Aminotroponimate Zinc(I) Complexes: Syntheses and Spectroscopic Analyses

Hari Pada Nayek,^[a] Anja Lühl,^[a] Stephan Schulz,^[b] Ralf Köppe,^{*[a]} and Peter W. Roesky^{*[a]}

Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 70th birthday

Low valent metal-metal bonded compounds have been the ongoing research interests during last few years.^[1] Following the first landmark discovery of decamethyldizincocene ($[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$; $\text{Cp}^* = \text{C}_5\text{Me}_5$) by Carmona,^[2] a great attention gradually revealing in inorganic and organometallic chemistry involving the synthesis and reactivity of low-valent metal-metal bonded organozinc compounds. Since the initial report, some low-valent dizinc compounds of the type R_2Zn_2 ($\text{R} = \text{EtMe}_4\text{Cp}$,^[3] $\{2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\}\text{N}(\text{Me})\text{C}\}_2\text{CH}$ (Dippnacnac),^[4] $2,6\text{-}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3$,^[5] $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{Me})\text{C}]_2$,^[6] $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{-NCH}]_2$,^[7] $\text{Me}_2\text{Si}[\text{N}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)]_2$,^[8] $1,2\text{-bis}[(2,6\text{-diisopropylphenyl})\text{imino}]\text{acenaphthene}$)^[9] have been synthesized and structurally characterized using different kinds of ligands. Limited information is available on the chemical reactivity of such compounds. The reactivity of $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ towards H_2O , $t\text{-BuOH}$, and NCXyl resulted in the formation of elemental zinc and the corresponding Zn(II) complexes through disproportionation pathways. The reaction with iodine occurred with oxidation and subsequent formation of $[(\eta^5\text{-Cp}^*)_2\text{Zn}]$ and ZnI_2 ,^[3] whereas no reaction was observed with H_2 , CO , and CO_2 . Very recently one of us reported on the reaction of $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ with the strong Lewis base 4-(dimethylamino)pyridine (dmap), yielding $[(\eta^5\text{-Cp}^*)\text{Zn-Zn}(\text{dmap})_2(\eta^5\text{-Cp}^*)]$, the first Lewis acid-base adduct of dizincocene. $[(\eta^5\text{-Cp}^*)\text{Zn-Zn}(\text{dmap})_2(\eta^5\text{-Cp}^*)]$,^[10] which on further reaction with $[\text{H}(\text{OEt}_2)_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ resulted base-stabilized $[\text{Zn}_2]^{2+}$ cation $[\text{Zn}_2(\text{dmap})_6][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$.^[11] Again, one of us succeeded recently to exchange Cp^* of $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ by reaction of it with $[\{2,4,6\text{-Me}_3\text{C}_6\text{H}_2\}\text{N}(\text{Me})\text{C}\}_2\text{CH}_2]$ (MesnacnacH) to synthesize $[(\text{Mesnacnac})_2\text{Zn}_2]$.^[12] Carmona *et al.* revealed the synthesis of $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{OR})(\text{L})_x]$ ($\text{R} = 2,6\text{-}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$ and C_5Me_5 ; $\text{L} = 4\text{-pyrrolidinopyridine}$).^[13] Moreover, reactions of $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ with bis(iminodi(phenyl)phosphorano)methanes yielded both homo- and heteroleptic Zn(I) complexes.^[14]

Obviously the organic ligands have a great impact on the nature of the Zn-Zn bond, such as bond length, bond strength, and orbital composition. Based on these observations we were interested in studying the nature of the Zn-Zn bond in more detail including the spectroscopic properties.

Herein, we report on the synthesis and characterization of two new zinc-zinc bonded compounds starting from $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$. The details of the vibrational modes supported by DFT^[15] calculations of the new compounds were investigated.

We are working for some time on aminotroponimate zinc compounds. These complexes were studied in detail for the catalytic hydroamination catalysis.^[16] In this context we were interested in preparing low valent aminotroponimate zinc-zinc bonded compounds. Reaction of the aminotroponimines *N*-isopropyl-2-(isopropylamino)troponimine $[\{(i\text{Pr})_2\text{ATI}\}\text{H}]$ ^[17] and 4-bromo *N*-isopropyl-2-(isopropylamino)troponimine $[\{4\text{-Br}(i\text{Pr})_2\text{ATI}\}\text{H}]$ ^[18] with $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ in toluene resulted at room temperature in the formation of $[\{(i\text{Pr})_2\text{ATI}\}_2\text{Zn}_2]$ (**1**) and $[\{4\text{-Br}(i\text{Pr})_2\text{ATI}\}_2\text{Zn}_2]$ (**2**). The Zn-Zn bond is preserved under these protolytic conditions in the products (Scheme 1).

Scheme 1. Synthesis of **1** and **2**.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic data for compounds **1** and **2** are consistent with the solid-state structures (Figure 1).

[a] Dr. H. P. Nayek, Dipl.-Chem. A. Lühl, Dr. R. Köppe, Prof. Dr. P. W. Roesky
Institut für Anorganische Chemie
Karlsruhe Institute of Technology (KIT)
Engesserstrasse 15, 76131 Karlsruhe (Germany)
Email: roesky@kit.edu
Fax : (+49)721-608-4854

[b] Prof. Dr. S. Schulz
University of Duisburg-Essen
Universitätsstr. 5-7, S07 S03 C30, 45117, Essen, Germany
Fax: Int (+) 201 1833830; Phone: Int (+)201 1834635
E-mail: stephan.schulz@uni-due.de

No bridging hydride resonances were observed in the expected range ($\delta = 4\text{--}5$ ppm)^[19] in the ^1H NMR spectra of the complexes and the IR spectrum had no absorption peak between 1000 and 1500 cm^{-1} , which is the typical range for Zn_2H_2 four ring systems.

Crystals of **1** and **2** suitable for single crystal X-ray diffraction analysis were obtained from a solution of **1** and **2** in toluene at -30°C . The data confirm the dimeric nature of **1** and **2** with the central Zn–Zn bond. Compound **1** and **2** crystallize as yellow needles in the orthorhombic space group *Pbcn* and the monoclinic space group *C2/c* respectively.^[20] Figure 1 shows the molecular structures of compounds **1** and **2**.

Figure 1. Molecular structure of **1** (top) and **2** (bottom) showing the atom labeling scheme. H atoms are presented by small black spheres. Selected bond lengths [Å] and angles [°] **1**: Zn1–Zn1' 2.3534(7), Zn1–N1 2.02(2), Zn1–N2 2.02(2), N1–Zn1–N2 80.04(7), N1–Zn1–Zn1' 142.51(5), N2–Zn1–Zn1' 135.67(5); **2**: Zn1–Zn1' 2.3570(8), Zn1–N1 2.017(3), Zn1–N2 2.012(3), N1–Zn1–N2 81.12(12), N1–Zn1–Zn1' 140.17(9), N2–Zn1–Zn1' 138.64(9).

The two ligands are arranged in a nearly orthogonal orientation with a N1–Zn1–Zn1'–N1' torsion angle of 79.2° (**1**) and 68.2° (**2**), thus providing effective steric protection of the Zn–Zn bond. The Zn–Zn distances are 2.3534(7) in **1** and 2.3570(8) Å in **2**. They are only about 0.05 Å longer than that of 2.305(3) Å reported for $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ but close to $[\text{Dippnacnac}_2\text{Zn}_2]$ (2.3586(7) Å) and shorter than $[\text{Mesnacnac}_2\text{Zn}_2]$ (2.3813(8) Å). However, the Zn–Zn bond lengths for **1** and **2** are notably shorter than the Zn...Zn separation of 2.4513(9) Å in the related zinc hydride dimer, $\text{RZn}(\mu\text{-H})_2\text{ZnR}$ ($\text{R} = [(\text{2,6-Me}_2\text{C}_6\text{H}_3)\text{N}(\text{Me})\text{C}(\text{CH}_3)_2]$).^[18] The zinc atoms in **1** and **2** adopt a trigonal planar geometry with the Zn–N bond distances of 2.02(2), 2.02(2) (**1**) and 2.012(3), 2.017(3) (**2**) Å. The Zn–N bond distances are in the range of $[(\text{iPr})_2\text{ATI}]_2\text{Zn}$ (1.988(2)–2.006(3) Å),^[21] $[\text{Dippnacnac}_2\text{Zn}_2]$ (2.005(3)–2.014(3) Å) and $[\text{Mesnacnac}_2\text{Zn}_2]$ (2.005(2)–2.000(3) Å).

To confirm the experimental data of compounds **1** and **2** we performed quantum chemical DFT calculations (RI-BP86 level, def2-TZVP basis sets for all atoms). The structural parameters obtained are in sound agreement with the results of the single crystal X-ray structure analysis ($r(\text{Zn-Zn})$ (exp. data in brackets): **1**: 2.371 Å (2.353 Å), **2**: 2.369 Å (2.357 Å)). The molecular symmetry is close to D_{2d} symmetry. The torsional angle $\angle(\text{N-Zn-Zn-N})$ was calculated to be 92° for both species. To differentiate **1** from the possible hydride product $[(\text{iPr})_2\text{ATI}]_2\text{Zn}(\mu\text{-H})_2\text{Zn}\{(\text{iPr})_2\text{ATI}\}$ **3** we furthermore calculated its structure and vibrational spectrum. The ground state of this molecule is formed by a Zn_2H_2 four membered ring and the shape is almost of D_{2h} symmetry. The most intense band in the infrared spectrum was calculated being at 1076 cm^{-1} (Zn_2H_2 stretching mode; b_{2u} representation). As both the overall molecular symmetry of the experimentally determined structure as well as the measured IR spectrum are not in line with the results of the calculations on **3** the formation of this hydride species can definitely be ruled out.

Quantum chemical calculations support the interpretation of vibrational spectroscopy data. Information on the bonding forces – especially on the Zn–Zn bond – can be obtained. Whereas a detailed normal coordinate analysis on Zn–Zn bond containing species with inversion symmetry was available only on $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ (D_{5h} symmetry) to date^[22] such an investigation is out of reach for **1** and **2** due to its lower symmetry: the number of internal coordinates – even in the totally symmetric irreducible representation a_g – is too high (51 coordinates). Still, a statement on which emissions of the totally symmetric representation in the Raman spectrum are responsible for the Zn–Zn motion is given after the analysis of the eigenvectors of a quantum chemical frequency calculation. In the case of compound **1** we find for the very first time a stretching motion of the Zn–Zn bond which is almost uncoupled to other vibrations: it is found in the Raman spectrum at 330.4 cm^{-1} (calc. 322 cm^{-1}). For compound **2** the Zn–Zn stretching and the symmetric deformation mode $\delta(\text{Zn-N-C})$ seem strongly be coupled to each other (exp. 280.9 cm^{-1} , 331.0 cm^{-1} ; calc. 276.8 cm^{-1} , 355.5 cm^{-1}).

Figure 2. Comparison of the a) experimental and b) theoretical Raman spectrum of **1**.

It is interesting how to compare the Zn–Zn bonds in **1** and **2** with those of $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ ^[22] and of the dmap stabilized dizinc dication $[\text{Zn}_2(\text{dmap})_6]^{2+}$.^[11] By means of a normal coordinate analysis in $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ two vibrational modes with Zn–Zn stretching motion coupled to the deformation $\delta(\text{Zn-C}_{\text{ring}}\text{-C}_{\text{methyl}})$ as

well as to the stretching mode $\nu(\text{Zn-C}_{\text{ring}})$ were found (exp. 236.0 cm^{-1} , calc. 228.6 cm^{-1} (potential energy distribution (PED) 44% $\nu(\text{Zn-Zn})$, 53 % $\delta(\text{Zn-C}_{\text{ring}}\text{-C}_{\text{methyl}})$; exp. 373.6 cm^{-1} , calc. 381.8 cm^{-1} (PED: 27% $\nu(\text{Zn-Zn})$, 56% $\nu(\text{Zn-Zn})$, 15 % $\delta(\text{Zn-C}_{\text{ring}}\text{-C}_{\text{methyl}})$). In $[\text{Zn}_2(\text{dmap})_6]^{2+}$ three absorptions of lower energy with respect to **1**, **2** and $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ (exp. 289.8 cm^{-1} , 233.9 cm^{-1} ; calc. 288.1 cm^{-1} , 263.1 cm^{-1} , 237.4 cm^{-1}) are found in the totally symmetric representation (orientational DFT calculation (BP86, def2-TZVP basis sets)). Comparing the energies of the modes attributed to a Zn-Zn motion we assume the Zn-Zn bonds in **1**, **2** and $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ to be of comparable strength, whereas the Zn-Zn bond strength in $[\text{Zn}_2(\text{dmap})_6]^{2+}$ is slightly lower probably due to its dicationic nature.

A further method to gain information on the strength of the Zn-Zn bond using purely theoretical results is the population analysis based on occupation numbers (Ahlrichs-Heinzmann population analysis).^[23] The shared electron numbers (SEN) are a reliable measure on the covalent bond strength in these molecules.

Figure 3. Comparison of the a) experimental and b) theoretical IR spectrum of **1**.

The SENs obtained for the Zn-Zn bonds in **1**, **2** and $[\text{Zn}_2(\text{dmap})_6]^{2+}$ are identical (1.32) and give rise for a strong single bond; the SEN(Zn-Zn) of $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ is slightly higher (1.45). We interpret stabilization of Zn-N bonding in $[\text{Zn}_2(\text{dmap})_6]^{2+}$ to be slightly higher compared to **1** and **2** (sums of SEN(Zn-N): **1**: 4.77; **2**: 4.76; $[\text{Zn}_2(\text{dmap})_6]^{2+}$: 5.01).

In conclusion, two aminotroponimate stabilized low valent zinc-zinc bonded compounds were synthesized and characterized by single crystal X-ray diffraction and spectroscopic methods. Quantum chemical investigations were performed to demonstrate the experimental findings. For the very first time a stretching motion of the Zn-Zn bond which is almost uncoupled to other vibrations was found in the Raman spectrum. Future investigation will concentrate on the synthesis of new zinc-zinc bonded compounds and their potential use in small molecule activation, generation of heterometallic metal-metal bonded compounds.

Experimental Section

General: All synthesis steps were performed with strong exclusion of air and external moisture (Ar atmosphere at a high-vacuum, double-manifold Schlenk line or Ar

atmosphere in a glove box). Toluene and pentane were dried and freshly distilled prior to use.

Synthesis of compound 1 and 2: To a mixture of $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ (0.05 g, 0.12 mmol) and $[(i\text{-Pr})_2\text{ATI}]\text{H}$ (0.051 g, 0.25 mmol) (**1**) or $[\text{4-Br}(i\text{-Pr})_2\text{ATI}]\text{H}$ (0.071 g, 0.25 mmol) (**2**) in 10 mL of toluene was added at room temperature. The mixture was stirred for 4 hours. The solvent was evaporated to get a yellow solid. The solid was washed with 10 mL of pentane and dried in vacuum. The yellow solid was again dissolved in a minimum amount (around 2 mL) of toluene and kept at -30°C . Yellow crystals, suitable for X-ray diffraction were obtained after one day.

1. Yield: 0.038 g, 56%, NMR: ^1H NMR (C_6D_6 , 300 MHz, 25°C): δ = 1.39 [d, $J_{\text{H,H}}$ = 6.3 Hz, 24 H, $\text{CH}(\text{CH}_3)_2$], 3.95 [sept, $J_{\text{H,H}}$ = 6.2, 4 H, $\text{CH}(\text{CH}_3)_2$], 6.38 [t, $J_{\text{H,H}}$ = 9.1 Hz, 2 H, Ar], 6.64 [d, $J_{\text{H,H}}$ = 11.6 Hz, 4 H, Ar], 7.01 [t, $J_{\text{H,H}}$ = 10.6 Hz, 4 H, Ar]. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75 MHz): δ = 26.0, 49.1, 110.5, 117.1, 134.3, 160.9 ppm. Elemental analysis: Calculated: C: 58.11, H: 7.13, N: 10.42, Found: C: 57.14, H: 7.07, N: 9.78.

2. Yield: 0.045 g, 52%, NMR: ^1H NMR (C_6D_6 , 300 MHz, 25°C): δ = 1.28 [d, $J_{\text{H,H}}$ = 6.2 Hz, 24 H, $\text{CH}(\text{CH}_3)_2$], 3.74 [sept, $J_{\text{H,H}}$ = 6.2, 4 H, $\text{CH}(\text{CH}_3)_2$], 6.20 [t, $J_{\text{H,H}}$ = 13.3 Hz, 2 H, Ar], 7.25 [d, $J_{\text{H,H}}$ = 12.3 Hz, 4 H, Ar]. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75 MHz): δ = 25.8, 49.2, 109.6, 111.5, 136.5, 159.8 ppm. Elemental analysis: Calculated: C: 44.92, H: 5.22, N: 8.05, Found: C: 45.44, H: 5.06, N: 7.89.

Spectroscopic measurements: NMR spectra were recorded on a Bruker Avance II 300 MHz NMR spectrometer. Raman spectra of polycrystalline samples were measured using a Bruker Senterra (**1**, excitation 785 nm) and Bruker Multiram (**2**, excitation 1064 nm). IR spectra for solid **1** and **2** were recorded in the range 4000–400 cm^{-1} by means of an ATR unit (DuraSampIR unit, Bruker Tensor 37 FTIR spectrometer). Raman and FTIR spectra were recorded with a resolution of 2 cm^{-1} .

Crystal data for **1**: $\text{C}_{26}\text{H}_{38}\text{N}_4\text{Zn}_2$, $M = 537.34$, orthorhombic, $a = 15.934(3)$ Å, $b = 17.257(4)$ Å, $c = 9.4663(19)$ Å, $V = 2603.0(9)$ Å³, $T = 200(2)$ K, space group $Pbcn$, $Z = 4$, $\mu(\text{MoK}\alpha) = 1.863$ mm⁻¹, 25999 reflections measured, 3514 independent reflections ($R_{\text{int}} = 0.0830$). The final R values were 0.0465 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1201 (all data). The goodness of fit on F^2 was 1.064.

Crystal data for **2**: $\text{C}_{26}\text{H}_{36}\text{Br}_2\text{N}_4\text{Zn}_2\cdot\text{C}_7\text{H}_8$, $M = 787.28$, monoclinic, $a = 20.2931(8)$ Å, $b = 5.9614(2)$ Å, $c = 30.4380(13)$ Å, $\beta = 111.013(3)^\circ$, $V = 3437.4(2)$ Å³, $T = 200(2)$ K, space group $C2/c$, $Z = 4$, $\mu(\text{MoK}\alpha) = 3.748$ mm⁻¹, 22914 reflections measured, 4640 independent reflections ($R_{\text{int}} = 0.0731$). The final R values were 0.0530 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1554 (all data). The goodness of fit on F^2 was 1.021. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC-790136 (**1**), and 790137 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Quantum chemical calculations: Theoretical DFT calculations were based on the RI-BP86 level^[24] as implemented in the program system TURBOMOLE.^[25] The basis sets used were of def2-TZVP quality for all atoms.^[26] The calculations were restricted to the symmetry D₂. Vibrational frequencies and IR intensities were calculated by means of the module AOFORCE.^[27] Raman scattering cross sections were obtained after calculation of the polarizability derivatives with the help of the modules EGRAD^[28] and INTENSE. Shared electron numbers were calculated by means of a population analysis based on occupation numbers.^[23]

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft, DFG Center for Functional Nanostructures (CFN), the Leibniz Rechenzentrum der Bayerischen Akademie der Wissenschaften, the Landesstiftung Baden-Württemberg gGmbH, and the Fonds der Chemischen Industrie.

Keywords: Metal-metal interactions • Raman Spectroscopy • X-Ray Diffraction • Zinc • Zinc-Zinc Bond

[1] S. Schulz, *Chem. Eur. J.* **2010**, *16*, 6416–6428.

- [2] a) I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science*, **2004**, 305, 1136-1138; b) D. del Río, A. Galindo, I. Resa, E. Carmona, *Angew. Chem.* **2005**, 117, 1270-1273; *Angew. Chem. Int. Ed.* **2005**, 44, 1244-1247.
- [3] A. Grirrane, I. Resa, A. Rodríguez, E. Carmona, E. Alvarez, E. Gutierrez-Puebla, A. Monge, A. Gilando, D. del Río, A. Anderson, *J. Am. Chem. Soc.* **2007**, 129, 693-703.
- [4] Y. Wang, B. Quillian, P. Wei, H. Wang, X. Yang, Y. Xie, R. B. King, P. V. R. Schleyer, H. Fritz, III, G. H. Robinson, *J. Am. Chem. Soc.* **2005**, 127, 11944-11945.
- [5] Z. Zhu, M. Brynda, R. J. Wright, R. C. Fischer, W. A. Merrill, E. Rivard, R. Wolf, J. C. Fettingter, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2007**, 129, 10847-10857.
- [6] X. Yang, J. Yu, Y. Liu, Y. Xie, H. F. Schaefer, Y. Liang, B. Wu, *Chem. Commun.* **2007**, 2363-2365.
- [7] P. Yang, X. Yang, J. Yu, Y. Liu, C. Zhang, Y. Deng, B. Wu, *Dalton Trans.* **2009**, 5773-5779
- [8] Y. Tsai, D. Lu, Y. Lin, J. Hwang, J. K. Yu, *Chem. Commun.* **2007**, 4125-4127.
- [9] I. L. Fedushkin, A. A. Skatova, S. Y. Ketkov, O. V. Eremenko, A. V. Piskunov, G. K. Fukin, *Angew. Chem.* **2007**, 119, 4380-4383; *Angew. Chem. Int. Ed.* **2007**, 46, 4302-4305.
- [10] D. Schuchmann, U. Westphal, S. Schulz, U. Flörke, D. Bläser, R. Boese, *Angew. Chem.* **2009**, 121, 821-824; *Angew. Chem. Int. Ed.* **2009**, 48, 807-810.
- [11] S. Schulz, D. Schuchmann, I. Krossing, D. Himmel, D. Bläser, R. Boese, *Angew. Chem.* **2009**, 121, 5859-5862; *Angew. Chem. Int. Ed.* **2009**, 48, 5748-5751.
- [12] S. Schulz, D. Schuchmann, U. Westphal, M. Bolte, *Organometallics*, **2009**, 28, 1590-1592
- [13] M. Carrasco, R. Peloso, A. Rodríguez, E. Alvarez, C. Maya, E. Carmona, *Chem. Eur. J.*, **2010**, 16, 9754-9757.
- [14] S. Schulz, S. Gondzik, D. Schuchmann, U. Westphal, L. Dobrzycki, R. Boese, S. Harder, *Chem. Commun.*, **2010**, accepted
- [15] a) R.G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York **1988**; b) T. Ziegler, *Chem. Rev.* **1991**, 91, 651-667.
- [16] a) M. Dochnahl, K. Löhnwitz, J. Pissarek, M. Biyikal, S. R. Schulz, S. Schön, N. Meyer, P. W. Roesky, S. Blechert, *Chem. Eur. J.* **2007**, 13, 6654-6666; b) J. Herrmann, G. A. Luinstra, P. W. Roesky, *J. Organomet. Chem.* **2004**, 689, 2720-2725; c) M. Dochnahl, K. Löhnwitz, A. Lühl, J. Pissarek, M. Biyikal, P. W. Roesky, S. Blechert, *Organometallics*, **2010**, 29, 2637-2645; d) K. Löhnwitz, M. J. Molski, A. Lühl, P. W. Roesky, M. Dochnahl, S. Blechert, *Eur. J. Inorg. Chem.* **2009**, 1369-1373; e) N. Meyer, P. W. Roesky, *Organometallics*, **2009**, 28, 306-311; f) M. Biyikal, K. Löhnwitz, M. Dochnahl, P. W. Roesky, S. Blechert, *Eur. J. Inorg. Chem.* **2010**, 7, 1070-1081.
- [17] H. V. R. Dias, W. Jin, R. E. Ratcliff, *Inorg. Chem.* **1995**, 34, 6100-6105.
- [18] M. Dochnahl, K. Löhnwitz, J. Pissarek, P. W. Roesky, S. Blechert, *Dalton Trans.* **2008**, 2844-2848.
- [19] H. Hao, C. Cui, H. W. Roesky, G. Bai, H. Schmidt, M. Noltemeyer, *Chem. Commun.* **2001**, 1118-1119.
- [20] See Supporting Information
- [21] S. Marks, P. W. Roesky, *unpublished results*.
- [22] D. del Río, I. Resa, A. Rodríguez, L. Sanchez, R. Köppe, A. J. Downs, C. Y. Tang, E. Carmona, *J. Phys. Chem. A*, **2008**, 112, 10516.
- [23] R. Heinzmann, R. Ahlrichs, *Theoret. Chim. Acta*, **1976**, 42, 33.
- [24] a) A. D. Becke, *Phys. Rev. A* **1988**, 38, 3098; b) S. H. Vosko, L. Wilk, M. Nussair, *Can. J. Phys.* **1980**, 58, 1200; c) J. P. Perdew, *Phys. Rev. B* **1986**, 33, 8822; J. P. Perdew, *Phys. Rev. B* **1986**, 34, 7406.
- [25] a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, 162, 165; b) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, 102, 346.
- [26] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, 97, 2571.
- [27] P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Letters*, **2004**, 384, 103.
- [28] D. Rappoport, F. Furche, *J. Chem. Phys.* **2007**, 126, 201104.

Received: ((will be filled in by the editorial staff))
 Revised: ((will be filled in by the editorial staff))
 Published online: ((will be filled in by the editorial staff))

Entry for the Table of Contents (Please choose one layout only)

Zinc–Zinc Bond

*Hari Pada Nayek, Anja Lühl,
Stephan Schulz, Ralf Köppe,* Peter
W. Roesky** Page –
Page

Aminotroponimate Zinc(I) Complexes: Syntheses and Spectroscopic Analyses

Aminotroponimates found to be a new type and very effective ligand for stabilization low valent Zn(I)-Zn(I) bonded compound. For the first time a stretching motion of the Zn-Zn bond which is almost uncoupled to other vibrations was found in the Raman spectrum.

Supporting Information

Aminotroponimate Zinc(I) Complexes: Syntheses and Spectroscopic analyses

Hari Pada Nayek,^[a] Anja Lühl,^[a] Stephan Schulz,^[b] Ralf Köppe*^[a] and Peter W. Roesky*^[a]

Institut für Anorganische Chemie, Karlsruhe Institute of Technology (KIT),

Engesserstrasse 15, 76131 Karlsruhe, Germany

University of Duisburg-Essen, Universitätsstr. 5-7, S07 S03 C30, 45117 Essen, Germany

Details of the X-ray diffraction measurement, structure solution and refinement

General

Data were collected on diffractometer equipped with a STOE imaging plate detector system IPDS2T using MoK α radiation with graphite monochromatization ($\lambda = 0.71073$ Å) at 200 K. Structure solution was performed by direct methods, full-matrix-least squares refinement against F₂ using SHELXS-97 and SHELXL-97 software.^[1]

Table S1 Crystal data and experimental details of the single-crystal X-ray analyses of **1** and **2**

Compound	1	2•toluene
Empirical formula	C ₂₆ H ₃₈ N ₄ Zn ₂	C ₃₃ H ₄₄ Br ₂ N ₄ Zn ₂
Formula weight /g·mol ⁻¹	537.34	787.28
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbca</i>	<i>C2/c</i>
<i>a</i> /Å	15.934(3)	20.2931(8)
<i>b</i> /Å	17.257(4)	5.9614(2)
<i>c</i> /Å	9.4663(19)	30.4380(13)
β /°	—	111.013(3)
<i>V</i> /Å ³	2603.0(9)	3437.4(2)
<i>Z</i>	4	4
ρ_{calc} /g·cm ⁻³	1.371	1.521
$\mu(\text{MoK}\alpha)$ /mm ⁻¹	1.863	3.748
Absorption correction type	Integration (X-Shape)	Integration (X-Shape)
Min/Max transmission	0.4697/0.8217	0.3547/0.8514
2 θ range /°	4 -58	4-58
Reflections measured	25999	22914
Independent reflections	3514	4640
<i>R</i> (int)	0.0830	0.0731
Ind. reflections ($I > 2\sigma(I)$)	2862	3657
Parameters	145	180
<i>R</i> ₁ ($I > 2\sigma(I)$)	0.0465	0.0530
<i>wR</i> ₂ (all data)	0.1201	0.1554
GooF (all data)	1.064	1.021
Max. peak/hole /e ⁻ ·10 ⁻⁶ pm ⁻³	0.766/-1.067	0.851/-0.599

^{a)} $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, ^{b)} $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

Raman Spectrum

Figure S1 Raman spectrum of **2**

FT-IR Spectrum

Figure S2 Infrared spectrum of **2**

Results of DFT Calculation on 1 (RI-BP86/def2-TZVP basis sets)

a) Cartesian coordinates (atomic units)

0.00000000	0.00000000	-2.24004728	zn
1.72028522	1.78508894	-5.15204018	n
-1.72028522	-1.78508894	-5.15204018	n
0.87017785	1.11947402	-7.43676712	c
-0.87017785	-1.11947402	-7.43676712	c
1.46648413	2.52259292	-9.65441381	c
-1.46648413	-2.52259292	-9.65441381	c
1.08009868	2.07527662	-12.21765752	c
-1.08009868	-2.07527662	-12.21765752	c
0.00000000	0.00000000	-13.42924563	c
2.40926850	4.31443342	-9.27936502	h
-2.40926850	-4.31443342	-9.27936502	h
1.77892761	3.57383804	-13.45892946	h
-1.77892761	-3.57383804	-13.45892946	h
0.00000000	0.00000000	-15.49157117	h
0.00000000	0.00000000	2.24004728	zn
1.72028522	-1.78508894	5.15204018	n
-1.72028522	1.78508894	5.15204018	n
0.87017785	-1.11947402	7.43676712	c

-0.87017785	1.11947402	7.43676712	c
1.46648413	-2.52259292	9.65441381	c
-1.46648413	2.52259292	9.65441381	c
1.08009868	-2.07527662	12.21765752	c
-1.08009868	2.07527662	12.21765752	c
0.00000000	0.00000000	13.42924563	c
2.40926850	-4.31443342	9.27936502	h
-2.40926850	4.31443342	9.27936502	h
1.77892761	-3.57383804	13.45892946	h
-1.77892761	3.57383804	13.45892946	h
0.00000000	0.00000000	15.49157117	h
3.55992717	3.83713792	-4.83490132	c
2.21676094	6.36755982	-4.35707835	c
1.11908807	6.27175187	-2.59456468	h
3.59614744	7.91258527	-4.17630201	h
0.90875988	6.83674912	-5.90002807	h
5.39091069	3.20072046	-2.68416953	c
4.70660593	4.01202094	-6.56948353	h
6.81807359	4.69844008	-2.48606997	h
6.37201462	1.40902348	-3.05513855	h
4.37851753	3.02041149	-0.87799424	h
-3.55992717	-3.83713792	-4.83490132	c
3.55992717	-3.83713792	4.83490132	c
-3.55992717	3.83713792	4.83490132	c

-2.21676094	-6.36755982	-4.35707835	c
2.21676094	-6.36755982	4.35707835	c
-2.21676094	6.36755982	4.35707835	c
-1.11908807	-6.27175187	-2.59456468	h
1.11908807	-6.27175187	2.59456468	h
-1.11908807	6.27175187	2.59456468	h
-3.59614744	-7.91258527	-4.17630201	h
3.59614744	-7.91258527	4.17630201	h
-3.59614744	7.91258527	4.17630201	h
-0.90875988	-6.83674912	-5.90002807	h
0.90875988	-6.83674912	5.90002807	h
-0.90875988	6.83674912	5.90002807	h
-5.39091069	-3.20072046	-2.68416953	c
5.39091069	-3.20072046	2.68416953	c
-5.39091069	3.20072046	2.68416953	c
-4.70660593	-4.01202094	-6.56948353	h
4.70660593	-4.01202094	6.56948353	h
-4.70660593	4.01202094	6.56948353	h
-6.81807359	-4.69844008	-2.48606997	h
6.81807359	-4.69844008	2.48606997	h
-6.81807359	4.69844008	2.48606997	h
-6.37201462	-1.40902348	-3.05513855	h
6.37201462	-1.40902348	3.05513855	h
-6.37201462	1.40902348	3.05513855	h

-4.37851753 -3.02041149 -0.87799424 h

4.37851753 -3.02041149 0.87799424 h

-4.37851753 3.02041149 0.87799424 h

b) Population analysis based on occupation numbers

(Zn: 18 MAOs, H: 1 MAO, N,C: 5 MAOs)

1 zn - 2 n = 1.1927

1 zn - 4 c = 0.1055

1 zn - 16 zn = 1.3239

1 zn - 31 c = 0.0495

1 zn - 32 c = 0.0286

1 zn - 33 h = 0.0218

1 zn - 36 c = 0.0331

1 zn - 40 h = 0.0253

1 zn - 57 c = 0.0211

1 zn - 69 h = 0.0286

2 n - 4 c = 1.6466

2 n - 5 c = 0.0288

2 n - 6 c = 0.0184

2 n - 31 c = 1.2117

2 n - 32 c = 0.0274

2 n - 36 c = 0.0236

2 n - 37 h = 0.0105

4 c - 5 c = 1.4768

4 c - 6 c = 1.6899

4 c - 7 c = 0.0706

$4\text{ c} - 8\text{ c} = 0.0342$
 $4\text{ c} - 11\text{ h} = 0.0301$
 $4\text{ c} - 31\text{ c} = 0.0416$
 $6\text{ c} - 7\text{ c} = 0.0103$
 $6\text{ c} - 8\text{ c} = 1.8419$
 $6\text{ c} - 10\text{ c} = 0.0356$
 $6\text{ c} - 11\text{ h} = 1.3220$
 $6\text{ c} - 13\text{ h} = 0.0223$
 $6\text{ c} - 31\text{ c} = 0.0152$
 $6\text{ c} - 37\text{ h} = 0.0230$
 $8\text{ c} - 9\text{ c} = 0.0473$
 $8\text{ c} - 10\text{ c} = 1.8066$
 $8\text{ c} - 11\text{ h} = 0.0278$
 $8\text{ c} - 13\text{ h} = 1.3434$
 $8\text{ c} - 15\text{ h} = 0.0210$
 $10\text{ c} - 13\text{ h} = 0.0245$
 $10\text{ c} - 15\text{ h} = 1.3484$
 $11\text{ h} - 31\text{ c} = 0.0180$
 $11\text{ h} - 37\text{ h} = 0.0187$
 $31\text{ c} - 32\text{ c} = 1.3292$
 $31\text{ c} - 33\text{ h} = 0.0222$
 $31\text{ c} - 34\text{ h} = 0.0285$
 $31\text{ c} - 35\text{ h} = 0.0279$
 $31\text{ c} - 36\text{ c} = 1.3101$
 $31\text{ c} - 37\text{ h} = 1.3110$
 $31\text{ c} - 38\text{ h} = 0.0302$
 $31\text{ c} - 39\text{ h} = 0.0265$
 $31\text{ c} - 40\text{ h} = 0.0236$
 $32\text{ c} - 33\text{ h} = 1.3563$
 $32\text{ c} - 34\text{ h} = 1.3597$
 $32\text{ c} - 35\text{ h} = 1.3604$
 $32\text{ c} - 36\text{ c} = 0.0329$
 $32\text{ c} - 37\text{ h} = 0.0274$
 $33\text{ h} - 34\text{ h} = 0.0187$
 $33\text{ h} - 35\text{ h} = 0.0181$

34 h - 35 h = 0.0183
 36 c - 37 h = 0.0283
 36 c - 38 h = 1.3584
 36 c - 39 h = 1.3621
 36 c - 40 h = 1.3653
 38 h - 39 h = 0.0189
 38 h - 40 h = 0.0196
 39 h - 40 h = 0.0182

c) Vibrational frequencies and intensities

	Representation	ν/cm^{-1}	IR intensity/ km mol^{-1}	Raman cross section (par/unpol.) (max. 100 %)
1	a	11.45	0.00000	0
2	b2	15.46	0.00146	0
3	b3	15.86	0.00297	0
4	b2	34.54	0.06508	6.05
5	b3	35.39	0.00026	2.37
6	b1	48.27	0.37828	0.86
7	a	51.32	0.00000	0.5
8	b3	61.40	0.26336	0.04
9	b2	67.81	0.00410	1.51
10	b3	73.51	0.61090	1.64
11	b2	76.89	0.47185	0.58
12	a	77.12	0.00000	0.58

13	b1	82.90	0.18146	0.02
14	a	96.94	0.00000	3.3
15	b2	114.06	0.01387	0.43
16	b3	118.65	0.77987	0
17	b1	143.25	0.39546	0.01
18	a	144.64	0.00000	0.8
19	b1	151.03	0.02376	0
20	b3	153.61	1.39997	0.14
21	b2	154.37	0.14681	0.05
22	a	158.08	0.00000	2.33
23	b2	178.39	1.80633	0.13
24	b3	185.02	1.42093	0
25	b1	206.56	47.56640	0.05
26	b2	208.51	0.02383	0.01
27	b1	209.94	13.94570	0
28	b3	210.17	0.00003	0.09
29	a	210.42	0.00000	0.29
30	b2	231.45	0.46331	0.03
31	b3	231.77	1.30870	0
32	b1	240.17	1.24829	0.01
33	a	240.32	0.00000	0.3
34	b2	241.90	0.10278	0.41
35	b3	243.53	0.00195	0.08

36	a	264.31	0.00000	0.84
37	b1	285.65	32.02434	0.08
38	b3	311.49	0.40133	0.73
39	b2	311.61	1.40335	0.36
40	a	322.36	0.00000	1.95
41	b3	345.76	5.84058	0
42	b2	345.82	4.72572	0.05
43	b1	373.58	6.63743	0
44	a	374.23	0.00000	0.61
45	b2	383.32	0.12812	0.1
46	b3	383.89	0.00234	0.13
47	b1	411.46	5.07163	0.05
48	a	412.73	0.00000	0.02
49	b1	432.35	27.72467	0.05
50	a	435.13	0.00000	2.2
51	b1	464.49	29.92732	0.36
52	a	466.25	0.00000	2.89
53	b3	487.33	0.09979	0.02
54	b2	487.39	0.88467	0.02
55	b1	498.24	26.68483	0.08
56	a	499.58	0.00000	0.21
57	b3	510.02	0.25385	0.19
58	b2	510.24	0.33332	0.03

59	b2	563.68	0.11297	0.07
60	b3	563.82	6.35222	0.21
61	b3	605.00	0.23173	0
62	b2	605.02	0.40634	0
63	b3	712.91	75.42144	0
64	b2	713.01	40.80386	0.12
65	a	715.47	0.00000	0.34
66	b1	715.48	6.98701	0.15
67	b1	746.25	14.72101	0.07
68	a	747.27	0.00000	0.87
69	b3	752.97	9.52386	0.25
70	b2	752.99	2.56724	0.33
71	b1	813.21	10.70368	0.02
72	a	813.31	0.00000	0.05
73	b2	827.89	5.75060	0
74	b3	827.93	0.82652	0.01
75	b1	839.89	59.32084	0.02
76	a	840.63	0.00000	0.11
77	b3	852.63	1.36974	0.06
78	b2	852.78	7.77945	0.01
79	b1	877.89	27.83239	0.17
80	a	878.10	0.00000	2.37
81	b1	904.45	0.36292	0.01

82	b3	904.57	0.53818	0.02
83	b2	904.89	0.01013	0
84	a	905.03	0.00000	0.07
85	b1	919.80	0.79567	0
86	a	919.87	0.00000	0.27
87	b3	920.54	1.84789	0.03
88	b2	920.81	1.61845	0
89	b2	934.31	12.23071	0.12
90	b3	934.38	10.04428	0.24
91	b3	936.09	0.64205	0
92	b2	936.11	0.01274	0.07
93	b1	937.27	2.27237	0
94	a	937.28	0.00000	0.06
95	b1	953.59	122.23774	0.25
96	a	954.60	0.00000	1.68
97	b1	991.99	10.34145	0.04
98	a	992.03	0.00000	3.47
99	b3	1064.36	19.32499	0
100	b2	1064.60	12.27954	0
101	b1	1107.62	2.56643	0
102	b3	1108.07	8.96160	0.11
103	a	1108.10	0.00000	0.2
104	b2	1108.20	6.90761	0

105	b1	1126.55	4.90033	0.08
106	a	1127.23	0.00000	0.22
107	b3	1139.56	42.40242	0.18
108	b2	1140.07	52.31671	0.05
109	b1	1156.23	0.08919	0.02
110	b2	1156.28	27.32143	0.04
111	b3	1156.53	25.04042	0.07
112	a	1156.65	0.00000	0.08
113	b3	1220.82	20.67043	0.11
114	b2	1220.84	25.82925	0.03
115	a	1234.72	0.00000	1.18
116	b1	1234.77	20.79963	0
117	b2	1282.03	45.04033	0
118	b3	1282.17	36.38510	0
119	b3	1302.30	2.23982	0.05
120	b1	1302.83	2.28708	0
121	b2	1304.22	38.61197	0.01
122	a	1304.95	0.00000	0.07
123	b1	1340.52	2.01918	0
124	b3	1341.02	13.22489	0.01
125	b2	1341.27	15.11564	0
126	a	1341.59	0.00000	0
127	a	1348.02	0.00000	1.8

128	b1	1348.37	46.56726	0
129	b2	1351.51	0.45322	0
130	b3	1351.60	4.66141	0
131	b1	1357.82	81.77976	0.02
132	b3	1359.42	3.01179	0.04
133	b2	1359.49	17.61157	0.04
134	a	1359.77	0.00000	1.73
135	b1	1377.60	267.11024	0.28
136	a	1378.09	0.00000	7.38
137	b3	1381.19	27.03130	1.11
138	b2	1381.20	17.91955	0.77
139	b1	1399.63	474.86436	0.03
140	a	1403.00	0.00000	22.81
141	b2	1426.81	35.65438	0.17
142	b3	1427.23	73.01101	0.14
143	b1	1429.93	1.97867	0
144	a	1431.06	0.00000	0.11
145	b2	1433.74	22.32436	0.05
146	b1	1433.99	0.29402	0
147	b3	1435.79	58.44647	0.36
148	b2	1436.33	110.49001	0.1
149	b3	1438.13	24.58984	0
150	a	1438.37	0.00000	0.09

151	b2	1442.34	0.27725	0
152	b1	1443.76	6.61371	0.02
153	b3	1443.79	7.98168	0.06
154	a	1444.62	0.00000	0.11
155	b2	1453.93	0.29963	0
156	b1	1456.42	21.71387	0.02
157	a	1459.32	0.00000	0.06
158	b3	1460.20	11.30151	0
159	b3	1492.97	167.35255	2.31
160	b2	1493.04	235.27071	1.21
161	b1	1493.95	691.66688	0.46
162	a	1495.59	0.00000	0.87
163	b2	1568.74	1.06448	1.4
164	b3	1568.81	3.68592	2.31
165	b1	1590.44	245.59068	0.86
166	a	1591.16	0.00000	13.95
167	b2	2927.30	11.99192	0.06
168	b3	2927.36	56.50655	0.01
169	b1	2927.48	19.24335	0.05
170	a	2927.61	0.00000	0.13
171	b2	2958.72	39.52544	0
172	b1	2958.74	8.52330	0
173	a	2958.86	0.00000	0.08

174	b3	2958.88	23.07990	0.01
175	b3	2962.43	11.55334	0
176	b2	2962.48	48.63314	0
177	a	2962.75	0.00000	1.27
178	b1	2962.77	53.74276	0.12
179	b2	3027.02	4.35483	0
180	a	3027.10	0.00000	0.13
181	b3	3027.27	0.16715	0
182	b1	3027.37	0.11286	0.02
183	b2	3033.02	69.44797	0.13
184	b3	3033.21	152.13703	0.08
185	b1	3033.34	43.76862	0.18
186	a	3033.66	0.00000	0.36
187	b2	3037.60	1.43965	0.02
188	a	3037.74	0.00000	0.02
189	b1	3037.77	42.17575	0.02
190	b3	3037.85	28.18225	0.03
191	b2	3040.54	61.88732	0
192	b1	3040.54	30.01049	0.25
193	b3	3040.58	0.03261	0.01
194	a	3040.71	0.00000	0.09
195	b1	3062.61	33.05659	0
196	a	3062.65	0.00000	0.07

197	b3	3066.77	3.60412	0.48
198	b2	3066.77	20.66233	0.15
199	b1	3102.64	51.06983	0
200	a	3102.66	0.00000	0.71
201	b3	3111.84	9.58630	0
202	b2	3111.86	31.76335	0
203	b1	3113.84	8.26437	0.06
204	a	3113.88	0.00000	0.23

2. Results of DFT Calculation on 2 (RI-BP86/def2-TZVP basis sets)

a) Cartesian coordinates (atomic units)

```

0.00000000  0.00000000 -2.23875360  zn
1.71890204  1.78912592 -5.15324573  n
1.71890204 -1.78912592 -5.15324573  n
0.87087200  1.11596368 -7.43409018  c
0.87087200 -1.11596368 -7.43409018  c
1.47013095  2.51036874 -9.65660962  c
1.47013095 -2.51036874 -9.65660962  c
1.09107550  2.08340955 -12.22197463  c
1.09107550 -2.08340955 -12.22197463  c
0.00000000  0.00000000 -13.40380465  c
2.41186496  4.30392094 -9.28944023  h
2.41186496 -4.30392094 -9.28944023  h
1.78424756  3.57391463 -13.46839071  h

```


1.78424756	-3.57391463	-13.46839071	h
0.00000000	0.00000000	-17.04341640	br
0.00000000	0.00000000	2.23875360	zn
1.71890204	-1.78912592	5.15324573	n
1.71890204	1.78912592	5.15324573	n
0.87087200	-1.11596368	7.43409018	c
0.87087200	1.11596368	7.43409018	c
1.47013095	-2.51036874	9.65660962	c
1.47013095	2.51036874	9.65660962	c
1.09107550	-2.08340955	12.22197463	c
1.09107550	2.08340955	12.22197463	c
0.00000000	0.00000000	13.40380465	c
2.41186496	-4.30392094	9.28944023	h
2.41186496	4.30392094	9.28944023	h
1.78424756	-3.57391463	13.46839071	h
1.78424756	3.57391463	13.46839071	h
0.00000000	0.00000000	17.04341640	br
3.56027627	3.84135227	-4.83830689	c
2.21567407	6.37032951	-4.35875464	c
1.11749618	6.27327095	-2.59672479	h
3.59541362	7.91432082	-4.17606636	h
0.90813084	6.84234571	-5.90124208	h
5.39320898	3.20319686	-2.69004820	c
4.70544174	4.01601089	-6.57369079	h

6.82152721	4.69977039	-2.49482582	h
6.37294979	1.41101992	-3.06170717	h
4.38303757	3.02546467	-0.88242582	h
3.56027627	-3.84135227	-4.83830689	c
3.56027627	-3.84135227	4.83830689	c
3.56027627	3.84135227	4.83830689	c
2.21567407	-6.37032951	-4.35875464	c
2.21567407	-6.37032951	4.35875464	c
2.21567407	6.37032951	4.35875464	c
1.11749618	-6.27327095	-2.59672479	h
1.11749618	-6.27327095	2.59672479	h
1.11749618	6.27327095	2.59672479	h
3.59541362	-7.91432082	-4.17606636	h
3.59541362	-7.91432082	4.17606636	h
3.59541362	7.91432082	4.17606636	h
0.90813084	-6.84234571	-5.90124208	h
0.90813084	-6.84234571	5.90124208	h
0.90813084	6.84234571	5.90124208	h
5.39320898	-3.20319686	-2.69004820	c
5.39320898	-3.20319686	2.69004820	c
5.39320898	3.20319686	2.69004820	c
4.70544174	-4.01601089	-6.57369079	h
4.70544174	-4.01601089	6.57369079	h
4.70544174	4.01601089	6.57369079	h

6.82152721 -4.69977039 -2.49482582 h
 6.82152721 -4.69977039 2.49482582 h
 6.82152721 4.69977039 2.49482582 h
 6.37294979 -1.41101992 -3.06170717 h
 6.37294979 -1.41101992 3.06170717 h
 6.37294979 1.41101992 3.06170717 h
 4.38303757 -3.02546467 -0.88242582 h
 4.38303757 -3.02546467 0.88242582 h
 4.38303757 3.02546467 0.88242582

b) Population analysis based on occupation numbers

(Zn, Br: 18 MAOs, H: 1 MAO, N,C: 5 MAOs)

1 zn - 2 n = 1.1906
 1 zn - 4 c = 0.1069
 1 zn - 16 zn = 1.3218
 1 zn - 31 c = 0.0487
 1 zn - 32 c = 0.0283
 1 zn - 33 h = 0.0217
 1 zn - 36 c = 0.0330
 1 zn - 40 h = 0.0251
 1 zn - 57 c = 0.0206
 1 zn - 69 h = 0.0280
 2 n - 4 c = 1.6546
 2 n - 5 c = 0.0298

$$\begin{aligned}
2 \text{ n} - 6 \text{ c} &= 0.0181 \\
2 \text{ n} - 31 \text{ c} &= 1.2105 \\
2 \text{ n} - 32 \text{ c} &= 0.0275 \\
2 \text{ n} - 36 \text{ c} &= 0.0236 \\
2 \text{ n} - 37 \text{ h} &= 0.0104 \\
4 \text{ c} - 5 \text{ c} &= 1.4818 \\
4 \text{ c} - 6 \text{ c} &= 1.6955 \\
4 \text{ c} - 7 \text{ c} &= 0.0696 \\
4 \text{ c} - 8 \text{ c} &= 0.0363 \\
4 \text{ c} - 11 \text{ h} &= 0.0318 \\
4 \text{ c} - 31 \text{ c} &= 0.0417 \\
6 \text{ c} - 8 \text{ c} &= 1.8681 \\
6 \text{ c} - 10 \text{ c} &= 0.0221 \\
6 \text{ c} - 11 \text{ h} &= 1.3277 \\
6 \text{ c} - 13 \text{ h} &= 0.0255 \\
6 \text{ c} - 31 \text{ c} &= 0.0151 \\
6 \text{ c} - 37 \text{ h} &= 0.0226 \\
8 \text{ c} - 9 \text{ c} &= 0.0543 \\
8 \text{ c} - 10 \text{ c} &= 1.7476 \\
8 \text{ c} - 11 \text{ h} &= 0.0311 \\
8 \text{ c} - 13 \text{ h} &= 1.3473 \\
10 \text{ c} - 13 \text{ h} &= 0.0256 \\
10 \text{ c} - 15 \text{ br} &= 1.0315 \\
11 \text{ h} - 31 \text{ c} &= 0.0179
\end{aligned}$$

$$11 \text{ h} - 37 \text{ h} = 0.0185$$

$$31 \text{ c} - 32 \text{ c} = 1.3268$$

$$31 \text{ c} - 33 \text{ h} = 0.0221$$

$$31 \text{ c} - 34 \text{ h} = 0.0288$$

$$31 \text{ c} - 35 \text{ h} = 0.0278$$

$$31 \text{ c} - 36 \text{ c} = 1.3082$$

$$31 \text{ c} - 37 \text{ h} = 1.3117$$

$$31 \text{ c} - 38 \text{ h} = 0.0303$$

$$31 \text{ c} - 39 \text{ h} = 0.0265$$

$$31 \text{ c} - 40 \text{ h} = 0.0236$$

$$32 \text{ c} - 33 \text{ h} = 1.3558$$

$$32 \text{ c} - 34 \text{ h} = 1.3596$$

$$32 \text{ c} - 35 \text{ h} = 1.3600$$

$$32 \text{ c} - 36 \text{ c} = 0.0325$$

$$32 \text{ c} - 37 \text{ h} = 0.0270$$

$$33 \text{ h} - 34 \text{ h} = 0.0187$$

$$33 \text{ h} - 35 \text{ h} = 0.0181$$

$$34 \text{ h} - 35 \text{ h} = 0.0183$$

$$36 \text{ c} - 37 \text{ h} = 0.0281$$

$$36 \text{ c} - 38 \text{ h} = 1.3584$$

$$36 \text{ c} - 39 \text{ h} = 1.3620$$

$$36 \text{ c} - 40 \text{ h} = 1.3648$$

$$38 \text{ h} - 39 \text{ h} = 0.0189$$

$$38 \text{ h} - 40 \text{ h} = 0.0196$$

$$39 \text{ h} - 40 \text{ h} = 0.0181$$

c) Vibrational frequencies and intensities

	Representation	ν/cm^{-1}	IR intensity/ km mol^{-1}	Raman cross section (par/unpol.) (max. 100%)
1	b3	8.27	0.12150	12.79
2	b2	8.45	0.15933	13.72
3	a	10.96	0.00000	92.18
4	b2	27.83	0.04873	1.19
5	b3	31.70	0.00004	1.2
6	b1	47.54	0.54765	0.41
7	b2	49.34	0.00053	0.24
8	b3	50.00	0.02018	0.08
9	a	50.27	0.00000	0.52
10	b3	60.67	0.27808	0
11	b2	71.32	0.30753	0
12	a	71.67	0.00000	0.22
13	b1	79.58	0.38232	0
14	b3	80.13	0.17063	0.55
15	a	84.41	0.00000	1.73
16	b2	86.64	0.22676	0.63
17	b2	119.73	0.15872	0.01

18	b3	129.26	0.27606	0
19	b1	141.14	0.00190	0.02
20	a	141.55	0.00000	3.1
21	b1	150.57	0.06009	0
22	b2	153.22	0.42402	0.79
23	a	154.01	0.00000	5.09
24	b3	158.71	0.76548	0.08
25	b3	175.55	2.55038	0.06
26	b2	176.92	0.54530	0.02
27	b1	180.38	48.48683	0.03
28	a	207.70	0.00000	0.07
29	b2	207.95	0.00976	0.02
30	b1	208.05	2.98088	0.03
31	b3	209.63	0.00177	0.07
32	a	215.88	0.00000	0.46
33	b1	223.18	15.68789	0.01
34	b2	229.32	0.73014	0
35	b3	229.49	0.21041	0.03
36	b2	235.43	0.14135	0.05
37	b3	238.34	0.36860	0.04
38	b1	239.97	1.29061	0
39	a	240.14	0.00000	0.51
40	b3	276.77	0.00000	0.4

41	b2	281.71	0.92032	0.02
42	a	281.77	0.71429	0.16
43	b2	328.39	1.33490	0.45
44	b3	328.49	0.05936	0.15
45	b1	333.40	47.37517	0.11
46	b2	345.20	5.74214	0.01
47	b3	345.22	5.86495	0.1
48	a	355.47	0.00000	7.5
49	b3	375.41	4.89726	0.01
50	b2	375.65	0.00000	0.7
51	a	384.99	0.17764	0.11
52	b1	385.51	0.20682	0.11
53	b3	432.01	32.24806	0.01
54	a	434.86	0.00000	5.67
55	b2	451.08	5.71809	0.11
56	b2	452.23	0.00000	2.02
57	b3	490.80	2.50841	0.02
58	b1	491.17	0.00000	2.8
59	a	502.40	0.11168	0.17
60	b1	502.64	1.37268	0.01
61	b2	507.97	0.07957	0.03
62	a	508.06	0.85594	0.03
63	b3	517.19	162.77343	0.13

64	b3	518.55	0.00000	0.36
65	b2	561.16	0.05732	0.03
66	b1	561.32	6.74531	0.15
67	a	608.22	2.55963	0
68	b2	608.26	2.96925	0
69	b1	708.19	0.00000	0.25
70	b3	708.21	11.90995	0.15
71	a	756.66	68.76481	0.14
72	b1	757.92	0.00000	4.56
73	b2	763.80	1.24410	0.21
74	b3	763.89	8.86016	0.3
75	b2	787.48	33.37365	0.05
76	b3	787.58	35.50006	0
77	b1	805.96	16.72625	0.02
78	a	806.15	0.00000	0.03
79	b3	838.70	5.83164	0.04
80	b2	838.73	0.83539	0
81	a	839.45	61.62641	0
82	b2	840.18	0.00000	0.4
83	b3	875.74	42.92379	0.16
84	b1	875.78	0.00000	8.94
85	b2	904.99	0.31135	0.02
86	b3	905.04	0.01516	0.01

87	a	905.39	0.00449	0
88	b3	905.58	0.00000	0.04
89	b2	918.66	3.78273	0.01
90	a	918.81	2.00523	0.03
91	b1	920.46	0.16091	0
92	b3	920.53	0.00000	0.28
93	a	925.46	0.02537	0.01
94	b2	925.62	0.17328	0.02
95	b2	933.42	10.97188	0.07
96	b3	933.49	9.13287	0.19
97	b1	934.06	0.68166	0.01
98	a	934.06	0.00000	0.22
99	b1	954.26	118.93916	0.13
100	b2	955.23	0.00000	1.19
101	a	1015.43	86.45866	0.09
102	b3	1015.61	0.00000	18.26
103	b3	1083.20	36.49247	0.02
104	b2	1083.54	27.51145	0
105	b1	1107.51	4.52096	0
106	a	1107.93	7.85613	0.08
107	b2	1107.98	0.00000	0.71
108	b1	1108.05	7.14292	0
109	b3	1125.91	1.51516	0.08

110	a	1126.57	0.00000	0.19
111	b1	1154.38	0.20264	0
112	b2	1154.94	0.94575	0
113	b3	1156.33	0.11585	0.02
114	b2	1156.70	0.00000	0.16
115	b3	1163.91	78.44017	0.05
116	b1	1164.27	64.54326	0.11
117	a	1238.20	0.00000	1.88
118	b3	1238.23	40.13297	0
119	b2	1282.14	39.22702	0
120	a	1282.28	30.48690	0.01
121	b2	1301.81	2.99135	0.04
122	b3	1302.40	3.14189	0
123	b1	1303.75	40.11823	0.01
124	b2	1304.49	0.00000	0.18
125	b3	1339.36	16.74111	0.1
126	a	1339.44	11.15409	0.18
127	b3	1341.37	2.47740	0
128	b2	1341.95	10.21247	0
129	a	1342.28	24.05493	0
130	b1	1342.43	0.00000	0.01
131	b3	1349.18	0.00000	4.06
132	a	1349.54	43.95254	0

133	b2	1356.88	6.35240	0.14
134	b2	1356.93	0.25479	0.07
135	b3	1358.62	96.61151	0.01
136	b1	1360.55	0.00000	4.82
137	a	1360.90	7.75082	0
138	b1	1360.92	24.87736	0
139	b2	1376.94	335.90304	0.35
140	a	1377.52	0.00000	26.76
141	b3	1395.45	127.24168	0.36
142	b3	1395.83	143.28368	0.46
143	b2	1401.56	648.29468	0.04
144	b1	1405.18	0.00000	100
145	a	1430.12	3.39968	0
146	b2	1430.76	10.47782	0
147	b1	1431.15	0.35211	0.01
148	b3	1431.25	0.00000	0.19
149	a	1433.89	0.83150	0
150	b1	1434.55	5.46845	0
151	b2	1437.94	11.56473	0.01
152	b3	1438.33	0.00000	0.23
153	b2	1442.46	3.10517	0
154	b3	1444.00	6.26863	0.02
155	b1	1444.02	10.73287	0.02

156	a	1444.79	0.00000	0.22
157	b3	1453.71	3.24781	0
158	b2	1456.48	19.91388	0.01
159	a	1459.35	0.00000	0.26
160	b2	1460.03	5.69913	0.01
161	b3	1481.52	168.28345	1.7
162	b1	1481.61	219.67871	0.92
163	b2	1486.12	1005.31098	0.43
164	b3	1488.16	0.00000	0.53
165	a	1547.98	8.07666	1.18
166	b3	1548.10	22.63183	2.08
167	b2	1573.56	102.33310	1.14
168	a	1574.06	0.00000	68.07
169	b1	2928.91	11.18751	0.02
170	b3	2928.97	52.47033	0
171	a	2929.08	16.15416	0.02
172	b2	2929.19	0.00000	0.12
173	b2	2959.84	35.70994	0
174	b3	2959.87	9.72657	0
175	b1	2959.99	0.00000	0.05
176	a	2959.99	22.54276	0.01
177	b1	2963.46	7.88058	0
178	b2	2963.51	43.65442	0

179	a	2963.75	0.00000	0.8
180	b3	2963.78	61.82202	0.06
181	b3	3028.57	3.72595	0
182	b2	3028.64	0.00000	0.22
183	b1	3028.78	1.29282	0
184	a	3028.90	0.19642	0.01
185	b2	3034.39	58.90160	0.08
186	b1	3034.58	133.88530	0.05
187	b3	3034.73	51.62386	0.08
188	a	3034.99	0.00000	0.24
189	b1	3038.22	0.06131	0
190	b2	3038.34	0.00000	0.02
191	b3	3038.39	43.03613	0.02
192	b2	3038.44	35.86518	0.02
193	b3	3041.65	24.11249	0.12
194	b1	3041.66	66.40805	0
195	a	3041.74	0.42247	0.01
196	b3	3041.85	0.00000	0.1
197	b2	3093.43	0.10181	0.06
198	a	3093.43	0.01561	0.17
199	b2	3094.00	12.57824	0.01
200	b3	3094.01	0.00000	0.04
201	b1	3116.58	5.02616	0

202	b2	3116.59	17.32321	0
203	b3	3117.63	0.28355	0.02
204	a	3117.65	0.00000	0.12

3. Results of DFT Calculation on $\text{Zn}_2(\text{DMAP})_6^{2+}$ (RI-BP86/def2-TZVP basis sets)

a) Cartesian Coordinates (atomic units)

```

0.00000000  0.00000000  2.29776591  zn
0.00000000  0.00000000 -2.29776591  zn
3.52413424 -0.13632821  4.38816438  n
3.94253439 -1.52685661  6.49284134  c
6.22181237 -1.60861111  7.76809356  c
8.30938088 -0.16482716  6.88153016  c
7.85724633  1.28549269  4.66212167  c
5.50752856  1.22725544  3.52340253  c
2.34152716 -2.63269156  7.17591495  h
6.37339907 -2.78833874  9.44446602  h
9.33238332  2.44771003  3.82784916  h
5.15962173  2.32487914  1.80987587  h
1.88013081  2.98382567 -4.38816438  n
-1.64400343  3.12015388  4.38816438  n
-3.52413424  0.13632821 -4.38816438  n
-1.88013081 -2.98382567  4.38816438  n
1.64400343 -3.12015388 -4.38816438  n
3.29356380  2.65090663 -6.49284134  c
-0.64897058  4.17776324  6.49284134  c
-3.94253439  1.52685661 -6.49284134  c
-3.29356380 -2.65090663  6.49284134  c
0.64897058 -4.17776324 -6.49284134  c
4.50400427  4.58394202 -7.76809356  c

```

-1.71780810	6.19255312	7.76809356	c
-6.22181237	1.60861111	-7.76809356	c
-4.50400427	-4.58394202	7.76809356	c
1.71780810	-6.19255312	-7.76809356	c
4.29743495	7.11372135	-6.88153016	c
-4.01194593	7.27854851	6.88153016	c
-8.30938088	0.16482716	-6.88153016	c
-4.29743495	-7.11372135	6.88153016	c
4.01194593	-7.27854851	-6.88153016	c
2.81535384	7.44732127	-4.66212167	c
-5.04189249	6.16182858	4.66212167	c
-7.85724633	-1.28549269	-4.66212167	c
-2.81535384	-7.44732127	4.66212167	c
5.04189249	-6.16182858	-4.66212167	c
1.69092989	5.38328736	-3.52340253	c
-3.81659866	4.15603192	3.52340253	c
-5.50752856	-1.22725544	-3.52340253	c
-1.69092989	-5.38328736	3.52340253	c
3.81659866	-4.15603192	-3.52340253	c
3.45074135	0.71147622	-7.17591495	h
1.10921419	3.34416778	7.17591495	h
-2.34152716	2.63269156	-7.17591495	h
-3.45074135	-0.71147622	7.17591495	h
-1.10921419	-3.34416778	-7.17591495	h
5.60147171	4.12535613	-9.44446602	h
-0.77192735	6.91369487	9.44446602	h
-6.37339907	2.78833874	-9.44446602	h
-5.60147171	-4.12535613	9.44446602	h
0.77192735	-6.91369487	-9.44446602	h
2.54641259	9.30593605	-3.82784916	h
-6.78597073	6.85822601	3.82784916	h
-9.33238332	-2.44771003	-3.82784916	h
-2.54641259	-9.30593605	3.82784916	h
6.78597073	-6.85822601	-3.82784916	h
0.56640647	5.63080306	-1.80987587	h

-4.59321526	3.30592392	1.80987587	h
-5.15962173	-2.32487914	-1.80987587	h
-0.56640647	-5.63080306	1.80987587	h
4.59321526	-3.30592392	-1.80987587	h
10.58311698	-0.17214146	8.07292802	n
12.67356138	1.34149963	7.09449337	c
14.31775007	1.09213700	8.32178304	h
12.19700783	3.36712403	7.05929761	h
13.20845173	0.75112297	5.17129769	h
10.96188626	-1.69473107	10.34525234	c
12.90218678	-1.44020088	11.01023279	h
9.67456052	-1.11473303	11.87415650	h
10.67012177	-3.71923221	9.96319639	h
5.44063737	9.07917743	-8.07292802	n
-5.14247961	9.25131889	8.07292802	n
10.58311698	0.17214146	-8.07292802	n
-5.44063737	-9.07917743	8.07292802	n
5.14247961	-9.25131889	-8.07292802	n
5.17500793	11.64637593	-7.09449337	c
-7.49855345	10.30487630	7.09449337	c
12.67356138	-1.34149963	-7.09449337	c
-5.17500793	-11.64637593	7.09449337	c
7.49855345	-10.30487630	-7.09449337	c
6.21305665	12.94560379	-8.32178304	h
-8.10469342	11.85346679	8.32178304	h
14.31775007	-1.09213700	-8.32178304	h
-6.21305665	-12.94560379	8.32178304	h
8.10469342	-11.85346679	-8.32178304	h
3.18248897	12.24648064	-7.05929761	h
-9.01451886	8.87935661	7.05929761	h
12.19700783	-3.36712403	-7.05929761	h
-3.18248897	-12.24648064	7.05929761	h
9.01451886	-8.87935661	-7.05929761	h
5.95373430	11.81441623	-5.17129769	h
-7.25471743	11.06329326	5.17129769	h

13.20845173	-0.75112297	-5.17129769	h
-5.95373430	-11.81441623	5.17129769	h
7.25471743	-11.06329326	-5.17129769	h
6.94862329	8.64590644	-10.34525234	c
-4.01326297	10.34063751	10.34525234	c
10.96188626	1.69473107	-10.34525234	c
-6.94862329	-8.64590644	10.34525234	c
4.01326297	-10.34063751	-10.34525234	c
7.69834394	10.45352108	-11.01023279	h
-5.20384284	11.89372196	11.01023279	h
12.90218678	1.44020088	-11.01023279	h
-7.69834394	-10.45352108	11.01023279	h
5.20384284	-11.89372196	-11.01023279	h
5.80266739	7.82104867	-11.87415650	h
-3.87189314	8.93578170	11.87415650	h
-9.67456052	1.11473303	-11.87415650	h
-5.80266739	-7.82104867	11.87415650	h
3.87189314	-8.93578170	-11.87415650	h
8.55601046	7.38098041	-9.96319639	h
-2.11411131	11.10021262	9.96319639	h
10.67012177	3.71923221	-9.96319639	h
-8.55601046	-7.38098041	9.96319639	h
2.11411131	-11.10021262	-9.96319639	h

b) Population analysis based on occupation numbers

(Zn: 18 MAOs, H: 1 MAO, N,C: 5 MAOs)

$$1 \text{ zn} - 2 \text{ zn} = 1.3292$$

$$1 \text{ zn} - 3 \text{ n} = 0.8352$$

$$1 \text{ zn} - 4 \text{ c} = 0.0350$$

$$1 \text{ zn} - 8 \text{ c} = 0.0709$$

$$1 \text{ zn} - 12 \text{ h} = 0.0166$$

$$3 \text{ n} - 4 \text{ c} = 1.6165$$

$$3 \text{ n} - 5 \text{ c} = 0.0172$$

$$3 \text{ n} - 6 \text{ c} = -0.0110$$

$$3 \text{ n} - 7 \text{ c} = 0.0190$$

$$3 \text{ n} - 8 \text{ c} = 1.6155$$

$$3 \text{ n} - 9 \text{ h} = 0.0101$$

$$3 \text{ n} - 12 \text{ h} = 0.0102$$

$$4 \text{ c} - 5 \text{ c} = 1.8633$$

$$4 \text{ c} - 6 \text{ c} = 0.0459$$

$$4 \text{ c} - 7 \text{ c} = -0.0120$$

$$4 \text{ c} - 8 \text{ c} = 0.0426$$

$$4 \text{ c} - 9 \text{ h} = 1.3372$$

$$4 \text{ c} - 10 \text{ h} = 0.0220$$

$$5 \text{ c} - 6 \text{ c} = 1.6895$$

$$5 \text{ c} - 7 \text{ c} = 0.0825$$

$$5 \text{ c} - 8 \text{ c} = -0.0128$$

$$5 \text{ c} - 9 \text{ h} = 0.0211$$

$$5 \text{ c} - 10 \text{ h} = 1.3410$$

$$5 \text{ c} - 63 \text{ n} = 0.0116$$

$$5 \text{ c} - 68 \text{ c} = 0.0150$$

$$6 \text{ c} - 7 \text{ c} = 1.6872$$

$$6 \text{ c} - 8 \text{ c} = 0.0462$$

$$6 \text{ c} - 10 \text{ h} = 0.0172$$

$$6 \text{ c} - 11 \text{ h} = 0.0162$$

$$6 \text{ c} - 63 \text{ n} = 1.5268$$

$$6 \text{ c} - 64 \text{ c} = 0.0218$$

$$6 \text{ c} - 68 \text{ c} = 0.0216$$

$$7 \text{ c} - 8 \text{ c} = 1.8993$$

$$7 \text{ c} - 11 \text{ h} = 1.3445$$

$$7 \text{ c} - 12 \text{ h} = 0.0213$$

$$7 \text{ c} - 63 \text{ n} = 0.0104$$

$$7 \text{ c} - 64 \text{ c} = 0.0146$$

$$8 \text{ c} - 11 \text{ h} = 0.0313$$

$$8 \text{ c} - 12 \text{ h} = 1.3331$$

$$10 \text{ h} - 68 \text{ c} = 0.0124$$

$$11 \text{ h} - 64 \text{ c} = 0.0125$$

$$63 \text{ n} - 64 \text{ c} = 1.2298$$

$$63 \text{ n} - 65 \text{ h} = 0.0116$$

$$63 \text{ n} - 68 \text{ c} = 1.2288$$

$$63 \text{ n} - 69 \text{ h} = 0.0116$$

$$64 \text{ c} - 65 \text{ h} = 1.3388$$

$$64 \text{ c} - 66 \text{ h} = 1.3400$$

$$64 \text{ c} - 67 \text{ h} = 1.3408$$

$$64 \text{ c} - 68 \text{ c} = 0.0114$$

$$65 \text{ h} - 66 \text{ h} = 0.0198$$

$$65 \text{ h} - 67 \text{ h} = 0.0196$$

$$66 \text{ h} - 67 \text{ h} = 0.0151$$

$$68 \text{ c} - 69 \text{ h} = 1.3392$$

$$68 \text{ c} - 70 \text{ h} = 1.3401$$

$$68 \text{ c} - 71 \text{ h} = 1.3400$$

$$69 \text{ h} - 70 \text{ h} = 0.0197$$

$$69 \text{ h} - 71 \text{ h} = 0.0196$$

$$70 \text{ h} - 71 \text{ h} = 0.0151$$

c) Vibrational frequencies and intensities of $[\text{Zn}_2(\text{DMAP})_6]^{2+}$

	Representation	ν/cm^{-1}	IR intensity/ km mol^{-1}
1	au	2.48	0.00974
2	eu	8.57	0.20994
3	eu	8.57	0.20994
4	eu	11.97	0.47140
5	eu	11.97	0.47140
6	eg	12.54	0.00000
7	eg	12.54	0.00000
8	ag	15.64	0.00000
9	eu	19.01	0.40658
10	eu	19.01	0.40658
11	eg	19.96	0.00000
12	eg	19.96	0.00000
13	au	21.24	2.30828
14	ag	29.22	0.00000
15	au	32.44	0.00867
16	eg	33.22	0.00000
17	eg	33.22	0.00000
18	ag	51.08	0.00000
19	eu	51.34	0.74089
20	eu	51.34	0.74089
21	eg	51.72	0.00000

22	eg	51.72	0.00000
23	au	51.72	0.67968
24	ag	61.74	0.00000
25	au	66.37	2.13579
26	eu	72.43	3.24337
27	eu	72.43	3.24337
28	eg	78.52	0.00000
29	eg	78.52	0.00000
30	eu	83.64	0.11777
31	eu	83.64	0.11777
32	ag	84.05	0.00000
33	eg	84.18	0.00000
34	eg	84.18	0.00000
35	au	84.57	0.26924
36	ag	90.56	0.00000
37	eu	105.44	0.24236
38	eu	105.44	0.24236
39	eg	107.13	0.00000
40	eg	107.13	0.00000
41	au	107.14	0.28998
42	ag	107.60	0.00000
43	au	142.25	29.51498
44	eu	149.40	15.64872
45	eu	149.40	15.64872
46	eg	150.94	0.00000
47	eg	150.94	0.00000
48	ag	155.45	0.00000
49	eu	155.52	3.20147
50	eu	155.52	3.20147
51	eg	155.98	0.00000
52	eg	155.98	0.00000
53	au	156.56	2.60779
54	ag	166.01	0.00000

55	eu	171.01	5.18651
56	eu	171.01	5.18651
57	eg	175.53	0.00000
58	eg	175.53	0.00000
59	au	176.55	30.95019
60	ag	237.42	0.00000
61	eu	249.10	1.95312
62	eu	249.10	1.95312
63	au	249.60	10.54239
64	eg	250.51	0.00000
65	eg	250.51	0.00000
66	ag	263.05	0.00000
67	eu	280.92	10.30811
68	eu	280.92	10.30811
69	eg	281.40	0.00000
70	eg	281.40	0.00000
71	au	281.51	33.32917
72	ag	288.15	0.00000
73	eg	384.82	0.00000
74	eg	384.82	0.00000
75	eu	385.20	19.59807
76	eu	385.20	19.59807
77	au	386.30	16.56312
78	ag	388.89	0.00000
79	eu	408.14	0.51188
80	eu	408.14	0.51188
81	eg	408.70	0.00000
82	eg	408.70	0.00000
83	ag	411.81	0.00000
84	au	412.28	1.97174
85	eu	474.22	3.95685
86	eu	474.22	3.95685
87	au	474.25	3.93142

88	eg	474.32	0.00000
89	eg	474.32	0.00000
90	ag	474.54	0.00000
91	ag	522.27	0.00000
92	eu	522.32	25.54160
93	eu	522.32	25.54160
94	eg	522.62	0.00000
95	eg	522.62	0.00000
96	au	522.81	35.25142
97	au	544.05	16.29553
98	eu	544.17	17.55380
99	eu	544.17	17.55380
100	eg	544.17	0.00000
101	eg	544.17	0.00000
102	ag	545.26	0.00000
103	eg	654.66	0.00000
104	eg	654.66	0.00000
105	eu	654.92	0.25439
106	eu	654.92	0.25439
107	au	655.11	1.62688
108	ag	655.51	0.00000
109	au	725.68	0.51051
110	eu	725.75	0.25663
111	eu	725.75	0.25663
112	ag	725.79	0.00000
113	eg	725.81	0.00000
114	eg	725.81	0.00000
115	au	750.23	6.83955
116	ag	750.26	0.00000
117	eu	751.40	7.40548
118	eu	751.40	7.40548
119	eg	751.58	0.00000
120	eg	751.58	0.00000

121	ag	801.40	0.00000
122	eu	801.83	76.24802
123	eu	801.83	76.24802
124	eg	801.92	0.00000
125	eg	801.92	0.00000
126	au	802.44	65.77443
127	eu	806.83	0.89824
128	eu	806.83	0.89824
129	eg	807.71	0.00000
130	eg	807.71	0.00000
131	ag	808.31	0.00000
132	au	809.51	0.06173
133	eu	937.79	11.08808
134	eu	937.79	11.08808
135	eg	937.91	0.00000
136	eg	937.91	0.00000
137	au	938.12	7.12289
138	ag	938.19	0.00000
139	eu	939.05	2.93855
140	eu	939.05	2.93855
141	ag	939.79	0.00000
142	eg	939.94	0.00000
143	eg	939.94	0.00000
144	au	942.13	0.01457
145	eu	957.33	0.72554
146	eu	957.33	0.72554
147	eg	958.60	0.00000
148	eg	958.60	0.00000
149	ag	959.19	0.00000
150	au	960.92	4.13111
151	eg	993.35	0.00000
152	eg	993.35	0.00000
153	eu	993.38	275.52215

154	eu	993.38	275.52215
155	au	993.83	171.01603
156	ag	996.85	0.00000
157	eg	1042.79	0.00000
158	eg	1042.79	0.00000
159	eu	1042.81	24.80026
160	eu	1042.81	24.80026
161	au	1042.81	48.55436
162	ag	1042.82	0.00000
163	eu	1050.85	83.96037
164	eu	1050.85	83.96037
165	eg	1051.28	0.00000
166	eg	1051.28	0.00000
167	au	1052.02	49.38364
168	ag	1054.26	0.00000
169	eu	1097.14	0.01742
170	eu	1097.14	0.01742
171	ag	1097.15	0.00000
172	eg	1097.15	0.00000
173	eg	1097.15	0.00000
174	au	1097.17	0.00567
175	eu	1102.36	7.01909
176	eu	1102.36	7.01909
177	au	1102.38	19.92516
178	eg	1102.59	0.00000
179	eg	1102.59	0.00000
180	ag	1103.14	0.00000
181	au	1103.57	0.25795
182	eu	1103.57	0.07616
183	eu	1103.57	0.07616
184	eg	1103.57	0.00000
185	eg	1103.57	0.00000
186	ag	1103.59	0.00000

187	ag	1160.56	0.00000
188	au	1160.57	0.61310
189	eu	1160.75	0.82130
190	eu	1160.75	0.82130
191	eg	1160.78	0.00000
192	eg	1160.78	0.00000
193	eg	1208.35	0.00000
194	eg	1208.35	0.00000
195	eu	1208.64	238.94861
196	eu	1208.64	238.94861
197	au	1213.26	101.10995
198	ag	1218.26	0.00000
199	eg	1221.76	0.00000
200	eg	1221.76	0.00000
201	ag	1221.78	0.00000
202	au	1221.79	69.71715
203	eu	1221.79	35.14388
204	eu	1221.79	35.14388
205	au	1314.44	35.66027
206	ag	1314.57	0.00000
207	eg	1314.74	0.00000
208	eg	1314.74	0.00000
209	eu	1314.81	11.14584
210	eu	1314.81	11.14584
211	au	1326.84	10.07368
212	eg	1326.95	0.00000
213	eg	1326.95	0.00000
214	eu	1327.02	5.68693
215	eu	1327.02	5.68693
216	ag	1327.39	0.00000
217	au	1372.42	150.16238
218	eu	1373.37	235.81478
219	eu	1373.37	235.81478

220	eg	1373.41	0.00000
221	eg	1373.41	0.00000
222	ag	1373.44	0.00000
223	au	1401.16	1.85439
224	eg	1401.16	0.00000
225	eg	1401.16	0.00000
226	eu	1401.18	0.57306
227	eu	1401.18	0.57306
228	ag	1401.18	0.00000
229	eu	1434.79	2.43219
230	eu	1434.79	2.43219
231	ag	1434.80	0.00000
232	eg	1434.81	0.00000
233	eg	1434.81	0.00000
234	au	1434.81	0.05428
235	au	1437.25	44.26467
236	eu	1437.34	71.71335
237	eu	1437.34	71.71335
238	eg	1437.37	0.00000
239	eg	1437.37	0.00000
240	ag	1437.47	0.00000
241	ag	1441.54	0.00000
242	au	1441.65	0.06155
243	eu	1441.78	1.16529
244	eu	1441.78	1.16529
245	eg	1441.80	0.00000
246	eg	1441.80	0.00000
247	ag	1446.21	0.00000
248	au	1446.21	31.14703
249	eu	1446.22	43.10978
250	eu	1446.22	43.10978
251	eg	1446.22	0.00000
252	eg	1446.22	0.00000

253	ag	1462.10	0.00000
254	au	1462.15	16.68955
255	eg	1462.16	0.00000
256	eg	1462.16	0.00000
257	eu	1462.17	7.29844
258	eu	1462.17	7.29844
259	au	1473.30	46.72180
260	ag	1473.49	0.00000
261	eu	1473.81	71.02599
262	eu	1473.81	71.02599
263	eg	1473.89	0.00000
264	eg	1473.89	0.00000
265	eg	1514.13	0.00000
266	eg	1514.13	0.00000
267	eu	1514.41	34.99369
268	eu	1514.41	34.99369
269	au	1514.54	87.27276
270	ag	1514.81	0.00000
271	au	1522.79	217.18786
272	eg	1523.25	0.00000
273	eg	1523.25	0.00000
274	eu	1523.41	423.43552
275	eu	1523.41	423.43552
276	ag	1523.84	0.00000
277	eg	1613.20	0.00000
278	eg	1613.20	0.00000
279	eu	1613.47	1162.07718
280	eu	1613.47	1162.07718
281	au	1613.60	701.07469
282	ag	1618.18	0.00000
283	eg	2948.01	0.00000
284	eg	2948.01	0.00000
285	eu	2948.03	85.96638

286	eu	2948.03	85.96638
287	au	2948.04	104.81572
288	ag	2948.04	0.00000
289	eg	2953.53	0.00000
290	eg	2953.53	0.00000
291	eu	2953.55	76.85900
292	eu	2953.55	76.85900
293	au	2953.62	82.43497
294	ag	2953.82	0.00000
295	ag	2999.86	0.00000
296	eu	2999.87	27.97722
297	eu	2999.87	27.97722
298	eg	2999.88	0.00000
299	eg	2999.88	0.00000
300	au	2999.88	26.02530
301	au	3002.50	34.69192
302	eg	3002.50	0.00000
303	eg	3002.50	0.00000
304	ag	3002.50	0.00000
305	eu	3002.50	41.86132
306	eu	3002.50	41.86132
307	eg	3081.63	0.00000
308	eg	3081.63	0.00000
309	au	3081.63	2.66554
310	eu	3081.64	1.61107
311	eu	3081.64	1.61107
312	ag	3081.64	0.00000
313	au	3091.02	10.20056
314	eg	3091.29	0.00000
315	eg	3091.29	0.00000
316	eu	3091.32	22.84393
317	eu	3091.32	22.84393
318	ag	3091.32	0.00000

319	au	3091.36	11.08701
320	ag	3091.50	0.00000
321	eg	3091.52	0.00000
322	eg	3091.52	0.00000
323	eu	3091.61	10.63851
324	eu	3091.61	10.63851
325	eu	3107.37	1.69462
326	eu	3107.37	1.69462
327	eg	3107.39	0.00000
328	eg	3107.39	0.00000
329	au	3108.25	17.73389
330	ag	3108.40	0.00000
331	eu	3148.85	4.85865
332	eu	3148.85	4.85865
333	eg	3148.85	0.00000
334	eg	3148.85	0.00000
335	au	3148.93	14.20762
336	ag	3149.00	0.00000
337	au	3150.54	0.26747
338	eg	3150.55	0.00000
339	eg	3150.55	0.00000
340	eu	3150.57	8.11739
341	eu	3150.57	8.11739
342	ag	3150.61	0.00000

[1] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, 64, 112-122..

DuEPublico

Duisburg-Essen Publications online

UNIVERSITÄT
DUISBURG
ESSEN

Offen im Denken

ub

universitäts
bibliothek

This text is made available via DuEPublico, the institutional repository of the University of Duisburg-Essen. This version may eventually differ from another version distributed by a commercial publisher.

DOI: 10.1002/chem.201002443

URN: urn:nbn:de:hbz:464-20201110-092856-2

This is the peer reviewed version of the following article: Chemistry - A European Journal, 2011, Volume 17, Issue 6, Pages 1773-1777, which has been published in final form at: <https://doi.org/10.1002/chem.201002443>

All rights reserved.