

Metal–Metal Distances at the Limit: Cr–Cr 1.73 Å – the Importance of the Ligand and its Fine Tuning

Awal Noor,^[a] Germund Glatz,^[a] Robert Müller,^[b] Martin Kaupp,^{*,[b]} Serhiy Demeshko,^[c] and Rhett Kempe^{*,[a]}

Keywords: Chemical bonding; Chromium; Metal–metal bonds; Multiple bonds; N ligands

Abstract. The synthesis and structure of a homobimetallic chromium complex is reported. The ligand used to stabilise the quintuply bonded metals is a sterically fine-tuned guanidinate. A

chromium–chromium bond length of 1.7293(12) Å was observed. It is the shortest metal–metal distance reported for a stable compound yet.

Quintuple Bonds

The shortest metal–metal bond in a stable compound has been of interest to natural scientists and chemists in particular for decades. In this context, the element chromium plays a decisive role. Because of their electron configuration, chromium and the higher homologues of group 6 transition metals are able to form metal–metal bonds of high formal bond orders [1]. Within group 6, chromium exhibits the smallest ion radius and is ideally suited to form exceptionally short metal–metal bonds. The search for shorter metal–metal distances in coordination compounds has recently been reignited by the pioneering work of *Power* and co-workers, reporting quintuple bonding between chromium atoms [2]. Interestingly, the first compound of this kind ArCr–CrAr [Ar = C₆H₃-2,6-(C₆H₃-2,6-{isopropyl}₂)₂] exhibited a Cr–Cr distance of 1.8351(4) Å [2], which is slightly longer than the shortest formally quadruply bonded chromium complexes [3]. For almost 30 years an aryl Cr^{II} compound, structurally characterised by *Cotton* and *Koch* [4] and first prepared by *Hein* and *Tille* more than 40 years ago [5], was reported to have the shortest experimentally observed metal–metal distance, 1.830(4) Å, of a stable mol-

ecule [6]. *Hein* and *Tille* also proposed the dimeric structure for this compound [5]. The chromium–chromium bond length of Cr₂ generated by laser-evaporation of the metal and flash photolysis of Cr(CO)₆ is about 1.68 and 1.71 Å, respectively [7, 8]. Similar distances were calculated for Cr₂ [9]. For the Cr₂ dimer a formally sextuple bond is assumed. Hence, quintuply bonded complexes could be expected to exhibit bond lengths between that observed for ArCr–CrAr and 1.68 Å. Consequently, a number of compounds with shorter Cr–Cr distance have been synthesised. *Theopold*, *Landis* and co-workers reported on an N ligand stabilised homobimetallic chromium complex [distance (Cr–Cr) 1.8028(9) Å] with quintuple bonding, as suggested by DFT-based NRT and NBO analyses [10]. The compound was synthesised by subsequent adding of sodium and a Cr^{III} chloride to a sterically demanding diazadiene affording a monochloro chromium complex which was further reduced by potassium graphite. The problem with the used ligand is its redox ambiguity making it difficult to judge the oxidation state of the chromium atoms of the multiply bonded dimer. Multiconfigurational quantum chemical calculations suggested a formal oxidation state of 1.5+ for each of the chromium atoms and a bond order of 3.43, based on natural orbital occupations [11]. Derivatives of ArCr–CrAr show variations in the metal–metal distances between 1.8077(7) Å and 1.8351(4) Å. Packing forces rather than electronic effects seem to dominate the different distances [12]. Distances of 1.74 and 1.75 Å for N ligand stabilised chromium dimers were reported simultaneously by *Tsai* et al. and our own group, respectively [13–15]. These examples represent the class of ultra-short metal–metal bonded homobimetallics. Calculations indicate quintuple bonding. The Cr–Cr bond lengths are intermediate between the quadruply bonded Cr^{II}–Cr^{II} complexes and the gas phase Cr₂ molecule with its formal sextuple bond. An important aspect in the context of ultra-short metal–metal distances is the *Hein*–*Cotton* principle

* Prof. Dr. M. Kaupp,
E-Mail: Kaupp@Mail.Uni-Wuerzburg.de

* Prof. Dr. R. Kempe
E-Mail: Kempe@uni-bayreuth.de

[a] Lehrstuhl Anorganische Chemie II
Universität Bayreuth
95440 Bayreuth, Germany

[b] Institut für Anorganische Chemie
Universität Würzburg
Am Hubland
97074 Würzburg, Germany

[c] Institut für Anorganische Chemie
Georg-August-Universität Göttingen
Tammannstraße 4
37077 Göttingen, Germany

Supporting information for this article is available on the WWW under www.zaac.wiley-vch.de or from the author.

[13], that is the X–Y–Z ligand arrangement, which brings the two metal atoms into close proximity in the first place (Figure 1) [13–15].

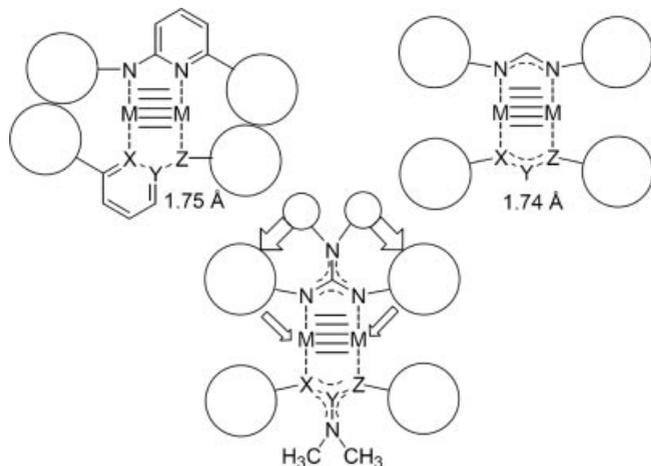


Figure 1. The role of the ligand in stabilising ultra-short metal–metal bonds: aminopyridinates (left, top) vs. amidinates (right, top) vs. guanidinate (bottom).

By comparing the two ligand families which were used to stabilise ultra-short chromium–chromium bonds, aminopyridinates and amidinates (Figure 1, top), the two-wings-up arrangement observed for amidinates (Figure 1, top right) apparently causes much less inter-ligand repulsion within the bimetallic complex than the wing-up-wing-down arrangement observed for aminopyridinates (Figure 1, top left). This allows the generation of a closer N–C–N-pincer and/or an alignment of nitrogen atom based orbitals that interact with chromium (lone pairs) towards each other resulting in shorter Cr–Cr distances. Gradual closing of this pincer by applying steric pressure via the substituent at the bridging carbon atom should give rise to a further reduced distance between the clamped metal atoms (Figure 1, bottom). Guanidinate appears to be ideally suited in this regard. The π -system can be delocalised with a planar arrangement of the three nitrogen atoms and their residues (Figure 1, bottom) which should become “frozen” between two bulky 2,6-alkyl phenyl “wings” avoiding an out of plane arrangement of the substituent of the non-coordinating nitrogen atom. Consequently, the substituent of the non metal-bonded nitrogen atom is ideally suited to push the

two “wings” further down resulting in a shortening of the metal–metal bond. A ligand introduced by *Hessen* and co-workers recently seems to be ideal in this regard [16]. Additionally, the potential of guanidinate to stabilise short metal–metal distances was shown by *Gambarotta* and co-workers recently [17]. We show here that the strategy discussed above was successfully applied to synthesise the coordination compound with the shortest metal–metal distance observed yet.

The reaction of lithium guanidinate $\text{Li}[\text{Me}_2\text{NC}(\text{NAr})_2]$ (**1**, Ar = 2,6-diisopropylphenyl) with CrCl_2 in THF afforded, after removal of the solvent and subsequent extraction with hexane, the Cr^{II} complex **2** as blue crystalline material in good yield (Scheme 1). The ^1H NMR shows only broad signals and magnetic susceptibility experiments provide a magnetic moment $\mu_{\text{eff}}(298.8\text{ K}) = 2.70 \mu_{\text{B}}$ per chromium. The X-ray crystal structure analysis shows compound **2** to be dimeric in the solid state. The coordination pattern around each metal centre can be best described as slightly distorted square planar (Figure 2) [18]. Considerable interaction of the lone pair of the Me_2N moiety with

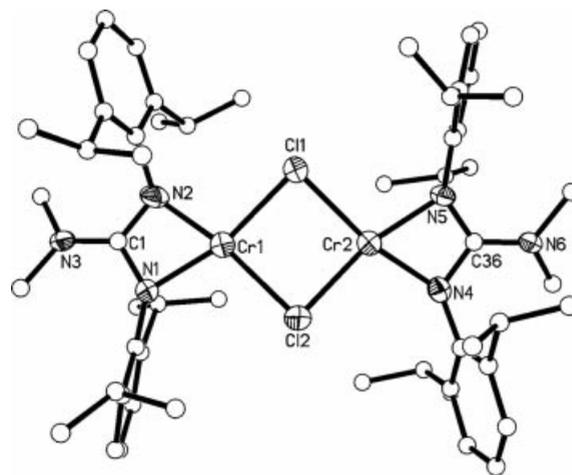
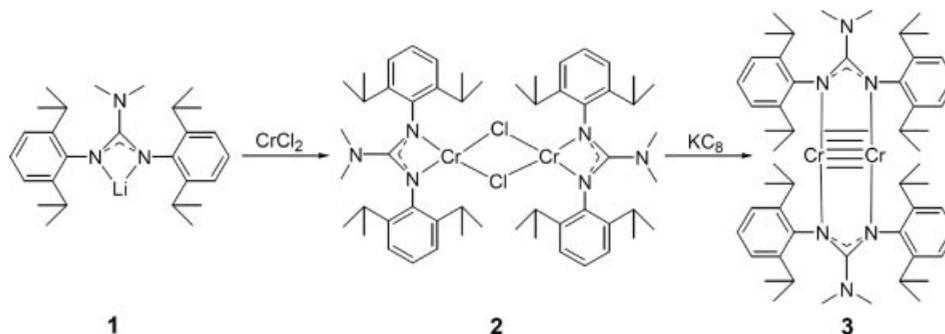


Figure 2. Molecular structure of **2** [ORTEP representation (on the 50% probability level) for all non carbon atoms]; hydrogen atoms have been omitted for clarity. Selected bond lengths /Å and angles /°: C1–N2 1.323(9), C1–N3 1.347(8), C1–N1 1.361(9), N1–Cr1 2.030(6), N2–Cr1 1.995(6), N4–Cr2 2.012(6), N5–Cr2 2.017(6), Cl1–Cr2 2.3713(6), Cl1–Cr1 2.383(2), Cl2–Cr2 2.366(2), Cl2–Cr1 2.389(3); N2–Cr1–N1 65.9(2), Cl1–Cr1–Cl2 88.77(8).



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

the conjugated NCN moiety is indicated by very similar C–N distances [C1–N2 1.323(9), C1–N3 1.347(8), C1–N1 1.361(9) Å], which is also in accordance with the structure of a yttrium complex of the same ligand [17].

Subsequent reduction of **2** with KC_8 in THF resulted in a sudden colour change from royal blue to orange red. After work up, **3** was isolated as orange crystalline material. The ^1H NMR shows four doublets for the non equivalent CH_3 -protons of the isopropyl groups at -1.08 , 1.13 , 1.64 and 1.87 ppm and two septets for the CH -proton of the isopropyl groups at 3.30 and 5.18 ppm. However, a single set of signals was observed for CH_3 -N and aromatic protons. This might be attributed to the rigid behaviour of the compound arising from the steric crowding. X-ray crystal structure analysis shows **3** to be a bridged homobimetallic

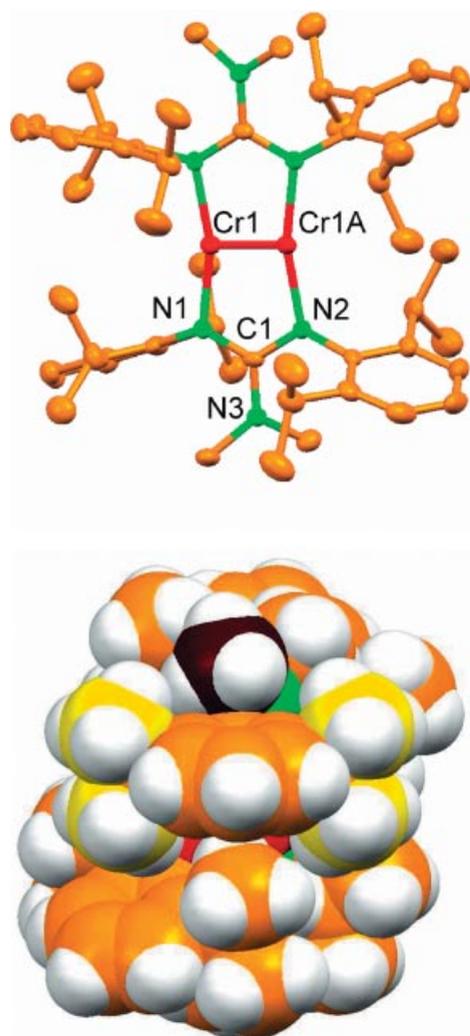


Figure 3. Molecular structure of **3** [ORTEP representation top (hydrogen atoms have been omitted for clarity.) and space filling model bottom (carbon atom of one of the methyl group of the dimethylamine moiety has been coloured brown and isopropyl residues of one of the 2,6-diisopropylphenyl moiety has been coloured yellow for clarity.)]; selected bond lengths /Å and angles $^\circ$: C1–N2 1.352(4), C1–N3 1.371(4), C1–N1 1.332(4), N1–Cr1 2.022(3), N2–Cr1 2.013(3), Cr1–Cr1A 1.7293(12); N2–C1–N1 115.4(3).

complex with an exceptionally short metal–metal distance of 1.7293(12) Å (Figure 3) [19]. It is the shortest Cr–Cr distance as well as the shortest metal–metal bond reported for a stable compound. The chromium–chromium distance is 0.1 Å shorter than that observed in the two examples that had been the classics in terms of the shortest metal–metal bond for nearly 30 years [4, 6]. The Cr–N bond lengths of [N1–Cr1 2.022(3), N2–Cr1 2.013(3)] are comparable to the known quintuply bonded amidinate chromium complexes [14, 15]. The C1–N1, C1–N2 and C1–N3 bond lengths of the ligand back bone are C1–N2 1.352(4), C1–N1 1.332(4) and C1–N3 1.371(4) Å respectively, indicating the delocalisation of the π -system over the three nitrogen atoms. The space-filling plot of **3** (Figure 3, bottom) shows how the methyl groups of the dimethylamine moieties are locked between the two isopropyl substituents of the “wings” and how these methyl groups or moieties put “steric pressure” on the phenyl groups of that “wings”. The magnetic susceptibility measurement of **3** in the range of 300 to 2 K are indicative of a $S = 0$ ground state, as could be expected for strongly coupled d^5 – d^5 bonding electrons [2]. Some positive contribution of temperature-independent paramagnetism (*TIP*) as characteristic for 3d metal ions [20] amounts $535 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$ for **3**.

To investigate the electronic structure of **3** we employed DFT calculations [21] with subsequent natural population analyses (NPA) [22] and inspection of the electron-localisation function (ELF) [23]. All calculations were carried out on a model structure of **3**, namely **3a**, in which the isopropyl substituents were replaced with hydrogen atoms [24]. The results show **3a** to be almost identical to **4a** in terms of its electronic structure (Figure 4) [13], which supports the assumption that the observed bond lengths are rather determined by the sterics of the ligands instead of substantial changes in the electronic structure.

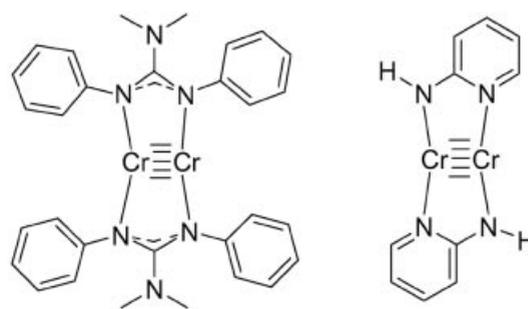


Figure 4. Structure of **3a** (left) and **4a** (right).

For the Cr–Cr bond in **3a**, a Wiberg bond index [25] of 4.43 was obtained. By comparison with an index of 4.36 for complex **4a**, a similar bond order is apparent. NPA revealed no significant differences for the metal charges nor for the relative 4s and 3d populations. Canonical MO patterns as well as ELF results (see Supporting Information) also compare the essentially similar electronic structure of the two complexes.

In conclusion we introduced the coordination compound showing the shortest metal–metal bond observed yet and emphasise the importance of the ligand and its steric fine tuning to observe such short Cr–Cr bonds.

Supporting Information (see footnote on the first page of this article): Experimental details of the complex syntheses and characterisation of the SQUID measurements and details of the calculations.

References

- [1] G. Frenking, R. Tonner, *Nature* **2007**, *446*, 276–277.
- [2] T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long, P. P. Power, *Science* **2005**, *310*, 844–847.
- [3] The role of metal–metal bonds, magnetic coupling ligand artefacts and the questionable strength in quadruply bonded chromium complexes possessing supershort Cr–Cr distance was reviewed in: J. J. H. Edema, S. Gambarotta, *Inorg. Chem.* **1991**, *11*, 195–214.
- [4] F. A. Cotton, S. A. Koch, *Inorg. Chem.* **1978**, *17*, 2021–2024.
- [5] F. Hein, D. Tille, *Z. Anorg. Allg. Chem.* **1964**, *329*, 72–82.
- [6] Interestingly, a little more than a month before a homobimetallic Cr^{II} compound with a Cr–Cr distance of the same length 1.828(2) Å, tetrakis(2-methoxy-5-methylphenyl)dichromium was submitted. It appeared in print one issue later: F. A. Cotton, S. A. Koch, M. Millar, *Inorg. Chem.* **1978**, *17*, 2084–2086. The metal–metal distances in both compounds are statistically indistinguishable from each other and the formal bond order is four.
- [7] V. E. Bondybey, J. H. English, *Chem. Phys. Lett.* **1983**, *94*, 443–447.
- [8] Spectroscopy of flash photolysis products of Cr(CO)₆ are indicative of the same distance: Yu. M. Efremov, A. N. Samoilova, L. V. Gurvich, *Opt. Spectrosk.* **1974**, *36*, 654–657.
- [9] B. O. Roos, *Collect. Czech. Chem. Commun.* **2003**, *68*, 265–274.
- [10] K. A. Kreisel, G. P. A. Yap, O. Dmitrenko, C. R. Landis, K. H. Theopold, *J. Am. Chem. Soc.* **2007**, *129*, 14162–14163.
- [11] G. La Macchia, F. Aquilante, V. Veryazov, B. O. Roos, L. Gagliardi, *Inorg. Chem.* **2008**, *47*, 11455–11457.
- [12] R. Wolf, C. Ni, T. Nguyen, M. Brynda, G. J. Long, A. D. Sutton, R. C. Fischer, J. C. Fettinger, M. Hellman, L. Pu, P. P. Power, *Inorg. Chem.* **2007**, *46*, 11277–11290.
- [13] A. Noor, F. R. Wagner, R. Kempe, *Angew. Chem.* **2008**, *120*, 7356–7359; *Angew. Chem. Int. Ed.* **2008**, *47*, 7246–7249.
- [14] Y.-C. Tsai, C.-W. Hsu, J.-S. K. Yu, G.-H. Lee, Y. Wang, T.-S. Kuo, *Angew. Chem.* **2008**, *120*, 7250–7253; *Angew. Chem. Int. Ed.* **2008**, *47*, 7250–7253.
- [15] C.-W. Hsu, J.-S. K. Yu, C.-H. Yen, G.-H. Lee, Y. Wang, Y.-C. Tsai, *Angew. Chem.* **2008**, *120*, 10081–10084; *Angew. Chem. Int. Ed.* **2008**, *47*, 9933–9936.
- [16] S. Ge, A. Meetsma, B. Hessen, *Organometallics* **2008**, *27*, 313–3135.
- [17] Guanidines were recently used to break the 1.80 Å barrier of the Cr–Cr multiple bond between Cr^{II} atoms S. Horvath, S. I. Gorelsky, S. Gambarotta, I. Korobkov, *Angew. Chem. Int. Ed.* **2008**, *47*, 9937–9940.
- [18] $P\bar{1}$; $a = 18.0850(17)$, $b = 18.1010(17)$, $c = 18.1180(2)$ Å; $\alpha = 75.711(8)$, $\beta = 76.094(8)$, $\gamma = 89.885(5)^\circ$; $R_1 = 0.0626$, wR_2 (all data) = 0.1315.
- [19] $Pccn$; $a = 13.4340(8)$, $b = 19.7350(11)$, $c = 19.8000(13)$ Å; $\alpha = \beta = \gamma = 90.00^\circ$; $R_1 = 0.0490$ [$I > 2\sigma(I)$], wR_2 (all data) = 0.0932.
- [20] O. Kahn, *Molecular Magnetism*, VCH, New York, **1996**, pp. 380.
- [21] All structure optimisations were carried out at BP86/TZVP DFT level. NPA and ELF analyses were based on single point calculations at B3LYP/TZVPP level.
- [22] See for instance: A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.
- [23] A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.* **1990**, *92*, 5397–5403.
- [24] The employed model structure was based on X-ray structure data of **3**, but the positions of all hydrogen atoms were optimised.
- [25] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083–1096.

Received: February 26, 2009
Published Online: May 11, 2009