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Highlights :

- Candidates for self-assembled halogen-bonded nanoarchitectures
- X-ray structure of iodo derivative of bis-salphen zinc complex

Journal Pre-proof

Synthesis and Characterization of Iodo Derivatives of Bis-salphen Complexes.

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Abstract: Two new iodo derivatives of bis-salphen zinc complexes [salphen = N,N'-bis(salicylideneimine)-1,2-diaminobenzene] have been synthesized and fully characterized. The ¹H NMR, ¹³C NMR, IR, UV-Vis, TGA, elemental analysis and MALDI mass spectral data of these complexes are presented. In addition, X-Ray single crystal diffraction analysis of complex 1 has been recorded. These two compounds present a great potential interest for generating 2D covalent organic nanoarchitecture.

Keywords: Metal-Salophen complexes / Crystal structure / Zinc / NMR / TGA

1. Introduction

Metal-salphen or bis-salphen are promising molecules for engineering two-dimensional nanomaterials since their planar structure is ideal to favor flat adsorption on surfaces.[1-7] These molecules can be prepared using a one-step process. This makes these compounds accessible, cost-effective synthesis and easy to functionalized. [8] These compounds have surprisingly received little attention as sources of supramolecular planar building blocks [9, 10] for engineering complex two-dimensional nanoarchitectures. Directional and selective intermolecular interactions have been successfully exploited to control the lateral arrangement of molecular building blocks. Large-scale two-dimensional organic nanoarchitectures have thus been engineered taking advantage of intermolecular hydrogen-bonds [11-14] and halogen bonds. [15-17] Molecular building blocks with halogens also have an interesting potential to create novel on-surface synthesized 2D covalent organic nanoarchitectures. [18-20]

Herein, we present two molecules which are ideal candidates as molecular building block to elaborate complicated self-assembled halogen-bonded nanoarchitectures. [21] These molecules are composed of two iodo derivatives of bis-Zn(II)salphen complexes **1-2** (Scheme 1). These two molecules differ by the position of the iodine atoms on the four external phenyl rings. These different designs are expected to lead to totally different molecular arrangements as it has already been noticed in our precedent work [21]. Indeed, we showed that a tiny modification of the skeleton of the molecule can drastically affect its self-assembly. [21] The synthetic work is presented as well as the ¹H NMR, ¹³C NMR, IR, TGA, UV-Vis and MS spectra. The X-Ray analysis of complex **1** is also shown.

Scheme 1

2. Experimental

Physical Measurements. IR spectra were measured on a PerkinElmer Spectrum 100 FT-IR spectrometer with samples as KBr pellets. UV-Vis spectra were recorded on a Varian Cary 5000 spectrophotometer. MS spectra were recorded by the Service de Spectrométrie de Masse of Paul Sabatier University using Waters MALDI micro MX spectrometer for matrix-assisted laser desorption ionization (MALDI; matrix: trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB); $\lambda=337\text{nm}$). NMR experiments were performed at 298K on a Bruker AVANCE I 500MHz spectrometer equipped with a 5 mm Z-gradient TCI cryoprobe and on a Bruker AVANCE III HD 500MHz equipped with a 5 mm Z-gradient BBO PRODIGY cryoprobe. Full assignments of ^1H and ^{13}C spectra were made with the assistance of COSY, HMBC and HSQC spectra. Coupled TG/DTA measurements were performed on about 15 mg of each sample, using a Setaram-Labsys apparatus, from ambient to 1000 °C. A 100 ml min $^{-1}$ Helium flow was used and the warming up was realized with a 15 °C min $^{-1}$ ramp rate. Mass loss was given with an accuracy done near 0.01%.

General methods for the preparation of complexes. All of solvents and materials were used without further purifications. The synthesis of complexes **1** and **2** follows the procedure given by Kleij et al. [22] The bis-salphen complexes were prepared in a yield of around 60% by a one-pot protocol consisting of four condensation and two metalation stages. The high selectivity for the targeted complexes **1-2** was obtained by combining the tetramine and $\text{Zn}(\text{OAc})_2$ in DMSO to which the salicylaldehyde reagent was added as a solution in the same solvent. Procedures using other solvent as THF or mixture of solvents as THF/MeOH as used in Lin's publication [23] afforded lower yields or intractable mixtures of components.

2.1 Preparation of complexes **1-2**

2.1.1. Synthesis of complex **1**: $[(\mu_2\text{-}1,2,4,5\text{-tetrakis}(\text{N}-(5\text{-iodosalicylidenealdiminato}))\text{benzene})\text{-bis}(\text{N,Ndimethylformamide})\text{-di-zinc(II)}]$

To a solution of 1,2,4,5-tetraaminobenzene tetrahydrochloride (100 mg, 0.352 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (309.1 mg, 1.408 mmol) in DMSO (30mL) was added a solution of 4-iodosalicylaldehyde (349.3 mg, 1.408 mmol) in DMSO (10 mL). The reaction mixture was stirred for 18 h and then filtered

(fraction 1 = 215.8 mg). A second fraction of product was obtained by addition of MeOH (200 mL) to the mother liquor which gave after filtration another fraction (25.6 mg). Total yield: 241mg (0.203 mmol, 58 %). This complex is almost insoluble in THF, DMF or DMSO. In order to analyze it by ^1H NMR, an additive (i.e., NBu_4OAc) was needed to solubilize it in DMSO. ^1H NMR (500 MHz, DMSO-d^6 + NBu_4OAc , 25°C) δ 8.95 (s, 4H, H_d), 8.14 (s, 2H, H_e), 7.07 (d, $^3J = 7.6$ Hz, 4H, H_c), 7.03 (d, $^4J = 1.7$ Hz, 4H, H_a), 6.76 (d, $^3J = 8.1$ Hz, 4H, H_b). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO-d^6 + NBu_4OAc , 25°C) δ 172.64 (C^1), 162.12 (C^7), 139.96 (C^8), 137.38 (C^5), 132.34 (C^2), 121.32 (C^4), 120.04 (C^6), 104.34 (C^9), 103.24 (C^3). The signals corresponding to the additive (NBu_4OAc) are not listed here. MS (MALDI+, DCTB): calcd for $\text{C}_{34}\text{H}_{18}\text{I}_4\text{N}_4\text{O}_4\text{Zn}_2$ $[\text{M}]^+ = 1185.9$; found: 1185.9. Anal. Calcd for $\text{C}_{34}\text{H}_{18}\text{I}_4\text{N}_4\text{O}_4\text{Zn}_2 \cdot 1\text{H}_2\text{O}$: C, 33.95; H, 1.68; N, 4.66. Found: C, 33.26; H, 1.20; N, 4.56. IR (KBr pellet): $\nu = 1602$ s, 1581 s, 1492 s, 1459 m, 1414 m, 1383 m, 1298 w, 1246 w, 1199 w, 1171 m, 1136 w, 1064 w, 948 w, 915 m, 857 w, 777 w, 733 w, 584 w, 496 w. cm^{-1} . UV-Vis (in THF with NBu_4OAc) (λ [nm], ϵ [$\text{M}^{-1}\text{cm}^{-1}$]) (502 (sh), 58970; 480, 67270; 430, 50340; 330, 41930; 264, 46918).

2.1.2. Synthesis of complex 2: $[(\mu_2\text{-}1,2,4,5\text{-tetrakis}(\text{N-(4-iodosalicylidenealdiminato)})\text{benzene})\text{-bis}(\text{N,Ndimethylformamide})\text{-di-zinc(ii)}]$

To a solution of 1,2,4,5-tetraaminobenzene tetrahydrochloride (100 mg, 0.352 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (309.1 mg, 1.408 mmol) in DMSO (30 mL) was added a solution of 5-iodosalicylaldehyde (349.3 mg, 1.408 mmol) in DMSO (10 mL). The reaction mixture was stirred for 18h and then filtered (fraction 1 = 231.8 mg). A second fraction of product was obtained by addition of MeOH (200 mL) to the mother liquor which gave after filtration another fraction (50.4 mg). Total yield: 282mg (0.238 mmol, 68%). This complex is almost insoluble in THF, DMF or DMSO. In order to analyze it by ^1H NMR, an additive (i.e., NBu_4OAc) was needed to solubilize it in DMF. ^1H NMR (500 MHz, DMF-d^7 + NBu_4OAc , 25°C) δ 9.08 (s, 4H, H_d), 8.35 (s, 2H, H_e), 7.64 (d, $^4J = 2.6$ Hz, 4H, H_c), 7.35 (d, $^3J = 9.0$, 2.5Hz, 4H, H_a), 6.52 (d, $^3J = 8.1$ Hz, 4H, H_b). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMD-d^7 + NBu_4OAc , 25°C) δ 172.73 (C_1), 160.98 (C_7), 143.50 (C_5), 141.19 (C_3), 140.30 (C_8), 126.50 (C_2), 123.49 (C_6), 104.04 (C_9), 69.79 (C_4). The signals corresponding to the additive (NBu_4OAc) are not listed here. MS (MALDI+, DCTB): calcd for $\text{C}_{34}\text{H}_{18}\text{I}_4\text{N}_4\text{O}_4\text{Zn}_2$ $[\text{M}]^+ = 1185.9$; found: 1185.9. Anal. Calcd for $\text{C}_{34}\text{H}_{18}\text{I}_4\text{N}_4\text{O}_4\text{Zn}_2 \cdot 1\text{H}_2\text{O}$: C, 33.95; H, 1.68; N, 4.66. Found: C, 33.13; H, 1.17; N, 4.59. IR (KBr pellet): $\nu = 1606$ s, 1510 s, 1491 m, 1456 s, 1406 m, 1374 m, 1305 m, 1246 w, 1164 s, 948 w, 872 w, 829 m, 783 w, 625 m, 557 w, 496 w. cm^{-1} .

2.2. X-Rays study

The crystallographic data of compound 1 were collected at 193(2) K using a Bruker-AXS D8-Venture diffractometer equipped with a CMOS detector (Photon 100) and a 30W air-cooled microfocus source using Cu $\text{K}\alpha$ radiation ($\lambda = 1.54178$ Å). Phi- and omega-scans were used. The space group was determined on the basis of systematic absences and intensity statistics. Semi-empirical absorption correction was employed. [24] The structure was solved using an intrinsic phasing method (SHELXT), [25] and refined using the least-squares method on F2. [26] All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically at calculated positions using a riding model with their isotropic displacement parameters constrained to be equal to 1.5 times the equivalent isotropic displacement parameters of their pivot atoms for terminal sp^3 carbon and 1.2 times for all other carbon atoms. A counter cation NBu_4^+ is partially disordered: equal xyz and Uij constraints (EXYZ and EADP) and several restraints (SAME, SIMU, DELU) were applied to model the disorder over 2 positions. Hydrogen atoms of the H_2O molecule were located by difference Fourier map and were refined using restraints DFIX and SADI to get suitable target values.

Selected data for **1** : $C_{34}H_{18}Br_2I_4N_4O_4Zn_2$, 4 ($C_{16}H_{36}N$), 2 Br, 2 (H_2O) $M = 2510.36$, triclinic, space group $P\bar{1}$, $a = 10.9172(3)$ Å, $b = 17.1431(5)$ Å, $c = 17.1840(5)$ Å, $\alpha = 117.6852(13)^\circ$, $\beta = 103.5977(16)^\circ$, $\gamma = 90.8450(16)^\circ$, $V = 2739.18(14)$ Å³, $Z = 1$, crystal size $0.25 \times 0.08 \times 0.04$ mm³, 37748 reflections collected (9683 independent, $R_{int} = 0.0560$), 636 parameters, 259 restraints, $R1 [I > 2\sigma(I)] = 0.0368$, $wR2$ [all data] = 0.0901, largest diff. peak and hole: 1.819 and -0.836 eÅ⁻³.

3. Results and discussion

3.1 NMR analysis

Complexes **1-2** (scheme 1) are sparingly soluble under non-polar conditions. The NMR analysis was therefore made under polar conditions (DMSO- d_6 for **1** and DMF- d_7 for **2**) with a necessary additive agent (NBu₄OAc). The analysis confirms the proposed connectivity patterns (*cf* Figure 1 and Figures S1-S3). The numbering system used for the assignments of signals is provided in Figure 1 and in the Supporting Information.

Figure 1: Complex 1: ¹H NMR (500MHz, DMSO- d_6 , 25°C) (aromatic region)

3.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) are used up to 1000°C at He atmosphere to investigate the thermal stability of complexes **1** and **2**. The measurements reveal that the complex **1** and complex **2** are stable up to approximately 400°C and 300°C respectively. The thermogravimetric plots (TGA and DTG) of complexes **1** and **2** as weight loss versus temperature are shown in supplementary materials (Figures S4-S5). The thermal decomposition of the two complexes essentially takes place in one stage. This

stage is probably related to the omission of the four bromine atoms with a mass loss of 53% for **1** at 420°C and 45% for **2** at 380°C compared to the calculated 43% for both complexes.

3.3 FT-IR Spectra

The experimental IR spectra of the complexes **1** and **2** are shown Figure 2. These spectra look almost identical except at low frequencies (around 600cm⁻¹ and 800cm⁻¹). The calculated spectra (Figure 3) are in close agreement with the experimental ones. Indeed, the experimental observed differences between complexes **1** and **2** at low frequencies are also observed on the theoretical spectra. In order to get the calculated IR spectra, the optimized geometry of complex **1** and complex **2** have been obtained using Density Functional Theory (DFT) with Gaussian09 software [27] using PBE0 functional.[28] All atoms were described using a double zeta quality basis set (LANL2DZ).[29]

Figure 2: Experimental IR spectra of complex **1** (black) and complex **2** (red) (2000-400cm⁻¹)

Figure 3: Calculated IR spectra of complex **1** (black) and complex **2** (red) (2000-400cm⁻¹)

3.4 UV-Vis Analysis

The experimental UV-vis spectrum of complex **1** is shown in Figure 4. The spectrum was taken in THF with an additive agent (NBu₄Br) in order to increase the solubility. In the UV-Vis range, it shows five peaks as follows: 502nm (shoulder), 480nm (strong), 430nm (medium), 330 nm (medium) and 264nm (medium). It has to be noted that the same spectrum is obtained in DMSO with NBu₄OAc as additive agent.

Figure 4: Experimental UV-Vis spectrum of complex **1** in THF with (NBu₄Br) as additive agent.

3.5 X-Rays analysis

The X-Ray molecular structure of complex **1** is shown in Figure 5 and Figures S6-S7. Crystals suitable for single-crystal XRD were obtained by adding an additive (NBu₄Br) to a solution of complex **1** in THF. As a consequence, one bromine atom of the additive appears to bind to one molecular central zinc atom. Complex **1** crystallizes in a triclinic lattice and its asymmetric unit comprises one half of a centrosymmetric dinuclear complex, a tetrabutylammonium cation, a molecule of NBu₄Br and a water molecule coming from the chemical reaction medium. The coordination geometry can be viewed as a distorted five-coordinated square pyramid with a τ_5 value [30] of 0.14, fairly close to the value of 0 for an ideal square pyramid. The axial site is occupied by the Zn atom, its deviation from the mean plane defined by O1, O2, N1 and N2 is 0.5478(6) Å. The Zn-O and Zn-N distances Zn1-O1, Zn1-O2, Zn1-N1 and Zn1-N2 found within the salphen complex are similar to other bis-salphen zinc complexes described [1.985(3), 1.995(3), 2.123(3) and 2.108(3) Å respectively]. [22, 31, 32] The C1-C6 ring is almost coplanar with the central phenyl ring C15-C17A (tilting angle of 4.56°) whereas the C8-C13 is tilted by 12.8°. Only the anionic part of the complex **1** is represented in Figure 5 for clarity. Crystallographic data are shown on Supplementary materials.

Figure 5: Molecular view of anionic part of the complex **1**. Thermal ellipsoids represent 50% probability level. H and disordered atoms are omitted for clarity.

Selected bond lengths [Å] and angles [°]: Zn1–O1 1.985(3), Zn1–O2 1.995(3), Zn1–Br1 2.445(1), Zn1–N1 2.123(3), Zn1–N2 2.108(3); O1–Zn1–O2 89.69(6), O1–Zn1–N1 87.89(12), O1–Zn1–N2 144.02(13), O2–Zn1–N1 152.40(13), O2–Zn1–N2 89.07(12), N1–Zn1–N2 77.12(12) O1–Zn1–Br1 105.34(9), O2–Zn1–Br1 107.23(10), N2–Zn1–Br1 109.33(9), N1–Zn1–Br1 99.92(9)

4. Conclusions

In conclusion, two new iodo derivatives of bis-salphen zinc complexes have been synthesized and fully characterized. These molecules, stable at room temperature, quite easy to make, chemically pure, readily available, will in the future be used as molecular building block to engineer novel two-dimensional halogen-bonded self-assembled nanoarchitecture.

CCDC-1951509 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Author statement

Mélia Lacaze : Investigation ; **Nathalie Saffon-Merceron** : Investigation, Formal analysis ; **Fabien Silly** : Conceptualization ; **Jacques Bonvoisin** : Conceptualization, Writing - Review & Editing, Validation, Supervision

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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References

- [1] G. Salassa, M.J.J. Coenen, S.J. Wezenberg, B.L.M. Hendriksen, S. Speller, J. Elemans, A.W. Kleij, Extremely Strong Self-Assembly of a Bimetallic Salen Complex Visualized at the Single-Molecule Level, *Journal of the American Chemical Society*, 134 (2012) 7186-7192.
- [2] M.T. Raisanen, F. Mogeles, S. Feodorow, B. Rieger, U. Ziener, M. Leskela, T. Repo, Alkyl chain length defines 2D architecture of salophen complexes on liquid-graphite interface, *European Journal of Inorganic Chemistry*, (2007) 4028-4034.
- [3] Y.C. Zhang, B. Chilukuri, T.B. Hanson, Z.M. Heiden, D.Y. Lee, Connecting Solution-Phase to Single-Molecule Properties of Ni(Salophen), *Journal of Physical Chemistry Letters*, 10 (2019) 3525-3530.
- [4] L. Mengozzi, M. El Garah, A. Gualandi, M. Iurlo, A. Fiorani, A. Ciesielski, M. Marcaccio, F. Paolucci, P. Samori, P.G. Cozzi, Phenoxylaluminum(salophen) Scaffolds: Synthesis, Electrochemical Properties, and Self-Assembly at Surfaces of Multifunctional Systems, *Chemistry-a European Journal*, 24 (2018) 11954-11960.
- [5] M. Bazarnik, B. Bugenhagen, M. Elsebach, E. Sierda, A. Frank, M.H. Prosenc, R. Wiesendanger, Toward Tailored All-Spin Molecular Devices, *Nano Letters*, 16 (2016) 577-582.
- [6] A. DiLullo, S.H. Chang, N. Baadji, K. Clark, J.P. Klockner, M.H. Prosenc, S. Sanvito, R. Wiesendanger, G. Hoffmann, S.W. Hla, Molecular Kondo Chain, *Nano Letters*, 12 (2012) 3174-3179.
- [7] M. Viciano-Chumillas, D.Z. Li, A. Smogunov, S. Latil, Y.J. Dappe, C. Barreteau, T. Mallah, F. Silly, Tailoring the Structure of Two-Dimensional Self-Assembled Nanoarchitectures Based on Ni-II-Salen Building Blocks, *Chemistry-a European Journal*, 20 (2014) 13566-+.
- [8] C.J. Whiteoak, G. Salassa, A.W. Kleij, Recent advances with pi-conjugated salen systems, *Chemical Society Reviews*, 41 (2012) 622-631.
- [9] A.W. Kleij, M. Kuil, D.M. Tooke, M. Lutz, A.L. Spek, J.N.H. Reek, Zn-II-salphen complexes as versatile building blocks for the construction of supramolecular box assemblies, *Chemistry-a European Journal*, 11 (2005) 4743-4750.

- [10] S.J. Wezenberg, A.W. Kleij, Material applications for salen frameworks, *Angewandte Chemie-International Edition*, 47 (2008) 2354-2364.
- [11] J.A. Gardener, O.Y. Shvarova, G.A.D. Briggs, M.R. Castell, Intricate Hydrogen-Bonded Networks: Binary and Ternary Combinations of Uracil, PTCDI, and Melamine, *Journal of Physical Chemistry C*, 114 (2010) 5859-5866.
- [12] F. Silly, A.Q. Shaw, M.R. Castell, G.A.D. Briggs, M. Mura, N. Martsinovich, L. Kantorovich, Melamine structures on the Au(111) surface, *Journal of Physical Chemistry C*, 112 (2008) 11476-11480.
- [13] Y.L. Yang, C. Wang, Hierarchical construction of self-assembled low-dimensional molecular architectures observed by using scanning tunneling microscopy, *Chemical Society Reviews*, 38 (2009) 2576-2589.
- [14] S. Uemura, M. Aono, T. Komatsu, M. Kunitake, Two-Dimensional Self-Assembled Structures of Melamine and Melem at the Aqueous Solution-Au(111) Interface, *Langmuir*, 27 (2011) 1336-1340.
- [15] G. Berger, J. Soubhye, F. Meyer, Halogen bonding in polymer science: from crystal engineering to functional supramolecular polymers and materials, *Polym Chem-Uk*, 6 (2015) 3559-3580.
- [16] F. Silly, Selecting Two-Dimensional Halogen Halogen-Bonded Self-Assembled 1,3,5-Tris(4-iodophenyl)benzene Porous Nanoarchitectures at the Solid-Liquid Interface, *Journal of Physical Chemistry C*, 117 (2013) 20244-20249.
- [17] F. Silly, Concentration-Dependent Two-Dimensional Halogen-Bonded Self-Assembly of 1,3,5-Tris(4-iodophenyl)benzene Molecules at the Solid-Liquid Interface, *Journal of Physical Chemistry C*, 121 (2017) 10413-10418.
- [18] L. Dong, P.N. Liu, N. Lin, Surface-Activated Coupling Reactions Confined on a Surface, *Accounts Chem Res*, 48 (2015) 2765-2774.
- [19] Q.T. Fan, J.M. Gottfried, J.F. Zhu, Surface-Catalyzed C-C Covalent Coupling Strategies toward the Synthesis of Low-Dimensional Carbon-Based Nanostructures, *Accounts Chem Res*, 48 (2015) 2484-2494.
- [20] D. Peyrot, F. Silly, On-Surface Synthesis of Two-Dimensional Covalent Organic Structures versus Halogen-Bonded Self-Assembly: Competing Formation of Organic Nanoarchitectures, *Acs Nano*, 10 (2016) 5490-5498.
- [21] F. Silly, C. Viala, J. Bonvoisin, Two-Dimensional Halogen-Bonded Porous Self-Assembled Nanoarchitectures of Copper beta-Diketonato Complexes, *Journal of Physical Chemistry C*, 122 (2018) 17143-17148.
- [22] E.C. Escudero-Adan, M.M. Belmonte, E. Martin, G. Salassa, J. Benet-Buchholz, A.W. Kleij, A Short Desymmetrization Protocol for the Coordination Environment in Bis-salphen Scaffolds, *Journal of Organic Chemistry*, 76 (2011) 5404-5412.
- [23] K.L. Kuo, C.C. Huang, Y.C. Lin, Synthesis and photophysical properties of multinuclear zinc-salophen complexes: enhancement of fluorescence by fluorene termini, *Dalton Transactions*, (2008) 3889-3898.
- [24] Bruker, SADABS, Bruker AXS Inc., in, Madison, Wisconsin, USA, 2008.
- [25] ShelXT, G.M. Sheldrick, University of Göttingen, *Acta Crystallogr. Sect A*, 71 (2015) 3-8.
- [26] ShelXL, G.M. Sheldrick, University of Göttingen, *Acta Crystallogr. Sect C*, 71 (2015) 3-8.
- [27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian09, in, Gaussian, Inc., Wallingford CT, 2013.