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Registry No. I, 20734-58-1; II, 71138-60-8; [(1,8-bis(dimethylamino)naphthalene)BF_2]$^+$[BF_4]$^-$, 71138-62-0; (1,8-bis(dimethylamino)naphthalene)decaborane(14), 71129-90-3; (1,8-bis(dimethylamino)naphthalene)pentaborane(9), 71129-91-4; B_2H_6, 19287-45-7; BF_3, 7637-07-2; B_5H_9, 19624-22-7; $B_{10}H_{14}$, 17702-41-9.

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Correspondence

Metal–Metal Bonding in Transition-Metal Compounds

Sir:

The characterization of binuclear transition-metal complexes containing "short" metal–metal bonds has provoked much activity recently in both experimental and theoretical chemistry.[1] Binuclear complexes are known for most transition elements, but those containing the Cr_2 unit have been of particular interest since they show a wide variation in metal–metal bond lengths (several species have $R_e < 1.9$ Å) and their electronic structure is amenable to theoretical investigation via MSW–SCF–Xα and conventional CI procedures.[2] Molecules and solids containing dimers or larger aggregates of transition-metal atoms are however difficult to treat accurately by quantum chemistry techniques because of the important electronic effects associated with the incomplete atomic d-electron shells. In this situation one may fall back on a more qualitative discussion of bonding in such systems. One way of thinking about compounds containing metal–metal bonds is to take as reference systems one or more homonuclear transition-metal systems in which the bonding factors are well understood and try to assess the effects of ligands as changes in the electronic environment of the metal–metal bonds.

Reasonably accurate molecular orbital theories exist for only two homonuclear transition-metal systems, namely, the perfectly periodic bulk metals M_∞[3,4] and the diatomic molecules M_2 of the 3d transition elements.[5] In this paper, I suggest that, for complexes in which the metal formal oxidation state is low ($\leq +2$) and ligand–ligand repulsions do not have a dominating effect on structure, the systems M_2 and M_∞ can serve as useful reference points in a discussion of metal–metal bonding in transition-metal compounds. An important qualitative bonding principle, which offers the basis for a working hypothesis for all systems containing aggregates of transition-metal atoms,[6] has emerged from these recent detailed MO studies: simply put, it suggests that structural properties of metal–metal bonds are the result of the competition of *attractive* forces between adjacent transition-metal atoms due to the metal d electrons and repulsive forces due to the overlap of metal s (p) electrons with the adjacent metal atom cores, provided that one is dealing with low-spin systems. In high-spin systems of large multiplicity and in bulk ferromagnets, the spin correlation energy, which acts as an effective repulsive force, must also be considered.

The cores of transition-metal atoms occupy a significant fraction, η, of the equilibrium atomic volume ($0.2 \leq \eta \leq 0.35$) compared with s,p-bonded metals ($\eta < 0.1$). As a result the bottom of the conduction band in transition metals, which corresponds to the lowest s,p-bonding (valence) MO in a molecule, may be close to or even above the s-orbital energy of the free metal atom when the solid is near its equilibrium volume: hence as one puts electrons into the s,p band, the system is destabilized relative to the free metal atoms.[3] On the other hand for partially filled "d bands", the d-electron interactions are strongly attractive and become more so rapidly as the internuclear distance R decreases (the cohesive energy due to the d electrons varies roughly as $1/R^5$).[3,6] The equilibrium structure occurs when these two opposing forces cancel one another. The bonding between transition-metal atoms is thus rather different from that encountered with main-group elements. Usually we argue that large orbital overlap is directly related to significant net bonding for incomplete shells, but this qualitative argument is spoiled in transition metals because it fails to take into account the large destabilizing energy shifts due to the core repulsion experienced by the s,p electrons in structures near equilibrium atomic volume.

Local density functional calculations on the 3d diatomic molecules have suggested a similar picture of metal–metal bonds in M_2 systems.[5] At large separations, bonding 4s-like orbitals provide an attractive force which, neglecting the effects of spin correlation and d electrons, would give a bonding contribution varying from ~0.5 eV (K_2) to ~2 eV (Cu_2), the increase resulting from the contraction of the outer parts of the 4s orbitals. As d-orbital overlap becomes substantial, an additional force draws the nuclei together and increases the binding energy, provided that the molecular orbitals of d-orbital parentage are incompletely filled—thus this remark does not apply to the dimers of the group 1B metals (d^{10} systems). The equilibrium separation is determined by the point where this force, together with the s (p) force, which becomes repulsive at small R due to core penetration, balances the electrostatic repulsion due to incomplete screening of the

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nuclei. At the beginning and end of the 3d transition series, the calculated[5] equilibrium internuclear distances R_e are shorter than the nearest-neighbor distance in the bulk, especially at the right-hand end of the series, e.g., for Fe_2, Co_2, and Ni_2, $R_e = R_{bulk} - (0\text{–}4\ \text{Å})$. The binding in these systems is accordingly attributed to the overlap of the d orbitals since at these short distances core penetration cancels out most of the energy gain from the strong overlap of the 4s orbitals. On the other hand, in the middle of the series the half-filled, high-spin atomic d shell gives rise to repulsion like a closed shell, and Cr_2 for example is thought to have a large R_e value with only a single bond of s-electron character—it is just too expensive in energy to flip the d-electron spins to make additional bonds. Accordingly, the theoretical interpretation of the common occurrence of Cr_2L_n complexes (low spin) with short Cr–Cr bonds is that in going from Cr_2 to Cr_2L_n the difference is that ligands (L) can move the metal s- (p-) electron density out into the metal–ligand bonds: the attractive d-electron force between the metal centers is then sufficient to overcome the spin-correlation energy and the Cr–Cr bond contracts dramatically with respect to high-spin Cr_2.

While the spin-correlation energy seriously complicates a full theoretical treatment of the M_2 systems (especially the estimation of binding energies), this is less of a problem in bi- and polynuclear metal compounds where the spins may be saturated by the extra bonds and low-spin states are common. Hence in choosing a homonuclear metal reference system to which some M_nL_m complex may be related, one must pay attention to the spin states of the two systems since the spin-correlation energy can be an important factor providing an effective repulsive interaction. In the homonuclear diatomic molecules one can say that relative to the bulk metal the repulsive s- (p-) electron forces can be substantially alleviated as the s-electron density "spills out" into empty space, and in systems of small spin multiplicity one *expects* contraction of the bond under the influence of the attractive d-electron force. I thus believe that the competition between attractive d-electron forces and repulsive s- (p-) electron forces is the principal factor governing the stereochemistry of metal–metal bonds. This principle can be generalized to the statement that metal–metal bond length variation in bi- and polynuclear transition-metal compounds should be a reflection of the ability of the ligands to remove the s- (p-) electron density from the vicinity of the metal atom (so as to reduce core penetration at the metal atom sites), leaving d-electron bonds that are much like those found in the bulk metal and metal diatomics: implicit in this view is that the d-electron density is not changed too much by ligation, i.e., that the d electrons only play a relatively minor role in ligand bonding, and this seems consistent with ESR measurements on transition-metal complexes. Other things being equal, one thus expects ligands that are Lewis acids to be associated with shorter metal–metal bonds than are basic ligands.

An illustration of these remarks can be found in the structural systematics of transition-metal carbonyls containing two or more metal atoms. In the conventional synergic bonding mechanism, the carbonyl 5σ orbitals donate electron density to the metal unit, while electron density is pushed off the cluster through hybridization between the metal $d\pi$ orbitals and the carbonyl 2π levels. The carbonyl 5σ orbital is a sp-hybrid orbital, and so this bonding mechanism implies that the sp-electron density at each metal atom is enhanced as carbonyl ligands are brought up to the metal cluster, but there is no compensating increase in d-electron density. Hence we may expect metal carbonyls to have longer metal–metal bond lengths than in the corresponding homonuclear metal systems, although this comparison may be upset by the spin-correlation energy balance in the middle of the transition-metal series (it ought to be valid for the group 8 metals where polynuclear metal carbonyls are found[7]). The carbonyl shell round the metal unit can also be thought of as a layer of dielectric (insulating) material, and so in comparison with a metal cluster embedded in bulk metal, it is reasonable to presume that the metal cluster sp electrons are more confined in metal cluster carbonyls than in the bulk metals: one thus also expects metal–metal bond lengths in cluster carbonyls to be greater than in the bulk metals. Consideration of the fragmentary structural data on M_2 systems, the structural systematics of the bulk metals, and the data for metal carbonyls shows these expectations to be borne out in practice.[6] Moreover the exceptional structures of the "two-dimensional" cluster carbonyls $M_3(CO)_6^{2-}$ (M = Ni, Pt)[7] and oligomers of this planar fragment can also be simply understood from this point of view: in these systems the metal sp electrons are *not* confined by ligands above and below the molecular plane, and so just as I have argued for the homonuclear metal dimers, some of the repulsive sp force between metal atoms can be relieved by the sp-electron density spilling out into the vacuum. As a result the M–M bonds in the $M_3(CO)_6$ unit are significantly shorter than in the bulk metals, and this remains true in the oligomers $[M_3(CO)_6]_n^{2-}$, n, > 1, in which interfragment M–M bonds are significantly longer than in the bulk metals.[6,7]

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Additions and Corrections

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Ronald F. Ziolo* and Jan M. Troup: Threefold Configuration Tellurium(IV). Crystal Structure of Trimethyltelluronium Tetraphenylborate.

Page 2271. The superscript "1" should not appear behind Ronald F. Ziolo's name. His corresponding address is: Xerox Corp., Webster Research Center, Webster, NY 14580.—Ronald F. Ziolo