THE RICE INSTITUTE

The Crystal Structure of Some Cobalt Complexes

by

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A THESIS
SUBMITTED TO THE FACULTY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Arts

Jurg Waser

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ACKNOWLEDGEMENT

I wish to express my gratitude to Professor Jurg Waser for his constant advice and willing guidance during this work.
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SUMMARY

The crystal structures of the alkaline earth salts of ethylene diamine tetracetato-cobaltic complex, \( \text{Me}(\text{CoY})_2x\text{H}_2\text{O} \) (Me = Ca, Ba, Sr), were studied by means of X-ray diffraction of single crystals. The unit cell dimensions and crystal symmetries of the crystals are listed in the following table. Two modifications of the strontium salt were found.

<table>
<thead>
<tr>
<th></th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
<th>( \alpha_1 )</th>
<th>( \alpha_2 )</th>
<th>( \alpha_3 )</th>
<th>CRYSTAL SYMMETRY</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ba}(\text{CoY})_2x\text{H}_2\text{O} )</td>
<td>6.58</td>
<td>13.80</td>
<td>19.60</td>
<td>90°</td>
<td>95°11'</td>
<td>90°</td>
<td>monoclinic</td>
</tr>
<tr>
<td>( \text{Ca}(\text{CoY})_2x\text{H}_2\text{O} )</td>
<td>6.51</td>
<td>11.54</td>
<td>11.90</td>
<td>68°13'</td>
<td>86°26'</td>
<td>84°29'</td>
<td>triclinic</td>
</tr>
<tr>
<td>( \text{Sr}(\text{CoY})_2x\text{H}_2\text{O} )</td>
<td>6.52</td>
<td>11.47</td>
<td>12.25</td>
<td>67°54'</td>
<td>88°44'</td>
<td>84°1'</td>
<td>triclinic</td>
</tr>
<tr>
<td>( \text{Sr}(\text{CoY})_2x\text{H}_2\text{O} )</td>
<td>6.48</td>
<td>13.57</td>
<td>19.27</td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
<td>orthorhombic</td>
</tr>
</tbody>
</table>

Fourier projections of the calcium and triclinic strontium salt were made but only preliminary parameters \( y \) and \( z \) for the atoms have been obtained. The projections are in agreement with the hypothesis that two nitrogen atoms and four oxygen atoms of the same ethylene diamine tetracetate ion form bonds with a central cobalt atom.
I. INTRODUCTION

Polyamino polyacids and their ions have the ability of forming soluble complexes with polyvalent metal ions, giving a very low concentration of the cation. A very interesting compound of this class is ethylenediamine tetracetic acid (H$_4$Y).

Chemical properties of this acid, especially its complex formation, have been studied extensively by Schwarzenbach (1948, 49).

Cobaltic ion is well known to form complexes with coordination number six, such as Co(CH$_3$)$_6^{3-}$, Co(H$_2$)$_6^{++}$, etc. The corresponding complex with ethylene diamine tetracetic acid (H$_4$Y) has the formula CoY$^-$.

Schwarzenbach cites chemical evidence, which makes it likely that in the structure of this cobaltic complex there are coordination linkages between two nitrogens and four carboxyl oxygens and the central cobaltic ion as shown in the diagram.
In this paper, the structure of the cobaltic complex of ethylene diamine tetracetic acid is studied by means of X-ray diffraction. Single crystals of the barium, calcium and strontium salt of this complex (of the general formula $\text{Me(CoY)}_2\text{H}_2\text{O}$) were used in obtaining the diffraction patterns on which the structure analysis was based.
The procedure of preparing the calcium and strontium salts of the cobaltic complex was the one suggested by Schwarzenbach (1949). Fifteen grams of ethylene diamine tetracetic acid and 0.2 gram equivalent of the base (CaCO$_3$, SrCO$_3$) were mixed with 50 cc. of water, in a stoppered flask.

To oxidize the cobalt the mixture was cooled in an ice bath and shaken with 4 cc. of bromine in ten cc. of glacial acetic acid, until the violet color had gradually changed into blue or bluish green. Four cc. of concentrated hydrochloric acid were added to the flask which was always kept in the cold. The bromine complex, Me[Co(HY)Br]$_2$$\times$10H$_2$O, which precipitated as green short prisms or platelets, was purified by dissolving it in a small amount of the corresponding base. The solution was filtered and acidified with a little hydrochloric acid. The bromocomplex precipitated out and was collected by filtering with suction. It was washed with ice water and alcohol and then dried in air.

To remove the bromine the slightly soluble green bromo salt was mixed with some water and the calculated amount of Ag$_2$O. The reaction mixture was warmed briefly and the silver bromide formed was removed by filtering while hot. The violet salt Me(CoY)$_2$$\times$9H$_2$O (Me = Ca, Sr) crystallized from the filtrate on cooling in the form of violet long needles.

Calcium and strontium salts were prepared in this way, while a sample of the barium salt had been kindly furnished by Professor Schwarzenbach.
III. DETERMINATION OF UNIT CELL DIMENSIONS

A precession camera (Buerger, 1944) as well as a Weissenberg camera (Buerger, 1942) were used in taking the X-ray diffraction pictures of the cobaltic complex crystals. The precession camera records reflections corresponding to reciprocal lattice planes perpendicular to the X-ray beam, while in the Weissenberg camera reflections corresponding to reciprocal lattice net parallel to the beam are registered. Since in both instruments the crystal is mounted with the same axis almost perpendicular to the beam it is feasible to record reflections of three or more zones whose axes are non-coplanar with the same mounting of a crystal.

The crystals were mounted in such a way that their needle axis was nearly parallel to the axis of the goniometer head. In each case, a Weissenberg photograph was taken first with the needle axis as the axis of rotation. The pictures contained reflections (OKL). Despite a general resemblance, the patterns from different crystals indicated different symmetries. Two preparations of the strontium salt gave two different modifications. One showed no symmetry on the Weissenberg picture except for the center always present in equatorial photographs (pattern $C_2$, in Buerger nomenclature 1942). The other modification of the strontium salt produced a pattern with two mirror lines, at ninety degrees to each other and a diamond net ($C_{2i}$, D). Further exploration showed the first form to be triclinic, the second orthorhombic. Subsequent preparations of the strontium salt yielded always the triclinic form. The difference between the two forms is not likely due to different
chemical formulas, because their diffraction patterns bear close resemblance to each other. This polymorphism of the strontium salts was, however, not pursued further. The calcium (0KL) pictures had the same symmetry as those of the triclinic form of the strontium crystals, while the barium pictures had two mirror lines at right angles to each other, similar to those of the orthorhombic strontium pictures, but a rectangular net (C2I , n). The barium crystals were later found to be monoclinic.

The precession pictures were taken with the following orientations of the crystals. For the barium and orthorhombic strontium crystals the mirror lines were taken to define reciprocal axes B2 and B3 (B2 > B3). The crystals were adjusted so that the axis B1 reciprocal to the needle axis was parallel to the mounting axis of the goniometer head. The axes B2 and B3 were in turn parallel (or nearly parallel) to the vertical axis of the film. For the precession pictures of the triclinic calcium and strontium crystals analogous orientations were chosen, the above mirror lines being replaced by zone lines of strong intensity and approximately ninety degrees to each other. The vectors B2 and B3 were defined according to these zone lines.

The three vectors A1, A2, A3 and three angles $\alpha_1$, $\alpha_2$, $\alpha_3$ of the direct lattice are defined in terms of the reciprocal vectors B1, B2, B3 by the relations

$$A_1 = \frac{B_1 \delta B_2}{(B_1 B_2 B_3)}$$
The corresponding reciprocal lattice angles are $\beta_1$, $\beta_2$, $\beta_3$. The angle $\beta_1$ was measured from the Weissenberg picture as the distance between the two zone lines chosen as $b_2$ and $b_3$, and the angles $\beta_2$ and $\beta_3$ were recorded on the corresponding precession pictures. The reciprocal lattice constants were obtained by measuring the precession pictures on which a short exposure of quartz powder lines had been superimposed. The lattice constants of quartz being well established, the spacings of these lines served to minimize possible errors in our measurement caused by film shrinkage, etc. The length of $b_1$ was obtained from precession pictures of both orientations, and there was good agreement between the two values.

Cobaltic ion fluoresces in Cu K radiation, which was used here. This did not blacken the film unduly, however, since n-layer screens were used, slits admitting only the chosen diffracted beams, lying on the surface of a cone. A large part of the fluorescent radiation was therefore shielded off by these screens. Since for the determination of the unit cell dimensions only the positions of the diffracted beams are involved and not the intensities, Cu K radiation can safely be used.

The lattice constants and crystal symmetries of the barium, calcium and strontium crystals are listed in Table III-1.
The diffraction patterns of these crystals were found to have different extinctions which will be discussed separately in the forthcoming paragraphs.

A. Triclinic Calcium and Strontium Salts: In the diffraction patterns of the triclinic calcium and strontium salts only reflections with \( k + \ell \) even appeared, which indicates that the lattices are \( A_1 \) end centered. Since both salts belong to the triclinic system, the lattices can be described in a simpler way by transforming the end-centered unit cells into primitive ones. The results are listed in the following table:

<table>
<thead>
<tr>
<th>CRYSTAL</th>
<th>( A_1 ) Å</th>
<th>( A_2 ) Å</th>
<th>( A_3 ) Å</th>
<th>( \alpha_1 )</th>
<th>( \alpha_2 )</th>
<th>( \alpha_3 )</th>
<th>CRYSTAL SYMMETRY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(CoY)(_2)(x)(SH(_2))(_0)</td>
<td>6.58</td>
<td>13.80</td>
<td>19.60</td>
<td>90°</td>
<td>95°11'</td>
<td>90°</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Ca(CoY)(_2)(x)(SH(_2))(_0)</td>
<td>6.51</td>
<td>11.54</td>
<td>22.26</td>
<td>83°</td>
<td>88°50'</td>
<td>84°30'</td>
<td>triclinic</td>
</tr>
<tr>
<td>Sr(CoY)(_2)(x)(SH(_2))(_0)</td>
<td>6.52</td>
<td>13.26</td>
<td>19.68</td>
<td>94°5'</td>
<td>94°16'</td>
<td>94°</td>
<td>triclinic</td>
</tr>
<tr>
<td>Sr(CoY)(_2)(x)(SH(_2))(_0)</td>
<td>6.48</td>
<td>13.57</td>
<td>19.27</td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
<td>orthorhombic</td>
</tr>
</tbody>
</table>
The space group symmetry of these crystals is therefore $C_{\frac{1}{2}}^{-1}$ or $C_{1}^{-2}$, which differ by the absence or presence of symmetry centers.

B. Barium Salt: Reflections (0k0) are present only if k even. These absences would be explained by the space groups $P2_{1}/m$ and $P2_{1}$.

C. Orthorhombic Strontium Salt: One specimen of the strontium salt has orthorhombic symmetry. The only rigid extinction rule is that reflections (Ok0) are absent when k is odd, which leads to the probable space group $D_{2}^{2}-P2_{1}2_{1}2_{1}$. Only very few of the reflections (Ok0) with k odd and of the reflections (hk0) with h odd are present and they are exceedingly weak. In a good approximation the crystal has the probable

<table>
<thead>
<tr>
<th>Transformation matrix</th>
<th></th>
<th>Lattice constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_i = \alpha_{ik}A$</td>
<td>$a_1 , \text{Å}$</td>
<td>$a_2 , \text{Å}$</td>
</tr>
<tr>
<td><strong>Ca crystal</strong></td>
<td>6.51</td>
<td>11.54</td>
</tr>
<tr>
<td></td>
<td>6.52</td>
<td>11.47</td>
</tr>
<tr>
<td><strong>Sr crystal</strong></td>
<td>6.51</td>
<td>11.54</td>
</tr>
</tbody>
</table>
group symmetry \( C_{2v}^{2} - \text{Pn2}_1 \alpha \).

The pseudo extinctions mentioned are characteristic also of the space group \( \text{D}_{4h}^{16} - \text{Pmmn} \). The set of general positions in this space group is eight-fold and there are four-fold positions also, located on the inversion centers and on the mirror planes. Since there are only four complexes in the unit cell and since these complexes have no symmetry, this space group is eliminated.

The space group \( C_{2v}^{2} - \text{Pn2}_1 \alpha \) has a general set of four-fold positions only. There are two strontium ions per unit cell (and \( 18 = 4n - 2 \) water molecules) so that this space group symmetry can be approximate only. It is likely that it concerns the complex ions and most of the water molecules, while the two strontium ions and the remaining two water molecules are responsible for the weak reflections which disagree with the extinction rules. The fact that these spots are very weak means probably that the strongly scattering strontium ions are in very special positions.

The number of "molecules" per unit cell follows from the densities of the crystals, which were determined by suspension in a mixture of chloroform and ethylene dibromide. The results are collected in the following tables. The close relationship in the unit cell dimensions and diffraction patterns of the calcium and the triclinic strontium crystals makes it appear likely that the two substances are isomorphous.
### TABLE III-3

<table>
<thead>
<tr>
<th>Crystal</th>
<th>M(mol.u.t)</th>
<th>( \rho ) gm/cc</th>
<th>Vol. of unit cell ( \AA^3 )</th>
<th>Z(no. of &quot;mol&quot; per unit cell)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba crystal</td>
<td>993</td>
<td>2.001</td>
<td>1778</td>
<td>2</td>
</tr>
<tr>
<td>Ca crystal</td>
<td>896</td>
<td>1.789</td>
<td>826.1</td>
<td>1</td>
</tr>
<tr>
<td>Sr crystal (triclinic)</td>
<td>943.6</td>
<td>1.874</td>
<td>844.5</td>
<td>1</td>
</tr>
<tr>
<td>Sr crystal (orthorhombic)</td>
<td>943.6</td>
<td>1.874</td>
<td>1694</td>
<td>2</td>
</tr>
</tbody>
</table>

### TABLE III-4

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Ba(COY)(_2)(_x)H(_2)O</th>
<th>Ca(COY)(_2)(_x)H(_2)O</th>
<th>Sr(COY)(_2)(_x)H(_2)O</th>
<th>Sr(COY)(_2)(_x)H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>a(_1) Å</td>
<td>6.58</td>
<td>6.51</td>
<td>6.52</td>
<td>6.48</td>
</tr>
<tr>
<td>a(_2) Å</td>
<td>13.80</td>
<td>11.54</td>
<td>11.47</td>
<td>13.57</td>
</tr>
<tr>
<td>a(_3) Å</td>
<td>19.60</td>
<td>11.90</td>
<td>12.25</td>
<td>19.27</td>
</tr>
<tr>
<td>(\alpha)(_1)</td>
<td>90°</td>
<td>63°13'</td>
<td>67°54'</td>
<td>90°</td>
</tr>
<tr>
<td>(\alpha)(_2)</td>
<td>95°11'</td>
<td>88°26'</td>
<td>88°44'</td>
<td>90°</td>
</tr>
<tr>
<td>(\alpha)(_3)</td>
<td>90°</td>
<td>84°29'</td>
<td>84° 1'</td>
<td>90°</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Crystal Symmetry</th>
<th>monoclinic</th>
<th>triclinic</th>
<th>triclinic</th>
<th>orthorhombic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space Group</td>
<td>P2(_1)/n or P2(_1)</td>
<td>P1 or P1'</td>
<td>P1 or P1'</td>
<td>P2(_2)_2</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
IV. MEASUREMENT OF INTENSITIES

The unit cell dimensions are calculated from the positions of the reflections without reference to the intensities. But to find the arrangement of atoms in the unit cell, it is necessary to consider the intensities of the diffracted beams. The relative intensities were obtained by visual comparison of the films with an intensity scale to be described later. No effort was made to bring these intensities onto an absolute scale by instrumental means.

All the diffraction pictures, used in intensity measurements, were taken with the Weissenberg camera loaded with three sheets of film and two intervening sheets of brass foil, 0.001 inch thick. Mo K rather than Cu K radiation was used, since the shorter wavelength was less absorbed by the crystals. Besides the fluorescence of cobalt in Cu K radiation is undesirable in intensity work. Each diffraction spot was recorded on the three successive films at the same time, but weakened by the same factor after each passage through brass foil and film. Brass foil of the thickness chosen was used here because of its favorable absorption factor for Mo K radiation.

The absorption factor of the brass foil plus one sheet of film was determined in the following way. A prominent spot on a Weissenberg picture was selected as reference and the crystal was allowed to oscillate over ten degrees in the neighborhood of this spot, thus producing a narrow strip of the diffraction pattern containing the reference spot. Seven such strips were taken with different exposure times in the ratio
of $2^{0.1}$, $2^{0.2}$, $2^{0.3}$, $2^{0.4}$, $2^{0.5}$, and $2^{2.0}$, tube current and voltage being carefully regulated. A careful comparison of the three records showed that the density of the reference spot with the relative exposure time $2^{2.0}$ on the second film fell between those on the first film with the respective exposure times $2^{0.2}$ and $2^{0.1}$ and that the same relationship obtained between the second and third film. The absorption factor of the brass foil is therefore approximately

$$\frac{2^{2.0}}{2^{0.15}} = 2^{1.85} = 3.60$$

Once the absorption factor had been determined, a set of intensity scales was prepared using again three films with intervening brass foils and the same reference spot. Eight exposures were made on different places of the film, forming eight strips on each film. Each strip contained the reference spot with the following exposure times.

<table>
<thead>
<tr>
<th>Strip No.</th>
<th>Exposure Time</th>
<th>Relative Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3600.3 sec</td>
<td>$3.6^1 = 1.2^7$</td>
</tr>
<tr>
<td>2</td>
<td>3000.3</td>
<td>$3.6^6/7 = 1.2^6$</td>
</tr>
<tr>
<td>3</td>
<td>2490.3</td>
<td>$3.6^5/7 = 1.2^5$</td>
</tr>
<tr>
<td>4</td>
<td>2080.6</td>
<td>$3.6^4/7 = 1.2^4$</td>
</tr>
<tr>
<td>5</td>
<td>1730.7</td>
<td>$3.6^3/7 = 1.2^3$</td>
</tr>
<tr>
<td>6</td>
<td>1442.4</td>
<td>$3.6^2/7 = 1.2^2$</td>
</tr>
<tr>
<td>7</td>
<td>1201.3</td>
<td>$3.6^1/7 = 1.2^1$</td>
</tr>
<tr>
<td>8</td>
<td>1007.8</td>
<td>$3.6^0 = 1.2^0$</td>
</tr>
</tbody>
</table>
The ratio between the longest and shortest exposures was chosen to be
3.6, the absorption factor of the brass foil used. Therefore the weakest
strip on the first (or second) film had the same density as the strongest
strip on the second (or third) one. Starting from the weakest strip on
the third film, the strips were numbered consecutively from 0 to 21 in
the order of increasing density corresponding to the relative exposures
of \((1.2)^0, (1.2)^1, (1.2)^2, \ldots, (1.2)^{21}\).

Intensity pictures of calcium and strontium crystals were taken
only and, for the time being, only of reflections \(0k\ell\). The pictures
were indexed and the intensities of each diffracted beam compared with
the scale. Average values from the three successive films were taken
to obtain better accuracy, and the densities of very weak spots were
interpolated by an extension of the scale. These intensity data were
used in the Fourier and Patterson analyses to be described in the fol-
lowing section.
V. FOURIER ANALYSIS

The projection of the electron density \( \rho(y,z) \) along the axis \( \mathbf{a}_1 \) onto the plane (100) can be represented by a Fourier series

\[
\rho(y,z) = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} F(0k\ell) e^{-2\pi i(ky + \ell z)}
\]

The coefficients \( F(0k\ell) \) in this series are the structure factors which characterize the arrangement of the atoms in the unit cell and are related to the intensities of the diffracted beams. A projection along \( \mathbf{a}_1 \) was chosen as there would be expected few superpositions of atoms due to the shortness of this axis.

For an ideally imperfect crystal the relative intensities of the diffracted beams can be expressed as the product of Lorentz and polarization factors with the square of the absolute value of structure factor \( |F|^2 \)

\[
I(0k\ell) = \text{const.} \frac{1}{\sin^2 \phi / 2} |F(0k\ell)|^2
\]

From the observed \( I \)'s values of \( |F|^2 \) and \( |F| \) were obtained by using the convenient table of the trigonometric function in (v-2) of Lu (1943). In general the structure factor is a complex number,

\[
F(0k\ell) = |F(0k\ell)| e^{i\beta}
\]
where $e^{i\beta}$ is the phase component, $\beta$ being the phase angle of the diffracted beam. To calculate the electron density $\rho(y, z)$ from equation (V-1) the phase component $e^{i\beta}$ of the structure factors must be known as well as their absolute values. If centers of symmetry are present, the phases are limited to the values 0 and $\pi$, as may be seen from the following.

The structure factor, as mentioned before, is a function of the atomic arrangements. It has the form

$$F(Ok\ell) = \sum_i f_i e^{-2\pi i(ky_1 + \ell z_1)} \quad (V-3)$$

Here $f_i$ is the atomic scattering factor of the ith atom, $x_1, y_1, z_1$ are the coordinates of the ith atom, and the summation is carried over all the atoms in the unit cell. If a unit cell has a center of symmetry at the origin there must be for any atom at position $(x, y, z)$ an identical one at $(z, y, z)$ so that from (V-3)

$$F(Ok\ell) = \sum_i f_i e^{-2\pi i(ky_1 + \ell z_1)}$$

$$= \sum_i f_i e^{-2\pi i(ky_1 + \ell z_1)}$$

or $F(Ok\ell) = F^*(Ok\ell)$. Therefore the structure factors must be real and $\beta = 0$ or $\gamma$. The imaginary parts of the exponential functions in (V-1) cancel and the projection is given by

$$\rho(y, z) = \sum_{k=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} F(Ok\ell) \cos 2\pi(ky + \ell z) \quad (V-4)$$
If there is a center of symmetry, the problem of determining the phase components is simplified to the one of determining their signs. Since each unit cell contains one formula of Me(CoY)$_2$xH$_2$O, it was reasonable to assume that the two complex ions (CoY)$^-$ were arranged symmetrically with respect to a center which in turn was occupied by the metal ion (Ca$^{++}$ or Sr$^{++}$). A preliminary determination of the signs of the structure factors was based upon the isomorphism of the calcium and the triclinic strontium salts previously mentioned. Since both crystals are isomorphous to each other, they should have essentially the same structure, except for the replacement of calcium by strontium. The difference between the structure factors of the strontium and the calcium salts should be nearly the same as the difference between the atomic scattering factors of strontium and calcium ions.

$$F(Sr) - F(Ca) = f(Sr^{++}) - f(Ca^{++})$$

However, only relative values $F'(Okl) = K \times F(Okl)$ had been measured. To correlate the relative values of the structure factors from the two isomorphous crystals, one must bring them to the same scale.

The scale factor for the observed structure factors was estimated by the following method. If the squares of a reasonably large number of structure factors in a narrow range of $\theta$ are averaged over all $h, k, \ell$. 
\[
|F(hk\ell)|^2 = \sum_j f_j^2 \exp 2\pi i \left( h(x_j - x_\ell) + k(y_j - y_\ell) + \ell(z_j - z_\ell) \right)
\]

The final double sum is apt to be very small since different terms of similar magnitude have random phase and tend to cancel,

\[
|F(hk\ell)|^2 \sim \sum_j f_j^2(\theta)
\]

In a better approximation the contributions of the heavy atoms to this sum would have to be accounted for, but at this stage the coordinates of the cobalt atoms were not known. In this work the averaging was further carried over \(k\) and \(\ell\) only. If the scale factor \(K\) is defined as the ratio of observed over the actual value of the structure factor, it follows from the above that

\[
K^2 = \frac{|F'(0k\ell)|^2}{|F(0k\ell)|^2} = \frac{|F'(0k\ell)|^2}{\sum_j f_j^2(\theta)}
\]

Reflections with \(\sin \theta\) between 0.1 and 0.2 were taken to calculate

\[
|F'(0k\ell)|^2 = \sum_\ell \frac{1}{k} f_j^2 |F'(0k\ell)|^2 / \sum_\ell f_j^2(\theta). \quad \text{The atomic form factors } f_j(\theta) \text{ were taken from the Internationale Tabellen at } \sin \theta = 0.15.
\]

The constant \(K\) was calculated from the observed data from calcium.
and strontium crystals separately. It was found to be 0.0338 for calcium and 0.0326 for strontium crystals. Since the two scale factors turned out so close to each other, it was assumed that the relative observations from both salts were on the same scale so that

\[ F'(\text{Sr}) - F'(\text{Ca}) = K[f(\text{Sr}^{2+}) - f(\text{Ca}^{2+})], \]

the scattering due to complex ions and water molecules being the same in both cases.

Therefore,

\[ K = \frac{F'(\text{Sr}) - F'(\text{Ca})}{f(\text{Sr}^{2+}) - f(\text{Ca}^{2+})} = \frac{\frac{1}{2} |F'(\text{Sr})| - \frac{1}{2} |F'(\text{Ca})|}{f(\text{Sr}^{2+}) - f(\text{Ca}^{2+})} \]

Since the signs of the structure factors were known, there are four possible combinations of the positive and negative signs. But as the constant \( K \) must be positive from its nature as scale factor, the two combinations leading to negative values of \( K \) can be discarded. For each pair of reflections two alternatives remain. They are conveniently divided into two groups according to whether \( |F'(\text{Sr})| \geq |F'(\text{Ca})| \). The resulting possibilities are recorded in the following table.
<table>
<thead>
<tr>
<th>SCALE FACTOR K</th>
<th>SIGNS</th>
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<td>F'(Sr)</td>
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The two possible values for the scale factor were calculated for each pair of reflections. For most of the reflections, one of the values fell in the range 0.01 - 0.04, while the other was far from it so that the choice of the proper sign offered no difficulty in these cases. A number of reflections were discarded since no decision could be made on their signs. The first electron density map of the calcium crystal was calculated by Patterson and Tomell strips using these signs. Contour lines at equal altitude intervals were drawn to show the location of the peaks on which the resolved atoms should fall.

On the first Fourier projection there appeared a heavy peak at the origin, presumably representing the calcium ion and two other heavy ones related by a center of symmetry. These two obviously should be the two cobaltic ions. To interpret the remaining peaks of much lower magnitude an ideal model of the complex \((CoY)^7\) was made with theoretical bond dis-
tances and angles (Pauling, 1940) and, in accordance with Schwerzenbach's views, with the cobaltic ion octahedrally surrounded by two nitrogen atoms and four oxygen atoms. It was found that essentially only two such models could be constructed, one being the mirror image of the other. The arrangement of the oxygens and nitrogens surrounding the cobalt, as well as of the carbons attached to them was given quite uniquely by the assumed angles and distances, but for the peripheral carbons and oxygens some flexibility remained. The assumed centers of symmetry in the crystal would of course require the presence of one molecule of each kind per unit cell. They could be conveniently arranged with respect to the centers of inversion so as not to interfere with one another or the molecules in neighboring cells.

With the help of this model, most of the maxima were easily identified, except for two carbon atoms in each acid molecule, which did not correspond to peaks at appropriate positions. No attempt was made to locate the water molecules.

The structure factors of this idealized atomic arrangement were calculated, and their signs were combined with the observed structure factors to compute a second Fourier projection. The electron density map obtained is shown in figure 1. For all the lower peaks, the contour lines are at an arbitrary but constant interval, while for the high peaks, representing the calcium and the two cobaltic ions, the contour lines are at double this interval. The atoms composing the complex ion are labeled, and the chemical bonds are indicated with broken lines. Comparing the first and second projections, there was no change in the posi-
tions of the calcium and cobaltic ions, and very little change for the six atoms around it. But those farther removed from the cobalt were shifted as much as 0.5 Å to 1 Å.

The structure factors $F(0k\ell)$ were calculated for the atomic configurations from the second projection. Fair agreement was obtained between factors for a large fraction of the values, but for the remainder the agreement was poor. This indicates that the parameters of the carbon and oxygen atoms should be further adjusted.

In the second projection the lower peaks of the lighter atoms might deviate from their true positions and there was a number of false peaks which could not be distinguished from the true ones. The errors were most likely due to the following two facts: (1) Some terms were left out in summing the Fourier series because of the doubtfulness of their signs. (2) The "diffraction waves" (Bragg and West, 1930) due to the "breaking-off error" for the heavy atoms, calcium and cobalt, were of a magnitude comparable with that of the lower peaks of the lighter atoms.

Two ways present themselves to minimize the "breaking-off error". An artificial temperature factor $\exp(-a \sin^2 \theta)$ may be introduced such that $F'' = F' \exp(-a \sin^2 \theta)$. The temperature factor acts as a convergence factor, decreasing the importance of the coefficients as $\sin \theta$ increases. It causes the peaks in the projection to be broadened.

Another method is to calculate a synthetic Fourier projection using as coefficients the structure factors calculated from the already known parameters of $\text{Co}^{+++}$ and $\text{Me}^{+++}$ and breaking off the series at the same value of $\sin \theta$. This function is then subtracted from the electron
density projection. The resulting map will contain the light peaks not affected by the "diffraction waves" from the heavy atoms. Probably a set of improved parameter values would be obtained by this procedure.

To gain confirmation of the present interpretation of $\rho(y,z)$ for the calcium salt a projection was made for the strontium salt using a different method of determining the signs. Assuming the cobaltic ions to have the same $(y,z)$ coordinates in both calcium and strontium crystals, structure factors with $\text{Sr}^{++}$ and $\text{Co}^{++}$ only were calculated for all the reflections. Since the atomic number of strontium is larger than that of calcium, it is expected that the signs of most terms can be determined by considering $\text{Sr}^{++}$ and $\text{Co}^{++}$ alone. But the "breaking off error" would be worse for $\text{Sr}^{++}$ also.

The signs of one hundred and two terms out of hundred and twenty-four observed structure factors were considered reasonably assured by this procedure and were used in calculating an electron density projection. Figure 2 represents a contour map of this projection, with contour lines drawn in the same way as those for calcium. The arrangement of the peaks in the unit cell is very similar to that of fig. 1 and serves to check the original assumption that the calcium and the strontium salts have essentially the same structure. The cobaltic ions have exactly the same parameters in both crystals, but the peaks for the lighter atoms are not all located at the same positions. Since not all of the terms used in the projection for the strontium salt can be presumed certain, and since the "breaking off" error for strontium is large, this difference may not be significant. It is hoped that a detailed analysis
of the differences between the two projections may lead to improved parameter values for both.

It was recently proposed that electron densities can be obtained without a knowledge of the phases of the diffracted beams. The procedure made use of the Patterson function (Patterson, 1934).

\[ P(y, z) = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} |F(Ok \ell)|^2 \cos 2\pi \left( k\frac{y}{a} + l\frac{z}{b}\right) \]  

(V-5)

which gives peaks at vector distances from the origin equal to vector distances between pairs of maxima in the electron density projection. It has been shown (Buerger, 1950) that by superposing the origin of one sheet of the Patterson projection on a suitable peak on a similar sheet and recording only peaks appearing on both sheets, it should be possible to resolve the vector map to give essentially a projection of the electron density. One superposition may suffice for complete resolution if the peak on which the origin is superposed corresponds to a vector between maxima in electron density, which are related by a center of symmetry. The resolution will, however, not be complete if this vector accidentally corresponds to other interatomic vectors also.

This method was tried on the calcium crystal. A Patterson projection along the needle axis was calculated by equation (V-5). The contour map obtained is shown in figure 3. In addition to the one at the origin, two heavy peaks appeared, each of which contains mainly the interactions between the calcium and cobalt and the two cobalt ions. Contour lines were drawn at arbitrary but equal intervals, and at double this interval
Fig. 3
for the heavy peaks.

An effort was made to resolve this projection by superposing the origin of one sheet on the peak due to the interaction between the two cobaltic ions the parameters of which were deduced from the Fourier projection. On a third sheet the lower of the two numbers was recorded for each point at which \( P(y, z) \) had been calculated. The result did show a number of resolved peaks, but not enough to obtain improvement of the parameters deduced from the Fourier projection. This disappointing outcome is doubtlessly due to the fact that the projections of the three heavy atoms are almost equally spaced along the diagonal of the \((ac^2b_3)\) net.

Despite the fact that the present parameter values of the carbon and oxygen atoms are by no means final, it is clear that the idea that the cobaltic ion is octahedrally surrounded by two nitrogens and four carboxyl oxygens is essentially correct.
BIBLIOGRAPHY