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

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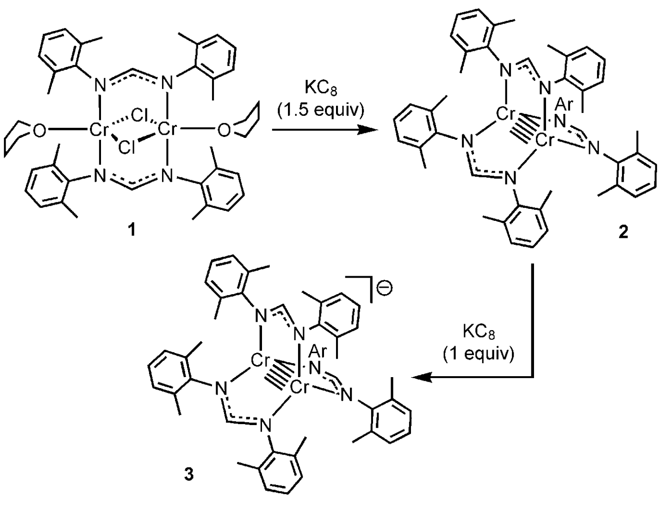
*In memory of F. Albert Cotton*

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, $[Re_2Cl_8]^{2-}$, 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 (M = Cr, Mo, W, U; R = H, F, Cl, Br, CN, 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 [Ar′CrCrAr′] (Ar′ = $C_6H_3$-2,6-($C_6H_3$-2,6-$i$$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 $[Cr_2(\mu\text{-}\eta^2\text{-}{}^{H}L^{iPr})_2]$ (${}^{H}L^{iPr}$ = *N*,*N*′-bis(2,6-diisopropylphenyl)-1,4-diazadiene) 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 $[Mo_2\{\mu\text{-}\eta^2\text{-}(DippN)_2SiMe_2\}_2]$ (Dipp = 2,6-$i$Pr$C_6H_3$), 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 $Ar^{Xyl}NC(H)NAr^{Xyl}$ ($Ar^{Xyl}$ = 2,6-$C_6H_3$-$(CH_3)_2$) to stabilize mixed-valent $Cr_2^{3+}$ complex $[Cr_2(Ar^{Xyl}NC(H)NAr^{Xyl})_3]$ (**2**) with formal Cr–Cr bond order of 4.5 and its one-electron reduced $Cr_2^{2+}$ species $[Cr_2(Ar^{Xyl}NC(H)NAr^{Xyl})_3]^-$ (**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 $[\{Cr(thf)\}_2(\mu\text{-}Cl)_2\{\mu\text{-}\eta^2\text{-}(Ar^{Xyl}NC(H)NAr^{Xyl})\}_2]$ (**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



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

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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 $\varepsilon = 2055$ and $2730\,\text{mol}^{-1}\,\text{L}\,\text{cm}^{-1}$.

The solid-state molecular structure of compound **2** (Figure 1) was deciphered by X-ray crystallography.[19] In 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 1 b), 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)°, and N-Cr2-N bond angles of 107.57(10), 126.00(10), 122.73(11)°. 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) Å for **2** is significantly shorter than the Cr–Cr quintuple-bond length of 1.8351(4) Å of complex [Ar′CrCrAr′].[12] Complex **2** has a formal shortness ratio (FSR) of 0.766 (cf. FSR($N_2$) = 0.786).[4]

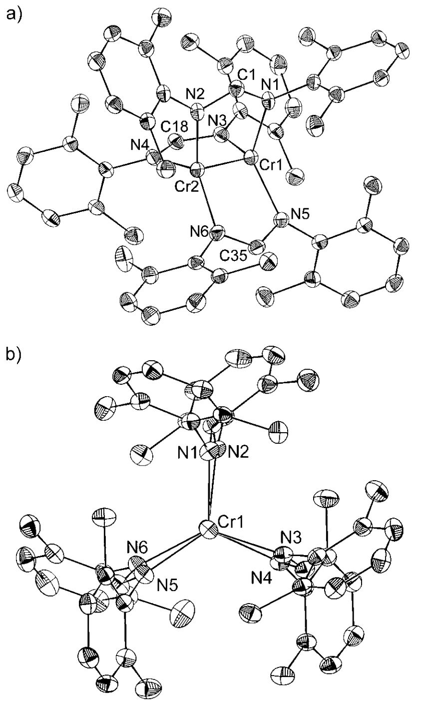


***Figure 1.*** Solid-state structure of $[\text{Cr}_2(\text{Ar}^{\text{Xyl}}\text{NC(H)NAr}^{\text{Xyl}})_3]$ (**2**) viewed a) normal to and b) along the metal–metal axis with thermal ellipsoids at 30% probability.

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 $\text{Cr}_2$ 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, $d_{z^2} + d_{z^2}$, 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 $E_{1/2} = -2.14$ V (relative to $\text{Fc}/\text{Fc}^+$) over the course of the cathodic sweep. Accordingly, reduction of THF solutions of **2** with $\text{KC}_8$ 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 $\text{K(crypt[222])}[\text{Cr}_2\{\text{Ar}^{\text{Xyl}}\text{NC(H)NAr}^{\text{Xyl}}\}_3]$ (K(crypt[222])[**3**]) in 83% yield. After workup the product showed a diamagnetic NMR spectrum in [D$_8$]THF with sharp resonances between $\delta = 0$ and 8 ppm for $^1$H, 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 $\varepsilon = 3200\,\text{mol}^{-1}\,\text{L}\,\text{cm}^{-1}$.

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 2 b). The most remarkable feature of **3** is that the Cr–Cr bond contracts significantly to a distance of 1.7397(9) Å, a difference of about 0.08 Å 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) Å 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 Å, 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 the Cr–Cr σ bond ($d_{z^2} + d_{z^2}$), 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

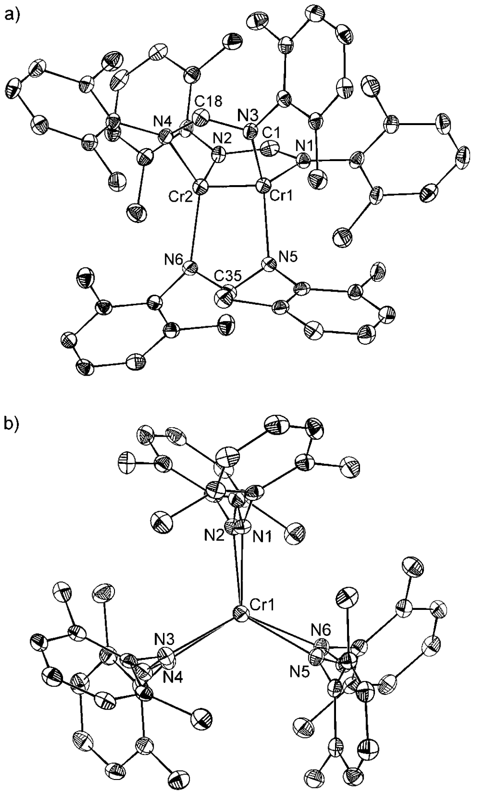
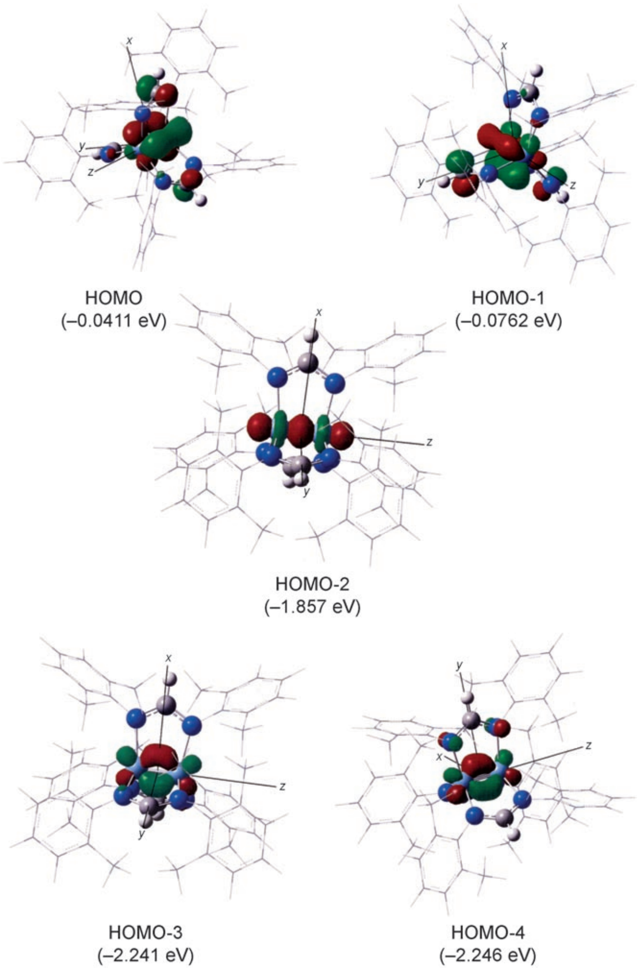


***Figure 2.*** Molecular structure of the anion in K(crypt[222])[**3**]·3THF viewed a) normal to and b) along the metal–metal axis with thermal ellipsoids at 30% probability. The cation, THF solvate, and hydrogen atoms have been omitted for clarity.

Cr–N π bonding in $[Cr_2(\mu\text{-}\eta^2\text{-}{}^{H}L^{iPr})_2]$,[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 pyramidality effect in quadruply bonded $Cr_2$ complexes, whereby the Cr–Cr distance is correlated to the average pyramidality angle (Cr-Cr-L). They explained the pyramidality effect in terms of major changes in hybridization affecting the metal–metal σ and π bonding. Accordingly, the pyramidality 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–metal bond length of **3** is associated with the largest Cr-Cr-L bond angle found so far.



HOMO
(−0.0411 eV)

HOMO-1
(−0.0762 eV)

HOMO-2
(−1.857 eV)

HOMO-3
(−2.241 eV)

HOMO-4
(−2.246 eV)

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

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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[19] Crystallographic data for **2**·Et$_2$O: $C_{55}H_{67}N_6OCr_2$, $M_r = 932.15$, $T = 150(2)$ K, monoclinic, space group $P2_1/n$, $a = 15.8060(6)$, $b = 17.3373(9)$, $c = 18.8494(8)$ Å, $\beta = 106.617(2)°$, $V = 4949.6(4)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.251$ Mg m$^{-3}$, $\mu = 0.484$ mm$^{-1}$, 20355 reflections collected, 8686 independent reflections ($R_{int} = 0.0696$), final $R$ indices $[I > 2\sigma(I)]$: $R_1 = 0.0475$, $wR_2 = 0.1005$, $R$ indices (all data): $R_1 = 0.1021$, $wR_2 = 0.1182$. K(crypt[222])[**3**]·3 THF: $C_{81}H_{117}N_8KO_9Cr_2$, $M_r = 1489.93$, $T = 150(2)$ K, monoclinic, space group $P2_1/c$, $a = 23.1962(4)$, $b = 26.1563(6)$, $c = 26.4577(6)$ Å, $\beta = 97.2449(12)°$, $V = 15924.4(6)$ Å$^3$, $Z = 8$, $\rho_{calcd} = 1.243$ Mg m$^{-3}$, $\mu = 0.385$ mm$^{-1}$, 73852 reflections collected, 27954 independent reflections ($R_{int} = 0.1078$), final $R$ indices $[I > 2\sigma(I)]$: $R_1 = 0.0596$, $wR_2 = 0.1136$, $R$ indices (all data): $R_1 = 0.1693$, $wR_2 = 0.1468$. CCDC-675770 (**2**·Et$_2$O) and -675771 (K(crypt[222])[**3**]·3 THF) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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