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Synthesis and structural studies on Ni(II) dithiocarbamates: Exploring intramolecular Ni $\cdots$ H–C interactions

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ABSTRACT

Five new Ni(II) dithiocarbamates with NiS₄, NiS₂PN and NiS₂PCl coordination spheres viz. [Ni(bupmbzdtc)₂] (**1**), [Ni(bupmbzdtc)(PPh₃)(NCS)] (**2**), [Ni(bupmbzdtc)(PPh₃)Cl] (**3**), [Ni(4-dpmpzdtc)(PPh₃)Cl] (**4**) and [Ni(pbbzbudtc)(PPh₃)(NCS)] (**5**) where, bupmbzdtc = *N*-butyl(*p*-

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methylbenzyl)dithiocarbamate anion, 4-dmpzdtc = 4-(diphenylmethyl)piperazinecarbodithioato anion, pbbzbudtc = *N*-(*p*-bromobenzyl)butyl-dithiocarbamate anion and PPh₃ = triphenylphosphine, were synthesized and characterized by UV, IR, NMR and single crystal X-ray diffraction methods. Spectral results suggest square planar geometry around the Ni(II) metal center for all the synthesized complexes. Single crystal X-ray structural analyses agree to these findings but also show evidence of intramolecular C-H...Ni interactions (2.815 for **3** and 2.869 Å for **5**) in complexes **3** and **5** in the solid state analyzed further by computational (DFT) methods. Herein, these and other structural aspects of homo- (**1**) and heteroleptic dithiocarbamate complexes (**2** - **5**) of Ni(II) are discussed.

Keywords: Dithiocarbamate; X-ray structural analysis; NMR; C-H...Ni interaction

1. Introduction

Transition metal dithiocarbamates are important due their contribution in supramolecular architectures [1], biological significance [2-5] and industrial applications [6, 7]. Most importantly they have found use as single source precursors for metal sulfide nanoparticles and thin films as the solubility, volatility and decomposition properties of these complexes can be tuned by changing the amine substituents [8-12]. Additionally, the advantage of dithiocarbamate complexes is their easy preparation from inexpensive raw materials.

Studies of homoleptic Ni(II) dithiocarbamates (Ni(dtc)₂) with planar NiS₄ are found in relatively large extent in the literature whereas investigations concerning their reactivity are less abundant. It has been shown that Ni(dtc)₂ exhibit interesting variation in reactivity with soft Lewis bases like phosphines and hard nitrogenous bases [9-11, 13-17]. Also, the rigid core of M(II) dithiocarbamates (M = Ni or Pd or Pt), where thirteen atoms lie in an approximate plane, (in mixed ligand complexes the approximate plane covers generally at least nine atoms) offers a

possibility of various secondary supramolecular synthons such as $M \cdots H-C$, (MS_2C chelate) $\pi \cdots H-C$ and $\pi-\pi$ interactions besides hydrogen bonding [1, 18-22]. Among which, recently attention has been focused on $M \cdots H-C$ interactions in d^8-ML_4 complexes and in some cases it was found that the proton involved in the interaction displayed hydridic character [23]. The emphasis of this work is to study the chemistry involving the synthesis and reactivity of Ni(II) dithiocarbamates and also to analyze the structural inferences mainly in the context of $M \cdots H-C$ interactions in d^8-ML_4 . In this paper we report the synthesis (Scheme 1), spectral and structural studies of complexes with NiS_4 , NiS_2PN and NiS_2PCl coordination spheres viz. $[Ni(bupmbzdtc)_2]$ (**1**), $[Ni(bupmbzdtc)(PPh_3)(NCS)]$ (**2**), $[Ni(bupmbzdtc)(PPh_3)Cl]$ (**3**), $[Ni(4-dpmpzdtc)(PPh_3)Cl]$ (**4**) and $[Ni(pbbzbudtc)(PPh_3)(NCS)]$ (**5**) where, bupmbzdtc = N-butyl(p-methylbenzyl)dithiocarbamato anion, 4-dpmpzdtc = 4-(diphenylmethyl)piperazinecarbodithioato anion, pbbzbudtc = N-(p-bromobenzyl)butyl-dithiocarbamato anion and PPh_3 = triphenylphosphine. The synthesized compounds have been characterized by UV, IR and NMR spectroscopy. Single crystal X-ray crystal structural analysis of **1** - **5** are also reported with a specific attention on intramolecular $M \cdots H-C$ interactions analyzed further by computational (DFT) methods.

2. Experimental

All the reagents and solvents were commercially available analytical grade materials and were used as supplied, without further purification. IR spectra were recorded on Bruker VERTEX 70 spectrometer (range $4000-400\text{cm}^{-1}$). UV-Vis spectra were recorded in CH_2Cl_2 on a PerkinElmer Lambda 45 spectrophotometer. 1H , ^{13}C and ^{31}P NMR spectra were recorded on Bruker Avance 500 MHz spectrometer operating at 303K, using $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded in proton decoupled mode. In 1H and ^{13}C NMR runs the chemical shifts

are referenced to the signal of the internal tetramethylsilane (TMS) and in ^{31}P NMR to the signal of the external 85 % orthophosphoric acid in a 1 mm diameter capillary tube inserted coaxially inside the 5 mm NMR-tube.

2.1. Synthesis of complexes

2.1.1. Bis(*N*-butyl(*p*-methylbenzyl)dithiocarbamato)nickel(II), $[\text{Ni}(\text{bupmbzdtc})_2]$ (**1**)

A mixture of *N*-butyl(*p*-methylbenzyl)amine (177 mg, 1 mmol) and CS_2 (76 mg, 1 mmol) in ethanol (50 mL) was kept at $-5\text{ }^\circ\text{C}$ for 10 minutes and to this pale yellow solution, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (145 mg, 0.5 mmol) in water (25 mL) was then added slowly with vigorous stirring. The dark green precipitate obtained was filtered, washed with ether and water, allowed residual water to evaporate, and dried in a desiccator. Single crystals suitable for X-ray analysis were obtained by recrystallization from chloroform. Yield: 80 %, dec. $>250\text{ }^\circ\text{C}$; IR (KBr, cm^{-1}): 2963, 2928 (C-H), 1490 (C=N), 961 (C-S); *Anal.* Calc. for $\text{C}_{26}\text{H}_{36}\text{N}_2\text{NiS}_4$: C, 55.41; H, 6.44; N, 4.97. Found: C, 55.26; H, 6.28; N, 4.87%.

2.1.2. (*N*-butyl(*p*-methylbenzyl)dithiocarbamato)(isothiocyanato)(triphenylphosphine) nickel(II), $[\text{Ni}(\text{bupmbzdtc})(\text{PPh}_3)(\text{NCS})]$ (**2**)

A mixture of $\text{Ni}(\text{bupmbzdtc})_2$ (**1**) (282 mg, 0.5 mmol), PPh_3 (260 mg, 1 mmol), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (145 mg, 0.5 mmol) and KSCN (97 mg, 1 mmol) was refluxed for 3h in acetonitrile-methanol mixture (2:1, 75 mL) and was then concentrated to *ca.* 25 mL. The dark purple-red solution obtained was filtered and was allowed to evaporate. After 2 days, the solid precipitate was filtered and dried in a desiccator. Single crystals suitable for X-ray analysis were obtained by recrystallization from the same solvent mixture. Yield: 75 %, dec. $195\text{ }^\circ\text{C}$; IR (KBr,

cm⁻¹): 3073, 3051, 3006, 2928 (C-H), 1514 (C=N), 997 (C-S); *Anal.* Calc. for C₃₂H₃₃N₂NiPS₃: C, 60.86; H, 5.27; N, 4.44. Found: C, 60.62; H, 5.18; N, 4.32%.

2.1.3. (Chloro)(*N*-butyl(*p*-methylbenzyl)dithiocarbamato)(triphenylphosphine) nickel(II), [Ni(*bupmbzdtc*)(PPh₃)Cl] (**3**)

A mixture of Ni(*bupmbzdtc*)₂ (**1**) (282 mg, 0.5 mmol), PPh₃ (260 mg, 1 mmol) and NiCl₂·6H₂O (120 mg, 0.5 mmol) was refluxed for 2 h in chloroform (50 mL) and then concentrated to *ca.* 25 mL. The purple-red solution obtained was filtered and allowed to evaporate. The solid precipitate was filtered and dried in a desiccator. Single crystals suitable for X-ray analysis were obtained by recrystallization from chloroform. Yield: 70 %, dec. 190 °C; IR (KBr, cm⁻¹): 3062, 3023, 2931 (C-H), 1510 (C=N), 997 (C-S); *Anal.* Calc. for C₃₁H₃₃ClNNiPS₂: C, 61.15; H, 5.46; N, 2.30. Found: C, 61.08; H, 5.29; N, 2.21%.

2.1.4. Bis(4-(diphenylmethyl)piperazinecarbodithioato) nickel(II), [Ni(4-*dpmpzdtc*)₂]

The preparation and its single crystal X-ray structure was reported already [9].

2.1.5. (Chloro)(4-(diphenylmethyl)piperazinecarbodithioato)(triphenylphosphine) nickel(II), [Ni(4-*dpmpzdtc*)(PPh₃)Cl] (**4**)

A mixture of Ni(4-*dpmpzdtc*)₂ (357 mg, 0.5 mmol), PPh₃ (260 mg, 1 mmol) and NiCl₂·6H₂O (120 mg, 0.5 mmol) was refluxed for 2 h in chloroform (50 mL) and then concentrated to *ca.* 25 mL. The purple-red solution obtained was filtered and allowed to evaporate. The solid precipitate was filtered and dried in a desiccator. Single crystals suitable for X-ray analysis were obtained by recrystallization from a mixture of acetone and chloroform (1:1). Yield: 70 %, dec. 175 °C; IR (KBr, cm⁻¹): 3066, 3002, 2969, 2909 (C-H), 1522 (C=N), 987

(C-S); *Anal.* Calc. for $C_{39}H_{40}ClN_2NiOPS_2$: C, 63.13; H, 5.43; N, 3.78. Found: C, 62.92; H, 5.32; N, 3.68%.

2.1.6. *Bis(N-(p-bromobenzyl)butyldithiocarbamato)nickel(II)*, $[Ni(pbbzbudtc)_2]$

The same procedure as described in section 2.1.1 and *N*-(*p*-bromobenzyl)butylamine was used instead of *N*-butyl(*p*-methylbenzyl)amine.

2.1.7. *(N-(p-bromobenzyl)butyldithiocarbamato)(isothiocyanato)(triphenylphosphine) nickel(II)*, $[Ni(pbbzbudtc)(PPh_3)(NCS)]$ (**5**).

A mixture of $Ni(pbbzbudtc)_2$ (347 mg, 0.5 mmol), PPh_3 (260 mg, 1 mmol), $Ni(NO_3)_2 \cdot 6H_2O$ (145 mg, 0.5 mmol) and KSCN (97 mg, 1 mmol) was refluxed for 3 h in acetonitrile-methanol solvent mixture (2:1, 75 mL) and was then concentrated to *ca.* 25 mL. The dark purple-red solution obtained was filtered and was allowed to evaporate. After 2 days, the solid separated was filtered and dried in a desiccator. Single crystals suitable for X-ray analysis were obtained by recrystallization from acetonitrile:dichloromethane (1:1) mixture. Yield: 78 %, dec. 189 °C; IR (KBr, cm^{-1}): 3070, 3050, 2966, 2927 (C-H), 1509 (C=N), 969 (C-S); *Anal.* Calc. for $C_{31}H_{30}BrN_2NiPS_3$: C, 53.47; H, 4.34; N, 4.02. Found: C, 53.16; H, 4.26; N, 3.96%.

2.2. X-ray crystallography

Agilent Supernova (Cu/Mo dual flux micro-focus sources) diffractometer was used to acquire the data at 123 K using Cu- K_α radiation ($\lambda = 1.54184 \text{ \AA}$). Data collections and reductions, as well as analytical numeric absorption corrections using multifaceted crystal models, were all made by program *Crysalis^{Pro}* [24]. All the structures were solved by direct methods using *SHELXS* [25] and were refined using *SHELXL-97* [25] both implemented in program *Olex²* [26]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms could be located

from the difference Fourier map and case sensitively were refined either isotropically without restrictions (H atoms involved in the C–H...Ni contacts) or as riding atoms with isotropic parameters 1.2 (hydrogens associated to methylene of sp^2 carbon atoms) or 1.5 (methyl hydrogens) times to their host atoms. Details of crystal data, data collection and refinement parameters for complexes **1** - **5** are summarized in Table 1. Selected bond lengths and bond angles for **1** - **5** are given in Table 2. The figures of molecular unit are drawn using program Olex² with thermal ellipsoids presented at the 50 % level of probability. Packing figures are made using program Mercury [27].

2.3. DFT calculations

All DFT calculations were carried out using Gaussian09 [28] and were done in the gas phase using PBE0 hybrid functional [29] with Def2-TZVP basis sets for all atoms [30]. Grimme's D3 dispersion correction was also included into all calculations [31]. In search of energy minima vibrational analyses were carried out to confirm that no imaginary frequencies were present. Potential energy surface (PES) scan of model complex **3'** was carried by taking the optimized structure as a starting point and disrupting the essential H...Ni distance in ± 0.02 Å increments from its minimum, freezing this distance and allowing the rest of the system to relax to its minimum energy (see Fig. 8 for graphical presentation of E vs. H...Ni distance). Multifunctional wavefunction analyzer (multiwfn) was used to carry out analyses based on Bader's atoms in molecules theory [32] whereas natural bonding orbital (NBO) analyses were carried out with the NBO version 3.1 code implemented in the Gaussian 09 program package [33].

3. Results and discussion

3.1. Electronic spectral studies

Electronic spectra show bands at 630, 618 and 630 nm for complexes **1**, **3** and **4** respectively due to $d_{xy} \rightarrow d_{x^2-y^2}$ transition [34]. The intense bands observed at 420, 482, 477, 506 and 484 nm for complexes **1** - **5** respectively are assigned to $d_z^2 \rightarrow d_{x^2-y^2}$ transition based on the single crystal electronic spectral studies of the similar complexes [34]. Intra ligand charge transfer bands were observed below 350 nm. Electronic spectral data suggests that geometry around the metal in all the cases (**1** - **5**) is most likely square planar [9-11, 14-17].

3.2. IR spectral studies

The ν_{C-N} and ν_{C-S} bands are characteristic of complexes with dithiocarbamate ligands. IR spectra show ν_{C-N} bands at 1490, 1514, 1510, 1522 and 1509 cm^{-1} for **1** - **5** respectively. The increase in wave number for the mixed ligand complexes (**2** - **3**) compared to that of parent (**1**) exemplifies the increasing drift of electron density from the dithiocarbamate towards the metal center thereby increasing the polar thioureide structures in **2** - **3**. Similarly, the parent complex of **4** showed the ν_{C-N} band at the lower wave number of 1516 cm^{-1} [9]. The band due to N-coordinated NCS^- anion was observed at 2094 and 2093 cm^{-1} for **2** and **5** respectively. For all the complexes the ν_{C-S} bands were observed without any splitting around 1000 cm^{-1} confirming the isobidentate coordination.

3.3. NMR Spectral studies

3.3.1. ^1H NMR

Compounds **2** - **5** showed a set of closely spaced resonances for protons from dithiocarbamate moiety due to asymmetric NiS_2PN (**2** and **5**) and NiS_2PCl (**3** and **4**) coordination spheres respectively. However, for complex **1** with symmetric coordination environment around nickel, each group of protons give rise to only one signal. In **1** - **3** and **5**, the benzylic protons are strongly deshielded as they were flanked by electron withdrawing

dithiocarbamate and aryl groups. The α -CH₂ protons of butyl group are also considerably deshielded due to their close proximity to electron withdrawing NCS₂ fragment whereas, the degree of deshielding diminishes while going further down the alkyl chain. Aromatic protons resonate in the region of 7.0 - 7.74 ppm.

3.3.2. ¹³C NMR

Normally, the NCS₂ carbon in free ligand (potassium salt of dithiocarbamate) resonates around 215 ppm [18-21] and complexation results in an upfield shift and thereby resonance appears around 205 - 210 ppm [9-11, 13-17] in homoleptic Ni(dtc)₂ complexes. In heteroleptic complexes with the general formula of [Ni(dtc)(PPh₃)X] where X = SCN⁻ or Cl⁻ or CN⁻, the same carbon appears around 200 - 205 ppm. It has already been reported that [35], in dithiocarbamate complexes ν_{C-N} (thioureide) band values in IR spectrum and $>N^{13}CS_2$ chemical shifts in ¹³C NMR spectrum are inversely proportional to each other. The same effect is also observed in our case (refer Table 2). Aromatic carbons are resonating in the range of 122.7 - 143.9 ppm. The benzylic and α -CH₂ carbons (of butyl group) are significantly deshielded and they were observed around 52 and 48 ppm respectively for **1** - **3** and **5**. In **2**, **3** and **5** the α -carbon appeared as two separate signals due to asymmetric coordination environment around the nickel. However, such difference is not witnessed for remaining carbons of the butyl group in dithiocarbamate moiety (except **3**) and the peaks corresponding to these carbons are observed at 28.7 (β -CH₂), 19.9 (γ -CH₂) and 13.6 ppm (δ -CH₃), respectively. The assignment of α and β carbon signals for **4** are based on the 2D NMR spectral studies of the structurally similar compounds reported already [9].

3.3.3. ³¹P NMR

^{31}P chemical shifts of complexes with NiS_2PN (**2** and **5**) and NiS_2PCl (**3** and **4**) coordination spheres showed clear differences and they were observed around 22 and 29 ppm, respectively. In the absence of impact from dithiocarbamate backbone, the observed dissimilarity could be attributed to the difference in electron withdrawing properties of the auxiliary ligands, like NCS^- and Cl^- . As observed earlier [9, 10] the pronounced deshielding of coordinated phosphorus in **2** - **5** compared to the free triphenylphosphine ($\delta = -5$ ppm) [36] confirms the effective bonding.

3.4. Single crystal X-ray diffraction analysis

We were successful in obtaining good quality single crystals of all complexes **1** - **5** which allowed a detailed single crystal X-ray analysis of their solid state structures (see Figures 1 - 5 for molecular structures and packing schemes). Homoleptic complex **1** crystallizes in the monoclinic space group $C2/c$ with half a molecule in the asymmetric unit (Fig. 1). The Ni(II) ion lies at the center of inversion thus resulting in a zero mean plane deviation of the NiS_4 unit from planarity. The coordination environment, however, deviates from ideal square planarity as the S–Ni–S bite angles and inter-ligand S–Ni–S angles are roughly 80° and 100° , respectively (refer to Table 2). The planarity of the coordination environment of Ni(II) in **1** is in accordance with the observed diamagnetism of the complex. The observed planarity extends throughout dithiocarbamate fragments of the ligand backbones, thus showing evidence of delocalization of the π -electrons over the C–S and C–N bonds. This is also supported by the respective bond distances which imply partial double bond character for both C–S and C–N bonds and are similar to other dithiocarbamate complexes [9-11, 13-21]. In the lack of functional groups that would influence in strong directional intermolecular binding, the solid state packing of **1** is seemingly governed by weak van der Waals interactions.

Fig. 1 Molecular conformation with selective atom numbering for **1** derived from its crystal structure.

Complex **2**, which is a heteroleptic complex derived from **1** with thiocyanate and triphenylphosphine auxiliary ligands, crystallizes in the triclinic space group *P*-1 with two discrete molecules in the unit cell and one in the asymmetric unit. The Ni(II) coordination environment shows a slight deviation from planarity (0.046 Å). The geometry around the central metal ion in this heteroleptic complex is closer to perfect square planar than in **1** as the auxiliary ligands provide ca. 90° N–Ni–P bonding angle [N(2)–Ni(1)–P(5) = 89.98(5)°; S(24)–Ni(1)–S(25) = 79.05(2)]. The bonding parameters of the dithiocarbamate functional group are mostly similar to its parent complex **1**. However, the Ni–S bonds exhibit mild asymmetry caused by PPh₃, which (being a good π -acceptor and thus a stronger *trans*-influencing ligand compared to NCS[−]), induces elongation of the Ni–S bond *trans* to the Ni–P bond (Table 2). The intermolecular contacts between the heteroleptic complex units in the solid state occur mostly via

the auxiliary ligands in the form of C–H⋯phenyl and C–H⋯NCS[−] interactions. For example, an infinite chain of molecular units is formed along the unit cell *b*-axis via a contact between PPh₃ and *p*-methylbenzyl groups of adjacent molecules (Fig. 2).

Fig. 2 Molecular conformation of **2** with selective atom labeling shown and partial view of selected intermolecular contacts (below) present in its crystal structure.

Complex **3** crystallizes in monoclinic crystal system (space group *Pn*) and comprises of one molecule in the asymmetric unit and two in the unit cell. The structure consists of distorted square planar metal coordination with a NiS₂PCl coordination sphere. Replacing the NCS[−] ligand

(**2**) to Cl^- (**3**) does not significantly alter the intramolecular bonding parameters regarding the backbone of the molecular unit. The nickel atom in **3** deviates from the mean plane of the square planar geometry by 0.070 Å, *i.e.* slightly more in contrast to complex **2**. As in **2**, the deviation from the perfect square planar coordination geometry also arises from the small dithiocarbamate bite angle and interligand coordination angle (P–Ni–Cl) which is probably affected by the steric influence between the PPh_3 and Cl^- ligands. Similarly to **2**, the strong *trans* influencing ligand PPh_3 (vs. Cl^-) induces a small elongation of the Ni–S bond *trans* to the Ni–P bond [$d(\text{Ni1–S25}) = 2.2293(7)$ Å; $d(\text{Ni1–S24}) = 2.1742(7)$ Å]. The C–N and C–S distances are comparable to **1** and **2**. Intermolecular contacts occur mostly between the aliphatic and aromatic functional groups whereas Cl^- , being more sterically shielded than NCS^- anion in **2**, plays a smaller role. Hence, similar C–H $\cdots$ phenyl contact patterns to **2** can also be observed in **3** (Fig. 3).

Fig. 3 Molecular conformation of **3** with selective atom labeling and partial view of selected intermolecular contacts (Below) present in its crystal structure.

Heteroleptic complex **4** (Fig. 4), with its bulky piperazine derived dithiocarbamate backbone, is different to other complexes in this study. It crystallizes in triclinic space group $P\bar{1}$ and its asymmetric unit comprises of two complex molecules ($Z'=2$) and two acetone solvent molecules whereas a total of four molecules occupy the unit cell ($Z=4$). In regards to the bonding parameters the two distinct molecules exhibit similar metal-ligand distances and angles to each

other and comparable to other heteroleptic complexes presented in this study (central metal ions in the two asymmetric units deviate from the mean plane by 0.052 Å (Ni1) and 0.053 Å (Ni1B), respectively). Piperazine rings in the dithiocarbamate fragment are in chair conformation. This enables an interaction between two adjacent molecular units in the solid state via the piperazine methylene groups and the dithiocarbamate moieties (Fig. 4). The overall packing is dominated by aliphatic and aromatic van der Waals interactions.

Fig. 4 Molecular conformation with selective atom numbering of **4** (only one of the two molecules existing in an asymmetric unit is shown, also solvent molecules (acetone) are removed for clarity), and partial view of C–H $\cdots$ S₂CN intermolecular contacts (down) observed in its crystal structure.

Complex **5** (Fig. 5) is a close structural analog to **2** but with the *para*-methyl substituent in the dithiocarbamate ligand replaced with a bromine. It crystallizes in triclinic system with space group *P*–1 with two discrete complex molecules in the unit cell and one in the asymmetric unit. The most obvious difference between the structure of **5** and other studied heteroleptic complexes (**2** - **4**) is the out-of-plane distortion of the NCS[–] auxiliary ligand in **5** [dihedral angle N(2)–Ni(1)–S(24)–S(25) = 171.07(6)]. As the steric properties around the coordination center in **5** are similar to **2**, wherein planar coordination geometry is observed, the reason for the non-planarity in **5** most likely arises from packing effects. Close observation of the intermolecular interactions in crystal structure of **5** reveals a relatively short contact between the thiocyanate group's S atom and Br atom of the 4-bromobenzyl group of the adjacent molecule (Fig. 5). By considering the interatomic distance [Br(32)–S(4) = 3.4906(7) Å] and angle [C(32)–Br(32)–S(4) = 169.88(6)°] this contact can be described as a halogen bond [37]. Interestingly, the NCS[–] group associated with the halogen bond is bent to the direction of this halogen bond. It can be therefore assumed that the attractive NCS[–] $\cdots$ Br halogen bonding interaction is one of the main underlying reasons behind the geometrical differences between the coordination units in **2** and **5**. In addition to the out-of-plane bending, an increased degree of asymmetry is observed in the Ni–S bonds in **5** compared to **2**; i.e. roughly 0.08 Å vs. 0.05 Å respectively for **5** and **2** (see Table 2).

Fig. 5 Molecular conformation with selective atom numbering for compound **5**, and partial view of halogen bonding between Br and S atoms.

The presented structural data shows that the alteration of the dithiocarbamate ligand backbone has a very limited effect on the coordination geometry of the respective metal complexes whereas changing the auxiliary ligands tends to have more influence on the bond parameters and thereby to the geometry as well. Only when a direct interference between the dithiocarbamate ligand backbone and the coordination environment occurs, such as the halogen bonding interaction between the 4-bromobenzyl functionality and NCS^- in **5**, a more significant change is observed. Indeed, the incorporation of functionalities to the dithiocarbamate ligand, that give rise to strong and directional intermolecular interactions, is an attractive way to modify both the coordination geometry and solid state packing of these compounds. Another interesting

aspect regarding these compounds is their structural isomerism which arises from the possibility of unsymmetrical substitution of functional groups to the carbamic nitrogen. Therefore, the dithiocarbamate complexes **2**, **3** and **5** can occur in two forms as shown in Fig. 6. In the solid state, complexes **2** and **5** are in isomeric form B whereas **3** exists in form A. Similarly, homoleptic complexes with the NiS₄ coordination sphere and asymmetric dithiocarbamate ligands also exhibit structural isomerism in respect to the carbamic substitution. To exemplify, both **1** and its bis(N-benzylbutyldithiocarbamato)nickel(II) analog [10] exhibit solid state structures wherein the bulky benzyl groups of the dithiocarbamate ligands are in the opposite side in respect to each other. This can be illustrated by, for example, comparing them to alkenes with “*E*” configuration by considering the planar >NCS₂NiS₂CN< fragment as equivalent to the C=C alkene moiety. This type of structural isomerism can give rise to challenges regarding rational design of dithiocarbamate complexes but, on the other hand, it further enriches their structural chemistry.

Fig. 6 Form A and B for complexes **2**, **3** and **5**.

3.5. Ni...H–C interactions

In the solid state structure of **3** and **5** (Fig. 7), relatively low intramolecular distances (2.815 and 2.869 Å respectively) are present between the metal and a phenyl *ortho* hydrogen

belonging to the PPh_3 group. Both these contacts have an intramolecular $\text{Ni}\cdots\text{H}-\text{C}$ angle of roughly 120° with the *ortho* hydrogen hovering at the near axial position of the pseudo square-pyramidal geometry. Generally, three types of different $\text{M}\cdots\text{H}-\text{C}$ contacts namely (i) agostic (ii) anagostic and (iii) hydrogen bonding are observed in square-planar $d^8\text{-ML}_4$ complexes [38-41]. The agostic interaction ($d(\text{M}\cdots\text{H})$ 1.8 - 2.3 Å; $\angle\text{M}\cdots\text{H}-\text{C}$ $90\text{--}140^\circ$) is referred to as 3 centered 2 electron (3c-2e) interaction. The anagostic (3c-4e) interaction is largely electrostatic in nature with the comparatively long $\text{M}\cdots\text{H}$ distances of 2.3 - 2.9 Å and $\angle\text{M}\cdots\text{H}-\text{C}$ of $110 - 170^\circ$ whereas the hydrogen bonding involves 3c-4e interaction with nearly linear geometry. The anagostic and hydrogen bonding interactions require the presence of a fully occupied and axially oriented $\text{M}(\text{dz}^2)$ orbital whereas agostic interaction is a covalent interaction between an occupied $\sigma(\text{C}-\text{H})$ orbital and a partially vacant metal orbital. In dithiocarbamate complexes the $\text{M}\cdots\text{H}-\text{C}$ interactions have been in general described as anagostic interactions [18-21] that in most cases occur between separate molecular units (intermolecular interactions). On the other hand, few recent reports show that $\text{M}\cdots\text{H}-\text{C}$ interactions can also be present within the complex units. In a recent interesting report by Scherer *et al.* $\text{M}\cdots\text{H}-\text{C}$ interactions were studied in the context of square-planar $d^8\text{-ML}_4$ complexes using experimental (X-ray diffraction and IR spectral studies under high pressure) and computational methods [42]. They concluded that the $\text{M}\cdots\text{H}-\text{C}$ (where M = square-planar d^8 metal) interaction is weakly attractive and, in fact, shows features fitting to that of 3c-2e agostic interaction. The report further states that “*the expression “anagostic interactions”, which describes $\text{M}\cdots\text{H}-\text{C}$ interactions in square planar $d^8\text{-ML}_4$ in terms of repulsive 3c-4e interactions, should be used more carefully*” as the “*bonding concept is based on a purely electrostatic description in terms of crystal field theory and ignores the*

consequences of strong covalent metal–ligand interactions.” Hence, there are differences of opinion on the nature and description of $d^8\text{-M}\cdots\text{H-C}$ interactions.

Fig. 7 C–H $\cdots$ Ni contacts observed in crystal structures of **3** and **5**. Distances are reported in Å.

3.6. DFT analysis

The C–H $\cdots$ Ni interactions in **3** and **5** (Fig. 7) satisfy the geometrical requirements of anagostic interaction (γ type) in terms of specified H $\cdots$ Ni distances (2.815 Å in **3** and 2.869 Å in **5**, taken from riding H atoms; normalization of the H atoms would result in slightly smaller distances) as well as C–H $\cdots$ Ni angles (119.77° in **3** and 120.99° in **5**). The pertinent question to be answered is the nature of the interaction; that is, whether it can be described as anagostic or weakly agostic interaction? In the absence of experimental (X-ray diffraction or IR studies under high pressure) evidence we conducted a theoretical evaluation of a model system **3'** consisting of Ni(II) dimethyldithiocarbamate complex (Fig. 8) with chloride and triphenylphosphine auxiliary ligands (structural analog of **3**). Geometry optimization of the model system, using DFT (PBE0/Def2-TZVP level of theory with Grimme's D3 dispersion correction), yielded an energy minimum structure with bonding parameters surrounding the Ni(II) center well comparable to

those observed in solid state structure of **3**. The same energy minimum structure was obtained regardless of whether starting the optimization from geometry similar to **3** or **4**. The most notable difference in geometries between **3** and **3'** is the C–H···Ni distance which is roughly 0.1 Å longer in **3'**. Such a difference can be explained by packing effects in the experimental structure, but only if the C–H···Ni interaction can be easily displaced from its energy minimum geometry. In order to clarify this we conducted a PES scan of the system along the Ni···H distance of **3'**. As evidenced by the PES graph (Fig. 8, right) the C–H···Ni interaction has a clear but very shallow energy minimum as disruption of the H···Ni distance by ± 0.2 Å results only in ca. 1 kJ/mol energy penalty. This offers an explanation to the difference of H···Ni distances between the geometries of **3** and **3'** and also why no C–H···Ni short contacts ($d(\text{H}\cdots\text{Ni}) < 2.9$ Å) are observed in the crystal structures of **2** and **4**, as such a small loss of intramolecular stabilization energy is easily compensated by the intermolecular packing interactions. Since, it is a weak interaction the expected deshielding of *ortho* proton (characteristic of anagostic interaction) of PPh₃ in PMR was not observed clearly and the signal merged with the other aromatic proton signals. Thus far we have recognized the C–H···Ni interaction to be attractive but not yet know much about its nature. Atoms in molecules (AIM) analysis, which is a convenient way of analyzing intramolecular (in addition to intermolecular) interactions, show no bond critical points between the H and Ni atoms of the C–H···Ni fragment. Nor does analyzing the NBO atomic charges and C–H distances give any indication that the particular H atom, involved in the C–H···Ni contact, would be noticeably different to other aromatic H atoms in the PPh₃ system. A slight deviation of Wiberg bond index [43] from zero (0.0026 between the H and Ni atoms) can however be taken as an indication of a weak C–H···Ni interaction. In overall, we can conclude

that the C–H···Ni contacts found in crystal structures of studied dithiocarbamate complexes are most likely weakly attractive and show the characteristics of anagostic interaction.

Fig. 8 DFT optimized structure of **3'** (left) and results of the PES scan along the C–H···Ni distance (right). Distances are reported in Å.

4. Conclusions

Three different homoleptic dithiocarbamate Ni(II) complexes were synthesized and subjected to ligand exchange reactions with soft Lewis acids and hard nitrogenous bases. The five new complexes, with three different coordination spheres (NiS₄, NiS₂PN and NiS₂PCl), were analyzed by spectral and single crystal X-ray techniques. The analyses confirm the completion of the described ligand exchange reactions thus verifying the validity of this method as a convenient route to produce heteroleptic systems with different types of ligands. All five complexes exhibit distorted square planar geometry due to the characteristic bite angle associated with the dithiocarbamate unit. They also show rich structural chemistry in the solid state with different types of packing interactions, such as halogen bonding and C–H··· π , governing the intermolecular ordering. Interestingly, two (**3** and **5**) of the five synthesized systems show

intramolecular C-H...Ni contacts in the solid state which led us to study their nature with DFT methods. A thorough computational analysis of a model system showed that a weak anagostic interaction most likely occurs between the H and Ni atoms which, on the other hand, is not strong enough to alone dictate the complex conformation. However, if desired, this type of interaction could be strengthened by the selection a more suitable auxiliary ligand and thus be used a tool to control the complex geometry.

Appendix A. Supplementary data

Crystallographic data have been deposited with Cambridge Crystallographic Data Collection Centre: Deposition number(s) CCDC1429012-1429016, for compounds **1** - **5** respectively. Copies of the data can be obtained free of charge on request quoting the deposition number from, The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or [www:http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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Scheme 1 Synthesis of complexes 1-5.

Table 1
Crystallographic data of **1–5**.

Complex	1	2	3	4	5
Empirical formula	C ₂₆ H ₃₆ N ₂ NiS ₄	C ₃₂ H ₃₃ N ₂ NiPS ₃	C ₃₁ H ₃₃ CINNiPS ₂	C ₃₉ H ₄₀ CIN ₂ NiOPS ₂	C ₃₁ H ₃₀ BrN ₂ NiPS ₃
Formula weight	563.52	631.46	608.83	741.98	696.34
Temperature/K	123.01(10)	123.01(10)	123.01(10)	123.00(10)	123.01(10)
Crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic
Space group	<i>C2/c</i>	<i>P-1</i>	<i>Pn</i>	<i>P-1</i>	<i>P-1</i>
a/Å	15.2695(7)	10.5741(7)	9.36017(13)	9.41788(9)	9.8257(8)
b/Å	9.9696(4)	11.6978(13)	9.40553(15)	10.65206(11)	11.2400(14)
c/Å	18.5320(7)	13.9524(12)	16.3594(3)	36.5502(5)	15.8451(14)
α /°	90	102.386(8)	90	89.5887(10)	109.932(10)
β /°	104.740(4)	91.985(6)	91.8965(13)	86.9179(9)	93.562(7)
γ /°	90	109.965(8)	90	84.8890(8)	109.442(9)
Volume/Å ³	2728.31(19)	1573.4(3)	1439.45(4)	3646.84(7)	1520.6(3)
Z	4	2	2	4	2
ρ_{calc} mg/mm ³	1.372	1.333	1.405	1.351	1.521
μ /mm ⁻¹	4.009	3.406	3.863	3.181	5.064
F(000)	1192.0	660.0	636.0	1552.0	712.0
Crystal size/mm ³	0.148 × 0.083 × 0.043	0.328 × 0.149 × 0.054	0.220 × 0.198 × 0.132	0.360 × 0.138 × 0.047	0.237 × 0.185 × 0.115
Radiation	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)
2 θ range for data collection	9.87 to 135.99°	6.532 to 135.978°	10.738 to 135.994°	7.266 to 135.998°	8.734 to 135.984°
Index ranges	-18 ≤ h ≤ 18, -11 ≤ k ≤ 11, -15 ≤ l ≤ 22	-12 ≤ h ≤ 8, -13 ≤ k ≤ 14, -16 ≤ l ≤ 15	-11 ≤ h ≤ 7, -10 ≤ k ≤ 11, -19 ≤ l ≤ 19	-6 ≤ h ≤ 11, -12 ≤ k ≤ 12, -43 ≤ l ≤ 42	-8 ≤ h ≤ 11, -13 ≤ k ≤ 11, -19 ≤ l ≤ 18
Reflections collected	4541	9156	4684	22349	8883
Independent reflections	2459 [R _{int} = 0.0252, R _{sigma} = 0.0371]	5679 [R _{int} = 0.0252, R _{sigma} = 0.0392]	3019 [R _{int} = 0.0203, R _{sigma} = 0.0292]	13174 [R _{int} = 0.0376, R _{sigma} = 0.0519]	5488 [R _{int} = 0.0232, R _{sigma} = 0.0334]
Data/restraints/parameters	2459/0/153	5679/0/354	3019/2/336	13174/0/851	5488/0/353
Goodness-of-fit on F ²	1.046	1.024	1.032	1.153	1.020
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0314, wR ₂ = 0.0745	R ₁ = 0.0322, wR ₂ = 0.0806	R ₁ = 0.0199, wR ₂ = 0.0507	R ₁ = 0.0561, wR ₂ = 0.1414	R ₁ = 0.0255, wR ₂ = 0.0636
Final R indexes [all data]	R ₁ = 0.0369, wR ₂ = 0.0772	R ₁ = 0.0365, wR ₂ = 0.0845	R ₁ = 0.0201, wR ₂ = 0.0509	R ₁ = 0.0602, wR ₂ = 0.1437	R ₁ = 0.0276, wR ₂ = 0.0651
Largest diff. peak/hole / e Å ⁻³	0.47/-0.18	0.59/-0.42	0.22/-0.24	0.61/-0.46	0.30/-0.45

Table 2Selected bond distances and angles for **1–5**.

1	2		3		4		5		
<i>Bond distances</i>									
Ni1–S2 ¹	2.1995(5)	Ni1–S24	2.1730(5)	Ni1–Cl2	2.1951(7)	Ni1–Cl2	2.1784(11)	Ni1–S25	2.2482(6)
Ni1–S2	2.1995(5)	Ni1–S25	2.2206(6)	Ni1–S25	2.2289(7)	Ni1–S24	2.1872(10)	Ni1–S24	2.1663(6)
Ni1–S3 ¹	2.2058(5)	Ni1–P5	2.1923(6)	Ni1–S24	2.1741(8)	Ni1–S25	2.2182(11)	Ni1–P5	2.2081(6)
Ni1–S3	2.2059(5)	Ni1–N2	1.8547(16)	Ni1–P5	2.2071(7)	Ni1–P5	2.2037(11)	Ni1–N2	1.8659(16)
S2–C4	1.7243(19)	S24–C26	1.7342(18)	S25–C26	1.716(3)	Ni1B–Cl2B	2.1786(11)	S25–C26	1.7201(18)
S3–C4	1.733(2)	S25–C26	1.7165(18)	S24–C26	1.725(3)	Ni1B–S24B	2.1851(10)	S24–C26	1.7204(18)
N5–C4	1.311(3)	S4–C3	1.6134(19)	N27–C26	1.319(3)	Ni1B–S25B	2.2176(10)	N27–C26	1.312(2)
¹ 1/2–X,1/2–Y,1–Z		N2–C3	1.162(3)			Ni1B–P5B	2.2111(10)	N2–C3	1.167(3)
		N27–C26	1.312(2)			S24B–C26B	1.740(4)	S4–C3	1.6242(19)
						S24–C26	1.739(4)		
						S25–C26	1.723(4)		
						S25B–C26B	1.723(4)		
						N27–C26	1.291(5)		
						N27B–C26B	1.294(5)		
<i>Bond angles</i>									
S2–Ni1–S3	79.469(18)	S24–Ni1–S25	79.05(2)	Cl2–Ni1–S25	93.74(3)	Cl2–Ni1–S25	91.24(4)	S24–Ni1–S25	78.63(2)
S2 ¹ –Ni1–S3	100.529(18)	S24–Ni1–P5	96.64(2)	Cl2–Ni1–P5	92.91(3)	Cl2–Ni1–P5	96.39(4)	S24–Ni1–P5	92.62(2)
S2 ¹ –Ni1–S3 ¹	79.471(18)	N2–Ni1–S25	94.17(5)	S24–Ni1–S25	78.37(3)	S24–Ni1–S25	78.73(4)	N2–Ni1–S25	94.01(5)
S2–Ni1–S3 ¹	100.531(18)	N2–Ni1–P5	89.98(5)	S24–Ni1–P5	94.62(3)	S24–Ni1–P5	93.59(4)	N2–Ni1–P5	95.21(5)
C4–S2–Ni1	85.86(7)	C26–S24–Ni1	86.80(6)	C26–S25–Ni1	86.04(9)	Cl2B–Ni1B–S25B	90.85(4)	C26–S25–Ni1	84.95(6)
C4–S3–Ni1	85.47(7)	C26–S25–Ni1	85.73(6)	C26–S24–Ni1	87.52(9)	Cl2B–Ni1B–P5B	96.80(4)	C26–S24–Ni1	87.54(6)
S2–C4–S3	109.10(11)	C3–N2–Ni1	175.54(15)	C26–N27–C35	120.8(2)	S24B–Ni1B–S25B	78.71(4)	C3–N2–Ni1	161.29(15)
N5–C4–S2	125.67(15)	N2–C3–S4	179.77(18)	C26–N27–C28	122.0(2)	S24B–Ni1B–P5B	93.55(4)	N2–C3–S4	178.66(16)
N5–C4–S3	125.23(15)	S25–C26–S24	108.26(10)	S25–C26–S24	107.88(15)	C26–S24–Ni1	87.12(13)	S25–C26–S24	108.80(10)
¹ 1/2–X,1/2–Y,1–Z		N27–C26–S24	125.03(14)	N27–C26–S25	126.10(19)	C26–S25–Ni1	86.51(13)	N27–C26–S25	127.14(14)
		N27–C26–S25	126.71(14)	N27–C26–S24	120.0(2)	C26B–S24B–Ni1B	87.21(12)	N27–C26–S24	124.04(14)
						C26B–S25B–Ni1B	86.61(13)		

Table 3
NMR chemical shifts (ppm) of **1–5**.

Compound	Nucleus	Benzylic	α -CH ₂	β -CH ₂	γ -CH ₂	δ -CH ₃ / -CH-	Aromatic	>N ¹³ CS ₂ (Thioureide)
1	¹ H	4.75 (s)	3.45 (t)	1.57 (m)	1.28 (m)	0.89 (t)	7.15–7.19 (m)	–
	¹³ C	51.5	48.1	28.7	19.9	13.6	128.1–138.0	207.8
2	¹ H	4.52 (s) 4.72 (s)	3.25 (t) 3.44 (t)	1.43 (m) 1.55 (m)	1.17 (m) 1.27 (m)	0.80 (s) & 0.89 (t)	7.0–7.74 (m)	–
	¹³ C	51.5 51.8	48.0	28.7	19.9		128.2–138.5	204.2
	³¹ P	–	–	–	–	–	22.5	–
3	¹ H	4.61 (s) 4.74 (s)	3.32 (s) 3.44 (s)	1.49 (s)	1.20 (s) 1.22 (s)	0.82 (s) 0.89 (s)	7.09–7.67 (m)	–
	¹³ C	51.3 51.5	47.7 48.1	28.6 28.7	19.8 19.9	13.5 & 13.6	128.2–138.3	204.8
	³¹ P	–	–	–	–	–	29.3	–
4	¹ H	–	3.65 (s) 3.75 (s)	2.17 (s) 2.40 (s)	–	4.24 (s)	7.19–7.66 (m)	–
	¹³ C	–	46.5	50.7	–	75.5	127.4–141.6	203.0
	³¹ P	–	–	–	–	–	29.3	–
5	¹ H	4.52 (s) 4.72 (s)	3.25 (s) 3.44 (s)	1.43 (s) 1.54 (s)	1.16 (s) 1.28 (s)	0.80 (s) 0.90 (s)	6.98–7.74 (m)	–
	¹³ C	50.9 51.4	48.3	28.7	19.6 19.9	13.5 13.6	122.7–143.9	205.2
	³¹ P	–	–	–	–	–	22.2	–

In **1–3**, the *p*-CH₃ protons resonate at 2.34 ppm and the corresponding carbon resonates at 21.1 ppm.