

Angular distortions from the ideal octahedral arrangement are minor (Table 5) and do not seem to follow any particular pattern. The planes defined by the six nitro groups of the two octahedra are twisted with respect to those defined by four N atoms lying in a plane. Thus the nitro group O(11)–N(1)–O(12) (plane *D*) is twisted 51.8, 80.1 and 40.5° from the planes N(1), N(3), N(6), N(5) (*A*), N(2), N(3), N(4), N(6) (*B*) and N(1), N(2), N(5), N(4) (*C*) respectively. The nitro groups themselves form angles of 60.4, 58.3 and 76.2° with each other in one octahedron and 57.5, 57.0 and 67.5° in the second.

Siebert (1978) reported that the solubility of the facial isomer in various solvents is much lower than that of the meridional. This might be due to intra- and intermolecular hydrogen bonding. This could be confirmed by some short intra- and intermolecular N(ammonia)⋯O(nitro) distances ranging from 2.7–3.0 Å (intramolecular) and 3.0–3.3 Å (intermolecular) respectively. These data fall well within the range given for O–H–N interactions (Wells, 1975). The argument for hydrogen bonding is also supported by relatively short O⋯H distances, the shortest being

1.7 Å (intramolecular) and 2.2 Å (intermolecular) respectively.

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X-ray Structure of Ammonium Perchlorate.

I. X-ray Data Collection and Estimation of Variances of the Intensities

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Abstract

X-ray diffraction data have been collected at 295 K for a single crystal of ammonium perchlorate, NH₄ClO₄. Intensities for 5560 reflexions, excluding test reflexions, were recorded on a Stoe–Philips four-circle diffractometer up to $\sin \theta/\lambda = 0.86 \text{ \AA}^{-1}$. On average, five symmetry-related reflexions within a form were measured on the orthorhombic crystal, space group *Pnma*. Variances for the observed intensities were calculated from Poisson counting statistics together with the information obtained from the repeated recording of twelve test reflexions. An analysis of the scatter observed among symmetry-related reflexions after absorption correction gave no indication of anisotropic systematic errors in the data set. It suggested, moreover, that the estimation of the

variances was reasonable. The agreement among symmetry-related reflexions, $R_w = [\sum w(F_o^2 - \bar{F}_o^2)^2 / \sum wF_o^4]^{1/2}$, was 0.018.

Introduction

In an X-ray redetermination of the crystal structure of ammonium perchlorate, Peyronel & Pignedoli (1975) described the structure in terms of the non-centrosymmetric space group *Pna2₁*. This result was in conflict with earlier reported two-dimensional (Smith & Levy, 1962) and three-dimensional (Choi, Prask & Prince, 1974) neutron diffraction studies, in which the structure was reported to crystallize in the centrosymmetric space group *Pnma*.

Peyronel & Pignedoli's result indicated that ammonium perchlorate might have interesting physical properties. We decided to study this material further, with the aim of relating the absolute atomic arrangement to the polar properties by means of anomalous-scattering techniques. In order to create a solid experimental basis for this study, we decided to recollect a carefully measured set of X-ray intensities. Accurate measurement of integrated intensities together with estimates of the variances are especially important in such applications as determination of the absolute atomic arrangement by anomalous dispersion or in electron density studies. The accurate measurement of structure factors and the estimation of their errors have been the subject of many papers: see, for example, Arndt & Mathieson (1969), Abrahams (1974) and Hope (1975).

It was found later that physical tests for piezo- and pyro-electricity on crystals grown in Uppsala gave no indication of acentricity. The same was true for crystals grown at Bell Laboratories, Murray Hill, where the material was also tested for second harmonic generation which was found to be less than 3×10^{-5} of that of quartz (Abrahams, 1976). We can therefore conclude that these crystals provide no physical evidence for the assignment of the point group $mm2$.

In a re-refinement based on the X-ray data of Peyronel & Pignedoli (1975), Choi, Prask & Prince (1976) have shown that the structure can be refined successfully in space group $Pnma$. At this stage, when it became clear that the crystals could not possess any polar properties, the data collection was almost complete. The original aim to relate these properties to the absolute atomic arrangement was abandoned. However, we still found it of interest to analyse our X-ray data further, particularly with the intention of making an *a priori* estimate of the variances of the observed intensities to be used for weighting purposes in the least-squares refinements.

The e.s.d.'s in the derived parameters will be calculated correctly only if the least-squares weights are correctly estimated. A weighting formula often used is $w^{-1} = \sigma_c^2(F_o^2) + k^2 F_o^4$, where σ_c^2 is based on Poisson counting statistics and k is a constant typically 0.01–0.05. If this formula is used, k must not be modified in the refinements to give a better weighting analysis. It appears to us that such a change of k or the use of a

weighting formula, where the weight is a function of $\Delta F = (F_o - F_c)$, is totally unjustifiable (e.g. Nielsen, 1977). The discrepancy ΔF is, in most cases, likely to be associated with inadequacies in the model and not just with errors in the observed data. Using a somewhat pointed formulation, a weighting formula based on ΔF would tend to fit the observed data to the assumed model by changing their weights rather than fit the model to the observed data.

Crystal data

Ammonium perchlorate, NH_4ClO_4 , FW 117.49. Orthorhombic, $a = 9.2250$ (3), $b = 5.8154$ (3), $c = 7.4560$ (3) Å, $V = 400.00$ Å³, $Z = 4$, $D_x = 1.951$, $D_m = 1.95$ Mg m⁻³, $F(000) = 240$, $\mu(\text{Mo } K\alpha) = 0.828$ mm⁻¹. Space group $Pnma$.

Experimental

Crystals of ammonium perchlorate were grown from an aqueous solution of commercial NH_4ClO_4 . The cell dimensions were determined by least-squares refinement from the measured θ values of 17 reflexions recorded on powder photographs taken with a Guinier–Hägg focusing camera at room temperature, monochromatized Cr $K\alpha_1$ radiation ($\lambda = 2.289753$ Å) and CoP_3 ($a = 7.707780$ Å) as an internal standard.

The intensities were collected at room temperature on a Stoe–Philips four-circle diffractometer, controlled by a PDP8/I computer, with graphite-monochromatized Mo $K\alpha$ radiation and an ω – 2θ scan mode. A small crystal ($0.15 \times 0.15 \times 0.10$ mm) was chosen for the data collection to give low absorption and, more importantly, to maintain the crystal bathed in the narrow homogeneous area of the X-ray beam.

All equivalent reflexions were measured in the interval $0 < \sin \theta/\lambda < 0.6$ Å⁻¹, whereas the set of reflexions in the interval $0.6 < \sin \theta/\lambda < 0.86$ Å⁻¹ was somewhat reduced due to physical limitations of the diffractometer. 5560 reflexions were measured (excluding test reflexions).

The importance of choosing a large number of test reflexions has been stressed (e.g. Abrahams, 1973), but

Table 1. Contributions to the variance of I^0

Intensity	500	1000	5000	33 000	280 000		
$K^2 \sigma_c^2/I^0^2$	382	110	13.0	2.0	3.6	$\times 10^{-5}$	
p^2		2.9×10^{-5} for all reflexions					
Time (arbitrary units)	0	1310	2750	4075	5510	6945	7725
$S^2(K)/K^2$	0	0.2	0.7	4.6	8.2	12.6	15.3 $\times 10^{-5}$

these recommendations seem to be seldom followed. In the present case, twelve test reflexions were monitored at regular intervals. The strongest reflexion in the data set was chosen as one of the test reflexions. This strong reflexion showed a small increase (2%) during the first ten days of data collection, indicating a change in secondary extinction. When an increase was no longer observed, all (36) strong reflexions were remeasured.

The intensities of the test reflexions started to decrease after about one third of the intensities had been collected. The decrease was uniform over all test reflexions, except for the extinction-affected test reflexion, where the decrease was only 20% of that of the other reflexions. A plot of the total integrated intensity of a test reflexion *versus* time is shown in Fig. 1. The intensities of the test reflexions had decreased by about 6% by the end of the experiment. A scaling function K was determined as the average of the individual scaling functions k_i for the different test reflexions (excluding the extinction test reflexion). K consists of two line segments with slopes $-0.060(100) \times 10^{-3}$ and $-1.154(170) \times 10^{-3}$, respectively (Fig. 1). The observed intensities of all reflexions were brought to a common scale with the overall scaling function, K .

The variance σ_c^2 of the measured intensity arising from counting statistics is readily obtained from the experiment. However, there are other random errors affecting the intensities in addition to Poisson statistics (Abrahams, 1969). These errors may be assessed by repetition of the measurement on the same Bragg reflexion or, less good, on symmetry-related reflexions. Symmetry-related reflexions may be affected by anisotropic systematic errors (which may later be corrected

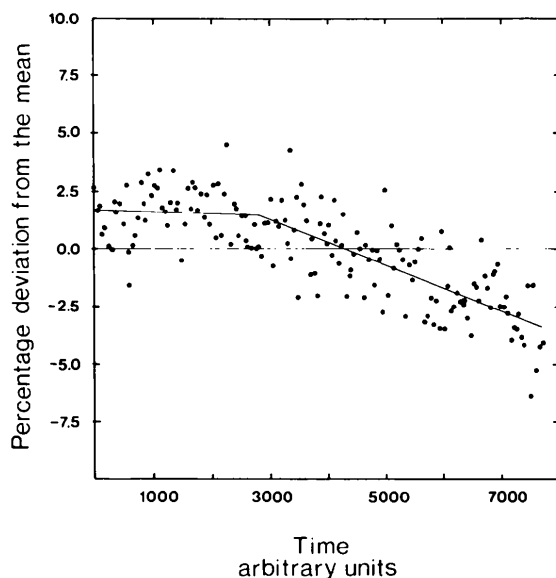


Fig. 1. The percentage deviation of the 006 test reflexion from its average intensity *versus* elapsed time. Time is given in arbitrary units.

for), and the scatter observed may then not be related to random errors alone.

The twelve test reflexions measured in the present experiment were used to estimate this addition to σ_c^2 following a procedure given by McCandlish, Stout & Andrews (1975), where it is assumed that the variance of the scaled intensity I^0 is of the form

$$\sigma^2(I^0) = K^2 \sigma_c^2(I_0) + K^2 P^2 I_0^2 + S^2(K) I_0^2 \quad (1)$$

The instability constant P was determined for every test reflexion from the observed scatter in this reflexion about its scaling function k_i . The average value of P , 0.0054 (14), was then used for all other reflexions. The scaling function K is the average of individual scaling functions k_i . The uncertainty, $S^2(K)$, of K then gives a time-dependent contribution to the variance of the scaled intensity. Consider the relative error

$$\frac{\sigma(I^0)}{I^0} = \left[\frac{K^2 \sigma_c^2}{I_0^2} + P^2 + \frac{S^2(K)}{K^2} \right]^{1/2}$$

The three terms on the right hand side, *i.e.* the contributions to the total variance from counting statistics, instability and uncertainty in the scaling function, are compared in Table 1. The first term is a function of reflexion intensity and scaling function K , the second term is constant for all reflexions and the third term is a function of K and variance of K (*i.e.* X-ray exposure time). In the present case, the variations in k_i were very small. It is seen from the table that the counting statistics term is by far the most important for all but the strongest reflexions. (Only 9% of the reflexions had an intensity exceeding 5000.) The contribution to the variance from the uncertainty in K will be very small for all reflexions, since the strong reflexions were measured at the beginning of the experiment when $S^2(K)/K^2$ was still very small.

Observed structure factors and their variances

The intensities and e.s.d.'s calculated from (1) were corrected for Lorentz-polarization and absorption effects. The absorption correction was made by the Gaussian quadrature method with a $4 \times 4 \times 4$ grid. The description of the crystal was in terms of its eleven rational boundary planes. The calculated transmission factors were in the range 0.910–0.922.

A test for possible multiple diffraction was made with *MULREF* (Coppens, 1968; Helmholdt & Vos, 1977). It was found that, for about 50% of the strong and medium intensity reflexions, there was risk of multiple diffraction from the 48 strongest reflexions in the material. For the weak reflexions, the analysis indicated no such risk. Earlier in the data collection, no significant intensity was observed for reflexions predicted absent due to space-group extinction. Symmetry-

related reflexions were measured for all reflexions. Within a form, some reflexions incurred the risk of multiple-diffraction contribution, while others did not. However, an analysis of the data showed that no significant intensity differences could be detected between these two types of reflexions. It was therefore concluded that the data material was not affected by multiple diffraction. This may be attributed to the small number of strong reflexions in the data set.

After averaging symmetry-related reflexions, the original data set of 5560 reflexions was reduced to 1123. The agreement among symmetry-related reflexions, $R = \sum (F_o^2 - \bar{F}_o^2) / \sum F_o^2$ and $R_w = [\sum w(F_o^2 - \bar{F}_o^2)^2 / \sum wF_o^4]^{1/2}$, was 0.0136 and 0.0176, respectively. The weights used were $w^{-1} = \sigma^2(F_o^2)$. The contributions from averaging *identical* reflexions, such as test reflexions, were not included in the calculation of these R values.

The additional errors in F_o^2 introduced in the absorption correction through the uncertainties in absorption coefficient μ and crystal dimensions were estimated as

$$\sigma_{\text{abs}}^2(F_o^2) = \sigma^2 \bar{l}^2 \left(\frac{\sigma^2(\mu)}{\mu^2} + \frac{\sigma^2(\bar{l})}{\bar{l}^2} \right) F_o^4.$$

The errors in the crystal dimensions were assumed to be isotropic. The relative errors in μ and \bar{l} were estimated as 0.04 and 0.10, respectively. (\bar{l} is the mean path length of the X-ray beam through the crystal.) The total variance used for the structure factors was thus

$$\sigma^2(F_o^2) = \sigma_{\text{av}}^2(F_o^2) + \sigma_{\text{abs}}^2(F_o^2).$$

In the present case $\mu = 0.828 \text{ mm}^{-1}$, and $\bar{l} \sim 0.1 \text{ mm}$ for all reflexions. Thus $\sigma_{\text{abs}}^2 \sim 8 \times 10^{-5} F_o^4$. Comparing this value of σ_{abs}^2 with the values given in Table 1, we see that in the present case σ_{abs}^2 will make a non-negligible contribution only for strong reflexions. It is doubtful, however, whether additions should be made to the variances from the absorption correction as there are obvious difficulties in estimating the random errors in the quantities μ and \bar{l} involved.

Data quality control

The data used in the refinements should be free from systematic effects other than those included in the least-squares model. Furthermore, the variances derived from the random errors in the observations should be correctly estimated. Discrepancies between observed and calculated structure factors in a least-squares refinement depend on F_o^2 and F_c^2 and also on the weight used, normally $1/\sigma^2(F_o^2)$. In order to ascertain whether these discrepancies are due mainly to errors in F_c^2 (*i.e.* in the model) or are also due to errors in F_o^2 , an *a priori* analysis of the quality of the observed data set is important.

The quality of the observed data set may be assessed by an analysis of (*a*) test reflexions and (*b*) symmetry-related reflexions. The analysis of the test reflexions gives a scaling function for all reflexions together with an estimate of random errors other than those from counting statistics. If the scaling functions for different test reflexions differ, this is an indication that the data set will be less suitable for work demanding a high accuracy, *e.g.* electron density analyses.

The question arises as to whether the variance of F_o^2 as obtained from counting statistics and analysis of test reflexions is consistent with the scatter observed among symmetry-related reflexions. In Fig. 2, a normal probability plot (Abrahams & Keve, 1971) is shown where observed quantities $\delta R = (F_o^2 - \bar{F}_o^2) / \sigma(F_o^2)$ are plotted *versus* the values expected for a normal distribution (0,1). \bar{F}_o^2 is the average of the symmetry-related reflexions in a form. The plot is perfectly linear with no observed quantity δR exceeding 4.0. The 0.87 slope indicates a slight overestimate of the variances. The linearity suggests that there are no appreciable anisotropic systematic errors in the data set, *i.e.* no errors which affect symmetry-related reflexions differently.

Systematic errors can, in principle, be corrected for after data collection if they cannot be avoided during the experiment. Unfortunately, some types of correction (*e.g.* extinction) often have to be made at the refinement stage, and may therefore be strongly coupled to other refined parameters. If such systematic errors are anisotropic, the averages of symmetry-related reflexions can clearly not be taken at the data-reduction

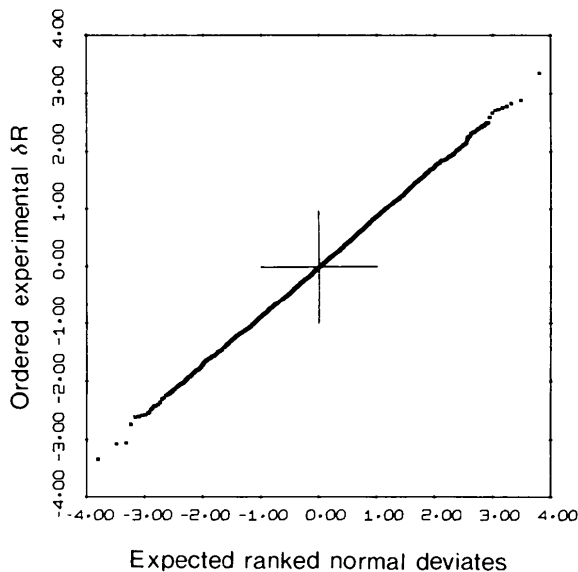


Fig. 2. Normal probability plot of quantities $(F_o^2 - \bar{F}_o^2) / \sigma(F_o^2)$ versus expected values for a normal distribution (0,1). All 5555 reflexions for which at least two symmetry-related reflexions were measured have been included. The slope of a least-squares line through the points is 0.87; the y intercept is -0.01 .

stage. For example, isotropic extinction can result in an anisotropic effect on the intensities depending on the crystal shape. If systematic errors or, rather, systematic effects are detected for which no correction can be made, the obvious conclusion is that the data set is not suitable for high-accuracy work.

Problems in this connexion are the isotropic systematic errors which may be difficult to detect. An example is thermal diffuse scattering which will always affect the data but for which it is difficult to make a correction. The effect of TDS is reduced at low temperatures and low-temperature work is therefore to be preferred.

The agreement among symmetry-related reflexions, as expressed by a discrepancy index R , can also be used as a measure of the quality of the data set. Repeated measurements of identical reflexions should not be included in the calculation of this R value. It is suggested that this number be quoted for all data sets where symmetry-related reflexions have been measured.

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X-ray Structure of Ammonium Perchlorate.

II. Conventional Refinement *versus* Refinement with Multipole Deformation Density Functions

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Abstract

The crystal structure of ammonium perchlorate, $\text{NH}_4^+\text{ClO}_4^-$, has been refined from X-ray data collected at 295 K. A deformation model has proved more successful than a conventional spherical free-atom model in describing the observed structure factors. The deformation refinement with Hirshfeld-type deformation density functions [Hirshfeld (1977). *Isr. J. Chem.* **16**, 226–229] gave a final $R_p(F^2) = 0.0276$ compared with 0.0669 for a conventional refinement. The bias introduced by the bonding density is demon-

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strated by a shift in the refined O atom positions towards the Cl atom in the conventional refinement. The shifts in the positional parameters of O atoms were up to 7σ . No significant changes were found in the thermal parameters. The Cl–O lengths obtained in the two refinements differed by ~ 0.01 Å. A small isotropic extinction correction applied in the conventional refinement proved unnecessary in the deformation refinement. The disordered ammonium ion is described by a model in which the H atoms are randomly distributed on a sphere centred on the N atom. The results from the deformation refinement are compared with a high-order refinement from data with $\sin \theta/\lambda > 0.7$ Å⁻¹.