The Crystal Structure of CsCoCl₃·2H₂O

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Violet platy crystals of CsCoCl₃·2H₂O were prepared by slow evaporation at room temperature of an aqueous solution containing CsCl and CoCl₂ in the molar ratio 5.26:1.00, (Benrath ¹). The correct composition of the compound was checked by chemical analysis: 17.79 % Co and 31.86 % Cl (calc. 17.77 and 32.07 resp.). The violet dihydrate converts into the blue anhydride when exposed to the atmosphere. The crystals used for the structure investigation were therefore sealed into thin-walled glass capillaries.

The space group Pcca was unequivocally established by means of precession photographs, applying Zr-filtered Mo-radiation. The unit cell dimensions, \( a = 8.914(5) \), \( b = 7.174(5) \), and \( c = 11.360(5) \AA \), were determined from a powder photograph using Nelson and Riley’s extrapolation method ¹ (Mn-filtered FeKα radiation). The density found by flotation was 3.01 g·cm⁻³ in fair agreement with a calculated density of 3.06 g·cm⁻³ assuming four formula units per unit cell. Preliminary Weissenberg photographs of several crystals revealed a severe splitting of most of the reflexions. Nevertheless, a regular structure analysis was endeavoured. A crystal fragment of the approximate dimensions 0.2 × 0.2 × 1.5 mm, cut from a large crystal plate, was finally chosen for the collection of three-dimensional intensity data.

The data collection was performed by means of an automatic equi-inclination diffractometer (STOE & CIE, Darmstadt, DBK). MoKα-radiation was selected using a LiF monochromator. Harmonics were excluded by using a scintillation detector with proper settings of a pulse height discriminator. The relative intensities of non-extinct reflexions 0kl through 7kl \( (\theta_{\text{max}} = 30°) \) were measured by ω-scanning. 331 reflexions having net intensities less than twice the standard deviation, calculated from counting statistics, were rejected as non-observable. This left a total of 559 independent observations. The intensities were transformed to relative structure factors by conventional calculations. In view of the rather poor quality of the crystal no correction for absorption was made, although \( \mu \) for MoKα is 28.4 cm⁻¹.

CsCoCl₃·2H₂O was expected to be isostructural with CsMnCl₂·2H₂O which has been investigated by Stig J. Jensen et al. ⁴ A set of structure factors based on the parameters of CsMnCl₂·2H₂O were calculated. Atomic scattering factors were taken from International Tables ⁴ except for Cs where the values given by Cromer and Waber ² were used. The value of the residual \( R = \sum |F_o| - |F_c|/\sum |F_o| \) was 0.179. Then a full-matrix least squares refinement was carried out with isotropic temperature factors. The weighting function used was \( 1/w = -F + \sqrt{\sigma(F^2) + 1.05F^2} \), where \( \sigma(F^2) \) is the standard deviation based on Poisson counting statistics. The refinement was terminated with the residuals \( R = 0.080 \) and \( wR = 0.094 \). A tentative refinement applying anisotropic temperature factors did not significantly change the positional parameters, which are listed in Table 1.

CsCoCl₃·2H₂O is isostructural with CsMnCl₂·2H₂O and α-RbMnCl₂·2H₂O, which have been described in detail by Stig J. Jensen. ⁴ The transition metal is octahedrally surrounded by four chlorine atoms and two water molecules, the latter occupy-

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**Table 1. Positional and thermal parameters for CsCoCl₃·2H₂O.**

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( B )</th>
</tr>
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<tbody>
<tr>
<td>Cs</td>
<td>0.2500</td>
<td>0.0000</td>
<td>0.1455</td>
<td>2.15</td>
</tr>
<tr>
<td>Co</td>
<td>0.0000</td>
<td>0.4727</td>
<td>0.2500</td>
<td>0.78</td>
</tr>
<tr>
<td>Cl I</td>
<td>0.2500</td>
<td>0.5000</td>
<td>0.1529</td>
<td>1.18</td>
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<tr>
<td>Cl II</td>
<td>0.0866</td>
<td>0.2344</td>
<td>0.3879</td>
<td>1.37</td>
</tr>
<tr>
<td>O</td>
<td>0.0659</td>
<td>0.6795</td>
<td>0.3861</td>
<td>1.77</td>
</tr>
</tbody>
</table>

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ing cis positions of the distorted octa-
edron. The distances from the central Co-
atom to the chlorine and oxygen atoms are:
Co—Cl I 2.494(3) Å, Co—Cl II 2.444(5) Å,
and Co—O 2.070(13) Å. The oxygen atoms
have four chlorine atoms as nearest neigh-
bours outside the octahedron. Two of these
Cl—O distances are rather short, both
3.17(1) Å, and the corresponding angle
Cl—O—Cl is 108.2(4)°. This structural
feature which is also observed in
CsMnCl$_3$.2H$_2$O and in α-RbMnCl$_3$.2H$_2$O
is taken as evidence for hydrogen bonding
as suggested by Stig J. Jensen.\textsuperscript{a}

All the crystallographic calculations were
carried out at Northern Europe University
Computing Center (NEUCC) using the
program system “X-Ray 63” edited by
Stewart.

A list of structure factors may be ob-
tained from the authors.

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