Acta Cryst. (1954). **7**, 795

Crystal Chemical Studies of the 5*f*-Series of Elements. XXIII. On the Crystal Chemistry of Uranyl Compounds and of Related Compounds of Transuranic Elements

By W. H. Zachariasen

Argonne National Laboratory and Department of Physics, University of Chicago, Chicago, Illinois, U.S.A.

(*Received* 23 *July* 1954)

The crystal chemistry of uranyl compounds and of compounds containing the groups $(NpO_2)^{+2}$, $(PuO_2)^{+2}$, $(AmO_2)^{+2}$, $(PuO_2)^{+1}$ and $(AmO_2)^{+1}$ is discussed on the basis of the available structural information.

All of these (XO_2) groups have the symmetrical collinear shape O–X–O. In all of the known crystal structures the X atom forms additional and longer bonds to other oxygen atoms or to fluorine atoms. Four, five and six such secondary bonds have been observed. The bond length within the XO_2 group as well as the length of the secondary bonds have been found to vary greatly from one structure to another. Empirical rules governing this variation in bond length are given.

Introduction

Most of the known compounds of hexavalent uranium, neptunium, plutonium and americium can be regarded as salts of radicals $(XO_2)^{+2}$, and recently the existence of similar radicals $(XO_2)^{+1}$ has been demonstrated in pentavalent plutonium and americium compounds. It is the purpose of the present article to give a brief discussion of the crystal chemistry of the group of compounds containing such radicals $(XO_2)^{+2}$ or $(XO_2)^{+1}$.

Crystal structure information has been reported for a number of compounds of the type under consideration, particularly for uranyl compounds. However, because of the unfavorable situation as to scattering power and excessive absorption, it is not an easy matter by means of X-ray diffraction data to find the positions of light atoms in the presence of uranium or still heavier atoms. Hence, the light atom parameters have been determined with accuracy only in a few isolated cases. In most instances positions have been assigned to the light atoms purely on the basis of steric considerations. Some results obtained in this indirect manner may prove to be correct. Unfortunately it is not always possible *a priori* to assess the reliability.

The shape and size of the XO_2 radicals

The collinear shape, O–U–O, for the uranyl group was first demonstrated by Fankuchen (1935) in his structural study of sodium uranyl acetate. The conclusion as to shape was a consequence of the observed space-group symmetry, the uranium atom being situated on a threefold axis. Fankuchen was, however, not able to make an experimental determination of the U–O distances. He assumed that the two U–O distances were equal and guessed the U–O bond length to be 2·2 Å. Samson & Sillén (1947), in their structure determination of $BaUO_2O_2$, deduced the uranium (no degrees of freedom) and barium (two degrees of freedom) positions from the intensity data, but placed the oxygen atoms in the structure purely on the basis of steric arguments. The symmetrical collinear shape of the uranyl group was a consequence of uranium being at an inversion center. Samson & Sillén assumed the U–O distance to be 1·90 Å, apparently as a guess, since other interatomic distances in the structure would be equally or more reasonable if the U–O distance was taken to be 1·7 Å. Hoard & Stroupe (1949), in their investigation of the structure of $RbUO_2(NO_3)_3$, likewise found the positions of the heavy atoms with the aid of intensities and used spatial considerations to assign positions to the light atoms. Their conclusions agreed with the earlier studies as to the shape of the uranyl group; but their suggested U–O bond length of 1·58 Å was much smaller than either of the earlier guesses. Hoard & Stroupe's low value for the bond length would seem to be the most reliable of the guessed values, for an unreasonably small Rb–O distance would result if the U–O bond length was increased by more than about 0·10–0·15 Å.

The first direct determination of the light-atom parameters in a uranyl compound was carried out for $CaUO_2O_2$ (Zachariasen, 1948*a*). Again, the symmetrical collinear shape of the uranyl group followed from space-group symmetry; but the U–O bond length was deduced from intensity considerations, the result being $1{\cdot}91 \pm 0{\cdot}10$ Å. In a number of subsequent structural studies of uranyl compounds the U–O bond length of 1·91 Å was assumed in the firm belief that there was little variation in bond length from one structure to another.

Two direct and quite precise structure determinations for uranyl compounds have recently been carried out. The precision was attained by means of accurate measurement of intensities and of accurate evaluation of absorption corrections. The two investigated compounds are $K_3UO_2F_5$ (Zachariasen, 1954*a*) and $MgUO_2O_2$ (Zachariasen, 1954*b*). In both structures the uranyl group was found to be collinear within the experimental error, even though this shape was not required by the space-group symmetry. However, the two determinations of the bond length gave quite different results, namely U–O = 1·92±0·03 Å in $MgUO_2O_2$ and U–O = 1·76±0·03 Å in $K_3UO_2F_5$. It has thus been shown that the uranyl bond length does vary greatly from one structure to another, and this observation is the more interesting because it was entirely unexpected. In order to try to understand the nature of this variation in bond length it becomes necessary to examine the atomic configuration about uranium beyond the two nearest oxygen atoms. The discussion of this variation will therefore have to be postponed to the next section in this article.

As to the structure of the radicals $(NpO_2)^{+2}$, $(PuO_2)^{+2}$ and $(AmO_2)^{+2}$ there is no direct information. However, compounds involving these radicals are invariably isostructural with the corresponding uranyl compounds. Since the symmetrical collinear shape has been firmly established for the uranyl group, it is thus justifiable to conclude that these other radicals have the same shape. The edge of the unit cube for the compounds in the isostructural series $Na(XO_2)(CH_3CO_2)_3$ varies as follows:

X	a (Å)	Observer
U	10·692±0·001	Fankuchen (1935)
Np	10·680±0·002	Zachariasen (1949)
Pu	10·664±0·002	Zachariasen (1949)
Am	10·655±0·001	Ellinger (1953)

Accordingly, there is a small contraction in the dimensions of the XO_2^{+2} radicals with increasing atomic number. This is, of course, the well known 5*f* contraction. The contraction in bond length in going from one XO_2^{+2} group to the next in a series of isostructural compounds U–Am is estimated to be 0·01 Å or less.

The isostructural compounds $KPuO_2CO_3$, $NH_4PuO_2CO_3$ and $RbAmO_2CO_3$ have recently been studied both chemically (Asprey, Penneman & Staritzski, 1954) and structurally (Ellinger & Zachariasen, 1954). These compounds were shown to contain symmetrical collinear groups $(PuO_2)^{+1}$ and $(AmO_2)^{+1}$, the shape being in accordance with the space-group symmetry. However, only microcrystalline material being available, it was not possible to get a direct determination of the Pu–O or Am–O bond lengths. These distances were guessed to be 1·94 Å and 1·93 Å respectively on the assumption that the U–O distance in the uranyl group has the constant value of 1·93 Å. In view of the recent result that the uranyl bond length varies considerably the guesses as to the dimensions of the $(PuO_2)^{+1}$ and $(AmO_2)^{+1}$ will have to be reconsidered. The bond length Pu–O = 1·7 Å in the compounds under consideration now seems more reasonable than the value suggested earlier, and the Am–O distance is presumably 0·01 Å shorter.

Another recent investigation is of the compound $KAmO_2F_2$ (Asprey, Ellinger & Zachariasen, 1954), which was shown to be isostructural with $CaUO_2O_2$. Direct determination of the X–O bond was again not feasible.

Although reliable information about bond lengths is lacking except for the uranyl group, it has been conclusively shown that the uranyl group serves as the prototype for a whole series of radicals $(XO_2)^{+2}$ and $(XO_2)^{+1}$, all of them being of symmetrical collinear shape.

The secondary bonds

It would be completely misleading to imply in speaking of XO_2 groups that the heavy central atom forms no other bonds than the two X–O bonds to which the attention so far has been directed. Invariably the atom X forms other bonds. However, it is true that the two X–O bonds are considerably shorter than the other bonds which are formed, so that there is justification for the reference to XO_2 groups. It is convenient to call the two short bonds primary bonds and other bonds secondary. In order to differentiate between primary and secondary bonds to oxygen atoms, the designation O_I will be used for an oxygen atom of the XO_2 group and O_{II} for other oxygen atoms. The only secondary bonds with which this article will be concerned are X–O_{II} and X–F bonds for the simple reason that structural information is available only for oxygen and fluorine compounds.

The central atom X has been observed to form six, five or four secondary bonds to oxygen or fluorine atoms. Six secondary bonds represent the usual situation. $K_3UO_2F_5$ is the only structure in which five secondary bonds occur, and four secondary bonds have been found only in the $BaUO_2O_2$ and the $MgUO_2O_2$

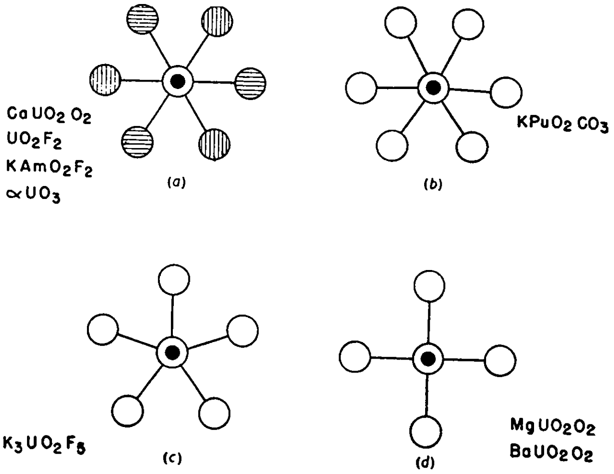

Fig. 1. The various observed atomic configurations about the X atom. The XO_2 group is drawn normal to the paper. The figures are somewhat idealized as to bond angles.

structures. The various observed atomic configurations about the X atom are shown in schematical and somewhat idealized form in Fig. 1. The most common configuration is that shown in Fig. 1(*a*). The XO_2 group is normal to the paper while of the O_{II} or F atoms three are at a height of about 0·5 Å above and three 0·5 Å below the plane of the paper. Accordingly, the angle between a primary and a secondary bond is about 75–80°. In two structures, namely $RbUO_2(NO_3)_3$ and $KPuO_2CO_3$, the six secondary bonds all lie in the plane normal to the XO_2 axis, as shown in Fig. 1(*b*). Such a configuration is made possible in these structures without causing unreasonably small O_{II}–O_{II} separations by the fact that every other edge of the hexagon formed by the O_{II} atoms is also the edge of a NO_3 or CO_3 group. The five or four secondary bonds in the configurations depicted in Fig. 1(*c*) and Fig. 1(*d*) respectively are accurately or approximately normal to the X–O_I bonds.

Observations as to the lengths of secondary (as well as of primary) bonds are compiled in Table 1. The table includes some results deduced from purely steric considerations which are believed to be reliable because the bond length in question is insensitive to variations in the light-atom parameters. It is immediately apparent from this table that the bond lengths are not primarily determined by the number of bonds formed by the X atom. Thus the observed primary bond lengths in $CaUO_2O_2$, $K_3UO_2F_5$ and $MgUO_2O_2$ show no obvious relationship to the number of secondary bonds.

Table 1. *Observed bond lengths*

Compound	Bond	Bond length (Å)	Bond strength, *s*
$K_3UO_2F_5$	U–2 O_I	1·76±0·03	1·63
$MgUO_2O_2$	U–2 O_I	1·92±0·03	1·33
$CaUO_2O_2$	U–2 O_I	1·91±0·10	1·25
UOO_2	U–2 O_I	2·08±0·01	1·00
$MgUO_2O_2$	U–4 O_{II}	2·18±0·02	0·83
$BaUO_2O_2$	U–4 O_{II}	2·17±0·10	0·75
UOO_2	U–6 O_{II}	2·39±0·10	0·67
$CaUO_2O_2$	U–6 O_{II}	2·29±0·02	0·58
$RbUO_2(NO_3)_3$	U–6 O_{II}	2·72±0·10	0·36
$NaUO_2(CH_3CO_2)_3$	U–6 O_{II}	2·45±0·10	0·33
$KPuO_2CO_3$	Pu–6 O_{II}	2·55±0·10	0·25
$K_3UO_2F_5$	U–5 F	2·24±0·02	0·55
UO_2F_2	U–6 F	2·50±0·10	0·33
$KAmO_2F_2$	Am–6 F	2·47±0·10	0·29

However, there does seem to be a very good correlation between observed bond length and bond strength, as defined below. The normal valence of an atom will be divided between the various bonds from the atom to its neighbors, each bond being assigned a fraction of the valence, the bond strength s_i. Thus Σs_i equals the normal valence of the atom. It is further assumed that equivalent bonds have equal strength, and that there is detailed balancing of valences. As an illustration, consider the $CaUO_2O_2$ structure in which the bonds formed by the various atoms are as follows:

Ca –6 O_I = 2·45 Å
Ca –2 O_{II} = 2·44
O_I –1 U = 1·91
O_I –3 Ca = 2·45

U –2 O_I = 1·91 Å
U –6 O_{II} = 2·29
O_{II} –3 U = 2·29
O_{II} –1 Ca = 2·44

Since all the eight Ca–O bonds may be considered equivalent, each bond is to be assigned the strength 0·25. Three such bonds end on an O_I atom, and thus the O_I–U bond must be given a strength $s = 1{\cdot}25$ in order that the total bond strength equal the normal valence of oxygen. Considering next an O_{II} atom, a strength of 0·25 is involved in the O_{II}–Ca bond, leaving a strength of 1·75 to be divided equally between the three equivalent O_{II}–U bonds, so that $s = 0{\cdot}58$ for each. The s values listed in Table 1 have all been obtained in the manner illustrated by this example. It is seen from Table 1 that, except for minor deviations, there is a monotonic increase in primary and secondary bond length with decreasing bond strength. In Fig. 2 the observed bond distances are plotted as a function of s, and it is seen that the observed X–O distances for primary and secondary bonds lie close to a single smooth curve.

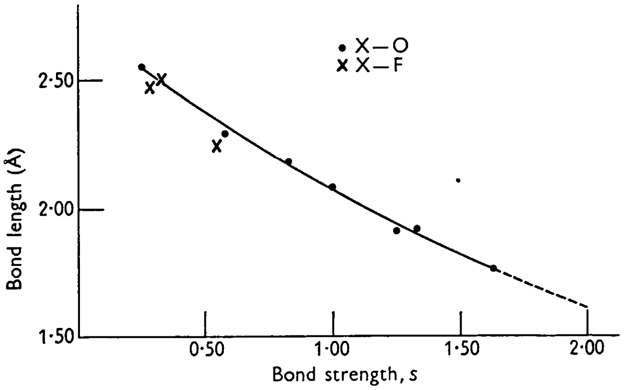

Fig. 2. The bond length plotted against the bond strength.

The empirical relation between bond length and strength illustrated in Fig. 2 may be restated in words as follows: The X–O_I bond is shortest when the O_I atom is not bonded to any atom other than the X atom. When this is the case the U–O_I distance, according to Fig. 2, is about 1·60 Å. If the O_I atom does form bonds to other atoms, there is an increase in the X–O_I bond length, the magnitude of the effect increasing with the number and the valence of the

Table 2. U–O *bond lengths empirically predicted*

		Six secondary bonds		Four secondary bonds	
s	U–O_I	*s*	U–O_{II}	*s*	U–O_{II}
2·00	1·60 Å	0·33	2·6 Å	0·50	2·4 Å
1·75	1·70	0·42	2·5	0·63	2·3
1·50	1·82	0·50	2·4	0·75	2·23
1·25	1·95	0·58	$2{\cdot}3_5$	0·88	2·15
1·00	2·08	0·66	2·3	1·00	2·08
0·75	2·23	0·75	2·23		

other atoms to which the O_I atom is bonded. The secondary bond length depends both upon the primary bond length and upon the number of secondary bonds (and, of course, upon the nature of the bonded atom). The secondary bond length increases with decreasing primary bond length and with increasing number of secondary bonds. The interrelationship between primary and secondary bond lengths is shown in Table 2, the tabulated data being taken from the curve of Fig. 2.

Earlier in this article reference was made to the fact that guesses as to the length of the uranyl bond were made independently by Fankuchen, by Samson & Sillén, and by Hoard & Stroupe. It may be of interest to compare these various guesses with the values to be anticipated on the basis of the smooth curve of Fig. 2, and this comparison is made in Table 3.

Table 3. *Guessed and predicted uranyl bond lengths*

Compound	s	U–O_I guessed	U–O_I predicted
$NaUO_2(CH_3CO_2)_3$	2·00	2·2 Å	1·60 Å
$RbUO_2(NO_3)_3$	1·93	1·58	1·63
$BaUO_2O_2$	1·50	1·90	1·82

The variation from U–O_I = 2·08 Å for $s = 1$ to U–O_I = 1·60 Å for $s = 2$ is much greater than the normal contraction of 14% in going from a single to a double bond, but is close to the usual single–triple bond contraction. This suggests that for $s = 2$ the most important electronic configurations may be $O{:}X{:}{:}{:}O$ and $O{:}{:}{:}X{:}O$, rather than $O{:}{:}X{:}{:}O$. Except for this last statement, the writer has throughout the article with intent refrained from trying to give 'theoretical' explanations of the empirical data. Such 'interpretations' seem to this writer to have little sense unless and until there is an adequate theoretical explanation for the pronounced tendency of the elements U–Am in their pentavalent and hexavalent states to form collinear symmetrical groups $(XO_2)^{+2}$ and $(XO_2)^{+1}$, and for the virtual non-existence of a similar tendency in the case of homologous elements in the periodic system.

On uranates

Crystal-structure information has been reported for the orthouranates of barium, of calcium and strontium, and of magnesium. In addition, the main structural features are known for the isostructural series $R_2UO_2O_2$, where R = K, Na, Li (Zachariasen, 1945).

As pointed out above and as shown in Fig. 1, the uranium atom forms four secondary oxygen bonds in the $BaUO_2O_2$ and in the $MgUO_2O_2$ structures, while six secondary oxygen bonds are found in the structures of all the other orthouranates which have been investigated. In all of the structures an O_{II} atom is bonded to more than one uranium atom, the O_I atom only to one uranium atom. An O_{II} atom is shared between three different uranium atoms in the calcium, strontium and alkali orthouranates in the manner shown in Fig. 3(*a*) so as to form infinite layers of composition UO_2O_2 in which all uranate groups are normal to the layers. If the O_{II} atoms are replaced by fluorine atoms one obtains the layers observed in UO_2F_2.

In the barium and magnesium compounds each O_{II} atom is shared between two uraniums; however, this sharing is done in entirely different ways in the two structures. In the former compound the angle between the two O_{II}–U bonds at the O_{II} atom is approximately 180° (the drawing in Fig. 3(*b*) as well as in Fig. 3(*c*) is admittedly idealized) and in the latter compound this bond angle is approximately 90°. As a consequence infinite layers are formed in the barium compound and infinite chains in the magnesium compound.

There is no structural information whatsoever available for di-orthouranates or any other group of uranates. It may be mentioned as a purely speculative suggestion that the simplest way of obtaining the di-orthouranate composition of 3½ oxygen atoms per

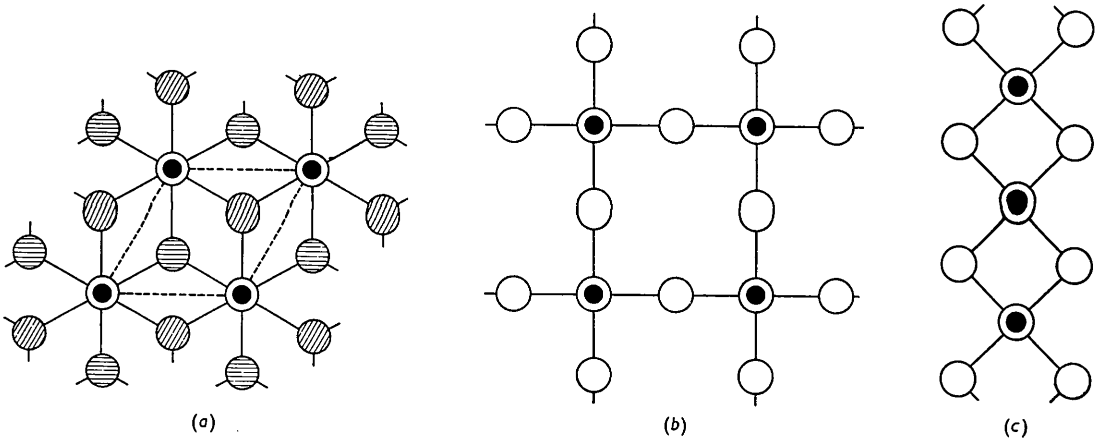
(*a*) (*b*) (*c*)

Fig. 3. (*a*) The structure of the endless hexagonal orthouranate layer first observed in the calcium compound. (*b*) The tetragonal orthouranate layer observed in somewhat distorted form in the barium compound. (*c*) The orthouranate chain observed in the magnesium compound, shown in somewhat idealized form.

uranium is to join together two orthouranate layers or two orthouranate chains by means of shared O_I atoms. If this suggestion proves to be correct, the di-orthouranates should be designated as $R_2U_2O_3O_4$, corresponding to the presence of $1\frac{1}{2}$ O_I and 2 O_{II} atoms per uranium. According to this guess as to the constitution of the di-orthouranates, each uranium forms two primary $U\text{–}O_I$ bonds, but there are no uranyl groups (UO_2). Instead, two uranyl groups are joined together to form configurations $O_I\text{–}U\text{–}O_I\text{–}U\text{–}O_I$ with the infinite layers or chains normal to this axis.

Anhydrous UO_3 is known to exist in several crystalline forms, but structural information has been reported for only one of them. The hexagonal form of UO_3 is said (Zachariasen, 1948*b*) to have a very simple structure with one molecule per unit cell with $a_1 = 3{\cdot}971$ Å, $a_3 = 4{\cdot}168$ Å. Positions were assigned to the oxygen atoms purely on the basis of steric considerations as follows:

$$1\ \mathrm{U}\ \text{in}\ (0, 0, 0),\quad 1\ \mathrm{O_I}\ \text{in}\ (0, 0, \tfrac{1}{2}),\quad 2\ \mathrm{O_{II}}\ \text{in}\ (\tfrac{1}{3}, \tfrac{2}{3}, z)$$

with $z \approx 0{\cdot}17$. It is readily seen that the proposed structure can be described as an infinite stack of the hexagonal layers first observed in the $CaUO_2O_2$ structure. These layers are stacked directly on top of one another in such a way that the O_I atoms are shared. The formula, accordingly, should be written UOO_2. There are no uranyl groups; instead uranyl groups are joined together to form an endless linear chain $\text{–}O_I\text{–}U\text{–}O_I\text{–}U\text{–}O_I\text{–}$.

References

Aspey, L. B., Ellinger, F. & Zachariasen, W. H. (1954). *J. Amer. Chem. Soc.* In press.

Asprey, L. B., Penneman, R. & Staritzski, E. (1954). *J. phys. Chem.* **58**, 403.

Ellinger, F. (1953). Private communication.

Ellinger, F. & Zachariasen, W. H. (1954). *J. phys. Chem.* **58**, 405.

Fankuchen, I. (1935). *Z. Kristallogr.* **91**, 473.

Hoard, J. L. & Stroupe, J. D. (1949). National Nuclear Energy Series, Division III, vol. 2, chap. 2, p. 15.

Samson, S. & Sillén, L. G. (1947). *Ark. Kemi Min. Geol.* **25**, No. 21.

Zachariasen, W. H. (1945). Manhattan Project Report CP-2611, p. 14.

Zachariasen, W. H. (1948*a*). *Acta Cryst.* **1**, 281.

Zachariasen, W. H. (1948*b*). *Acta Cryst.* **1**, 265.

Zachariasen, W. H. (1949). *Acta Cryst.* **2**, 388.

Zachariasen, W. H. (1954*a*). *Acta Cryst.* **7**, 783.

Zachariasen, W. H. (1954*b*). *Acta Cryst.* **7**, 788.

Acta Cryst. (1954). **7**, 799

A Test of the Usefulness of Direct Mathematical Methods in the Structure Analysis of a Protein

By M. F. Perutz and V. Scatturin

Medical Research Council Unit for the Study of the Molecular Structure of Biological Systems, Cavendish Laboratory, Cambridge, England

(*Received* 20 *August* 1954)

A test was made to see how large a fraction of the $h0l$ reflexions of horse methaemoglobin obeyed sign relations of the type: $S(h0l) = S(h'0l')S(h+h',0,l+l')$. Thirty sign relations were found between the 16 strongest reflexions chosen for the test; 22 of these held and 8 failed. A further 56 sign relations were found between any two strong and any one medium reflexion; 30 of these held and 26 failed. The results suggest that direct mathematical methods are not likely to give correct results in the structure analysis of proteins, except perhaps in very favourable cases.

There has been some debate whether direct mathematical methods, such as inequalities (Harker & Kasper, 1948) or sign relations (Sayre, 1952; Cochran, 1952; Zachariasen, 1952), could be usefully applied to the structure analysis of proteins. The recent determination of the signs of the inner 100 $h0l$ reflexions of horse methaemoglobin by the isomorphous replacement method (Green, Ingram & Perutz, 1954) provides an opportunity for testing the validity of such procedures. The unitary structure factors of haemoglobin are too small to apply inequalities. However, Cochran (1952) has shown that this is not necessary, because whenever inequalities give a relationship between three large structure factors it is of the form

$$S(hkl) = S(h'k'l')S(h+h',k+k',l+l')\,. \qquad (1)$$

The first application of this type of sign relation to proteins is due to Kendrew (1952). He treated a particularly favourable case: a projection of myoglobin in which the polypeptide chains are probably viewed end-on, simulating in appearance a structure with only a few well-resolved atoms. Such simple