Biradicals

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[(dpp-bian)Zn–Zn(dpp-bian)]: A Zinc–Zinc-Bonded Compound Supported by Radical-Anionic Ligands**

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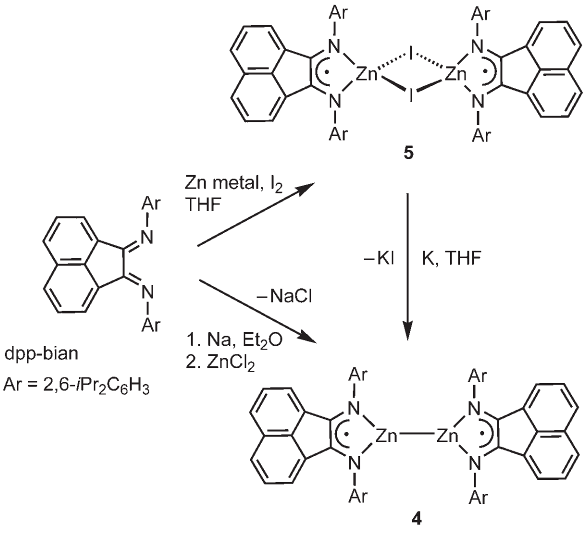
Dedicated to Professor Gleb A. Abakumov on the occasion of his 70th birthday

In 2004, Carmona and co-workers reported the isolation of the first molecular zinc compound having a direct metal–metal bond, [Cp*Zn–ZnCp*] (**1a**; Cp* = C_5Me_5).[1] Following this pioneering work, Robinson and co-workers synthesized the three-coordinate zinc ketiminate derivative [{HC(CMeNAr)$_2$}Zn–Zn{HC(CMeNAr)$_2$}] (**2**) (Ar = 2,6-iPr$_2$C$_6$H$_3$).[2] A further breakthrough in this field was the synthesis by Power and co-workers of the two-coordinate compound, [Ar′Zn–ZnAr′] (**3**) (Ar′ = 2,6-(2,6-iPr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$), in which stabilization of Zn–Zn bonding was achieved using a bulky aryl ligand.[3] While our paper was being submitted, another dizincocene, [(C$_5$Me$_4$Et)Zn–Zn(C$_5$Me$_4$Et)] (**1b**), was prepared and investigated by X-ray crystallography as well as computationally.[1d] So far, compounds **1**–**3** are the only examples of zinc organic derivatives which have a direct Zn–Zn bond. The metal–metal bonds in these compounds (**1a**: 2.305(3); **1b**: 2.295(3); **2**: 2.3586(7); **3**: 2.3591(9) Å) are significantly shorter than the sum of zinc covalent radii (2.5 Å).[4] Density functional theory (DFT) calculations (B3LYP) for **1**–**3** showed that in **1a**[1b] and **2**[2] the metal 4s orbitals mainly contribute to the Zn–Zn bond, whereas in **3** this bond is formed from the overlap of 4p$_z$ orbitals.[3]

Earlier we showed that the use of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) allowed the preparation of monomeric complexes of Group 1, 2, and 13 metals with the dpp-bian ligand in its anionic forms ([dpp-bian]$^{n-}$, n = 1–4).[5] Aggregation of alkaline-earth or aluminum complexes of [dpp-bian]$^{n-}$ (n = 1, 2) is prevented by two factors: the rigidity of the diimine fragment and the bulkiness of 2,6-iPr$_2$C$_6$H$_3$ substituents. Also the dpp-bian is able to stabilize the low oxidation state of germanium, thus providing two- and three-coordinate Ge^{II} species with the dianionic and radical-anionic dpp-bian ligand, [(dpp-bian)Ge][6] and [(dpp-bian)GeCl].[7] Being inspired by the development of the Zn–Zn chemistry and to get more insight in solution behavior of zinc–zinc-bonded species we have attempted the synthesis of a Zn–Zn compound stabilized with the radical-anionic dpp-bian. Herein we report on the synthesis and characterization by single-crystal X-ray analysis and ESR spectroscopy of the first zinc–zinc-bonded compound supported by radical-anionic ligands, [(dpp-bian)Zn–Zn(dpp-bian)] (**4**), as well as examination of its electronic structure by computation (DFT).

In contrast to magnesium, which reacts with dpp-bian in the presence of 1 mol% of MgI$_2$ to give quantitative formation of [(dpp-bian)Mg(thf)$_3$], zinc metal does not react with dpp-bian in the presence of ZnI$_2$ in THF under the same conditions. However, stirring of dpp-bian with a large excess of zinc granules in THF in the presence of 0.5 mol equivalents of ZnI$_2$ (formed in situ from the Zn and I$_2$ in THF) at 20 °C for several minutes affords the cherry-red compound [{(dpp-bian)ZnI}$_2$] (**5**) in 64% yield (Scheme 1).

In solution compound **5** gives an ESR signal (2-methyltetrahydrofuran (Me-THF), 280 K: septet, g_i = 2.0027, $a_i(^{127}I)$ = 0.24 mT, $a_i(2\times{}^{14}N)$ = 0.51 mT) which clearly indicates the presence of the dpp-bian radical-anion. The ^{14}N hyperfine coupling constant in **5** is only slightly different to those in Zn–DAD (DAD = 1,4-di-*tert*-butyl-1,3-diazadiene) radical-anionic species such as [(DAD)$^{\bullet-}$Zn(DAD)^0]OTf



Scheme 1. Synthetic pathways to compounds **4** and **5**.

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($OTf = [CF_3SO_3]^-$) and $K[(DAD)^{\bullet -}Zn(DAD)^{2-}]$ (both 0.54 mT).[8]

The target compound [(dpp-bian)Zn–Zn(dpp-bian)] (**4**) can be prepared in two ways. The first one uses alkali-metal reduction of **5** similar to the preparation of **2** and **3**.[2,3] At room temperature the reduction of **5** with potassium in THF is complete within 3 h and gives a deep, gold-red solution along with a precipitate of KI (Scheme 1). In contrast to the colorless compounds **1**–**3**, complex **4** has a deep color which is typical for metal–dpp-bian derivatives.[5] Crystallization from toluene affords compound **4** as black block crystals in 52 % yield. However, a more convenient synthetic approach to **4** is the direct reaction of $ZnCl_2$ with the sodium salt of dpp-bian dianion[5a] which can be generated in situ from dpp-bian and Na in diethyl ether (Scheme 1). Note that in this reaction the metal-cation exchange and the reduction processes take place simultaneously. In this way we were able to prepare compound **4** on a scale of several grams. Crystallization from diethyl ether affords compound **4** in 85 % yield.

According to the X-ray crystal-structure analyses compounds **4** (Figure 1) and **5** (Figure 2) are binuclear zinc species. In the case of **4** the X-ray analysis has been carried out on the crystals obtained from both diethyl ether and toluene. The geometrical parameters of both structures are very similar: Zn–Zn bond lengths are 2.3321(2) Å (crystals from Et_2O) and 2.3386(6) Å (crystals from toluene) and these fit well into the range found in **1**–**3**.

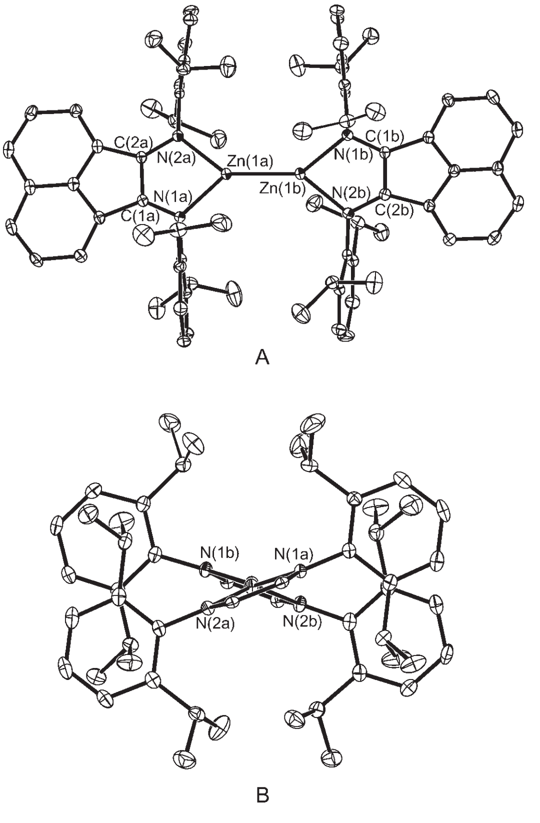

Figure 1. A) Molecular structure of **4** (recrystallized from Et_2O; thermal ellipsoids are set at 40% probability). Selected bond lengths [Å] and angles [°]: Zn(1a)–Zn(1b) 2.3321(2), Zn(1a)–N(1a) 2.0133(10), Zn(1b)–N(1b) 2.0153(10), Zn(1a)–N(2a) 2.0287(12), Zn(1b)–N(2b) 2.0381(12), N(1a)–C(1a) 1.3244(17), N(1b)–C(1b) 1.3323(17), N(2a)–C(2a) 1.3357(15), N(2b)–C(2b) 1.3233(16), C(1a)–C(2a) 1.4414(18), C(1b)–C(2b) 1.4453(18); N(1a)-Zn(1a)-N(2a) 83.63(4), N(1b)-Zn(1b)-N(2b) 83.77(4). B) Projection along the Zn–Zn bond (the naphthalene moieties are omitted for clarity).

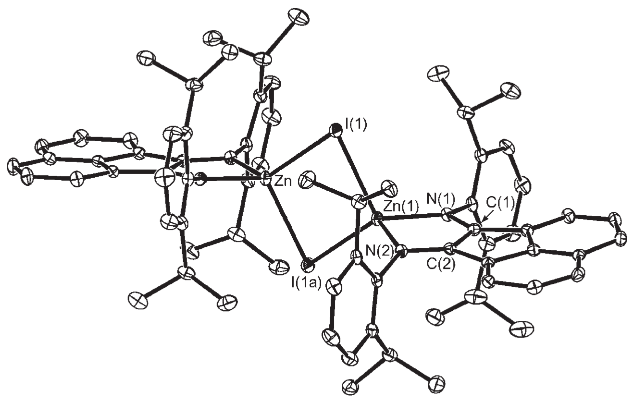

Figure 2. Molecular structure of **5** (thermal ellipsoids are set at 40% probability). Selected interatomic distances [Å] and angles [°]: Zn(1)···Zn 3.346(2), Zn(1)–N(1) 1.9885(10), Zn(1)–N(2) 1.9908(13), Zn(1)–I(1) 2.5959(2), Zn(1)–I(1a) 2.6664(2), N(1)–C(1) 1.3346(19), N(2)–C(2) 1.3296(15), C(1)–C(2) 1.447(2), N(1)-Zn(1)-N(2) 87.25(5); N(1)-Zn-I(1a) 117.35(4); N(2)-Zn(1)-I(1) 126.19(3), N(1)-Zn(1)-I(1a) 16.56(4), I(1)-Zn(1)-I(1a) 101.116(7), Zn(1)-I(1)-Zn 78.721(7).

In contrast to **2** both metallacycles in **4** are nearly planar (Figure 1 B). The twist of the two dpp-bian ligands around the Zn–Zn bond (the dihedral angle between two planes C_2N_2Zn is ca. 42°) is likely a result of steric repulsion between the *i*Pr groups occurring in coplanar or orthogonal orientations of the dpp-ligands.) The same twist of the dpp-bian ligands is observed in the magnesium complex $[(dpp\text{-}bian)_2Mg]$,[9a] in which the Mg^{2+} ion plays the role of the binuclear $\{Zn–Zn\}^{2+}$ ion in **4**. The dimeric structure of **5** formed through the bridging iodine atoms: the Zn···Zn separation is 3.346(2) Å.

The X-ray crystallography data allow elucidation of the radical-anionic character of dpp-bian ligands in both molecules **4** and **5**. Population of the LUMO on going from neutral dpp-bian to its radical-anion and further to the dianion must result in shortening of the central C(1)–C(2) bond and elongation of the C(1)–N(1) and C(2)–N(2) bonds. The bonds C(1)–N(1) and C(2)–N(2) in **4** (1.323(1)–1.335(1) Å) and in **5** (1.334(1), 1.329(1) Å) are longer than in free dpp-bian (both 1.282(4) Å),[10] but shorter than in its dianion in $[(dpp\text{-}bian)Mg(thf)_3]$ (1.401(6) and 1.378(7) Å)[5b] and almost of the same length as in the radical-anionic complex $[(dpp\text{-}bian)_2Mg]$ (N(1)–C(1) 1.338(2), N(2)–C(2) 1.340(2) Å).[9a]

To probe whether compound **4** retains its Zn–Zn bond in solution we investigated **4** by the ESR spectroscopy. As expected, biradical **4** shows a broad unresolved ESR signal ($\Delta H \approx 5$ mT) in solution at room temperature. In contrast to **5**, complex **4** does not exhibit any signal attributable to single radical-anionic species in the range 130–300 K. At 130 K, compound **4** exhibits a half-field signal ($\Delta m_s = 2$) characteristic of a biradicals in Me-THF or toluene. The zero-field splitting parameters of the $g = 2$ ESR signal (toluene, $D =$ 6.39 mT, $E = 1.01$ mT, Figure 3) allows the unpaired electron separation to be estimated at 7.57 Å in molecule **4**. This parameter is in perfect agreement with a distance of 7.78 Å

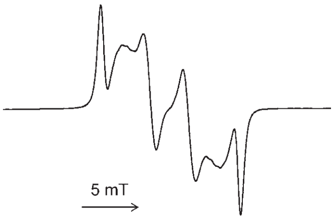

Figure 3. The ESR signal of compound **4** in toluene at 130 K.

between the imino carbon atoms C(1a)–C(1b) and C(2a)–C(2b) in **4** determined by single-crystal X-ray analysis. For comparison the respective values in [(dpp-bian)$_2$Mg] are 5.28 and 5.65 Å (from ESR[9b] and X-ray data,[9a] respectively). Further comparison can be made with the mononuclear biradical compound [(DAD)$^{\bullet-}{}_2$Zn], in which the corresponding unpaired electron separation is 4.75 Å.[11]

The electronic structure of complex **4** was examined by DFT calculations[12] at the B3LYP/6-31G* level using a D_2 molecule with unsubstituted phenyl groups as a model system. The same level of theory was employed earlier to analyze Zn–Zn bonding in **3**.[3] In contrast to the single-point computation[3] we performed geometry optimization for both singlet and triplet states of the molecule with the coplanar and perpendicular conformation of the two ligands. The triplet ground-state configuration appears to be 13.1 kcal mol^{-1} more stable than the lowest singlet state which agrees well with the ESR data. The perpendicular geometry minimum lies 2.3 kcal mol^{-1} lower than the coplanar one. A single-point computation shows that a change of the N-Zn-Zn-N dihedral angle from 90 to 42° (value found in the X-ray structure) leads to a small electronic energy increase (1.6 kcal mol^{-1}). Minor energy changes indicate that the dihedral angle observed experimentally is a result of mutual repulsion of the bulky isopropyl groups. The calculated Zn–Zn distance in the triplet perpendicular conformation (2.31453 Å) is in a good agreement with the X-ray data presented in Figure 1.

Two degenerate semioccupied MOs of the perpendicular triplet system (HOMO and HOMO−1; −3.95 eV) are localized on the dpp-bian ligands. The Zn–Zn bond is formed mainly by the overlap of the Zn 4s orbitals in the HOMO−2 (−5.36 eV). The degenerate LUMO orbitals (LUMO and LUMO+1; −1.71 eV) and the two next unoccupied orbitals (LUMO+2 and LUMO+3; −0.27 eV) represent ligand MOs (Figure 4). According to the natural bond orbital (NBO) analysis the Zn s, p, and d wave-function contributions to the Zn–Zn bond are 93.9, 3.7, and 2.4 %, respectively. Zn–Zn bonding in **4** differs, therefore, from that in **3** where the Zn 4p$_z$ orbitals form the metal–metal bond.[3] This difference is explained by the Zn environments in the two systems. In the dpp-bian derivative, the Zn atom interacts with two nitrogen atoms whereas in **3** one Zn–C bond is formed to the ligand. Indeed, in **2**, which has two Zn–N bonds for each metal atom, the Zn–Zn bond has 95 % s character.[2] However, in **2** the Zn–Zn σ-bonding orbital is the HOMO, whereas in **4** the HOMO is a ligand orbital. The Zn natural charge in our model system derived from the NBO analysis is +0.842 which correlates well with the formal +1 oxidation state of the metal atoms.

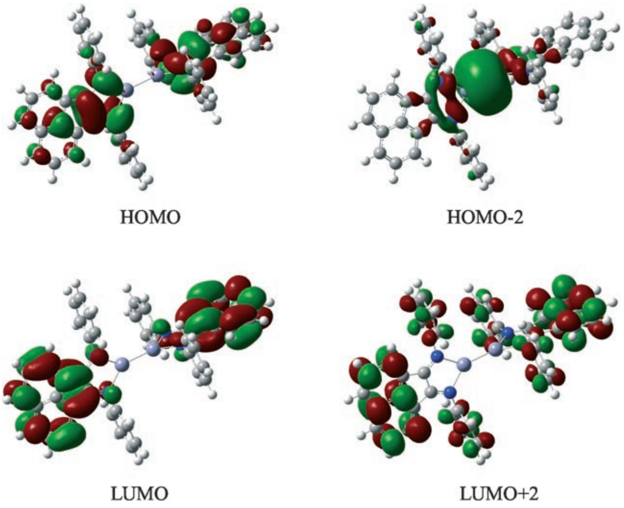

Figure 4. Representation of the frontier orbitals, HOMO−2, and LUMO+2 of **4** from DFT calculations; Zn blue-gray, N dark blue, C gray, H white.

In conclusion, a new zinc–zinc-bonded compound supported by radical-anionic ligands has been synthesized by a straightforward procedure. The use of a spin labeled ligand, the dpp-bian radical-anion, allowed the confirmation of the presence of Zn–Zn bonding in solution. DFT calculations confirm the biradical nature of the compound and indicate that the Zn–Zn bond is formed mainly by the metal s orbitals. A study of the reactivity of the Zn–Zn bond in **4** and related bian-based compounds will be subjects of further research.

Experimental Section

All manipulations were carried out on vacuum lines using Schlenk technique. The solvents THF, Et$_2$O, and toluene were distilled from sodium/benzophenone prior to use. The ESR spectra were recorded on a Bruker EMX instrument equipped with an ER 041X microwave bridge. ZnCl$_2$ was purchased from Aldrich. Diimine dpp-bian was prepared according to the published procedure.[13]

4: ZnCl$_2$ (0.27 g; 2 mmol) was added to a solution of (dpp-bian)Na$_2$ (generated in situ from dpp-bian (1.0 g; 2 mmol) and sodium (0.092 g; 4 mmol) in Et$_2$O (50 mL). Within a few minutes the stirred solution changed color from bright green to gold-red and NaCl precipitated. After filtration, slow evaporation of the solvent from the filtrate afforded compound **4** as deep red, almost black crystals (1.0 g, 85 %). M.p. > 300 °C (the sample was unchanged in the temperature range of 20–300 °C). IR (nujol): $\tilde{\nu} = 1923$ w, 1861 w, 1796 w, 1623 m, 1538 s, 1319 m, 1254 w, 1181 w, 1111 w, 938 m, 861 m, 800 w, 758 vs, 669 w, 615 w, 546 w, 450 m cm^{-1}. Elemental analysis calcd (%) for $C_{72}H_{80}N_4Zn_2 \cdot Et_2O$ (1206.34): C 75.67, H 7.52; found C 75.11, H 7.46. Crystal data for **4** crystallized from diethyl ether: $M_r = C_{76}H_{90}N_4OZn_2$, monoclinic, space group $P2_1/c$, $a = 18.8890(9)$, $b = 14.1495(6)$, $c = 25.6573(12)$ Å, $\beta = 105.0550(10)°$, $V = 6622.1(5)$ Å^3, $Z = 4$, $T = 100(2)$ K, $F_{000} = 2568$, $\mu = 0.771$ mm^{-1}, $\theta = 1.66$–$27.50°$, reflections collected 44000, independent reflections 15200 ($R_{int} = 0.0405$), $GOF = 0.974$, $R = 0.0402$, $wR^2 = 0.0896$, largest diff. peak and hole 0.460/−0.235 e Å^{-3}. Crystal data for **4** crystallized from toluene: $M_r = C_{79}H_{88}N_4Zn_2$, monoclinic, space group $P2_1/c$, $a = 18.6853(13)$, $b = 14.1138(11)$, $c = 25.881(2)$ Å, $\beta = 103.491(2)°$, $V = 6637.0(9)$ Å^3, $Z = 4$, $T = 100(2)$ K, $F_{000} = 2600$, $\mu = 0.769$ mm^{-1}, $\theta =$

1.62–26.00°, reflections collected 38794, independent reflections 13021 ($R_{int} = 0.0685$), $GOF = 1.020$, $R = 0.0573$, $wR^2 = 0.1231$, largest diff. peak and hole 0.844/−0.456 e Å^{-3}.

5: Excess of zinc (7.4 g, granules, diameter ca. 5 mm) was stirred with I_2 (0.254 g, 1 mmol) in THF (40 mL) until the color of iodine had completely disappeared. Addition of dpp-bian (1.0 g; 2 mmol) and stirring of the mixture for several minutes at room temperature led to the formation of deep cherry-red solution, which was decanted from the excess metal. Evaporation of the solvent in vacuum left an oily residue which was dissolved in Et_2O (25 mL). Within several minutes 0.95 g (64%) of **5** precipitated in a form microcrystalline solid. Recrystallization from hot toluene afforded deep red X-ray-quality crystals. M.p. > 300 °C (the sample was unchanged in the temperature range of 20–300 °C). IR (nujol): $\tilde{\nu} = 1531$ s, 1315 w, 1250 w, 1184 w, 1142 w, 1104 w, 942 w, 865 w, 819 w, 800 m, 754 s, 669 w, 619 w, 546 w cm^{-1}. Elemental analysis calcd (%) for $C_{72}H_{80}I_2N_4Zn_2 \cdot C_7H_8$ (1478.16): C 64.19, H 6.00; found C 64.05, H 5.98. Crystal data for **5**: $M_r = C_{79}H_{88}I_2N_4Zn_2$, triclinic, space group $P\bar{1}$, $a = 13.6474(7)$, $b = 14.1559(7)$, $c = 20.7590(10)$ Å, $\alpha = 95.6190(10)°$, $\beta = 104.9990(10)°$, $\gamma = 113.1040(10)°$, $V = 3472.2(3)$ Å^3, $Z = 2$, $T = 100(2)$ K, $F_{000} = 1512$, $\mu = 1.626$ mm^{-1}, $\theta = 1.69$–27.50°, reflections collected 33346, independent reflections 15760 ($R_{int} = 0.0229$), $GOF = 1.028$, $R = 0.0286$, $wR^2 = 0.0667$, largest diff. peak and hole 0.713/−0.400 e Å^{-3}.

CCDC-632011 (**4** from Et_2O) and CCDC-632012 (**5**) contains 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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