Bi(III) Complexes Containing Dithiocarbamate Ligands: Synthesis, Structure Elucidation by X-ray Diffraction, Solid-State $^{13}$C/$^{15}$N NMR, and DFT Calculations

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We report on syntheses, characterisation by nuclear magnetic resonance (NMR) spectroscopy, X-ray diffraction (XRD) measurements, and density functional theory (DFT) calculations of electronic/molecular structure and NMR chemical shifts of complexes of Bi(III), having the molecular formulae: [Bi(S$_2$CN (C$_6$H$_5$)$_2$)$_3$] (1), [Bi(S$_2$CN(C$_6$H$_5$)$_2$)$_2$(C$_5$H$_7$N$_2$NO$_3$)] (2), and [Bi$_2$(S$_2$CN (C$_6$H$_5$)$_2$)$_2$•H$_2$O] (3). The powder XRD patterns of complexes (1) and (2) resembled the corresponding calculated powder XRD patterns for previously reported single crystal structures. Single crystal XRD structure of complex (3), reported in this work, adopted an orthorhombic system with a space group Pbca with $a = 10.9956(3)$ Å, $b = 27.7733(8)$ Å, $c = 35.1229(10)$ Å and $\alpha = \beta = \gamma = 90^\circ$. The experimental solid-state $^{13}$C/$^{15}$N NMR data of the complexes (1)-(3) were in accord with their X-ray single crystal structures. The unit cell of the complex (3) shows a weak supramolecular Bi...S interaction leading to the formation of a non-centrosymmetric binuclear molecule [Bi$_2$(S$_2$CN (C$_6$H$_5$)$_2$)$_2$•H$_2$O], which displays structural inequivalence in both $^{13}$C/$^{15}$N NMR, and XRD data. Assignments of resonance lines in solid-state $^{13}$C/$^{15}$NMR spectra of complexes (1)-(3) were assisted by chemical shift calculations using periodic DFT methods. The findings of the present multidisciplinary approach will contribute in designing molecular models and further understanding of the structures and properties of (diamagnetic) metal complexes, including heavy metal ones.

1. Introduction

There has been growing interest in bismuth(III) biocoordination chemistry,[1–5] particularly in the light of the applications of bismuth compounds in pharmaceutical industry, especially, in the treatment for cancer,[6] gastrointestinal diseases,[7] as antimicrobial agent,[8,9] in cosmetic industry,[10] etc. In addition, bismuth has found several industrial applications,[11] e.g. nontoxic replacement for mercury electrodes in electrochemical detection of trace heavy metals,[12] and replacement for lead in brass[13] and solders,[14] in permanent magnets,[15–16] as lubricant additives,[11,17] in solar cells and photolithography,[18,19] as single-source precursors for the preparation of Bi$_2$S$_3$ nanoparticles,[20–27] as photocatalytic enhancer,[28,29] in extraction of gold, mercury, and platinum from water,[30–32] to mention but a few. Bismuth(III) being a soft Lewis acid preferentially bonds with soft bases or with ligands containing soft donating sites such as dithiocarbamates, R$_2$NCS$_2$–, xanthates, ROCS$_2$–, or dithiophosphates, (RO)$_2$PS$_2$– (R indicating alkyl or aryl groups).[33] However, a variety of bismuth(III) coordination compounds with hard or borderline Lewis bases with nitrogen/oxygen donor atoms, e.g., 1,10-phenanthroline (PHEN), have been actively studied.[34–36] From structure-property relationship perspectives, homoleptic ternary bismuth(III) dithiocarbamates are interesting, because they often form structural varieties such as ‘bridged’ networks due to weak Bi...S supramolecular interactions between the molecular units.[37] This ability of dithiocarbamates to form cross-links has found industrial applications, e.g. as in covalent cross-linking of proteins[38] and vulcanisation of rubber.[39,40] On the other hand, heteroleptic dithiocarbamates have received special attention due to their applications as nanomaterials.[19,23–25,41,42]

The ability to form weak secondary Bi...S interactions results in various supramolecular aggregations or polymorphic Bi(III) compounds.[30,46–50] A large number of single-crystal structures of complexes containing Bi(III) and sulfur donor ligands have been reported, among which the first examples to be structurally characterised[51] were those containing the tris (diethylidithiocarbamate) ligand and associated derivates. A large variety of mixed ligand and halogen substituted complexes of Bi(III) complexes e.g. Bi(S$_2$CN(R$^1$)$_2$S$_2$CN(R$^2$)$_2$)$_3$, Bi(S$_2$CN (R$^1$)$_2$)X, Bi(S$_2$CN(R$^1$)$_2$)X$_2$, Bi(S$_2$CN(R$^1$)$_2$)XY (where R$^1$, R$^2$ = alkyl or...
aryl groups, X=Cl, Br, I, etc., and Y = bipyrindine, PHEN, etc.) are described by Glen et al.[32,33] Heard et al.[34] and the references therein. The structures adopted by these complexes can be complicated with varied and irregular stereochemistry, often due to the presence of lone pairs on the Bi(III) or due to the formation of polymeric and oligomeric systems by bridging halide and dithiocarbamate groups (through intermolecular Bi···S interactions) as well as long range molecular contacts.[49,50] This means that a concise overview of the diversity of the possible structures and the functions of the materials is tedious but possible with the application of combination of experimental and theoretical methods.

Solid-state nuclear magnetic resonance (ss-NMR) has become the state-of-the-art method for obtaining structural information at the atomic level and, because it is applicable even in highly heterogeneous and complex molecular environments, largely irrespective of solubility and crystallinity,[56] ss-NMR can be the method of choice to study such complex systems. Also, when complemented with quantum mechanical calculations (of the atomic/molecular structure and properties), it can be used for rational design and development of new materials and provide insights into the structures of novel molecules that are often difficult to crystallise and to solve structure by crystallography. In spite of having those advantages, there has been very limited study of Bi(III) dithiocarbamate complexes using the experimental ss-NMR[46–50] or quantum mechanical modelling and molecular property calculations.[46] This article attempts to fill that research gap by following a multidisciplinary approach for molecular structure and property calculations wherein the results from experimental ss-NMR, X-ray crystallography, and density functional theory (DFT) methods are compared and complemented. This combination is often referred to as “NMR Crystallography” methods, which has gained interests of many researchers in organic, inorganic, and also in biomolecular disciplines.[37–41]

In this article, three bismuth(III) dithiocarbamate complexes, viz., tris(diethylidithiocarbamato-S,S)bismuth(III), [Bi(S$_2$CN(CH$_3$)$_3$)$_3$]$_2$ (1),[36,42] (nitrato-O,O')PHEN-N,V'bis(diethylidithiocarbamato-S,S)bismuth(III), [Bi(S$_2$CN(CH$_3$)$_3$)$_3$][NO$_3$](PHEN-N,V') (2),[36,43] and tris(N,V'-cyclopentamethyleneidithiocarbamato-S,S) bismuth(III), [Bi$_2$(S$_2$CN(CH$_3$)$_3$)$_3$iPr$_3$H$_2$O] (3) are considered. The reported complex (1) crystallised into a monoclinic system with space group P2$_1$/c. At least four crystal structures with slightly varying lattice parameters have been found in the Cambridge structural database (CSD) (CCDC #910136,[40] #600513,[47] #1137722,[51] and #179931[50]). In all these structures, the [Bi$_2$(S$_2$CN(CH$_3$)$_3$)$_3$] molecule exists as a binuclear complex, where two of the six dithiocarbamate ligands are bridged via Bi···S bonds and a centrosymmetrical dimer molecule is present in the unit cell. In each of these molecules, both Bi(III) atoms are seven-coordinated and the geometry of each monomer [Bi(S$_2$CN(CH$_3$)$_3$)$_3$] is distorted pentagonal bipyramidal around Bi(III). Each of the central Bi atoms is surrounded equatorially by five S atoms and axially by two S atoms. Since the experimental powder X-ray diffraction (PXRD) pattern for our complex (1) closely resembles those calculated for the reported crystal structure(s), the crystal structure determination is not attempted herein.

For complex (2), a monoclinic system with space group P2$_1$/n (CCDC No. 256686) is reported.[83] It is a mononuclear complex, where the Bi(III) is eight-coordinated and attains a capped distorted pentagonal bipyramidal geometry. Around the central Bi(III) atom, two S atoms, two N atoms, and one O atom occupy equatorial positions and two S atoms and one O atom occupy axial positions. The bulky PHEN ligand, which fills the geometrical void around Bi atom, hinders the supramolecular Bi···S interactions thus avoiding the formation of bridged networks. We have observed close resemblance between the experimental PXRD patterns for our complex (2) and the calculated patterns for the reported crystal structure and hence we did not attempt to solve the crystal structure in this report.

For complex (3), a single-crystal X-ray diffraction structure is reported in this work (CCDC #1880334). This complex crystallised into an orthorhombic system with space group Pbcn. It is a binuclear complex [Bi$_2$(S$_2$CN(CH$_3$)$_3$)$_3$iPr$_3$H$_2$O] wherein two non-centrosymmetrically related molecules associate via a pair of Bi···S interactions.

For all three complexes, the X-ray structure (after DFT geometry optimisation) was used as the input for NMR nuclear shielding calculations using the GIPAW (gauge-including projector augmented wave) method.[64–67] The computational analysis is complemented by the recording of 1D (one-dimensional) $^{13}$C and $^{15}$N cross-polarisation (CP) magic-angle-spinning (MAS) NMR spectra. Building upon our recent studies of heavy metal coordination complex crystals by such an “NMR crystallography” investigation,[46,48,69] we present here the application of this approach to three other bismuth crystals.

2. Results and Discussion

The solution-state $^1$H and $^{13}$CNMR data of both complexes (1) and (2) (see Figs. S1-S4 in the ESI) correlate well with their isolated molecular structures, i.e. both $^1$H and $^{13}$C spectra show one set of signals for each inequivalent atom in the molecule. The $^1$H NMR spectra of (2) confirm the PHEN to dithiocarbamate ligand ratios as 1:2. The $^1$H and $^{13}$C chemical sites of PHEN are slightly more deshielded upon bonding as compared to the uncoordinated (free) PHEN ligand.[84] The methylene and methyl protons are slightly more shielded and deshielded, respectively, when going from complex (1) to (2). The dithiocarbamate as well as the PHEN carbons also show small but non-negligible differences in the $^{13}$C chemical shifts for both complexes (1) and (2). For example, the dithiocarbamate carbon of complex (2) is additionally shielded by ca. 0.6 ppm due to the incorporation of PHEN into complex (1).

The experimental PXRD pattern of complex (1) shows excellent matching to the corresponding calculated PXRD data for the reported structure(s) (see Figure 1a), which confirms that complex (1) has the crystal structure type identical to that of the reported ones.[46,47,51] On the other hand, for complex (2) the calculated PXRD pattern shows minor deviations, in terms of peak intensities as well as the 20 values, when
Crystal structure was determined for complex (3), i.e. tris (N,N'-cyclo-pentamethylenedithiocarbamato)bismuth(III),  
\([\text{Bi}_3(\text{SCN}(\text{CH}_2)_5)_6\text{H}_2\text{O}])
\); crystallographic data for complex (3) is given in Table 1 and selected geometric parameters are collected in Tables 2 and 3. In this complex, two non-centrosymmetrically related molecules associate via a pair of Bi—S interactions (see Figure 3). In the unit cell, there are eight pairs of such non-centrosymmetric dimers (see Figure 4). The dimeric molecules are arranged in a ‘zigzag’ manner to form a layer along the axis \(c\), in which, two Bi1 units are followed by two Bi2 units. The Bi1 and Bi2 units in alternate layers are exposed to the solvent void, appearing to form a cage-like structure around the solvent molecule. The Bi atom is coordinated by three dithiocarbamate ligands, each of which forms asymmetric Bi—S interactions. The degree of asymmetry in the Bi—S bonds formed by the three ligands varies with the greatest asymmetry being found in the Bi1—S9 and Bi1—S10 bonds (see Table 2). Three of the six C—N bonds (S5-CN groups), particularly in the Bi1 molecule, have bond distances between 1.32(1)—1.335(9), while the remaining three C—N bonds in the Bi2 molecules are slightly longer i.e. 1.342(9)—1.35(1). Six of the twelve inter-ligand S—Bi—S bonds, in each molecule, are close to 90° (vary between 83—92°); three S—Bi—S bonds show a deviation of 30° from being linear; remaining three S—Bi—S bonds are between 112—120°. To a first approximation, the coordination geometry in the complex can be considered having a distorted square antiprism geometry with four S atoms occupying the corners of the basal plane, Bi atom at the centre (e.g. Bi2—S11—S12—S8—S9), while two S atoms (i.e. S7 and S10) occupying near axial positions (see Figure 3a/b). As seen from the torsional angles of ca. 150° in Table 3, the lone pair electrons on the Bi atom disturbs the near perfect planarity of

**Table 1.** Selected crystallographic data for complex (3) \([\text{Bi}_3(\text{SCN}(\text{CH}_2)_5)_6\text{H}_2\text{O}])
\)

| Empirical formula | \(\text{C}_{86}\text{H}_{79}\text{Bi}_3\text{N}_3\text{O}_3\text{S}_{12}\) |
|-------------------|--------------------------------------------------|
| Formula weight    | 1395.58                                          |
| Temperature (K)   | 296 (2)                                          |
| Crystal system    | Orthorhombic                                     |
| Space group       | Pbca                                             |
| \(a\) (Å)         | 10.9956(3)                                       |
| \(b\) (Å)         | 27.7733(8)                                       |
| \(c\) (Å)         | 35.1229(10)                                      |
| \(\alpha\) (°)    | 90.00                                            |
| \(\beta\) (°)     | 90.00                                            |
| \(\gamma\) (°)    | 90.00                                            |
| \(V\) (Å\(^3\))   | 10726.0 (5)                                      |
| \(Z\)             | 8                                               |
| \(F(000)\)        | 5472                                             |
| Range of \(h, k,\) and \(l\) | -13/13, -35/28, -43/35                          |
| \(\theta\) range  | 147.4—26.89                                      |
| \(D_\text{g}\) (g cm\(^{-1}\)) | 1.728                                           |
| \(\mu\) (Mo-K\(\alpha\)) (mm\(^{-1}\)) | 7.055                                           |
| Crystal size (mm) | 0.31\(\times\)0.19\(\times\)0.12               |
| Independent/observed reflections | 11322/8660                                    |
| \(R\) | 0.0358/0.0906                                    |
| GOF               | 1.091                                            |
| CCDC deposition No.| 188053                                           |

\(a\) : \(R_1 = \sum |F_\text{cal}|-|F_\text{obs}|/\sum |F_\text{obs}|\). \(wR_2 = \sum w(F_\text{cal}^2 - F_\text{obs}^2)^2/\sum wF_\text{obs}^2\).
The basal ligand planes by ca. 30°. Selected bond lengths and angles for the "full-opt" structure are also listed in Tables 2 and 3, respectively. The bond parameters have changed very slightly after full optimisation of the crystal structure.

The $^{13}$C and $^{15}$N solid-state CP-MAS NMR spectra of the polycrystalline samples of complexes (1)-(3) are depicted in Figs. 5 and 6, respectively, while the suggested spectral assignments are listed in Tables 4–6. It is a known fact that the efficiency of the polarisation transfer in a CP-MAS experiment depends on the strength of the heteronuclear dipole-dipole interactions as well as the relaxation parameters such as proton spin-lattice relaxation time ($T_1^p$) and the competition between the CP contact time ($t_{cp}$) and the spin-lattice relaxation time of protons during CP ($T_1^p$). Since these parameters are usually different for different chemical groups, the integrated intensity ratios of signals can only be used for semiquantitative analysis of groups that are chemically similar. Keeping this in mind, in our case, to quantify the number of sites of each kind the resonance lines corresponding to chemically and magnetically equivalent atoms in the molecule are compared. Additionally, in a semi-empirical way, the chemical shifts of the dithiocarbamate carbon and nitrogen atoms can be correlated to the $\pi$-bonding in the $S_x$CN fragment, i.e. the $\pi$-bond orders of the $\pi$-bonds will be maximum for equal or symmetric $\pi$-bonds while it will decrease with increasing inequality (asymmetry) of the three $\pi$-bonds. As with free dithiocarbamate ligands, nearly equal CS $\pi$-bonds will result in higher $\pi$-bond orders and higher chemical shift values for carbon atoms. On the other hand, main group metals like

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**Table 2. Selected bond distances for complex (3) [Bi$_2$(CN(CH$_2$)$_5$)$_3$]$_n$·H$_2$O.**

| Bonds          | Length[A] | Length[B] | Bonds          | Length[A] | Length[B] | Bonds          | Length[A] | Length[B] | Bonds          | Length[A] | Length[B] |
|----------------|-----------|-----------|----------------|-----------|-----------|----------------|-----------|-----------|----------------|-----------|-----------|
| Bi2-S7         | 2.982(2)  | 2.972     | N4-C21         | 1.451(9)  | 1.467     | Bi1-S1        | 2.718(2)  | 2.742     | N1-C6         | 1.493(9)  | 1.468     |
| Bi2-S11        | 2.676(2)  | 2.707     | N5-C23         | 1.501(1)  | 1.468     | Bi1-S5        | 2.946(2)  | 2.908     | N2-C8         | 1.486(9)  | 1.467     |
| Bi2-S12        | 2.946(2)  | 2.919     | N5-C31         | 1.494(9)  | 1.466     | Bi1-S4        | 2.938(2)  | 2.904     | N2-C10        | 1.471(1)  | 1.465     |
| Bi2-S8         | 2.672(2)  | 2.723     | N6-C28         | 1.460(9)  | 1.470     | Bi1-S3        | 2.679(2)  | 2.698     | N3-C12        | 1.474(9)  | 1.465     |
| Bi2-S9         | 2.982(2)  | 2.916     | N6-C35         | 1.480(9)  | 1.467     | Bi1-S5        | 2.678(2)  | 2.702     | N3-C32        | 1.468(9)  | 1.467     |
| Bi2-S10        | 2.663(2)  | 2.708     | C21-C20        | 1.501(1)  | 1.524     | Bi1-S6        | 2.919(2)  | 2.885     | C12-C13       | 1.51(1)   | 1.521     |
| Bi2-S2         | 3.314(2)  | 3.282     | C19-C20        | 1.521(1)  | 1.522     | Bi1--S12      | 3.331(2)  | 3.284     | C4-C5         | 1.54(1)   | 1.527     |

[a] Experimental; [b] “full-opt” DFT optimised. Bond lengths in Å unit.

**Table 3. Selected bond angles for complex (3) [Bi$_2$(CN(CH$_2$)$_5$)$_3$]$_n$·H$_2$O.**

| Bonds          | Angles[A] | Angles[B] | Bonds          | Angles[A] | Angles[B] | Bonds          | Angles[A] | Angles[B] | Bonds          | Angles[A] | Angles[B] |
|----------------|-----------|-----------|----------------|-----------|-----------|----------------|-----------|-----------|----------------|-----------|-----------|
| S2-Bi1-S6-C15  | 149.4(3)  | 146.65    | S9-Bi2-S12-C22 | 150.1(3)  | 150.43    | S2-Bi1-S7-C16  | 150.1(3)  | 150.43    | S7-Bi2-S9-C27 | 151.5(3)  | 152.47    |
| S2-Bi1-S6-C15  | 149.4(3)  | 146.65    | S9-Bi2-S12-C22 | 150.1(3)  | 150.43    | S2-Bi1-S7-C16  | 150.1(3)  | 150.43    | S7-Bi2-S9-C27 | 151.5(3)  | 152.47    |
| S2-Bi1-S6-C15  | 149.4(3)  | 146.65    | S9-Bi2-S12-C22 | 150.1(3)  | 150.43    | S2-Bi1-S7-C16  | 150.1(3)  | 150.43    | S7-Bi2-S9-C27 | 151.5(3)  | 152.47    |

[a] Experimental; [b] “full-opt” DFT optimised.
bismuth with chelating dithiocarbamate ligands usually result in asymmetrical CS bonds and lower chemical shifts for $S_2\text{CN}$ carbons when compared to the free ligands. Also, due to the so-called "mesomeric effect", CN bonds in dithiocarbamate complexes attain a partial double bond character, which gives rise to a negative surplus charge at $S_2\text{CN}$ carbons (low chemical shift) while a surplus positive charge at the nitrogen atoms (high chemical shift). Therefore, the effective chemical shift observed for a given ligand in a complex depends on the sum total of all the effects mentioned above.

In the $^{13}\text{C}$ CP-MAS NMR spectrum of (1), the most informative region of the dithiocarbamate ligand, i.e. $S_2\text{CN}$-carbon nuclei, resulted in two partially resolved $^{13}\text{C}$ resonance signals at 202.08 and 200.59 ppm with relative integral intensities of 1:2 (see Figure 5a). On the other hand, $^{15}\text{N}$ CP-MAS NMR experiment resulted in three distinct resonance signals over a range of 186–176 ppm with relative integral

**Figure 2.** Ball and stick model structure of the complexes: (a) $[\text{Bi(DEDTC)}_3]_2$ (1) and (b) $[\text{Bi(DEDTC)}_2(\text{NO}_3)(\text{PHEN})]$ (2) showing the atom labelling scheme. H-atoms are omitted for clarity. (DTC-$S_2\text{CN}$, PHEN-$1,10$-phenanthroline).

**Figure 3.** Binuclear molecules of complex (3) $[\text{Bi}_2(S_2\text{CN(CH}_2)_5)]_6\text{H}_2\text{O}$ (a) and clear view of a pentagonal bipyramidal geometry involving $\text{Bi}_2$ (lone pair)-$S12-S11-S8-S9$ as the basal plane while $S7$ and $S10$ occupying near axial positions ($S9$ deviates by ca. $30^\circ$) (b). Displacement ellipsoids are shown at the $50\%$ probability level. H-atoms are omitted for clarity.

**Figure 4.** Unit cell representation of complex (3) $[\text{Bi}_2(S_2\text{CN(CH}_2)_5)]_6\text{H}_2\text{O}$ (projection onto the $bc$ plane).
Table 4. Experimental and GIPAW/PBE calculated $^{13}$C and $^{15}$N chemical shifts for complex (1) [Bi$_2$(CN(C$_6$H$_5$)$_3$)$_2$].

| Atoms | H-opt | Full-opt | Expt. (± 0.04) |
|-------|-------|----------|---------------|
| $^{13}$C Chemical shifts (ppm) | | | |
| $-$S$_2$CN | C1 | 203.5 | 203.3 | 202.08 |
| | C6 | 199.5 | 200.27 | 200.59 |
| | C1 | 197.9 | 202.5 | 200.59 |
| $-$CH$_3$ | C12 | 57.3 | 51.3 | 52.97 |
| | C14 | 58.1 | 49.6 | 51.46 |
| | C9 | 47.8 | 47.6 | 48.70 |
| | C7 | 47.7 | 47.3 | 48.70 |
| | C6 | 50.4 | 47.2 | 48.17 |
| | C2 | 49.0 | 46.6 | 48.17 |
| $-$CH$_3$ | C8 | 11.7 | 11 | 12.85 |
| | C10 | 10.0 | 9.3 | 12.85 |
| | C13 | 7.9 | 8.5 | 12.44 |
| | C3 | 7.9 | 8.5 | 11.76 |
| | C5 | 9.3 | 7.7 | 11.76 |
| | C15 | 7.2 | 6.3 | 10.86 |
| RMSD | 3.3 | 2.9 | |
| $^{15}$N Chemical shifts (ppm) | | | |
| $-$S$_2$CN | N2 | 203.0 | 197.1 | 185.83 |
| | N1 | 184.2 | 183.8 | 180.53 |
| | N3 | 186.7 | 183.6 | 176.32 |
| RMSD | 11.8 | 8.0 | |

Table 5. Experimental and GIPAW/PBE calculated $^{13}$C and $^{15}$N chemical shifts for complex (2) [Bi$_2$(CN(C$_6$H$_5$)$_3$)$_2$(NO)$_2$][PHEN].

| Atoms | H-opt | Full-opt | Expt. (± 0.04) |
|-------|-------|----------|---------------|
| $^{13}$C Chemical shifts (ppm) | | | |
| $-$S$_2$CN | C1 | 196.1 | 202.9 | 200.37 |
| | C6 | 199.5 | 201.0 | 197.72 |
| PHEN | C11 | 155.8 | 157.3 | 153.95 |
| | C20 | 156.7 | 156.4 | 153.22 |
| | C15 | 146.5 | 145.9 | 143.62 |
| | C16 | 139.7 | 145.4 | 139.10 |
| | C13 | 138.5 | 143.4 | 135.66 |
| | C18 | 132.8 | 138.0 | 130.63 |
| | C21 | 128.5 | 133.9 | 130.03 |
| | C14 | 130.9 | 132.3 | 130.03 |
| | C22 | 125.1 | 132.3 | 130.03 |
| | C17 | 121.1 | 131.8 | 127.7 |
| | C12 | 123.0 | 127.7 | 126.07 |
| | C12 | 123.0 | 126.3 | 124.44 |
| $-$CH$_3$ | C4 | 92.0 | 53.7 | 51.35 |
| | C2 | 53.1 | 51.6 | 50.44 |
| | C9 | 50.5 | 47.7 | 49.46 |
| | C7 | 46.2 | 47.0 | 48.44 |
| $-$CH$_3$ | C5 | 12.3 | 12.2 | 15.00 |
| | C3 | 11.5 | 9.4 | 13.28 |
| | C8 | 8.3 | 9.2 | 13.28 |
| | C10 | 3.7 | 5.1 | 9.62 |
| RMSD | 9.4 | 3.9 | |
| $^{15}$N Chemical shifts (ppm) | | | |
| $-$NO$_2$ | N5 | 356.8 | 380.0 | 374.11 |
| | N4 | 300.0 | 299.6 | 279.15 |
| PHEN | N3 | 303.9 | 294.5 | 276.75 |
| $-$S$_2$CN | N1 | 240.1 | 188.3 | 187.68 |
| | N2 | 188.4 | 186.0 | 186.39 |
| RMSD | 29.1 | 12.4 | |

Table 6. $^{13}$C and $^{15}$N NMR chemical shift parameters for complex (3) [Bi$_2$(S$_2$C(C$_6$H$_5$)$_3$)$_2$H$_2$O].

| Atoms | H-opt | Full-opt | Expt. (± 0.1) |
|-------|-------|----------|---------------|
| $^{13}$C chemical shifts | | | |
| $-$S$_2$CN | C1 | 198.9 | 200.6 | 200.8 |
| | C27 | 197.7 | 199.9 | 200.8 |
| | C22 | 196.9 | 199.8 | 200.2 |
| | C15 | 196.9 | 199.1 | 198.3 |
| | C7 | 195.5 | 198.9 | 198.0 |
| | C16 | 194.7 | 196.4 | 196.2 |
| $-$CH$_3$ | NCH$_3$ | 53.9 | 52.1 | 53.4 |
| | CH$_3$ | 25.2 | 25.1 | 26.5 |
| RMSD | 2.1 | 0.9 | |
| $^{15}$N chemical shifts | | | |
| $-$S$_2$CN | N2 | 186.8 | 185.7 | 180.1 |
| | N4 | 182.5 | 182.4 | 177.2 |
| | N3 | 181.8 | 180.9 | 175.4 |
| | N1 | 179.3 | 178.9 | 175.4 |
| | N5 | 178.1 | 178.9 | 173.2 |
| | N6 | 175.7 | 178.6 | 171.9 |
| RMSD | 5.8 | 5.6 | |

intensities of 1:1:1 (see Figure 6a). As can be seen in Table S1 (in the ESI), the XRD measured C11-($S$S) bond lengths are comparatively less asymmetric compared to C1-($S$S) and C6-($S$S) bonds. Therefore, based on our earlier discussion about the effect of the CS bond symmetry on the chemical shifts, one can expect a higher $^{13}$C chemical shift for C11 atom. Additional details about the effect of the CS bond symmetry and CN bond lengths on the $^{13}$C/$^{15}$N chemical shifts are included in the later part of this discussion. The $^{15}$N resonance line at 180.53 ppm is comparatively broader than the other two signals. This broadness of the $^{15}$N resonance line may be due to restricted C$_2$H$_4$ side chain motion or a structural disorder in this particular dithiocarbamate group in the complex. Based on our DFT calculations, we have assigned this broad signal to N1 atom (see Table 4 and Figure 5a). It can be noted that complex (1) exists as a centrosymmetric dimer in the solid-state via a weak supramolecular Bi...Bi interaction (bond length 3.21 Å). The $^{15}$C/$^{15}$N solid-state CP-MAS NMR data can be used to distinguish between ‘bridged’ and ‘terminal’ ligands. This is because for the ‘bridged’ type of a ligand, the $^{13}$C/$^{15}$N chemical shifts are often higher/lower compared to a ‘terminal ligand’. Both $^{13}$C and $^{15}$N spectra have indicated the presence of at least three structurally inequivalent dithiocarbamate ligands in the unit cell. It is a well-established fact that, especially in metal-dithiocarbamate complexes, the $^{13}$N chemical shifts are more sensitive to the subtle structural changes than $^{13}$C chemical shifts. This is evident from the larger chemical shift range of signals for $^{15}$N sites (ca. 10 ppm) than for $^{13}$C sites (ca. 1.5 ppm) in dithiocarbamate ligands of different metal dithiocarbamate complexes. Additionally, in the $^{13}$C CP- MAS NMR spectrum, one observes $^{13}$C resonances corresponding to six methylene in the range of ca. 53–48 ppm with an integrated intensity ratio of 1:1:2:2 and six methyl carbons in the range of ca. 10.8–12.8 ppm with an integrated intensity ratio of 2:1:2:1 (Figure 5a). The solid-state NMR spectral assignments for selected carbon and nitrogen sites based on DFT calculations are suggested in Table 4.
The $^{13}$C and $^{15}$N CP-MAS NMR spectra of complex (2) show very distinctive signals for dithiocarbamate and PHEN ligand atoms (see Figs. 5b and 6b). Both dithiocarbamate carbon and nitrogen atoms show two well-resolved resonance lines, with an integral ratio of 1:1, indicating the presence of at least two inequivalent dithiocarbamate ligands (or $S_2CN$ groups) in the asymmetric part of the unit cell, which is consistent with the crystal structure of the complex. In contrast to complex (1), the $^{13}$C chemical shift difference between the two dithiocarbamate carbons has increased to ca. 2.6 ppm while for $^{15}$N it has
reduced to ca. 1.3 ppm. The methyl carbons show well-resolved $^{13}$C signals while the resonance lines for methylene carbons are severely overlapped. The well-resolved $^{13}$C signals corresponding to twelve PHEN carbons appear over a range of 154.95-124.44 ppm.

Figures 5c and 6c, respectively, depict $^{13}$C and $^{15}$N CP-MAS NMR spectra of complex (3). The $^{13}$C spectrum consists of five closely spaced resonance lines between 201 and 196 ppm, which correspond to $\text{S}_2\text{CN}$ groups, with relative integral intensities of 2:1:1:1:1. These integrals indicate the presence of at least six inequivalent dithiocarbamate ligands (or $\text{S}_2\text{CN}$ groups) in the asymmetric part of the unit cell, which is consistent with the single-crystal structure for the complex (3). The $^{13}$C resonances for twelve $-\text{NCH}_2$ and eighteen $-\text{CH}_2-$ are severely overlapped and appear in the range of chemical shifts between 51–56 ppm and 24–29 ppm, respectively. On the other hand, the $^{15}$N spectrum consists of five well resolved resonances in the range of chemical shifts between 171–180 ppm, having the relative integral intensities of 1:1:2:1:1, again indicating the presence of at least six inequivalent dithiocarbamate ligands. Overall, the $^{13}$C and $^{15}$N CP-MAS NMR data of complexes (1)-(3) agree well with single crystal XRD data indicating that the systems under consideration contain a minimum of three, two, and six, respectively, structurally inequivalent dithiocarbamate groups.

The experimental chemical shifts for complexes (1)-(3) are compared with those calculated from DFT/GPaw approach in Tables 4–6, respectively, and are sorted in order of decreasing chemical shifts. In CASTEP, the $^{13}$C and $^{15}$N chemical shift calculations were performed at both the “H-opt” and “full-opt” geometry of complexes (1)-(3). The strong forces on the non-hydrogen atoms (> 2 eV/Å) in the “H-opt” structure indicated that the structural model derived from diffraction requires optimisation of the atomic coordinates for all atoms. For the “full-opt” structures, the forces on all atoms were reduced below 0.03 eV/Å. The CASTEP calculated bond lengths and bond angles are compared with the actual (experimental) values in Tables S1–S4 for complexes (1) and (2) in the ESI and in Tables 2 and 3 for complex (3). For all three complexes (1)-(3), the calculated bond parameters show some significant differences to the experimental values. It can be seen from these tables that the DFT functional PBE, for example, underestimates the longer Bi–S bond distances whereas the shorter Bi–S bond distances were overestimated. Also, all calculated bond distances for (S$_2$)C–N were comparable with small variations between 1.34–1.35 Å whereas the experimental values varied between 1.31–1.35 Å. Similar discrepancies between the experimental and DFT/PBE calculated bond parameters can be observed for other bonds as well. However, overall, there is a good agreement between the experimental and ‘full-opt’ structures, which can be seen from their RMSD values: The heavy atom RMSD between the “H-opt” and “full-opt” structures of (1), (2), and (3) were 0.074 Å, 0.08 Å, and 0.15/0.08 Å, respectively (Figs. S5–S7).

The NMR chemical shifts are known to be very sensitive even to small variations in the bond parameters. Therefore, the geometry optimisation of the X-ray structures will have a large and direct effect on the calculated chemical shifts. As can be seen from the larger RMSD values (see Tables 4–6), the calculated $^{13}$C and $^{15}$N chemical shifts for the “H-opt” structure show larger deviations from the experimental values than the “full-opt” structures. Although the calculated $^{13}$C and $^{15}$N chemical shifts for the “H-opt” structure qualitatively represent the experimental spectral pattern, the dithiocarbamate ligands show deviations in terms of the chemical shift range as well as the relative chemical shift difference between the inequivalent sites. For example, in case of complex (1), the experimental $^{13}$C/$^{15}$N chemical shift ranges for $-\text{S}_2\text{CN}$ sites are smaller (1.5/9.5 ppm) compared to the calculated ones (5.6/18.8 ppm) while the corresponding chemical shift ranges for the “full-opt” structure were 0.8/13.5. The plots of experimental vs. calculated $^{13}$C chemical shifts for “H-opt” and “full-opt” structure of complex (1) are depicted in Figure S8, showing excellent linear correlations ($R^2$ close to unity) between them. It is interesting to note that the $^{13}$C resonance lines for the bridged dithiocarbamate ligand shifted downfield compared to terminal dithiocarbamate ligands (see Table 4, Figs. 2a and 5a). Moreover, the methyl and methylene $^{13}$C resonance lines for the bridged dithiocarbamate ligand (C11-C15) are distinctive, while the $^{13}$C resonance line for the two methylene (C7/C9 and C2/C4) and two methyl (C8/C10 and C3/C5) groups of each terminal ligand overlap. In contrast to the dithiocarbamate $^{13}$C resonance lines, the chemical shift for the bridged nitrogen (N3) is smaller while the terminal nitrogens are deshielded (see Table 4, Figs. 3a and 5a). The experimental CN bond lengths are distinctive for all three dithiocarbamate ligands while for the “full-opt” structure, the C11-N3 bond length is shorter (stronger) compared to the other two CN bonds (see Table S1 in the ESI). It has been often noted that dithiocarbamate ligands with stronger CN bonds result in higher $^{13}$C and lower $^{15}$N chemical shift values for the $\text{S}_2\text{CN}$ group.[46,48,71,72] A similar trend is observed in our case as well where the stronger CN bond resulted in larger $^{13}$C chemical shift.

For complex (2), the major deviations in the calculated chemical shifts were observed for C1, C4, N3, and N5 atoms for the “H-opt” structure (see Table 5 and Figure 2b). On the other hand, as evident from the lower RMSD values (see Table 5), the calculated $^{13}$C/$^{15}$N chemical shifts for the “full-opt” structure of complex (2) showed much better agreement with the experimental values than the “H-opt” structure. The linear regression plots of experimental vs. calculated $^{13}$C/$^{15}$N chemical shifts for “H-opt” and “full-opt” structures of complex (2) are depicted in Figure S9, where the chemical shifts for the “full-opt” structure show better agreement ($R^2$ close to unity) with the experimental values.

For complex (3), as can be seen from Table 6 and Figure 5c, the chemical shifts for the bridged dithiocarbamate carbons (C1 and C22) are larger compared to terminal dithiocarbamate carbons except for C27 (see Figure 3). However, the difference between the calculated chemical shifts for C27 and C22 (full-opt) is only 0.1 ppm, which is much lower than the accuracy limit for such calculations. On the other hand, the $^{15}$N chemical shifts for the bridged ligands (N1 and N5) are smaller compared to other terminal ligands, except for N6 (see Table 6 and...
of complexes (1)-(3). In case of complexes (1) and (3), of particular interest was the $^{13}$C and $^{15}$N chemical shifts for the ‘bridging’ and ‘terminal’ dithiocarbamate ligands, where the results of GIPAW calculations supported the theory of ‘meso-meric effect’ that the $^{13}$C chemical shifts for the ‘bridging’ dithiocarbamate carbons are slightly larger than the ‘terminal’ ones and vice versa for the $^{15}$N chemical shifts. Because of large forces on atoms of the experimental XRD structures, the best correspondence with the experimental NMR chemical shifts were obtained when the atomic positions of all atoms in the single crystal structures of both complexes were optimised. The present approach can be applied to get complementary structural information of computationally demanding d- and f-block systems and to refine the crystal structures.

Deposition Number 1880534 (for 3) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Supporting Information Summary

The supporting information contains details about the experimental methods and simulations, tables providing an additional information about bond parameters of the complexes and GIPAW calculated nuclear shielding values, and figures depicting solution-state $^1$H and $^{13}$CNMR spectra, overlay of experimental and calculated structures, and linear regression plots of experimental vs. GIPAW/PBE calculated $^{13}$C/$^{15}$N chemical shifts.

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Conflict of Interest

The authors declare no conflict of interest.

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