SHORT COMMUNICATIONS

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

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In the crystal structures of $CuK_2(SO_4)_2.6H_2O$ and $CuCs_2(SO_4)_2.6H_2O$, determined recently by neutron diffraction, one of the water hydrogen atoms has K–H and Cs–H distances similar in length to the K–O and Cs–O distances. Because of the small size of the H atoms it is not necessary to assume that the H atoms are coordinated to the alkali atoms. However two of the criteria for hydrogen bonding have to be restricted: when M is a cation with small formal charge and high coordination number, the angles M–*D*–H can have values between 70 and 90° and both the donor atom (*D*) and the acceptor atom (*A*) of the hydrogen bond (*D*–H···*A*) can belong to the same coordination polyhedron around the cation M.

Introduction

In a recent paper eight criteria were discussed, which can be used to predict the location of hydrogen bonds and the position of hydrogen atoms in crystal structures where the heavy atom parameters are well known but the evidence for the hydrogen atom positions is ambiguous or lacking (Baur, 1972). One part of the discussion involved the question whether or not hydrogen atoms can be coordinated to cations. Such coordination has been postulated but never proved conclusively because no neutron diffraction evidence on this point was available so far. If hydrogen atoms can be coordinated to cations this would affect the two criteria: '(1) The angles M–*D*–H will be at least 90° (and usually over 100°)'; and '(3) no hydrogen atoms will be located in the edges of coordination polyhedra around cations'. The symbol M represents any cation, and *D* is the donor atom of the hydrogen bond.

Coordination in Tutton's salts

New evidence regarding this problem is provided by neutron-diffraction studies on two members of the isomorphous series of Tutton's salts, $CuK_2(SO_4)_2.6H_2O$ (Robinson & Kennard, 1972), and $CuCs_2(SO_4)_2.6H_2O$ (Shields & Kennard, 1972). The coordinations around the alkali atoms in these two salts and in $Cu(NH_4)_2(SO_4)_2.6H_2O$ (Brown & Chidambaram, 1969) are compared in Table 1(*a*), in which all X–O distances up to a limit of 4·0 Å are included (where X=K, NH_4 and Cs). The coordination number of the K^+ ion is clearly eight. The ammonium ion could be called either seven- or eight-coordinated if bond length were the sole criterion; however, since the hydrogen atom positions are known from the neutron-diffraction investigation, the coordination number can be judged on the basis of the N–H···O bonds formed. The NH_4^+ ion is five-coordinated, the three shortest distances are normal N–H···O bonds, and the next two distances (3·007 and 3·121 Å) correspond to a bifurcated bond. The coordination number of the Cs atom could be 7, 9 or 11 depending on how the cut-off point is chosen; it was assumed here that Cs is 9-coordinated. The fact that the NH_4^+ group, despite its larger radius, has a smaller coordination number than the K^+ ion is connected with its capacity for hydrogen bonding, and agrees with the observations made in a comparison of 30 crystal structures containing NH_4^+ (Khan & Baur, 1972). In a certain sense it could be argued that these three $CuX_2(SO_4)_2.6H_2O$ structures are not exactly isostructural because the coordination numbers of some of the oxygen atoms are different in the three compounds: atom O(4) is only once coordinated to NH_4^+, but twice to K^+, and three times to Cs^+.

Five of the six crystallographically different hydrogen atoms which belong to water molecules have normal distances to the Cu and X atoms in all three salts. This is not true, however, of the sixth one, H(17), which forms a hydrogen bond between the water oxygen O(*w*8) and the sulphate group oxygen O(4) [Table 1(*b*)]. In the ammonium salt the distance from H(17) to N of 3·101 Å is longer than the average N–O distance; the distances from H(17) to the ammonium hydrogen atoms are all longer than 2.7 Å, which is more than twice the van der Waals radius of hydrogen. In the potassium salt the distance K–H(17) is almost as short as the average K–O distance, whereas in the cesium salt Cs–H(17) is shorter than the average Cs–O distance. Moreover, in the Cs salt both the donor and the acceptor atom of the hydrogen bond involving H(17) are coordinated to the Cs^+ ion [see X–O(4) in Table 1(*a*)]. Because the internal geometry of the water molecule H(17)–O(*w*8)–H(18) is normal [Table 1(*b*)], there is no doubt that the coordinates of the atoms are correct. All three structures have been carefully refined to low *R* values using neutron-diffraction data.

Consequently, $CuK_2(SO_4)_2.6H_2O$ and $CuCs_2(SO_4)_2.6H_2O$ show the first well documented examples of hydrogen bonds which are exceptions to the two above-mentioned criteria: the angles K–O(*w*8)–H(17) and Cs–O(*w*8)–H(17) are both smaller than 90° and the K–H(17) and Cs–H(17) distances are relatively short when compared with the K–O and Cs–O distances, whereas O(*w*8)–H(17)–O(4) is in the edge of the Cs polyhedron. It appears, therefore, that H(17) might be coordinated to the alkali atoms in these two salts. In order to judge the existence or nonexistence of a bond between two atoms, and whether or not a certain atom belongs to the coordination polyhedron of another atom, the distance between these atoms is com-

Table 1. *Tutton's salts*, $CuX_2(SO_4).6H_2O$, *where* X = K, NH_4 *and* Cs

(*a*) Coordinations around the X atoms and (*b*) hydrogen bonding geometry involving hydrogen atom H(17). Bond distances and angles calculated using parameters taken from Robinson & Kennard (1972), Shields & Kennard (1972) and Brown & Chidambaram (1969). Estimated standard deviations are given in parentheses. The numbers after the X–O distances show how the bonds rank according to length.

		K-salt		NH_4-salt		Cs-salt	
(*a*)	X–O(5)	2·787 (4) Å	1	2·860 (2) Å	1	3·164 (4) Å	3
	X–O(6)	2·829 (4)	2	2·899 (2)	2	3·118 (5)	2
	X–O(3)	2·899 (4)	5	2·983 (2)	3	3·100 (5)	1
	X–O(3′)	2·978 (4)	6	3·007 (2)	4	3·170 (5)	4
	X–O(4′)	2·880 (5)	4	**3·121 (2)**	**5**	3·223 (5)	7
	X–O(*w*7)	3·096 (4)	7	3·149 (2)	6	3·424 (6)	8
	X–O(*w*8)	2·872 (4)	3	3·189 (2)	7	3·210 (5)	6
	X–O(4″)	**3·141 (5)**	**8**	3·282 (2)	8	3·189 (5)	5
	X–O(4)	3·713 (5)	9	3·633 (2)	9	**3·315 (5)**	**9**
	X–O(*w*9)	3·782 (4)	10	3·692 (2)	10	3·873 (5)	11
	X–O(5′)	3·901 (4)	11	3·912 (2)	11	3·868 (5)	10
	mean	(of 8) 2·935		(of 5) 2·974		(of 9) 3·235	
(*b*)	X ——H(17)	2·945 (6)		3·101 (3)		3·105 (8)	
	O(*w*8)–H(17)	0·978 (5)		0·978 (3)		0·986 (9)	
	O(*w*8)–H(18)	0·960 (5)		0·978 (3)		0·981 (11)	
	H(17)–O(4)	1·733 (5)		1·730 (2)		1·798 (2)	
	O(*w*8)–O(4)	2·711 (3)		2·707 (2)		2·780 (5)	
	O(*w*8)–H(17)–O(4)	178·0 (5)°		178·1 (3)°		173·3 (7)°	
	H(17)–O(*w*8)–H(18)	105·6 (4)		105·9 (2)		105·3 (7)	
	X ——O(18)–H(17)	84·6 (3)		76·0 (2)		75·0 (5)	

pared against our experience with other compounds, which is conveniently done by comparing it with the sum of the two appropriate radii. In case we know nothing about the type of bond which could be expected, it is best to compare the distance against the sum of the *atomic* radii (Slater, 1965). These radii are remarkably successful in predicting essentially correct bonding distances in a variety of very different bonding situations. The values of Slater's atomic radii are: 2·20 for K, 2·60 for Cs, 0·60 for O and 0·25 Å for H; the sums of the Slater radii are: K–O 2·80, K–H 2·45, Cs–O 3·20 and Cs–H 2·85 Å. Therefore, it seems that although H(17) does have X–H(17) distances which are similar to the X–O distances, this does not mean that this hydrogen atom is coordinated or bonded to the alkali ions. These short distances found for K–H(17) and Cs–H(17) show, however, that the electrostatic repulsion between a hydrogen atom and a cation with a small formal charge and a high coordination number is sufficiently small so that M–*D*–H angles smaller than 90° are possible, and M–H distances can occur, which are relatively short when compared with the M–O distances. One small indication of repulsion between atoms H(17) and Cs is the value of the angle O(*w*8)–H(17)–O(4), which is 173·3°, and therefore smaller than the corresponding angles in the NH_4^+ and K^+ Tutton's salts. Atom H(17) is placed slightly away from the Cs atom. If the angle O(*w*8)–H(17)–O(4) were 180°, H(17) would be 3·04 Å from the Cs atom and the angle Cs–O(*w*8)–H(17) would measure 71°. Another indication is that the distance Cs–O(4) to the acceptor atom of the hydrogen bond is the longest of the distances considered to belong to the coordination polyhedron around the Cs-atom.

Conclusion

The criteria (1) ('the angles M–*D*–H will be at least 90° and usually over 100°') and (3) ('no hydrogen atoms will be located in the edges of coordination polyhedra around cations') will be well obeyed in cases of cations of high formal charge and small coordination number. In cases of cations of low formal charge and/or high coordination number the angle M–*D*–H can be as small as about 70° and the edge of a coordination polyhedron can contain a hydrogen bond. The restriction proposed here for criteria (1) and (3) is similar to the limitations put by Pauling (1960) on the validity of his rules for complex ionic structures. These revised conclusions are in general agreement with the discussion given by Falk & Knop (1972) and with the observations made on $Sr(OH)_2$ (Grueninger & Bärnighausen, 1969; Baur, 1972).

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