Criteria for hydrogen bonding. II. A hydrogen bond in the edge of a coordination polyhedron around a cation. 

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The bond length Cs–O(4) given in Table 1 in Acta Cryst. (1973), B29, 139 should be 3.515 Å.

Because of a misprint the value of the bond length Cs–O(4) in Table 1 (Baur, 1973) reads as 3.315 Å. The correct value of Cs–O(4) is 3.515 Å. Therefore the statement (Baur, 1973) "that the distance Cs–O(4) to the acceptor atom of the hydrogen bond is the largest of the distances considered to belong to the coordination polyhedron around the Cs-atom" is correct after all, even though it is not apparent from Table 1 as it was printed. Since atom O(4) is the acceptor atom of the hydrogen bond located in the edge of the coordination polyhedron around the Cs atom it is significant that Cs–O(4) is a long bond.

Reference


Orientation relation in the transformation of the NaCl-related to the CsCl-related structure in rubidium nitrate.

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The structure transformation RbNO₃ I(NaCl-like) → II → III(CsCl-like) proceeds topotaxically, with an orientation relation in which [100]ₜ || [100]ₜI. Despite the presence of the complex ion the relation is similar to one of the relations observed in the transformations NaCl-type ↔ CsCl-type in NH₄Br.

It has already been shown that the forward and reverse transformations CsCl-type (simple cubic) ↔ NaCl-type (f.c.c.) are topotaxic in that definite orientation relations result, and there is evidence that at least on supercooling the mechanism is martensitic (Fraser & Kennedy, 1972; Kennedy, Patterson, Chaplin & Mackay, 1973). It has not been known how far crystal-chemical relations can result in topotaxy when in addition to a large lattice deformation, the planar complex ions such as NO₃⁻, CO₃²⁻, must tilt during the transformation. Rubidium nitrate affords a test of this. In rubidium nitrate an NaCl-like f.c.c. phase (I) (having randomized orientations of anions) (Kennedy, 1970a; Strømme, 1971) is linked to a CsCl-like cubic phase III (Korhonen, 1951) through a phase II which is stable between 219 and 284°C. Phase II is commonly considered to be rhombohedral, calcite-like (e.g. Salhotra, Subbarao & Venkateswarlu, 1968) but tetragonal symmetry has also been suggested (Brown & McClaren, 1962). The primitive cubic cell of phase III is a sub-cell, the plane of the anion being differently oriented in neighbouring sub-cells. The volume change III → I || [100] is 16% is the same as in CsCl and NH₄Br, but ΔVₐₐ = 0 and ΔVₐₐ = 1 is small, the remainder being accounted for by thermal expansion of II (Salhotra, Subbarao & Venkateswarlu, 1968). Because of the disruption previously observed at the transformation III → II in needle-like crystals it has been considered that in practice the large structure and volume change do not permit topotaxy (Brown & McClaren, 1962). Topotaxy in the transformation II → I (Kennedy, 1966), and in I → II with fine twinning (Kennedy, 1970a) has already been reported. The present work shows that a definite orientation relation is also maintained between the NaCl-like phase I and the CsCl-like phase III during the transformations I → II → III.

Single crystals of RbNO₃ I were grown from the melt at 310°C on glass cover-slips on a flat heater carried on the goniometer head of an X-ray camera, which itself carried a detachable polarising microscope. Form I was oriented, and the orientation of III determined, by precession and front-reflexion Laue photographs, the X-rays being transmitted through the glass.

The resulting finely twinned specimens of phase II detwinned after 15 min, giving up to six reproducible orientations. When such detwinned specimens were maintained slightly below 219°C fine platelets of phase III appeared in three orientations within each single block of phase II (Kennedy, 1970b). The traces of the platelets were parallel to the traces of the twin-plane of the calcite-like structure. The platelets grew first into blocks and then into an irregular shape. Fine remnants of phase II trapped between adjacent regions of phase III could be supercooled to 164°C. Only one type of orientation was found both in individual specimens, and in repeated experiments:

\[
\begin{align*}
(001)_I & \parallel [011]_I, \\
[100]_I & \parallel [100]_I.
\end{align*}
\]

This however is a mean orientation. The reflexions were split into several components which corresponded to individual orientations differing from this mean by up to 5°. The splitting of the reflexions is probably due to variants of an irrational relation. This result is the converse of relation C of Kennedy, Patterson, Chaplin & Mackay (1973).
for NH₄Br II \( \rightarrow \) I and close to relation C of Fraser & Kennedy (1972) for NH₄Br I \( \rightarrow \) II, and is probably a secondary orientation in CsCl (Chatterji, Mackay & Jeffery, 1970). The commonly accepted lattice correspondence relates f.c.c. and primitive cubic (or rhombohedral) through the primitive rhombohedron of the f.c.c. lattice (Shoji, 1931) the lattice transformation being effected by a pure strain the principal axis of which is the common [111] direction. This is only one component of the total deformations that would also accommodate the structures, but the additional rotation that would produce the present relation is unexpectedly large. In fact the relation corresponds to the Bain strain (principal axis [100]), which would have to be combined with shears to produce the structure of III. Whilst the twinning in the transformation I \( \rightarrow \) II was consistent with a martensitic mechanism, detailed discussion of the mechanism of II \( \rightarrow \) III especially awaits further investigations.

The results already obtained nevertheless imply topotaxy not only between the NaCl-like and CsCl-like phases, but also between the RbNO₃ II and low-RbNO₃ structures. They support the view that a large structure change is consistent with topotaxy in chemical compounds; and they imply that though a particular variation may be favoured, the transformations of compounds of complex ions can follow the same geometry that applies to compounds of simple or near-spherical ions.

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References


