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The structures of hexagonal $CsCdCl_3$ and tetragonal Cs_2CdCl_4.*

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$CsCdCl_3$ has been reported by Ferrari & Baroni (1927) as cubic, perovskite type, with $a=5{\cdot}21$ Å. Subsequently, Naráy-Szabo (1947–1948) indicated monoclinic symmetry with dimensions near $a=b=c=10{\cdot}42$ Å and $\beta=90°$. Our observations indicate that crystals of $CsCdCl_3$ grown from the melt develop with hexagonal symmetry, while those grown from solution are predominantly hexagonal with small amounts of a cubic modification present. Single-crystal studies of the cubic form lead to the small cell, and, within the limits of accuracy of our intensity data, to the perovskite type as reported. The dimensions of the hexagonal phase are: $a=7{\cdot}418\pm0{\cdot}004$ and $c=18{\cdot}39\pm0{\cdot}03$ Å, with six molecules in the unit cell. Powder patterns of the two forms exhibit a striking similarity.

Multifilm Weissenberg patterns were obtained with Cu $K\alpha$ radiation. No space group could be assigned because of the presence of many structural extinctions. However, the structural problem is similar to that described by Wells (1947) for cesium cupric chloride. For this compound he considered those structures which could be derived from six close-packed layers of $CsCl_3$ composition with octahedral vacancies available for copper atoms. One of the possible configurations was found to lead to the correct structure for $CsCdCl_3$, based on space group $P6_3/mmc$. All atoms are in the following special positions: $2\mathrm{Cs_I}$ in (*b*), $4\mathrm{Cs_{II}}$ in (*f*), $z=0{\cdot}091$, $2\mathrm{Cd_I}$ in (*a*), $4\mathrm{Cd_{II}}$ in (*f*), $z=0{\cdot}838$, $6Cl_{\mathrm{I}}$ in (*h*), $x=0{\cdot}509$, and $12Cl_{\mathrm{II}}$ in (*k*), with $x=0{\cdot}834$, and $z=0{\cdot}0838$. The coordinates were determined from electron density maps followed by a least-squares refinement. The reliability index R was 19% based on 226 reflections. As evidenced by the space group and coordinates, this form of $CsCdCl_3$ is isostructural with hexagonal $BaTiO_3$ (Burbank & Evans, 1948).

Each cadmium atom is bonded to six chlorine neighbors at the corners of an octahedron. For $\mathrm{Cd_I}$, the octahedron is formed by $\mathrm{Cl_{II}}$ atoms which share corners with other octahedra. For this configuration, $\mathrm{Cl_{II}-Cl_{II}}=3{\cdot}70$ Å for chlorine atoms in a plane at the same height z, $\mathrm{Cl_{II}-Cl_{II}}=3{\cdot}73$ Å for chlorine atoms between these planes, and $\mathrm{Cd_I-6Cl_{II}}=2{\cdot}64$ Å. On the other hand, each $\mathrm{Cd_{II}}$ is the center of an octahedron formed by $3\mathrm{Cl_I}$ and $3\mathrm{Cl_{II}}$, with the three $\mathrm{Cl_I}$ atoms common to two octahedra. Thus, two octahedra formed with $\mathrm{Cd_{II}}$ atoms at the centers share faces. For the shared octahedra, $\mathrm{Cd_{II}-Cd_{II}}=3{\cdot}23$ Å with the $\mathrm{Cd_{II}}$ atoms shifted away from their octahedral "centers" towards the planes of the $\mathrm{Cl_{II}}$ atoms. Within the shared face, $\mathrm{Cl_I-Cl_I}=3{\cdot}51$ Å, $\mathrm{Cl_{II}-Cl_{II}}=3{\cdot}73$ Å, $\mathrm{Cl_I-Cl_{II}}=3{\cdot}69$ Å, and $\mathrm{Cd_{II}-3Cl_I3Cl_{II}}=2{\cdot}59$ Å. All Cs–Cl distances are about $3{\cdot}70$ Å with the exception of $\mathrm{Cs_{II}-3Cl_{II}}=3{\cdot}87$ Å. All bond distance errors for the metal–chlorine or chlorine–chlorine separations are about $\pm0{\cdot}04$ Å.

The shift of the $\mathrm{Cd_{II}}$ atoms is associated with a substantial decrease in the $\mathrm{Cl_I-Cl_I}$ distances, resulting in an appreciable distortion of the shared octahedra.

The cell dimensions for $CsCdCl_3$ are substantially larger than those for hexagonal $BaTiO_3$. However, the c/a ratios are comparable and it is observed that for $CsCdCl_3$, the deviations from the idealized close-packed structure lead to bond length variations and distortions of the octahedra which follow closely similar variations and distortions observed for $BaTiO_3$.

Cs_2CdCl_4 is tetragonal with $a=5{\cdot}26$ and $c=16{\cdot}88$ Å, and two molecules in the cell. The space group is I_4/mmm and the compound is isostructural with K_2NiF_4 (Balz, 1953). Atoms are in the following positions: 4Cs in (*e*), $z=0{\cdot}357$, 2Cd in (*a*), $4\mathrm{Cl_I}$ in (*c*) and $4\mathrm{Cl_{II}}$ in (*e*), with $z=0{\cdot}149$. Positions were determined from single-crystal Weissenberg and precession data.

Each octahedron shares four corners with four other octahedra. In the xy plane, $\mathrm{Cl_I-Cl_I}=3{\cdot}72$ Å while in the xz plane, $\mathrm{Cl_I-Cl_{II}}=3{\cdot}64$ Å. $\mathrm{Cd-4Cl_I}=2{\cdot}64$ and $\mathrm{Cd-2Cl_{II}}=2{\cdot}51$ Å. For the caesium–chlorine coordination $\mathrm{Cs-4Cl_{II}}=3{\cdot}72$, $\mathrm{Cs-1Cl_{II}}=3{\cdot}51$, and $\mathrm{Cs-4Cl_I}=3{\cdot}57$ Å.

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