A new zinc–zinc-bonded compound with a dianionic α-diimine ligand: synthesis and structure of $[Na(THF)_2]_2 \cdot [LZn–ZnL]$ (L = $[(2,6\text{-}{}^iPr_2C_6H_3)N(Me)C]_2{}^{2-}$)†

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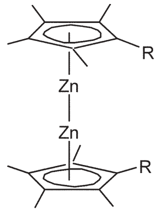
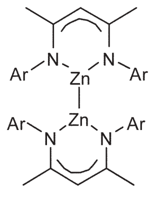
The synthesis and structure of a Zn–Zn-bonded compound supported by a doubly reduced α-diimine ligand, $[Na(THF)_2]_2 \cdot [LZn–ZnL]$ (L = $[(2,6\text{-}{}^iPr_2C_6H_3)N(Me)C]_2{}^{2-}$) are reported, with a Zn–Zn bond length of 2.399(1) Å.

The recent report by Carmona *et al.*[1] of the landmark compound with the first Zn–Zn bond, Cp*Zn–ZnCp* (**1**, Cp* = C_5Me_5), has attracted much interest not only in the theoretical study of the Zn–Zn bond nature,[2] but also in the synthesis and characterization of new Zn–Zn-bonded compounds. The second example, RZnZnR (**2**, R = $HC[C(Me)N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2$), synthesized by Robinson's group,[3] followed shortly afterwards using a bidentate β-diketiminate ligand. Furthermore, Power *et al.*[4] characterized Ar′ZnZnAr′ (**3**) and Ar′Zn(μ-Na)(μ-H)ZnAr′ (**4**) where Ar′ = $C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}{}^iPr_2)_2$, the latter featuring a different type of Zn–Zn bond bridged by a sodium and a hydrogen atom. Very recently another dizincocene Cp′Zn–ZnCp′ (**5**, Cp′ = C_5Me_4Et), an analog of **1**, has been reported by Carmona's group, along with computations on the electronic structure and the bonding properties of the two compounds and related dizincocenes.[5] It is found that the nature of the Zn–Zn bond depends largely on the ligand employed. For instance, the Zn–Zn bond length in **1** and **5** ($\sim$2.30 Å) is shorter than that in **2–4** ($\sim$2.36 Å), despite the lower coordination number of the zinc atom in the latter compounds. Moreover, DFT studies indicated that the Zn–Zn bond in **1**, **2** and **5** is formed mainly by the zinc 4s orbitals, while in **3** it contains mainly $4p_z$ character. Therefore, tuning of ligand properties may be a key to enriching the Zn–Zn bond family and to exploring the chemistry of these compounds. Here we report the synthesis and structure of a Zn–Zn-bonded compound bearing a doubly reduced α-diimine ligand, $[Na(THF)_2]_2 \cdot [LZn–ZnL]$ (**6**, L = $[(2,6\text{-}{}^iPr_2C_6H_3)N(Me)C]_2{}^{2-}$).



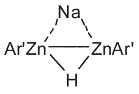
1 R = Me
5 R = Et



2 Ar = 2,6-$^iPr_2C_6H_3$

Ar′Zn—ZnAr′

3



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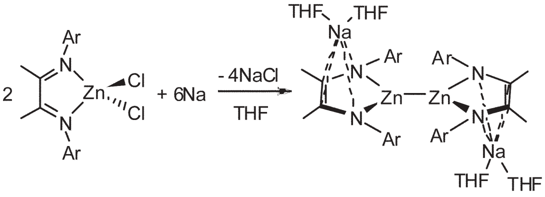
Ar′ = 2,6-(2,6-$^iPr_2C_6H_3)_2C_6H_3$

The title compound was synthesized by reduction of L^0ZnCl_2[6] (L^0 denotes the neutral α-diimine ligand) with sodium metal in THF (eqn (1), Ar = 2,6-$^iPr_2C_6H_3$).‡



(1)

Upon storage at −40 °C orange crystals were isolated, which differ significantly from the colorless appearance of the crystals of **1–5**.

The crystal structure§ of **6** reveals a centrosymmetric $[LZn]_2$ dimer with a Zn–Zn bond. The trigonal coordinated zinc atom is slightly deviated (0.40 Å) from the C_2N_2 plane, and the two C_2N_2 planes adopt a parallel but not coplanar orientation (a vertical separation of $\sim$1.28 Å between the two C_2N_2 planes). This is in contrast to either the nearly orthogonal (**2** and **3**)[3,4] or the planar (**4**)[4] conformations found in the known Zn–Zn-bonded compounds. The planes of the substituted N-phenyl groups in **6** are nearly perpendicular to the metallacycle C_2N_2Zn, with a dihedral angle of 75.2 and 77.4° (Fig. 1).

The Zn–Zn bond length in **6** is 2.3994(6) Å, about 0.04 Å longer than those in **2–4**, and about 0.1 Å longer than in the dimetallocenes **1** and **5**. Notably, while this bond length is about 0.05 Å shorter than the Zn···Zn separation (2.4513(9) Å) in a zinc hydride compound $[RZn(\mu\text{-}H)_2ZnR]$ (**7**, R as in **2**),[7] it is very close to that (2.4084(3) Å) in $Ar'Zn(\mu\text{-}H)_2ZnAr'$ (**8**, Ar′ as in **3** and **4**).[4] However, in the ^1H NMR spectrum of **6** no signal appears corresponding to the bridging hydride, which was located at 4.59 and 4.84 ppm for **7** and **8**, respectively, thus ruling out the presence of hydrogen bridges.

The most interesting structural feature of **6** is that there are two sodium ions in the molecule, each coordinated by two THF molecules. The two $[Na(THF)_2]^+$ units are situated above and

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† Electronic supplementary information (ESI) available: Details of the computations. See DOI: 10.1039/b703200e

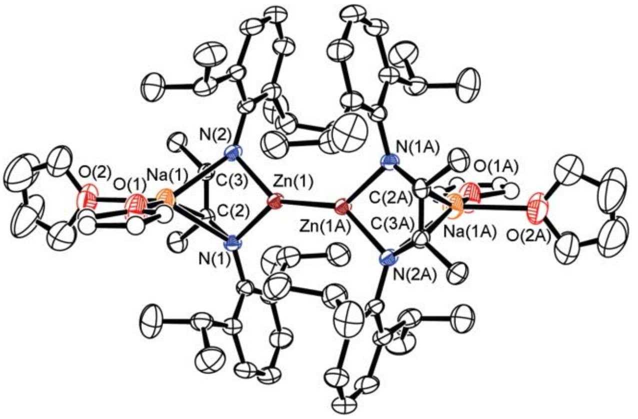

Fig. 1 The molecular structure of **6** (thermal ellipsoids set at 30% probability level; C atoms on one THF are drawn as smaller spheres for clarity). Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): Zn(1)–Zn(1A)* 2.3994(6), Zn(1)–N(1) 2.017(2), Zn(1)–N(2) 2.019(2), Na(1)–C(2) 2.619(3), Na(1)–C(3) 2.610(3), Na(1)–N(1) 2.659(3), Na(1)–N(2) 2.648(3), Zn(1)···Na(1) 3.1650(14); N(1)–Zn(1)–N(2) 82.02(9), N(1)–Zn(1)–Zn(1A) 138.71(7), N(2)–Zn(1)–Zn(1A) 139.03(7). * ($-x$, $2-y$, $1-z$).

below the two five-membered metallacycles, respectively, and each Na^+ ion is π-bonded (η^4-) to one N–C=C–N moiety (Fig. 1). The projection of the Na atom on the C_2N_2Zn plane deviates from the ring centroid by ∼0.3 Å, being closer to the C and N atoms than to Zn. It is noted that, apart from the solvation, the way the Na^+ is bound in **6** is dramatically different from that in some other metal-metal-bonded systems with terphenyl ligands, *e.g.*, $Na_2[GaR]_3$,[8] $Na_2[GaR]_2$,[9] and compound **4**,[4] where the sodium ions bridge the central metals and interact with the flanking aryl rings. Furthermore, the solvated $[Na(THF)_2]^+$ ions provide considerable additional shielding for the central Zn–Zn bond, as shown in the space filling structure (Fig. 2). The two aryl substituents in each ligand are bent toward each other such that the distance between the isopropyl groups on one side is significantly larger than on the other side (CH···CH about 4.07 and 6.66 Å, respectively). Most conveniently, the volume of the widened side is filled by the $[Na(THF)_2]^+$ unit (Fig. 2(b)).

The redox processes involved in the reaction are also worth noting, as the Zn^{2+} ion in the precursor was reduced to monovalent Zn^+, while each α-diimine ligand took two electrons to form a dianion $[L]^{2-}$. Ligand L^0 and its derivatives are well known because of the high activity of their late transition metal complexes—Brookhart's catalysts —in catalytic olefin polymerization.[10] The reduction of related α-diimine units to mono- or dianions has been reported;[11] in particular, crystals of $[Na_2(OEt_2)_3]^{2+}[L']^{2-}$ (L′ = bis[*N*-(2,6-diisopropylphenyl)imino] acenaphthene) have been isolated[12] in which one of the ether-solvated Na^+ ions is π-bonded to the enediamido C_2N_2 moiety, similar to that in compound **6**. Furthermore, such π-bond modes have also been observed in some Zn-diimine/enediamido systems containing K^+ cation, *e.g.*, K[ZnR(*t*-BuNCHCHN-*t*-Bu)] (R = CH_3, CH_2Ph)[13] and $K(THF)_3[Zn(t\text{-BuNCHCHN-}t\text{-Bu})_2]$.[14]

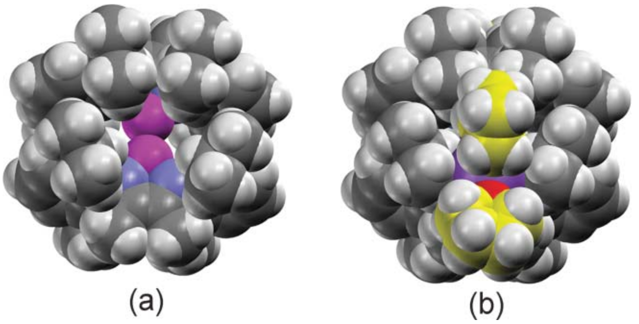
(a) (b)

Fig. 2 Space filling diagrams of **6**. (a) The [LZn–ZnL] backbone without $[Na(THF)_2]^+$; (b) The whole molecule showing the $[Na(THF)_2]^+$ units that provide effective protection for the Zn–Zn bond. Zn, pink; N, blue; Na, purple; O, red. Carbon atoms of THF are in yellow.

DFT studies[15] of a model $Na_2[(CHNH)_2Zn–Zn(NHCH)_2]$ (**6H**) were performed at the DZP BP86 level. The theoretical Zn–Zn bond distance (2.373 Å) for **6H** agrees well with the experimental data (2.3994(6) Å) for **6**, and both fall in the range (2.28–2.40 Å) of the experimental and theoretical studies to date.[5] The Wiberg bond index (WBI) gives a Zn–Zn bond order of 0.69 for **6H**, which is smaller than similarly theoretical Zn–Zn bond orders for the known compounds **1–5**. The DFT predicted bond dissociation energy *E*(Zn–Zn) of 57 kcal mol^{-1} for **6H** is also slightly smaller than the similar DFT theoretical result (67 kcal mol^{-1}) for the Zn–Zn bond in **1**.[2b] Together with the slightly lengthened bond distance, our theoretical results may suggest a weaker Zn–Zn bond in **6** than in the analogs **1–5**.

As shown in Fig. 3, the HOMO−2 involves the Zn–Zn σ-bond and some N→Zn coordination bonding. The LUMO is localized on the ligands with π-symmetry. Thus the Zn–Zn bond is formed mainly by the 4s orbitals, and the natural bond orbital (NBO) analysis shows that this Zn–Zn σ-bond is composed of 95% s, 4% p, and 1% d character. This is similar to the composition of the Zn–Zn bond in **1**, **2** and **5**,[3,5] but is different from that of **3**,[4] which has mostly $4p_z$ character. The natural charges on the Zn and Na atoms are +0.75 and +0.84, respectively, while the negative charges are delocalized on the ligand N–C=C–N moiety with a total value

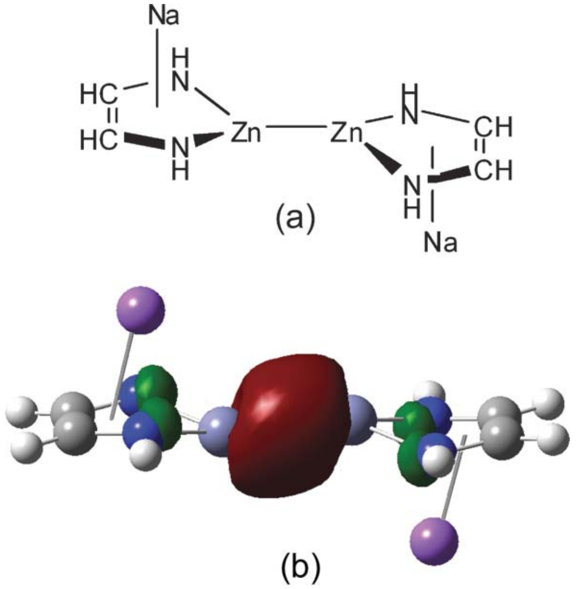

Fig. 3 The structure (a) and the Zn–Zn bonding orbital (HOMO−2, b) of the model compound **6H** from DFT computations. For other frontier orbitals see ESI.†

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approaching −2 on the four atoms. This charge distribution further confirms that the neutral α-diimine ligand L^0 in the precursor is reduced to a dianion during the reaction.

In conclusion, we report the synthesis and structure of a new Zn–Zn-bonded compound supported by two α-diimine dianions, which are π-bonded by solvated sodium ions. Investigation of the reactivity of this compound and synthesis and characterization of similar compounds with a Zn–Zn bond are planned.

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Notes and references

‡ *Synthesis* of **6**: under an inert atmosphere of dry argon, $LZnCl_2$ (1.50 g, 2.78 mmol) and sodium (0.20 g, 8.70 mmol) were combined with 40 mL of THF at ambient temperature. The mixture was stirred for 10 d and filtered to yield a dark red solution, which was concentrated to about 10 mL and stored at *ca.* −40 °C. Orange crystals were isolated after a week (0.96 g, 54%). Mp 150 °C (decomp.). ^1H NMR (400 MHz, C_6D_6): δ = 1.02 (d, 24H, J = 6.8 Hz, $CH(CH_3)_2$), 1.28 (m, 40H, $CH(CH_3)_2$ + THF), 1.64 (s, 12H, N–CCH_3), 3.16 (m, 8H, $CH(CH_3)_2$), 3.40 (t, 16H, J = 6.4 Hz, THF), 7.10–7.16 ppm (m, 12H, C_6H_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 15.7 (N–CCH_3), 23.5 ($CH(CH_3)_2$), 25.8 ($CH(CH_3)_2$), 28.3 (THF), 68.0 (THF), 121.4 (p-C_6H_3), 122.6 (o-C_6H_3), 144.5 (N–CCH_3), 128.0 ppm (i-C_6H_3 and m-C_6H_3).

§ X-Ray intensity data were collected on a Bruker SMART APEX II diffractometer at 293 K. The structure was solved by direct methods using the SHELXL-97 program. *Crystal data*: $C_{72}H_{112}N_4Na_2O_4Zn_2$: monoclinic, space group $P2_1/n$, a = 13.0184(2), b = 20.3636(4), c = 13.8961(3) Å, β = 90.332(1)°, V = 3683.81(12) Å^3, D_c = 1.149 g cm^{-3}, Z = 2, μ = 0.709 mm^{-1}; 22949 reflections measured, 8772 unique (R_{int} = 0.0343), no. of observed reflections 5871 ($I > 2\sigma(I)$); $R1$ = 0.0515, $wR2$ = 0.1392 for observed reflections ($I > 2\sigma(I)$). CCDC 638804. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703200e

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15 Computations: The structure of the model compound was optimized at the DFT level (BP86) with DZP++ basis set with the Gaussian-94 program (reference in ESI†).