

The Structure of the Iron(III) Complex with Sodium Tartrate (FeTNa)

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The composition and structure of the iron complex with sodium tartrate, $\text{Fe}(\text{C}_4\text{H}_2\text{O}_6)_2 \cdot \text{Na}_5 \cdot 14\text{H}_2\text{O}$, have been determined and refined. The crystals are triclinic, $P\bar{1}$, with $a=10.909$ (5), $b=10.222$ (5), $c=6.998$ (5) Å, $\alpha=102.96$ (5), $\beta=100.64$ (5), $\gamma=111.10$ (5)°. Three oxygen atoms of two molecules of DL-tartaric acid are connected to one iron atom (the two oxygen atoms of the hydroxyl groups plus an oxygen atom from one of the carboxyl groups). Five (out of six) oxygen atoms belonging to the tartaric acid contribute to one to three hydrogen bonds with H_2O molecules as acceptors. Two (out of 14) hydrogen atoms of H_2O do not form hydrogen bonds.

Introduction

Fe(III)-tartrate complexes have long been known (Franke, 1931; Pavlinova, 1949; Piatnitsky & Gendler, 1956; Jayme & Bergmann, 1958; Hanby & Jonson, 1969) and presumably there are no less than ten similar compounds with various quantitative relationships between the components. From chemical data it has been assumed that in an alkaline medium the iron atom, being a central one, is linked to the oxygen atoms belonging to the hydroxyl groups of the ligands, although no structural evidence for this has yet been adduced. This is due to difficulties experienced in the crystal preparation of Fe(III)-tartrate complexes.

Yellow crystals of a prismatic shape are precipitated after several days of storage of aqueous FeTNa prepared by mixing 0.3M $\text{Fe}(\text{NO}_3)_3$ with 0.9M $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ (sodium tartrate) in 2.5M NaOH solution. We have not been able to obtain reliable chemical data for these crystals because of the difficulties encountered in extraction of the crystals from the solution and in their decomposition upon drying. The chemical analyses have shown the presence of Fe, Na, tartaric acid and water in the crystals, but since their quantitative ratios were ambiguous diffraction data were used to obtain the true composition.

Experiment

Accurate measurements of unit-cell dimensions as well as the determination of the intensity values for a 0.7×0.5 mm prismatic crystal were made on the AFC automatic diffractometer of the Rigaku firm with the amiable assistance of its employees, Dr Mitsuru Yoshimatsu and Mr Yoshimitsu Suzuki. Mo $K\alpha$ radiation and a graphite monochromator were used. Cell parameters for space group $P\bar{1}$ were as follows: $a=10.909$ (5), $b=10.222$ (5), $c=6.998$ (5) Å, $\alpha=102.96$ (5)°, $\beta=100.64$ (5)°, $\gamma=111.10$ (5)°, $V=678.5$ Å³. All reflexions were measured within a sphere of radius $S=0.6$. The specific weight was measured by flotation in a mixture of bromoform and ethyl alcohol, and amounted to

1.77 (1) g cm⁻³ resulting in a molecular weight of the cell contents equal to 720. This molecular weight covers a number of possible combinations of four components of chemical composition. The system of programs X-RAY-70 composed by Andrianov, Tarnopolsky & Shibaeva (1969) was used for the structural calculations.

Determination of structure and composition

Uncertainty in the chemical data stemmed from the following observations: there are one or two iron atoms, four to seven sodium atoms, one to three molecules of tartaric acid and an uncertain number of water molecules per cell.

The highest peaks of the Patterson function are shown schematically in Fig. 1. Two peaks located on the long diagonal of the bc plane (40% of the height of the starting peak) probably correspond to Fe or Na atoms along this diagonal with a period of $\frac{1}{2}$. The weaker peaks correspond to oxygen atoms, forming a similar octahedral coordination around each of the cations along the diagonal. The Patterson function does not give us a precise answer about the number of Fe and Na atoms in the cell. In order to obtain additional information on this subject direct methods have been employed (Andrianov *et al.*, 1969).

At first we were uncertain whether we were dealing with the centrosymmetric structure because the E -statistics (Karle & Karle, 1965) failed to provide unambiguous results and in the process of crystallization of a mixture of D and L configurations it was unwise to exclude the possibility of separation of the racemic mixture.

It was assumed that the E -synthesis would at least lead to the determination of the centrosymmetric portion of the structure.

Table 1 presents the coordinates and the heights of the first ten peaks of such an E -synthesis which showed good agreement with the Patterson function. Analysis of the peak heights and their positions indicated that the cell contained one iron atom and five sodium atoms.

By placing one iron atom and one sodium atom at the centres of the $P\bar{1}$ unit cell and by changing the coordinates of the remaining sodium atoms and part of the oxygen atoms (Table 1) in accordance with the altered positions of the symmetry centres and the origin we performed three consecutive cycles of Fourier synthesis. As a result all the oxygen and carbon atoms were revealed and the difference syntheses showed the positions of the hydrogen atoms. At this stage the chemical composition for $\text{Fe}(\text{C}_4\text{H}_2\text{O}_6)_2 \cdot \text{Na}_5 \cdot 14\text{H}_2\text{O}$ was completely determined. The refinement of coordinates and isotropic thermal constants for the atoms was by the

least-squares method combined with Cruickshank's (1965) weighting scheme. The atomic scattering factors used were those of Cromer & Mann (1968) for neutral atoms, with Cromer's (1965) anomalous scattering corrections. Absorption was neglected. The refinement terminated at $R=0.055$; the final results are given in Tables 2 and 3.

Description of the structure

The projection of the structure along the c axis is shown in Fig. 2. The iron atom is surrounded by two ligands which are molecules of tartaric acid. The Fe coordination is octahedral; four (out of six) oxygen atoms belong to two hydroxyl groups of each molecule and are strongly linked to Fe (1.98 Å) while two opposite octahedral summits (distorted towards a tetra-

Table 1. The highest peaks of the E -synthesis in space group $P\bar{1}$

| No. | x | y | z | Height | Atoms |
|-----|-------|-------|-------|--------|---------|
| 1 | 0.501 | 0.375 | 0.130 | 427 | Fe + Na |
| 2 | 0.494 | 0.118 | 0.371 | 270 | Na + Na |
| 3 | 0.637 | 0.266 | 0.184 | 183 | O + O |
| 4 | 0.344 | 0.222 | 0.849 | 179 | O + O |
| 5 | 0.380 | 0.257 | 0.302 | 157 | O + O |
| 6 | 0.634 | 0.000 | 0.437 | 153 | O + O |
| 7 | 0.654 | 0.021 | 0.908 | 150 | O + O |
| 8 | 0.647 | 0.513 | 0.406 | 149 | O + O |
| 9 | 0.904 | 0.172 | 0.018 | 145 | Na |
| 10 | 0.897 | 0.426 | 0.748 | 141 | Na |

Table 2. Atomic coordinates

| | x/a | y/b | z/c | B |
|-------|------------|------------|------------|-----------|
| Fe | 0 | 0 | 0 | 1.16 (1) |
| Na(1) | 0 | 0.5000 | 0.5000 | 1.98 (3) |
| Na(2) | 0.4013 (2) | 0.7985 (2) | 0.8798 (2) | 2.55 (3) |
| Na(3) | 0.0109 (1) | 0.7624 (2) | 0.2645 (2) | 1.89 (2) |
| O(1) | 0.8543 (3) | 0.0957 (3) | 0.9690 (4) | 1.64 (4) |
| O(2) | 0.3730 (3) | 0.0068 (3) | 0.0864 (4) | 2.07 (5) |
| O(3) | 0.8584 (2) | 0.8611 (3) | 0.7415 (4) | 1.47 (4) |
| O(4) | 0.8814 (2) | 0.8722 (3) | 0.1286 (4) | 1.42 (4) |
| O(5) | 0.3713 (3) | 0.4781 (3) | 0.2288 (4) | 2.18 (5) |
| O(6) | 0.1606 (3) | 0.4155 (3) | 0.0325 (4) | 2.21 (5) |
| O(7) | 0.4011 (3) | 0.5772 (3) | 0.6629 (5) | 2.74 (5) |
| O(8) | 0.1216 (3) | 0.3510 (3) | 0.5391 (4) | 2.21 (5) |
| O(9) | 0.1450 (3) | 0.6328 (3) | 0.3228 (4) | 2.25 (5) |
| O(10) | 0.1670 (3) | 0.9928 (3) | 0.5322 (5) | 2.78 (5) |
| O(11) | 0.1620 (3) | 0.6467 (3) | 0.8304 (4) | 2.32 (5) |
| O(12) | 0.4645 (4) | 0.7589 (4) | 0.2004 (6) | 4.06 (7) |
| O(13) | 0.3711 (4) | 0.8937 (4) | 0.5787 (6) | 4.05 (7) |
| C(1) | 0.2638 (3) | 0.0132 (4) | 0.1003 (5) | 1.47 (5) |
| C(2) | 0.2621 (3) | 0.1643 (4) | 0.1949 (5) | 1.63 (6) |
| C(3) | 0.2458 (3) | 0.2269 (3) | 0.0137 (5) | 1.37 (5) |
| C(4) | 0.2583 (3) | 0.3854 (4) | 0.0977 (5) | 1.42 (5) |
| H(1) | 0.346 (7) | 0.245 (8) | 0.301 (11) | 0.2 (1.6) |
| H(2) | 0.324 (7) | 0.231 (8) | 0.960 (11) | 0.9 (1.6) |
| H(3) | 0.481 (7) | 0.565 (8) | 0.727 (11) | 6.8 (1.7) |
| H(4) | 0.410 (7) | 0.586 (8) | 0.536 (11) | 4.4 (1.7) |
| H(5) | 0.113 (7) | 0.273 (8) | 0.426 (11) | 4.1 (1.7) |
| H(6) | 0.217 (7) | 0.429 (8) | 0.589 (11) | 6.1 (1.7) |
| H(7) | 0.236 (7) | 0.705 (8) | 0.400 (11) | 2.3 (1.6) |
| H(8) | 0.168 (7) | 0.563 (8) | 0.237 (11) | 3.7 (1.6) |
| H(9) | 0.171 (7) | 0.063 (8) | 0.454 (11) | 5.3 (1.7) |
| H(10) | 0.145 (7) | 0.040 (8) | 0.663 (11) | 7.7 (1.7) |
| H(11) | 0.143 (7) | 0.728 (8) | 0.900 (11) | 4.9 (1.4) |
| H(12) | 0.174 (7) | 0.583 (7) | 0.914 (11) | 4.4 (1.4) |
| H(13) | 0.444 (7) | 0.651 (8) | 0.184 (11) | 6.8 (1.4) |
| H(14) | 0.554 (7) | 0.826 (8) | 0.310 (11) | 7.2 (1.4) |
| H(15) | 0.306 (7) | 0.944 (7) | 0.573 (11) | 3.1 (1.4) |
| H(16) | 0.440 (7) | 0.923 (7) | 0.546 (11) | 7.4 (1.4) |

Table 3. Interatomic distances (Å) and angles (°)

| Fe octahedron | | Na(1) octahedron | |
|---|-----------|------------------|-----------|
| Fe-O(1) | 2.149 (3) | Na(1)-O(8) | 2.380 (4) |
| Fe-O(3) | 1.978 (3) | Na(1)-O(9) | 2.412 (4) |
| Fe-O(4) | 1.983 (3) | Na(1)-O(11) | 2.397 (3) |
| Average | 2.036 | Average | 2.396 |
| O(1)-Fe-O(3) | 77.5 (1) | O(8)-Na(1)-O(9) | 86.3 (1) |
| O(1)-Fe-O(4) | 86.8 (1) | O(8)-Na(1)-O(11) | 80.0 (1) |
| O(3)-Fe-O(4) | 83.9 (1) | O(9)-Na(1)-O(11) | 86.8 (1) |
| Na(2) octahedron | | Na(3) octahedron | |
| Na(2)-O(2 ₁) | 2.444 (4) | Na(3)-O(1) | 2.711 (4) |
| Na(2)-O(2 ₂) | 2.475 (3) | Na(3)-O(4) | 2.298 (4) |
| Na(2)-O(7) | 2.424 (4) | Na(3)-O(6) | 2.355 (4) |
| Na(2)-O(11) | 2.419 (4) | Na(3)-O(8) | 2.359 (4) |
| Na(2)-O(12) | 2.389 (5) | Na(3)-O(9) | 2.341 (4) |
| Na(2)-O(13) | 2.528 (5) | Na(3)-O(10) | 2.432 (4) |
| Average | 2.447 | Average | 2.399 |
| O(2 ₁)-Na(2)-O(2 ₂) | 82.8 (1) | O(1)-Na(3)-O(4) | 73.2 (1) |
| O(2 ₁)-Na(2)-O(11) | 88.4 (1) | O(1)-Na(3)-O(6) | 90.5 (1) |
| O(2 ₁)-Na(2)-O(12) | 84.1 (1) | O(1)-Na(3)-O(9) | 97.2 (1) |
| O(2 ₁)-Na(2)-O(13) | 88.6 (1) | O(1)-Na(3)-O(10) | 81.4 (1) |
| O(2 ₂)-Na(2)-O(7) | 103.1 (1) | O(4)-Na(3)-O(6) | 71.9 (1) |
| O(2 ₂)-Na(2)-O(12) | 97.2 (1) | O(4)-Na(3)-O(8) | 101.2 (1) |
| O(2 ₂)-Na(2)-O(13) | 72.6 (1) | O(4)-Na(3)-O(10) | 92.2 (1) |
| O(7)-Na(2)-O(11) | 85.3 (1) | O(6)-Na(3)-O(8) | 88.3 (1) |
| O(7)-Na(2)-O(12) | 97.3 (1) | O(6)-Na(3)-O(9) | 99.0 (1) |
| O(7)-Na(2)-O(13) | 91.0 (1) | O(8)-Na(3)-O(9) | 88.5 (1) |
| O(11)-Na(2)-O(12) | 90.7 (1) | O(8)-Na(3)-O(10) | 98.6 (1) |
| O(11)-Na(2)-O(13) | 98.3 (1) | O(9)-Na(3)-O(10) | 96.0 (1) |
| Tartaric acid | | | |
| C(1)-O(1) | 1.276 (4) | C(4)-O(5) | 1.270 (4) |
| C(1)-O(2) | 1.237 (5) | C(4)-O(6) | 1.248 (5) |
| C(1)-C(2) | 1.546 (5) | C(4)-C(3) | 1.541 (6) |
| C(2)-O(3) | 1.420 (5) | C(3)-O(4) | 1.404 (4) |
| C(2)-H(1) | 1.00 (5) | C(3)-H(2) | 0.99 (8) |
| C(2)-C(3) | 1.552 (6) | | |
| O(1)-C(1)-O(2) | 125.4 (3) | O(5)-C(4)-O(6) | 124.2 (3) |
| O(1)-C(1)-C(2) | 114.4 (2) | O(5)-C(4)-C(3) | 116.2 (3) |
| O(2)-C(1)-C(2) | 119.8 (3) | O(6)-C(4)-C(3) | 119.3 (3) |
| O(3)-C(2)-C(3) | 106.9 (3) | O(4)-C(3)-C(2) | 106.3 (3) |
| O(3)-C(2)-C(1) | 108.5 (2) | O(4)-C(3)-C(4) | 114.2 (3) |
| C(1)-C(2)-C(3) | 104.9 (3) | C(2)-C(3)-C(4) | 106.0 (5) |
| O(3)-C(2)-H(1) | 112 (4) | O(4)-C(3)-H(2) | 113 (3) |
| C(1)-C(2)-H(1) | 119 (5) | C(4)-C(3)-H(2) | 109 (4) |
| C(3)-C(2)-H(1) | 104 (4) | C(2)-C(3)-H(2) | 106 (5) |

Table 3 (cont.)

| H ₂ O and H-bonds | | | |
|------------------------------|-----------|-------------------|-----------|
| O(7)—H(3) | 0.97 (8) | O(8)—H(5) | 0.95 (8) |
| O(7)—H(4) | 0.93 (8) | O(8)—H(6) | 1.00 (6) |
| H(3)—O(7)—H(4) | 106 (7) | H(5)—O(8)—H(6) | 110 (6) |
| O(7)—O(5 ₁) | 2.751 (5) | O(8)—O(3) | 2.681 (4) |
| H(3)—O(5 ₁) | 1.81 (8) | H(5)—O(3) | 1.75 (8) |
| O(7)—H(3)—O(5 ₁) | 164 (7) | O(8)—H(5)—O(3) | 164 (7) |
| O(7)—O(5 ₂) | 2.888 (5) | O(8)—O(7) | 2.902 (5) |
| H(4)—O(5 ₂) | 2.07 (7) | H(6)—O(7) | 1.91 (6) |
| O(7)—H(4)—O(5 ₂) | 147 (6) | O(8)—H(6)—O(7) | 176 (7) |
| O(9)—H(7) | 0.95 (6) | O(10)—H(9) | 0.99 (9) |
| O(9)—H(8) | 0.97 (8) | O(10)—H(10) | 1.05 (8) |
| H(7)—O(9)—H(8) | 99 (6) | H(9)—O(10)—H(10) | 103 (7) |
| O(9)—O(13) | 2.809 (5) | O(10)—O(3) | 2.713 (5) |
| H(7)—O(13) | 1.91 (6) | H(9)—O(3) | 1.75 (9) |
| O(9)—H(7)—O(13) | 155 (7) | O(10)—H(9)—O(3) | 163 (6) |
| O(9)—O(6) | 2.733 (5) | O(10)—O(4) | 2.708 (5) |
| H(8)—O(6) | 1.79 (8) | H(11)—O(4) | 1.66 (8) |
| O(9)—H(8)—O(6) | 163 (6) | O(10)—H(10)—O(4) | 176 (3) |
| O(11)—H(11) | 0.98 (8) | O(12)—H(13) | 1.02 (8) |
| O(11)—H(12) | 1.00 (8) | O(12)—H(14) | 1.01 (6) |
| H(11)—O(11)—H(12) | 115 (7) | H(13)—O(12)—H(14) | 110 (6) |
| O(11)—O(1) | 2.776 (5) | O(12)—O(5) | 2.746 (5) |
| H(11)—O(1) | 1.81 (8) | H(13)—O(5) | 1.78 (8) |
| O(11)—H(11)—O(1) | 167 (6) | O(12)—H(13)—O(5) | 156 (7) |
| O(11)—O(6) | 3.007 (5) | O(13)—H(15) | 1.01 (9) |
| H(12)—O(6) | 2.03 (8) | O(13)—H(16) | 0.91 (9) |
| O(11)—H(12)—O(6) | 167 (5) | H(15)—O(13)—H(16) | 113 (7) |
| O(13)—O(10) | 2.755 (6) | | |
| H(15)—O(10) | 1.76 (8) | | |
| O(13)—H(15)—O(10) | 168 (6) | | |

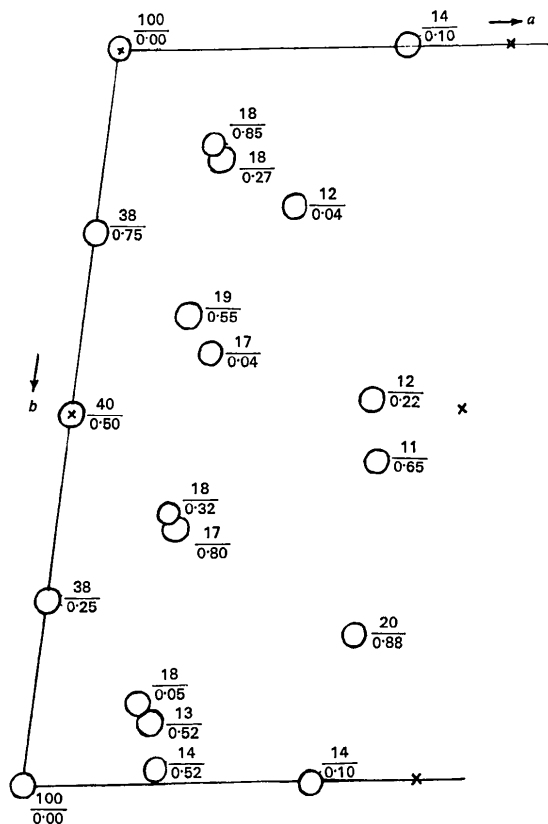


Fig. 1. Schematic representation of the highest peaks of the Patterson function for FeTNa (only half the projection along the *c* axis is shown). The upper number refers to the respective height of the peak (the starting peak is defined as 100), the lower number is the fractional *z* coordinate.

gonal bipyramid) are each occupied by an oxygen atom of one of the carboxyl groups (2.15 Å). The sodium atoms also have octahedral coordination with Na—O average distances of 2.40 to 2.45 Å for different octahedra. Five (out of six) oxygen atoms of the tartaric acid are involved in hydrogen bonds with H₂O molecules as acceptors [O(1) and O(4) in one H-bond, O(3) and O(6) in two H-bonds, O(5) in three H-bonds]. Thus, the charge on the complex ion $\text{Fe}(\text{C}_4\text{H}_2\text{O}_6)_2^{5-}$ is compensated in the structure not directly by Na ions but to a large extent through H-bonds to H₂O molecules. This is similar to the arrangement in solution.

Twelve (out of fourteen) hydrogen atoms of the H₂O molecules are involved in hydrogen bonds. The bonding strength varies widely and the O—O distances vary in the range 2.68 to 3.01 Å. Each H₂O molecule contributes to one [O(12)], two [(O(8), O(9), O(11), O(13))] and three [O(7), O(10)] H-bonds not only as a donor, but in three cases [O(7), O(10), O(13)] as an acceptor.

The bonding of three (out of six) oxygen atoms of the tartaric acid molecules to Fe causes considerable distortion of the molecular geometry (Fig. 3) as compared with crystals of tartaric acid and its salts. The angle between the two flat groups in the molecule is reduced from 54.6° (Okaya, Stemple & Kay, 1966) to 36.5°; the oxygen spacing between hydroxyl groups is decreased from 2.86 to 2.65 Å. One-half of the molecule remains flat—deviations of C(3), C(4), O(4), O(5), O(6) from the plane through them do not exceed 0.01 Å—while the other half, which includes O(1) and O(3) associated with Fe, is distorted considerably with deviations of up to 0.19 Å from the plane.

The carboxyl groups of the molecule are not crystallochemically equivalent. O(1) is linked to Fe and Na, contributing to one H-bond, O(2) is linked to two Na atoms and is not involved in H-bonds; O(5) is not linked to the cations and behaves as an acceptor in three H-bonds; O(6) is linked to one

Table 4. *Observed and calculated structure amplitudes*

| h | k | l | Observed | Calculated |
|---|---|-----|----------|------------|
| 0 | 0 | 0 | 100 | 100 |
| 0 | 0 | 1 | 100 | 100 |
| 0 | 0 | 2 | 100 | 100 |
| 0 | 0 | 3 | 100 | 100 |
| 0 | 0 | 4 | 100 | 100 |
| 0 | 0 | 5 | 100 | 100 |
| 0 | 0 | 6 | 100 | 100 |
| 0 | 0 | 7 | 100 | 100 |
| 0 | 0 | 8 | 100 | 100 |
| 0 | 0 | 9 | 100 | 100 |
| 0 | 0 | 10 | 100 | 100 |
| 0 | 0 | 11 | 100 | 100 |
| 0 | 0 | 12 | 100 | 100 |
| 0 | 0 | 13 | 100 | 100 |
| 0 | 0 | 14 | 100 | 100 |
| 0 | 0 | 15 | 100 | 100 |
| 0 | 0 | 16 | 100 | 100 |
| 0 | 0 | 17 | 100 | 100 |
| 0 | 0 | 18 | 100 | 100 |
| 0 | 0 | 19 | 100 | 100 |
| 0 | 0 | 20 | 100 | 100 |
| 0 | 0 | 21 | 100 | 100 |
| 0 | 0 | 22 | 100 | 100 |
| 0 | 0 | 23 | 100 | 100 |
| 0 | 0 | 24 | 100 | 100 |
| 0 | 0 | 25 | 100 | 100 |
| 0 | 0 | 26 | 100 | 100 |
| 0 | 0 | 27 | 100 | 100 |
| 0 | 0 | 28 | 100 | 100 |
| 0 | 0 | 29 | 100 | 100 |
| 0 | 0 | 30 | 100 | 100 |
| 0 | 0 | 31 | 100 | 100 |
| 0 | 0 | 32 | 100 | 100 |
| 0 | 0 | 33 | 100 | 100 |
| 0 | 0 | 34 | 100 | 100 |
| 0 | 0 | 35 | 100 | 100 |
| 0 | 0 | 36 | 100 | 100 |
| 0 | 0 | 37 | 100 | 100 |
| 0 | 0 | 38 | 100 | 100 |
| 0 | 0 | 39 | 100 | 100 |
| 0 | 0 | 40 | 100 | 100 |
| 0 | 0 | 41 | 100 | 100 |
| 0 | 0 | 42 | 100 | 100 |
| 0 | 0 | 43 | 100 | 100 |
| 0 | 0 | 44 | 100 | 100 |
| 0 | 0 | 45 | 100 | 100 |
| 0 | 0 | 46 | 100 | 100 |
| 0 | 0 | 47 | 100 | 100 |
| 0 | 0 | 48 | 100 | 100 |
| 0 | 0 | 49 | 100 | 100 |
| 0 | 0 | 50 | 100 | 100 |
| 0 | 0 | 51 | 100 | 100 |
| 0 | 0 | 52 | 100 | 100 |
| 0 | 0 | 53 | 100 | 100 |
| 0 | 0 | 54 | 100 | 100 |
| 0 | 0 | 55 | 100 | 100 |
| 0 | 0 | 56 | 100 | 100 |
| 0 | 0 | 57 | 100 | 100 |
| 0 | 0 | 58 | 100 | 100 |
| 0 | 0 | 59 | 100 | 100 |
| 0 | 0 | 60 | 100 | 100 |
| 0 | 0 | 61 | 100 | 100 |
| 0 | 0 | 62 | 100 | 100 |
| 0 | 0 | 63 | 100 | 100 |
| 0 | 0 | 64 | 100 | 100 |
| 0 | 0 | 65 | 100 | 100 |
| 0 | 0 | 66 | 100 | 100 |
| 0 | 0 | 67 | 100 | 100 |
| 0 | 0 | 68 | 100 | 100 |
| 0 | 0 | 69 | 100 | 100 |
| 0 | 0 | 70 | 100 | 100 |
| 0 | 0 | 71 | 100 | 100 |
| 0 | 0 | 72 | 100 | 100 |
| 0 | 0 | 73 | 100 | 100 |
| 0 | 0 | 74 | 100 | 100 |
| 0 | 0 | 75 | 100 | 100 |
| 0 | 0 | 76 | 100 | 100 |
| 0 | 0 | 77 | 100 | 100 |
| 0 | 0 | 78 | 100 | 100 |
| 0 | 0 | 79 | 100 | 100 |
| 0 | 0 | 80 | 100 | 100 |
| 0 | 0 | 81 | 100 | 100 |
| 0 | 0 | 82 | 100 | 100 |
| 0 | 0 | 83 | 100 | 100 |
| 0 | 0 | 84 | 100 | 100 |
| 0 | 0 | 85 | 100 | 100 |
| 0 | 0 | 86 | 100 | 100 |
| 0 | 0 | 87 | 100 | 100 |
| 0 | 0 | 88 | 100 | 100 |
| 0 | 0 | 89 | 100 | 100 |
| 0 | 0 | 90 | 100 | 100 |
| 0 | 0 | 91 | 100 | 100 |
| 0 | 0 | 92 | 100 | 100 |
| 0 | 0 | 93 | 100 | 100 |
| 0 | 0 | 94 | 100 | 100 |
| 0 | 0 | 95 | 100 | 100 |
| 0 | 0 | 96 | 100 | 100 |
| 0 | 0 | 97 | 100 | 100 |
| 0 | 0 | 98 | 100 | 100 |
| 0 | 0 | 99 | 100 | 100 |
| 0 | 0 | 100 | 100 | 100 |

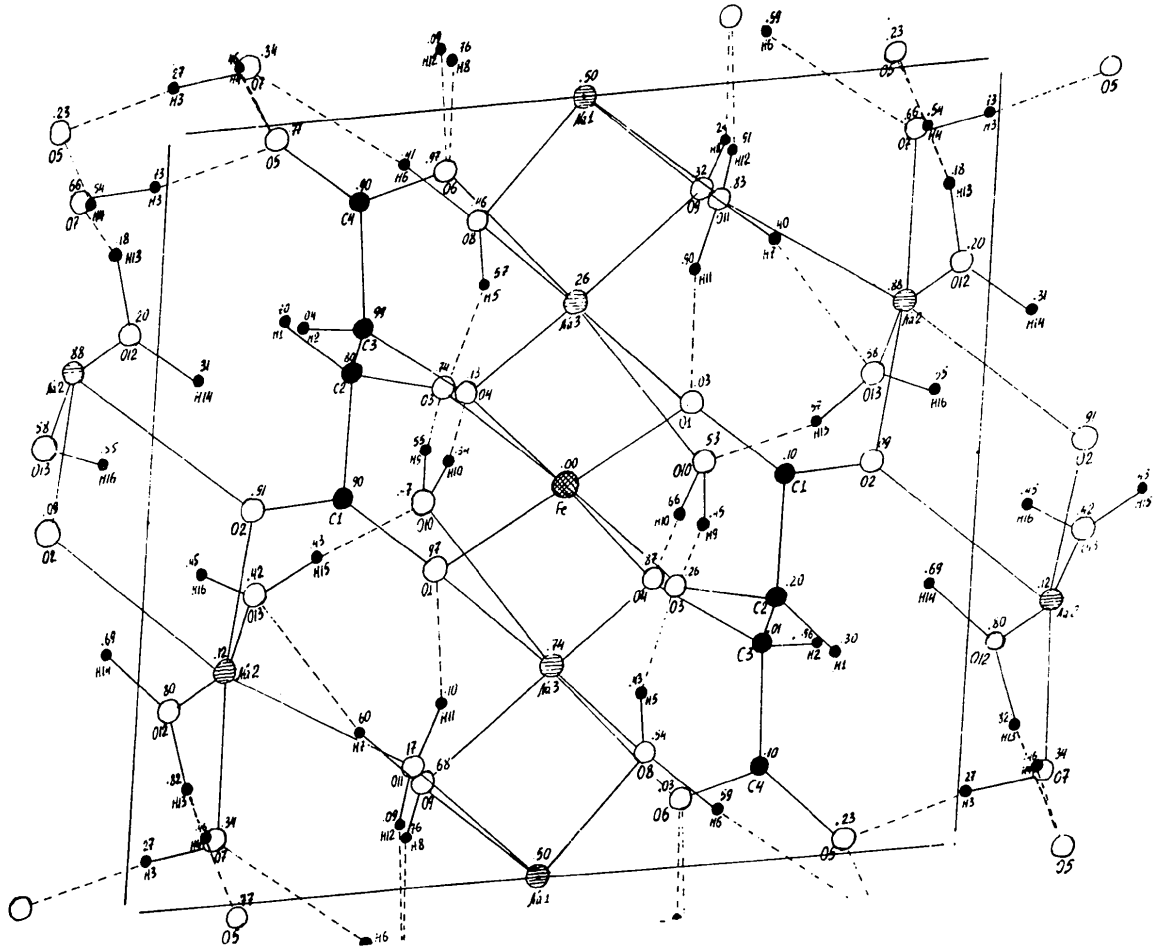


Fig. 2. Representation of the FeTNa structure projected along the *c* axis.

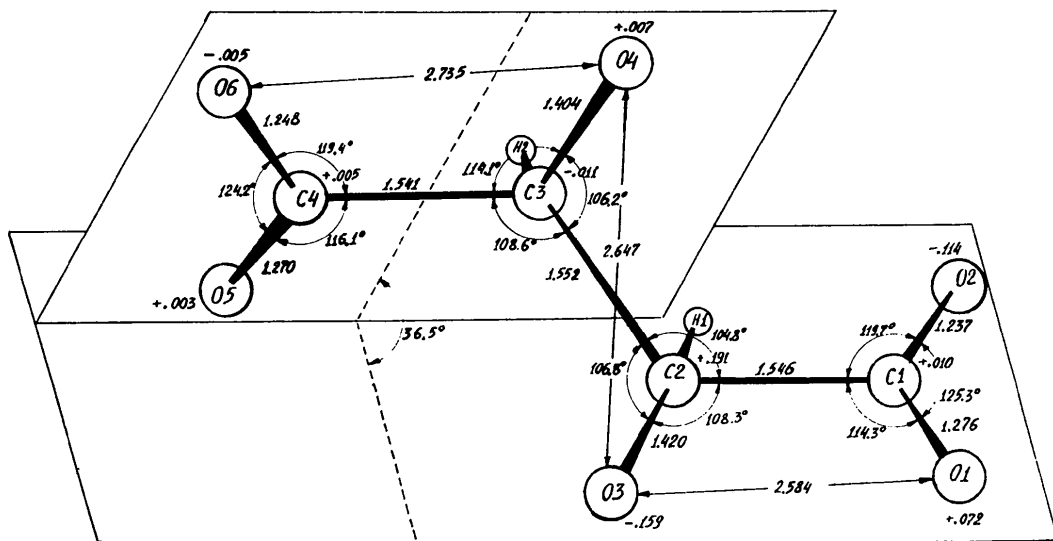


Fig. 3. Molecule of tartaric acid in the FeTNa structure represented in perspective; interatomic distances, angles and atomic deviations from the root-mean-square planes are shown.

Na and contributes to two H-bonds. The distances C(1)–O(1) and C(1)–O(2) (1.276 and 1.237 Å) are greater than C(4)–O(5) and C(4)–O(6) (1.270 and 1.248 Å), but the difference is not statistically significant.

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Acta Cryst. (1975). **B31**, 2848

The Crystal Structure of the Hydrochloride of 6,9-endo-Methylenhomopseudopelletierine, a Tricyclic Tropane Congener

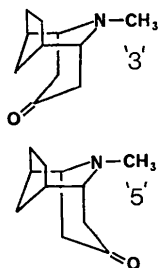
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(Received 22 April 1975; accepted 12 May 1975)

The structure of 6,9-endo-methylenhomopseudopelletierine.HCl was determined from film data, and refined by block-diagonal least-squares calculations to $R=0.073$ for 1556 observed data. The crystals are orthorhombic, space group *Pbca*, with $a=10.69$, $b=10.13$, $c=20.32$ Å, $Z=8$. The molecule approximates symmetry *m*, with the mirror plane passing through the Cl⁻ ion and the carbonyl and *N*-methyl groups of the *N*-methyl- γ -piperidone ring which has a flattened chair conformation.

Introduction

The Robinson–Schöpf (Schöpf, 1937) reaction of *cis*-cyclopentane-1,3-dialdehyde, methylamine hydrochloride and acetonedicarboxylic acid in a phosphate-buffered aqueous solution yields a single tricyclic amino ketone in high yield (Alder, Wirtz & Koppberg, 1956). A detailed study of the stereochemical course of this reaction by n.m.r. spectroscopy (Paquette & Heimaster, 1966) showed that in solution the molecule was 'best described as a mobile equilibrium of conformers' shown below.



The determination of the exact conformation of the *N*-methyl- γ -piperidone ring was of interest, and a crystal structure determination was therefore undertaken.

Experimental

Crystals of the hydrochloride, C₁₁H₁₈NOCl, were supplied by Dr Paquette. A well formed rectangular parallelepiped 0.8 × 0.3 × 0.3 mm was used for all X-ray work.

Oscillation, Weissenberg and precession photographs showed the cell to be orthorhombic, space group *Pbca* from systematic absences: $0kl$ for k odd, $h0l$ for l odd, $hk0$ for h odd. Accurate unit-cell dimensions were measured from calibrated zero-layer photographs. $a=10.69$ (1), $b=10.13$ (1), $c=20.32$ (2) Å; $d_{\text{obs}}=1.24$ g cm⁻³, measured by flotation in a chlorobenzene–bromobenzene mixture. $Z=8$.

Integrated multiple-film intensities were collected by the equi-inclination Weissenberg method with Ni-filtered Cu $K\alpha$ radiation for layers $0kl$ to $8kl$; $h0l$, $h1l$ and $hk0$ were collected for scaling purposes. The inten-