Crystallography and the Physical Sciences in the 20th and 21st Centuries

Larry R. Falvello

University of Zaragoza - C.S.I.C., Department of Inorganic Chemistry and I.C.M.A., Pedro Cerbuna 12, 50009 Zaragoza, Spain.
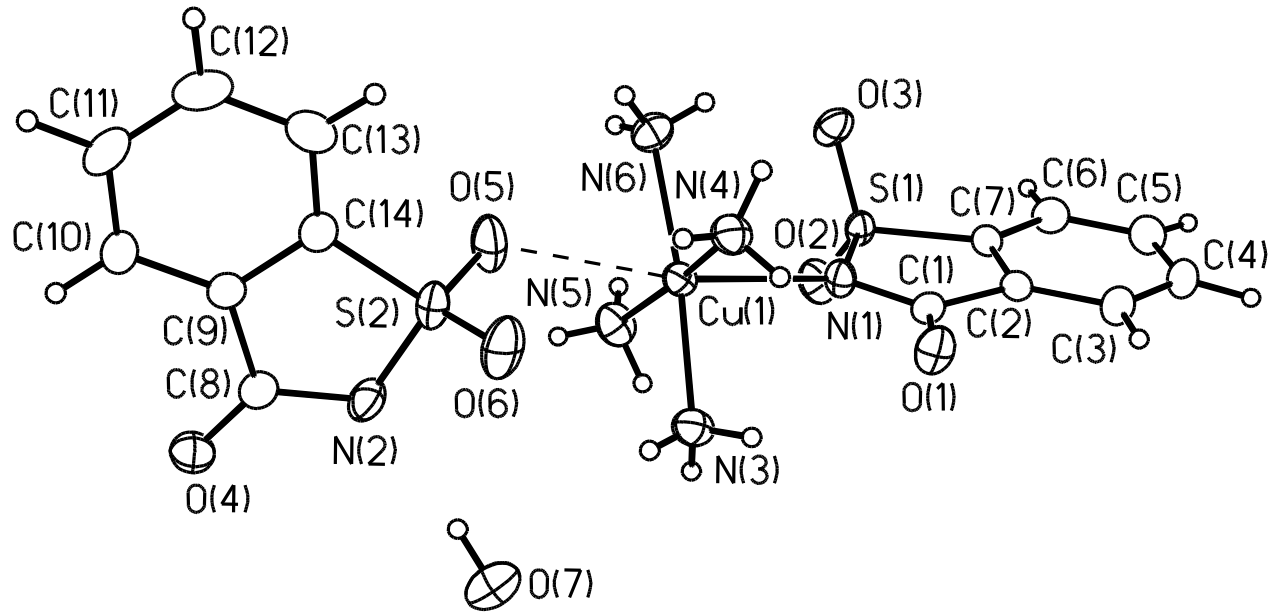
NMI3-II General Assembly, Zaragoza
25 September, 2014

GOBIERNO DE ESPAÑA
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

EIMM

/icma / Instituto de Ciencia de Materiales de Aragón /

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

Universidad Zaragoza

"The ORTEP"

Shows:

    Atom names (including element)

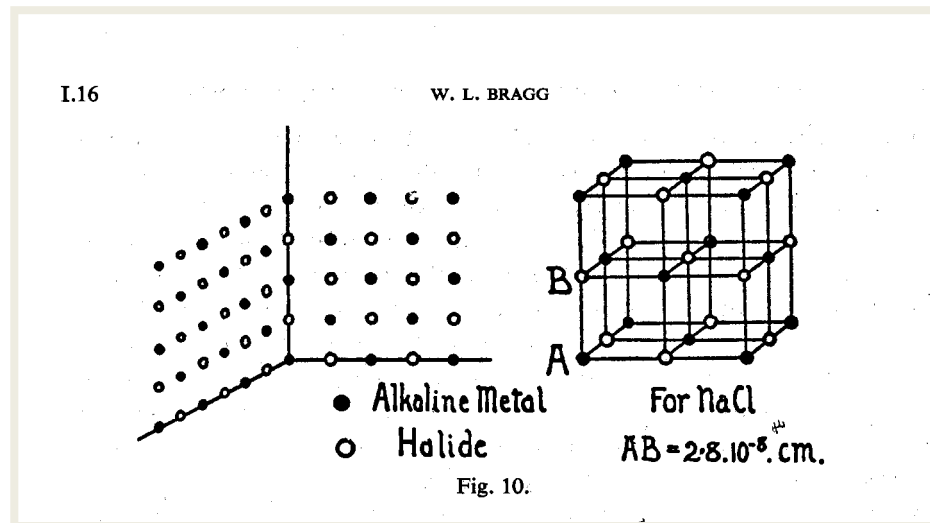   Atomic arrangement

    Displacement ellipsoids

Crystal Structures in the Physical Sciences
- Single-structure discoveries
- Multiple-structure discoveries

1912/1913/1914 – Crystal structures of NaCl and other substances

"The Structure of Crystals as Indicated by their Diffraction of X-rays," W. L. Bragg, *Proceedings of the Royal Society London,* **1913**, <u>A89</u>, 248-277.

I.16   W. L. BRAGG

● Alkaline Metal
○ Halide

For NaCl
$AB = 2.8 . 10^{-8} . cm.$

Fig. 10.

Crystal Structures in the Physical Sciences

- Single-structure discoveries
- Multiple-structure discoveries

Pauling's Rules

THE PRINCIPLES DETERMINING THE STRUCTURE OF COMPLEX IONIC CRYSTALS

By LINUS PAULING

1.   The Relative Stability of Alternative Structures of Ionic Crystals.— The elucidation of the factors determining the relative stability of alternative crystalline structures of a substance would be of the greatest significance in the development of the theory of the solid state. Why, for example, do some of the alkali halides crystallize with the sodium chloride structure and some with the cesium chloride structure? Why does titanium dioxide under different conditions assume the different structures of rutile, brookite and anatase?   Why does aluminum fluosilicate, $Al_2SiO_4F_2$, crystallize with the structure of topaz and not with some other structure?   These questions are answered formally by the statement that in each case the structure with the minimum free energy is stable. This answer, however, is not satisfying; what is desired in our atomistic and quantum theoretical era is the explanation of this minimum free energy in terms of atoms or ions and their properties.

Outline

- General background – some numbers.

- The importance of non-crystallographic chemistry in one major area of structure science – macromolecular crystallography.

- An aside regarding funding.

- Why coordination chemists are so hooked on crystallography.

- An important one-structure discovery in inorganic chemistry – the quadruple bond.

- An important multi-structure analysis in inorganic chemistry – the delta component of the quadruple bond.

- New light in the future?

- Data bases.

- A few closing images.

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The NobelPrize in Physics 1994

The Royal Swedish Academy of Sciences has awarded the 1994 Nobel Prize in Physics for pioneering contributions to the development of neutron scattering techniques for studies of condensed matter.

Clifford G. Shull, MIT, Camebridge, Massachusetts, USA, receives one half of the 1994 Nobel Prize in Physics for development of the neutron diffraction technique.

Betram N. Brockhouse, McMater University, Hamilton, Ontario, Canada, receives one half of the 1994 Nobel Prize in Physics for the development of neutron spectroscopy.

Shull made use of **elastic scattering** i.e. of neutrons which change direction without losing energy when they collide with atoms.

Because of the wave nature of neutrons, a diffraction pattern can be recorded which indicates where in the sample the atoms are situated. Even the placing of light elements such as hydrogen in metallic hydrides, or hydrogen, carbon and oxygen in organic substances can be determined.

The pattern also shows how atomic

Brockhouse made use of **inelastic scattering** i.e. of neutrons, which change both direction and energy when they collide with atoms. They then start or cancel atomic oscillations in crystals and record movements in liquids and melts. Neutrons can also interact with spin waves in magnets.

With his 3-axis spectrometer Brockhouse measured energies of phonons (atomic vibrations) and magnons

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Sold! Nobel Prize for Neutron Discovery Auctioned for $329,000

By Megan Gannon, News Editor | June 04, 2014 11:01am ET

The 1935 Nobel Prize Medal that was presented to James Chadwick for his discovery of the neutron.

Credit: Courtesy of Sotheby's

View full size image

Pin it

The 1935 Nobel Prize in physics that was awarded to English scientist James Chadwick for his discovery of the neutron was sold at auction this week for $329,000.

Sotheby's auction house, which handled the sale yesterday (June 3) in New York, estimated that the Nobel gold medal and its accompanying diploma would sell for between $200,000 and $400,000. Sotheby's did not release any information about the buyer. The seller was a collector of medals and coins, who bought Chadwick's Nobel gold medal and diploma from the famed physicist about 20 years ago.

In the year **(2002) 2014**:

The Cambridge Structural Database holds more than **(250,000) 717,895** crystal structures (> 628,684 distinct compounds). Of these entries, 1641 have the "radiation source: neutrons" attribute.

The Protein Data Bank has some **(17,443) 103,199** macromolecular structures (as of 9 September, 2014).
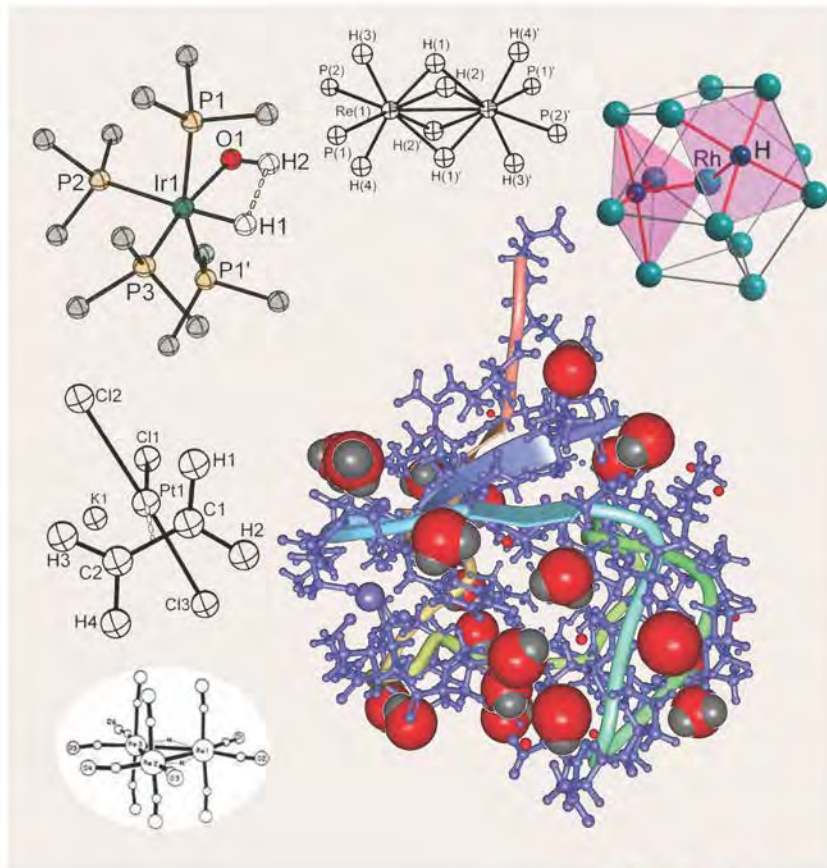
The Inorganic Crystal Structure Database holds more than **(50,000) 169,800** structures.

ACA RefleXions

American Crystallographic Association

Number 4

Winter 2009

ACA 2010
Transactions Symposium
The First Element

In the year **2014**:

The Protein Data Bank held some **103,199** macromolecular structures (as of 9 September, 2014).
(+155)
The Protein Data Bank held some **103,354** macromolecular structures (as of 16 September, 2014).
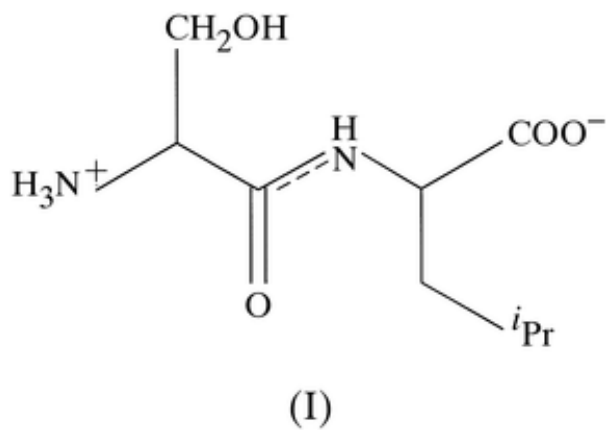(+203)
The Protein Data Bank has some **103,557** macromolecular structures (as of 23 September, 2014).
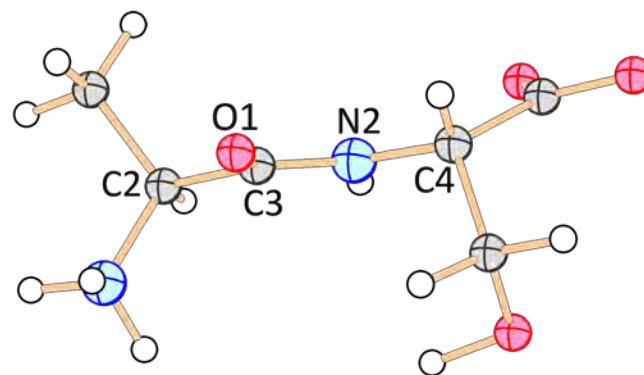
Protein Components -- The Peptide Bond

Emil Fischer biography:

http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1902/fischer-bio.html

"He was able to establish the type of bond that would connect [amino acids] together in chains, namely, the peptide bond, and by means of this he obtained the dipeptides and later the tripeptides and polypeptides."

(I)

J. Slowikowska & J. Lipkowski
L-seryl-L-leucine *Acta Cryst.* (2001). C**57**, 187-189 [doi:10.1107/S0108270100016164]

Acta Cryst. B34, 1939-1942. L-alanyl-L-serine C2-C3-N2-C4 = 177.98(2)º

Beginnings

Astbury, W. T. & Street, A. (1931). *Trans. R. Soc. Lond.*, <u>A230</u>, 75-101. "X-ray studies of the structures of hair, wool and related fibres. I. General."

Astbury, W. T. (1933). *Trans. Faraday Soc.*, <u>29</u>, 193-211. "Some Problems in the X-ray Analysis of the Structure of Animal Hairs and Other Protein Fibers."

Astbury, W. T. & Woods, H. J. (1934). *Trans. R. Soc. Lond.*, <u>A232</u>, 333-394. "X-ray studies of the structures of hair, wool and related fibres. II. The molecular structure and elastic properties of hair keratin."

Astbury, W. T. & Sisson, W. A. (1935). *Proc. R. Soc. Lond.*, <u>A150</u>, 533-551. "X-ray studies of the structures of hair, wool and related fibres. III. The configuration of the keratin molecule and its orientation in the biological cell."

Unstretched keratin fibers had a repeat distance measured as 5.1 Å.

Macromolecular Structure: Beginnings

J. D. Bernal & D. Crowfoot (1934). *Nature* <u>133</u> 794-795. X-Ray Photographs of Crystalline Pepsin.

FOUR weeks ago, Dr. G. Millikan brought us some crystals of pepsin prepared by Dr. Philpot in the laboratory of Prof. The Svedberg, Uppsala. They are in the form of perfect hexagonal bipyramids up to 2 mm. in length, of axial ratio $c/a = 2 \cdot 3 \pm 0 \cdot 1$.

It was clearly necessary to avoid alteration of the crystals, and this was effected by drawing them with their mother liquor and without exposure to air into thin capillary tubes of Lindemann glass. The first photograph taken in this way showed that we were dealing with an unaltered crystal. From oscillation photographs with copper $K\alpha$-radiation, the dimensions of the unit cell were found to be $a = 67$ A., $c = 154$ A., correct to about 5 per cent. This is a
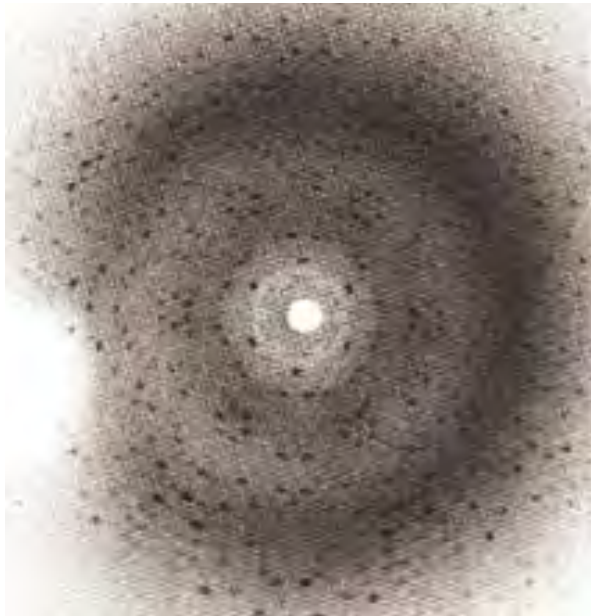
Guy Dodson
Biogr. Mems Fell. R. Soc. 2002 **48, 179-219**
doi: 10.1098/rsbm.2002.0011

"Dorothy has often been given the credit for this hugely important X-ray experiment but she always made it clear that it was Bernal who took the first photographs and had the critical insight to keep the crystal wet. Dorothy in her experiments with the crystals also observed that the X-ray reflections weakened with exposure to the radiation, a continuing problem with macromolecular crystals until the recent introduction of cryo-techniques. The question arose as to whether the radiation damage affected the enzyme's activity. Experiments showed that it remained active, proving that the loss of diffraction was due to damage to the crystal lattice, not to chemical and structural changes in the molecule."
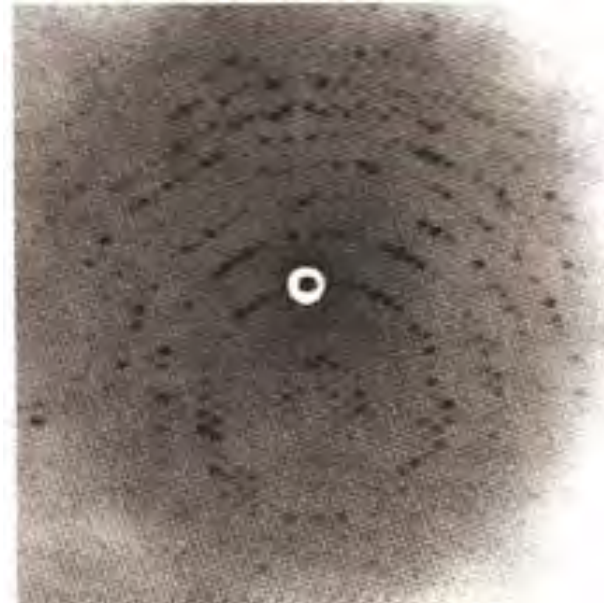
Macromolecular Structure: Beginnings

Diffraction photo from pepsin

Oscillation photo from horse met-hemoglobin, taken by Max Perutz in the late 1930's.

from Judson
Photograph courtesy of Max Perutz

from Judson
Photograph courtesy of Max Perutz

Macromolecular Structure: Beginnings

Crowfoot, Dorothy (1939). *Proc. Roy. Soc. Lon. Series B: Biological Sciences* <u>127</u>, 35-36. *X-ray studies of protein crystals.*
"So far, of only seven proteins -- pepsin, insulin, excelsin, lactoglobulin, haemoglobin, chymotrypsin, and tobacco seed globulin -- have sufficient X-ray measurements been made to cover even the first stages of crystallographic examination, the determination of unit cell size and cell molecular weight."

Macromolecular Structure: Beginnings

Upon being appointed Cavendish Professor at Cambridge (1937), "Lawrence's first task was to deal with major staff changes..... Bernal and his team of biological crystallographers left the Cavendish.... Lawrence brought in [among others] Henry Lipson, Egon Orowan, and Paul Ewald to continue the work in crystallography, joining Max Perutz, who was the sole remaining member of Bernal's group. Perutz, a refugee student from Vienna, was working on the structure of haemoglobin protein crystals and Lawrence obtained a grant from the Rockefeller Foundation to enable him to continue: 'Some fortunate intuition made me feel that this line of research must be pursued, although it seemed absolutely hopeless to think of getting out the structure of so vast a molecule.'" W. L. Bragg, autobiographical notes, p. 92, quoted in John Jenkin, *William and Lawrence Bragg, Father and Son.* Oxford University Press, 2008.

Macromolecular Structure: Beginnings

Following the Second World War, "'It was a strange time at the Cavendish because Rutherford's influence had been removed... It was as if some mighty forest tree had fallen, and saplings hitherto starved of light and nourishment were beginning a more normal development.... But probably the work which in future years will be regarded as the outstanding contribution of the Cavendish Laboratory in these after-war years was the start of the investigation of biological molecules by X-rays.'"

...

"The Medical Research Council agreed to support the protein research, and for a long time the results were 'very meagre indeed... Perutz at times became quite discouraged... Why I continued to be optimistic I shall never understand.' In 1946 John Kendrew joined the group but, having realized that a helical structure was likely, they failed to solve the protein structure because of an ignorance of one piece of chemistry and an erroneous assumption regarding the helix. Lawrence never forgave himself and determined in future to seek the best chemistry advice before publishing."

W. L. Bragg, autobiographical notes, p. 92, quoted in John Jenkin, *William and Lawrence Bragg, Father and Son.* Oxford University Press, 2008.

first concepts, beginnings

Bragg, W. Lawrence, Kendrew, J. C. & Perutz, M. F. (1950). *Proceedings of the Royal Society of London, Series A: Mathematical, Physical and Engineering Sciences,* 203, 321-357. Polypeptide chain configurations in crystalline proteins.

ABSTRACT. A systematic survey has been made of chain models which conform to established bond lengths and angles, and which are held in a folded form by N---H...O bonds. An attempt is made to reduce the no. of possibilities by comparing vector diagrams with Patterson projections. The evidence favors chains of the general type proposed for α-keratin by Astbury. These chains have a dyad axis with 6 residues in a repeat distance of 10.2 A. and are composed of approx. coplanar folds. These chains are placed in the myoglobin structure, and a comparison is made between calcd. and observed F values for a zone parallel to the chains; the agreement is remarkably close. The 3-dimensional Patterson of hemoglobin shows how cautious one must be in accepting this agreement as significant. Successive portions of the rod of high vector d. which has been supposed to represent the chains give widely different projections and show no evidence of a dyad axis. The evidence is still too slender for definite conclusions to be drawn. A further intensive study of myoglobin may lead to a detn. of the chain structure.

Secondary structure: the alpha hélix and the beta sheet

'From the spring of 1948 through the spring of 1951.... rivalry sputtered and blazed between Pauling's lab and Bragg's -- rivalry over protein..... Pauling was working up from the simpler structures of components. In January 1948, he went to Oxford as a visiting professor for two terms, to lecture on the chemical bond and on molecular structure and biological specificity.

"In Oxford, it was April, I believe, I caught cold. I went to bed, and read detective stories for a day, and got bored, and thought why don't I have a crack at that problem of alpha keratin."

...

He knew that the peptide bond, at the carbon-to-nitrogen link, was always rigid: And this meant that the chain could turn corners only at the alpha carbons.'
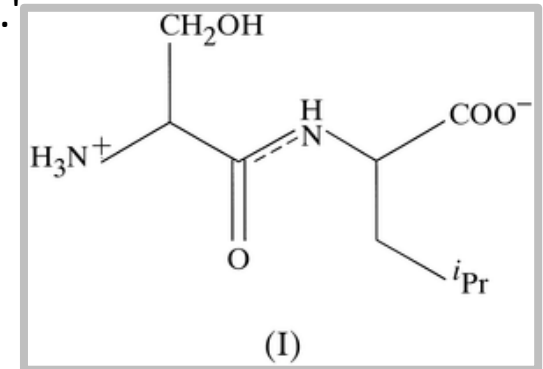
--- Judson, *The Eighth Day of Creation.*

Pauling, L. & Corey, R. B. (1950). J. Am. Chem. Soc. 5349

TWO HYDROGEN-BONDED SPIRAL CONFIGURATIONS OF THE POLYPEPTIDE CHAIN

Sir:

During the past fifteen years we have been carrying on a program of determination of the detailed atomic arrangements of crystals of amino acids, peptides, and other simple substances related to proteins, in order to obtain structural information that would permit the precise prediction of reasonable configurations of proteins.

One of these spirals is the three-residue spiral, in which there are about 3.7 residues per turn and each residue is hydrogen-bonded to the third residue from it in each direction along the chain. The unit translation per residue is 1.47 Å. There is evidence that indicates strongly that this configuration is present in α-keratin, contracted myosin, and some other fibrous proteins and also in hemoglobin and other globular proteins.[1]

The pitch of this helix is 5.4 Å, not 5.1 Å.

Pauling, L. & Corey, R. B. (1951). Proc. Natl. Acad. Sci. <u>37</u>, 282-285.

THE POLYPEPTIDE-CHAIN CONFIGURATION IN HEMOGLOBIN AND OTHER GLOBULAR PROTEINS

By Linus Pauling and Robert B. Corey

Gates and Crellin Laboratories of Chemistry,* California Institute of Technology, Pasadena, California

Communicated March 31, 1951

In the immediately preceding papers we have described several hydrogen-bonded planar-amide configurations of polypeptide chains, and have discussed the evidence bearing on the question of their presence in fibrous proteins. It seems worth while to consider the possibility that these configurations—the pleated sheet, the 3.7-residue α helix, the 5.1-residue γ helix, and the three-chain collagen helix—are represented in molecules of the globular proteins.

The First Structures

A Three-Dimensional Model of the Myoglobin Molecule Obtained by X-Ray Analysis
By Kendrew, J. C.; Bodo, G.; Dintzis, H. M.; Parrish, R. G.; Wyckoff, H.; Phillips, D. C., Medical Research Council Unit for Molecular Biology, Cavendish Laboratory, Cambridge, Davy Faraday Laboratory, The Royal Institution, London
A report of the method used to obtain a 3-dimensional model of the myoglobin mol. by x-ray analysis.
-- 6 Å resolution, ~ 600 data. MIR. Eight lengths of α-helix, 70% of the sequence.
Later 2 Å data were measured with the Arndt diffractometer at the Royal Institution.

Architecture of a protein molecule
KENDREW J. C. (1958). *Nature,* 182, 764-767.
The crystal structure of myoglobin. IV. A Fourier projection of sperm-whale myoglobin by the method of isomorphous replacement
By Bluhm, M. M.; Bodo, G.; Dintzis, H. M.; Kendrew, J. C.
Proceedings of the Royal Society of London, Series A: Mathematical, Physical and Engineering Sciences (1958), 246, 369-89. DOI:10.1098/rspa.1958.0145
 By 2 methods heavy atoms are attached at specific sites (Hg or Au). An electron d. projection is computed. The relative positions of the 2 protein mols. in the unit cell are established.

A THREE-DIMENSIONAL MODEL OF THE MYOGLOBIN MOLECULE OBTAINED BY X-RAY ANALYSIS

By Drs. J. C. KENDREW, G. BODO, H. M. DINTZIS, R. G. PARRISH and H. WYCKOFF

Medical Research Council Unit for Molecular Biology, Cavendish Laboratory, Cambridge

AND

D. C. PHILLIPS
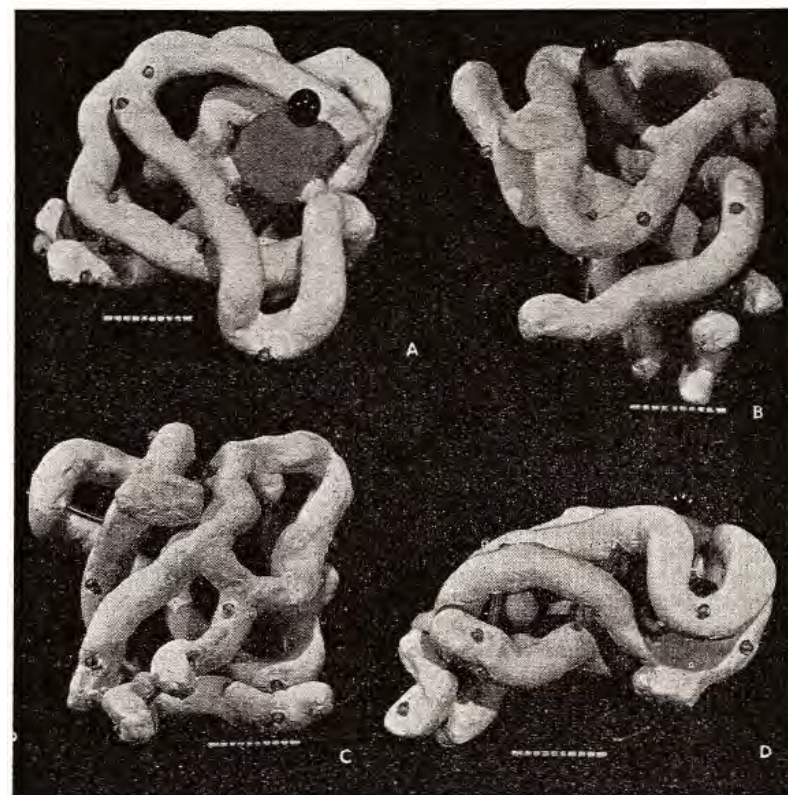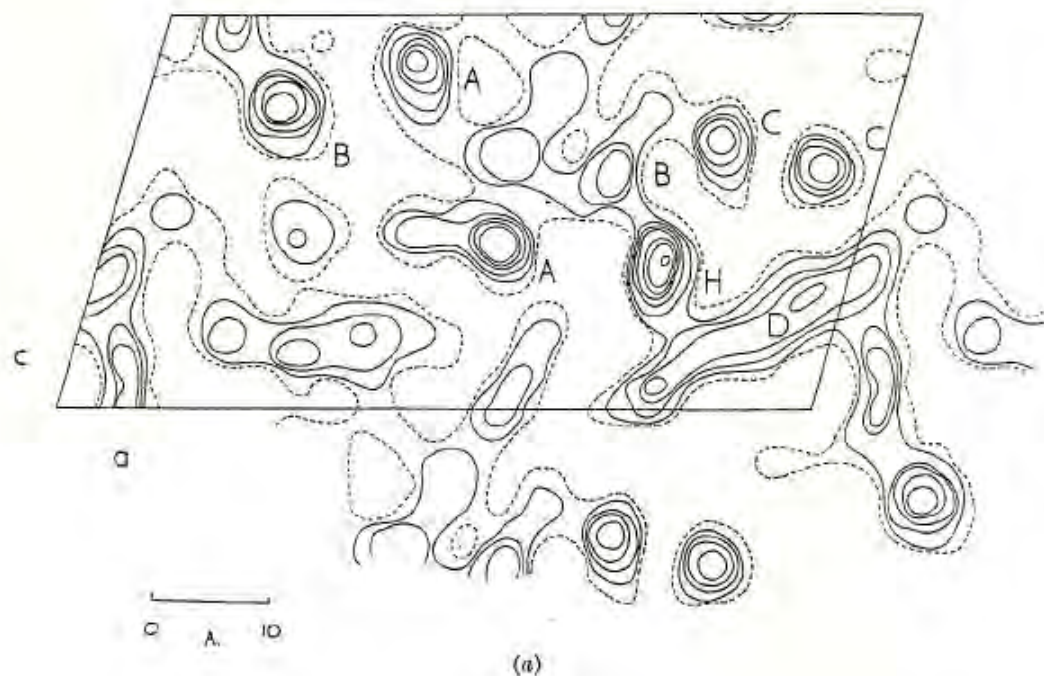
Davy Faraday Laboratory, The Royal Institution, London

Fig. 2. Photographs of a model of the myoglobin molecule. Polypeptide chains are white; the grey disk is the hæm group. The three spheres show positions at which heavy atoms were attached to the molecule (black: Hg of p-chloro-mercuri-benzene-sulphonate; dark grey: Hg of mercury diammine; light grey: Au of auri-chloride). The marks on the scale are 1 A. apart

The First Structures

Structure of hemoglobin. A three-dimensional Fourier synthesis at 5.5-A. resolution, obtained by x-ray analysis,

Perutz, M. F.; Rossmann, M. G.; Cullis, Ann F.; Muirhead, Hilary; Will, Georg; North, A. C. T.

Structure of hemoglobin. VIII. A three-dimensional Fourier synthesis at 5.5-A. resolution: determination of the phase angles

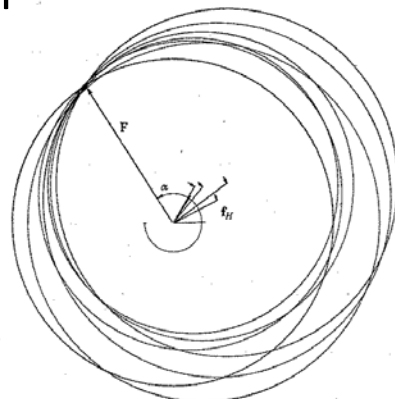Cullis, Ann F.; Muirhead, Hilary; Perutz, M. F.; Rossmann, M. G.; North, A. C. T.
horse oxyhemoglobin

FIGURE 7. Phase circles for the $91\bar{2}$ reflexion.

Figures 7 and 8 show examples of three phase circles, drawn for the $91\bar{2}$, $11\bar{2}$ and 317 reflexions. In $91\bar{2}$ all the circles intersect at a point and marked anomalous scattering is observed in several derivatives with $|F_H(hkl)| < |F_H(\bar{h}\bar{k}l)|$, confirming the choice of phase angle. In $11\bar{2}$ isomorphous replacement gives an ambiguous
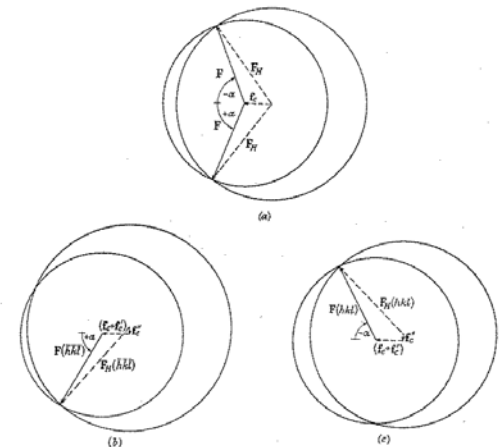
FIGURE 6. Isomorphous replacement and anomalous scattering. (a) Shows the effect on **F** of isomorphous replacement by a single heavy atom chosen as origin. (b) and (c) Show the effect of anomalous scattering by the heavy atom on F_H. The direction of the anomalous scattering factor f_c'' is 90° in advance of the phase of f_c. Its orientation is the same for $f(hkl)$ and $f(\bar{h}\bar{k}l)$. The resulting difference in the amplitudes of $F_H(hkl)$ and $F_H(\bar{h}\bar{k}l)$ solves the ambiguity in (a).

Elements of the technique, **diffraction measurement:** The four-circle diffractometer

Apparatus for Measuring Complete Single-Crystal X-Ray Diffraction Data by Means of a Geiger Counter Diffractometer*

THOMAS C. FURNAS, JR., AND DAVID HARKER

Protein Structure Project, Polytechnic Institute of Brooklyn, 55 Johnson Street, Brooklyn 1, New York

(Received October 28, 1953)

A device for measuring x-ray diffractions from a single crystal is described. The heart of the apparatus is an "Eulerian Cradle," so named because it permits rotation of the crystal about each of the Eulerian axes. It is used for orienting single crystals in an x-ray beam, in order to bring each reciprocal lattice point into the equatorial plane for Geiger counter measurement of the intensity. It eliminates the need for raising the Geiger tube out of the equatorial plane and suggests that the reciprocal lattice be surveyed by either "zone" or "cone" schemes. These are described, and the "cone" scheme is shown to permit a complete hemisphere of the reciprocal lattice to be surveyed with only a single mounting of any crystal. Fine points concerning

STRUCTURE determination in the case of crystalline proteins presents several problems which have necessitated a re-evaluation of conventional techniques for collecting data.

(1) Crystalline proteins have such large unit cells that many thousands of separate integrated intensity measurements must be made on a single crystal species.

(2) There are uncertainties regarding the absolute identity of two crystals grown at different times from different batches.

(3) Many crystalline proteins are destroyed by exposure to x-rays (ribonuclease crystals survive only 50 to 100 hr under our experimental conditions).
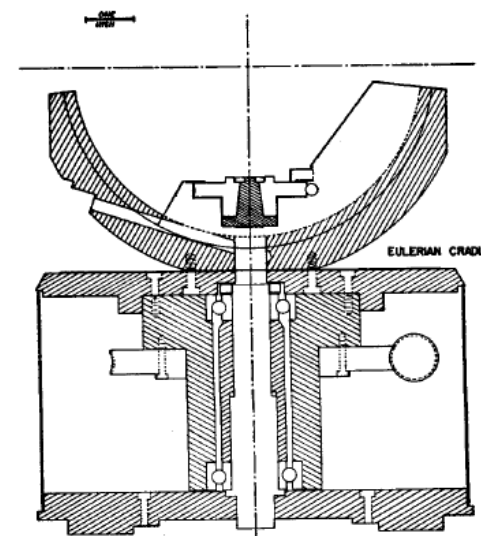
DESCRIPTION OF APPARATUS

We have named our instrument an "Eulerian Cradle," because of its shape and the fact that it

FIG. 2. Cross-sectional view of Eulerian Cradle (see text and Figs. 3 and 4 for details).

25

445. *Phosphine Oxide Complexes. Part IV.*[1] *Tetrahedral, Planar, and Binuclear Complexes of Copper*(II) *with Phosphine Oxides, and Some Arsine Oxide Analogues.*

By D. M. L. GOODGAME and F. A. COTTON.

Some phosphine oxide complexes of copper(II) have been prepared, along with the arsine oxide analogues of two of them, and physical measurements made in order to determine the co-ordination symmetries. It appears that the co-ordination is tetrahedral in $[Cu(Ph_3PO)_2Cl_2]$ and $[Cu(Ph_3PO)_2Br_2]$, as in the analogous manganese(II), cobalt(II), and nickel(II) compounds. The triphenylarsine oxide analogues of these complexes do not seem to be tetrahedral. The complex cation $[Cu(Me_3PO)_4]^{2+}$ appears to be square, and the complex $CuCl_2,4(HO\cdot CH_2)_3PO$ also appears to contain tetragonally co-ordinated copper(II). The complex $Cu(CH_3\cdot CO_2)_2,Ph_3PO$ is very probably a carboxylate-bridged dimer.

Kuznetzov, V. G. & Koz'min, P. A. (1963) *J. Struct. Chem.* <u>4</u>, 49. [*Zhurnal Strukturnoi Khimii* (1963) <u>4</u>, 55-62].

Crystal structure of "(pyH)HReCl$_4$":

Twinning problems.

Charge balanced by isolated H$^+$.

The cryst. structure of the pyridine deriv. of the tetrachloride of bivalent Re, (pyH)HReCl$_4$ was detd. from 2-dimensional projections of the interat. vectors and the electron d. The space group is D$^{19}_{2h}$- Cmmm, the calcd. unit cell parameters are a 7.55 $\pm$ 0.22; b 16.31 $\pm$ 0.04, and c 8.25 $\pm$ 0.02 kX, the observed d. = 2.69 and Z = 4. The basic structure seems to consist of dimeric ions [Re$_2$Cl$_8$]$^{4-}$ exhibiting the form of a square prism in which, besides the 4 covalent bonds Re-(1 of 2.43 kX length, the bond Re-Re of 2.22 kX length exists, thereby the coordination no. of Re is 5. The direction of the Re-Re bond is parallel to the x axis, while the planes of the chloride squares are perpendicular to this same axis. The planes of the pyH$^+$ ion lay in such a way that the N atom is surrounded by 4 Cl atoms belonging to 4 different [Re$_2$Cl$_8$]$^{4-}$ groups. The free H atoms are postulated to occupy symmetry centers between the Cl atoms. The inferred structure accounts satisfactorily for the observed diamagnetic character of the compd. 15 references.
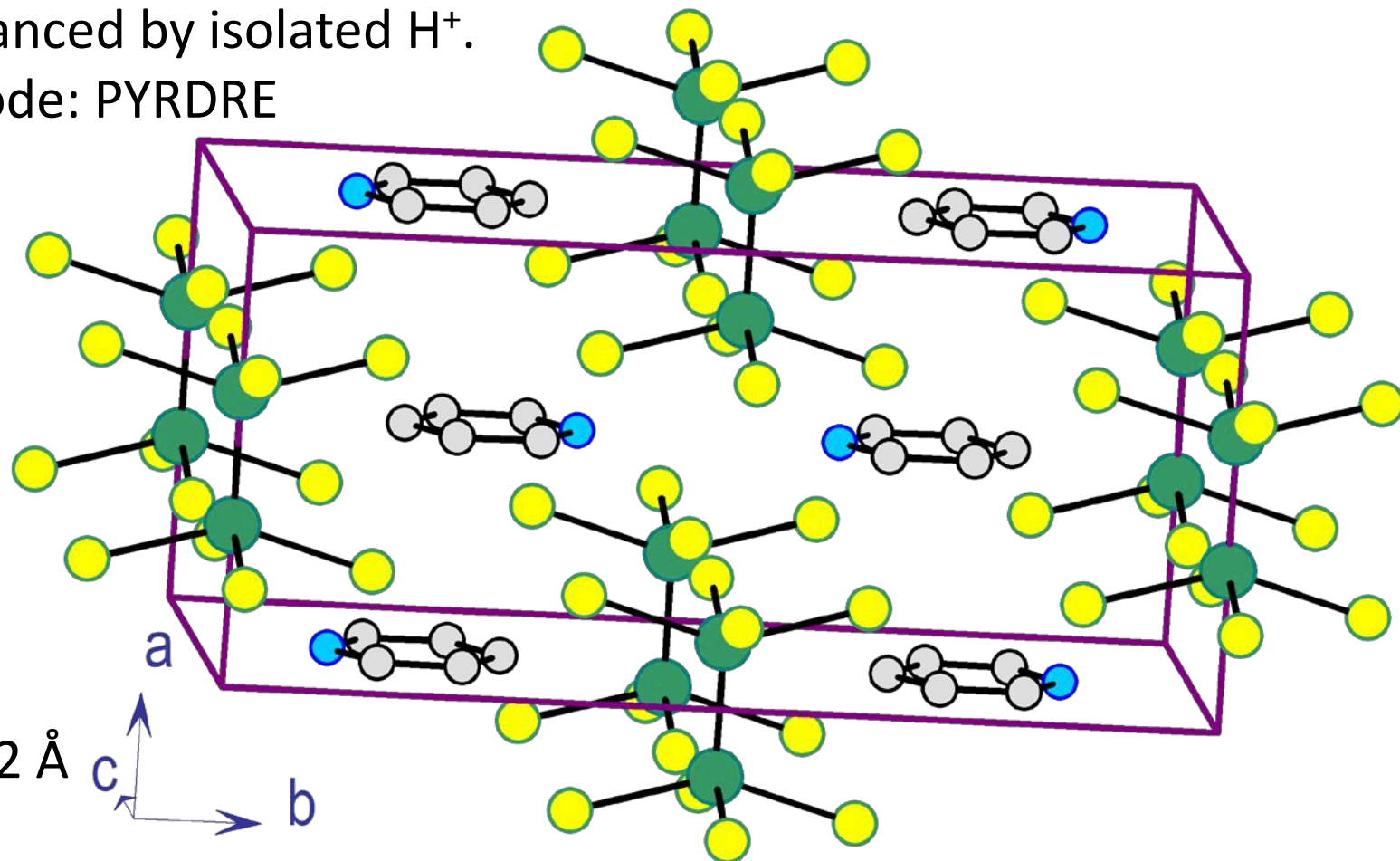
Kuznetzov, V. G. & Koz'min, P. A. (1963) *J. Struct. Chem.* <u>4</u>, 49. [*Zhurnal Strukturnoi Khimii* (1963) <u>4</u>, 55-62].

Crystal structure of "(pyH)HReCl$_4$":

Twinning problems.

Charge balanced by isolated H$^+$.

CCDC Refcode: PYRDRE

Re---Re 2.22 Å

Diamagnetism attributed to the formation of an Re---Re bond.

The quadruple bond - $K_2[Re_2Cl_8]$
F. A. Cotton, *et al., Science,* **1964**, <u>145</u>, 1305.

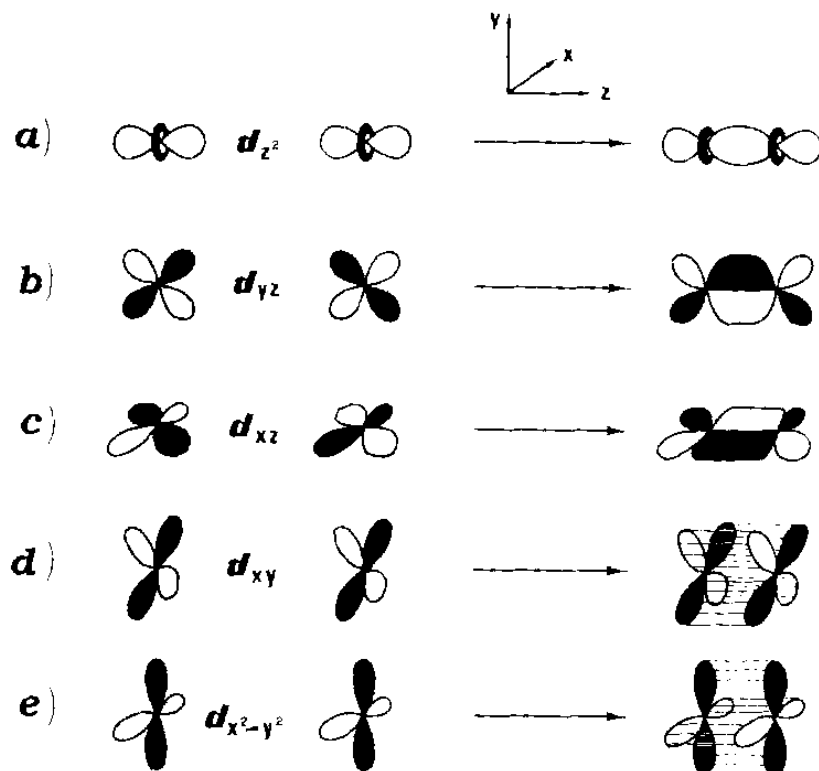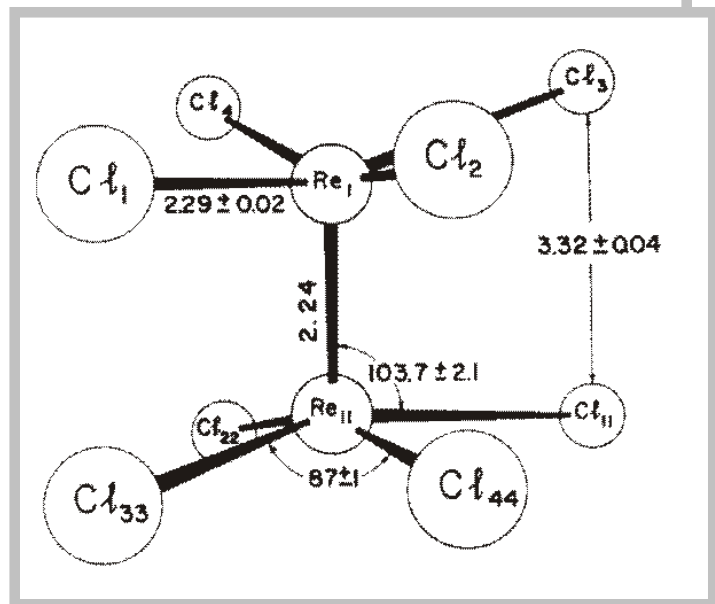# Mononuclear and Polynuclear Chemistry of Rhenium (III): Its Pronounced Homophilicity

Abstract. *Extensive chemical, spectrophotometric, and x-ray structural studies have shown that trivalent rhenium is strongly homophilic—that is, it tends to form bonds to other Re^{III} atoms—and it forms at least three different series of $[ReX_4]_n^{n-}$ complexes. The mononuclear, square complex, $[ReBr_4]^-$, adds two water molecules to give* trans-$[ReBr_4(H_2O)_2]^-$. *The binuclear complexes $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ have strong Re-Re bonds, unsupported by halide bridges. The trinuclear species, $[Re_3X_{12}]^{3-}$ or $Re_3X_9L_3$, contain the triangular Re_3X_9 clusters. Use of $ReCl_3$ appears always to lead directly to products containing Re_3Cl_9; this unit exists in $ReCl_3$ itself and does not appear to be kinetically labile. The $[Re_2X_8]^{2-}$ ions are obtained by reduction of ReO_4^- in aqueous HCl or HBr. Salts of $[ReBr_4(H_2O)_2]^-$ can be obtained directly from solutions of $ReBr_3$ in HBr along with numerous other compounds, some containing trinuclear clusters.*

overlap would be zero). We believe that an absorption band at about 36,000 cm^{-1} can be assigned to the $\delta \rightarrow \delta^*$ transition (which is $a_{1g} \rightarrow b_{2u}$ electric-dipole-allowed with z polarization), thus fixing the energy of the δ bond at about 60 kcal/mole. Since the Cl-Cl

This would appear to be the first quadruple bond to be discovered.

F. A. Cotton, N. F. Curtis
C. B. Harris, B. F. G. Johnson
S. J. Lippard, J. T. Mague
W. R. Robinson, J. S. Wood
*Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge*

Cambridge Database 2014 Author Statistics

Rank	Structures	Author
1.	5256	White,A.H.
2.	4508	Skelton,B.W.
3.	4276	Rheingold,A.L.
4.	4172	Jones,P.G.
5.	3908	Hursthouse,M.B.
6.	2824	Fun,H.-K.
7.	2801	Howard,J.A.K.
8.	2727	Struchkov,Yu.T.
9.	2644	Spek,A.L.
10.	2584	Cotton,F.A.
11.	2569	Hitchcock,P.B.
12.	2547	Frohlich,R.
13.	2379	Clegg,W.
14.	2338	Slawin,A.M.Z.
15.	2258	Mak,T.C.W.

The Crystal and Molecular Structure of Dipotassium Octachlorodirhenate(III) Dihydrate, $K_2[Re_2Cl_8]2H_2O$

F. A. Cotton, C. B. Harris

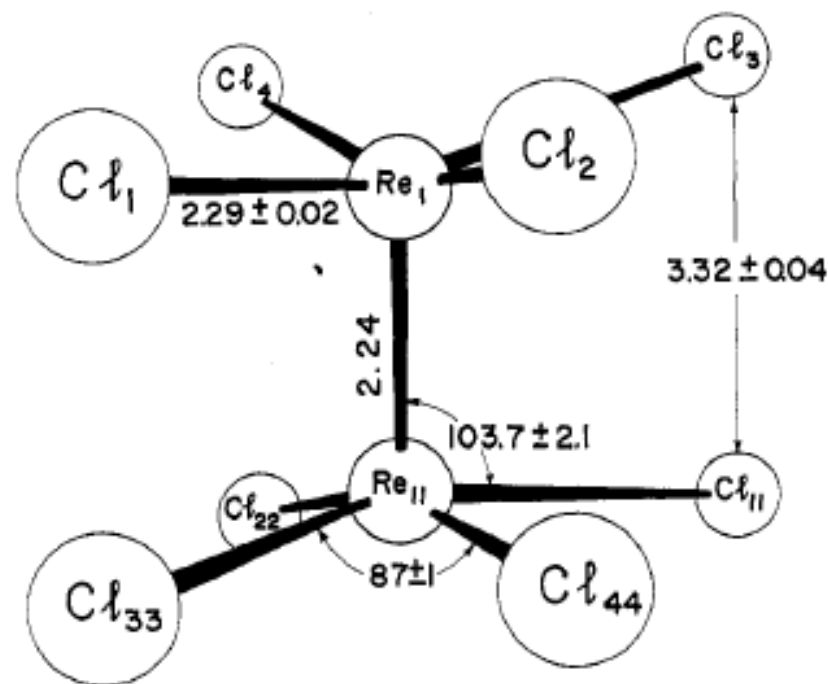## The Crystal and Molecular Structure of Dipotassium Octachlorodirhenate(III) Dihydrate, $K_2[Re_2Cl_8] \cdot 2H_2O$[1]

By F. A. COTTON AND C. B. HARRIS

Intensity data were collected by the equi-inclination Weissenberg method with Cu $K\alpha$ radiation using a crystal with approximate dimensions $0.02 \times 0.02 \times 0.05$ mm. The levels $0kl$–$4kl$ were recorded; 579 reflections within half a sphere ($h \geqslant 0$) with $\sin \theta/\lambda \leqslant 45°$ were recorded.

Intensities were estimated visually using an intensity wedge

The structure was solved and developed in space group P1, after which the correct space group was established by examination of the structure.

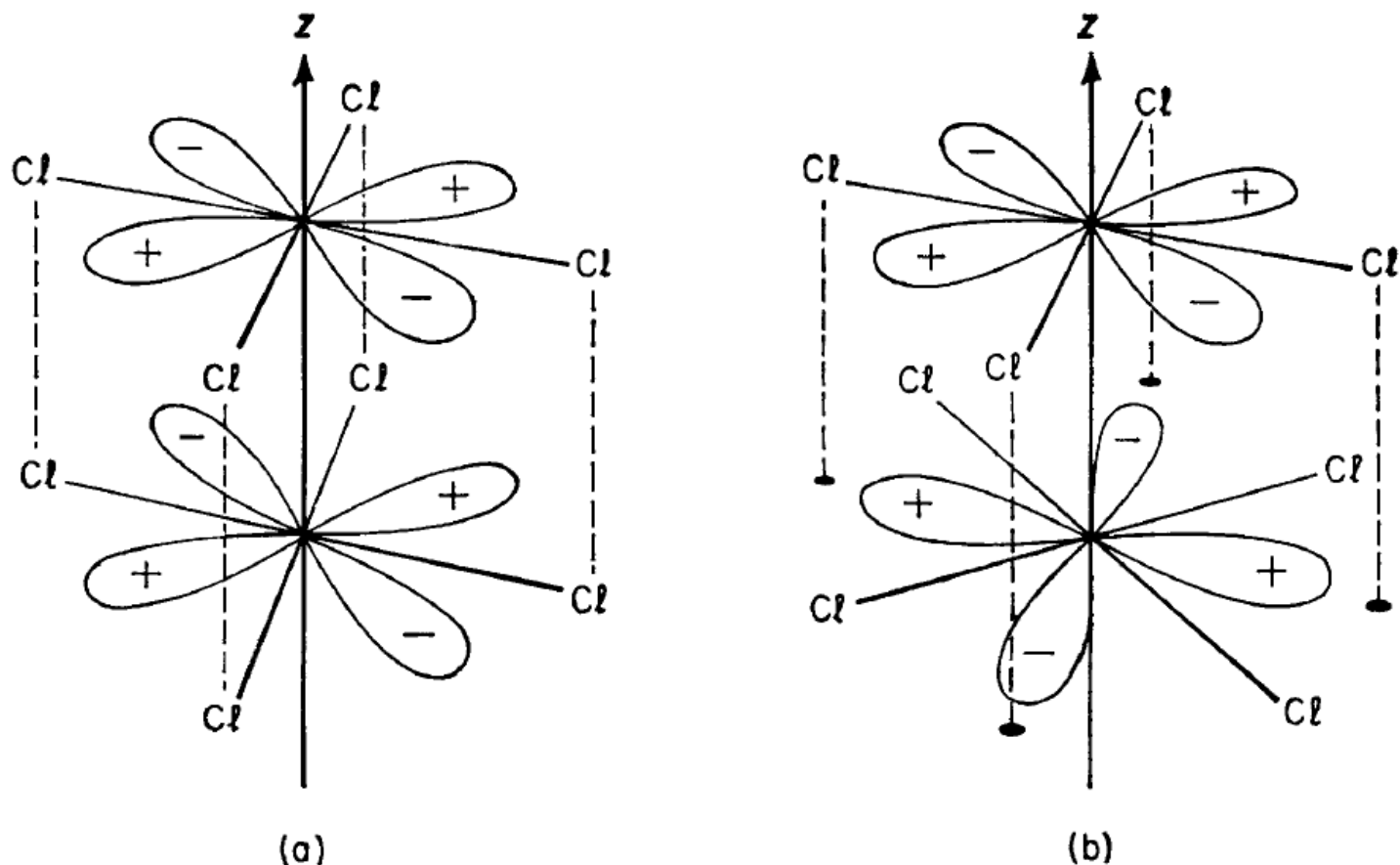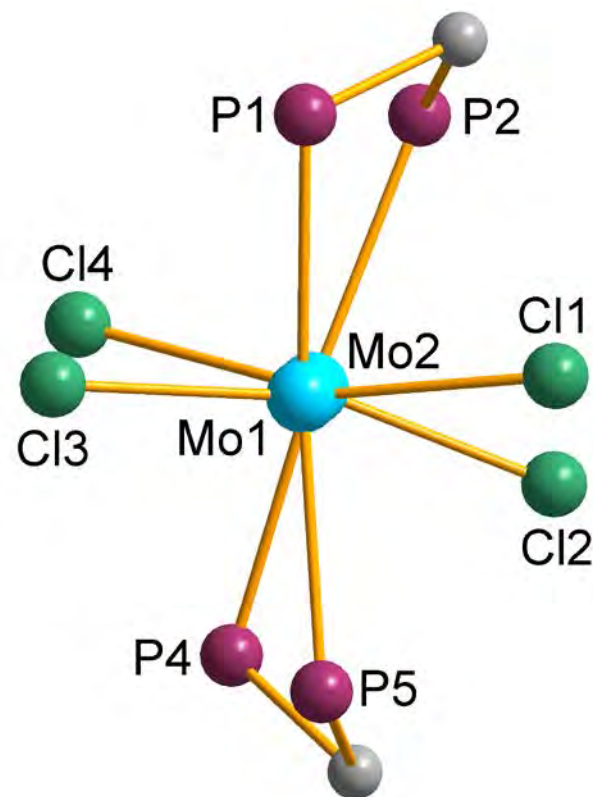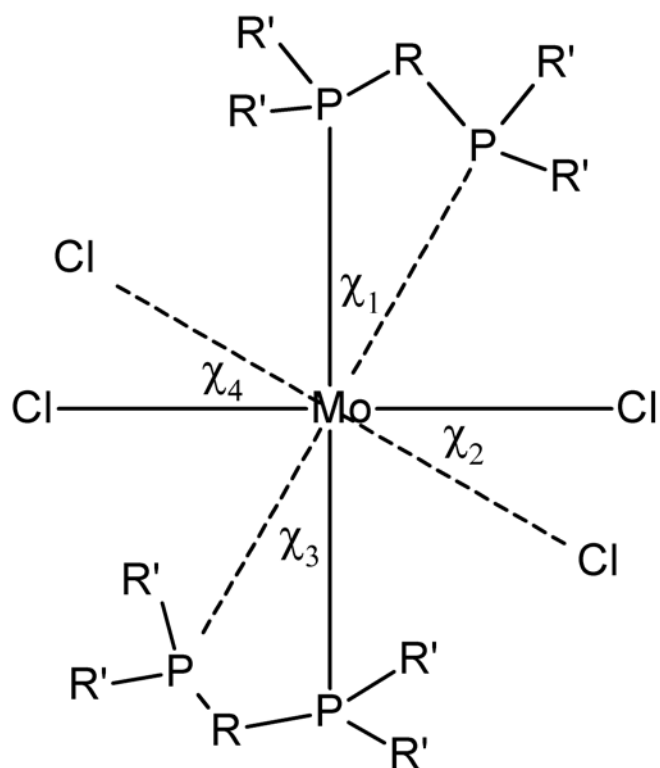# Relationship between δ bond strength and bond length.

Figure 2 Sketches showing (a) the maximization of δ overlap in the eclipsed configuration and (b) how it becomes zero for a staggered configuration.

F. A. Cotton. Centenary Lecture, delivered at a meeting of The Chemical Society in Bristol, February 4, 1974.

The δ bond is affected by rotation

The orbital overlap for the δ component varies with $\cos 2\chi$.
F. A. Cotton, P. E. Fanwick, J. W. Fitch, H. D. Glicksman & R. A. Walton (1979). *J. Am. Chem. Soc.* <u>101</u>, 1752-1757.

Preparation and Structure of the Bridged Form of $Mo_2Cl_4([CH_3)_2PCH_2CH_2P(CH_3)_2]_2$. Dependence of the Mo_2 Quadruple Bond Length on Torsional Angle

F. Albert Cotton & Gregory L. Powell (1983). *Inorg. Chem.* 22, 1507-1510.

Preparation and crystal structure of β-$Mo_2Cl_4(dmpe)_2$, with Mo---Mo bond length 2.183(3) Å and mean χ of 40.0(1)°.
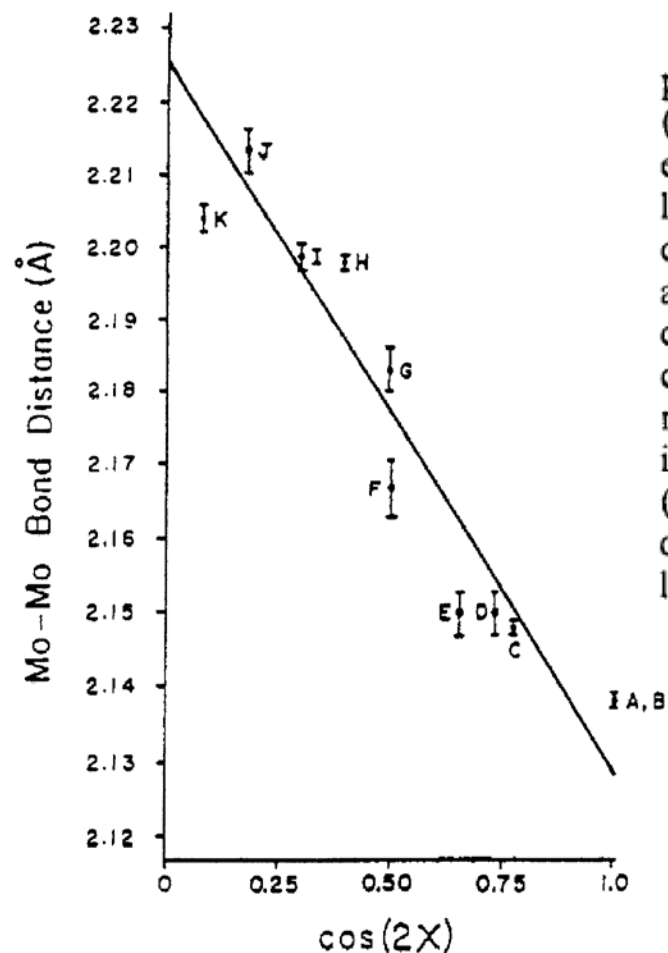This result was combined with data from the previously characterized $Mo_2Cl_4(dppm)_2$ and $Mo_2Br_4(arphos)_2$.
A linear relationship was observed between the Mo---Mo distance and $\cos(2\chi)$.

> There are relatively few occasions in chemistry where bonding theory reliably predicts a simple relationship between one structure parameter and another and where it is also feasible to obtain experimental confirmation of the relationship, free of other, complicating factors. This report is concerned with one such case.

Steric and Electronic Factors Influencing the Structures of Bridged (β-Type) $M_2Cl_4(LL)$, (M = Mo, Re) Compounds: A Refined Correlation of Bond Length with Torsion Angle. Fred L. Campbell, III, F. Albert Cotton,* and Gregory L. Powell (1985). *Inorg. Chem.* <u>24</u>, 4384-4389. New compounds: β-M_2Cl_4(depe)2 (M = Mo, Re)
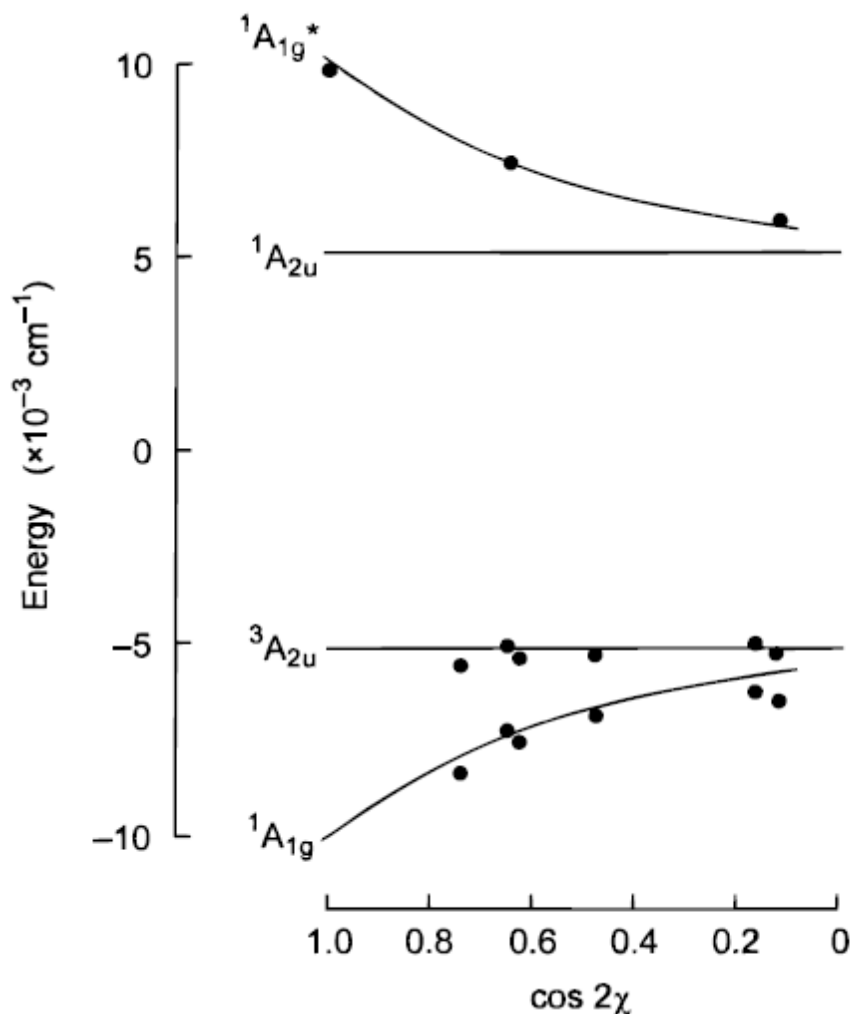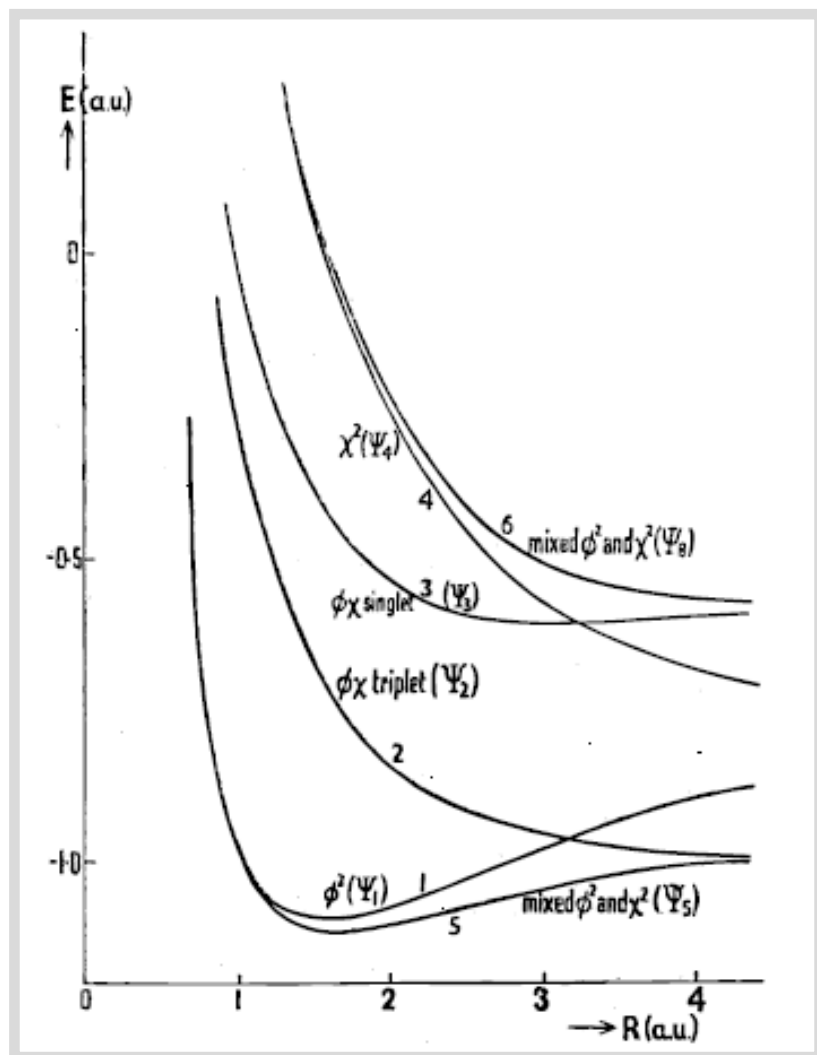

We have prepared the triply bonded β-Re_2Cl_4(depe)$_2$ for the purpose of calibrating empirically the effect of changing Ph_2P to (alkyl)$_2$P on the metal–metal bond length. This molecule has an essentially staggered structure (χ = 43.7°) and a Re–Re bond length of 2.211 (1) Å. These features may be compared to the corresponding ones in Re_2Cl_4(dppe)$_2$[10] in which we have χ = 34.0° and a Re–Re distance of 2.244 (1) Å. Each of these dirhenium compounds has a triple bond based on the $\sigma^2\pi^4\delta^2\delta^{*2}$ electron configuration (i.e., a net of one σ and two π bonds). In these cases no barrier to rotation is imposed and bond strength should be independent of the angle of rotation. Thus, the difference of 0.033 (2) Å in the Re–Re bond lengths should be due essentially to the different properties (steric and electronic) of the depe and dppe ligands.

The new least-squares line has a correlation coefficient (−0.9547) that is statistically far superior to that of the previous line. This new line yields values of 2.128 and 2.225 Å for χ = 0 and 45°, respectively. The overall change in Mo–Mo distance upon loss of δ bonding becomes 0.097 Å.

Figure 6. Plot of corrected Mo–Mo distances vs. cos 2χ. The corrections are explained in the text. Compounds are identified by the same capital letters as in Figure 1b. Mo_2Cl_4(depe)$_2$ is point K.

The Whole Story of the Two-Electron Bond, with the δ Bond as a Paradigm

F. A. Cotton and D. G. Nocera (2000). *Acc. Chem. Res.* <u>33</u>, 483-490.

Citation: Discussion Meeting Issue, "Biology with free-electron X-ray lasers," organized and edited by John C.H. Spence and Henry N. Chapman, *Philosophical Transactions of The Royal Society B* July 17, 2014; 369 (1647), DOI: [10.1098/rstb.2013.0500 1471-2970](#).

"Serial femtosecond crystallography (SFX)"

http://www-ssrl.slac.stanford.edu/stohr/xfels.pdf
"X-Ray Free Electron Lasers: Principles, Properties and Applications" Claudio Pellegrini, UCLA, and Joachim Stöhr, SSRL

http://www.ccdc.cam.ac.uk/pages/Home.aspx :

"The CCDC grew out of the activities of the crystallography group led by Dr Olga Kennard OBE FRS in the Department of Organic, Inorganic and Theoretical Chemistry of the University of Cambridge. From 1965, the group began to collect published bibliographic, chemical and crystal structure data for all small molecules studied by X-ray or neutron diffraction. With the rapid developments in computing taking place at this time, this collection was encoded in electronic form and became known as the Cambridge Structural Database (CSD).

The CSD was one of the first numerical scientific databases to begin operations anywhere in the world,…."
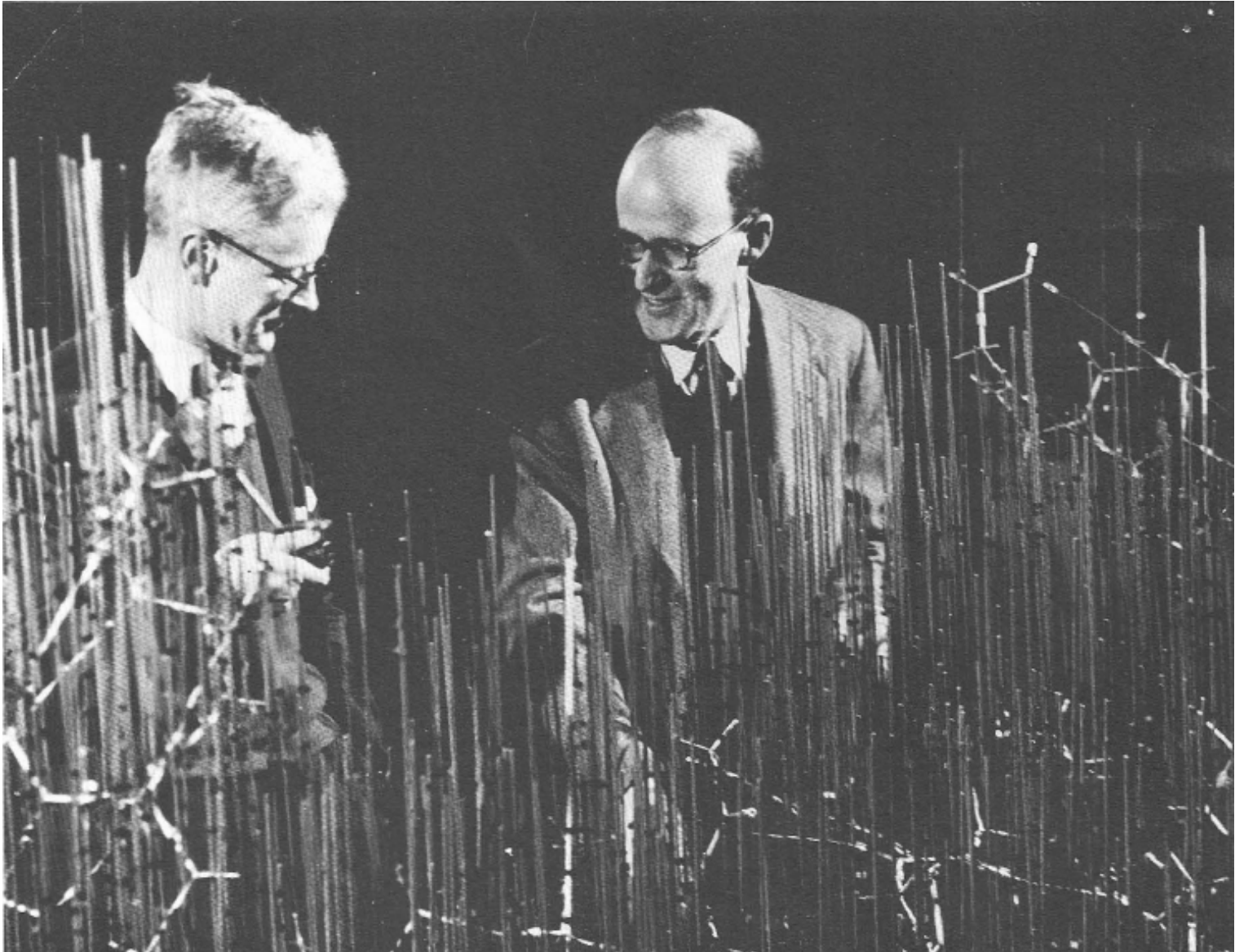
Advanced experimentation

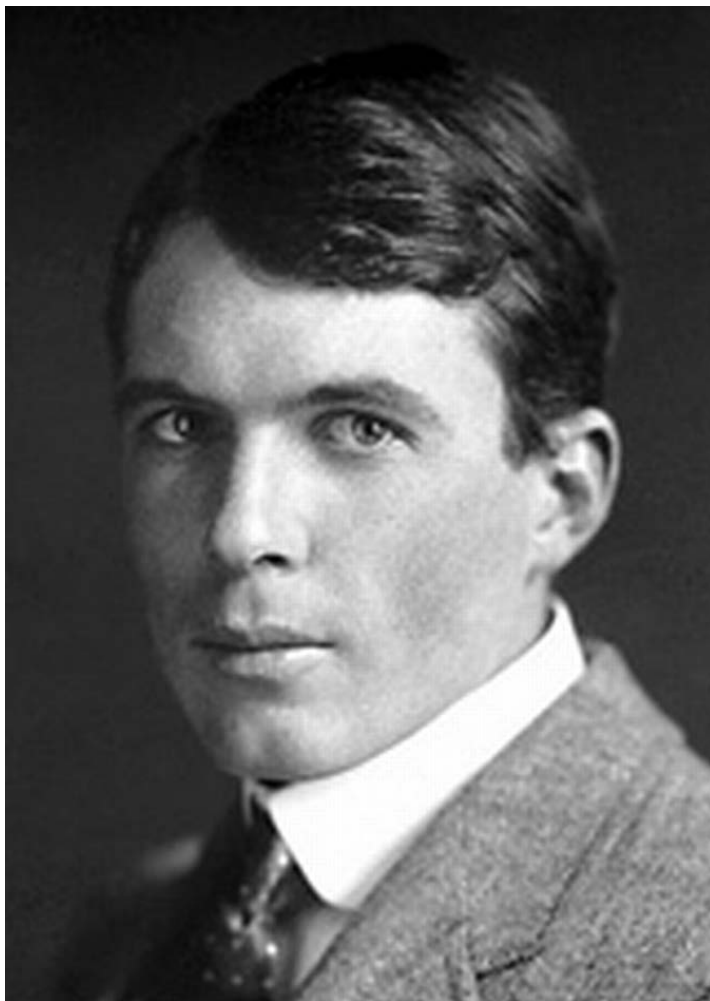Integration of diffraction (scattering) with other experimental and theoretical techniques

Massive acquisition of data

"Knowledge synthesis"

Chemical and physical insight applied to crystallographic analysis

Elements of the technique, visualization: Wire models

William Lawrence Bragg 1915

MULTIPLE BONDS
BETWEEN
METAL ATOMS

third edition

Edited by
F. Albert Cotton, Carlos A. Murillo, and Richard A. Walton

MY LIFE IN THE
GOLDEN AGE
OF CHEMISTRY
More Fun Than Fun

F. A. COTTON