*Acta Cryst.* (1963). **16**, 243

# The Refinement of the Crystal Structure of $KICl_4 . H_2O$

By R. J. Elema, J. L. de Boer and Aafje Vos

*Laboratorium voor Structuurchemie, Rijksuniversiteit, Groningen, The Netherlands*

(*Received* 13 *April* 1962)

A refinement of the crystal structure of $KICl_4 . H_2O$ has shown, that the I–Cl bond lengths in the $ICl_4^-$ ion range from 2·42 to 2·60 Å, with an e.s.d. of 0·01 Å. These bond lengths are significantly larger than both the average value, 2·34 Å, reported by Mooney and the sum of the covalent radii, 2·32 Å. The structure is compatible with a bonding scheme in which delocalized molecular orbitals are formed by a linear combination of *p* orbitals of the halogen atoms.

## Introduction

In homo-polyhalide ions, such as $Br_3^-$, $I_5^-$ *etc.*, the bond lengths are appreciably larger than the sum of the covalent radii. The difference is of the order of 0.2 Å. (For a review, see Wiebenga *et al.*, 1961). Also, for the $ICl_2^-$ ions in piperazinium di-dichloroiodide (Rømming, 1958), the I–Cl bond lengths are respectively 0·37 and 0·15 Å larger than the sum of the covalent radii, 2·32 Å (Pauling, 1960). Values near the sum of the covalent radii were reported previously for the bond lengths in the mixed-polyhalide ions in $KICl_4 . H_2O$, $NH_4BrICl$, and $N(CH_3)_4ICl_2$ by Mooney (1937*a*; 1937*b*; 1939). During a refinement of the crystal structures of $N(CH_3)_4ICl_2$ and $KICl_4 . H_2O$ in our laboratory, it was found, however, that the interatomic distances in the polyhalide ions are considerably larger than the values determined by Mooney. The work on $N(CH_3)_4ICl_2$ is still in progress; the structure of $KICl_4 . H_2O$ will be described in this paper. We also intend to refine the crystal structure of $NH_4BrICl$.

During Mooney's structure determination of $KICl_4 . H_2O$ it was not realized that the crystals contain water of crystallization. The presence of water molecules was discovered by Cornwell & Yamasaki (1957) by chemical analysis and confirmed by our electron-density maps.

## Experimental

The substance was prepared by the Wells & Wheeler method described by Mooney (1937*a*). Needles along [001] and plates parallel to (100) could be obtained from the reaction mixture. In air the crystals decompose and KCl is formed on their surface. They were therefore mounted in thin-walled glass capillaries.

Table 1. *Crystallographic data*

Monoclinic, space group $P2_1/n$
Four units $KICl_4 . H_2O$ per unit cell
With $\lambda(\text{Cu } K\alpha_1) = 1{\cdot}54051$ Å, $\lambda(\text{Cu } K\alpha_2) = 1{\cdot}54433$ Å
$a = 13{\cdot}282$, $b = 14{\cdot}351$, $c = 4{\cdot}284$ Å, $\beta = 95{\cdot}72°$

The crystallographic data are listed in Table 1. The cell dimensions were determined with an accuracy better than $0{\cdot}5\,^0/_{00}$ from back-reflexion photographs.

The intensities were measured from photographs taken with zirconium-filtered molybdenum radiation. The absorption coefficient is 62 $cm^{-1}$. The errors due to absorption were small and no absorption corrections were applied. The intensities of 59 independent reflexions $0kl$ were obtained from integrated anti-equi-inclination Weissenberg photographs ($\mu = 40°$) of a plate parallel to (100) with approximate dimensions of $0{\cdot}26 \times 0{\cdot}43 \times 0{\cdot}43$ mm (Kartha, 1952) and those of 252 independent reflexions $hk0$ from zero-layer-line Weissenberg photographs of a thin needle ($R \simeq 0{\cdot}06$ mm) along the $c$ axis; strong reflexions $hk0$ were measured from integrated exposures, and the weak ones were estimated visually from ordinary photographs of long exposure time. Only 647 reflexions were determined from the higher layer lines about the $c$ axis. Their intensities were estimated visually from non-integrated equi-inclination Weissenberg photographs with a limited oscillation range. Allowance was made for the variable size of the spots by taking the harmonic mean of the intensities estimated for the extended and contracted reflexion spots (Phillips, 1956). No reflexions with relatively low values of $\xi$, for which this procedure is not valid, were measured.

## Refinement

Starting from Mooney's final coordinates for the K, I and Cl atoms, we calculated the structure factors of the reflexions $hk0$ and $0kl$. For $K^+$, and later for O also, use was made of the scattering factors calculated by Berghuis *et al.* (1955). The scattering factor for I was taken from the table calculated by Thomas & Umeda (1957) and was corrected for the anomalous component $\Delta f'$ (Dauben & Templeton, 1955).

For the (partly negatively charged) Cl-atoms a scattering factor $\frac{3}{4} f(\text{Cl}) + \frac{1}{4} f(\text{Cl}^-)$ was used with $f$-values determined by Tomiie & Stam (1958). The first [100] and [001] $F$(obs.)-syntheses clearly indicated the positions of the oxygen atoms.

The projections were refined in successive cycles of

Table 2. *Observed and calculated structure factors, observed reflexions only*

| h | $F_o$ | $F_c$ |
|---|---|---|
| hk0 | | |
| k = 0 | | |
| 2 | 87 | 148- |
| 4 | 76 | 79 |
| 6 | 37 | 27- |
| 8 | 106 | 109- |
| 10 | 90 | 96 |
| 12 | 92 | 92- |
| 14 | 18 | 20 |
| 18 | 12 | 18- |
| k = 1 | | |
| 1 | 43 | 38- |
| 2 | 70 | 76- |
| 3 | 113 | 120 |
| 5 | 216 | 252- |
| 6 | 89 | 79- |
| 7 | 121 | 124 |
| 8 | 81 | 70 |
| 9 | 18 | 19- |
| 10 | 28 | 22- |
| 12 | 21 | 19 |
| 13 | 48 | 49 |
| 15 | 35 | 38- |
| 16 | 13 | 16- |
| 17 | 48 | 42 |
| k = 2 | | |
| 0 | 116 | 137 |
| 1 | 89 | 94 |
| 2 | 97 | 96- |
| 3 | 74 | 82- |
| 4 | 46 | 29- |
| 5 | 62 | 60 |
| 6 | 63 | 58 |
| 7 | 54 | 47 |
| 8 | 48 | 45- |
| 10 | 84 | 87 |
| 11 | 76 | 75 |
| 12 | 76 | 73- |
| 13 | 46 | 49- |
| 16 | 13 | 10 |
| 17 | 20 | 14- |
| 18 | 12 | 12- |
| 19 | 18 | 16- |
| k = 3 | | |
| 2 | 70 | 68- |
| 4 | 17 | 18 |
| 5 | 48 | 40- |
| 6 | 125 | 130- |
| 7 | 76 | 81 |
| 8 | 34 | 32 |
| 9 | 14 | 11 |
| 10 | 39 | 26- |
| 11 | 32 | 27- |
| 12 | 14 | 19- |
| 13 | 11 | 7- |
| 14 | 47 | 46 |
| 15 | 32 | 31- |
| 16 | 45 | 43- |
| 17 | 30 | 31 |
| 18 | 38 | 42 |
| k = 4 | | |
| 1 | 120 | 131 |
| 2 | 63 | 64- |
| 3 | 20 | 14- |
| 4 | 18 | 10- |
| 5 | 35 | 25 |
| 6 | 24 | 19- |
| 7 | 35 | 36 |
| 8 | 68 | 62 |
| 9 | 84 | 91- |
| 10 | 13 | 10 |
| 11 | 76 | 77 |
| 12 | 23 | 17- |
| 13 | 52 | 55- |
| 15 | 24 | 25 |
| 19 | 12 | 22- |
| k = 5 | | |
| 1 | 127 | 134 |
| 2 | 28 | 24- |
| 3 | 44 | 38- |
| 4 | 161 | 181 |
| 5 | 37 | 31 |
| 6 | 123 | 127- |
| 7 | 29 | 27- |
| 8 | 72 | 71 |
| 9 | 8 | 12- |
| 10 | 46 | 44- |
| 11 | 9 | 9 |
| 12 | 9 | 13- |
| 13 | 60 | 55- |
| 14 | 37 | 38 |
| 15 | 11 | 16 |
| 16 | 37 | 34- |
| 18 | 29 | 29 |
| k = 6 | | |
| 0 | 95 | 93- |
| 1 | 167 | 183 |
| 2 | 116 | 119 |
| 3 | 91 | 92- |
| 4 | 103 | 102- |
| 5 | 21 | 20 |
| 6 | 66 | 60- |
| 8 | 70 | 67 |
| 9 | 77 | 73- |
| 10 | 39 | 37- |
| 11 | 59 | 60 |
| 12 | 53 | 50 |
| 13 | 37 | 39- |
| 15 | 11 | 14 |
| 17 | 14 | 9 |
| k = 7 | | |
| 1 | 85 | 84 |
| 2 | 44 | 44- |
| 3 | 125 | 134- |
| 4 | 93 | 92 |
| 5 | 87 | 90 |
| 6 | 60 | 55- |
| 7 | 107 | 109- |
| 8 | 59 | 59 |
| 9 | 68 | 66 |
| 10 | 33 | 32 |
| 12 | 19 | 17- |
| 13 | 26 | 23- |
| 14 | 11 | 17 |
| 15 | 33 | 34 |
| 16 | 33 | 33- |
| 17 | 14 | 21- |
| k = 8 | | |
| 0 | 94 | 94- |
| 2 | 105 | 109 |
| 3 | 43 | 40- |
| 4 | 62 | 61- |
| 5 | 75 | 79- |
| 6 | 22 | 16- |
| 7 | 12 | 13 |
| 8 | 70 | 73 |
| 9 | 32 | 27- |
| 10 | 64 | 70- |
| 11 | 27 | 29 |
| 12 | 43 | 43 |
| 14 | 46 | 39- |
| 15 | 11 | 14- |
| 18 | 12 | 16 |
| k = 9 | | |
| 3 | 84 | 86- |
| 5 | 73 | 70 |
| 7 | 31 | 34- |
| 8 | 11 | 12- |
| 9 | 53 | 51 |
| 10 | 34 | 29 |
| 13 | 41 | 41- |
| 15 | 49 | 45 |
| 17 | 20 | 28- |
| 19 | 22 | 24 |
| k = 10 | | |
| 0 | 38 | 33- |
| 2 | 66 | 66 |
| 3 | 49 | 47 |
| 4 | 25 | 21- |
| 5 | 11 | 15 |
| 6 | 10 | 10 |
| 7 | 34 | 31- |
| 8 | 40 | 43 |
| 9 | 31 | 35 |
| 10 | 57 | 57- |
| 11 | 22 | 28- |
| 12 | 13 | 17 |
| 13 | 19 | 21 |
| 14 | 50 | 43- |
| 15 | 11 | 10- |
| k = 11 | | |
| 2 | 76 | 73 |
| 3 | 53 | 48- |
| 4 | 61 | 54- |
| 5 | 27 | 29 |
| 6 | 43 | 45 |
| 7 | 40 | 39- |
| 8 | 49 | 58- |
| 9 | 48 | 49 |
| 12 | 18 | 20 |
| 13 | 11 | 2- |
| 14 | 37 | 29- |
| 15 | 14 | 16 |
| 16 | 28 | 32 |
| k = 12 | | |
| 1 | 94 | 89- |
| 2 | 30 | 26 |
| 3 | 110 | 103 |
| 4 | 45 | 38- |
| 7 | 30 | 32- |
| 9 | 53 | 61 |
| 11 | 39 | 44- |
| 12 | 13 | 15 |
| 13 | 26 | 30 |
| k = 13 | | |
| 1 | 23 | 25 |
| 2 | 62 | 56 |
| 3 | 13 | 13 |
| 4 | 106 | 104- |
| 5 | 33 | 29- |
| 6 | 58 | 57 |
| 7 | 10 | 5 |
| 8 | 59 | 61- |
| 10 | 10 | 18 |
| 12 | 17 | 18 |
| 14 | 27 | 29- |
| 16 | 23 | 23 |
| k = 14 | | |
| 0 | 43 | 38 |
| 1 | 64 | 63- |
| 2 | 44 | 43- |
| 3 | 37 | 34 |
| 4 | 9 | 10 |
| 5 | 12 | 11- |
| 6 | 10 | 12- |
| 7 | 38 | 37- |
| 9 | 56 | 58 |
| 10 | 18 | 24 |
| 11 | 19 | 28- |
| 12 | 11 | 15- |
| 13 | 14 | 21 |
| 14 | 12 | 15 |
| k = 15 | | |
| 2 | 34 | 30 |
| 3 | 28 | 30 |
| 4 | 32 | 33- |
| 5 | 24 | 27- |
| 6 | 26 | 27 |
| 7 | 35 | 37 |
| 9 | 17 | 20- |
| 12 | 12 | 19 |
| 13 | 12 | 0 |
| 14 | 19 | 25- |
| 15 | 17 | 22- |
| k = 16 | | |
| 0 | 18 | 20 |
| 1 | 10 | 10- |
| 2 | 35 | 37- |
| 3 | 15 | 17 |
| 4 | 7 | 9 |
| 5 | 15 | 12- |
| 7 | 14 | 18- |
| 8 | 17 | 15- |
| 10 | 30 | 34 |
| 12 | 28 | 32- |
| 14 | 19 | 15 |
| k = 17 | | |
| 1 | 11 | 15- |
| 2 | 14 | 16 |
| 3 | 29 | 26 |
| 4 | 19 | 19 |
| 5 | 39 | 40- |
| 7 | 39 | 38 |
| 9 | 12 | 16- |
| k = 18 | | |
| 0 | 62 | 59 |
| 1 | 28 | 28 |
| 2 | 33 | 32- |
| 4 | 20 | 20 |
| 8 | 14 | 20- |
| 9 | 23 | 21- |
| 10 | 15 | 23 |
| 12 | 21 | 23- |
| k = 19 | | |
| 2 | 14 | 15- |
| 3 | 24 | 20 |
| 4 | 31 | 32 |
| 5 | 34 | 35- |
| 6 | 34 | 36- |
| 7 | 22 | 20 |
| 8 | 17 | 18 |
| k = 20 | | |
| 0 | 21 | 22 |
| k = 22 | | |
| 0 | 19 | 9- |
| hk1 | | |
| k = 0 | | |
| 17- | 41 | 48 |
| 15- | 51 | 51- |
| 13- | 50 | 59 |
| 9- | 90 | 97- |
| 7- | 182 | 218 |
| 5- | 90 | 101- |
| k = 1 | | |
| 14- | 60 | 62 |
| 12- | 88 | 96- |
| 11- | 45 | 46- |
| 10- | 64 | 64 |
| 9- | 51 | 53 |
| 8- | 90 | 100- |
| 5- | 73 | 73 |
| 4- | 82 | 85 |
| 0 | 122 | 172 |
| 3 | 99 | 103- |
| 4 | 39 | 35 |
| k = 2 | | |
| 14- | 39 | 43- |
| 13- | 33 | 30 |
| 10- | 24 | 22- |
| 9- | 43 | 40- |
| 8- | 40 | 40- |
| 7- | 101 | 105 |
| 6- | 104 | 120 |
| 5- | 73 | 75- |
| 4- | 52 | 50- |
| 0 | 61 | 66- |
| 4 | 113 | 121 |
| 5 | 116 | 122- |
| 6 | 66 | 69- |
| k = 3 | | |
| 13- | 47 | 42 |
| 10- | 28 | 29 |
| 9- | 62 | 64 |
| 7- | 37 | 34- |
| 6- | 41 | 36 |
| 3- | 32 | 31 |
| 0 | 68 | 69 |
| 2 | 33 | 25 |
| 3 | 130 | 143- |
| 4 | 72 | 73 |
| 5 | 32 | 29 |
| 7 | 67 | 67 |
| 8 | 73 | 73- |
| k = 4 | | |
| 8- | 74 | 76- |
| 6- | 66 | 69 |
| 5- | 38 | 37- |
| 4- | 105 | 118- |
| 3- | 37 | 32- |
| 2- | 90 | 92 |
| 1- | 121 | 127- |
| 0 | 36 | 32 |
| 1 | 95 | 98 |
| 2 | 65 | 64- |
| 3 | 51 | 49 |
| 4 | 147 | 160 |
| 5 | 23 | 19 |
| 6 | 144 | 163- |
| 8 | 77 | 78 |
| k = 5 | | |
| 13- | 68 | 68 |
| 11- | 71 | 71- |
| 10- | 27 | 23- |
| 9- | 73 | 76 |
| 8- | 37 | 34 |
| 7- | 88 | 88- |
| 6- | 93 | 94 |
| 4- | 23 | 20- |
| 3- | 90 | 91 |
| 2- | 72 | 66 |
| 1- | 94 | 101- |
| 0 | 49 | 48- |
| 3 | 77 | 78- |
| 6 | 99 | 101- |
| 9 | 81 | 82- |
| k = 6 | | |
| 15- | 52 | 55 |
| 11- | 31 | 31- |
| 10- | 32 | 32 |
| 8- | 83 | 86- |
| 7- | 99 | 95- |
| 6- | 107 | 112 |
| 5- | 106 | 105 |
| 4- | 107 | 113- |
| 3- | 71 | 66- |
| 2- | 81 | 76 |
| 0 | 32 | 31- |
| 1 | 56 | 54 |
| 2 | 50 | 47- |
| 3 | 57 | 56- |
| 4 | 71 | 68 |
| 5 | 40 | 38 |
| 6 | 70 | 71- |
| 7 | 33 | 32- |
| 9 | 48 | 41 |
| 11 | 37 | 34 |
| k = 7 | | |
| 12- | 59 | 63 |
| 11- | 61 | 65- |
| 10- | 106 | 113- |
| 8- | 62 | 58 |
| 4- | 34 | 32- |
| 3- | 103 | 104 |
| 2- | 93 | 95 |
| 1- | 76 | 71- |
| 0 | 102 | 106- |
| 1 | 51 | 51 |
| 2 | 105 | 104 |
| 4 | 56 | 50- |
| 7 | 43 | 37 |
| 8 | 36 | 39 |
| 9 | 54 | 48- |
| 12 | 39 | 40 |
| k = 8 | | |
| 9- | 43 | 41 |
| 7- | 58 | 59- |
| 6- | 43 | 39 |
| 5- | 115 | 120 |
| 3- | 104 | 101- |
| 2- | 90 | 78- |
| 1 | 53 | 49 |
| 2 | 110 | 103- |
| 3 | 68 | 69- |
| 4 | 47 | 43 |
| 5 | 82 | 09 |
| 7 | 108 | 104- |
| 9 | 44 | 36 |
| k = 9 | | |
| 12- | 31 | 31 |
| 10- | 53 | 50- |
| 8- | 49 | 46 |
| 4- | 72 | 73- |
| 2- | 37 | 33 |
| 0 | 111 | 116- |
| 1 | 52 | 50- |
| 2 | 128 | 135 |
| 3 | 46 | 41 |
| 8 | 65 | 63 |
| 10 | 77 | 76- |
| 12 | 67 | 68 |
| k = 10 | | |
| 9- | 38 | 37 |
| 6- | 36 | 37- |
| 5- | 81 | 85 |
| 4- | 45 | 43 |
| 3- | 81 | 78- |
| 2 | 61 | 59 |
| 3 | 52 | 50- |
| 4 | 53 | 49- |
| 5 | 72 | 69 |
| 6 | 59 | 53 |
| 7 | 109 | 108- |
| 8 | 62 | 58- |
| k = 11 | | |
| 11- | 61 | 58 |
| 10- | 45 | 46- |
| 9- | 47 | 45- |
| 8- | 32 | 32 |
| 6- | 30 | 27- |
| 3- | 59 | 55- |
| 1- | 75 | 73 |
| 0 | 56 | 55- |
| 1 | 72 | 68- |
| 2 | 83 | 81- |
| 3 | 43 | 40 |
| 4 | 37 | 32- |
| 7 | 52 | 52- |
| 9 | 39 | 38 |
| k = 12 | | |
| 10- | 33 | 31- |
| 8- | 47 | 43 |
| 6- | 89 | 89- |
| 5- | 27 | 31 |
| 4- | 96 | 96 |
| 3- | 26 | 26- |
| 2- | 34 | 27- |
| 1- | 31 | 29 |
| 2 | 63 | 61 |
| 4 | 35 | 40- |
| 6 | 51 | 48 |
| 8 | 52 | 48- |
| k = 13 | | |
| 11- | 64 | 66 |
| 9- | 59 | 59- |
| 5- | 26 | 24 |
| 3- | 62 | 61- |
| 1- | 50 | 47 |
| 1 | 95 | 98- |
| k = 14 | | |
| 8- | 38 | 37 |
| 6- | 42 | 41- |
| 5- | 43 | 40- |
| 4- | 64 | 64 |
| 1- | 41 | 35- |
| 0 | 45 | 42- |
| 2 | 43 | 36 |
| 4 | 39 | 40- |
| 6 | 61 | 59 |
| k = 15 | | |
| 5- | 35 | 31 |
| 2- | 41 | 40- |
| 1- | 36 | 34 |
| 0 | 41 | 44 |
| 1 | 39 | 42- |
| 2 | 40 | 40- |
| 8 | 38 | 38- |
| k = 16 | | |
| 5- | 36 | 42- |
| 3 | 50 | 59 |
| 5 | 50 | 47- |
| 7 | 54 | 43 |
| k = 17 | | |
| 2- | 43 | 42- |
| 0 | 47 | 48 |
| 2 | 37 | 37- |
| k = 18 | | |
| 5 | 43 | 39- |
| k = 19 | | |
| 0 | 30 | 27 |
| hk2 | | |
| k = 0 | | |
| 0 | 54 | 53- |
| 4 | 47 | 45 |
| 6 | 57 | 54 |
| 8 | 40 | 36- |
| 10 | 78 | 77 |
| 12 | 23 | 44- |
| 14 | 45 | 40 |
| k = 1 | | |
| 6- | 32 | 31 |
| 5- | 47 | 44- |
| 0 | 25 | 22- |
| 3 | 86 | 93 |
| 4 | 72 | 73 |
| 5 | 42 | 45- |
| 7 | 73 | 75 |
| 9 | 71 | 62- |
| 12 | 23 | 29- |
| 15 | 38 | 44- |
| k = 2 | | |
| 9- | 95 | 112 |
| 8- | 55 | 51- |
| 5- | 24 | 25 |
| 4- | 85 | 92 |
| 0 | 97 | 105 |
| 3 | 47 | 56- |
| 4 | 75 | 77 |
| 7 | 28 | 34 |
| 8 | 63 | 59- |
| 9 | 39 | 91- |
| 10 | 40 | 36 |
| 14 | 37 | 37 |
| k = 3 | | |
| 9- | 40 | 39- |
| 8- | 95 | 102- |
| 6- | 95 | 99 |
| 5- | 80 | 72- |
| 4- | 153 | 171- |
| 3- | 53 | 67 |
| 2 | 75 | 77- |
| 3 | 78 | 77 |
| 4 | 170 | 169 |
| 5 | 61 | 63- |
| 6 | 95 | 98- |
| 8 | 93 | 88 |
| 9 | 50 | 49- |
| k = 4 | | |
| 11- | 72 | 76- |
| 9- | 63 | 69 |
| 8- | 61 | 61- |
| 7- | 62 | 60- |
| 3- | 142 | 150 |
| 2- | 16 | 19 |
| 1- | 117 | 132- |
| 0 | 26 | 26 |
| 1 | 159 | 158 |
| 2 | 25 | 22 |
| 3 | 133 | 129- |
| 4 | 24 | 22 |
| 7 | 48 | 46 |
| 8 | 65 | 54- |
| 9 | 67 | 70- |
| 11 | 65 | 68 |
| 13 | 31 | 40- |
| k = 5 | | |
| 9- | 23 | 28 |
| 8- | 77 | 73- |
| 7- | 38 | 35- |
| 6- | 84 | 86 |
| 5- | 35 | 30 |
| 4- | 67 | 73 |
| 2- | 97 | 105 |
| 1- | 61 | 63- |
| 1 | 56 | 60- |
| 2 | 97 | 94- |
| 4 | 59 | 59 |
| 5 | 47 | 42 |
| 6 | 91 | 92- |
| 7 | 22 | 22- |
| 8 | 54 | 57 |
| 9 | 40 | 33 |
| 13 | 30 | 23 |
| 14 | 34 | 33 |
| k = 6 | | |
| 13- | 31 | 39 |
| 12- | 22 | 27 |
| 11- | 51 | 51- |
| 10- | 54 | 53- |
| 9- | 49 | 43 |
| 7- | 57 | 55- |
| 6- | 23 | 25 |
| 4- | 35 | 31 |
| 3- | 42 | 37 |
| 2- | 42 | 42 |
| 1- | 47 | 48- |
| 0 | 66 | 71- |
| 1 | 43 | 42 |
| 3 | 43 | 44 |
| 6 | 30 | 23 |
| 7 | 40 | 49 |
| 9 | 41 | 38- |
| 10 | 49 | 46- |
| 11 | 49 | 49 |
| k = 7 | | |
| 10- | 47 | 45 |
| 7- | 53 | 46- |
| 6- | 50 | 52 |
| 5- | 108 | 100 |
| 4- | 22 | 22- |
| 3- | 30 | 26- |
| 2 | 35 | 32- |
| 3 | 44 | 46- |
| 4 | 20 | 22 |
| 5 | 79 | 78 |
| 6 | 40 | 42- |
| 7 | 44 | 42- |
| 10 | 43 | 39- |
| k = 8 | | |
| 12- | 59 | 65 |
| 10- | 60 | 62- |
| 7- | 48 | 42 |
| 5- | 69 | 58- |
| 4- | 31 | 28- |
| 2- | 73 | 81 |
| 1- | 36 | 28- |
| 0 | 122 | 127- |
| 1 | 14 | 25 |
| 2 | 79 | 74 |
| 5 | 69 | 63 |
| 8 | 33 | 36 |
| 10 | 59 | 59- |
| 12 | 54 | 56 |
| k = 9 | | |
| 9- | 22 | 28 |
| 7- | 109 | 106- |
| 6- | 36 | 30- |
| 5- | 114 | 101 |
| 4- | 31 | 29 |
| 3- | 72 | 70- |
| 1- | 47 | 48 |
| 1 | 67 | 59 |
| 3 | 71 | 59- |
| 5 | 105 | 109 |
| 6 | 28 | 30 |
| 7 | 98 | 95- |
| k = 10 | | |
| 12- | 42 | 61 |
| 11- | 31 | 34 |
| 10- | 42 | 41- |
| 8- | 44 | 33 |
| 6- | 28 | 31- |
| 4- | 47 | 46- |
| 3- | 24 | 26- |
| 2- | 75 | 64 |
| 1- | 86 | 85 |
| 0 | 115 | 117- |
| 1 | 83 | 79- |
| 2 | 75 | 70 |
| 8 | 34 | 36 |
| 10 | 43 | 42- |
| 12 | 54 | 51 |
| k = 11 | | |
| 6- | 85 | 79- |
| 5- | 61 | 60 |
| 4- | 61 | 56 |
| 3 | 29 | 30- |
| 4 | 67 | 65- |
| 5 | 59 | 54 |
| 6 | 63 | 65 |
| 7 | 29 | 32- |
| 8 | 20 | 23- |
| k = 12 | | |
| 13- | 26 | 32- |
| 11- | 43 | 50 |
| 1- | 60 | 64 |
| 0 | 35 | 35- |
| 1 | 56 | 58- |
| 11 | 49 | 42- |
| k = 13 | | |
| 6- | 61 | 62- |
| 4- | 29 | 28 |
| 1- | 22 | 22- |
| 6 | 60 | 60 |
| k = 14 | | |
| 11- | 35 | 39 |
| 3- | 48 | 36- |
| 1- | 50 | 46 |
| 0 | 29 | 26 |
| 1 | 51 | 49- |
| 3 | 32 | 34 |
| 11 | 43 | 39- |
| k = 15 | | |
| 6- | 30 | 35- |
| 5- | 54 | 53- |
| 4- | 29 | 30 |
| 3- | 44 | 32 |
| 3 | 42 | 38 |
| 4 | 42 | 32- |
| 5 | 53 | 45- |
| 6 | 40 | 37 |
| k = 16 | | |
| 2- | 51 | 46- |
| 0 | 67 | 71 |
| 2 | 43 | 41- |
| k = 17 | | |
| 3- | 55 | 40 |
| 3 | 37 | 39 |
| 5 | 45 | 41- |
| hk3 | | |
| k = 0 | | |
| 5 | 54 | 62- |
| 7 | 123 | 125 |
| 9 | 51 | 51- |
| k = 1 | | |
| 0 | 86 | 96 |
| 2 | 19 | 16 |
| 3 | 57 | 55- |
| 9 | 41 | 37- |
| 10 | 40 | 42 |
| 12 | 62 | 61- |
| 14 | 34 | 32 |
| k = 2 | | |
| 9- | 32 | 30- |
| 8- | 52 | 49- |
| 7- | 40 | 42 |
| 0 | 35 | 30 |
| 5 | 51 | 53- |
| 6 | 57 | 57- |
| 7 | 66 | 64 |
| 14 | 28 | 27 |
| k = 3 | | |
| 11- | 71 | 87- |
| 10- | 37 | 40 |
| 9- | 61 | 68 |
| 8- | 50 | 52- |
| 7- | 34 | 34- |
| 0 | 55 | 56 |
| 9 | 44 | 41- |
| k = 4 | | |
| 3- | 58 | 63- |
| 6- | 103 | 119 |
| 4 | 52 | 55 |
| 5 | 26 | 26- |
| 6 | 58 | 57- |
| 8 | 51 | 48 |
| k = 5 | | |
| 11- | 62 | 61- |
| 9- | 50 | 51 |
| 6- | 55 | 58- |
| 0 | 26 | 24- |
| 6 | 57 | 48 |
| 7 | 56 | 54 |
| 9 | 42 | 42- |
| 11 | 51 | 50 |
| 13 | 40 | 41- |
| k = 6 | | |
| 9- | 33 | 33 |
| 8- | 26 | 27- |
| 6- | 49 | 45 |
| 5- | 41 | 37 |
| 4- | 50 | 45- |
| 3- | 43 | 37- |
| 2- | 32 | 33 |
| 0 | 25 | 24 |
| 2 | 43 | 40- |
| 3 | 49 | 49- |
| 4 | 74 | 73 |
| 5 | 67 | 67 |
| 6 | 62 | 64- |
| 7 | 49 | 46- |
| 8 | 52 | 52 |
| k = 7 | | |
| 9- | 34 | 40 |
| 5- | 40 | 37 |
| 4- | 39 | 37- |
| 2- | 56 | 50 |
| 1- | 46 | 43- |
| 0 | 77 | 81- |
| 1 | 53 | 51 |
| 2 | 50 | 46 |
| 3 | 50 | 50- |
| 8 | 51 | 49 |
| 10 | 66 | 65- |
| 11 | 42 | 37 |
| 12 | 36 | 37 |
| k = 8 | | |
| 9- | 31 | 32 |
| 7- | 73 | 78- |
| 5- | 62 | 58 |
| 4- | 37 | 36- |
| 3- | 54 | 52- |
| 2- | 47 | 53 |
| 1- | 37 | 29 |
| 2 | 46 | 45 |
| 3 | 57 | 66- |
| 5 | 76 | 74 |
| 6 | 24 | 27- |
| 7 | 40 | 37- |
| 9 | 26 | 28 |
| k = 9 | | |
| 12- | 51 | 57 |
| 10- | 55 | 57- |
| 8- | 40 | 43 |
| 3- | 31 | 31- |
| 2- | 94 | 100 |
| 1- | 25 | 25 |
| 0 | 63 | 64- |
| 2 | 41 | 35 |
| 4 | 52 | 49- |
| k = 10 | | |
| 8- | 35 | 40 |
| 7- | 74 | 84- |
| 6- | 43 | 41- |
| 5- | 49 | 45 |
| 4- | 42 | 37 |
| 3- | 30 | 32- |
| 2- | 30 | 36- |
| 1 | 26 | 26 |
| 3 | 51 | 48- |
| 4 | 30 | 31- |
| 5 | 53 | 43 |
| 6 | 24 | 24 |
| k = 11 | | |
| 9- | 37 | 33- |
| 7- | 31 | 32 |
| 4- | 25 | 24- |
| 2- | 55 | 52 |
| 1- | 54 | 56 |
| 0 | 37 | 35- |
| 1 | 50 | 48- |
| 3 | 30 | 34 |
| 9 | 32 | 34 |
| 10 | 28 | 28- |
| 11 | 31 | 33- |
| k = 12 | | |
| 6- | 33 | 37- |
| 4- | 35 | 32 |
| 2- | 42 | 39- |
| 4 | 64 | 65- |
| 6 | 54 | 55 |
| k = 13 | | |
| 3- | 31 | 27- |
| 1- | 61 | 64 |
| 1 | 35 | 34- |
| 3 | 44 | 39 |
| 9 | 35 | 37 |
| 11 | 42 | 42- |
| k = 14 | | |
| 6- | 42 | 43- |
| 4- | 28 | 27 |
| 2- | 33 | 32- |
| 0 | 20 | 24 |
| 4 | 44 | 41- |
| k = 15 | | |
| 2- | 26 | 26- |
| 0 | 40 | 38 |
| k = 16 | | |
| 7- | 30 | 35 |
| 5- | 39 | 40- |
| 3- | 39 | 40 |
| k = 17 | | |
| 0 | 35 | 35 |
| k = 19 | | |
| 0 | 23 | 13 |
| hk4 | | |
| k = 0 | | |
| 0 | 131 | 148 |
| 8 | 43 | 49- |
| 10 | 39 | 40 |
| 12 | 43 | 40- |
| k = 1 | | |
| 6 | 39 | 40- |
| 7 | 44 | 43 |
| 8 | 17 | 18 |
| k = 2 | | |
| 0 | 55 | 59 |
| 6 | 17 | 18 |
| 10 | 38 | 38 |
| 11 | 33 | 33 |
| 12 | 29 | 30- |
| k = 3 | | |
| 3- | 30 | 22- |
| 6 | 45 | 50- |
| 7 | 23 | 25 |
| 8 | 19 | 18 |

Table 2 (*cont.*)

| h | $F_o$ | $F_c$ |
|---|---|---|
| | k = 4 | |
| 11- | 45 | 47- |
| 9- | 42 | 45 |
| 8- | 22 | 25 |
| 5 | 18 | 16 |
| 7 | 27 | 25 |
| 8 | 21 | 21 |
| 9 | 35 | 35- |
| 11 | 35 | 35 |
| 13 | 22 | 26- |
| | k = 5 | |
| 13- | 21 | 28- |
| 10- | 18 | 19 |
| 8- | 31 | 36- |
| 6 | 45 | 49- |
| 8 | 35 | 35 |
| | k = 6 | |
| 12- | 27 | 28 |
| 11- | 35 | 35- |
| 10- | 21 | 19- |
| 9- | 37 | 36 |
| 8- | 36 | 39 |
| 6- | 19 | 19- |
| 0 | 43 | 44- |
| 4 | 30 | 26- |
| 6 | 20 | 21- |
| 8 | 27 | 27 |
| 9 | 36 | 35- |
| 11 | 25 | 26 |
| 12 | 19 | 20 |
| | k = 7 | |
| 9- | 33 | 35 |
| 8- | 32 | 33- |
| 7- | 49 | 52- |
| 6- | 27 | 25 |
| 5- | 42 | 42 |
| 3 | 44 | 45- |
| 4 | 36 | 39 |
| 5 | 46 | 49 |
| 6 | 26 | 27- |
| 7 | 43 | 46- |
| 9 | 26 | 24 |
| | k = 8 | |
| 12- | 29 | 26 |
| 10- | 41 | 42- |
| 8- | 37 | 35 |
| 5- | 16 | 23 |
| 4- | 32 | 29- |
| 2- | 53 | 52 |
| 0 | 43 | 43- |
| 2 | 48 | 51 |
| 4 | 28 | 24- |
| 5 | 33 | 28- |
| 8 | 33 | 32 |
| 10 | 33 | 32- |
| | k = 9 | |
| 9- | 26 | 25 |
| 7- | 27 | 24- |
| 5- | 46 | 41 |
| 3- | 38 | 38- |
| 3 | 47 | 44- |
| 5 | 27 | 27 |
| 9 | 27 | 25 |
| | k = 10 | |
| 10- | 32 | 34- |
| 7- | 22 | 19 |
| 3- | 16 | 18- |
| 2- | 40 | 36 |
| 0 | 25 | 20- |
| 2 | 27 | 27 |
| 3 | 25 | 20 |
| 8 | 24 | 21 |
| 10 | 20 | 23- |
| | k = 11 | |
| 9- | 27 | 24 |
| 8- | 33 | 33 |
| 7- | 19 | 20- |
| 4- | 39 | 37 |
| 3- | 22 | 23- |
| 2- | 35 | 31- |
| 2 | 28 | 28 |
| 3 | 26 | 22- |
| 4 | 28 | 27- |
| 6 | 26 | 24 |
| 8 | 25 | 24 |
| | k = 12 | |
| 9- | 29 | 34- |
| 4- | 20 | 21- |
| 3- | 48 | 48- |
| 1- | 43 | 43 |
| 1 | 48 | 46- |
| 3 | 44 | 43 |
| 9 | 29 | 29 |
| | k = 13 | |
| 8- | 32 | 32 |
| 4- | 47 | 48 |
| 2- | 30 | 28- |
| 2 | 32 | 29 |
| 4 | 47 | 47- |
| 6 | 30 | 29 |
| 8 | 28 | 27- |
| | k = 14 | |
| 9- | 28 | 32- |
| 3- | 25 | 21- |
| 2- | 20 | 23- |
| 1- | 36 | 34 |
| 0 | 24 | 18 |
| 1 | 31 | 29- |
| | k = 18 | |
| 0 | 33 | 29 |
| | hk5 | |
| | k = 1 | |
| 0 | 48 | 48 |
| 8 | 19 | 20- |
| 10 | 33 | 31 |
| | k = 2 | |
| 8 | 23 | 22 |
| | k = 3 | |
| 7 | 18 | 21 |
| 9 | 30 | 28- |
| 11 | 33 | 34 |
| | k = 4 | |
| 8 | 23 | 23 |
| | k = 5 | |
| 13- | 25 | 27 |
| 11- | 27 | 28- |
| 9- | 32 | 34 |
| 6 | 21 | 22- |
| 9 | 29 | 29- |
| | k = 6 | |
| 3- | 27 | [illegible] |
| 6 | 26 | 23- |
| | k = 7 | |
| 12- | 25 | 23 |
| 11- | 20 | 24- |
| 10- | 33 | 39- |
| 8- | 18 | 21 |
| 0 | 34 | 33- |
| | k = 8 | |
| 7- | 26 | 24- |
| 5 | 31 | 31 |
| 7 | 35 | 33- |
| | k = 9 | |
| 10- | 25 | 25- |
| 4- | 21 | 21- |
| 0 | 45 | 42- |
| 2 | 35 | 37 |
| 8 | 23 | 24 |
| 10 | 24 | 25- |
| | k = 10 | |
| 5- | 36 | 33 |
| 3- | 29 | 26- |
| 3 | 19 | 20- |
| 5 | 29 | 27 |
| 7 | 31 | 29- |
| | k = 11 | |
| 11- | 23 | 26 |
| 3- | 25 | 24- |
| 1- | 27 | 21 |
| 0 | 25 | 21- |
| 1 | 29 | 27- |
| 2 | 28 | 26 |
| | k = 12 | |
| 8- | 18 | 20 |
| 6- | 36 | 33- |
| 4- | 34 | 33 |
| 2 | 18 | 21 |
| 6 | 25 | 20 |
| | k = 13 | |
| 11- | 25 | 26 |
| 9- | 25 | 24- |
| 1- | 28 | 23 |
| 1 | 29 | 32- |
| | k = 14 | |
| 4- | 21 | 25 |

structure-factor calculations and difference Fourier syntheses. The scale factor was determined by comparing calculated and observed structure factors. The atomic shifts were calculated in the usual way (Cochran, 1951). A first estimate of the corrections in the temperature factors was made by using Hamilton's formula (Hamilton, 1955). Further corrections were estimated by comparing successive difference Fourier syntheses. For all atoms the [001] difference Fourier syntheses indicated a larger thermal motion in the $y$-direction than the [100] difference maps. This discrepancy may be due to systematic absorption errors in the reflexion intensities or to some disorder because of decomposition, which may be different for the two crystals used. Only isotropic temperature factors $\exp(-B\sin^2\theta/\lambda^2)$ were therefore considered. The values of $B$ were assumed to be equal for the four independent Cl atoms. The final temperature parameters are $B(\mathrm{K})=3\cdot2$, $B(\mathrm{I})=1\cdot9$, $B(\mathrm{Cl})=3\cdot0$ and $B(\mathrm{O})=3\cdot5$ Å$^2$.

The three-dimensional refinement was carried out with the reflexions obtained from the zero and higher layer-line photographs about the $c$ axis. The temperature factors from the two-dimensional refinement were used. For each $l$ level an individual scale factor was determined by comparing calculated and observed structure factors.

At the end of the refinement the reliability factor $R$ was 0·07 for the observed reflexions listed in Table 2. The calculated values in this table are based on the final coordinates in Table 3 and the thermal parameters from the two-dimensional refinement.

Only a rough estimate of the errors in the final coordinates could be made, as the final difference Fourier synthesis still shows systematic deviations due to errors in the thermal parameters. The estimated 'standard deviations' in Table 3 correspond to 1·5 times the value calculated with Cruickshank's formula (Cruickshank, 1949).

Table 3. *Final coordinates*

| Atom* | $x$ | S.d. | $y$ | S.d. | $z$ | S.d. |
|---|---|---|---|---|---|---|
| K | −0·0791 | 0·0007 | 0·8409 | 0·0006 | 0·7767 | 0·0023 |
| I | 0·2041 | 0·0002 | 0·4408 | 0·0001 | 0·4989 | 0·0004 |
| $Cl_1$ | 0·2292 | 0·0007 | 0·2807 | 0·0005 | 0·7435 | 0·0020 |
| $Cl_2$ | 0·1866 | 0·0007 | 0·5955 | 0·0005 | 0·2466 | 0·0020 |
| $Cl_3$ | 0·3824 | 0·0006 | 0·4884 | 0·0006 | 0·7574 | 0·0021 |
| $Cl_4$ | 0·0398 | 0·0006 | 0·3953 | 0·0006 | 0·2523 | 0·0020 |
| O | −0·043 | 0·003 | 0·208 | 0·002 | 0·693 | 0·015 |

* The numbering refers to Fig. 1.

## Discussion of the structure

In Fig. 1 the structure is viewed down the $c$ axis. The distances between non-bonded atoms (ions) smaller than 3·6 Å are indicated in this figure. Equivalent iodine atoms in the $z$-direction have a spacing $c=4\cdot284$ Å. The observed interatomic distances may be compared with the corresponding sums of the van der Waals or ionic radii, which are 1·33, 2·15, 1·80 and 1·40 Å for $K^+$, I, Cl and O respectively (Pauling, 1960, p. 514 and 260).

The positions of the hydrogen atoms in the water molecules could not be obtained from the electron-density maps. It is most likely that the more negative part of the oxygen atom in these molecules is directed towards the $K^+$ ions, which implies that the H atoms are near the Cl atoms. All O $\cdots$ Cl distances are larger than the O $\cdots$ Cl distances observed for the O–H $\cdots$ $Cl^-$ bonds in hydrochlorides, *e.g.* 3·12 and 3·16 Å in adeninehydrochloride (Broomhead, 1951) and 3·07 and 3·24 Å in isoleucine hydrochloride (Trommel & Bijvoet, 1954). The comparatively large value of the O–H $\cdots$ Cl distance in $KICl_4.H_2O$ may occur because the Cl atoms in this compound are less negatively charged than the $Cl^-$ ions in the hydrochlorides.

The structure of the $ICl_4^-$ ion is given in Fig. 2; the e.s.d. in the bond lengths and angles are 0·01 Å and 0·3° respectively. The plane through I with the best fit to the Cl atoms is given by

$$-0\cdot4177x'+0\cdot3344y'+0\cdot8448z'=2\cdot5662$$

where $x'=ax\sin\beta$, $y'=by$ and $z'=cz+ax\cos\beta$ are the atomic coordinates measured in Ångström units in the orthogonal coordinate system $a^*$, $b$, $c$. All four Cl atoms atoms lie at the same side of the plane at

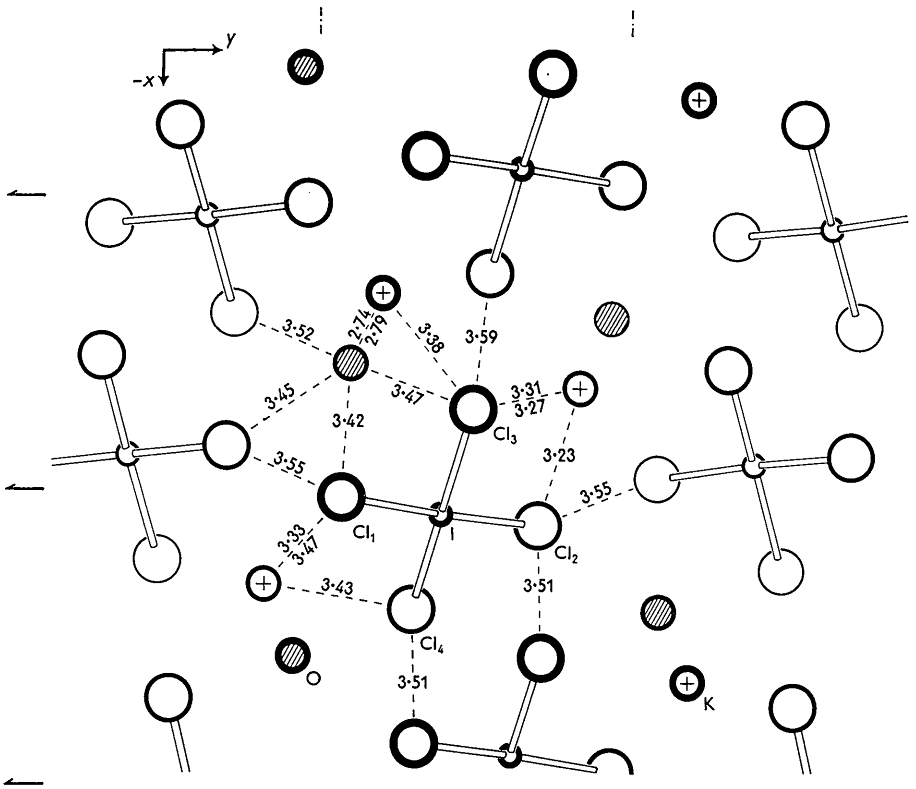


Fig. 1. Projection of the structure along [001] on the (001) plane.

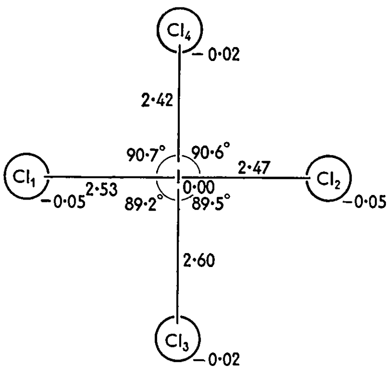


Fig. 2. Bond lengths and angles in the $ICl_4^-$ ion, the angles $Cl_1$–I–$Cl_2$ and $Cl_3$–I–$Cl_4$ are 177·3 and 179·1° respectively.

perpendicular distances of 0·02 and 0·05 Å (e.s.d. 0·01 Å) respectively, as indicated in the figure. This means that the $ICl_4^-$ ion in $KICl_4.H_2O$ is slightly pyramidal.

The valence angles show only slight deviations from the values 90 and 180°, which are characteristic for the polyhalide ions.

The bond lengths are considerably larger than the values, 2·33 and 2·35 Å, reported by Mooney, and show appreciable differences. Fig. 1 shows that the variation in the bond lengths may be due to cation influence as suggested by Havinga & Wiebenga (1959) for the asymmetric $I_3^-$ ions in $CsI_3$ and $NH_4I_3$. The atoms $Cl_1$, $Cl_2$, $Cl_3$ and $Cl_4$ are close to 2, 1, 3 and 1 $K^+$ ions respectively. As in $CsI_3$ and $NH_4I_3$, the terminal atoms of the longer bonds are surrounded by more cations at short distances than those of the shorter ones.

A qualitative explanation of the structural features of the polyhalogen complexes has been given by Havinga & Wiebenga (1959) in terms of L.C.A.O. molecular orbitals involving only outer *p* orbitals of the atoms. The relatively small bond lengths in the mixed-polyhalide ions investigated by Mooney could, however, not satisfactorily be explained (Rundle, 1961). For the mixed-polyhalide ions other bonding schemes are therefore in use as well. For $ICl_4^-$, for instance, Pauling (1960) assumes localized bonds established by four equatorial $sp^3d^2$ hybrid orbitals of iodine and one *p* orbital of each chlorine. Rundle (1961) proposes an extension of the original molecular orbital scheme, in which also *d* orbitals are used. The experimental evidence above indicates, however, that the bonds in the $ICl_4^-$ ion may be explained by considering delocalized molecular orbitals in which only *p* orbitals participate.

We are grateful to Prof. E. H. Wiebenga for suggesting the structure refinement and for reading the manuscript.

The Patterson and Fourier syntheses and the structure factors were calculated on a ZEBRA computer with programs devised by Dr D. W. Smits. For the calculation of the bond lengths and angles, and the best plane through the $ICl_4^-$ ion, a program devised by Dr D. Rogers was used. We wish to thank Mr H. Schurer for operating ZEBRA.

### References

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BROOMHEAD, J. M. (1951). *Acta Cryst.* **4**, 92.

COCHRAN, W. (1951). *Acta Cryst.* **4**, 408.

CORNWELL, C. D. & YAMASAKI, R. S. (1957). *J. Chem. Phys.* **27**, 1060.

CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.

DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.

HAVINGA, E. E. & WIEBENGA, E. H. (1959). *Rec. Trav. Chim. Pays-Bas*, **78**, 724.

HAMILTON, W. C. (1955). *Acta Cryst.* **8**, 199.

KARTHA, G. (1952). *Acta Cryst.* **5**, 549.

MOONEY, R. C. L. (1937*a*). *Z. Kristallogr.* **98**, 377.

MOONEY, R. C. L. (1937*b*). *Z. Kristallogr.* **98**, 324.

MOONEY, R. C. L. (1939). *Z. Kristallogr.* **100**, 519.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca, New York: Cornell University Press.

PHILLIPS, D. C. (1956). *Acta Cryst.* **9**, 819.

RØMMING, C. (1958). *Acta Chem. Scand.* **12**, 668.

RUNDLE, R. E. (1961). *Acta Cryst.* **14**, 585.

THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.

TOMIIE, Y. & STAM, C. H. (1958). *Acta Cryst.* **11**, 126.

TROMMEL, J. & BIJVOET, J. M. (1954). *Acta Cryst.* **7**, 703.

WIEBENGA, E. H., HAVINGA, E. E. & BOSWIJK, K. H. (1961). *Advances in Inorganic Chemistry and Radiochemistry*, Vol. III, p. 133. New York: Academic Press.

---

*Acta Cryst.* (1963). **16**, 247

# The Crystal Structure of Decammine-$\mu$-peroxodicobalt Pentanitrate

BY NILS-GÖSTA VANNERBERG AND CYRILL BROSSET

*Department of Inorganic Chemistry, Chalmers University of Technology, Göteborg, Sweden*

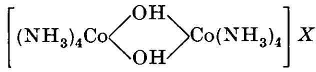
(*Received* 2 *April* 1962)

The compound $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$ has been prepared and its structure determined. The space group is $P4_2nm$ with $a = b = 11{\cdot}94$ and $c = 8{\cdot}06$ Å. The two cobalt atoms are linked together by a peroxide group. The bonding is similar to that in the olefin complex.

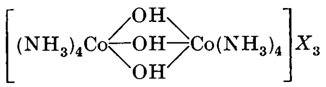
Table 1. *Some dinuclear cobalt complexes*

Red diamagnetic compounds

$[(NH_3)_5Co—O_2—Co(NH_3)_5]X_4$



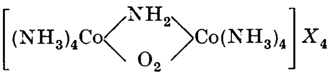
$\left[(NH_3)_4Co\begin{smallmatrix}OH\\OH\end{smallmatrix}Co(NH_3)_4\right]X_4$



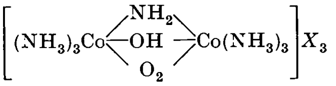
$\left[(NH_3)_4Co\begin{smallmatrix}OH\\OH\\OH\end{smallmatrix}Co(NH_3)_4\right]X_3$

Green paramagnetic compounds

$[(NH_3)_5Co—O_2—Co(NH_3)_5]X_5$



$\left[(NH_3)_4Co\begin{smallmatrix}NH_2\\O_2\end{smallmatrix}Co(NH_3)_4\right]X_4$



$\left[(NH_3)_3Co\begin{smallmatrix}NH_2\\OH\\O_2\end{smallmatrix}Co(NH_3)_3\right]X_3$

## Introduction

Dinuclear cobaltic $\mu$-peroxo coordination compounds were for the first time prepared by Fremy (1852). He prepared salts of the ion $[(NH_3)_5Co–O_2–Co(NH_3)_5]^{4+}$ and was also able to perform a complete and correct analysis of these compounds, which contain both the cobalt atoms in valency state +III and are coloured dark red. From these salts another series of salts can be prepared, which are characterized by their intense dark-green colour. The first salt in this series was prepared by Maquenne (1883). Later Vortman (1885) managed to prepare several compounds of this type. Maquenne and Vortman believed these compounds to contain an ion

$$[(NH_3)_5Co(III).O.OH.Co(III)(NH_3)_5]^{5+}\,.$$

Werner & Mylius (1898) proved, however, that there were no hydrogen atoms bonded to the bridging peroxide groups. In addition to compounds with one bridge, Werner (1910) prepared dinuclear cobaltic complexes containing two or three bridges. The bridging groups could be $OH^-$, $NH_2^-$ or $O_2^{2-}$. All these complexes were either red and diamagnetic or green and paramagnetic (Gleu & Rehm, 1938). In the red compounds the valency of the cobalt atoms is obviously +III; the cobalt valency in the green paramagnetic compounds is, however, not obvious. Both types are listed in Table 1. Werner (1910) proposed that the valency of the cobalt atoms in the green compound should be +III for one of them and +IV for the other. As the valency state +IV is very uncommon for cobalt, several authors, Gleu & Rehm (1938), Malatesta (1942), Thompson & Wilmarth (1952), Dunitz & Orgel