# A Solvated Zinc Analogue of the Calomel-Dication

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#### **Materials and Methods**

**Spectroscopy** NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer (<sup>1</sup>H, 250.1 MHz; <sup>13</sup>C, 62.9 MHz) in CD<sub>2</sub>Cl<sub>2</sub> at 298 K unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the residual solvent peak as internal standards. Chemical shifts are reported in parts per million, downfield shifted from TMS, and are consecutively reported as position ( $\delta_{\rm H}$  or  $\delta_{\rm C}$ ), relative integral, multiplicity (s = singlet, d = doublet, sept = septet, m = multiplet), coupling constant (J in Hz) and assignment. IR spectra were measured in an ATR setup with a Bruker Alpha FTIR spectrometer under an inert gas atmosphere in a glove-box.

**Elemental Analysis (EA) and Atomic Absorption Spectroscopy (AAS)** EA and AAS measurements for compound 1 were conducted at the University of Duisburg-Essen on an EURO EA Elemental Analyzer of the EURO VECTOR company (EA) and a M-Serie device of the Thermo Electron company (AAS). Measurements for compound 2 and 3 were conducted in the Microanalytical Laboratory Kolbe in Mülheim an der Ruhr.

**Spectrometry** Mass spectrometry was measured with a Waters LCT; Ionisation method: liquid injection field desorption ionization (LIFDI; special ionization cell obtained from Linden CMS GmbH, Leeste, Germany; http://www.linden-cms.de), solvent: CH<sub>2</sub>Cl<sub>2</sub>.

X-ray crystallography The X-ray diffraction intensities for  $1 \cdot \text{THF}$ ,  $2 \cdot 4 \text{ CH}_2\text{Cl}_2$  and [Zn(PMe<sub>3</sub>)<sub>4</sub>][BAr<sub>4</sub><sup>F</sup>]<sub>2</sub> were collected on an Agilent Technolgies SuperNova diffractometer with an Atlas CCD and Cu  $K_{\alpha}$  radiation from multilayer X-ray optics. The crystals were coated with a perfluoropolyether, picked up with a glass fiber and immediately mounted in the nitrogen cold gas stream of the diffractometer. The data were processed with CrysAlisPro [1]. Absorption corrections based on multiple-scanned reflections were carried out with ABSPACK in CrysAlisPro. The crystal structures were solved by direct methods using SHELXS-97 and refined with SHELXL-2014 [2]. In  $1 \cdot \text{THF}$ ,  $2 \cdot 4 \text{ CH}_2\text{Cl}_2$  and [Zn(PMe<sub>3</sub>)<sub>4</sub>][BAr<sub>4</sub><sup>F</sup>]<sub>2</sub>, standard similar distance restraints and restraints and constraints on atomic displacement parameters (ADPs) were used to model disordered regions. Anisotropic ADPs were introduced for all non-hydrogen atoms with the exception of a disordered THF solvent molecule in  $1 \cdot \text{THF}$ . The structure of  $[Zn(PMe_3)_4][BAr_4^F]_2$  is described in the noncentrosymmetric space group P1 but exhibits pseudo inversion symmetry (84 % fit). Assignment of the centrosymmetric space group  $P\overline{1}$  would require the central Zn atom of the tetrahedral  $[Zn(PMe_3)_4]^{2+}$  ion to reside on a crystallographic inversion centre, which would result in disorder by symmetry. Although the  $[Zn(PMe_3)_4]^{2+}$  ion is indeed found disordered over two positions in P1, the refined ratio of occupancies of the disorder sites of 0.898(2):0.102(2) significantly deviates from 0.5:0.5, as would be imposed by the  $\overline{1}$  site symmetry in the space group  $P\overline{1}$ . Therefore, the description in P1 is more appropriate for the structure of [Zn(PMe<sub>3</sub>)<sub>4</sub>][BAr<sub>4</sub><sup>F</sup>]<sub>2</sub>. A Flack x parameter of 0.36(3) [3], resulting from the refinement as a two-component inversion twin, lends support to this view. Hydrogen atoms were placed at geometrically calculated positions and refined with the appropriate riding model. The structure of [Zn(PMe<sub>3</sub>)<sub>4</sub>][BAr<sub>4</sub><sup>F</sup>]<sub>2</sub> was refined as a two-component inversion twin, affording a Flack x parameter of 0.36(3) [3]. CCDC 1032396-1032398 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.

- [1] CrysAlisPro Software system, Agilent Technologies UK Ltd, Oxford, UK.
- [2] G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122.
- [3] H. D. Flack, Acta Cryst 1983, A39, 876-881.

## Synthesis of $[Zn_2(THF)_6][BAr_4^F]_2(1)$

200 mg (0.498 mmol)  $Zn_2Cp_2^*$  and 1.046 g (0.997 mmol) [FeCp<sub>2</sub>][BAr<sub>4</sub><sup>F</sup>] were dissolved in 7 ml of THF at room temperature and stirred for 15 min, whereupon the initial blue solution immediately turned orange. A white precipitate was formed after addition of 20 ml of *n*-hexane. The white solid was isolated by filtration and washed with *n*-hexane (3x3 ml). Recrystallization by slow diffusion of *n*-hexane into a THF solution of  $[Zn_2(THF)_6][BAr_4^F]_2$  at -30 °C gave suitable colorless crystals for single crystal X-ray diffraction.

Yield: 1.015 g of colorless crystals (89 %).

*Elemental and AAS analysis* [%] calculated for C<sub>88</sub>H<sub>68</sub>B<sub>2</sub>F<sub>48</sub>O<sub>6</sub>Zn<sub>2</sub>: C, 46.19; H, 3.17; O, 4.20; Zn, 5.59; Found: C, 46.20; H, 3.20; O, 4.61; Zn, 5.29.

## Synthesis of [Zn<sub>2</sub>(PhNC)<sub>6</sub>][BAr<sub>4</sub><sup>F</sup>]<sub>2</sub> (2)

100 mg  $[Zn_2(THF)_6][BAr_4^F]_2$  (0.044 mmol) were dissolved in 3 ml of dichloromethane and 0.03 ml (0.297 mmol) of PhNC were added to the solution at room temperature. The resulting red solution was stirred for 1 h. 15 ml of *n*-hexane was added, giving a red precipitate, which was isolated by filtration and washed with *n*-hexane (4x2 ml). Recrystallization from a saturated dichloromethane solution of  $[Zn_2(PhNC)_6][BAr_4^F]_2$  at -30 °C gave suitable crystals for single crystal X-ray diffraction.

Yield: 70 mg of crystalline red powder (65 %).

*Elemental and AAS analysis* [%] calculated for C<sub>106</sub>H<sub>54</sub>B<sub>2</sub>F<sub>48</sub>N<sub>6</sub>Zn<sub>2</sub>: C, 51.45; H, 2.20; N, 3.40; Zn, 5.17; Found: C, 51.42; H, 2.29; N, 3.37; Zn, 5.27.

#### Synthesis of [Zn<sub>2</sub>(<sup>t</sup>BuNC)<sub>6</sub>][BAr<sub>4</sub><sup>F</sup>]<sub>2</sub> (3)

100 mg  $[Zn_2(THF)_6][BAr_4^F]_2$  (0.044 mmol) were dissolved in 3 ml dichloromethane and 25 mg (0.301 mmol) of 'BuNC were added to the solution at room temperature. The resulting red solution was stirred for 1 h. 15 ml of *n*-hexane was added, giving a red precipitate, which was isolated by filtration and washed with *n*-hexane (4x2 ml). Recrystallization from a saturated dichloromethane solution of  $[Zn_2(^tBuNC)_6][BAr_4^F]_2$  at -30 °C gave suitable crystals for single crystal X-ray diffraction.

Yield: 61 mg of crystalline white powder (59 %).

*Elemental and AAS analysis* [%] calculated for C<sub>94</sub>H<sub>78</sub>B<sub>2</sub>F<sub>48</sub>N<sub>6</sub>Zn<sub>2</sub>: C, 47.95; H, 3.34; N, 3.57; Zn, 5.44; Found: C, 46.98; H, 3.19; N, 3.39; Zn, 5.21.

**Table S1.** Crystallographic data and refinement details for  $1 \cdot \text{THF}$ ,  $2 \cdot 4 \text{ CH}_2\text{Cl}_2$  and $[Zn(PMe_3)_4][BAr_4^F]_2$ .

	$1 \cdot \text{THF}$	$2 \cdot 4 \operatorname{CH}_2\operatorname{Cl}_2$	[Zn(PMe <sub>3</sub> ) <sub>4</sub> ][BAr <sub>4</sub> <sup>F</sup> ] <sub>2</sub>
Empirical formula	$C_{92}H_{80}B_2F_{48}O_7Zn_2$	$C_{110}H_{62}B_2Cl_8F_{48}N_6Zn_2$	$C_{76}H_{60}B_2F_{48}P_4Zn$
$M_{ m r}$	2361.92	2815.61	2096.11
<i>T</i> [K]	113(2)	116(2)	100(2)
$\lambda$ [Å]	1.54184	1.54184	1.54184
Crystal size [mm <sup>3</sup> ]	$0.109 \times 0.089 \times 0.069$	$0.146 \times 0.054 \times 0.052$	$0.111 \times 0.080 \times 0.075$
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\overline{1}$	$P2_{1}/c$	<i>P</i> 1
<i>a</i> [Å]	12.6592(5)	15.1012(5)	13.0001(4)
<i>b</i> [Å]	14.0662(5)	16.1231(5)	13.4282(4)
<i>c</i> [Å]	14.2052(5)	24.7275(7)	14.1449(5)
α [°]	77.951(3)	90	102.570(3)
$\beta$ [°]	88.733(3)	102.147(3)	115.154(3)
γ [°]	85.817(3)	90	91.670(3)
V[Å <sup>3</sup> ]	2467.10(16)	5885.8(3)	2160.73(13)
Ζ	1	2	1
$\rho_{\text{calc.}} [\text{g cm}^{-3}]$	1.590	1.589	1.611
$\mu$ [mm <sup>-1</sup> ]	1.906	3.311	2.438
F (000)	1190	2804	1048
$\theta$ range [°]	3.181 - 74.193	3.295 - 74.929	3.405 - 74.267
Reflections collected / unique	18057 / 9694	25281 / 11758	15514 / 10115
<i>R</i> <sub>int</sub>	0.0365	0.0343	0.0260







Figure S2: <sup>13</sup>C NMR spectrum of 1 recorded at room temperature in CD<sub>2</sub>Cl<sub>2</sub>.

---62.84



Figure S3: <sup>19</sup>F NMR spectrum of 1 recorded at room temperature in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S4: <sup>11</sup>B NMR spectrum of 1 recorded at room temperature in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S5: IR spectrum of 1.

---6.63



for a  $[Zn(THF)_6]^+$  fragment.









Figure S8: <sup>13</sup>C NMR spectrum of 2 recorded at room temperature in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S9: <sup>19</sup>F NMR spectrum of 2 recorded at room temperature in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S11: IR spectrum of 2.







9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10 -11 -12 -13 -14 -15 -16 -17 -18 -19 -20 -21 -22 -23 -24 -25 -26 -27 -28 **Figure S14:** <sup>11</sup>B NMR spectrum of **3** recorded at room temperature in  $CD_2Cl_2$ .

13 12 11 10



Figure S15: IR spectrum of 3.



Figure S16: <sup>1</sup>H NMR recorded from the reaction between 1 and KCp\* in CD<sub>2</sub>Cl<sub>2</sub> at room temperature.



Figure S17: <sup>1</sup>H NMR recorded from the reaction between 2 and KDDP in  $C_6D_6$  at room temperature.



**Figure S18:** Molecular structure of  $[Zn(PMe_3)_4][BAr_4^F]_2$  in the crystal as determined by single crystal X-ray diffraction. Displacement ellipsoids are shown at the 50 % probability level. The disorder of the compound and the hydrogen atoms are omitted for clarity.





 $\begin{array}{c} -14 \ -16 \ -18 \ -20 \ -22 \ -24 \ -26 \ -28 \ -30 \ -32 \ -34 \ -36 \ -38 \ -40 \ -42 \ -44 \ -46 \ -48 \ -50 \ -52 \ -54 \ -56 \ -58 \ -60 \ -62 \ -64 \ -66 \ -68 \ -70 \ -72 \ -74 \ ppm \\ \hline \mathbf{Figure S20:} \ ^{31}P \ NMR \ spectrum \ of \ [Zn(PMe_3)_4] [BAr_4^F]_2 \ recorded \ at \ room \ temperature \ in \ CD_2Cl_2. \end{array}$