ON CHRIST'S POSTULATED BORON-OXYGEN POLYIONS IN SOME HYDRATED BORATES OF UNKNOWN CRYSTAL STRUCTURES[1]

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Recent systematic structural studies of the hydrated borates have made it possible to synthesize a set of "rules" (Christ, 1960; Edwards and Ross, 1960) which seemingly govern the nature of the complex boron-oxygen polyions existing in such crystals. Following these rules, Christ (1960) has postulated the type of polyion to be found in each of many hydrated borates of unknown crystal structures. This has allowed him to classify these compounds and assign structural formulas. The purpose of this note is to describe briefly the results of experimental tests of the predictions made by Christ as to the nature of the polyions in several hydrated borates.

The nuclear magnetic resonance (n.m.r.) technique provides one with a tool to use nuclei already present in a crystal as probes to explore the internal electric fields. The interactions between the nuclear electric quadrupole moments and the electric field gradients manifest themselves as a splitting of the normal resonance absorption signal into several components. A study of the magnitude and orientation dependence of this splitting allows one to determine the quadrupole coupling tensor which is the product of an unchangeable nuclear property, the nuclear electric quadrupole moment, and the gradient of the electric field at the nuclear site. The quadrupole coupling tensor is usually characterized by its largest component called the quadrupole coupling constant (q.c.c.), the ratio of the difference between the smallest and intermediate components to the largest component which is called the asymmetry parameter (η) and the orientation of the principal axes.

The field gradient tensor at a nuclear site depends upon the detailed charge distribution in the neighbourhood of the nucleus. In a crystal containing tightly bound complexes, the charge distribution is determined by the electrical forces that bind the atoms within the complexes and bind neighbouring complexes to form the crystal. There is evidence that the binding within the complexes is much the strongest so that the properties of the complexes in the solid do not differ very greatly from those they would exhibit if they were isolated. In these cases, it is often possible

to determine the nature of a complex by comparing the gross features of the quadrupole coupling tensors at some of the nuclear sites with what one would expect for an ideal or isolated complex.

In the hydrated borates, the boron atoms are tightly bound to oxygen atoms in either tetrahedral or triangular coordination. These BO_4 tetrahedra and BO_3 triangles may be expected to exist as discrete insular complexes or to form larger groupings or polyions by sharing oxygen atoms. Extrapolating from symmetry considerations for the ideal unit, one would predict that the q.c.c. for a B^{11} nucleus at the center of a BO_4 tetrahedron would be very small if the tetrahedron existed as a discrete unit in the crystal and somewhat larger if the tetrahedron were bound with other tetrahedra and triangles to form a condensed polyion such as a closed ring. For a B^{11} nucleus at the center of a BO_3 triangle, one would predict (1) that the q.c.c. would be considerably larger than in the case of a tetrahedron, (2) that the value of η would be very small, and (3) that the z (direction in which the tensor has its maximum component) principal axis would be nearly perpendicular to the plane containing the triangle. These predictions have been verified for discrete BO_4 tetrahedra in teepleite (Ross and Edwards, 1959) and for tetrahedra and a triangle in a closed ring in colemanite (Holuj and Petch, 1960). The characteristic values of the q.c.c. are unambiguous, falling at about 100, 500 and 2500 kc/sec for discrete tetrahedra, tetrahedra in closed-ring polyions and triangles, respectively.

We have studied the quadrupolar splitting of the B^{11} n.m.r. signals in single crystals of several hydrated borates. In the monoclinic and triclinic dimorphs of $Mg_2B_6O_{11} \cdot 15H_2O$, inderite and kurnakovite[1] respectively, the asymmetric unit has been found to contain three chemically different boron sites. At two of these sites the B^{11} q.c.c.'s have values characteristic of those found for tetrahedra in closed-ring polyions and at the third site the q.c.c. is characteristic of that found for triangles. The actual numerical values found for the q.c.c.'s at equivalent sites in inderite, kurnakovite and colemanite are in close agreement. It has been inferred that the complex boron-oxygen polyions in both inderite and kurnakovite each contain two BO_4 tetrahedra and one BO_3 triangle to form a closed ring similar to that found in colemanite (Christ and Clark, 1958). Whether the polyions exist in the form of polymerized chains as in colemanite, or as isolated polyions as in meyerhofferite (Christ and Clark, 1960) cannot be decided on the basis of the present n.m.r. work alone. The above result is in complete accord with Christ's prediction that inderite and kurnakovite possess a closed-ring polyion containing two tetrahedra and a triangle and belong to the inyoite-colemanite series.

In tincalconite, $Na_2B_4O_7 \cdot 5H_2O$, B^{11} signals have been observed for all twelve boron sites in the unit cell indicating that the crystal is not centro-symmetric. The spectrum also indicates the presence of a family of two-fold axes which repeat every 60° at right angles to the three-fold axis. The n.m.r. spectrum is thus consistent with the space group $R32$ rather than with $R\overline{3}$ which is commonly quoted (Palache, *et al.* 1951). The twelve boron sites fall into three four-membered groups with the members of each group arranged so that the group has a two-fold axis. Of the two unique sites in each group, one has a q.c.c. consistent with triangular coordination whereas the other has a q.c.c. characteristic of tetrahedral coordination in a condensed system. We therefore infer that the polyion in tincalconite is made up of two BO_4 tetrahedra and two BO_3 triangles such that the assembly possesses two-fold symmetry. The only polyion having such properties known to date is that reported by Morimoto (1956) for borax, $Na_2B_4O_7 \cdot 10H_2O$. Again we find that Christ has predicted that tincalconite contains the same polyions as borax.

In kernite, $Na_2B_4O_7 \cdot 4H_2O$, another member of the borax family, Christ has predicted that the same polyions occur as in borax but that the polyions have polymerized to form infinite chains. The B^{11} spectrum of kernite was studied some years ago by Watermann and Volkoff (1955). On examining their data, it is immediately evident that the polyion contains two tetrahedra and two triangles as in borax but lacks the two-fold symmetry of the borax polyion although the members of each pair of tetrahedra and triangles differ only slightly. The n.m.r. results provide a further test of whether the nature of the polyion in kernite is like that in borax. If the borax-type polyions polymerize to form kernite there might be sufficient distortion of the polyions to cause the two-fold symmetry to be lost but the relative orientations of the two BO_3 triangles would be expected to remain nearly the same. Our analysis of Watermann and Volkoff's results yields for the angle between the planes of the BO_3 triangles in the kernite polyion a value of $121 \pm 4.5°$ which is in good agreement with the value of 126.5° obtained from the atomic coordinates for the equivalent angle in borax.

Further studies are in progress but there now seems little doubt that, in the main, Christ's predictions will be found to be essentially correct.

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ON THE OCCURRENCE OF SIDEROTIL IN THAMES RIVER GRAVEL

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Thames river gravels consist mainly of flint, but commonly pyrite occurs as an accessory constituent (Midgley, 1958). One sample of such a gravel from Chertsey, Surrey, left to weather at the Building Research Station was found to contain a high proportion of pyrite pebbles, which were covered with a white crystalline powder. This powder under the microscope consisted of very small equant grains with a refractive index of about 1.535. A powder x-ray diffraction pattern obtained on a 10 cm diameter cylindrical camera with filtered cobalt K_α radiation suggested by reference to the A.S.T.M. index (1960) that the mineral was $FeSO_4 \cdot 5H_2O$ (Table 1, ii, iv).

An electron microscopic examination of the mineral showed it was composed of aggregates of small tabular crystals of about 0.05×0.15 micron (Fig. 2), or aggregates of crystals, 0.1×0.01 micron, in which the crystals were commonly arranged to give a "boat-shaped" outline (Fig. 3).