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Rare intermolecular M⋯H–C anagostic interactions in homoleptic Ni(II) / Pd(II) dithiocarbamate complexes

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New functionalized homoleptic dithiocarbamates of the form [M(L)₂] (M= Ni(II), L= L₁, N-(3-methoxybenzyl)-N-(methylbenzyl)dithiocarbamate (1), L₃, N-(3,4,5-trimethoxybenzyl)-N-(3-methylpyridyl)dithiocarbamate (3), L₄, N-(4-methoxybenzyl)-N-benzylidithiocarbamate (4), Pd(II), L₂, N-(N'-methyl-2-pyrrrole)-N-benzylidithiocarbamate (2)) have been synthesized and characterized by microanalysis and their structures have been investigated by X-ray crystallography. The four structures are all centrosymmetric with the metal located in a square plane with minor distortions, Pd(II) greater than Ni(II). The crystal structures of 1 and 2 revealed the existence of unique intermolecular C–H⋯M (Ni, Pd) anagostic interactions between the methylene hydrogen atom on the ligand substituents and the metal centres and these enable the formation of 1-D polymeric chains. Particularly geometric parameters (Pd⋯H–C = 2.61 Å; Pd⋯H–C = 173°) for the C–H⋯Pd interactions in 2 are at the border of anagostic and hydrogen bonding bonding. By contrast, 4 shows interactions between the methylene hydrogen and the CS₂Ni ring rather than the metal alone, while the interaction in 3 is intermediate between the two aforementioned types. These interactions are not retained in solution as revealed by their ¹H NMR studies. DFT calculations have been performed to analyse these rare interactions. 1, 3 and 4 are weakly conducting, σ = 10⁻¹⁰⁻¹⁻¹² S cm⁻¹ and show semiconductor behaviour in the 313-373 K range.

Introduction

Metal dithiocarbamate complexes have been widely studied because of their rich diversity of structures, interesting conducting, magnetic and optical properties, as photosensitisers in solar energy conversion processes, single source MOCVD precursor for the preparation of metal sulphides and nanocrystals and wide ranging applications. A resurgence of interest in the dithiocarbamate complexes arises due to the functionalisation of substituents on the N atom of the dithiocarbamate backbone that may provide structural scaffolds for novel molecular architectures and modify their chemical reactivity and physical properties. Crystal engineering of metal directed self assembly of coordination compounds afforded by S⋯H, O⋯H, N⋯H, S⋯S and C–H⋯π (chelate, CS,M) secondary interactions play key roles in organization of supramolecular networks. The existence of important C–H⋯M bonding interactions between the C–H hydrogen atom on the ligand fragment and metal centres providing agostic, anagostic or preagostic and hydrogen bonding interactions are less commonly observed in the organometallic complexes. As compared to agostic bonding, the nature of anagostic and hydrogen bonding interactions have been less explored in the literature. In fact the anagostic interactions comprising of 3c–2e bonds are the strongest and supported by a noticeable upfield chemical shift of the participating protons. By comparison, somewhat weaker anagostic interactions are largely electrostatic in nature and exhibit a downfield shift of the uncoordinated C–H protons. The anagostic interactions are stabilised by the electron deficient early transition metals whereas the anagostic interactions are typically associated by d⁴ or even d⁰ metal ions. The anagostic and anagostic interactions are characterized by the M⋯H–C distances of ~ 1.8-2.3 and 2.3-2.9 Å and M⋯H–C angles of ~ 90-140° and 110-170° respectively. In hydrogen bonding the late electron rich transition metals, Pt(II) and Au(III), have served as proton acceptors forming 3c–4e bond involving X-H⋯M type interactions where X is an electro negative atom such as nitrogen and oxygen. Such classical hydrogen bonds are nearly linear and accompanied with a downfield shift of the non bonded proton. The C–H bonds in the ligand fragment are believed to be weak hydrogen bond donors because of the relatively lower electronegativity of the carbon atom but are rarely involved in the metal assisted nonconventional intramolecular M–C⋯H hydrogen bond formation. However, it appears that the polar C–H bonds may be substantially engaged in the C–H⋯M anagostic / hydrogen bonding interactions. In spite of the aid of advanced quantum chemical calculations, in comparison to agostic interactions there is relatively scant evidence regarding structural characteristics i.e. geometrical parameters and optimum C–H⋯M bond lengths and bond angles for the anagostic and H-bonding interactions.

These metal mediated interactions are of significant importance due to their possible implications in the C–H bond activation. Considerable attention has been devoted to explore the
origin and nature of the anagostic / hydrogen bonding interactions with the aid of spectroscopic techniques, crystallography and theoretical studies.16h

The manifestation of multifaceted chemistry of dithiocarbamate complexes may be ascribed to the resonance structures (Fig.1) that this ligand provides in the complexes.

Fig. 1 Resonance structures of the dithiocarbamate ligand.

In recent years we and other groups have reported the existence of intra- and intermolecular anagostic interactions in some homo- and heteroleptic group 10 metal dithiocarbamate complexes.8e-9

Influenced by these observations and lack of examples with its nickel congener, Pd it was considered promising to undertake the synthesis, structural investigation and conducting properties of new functionalized Ni(II) and Pd(II) dithiocarbamate complexes.

The anagostic and borderline case of anagostic-hydrogen bonding interactions observed in the nickel (1) and palladium (2) complexes respectively have been discussed and their nature has been supported by DFT calculations.

Experimental section

Materials and methods

All reactions were carried out in open under ambient conditions. Reagent grade chemicals and solvents were obtained from commercial sources. The solvents were purified by standard procedures. Potassium salt of the ligands (Fig. 2), N-(3-methoxybenzyl)-N-(methylbenzyl)dithiocarbamate (KL1), N-(N'-methyl-2-pyryrole)-N-benzylidithiocarbamate (KL2), N-(3,4,5-trimethoxybenzyl)-N-(3-methylpyridyl)dithiocarbamate (KL3) and N-(4-methoxybenzyl)-N-benzylidithiocarbamate (KL4) were prepared according to literature procedures by the reaction of appropriate secondary amines with CS2 and KOH. The experimental details pertaining to melting point, elemental analysis, recording of IR, 1H and 13C (1H) NMR and UV-Vis. spectra and the measurement of pressed pellet electrical conductivity are the same as described earlier.6a-d

Synthesis and characterization of complexes

[ML2] (M=Ni(II), L=L1 (1), L2 (3), L4 (4); Pd(II), L=L2 (2))

The homoleptic complexes [ML2] were prepared adopting the general procedure. To a 10 mL stirred methanol–water (v/v) solution of KL1 (0.341, 1 mmol), KL2 (0.330, 1 mmol), KL3 (0.401, 1 mmol) or KL4 (0.341, 1 mmol) was added separately a (5 mL) solution of NiCl2.6H2O (0.118 g, 0.5 mmol) K2PdCl4 (0.163 g, 0.5 mmol) in the same solvent mixture. In each case the reaction mixture was additionally stirred for 4-6 h. The orange- to dark brown solid products thus formed were filtered off and washed with methanol followed by diethyl ether. The compounds were recrystallized in dichloromethane.

[Ni(L1)] (1) Yield: (76%, 0.252 g), m.p. 154-156°C. Anal. Calcd. for C19H20NiO3S5 (663.55): C 57.92, H 4.86, N 4.22 %. Found: C 57.61, H 4.97, N 4.13 %. IR (KBr, cm−1): 3476 (M-H), 1741 (C=S), 1610, 1000 (v(N-O)), 3408 (v(N-H)), 2971 (v(C-H)), 1530 (v(C=N)). 1H NMR (300.40 MHz, CDCl3) : δ 3.83 (s, 3H, -OCH3), 4.72 (s, 2H, -CH2CH2), 6.87 (s, 2H, -CH2Ph), 7.37, 7.61 (m, 2H, -C6H4Ph), 7.30-6.89 (m, 7H, Ar-H) ppm.

13C (1H) NMR (75.45 MHz, CDCl3) : δ 210.08 (CS), 160.16, 153.74 (C=O), 136.17, 134.88, 130.20, 123.97-123.58, 114.00, 113.94 (Ar-C), 55.37 -(OCH3), 50.86 -(CH2Ph), 48.13 -(CH2Ph), 34.46 (NCH2) ppm. UV-Vis. (CH3Cl2, λmax (nm), ε (M−1 cm−1)): 247 (9.4 × 104), 327 (9.2 × 103), 402.3 (1.6 × 105), 632 (121); σ = 0.159 × 10−10 S cm−1.

[Pd(L2)] (2) Yield: (87%, 0.285 g), m.p.174-176°C. Anal. Calcd. for C20H20PdO3S2 (654.19): C 51.17, H 4.60, N 98.52 %. Found: C 50.76, H 4.68, N 8.35 %. IR (KBr, cm−1): 1482 (v(C=S)), 978 (v(C=N)), 1340 (v(C=N)), 1297, 1231 (v(C=N)), 1160 (v(C=N)). 1H NMR (300.40 MHz, CDCl3) : δ 3.35 (s, 3H, -OCH3), 4.01 (s, 2H, -CH2CH2), 4.78 (s, 2H, -CH2CH2), 6.11, 6.09 (m, 3H, -C6H4Ph), 7.35-6.62 (m, 5H, -CH2H), 1.96 (OCH3) ppm. 13C (1H) NMR (75.45 MHz, CDCl3) : δ 211.89 (CS), 130.05, 133.92, 128.99-128.17, 124.32, 123.31, 116.42 (Ar-C), 50.94 -(CH2Ph), 43.29 -(CH2Ph), 34.65 (OCH3) ppm. UV-Vis. (CH3Cl2, λmax (nm), ε (M−1 cm−1)): 240 (4.0 × 104), 307 (1.15 × 105), 354 (1.5 × 105), 450 (1.30 × 105).

[Ni(L3)] (3) Yield: (81%, 0.318 g), m. p. 157-159°C. Anal. Calcd. for C24H20NiO4S (785.63): C 51.98, H 4.88, N 7.13 %. Found: C 52.62, H 4.97, N 7.02 %. IR (KBr, cm−1): 1464 (v(C=S)), 995 (v(C=N)). 1H NMR (300.40 MHz, CDCl3) : δ 3.83 (s, 3H, -OCH3), 4.64 (s, 2H, -CH2CH2), 4.78 (s, 2H, -CH2CH2), 8.61, 8.50 (m, 2H, -C6H4Ph), 7.73-6.45 (m, 4H, Ar-H) ppm.

13C (1H) NMR (75.45 MHz, CDCl3) : δ 210.01 (CS), 153.74 (meta, C=CH2(OCH3)), 149.94, 149.59 (CH2Ph), 138.20 (para, C=CH2(OCH3)), 136.10, 128.85, 123.97, 105.53 (Ar-C), 60.89 (para, OCH3), 56.34 (meta, OCH3), 51.30 (CH2Ph) ppm. UV-Vis. (CH3Cl2, λmax (nm), ε (M−1 cm−1)): 243 (1.93 × 103), 330 (1.62 × 103), 400 (3.05 × 103), 632 (167); σ = 0.212 × 10−11 S cm−1.

[Ni(L4)] (4) Yield: (74%, 0.245 g), m. p. 160-162°C. Anal. Calcd. for C27H22NiO5S4 (663.55): C 57.92, H 4.86, N 4.22 %. Found: C 57.63, H 4.91, N 4.15 %. IR (KBr, cm−1) 1488 (v(C=N)).

1H NMR (300.40 MHz, CDCl3) : δ 3.83 (s, 3H, -OCH3), 4.70 (s, 2H, -CH2CH2OCH3), 4.66 (s, 2H, -CH2CH2), 6.88 (m, 2-meta-H, -CH2CH2OCH3), 7.38-7.25 (m, 7H, Ar-H) ppm.

13C (1H) NMR (75.45 MHz, CDCl3) : δ 201.16 (CS), 158.08 (para C, -CH2(OCH3)), 132.77, 132.07, 130.57, 128.84 (Ar-C), 59.46 (OCH3), 45.01 -(CH2PhOCH3), 44.32 -(CH2PhOCH3) ppm. UV-Vis. (CH3Cl2, λmax (nm), ε (M−1 cm−1)): 245 (8.23 × 103), 329 (7.86 × 103).

Fig. 2 Structures of the potassium salt of dithiocarbamate ligands used in this work.
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x 10³), 400 (1.45 x 10³), 635 (114). \( \sigma_{\text{eff}} = 0.464 \times 10^{-12} \text{ S cm}^{-1} \).

X-ray structure determinations

Single crystals of the complexes 1-4 were grown by slow evaporation of the solution of products in CH\(_2\)Cl\(_2\). The X-ray diffraction data were collected on an Oxford X-calibur CCD diffractometer using Mo K\(_\alpha\) radiation with I, 3 and 4 at 293(2) K and 2 at 150(2) K. Data reductions were carried out using the CrysAlis program.\(^{13}\) The structures were solved by direct methods using SHELXS-97\(^{14}\) and refined on F\(^2\) by full matrix least squares method using SHELXL-97.\(^{14}\) Non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically fixed with displacement parameters equivalent to 1.2 times that of the atom to which they were bonded. The -OMe group in 1 was disordered over two sites in different aromatic rings. Populations were set at x and 1-x with x refining to 0.52(1). In 2 one ring in the ligand was disordered between N-methyl-2-pyrole and phenyl and both options were given a population of 0.50. Diagrams for all complexes were prepared using ORTEP\(^{15}\) and Mercury software.

Theoretical calculations

All calculations were carried out using the Gaussian 03 program.\(^{16}\) Structures were optimized using the B3LYP density functional together with basis sets LANL2DZ for Ni, Pd; 6-31+G* for S and 6-31G for the remaining atoms. Starting models were taken from the crystal structures with disorder removed but with hydrogen atoms given theoretical positions. Single point calculations were carried out on models of structures 1 and 2 using one and three molecules (Fig. 6).

Results and discussion

Synthesis and spectroscopy

The homoleptic complexes 1-4 were isolated in good yield by metathesis reactions of an aqueous-methanolic solution of the metal salts and potassium salt of the ligands (KL1–KL4, Scheme 1, Fig. 2) in 1:2 molar ratios. All complexes are stable to air and moisture and melt in the 154–176\( ^\circ\)C temperature range. The complexes have been characterized by microanalysis and their structures have been investigated by X-ray crystallography; 1 and 2 show intermolecular C-H···M interactions while 4 shows interactions between methylene hydrogen atom and the CS\(_2\)Ni ring while the interaction in 3 is intermediate between the two aforementioned types. The pressed pellet conductivity of 1, 3 and 4 has been studied.

\[
\text{NiCl}_2\cdot6\text{H}_2\text{O} / \text{K}_2\text{PdCl}_4 + 2\text{KCl} \rightarrow \text{MeOH/H}_2\text{O}, \text{rt}, 3-4 \text{ h} \rightarrow \text{M(L)}_2
\]

\[
\text{M=Ni, L=1 (1), L=3 (3), L=4 (4), M=Pd, L=L2 (2)}
\]

Scheme 1. General methodology for the synthesis of complexes 1-4.

All the complexes show \( \nu_{(C=O)} \) and \( \nu_{(C=S)} \) vibrations at 1464-1488 and 995-1013 cm\(^{-1}\) characteristic of coordinated dithiocarbamate ligands. A significant enhancement in the \( \nu_{(C=N)} \) frequency of the complexes in comparison to free dithiocarbamate ligands (160-193 cm\(^{-1}\)) indicates the dominant contribution of the canonical form (IV), Fig. 1. \(^{\text{1H NMR of all the complexes exhibit resonances characteristic of the ligand functionalities and integrate well to the corresponding protons. The}}\)

\( ^{\text{1H NMR of 1-4 show downfield shifting in } \delta \text{ 4.64-4.81 ppm region for the}}\)

\( \text{methylene hydrogen atoms due to metal-dithiocarbamate ligand coordination. Two close singlets are observed for these protons on each ligand functionality with a difference in peak position of } \delta \text{ 0.03-0.10 ppm. To confirm the existence of anagostic interactions observed in the crystal structure of 1 (vide infra) the}}\)

\( \text{low temperature proton NMR study was carried out down to liquid nitrogen temperature which could not reveal a significant}}\)

\( \text{downfield shift of the uncoordinated proton thereby confirming that the intermolecular C-H···M interactions are not retained in}}\)

\( \text{solution. This kind of difference between the solid state and solution structures in the case of intramolecular C-H···M}}\)

\( \text{hydrogen bonding is known.}^{11a-b} \text{ The intermolecular C-H···M}}\)

\( \text{interactions are rare and are generally not retained in solution but}}\)

\( \text{are stabilized in the solid state. In the } ^{\text{13C NMR an upfield shift of}}\)

\( \text{δ 5-15 ppm for the NCS}_2 \text{ carbon in the complexes (δ 201–211}}\)

\( \text{ppm) as compared to uncoordinated ligands (δ 215-216 ppm) is indicative of metal-ligand bonding.}}\)

Crystal Structures

The single crystals of 1-4 were obtained by slow evaporation of the solution of compounds in dichloromethane. Selected bond angles and bond lengths and crystallographic parameters are listed in Tables 1 and 3 respectively. The metal atoms occupy a crystallographic centre of symmetry in all the complexes, thus each asymmetric unit contains half a discrete molecule. Their ORTEP representations are shown in Fig. 3.

\[\text{Fig. 3 ORTEP diagrams of 1-4 with displacement ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity. In 1 the –OMe}}\]

\( \text{is disordered over the two } \text{meta sites: only one is shown. In 2, the ligand is}}\)

\( \text{disordered with N-methyl-2-pyrole and phenyl rings refined in}}\)
superimposed positions with 50% occupancy. The latter ring is not shown.

The basic structural features of all complexes are equivalent. The metal atom lies at the centre of a distorted square plane; the distortion varies, Pd greater than Ni. The distortion is caused due to small S(11)-M(1)-S(13) bite angles of 79.36(3), 79.39(4) and 79.60(4)° for M=Ni and 75.38(6)° for M=Pd. The Ni–S distances in the range 2.188(1) - 2.202(1) Å for 1, 3 and 4 are shorter than the Pd-S distance of 2.321(2), 2.324(2) Å for 2, values which are indicative of symmetrical (S,S) chelating behaviour of the dithiocarbamate ligands. The C(12)–N(14) bond lengths in the range 1.301(5)-1.316(8) Å are intermediate between the C–N bonds of 1.30 Å for the benzyl methylene hydrogens in 1 and 2 oriented the C-H hydrogen atom of the methylene group on the benzyl and pyrrole substituents, in close proximity of the metal coordination sphere forming C-H···M (Ni, Pd) intermolecular anagostic or preagostic interactions generating 1-D polymeric chain motif. In both complexes the methylene hydrogen atoms occupy vacant axial sites at the metal centres establishing a pseudo octahedral coordination environment. The Ni···H–C distance and ∠Ni···H–C angle of 2.78 Å and 137° in 1 (Fig. 4 a, b) are well within the range for the anagostic interactions.10 In 2, despite the larger size of palladium, the Pd···H–C distance of 2.61 Å is shorter than in the nickel complex and the ∠Pd···H–C angle of 173° is close to 180° (nearly linear) thus demonstrating the existence of spectacular C-H···Pd intermolecular electrostatic interactions which are on the borderline between the anagostic and hydrogen bonding interactions60 (Fig. 4c, d) and do not persist in solution (vide supra synthesis and spectroscopy).

However by contrast in 3, it is not clear whether the methylene hydrogen atom interacts more with the chelating NiS2C dithiocarbamate ring or with the nickel atom. Distances from the centre of gravity (CG) of the ring and the metal atom are 3.61 and 3.24 Å respectively with ∠C-H···CG and ∠C-H···Ni angles of 153 and 133°. The ∠H···CG···Ni and ∠H···Ni···CG angles are 91 and 64° respectively. In 4, the arrangement is clearer. Distances from the ring CG and the metal atom are 3.07 and 3.70 Å with C-H···CG and C-H···Ni angles of 137 and 134° and ∠H-CG-Ni and ∠H-Ni-CG angles of 102 and 54° respectively so that it is clear the interaction is with the ring66 (Fig. 5), rather than the metal as is shown in 1 and 2. The nearest S···S intermolecular contacts between the coordinated dithiocarbamate ligands in 1-4 are in the 4.273-5.989 Å range which are significantly larger than are expected for prominent S···S intermolecular associations. It can therefore be noted that in 3 and 4 the benzyl methylene hydrogen atoms are not involved in the anagostic interactions with the metal rather the interaction is with the ring.
From the DFT calculations it is possible to calculate the stabilization energy of the packing due to C-H···Ni/Pd interactions. To eliminate the stabilization effect due to other secondary interactions in 1 and 2 (Table 2) some model compounds were designed. Thus the aromatic rings in the ligand moieties were replaced by methyl group (Fig. 6) and single point calculations were performed. The energy difference of E(trimer)-3E(monomer) was -3.89 kcal/mol for 1 and -2.37 kcal/mol for 2. Thus, we can propose that these interactions are real anagostic / H-bonding interactions and affect the overall stability of the molecule in the supramolecular structure in the solid state.

It seems likely that the presence of the M···H interaction is caused due to steric effects and favourable packing of the molecules which leads to the close contact between the metal and the methylene hydrogen atom.

![Fig. 6 Structure of model compounds used for assessing the C-H···M anagogic interactions in 1 (model A, B) and borderline anagostic-hydrogen bonding interactions in 2 (model C, D).](image)

### Table 1. Selected bond distances and angles for 1-4

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<tr>
<th>Compound</th>
<th>D-H···A</th>
<th>d(D-H···A) (Å)</th>
<th>d(D···A) (Å)</th>
<th>θ (°)</th>
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<td>C24-H24···O28</td>
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<td>2</td>
<td>C37A-H37C···O24</td>
<td>2.94</td>
<td>3.88</td>
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<tr>
<td>3</td>
<td>C251-H25B···O24</td>
<td>2.47</td>
<td>3.42</td>
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<tr>
<td>4</td>
<td>C281-H281···O24</td>
<td>2.78</td>
<td>3.72</td>
<td>165</td>
</tr>
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</table>

Symmetry code: 1.*x,y,z 2.*x,1+y,z 3.3+x,1+y,1 4.-1/2-x,1/2+y,1 5.-1/2-x,-1/2+y,1 6.-1/2-x,-1/2+y,1 7.*x,1+y,z 8.3+x,1+y,1 9.1+x,y,z 10.1+y,z 11.1+z; x,1+y,z

### Absorption spectra

The electronic absorption spectra of 1-4 in dichloromethane solution (Fig. S1, ESI) show bands near 241.247 (ε= 1.9 x 10^4, 1.44–1.55 eV) but they show semiconductor property (Table 2) some model studies (vide supra) show bands near 521 nm (ε= 1.6 x 10^4 cm^−1) and 632.635 nm (ε= 114.167 M^−1 cm^−1) assignable to intraligand charge transfer (ILCT), ligand (S) to metal charge transfer (LMCT) and d-d transitions respectively consistent with square planar geometry about the metal centre.

### Pressed Pellet Conductivity

Pressed pellet electrical conductivity of 1, 3 and 4 was measured with a Keithly 236 source measure unit by employing the conventional two-probe technique. All the complexes are weakly conducting at room temperature (σ תורה = 10^−10–10^−12 S cm^−1, E_{on}=1.44–1.55 eV) but they show semiconductor property in the 313-373 K temperature range as their conductivity increases with increasing temperature (Fig. S2, ESI) and decreases with decrease in temperature. The weakly conducting nature of the complexes may be attributed to the lack of efficient S···S intermolecular interactions in the solid state (vide supra X-ray structures).

### Conclusions

Among new functionalized homoleptic Ni(II) and Pd(II) dithiocarbamate complexes (1-4), the X-ray crystallography revealed the existence of interesting intermolecular C-H···M (Ni, Pd) anagostic interactions generating 1-D polymeric chain motifs performe by crystal packing in 1 and 2. The geometric parameters revealed that the C-H···M interactions in 2 are on the borderline between anagostic and hydrogen bonding interactions. In these structures the vacant axial sites on the metal centres are occupied by the methylene hydrogen atoms on the ligand fragments thereby providing pseudo octahedral environments. However in 3 and 4, the interactions of the methylene hydrogen atom are subtly different. In 4 the prime interaction is with the NiS3C ring rather than the metal, while in 3 the interaction is intermediate between the two aforementioned types with the centre of gravity of the ring and...
the metal. These types of bonding interactions involving the metal centres are of considerable importance in the transition metals as well as main group chemistry due to their possible involvement in the C-H bond activation in the organic synthesis. Complex 1 having a methoxy group at the meta-position of benzene ring exhibits anagostic interactions while 4 having methoxy group at the para-position does not possess any such interactions. The former has overlapping aromatic rings of the functionalities (a feature also observed in 2) while the latter has the rings antagonistically placed. This may be a contributing factor in the favourable orientation of the methylene hydrogen atoms for the generation of these interactions. This study demonstrates that the crystal packing forces significantly influence the construction of metal assisted C-H intermolecular interactions rather than the functionalities on the N atom of the dithiocarbamate backbone in these complexes.

Table 3. Crystal data and refinement parameters

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<th>Compound</th>
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<th>3</th>
<th>4</th>
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<td>C$<em>{32}$H$</em>{32}$N$_2$NiO$_5$S$_4$</td>
<td>C$<em>{29}$H$</em>{33}$NiPdS$_4$</td>
<td>C$<em>{34}$H$</em>{33}$N$_2$NiO$_5$S$_4$</td>
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<td>10.3187(18)</td>
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<td>21.4036(11)</td>
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<td>10.309(7)</td>
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<td>γ (°)</td>
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<td>72.281(14)</td>
<td>103.041(11)</td>
<td>103.09(7)</td>
</tr>
<tr>
<td>V(Å$^3$)</td>
<td>760.24(14)</td>
<td>688.59(18)</td>
<td>907.7(2)</td>
<td>1580.27(19)</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>$\mu$ (Mo Kα) (mm$^{-1}$)</td>
<td>0.946</td>
<td>0.814</td>
<td>0.910</td>
<td>0.90</td>
</tr>
<tr>
<td>$\mu$ (Mo Kα) (mm$^{-1}$)</td>
<td>0.946</td>
<td>0.814</td>
<td>0.910</td>
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</tr>
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<td>0.946</td>
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<td>0.910</td>
<td>0.90</td>
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Acknowledgements

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Notes and references


