[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Electron Deficient Compounds[1]

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Recently Pitzer has proposed explanations of the electron deficient bonding in the boron hydrides[1a] and the aluminum alkyl dimers.[2] In his papers he has reviewed the structural investigations of these compounds quite extensively, and he has concluded that the evidence favors bridge-type structures rather than direct boron-to-boron or aluminum-to-aluminum bonds in the respective cases.

In this paper the bridge structures for these molecules will be accepted, but the possible nature of the bonds in the bridge will be reexamined. The proposal which will be made in this paper is in some respects similar to the "protonated double-bond" of Pitzer, but it will alter, or perhaps simply clarify, the nature of this bond in such a way that not only will it appear to be applicable to the boron hydrides, but the same proposal will serve as an adequate explanation of the bridge structure in the aluminum alkyls and the bonding in certain other peculiar compounds such as the tetramethylplatinum tetramer[3] and certain of the so-called interstitial compounds.[4]

Interstitial Compounds, MX.—In considering the nature of certain so-called interstitial compounds, particularly those of composition MX, where X is C, N or (in certain suboxides) O, it became apparent that these compounds are not suitably explained by an interstitial solution theory. An extensive survey of the literature of compounds of this type is presented in another paper,[4] but a brief summary of some of the important points relative to the nature of the bonding in these compounds seems pertinent here.

(1) Almost all the interstitial compounds, MX, have the sodium chloride-type structure. This is true whether the metal from which the "interstitial" phase is derived has a cubic closest-packed structure or not. (For most compounds of this type the corresponding metals have body-centered cubic or hexagonal closest-packed structures.) The sodium chloride-type structure is also the preferred type even if compound formation involves a considerable loosening of metal-to-metal bonds. (Metallic-like phases are known where the volume of the metal increases up to 33% upon formation of the monocarbide.)

(2) The "interstitial" phases are all very hard and have extremely high melting points, usually of the order of 1000° higher than that of the corresponding metal. This is true even where metal-to-metal bonds have been considerably weakened, as in those cases where there are large increases in volumes upon forming the "interstitial" phases.

Points (1) and (2) are interpreted as requiring good metal-to-nonmetal bonding to make up for weakened metal-to-metal bonds in some cases, and to augment this bonding in all cases. Since the sodium chloride structure prevails almost exclusively in these compounds the bonding must be octahedral, *i. e.*, six equal bonds from the nonmetal directed toward the corners of an octahedron. First row elements have only four stable orbitals for bond formation. Consequently, we conclude that *under certain circumstances an element may use one orbital to form more than one bond.* In accordance with the exclusion principle, however, this orbital may be occupied by no more than one electron pair.

To achieve octahedral bonding by a first row element the orbitals which suggest themselves are the 2p-orbitals. The p_x, p_y and p_z orbitals are mutually orthogonal, and have equal concentrations of the orbital in the positive and negative directions of the designated axis. It would seem quite reasonable to use a p-orbital to form two bonds at 180°, but using only one electron pair in the two bonds. Since any one such bond would have an electron pair within the bond one-half the time, we shall speak of such a bond as a "half bond." It is not to be confused with a one-electron bond which requires a bond orbital per atom.

Better octahedral bonding may be achieved by the nonmetal by using two equivalent sp-orbitals to form ordinary electron pair bonds. The two remaining p-orbitals may then form four "half bonds." The sp-orbitals are oppositely directed and at right angles to the remaining p-orbitals. Hybridization of the s-orbital with any one p-orbital would be equivalent to hybridization with any other. Consequently, resonance would make all six bonds equal. The bonds could then be regarded as two-thirds "half bonds" and one-third single bonds. Each bond would then have two-thirds the electron density of a single bond, and six such bonds would be roughly equivalent to four ordinary bonds. Since "half bonds" seem to be preferred in cases where one element has excess orbitals, it appears that a "half bond" must have somewhat more than half the bond energy of a single bond.

"Half bonds" of the type described above provide interstitial compounds with a resonating system of bonds.[4] This, in turn, provides for electrical conductivity just as it is provided for in

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[1] Supported in part by a grant from the Industrial Science Research Institute of the Iowa State College.

[1a] K. Pitzer, THIS JOURNAL, **67**, 1126 (1945).

[2] K. Pitzer and H. Gutowsky, *ibid.*, **68**, 2204 (1946).

[3] R. Rundle and J. H. Sturdivant, "The Crystal Structure of Trimethylplatinum Chloride and Tetramethylplatinum," submitted for publication in THIS JOURNAL.

[4] R. Rundle, "A New Interpretation of Interstitial Compounds," to be published in THIS JOURNAL.

graphite. The directed, strong bonds also serve to make interstitial compounds brittle, a property not often associated with electrical conductivity.

Conditions for Forming "Half Bonds."—The interstitial compounds are discussed here because they provide, in the author's opinion, the clearest indication to date for "half bonds" of the type described above. It is this concept of "half bonds" which we wish to apply to other electron deficient compounds.

It is, of course, clear that both interstitial compounds and metals are examples of electron deficient structures; that is, both have more bonds than bonding electron pairs. In metals the concept has been accepted that in this case the bonding electrons resonate among the various available bonds.

In metals, all the atoms present have a surplus of orbitals. The interstitial compounds and the other electron deficient molecules which will be discussed in this paper differ from metals in that there is one set of atoms, A, which has less valence electrons than stable bond orbitals, and another set, B, which may be thought of as deficient in stable orbitals; that is, B can use to a maximum the bond orbitals of the set, A, only if it uses some of its bond orbitals to form more than one bond.

For B to "over-tax" its stable orbitals in this fashion certain other requirements must be met. A and B must tend to form strong, essentially covalent bonds. Since A is to have more bond orbitals than bonding electrons it will, in general, be a metal. Similarly, B will generally be a nonmetal. Consequently, one important requirement is that A and B must not differ too greatly in electronegativity, or the bond will be essentially ionic. This means that A will not be among the most electropositive metals, and B will not usually be extremely electronegative. (Some suboxides appear to be interstitial compounds with properties similar to the carbides and nitrides, nevertheless.)

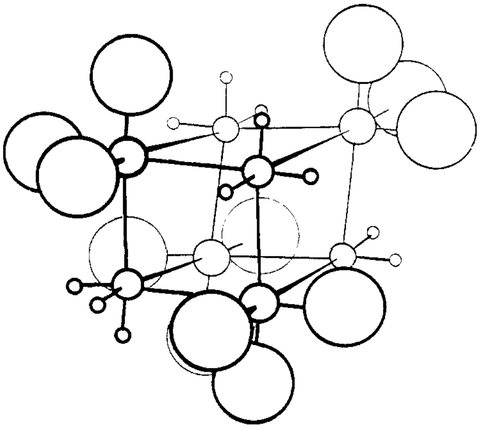


Fig. 1.—The tetramethylplatinum tetramer. Circles in decreasing order represent methyl, platinum, carbon of the "bridge" methyls and hydrogen.

Moreover, for B to be "orbital deficient" it will generally be limited to hydrogen and the first row elements where the stable bond orbitals are limited in number to one and four. (It is possible that second row elements, where there is still some tendency to retain the octet rule, may also fulfill the conditions for "orbital deficient" atoms.)

If B is a first row element having four orbitals, presumably the corresponding A must have more than four stable orbitals. Consequently A must belong to a higher order row of the periodic table in this case.

If B is hydrogen or a radical (such as methyl) having only one stable orbital, then A may be a metal with only four stable orbitals. The possibilities for A in this case include first and second row metals as well as those higher in the periodic table.

It will be our hypothesis that, if the above conditions are met, "half bonds" of the type described above will be possible. Of course, the orbital used by B for forming more than one bond must have suitable directional properties. It must not be concentrated in one direction, but preferably in two, *e. g.*, a p-orbital. With hydrogen the only available orbital is an s-orbital, but this orbital likewise appears satisfactory since it provides for equal overlap in all directions. One would expect, however, because of the size of hydrogen, the angle between the two bonds it forms would tend for steric reasons to be 180°.

The restrictions on "half bonds" listed above (and it may well be that further restrictions will have to be added) are so numerous that compounds fulfilling them are chemical oddities. They are not by any means limited to the boron hydrides and aluminum alkyl dimers, however. In fact, those "interstitial" compounds which appear to be of this type are very numerous.[4]

Tetramethylplatinum.—Recently the crystal structure determination of tetramethylplatinum has revealed that the compound is a tetramer.[3] The structure is shown in Fig. 1. In the tetramer some of the methyl groups form bonds to three platinum atoms with the bonds to platinum forming essentially right angles. There are neither sufficient electrons nor sufficient orbitals for these to be normal bonds, and, as might be expected, the observed platinum to carbon distance (about 2.50 Å.) is considerably greater than the sum of the covalent radii (2.08 Å.).

One cannot understand this electron deficient bonding of methyl to *three* platinums by any of the suggestions of Pitzer,[1,2] but it is understandable in terms of "half bonds" as described above.

Tetravalent platinum has six stable bond orbitals, the familiar d^2sp^3, octahedral orbitals. It can form only four normal, electron pair bonds with methyl radicals because of valence considerations. This leaves two unused, stable, bond orbitals for platinum. The methyl radical does not possess excess orbitals, so that the use of the extra orbitals of platinum cannot be satisfied, as in a metal, by allowing resonance of an electron pair among several bonds. Under these circumstances the conditions for forming "half bonds" are fulfilled. Carbon can supply p-orbitals which can be used to form six "half bonds" directed octahedrally. The structure of the compound is in accord with this use of bonds. Each p-orbital of carbon can be used to bond one platinum and one hydrogen; the bond angle will be 180°. It is probable that in tetramethylplatinum the methyl group forming the platinum bonds is distorted, so that the H–C–H angles are approximately 90° instead of tetrahedral. Again, to provide stronger bonds, sp hybrid orbitals may be used along with the other two p-orbitals, and resonance will make all six bonds similar.

About the only conceivable alternative to the above binding in the tetramethylplatinum tetramer is to assume that one methyl group is an ion. There is little reason to believe that the carbon–platinum bond should be ionic, and the ionic bonding provides little basis for understanding the peculiar structure of the tetramer.

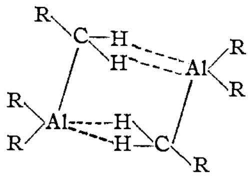
The Boron Hydrides.—Pitzer has discussed the boron hydrides and the application of the concept of a "protonated double bond" to these molecules in great detail. The remarks made in this paper will be directed primarily toward an interpretation of this bond as consisting of two hydrogen bridges, each of which consists of "half bonds"; that is, where hydrogen, using one electron pair and its 1s-orbital, bonds two boron atoms. One would expect boron to try to maintain tetrahedral bonds, so, in accord with Pitzer's picture, the two hydrogens of the bridge will lie above and below the plane of the rest of the molecule. Hydrogen for steric reasons would tend to make the B–H–B bond angle 180°, but the two hydrogens would repel each other. The resulting angles H–B–H in the bridge would then tend to be less than tetrahedral, and the B–H–B angle would tend to be less than 180°.

The bridge in the boron hydrides would contain two pairs of electrons, should effectively prevent rotation, and would thus have many of the properties of a double bond. Accordingly it may be thought of as a "protonated double bond." This nomenclature does not seem desirable to this writer, since it is probably not very different from the bridge in the aluminum alkyl dimers, and it would seem unwise to call these bridges "alkylated double bonds" (see the next section).

Probably the chief reason for supposing that there is something special about a "protonated double bond" is that dimethylborine forms a dimer, whereas trimethylboron does not. Actually, on the basis of "half bonds" presented here it might be supposed that carbon could use one of its orbitals to form two bonds, so that trimethylboron should dimerize.

Examining this case further, it appears that steric factors in a four-membered ring will become very important. This will be particularly true in the case of boron, whose covalent radius is but 0.88 Å.[5] Even if we allow carbon a 1.00 Å. covalent radius in "half bonds," a value which seems consistent with distances in certain "interstitial" carbides, the nearly square ring will have to have methyl–methyl and BH_2–BH_2 distances of about 2.6 Å. It is probable for steric reasons that the "ring" bridge cannot form in trimethylboron.[5a] The steric factor is not so important in the aluminum alkyls, since the covalent radius of aluminum is considerably greater.[5] It is probably only the small size of hydrogen that is unique about the "protonated double bond."

The Aluminum Alkyl Dimers.—In the aluminum alkyl dimers Pitzer and Gutowsky have found that, as long as one of the three alkyl groups attached to aluminum contains two hydrogens, the aluminum alkyl will dimerize.[2] Then they write the "natural" structure for the dimer as



The $\mathrm{Al}\begin{smallmatrix}\mathrm{H}\\ \mathrm{H}\end{smallmatrix}\mathrm{C}$ distance in the dimer must not greatly exceed 2.5 Å., or the over-all size of the dimer cannot be made to correspond with the gross aspects of electron diffraction data.[6,7,8] The bond cannot be a "protonated double bond," since this would involve very unlikely violation of the octet rule by aluminum. Pitzer and Gutowsky propose that the negative carbon is attracted to the positive aluminum core. The hydrogen atoms between aluminum and carbon must certainly interfere with this attraction. Indeed, the weak $\mathrm{C}\begin{smallmatrix}\mathrm{H}\\ \mathrm{H}\end{smallmatrix}$ dipole has its positive end directed toward aluminum. It is not clear, therefore, that the attraction will be sufficient to lead to an Al–C distance only 0.5 Å. greater than the normal, covalent distance. The polar nature of this bond is not unlike the hydrogen bond, but it seems unlikely that it can be so strong as a hydrogen bond between very electronegative elements. It is, therefore, difficult for this writer to believe the bond will have sufficient energy to overcome the decrease in entropy accompanying dimerization,

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(5) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1945, p. 179.

(5a) The referee has pointed out that trimethylboron also forms less stable complexes with trimethylamine, indicating less tendency for further bond formation; see Schlesinger, Flodin and Burg THIS JOURNAL, **61**, 1078 (1939).

(6) Davidson, Hugill, Skinner and Sutton, *Trans. Faraday Soc.*, **36**, 1212 (1940).

(7) L. Brockway and N. Davidson, THIS JOURNAL, **63**, 3287 (1941).

(8) Skinner and Sutton, *Nature*, **156**, 601 (1945).

On the basis of the suggestion of this paper no such structures need be assumed. Carbon in the methyl group may use one orbital to bond two atoms in this situation. It has two choices for this. It may use a p-orbital, presumably, in the bridge bond between aluminums, or it may use the p-orbital to bond two of its hydrogens. Actually, there is probably resonance between these choices.

If carbon uses one p-orbital to bond the two aluminums, the bond should tend to be straight, which is impossible because of the repulsion of the methyl in the other bridge bond. In this case, the p-orbital could not be used to best advantage in the resulting "bent" bond.

If, instead, carbon uses two sp^2 hybrid orbitals to form the aluminum bonds and a p-orbital to bond two hydrogens, then aluminum will have a negative formal charge and the two hydrogens will each have a positive formal charge 1/2. This situation is also not favorable, and it is hard to judge which of the cases would predominate. The nuclear arrangements (see below) need not be very different in the two cases, so presumably resonance will occur. Probably neither the bridge bond nor the hydrogen bonds can be exactly characterized as consisting of "half bonds." Nevertheless, it appears that the concept of the use of one orbital to form more than one bond is important in understanding the dimerization.

Bridge models have not been looked upon with much favor by those studying the structure of the aluminum alkyl dimers.[6,7,8] It seems to this writer that the elimination of bridge structures, and even the obtaining of unacceptably low Al–Al distances in ethane-like models, has resulted from the assumption that the radial distribution peak at about 3.3 Å. is due primarily to non-bonded Al–C distances in the molecule.[7] Since no models, making this assumption, can possibly have a large enough Al–Al distance, it seems likely that this radial distribution peak has been misinterpreted, and that the non-bonded Al–C distance is greater than 4 Å., corresponding to another important maximum of the radial distribution curve which is usually neglected in choosing a model.[7]

On the basis of the structure proposed here an approximate model can be given, and though the writer's present circumstances make it difficult to compare this model with electron diffraction scattering curves, the resulting model can be compared with the published radial distribution curve.[7]

Since aluminum forming four bonds will tend to be tetrahedral the carbons in the bridge will tend to lie above and below the plane of the rest of the molecule. The bond angle Al–C–Al will tend to be large for a four-membered ring no matter what sort of orbitals are chosen, so this angle will probably be larger than the C–Al–C angle in the ring. The Al–C distance in the ring should be considerably greater than the sum of the covalent radii, due to the "half bond" structure. The value of the bond distance will depend on which resonating form of the structure predominates. Probably the distance will be greater than 2.1 Å. and less than 2.3 Å. The Al–Al distance will then be greater than 3 Å. but probably less than 3.4 Å. The Al–C bonded distances outside the ring should be normal, *i. e.*, about 2.0 Å.[5] Since the C–Al–C angle in the ring should be less than tetrahedral, that angle outside the ring should be greater than tetrahedral. Al–C non-bonded distances should then be greater than 4 Å.

The final model should have approximately the following important distances: 4 Al–C distances about 2.0 Å., 4 Al–C distances (ring), 2.1 to 2.3 Å., 1 Al–Al distance and 11 C–C distances between 3 and 3.5 Å., 4 Al–C distances (non-bonded) greater than 4 Å., and 4 C–C distances considerably greater than 4 Å. The important Al–H distances will be about 2.6 Å. The important radial distribution peaks are at 2.0, 3.3 and about 4.3 Å., with a smaller peak at 2.6 Å. It would seem that the model proposed here is as consistent with the radial distribution curve as any other of the more successful models.

The bridge in the aluminum alkyl dimer, as suggested here, has much the same geometry and properties as the bridge in the boron hydrides. It will effectively prevent rotation about the Al–Al axis, and has many of the properties of a double bond. To regard it as a type of double bond does not, however, appear attractive.

No doubt a ring bridge of the type described above is quite sterically sensitive. One alkyl group attached to each carbon in the bridge could be directed away from the ring, but two alkyls on each bridge carbon would certainly introduce further strain. It seems quite reasonable that this should lead to instability of the dialkyl-substituted bridge, as observed by Pitzer and Gutowsky.[2]

In this respect it is interesting to consider the configuration at the bridge carbon (see Fig. 2). In one of the resonating forms discussed above a p-orbital is used as a bridge-orbital. The remaining orbitals should hybridize to give sp^2 bonds, directed at 120° in a plane.[9] The p-orbital of the bridge would be normal to this plane. In the other form, sp^2 orbitals would be used to form two bridge orbitals and one to hydrogen. The bond angle in the ring would no doubt be less than the ideal 120°, but the bond to hydrogen should be directed away from the ring. The two hydrogens sharing the p-orbital of carbon should lie on a line normal to the ring. Resonance between these forms should lead to three bonds to carbon in one plane, two in the ring and one directly away from it, and two others above and below the ring directed as shown in Fig. 2. With this configuration it is clear that disubstituted carbons

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(9) See, for example, L. Pauling, ref. 5, Chapter III.

would lead to serious steric interactions with the ring.

It seems worth while to point out that the resonating "half bond" structures described above would be expected to lead to high polarizabilities. This has been noted by Wiswall and Smyth,[10] and its relation to infrared absorption intensities has been discussed by Pitzer and Gutowsky.[2]

Other Alkyl Compounds of Second and Third Group Metals.—Pitzer and Gutowsky[2] feel that their proposal of a "polar" bond in the alkyl dimers may also explain the tendency of second group alkyl compounds to polymerize, since the metal in this case is more electropositive. It would also seem possible to explain this behavior on the basis that second group elements will have more surplus orbitals than third group elements, and polymerization beyond dimerization would be necessary to make most efficient use of these bond orbitals.

According to Pitzer, gallium and indium alkyls do not dimerize. Gallium and indium also do not form interstitial carbides of the type described earlier in this paper. A similar situation seems to obtain generally for the metals of the B subgroups of the periodic table. Apparently these metals do not tend to form "half bonds." To form "half bonds" it is necessary that bond strengths be large, so that there is a tendency for the elements concerned to form as many bonds as possible. Bond strengths of the B subgroup metals with the light elements are apparently insufficient for this purpose.

Discussion

The proposal of "half bonds," or bonding in which one atom forms more than one bond with a single bond orbital, using a single electron pair, has been applied to several types of compounds. The list could be extended. Already the author has met with some success in interpreting the structures of certain types of "interstitial" hydrides, but it seems best to make this the subject of another paper.

In this paper the relation of the present proposal to similar proposals made in the past will not be discussed. It seems sufficient to say that enough proposals have been made concerning electron deficient bonding so that any new proposal must have certain points which parallel previous proposals. It seems to the author, however, that the present proposal is more generally applicable to electron deficient structures, but at the same time is more specific in its nature.

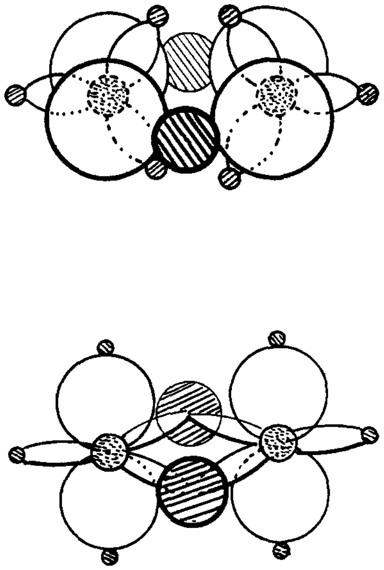

Fig. 2.—Resonating forms of ring of aluminum alkyl dimer. Shaded circles represent, in decreasing order, Al, C and H. Carbon bond orbitals for two possible resonating forms of the ring are shown (unshaded) to illustrate the similarity of ideal nuclear configurations for the two forms. In resonance the nuclei will presumably occupy intermediate positions. Above: Hybrid sp^2 orbitals to hydrogen, p-orbital to aluminums. Below: Hybrid sp^2 orbitals to aluminums and one hydrogen, p-orbital to two other hydrogens.

It also seems to the author that the present proposal departs less from accepted principles of valence, use of usual bond orbitals, etc., than most past proposals. It clearly violates no quantum mechanical principles. The rule that an atom can form only one covalent bond per orbital follows from the quantum mechanical exclusion principle *and* the fact that ordinary bonds contain an electron pair. The exclusion principle demands only that there be but one electron pair per orbital.

Summary

1. It is proposed that under appropriate conditions an atom may form more than one bond using a single bond orbital, and using a single electron pair in the orbital. Some of the "appropriate conditions" for this type of bonding are listed.

2. The proposal is shown to provide an explanation for electron deficient bonding in such diverse compounds as certain types of "interstitial" compounds, the tetramethylplatinum tetramer, the boron hydrides and the aluminum alkyl dimers.

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(10) R. Wiswall, Jr., and C. Smyth, *J. Chem. Phys.*, **9**, 352 (1941).