12. *Bond Lengths in Some Inorganic Molecules and Complex Ions.*

By A. F. Wells.

The bond lengths in the following groups of compounds are discussed: the methyl derivatives and the molecular chlorides and fluorides of the elements of the later Periodic Groups, oxy-ions, metallic carbonyls, cyanides, and phthalocyanines. It is concluded that the Schomaker–Stevenson equation, in conjunction with the usual $8 - N$ covalent radii, does not account sufficiently well for observed bond lengths to justify its use in detailed discussions of the nature of bonds. The experimental evidence for resonance with doubled-bonded structures in the above molecules and ions is examined. The arguments for formulating the oxy-ions of phosphorus, sulphur, and chlorine with double bonds are not acceptable. The apparent abnormal shortness of many bonds cannot be satisfactorily explained in the present state of our knowledge.

In recent years the concept of resonance has become widely, if somewhat uncritically, accepted. Most bonds are now regarded as having fractional bond order and varying degrees of ionic character. The valence-bond treatment in terms of resonance between a number of structures differing in distribution of bonding electrons has been adopted as one practical way of overcoming the difficulty of representing such structures. In organic chemistry experimental evidence for resonance comes chiefly from bond lengths and thermochemical data, it being assumed that covalent radii and bond energies are additive. In the case of inorganic molecules and complex ions, evidence for resonance comes largely from interatomic distances, supported in some cases by other physical properties such as dipole moments and force constants of bonds. In this paper it is proposed to discuss the bond lengths in some inorganic compounds, in particular those which could be, and previously were, formulated with simple electron-pair bonds. At the present time a discussion of bond lengths is essentially a discussion of covalent radii and electronegativity coefficients, though presumably we shall one day have no need for such concepts when it becomes possible to describe accurately the distribution of electron density in complex systems of atoms.

The Two Alternative Explanations of Bond Shortening.—It was first assumed that covalent radii could be assigned to atoms such that the sums of these radii were equal to the lengths of bonds between pairs of atoms. This simple additivity principle was introduced by Huggins in 1926, and an extensive set of covalent radii was proposed by Pauling and Huggins in 1934 and checked against the observed lengths of " essentially covalent " bonds. As more bond lengths were determined it was assumed that departures from the additivity rule indicated that the bonds concerned were not simple electron-pair bonds with equal sharing of the electrons between the two atoms. Explanations in terms of resonance with ionic and/or multiple-bonded structures were put forward to explain some of the discrepancies, and various *ad hoc* modifications were made to the simple additivity rule (*e.g.*, the effect on the covalent radius of an incomplete octet or formal charge, and the adjacent charge rule). Later it was found that the radii assigned to nitrogen, oxygen, and fluorine were incorrect, so that some bond lengths which originally supported the additivity rule were now seriously different from the expected values. For example, the O–F bond in OF_2 and $FO{\cdot}NO_2$ ($\approx 1{\cdot}42$ A.) is appreciably longer than the sum of the O and F radii which are consistent with O–C and F–C in dimethyl ether and fluoromethane respectively, *viz.*, $r_O = 0{\cdot}66$ and $r_F = 0{\cdot}64$ A., which with $r_C = 0{\cdot}77$ A. give O–C, 1·43, and F–C, 1·41 A., as observed, but O–F only 1·30 A. Clearly, the simple additivity rule could no longer be upheld, and since the discrepancies were worst for bonds involving the most electronegative elements it appeared reasonable to relate them to the difference between the electronegativities of the elements. Schomaker and Stevenson (*J. Amer. Chem. Soc.*, 1941, **63**, 37) suggested an empirical equation $r_{AB} = r_A + r_B - \beta(x_A \sim x_B)$, according to which the observed bond length should be less than the sum of the covalent radii (which sum would equal the length of a hypothetical 100% covalent bond) by an amount proportional to the difference between the Pauling electronegativity coefficients. This equation appears to have become generally accepted as the basis for discussion of bond lengths. It is therefore important that the experimental foundation for this admittedly empirical equation should be critically examined (in this connection see also Burawoy, *Trans. Faraday Soc.*, 1943, **39**, 79). We shall show that there is, in fact, no sound basis for such an equation. The reason for introducing a correction term dependent on the difference between the electronegativity coefficients was that the largest discrepancies occurred, after introducing the correct radii for nitrogen, oxygen, and fluorine, for bonds involving these, the most electronegative atoms. It does not seem to be generally appreciated that the improved agreement in the case of bonds from these more electronegative atoms necessarily leads to appreciable discrepancies for other bonds.

It is important to realise at the outset that the arguments for the nature of the bonds in many inorganic molecules and complex ions are essentially different from those applied to C–C bonds. In the case of the latter, their lengths are known to range from 1·20 to 1·54 A., so that if we find bonds of intermediate lengths, say 1·39 and 1·42 A., it is reasonable to suppose (1) that they are both multiple bonds, and (2) that they differ in multiplicity. In other cases, however, the situation is entirely different. For example, all Si–Cl bonds are observed to have a length of 2·00 ± 0·03 A. There are no other Si–Cl bond lengths to use as standards by which to judge these bonds, and it is therefore necessary to set up a standard bond length in some other way. It is assumed that there is a relation between the length of a single covalent Si–Cl bond and the lengths of the Si–Si and Cl–Cl bonds in the elements. This relation was first taken to be $r_{AB} = r_A + r_B$. This additivity relation gave 2·16 A. as the length of a single Si–Cl bond. Accordingly, Pauling assumed the bonds in silicon tetrachloride to have partial double-bond character. After correction for $0{\cdot}09(x_{Cl} - x_{Si})$, the estimated length becomes 2·05 A., reducing, though not entirely removing, the discrepancy between observed and estimated values. The need for an explanation in terms of double-bond character is also almost entirely removed. In the case of S–O bonds the situation is even more complex. The greatest length so far observed is about 1·50 A., but the sum of the radii is 1·78 A., or, corrected for electronegativity difference, 1·69 A. The conclusion has been drawn that all S–O bonds are double bonds (see later). We see that the evidence for the nature of, *e.g.*, Si–Cl or S–O bonds is of a different kind from that used for C–C bonds. There is a further complication, in that in some cases, where there is no " chemical " reason for supposing the bonds to be other than single bonds, the length of a particular bond A–B varies in a series of related molecules. It is then obviously important to know what length (if any) is to be used as the standard A–B bond length, because according to the value adopted the observed variations are to be described alternatively as shortenings or lengthenings.

Confusion has arisen because two reasons for bond shortening have been accepted, *viz.*, multiple-bond character and ionic character. It is necessary to consider (1) the origin of the " covalent radii " used in discussions of bond lengths, (2) to what extent the length of a bond A–B is constant in cases where there is no reason to expect differences in bond order, and (3) the experimental basis for the Schomaker–Stevenson equation. A complete analysis would also include an inquiry into the significance of electronegativity coefficients. Here we shall accept the Pauling values and merely remark that these numbers have not quite the simple meaning hitherto attached to them. For example, Pauling's statement that the metals are elements with $x_A \leqslant 2$ and non-metals those with $x_A > 2$ was possible because electronegativity coefficients were not assigned to certain groups of elements, notably those of the IB sub-group. Later estimates of $x_{Cu^{II}}$, $x_{Ag^{I}}$ and $x_{Au^{III}}$ give values such as 2·3, 1·8, and 2·9, respectively (Gordy, *J. Chem. Physics*, 1946, **14**, 305; Haïssinsky, *J. Phys. Radium*, 1946, **7**, 7). It will be more convenient to deal with point (2) after (3). We shall then discuss briefly the bonds in certain oxy-compounds and in metallic cyanides and carbonyls.

The Origin of the Standard Covalent Radii.—Discussion of bond lengths will be based on the covalent radii given in Table I. The Pauling electronegativity coefficients (x) are also given. With the exception of those for N and O these radii are equal to one-half of the interatomic

TABLE I.

	C.	N.	O.	F.
r	0·77	0·74	0·74	0·72
x	2·5	3·0	3·5	4·0
	Si.	P.	S.	Cl.
r	1·17	1·10	1·04	0·99
x	1·8	2·1	2·5	3·0
	Ge.	As.	Se.	Br.
r	1·22	1·21	1·17	1·14
x	1·7	2·0	2·4	2·8
	Sn.	Sb.	Te.	I.
r	1·40	1·41	1·37	1·33
x	1·7	1·8	2·1	2·4

distances in the elements, *i.e.*, in molecules or crystals in which the element is forming 8 – N bonds (N is the number of the Periodic Group). The radii for N and O are one half the N–N and O–O distances in $H_2N{\cdot}NH_2$ and HO·OH respectively.

The Schomaker–Stevenson Correction for Ionic Character of Bonds.—We shall consider first the bond lengths M–C and M–Cl in molecules $M(CH_3)_n$ and MCl_n, where $n = 8 - N$. These are set out in Table II, which shows the observed bond length, the sum of the covalent radii, and the sum corrected according to the Schomaker–Stevenson (S.-S.) equation. The bond lengths in the methyl compounds were used by Pauling to illustrate the truth of the additivity rule. The facts concerning these M–C and M–Cl bond lengths are as follows.

M–C *Bonds.* In all cases except N–C, O–C, and F–C the observed bond lengths are, to within the experimental error, identical with $r_M + r_C$. The introduction of an electronegativity correction to account for these three shorter bond lengths leads to discrepancies of up to 0·07 A. in the cases of Ge–C and Sn–C, for which no correction is required.

M–Cl *Bonds.* Here the situation is more complex for the following reasons. (*a*) C–Cl = $r_C + r_{Cl}$, *i.e.*, this is not consistent with Schomaker and Stevenson's equation if we adopt, as they do, the Pauling values of $x_C = 2{\cdot}5$ and $x_{Cl} = 3{\cdot}0$. (*b*) The length of O–Cl agrees with the Schomaker–Stevenson corrected value; the length of F–Cl is unfortunately not known. (*c*) For MCl_n, where M is less electronegative than Cl, agreement between the observed M–Cl and the Schomaker–Stevenson corrected value becomes better towards the bottom left-hand corner of Table II. In some cases there is better agreement between $r_{obs.}$ and $r_M + r_{Cl}$ (as in the case of I–Cl), in others $r_{obs.}$ lies between the S.-S. value and $r_M + r_{Cl}$ (Sb–Cl and As–Cl), while in other

TABLE II.

Bond lengths M–C *and* M–Cl *in molecules* $M(CH_3)_n$ *and* MCl_n.

	C–C.	C–Cl.	N–C.	N–Cl.	O–C.	O–Cl.	F–C.	F–Cl.
r, obs.	1·54	1·76	1·47	1·74 *	1·42	1·68	1·36	?
$r_A + r_B$	1·54	1·76	1·51	1·73	1·51	1·73	1·49	1·71
r_{AB} (S.-S.)	1·54	1·71	1·47	1·73	1·42	1·68	1·36	1·62
	$\Delta_C = 0{\cdot}22$.		$\Delta_4 = 0{\cdot}27$.		$\Delta_5 = 0{\cdot}26$.		$\Delta_5 =$?.	
	Si–C.	Si–Cl.	P–C.	P–Cl.	S–C.	S–Cl.	Cl–C.	Cl–Cl.
r, obs.	1·93	2·00	1·87	2·00	1·82	2·00	1·77	1·98
$r_A + r_B$	1·94	2·16	1·87	2·09	1·81	2·03	1·76	1·98
r_{AB} (S.-S.)	1·87	2·05	1·83	2·03	1·81	1·99	1·72	1·98
	$\Delta_1 = 0{\cdot}07$.		$\Delta_1 = 0{\cdot}13$.		$\Delta_2 = 0{\cdot}18$.		$\Delta_{Cl} = 0{\cdot}21$.	
	Ge–C.	Ge–Cl.	As–C.	As–Cl.	Se–C.	Se–Cl.	Br–C.	Br–Cl.
r, obs.	1·98	2·08	1·98	2·16	?	?	1·91	?
$r_A + r_B$	1·99	2·21	1·98	2·20	1·94	2·16	1·91	2·13
r_{AB} (S.-S.)	1·91	2·09	1·93	2·11	1·93	2·11	1·88	2·11
	$\Delta_1 = 0{\cdot}10$.		$\Delta_1 = 0{\cdot}18$.		$\Delta_1 =$?.		$\Delta_3 =$?.	
	Sn–C.	Sn–Cl.	Sb–C.	Sb–Cl.	Te–C.	Te–Cl.	I–C.	I–Cl.
r, obs.	2·18	2·30	[2·18]	2·37	[2·14]	2·36	2·10	2·32 (2·38)
$r_A + r_B$	2·17	2·39	2·18	2·40	2·14	2·36	2·10	2·32
r_{AB} (S.-S.)	2·10	2·27	2·12	2·29	2·10	2·28	2·09	2·27
	$\Delta_1 = 0{\cdot}12$.		[$\Delta_1 = 0{\cdot}19$.]		[$\Delta_1 = 0{\cdot}22$.]		$\Delta_1 = 0{\cdot}22 - 0{\cdot}28$.	

* In $N(CH_3)Cl_2$. [ ] indicates assumed value.

cases $r_{\text{obs.}}$ lies below the S.-S. value (Si–Cl and P–Cl). The above facts might appear to suggest that adjustment of either the value of β or the values of some of the electronegativity coefficients would improve the agreement. (We should, perhaps, remark here that these discrepancies would not be very important if it were not for the fact that the M–F bond lengths show much larger discrepancies in the same sense.) The following simple analysis shows, however, that no adjustment of the numerical values of the electronegativity coefficients can account for all the bond lengths in Table II if an equation of the S.-S. type is used.

We may classify the elements into five groups according to the relative values of x_M, x_C, and x_{Cl}: (1) $x_M < x_C < x_{Cl}$, (2) $x_M = x_C$, (3) $x_C < x_M < x_{Cl}$, (4) $x_M = x_{Cl}$, and (5) $x_C < x_{Cl} < x_M$. We can then calculate $\Delta = (\text{M–Cl}) - (\text{M–C})$ as a function of r_{Cl}, r_C, x_M, x_C, and x_{Cl}. Assuming Pauling's electronegativity coefficients and $\beta = 0{\cdot}09$, we find:

$$\Delta_1 = 0{\cdot}08,\ \Delta_2 = 0{\cdot}17 \text{ (for S)},\ \Delta_3 = 0{\cdot}23 \text{ (for Br)},\ \Delta_4 = 0{\cdot}27 \text{ (for N)},\ \Delta_5 = 0{\cdot}27 \text{ (for O, F)}.$$

For (C–Cl) – (C–C) and (Cl–Cl) – (Cl–C) we expect $\Delta_C = 0{\cdot}17$ and $\Delta_{Cl} = 0{\cdot}27$ respectively. Thus in all the lower left-hand region of Table II Δ_1 should be 0·08. It may be noted that Δ_1 is independent of the values assigned to r_M and x_M, so that no alteration in these quantities would improve the situation. Actually it varies from 0·07 to about 0·25. There is an alternative, *viz.*, that we accept the equality of x_C and x_{Cl}, but then Δ should in all cases equal 0·22. We conclude, therefore, that the S.-S. type of equation cannot reproduce the observed bond lengths in $M(CH_3)_n$ and MCl_n whatever the values of the electronegativity coefficients assigned to C and Cl. Proceeding from the apparent agreement between M–C in $M(CH_3)_n$ and $r_M + r_C$, Pauling observed that M–Cl in MCl_n is often shorter than $r_M + r_{Cl}$. On the basis of this shortening he argued that the bonds in these halides have some double-bond character. However, since we now know that the simple additivity rule breaks down for M–C when M is very electronegative, it would seem unjustifiable to draw conclusions from the deviations from the rule in the case of M–Cl when M is most electropositive. So far it has been tacitly assumed, in this paper as in many others, that all cases of bond shortening must be explained in the same way. For example, it has been argued that since double-bond character is unlikely in C–F ($r_{\text{obs.}} = 1{\cdot}36$, radius sum $= 1{\cdot}49$ A.) because of the octet rule,* therefore it is not reasonable to explain a similar degree of shortening in Si–Cl ($r_{\text{obs.}} = 2{\cdot}00$, radius sum $= 2{\cdot}16$ A.) by invoking double-bond character. We cannot, however, exclude the possibility that different reasons for bond shortening may be operating in Si–Cl and C–F.

In a recent paper Hildebrand (*J. Chem. Physics*, 1947, **15**, 727) concludes that "none of the properties of $SiCl_4$ requires for its explanation the assumption of 'double bond resonance'." This author's interpretation of certain data cannot, however, be accepted. He points out that the isotropic Raman bond-stretching frequencies (ν_1) for the bonds C–Cl, Si–Cl, etc., vary linearly with the observed bond lengths, and that this regularity "gives but scant basis for assuming that any one of these molecules has an exceptional character". It is difficult to see how such a plot of one measured property of the bonds against another measured property can provide information about the nature of the bonds. It merely indicates that there is a linear relation between certain properties of the actual bonds. If either property were plotted against some independent third function of the atoms concerned then changes in bond type might be expected to be revealed. If, for example, the frequency ν_1 is plotted against $r_A + r_B$ instead of r_{AB}, then the line passing through Si, Ge, and Sn does not pass through the point for C. This is to be expected if a sudden change in bond character takes place at Si–Cl, as suggested by Pauling. In fact, the interatomic distances in the halides MCl_4 (and MCl_3 of the Group Vb elements) show clearly that an electronegativity correction for bond lengths is not only quantitatively, but also qualitatively, in disagreement with observation, as shown by the following figures:

	r, obs.	$r_M + r_{Cl}$.	Correction required.	S.-S. correction.
C–Cl	1·76	1·76	0·00	0·045
Si–Cl	2·00	2·16	0·16	0·11
Ge–Cl	2·08	2·21	0·13	0·12
Sn–Cl	2·30	2·39	0·09	0·12
N–Cl	1·74	1·73	–0·01	0·00
P–Cl	2·00	2·09	0·09	0·08
As–Cl	2·16	2·20	0·04	0·09
Sb–Cl	2·37	2·40	0·03	0·11

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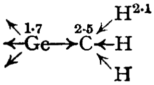
* It has, of course, been pointed out that resonance with structures of the type $[F_2C{=}F^+]F^-$ avoids the difficulty about the octet. Since, however, the physical nature of a bond intermediate between C–F, $C{=}F^+$, and an ionic bond is not clear, further discussion of this point is not profitable at present.

It is quite clear that the steadily increasing electronegativity correction is even qualitatively quite different from that required. The latter is zero for the first-row atoms C and N, large for Si and P, and progressively smaller for the heavier elements. This strongly suggests that some effect is operating for the second-row (and to a smaller extent for the heavier) atoms which is absent for the first-row elements. In this respect Pauling's explanation is certainly preferable to any electronegativity correction, though it cannot be regarded as certain that the explanation in terms of double-bond character is correct.

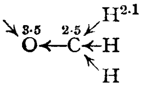
We have just seen that an electronegativity correction cannot account for the bond lengths in halide molecules. In certain cases it so happens that the S.-S. correction is of the required magnitude, as for Ge–Cl, but the Ge–C bond length agrees better with the simple radius sum :

	Observed.	$r_A + r_B$.	$r_A + r_B - 0{\cdot}09\ (x_A \sim x_B)$.
Ge–C	*1·98*	*1·99*	1·91
Ge–Cl	*2·08*	2·21	*2·09*

The additivity rule appears to apply to a whole group of M–C bond lengths *independently of the value of* x_M (in fact, to all except N–C, O–C, and F–C). The fact that no electronegativity correction is applicable to M–C in $M(CH_3)_n$ when $x_M < x_C$ would appear to be explicable on the following lines. The radius r_C is obtained from C–C in diamond, in which carbon forms four tetrahedral bonds, presumably with symmetrical sharing of electrons. In these methyl compounds we have two types of environment of carbon, according to whether (*a*) $x_M \leqslant x_C$ or (*b*) $x_M > x_C$. In (*a*) the carbon atom is surrounded by four atoms of comparable electronegativity, so that its effective radius is the same as in diamond, and there is no measurable shortening of M–C. In (*b*), however, the environment of carbon is quite different, as shown by the arrows, which point towards the more electronegative atom of a bond.



(*a*.)



(*b*.)

It is hardly to be expected that any simple arithmetical treatment based on the values of electronegativity coefficients (which are not measured physical constants) will give detailed agreement in all cases. Moreover, for the more metallic elements (except perhaps those of Group IV with the diamond structure) it is possible that one-half the interatomic distance in the *metal* may not be the value of r_M appropriate to discussions of bond lengths in *essentially covalent molecules*. We conclude that no simple correction based on electronegativity differences leads to the observed values of all bond lengths.

The length of a particular bond A–B depends also on the nature of the other atoms attached to A and B. Comparatively few data are available, and an unambiguous interpretation is not always possible. In the compounds $Sn(CH_3)_nCl_{4-n}$ the Sn–Cl bond length depends on *n* :

	Sn–Cl, A.		Sn–Cl, A.
$r_{Sn} + r_{Cl}$	2·39	$SnMeCl_3$	2·30±0·03
$SnMe_3Cl$	2·37±0·03	$SnCl_4$	2·30±0·02
$SnMe_2Cl_2$	2·34±0·03	$r_{Sn} + r_{Cl} - 0{\cdot}09\ (x_{Cl} - x_{Sn})$	2·27

It may be significant that the observed values lie, in a regular sequence, between the radius sum and the radius sum corrected for electronegativity difference. Skinner and Sutton (*Trans. Faraday Soc.*, 1944, **40**, 164) point out that it is unsatisfactory to regard the shortening as due to increased double-bond character of Sn–Cl (the Pauling explanation). This would imply that the more negative charge the tin atom acquires the more it wants, since the utilisation of an unshared pair of electrons from a chlorine atom increases the negative (or reduces the positive) charge on the tin atom. A somewhat analogous effect is found in the carbon fluorides (Brockway, *J. Physical Chem.*, 1937, **41**, 185) :

	Obs.	$r_C + r_X$.	Corrected (S.-S.).
C–Br in CBr_4	1·91	1·91	1·88
CH_3Br	1·91		
C–Cl in CCl_4	1·76	1·76	1·72
CH_3Cl	1·77		
C–F in CF_4	1·36	1·49	1·36
CH_3F	1·42		
CCl_3F	1·44		

There is apparently no alteration in C–Br or C–Cl on going from CX_4 to CH_3X, and the observed bond length agrees better with the sum of the radii than with the S.-S. corrected value. In the

TABLE III.

	C–F.	N–F.	O–F.	F–F.
r, obs.	1·36	1·37,[1] 1·45 [2]	1·36	1·44
$r_M + r_F$	1·49	1·46	1·46	1·44
r, corr. (S.-S.)	1·35	1·37	1·41	1·44
	Si–F.	P–F.	S–F.	Cl–F.
r, obs.	1·54	1·54	—	—
$r_M + r_F$	1·89	1·82	1·76	1·71
r, corr. (S.-S.)	1·69	1·65	1·62	1·62
		As–F.		
r, obs.		1·72		
$r_M + r_F$		1·93		
r, corr. (S.-S.)		1·75		

[1] Electron diffraction.
[2] Spectroscopic.

case of the fluorides the C–F bond is appreciably shorter in CF_4 than in CH_3F. No convincing explanation is forthcoming.

Bond Lengths in Fluorides MF_n ($n = 8 - N$).—The data are less complete than for the chlorides; those available are set out in Table III. The data, for SiF_4 and PF_3 in particular, speak for themselves.

Oxy-ions.—The observed bond lengths in the simplest oxy-ions are shown (in A.) in Table IV.

TABLE IV.

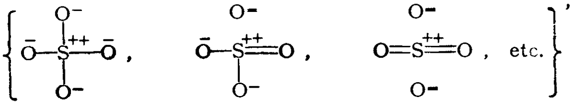
	BO_3^{3-}.	CO_3^{2-}.	NO_3^-.		
r, obs.	1·35	1·31	1·21		(3 equal coplanar bonds)
$r_M + r_O$	1·59	1·51	1·48		
r, corr. (S.-S.)	1·45	1·42	1·43		
r, obs./$(r_M + r_O)$	0·85	0·87	0·82		
r, obs./r, corr.	0·93	0·92	0·85		
	SiO_4^{4-}.	PO_4^{3-}.	SO_4^{2-}.	ClO_4^-.	
r, obs.	~1·60	~1·55	~1·50	~1·50	(4 equal tetrahedral bonds)
$r_M + r_O$	1·91	1·84	1·78	1·73	
r, corr. (S.-S.)	1·76	1·71	1·69	1·68	
r, obs./$(r_M + r_O)$	0·84	0·84	0·83	0·86	
r, obs./r, corr.	0·91	0·91	0·88	0·89	

[The bond lengths in the tetrahedral ions are not known with any great accuracy. For example, values from 1·44 to 1·56 A. have been recorded for Cl–O in crystalline perchlorates. The S–O bond length is probably nearer 1·44 A.; this value was obtained from $K\cdot SO_3\cdot NH_2$ (Brown and Cox, *J.*, 1940, 1) and appears to be the best S–O determination for a tetrahedral ion.]

The formulation of the tetrahedral ions with single bonds (co-ordinate links) has been rejected on the grounds that their lengths are far less than those of single bonds. The possibility that co-ordinate links might be shorter than normal covalent bonds has been dismissed by Phillips, Hunter, and Sutton (*J.*, 1945, 146), whose arguments we shall examine shortly. Since it is generally agreed that the octet of valency electrons is never exceeded in the first-row elements, only one double bond can be postulated in the triangular ions, and this must resonate between the three positions, since all the bonds have the same length, giving each bond one-third double-bond character. The following points are noteworthy in connection with the conventional resonance formulæ for oxy-ions and oxy-molecules.

(1) It is assumed that –M–O would have the same length as if O were forming two bonds, *i.e.*, that the radius of –O is the same as that of –O–.

(2) The types of resonance postulated are often not consistent with the observed bond lengths. For example, the S–O bond length is the same in SO_2 as in SO_3 (and probably also in SO_4^{2-}), whereas the bonds in the former should have 50% and in the latter $33\frac{1}{3}\%$ double-bond character. Similar difficulties arise in other cases, and it is found necessary to invoke also numbers of ionic structures, so that * " when a *more precise* description of the electronic structure is needed several of the resonating structures be enclosed in brackets, as in the following representation of the sulfate ion



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* Italics in quotations are introduced by the present author.

(Pauling, " The Nature of the Chemical Bond ", 1st edition, p. 225). After his discussion of $SiCl_4$, for which double-bond resonance structures are now known to be unnecessary, Pauling states (*op. cit.*, p. 214) : " In the above discussion of the silicon–chlorine distance, the possible direct effect of the ionic structures on the distance has been ignored. This seems to be justified in practice . . . and, moreover, it can be justified to some extent by theoretical arguments also. The ionic radius of an atom is a far more variable quantity than the covalent radius; it responds by large variations to change in co-ordination number, and *it may be expected to leave to the more precise covalent radius the burden of determining the equilibrium distance for bonds of mixed type.*"

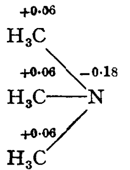
(3) In some of the resonating structures of, *e.g.*, the SO_4^{2-} ion, large groups of shared electrons appear around the central atom. The fact that the stereochemistry of these groups (10, 12, 14, 16) of electrons is unknown is not in itself a reason for objecting to these formulæ, but it is another matter to accept the rather arbitrary (but inevitable) assumption that the configuration of the bonds will be determined by the "classical" formula rather than by the resonance structures involving multiple bonds. Thus in the case of silicon tetrafluoride, for example, for which double-bonded structures are supposed to be very important, as well as ionic structures, Pauling says : " It seems that a single covalent bond to each attached atom plays the deciding part in the determination of bond directions." Again, in the case of nickel tetracarbonyl, where the Ni–C bonds are assumed to have appreciable double-bond character, " the single bonded structures are not to be ignored; they *seem* to play a *determinative part* with respect to the stereochemical properties of the central atom." In other words, the situation is that resonance with double-bonded structures is invoked to account for the short bond lengths, but the bond angles are supposed to be determined only by the single-bonded structures.

(4) The partial double-bond character resulting from the resonance is often not sufficient to account for the shortness of oxy-bonds, some of which are in fact quite as short as double bonds would be expected to be if we assumed the conventional relation between lengths of single and double bonds—see, for example, the discussion of the NO_3^- ion later.

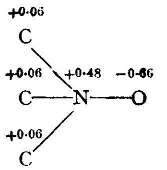
Double-bonded Structures for Oxy-ions, etc.—Phillips, Hunter, and Sutton have discussed the lengths of the " oxy-bonds " in a number of oxy-ions and molecules formed by phosphorus, sulphur and chlorine. The lengths of these bonds are, in general, as short as, or shorter than, those to be expected for double bonds, assuming Pauling's relation between the lengths of single and double bonds and that the use of $8 - N$ radii is valid. All these oxy-bonds have two points in common, apart from their short length, *viz.*, (1) they could all be formulated as co-ordinate links $M \rightarrow O$, and (2) the oxygen atom is forming only one bond. Phillips, Hunter, and Sutton first consider the possibility that a co-ordinate link might be shorter than a normal covalent bond, but dismiss this and finally conclude that all such bonds are best represented as double bonds. Their arguments may be summarised as follows. The N–O and B–O bonds in $(CH_3)_3NO$ and $(CH_3)_2O,BF_3$ respectively must be true co-ordinate links because of the octet rule. Their lengths are nearly equal to those to be expected for normal single covalent bonds. Also μ_{N-O} is nearly 70% of the value ($4{\cdot}8 \times d$) expected for symmetrical sharing of the electrons. Therefore, the co-ordinate link is not appreciably shorter than a normal single bond. On the other hand, the sulphur–oxygen bond, for example, is much shorter than the value expected for S–O and also has a much smaller dipole moment than $4{\cdot}8 \times d$; therefore the sulphur–oxygen bond cannot be a co-ordinate link. These arguments for the formulation of short SO, etc., bonds as double bonds cannot be accepted, for the following reasons.

Confusion has arisen because the term " co-ordinate link " has been used in two quite different senses : (1) to denote that the two electrons of the bond came from one atom—" Since the covalency of boron is limited to 4, the only kind of definite link which it can form in the complexes (with phosphines and sulphides) is a co-ordinate link "—and (2) to imply that the degree of asymmetry of sharing of the two electrons is similar in all co-ordinate links. (It is immaterial whether this is supposed to be $\overset{1+}{A}-\overset{1-}{B}$ or $\overset{x+}{A}-\overset{x-}{B}$.) The only possible interpretation of the statement : " If the S–O, P–O, and P–S bonds were co-ordinate links they should be even more polar than the N–O link, *because they are actually longer* ", is that Phillips, Hunter, and Sutton assume that there would be the same charge distribution in $S \rightarrow O$ in SO_4^{2-} etc., as in $N \rightarrow O$ in $(CH_3)_3NO$. This assumption is entirely without justification; without it there is clearly no necessary connection between the lengths and dipole moments of two different bonds such as S–O and N–O. The use of the term co-ordinate link in sense (1) is simply a convenient way of indicating the *origin* of the electrons. The use in sense (2) is an entirely different matter, for (2) is concerned with the *final sharing* of the electrons.

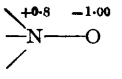
From dipole moments we can deduce the resultant formal charge distributions in molecules. For $(CH_3)_3N$ and $(CH_3)_3NO$ these are approximately as shown at (*a*) and (*b*), and for complete transfer of an electron we should have (*c*). The N–O bond in trimethylamine oxide is therefore not $\overset{1+}{\mathrm{N}}$–$\overset{1-}{\mathrm{O}}$ but closer to $\overset{\frac{1}{2}+}{\mathrm{N}}$–$\overset{\frac{1}{2}-}{\mathrm{O}}$. Again, although the bonds in BF_3 must be highly polar, the final



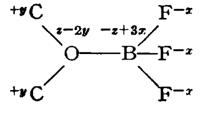
(*a*.)



(*b*.)



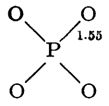
(*c*.)



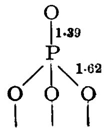
(*d*.)

charge distribution in $R_2O \rightarrow BF_3$ is the resultant of the original polarities of R_2O and BF_3 and the rearrangement of electrons which we call the formation of the co-ordinate link. The positive formal charge on B and the negative formal charge on O have both decreased, so that we have (*d*) and a B–O bond with dipole moment $z \times d$. The data from these compounds merely show that a bond of type (1) *can* be as long as an ordinary single covalent bond. It has *not* been shown that if a bond is abnormally short it *cannot* be of type (1). The low dipole moment of the short S–O bond indicates that x in $\overset{+x}{\mathrm{S}}$–$\overset{-x}{\mathrm{O}}$ is less than y in $\overset{+y}{\mathrm{N}}$–$\overset{-y}{\mathrm{O}}$ (the lengths being similar), but this does *not* prove that they are not co-ordinate links in sense (1). It is not admissible to deduce the origin (still less, the number) of the electrons in the short S–O, etc., bonds from dipole-moment data, and particularly to argue from the lengths of bonds such as N–O and B–O. If μ_{S-O} were *greater* than $4{\cdot}8 \times d$ (~7 D.) then it could be argued that more than two electrons are involved. Since it is *less* than 7 D., the moment can obviously be accounted for as well by 2 as by 4 electrons, a different degree of asymmetry of sharing being assumed. The following points are also relevant.

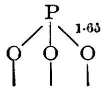
(*a*) The abnormal distances are found when oxygen is forming only one bond. Although the covalent radii are derived from elements or compounds in which phosphorus, sulphur, chlorine, and oxygen are forming respectively 3, 2, 1, and 2 bonds, they are applied to cases such as $(PO_4)^{3-}$ where phosphorus is forming 4 bonds and oxygen 1 bond. In the case of P–O bonds there are appreciable variations in length but also variations in the numbers of bonds formed by phosphorus and oxygen (numerals refer to A. units) :



$(PO_4)^{3-}$.

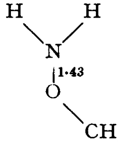


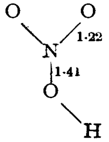
(P_4O_{10}).

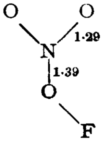


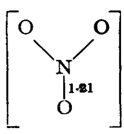
(P_4O_6).

Similar variations occur with other M–O bonds, the lengths varying also as the nature of the other atoms bonded to them is changed :









It would seem that the use of 8 — *N* radii in discussions of all such bond lengths needs justifying.

(*b*) The bond length in NO_3^- is 1·21 A., which is 85% of that in *O*-methylhydroxylamine (1·43 A.). Pauling's double-bond factor for first-row elements is 87%. Unfortunately, Phillips, Hunter, and Sutton do not extend their treatment to N–O bonds.

(*c*) Subsidiary evidence for double-bonded structures such as the non-existence of fluorine oxy-ions (because the octet cannot expand) can be interpreted in other ways (see later).

(*d*) The extension of Phillips, Hunter, and Sutton's ideas to more complex oxy-ions leads to difficulties of a stereochemical nature which call for further examination. Remarks already made about the spatial arrangement of bonds formed by groups of up to 16 electrons apply here.

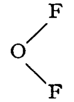
(*e*) The shortening of the P–O bonds which Phillips, Hunter, and Sutton propose to call double bonds is generally less than in the case of the Si–F bond :

	Sum of 8 — *N* radii, A.	Corrected sum (S.-S.), A.	Obs., A.
Si–F	1·89	1·69	1·54
P–O	1·84	1·70	1·65—1·55

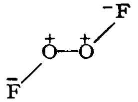
In a recent paper (Gordy, *J. Chem. Physics*, **1947**, **15**, 81) the Schomaker–Stevenson correction for single bonds has been extended to double bonds, using a different coefficient β (0·06 instead of 0·09) and a set of " double-bond radii ". It seems extremely doubtful whether further arithmetical work on these lines is profitable at present, in view of the uncertainties mentioned, and particularly in view of the fact that the original Schomaker–Stevenson equation does not account at all satisfactorily for the lengths of some single bonds between atoms of very different electronegativities. Gordy's treatment would also imply double bonds in many oxy-compounds, including those of nitrogen.

The Existence of the Halogen Oxy-acids.—Accepting the formulation of ClO_4^- with four double bonds, Phillips, Hunter, and Sutton claim that the non-existence of fluorine oxy-acids and salts is due to the fact that the valency group of fluorine is limited to the octet. It might be suggested that fluorine does not form oxy-ions simply because it is the only element which is more electronegative than oxygen. The formulation of fluorine oxy-ions with electron-pair bonds for each of which the two (unsymmetrically shared) electrons originate in the fluorine, would imply that fluorine would be the positive end of the polar bonds. We therefore expect stable oxy-ions to be formed only by elements more electropositive than oxygen, *i.e.*, by all the halogens except fluorine. Similarly, oxides of fluorine (except OF_2 and O_2F_2) should be unstable or non-existent.

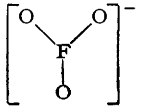
(*a*.)



(*b*.)



(*c*.)



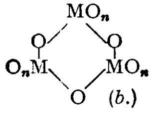
The " oxide " F_2O (*a*) has singly-bound F, not singly-bound O. The oxide F_2O_2 (*b*) is presumably of the same type ; its instability, like that of H_2O_2 and N_2H_4 and other symmetrical molecules and ions of this type, arises from the similar polarity of the central atoms. An ion FO_3^- (*c*) would be unstable for a different reason, *viz.*, that the F would be positive with respect to O.

The Stereochemistry of Condensed Pyro-ions.—We have pointed out that the spatial arrangement of the bonds in finite oxy-ions cannot, in the present state of our knowledge, be used as evidence for either single or double bonds to oxygen. In the case of pyro-ions, however, in which MO_n groups are joined up by sharing oxygen atoms, the oxygen bond angles should reflect the nature of the M–O bonds.

Pyro-ions range from the simplest binuclear ion (*a*) through cyclic ions of type (*b*) to infinite linear pyro-ions (*c*). The analogous molecules include

$O_nM—O—MO_n$

(*a*.)



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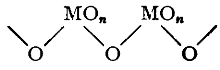
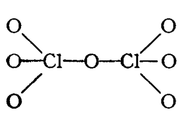
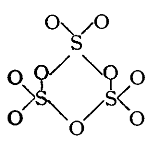


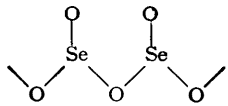
(*c*.)



(*d*.)

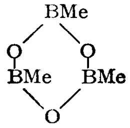


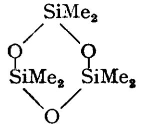
(*e*.)

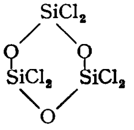


(*f*.)

and finally the infinite 2- and 3-dimensional oxy-networks in crystalline B_2O_3, SiO_2, etc. In addition to the ions of type (*b*) and molecules of type (*e*) there are cyclic molecules containing the M_xO_x ring system, such as







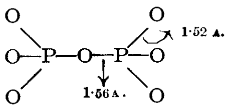
etc.

It would seem advisable to bear in mind what is known of the structures of all these types when considering the nature of the bonds in the simple oxy-ions. We shall write O″ for O shared between two M atoms and O′ for a terminal O atom. The sort of information we require is (1) the lengths of M–O″ compared with M–O′ bonds, and (2) the values of bond angles M–O″–M. Of particular interest would be cases in which M–O″ is appreciably less than $r_M + r_O$ and the angle M–O″–M is *not* 180°; double bonds would then appear inconsistent with ordinary stereochemical ideas. We shall consider these oxy-ions and molecules in two groups: (*a*) simple pyro-ions $O_nM–O–MO_n$, and (*b*) cyclic and more complex pyro-ions and molecules.

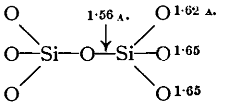
(a) *Simple pyro-ions and molecules.* No simple pyro-ions of the type $O_nM–O–MO_n$ are formed by elements of the first Periodic row. The second-row elements form

$$[O_3Si{\cdot}O{\cdot}SiO_3]^{6-},\ [O_3P{\cdot}O{\cdot}PO_3]^{4-},\ [O_3S{\cdot}O{\cdot}SO_3]^{2-},\ \text{and}\ O_3Cl{\cdot}O{\cdot}ClO_3.$$

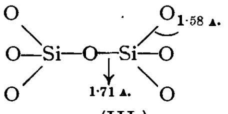
Structural data are available only for the pyrosilicate and pyrophosphate ions. In ZrP_2O_7 and isomorphous pyrophosphates (Levi and Peyronel, *Z. Krist.*, 1935, **92**, 100) the linear configuration (I) is found. No other pyrophosphate structures have been determined. Two configurations (both with linear Si–O–Si) have been found for the $Si_2O_7^{6-}$ ion, *viz.*, (II) in $Sc_2Si_2O_7$ (Zachariasen, *ibid.*, 1930, **73**, 1) and (III) in hemimorphite, $Zn_4(OH)_2Si_2O_7,H_2O$ (Ito and West, *ibid.*, 1932, **83**, 1). The discrepancies between (II) and (III) are so large that a discussion of the bond lengths is obviously out of the question. The configuration (IV) was found for the $S_2O_8^{2-}$ ion in the ammonium salt (Zachariasen and Mooney, *ibid.*, 1934, **88**, 63), with O–O = 1·46 A. as expected for a single bond, and the O bonds non-linear. However, the short length of the S–O″ bond (a double bond according to Phillips, Hunter, and Sutton) is surprising, and further study of this ion would appear desirable.



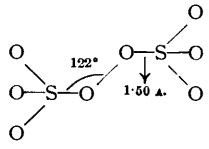
(I.)



(II.)



(III.)



(IV.)

(b) *Cyclic and other more complex oxy-ions and molecules.* Some boron–oxygen bond lengths (in A.) are summarised below. There is some doubt as to the best radius to assume for boron.

	B–O.		B–O.
H_3BO_3	1·36	$(B_3O_6)^{3-}$	B–O″ 1·38 B–O′ 1·33
$(B_5O_{10})^{5-}$	mean 1·35 (range 1·28—1·42)	$(BO_2)_n^{n-}$	B–O″ 1·34, 1·38 B–O′ 1·37
$B_3O_3(CH_3)_3$	1·39		
$B(OCH_3)_3$	1·38		

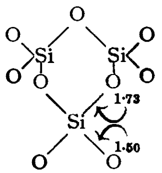
Bauer and Beach (*J. Amer. Chem. Soc.*, 1941, **63**, 1394) adopt a value 0·85 A., when $r_B + r_O = 1{\cdot}59$ A., and the S.-S. corrected value is 1·45 A. (assuming $x_B = 2{\cdot}0$). It is possible that the observed bond lengths are accounted for more satisfactorily by a tetrahedral radius of about 0·9 A. and a triangular radius of about 0·8 A.—Bauer and Beach tabulate the B–O distances without distinguishing between 3- and 4-covalent boron. There appears to be a small difference between B–O′ and B–O″ in $(B_3O_6)^{3-}$ but there are not sufficient accurate data for a discussion of this point [see the B–O bond lengths in the $(BO_2)_n^{n-}$ ion in calcium metaborate, above].

The most reliable Si–O bond lengths (A.) in $(SiO_4)^{4-}$ ions and in forms of crystalline silica are probably:

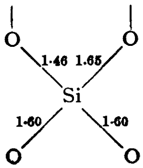
	Si–O.	
Quartz (low-temp.)	1·61, 1·62	(Wei, *Z. Krist.*, 1935, **92**, 355.)
Cristobalite (low-temp.)	1·59	(Nieuwenkemp, *ibid.*, p. 82.)
$ZrSiO_4$	1·62	

These values of about 1·60 A. are to be compared with $r_{Si} + r_O = 1{\cdot}91$ A. or corrected (S.-S.) 1·76 A. The oxygen bond angle in low-temperature cristobalite is stated to be about 150°.

For cyclic ions the data are far less satisfactory. Three determinations have been made of the structure of the cyclic $(Si_3O_9)^{6-}$ ion, with the following results (lengths in A.) :



In catapleite, $Na_2Zr(Si_3O_9),2H_2O$ (Brunowski, *Acta Physicochim., U.R.S.S.*, 1936, **5**, 863).



In benitoite, $BaTiSi_3O_9$ (Zachariasen, *Z. Krist.*, 1930, **74**, 139).

In wollastonite, $Ca_3Si_3O_9$, Si–O bond lengths from 1·48 to 1·76 A. were found (Barnick, Diss., Berlin, 1936), but little reliance can be placed on the precise values because the unit cell contains 60 atoms in general positions in the monoclinic space-group $P2_1/a$, involving the determination of 45 independent parameters. The bond lengths in benitoite are clearly unacceptable (unequal Si–O″ bonds). If the data for catapleite are accepted, the Si–O″ bonds are to be regarded as normal single bonds and the Si–O′ bonds as (single?) bonds showing the same abnormal shortening as in simple oxy-ions. Accurate data on the structures of cyclic silicon oxychlorides $(SiOCl_2)_n$ or of the molecules $(SiOR_2)_n$, where R is an organic radical, would be useful in a discussion of Si–O bond lengths.

Data on complex phosphorus oxy-ions or molecules are very scanty. The structure of the cyclic $(P_4O_{12})^{4-}$ ion in aluminium metaphosphate (Pauling and Sherman, *Z. Krist.*, 1937, **96**, 481) was not determined accurately * and no discussion of the P–O′ and P–O″ bond lengths is possible. The bond lengths in P_4O_6 and P_4O_{10} have already been given. The formulation of P–O bonds of length about 1·55—1·60 A. as double bonds would seem to call for the description of a bond of length 1·39 A. as a triple bond, but no satisfactory explanation of the extreme shortness of the P–O′ bond in P_4O_{10} has been given.

The only cyclic sulphur–oxygen molecule which has been studied is the trimeric S_3O_9 molecule (Westrik and MacGillavry, *Rec. Trav. chim.*, 1941, **60**, 794), but only approximate values of the bond lengths were determined (S–O″ 1·6, S–O′ 1·4 A.). There are no data on complex oxy-molecules of chlorine.

Probably the only conclusion to be drawn from this brief survey is that M–O′ is, in some cases at least, shorter than M–O″, although the difference is small in the case of boron. There is, however, so much uncertainty as to the precise values of the bond lengths, even in some simple MO_4 ions, that any detailed discussion of these bonds is out of the question until many of these crystal structures have been redetermined with greater accuracy.

Metallic Carbonyls, Complex Cyanides, and Phthalocyanines.—These compounds are of interest because the M–C bond lengths are appreciably shorter than the sums of the single-bond covalent radii, and resonance involving double-bonded structures has been generally accepted.

Carbonyls. We shall assume that in carbonyls it is the carbon and not the oxygen which is attached to the metal. In the account of the electron-diffraction study of $Ni(CO)_4$ it is stated (Brockway and Cross, *J. Chem. Physics*, 1935, **3**, 828) that " models were included in which the O atoms are attached to the Ni as well as those having C atoms adjacent to the Ni atom ", but no further reference is made to the former. The atomic separations were interpreted as due to the linear arrangement (bond lengths to ±0·03 A.)

$$\mathrm{Ni}\overset{1\cdot82}{\text{——}}\mathrm{C}\overset{1\cdot15}{\text{——}}\mathrm{O}$$

An infra-red study (Crawford and Cross, *ibid.*, 1938, **6**, 525) was inconclusive as regards the configuration of the molecule. In later studies of other carbonyls it has been assumed that carbon is attached to the metal atom. To account for the length of the Ni–C bond it is assumed that resonance between single bonded, $\mathrm{Ni{-}C{\equiv}O}$ (I.), and double bonded, $\mathrm{Ni{=}C{=}O}$ (II.), structures occurs, the 8 remaining $3d$ electrons of the Ni being used. The tetrahedral configuration was originally predicted for four sp^3 bonds, and it is stated (Brockway and Cross,

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* Care should be exercised when taking information from the " Strukturbericht ", which is essentially an uncritical compilation of data. The parameters in this complex structure were estimated from a model, and while the determination of the structure was an elegant piece of deductive work, the authors stated that the " atomic positions can be considered as experimentally verified only to within about 0·1—0·2 A. ". The " Strukturbericht ", however, gives P–O″ as 1·55 and 1·56 A. and P–O′ as 1·39 and 1·60 A., without a clear indication of the accuracy claimed by the authors.

loc. cit.) that the configuration of 4 groups attached to Ni by double bonds cannot be predicted since " the problem of 4 double bonds formed from d^4sp^3 has never been studied. Since structure (I) *probably* predominates in the resonance it is *likely* that its directional properties determine those of the normal state of the molecule, but in fact the observed tetrahedral configuration cannot be used as a criterion for the proposed resonance." The argument for resonance is based on the length (1·82 A.) of Ni–C as compared with the sum of the radii 1·23 + 0·77 = 2·00 A. The Pauling radius for tetrahedral Ni is derived as follows :

Octahedral radii (A.)	Ni^{II}	1·39	(from Ni–S in NiS_2)
	Ni^{III}	1·30	(from Ni–S in NiAsS)
	Ni^{IV}	1·21	(extrapolated)

Then :

	Ni^{IV}	octahedral	1·21
	Ni^{II}	planar	1·22
whence	Ni^0	tetrahedral	1·23 *by extrapolation*

Two points should be noted. (1) No justification for the second (or for that matter for the first) extrapolation is given ; the electronic structures for the last three states of the Ni atom are :

Ni^{IV} octahedral	(2, 8) 2, 6	6 + *4*	*2*	*6*	d^2sp^3
Ni^{II} planar		8 + *2*	*2*	*4*	dsp^2
Ni^0 tetrahedral		10	*2*	*6*	sp^3

(2) Pauling states (*op. cit.*, p. 172) : " It is found on examining the observed values of interatomic distances that square dsp^2 radii of atoms have the same values as the corresponding octahedral d^2sp^3 radii. . . . No reliable data are available for bivalent nickel, but it is probable that the equality holds for it also." In spite of this he extrapolates from Ni^{IV} = 1·21 and Ni^{II} = 1·22 A., *radii which should be equal according to the above statement.* In any case the Ni^{IV} octahedral radius is an extrapolated value of unknown accuracy. The weight to be attached to the value of 1·23 A. for the tetrahedral radius of Ni^0 is therefore a matter of personal opinion. However, it is true that the Ni–C distance in $Ni(CO)_4$ is shorter than the sum of 1·23 A. and one-half of the interatomic distance in diamond.

Metallic cyanides. The crystal structures of a number of complex metallic cyanides have been determined, and the configuration of the complex ion deduced, *e.g.*, $[Ag(CN)_2]^-$ linear, $[Ni(CN)_4]^{2-}$ planar, etc. It is conventional to write the formulæ of these ions with the carbon attached to the metal atom, as in $[N{-}C{-}Ag{-}C{-}N]^-$, but in no case has it been established that carbon rather than nitrogen is attached to the metal. (It is impossible to distinguish between these possibilities by *X*-ray methods. Although it is possible to differentiate carbon from nitrogen in organic compounds of certain types, it is not possible in metallic cyanides, not only because of the relatively strong scattering by the metal atom, but also because the complex electronic structure of the cyano-group leads to similar electron densities around the carbon and nitrogen peaks in Fourier projections.) What we do know, in fact, is that both C and N of CN can be attached to metal atoms, as in crystalline silver cyanide, in $[AuCN(C_3H_7)_2]_4$, and possibly in complex ferro- and ferri-cyanides. The Ni–C (?) distances in complex nickelocyanides have been found (Brasseur and Rassenfosse, *Bull. Soc. franç. Min.*, 1938, **61**, 129) to lie in the range 1·85—1·90 A., and although they are not very accurately known, they appear to be comparable with the value in nickel carbonyl. In spite of the above uncertainties, the structures of some new complex nickel cyanide ions have recently been discussed in exactly the same way as that of nickel carbonyl (Deasy, *J. Amer. Chem. Soc.*, 1945, **67**, 152).

Phthalocyanines. In nickel phthalocyanine (Robertson and Woodward, *J.*, 1937, 219) the nickel is bound to 4 coplanar nitrogen atoms, the Ni–N bond length being 1·83 A. The nitrogen atoms belong to a complex carbon–nitrogen ring system in which there is resonance between single and double bonds, as shown by the fact that all 16 C–N bonds have a length of 1·38 A. The Ni–N distance is shorter than the distance from N to the centre of the ring in the metal-free phthalocyanine (1·92 A.) (Robertson, *J.*, 1936, 1195). These two distances, 1·83 and 1·92 A., are not strictly comparable, however, because the introduction of the metal atom has apparently caused some alteration in the ring system. The C–N bond length in the metal-free compound is 1·34 A., and the ring is more distorted from true tetragonal symmetry than in the nickel derivative. Robertson points out that the Ni–N bond length is about equal to the length expected for a double bond, if this is calculated in the conventional way.

Conclusions.—The object in making this review of the lengths of certain bonds has been to present facts rather than to propound new theories. In the present state of our knowledge it would seem preferable to check some of the experimentally determined bond lengths and to determine other critical bond lengths rather than to attempt detailed discussion of the precise distribution of electron densities in bonds, as is implied by analyses of bond lengths in terms of covalent radii.

We conclude that the sums of the 8 — *N* covalent radii, either with or without a correction for electronegativity difference, do not agree sufficiently well with observed interatomic distances to justify the use of such radii in conjunction with an equation of the Schomaker–Stevenson type in detailed discussions of bond lengths. The values suggested for the covalent radii of certain elements have been too uncritically accepted. A number of bonds are inexplicably short, notably M–F in SiF_4 and PF_3, M–O in many oxy-ions and molecules, M–C in metallic carbonyls (and cyanides ?), and M–N in phthalocyanines. Perhaps the only feature common to all these bonds is that one atom of the bond is either appreciably more electronegative than the other, or is part of an atomic system in which its other bonding electrons are strongly bound, as in the carbon monoxide molecule, the cyano-group, the carbon–nitrogen ring of the phthalocyanine, or the triple bond –C≡C– in the case of the short H_3C–C bond in methylacetylene.

Two ways in which the environment of an atom in a molecule may differ from that in the molecule or crystal from which the 8 — *N* radius was derived are : (1) that it is forming a different number of bonds, and (2) that it is bonded to atoms of different electronegativities. Although the principle of assigning different " covalent radii " to an atom according to the number and type of orbitals used has long been established (compare Pauling's octahedral and tetrahedral radii), it is discarded in many discussions of bond lengths. The justification for using the 2-covalent radius of oxygen, for example, for a singly bound oxygen atom has not been established. It is somewhat surprising that while the longest S–O bond accurately measured has a length of only 1·44 A., as compared with the " corrected radius sum ", 1·76 A., no serious attempt seems to have been made to find a long S–O bond. The obvious compounds to study are those containing the system –S–O–, *e.g.*, esters of sulphonic acids. The value of the S–O bond length in the $S_2O_8^{2-}$ ion needs confirming. Finally, it could be argued that the existing bond-length data could be interpreted as showing that the length of a particular bond A–B is *not* dependent only on the 8 — *N* radii and electronegativity coefficients of A and B but is also dependent on the nature and number of the other atoms attached to A and B.

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[*Received, March* 18*th*, 1948.]