

the same chain (Figs. 1 and 2); however the second $\text{H}_2\text{O}(2)$ hydrogen, $\text{H}(22)$, links pairs of different chains along **a**, from $\text{O}(1)$ to $\text{O}(2^{\text{iv}})$ through a ClO_2^- anion: $\text{O}(1^{\text{iv}})-\text{Cl}^{\text{iv}}-\text{O}(2^{\text{iv}})$ in Fig. 2. Thus the number of connexions along **a**, higher than along **b**, explains the fact that the only good cleavage follows $\{010\}$.

Each of the six Na-coordinating oxygens is involved in a hydrogen bond with one oxygen of the neighbouring Na octahedra of the same chain, so reinforcing the link obtained by edge-sharing. The vertices of the shared edge $\text{H}_2\text{O}(3)-\text{H}_2\text{O}(3^*)$ form two H-bonds, in opposite directions, with the $\text{O}(1)$'s of the neighbouring Na^+ ions; a similar pair of H-bonds starts from the shared edge $\text{H}_2\text{O}(2)-\text{H}_2\text{O}(2')$ towards two $\text{H}_2\text{O}(1)$'s.

If ionic strengths of +0.25 and +0.75 are assigned, as contributions of each hydrogen, respectively to the farthest and the nearest oxygen involved in a hydrogen bond, the balance of electrostatic valences looks satisfactory for all oxygens except $\text{O}(2)$, which has an excess positive charge of +0.25; three different hydrogen atoms surround this oxygen.

Table 6 shows that each of the five oxygens in this structure exhibits a roughly tetrahedral environment, if all kinds of chemical interactions are taken into account, *i.e.* ionic, covalent and hydrogen-bonding. $\text{O}(2)$ and $\text{H}_2\text{O}(1)$ behave similarly in that both are involved in three different hydrogen bonds of similar length (the obvious difference between them is that $\text{O}(2)$ is never the nearest oxygen to any hydrogen).

The amount and the anisotropy of the thermal mo-

tion are largest for the ClO_2^- anion (Tables 3 and 4); the longest axes of the $\text{O}(1)$ and $\text{O}(2)$ ellipsoids lie roughly in the (100) plane, normal to the respective Cl-O bonds; the longest axis of the Cl ellipsoid forms an angle of 60° with **a** and lies roughly in the plane normal to (100), bisecting the $\text{O}(1)-\text{Cl}-\text{O}(2)$ angle.

There are no abnormally short non-bonding distances.

References

- ARTINI, E. (1922). *Atti Accad. Nazl. Lincei Rend. Classe Sci. Fis. Mat. Nat.* **31**, 65-67.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- CODA, A. (1959). *La struttura del clorito sodico triidrato*. Thesis, Univ. di Pavia.
- CODA, A., GIUSEPPETTI, G. & TADINI, C. (1965). *Period. Miner.* **34**, 27-47.
- CODA, A., GIUSEPPETTI, G. & TAZZOLI, V. (1968). *Annual Meeting, Chimica Inorganica*, Padova, pp. 161-166.
- COOPER, J. & MARSH, R. (1961). *Acta Cryst.* **14**, 202-203.
- FERRARIS, G. & FRANCHINI-ANGELA, M. (1972). *Acta Cryst.* **B28**, 3572-3583.
- GILLESPIE, R. B., SPARKS, R. A. & TRUEBLOOD, K. N. (1959). *Acta Cryst.* **12**, 867-872.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609-610.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040-1044.
- RIGANTI, V. (1959). *Gazz. Chim. Ital.* **89**, 2275-2279.

Acta Cryst. (1975). **B31**, 1037

The Structure of $\text{K}_3\text{RhCl}_6 \cdot \text{H}_2\text{O}$; a Comparison of Two Independent X-ray Structure Determinations

BY PETER MURRAY-RUST AND JUDITH MURRAY-RUST

Department of Chemistry, University of Stirling, Stirling, Scotland

(Received 16 October 1974; accepted 30 November 1974)

Two independent structure analyses of $\text{K}_3\text{RhCl}_6 \cdot \text{H}_2\text{O}$ are compared. The first is derived from data collected on a four-circle diffractometer [Cresswell, Fergusson, Penfold & Scaife. *J. Chem. Soc. Dalton*, (1972), pp. 254-262] which led to a final *R* of 0.072. The authors collected data on a linear diffractometer for two rotation axes and the final scaled and merged data led to a structure giving a final *R* of 0.046. The methods and extent of data collection and their treatment are compared. There was no significant difference in the cell dimensions and the derived atomic positions are shown to be identical within the standard deviations estimated by both groups. The r.m.s. amplitudes of vibration of the atoms differ significantly between the two studies and this is attributed to absorption effects. Final atomic and thermal parameters for the authors' investigation are tabulated.

Introduction

Although there has been considerable interest in the comparison of crystallographic data for a particular crystal collected by different groups on different in-

struments, this is often undertaken as part of a programme where care is taken to standardize experimental conditions, especially in the selection of the crystal. An example is the recent study published by the International Union of Crystallography Commission on

Crystallographic Apparatus (Abrahams, Hamilton & Mathieson, 1970). It is relatively infrequently that a structure is determined simultaneously by two different groups without either realizing that the data collection and structure refinement were being duplicated (an

example being Prout, Tickle & Wright (1973), where photographic and diffractometric data were unintentionally collected simultaneously for the same compound). We have recently determined the structure of $K_3RhCl_6 \cdot H_2O$ as part of a study of rhodium-chlorine

Table 1. *Comparison of crystal data, methods of data collection, structure refinement and other details of the two investigations*

The authors' study is represented by entries in the MRMR column and those for Cresswell, Fergusson, Penfold & Scaife (1972) under CFPS. Where the information is identical for both, it is located in the middle column.

	MRMR		CFPS
Crystal data			
Space group		<i>Pbcn</i>	
Unit-cell constants (Å) with standard deviations			
<i>a</i>	12.40 (1)		12.368 (9)
<i>b</i>	15.65 (2)		15.655 (6)
<i>c</i>	12.05 (1)		12.041 (10)
Cell constants determined		By diffractometer	
Crystal size (mm)	0.4 × 0.3 × 0.3		Sphere (diameter 0.2)
Absorption coefficient (cm ⁻¹)		38.4	
Data collection			
Radiation		Mo <i>K</i> α	
Filter		Zr	
Diffraction geometry	Weissenberg		Four-circle
Instrument	Hilger-Watts linear		Hilger-Watts Y 290
Method of use	Equi-inclination		Bisecting geometry
Scan mode	ω (fixed <i>Y</i>)		θ-2θ
Range of data collected	Layers 0 <i>kl</i> to 9 <i>kl</i> (2805 data and <i>h0l</i> to <i>h10l</i> (2569 data). All indices positive and <i>Y</i> _{max} = 55°.		All positive <i>h, k, l</i> up to θ _{max}
Multiple observation of reflexions	1761 data common to both of the above sets		None recorded
θ _{max} (°)	34		23
Merging <i>R</i> for multiply observed reflexions*	0.044		None
Layer scale factors	Obtained by comparison of reflexions common to both data sets		None
Total number of independent reflexions observed	3613		1472
E.s.d. of intensity [σ(<i>I</i>)]	(scan + background) ^{1/2}		[scan + background + 0.03 (integrated count) ²] ^{1/2}
Rejection criterion		<i>I</i> < 3σ(<i>I</i>)	
Reflexions used in refinement	2042		920
Treatment of data and refinement of structure			
Extinction correction		Not made	
Absorption correction	Not made		Spherical correction
Structure solution		Patterson and Fourier methods	
Refinement method		Full-matrix least-squares	
Weighting scheme (<i>w</i>)	1.0 if <i>F</i> _o ≤ 10.0, otherwise [1 + (<i>F</i> _o - 10) ² /225] ⁻¹		4 <i>F</i> _o ² /σ(<i>F</i> _o) ²
Scattering factors		<i>International Tables for X-ray Crystallography</i> (1968)	
Anomalous dispersion	Not corrected		Correction made
Standard deviations of parameters, σ(<i>p</i>)		Estimated from inverse normal matrix	
Thermal parameters	All atoms anisotropic		All atoms except oxygen anisotropic
Hydrogen atoms		Not located	
<i>R</i> †	0.046		0.072
<i>R</i> '†	0.053		0.052
Programs used	Powell & Griffiths (1969)		Reference 17 of CFPS

* $R = \sum |F_1 - F_2| / \sum \frac{1}{2} |F_1 + F_2|$.

† Residuals are given by: $R = (\sum ||F_o| - |F_c|| / \sum |F_o|)$, $R' = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$.

Table 2. Positional and thermal parameters ($\times 10^4$) obtained in the present study (MRMR), with e.s.d.'s in parentheses

The expression for the anisotropic temperature factor is given by $\exp(-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl])$.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	2147.1 (0.4)	1289 (0.3)	575.3 (0.4)	29 (0.3)	16 (0.2)	27 (0.3)	-4 (0.2)	3 (0.3)	0 (0.2)
Cl(1)	3469 (2)	1336 (1)	1991 (2)	41 (1)	27 (1)	39 (1)	-1 (1)	-10 (1)	0 (1)
Cl(2)	782 (2)	1281 (1)	-775 (2)	38 (1)	23 (1)	35 (1)	-6 (1)	5 (1)	-2 (1)
Cl(3)	2864 (2)	2554 (1)	-196 (2)	48 (1)	19 (1)	43 (1)	-13 (1)	-6 (1)	-7 (1)
Cl(4)	1415 (2)	46 (1)	1339 (2)	40 (1)	16 (1)	38 (1)	-7 (1)	3 (1)	5 (1)
Cl(5)	980 (2)	2066 (1)	1681 (2)	42 (1)	19 (1)	41 (1)	-2 (1)	14 (1)	-6 (1)
Cl(6)	3278 (2)	449 (1)	-576 (2)	43 (1)	25 (1)	45 (1)	3 (1)	-13 (1)	7 (1)
K(1)	1085 (1)	756 (1)	3840 (2)	50 (1)	18 (1)	39 (1)	0 (1)	-4 (1)	0 (1)
K(2)	2686 (1)	3329 (1)	2337 (1)	101 (2)	25 (1)	47 (1)	-19 (1)	-26 (1)	1 (1)
K(3)	4638 (1)	1643 (2)	4727 (2)	57 (2)	41 (1)	96 (2)	13 (1)	25 (1)	-7 (1)
O	902 (7)	4303 (5)	1643 (8)	77 (6)	29 (3)	108 (8)	-4 (4)	2 (6)	3 (4)

bonds and only when the structure had been completely solved was an independent study published by Cresswell, Fergusson, Penfold & Scaife (1972), hereinafter referred to as CFPS. We feel that comparison of our results (hereinafter MRMR) with those of CFPS show several interesting points and give some indication of the precision and accuracy available from diffractometric data.

Collection and treatment of data

The details of the two different crystals, the methods used to collect data and to refine the structure and other relevant information are given in Table 1. Table 2 lists our final positional and thermal parameters in the normal fashion, with standard deviations estimated from the inverted normal matrix. CFPS did not list their thermal parameters, giving instead the r.m.s. amplitudes of vibration of the atoms along the axes of

the thermal ellipsoids. As they did not list the direction cosines of these axes we are unable to reconstruct their original anisotropic temperature factors. For comparison of thermal parameters we have calculated the r.m.s. amplitudes given by our data and these are listed in Table 3.*

Table 3. Root-mean-square vibrational amplitudes (\AA) of atoms along the principal axes of the thermal ellipsoids ($\times 10^3$)

	Axis (1)	Axis (2)	Axis (3)
Rh	127	140	161
Cl(1)	147	182	197
Cl(2)	147	157	191
Cl(3)	111	187	213
Cl(4)	118	174	185
Cl(5)	135	158	208
Cl(6)	140	186	209
K(1)	160	167	199
K(2)	144	178	303
K(3)	160	244	284

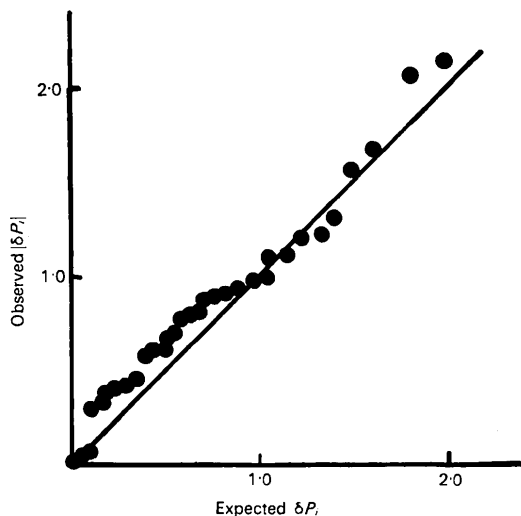


Fig. 1. Half-normal probability plot for the differences between the positional parameters of MRMR and CFPS. The quantity 'observed δp_i ' is given by $[|p_i(\text{MRMR}) - p_i(\text{CFPS})|] / [\sigma^2 p_i(\text{MRMR}) + \sigma^2 p_i(\text{CFPS})]^{1/2}$, and the 'expected δp_i ' as in Abrahams & Keve (1971). The straight line has unit slope and zero intercept.

Discussion

The two analyses allow a comparison between the different types of geometry used in the diffractometers and should show in particular whether they result in serious discrepancy between the results obtained. It is seen that the cell dimensions, while less accurately determined on the linear diffractometer, agree within the standard deviations estimated by both groups. Equi-inclination Weissenberg geometry is known to give rise under certain conditions to systematic errors (not present in other methods) in the measurement of intensities (Arndt & Willis, 1966). When these errors occur their effect will be transmitted to the derived parameters and their e.s.d.'s. The present comparison might be expected to show whether there are differences between the parameters derived from the different data

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30798 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

sets and whether a satisfactory account of these is given by the e.s.d.'s.

The e.s.d.'s of MRMR are approximately half those of CFPS, probably because of the larger number of reflexions used by MRMR, and their multiple measurement of many reflexions. This suggests that had CFPS collected an equivalently large data set the e.s.d.'s of both sets of parameters would be about equal. Consequently it is important to investigate whether the differences between the parameter sets are consistent with the e.s.d.'s, and only if these are larger than expected can a systematic difference between the methods be suspected. Apart from the geometry of the diffractometers, the main difference in the data was CFPS's use of an absorption correction; we might thus expect to see some significant differences in parameters linked to this effect.

Fig. 1 shows a half-normal probability plot (Abrahams & Keve, 1971) for the differences in positional parameters against expected values. It is essentially a straight line of slope 1.0 passing through the origin and suggests that the differences between the structures in their atomic positions are well described by the e.s.d.'s. In contrast Fig. 2(a) shows the normal probability plot for the differences between the r.m.s. amplitudes of vibration, where not only are these differences larger than expected from the e.s.d.'s, but show a systematic difference, $\sqrt{U_i^2}$ for MRMR always being lower than the corresponding value determined by CFPS. Regression analysis (coefficient=0.976) showed a good linear relationship where $\sqrt{U_i^2}$ (MRMR) = $0.994[\sqrt{U_i^2}(\text{CFPS})] - 0.012 \text{ \AA}$. The most likely explanation of this is that MRMR did not correct for absorption and since this effect is strongest for low values of θ , the apparent temperature factors will be too low. If the equation above is used to calculate 'corrected' values of $\sqrt{U_i^2}$ (MRMR) these agree with $\sqrt{U_i^2}$ (CFPS) within the errors suggested by the e.s.d.'s [Fig. 2(b)]. It should be noted that the effect is not very large, the r.m.s. amplitudes of MRMR being on average 6% too low. In conclusion, it appears that for routine structure determinations of moderate accuracy, the linear diffractometer (Arndt & Phillips, 1961) can give results equivalent to those obtained by the use of a four-circle machine.

We thank P. F. Caldwell for making the crystals.

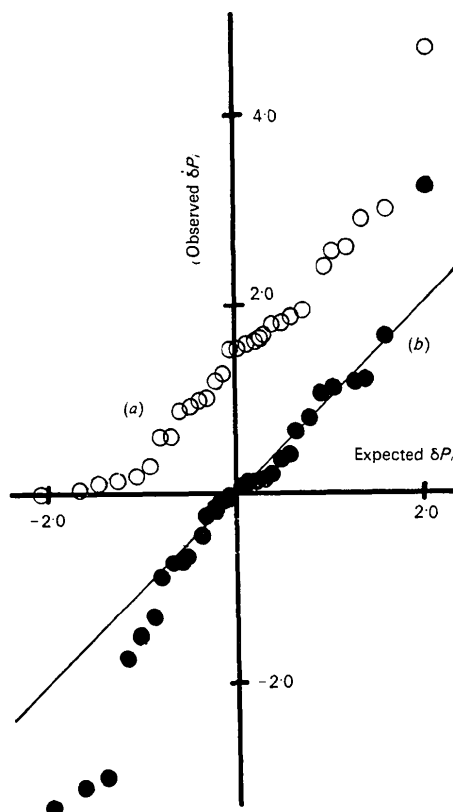


Fig. 2. (a) Normal probability plot for the difference between r.m.s. amplitudes of MRMR and CFPS. (b) Normal probability plot for the same after correction of the MRMR values as described in the text. The straight line is as in Fig. 1.

References

- ABRAHAM, S. C., HAMILTON, W. C. & MATHIESON, A. MCL. (1970). *Acta Cryst.* A26, 1-18.
 ABRAHAM, S. C. & KEVE, E. T. (1971). *Acta Cryst.* A27, 157-165.
 ARNDT, U. W. & PHILLIPS, D. C. (1961). *Acta Cryst.* 14, 807-818.
 ARNDT, U. W. & WILLIS, B. T. M. (1966). *Single Crystal Diffraction*, Chap. 9. Cambridge Univ. Press.
 CRESSWELL, P. J., FERGUSON, J. E., PENFOLD, B. R. & SCAIFE, D. E. (1972). *J. Chem. Soc. Dalton*, pp. 254-262.
International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.
 POWELL, M. T. G. & GRIFFITHS, A. (1969). CRYSTAL 69, Portsmouth Polytechnic.
 PROUT, C. K., TICKLE, I. J. & WRIGHT, J. D. (1973). *J. Chem. Soc. Perkin II*, pp. 528-530.