scattering power of the crystal.

Experimental

The compound, with provisional formula $[\text{FeRhCl}(\text{CO})_5\text{dppee}]$, where dppee is $\text{Ph}_2\text{PCH}(\text{=CH}_2)\text{PPh}_2$, was prepared by Dawson & Smith (1986) at Liverpool University; the largest crystal obtained, in crystallization from dichloromethane/heptane, had dimensions $320 \times 60 \times 50 \mu\text{m}^3$. Oscillation and Weissenberg photographs ($\text{Cu K}\alpha$) gave an approximate unit cell and probable space group, but the photographs were very weak and it was unlikely that our diffractometer would measure intensities satisfactorily. It seemed a good subject for a trial data collection by the Laue method.

On the SRS workstation 9.7, using components of an Arndt-Wonacott oscillation camera, Laue diffraction patterns were recorded for the above crystal, with $[201]$ parallel to the spindle, ten film packs at 18° intervals, each pack consisting of $F, F, \text{Al}, F, \text{Al}, F, \text{Al}, F, \text{Cu}, F$ where F stands for film, Al and Cu for metal foils, 200 and $38 \mu\text{m}$ thick respectively; crystal-to-film distance 64 mm, exposure time 6 s, SRS conditions 2 GeV, 158–146 mA. A sample Laue photograph is shown in Fig. 1; the reflections are substantially streaked, an indication that mosaic spread is greater than for a typical good quality crystal.

Intensity measurement

The films were scanned, $50 \times 50 \mu\text{m}$ raster, and the digitized images retained on magnetic tape. Subsequent processing used a series of programs which will shortly be fully described (Campbell *et al.*, 1988) in the stages outlined below.

Pattern prediction

The program *LGEM* on the ICL Perq computer allows quick pattern prediction and establishment of the approximate crystal orientation. *GENLAUE* (this and subsequent programs on a VAX 11/780) allows refinement of parameters to give a match between observed and predicted pattern; the match is judged first by visual examination on the terminal screen and then by the r.m.s. deviation of observed and calculated spot positions (better than 0.10 mm in this case, 0.05 mm desirable). The parameters adjusted are three angles defining crystal orientation, crystal-to-film distance, the position of X-ray beam incidence on the film, two of a^* , b^* and c^* (since the Laue pattern cannot establish absolute values), and β^* . The 'soft' limits d_{min} , λ_{min} and λ_{max} were judged by inspection of the photograph at 1.2, 0.3 and 2.1 Å.

Integration

All reflections to $2\theta_{\text{max}} = 43^\circ$ were integrated by the program *MOSLAUE*. The frame around each was octagonal, approximating to a circle, 0.75 mm across,

with background evaluated in a rim 0.05 mm outside. The actual diffraction spots are radially streaked, and up to 0.85 mm long and 0.4 mm across. The integration box was not ideal for this spot shape, but was the best available at the time.

Film-pack scaling

The program *AFSCALE* determines and applies the wavelength-dependent interfilm scale factors (as well as L_p factors). At this stage too, doublet and triplet reflections could be unscrambled (program *UNSCRAM*); the procedure uses the interfilm scale factors and the integrated intensities on successive films in the pack. These yielded, from each film pack, 300–350 reflection intensities measured as singlets, and 30–50 derived from doublet and triplet spots, with R factors (on intensity) between successive films in a pack in the range 10–15%.

Wavelength normalization and scaling and merging of all film packs

Each reflection intensity must be multiplied by a wavelength-dependent factor $1/f(\lambda)$ and a pack-scaling factor $c(i)$. Here both of these have been determined empirically, *i.e.* by internal comparisons of the same reflection or of symmetry-equivalent reflections measured at different wavelengths and/or in different film packs, using the program *LAUENORM* (Campbell *et al.*, 1988; Campbell, Habash, Helliwell & Moffat, 1986). The 3707 reflection intensities measured represent 830 unique reflections. In principle it should be possible to use the whole wavelength range, 0.3–2 Å, to

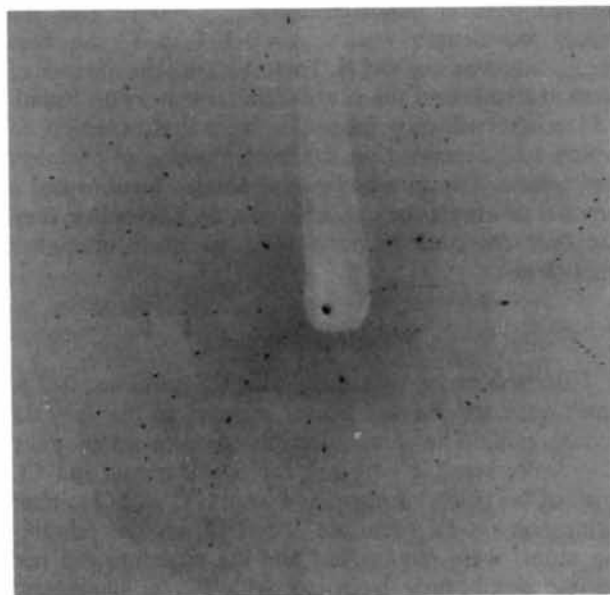


Fig. 1. Laue diffraction photograph of $\text{FeRhCl}(\text{CO})_5\text{dppee}$ — one of the set used for structure determination.

Table 1. Wavelength-normalization function, and distribution of reflection intensity measurements with respect to wavelength

In the wavelength range 0.58–0.91 Å, $f(\lambda)$ was fitted to a polynomial of order 8, and in the range 0.922–1.55 Å to one of order 6. A 14×14 matrix represents the overlaps among the 14 wavelength 'bins', i.e. the term N_{ij} is the number of reflections (or symmetry equivalent reflections) measured in both the i th and the j th wavelength bin. For the 0.58–1.55 Å data, N_{ij} varied from 1 to 55 with an average of 20.

Wavelength range (Å)	λ_{mean} (Å)	No. of intensities measured*	$f(\lambda)$
0.30–0.342	0.321	83	~0.0028†
0.342–0.385	0.364	99	~0.0042†
0.385–0.427	0.406	117	~0.0070†
0.427–0.470	0.409	132	~0.0119†
(Ag absorption edge, 0.486 Å; Rh absorption edge, 0.533 Å)			
0.580–0.621	0.601	149	0.0305
0.621–0.663	0.642	147	0.0414
0.663–0.704	0.683	136	0.0582
0.704–0.745	0.724	163	0.0822
0.745–0.786	0.766	145	0.1130
0.786–0.828	0.807	161	0.1495
0.828–0.869	0.848	175	0.1958
0.869–0.910	0.889	151	0.2703
(Br absorption edge, 0.929 Å)			
0.922–1.027	0.974	278	0.2152
1.027–1.131	1.079	179	0.3263
1.131–1.236	1.184	134	0.4670
1.236–1.341	1.288	103	0.6125
1.341–1.445	1.393	58	0.7589
1.445–1.550	1.498	34	1.0000

* After omitting 838 reflections with $|F| > 1.5\sigma(F)$; 425 measured intensities were outside the selected wavelength ranges.

† Not used in this structure refinement.

derive $f(\lambda)$, $c(i)$ and the intensities; in practice we have so far derived our most satisfactory data set by restricting the wavelength range to 0.58–1.55 Å. The internal consistency of this normalized, scaled and merged data is indicated by $R_{\text{merge}} = 0.12$ (for the whole wavelength range, $\lambda = 0.3$ –1.55 Å, the best R_{merge} achieved was 0.21). Table 1 shows the number of data available and the normalization curve $f(\lambda)$ found. 754 unique reflection intensities were thus obtained, of which 122 depended on the unscrambling of doublets and triplets. The data set lacks all axial reflections and a number of others such as $hh0$, hhh , $2h, hh$ because they are only recorded as parts of quadruplets or higher multiplets.

Structure solution

A Patterson series yielded Fe and Rh positions, 2.7 Å apart with the Fe–Rh vector parallel to the twofold screw axis. The first electron density map gave chemically sensible positions for two P atoms and Cl, three of the phenyl groups, and several C and O atoms; refinement (in $P2_1$) reached $R = 0.17$, but the remaining atoms were not evident and the structure did not deviate significantly from one with $P2_1/m$ symmetry. Therefore, solution and refinement were repeated in space group $P2_1/m$. The program *SHELX* (Sheldrick,

Table 2. Fractional coordinates and thermal parameters (Å²) with e.s.d.'s in parentheses

	x	y	z	U_{eq}		
Rh(1)	0.3970 (5)	−0.0692 (2)	0.0527 (2)	0.0758 (37)*		
P(3)	0.6245 (15)	−0.0783 (6)	0.2614 (9)	0.0726 (84)*		
Cl(5)	0.142 (6)	−0.082 (2)	−0.167 (4)	0.145 (13)		
C(1)	0.372 (7)	−0.157 (3)	0.045 (4)	0.108 (16)		
O(1)	0.366 (8)	−0.225 (3)	0.077 (5)	0.199 (20)		
C(4)	0.500 (10)	0.000	−0.062 (8)	0.148 (30)		
O(4)	0.622 (8)	0.000	−0.096 (4)	0.128 (17)		
C(10)	0.750 (7)	0.000	0.320 (4)	0.063 (15)		
C(9)	0.932 (9)	0.000	0.383 (5)	0.083 (19)		
C(11)	0.582 (4)	−0.099 (2)	0.421 (2)	0.090 (7)		
C(12)	0.419 (4)	−0.125 (2)	0.406 (2)	0.090 (6)		
C(13)	0.388 (4)	−0.146 (2)	0.529 (2)	0.090 (7)		
C(14)	0.517 (4)	−0.141 (2)	0.668 (2)	0.090 (7)		
C(15)	0.680 (4)	−0.115 (2)	0.684 (2)	0.090 (7)		
C(16)	0.713 (4)	−0.094 (2)	0.560 (2)	0.090 (7)		
C(41)	0.786 (3)	−0.138 (1)	0.251 (2)	0.069 (6)		
C(42)	0.809 (3)	−0.200 (1)	0.324 (2)	0.069 (6)		
C(43)	0.919 (3)	−0.248 (1)	0.301 (2)	0.069 (6)		
C(44)	1.007 (3)	−0.235 (1)	0.206 (2)	0.069 (6)		
C(45)	0.984 (3)	−0.173 (1)	0.133 (2)	0.069 (6)		
C(46)	0.874 (3)	−0.125 (1)	0.156 (2)	0.069 (6)		
C(3)	0.258 (14)	0.000	0.126 (7)	0.145 (32)		
O(3)	0.138 (8)	0.000	0.176 (5)	0.141 (19)		
C(2)	0.236 (†)	−0.083 (†)	−0.167 (†)	0.197 (58)		
O(2)	0.126 (20)	−0.077 (7)	−0.272 (10)	0.160 (4)		
<i>U</i> or U_{11} U_{22} U_{33} U_{23} U_{13} U_{12}						
Rh(1)	0.071 (4)	0.085 (4)	0.072 (4)	−0.004 (3)	0.005 (2)	−0.003 (3)
P(3)	0.085 (9)	0.062 (8)	0.072 (9)	0.010 (7)	0.016 (6)	−0.005 (7)

* Two atoms had anisotropic thermal vibration parameters.

† This atom was not refined in the last cycle.

1976) was used throughout; the metal atoms were treated as Rh with a site occupancy of 0.80 (equivalent to the mean of Fe and Rh); in the refinement, benzene rings were given ideal geometry, and P–C and C–O bond lengths were restrained to take values close to those expected. Initially, refinement led to U values very close to zero, a few being slightly negative; a factor, $\exp(-4\sin^2\theta/\lambda^2)$, was applied to all observed F 's after which the physically much more reasonable (relative) U values in Table 2 were obtained. The need for this 'damping' factor is not fully understood, but it is probably due to the neglect of absorption effects; a program to calculate and apply absorption corrections (before the normalization stage) will be written in due course.

At present R is 0.14 for 553 reflections with $I > 4\sigma(I)$ and the proposed molecular structure is shown in Fig. 2; 122 reflection intensities derived from doublet and triplet spots in the Laue diffraction pattern appear to be less accurate and have not been used in the refinement.

Results and discussion

Atom parameters are listed in Table 2,* selected bond lengths in Table 3, and the structure is illustrated in Fig. 2. By analogy with the recently reported structure of the

* Lists of observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44557 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

dppm (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) analogue of this compound (Jacobsen, Shaw & Thornton-Pett, 1986), we assign the Cl atom to be bonded to Rh rather than to Fe.

This completely new method of data measurement has clearly been sufficiently satisfactory to show that the molecule contains Fe and Rh joined by a bond of *ca* 2.7 Å, bridged by a dppee group, and with Cl attached to one of the metal atoms (and *trans* to P). The general validity of the structure determination is confirmed by the agreement of the *M*–P and *M*–Cl bond lengths with those found in the dppm analogue and similar structures; these distances were not in any way restrained in our refinement. The carbonyl groups C(3), O(3), C(4), O(4), treated as bridging here, could equally well be ‘semi-bridging’ (*i.e.* nearer to one metal atom than the other) and thus in complete agreement with the results of Jacobsen *et al.* (1986) and with the observed infra-red spectrum (Dawson & Smith, 1986). The disorder, the low resolution, and the lack of accuracy in the intensity measurements have made it impossible to locate these carbonyl groups, and C(2), O(2) with complete certainty – for all these atoms, if they are not in the pseudo-mirror plane the site-occupancy factor is 0.5.

There is room for much improvement in the accuracy of these intensity measurements and work is already in progress at Daresbury and Liverpool to this end. Software being developed includes ‘profile fitting’ at the intensity integration stage and a more suitable box size

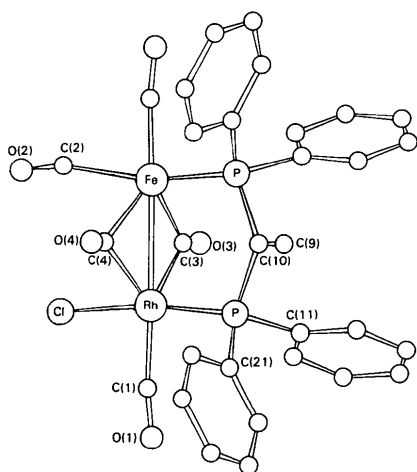


Fig. 2. Proposed molecular structure. A crystallographic mirror plane passes through C(3), O(3), C(4), O(4) and C(9), C(10); the molecular arrangement must be disordered with the Rh atoms randomly above and below this mirror plane. The present structure determination cannot show whether Cl is bonded to Rh or Fe; an Rh–Cl bond is expected, by analogy with the structure determined by Jacobsen, Shaw & Thornton-Pett (1986). The location of the carbonyl groups is not precise. [Drawing by PLUTO (Motherwell, 1976).]

Table 3. Bond lengths (Å)

Rh–Fe	2.74 (1)	Rh–C(1)	1.74 (6)
Rh–P	2.22 (1)	Rh–C(3)	2.08 (8)
Rh–Cl	2.41 (5)	Rh–C(4)	2.14 (9)

for the integration (Greenough, 1987). Further exploration of the wavelength normalization procedure should allow measurement of a much larger number of reflections from one film. For most purposes, the overlapping of harmonic reflections is not nearly as serious a problem as was once thought; Cruickshank, Helliwell & Moffat (1987) have shown that only 13% of the total number of unique reflections are experimentally inaccessible in a well designed Laue experiment (but, for direct-methods solution of a difficult structure the absence of this group of simple low-order reflections could be a serious disadvantage).

Laue diffraction patterns have considerable potential for new types of study in chemical crystallography. Their advantage lies in the very short exposure times and the substantial proportion of the reciprocal lattice that can be recorded in one or a few exposures (here for example, one, three, or six film packs can cover 40, 70, or 90% of the unique volume; or if $\lambda_{\min} = 0.3$ Å can be used, two film packs can give 70%, three 85%). One possible application is in structure determination from very small single crystals. Data can be recorded in very reasonable times – *e.g.* 40 s exposures for a microcrystal of an organic silicate of dimensions $12 \times 4 \times 125 \mu\text{m}^3$. High background intensity makes these more difficult, though by no means impossible to process. Many small crystals, from preparations which have failed to yield larger crystals, appear to have substantial mosaic spread to which the Laue geometry is particularly sensitive; the spots become radial streaks, which are more difficult to integrate and are more likely to overlap. For the organometallic crystal studied here, the low resolution and the disorder have both limited the accuracy of the structure determination; this was the largest and the best looking crystal from a batch and it is a salutary reminder that when a preparation yields only very small crystals they may often be of rather poor quality.

Other applications will be in the study of structural changes as a function of time. This has already been used to great effect in a kinetic study of the enzyme phosphorylase interacting with a substrate analogue; ‘snapshots’ of the structure were taken at intervals of 3–5 min (Hajdu *et al.*, 1987). That study involved difference procedures, *i.e.* the change in each measured $|F(hkl)|$ from that in the initial structure was used to calculate the difference electron density map; the present study shows that a complete structure can be established from Laue data recorded in a few seconds. A series of ‘snapshots’ of the structure could be obtained at intervals of 2–3 min or less.

We acknowledge financial support from SERC; the equipment was initially set up by Dr J. R. Helliwell, and we are grateful to him for this and for many useful discussions, and to Miss J. A. Clucas and Dr E. Towns for assistance in the taking of photographs.

References

- ANDREWS, S. J., HAILS, J. E., HARDING, M. M. & CRUICKSHANK, D. W. J. (1987). *Acta Cryst.* **A43**, 70–73.
- ANDREWS, S. J., PAPIZ, M. Z., MCMEEKING, R., BLAKE, A. J., LOWE, B. M., FRANKLIN, K. R., HELLIWELL, J. R. & HARDING, M. M. (1988). *Acta Cryst.* **B44**, 73–77.
- CAMPBELL, J. W., CLIFTON, I., CRUICKSHANK, D. W. J., ELDER, M., GREENOUGH, T. J., HABASH, J., HARDING, M. M., HELLIWELL, J. R., MACHIN, P. A., PAPIZ, M. Z. & ZUREK, S. (1988). *Acta Cryst.* In preparation.
- CAMPBELL, J. W., HABASH, J., HELLIWELL, J. R. & MOFFAT, K. (1986). *Inf. Q. Protein Crystallogr.* **18**, 23–32.
- CRUICKSHANK, D. W. J., HELLIWELL, J. R. & MOFFAT, K. (1987). *Acta Cryst.* **A43**, 656–674.
- DAWSON, R. H. & SMITH, A. K. (1986). *J. Organomet. Chem.* **309**, C56–C58.
- GREENOUGH, T. J. (1987). Personal communication.
- HAJDU, J., MACHIN, P. A., CAMPBELL, J. W., GREENOUGH, T. J., CLIFTON, I. J., ZUREK, S., GOVER, S., JOHNSON, L. N. & ELDER, M. (1987). *Nature (London)*, **329**, 178–181.
- HELLIWELL, J. R., MACHIN, P. A. & PAPIZ, M. Z. (1987). Editors. *Computational Aspects of Protein Crystal Data Analysis*, Proceedings of a Daresbury Study Weekend (January 1987). Warrington, UK: SERC Daresbury Laboratory.
- JACOBSEN, G. B., SHAW, B. L. & THORNTON-PETT, M. (1986). *J. Chem. Soc. Chem. Commun.* pp. 13–15.
- MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, UK.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, UK.
- WOOD, I. G., THOMPSON, P. & MATTHEWMAN, J. C. (1983). *Acta Cryst.* **B39**, 543–547.

Acta Cryst. (1988). **B44**, 146–151

Formation and Structure of a 2,3,9,10,16,17,23,24-Octacyanophthalocyanine–Potassium Complex in Thin Film

BY MICHIO ASHIDA, YASUKIYO UEDA AND HISAO YANAGI

Faculty of Engineering, Kobe University, Rokko, Kobe 657, Japan

NATSU UYEDA AND YOSHINORI FUJIYOSHI

Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan

AND J. R. FRYER

Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland

(Received 17 May 1987; accepted 23 November 1987)

Abstract

Dipotassium 2,3,9,10,16,17,23,24-octacyanophthalocyaninate [$K_2Pc(CN)_8$] has been synthesized as a thin film by reaction of tetracyanobenzene with KCl at 623 K in an evacuated sealed tube. The film was produced on a cleavage face of KCl crystals and is composed of slender tentacle-like crystallites. The molecular image of the crystal is observed by high-resolution electron microscopy and indicates that the crystal is an $H_2Pc(CN)_8-K$ complex. The crystal structure of the complex is determined from electron diffraction patterns and high-resolution electron micrographs. The unit-cell dimensions are $a = b = 1.57$ nm, $c = 0.674$ nm, and the space group is $P4/mcc$. The molecular arrangement in the crystal is determined directly from the molecular images. The planar molecules of $H_2Pc(CN)_8$ are in a layer normal to the c axis and are located at the corners of the square lattice. The

molecules are packed along the c axis and rotate alternately from the a axis by 27.4° . K atoms are surrounded at the center of the square by eight nitrile groups from octacyanophthalocyanine molecules in two successive layers. The crystal structure proposed from the molecular image is confirmed by comparison with a computer-simulated image.

Introduction

Since the molecular image of chlorinated copper phthalocyanine was observed by Uyeda, Kobayashi, Suito, Harada & Watanabe (1972), high-resolution electron microscopy (HREM) has been used, not only for the direct imaging of organic crystal structures (Kobayashi, Fujiyoshi & Uyeda, 1982), but also for determining molecular structure at the atomic level (Uyeda & Ishizuka, 1974; Uyeda, Kobayashi,