The Crystal Structure of $CsCoCl_3 \cdot 2H_2O$

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Violet platy crystals of $CsCoCl_3 \cdot 2H_2O$ were prepared by slow evaporation at room temperature of an aqueous solution containing CsCl and $CoCl_2$ 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 $c = 11.360(5)$ Å, were determined from a powder photograph using Nelson and Riley's extrapolation method [2] (Mn-filtered Fe$K\alpha$-radiation). The density found by flotation was 3.01 gcm^{-3} in fair agreement with a calculated density of 3.06 gcm^{-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 $0.2 \times 0.2 \times 1.5$ 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, DBR). Mo$K\alpha$-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 $7kl$ ($\theta_{max} = 30°$) 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 μ for Mo$K\alpha$ is 28.4 cm^{-1}.

$CsCoCl_3 \cdot 2H_2O$ was expected to be isostructural with $CsMnCl_3 \cdot 2H_2O$ which has been investigated by Stig J. Jensen *et al.*[3] A set of structure factors based on the parameters of $CsMnCl_3 \cdot 2H_2O$ were calculated. Atomic scattering factors were taken from *International Tables*,[4] except for Cs where the values given by Cromer and Waber [5] 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 $1/\sqrt{w} = -F + \sqrt{\sigma(F^2) + 1.05F^2}$, 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.

$CsCoCl_3 \cdot 2H_2O$ is isostructural with $CsMnCl_3 \cdot 2H_2O$ and α-$RbMnCl_3 \cdot 2H_2O$, which have been described in detail by Stig J. Jensen.[3,6] The transition metal is octahedrally surrounded by four chlorine atoms and two water molecules, the latter occupy-

Table 1. Positional and thermal parameters for $CsCoCl_3 \cdot 2H_2O$.

Atom	x	y	z	B
Cs	0.2500 (0)	0.0000 (0)	0.1455 (2)	2.15 (4)
Co	0.0000 (0)	0.4727 (4)	0.2500 (0)	0.78 (6)
Cl I	0.2500 (0)	0.5000 (0)	0.1529 (5)	1.18 (8)
Cl II	0.0866 (5)	0.2344 (5)	0.3879 (4)	1.37 (7)
O	0.0659 (13)	0.6795 (17)	0.3661 (10)	1.77 (23)

ing *cis* positions of the distorted octahedron. 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 neighbours 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 $CsMnCl_3 \cdot 2H_2O$ and in α-$RbMnCl_3 \cdot 2H_2O$ is taken as evidence for hydrogen bonding as suggested by Stig J. Jensen.[8]

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 obtained from the authors.

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