

## Short Communications

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**The chromium-carbon bond length in chromium hexacarbonyl.** By LINUS PAULING, *Institute for Physical Problems and Departments of Chemistry and Biology and Physics, University of California, San Diego, La Jolla, California 92037, U.S.A.*

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A discussion of the electronic structure of chromium hexacarbonyl by the semi-empirical valence-bond method is shown to lead to the conclusion that the bonds have about fifty per cent double-bond character, and that the bond length would accordingly be expected to be about 0.10 Å less than the single-bond length for  $d^2sp^3$  hybridization, 2.02 Å, and accordingly in agreement with the observed bond length, 1.916 ± 0.003 Å.

A recent paper (Whitaker & Jeffery, 1967) communicating a redetermination, with increased accuracy, of the bond lengths in chromium hexacarbonyl begins with the following two sentences: 'The valence bond theory and the molecular orbital theory predict different results for the chromium-carbon bond in chromium hexacarbonyl. The former suggests that the bonding consists of six  $\sigma$  hybrid bonds alone, giving a bond order of unity, while the latter suggests that there may in addition be  $\pi$  bonds which would increase the bond order to a maximum of 1.5'.

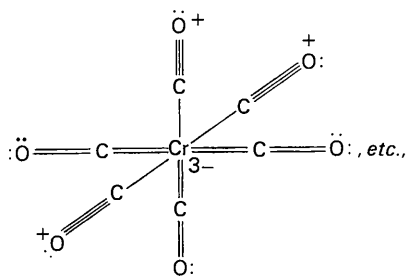
At the end of their paper the authors state that the observed bond length (1.916 ± 0.003 Å, corrected for thermal vibration; 1.909 Å, uncorrected) is smaller than the value to be expected for a chromium-carbon single bond, about 2.02 Å, that this difference must presumably be due to partial double-bond character, and that this is in agreement with molecular-orbital theory. The suggestion that it is not in agreement with valence-bond theory is not justified, and the initial statement that valence-bond theory leads to a structure with single bonds only is incorrect. Instead, for this molecule valence-bond theory leads to the definite conclusion that the bonds have fifty per cent double-bond character.

In my books (Pauling, 1939, p.234; 1940, p.253; 1960, p.335; 1967, p.180) the statement is made that the electron diffraction investigation of chromium hexacarbonyl (Brockway, Ewens & Lister, 1938) leads to the chromium-carbon bond length 1.92 Å, which is about 0.10 Å less than the value for a single bond, indicating that the bond has some double-bond character. A structure for chromium hexacarbonyl in which the chromium atom is bonded to the six surrounding carbon atoms by single bonds would not correctly be assigned to the molecule on the basis of the valence-bond theory. With such a structure the chromium atom would have associated with it six unshared electrons in the outer shell plus one electron for each of the single bonds, if the covalent bonds are bonds with no ionic character. Such a structure leads to a formal electrical charge of six units (negative) on the chromium atom, and is accordingly unacceptable, because of the violation of the electroneutrality rule (Langmuir, 1921; Pauling, 1948), which requires that the electric charge on each atom in a

stable structure differ from 0 by no more than one unit. The electronegativity difference of chromium (electronegativity 1.6) and carbon (electronegativity 2.5) corresponds to only 19% double-bond character, which would reduce the charge on the chromium atom from 6- to 5-; no reasonable amount of partial ionic character of the single bonds would lead to agreement with the electronegativity principle.

It was an argument of this sort, by Irving Langmuir, over forty-five years ago (Langmuir, 1921), that led to the initial assignment of double-bond character to the metal-carbon bonds in the metal carbonyls. Langmuir pointed out that the formal charge on the nickel atom in nickel tetracarbonyl would be 4- if the nickel atom formed single bonds with the four carbon atoms, and stated that this multiple electric charge on the nickel atom could not be considered acceptable. He pointed out that a structure with double bonds from the nickel atom to each carbon atom and double bonds from each carbon atom to the adjacent oxygen atom would assign zero formal charges to every atom, including the nickel atom. When Brockway & Cross (1935) made the electron-diffraction determination of the value of the bond length as 1.82 ± 0.03 Å they interpreted this result as showing that the bonds have a large amount of double-bond character. [Their value of the bond length is in agreement with the X-ray crystal-structure value, 1.84 Å (Ladell, Post & Fankuchen, 1952).] The difference in electronegativity of nickel and carbon, 0.07, corresponds to 12% ionic character of nickel-carbon bonds. Electroneutrality results from a total of seven bonds (three double bonds and one single bond) resonating among the four positions. It is a structure of this sort, with considerable double-bond character to the bonds, that is to be assigned to nickel tetracarbonyl by the valence-bond theory, and the structure is compatible with the observed bond lengths.

Similarly, the valence-bond theory leads to the assignment to chromium hexacarbonyl of a structure in which each of the six bonds has 50% double-bond character. This structure requires use in bonding of all nine outer orbitals ( $d^5sp^3$ ) of the chromium atom. There are twenty valence-bond structures of this sort,



and the normal state of the molecule is represented by the symmetrical resonance hybrid of the twenty structures, making nearly equal contributions. The formal charge of the chromium atom for these structures is  $3-$ . To be compatible with the electroneutrality principle, the structure would have to involve ionic character of the bonds great enough to neutralize two of the three negative charges. The amount of ionic character required is 22%, close to the value, 19%, that corresponds to the difference in electronegativity of chromium and carbon. It is accordingly likely that other structures, with a smaller amount of double-bond character, do not contribute, and that the six chromium-carbon bonds in the molecule are to be assigned 50% double-bond character.

The discussion of the bond length can be made with reasonable confidence. Whitaker & Jeffery (1967) pointed out that I had assigned the values 1.21, 1.22, and 1.23 Å, respectively to  $Ni^{IV}$ ,  $Co^{III}$ , and  $Fe^{II}$  as the octahedral covalent radii for  $d^2sp^3$  bonds, with three unshared electron pairs for each atom (Pauling, 1939, p. 169). The electronic structure of the chromium atom with oxidation number 0 and forming six covalent bonds is isoelectronic with that of these atoms, permitting the linear extrapolation of the values to the value 1.25 Å to be made with confidence. With the single-bond radius 0.77 Å for carbon, this leads to 2.02 Å for the chromium-carbon single bond length corresponding to such a structure.

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**Crystalline americium trihydroxide.** By W. O. MILLIGAN and M. L. BEASLEY, *Baylor University, Waco, Texas, U.S.A.* and M. H. LLOYD and R. G. HAIRE, *Oak Ridge National Laboratory\*, Oak Ridge, Tennessee, U.S.A.*

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Aging of amorphous precipitated hydrous americium gel under water yields rod-like or scroll-like particles of hexagonal  $Am(OH)_3$  ( $a = 6.426 \pm 0.002$ ,  $c = 3.745 \pm 0.002$  Å) isostructural with  $Nd(OH)_3$  ( $a = 6.422 \pm 0.002$ ,  $c = 3.742 \pm 0.002$  Å).

The addition of alkali to a trivalent americium salt solution yields a gelatinous precipitate, which, when washed and dried rapidly at room temperature, exhibits an amorphous type electron diffraction pattern, and which has been shown by electron microscopy to consist of particles about 15–20 Å in diameter (Milligan, Chetham-Strode & Keller, 1963).

In view of the fact that hydrous neodymia is amorphous under like conditions, becoming crystalline to form  $Nd(OH)_3$  on aging under water after several hours, it was suggested

The equation  $D(n) = D(1) - 0.60 \text{ Å} \log n$  (Pauling, 1960, p. 400) gives the correction  $-0.104 \text{ Å}$  for 50% double-bond character, and accordingly leads to an expected bond length about 1.91 Å in chromium hexacarbonyl, in satisfactory agreement with the observed bond length. There exists an uncertainty of about 0.03 Å in the correction for double-bond character, but the conclusion is nevertheless justified that the observed bond length in this molecule has very nearly the value expected from valence-bond theory.

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(Milligan & Dwight, 1965) that hydrous americium might exhibit a similar behavior. Such results would be of interest in providing additional information concerning the expected similarity of the lanthanides and the actinides.

A sample of hydrous americium gel was prepared from highly pure  $Am(NO_3)_3$ . Isotopic analysis by mass spectrometry established the americium to be  $^{241}Am$  with < 5 ppm of other isotopes, and cation impurities were determined to be less than 0.5%, the principal impurity being ~0.2% cerium. The gel was prepared by the addition of 0.06 M americium nitrate solution that was 2.2 M in  $HNO_3$  to a threefold excess of 10M  $NH_4OH$ . The precipitate was