**Electronic Supplementary Information** 

# Direct Investigation of Chalcogen Bonds by Multinuclear Solid-

## State Magnetic Resonance and Vibrational Spectroscopy

Vijith Kumar, Yijue Xu, César Leroy, and David L. Bryce\*

Department of Chemistry and Biomolecular Sciences, University of Ottawa, 10 Marie Curie Private, Ottawa, Ontario K1N 6N5, Canada. E-mail: dbryce@uottawa.ca; Fax: +1-613-562-5170; Tel: +1-613-562- 5800 ext. 2018

## Contents

	Page
S.1. Materials and methods	<b>S</b> 3
S.2. Synthesis of benzylic seleno and tellurocyanates	<b>S3</b>
S.3. Preparation of cocrystals	<b>S4</b>
S.4. Powder X-ray studies	<b>S4</b>
S.5. Single crystal X-ray studies	<b>S7</b>
S.6. <sup>13</sup> C, <sup>77</sup> Se, and <sup>125</sup> Te solid-state NMR spectroscopy	<b>S10</b>
S.8. Theoretical calculations	<b>S16</b>
S.9. CSD Analyses	<b>S23</b>
S.10. References	<b>S26</b>

#### S.1. Materials and methods

Commercially available anhydrous DMF was used for the synthesis of benzylic selenocyanates and anhydrous DMSO was used for the preparation of benzylic tellurocyanates. Starting materials were purchased from Sigma–Aldrich, TCI, or Apollo Scientific. All reactions were carried out under argon atmosphere with standard Schlenk techniques. AR grade solvents were used without any further purification for the preparation of cocrystals and for recrystallization. Melting points were determined with a MEL-TEMP electro thermal instrument. NMR spectra (<sup>1</sup>H, <sup>13</sup>C, <sup>77</sup>Se, and <sup>125</sup>Te) were recorded at ambient temperature on a Bruker AVII-300 spectrometer, with  $B_0 = 7.05$  T. DMSO- $d_6$  and CDCl<sub>3</sub> were used as solvents and all chemical shifts are given in ppm. IR spectra were obtained using an Agilent Cary 630 FTIR spectrometer. Raman spectra were obtained using a Horiba XploRA<sup>TM</sup> Plus Raman Microscope with two different laser wavelengths of 532 and 785 nm.

#### S.2. Synthesis of benzylic seleno and tellurocyanates

## S.2.1 Synthesis of 1,3-bis(selenocyanatomethyl)-benzene $(1)^1$

A solution of potassium selenocyanate (1.6 g, 10.8 mmol, 2.7 eq.) in anhydrous DMF (20 mL) was added dropwise over a period of 15 min to a solution of  $\alpha, \alpha'$ -dibromo-m-xylene (1 g, 3.6 mmol, 1 eq.) under an argon atmosphere. Upon stirring, the solution turns cloudy. The reaction was monitored by thin layer chromatography (eluent hexane/ethyl acetate 8/2). After completion of the reaction (typically 45 min), addition of 60 mL of warm water (40 °C) precipitated an off-white solid. Further, the solid was washed twice with 50 mL of warm water (40 °C) in an ultrasonic bath for 5 min. The solid product was filtered using Whatman filter paper and dried overnight at 70 °C. 95 % yield, off-white solid. Melting point: 107-109 °C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  in ppm 7.31-7.45 (m, 4H), 4.29 (s, 4H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>): 136.7 (2C), 129.9 (1C), 129.4 (1C), 129.2 (2C), 101.4 (2C), 32.1 (2C). <sup>77</sup>Se NMR (57.5 MHz, DMSO-*d*<sub>6</sub>): 292.6 (s, 2Se).

#### S.2.1. Synthesis of 1,4-bis(selenocyanatomethyl)-benzene $(2)^1$

A solution of potassium selenocyanate (1.6 g, 10.8 mmol, 2.7 eq.) in anhydrous DMF (20 mL) was added dropwise over a period of 15 min to a solution of  $\alpha, \alpha'$ -dibromo-p-xylene (1 g, 3.6 mmol, 1 eq.) under an argon atmosphere. Upon stirring, the solution turns cloudy. The reaction was monitored by thin layer chromatography (eluent hexane/ethyl acetate 8/2). After completion of the reaction (typically 30-40 min), addition of 60 mL of warm water (40 °C) precipitated an off-white solid. Further, the solid was washed twice with 50 mL of warm water (40 °C) in an ultrasonic bath for 5 min. The solid was filtered and dried

overnight at 70 °C. 94 % yield, white solid. Melting point: 149-152 °C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ in ppm 7.36 (s, 4H), 4.75 (t, 4H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>): 138.3 (2c), 129.5 (4c), 105.2 (2c), 32.8 (2c). <sup>77</sup>Se NMR (57.5 MHz DMSO-*d*<sub>6</sub>): 318.41 (s, 2Se).

#### S.2.3. Synthesis of benzylic tellurocyanate $(3)^2$

In a glove box, freshly crushed and finely ground tellurium (3.19 g, 0.025 mol) and powdered potassium cyanide (1.63 g, 0.025 mol) were placed in a round bottom flask and anhydrous dimethyl sulfoxide (25 mL) was added. The solution was heated to 110 °C under argon atmosphere for approximately 2 h until all the Te dissolved. Upon heating, the dark solution turns pale yellow. It was then cooled to room temperature and diluted with an additional 50 mL of anhydrous dimethyl sulfoxide. The *in situ* generated potassium tellurocyanate solution was added dropwise to a stirring solution of benzyl bromide (0.52 mL, 4.38 mmol, 1 eq.) in 25 mL of anhydrous dimethyl sulfoxide. After stirring for 2 h at ambient temperature, the reaction mixture was poured into cold water. The dark gray solid was filtered, dried and washed by decantation with warm petroleum ether. White needles. 58% yield, Melting point: 80 °C (starts to decompose). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  in ppm 7.26 (m, 4H), 7.14 (m, 1H) 4.10 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 141.7 (2C), 128.6 (1C), 128.3 (1C), 126.7 (2C), 16.2 (1C) <sup>125</sup>Te NMR (79.2 MHz CDCl<sub>3</sub>): 683.4 (s, 1Te).

#### S.3. Preparation of cocrystals

The preparation of cocrystals was carried out using slow evaporation of solvent or vapour diffusion at ambient temperature. ChB donors 1, 2, and acceptor systems such as tetrabutylammonium halides ((Bu<sub>4</sub>N)I, (Bu<sub>4</sub>N)Br, (Bu<sub>4</sub>N)Cl), 4,4'-bipyridine (BP) and 1,2-di(4-pyridyl)ethylene (DPE) were dissolved separately in acetone (1 eq of onium halides and 0.5 eq of BP and DPE for ChB donors). The two solutions were mixed and solvent then allowed to evaporate slowly at room temperature. The cocrystals of 1 and 2 with DPE are obtained by dissolving the two tectons in acetone and diethyl ether was diffused as a second less efficient solvent to obtain good quality crystals suitable for single crystal X-ray diffraction studies.

#### S.4. Powder X-ray studies

Pure ChB donors, ChB acceptors, and cocrystals were individually packed in an aluminium or glass sample holder and data sets were collected on a Rigaku Ultima IV powder diffractometer at 293 K ( $\pm 2$ ) (CuK $\alpha_1$  radiation with a wavelength of  $\lambda = 1.54056$  Å). The measurements were carried out in focused

beam geometry with a step-scan technique in  $2\theta$  range of  $5-50^{\circ}$ . Data were acquired by scintillation counter detector in continuous scanning mode with a step size of  $0.02^{\circ}$ . The experimental PXRD patterns of pure ChB donors and cocrystals, and simulated patterns generated from the single crystal structures are shown below. The comparison of simulated and experimental PXRD patterns confirms the structural uniformity of bulk cocrystal powders. A few additional peaks (much weaker than the intensity of the main phase) are occasionally present; this is probably related to some structural disorder or differences in data collection temperatures.



Fig. S1. Comparison of the experimental PXRD pattern of the cocrystal  $2 \cdot (Bu_4N)Cl$  (bottom, black) and the simulated pattern obtained from the single-crystal structure (top, red).



Fig. S2. Comparison of the experimental PXRD pattern of the cocrystal  $2 \cdot (Bu_4N)I$  (bottom, black) and the simulated pattern obtained from the single-crystal structure (top, red).



**Fig. S3.** Comparison of the experimental PXRD pattern of the cocrystal **1**·BP (bottom, black) and the simulated pattern obtained from the single-crystal structure (top, red).



**Fig. S4.** Comparison of the experimental PXRD pattern of the cocrystal  $2 \cdot BP$  (bottom, black) and the simulated pattern obtained from the single-crystal structure (top, red).

#### S.5. Single crystal X-ray studies

The crystals were mounted on a glass fibers or transparent MiTeGen MicroMounts<sup>TM</sup> precision tools prior to data collection. The data were collected on a Bruker Kappa Apex diffractometer equipped with MoK $\alpha$  radiation (wavelength of  $\lambda$ = 0.7103 Å) with an APEX II CCD detector at 200 ± 2 K. The raw data collection and processing were performed with the Bruker APEX III software package. Crystal structures of the complexes were solved using WinGX and Olex2 software packages with the direct method and refined against F2 using SHELXL97.<sup>3</sup> Packing diagrams were generated using Mercury 4.1.0 and POV-Ray.<sup>4</sup> Intermolecular interactions were analyzed with PLATON.<sup>5</sup> The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using difference Fourier maps or positioned geometrically. In cocrystal 2·DPE, 1,2-di(4-pyridyl)ethylene shows larger thermal ellipsoids and positional disorder. The disordered components are separated by PART instructions and occupancies are refined with the free variable and restraints (SADI, EADP, and FLAT). Crystallographic data and structural refinement details are provided in Table S1.

Name	1·DPE	2·DPE	3		
Empirical formula	C22H18N4Se2	$C_{22}H_{18}N_4Se_2$	C <sub>8</sub> H <sub>7</sub> NTe		
Molecular weight	496.32	496.32	244.75		
Crystal system, space group	monoclinic, C2/c	triclinic, P -1	monoclinic, P2 <sub>1</sub> /c		
Temperature (K)	200	200	293		
a (Å)	5.7217(7)	5.7832(5)	6.031(4)		
b (Å)	14.1966(2)	7.7601(7)	16.042(11)		
c (Å)	25.6661(3)	12.0835(1)	8.787(7)		
α(°)	90 77.499(2)		90		
β (°)	9.162(5)	78.664(2)	95.82(2)		
γ(°)	90	73.377(2)	90		
V (Å <sup>3</sup> )	2083.3(6)	502.02(8)	845.7(11)		
Z	4	1	4		
$\mu (mm^{-1})$	3.564	3.695	3.441		
Crystal size (mm <sup>3</sup> )	$0.26 \times 0.24 \times 0.19$	$0.34 \times 0.28 \times 0.22$	$0.18 \times 0.16 \times 0.08$		
F(000)	984	246	456		
Data collection and refinement					
Diffractometer	Bruker APEX-II CCE	area detector diffracto	meter		
Absorption correction	Based on multi-scan				
No. of reflections: measured, independent, observed	37092, 2057, 1326	32771, 1978, 1637	31142, 1938, 1709		
Rint	0.1498	0.1471	0.0407		
$\theta_{\min}$ (°)	1.6	2.7	2.5		
$\theta_{max}$ (°)	26.0	26.0	28		
$R_{all}, R_{obs}$	0.092, 0.047	0.038, 0.027	0.024, 0.019		
$wR_2_{all}, wR_2_{obs}$	0.127, 0.112	0.062, 0.059	0.041, 0.042		
GOOF	1.035	1.010	1.159		
No. of parameters	184	127	146		
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	0.61, -0.38	0.40, -0.37	0.43, -0.34		
CCDC number	1956411	1956409	1956410		

**Table S1.** Crystallographic data and structural refinement details for chalcogen-bonded compounds

### S.5.1. Single crystal X-ray representations



**Fig. S5.** Partial ball and stick representations (Mercury 4.1.1) showing the solid-state organization of pure ChB donors: (a) C–Se…NC ChBs in 2, (b) C–Se…NC ChBs in 1 and (c) C–Te…NC ChBs in 3. Color codes: grey, carbon; white, hydrogen; yellow, selenium; blue, nitrogen; brown, tellurium (dashed black lines denote ChBs).



**Fig. S6.** Space filling representation (Mercury 4.1.1) of the chalcogen bonds in cocrystal **2**·DPE along the extension of Se–CN covalent bonds (colour codes: grey, carbon; yellow, selenium; blue, nitrogen; white, hydrogen).



**Fig. S7.** Space filling representation (Mercury 4.1.1) of the chalcogen bonds in cocrystal **1** ·DPE along the extension of Se–CN covalent bonds (colour codes: grey, carbon; yellow, selenium; blue, nitrogen; white, hydrogen).

## S.6. <sup>77</sup>Se and <sup>125</sup>Te solid-state NMR spectroscopy

Experimental details are given in the main text.



**Figure S.8.** Experimental <sup>77</sup>Se CP/MAS SSNMR spectra acquired at 9.4 T for pure ChB donor **2** and the simulated spectrum. Spinning frequencies of 12.5 kHz and 3 kHz were used and isotropic peaks are indicated with black asterisks (343.0 ppm and 357.2 ppm).



**Figure S.9.** Experimental <sup>77</sup>Se CP/MAS SSNMR spectra acquired at 9.4 T for pure ChB donor **1** and the simulated spectrum. Spinning frequencies of 12.5 kHz and 3 kHz were used and isotropic peaks are indicated with black asterisks (365.3 ppm, 352.3 ppm, 336.4 ppm 321.9 ppm).



**Figure S.10.** Experimental <sup>77</sup>Se CP/MAS SSNMR spectra acquired at 9.4 T for  $2 \cdot BP$  and the simulated spectrum. Spinning frequencies of 12.5 kHz and 3 kHz were used and isotropic peak is indicated with a black asterisk (331.7 ppm).



**Figure S.11.** Experimental <sup>77</sup>Se CP/MAS SSNMR spectra acquired at 9.4 T for **2** ·DPE and the simulated spectrum. Spinning frequencies of 12.5 kHz and 3 kHz were used and the isotropic peak is indicated with a black asterisk (339.4 ppm).



**Figure S.12.** Experimental <sup>77</sup>Se CP/MAS SSNMR spectra acquired at 9.4 T for  $2 \cdot (Bu_4N)$ Cl and the simulated spectrum. Spinning frequencies of 8 kHz and 3 kHz were used and isotropic peaks are indicated with black asterisks (328.7 ppm and 318.1 ppm).



**Figure S.13.** Experimental <sup>77</sup>Se CP/MAS SSNMR spectra acquired at 9.4 T for  $2 \cdot (Bu_4N)Br$  and the simulated spectrum. Spinning frequencies of 12.5 kHz and 3 kHz were used and the isotropic peak is indicated with a black asterisk (314.3 ppm).



**Figure S.14.** Experimental <sup>77</sup>Se CP/MAS SSNMR spectra acquired at 9.4 T for  $2 \cdot (Bu_4N)I$  and the simulated spectrum. Spinning frequencies of 12.5 kHz and 3 kHz were used and the isotropic peak is indicated with a black asterisk (319.0 ppm).



**Figure S.15.** Experimental <sup>77</sup>Se CP/MAS SSNMR spectra acquired at 9.4 T for **1**·BP and the simulated spectrum. Spinning frequencies of 12.5 kHz and 3 kHz were used and the isotropic peak is indicated with a black asterisk (342.5 ppm).



**Figure S.16.** Experimental <sup>125</sup>Te CP/MAS SSNMR spectra acquired at 9.4 T for pure ChB donor **3** and the simulated spectrum. Spinning frequencies of 3 kHz and 5 kHz were used and the isotropic peak is indicated with a black asterisk (679.1 ppm).

**Table S2.** Parameters used to simulate the residual dipolar coupling patterns observed in the <sup>13</sup>C CP MAS NMR spectra. The unique component of the EFG tensor was placed along the C-N bond axis.

compound	$\delta_{iso}(^{13}C)$ /ppm	$C_{\rm Q}(^{14}{\rm N})/{\rm MHz}$	$\eta_{ m Q}(^{14} m N)^{a}$	$R_{\rm DD}(^{13}{\rm C}, {}^{14}{\rm N})^{\rm b}/{\rm Hz}$
<b>2</b> (site 1)	108.6 (0.1)	-4.3 (1.0)	0.32	1091.72
<b>2</b> (site 2)	107.4 (0.1)	-3.0 (1.0)	0.30	1854.50
$2 \cdot (Bu_4N)Cl$	106.9 (0.1)	-3.6 (1.0)	0.38	1521.57
$2 \cdot (Bu_4N)Br$	107.3 (0.1)	-1.4 (1.0)	0.31	1462.45
$2 \cdot (Bu_4N)I$	106.2 (0.1)	-3.0 (1.0)	0.30	1477.91
<b>2</b> ⋅BP	107.4 (0.1)	-3.1 (1.0)	0.38	1489.65
<b>2</b> ·DPE	107.3 (0.1)	-3.5 (1.0)	0.38	1485.72

a. Fixed to value calculated using DFT.  $|J_{iso}(^{13}C, ^{14}N)| < 10 \text{ Hz}$ 

b. Fixed to value determined directly from the X-ray structures.



**Fig. S17.** Experimental <sup>13</sup>C CP/MAS SSNMR spectra of the pure ChB donor **2** and respective cocrystals in two different magnetic fields.

#### **S.8** Computational Details

Density functional theory (DFT) was used to calculate the <sup>77</sup>Se magnetic shielding tensors with the Amsterdam Density Functional (ADF) software package,<sup>6,7</sup> using a statistically averaged orbital potential (SAOP)<sup>8</sup> and relativistic effects (spin–orbit or scalar). A diffuse function was included in the basis set for the chloride and bromide ions (i.e., ET/ET-QZ3P-2DIFFUSE), whereas the basis set used for all other atoms was quadruple- $\zeta'$  quadruply polarized (QZ4P). Relativistic effects were considered using the Zeroth Order Regular Approximation (ZORA). Cluster models were generated using atomic coordinates from the X-ray crystal structures with hydrogen atom geometry optimization, which was carried out within the general gradient approximation using the Perdew-Wang exchange and correlation functional (PW91)<sup>9</sup> with a triple- $\zeta'$  doubly polarized basis set (TZ2P). Data were extracted from the output files using EFGShield software version 4.3.<sup>10</sup> Experimental absolute shielding scales for selenium and tellurium,  $\sigma_{ref} = 2069$  ppm and 4333 ppm respectively,<sup>11</sup> were employed to convert the <sup>77</sup>Se and <sup>125</sup>Te magnetic shielding tensors to chemical shifts. The NLMO contributions to the magnetic shielding tensors were computed using the NBO 6.0<sup>12</sup> program that is implemented within ADF and the orbitals were visualized with the program adfview.

IR and Raman analysis was carried out using the GGA BP86<sup>13</sup> functional with the TZ2P basis set. The frequency assignments were done with the program adfspectra.

The molecular electrostatic surface potential (MESP) calculations were performed using the B3LYP hybrid functional in Gaussian 09 on the Wooki cluster at the University of Ottawa. The calculations were carried out using the Def2TZVP basis set. Models were constructed and visualized using GaussView 4.1 software.



**Fig. S18.** Electrostatic potential surfaces with an isodensity of 0.02 a.u. (B3LYP/Def2TZVP, GaussView 4.1) of the ChB donors **1**(a), **2**(b), and **3**(c). Each Ch atom possesses two electropositive regions ( $\sigma$ 1 and  $\sigma$ 2 in dark blue). The region ( $\sigma$ 1) along the prolongation of the electron withdrawing nitrile group is more electropositive than the region ( $\sigma$ 2) opposite the Ch-CH<sub>2</sub> bond. **1**:  $\sigma$ 1: 608.59 kJ/mol,  $\sigma$ 2: 522.47 kJ/mol; **2**:  $\sigma$ 1: 629.86 kJ/mol,  $\sigma$ 2: 522.47 kJ/mol; **3**:  $\sigma$ 1: 705.73 kJ/mol,  $\sigma$ 2: 628.81 kJ/mol.



**Fig. S19.** (a) A plot of the DFT calculated versus experimental <sup>77</sup>Se isotropic chemical shift for all the compounds in this study. Red outliers are 2 (two sites) and  $2 \cdot (Bu_4N)Cl$ . (b) A plot of the calculated <sup>77</sup>Se isotropic chemical shift as a function of ChB distance. (c) A plot of the calculated NLMO contributions to <sup>77</sup>Se isotropic magnetic shielding as a function of ChB distance. Orange circles represent the sum contributions from the sum of Se core orbitals. Green and blue diamonds represent bonding orbitals between selenium and methyl carbon and bonding orbitals between selenium and nitrile carbon, respectively. Pink and yellow squares represent the contributions from selenium lone pairs.

compound	distance	sum of Se CR	σ LP Se	$\pi$ LP Se	BD Se-CN	BD Se-CH <sub>2</sub>
$2 \cdot (Bu_4N)I$	3.506	3164	-90	-924	-703	80
$2 \cdot (Bu_4N)Br$	3.249	3489	222	-446	-654	-1031
<b>2</b> ·BP	2.897	2624	54	-871	-329	38
<b>2</b> ·DPE	2.865	2651	184	-852	-287	-208
1	3.01	2923	15	-633	-411	-211
	3.015	2895	-90	-1021	-365	126
	2.965	2827	-64	-559	-288	-248
	3.017	2691	-119	-586	104	-328
<b>1</b> ·BP	2.83	3411	-186	103	15	-1360

**Table S3**. Analysis of NLMO contributions to the isotropic magnetic shielding ( $\sigma_{iso}$  in ppm) of <sup>77</sup>Se in protonoptimized structures<sup>a</sup>

<sup>a</sup> CR: core orbital; LP: lone pair; BD: bonding orbital



**Fig. S20.** A plot of calculated principal components of <sup>77</sup>Se chemical shift tensors:  $\delta_{11}$  (blue circles),  $\delta_{22}$  (orange triangles) and  $\delta_{33}$  (green diamonds) as a function of ChB distance for model based on **2**·BP.



**Fig. S21.** Plots of the sum of Lewis and non-Lewis largest NLMO contributions to <sup>77</sup>Se isotropic magnetic shielding constants as a function of ChB distance for the models of  $2 \cdot (Bu_4N)Br$  (a) and  $2 \cdot BP$  (b). Orange circles represent the sum contributions from the sum of Se core orbitals. Green and blue diamonds represent bonding orbitals between selenium and methyl carbon and bonding orbitals between selenium and nitrile carbon, respectively. Black triangles represent the sum contributions from Br<sup>-</sup> lone pairs. Pink and yellow squares represent the contributions from selenium lone pairs.



Fig. S22. Computed <sup>77</sup>Se chemical shift tensor orientations for: 2 (a),  $2 \cdot BP$  (b),  $2 \cdot DPE$  (c),  $2 \cdot (Bu_4N)Br$  (d),  $2 \cdot (Bu_4N)I$  (e), 1 (f) and  $1 \cdot BP$  (g). The BP and DPE molecules involved in ChB with another Se atom are omitted for clarity.



**Fig. S23.** Distribution of interaction distances observed for Se/Te…N chalcogen bonds in the CSD (ConQuest Version 2.0.1).



**Fig S24.** Distribution of interaction distances observed for Se…Cl<sup>-</sup>, Se…Br<sup>-</sup>, Se…I<sup>-</sup> chalcogen bonds in the CSD (ConQuest Version 2.0.1).



**Fig S25.** Distribution of interaction distances observed for  $Te\cdots Cl^-$ ,  $Te\cdots Br^-$ ,  $Te\cdots I^-$  chalcogen bonds in the CSD (ConQuest Version 2.0.1).

#### S.10 References

- (a) A. M. S. Riel, H.-T. Huynh, O. Jeannin, O. Berryman and M. Fourmigué, *Cryst. Growth Des.*, 2019,
   19, 1418–1425; (b) H.-T. Huynh, O. Jeannin and M. Fourmigué, *Chem. Commun.*, 2017, 53, 8467–8469; (c) O. Jeannin, H.-T. Huynh, A. M. S. Rielab and M. Fourmigué, *New J. Chem.*, 2018, 42, 10502–10509.
- 2 H. K. Spencer, V. Lakshmikantham, and M. P. Cava, J. Am. Chem. Soc., 1977, 99, 1470-1473
- 3 G. M. Sheldrick, Acta Crystallogr. Sect. A., 2008, 64, 112.
- 4 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.*, 2008, **41**, 466.
- 5 A. L. Spek, Acta Crystallogr. Sect. D, 2009, 65, 148.
- 6 E. J. Baerends et al. Amsterdam Density Functional Software, *ADF2017*, SCM; Theoretical Chemistry;
   Vrije Universiteit: Amsterdam.
- 7 G. te Velde, F. M. Bickelhaupt, E. J. Baerends,; C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler J. Comput. Chem. 2001, 22, 931–967.
- 8 P. R. T. Schipper, O. V. Gritsenko, S. J. A. van Gisbergen, E. J. Baerends, E. J. J. Chem. Phys. 2000, 112, 1344–1352
- 9 J. P. Perdew, K. Burke, Y. Wang, Phys. Rev. B, 1996, 54, 16533-16539.
- 10 S. Adiga, D. Aebi, D. L. Bryce, Can. J. Chem. 2007, 85, 496-505.
- 11 C. J. Jameson, A. K. Jameson, Chem. Phys. Lett. 1987, 135, 254-259.
- E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold, F. NBO 6.0; Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013.
- 13 A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098-3100. (b) J. P. Perdew, *Phys. Rev. B* 1986, **33**, 8822-8824.