SHORT STRUCTURAL PAPERS

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Ammonium Azide

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Abstract. NH_4N_3, orthorhombic, *Pmna*, $Z = 4$, $a = 8{\cdot}948$ (3), $b = 3{\cdot}808$ (2), $c = 8{\cdot}659$ (3) Å, $D_c = 1{\cdot}352$ and $D_m = 1{\cdot}352$ g cm^{-3}. Final *R* was 0·054 for 233 observed neutron reflections and a constrained model in which two independent azide groups were treated as rigid bodies. The corrected N—N distance is 1·186 (4) Å in both azide groups. There are two strong N—H···N hydrogen bonds, with N—N distances of 2·975 (4) and 2·967 (3) Å.

Introduction. The general features of the structure of ammonium azide were determined by Frevel (1936). He determined the space group and the positions of the nitrogen atoms, and inferred, from the short N—N distances between the ends of the N_3 groups and the ammonium nitrogen, that the hydrogen atoms participated in strong N—H···N hydrogen bonds. We have refined the structure from three-dimensional neutron diffraction data.

A single crystal of ammonium azide with approximate dimensions 1 × 2 × 3 mm was mounted on a four-circle diffractometer at the National Bureau of Standards Research Reactor, and data were collected using a procedure described previously (Prince, 1972), in which a preliminary measurement is made at the peak position of each reflection, and at a background position on either side. If the peak intensity does not exceed the background intensity by at least 2σ, an upper limit to the integrated intensity is calculated, and the reflection is not measured further. Reflections with significant intensity are measured using a θ–2θ step scan. Of 359 independent reflections within the limiting sphere defined by a wavelength of 1·230 Å and a maximum 2θ angle of 106°, 234 had observable intensity. Because the crystals are hygroscopic, and also tend to sublime rapidly if exposed to the atmosphere, the crystal was sealed in a quartz tube. Hence it was not possible to make accurate measurements of the crystal, and no absorption corrections were made. This introduces an error in the data which can amount, in an extreme case, to about 12%. The effect of this error on refinement is partially compensated by the refinement algorithm described below.

The nitrogen atom positions, as given by Frevel, were used to determine the phases for a Fourier synthesis, from which hydrogen-atom positions were immediately located. The structure was then refined, using the program *RFINE* (Finger & Prince, 1975). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where the weights were initially assigned according to the formula $w = [\sigma_s^2 + (0{\cdot}02F)^2]^{-1}$ and σ_s is the standard deviation due to counting statistics. For the first few cycles isotropic temperature factors were used for all atoms. Then anisotropic temperature factors were introduced, along with an isotropic secondary-extinction parameter (Zachariasen, 1967). Weights were also modified according to a robust/resistant algorithm (Tukey, 1974; Nicholson, Buchanan & Prince, 1978) in which the modified weight, w', is related to the raw weight by: $w' = w(1 - 2x^2 + x^4)$ for $|x| \leq 1$ and $w' = 0$ for $|x| > 1$ where $x = w^{1/2}||F_o| - |F_c||/k$ and k is a scaling factor given by $9|\delta|_{\text{med}}$, where $|\delta|_{\text{med}}$ is the median value of $w^{1/2}||F_o| - |F_c||$ in the previous cycle. If the errors are Gaussian, $(3/2)|\delta|_{\text{med}}$ is an estimate of σ, the standard deviation of an observation of unit weight. Therefore $9|\delta|_{\text{med}}$ corresponds to 6σ, and the weights of 97% of the data are altered by 20% or less.

With this model the correlation between the extinction parameter and the scale factor proved to be very large (>0·96), and the refinement did not converge. It was necessary, therefore, to hold the extinction parameter at a value that appeared to give the minimum value of the *R* index. The modified weighting scheme caused one observed reflection to be rejected, so all subsequent refinements included 233 reflections.

This initial refinement gave $R = 0\cdot054$, $R_w = 0\cdot055$. Previous work on symmetric azides (Choi & Prince, 1976) showed, however, that azide groups could be treated as rigid bodies, with the incidental benefit that the rigid-body model provided a procedure for applying libration corrections. Accordingly, a model was constructed in which the thermal motions of both azide groups and the ammonium group were constrained (Prince & Finger, 1973; Finger & Prince, 1975) to conform to the motions of a rigid body (Schomaker & Trueblood, 1968), although the N—N distances in the azide groups, the direction of the N—N vector of the azide group perpendicular to a twofold axis, and the distances and angles in the ammonium group were allowed to vary. The thermal parameters refined were therefore components of **T** and **L** for the azide groups and components of **T**, **L**, and **S** for the ammonium group. The agreement indices for this model were $R = 0\cdot057$, $R_w = 0\cdot059$. Because it seemed unreasonable to neglect internal modes in the ammonium group, particularly the N—H stretching mode, a final refinement treated the azide groups as rigid, but the thermal parameters of the atoms in the ammonium group were unconstrained. This model gave $R = 0\cdot054$, $R_w = 0\cdot055$, identical with the unconstrained model. The constrained model had 40 parameters, as compared with 44 for the unconstrained model. We may conclude that the 4 additional parameters are not significant.

Table 1. *Final atomic coordinates in ammonium azide* ($\times 10^4$)

	x	y	z
N(1)	0	0	0
N(2)	1305 (5)	0	0
N(3)	5000	0	0
N(4)	5000	1098 (13)	1263 (5)
N(5)	2500	5443 (10)	2500
H(1)	2916 (9)	7082 (27)	3355 (10)
H(2)	3317 (9)	3927 (22)	2076 (9)

Table 2. *Rigid-body-motion parameters of the azide ions in ammonium azide*

Tensor elements are referred to an orthonormal coordinate system in which x is parallel to the azide group and z is perpendicular to the crystallographic b axis.

Tensor element	Azide I[N(1)—N(2)]	Azide II[N(3)—N(4)]
T_{11}	0·0315 (13) Å^2	0·0304 (14) Å^2
T_{22}	0·0248 (27)	0·0280 (28)
T_{33}	0·0231 (21)	0·0213 (19)
T_{12}	0	−0·0024 (15)
T_{23}	0·0016 (21)	0
L_{22}	0·0113 (20) rad^2	0·0098 (19) rad^2
L_{33}	0·0193 (30)	0·0187 (26)
L_{23}	−0·0072 (22)	0

Table 1 lists final positional and Table 2 lists rigid-body-motion parameters.* Fig. 1 is a stereoscopic pair (Johnson, 1965) showing the structure.

Discussion. Table 3 lists selected bond distances and angles in the ammonium azide structure. Corrections were calculated from the rigid-body model for the azide groups and from the riding model (Busing & Levy, 1964) for the ammonium group. The corrected N—N distances for the azide groups, 1·186 (4) Å in both groups, are in excellent agreement with those found previously (Choi & Prince, 1977) in a number of monovalent metal azides. The N—H···N distances and angles (see Table 3), are indicative of strong hydrogen

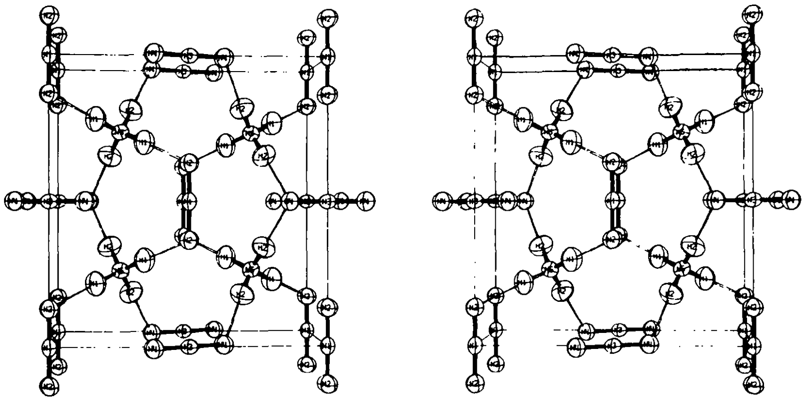

Fig. 1. Stereoscopic pair showing one unit cell of the ammonium azide structure, as seen looking down the b axis. The a axis is vertical and the c axis is horizontal.

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* Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33515 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected bond distances and angles in ammonium azide*

Distances and angles marked with an asterisk are involved in hydrogen bonds.

	Uncorrected	Corrected
N(1)–N(2)	1·168 (4) Å	1·186 Å
N(3)–N(4)	1·171 (4)	1·186
N(5)–H(1)*	1·037 (10)	1·067
N(5)–H(2)*	1·001 (9)	1·028
N(5)–N(2)*	2·967 (3)	
N(5)–N(4)*	2·975 (4)	
N(2)–H(1)*	1·930 (9)	
N(4)–H(2)*	1·974 (9)	
H(1)–N(5)–H(1′)	106·0 (1·1)°	
H(1)–N(5)–H(2)	110·3 (0·7)	
H(1)–N(5)–H(2′)	110·3 (0·7)	
H(2)–N(5)–H(2′)	109·6 (1·0)	
N(4)–N(5)–N(2)	109·4 (0·1)	
N(4)–N(5)–N(2′)	108·5 (0·1)	
N(4)–N(5)–N(4′)	112·5 (0·2)	
N(2)–N(5)–N(2′)	108·4 (0·1)	
N(5)–H(1)–N(2)*	177·9 (0·9)	
N(5)–H(2)–N(4)*	177·2 (0·7)	

bonds. The hydrogen bonds are nearly linear. The N–H bond distances within the ammonium group differ by about four times the estimated standard deviation, which is probably significant.

Differences in thermal ellipsoids between constrained and unconstrained models were insignificant, except that the shortest r.m.s. amplitudes for the hydrogen atoms, which were essentially parallel to the N–H bonds in both models, were about 0·02 Å shorter when the ammonium group was held rigid. This would seem to be a reasonable amplitude for an N–H stretching vibration within a strong hydrogen bond.

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Plutonium–Platinum Pu_2Pt*

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Abstract. Orthorhombic, *Pnma*, $Z = 4$, $a = 7{\cdot}046\ (3)$, $b = 4{\cdot}707\ (2)$, $c = 8{\cdot}865\ (4)$ Å, $\rho_c = 15{\cdot}20$ g cm^{-3}, $\mu = 1115$ cm^{-1}, $\lambda = 0{\cdot}70930$ Å. This structure belongs to the *C*23, $PbCl_2$ type.

Introduction. Kutaitsev, Chebotarev, Lebedev, Andrianov, Konev & Menshikova (1965) reported five compounds in the Pu–Pt system: Pu_5Pt_3, PuPt, $PuPt_2$, $PuPt_3$ and $PuPt_5$. They reported that PuPt has the CrB, *C*33 structure, $PuPt_2$ has the $MgCu_2$, *C*15 structure and that $PuPt_3$ has the $AuCu_3$, $L1_2$ structure. Cromer & Larson (1975) reported that Pu_5Pt_3 has the Mn_5Si_3, $D8_8$ structure.

The Pu–Pt system is much more complex than Kutaitsev *et al.* (1965) found. Cromer & Larson (1977) have since reported the existence and structure of $Pu_{31}Pt_{20}$. Land, Peterson & Roof (1978) have reinvestigated this system, particularly the platinum-rich end. They verified the presence of $PuPt_5$ and found that it has the $CaCu_5$, $D2_d$ structure. They also found the compound $PuPt_4$ and proposed an orthorhombic structure based on a distortion of two unit cells of $PuPt_5$ with the twofold Pt atoms removed. In addition, they found two high-temperature forms of $PuPt_3$, one of which appears to be of the Ni_3P, $D0_e$ type. The other $PuPt_3$ phase is poorly characterized.

In the present note the existence and structure of yet another phase, Pu_2Pt, is reported.

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