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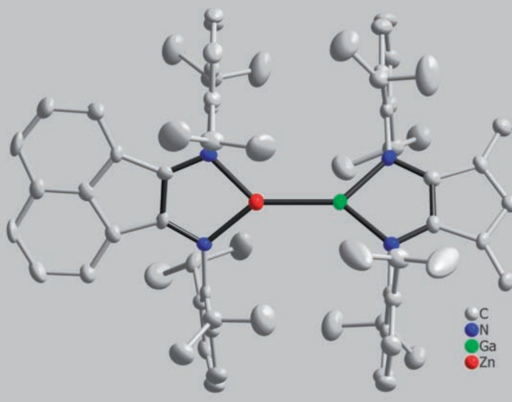

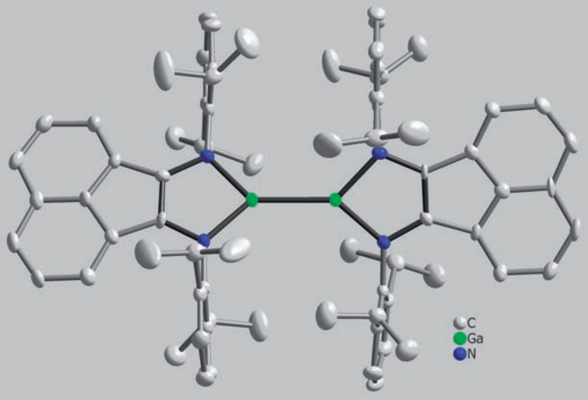

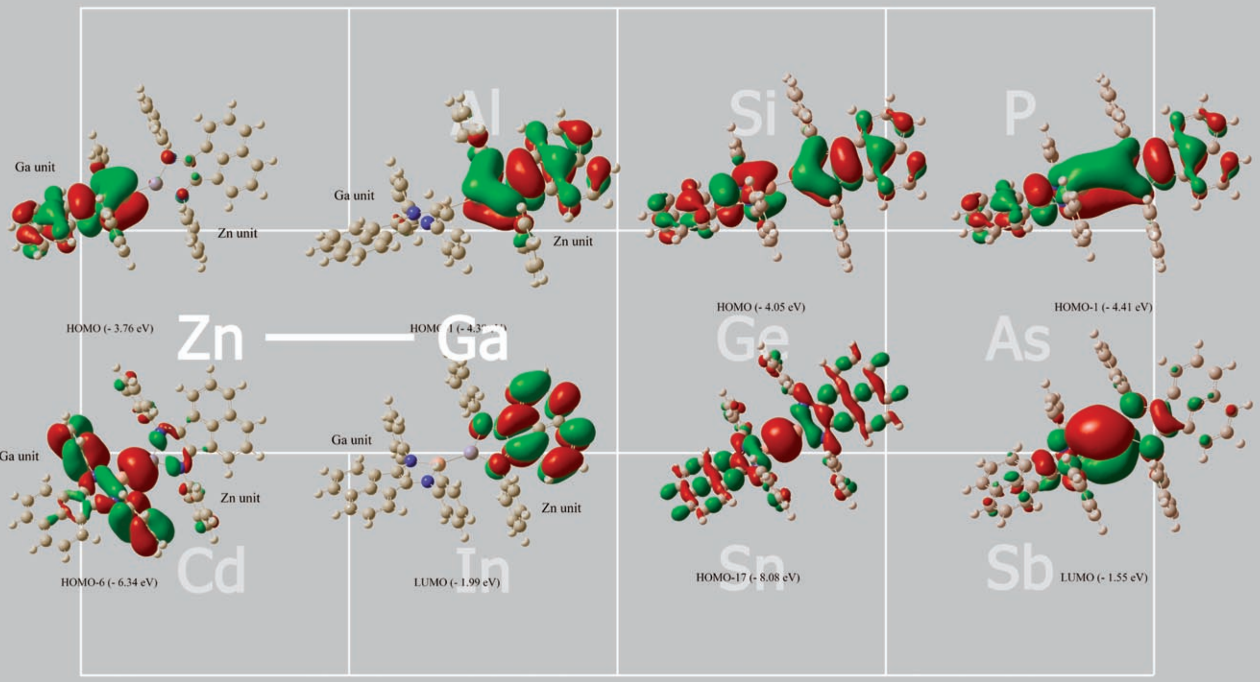

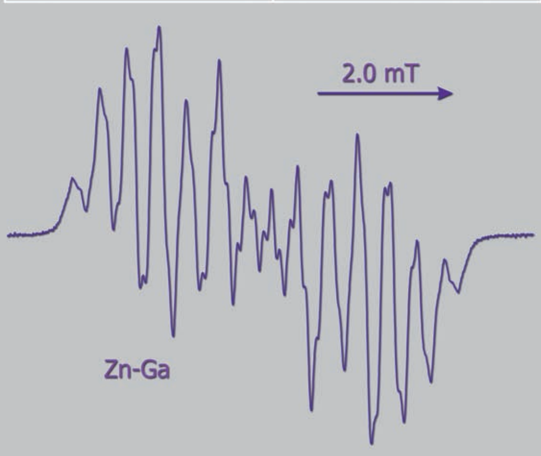

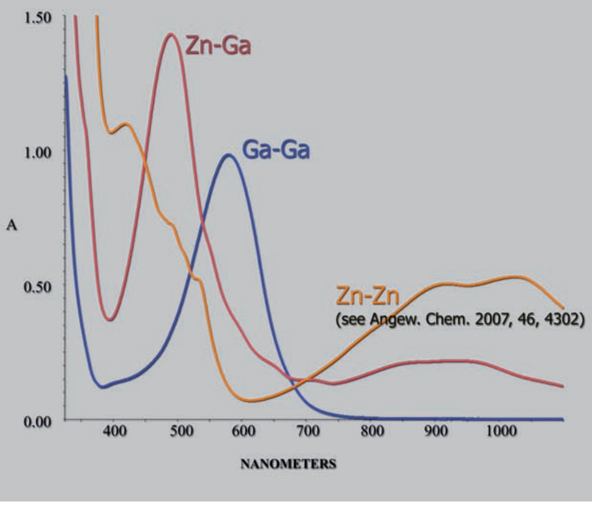

[(dpp-bian)Ga−Ga(dpp-bian)] and [(dpp-bian)Zn−Ga(dpp-bian)]: Synthesis, Molecular Structures, and DFT Studies of These Novel Bimetallic Molecular Compounds

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Abstract: 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene) (dpp-bian) stabilizes gallium–gallium and zinc–gallium bonds (compounds **1**–**3**). The compound [(dpp-bian)Ga−Ga(dpp-bian)] (**2**) was prepared by the reaction of $GaCl_3$ with K_3[dpp-bian] and the heterometallic [(dpp-bian)Zn−Ga(dpp-bian)] (**3**) was prepared by a simple one-pot reaction of [{(dpp-bian)ZnI}$_2$] with $GaCl_3$ and K_4[dpp-bian]. In contrast to [(dpp-bian)Zn−Zn(dpp-bian)] (**1**) and **3**, compound **2** is ESR silent, thus proving the dianionic character of both dpp-bian ligands. The solution ESR spectrum of **3** reveals the coupling of an unpaired electron with the gallium nuclei ^{69}Ga and ^{71}Ga ($A(^{69}\text{Ga})=0.97$, $A(^{71}\text{Ga})=1.23$ mT), thus confirming the presence of Zn−Ga bonds in solution. According to the results of the X-ray crystal structure analyses the metal–metal bond lengths in **2** (2.3598(3) Å) and **3** (2.3531(8) Å) are close to that found in **1** (2.3321(2) Å). The electronic structures of compounds **2** and **3** were studied by DFT (B3LYP/6–31G* level). The metal–metal π bond in **2** is mainly formed by overlap of the p orbitals of Ga in the HOMO and HOMO−1, the latter showing a stronger interaction. The s and p orbitals of Ga overlap in the deeper located HOMO−17 producing a Ga−Ga σ bond. In contrast to the Zn−Zn bond in **1**, which has 95 % s character, the NBO (natural bond order) analysis of **2** reveals 67.8 % s, 32.0 % p, and 0.2 % d character for the Ga−Ga bond. Compound **3** has a doublet electronic ground state. The unpaired electron occupies the α HOMO−1 localized at the Zn-containing fragment. The Ga−Zn bond is mainly formed by overlap of the metal orbitals in the α HOMO−6 and β HOMO−5. According to the results of the NBO analysis, the Zn wave functions are responsible for 28.7 % of the Zn−Ga bond, with 96.7 % s, 1.0 % p, and 2.3 % d character.

Keywords: EPR spectroscopy · gallium · metal–metal interactions · N ligands · structure elucidation · zinc

Introduction

With respect to the fact that most of the chemical elements are metals, studies concerning the character of metal–metal bonds are of fundamental interest. The isolation of thermally stable molecular species containing zinc–zinc bonds was one of the most recent achievements in this field.[1] Compounds with bonds between zinc and transition metals have been known since 1977,[2] whereas compounds containing main-group metals bonded to zinc are limited to the elements Ge, Sn,[3] and Sb.[4] In contrast to Group 14 and transition metals, the electropositive elements like alkaline earth metals and the lanthanides do not form stable molecules with homonuclear metal–metal bonds. However, homonuclear molecular species of aluminum, gallium, the elements between Group 12 and Group 14 metals, have attracted great attention in the last two decades.[5] Recently, we reported on the first Zn−Zn bonded compound supported by the radical anion ligand dpp-bian, [(dpp-bian)Zn−Zn(dpp-bian)] (**1**)[6] (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene). We could also demonstrate, that the use of dpp-bian allows the preparation of monomeric Al complexes with mono- and dianionic dpp-bian ligands

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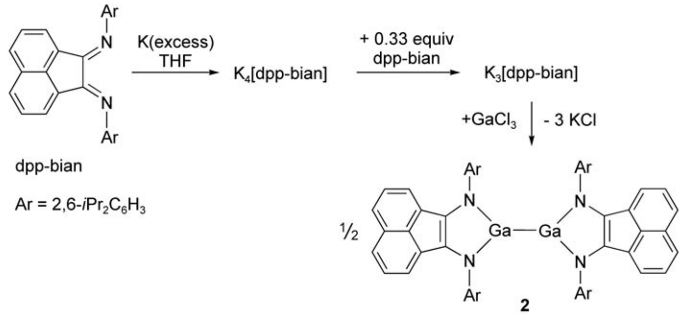
([dpp-bian]$^{n-}$, $n = 1, 2$).[7] Animated by the successful synthesis of the dizinc compound **1**, we suggested that the dpp-bian ligand may also be able to stabilize homonuclear bonds of Group 13 metals and possibly even heteronuclear bonds between Group 12 and Group 13 metals. The isolation of both, dpp-bian-supported digallium and dpp-bian-supported zinc–gallium compounds confirmed this suggestion. Here, we report on the preparation, the molecular structure, and the spectroscopic characteristics of these two compounds.

Results and Discussion

The compound [(dpp-bian)Ga−Ga(dpp-bian)] (**2**) has been prepared by reaction of $GaCl_3$ with K_3[dpp-bian] in diethyl ether/THF at room temperature (Scheme 1).

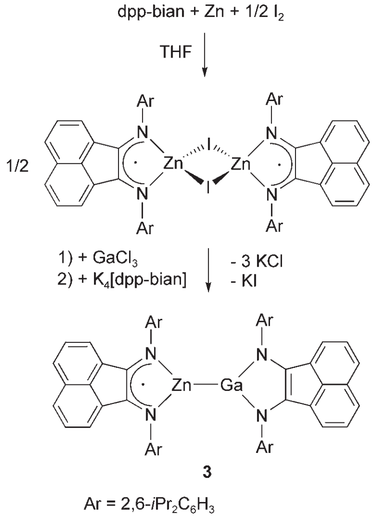


Scheme 1.

Solutions of K_3[dpp-bian] are obtained by addition of 0.33 equiv of dpp-bian to solutions of K_4[dpp-bian] in THF, the latter being the product of the reaction of dpp-bian with excess potassium. In the course of the formation of **2**, the cation exchange and the redox reactions $Ga^{3+} \rightarrow Ga^{2+}$ and $[\text{dpp-bian}]^{3-} \rightarrow [\text{dpp-bian}]^{2-}$ proceed simultaneously, accompanied with a change of the color of the reaction mixture from green to blue. Appropriate workup afforded compound **2** as deep blue crystals with 83 % yield. In contrast to **1**, compound **2** is ESR silent, thus proving the dianionic character of both dpp-bian ligands.

The heterometallic compound [(dpp-bian)Zn−Ga(dpp-bian)] (**3**) was obtained by a simple one-pot reaction of three reagents (Scheme 2).

The recently reported radical-anion derivative [{(dpp-bian)ZnI}$_2$] was used as a starting zinc-containing compound.[6] The addition of a solution of $GaCl_3$ in diethyl ether to a solution of this compound in THF did not cause visible changes. However, once a solution of K_4[dpp-bian] was added, the precipitation of potassium halide started and the color of the solution changed from brown to red-violet. Appropriate workup of the reaction mixture allowed the isolation of compound **3** as deep red crystals with 72 % yield.



Scheme 2.

To preclude the presence of an equimolar mixture of the homometallic species **1** and **2** formed by dismutation of **3**, we compared the UV/Vis spectrum of the product with those of **1** and **2** (Figure 1).

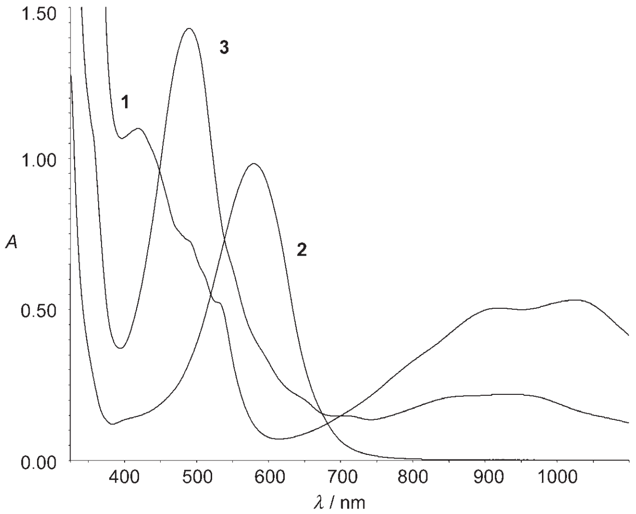


Figure 1. The absorption spectra of the complexes **1–3** in Et_2O.

In the present case UV/Vis spectroscopy is a suitable tool, since the absorption maxima of dpp-bian ligands in different anionic states vary significantly in their position.[8] The absorption maxima for **1**, **2**, and **3** are located at 418, 588, and 489 nm, respectively. The clear differences in the position of the maxima confirm that the reaction depicted in Scheme 2 does provide the novel heterometallic compound **3**. In contrast to **2**, compounds **1** and **3** exhibit absorptions in the near IR region due to the presence of the dpp-bian radical anion in solution.

As to expect, the ESR spectrum of **3** recorded in toluene gives rise to a signal (Figure 2) that clearly indicates the presence of dpp-bian radical anions.

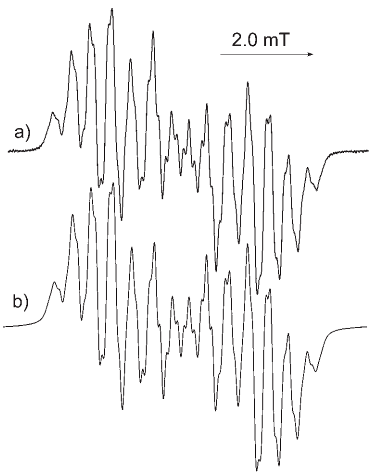


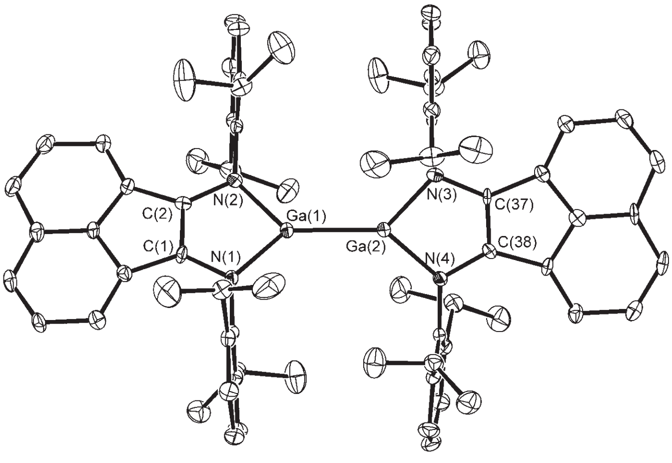
Figure 2. a) ESR spectrum of **3** in toluene at 330 K ($g=2.0020$); b) simulated spectrum ($A(^1H)=0.11$ (4H), $A(^{14}N)=0.38$ (2N); $A(^{69}Ga)=0.97$, $A(^{71}Ga)=1.23$ mT, line width = 0.13 mT).

The most important feature of the ESR spectrum, relating to the Zn–Ga bond, is the coupling of the unpaired electron with the gallium nuclei ^{69}Ga and ^{71}Ga, thus confirming the presence of Zn–Ga bonds in solution. This coupling ($A(^{69}Ga)=0.97$, $A(^{71}Ga)=1.23$ mT) is much smaller than that found for [(dpp-bian)GaCl$_2$][9] ($A(^{69}Ga)=1.58$, $A(^{71}Ga)=2.00$ mT) indicating a larger distance between the gallium atom and the center of the residence area of the unpaired electron in **3** than in [(dpp-bian)GaCl$_2$].

The molecular structures of **2** and **3** were determined by single-crystal X-ray analysis and are depicted in Figure 3. The crystal data and details of data collection are given in Table 1.

The most significant bond lengths of **2** and **3** are summarized in Table 2. For a better comparison the corresponding bond lengths of compound **1** are included in Table 2. According to the results of the X-ray crystal-structure analyses, compounds **1**,[6] **2**, and **3** are isotypic and crystallize in the space group $P2_1/c$. Since the electron cores of Zn^{II} and Ga^{III} are the same, these ions can not be distinguished in the X-ray crystal-structure analysis. However, due to their different formal oxidation states, the Zn and Ga ions require anionic ligands differing in the charge of one electron. It is known that the dpp-bian ligand is able to adopt variable oxidation states, forming metal complexes with one-, two-, three-, and fourfold negatively charged dpp-bian ligands.[10] On going from neutral dpp-bian to its mono- and further to its dianion, the molecular parameters of the dpp-bian skeleton change significantly with respect to the bond lengths within the diimine part as well as to the metal–nitrogen distances.

The metal–metal bond lengths in **2** (2.3598(3) Å) and **3** (2.3531(8) Å) are close to that in **1** (2.3321(2) Å). The increasing population of the LUMO on going from neutral dpp-bian to its radical anion and further to the dianion must result in a shortening of the central C–C bond and simultaneously in an elongation of the C–N distances within the diimine moiety. In fact, the C–N bonds in both metallocycles of **2** (av. 1.388 Å) are significantly elongated compared to those in **1** (av. 1.329 Å) and almost identical to the respective C–N distances in the magnesium complex [(dpp-bian)Mg(thf)$_3$] (av 1.389 Å) containing the dpp-bian dianion,[11] thus proving the dianionic character of both ligands in **2**.



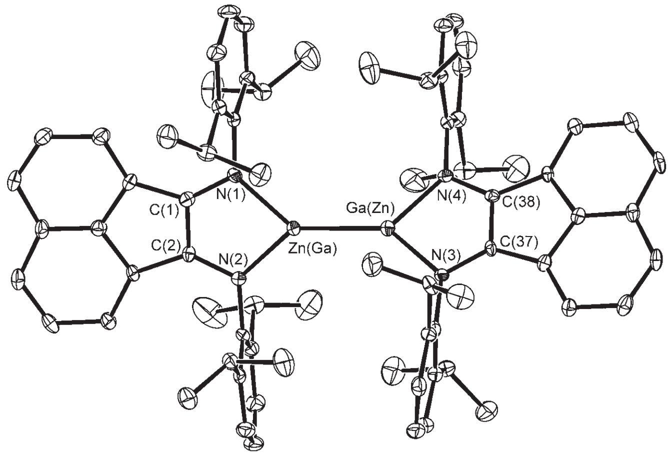


Figure 3. Top: Molecular structure of **2** (thermal ellipsoids shown at 40 % probability levels). Bottom: Molecular structure of **3** (thermal ellipsoids shown at 40 % probability levels).

Unexpectedly, the structure of the mixed Zn–Ga compound **3** shows no distinct differences between the geometries of the radical anionic and the dianionic dpp-bian ligands as well as between the metal–nitrogen bonds. This can be explained either by delocalization of the unpaired electron over both ligands or by superposition of the molecules in the crystal resulting in an averaging of the geometries of the two dpp-bian ligands. The latter explanation seems to be more plausible, because the ESR spectrum of **3** reveals hyperfine coupling only to two and not to four nitrogen atoms. Furthermore, the DFT calculations (see below) reveal an unsymmetrical electronic structure of molecule **3**. The C–C, C–N, and N–M bond lengths in the two metallocycles of **3** are the key in this discussion, since the respective bond lengths of **3** lie exactly in the middle of the range of distances observed for **1** and **2**. Thus, the half-sum of the averaged

Table 1. Crystal data and structure refinement details for **2** and **3**.

	2	**3**
formula	$C_{76}H_{90}Ga_2N_4O$	$C_{76}H_{90}GaN_4OZn$
M_r	1214.96	1210.61
T [K]	150(2)	150(2)
λ [Å]	0.71073	0.71069
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a [Å]	18.8445(3)	18.905(5)
b [Å]	14.1423(3)	14.139(5)
c [Å]	25.7557(5)	25.744(5)
β [°]	105.289(2)	105.207(5)
V [Å^3]	6621.1(2)	6640(3)
Z	4	4
ρ_{calcd} [g cm^{-3}]	1.219	1.211
μ [mm^{-1}]	0.860	0.813
$F(000)$	2576	2572
crystal size, [mm^3]	$0.24 \times 0.17 \times 0.03$	$0.26 \times 0.12 \times 0.05$
$\theta_{min}/\theta_{max}$	2.96/28.79	3.00/27.50
index ranges	$-25 \leq h \leq 25$	$-23 \leq h \leq 23$
	$-17 \leq k \leq 18$	$-18 \leq k \leq 18$
	$-34 \leq l \leq 31$	$-33 \leq l \leq 32$
reflns collected	46085	47525
independent reflns	14794	14540
R_{int}	0.0470	0.0704
completeness to $\theta = 27.50°$ [%]	95.2	95.2
max/min transmission	0.9746/0.8201	0.9605/0.8164
data/restraints/parameters	14794/0/766	14540/0/766
GOF on F^2	0.968	0.884
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0405$	$R_1 = 0.0447$
	$wR_2 = 0.0728$	$wR_2 = 0.0661$
R indices (all data)	$R_1 = 0.0884$	$R_1 = 0.1231$
	$wR_2 = 0.0865$	$wR_2 = 0.0794$
largest diff peak/hole [e Å^{-3}]	0.406/−0.420	0.374/−0.504

Table 2. Comparison of the main bond lengths in **1–3**.

	1[a]	**2**	**3**
M(1)–M(2)[b]	2.3321(2)	2.3598(3)	2.3531(8)
M(1)–N(1)	2.0133(10)	1.8624(18)	1.939(2)
M(1)–N(2)	2.0287(12)	1.8583(18)	1.945(2)
M(2)–N(3)	2.0153(10)	1.8551(17)	1.921(2)
M(2)–N(4)	2.0381(12)	1.8657(17)	1.939(2)
N(1)–C(1)	1.3244(17)	1.393(3)	1.355(3)
N(2)–C(2)	1.3357(15)	1.389(3)	1.349(3)
N(3)–C(37)	1.3323(17)	1.388(3)	1.349(3)
N(4)–C(38)	1.3233(16)	1.383(3)	1.364(3)
C(1)–C(2)	1.4414(18)	1.375(3)	1.412(3)
C(37)–C(38)	1.4453(18)	1.378(3)	1.408(3)

[a] The numbering scheme is the same as for complex **2** (Figure 2) [b] **1**: M(1) = M(2) = Zn; **2**: M(1) = M(2) = Ga; **3**: M(1) = Zn, M(2) = Ga or M(1) = Ga, M(2) = Zn.

C–N bond length (1.358 Å) in **1** and **2** is very close to the average value of the four C–N bonds in **3** (1.354 Å). The same is true for the M–N distances. The half-sum of the averaged M–N bond length in **1** and **2** (1.943 Å) agrees well with the averaged M–N distances in **3** (1.936 Å).

The electronic structures of compounds **2** and **3** were studied on the basis of DFT calculations[12] at the B3LYP/6–31G* level using molecules with unsubstituted phenyl fragments as model systems. Recently, we used such calculations to study the Zn–Zn bonding in **1**.[6] The optimization of the geometry of the molecules was carried out with regard to a coplanar and perpendicular conformation of the two ligands. The calculated distance between the two Ga atoms in **2** and between the Ga and the Zn atom in **3** is 2.29 and 2.31 Å, respectively. Taking into account that there is some repulsion caused by the isopropyl substituents at the phenyl rings of the dpp-bian ligands, the calculated metal–metal distances are in good agreement with the X-ray data. The difference in the electronic energy of the two conformations appears to be rather small (≈ 0.2 kcal mol^{-1}) for both compounds. On the other hand, the energies and shapes of some MO's differ substantially for the planar and perpendicular molecular geometry as shown by the respective values of −3.97 and −4.22 eV for the HOMO energy of **2**. For this reason, we performed the MO analysis for the conformers obtained from the optimized structures on the basis of single-point calculations changing the N-Ga(Zn)-Ga-N dihedral angle to 42°, a value which is close to that observed in the X-ray experiment.

In the singlet ground state of molecule **2**, the metal–metal π bond is mainly formed by overlap of the Ga p orbitals in the HOMO and HOMO−1, the latter showing a stronger interaction. The Ga s and p orbitals overlap in the deeper lying HOMO−17 (Figure 4) producing a σ Ga–Ga bond. The LUMO in **2** is derived from the p orbitals of the metal (Figure 4). However, the LUMO+1 and LUMO+2, which lie close together, are ligand-localized. In contrast to the Zn–Zn bond in **1** showing 95 % s character, the NBO (natural bond orbital) analysis of **2** reveals 67.8 % s, 32.0 % p, and 0.2 % d character for the Ga–Ga bond.

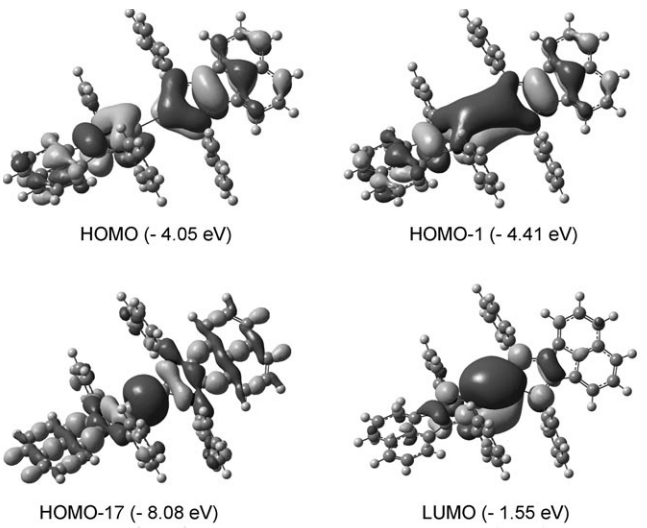
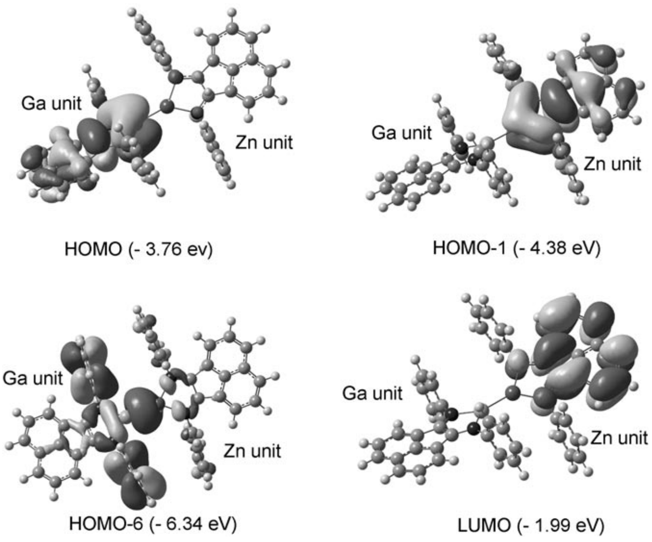

HOMO (- 4.05 eV)
HOMO-1 (- 4.41 eV)
HOMO-17 (- 8.08 eV)
LUMO (- 1.55 eV)

Figure 4. Representation of the frontier orbitals, HOMO−1 and HOMO−17 of **2** from DFT calculations.

Molecule **3** has a doublet electronic ground state. The unpaired electron occupies the α HOMO−1 localized at the Zn-containing fragment (Figure 5). This agrees well with the ESR results. The α and β HOMO's belong to the (dpp-bian)Ga moiety.



HOMO (- 3.76 ev) HOMO-1 (- 4.38 eV)

HOMO-6 (- 6.34 eV) LUMO (- 1.99 eV)

Figure 5. Representation of the key α orbitals in **3** resulting from DFT calculations.

The LUMO is localized at the ligand bonded to the Zn atom. The Ga−Zn bond is mainly formed by overlap of the metal orbitals in the α HOMO−6 and β HOMO−5. According to the results of the NBO analysis, the Zn wave functions are responsible for 28.7 % of the Zn−Ga bond with 96.7 % s, 1.0 % p, and 2.3 % d character. Consequently, the Ga orbitals contribute 71.3 % to the Zn−Ga bond with 70.8 % s, 28.4 % p, and 0.8 % d character. The natural charges for Ga and Zn in **3** are +0.509 and +1.279, respectively, while the charge of the metals in the symmetrical molecules **2** and **1** is +0.92 and +0.84,[6] respectively.

Conclusion

In conclusion, the first molecular compound containing a Zn−Ga bond has been synthesized. The basic finding of the investigations described above is the fact that the heterometallic compound [(dpp-bian)Zn−Ga(dpp-bian)] (**3**) is thermodynamically stable and does not dismutate into the respective symmetrical compounds **1** and **2**. On the basis of this finding, the synthesis of other molecular compounds with direct bonds between different metals, for example, between Zn and Al or Zn and Sc and so forth, seems to be very promising. The use of a spin-labeled ligand (i.e., dpp-bian radical anion) allowed the confirmation of the presence of Zn−Ga bonding in solution. DFT calculations demonstrate that the Ga and the Zn atom provide different orbital contributions to the metal–metal bond.

Experimental Section

All manipulations were carried out in vacuum lines by using Schlenk techniques. The solvents THF and Et$_2$O 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. The IR spectra were obtained on a Bruker Vertex 70 spectrometer. The ligand dpp-bian was prepared according to the published procedure.[13]

K$_4$[dpp-bian] and K$_3$[dpp-bian]: A solution of dpp-bian (0.375 g, 0.75 mmol) in THF (25 mL) was added to an excess of potassium metal (0.8 g, 20.51 mmol). The dpp-bian was completely reduced to the tetraanion within 4 h of vigorous stirring at room temperature. After decantation from unreacted potassium metal, the solution of K$_4$[dpp-bian] was used in situ either for the synthesis of **3**, or for the preparation of solutions of K$_3$[dpp-bian] by addition of 0.33 equiv of dpp-bian (0.125 g, 0.25 mmol).

[{(dpp-bian)ZnI}$_2$]: Excess zinc (7.4 g, granules) was stirred with I$_2$ (0.254 g, 1.0 mmol) in THF (40 mL) until the color of iodine completely disappeared. Addition of dpp-bian (0.5 g, 1.0 mmol) and stirring of the mixture for several minutes at room temperature led to the formation of a deep cherry-red solution of [{(dpp-bian)ZnI}$_2$], which was decanted from the excess of the metal and used in situ for the synthesis of **3**.

[(dpp-bian)Ga−Ga(dpp-bian)] (2): The addition of GaCl$_3$ (0.18 g, 1.0 mmol) dissolved in Et$_2$O (5 mL) to a rigorous stirred solution of K$_3$[dpp-bian] in THF (prepared in situ from dpp-bian (0.5 g, 1.0 mmol) and potassium (0.12 g) in THF (35 mL)) caused precipitation of KCl and a change in the color of the solution from green to blue. The mixture was stirred for another hour at room temperature. After evaporation of the solvent in vacuum, diethyl ether (40 mL) was added to the residue. The suspension formed was centrifuged and the solution was decanted from insoluble KCl. Slow evaporation of the solvent afforded compound **2** (0.49 g, 83 %) as deep-blue crystals. M.p. > 300 °C; IR (Nujol): $\tilde{\nu}$ = 1612 (m), 1596 (m), 1546 (w), 1360 (s), 1324 (m), 1254 (m), 1213(w), 1117 (s), 1057 (w), 1037 (w), 931 (s), 814 (s), 804 (s), 764 (vs), 671 (m), 616 (m), 453 (m), 418 cm^{-1} (s); elemental analysis calcd (%) for C$_{72}$H$_{80}$Ga$_2$N$_4$·C$_4$H$_{10}$O (1214.96): C 75.21, H 7.48; found: C 75.20, H 7.34; UV/Vis (Et$_2$O, 293 K): λ = 588 nm.

[(dpp-bian)Zn−Ga(dpp-bian)] (3): A solution of GaCl$_3$ (0.18 g, 1.0 mmol) in Et$_2$O (10 mL) was added to a solution of (dpp-bian)ZnI in THF [prepared in situ from dpp-bian (0.5 g, 1.0 mmol), I$_2$ (0.13 g, 0.5 mmol), and zinc (excess) in THF (20 mL)]. Then a solution of K$_4$[dpp-bian] in THF [prepared in situ from dpp-bian (0.5 g, 1.0 mmol) and potassium metal (0.16 g) in THF (25 mL)] was added, potassium halide precipitated, and the color of the mixture changed from brown to red-violet. After stirring for 1 h at room temperature, the solvent was removed in vacuum, diethyl ether (40 mL) was added to the residue, and the insoluble potassium halide was filtered off. Slow evaporation of the diethyl ether from the solution afforded compound **3** (0.87 g, 72 %) as deep red crystals. M.p. > 300 °C; IR (Nujol): $\tilde{\nu}$ = 1612 (m), 1596 (m), 1539 (s), 1359 (s), 1323 (s), 1259 (s), 1188 (m), 1116 (s), 1057 (w), 1038 (w), 932 (s), 871 (m), 802 (s), 762 (vs), 670 (m), 636 (m), 547 (w), 453 (m), 409 cm^{-1} (s); elemental analysis calcd (%) for C$_{72}$H$_{80}$Ga N$_4$Zn·C$_4$H$_{10}$O (1210.68): C 75.40, H 7.49; found: C 75.46, H 7.42; UV/Vis (Et$_2$O, 293 K): λ = 489 nm.

Single-crystal X-ray structure determination of 2 and 3: The crystallographic data of **2** and **3** were collected on a Xcalibur S Sapphire diffractometer (Oxford Diffraction) at 150 K. The structures were solved by direct methods by using SIR-2004[14] and refined by a full-matrix least-squares method on F^2 by using SHELXL-97.[15] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions by using a riding model. CCDC-641273 (**2**) and CCDC-641272 (**3**) 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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