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On the Structure of [Fe([9]aneN₃)₂]Cl₃.5H₂O: Some Caveats

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Abstract

The crystal structure of (1,4,7-triazacyclononane)-iron(III) chloride pentahydrate, $Fe(C_6H_{15}N_3)_2Cl_3.5H_2O$, has been reinvestigated, and the space group is shown to be $R32$ [$a = 8\cdot076$ (2), $c = 31\cdot363$ (6) Å, $Z = 3$] rather than $P3$. The new data comprised 3640 intensity measurements which, when averaged according to 32 symmetry, led to 1154 independent reflections; the final goodness-of-fit was 2·10 for 74 parameters and R was 0·0213 for 1140 reflections with $F^2 > 0$. The dimensions of the $[Fe([9]aneN_3)_2Cl_2]^+$ grouping are little changed from the earlier, $P3$ description [Boeyens, Forbes, Hancock & Wieghardt (1985). *Inorg. Chem.* **24**, 2926–2931]; however, the arrangement in the layer of water molecules (and one Cl^- ion) is quite different and entails considerable disorder. Possible reasons for the incorrect assignments of lattice type and Laue symmetry in the earlier investigation are examined, and some recommendations are made for avoiding such errors in the future.

Introduction

For several years I have been concerned with the problem of describing a crystal structure in the most appropriate space group, and in particular of reducing the chances of describing it in an incorrect space group (see, for example, Marsh, 1981, 1986; Schomaker & Marsh, 1979; Marsh & Herbstein, 1983). I recently came across, in the literature, an example where three components of the space group – the lattice, the Laue group and the presence or absence of a center of symmetry – seemed questionable. I have re-examined this structure and found that two of the three components were, indeed, incorrectly assigned. It is the purpose of this paper not only to describe the corrected structure but also to examine possible causes for the incorrect assignments in the hope of preventing similar problems in the future.

The crystal structure of $Fe(C_6H_{15}N_3)_2Cl_3.5H_2O$ – an Fe^{III} complex with triazacyclononane (Boeyens, Forbes, Hancock & Wieghardt, 1985; BFHW) – was described in the trigonal space group $P3$, with three independent complexes in the hexagonal unit cell. The reported structure raised three questions in my mind: (1) Is the hexagonal lattice rhombohedrally

centered rather than primitive? In the reported structure the three complexes are very nearly related by the rhombohedral centering operations, and all reflections violating the centering condition $(h - k - l = 3n)$ were reported as very weak (BFHW, supplementary material). (2) Is the Laue symmetry $\bar{3}m$ rather than $\bar{3}$? Surprisingly, the supplementary F table contained entries for only one-half of the asymmetric unit for the presumed $\bar{3}$ Laue symmetry, and only five pairs of reflections that would be equivalent if the true symmetry were $\bar{3}m$; for all five the agreement between the two F values (both calculated and observed) was excellent. (3) Is the structure centrosymmetric? The coordinates derived by BFHW corresponded quite closely to the centrosymmetric space group $R\bar{3}m$, and I was able to obtain refinement in this space group to an R of 0·081 for BFHW's data - the same R as reported for the $P3$ model of BFHW, but with the rhombohedrally forbidden reflections deleted.

To answer these questions, I have collected new data and redetermined the structure. To anticipate the results, the answer to questions (1) and (2) is Yes and the answer to (3) is No; the structure is properly described in space group $R32$.

Experimental

Since this is a reinvestigation, the experimentation was more extensive than usual and is described in more detail than usual.

Crystals were kindly provided by Professor Boeyens; they were red prisms, excellently formed. The one chosen for data collection was holohedral, point symmetry $2/m$, with major faces 101 and $\bar{1}0\bar{1}$ (0·18 mm apart), intermediate faces $0\bar{1}1$ and $01\bar{1}$ (0·34 mm) and $\bar{1}11$ and $1\bar{1}\bar{1}$ (0·32 mm), and minor faces 001 and $00\bar{1}$ (0·29 mm). Oscillation and Weissenberg photographs were first prepared, with the crystal oscillating about [011]; these photographs showed no violations of the rhombohedral-centering conditions. The crystal was then transferred to a Nonius CAD-4 diffractometer equipped with an Mo X-ray tube and a single-crystal monochromator; the aperture width was $(2 + \tan \theta)$ mm. Unit-cell dimensions (Table 1) were obtained from the setting angles of the 12 equivalent reflections (assuming $\bar{3}m$ symmetry) of the forms 4,5,11 and 1,3,31, centered at both the $+2\theta$ and the -2θ settings.

I first examined, with both ω and ω-2θ scans, the profiles of the eight violations of the rhombohedral conditions (0,0,10; 0,1,18; 0,1,19; 0,1,21; 1,1,23; 1,1,26; 1,1,28; 1,1,29) which were reported by BFHW (their supplementary material) to have F values greater than 10 e (corresponding to an intensity approximately 1% that of the strongest reflections). In the ω-2θ scans, none of the eight showed any significant increase in counting rate at the expected position, although all eight showed very large count-

Table 1. $Fe(C_6H_{15}N_3)_2Cl_3.5H_2O$: *crystal data*

	REM*	BFHW†
Space group	$R32$	$P3$
a (Å)	8·076 (2)	8·069 (8)
c (Å)	31·363 (6)	31·322 (9)
V	1771·5 (9)	1766 (4)
Z	3	3
No. of data		
Measured	3640	(975?)
Averaged	1159	975
Used	1159	815
R	0·021	0·082
No. of parameters	74	156

* This work.
† Boeyens, Forbes, Hancock & Weighardt (1985).

ing rates at one or the other end of the 2° scan range. Since each of these reflections lies on a reciprocal lattice row with h and k both small, successive reflections h, k, l and $h, k, l \pm 1$ have very similar orientations (φ and χ) and, because of the extreme length of the c axis, differ by less than 2° in 2θ; in the ω-2θ scans the large counting rate invariably occurred at the end of the scan closest to a strong reflection from the rhombohedral cell. The ω scans showed similar peaks at one end or the other except for the 0,0,10 reflection, which showed a small peak in the center of the scan - surely a tail of the 009 reflection. Thus neither the photographs nor the profile measurements gave any indication of violations of the rhombohedral conditions. It is highly probable that the apparent violations reported by BFHW were due to scan overlap problems; BFHW give no details of their scan techniques other than '$\omega/2\theta$'.

Let me note in passing that ω scans, often used to reduce the problem of scan overlap for large unit cells, may not always be effective. In the present case the ω scan for 0,0,10 seemed to suggest a very weak but valid reflection, with the peak well centered in the scan. However, the coupled ω-2θ scan showed no peak at the position of 0,0,10 but slightly increased counts (relative to neighboring background regions) throughout the scan that were clearly associated with 009 - diffuse scattering, perhaps, since the structure is disordered. In cases of this sort, then, erroneous space-group violations might be indicated by ω scans.

Intensities for the 3641 reflections within the hemisphere $\pm h$, $+k$, $\pm l$, $2 \leq 2\theta \leq 60°$ were surveyed by ω-2θ scans at a constant speed of 2° (in 2θ) per minute;* three check reflections ($2,\bar{3},11;0,2,\bar{1}\bar{1};30\bar{6}$) surveyed every 2·8 h showed no detectable decay. Backgrounds were recorded fore and aft of each scan. An empirical background correction, as a smooth function of 2θ, was then derived from the background

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* It is indeed possible to adjust the software parameters on a CAD-4 diffractometer so that all reflections will be collected at the same scan speed. However, the normal configuration encourages discrimination against the weak reflections - the ones often crucial in deciding on the correct space group.

Table 2. *Final parameters, space group R32*

	M^*	$x \times 10^4$	$y \times 10^4$	$z \times 10^5$	$U_{eq} \times 10^4$
Fe	3	0	0	0	208 (1)
Cl(1)	6	0	0	35242 (2)	413 (1)
N	18	1085 (2)	−1126 (2)	4033 (2)	283 (2)
C(1)	18	2833 (2)	506 (2)	5954 (5)	354 (3)
C(2)	18	2349 (2)	1994 (2)	7343 (5)	366 (3)
O(1)	3	0	0	18521 (37)	1212 (26)
Cl(2)	3	0	0	19109 (15)	823 (6)
O(2)	3	0	0	46178 (15)	804 (9)
O(3)	9	0	2986 (6)	50000	1234 (6)

		$x \times 10^3$	$y \times 10^3$	$z \times 10^4$	B_{iso}
H(N)	18	143 (2)	−186 (2)	283 (4)	2·8 (3)
H(C1)A	18	375 (2)	96 (2)	381 (5)	3·4 (3)
H(C1)B	18	331 (2)	5 (2)	828 (8)	3·6 (5)
H(C2)A	18	347 (3)	322 (2)	780 (8)	3·7 (5)
H(C2)B	18	165 (2)	166 (2)	1013 (5)	3·2 (3)
H(O1)†	6	100	−10	1800	4·0
H(O2)A†	3	0	100	4650	4·0
H(O2)B†	3	0	0	4330	4·0
H(O3)A	6	0	188 (4)	5000	2·2 (6)
H(O3)B	12	53 (3)	369 (3)	5003 (8)	0·3 (4)

* No. in cell.

† The multiplicities, coordinates and B's of these atoms were assumed.

measurements on the weak reflections $[I \leq 5\sigma(I)]$ and was applied to *all* reflections – a process that increases the precision of the backgrounds and reduces, but does not entirely eliminate, the effect of scan truncation on the stronger intensities (Destro & Marsh, 1987). Estimated variances $\sigma^2(I)$ included counting statistics for the scans, background variances from the derived function, and a term $(0·014S)^2$ where S is the scan count. The intensities and their variances were then corrected for absorption (range of transmission coefficients, 0·75 for $\bar{1}11$ at $2\theta = 6°$ to 0·80 for 8,1,19 at 58°). One intensity measurement was rejected as obviously aberrant.

The 3640 F^2 values were first averaged according to Laue symmetry $\bar{3}m$; there were six observations for most of the 688 independent forms. The r.m.s. value of the 688 GOF's, where

$$\text{GOF} = \{\textstyle\sum_{i=1}^{N} [(F_i^2 - \hat{F}^2)/\sigma(F_i^2)]^2/(N-1)\}^{1/2},$$

was 1·55. Later, when the structure was found to be noncentrosymmetric, averaging was repeated according to symmetry 32 with either two or four observations for most of the 1154 forms; the r.m.s. GOF was much improved, to 1·04, indicating that anomalous dispersion was very important. Variances $\sigma^2(F^2)$ were obtained from the variances of the individual contributors F_i^2 plus, again, an additional term $0·014\hat{F}^2$.

Initial refinement was in space group $R\bar{3}m$, starting with the parameters obtained from the earlier refinement based on BFHW's data. Convergence was reached at $R = 0·067$ for 681 $\bar{3}m$-averaged reflections with $F^2 > 0$ and a GOF, $\{\sum[(F_o^2 - F_c^2)/\sigma(F_o^2)]^2/(N-p)\}^{1/2}$, of 9·2 for $N = 688$ reflections and $p = 32$ parameters – obviously unsatisfactory numbers. Most of the largest residuals involved relatively weak reflections with $F^2(\text{cal.}) < F^2(\text{obs.})$, suggesting that the center of symmetry should be removed [so as to create out-of-phase 'B' terms that would tend to increase $F^2(\text{cal.})$ for the weaker reflections]. The two most

obvious methods of removing the center were to displace the methylene C atoms so as to destroy the mirror symmetry of the N–CH$_2$–CH$_2$–N groupings and to place the water molecules O(3) in ordered, fully occupied sites (they were, perforce, disordered in $R\bar{3}m$). Structure-factor calculations confirmed that these two changes would have a pronounced effect on the discrepant reflections, and also established the correct relative sense (with regards to destroying the center of symmetry) of the two changes. Least-squares refinement in $R32$ then proceeded to a final R of 0·0213 for 1140 reflections with $F^2 > 0$ and a GOF of 2·10 for 1154 total reflections and 74 parameters; maximum parameter shift/e.s.d. $= 0·1$ in the last cycle. The largest peaks in a difference map were at the Fe(0·56 e) and Cl(1) (0·43 e) sites and at the centers of the C–C and C–N bonds (0·3–0·4 e); the largest hole ($-0·45$ e) was near the Cl(2) site. Coordinates are given in Table 2.*

The locally developed program system $CRYM$ was used for all calculations. Atomic form factors for Fe, Cl$^-$, C, N, O and H were from *International Tables for X-ray Crystallography* (1974), with anomalous-dispersion corrections for Fe and Cl$^-$. (Consultation with several colleagues led to no consensus as to how best to distribute the positive charge. Refinement with Fe^{3+} instead of Fe^0 led to slightly worse agreement indexes, $R = 0·0223$ and GOF = 2·25.) When the chirality of the structure was reversed, convergence was reached at much worse indexes: 0·038 and 4·1. The final structure has the opposite chirality from that reported by BFHW; change of chirality can be attained by inverting the puckering of the en-type groups. The final value of the quantity $\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4$ was 0·00280.

Results

The bond lengths and angles in the Fe([9]aneN$_3$)$_2$ cation are little changed from those reported by BFHW other than being more precise by factors of about 10. All six Fe–N distances are now structurally equivalent, at 1·998 (1) Å; the 'trigonal twist distortion', φ, (BFHW) is 2·46 (2)° and the 'polar angle', ω, is 50·73 (4)°. The N–H···Cl distance is 3·186 (1) Å.

On the other hand, the description of the layer of *water molecules is appreciably altered. Within this layer, one site is shared equally by a water molecule* O(1) and a chloride ion Cl(2); the least-squares refinement seems to have been able to distinguish between these two atoms, and placed them 0·18 Å apart with quite different (and understandable) U_{ij}'s.

As a result of this disorder, the distance 2·91 Å designated by BFHW as a very short O–H···Cl hydrogen bond undoubtedly represents the average of a longer O–H···Cl bond and a shorter O–H···O bond; the variation in the bond length is accommodated by a large value ($0·18$ Å^2) for the major axis of the U_{ij} ellipsoid of the donor atom, O(3). The site of the remaining water molecule, O(2), is half populated. Thus, the arrangement in this layer is complicated; and while some of the H atoms could be placed in logical positions that survived least-squares refinement, the positions and occupation factors of others (Table 2) are conjectural. Uncertainties associated with the disorder are probably responsible for the GOF value of 2·1.

The disorder in this water layer results from the twofold axis in space group $R32$ which was not present in the earlier $P3$. This twofold axis is clearly dictated by the Laue symmetry (or, more accurately, by the point-group symmetry of the intensities, 32). In the $P3$ structure derived by BFHW, the twofold symmetry is satisfied, essentially within experimental error, by all the Fe, C and N atoms and by Cl(1) through Cl(6) (BFHW, Table III). For the remaining atoms – those in the 'water layer' – the relationships are not as exact; for example, Cl(9) must be paired with O(9), and Cl(8) with O(7). The very large e.s.d's in some of the coordinates [the reported e.s.d. in the z parameter of O(7) is over 0·6 Å!] might have suggested the presence of higher symmetry.

Discussion

Of the three space-group components that seemed questionable in the original investigation by BFHW – lattice, Laue group and centrosymmetry – the first two were incorrectly assigned. Let us examine each of these components with an eye toward reducing the risk of incorrect assignments in the future.

(1) *Determination of the correct lattice.* In most cases, the greatest worry in an automated (computer-controlled) search for the correct lattice is that the volume of the reduced unit cell will turn out to be too small: the search routine may overlook a category of reflections, either by chance or because they are systematically weak. Accordingly, many laboratories have adopted a procedure of searching for significant intensity at intermediate, fractional reciprocal-lattice points once a tentative unit cell has been established. Preliminary photography, in which reciprocal space is examined in a continuous rather than a discontinuous fashion, should be an even stronger safeguard.

In the present case, however, quite the opposite occurred: the primitive cell derived by BFHW was too *large*, by a factor of three. BFHW report that the space group and approximate cell constants were obtained by 'standard oscillation and Weissenberg

techniques'; more accurate cell dimensions and intensity data were obtained later on a Philips PW1100 diffractometer. What might have gone wrong? It is a reasonable scenario that the diffractometer was told that the unit cell is hexagonal but was not told of the rhombohedral centering, so that it sampled all possible reciprocal lattice points; enough of the reflections with $(h - k - l) \neq 3n$ showed significant intensity to convince BFHW that the cell was primitive. It now seems clear (see *Experimental*) that the apparently significant intensities of these 'forbidden' reflections were due to overlap by neighboring, allowed reflections.

This problem – the finding of significant intensity where none should occur – has serious ramifications. Systematic absences, whether due to lattice centering or to glide planes or screw axes, are commonly assigned by inspection of diffractometer output, and it is common lore that even a single violation of 'systematic' absences is adequate cause for rejection of the corresponding symmetry element. If the violation is artifactual, perhaps due to twinning or (as in the present case) to interference by neighboring reflections, an incorrect space-group assignment may result. In cases of this sort – where possible violations of systematic absences are very few in number or very weak in intensity – a very careful assessment of the apparent violations should be made. In particular, diffraction photographs, if available, should be closely inspected.

(2) *The Laue symmetry.*[*] Assigning the correct Laue group to a low-symmetry structure (triclinic, monoclinic or orthorhombic) usually presents no difficulty, since there is but one Laue group per crystal class. In higher symmetries, a choice must be made. For a structure based on a hexagonal lattice (as in the present case) the choice may be particularly difficult, since five distinct Laue symmetries ($\bar{3}$, $\bar{3}m1$, $\bar{3}1m$, $6/m$, and $6/mmm$) are compatible with a hexagonal lattice. When collecting intensity data on a diffractometer, it seems to be the custom (perhaps because of time pressures, real or perceived) to survey only a minimum number of reflections – a single asymmetric unit of the presumed Laue group. If the wrong Laue group is assigned, an insufficient sampling of data may result.

In the present example, the data collected by BFHW included only those reflections with h, k, and $l \geq 0$ – an asymmetric unit for Laue symmetry $\bar{3}m1$ or $6/m$ but only one-half the asymmetric unit for $\bar{3}$, the Laue symmetry for the space group $P3$ presumed by BFHW. If the entire asymmetric unit for $\bar{3}$ had

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[*] 'Laue symmetry' is used here in its classical sense – a *centrosymmetric* crystallographic point group. Because of anomalous dispersion it need not – and in this example does not – match the symmetry of the diffraction intensities.

been collected, it is quite likely that the higher, $\bar{3}m1$ Laue symmetry would have been recognized. The possible confusion over Laue groups is good reason to heed Ibers' (1967) suggestion that '*all* intensity data within a given range of scattering angle' be collected and examined.

(3) *Centrosymmetric or noncentrosymmetric?* This is one of the most vexing problems in crystallography: when the choice is a close one and systematic absences are of no help (as in the present example), how does one choose between a centrosymmetric and a noncentrosymmetric space group? I have suggested (Marsh, 1986) that, if a centrosymmetric model results in 'satisfactory agreement between I(obs.) and I(cal.)', '... there can be no profit in worrying about noncentrosymmetry'; this is because a noncentrosymmetric model must generate near-singularities in the refinement which will lead to poor (or no) convergence and to confusion over the correctness of the model. In the present case the standard R index for the centrosymmetric, $R\bar{3}m$ model was 0·067 (or 0·081 for the original, BFHW data) – not entirely satisfactory, but perhaps not *un*satisfactory. But the goodness-of-fit for the $R\bar{3}m$ structure was entirely unacceptable, at 9·2 (see *Experimental*). The need for including error estimates in evaluating the correctness of a model is clear.

In this example, where anomalous dispersion is appreciable (f'' for Fe, with Mo radiation, is 0·845 e; *International Tables for X-ray Crystallography*, 1974), the lack of a symmetry center could be detected at an earlier stage – when the intensity data were being averaged. As noted above, averaging in point group 321 gave a goodness-of-fit of 1·04, compared to 1·55 for $\bar{3}m$. We again see the advantage of retaining error estimates during this averaging; we also find strong support for Ibers' (1967) recommendation to collect a 'complete data set', so that comparisons of this sort can be made.

In summary, the task of assigning the correct space group may be more onerous than often assumed. Reflections may be overlooked or thought to be present when they are in fact absent, leading to a wrong lattice or to mistaken assignment of glide planes or screw axes; the Laue symmetry may not be readily obvious, particularly for high-symmetry structures; the choice between centrosymmetry and noncentrosymmetry may be a difficult one. Recommendations for improving the chances of a correct space-group assignment include: (1) a careful survey of the entire diffraction pattern, with photographic methods

being particularly helpful; (2) collection of more than one asymmetric unit of intensity data (see Ibers, 1967); (3) keeping careful account of experimental errors, for use in evaluating comparisons; (4) continual vigilance and skepticism throughout a structure analysis. At least some of these recommendations cannot be implemented solely by automated equipment in its present form; extensive human interaction is still needed.

Added comments. A referee has suggested that refinement, based on the new intensity data, might also be carried out in space group $P3$ in order to provide a 'fair comparison' with the $R32$ refinement. This cannot be done: the new data include no reflections which violate the rhombohedral centering conditions and therefore the refinement matrix would be singular (Schomaker & Marsh, 1979). Refinement in $R3$ should proceed normally; however, since the intensity data show point symmetry 32 within experimental error, the refined model derived from these data must do likewise. Perhaps refinement in $P3$ could include the weak superlattice reflections with $h - k - l \neq 3n$ reported by BFHW (but shown here to be anomalous), in order to remove the formal singularities. However, this experiment has already been carried out by BFHW. Their refinement in $P3$ was manifestly unsatisfactory: besides the very large e.s.d.'s for some atom coordinates as noted above (see *Results*), BHFW reported 'correlation problems, and the Fe–N, C–N and C–C bond lengths had to be constrained to prevent distortions of the complex cations'. By comparison, refinement in R32 proceeded normally.

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