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MODIFIED LEWIS THEORY
PART 2. COORDINATE AND NONINTEGRAL BONDS

ABSTRACT: The modification to Lewis's theory of valency proposed in Part 1 is extended to molecules containing coordinate bonds. A further modification to the theory is proposed to make it applicable to molecules containing nonintegral bonds (e.g., B_2H_6). [*Chem. Educ. Res. Pract. Eur.*: 2001, *2*, 179-182]

INTRODUCTION

In Part 1 of this series (Nelson, 2001), I showed how Lewis's theory of valency (Lewis, 1916, 1923) can be modified to make it consistent with the results of modern quantum-mechanical calculations on molecules containing polar covalent bonds and hypervalent atoms. This is by distinguishing between the valence shell (VS) of an atom and the Lewis shell (LS). The former has a capacity limited by the number of valence orbitals, while the latter can be larger, and accommodate the number of electrons proposed by Lewis. In this part, I show how the same modification helps in the treatment of molecules containing coordinate bonds, and present a further modification for molecules containing nonintegral bonds.

COORDINATE BONDS

Lewis postulated that bonds can be formed by an atom (X) sharing a pair of its electrons with another atom (Y), the former acting thereby as an electron donor and the latter as an electron acceptor:

$$X: + Y \rightarrow {}^+X:Y^- \qquad (1)$$

The resulting bond has been variously called a "coordinate link", "dative bond", "dipolar bond", and (because it comprises one covalent bond and one electrovalent bond) "semipolar double bond" (Gold et al., 1987). Sidgwick (1927) gave it the symbol $X \rightarrow Y$.

Quantum-mechanical calculations, however, indicate that the extent to which process 1 takes place varies widely. This is shown in Table 1, where I have brought together the results for a variety of bonds. The extent of charge transfer varies from 100% down to 0%.

That the degree to which process 1 takes place should vary is not in itself surprising. Chemists have long recognized that the degree of donation in, for example, $Ne \rightarrow BF_3$ is much less than in $H_3N \rightarrow BF_3$. They have also recognized that the degree of donation in ions like $[Ca(OH_2)_n]^{2+}$ is relatively small, the bonding arising mainly from electrostatic interaction between Ca^{2+} and $O^{\delta-}$.

TABLE 1: *Extent of charge transfer in coordinate bonds.**

Bond	Charge Transfer
$H_3P\rightarrow O$	~100%
$H_3N\rightarrow O$	~70%
$H_3N\rightarrow BH_3$	~20%
$F^-\rightarrow Al^{3+}$	~20%
$H_2O\rightarrow M^{3+}$ (M = Sc–Ga)	10–20%
$H_2O\rightarrow M^{2+}$ (M = Ca–Zn)	0–10%
$F^-\rightarrow BF_3$	~0%
* Sources: see Appendix.	

What is surprising about the results in Table 1 is the low degree of charge transfer in $F^-\rightarrow BF_3$. This arises because of the high polarity of the bonds in BF_3. Calculations give the charge distribution as about $B^{2+}(F^{2/3-})_3$ (Appendix). Thus if no sharing of electrons takes place, a bond can form by Coulombic attraction between F^- and B^{2+}. On the other hand complete sharing of an electron pair on the F^- ion to form a covalent bond would give $F:B^+$ and eliminate the Coulombic attraction. Calculations give the charge distribution in BF_4^- as about $B^{2+}(F^{3/4-})_4$, with the boron atom having almost exactly the same charge number as in BF_3 (Appendix). Thus in the process $F^- + BF_3 \rightarrow BF_4^-$, while there is a redistribution of charge among the fluorine atoms ($F^- + 3F^{2/3-} \rightarrow 4F^{3/4-}$), there is very little donation of electrons from F^- to B. This explains why the isoelectronic Ne atom is unable to form a stable adduct with BF_3.

These findings challenge the accepted conception of a coordinate bond. According to the above analysis, in $F^-\rightarrow BF_3$ the arrow is misleading: F^- is not a donor, BF_3 is not an acceptor, and there is no donation (except from F^- to $3F^{2/3-}$). We cannot say, as textbooks do, "boron trihalides readily add a halide ion to give an eight-electron species".

However, the distinction between VS and LS helps us again here. While the number of electrons in VS is affected by the polarity of bonds, the number in LS is not (Nelson, 2001). The above analysis has been entirely in terms of VS. In terms of LS, the boron atom in BF_3 has six electrons, and in BF_4^- eight. In the process $F^- + BF_3 \rightarrow BF_4^-$, therefore, the F^- ion has indeed acted as a donor, the BF_3 as an acceptor, there has been donation, and the symbol $F^-\rightarrow BF_3$ is appropriate. We can say after all that BX_3 adds X^- to give an 8-electron species.

Lewis's theory for coordinate bonds can therefore be recovered, provided that "valence shell" is replaced by "Lewis shell", and process 1 by

$$X: + Y \rightarrow {}^{\delta+}X: Y^{\delta-} \tag{2}$$

where the extent of donation (δ) and order of the bond (2δ) are left open to calculation.

NONINTEGRAL BONDS

Lewis had great difficulty in applying his theory to molecules like diborane and benzene for which a classical bond structure with integral bonds cannot be drawn (Lewis, 1923). This was probably because the concept of a nonintegral bond had not then been developed. It is now known that the basic valency rule

$$\sum_Y n\,(XY) = v(X) \tag{3}$$

holds for nonintegral bonds as well as integral ones (Nelson, 1997). Here $v(X)$ is the valency of X and $n(XY)$ is the bond number of the bond between X and Y. Thus for diborane, eq 3 gives $v = 3$ for the boron atoms and 1 for the hydrogen atoms if $n = 1$ for the terminal bonds and ½ for the bridging ones, as in the formula:

$$\begin{array}{ccccc} \text{H} & & \text{H} & & \text{H} \\ & \text{B} & & \text{B} & \\ \text{H} & & \text{H}_{0.5} & & \text{H} \end{array}$$
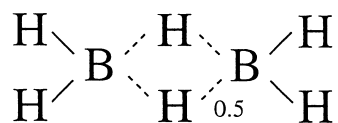
Similarly for benzene eq 3 gives $v = 4$ for the carbon atoms if $n = 1{\cdot}5$ for the carbon-carbon bonds. Bond number (n) must be distinguished from bond order (n'). The former denotes the number of valencies satisfied by a bond, the latter measures the strength of a bond relative to bonds having an integral bond number (Pauling, 1960). For the CC bonds in benzene, $n' \approx 1{\cdot}7$.

Other examples of nonintegral bonds are given in Table 2. Aluminium nitride and magnesium oxide belong to the series SiC, AlN, MgO, and NaF along which ionic character is expected to increase. Aluminium nitride has the wurzite structure with coordination numbers of four; the bond number of the aluminium-nitrogen bonds is accordingly ¾. This can be divided into covalent and ionic components, but the total is independent of ionicity (Nelson, 1997). Magnesium oxide has the sodium chloride structure with coordination numbers of six and hence a bond number of 2/6 or 1/3. Theoretical chemists are divided over whether this compound is completely ionic (Vidal-Valat et al., 1978; Causa' et al., 1986). The perlithiated molecule CLi_6 is octahedral. To get $v(C) = 4$ the carbon-lithium bonds must have $n = 2/3$; to get $v(Li) = 1$ there must also be a cage of lithium-lithium bonds with $n = 1/12$. This formulation accords with quantum-mechanical calculations (Reed & Weinhold, 1985).

TABLE 2: *Examples of nonintegral bonds.*

Species	Bond	Bond Number
B_2H_6	B(μ-H)	0·5
C_6H_6	CC	1·5
NO_2^-	NO	1·5
HF_2^-	HF	0·5
$(AlN)_\infty$	AlN	0·75
$(MgO)_\infty$	MgO	0·33
CLi_6	CLi	0·67
	LiLi	0·08

Lewis's theory can readily be extended to molecules of this kind if it is supposed that electrons can bind more than two atoms together, by spending a fraction of time between each pair. This can be indicated by using smaller or coloured colons, as in the following formula for B_2H_6:

$$\begin{array}{ccccc} \text{H} & & \text{H} & & \text{H} \\ & \text{B} & & \text{B} & \\ \text{H} & & \text{H}_{0.5} & & \text{H} \end{array}$$
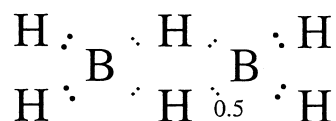
The colons indicate, as in other Lewis structures, that the electrons concerned share the same kind of motion, but when one is between one pair of atoms, the other will generally be between another pair.

The concept of a fractional bond pair corresponds exactly to that of a fractional bond. In Lewis's theory the bond pairs around an atom sum to v just like the bond numbers (eq 3). The value of the bond pairs in formulae is therefore automatically given by n, as in the above formula for B_2H_6.

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APPENDIX: SOURCES OF DATA

Charge distributions in BF_3, BF_4^-, and AlF_6^{3-} are from Robinson et al. (1997). I have scaled these as explained in Part 1. The remaining data are from Umeyama & Morokuma (1976), Wallmeier & Kutzelnigg (1979), and Åkesson et al. (1994). All the values are very approximate, being dependent on basis set and method of partitioning used.

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