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Bond Length and Bond Order in One of the Shortest Cr−Cr Bonds

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Multiconfigurational quantum chemical calculations on the R-diimines dichromium compound confirm that the Cr−Cr bond, 1.80 Å, is among the shortest Cr^I-Cr^I bonds. However, the bond between the two Cr atoms is only a quadruple bond rather than a quintuple bond. The reason why the bond is so short has to be attributed to the strain in the NCCN ligand moieties.

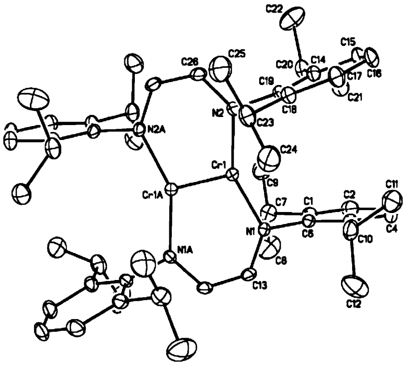

Figure 1. Structure of the R-diimine dichromium compound.

The Cr atom plays an important role in multiple bond chemistry.[1] Because of its electronic configuration, Cr, together with Mo and W, the other members of group 6, is one of the best candidates for the formation of the highest bond order involving d-block elements, namely, the sextuple bond.[2−5] The latter requires the involvement of the six valence electrons on each center, which are distributed into the *n*d and the $(n + 1)$s orbitals. Recent synthetic work by several groups has highlighted the existence of very short Cr−Cr bonds, corresponding to high-order multiple bonds and a low oxidation state of Cr. Nguyen et al.[6] have characterized the Ar′CrCrAr′ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-Pr^i_2)$_2$) species, with a short Cr−Cr bond of 1.8351(4) Å as well as a trans-bent, planar $C_{ipso}-Cr-Cr-C_{ipso}$ core structure, Cr−Cr−C = 102.78(3)°. This system also presents a relatively short [2.294(3) Å] secondary Cr−C interaction involving an *ipso*-carbon of one of the flanking aryl rings. We performed high-level multiconfigurational CASPT2 calculations[7,8] on the MeMMMe, PhMMPh, (MeMMMe)-(C_6H_6)$_2$, $Ar^§MMAr^§$, $Ar^\#MMAr^\#$ species, where M = Cr, Fe, Co, $Ar^§ = C_6H_4$-2(C_6H_5), and $Ar^\# = C_6H_3$-2,6(C_6H_3-2,6-Me_2)$_2$, in order to determine the extent of secondary metal−arene interaction involving the flanking aryl rings of the terphenyl ligands in quintuply bonded Ar′CrCrAr′ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-Pr^i_2)$_2$).

More recently, Kreisel et al.[9] synthesized a dichromium compound (Figure 1) coordinated by diazadienes (or R-diimines). The geometry around each Cr atom is trigonal planar, with each metal being coordinated by two N atoms from two different diazadiene ligands as well as by the neighboring Cr atom. The interesting feature is the very short Cr−Cr distance of 1.8028(9) Å, making it one of the shortest metal−metal distances. It should be noticed that recently two papers[10,11] have reported even shorter Cr−Cr distances. Complementary closed-shell density functional theory (DFT) calculations were performed at the BLYP/6-311g level using a model complex where the 2,6-diisopropylphenyl substituents were replaced by H atoms. Geometry optimizations on the model complex gave bond distances in good agreement with the experimental compound. Natural bond order

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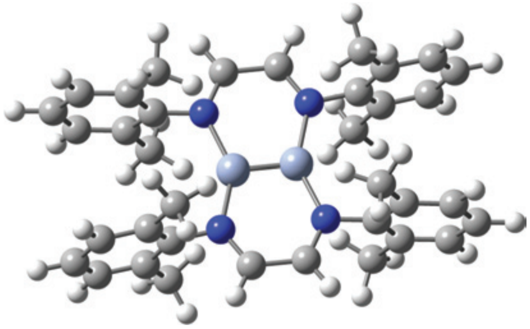

Figure 2. Structure of the model compound used in the calculation.

(NBO)[12] and natural resonance theory analysis were performed, showing the formation of a quintuple bond between the two Cr atoms (bond order 4.3). Earlier studies[8] indicate that this result is partly an artifact due to the use of a closed-shell DFT wave function. We decided to study the above compound using the multiconfigurational quantum chemical approach CASSCF/CASPT2 in order to obtain a better understanding of the electronic structure of the system and the nature of the Cr−Cr bond. The method has been very successful in earlier studies of metal−metal bonding.[13−20] We slightly reduced the size of the experimental compound by replacing the isopropyl substituents by methyl groups (Figure 2). Preliminary DFT calculations were performed using the B3LYP functional and DZP basis sets. A total of 2 degrees of freedom were investigated, namely, the Cr−Cr and Cr−N bond distances. For each point on the grid, corresponding to a given value of the Cr−Cr and Cr−N distances, the rest of the geometry was fully optimized at the DFT level of theory. Successive CASPT2 geometry optimization of the Cr−Cr and Cr−N bonds was performed at each point of the grid. The whole geometry has been slightly modified to fulfill C_{2v} symmetry. Because the distortion of the real compound from C_{2v} is minimal, we do not think that this geometry constraint will affect the final result. The active orbitals included in the CASSCF wave function are linear combinations of the Cr 3d orbitals forming the quintuple bond. An interesting bonding between the Cr 3dδ orbitals and the nitrogen π orbitals was found, and these orbitals had to be added to the active space. We selected two of the nitrogen π orbitals having the correct symmetry to interact with Cr 3dδ orbitals. Finally one more orbital, which is mainly Cr 4s, was also included, resulting in a total active space of 12 electrons in 13 orbitals. The molecular orbitals included in the active space, together with their occupation numbers, are reported in the Supporting Information.

Table 1. Cr−Cr and Cr−N Bond Distance (in Å), Computed at the CASPT2 and DFT Levels of Theory, Together with the Experimental Values

	Cr−Cr	Cr−N
CASPT2	1.799	1.909
B3LYP	1.726	1.911
BLYP (from ref 9)	1.764	1.904
exp (from ref 9)	1.803	1.914

In Table 1, the Cr−Cr and Cr−N bond distances, optimized at the CASPT2 and closed-shell B3LYP levels of theory, are reported, together with the corresponding experimental values. CASPT2 distances are in good agreement with the experiment, while closed-shell B3LYP slightly underestimates the Cr−Cr bond distance. The nature of this particularly short Cr−Cr bond has been analyzed in terms of the electronic configuration of the ground state of the compound and the molecular orbitals intervening in the bond.

Inspection of the wave function shows that the closed-shell configuration, (Cr−Cr)σ^2(Cr−Cr)π^4(Cr−Cr)δ^2-(Cr−N)π^4, dominates with a weight of 0.6, while all other configurations (about 185 000) contribute with weights lower than 0.05. The most important among them correspond to double excitations from the bonding orbitals to their antibonding counterparts. Their presence is responsible for the fractional occupation number of the orbitals and the multiconfigurational character of the wave function. A total of 10 molecular orbitals are almost completely localized on the Cr−Cr moiety, while the remaining 3 are more delocalized. The occupation numbers of the active orbitals can be used to determine the effective bond order (EBO) between the two Cr atoms, calculated as half the difference between the sum of the occupation numbers of the bonding orbitals minus the sum of the occupation numbers of the antibonding orbitals.[2]

The presence of delocalized orbitals in the active space makes the evaluation of the EBO less straightforward because their contribution to the Cr−Cr bond cannot be univocally assigned. A localization of the orbitals has therefore been performed according to a procedure described in the Supporting Information.

With this approach, a value of 3.43 has been obtained for the EBO, which differs significantly from the bond order of 4.28 proposed by Kreisel et al.[9] but is consistent with the value of 3.5 that we obtained from NBO analysis based on LoProp[21] densities. We thus consider the present Cr−Cr bond as a quadruple bond rather than a quintuple bond because one of the 3dδ orbitals is mainly involved in the π bonding with the nitrogen ligands. It should be pointed out at this point that it is a matter of semantics to describe a bond with a bond order of 3.5 as a quadruple bond or a quintuple bond where a couple of bonds are very weak. Both descriptions are possible, but what is important is that the quantitative measure of a bond order is given by its EBO.

The EBO of 3.43 obtained in this case is similar in value to the EBO of 3.52 obtained for the model compound PhCrCrPh or of 3.43 obtained for the Ar′CrCrAr′ species

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synthesized by Nguyen et al.[6] In the above case, the Cr−Cr bond distance, 1.84 Å, is longer than that in the present R-diimines Cr−Cr compound, 1.80 Å.

Such a situation naturally raises the question, why is the Cr−Cr bond shorter here than in the earlier cases even if the bond order is smaller? One should, of course, realize that there is no simple linear relationship between the bond order and the bond length. Many other factors determine a bond length, and here we believe that the strain in the NCCN ligand moieties is the key factor that holds the two Cr atoms in place and limits the variations in the bond distance. So, it is the specific ligands used here that make the Cr−Cr bond so short. This effect is even more obvious in the two recently synthesized systems.[10,11]

The formal oxidation state of Cr is not straightforward. Kreisel et al.[9] point to the fact that the oxidation state could be 2+, 1+, or 0 because of the redox ambiguity of diimine and other imine-containing ligands. On the basis of geometrical arguments, they concluded that the most likely oxidation state is between 1+ and 2+. This conclusion is well supported by the present study. The Cr atoms lose the 4s electrons, which go to the ligands. In addition, π bonds are formed between Cr and N, half a bond per Cr−N pair. This gives an oxidation number of 1.5+. The Cr−Cr bond is then essentially a quadruple bond with a small extra contribution from the delocalized CrN π bonding orbitals. This is quite different from the Cr−Cr bond of Ar′CrCrAr′, where all five Cr 3d orbitals are involved in the bond. Still the bond order is about the same because the δ orbitals in Ar′CrCrAr′ form only quite weak bonds.

In conclusion, we have performed multiconfigurational quantum chemical calculations on the R-diimines dichromium compound recently synthesized by Kreisel et al.[9] Our calculations confirm that the Cr−Cr bond, 1.80 Å, is among the shortest $Cr^{I}-Cr^{I}$ bonds to date. However, inspection of the wave function and the relevant molecular orbitals shows that the bond between the two Cr atoms has an EBO of 3.43 and not of 4.28 as proposed by Kreisel et al.[9] The analysis of the electronic structure shows that the electronic structure is best described with a formal oxidation state of 1.5+ for each of the Cr atoms. This leads to a bond that comprises between four and five 3d electrons per atom. Taking into account the weakness of the δ bond, this is consistent with the computed bond order. We are currently investigating similar species in order to try to understand how one could influence the length and strength of a metal−metal multiple bond by using different central metals and different ligands.

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Supporting Information Available: Details of the calculations, localization procedure, Cartesian coordinates of the structures, and pictures of the active molecular orbitals. This material is available free of charge via the Internet at http://pubs.acs.org.

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