Zinc–Zinc Bonds

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Structural Characterization of a Base-Stabilized $[Zn_2]^{2+}$ Cation[**]

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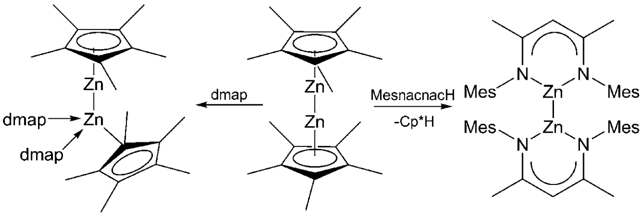
Dedicated to Professor Martin Jansen on the occasion of his 65th birthday

The landmark discovery of decamethyldizincocene $[Cp^*_2Zn_2]$ (**1**; $Cp^* = C_5Me_5$) by Carmona et al. in 2004[1] has led to increasing research on the synthesis of low-valent metal complexes of Group 2 and 12 metals in recent years and several complexes containing Mg–Mg,[2] Cd–Cd,[3,4] Hg–Hg[4] and Zn–Zn[5–11] bonds, which are typically kinetically stabilized by use of sterically demanding or chelating organic substituents, have been synthesized. However, it should be noted that the first molecular complex with a Zn–Zn bond, Zn_2H_2, was trapped in an argon matrix at 12 K and characterized by vibrational spectroscopy and computational calculations.[12] With respect to the rather large number of organometallic complexes containing a direct Zn–Zn bond it is somehow surprising how little is know about the $[Zn_2]^{2+}$ cation, even though this was obtained in a melt of Zn in $ZnCl_2$ and characterized by Raman spectroscopy 40 years ago.[13] The low stability of the $[Zn_2]^{2+}$ cation is in marked contrast to that of the intensively studied $[Hg_2]^{2+}$ and $[Cd_2]^{2+}$ cations and has been subject of several computational investigations.[14] In addition, a very few reports demonstrated the presence of $[Zn]^+$ cations in microporous materials.[15]

Recently, we became interested not only in the synthesis but also in the reactivity of low-valent organozinc complexes. Our initial studies focused on reactions of $[Cp^*_2Zn_2]$ (**1**) because of the promising steric and electronic flexibility of the Cp* substituent.[16] The reaction with 4-dimethylamino pyridine (dmap), which we have shown to be a valuable Lewis base for the synthesis of base-stabilized monomeric Group 13/15 compounds,[17] resulted in the formation of $[Cp^*Zn{-}Zn(dmap)_2Cp^*]$ (**2**),[18] in which the dmap molecules bind in a geminal coordination mode to only a single Zn atom. Disproportionation reaction into elemental zinc and the corresponding Zn^{II} compound, as observed in reactions of **1** with Lewis bases, did not occur.[1,5] At the same time Jones et al. showed that low-valent organomagnesium(I) complexes reacted with Lewis bases to form the vicinal coordinated adducts.[19] We reported the reaction of **1** with $[\{(2,4,6\text{-}Me_3C_6H_2)N(Me)C\}_2CH]H$ (MesnacnacH), which proceeded with protonation of the Cp* substituent and subsequent formation of the new low-valent Zn–Zn bonded complex $[(Mesnacnac)_2Zn_2]$ (**3**, Scheme 1).[20]



2 **1** **3**

Scheme 1. Reactions of **1**.

To elucidate, if this specific reaction might give a general access to low-valent organozinc complexes, we began to investigate the reaction of both **1** and **2** with protonating reagents. Herein, we report on the reaction of **2** with $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$, which proceeds at relatively low temperature with elimination of Cp*H and subsequent formation of $[Zn_2(dmap)_6][Al\{OC(CF_3)_3\}_4]_2$ (**4**) containing the base-stabilized $[Zn_2]^{2+}$ cation [Eq. (1)].

$$[Cp^*_2Zn_2(dmap)_2] \xrightarrow[-2Cp^*H]{2[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]} [Zn_2(dmap)_6][Al\{OC(CF_3)_3\}_4]_2 \quad (1)$$

A solution of **2** in CH_2Cl_2 reacts with two equivalents of $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$ at −30 °C forming **4**, which was isolated after crystallization at −30 °C as a colorless crystalline solid. NMR spectra (^1H, ^{13}C, ^{19}F) of **4** show resonances only arising from the dmap group and the aluminate anion, whereas no indication for the presence of a Cp* group was found.[21] Single crystals of **4** were obtained from a solution in CH_2Cl_2 stored at −30 °C.[22] Compound **4** consists of a base-stabilized $[Zn_2(dmap)_6]^{2+}$ cation and two $[Al\{OC(CF_3)_3\}_4]^-$ anions (Figure 1). The Zn atoms adopt tetrahedral coordination spheres with the Zn–N bond lengths (2.136(5) Å) slightly elongated compared to those in **2** (2.115(2), 2.125(2) Å). The

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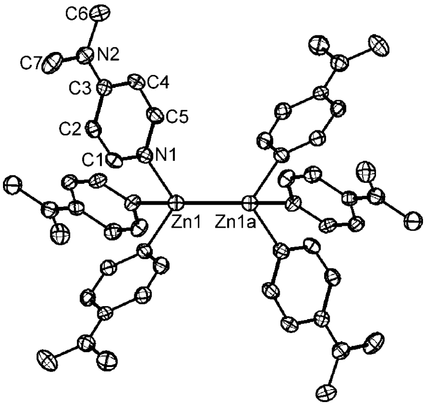

Figure 1. Molecular structure of the $[Zn_2(dmap)_6]^{2+}$ ion of **4**. H atoms and the $[Al\{OC(CF_3)_3\}_4]^-$ ions are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–Zn1a 2.419(2), Zn1–N1 2.136(4); N1-Zn1-N2 93.50(16), N1-Zn1-Zn1′ 122.75(11).

central Zn–Zn bond distance of **4** (2.419(1) Å) is almost identical to that of **2** (2.418(1) Å), whereas other $[Zn_2R_2]$ complexes typically show shorter Zn–Zn bonds, ranging from 2.29 to 2.35 Å. Only **3** (R = Mesnacnac, 2.3813(8) Å) and the doubly reduced diimine derivative (R = $[(2,6\text{-}i\mathrm{Pr}_2C_6H_3)N(Me)C]_2$, 2.3994(6) Å)[8] show comparable Zn–Zn bond lengths. The $[Al\{OC(CF_3)_3\}_4]^-$ ion is disordered.[23] Theoretical calculations of **4** at the BP86/def-SV(P) level revealed a gas-phase minimum structure **4′** with S_6 symmetry.[24] An alternative structure with the Zn atoms connected by two bridging hydrogen atoms was unstable and split into separated $[(dmap)_3ZnH]^+$ ions during the geometry optimization. The calculated Zn–Zn (2.399 Å) and Zn–N bond lengths (2.161 Å) of **4′** agree very well with the experimental values observed for **4** and the recently calculated base-free $[Zn_2]^{2+}$ ion (2.46 Å),[25] whereas the calculated value of **1** (2.331 Å) is shorter.[26]

The characterization of the $[Zn_2]^{2+}$ ion in $Zn/ZnCl_2$ glasses was exclusively based on Raman spectra,[13] which show a strong absorption band at 175 ± 5 cm^{-1}. In contrast, no single mode but four distinctive Raman and three IR active modes were identified for $[Cp^*{}_2Zn_2]$ (**1**).[27]

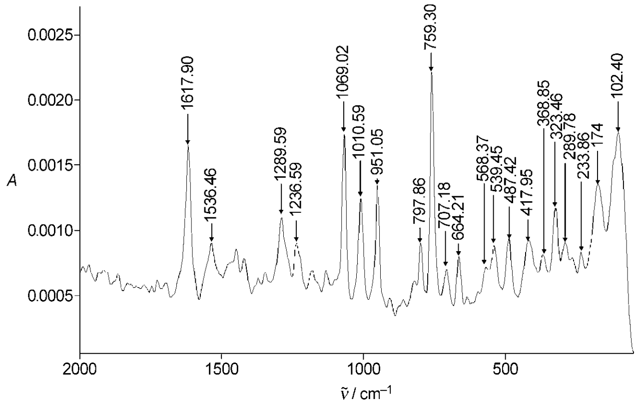

Figure 2. Raman spectrum of **4** between 100 and 2000 cm^{-1} (50 mW, 8 cm^{-1}).

The IR and Raman spectra of **4** are somewhat complex because of the presence of the Lewis base dmap and the anion $[Al\{OC(CF_3)_3\}_4]^-$ (Figure 2). However, the anion modes were identified by comparison with spectra of known complexes,[28] and the dmap modes by comparison with pure dmap and dmap coordinated zinc complexes.[29] In addition, the IR and Raman spectra of **4** were simulated using DFT methods.

The IR spectrum of **4** shows characteristic strong vibrations for the anion at 1353, 1260, 1240, 968, 725, and 442 cm^{-1}, which correspond very well with experimental and calculated data.[28] The bands at 2962, 1614, 1536, 1065, 1006, and 811 cm^{-1} agree with calculated bands of the dmap-stabilized dication and can be assigned to vibrations of the dmap group; comparing the IR spectra of **4** with those of dmap, $[(dmap)_2ZnCl_2]$, and $[(dmap)_2ZnMe_2]$ confirms this assignment.[29] Theoretical calculations of **4′** with BP86/def-SV(P) predict three Zn-Zn stretch vibrations coupled with dmap torsion vibrations, at 249, 279, and 305 cm^{-1}, but owing to their a_g symmetry they should not be visible in the IR spectrum. The calculated force constant of the Zn–Zn bond of 1.09 mdyne Å^{-1} is in between that reported for $[Zn_2]^{2+}$ in $Zn/ZnCl_2$[13] (0.6 mdyne Å^{-1}) and in **1** (1.42 mdyne Å^{-1}).[27]

The experimental Raman spectrum of **4** shows characteristic bands for the anion at 1290, 798, 759, 539, and 323 cm^{-1} and typical dmap absorptions. In addition, a vibration observed at 174 cm^{-1} corresponds very well with the calculated a_g vibration of **4′** (171 cm^{-1}), which exhibits significant Zn–Zn stretching vibration character. A strong band at 175 cm^{-1} was reported for the $Zn/ZnCl_2$ glasses,[13] in which the $[Zn_2]^{2+}$ ion probably exists as Zn_2Cl_2 unit. Theoretical calculations (BP86/SVP) predict an a_{1g} vibration for Zn_2Cl_2 at 194 cm^{-1}.

Compound **4** is the first structurally characterized complex containing the $[Zn_2]^{2+}$ ion. Coordination of the strong Lewis base dmap may have a stabilizing effect for the $[Zn_2]^{2+}$ unit as is suggested by recent studies on the stability of base-stabilized, dimeric Mg_2Cl_2.[30] DFT calculations were performed to evaluate the stability of the base-stabilized dication $[Zn_2(dmap)_6]^{2+}$. Coulomb explosion of the dication with subsequent formation of two equivalents of $[Zn(dmap)_3]^+$ was found to be strongly endergonic at 298.15 K both in the gas phase ($\Delta H^0 = 146$ kJ mol^{-1}; $\Delta G^0 = 89$ kJ mol^{-1}) as well as in solution ($\Delta G^0 = 183$ kJ mol^{-1}), since the Gibbs solvation energies of $[Zn(dmap)_3]^+$ (−113 kJ mol^{-1}) and $[Zn_2(dmap)_6]^{2+}$ (−321 kJ mol^{-1}) are strongly exergonic. According to these calculations, the base-stabilized dication is stable in solution. According to NBO analysis, the Zn atoms in $[Zn_2(dmap)_6]^{2+}$ have a positive charge of 0.61 (Mulliken: 0.41), which is practically equal to the base-free zinc atom (0.60) in $[Cp^*Zn\text{-}Zn(dmap)_2Cp^*]$ (**2**), in which the dmap-coordinated zinc atom (1.15) carries a significantly higher electronic charge. The NBO analysis (Wiberg bond index) shows a bond order of 0.90, which is in between the values reported for **1** (0.93) and **2** (0.85). In accordance with the $3d^{10}4s^14p^0$ electron configuration of a Zn^+ ion, a molecular-orbital study revealed mainly (76%) s character of the Zn–Zn bond (p: 23%, d: < 1%). The Zn–N bond order of 0.23 shows a mainly electrostatic coordination of the dmap ligands. Interestingly, the calculated negative charge of the aromatic N atom in dmap increases by coordination to the Zn from −0.52 to −0.63 (Mulliken: −0.12 to −0.25). The loss of electron density in the electron lone pair owing to coordination seems to be overcompensated mainly by the aromatic π system, as the negative charge of the N atom in the dimethylamino group remains almost unchanged upon coordination (NBO: −0.47 to −0.46; Mulliken: −0.31 to −0.30).

Experimental Section

All manipulations were performed under an argon atmosphere. Solvents were dried over Na/K alloy and degassed prior to use. ^{1}H, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 500 spectrometer and are referenced to internal CD_2Cl_2 (^{1}H: $\delta = 5.32$ ppm; ^{13}C: $\delta = 53.5$ ppm). IR spectra were recorded on a ALPHA-T FT-IR spectrometer and Raman spectra on a Bruker IFS 55 EQUINOX (with FRA 106 Raman attachment). Melting points were measured in sealed capillaries and were not corrected.

4: [Cp*Zn-Zn(dmap$_2$)Cp*] (**2**; 0.16 g, 0.25 mmol) dissolved in CH_2Cl_2 (10 mL) was added dropwise at −30 °C to a solution of $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$ (0.42 g, 0.5 mmol) in CH_2Cl_2 (10 mL) and stirred for 15 min at −30 °C. The resulting solution was concentrated in vacuum and stored at −30 °C. Colorless crystals of **4** (0.20 g, 0.07 mmol, 28 % based on **2**) were obtained after 24 h. The yield of isolated crystals of **4** increased to 64 % when a cold solution (−30 °C) of dmap (0.12 g, 1 mmol) in CH_2Cl_2 (20 mL) was added after the reaction of **2** and $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$ was completed.

Melting point: 120 °C (dec.). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): $\delta = 3.08$ (s, 6H, NMe$_2$), 6.61 (m (AA′XX′ spin system, 4H, C3-H), 7.89 ppm (m, 2H, C2-H). $^{13}C\{^{1}H\}$-NMR (125 MHz, CD_2Cl_2, 25 °C): $\delta = 39.5$ (N*Me*$_2$), 107.8 (C3), 121.6 (m, $^{1}J_{C,F} = 293.51$ Hz), 147.9 (C2), 156.2 ppm (C4). $^{19}F\{^{1}H\}$ (235 MHz, CD_2Cl_2, 25 °C): $\delta = -75.8$ ppm.

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[22] Bruker AXS SMART APEX CCD diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å; $T = 173(1)$ K). The structure was solved by Direct Methods (SHELXS-97, G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467) and refined by full-matrix least-squares on F^2. Semi-empirical absorption corrections were applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model. (SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, Universität Göttingen, **1997**). **4**: $C_{42}H_{60}N_{12}Zn_2\cdot 2[C_{16}F_{36}O_4Al]$, $M_r = 2799.04$, colorless crystal ($0.28 \times 0.23 \times 0.16$ mm); trigonal, space group $P\bar{3}$; $a = 16.9177(6)$, $b = 16.9177(6)$, $c = 10.4632(4)$ Å; $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 2593.45(16)$ Å^3; $Z = 1$; $\mu = 0.666$ mm^{-1}; $\rho_{calcd} = 1.792$ g cm^{-3}; 22 524 reflexes ($2\theta_{max} = 48°$), 2687 unique ($R_{int} = 0.0584$); 256 parameters; largest max./min. in the final difference Fourier synthesis 1.698 e Å^{-3}/−0.744 e Å^{-3}; max./min. transmission 0.75/0.64; $R_1 = 0.0761$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.2167. CCDC 723381 (**4**) 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.

[23] This causes a disc-like density distribution perpendicular to the respective Al−O bonds, indicating that the Al-O-C bonds are not linear. The disorder could not be reasonably resolved and is expected to be transferred to the C atoms of the CF_3 groups, even though this does not show up. As is oftern the case, the fluorine atoms of the CF_3 groups are also disordered.

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