

Quintuple Bonds

Remarkably Short Metal–Metal Bonds: A Lantern-Type Quintuply Bonded Dichromium(I) Complex**

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In memory of F. Albert Cotton

The field of quadruply bonded dinuclear complexes in which two metal atoms are embraced by eight ligands has been considered mature. The bonding and electronic structures of these compounds have been well understood,^[1–4] ever since the discovery of the first dimetal species containing a quadruple bond, $[\text{Re}_2\text{Cl}_8]^{2-}$, over 40 years ago.^[5] The quest for thermally stable and isolable dinuclear complexes with higher bond orders is one aim of chemists in this field. From the synthetic point of view, quintuply bonded dinuclear complexes have become the focus in the past few years. On the theoretical side, the hypothetical RMMR molecules ($\text{M} = \text{Cr}, \text{Mo}, \text{W}, \text{U}$; $\text{R} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{CN}, \text{Me}$) have been highlighted, particularly the *trans*-bent structures. These feature a quintuple bond between two metal atoms, and for RCrCrR , the calculated Cr–Cr bond lengths are in the range of 1.64–1.78 Å.^[6–11] Experimentally, a recent landmark advance was the isolation of a quintuply bonded dichromium(I) complex supported by two monodentate bulky carbyl ligands $[\text{Ar}'\text{CrCrAr}']$ ($\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2)_2$),^[12] in which, coincidentally, a *trans*-bent (C_{2h}) geometry is adopted and the two chromium atoms share five electron pairs in five bonding molecular orbitals according to computational analyses.^[13, 14] Moreover, D_{2h} -symmetric $[\text{Cr}_2(\mu-\eta^2\text{-}^i\text{Pr})_2]$ ($^i\text{Pr} = N,N'$ -bis(2,6-diisopropylphenyl)-1,4-diaza-

diene) was recently reported to feature a very short Cr–Cr distance of 1.8028(9) Å and calculated to display some degree of fivefold bonding.^[15]

We have been interested in the pursuit of low-coordinate and multiply bonded dinuclear complexes since our first report on the unconventional quadruply bonded dimolybdenum complex $[\text{Mo}_2\{\mu-\eta^2\text{-(DippN)}_2\text{SiMe}_2\}_2]$ (Dipp = 2,6-*i*PrC₆H₃), in which each Mo atom is ligated by only two nitrogen atoms.^[16] Accordingly, we were interested in the preparation of multiply bonded dinuclear complexes supported by ancillary ligands which can minimize the metal–ligand π -bonding interaction and maximize the metal–metal interaction. Inspired by the hypothetical eclipsing molecule M_2L_6 , proposed by Hoffmann et al.,^[17] in which M–M could be a quintuple bond, we set out to explore the possibility of synthesizing such complexes. Here we report the use of amidinate ligand $\text{Ar}^{\text{Xyl}}\text{NC(H)NAr}^{\text{Xyl}}$ ($\text{Ar}^{\text{Xyl}} = 2,6\text{-C}_6\text{H}_3\text{-(CH}_3)_2$) to stabilize mixed-valent Cr_2^{3+} complex $[\text{Cr}_2(\text{Ar}^{\text{Xyl}}\text{NC(H)NAr}^{\text{Xyl}})_3]$ (**2**) with formal Cr–Cr bond order of 4.5 and its one-electron reduced Cr_2^{2+} species $[\text{Cr}_2(\text{Ar}^{\text{Xyl}}\text{NC(H)NAr}^{\text{Xyl}})_3]^-$ (**3** with formal Cr–Cr bond order of 5.0). Both of these species have very short Cr–Cr bonds; the bonding in these two compounds was studied theoretically.

Reduction of dichromium bis(amidinate) dichlorido complex $[\{\text{Cr}(\text{thf})_2(\mu\text{-Cl})_2\{\mu-\eta^2\text{-(Ar}^{\text{Xyl}}\text{NC(H)NAr}^{\text{Xyl}})_2\}]$ (**1**),^[18] in which the Cr–Cr distance is 2.612(1) Å, with KC_8 gave red-brown mixed-valent dichromium tris(amidinate) compound **2** in 47% yield (Scheme 1). Compound **2** is paramagnetic, as

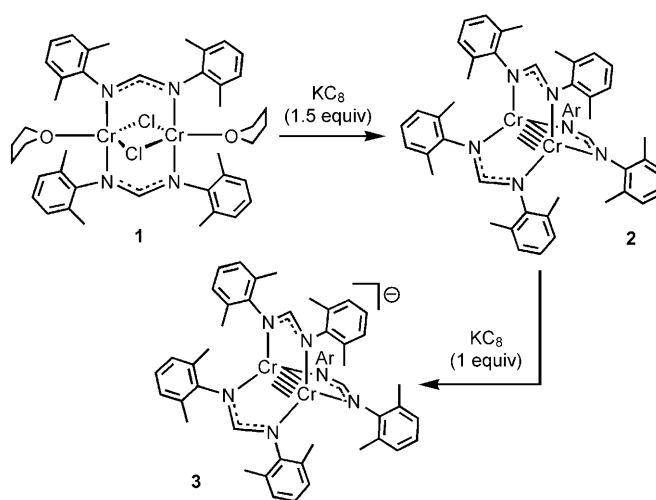
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Scheme 1. Synthesis of **2** and **3**.

evidenced by its solid-state magnetic moment of about $2.21 \mu_B$, and accordingly has one unpaired electron. The electronic absorption spectrum of **2** displays a strong absorption at 250 nm arising from the ligands and two absorptions at 389 and 572 nm with $\epsilon = 2055$ and $2730 \text{ mol}^{-1} \text{ L cm}^{-1}$.

The solid-state molecular structure of compound **2** (Figure 1) was deciphered by X-ray crystallography.^[19] In

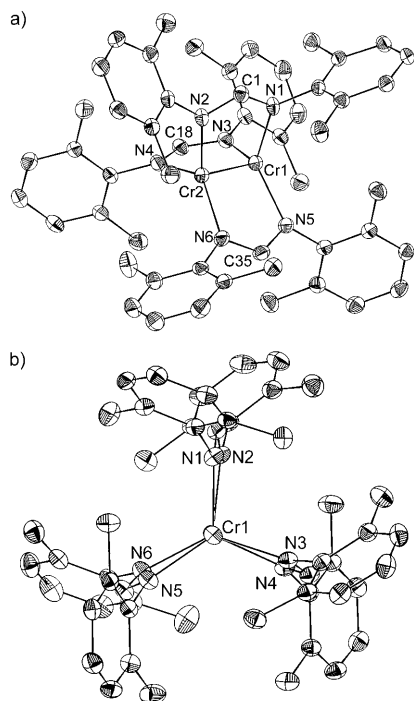


Figure 1. Solid-state structure of $[\text{Cr}_2(\text{Ar}^{\text{Xyl}}\text{NC}(\text{H})\text{NAr}^{\text{Xyl}})_3]$ (**2**) viewed a) normal to and b) along the metal–metal axis with thermal ellipsoids at 30% probability.

contrast to the D_{3h} -symmetric trigonal paddlewheel Fe and Co amidinates,^[20,21] in which all degenerate molecular orbitals are evenly occupied, **2** is substantially distorted from D_3 symmetry (Figure 1b), as evidenced by significant deviation from trigonal geometry at both Cr atoms with N–Cr1–N bond angles of $106.96(10)$, $123.15(11)$, and $125.53(11)^\circ$, and N–Cr2–N bond angles of $107.57(10)$, $126.00(10)$, $122.73(11)^\circ$. Although contributions from packing forces can not be completely ignored,^[20] the structural distortion of **2** is essentially attributed to the Jahn–Teller effect^[22] (vide infra). The metal–metal bond length of $1.8169(7) \text{ \AA}$ for **2** is significantly shorter than the Cr–Cr quintuple-bond length of $1.8351(4) \text{ \AA}$ of complex $[\text{Ar}'\text{CrCrAr}']$.^[12] Complex **2** has a formal shortness ratio (FSR) of 0.766 (cf. $\text{FSR}(\text{N}_2) = 0.786$).^[4]

Since **2** has one unpaired electron, we subjected it to a detailed EPR study. In toluene **2** is EPR-silent at room temperature, but axial symmetry displayed at low temperature (77 K) suggests that the unpaired electron resides in an orbital perpendicular to the z axis (coincident with the Cr–Cr axis), namely, $d_{x^2-y^2}$ or d_{xy} (Figure S2, Supporting Information). In fact, DFT calculations on complex **2** reproduced the geometrical features of the solid-state structure of **2**. The calculated SOMO has mostly metal $d_{x^2-y^2}$ character and hence

is perpendicular to the z axis, which is clearly consistent with the anisotropic EPR spectra of **2**. Fivefold bonding between two Cr atoms, arising from a $\sigma^2\pi^4\delta^3$ configuration for the Cr_2 core is consequently implied. The bonding scheme of **2** was further corroborated by unrestricted DFT calculations (BP86), and the metal–metal orbital surfaces are shown in Figure S2 (Supporting Information). The symmetries of SOMO and SOMO–1, mainly $d_{x^2-y^2} + d_{x^2-y^2}$ and $d_{xy} + d_{xy}$, correspond to δ bonds. The SOMO–2, $d_z + d_z$, corresponds to Cr–Cr σ bonding, while SOMO–3 and SOMO–5, $d_{xz} + d_{xz}$ and $d_{yz} + d_{yz}$, are Cr–Cr π bonds. The nondegeneracy of SOMO and SOMO–1 is consistent with the Jahn–Teller structural distortion observed in complex **2**.^[23]

The cyclic voltammogram of a solution of **2** (THF/tetrabutylammonium phosphate) shows a reversible reduction wave at $E_{1/2} = -2.14 \text{ V}$ (relative to Fc/Fc^+) over the course of the cathodic sweep. Accordingly, reduction of THF solutions of **2** with KC_8 in the presence of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt[222]) gave extremely air- and moisture-sensitive dark purple species $\text{K}(\text{crypt}[222])[\text{Cr}_2(\text{Ar}^{\text{Xyl}}\text{NC}(\text{H})\text{NAr}^{\text{Xyl}})_3]$ ($\text{K}(\text{crypt}[222])(\text{3})$) in 83 % yield. After workup the product showed a diamagnetic NMR spectrum in $[\text{D}_8]\text{THF}$ with sharp resonances between $\delta = 0$ and 8 ppm for ^1H , and $\delta = 0$ and 230 ppm for ^{13}C . The electronic absorption spectrum of **3** has a strong absorption at 250 nm and a broad absorption at 488 nm, with $\epsilon = 3200 \text{ mol}^{-1} \text{ L cm}^{-1}$.

The solid-state molecular structure of **3** (Figure 2) was elucidated by X-ray crystallography.^[19] In comparison with the distorted structure of **2**, the lantern structure is still conserved, except that it displays a more symmetrical D_3 -symmetric structure (Figure 2b). The most remarkable feature of **3** is that the Cr–Cr bond contracts significantly to a distance of $1.7397(9) \text{ \AA}$, a difference of about $0.08 \text{ \AA}$ when compared to **2**. The FSR of the Cr–Cr bond in **3** is 0.733. The magnitude of this change suggests that the additional electron resides in the $d_{x^2-y^2}$ - or d_{xy} -based molecular orbital if the z axis is coincident with the Cr–Cr bond, and therefore the dimetal core has a $\sigma^2\pi^4\delta^4$ configuration. The increase in average Cr–N distance from $2.044(3)$ in **2** to $2.092(3) \text{ \AA}$ in **3** on one-electron reduction indicates substantially weaker interactions between Cr and ligands compared to quadruply bonded $\text{Cr}_2(\text{amidinate})_4$ complexes,^[4] which, as a consequence, enhance the overlap of $d_{x^2-y^2}$ and $d_{x^2-y^2}$, and d_{xy} and d_{xy} , to form two δ bonds. The extremely short Cr–Cr bond of **3** is the shortest known metal–metal bond in an isolable compound. It is also the first metal–metal bond shorter than $1.8 \text{ \AA}$, and it lies in the range of those of hypothetical quintuply bonded Cr–Cr complexes.^[11]

We examined the nature of the bonding in **3** by DFT calculations (BP86). The geometry of the optimized structure was in close agreement with the crystal structure of **3**. Considerable metal–metal bonding can be found from HOMO to HOMO–4 (Figure 3). Orbital HOMO–2 corresponds to the Cr–Cr σ bond ($d_z + d_z$), while the degenerate HOMO–3 and HOMO–4 display Cr–Cr π -bonding interactions ($d_{xz} + d_{xz}$ and $d_{yz} + d_{yz}$). Almost degenerate Cr–Cr δ -bonding character is apparently displayed by HOMO ($d_{x^2-y^2} + d_{x^2-y^2}$) and HOMO–1 ($d_{xy} + d_{xy}$). In contrast to the significant

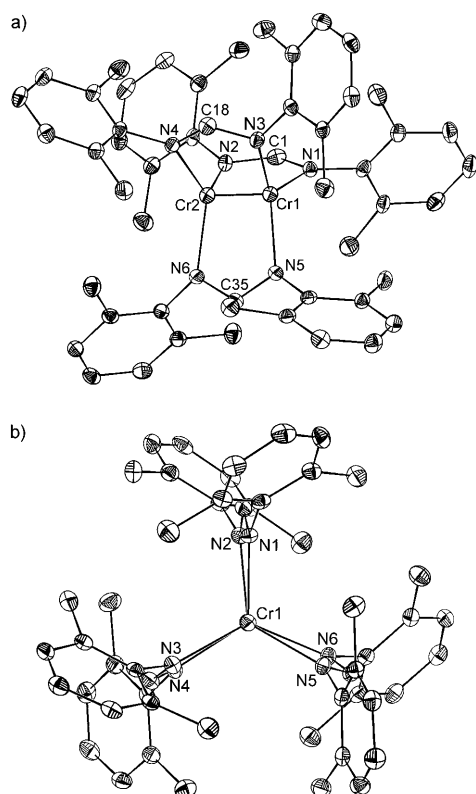


Figure 2. Molecular structure of the anion in K(crypt[222])[3]·3 THF viewed a) normal to and b) along the metal–metal axis with thermal ellipsoids at 30% probability. The cation, THF solvate, and hydrogen atoms have been omitted for clarity.

Cr–N π bonding in $[\text{Cr}_2(\mu\text{-}\eta^2\text{-H}^i\text{Pr})_2]$,^[15] no π bonding is observed between $d_{x^2-y^2}$ and d_{xy} orbitals of Cr atoms and N donors. These observations suggest two strong Cr–Cr δ bonds and consequently an extremely short Cr–Cr bond.

It could be argued that the very short Cr–Cr distances of **2** and **3** are due to the bridging nature of the amidinate ligand, which pushes the Cr atoms close together. However, the reported amidinate-bridged paddlewheel Cr_2 compounds have Cr–Cr bond lengths that range from 1.844(2) to 2.612(1) Å.^[4,18,24–28] Accordingly, the amidinate ligands can accommodate Cr–Cr distances that vary by almost 1 Å. As a result, we conclude that the extremely short Cr–Cr distances in **3** is a consequence of interactions of the d^5 Cr atoms, and not due to the constraint of the ligands; thus, the five bonding orbitals (1 σ , 2 π , and 2 δ) of **3** are filled with five pairs of electrons.

Mota et al.^[29] proposed a pyramidal effect in quadruply bonded Cr_2 complexes, whereby the Cr–Cr distance is correlated to the average pyramidal angle (Cr–Cr–L). They explained the pyramidal effect in terms of major changes in hybridization affecting the metal–metal σ and π bonding. Accordingly, the pyramidal angles of compounds **2** and **3** would predict Cr–Cr distances of 1.808 and 1.740 Å, remarkably close to the experimental values of 1.817 and 1.740 Å, respectively. Given the weak δ bonding, it seems reasonable to assume that quadruple and quintuple bonds have essentially the same behavior, and the shortest metal–

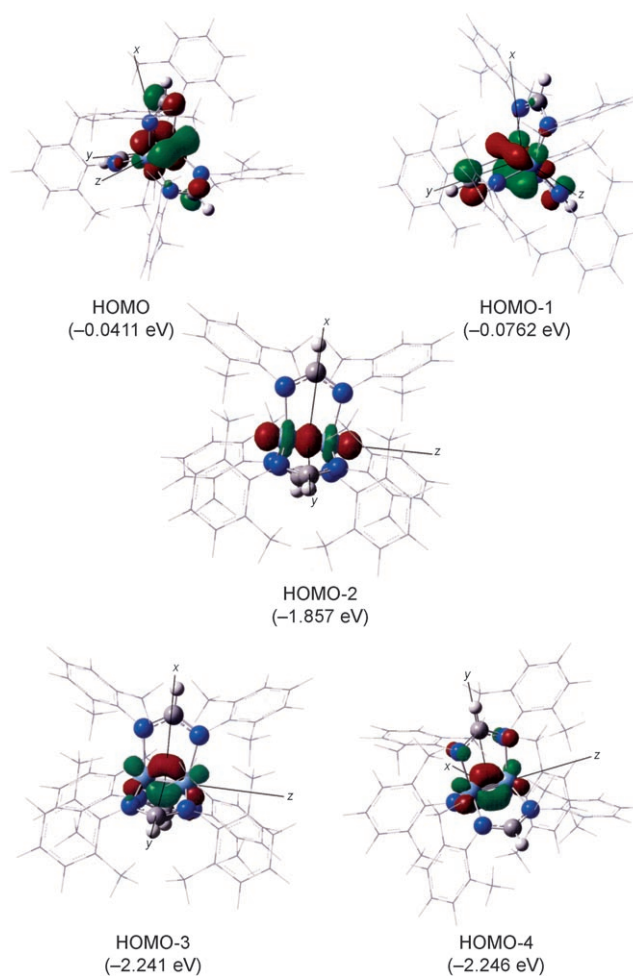


Figure 3. Frontier orbitals of **3**.

metal bond length of **3** is associated with the largest Cr–Cr–L bond angle found so far.

In summary, we have shown that associating two Cr atoms with three formamidinate ligands allows the isolation of a lantern-type dichromium compound with unambiguous quintuple bonding. We anticipate that the discovery of the shortest metal–metal bond may aid the development of systematic syntheses of more compounds with very short metal–metal bonds. Reactivity studies on complexes **2** and **3**, in which each Cr atom is ligated by three nitrogen donors, are also underway.

Experimental Section

Experimental details for the synthesis and characterization of and computations on complexes **2** and **3** are provided in the Supporting Information.

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