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Comments on the structure of $KBrF_4$.*

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Sly & Marsh (1957) have suggested an alternative structure for the compound $KBrF_4$ (Siegel, 1956). These authors propose a square configuration for the BrF_4^- ion, whereas I report a tetrahedral arrangement.

I agree with Sly & Marsh that the planar configuration is the one to be expected. However, it is not possible to distinguish between the two cases with certainty even if one places considerable reliability on the few isolated discrepancies.

In order to determine the fluorine positions, it is necessary to consider reflections hkl with l odd. Unfortunately, only a limited number of such reflections are observed on the powder pattern, and these generally suffer interference. Only a few reflections of this class (211, 213, 215) are observed in a single-crystal oscillation pattern, but interferences arise here from powder lines of decomposition products. Contrary to a statement by Sly & Marsh concerning the ability to resolve intensities from the powder pattern, the fact remains that it has been possible, with only a few exceptions, to evaluate intensities with reasonable consistency from line profiles in the microphotometer tracings. The agreement between observed and calculated $\sin^2\theta$ values certainly indicates some measure of resolution.

The 215 reflection, when corrected for the effects of 224, has an $I_o^{\frac{1}{2}}$ value of 33. Since this value includes the intensity from a non-resolvable neighboring impurity maximum, the true $I_o^{\frac{1}{2}}$ value must be less than 33 and is so indicated. However, it is doubtful that the interfering line has a high enough intensity to make up the difference between my observed and calculated intensities. Hence, the value given by Sly & Marsh appears to be reasonable. The 415 reflection is distinct. My calculated value of $I_c^{\frac{1}{2}}$ (1·2 and not 12 as given) is obviously low. The planar configuration also gives a low calculated value, but it is certainly a more reasonable one.

The 413 reflection is poorly resolved from its neighbors. However, the intensity is sufficiently high to permit its position and intensity to be determined. The tetrahedral case accounts for this reflection. However, the intensity calculated for the planar configuration is low, and, for the intensity scale used, the line would show near-zero intensity on the film. The only other discrepancy arises in the 114 reflection. Here, the planar configuration also gives a low calculated intensity. Data at the larger angles are not too reliable for evaluation. Finally, if we restrict ourselves only to the 215 and 415 reflections, major changes in the z coordinate of the tetrahedral fluorines will be required in order to improve intensities. Such shifts would, of course, modify the entire set of calculated intensities. Presumably, only minor changes in coordinates would be required for the planar fluorines in order to effect better agreement for the two reflections.

The discrepancy warrants a review of the structure under conditions of improved resolution. Accordingly, a new structure determination has been initiated.

References

Siegel, S. (1956). *Acta Cryst.* **9**, 493.
Sly, W. G. & Marsh, R. E. (1957). *Acta Cryst.* **10**, 378.

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Comments on Pauling's paper on effective metallic radii for use in the β-wolfram structure.

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The author's determination of a set of effective coordination number (12) radii for compounds A_3B having the β-wolfram structure (Geller, 1956) was recently criticized by Pauling (1957), who states that by the application of his resonating-valence-bond theory he obtains different radii which not only lead to better agreement with the measured cell edges but also are nearly the same as his R(L12) metallic radii formulated in 1947.

In the following we discuss Pauling's criticism under three headings:

(1) Has it been demonstrated that the resonating-valence-bond theory applies to compounds with the β-W structure?

(2) If not, has a new and justifiable technique been used to obtain a set of metallic radii?

(3) Are the new results, judged merely as an empirical correlation, an improvement on those of this author?

(1) The set of radii for the 32 compounds A_3B was obtained by Pauling by weighting the contributions to the interatomic distances in accordance with the relative numbers of atoms of each kind in the compound, i.e. 3:1. As he points out, the resonating-valence-bond theory requires a recognition of the coordination and valence of the atoms and the strength of bonds. However, because the 3:1 weighting alone suffices to give a seemingly good set of radii, these considerations, ordinarily a basic

part of the theory, are ignored. This procedure is equivalent to finding that the theory does not apply to these compounds.

Pauling thus excludes the theoretical considerations*; he derives his final results by neglecting the valency as a correction on the weighting. If valencies were considered, the proper weighting of the contributions to the A–B distances would be as dissimilar as 5:1 for V_3As and 2:1 for Ti_3Ir. By using the value 3:1 for all compounds in the group, he abandons the underlying theory.

The importance of the short (A–A) interactions should not be overlooked in attempting to determine the nature of the bonding in these compounds. In fact, these are probably just the bonds that cause the difficulty in applying the resonating-valence-bond theory. It is, however, not necessary to consider these A–A bonds in establishing that a certain constancy of the radii exists in the A–B interactions in these compounds, and as a result it is possible to reproduce the lattice constants of this structure type with unusual accuracy. (The same could not be done for intermetallic compounds with the CsCl structure, for example.) Pauling suggests that he has included these short bonds by his weighting in accordance with the number of atoms of each kind in the unit cell. Actually each A atom has effective CN(14), each B atom effective CN(12). Even if the longer (A–A) distances are neglected, there are 4 B atoms and only 2 A atoms coordinated to an A.

Thus far, we have seen that the principal features of the resonating-valence-bond theory have not been applied by Pauling in his explanation. Nor does his new criterion for the test of the theory, namely the agreement of his β-W set of radii with the R(L12) radii (Pauling, 1947), show the validity of the theory in the case of compounds with the β-W structure. A mean deviation is useful as a measure of agreement only when individual deviations are not significantly different from the mean. The agreement of many of Pauling's β-W with R(L12) radii is extremely good, but individual deviations for those which do not agree well are very large. Out of twenty listed radii, eight have deviations $\geq 0{\cdot}024$ Å. The mean deviation of these eight is 0·045 Å; the largest listed deviation is 0·077 (for As). The mean deviation for the other twelve (range 0·001 to 0·018 Å) is 0·008 Å. (Incidentally, the overall standard deviation is 0·031 Å, but this also is not too meaningful because the type of distribution function for the deviations is not known.) The large deviations for Ti and Zr are explained, but some other differences, notably for As, Si and Ge, are neglected.

There now exists an even more extreme example of such unexplained deviations. In a paper by Matthias, Wood, Corenzwit & Bala (1956), the compounds Nb_3Sb and V_3Sb with β-W structure are discussed. The lattice constants of these compounds are 5·26 and 4·92 Å respectively. The radius derived for Sb, 1·504 Å, using Pauling's formula $[a_0 = 1{\cdot}7888(\frac{3}{2}R_A+\frac{1}{2}R_B)]$ is about 0·09 Å different from his R(L12) radius (Pauling, 1947). This discrepancy is even larger than that for As. It changes the overall mean deviation to 0·03 Å and that of the nine with largest individual discrepancy to 0·050 Å. (The overall standard deviation now is 0·036 Å.)*

(2) The second question—is the new technique given by Pauling in his present paper a justifiable one?—centers around the point as to whether the 3:1 weighting is valid. This type of weighting is new and requires detailed justification by theory and by application in other instances. Although the rule of simple additivity leaves much to be desired, it is in general use (see first footnote). In *The Nature of the Chemical Bond* (p. 418), Pauling discusses briefly structures involving packing of atoms of different sizes, for example, $MgZn_2$ in which Zn has CN(12) and Mg CN(16). However, when discussing distances in this compound he employs the simple additivity rule. He also follows this procedure in treating Al_4Ba. In the V_3Au case, Pauling says 'The fallacy in Geller's argument is, of course, that of giving the radii of the small atom V and the large atom Au the same weight'. Now suppose, as he suggests, that the R(L12) radii of the 1947 paper and the 3:1 weighting were used. The values obtained for several compounds are shown in the following table† and compared with the observed values:

	Pauling's method	Observed	Δ
V_3Si	4·767 Å	4·722 Å	0·045 Å
V_3Ge	4·812	4·769	0·043
V_3As	4·834	4·75	0·084
Nb_3Sb	5·337	5·26	0·077
V_3Sb	5·012	4·92	0·092
Ti_3Ir	5·148	5·007	0·141
Ti_3Pt	5·175	5·033	0·142
Ti_3Au	5·223	5·096	0·127

Perhaps one might accept the argument for the contraction of Ti, but the discrepancies for the others are rather large, especially by Pauling's own criteria. Thus, although this kind of weighting of the R(L12) radii gives a satis-

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[*] Pauling's theory (1947) is usually applied on an atomistic basis, i.e. one considers the coordination of the crystallographically different atoms. Bond numbers are assigned to the bonds in a logical manner; the weighting which occurs is in accordance with the relationships:

$$R_A(n) = R_A(1) - 0{\cdot}300 \log n\,, \qquad (1)$$

$$R_B(n) = R_B(1) - 0{\cdot}300 \log n\,, \qquad (2)$$

$$R_A(n) + R_B(n) = D_n = D(1) - 0{\cdot}600 \log n\,, \qquad (3)$$

where n is the bond number, $R_A(n)$ and $R_B(n)$ are the observed radii of atoms A and B associated with bond number n, $R_A(1)$ and $R_B(1)$ the single-bond radii and $D(1)$ the sum of the single-bond radii. (It is seen that (3) is an expression of the simple additivity rule.) The sum of the bond numbers assigned to bonds from a given atom must equal the valence of the atom. In more complicated cases, it is necessary to assume various bond numbers, solve for the single-bond radii and show that these check well with the theoretical values. Thus, for example, when an atom distributes its d character differently among the orbitals in bonds to different atoms, the single-bond radius may be different for different bonds. This type of application is illustrated by the case of Nb_3Pt in the author's earlier paper (Geller, 1956). In some cases, the possibility of electron transfer from one atom to another producing a change of valencies and single-bond radii is also recognized.

[*] It should be pointed out that I was not attempting, in my earlier paper, to stress the similarities between my radii and the CN(12) radii of Pauling, but rather the differences. Thus it would not matter what the mean deviation between my radii and the R(L12) radii would be.

[†] The differences between this table and Pauling's Table 2 (which shows almost perfect agreement for the titanium compounds) arise because of the large difference between the R(L12) and his new β-W radii for Ti, As, Ge, and Si.

factory result when applied to V$_3$Au, it does not do so for many other compounds.

(3) Finally, are the new results, judged simply as an empirical correlation, an improvement on those of this author? The mean deviation in lattice constant obtained by the author for the 32 compounds is 0·01 Å, the range is 0·00–0·03 Å; for 31 compounds it is 0·00–0·02 Å. In this case, therefore, the mean deviation may be given as a meaningful measure of agreement. It was pointed out (Geller, 1956) that the accuracy of the measured lattice constants would not seem to warrant an attempt to obtain better agreement of predicted with measured lattice constants. Pauling has obtained a mean deviation in lattice constant of 0·004 Å. However, the range is 0·000–0·030 Å. Four of the deviations are greater than or equal to five times the mean deviation. Thus, the accuracy claimed by Pauling is illusory, and the results are really no better than those originally obtained by the author.

It is therefore necessary to conclude in answer to the three questions put at the introduction (1) that Pauling has not demonstrated that the resonating-valence-bond theory applies to the compounds with the β-W structure; (2) that the technique used to obtain his β-W radii is new and has not been justified in detail; (3) that the new results are no better than those of this author. The latter have the advantages that (1) they adhere to the generally accepted idea of simple additivity of radii for prediction of interatomic distances, and (2) they recognize the shortcomings of the experimental data.

References

GELLER, S. (1956). *Acta Cryst.* **9**, 885.

MATTHIAS, B. T., WOOD, E. A., CORENZWIT, E. & BALA, V. B. (1956). *J. Phys. Chem. Solids.* **1**, 188.

PAULING, L. (1945). *The Nature of the Chemical Bond.* Ithaca: Cornell University Press.

PAULING, L. (1947). *J. Amer. Chem. Soc.* **69**, 542.

PAULING, L. (1957). *Acta Cryst.* **10**, 374.

Acta Cryst. (1957). 10, 382

Some pyridine-*N*-oxide derivatives.*

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A survey was undertaken some months ago of pyridine-*N*-oxide derivatives with a view to obtaining cell data of crystalline specimens to aid in a diligent choice of compounds for complete X-ray analysis. Two such compounds have meantime been so analyzed to furnish bond data for theoretical chemists (Eichhorn, 1956, 1957; Jaffe & Doak, 1955).

Table 1 reproduces the data of the eight crystalline compounds investigated. The authors have to thank Dr H. J. den Hertog of the Wageningen Agricultural Institute and Dr E. Ochiai of the University of Tôkyo for the many samples placed at their disposal. The carbinol was first prepared by synthesis at C.I.T. by Dr R. L. Bixler, who was good enough to let us have a sufficient quantity for our experiments. Great difficulties were initially experienced with the purification of this compound since it would not properly dissolve in many of the commonly used organic solvents. With dioxane, however, the carbinol combines to give a molecular compound of uncertain dioxane content, yielding beautiful silky needles which will lose dioxane after some standing; the needles finally revert to powder.

Table 1. *Crystallographic data*

d_f and d_x are the densities, measured respectively by flotation (usually with the aid of an electrically driven centrifuge) and determined by calculation from the molecular weight and the cell volume. The translation distances were determined from oscillation photographs (Cu $K\alpha$ = 1·5418 Å), and their precision should be of the order of 0·02 Å. The axial angles should have a precision of about 0·1°; the d_f value for the last compound in the table is not very reliable.

4-Nitro-P*N*O

$Pmna$; $Z = 4$; $d_f = 1{\cdot}520$, $d_x = 1{\cdot}550$ g.cm.$^{-3}$
$a = 12{\cdot}53$, $b = 6{\cdot}04$, $c = 7{\cdot}93$ Å

4-Chloro-P*N*O

$Fddd$; $Z = 16$; $d_f = 1{\cdot}444$, $d_x = 1{\cdot}440$ g.cm.$^{-3}$
$a = 19{\cdot}69$, $b = 12{\cdot}87$, $c = 9{\cdot}54$ Å

4-Cyano-P*N*O

$P2_1/c$; $Z = 4$ with sub-cell $c' = \frac{1}{2}c$; $d_f = 1{\cdot}355$, $d_x = 1{\cdot}360$ g.cm.$^{-3}$
$a \sin\beta = 11{\cdot}31$, $b = 5{\cdot}90$, $c = 7{\cdot}89$ Å

4,4′-*trans*-Azo-P*N*O

$P2_1/n$; $Z = 2$; $d_f = 1{\cdot}497$, $d_x = 1{\cdot}504$ g.cm.$^{-3}$
$a = 4{\cdot}56$, $b = 12{\cdot}75$, $c = 9{\cdot}75$ Å, $\beta = 114{\cdot}6°$

4,4′-*cis*-Azo-P*N*O

$P2_1/a$; $Z = 4$; d_f = ?, $d_x = 1{\cdot}237$ g.cm.$^{-3}$
$a = 15{\cdot}44$, $b = 22{\cdot}01$, $c = 3{\cdot}76$ Å, $\beta = 114{\cdot}9°$

4-Hydroxy-P*N*O

$P1$ or $P\bar{1}$; $Z = 2$; $d_f = 1{\cdot}536$, $d_x = 1{\cdot}541$ g.cm.$^{-3}$
$a = 3{\cdot}85$, $b = 7{\cdot}10$, $c = 13{\cdot}10$ Å, $\alpha = 116{\cdot}5°$, $\beta = 121{\cdot}0°$, $\gamma = 93{\cdot}7°$

4-Pyridyl-*N*O-carbinol

$P2_1/c$; $Z = 4$; d_f = ?, $d_x = 1{\cdot}233$ g.cm.$^{-3}$
$a = 13{\cdot}89$, $b = 3{\cdot}93$, $c = 12{\cdot}33$ Å, $\beta = 90{\cdot}0°$

X Dioxane . *Y* 4-pyridyl-*N*O-carbinol

$P2_1/c$; Z = ?; $d_f = 1{\cdot}11$, d_x = ? g.cm.$^{-3}$
$a = 7{\cdot}58$, $b = 5{\cdot}95$, $c \sin\beta = 12{\cdot}74$ Å

The authors are very much indebted to Dr Linus Pauling and Dr Robert B. Corey whose interest stimulated this research.

References

EICHHORN, E. L. (1956). *Acta Cryst.* **9**, 787.

EICHHORN, E. L. (1957). To be published.

JAFFE, H. H. & DOAK, G. O. (1955). *J. Amer. Chem. Soc.* **77**, 4441.

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