methanol the dissociated dinitrophenolate–metaphosphate pair collapses back to dinitrophenyl phosphate faster than the rate at which the acceptor methanol can diffuse away, then the forward reaction will necessarily follow the preassociative path (see Scheme I). The heterolytic cleavage may still be rate limiting, but only when the acceptor is positioned appropriately (preassociatively) to receive the phospho group will heterolysis lead to products. The stereochemical data reported here require that if the word "metaphosphate" is used to describe the nature of phosphorus and its associated ligands in the intermediate of such monoester solvolysis, it be recognized that the "metaphosphate" may suffer only two fates: collapse back to reform the starting material of unchanged configuration at phosphorus or reaction forward to form product with inversion at the phosphorus center.

Registry No. Phenyl [(R)-^{16}O,^{17}O,^{18}O]phosphate, 80630-84-8; methyl [(S)-^{16}O,^{17}O,^{18}O]phosphate, 80630-85-9; 2,4-dinitrophenyl [(R)-^{16}O,^{17}O,^{18}O]phosphate, 80630-86-0; 2,4-dinitrophenyl [(R)-^{16}O,^{17}O,^{18}O]phosphate mono-2,6-lutidinium salt, 80630-89-3; 1-S-[^{16}O,^{17}O,^{18}O]phospho-(S)-propane-1,2-diol, 80630-90-6.

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A Theoretical Study of the Cr–Cr Quadruple Bond

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Recently there has been a great deal of interest both experimentally and theoretically on binuclear transition-metal compounds that are characterized by quadruple bonding, or so-called "δ" bonding.[1] Many of these compounds have now been reported, but we would like here to focus on those cases involving two d^4 transition-metal atoms. Their bonding is generally represented as in Figure 1. This figure shows eight ligands such as $M_2Cl_8^{4-}$ or $M_2(CH_3)_8^{4-}$ in an eclipsed conformation. In addition there are very many bridged compounds involving OCO (as acetate, formate, etc.) and NCO (aminato) bridging ligands. Fifth- and sixth-position ligands (along the z axis of the figure) are also common and are suspected of influencing the metal–metal bond. The dimolybdenum compounds generally have bond lengths between 2.0 and 2.2 Å, while the dichromium compounds show a wide variety of lengths from the "super short" bond length of about 1.85 Å to the "super long" bond length of about 2.6 Å.[2] For comparison the metal–metal bond in metallic chromium is 2.3 Å. In spite of the super short lengths reported, the ligands are
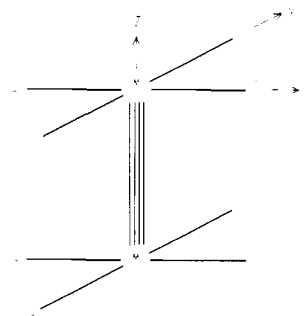
(1) See, for example, F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975); F. A. Cotton, *Acc. Chem. Res.*, **11**, 225 (1978); F. A. Cotton, *Pure Appl. Chem.*, **52**, 2331 (1980).
(2) F. A. Cotton, W. H. Ilsley, and W. Kaim, *J. Am. Chem. Soc.*, **102**, 3464 (1980).
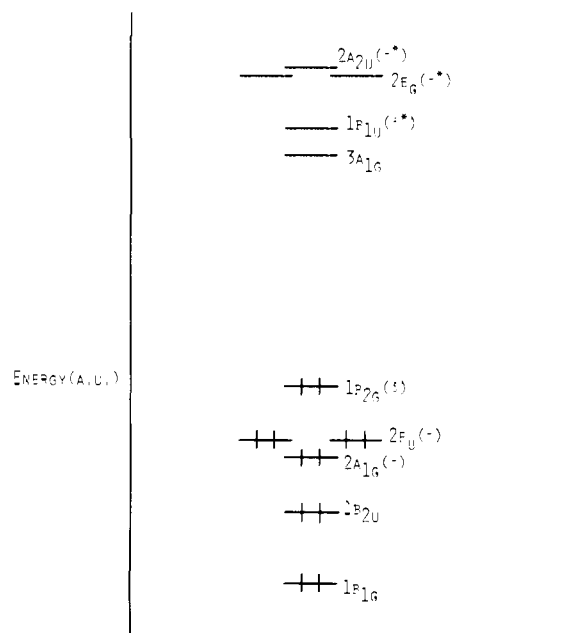
Figure 1. "Quadruple bond".

Figure 2. Frontier molecular orbitals for $Cr_2Cl_8^{4-}$ obtained from the symmetry- and spin-restricted procedure.

always eclipsed. Since this arrangement places the ligands closer than suggested by their van der Waals radii, one would expect steric crowding to be an important effect. These compounds are generally diamagnetic and are characterized by a weakly allowed z-polarized transition, the energy of which is sensitive to the metal–metal bond length as well as the electronic properties of the ligands.[3]

The bonding in these complexes was first examined by Cotton[4] and described in terms of bonding (and antibonding) orbitals of the form

$$\sigma = 2^{-1/2}(d_{z^2}(A) + d_{z^2}(B))$$

$$\pi = 2^{-1/2}(d_{xz}(A) + d_{xz}(B))$$

$$\pi' = 2^{-1/2}(d_{yz}(A) + d_{yz}(B))\delta = 2^{-1/2}(d_{xy}(a) + d_{xy}(B))$$

where A and B are the two metal atoms. The fourth or δ bond is the in-phase combination between the two d_{xy} orbitals with lobes that bisect the LXL angle of Figure 1. These bonds are shown in Figure 2; the molecular orbital picture inferred by Cotton[4] is given as Figure 3. The $d_{x^2-y^2}$ atomic orbitals interact with the ligands and are found at much higher energy.

On the other hand, it has been long known that this simple idea could not explain many of the known properties of the Cr–Cr systems. Most damaging was the observation that the singlet excitations of the δ→δ* type should be strongly allowed and at

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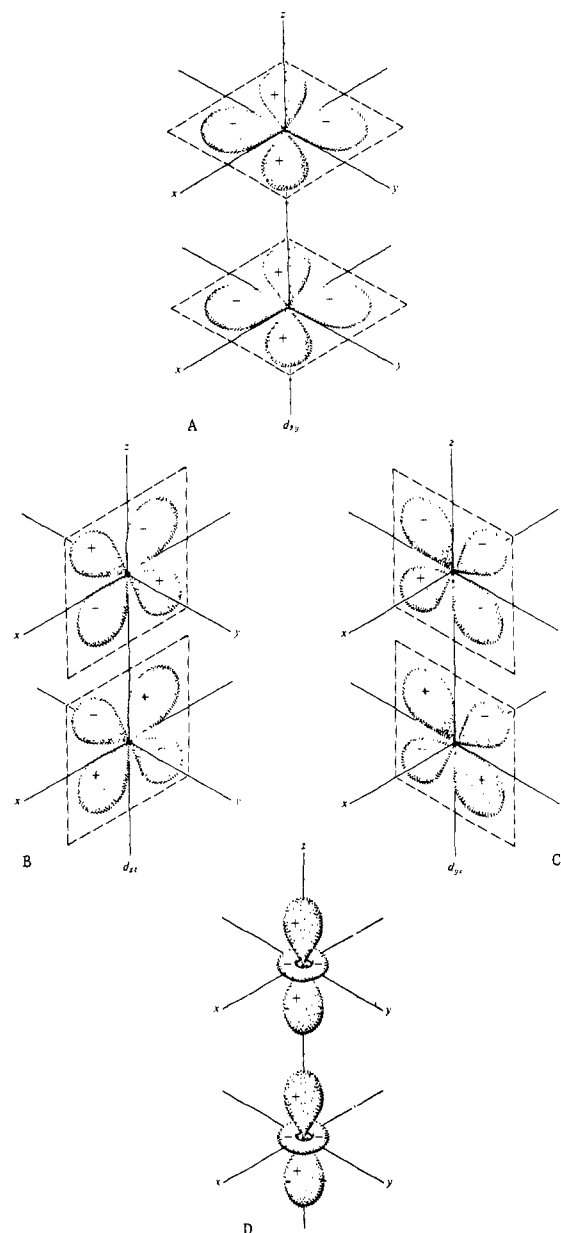
Communications to the Editor

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Figure 3. "d" bonding molecular orbitals obtained from the symmetry-restricted procedure.
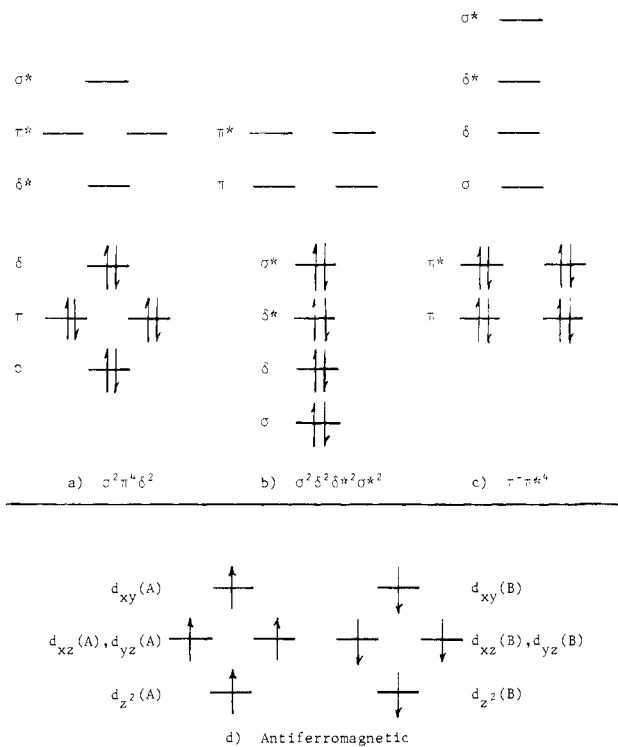

Figure 4. Dominant configurations of this study: a, the orbitals of Figure 2; a, b, and c obtained from the orbitals pictured in Figure 3. The orbitals of d are completely localized on either atom A or atom B.

high energy, and the corresponding triplet would lie well below the singlet represented in Figure 2, contrary to the experimentally observed diamagnestism.[1] Preliminary work by this group suggested an alternative approach to this problem. Several years ago it was noted[5] that performing a simple 2×2 configuration interaction between the δ-bond state of Figure 2 and the doubly excited state $(\delta\delta \rightarrow \delta^*\delta^*)$ lowered the energy nearly 180 kcal/mol. The resultant two-determinant wave function suggested a valence-bond description might be more appropriate. This is not surprising since the overlap between two d_{xy} orbitals at the Cr–Cr bonding distance is less than 0.01. This corresponds to a hydrogen molecule with a bond length of nearly 3.5 Å. At this distance the hydrogen molecule consists mostly of localized hydrogen atoms. This description of H_2 is not possible within MO theory unless one includes the doubly excited state $|\sigma^*\sigma^*|$ along with the reference state, $|\sigma\sigma|$[6]

After examining this question further, we report here preliminary results on the dichromium system, using the INDO model,[7]

that suggest that previous studies on these complexes may not be complete. At the self-consistent field molecular orbital level we examined the configurations shown in Figure 4. In this figure the δ-bond state is labeled $\sigma^2\pi^4\delta^2$. The $\sigma^2\delta^2\delta^{*2}\sigma^{*2}$ configuration of Figure 4b we find much lower than the δ-bonded state, as did Benard.[8] By far the lowest energy is obtained by a UHF calculation without spin or space restrictions. The orbitals obtained from this calculation are completely localized, with four α-spin electrons on Cr(A) and four β-spin electrons on Cr(B). This picture corresponds to two antiferromagnetically coupled chromium centers and formally should have a value of $\langle S^2 \rangle$ equal to 4 $(s_z = 0)$. The calculated value for $\langle S^2 \rangle$ for a Cr–Cr bond length of 3.0 Å is 3.996. The corresponding eight open-shell nonet $(s_z = 4)$ is everywhere higher in energy than the antiferromagnetic state, demonstrating that the weak antiferromagnetic coupling is stronger than the Hund's rule stability. Figure 5 summarizes these results. All of the curves appear to be very shallow; a 0.8-Å change about the minimum in any curve costs no more than 6 kcal/mol. This feature was also noted by Benard[8] and may be responsible for the wide variations in bond lengths.

We have performed geometry optimizations at the SCF level on $Cr_2Cl_8^{4-}$ and $Cr_2(CH_3)_8^{4-}$ that indicate the preferred conformations are eclipsed, as is generally observed. In addition we have performed extensive configuration interaction (CI) calculations that include all the configurations shown in Figure 4. It should be noted that the antiferromagnetic state is quadruply excited relative to the δ-bonded state and can only couple to it via doubles. In addition we note that a singles- and doubles-only CI from closed-shell reference functions[8] cannot completely generate the antiferromagnetic situation which has eight open-shell orbitals. The results of our CI calculations indicate that the antiferromagnetic description is dominant and that there exists no covalent bonds between the two Cr atoms. Much of the stability of $Cr_2Cl_8^{4-}$ relative to monomeric dissociation is associated with the presence of four positive countercharges located anywhere reasonable within the complex: $Cr_2(CH_3)_8^{4-}$ is stable even in the absence of countercharges.[9] Experimentally the former is not known to exist,

(5) M. C. Zerner and A. D. Bacon, presented at the Sanibel Symposia, 1977; see also W. C. Trogler, *J. Chem. Ed.*, **57**, 424 (1980).

(6) J. A. Pople, observations to ref 5.

(7) A. D. Bacon and M. C. Zerner, *Theor. Chim. Acta*, **53**, 21 (1979).

(8) M. Benard, *J. Am. Chem. Soc.*, **100**, 2354 (1978).

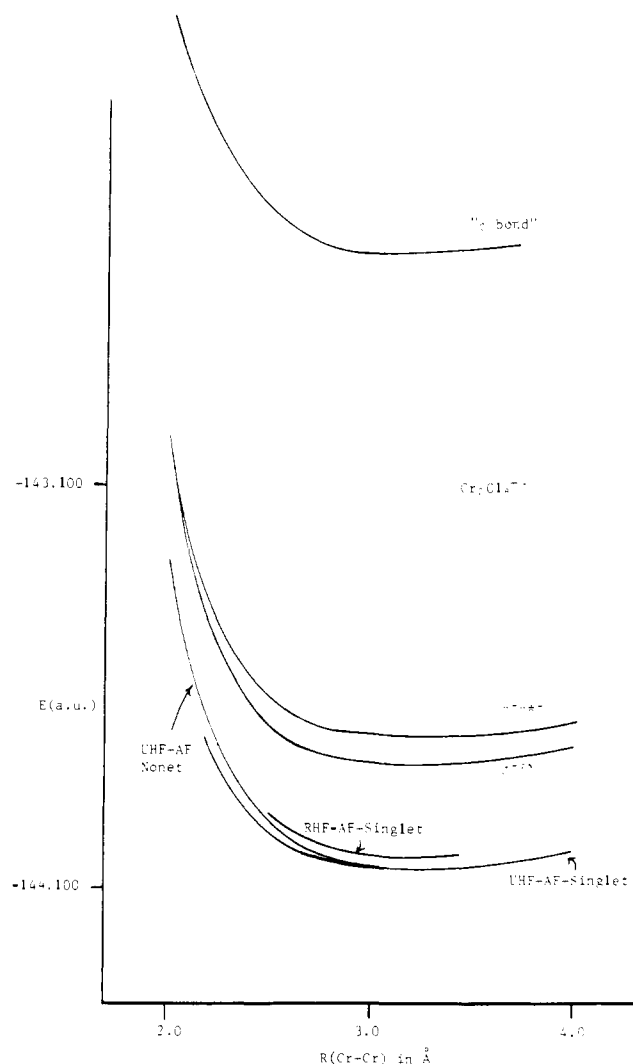(9) A more complete report on the studies reported here is in preparation.

Figure 5. Summary of results for calculations on $Cr_2Cl_8^{4-}$ see text.

while the latter is well characterized.[10]

Although the minimum of our potential is between 2.5 and 3.5 Å for any reasonable choice of four point charges or four Li atoms and these potential energy curves are relatively flat, experimental bond lengths are shorter and are reported between 1.85 and 2.6 Å. The reason for this discrepancy is not clear. From the experimental side these flat potentials may be greatly influenced by crystal forces: we have calculated for only a single molecule. From the theoretical side, basis-set deficiencies or correlation effects may be operative. We find, however, that no reasonable change in INDO parameters changes these geometry predictions significantly, and such changes usually mimic basis-set effects. Preliminary studies with much larger CI's do suggest a shortening of the bond, but only by about 0.3 Å.

Although the importance of the antiferromagnetic state might be expected to decrease with decreasing Cr–Cr bond distance (and increasing 3d–3d orbital interaction), this decrease is not significant for bond lengths as short as 2.0 Å. This is obvious from an examination of the spin density matrix or the expectation value of S^2 ($\langle S^2 \rangle = 3.736$ at 2.0 Å). For completeness we also mention that small basis sets generally favor spin polarization in a UHF treatment that may disappear as the size of the basis set is increased. The energy lowering accompanying spin polarization in cases in which there are basis set deficiencies, however, is never as large as we find for these Cr–Cr complexes. The antiferromagnetic state is clearly lowest in energy in the entire range of Cr–Cr bond lengths studied (Figure 5).

(10) A. P. Sattelberger and J. P. Fackler, *J. Am. Chem. Soc.*, **99**, 1258 (1977).

No extrapolation of these results can yet be made for the molybdenum complexes since the d orbitals of Mo are considerably larger than those on Cr. The larger d orbitals would result in larger d–d overlap and suggests the possibility of stronger covalent coupling between Mo centers. The much more uniform distribution of the bond lengths in the Mo–Mo complexes may in fact be an indication that δ bonding is important for these compounds.[9,11]

Recent MC SCF (multiconfiguration self-consistent field) calculations by Goodgame and Goddard on the "sextuple bond" of Cr_2[12] are in essential agreement with our findings on the "δ-bonded" $Cr_2X_8^{4-}$ complexes examined here in that they emphasize the importance of antiferromagnetic coupling in Cr–Cr bonding. It is interesting to note that their calculated Cr–Cr bond length is between 3.06 and 3.25 Å depending on the method utilized, much longer than the reported length of 1.7 Å. The experimental evidence for this short bond length, however, is not strong.[12,13]

Registry No. $Cr_2Cl_8^{4-}$, 63448-50-0.

(11) The reference list above is in no sense complete, as literally hundreds of valuable contributions on the subject of multiply bonded binuclear systems have appeared in the last few years.
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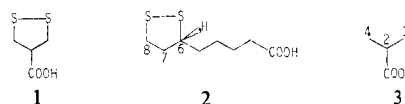
Biosynthesis of Sulfur Compounds. Investigations of the Biosynthesis of Asparagusic Acid

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Asparagusic acid (**1**) is a naturally occurring 1,2-dithiolane that

has been isolated from both the roots and edible portions of asparagus plants (*Asparagus officinalis* L.).[1-3] The substance is a plant-growth inhibitor, exerting activity comparable to abscisic acid,[1,2] and it also possesses potent nematicidal activity.[3] Previous investigations of the biosynthesis of naturally occurring 1,2-dithiolanes appear to have been confined to the enzyme cofactor α-(+)-lipoic acid (**2**).[4-7] We now report the results of experiments that show that the 1,2-dithiolane ring system of asparagusic acid is biosynthesized by a different mechanism than is involved in the biosynthesis of lipoic acid.

Our initial investigation of the biosynthesis of asparagusic acid was based upon a presumed analogy with lipoic acid biosynthesis. Since octanoic acid is the precursor of lipoic acid,[4] it was hy-

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