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Synthesis and structural characterization of a few thiocarboxylatonickel(II) complexes

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ABSTRACT

Thiobenzoate complexes of Ni(II), [Ni(dppe)(SCOPh)₂] (1), [Ni(en)(SCOPh)₂] (2), [Ni(opda)(SCOPh)₂] (3), [Ni₂(SCOPh)₄·EtOH] (4) [Ni₂(SCOPh)₄·CH₃CN] (5) [where dppe = bis(diphenylphosphino)ethane; en = ethylenediamine; opda = orthophenylenediamine] were synthesized and characterized structurally by X-ray crystallography. Electronic absorption spectra were recorded for all the complexes and the same has been computed using time dependent density functional theory for a representative compound (1). Bonding between Ni–Ni atoms in the dimeric unit has been confirmed in 4 and 5 on the basis of X-ray structural analyses and magnetic moment measurements. NBO calculations have been carried out to understand the nature of bonding.

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1. Introduction

During past several years much attention was attracted by transition metal chalcogeno complexes due to their structural diversity [1], relevance to catalysis [2] and biological applications as models for metalloenzymes [3]. Thiocarboxylates represent a very interesting class of ligands as they possess both soft sulfur and hard oxygen donor sites. A variety of thiocarboxylate complexes are known where either sulfur or oxygen or even both of them are involved in bonding with metal. Vittal and co-workers have synthesized a number of mononuclear and multinuclear thiocarboxylates which include neutral as well as anionic complexes [4]. Some of these have been found to be useful as the single source precursors for the synthesis of metal sulfides [5]. During past few years we have synthesized a few mono and bimetallic thiocarboxylate complexes [6]. Some of these exhibited unusual structural features and interesting properties. The heterobimetallic thiocarboxylates containing Pb/Cu and Cd/Cu were used to prepare corresponding ternary oxides and sulfides respectively [7]. A search in the literature revealed that studies on Ni(II) thiocarboxylates are scanty though a number of studies have been made on corresponding carboxylates [8].

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2. Experimental

2.1. Materials and physical measurements

Solvents used were purified using standard methods. Thiobenzoic acid, diphenylphosphinoethane (Sigma–Aldrich) and NiCl₂·6H₂O (s.d.fine chemicals) were used as such without further purification. The precursors NiCl₂(dppe) [9], NiCl₂(en)₂ [10], NiCl₂(opda) [11] were prepared by following the methods described in the literature. IR spectra were recorded using Perkin-Elmer RX-1, FTIR and Varian-3100 FTIR instruments. Electronic spectra were recorded on a Shimazdu UV-1700 PharmaSpec spectrophotometer using freshly prepared solutions of compounds in chloroform or DMSO.

2.2. Synthesis of complexes

2.2.1. Synthesis of $[Ni(dppe)(SCOPh)_2]$ (1)

Methanolic solution (10 mL) of thiobenzoic acid (59 μ L, 0.5 mmol) was added drop wise to a methanolic solution (10 mL) of sodium hydroxide (0.020 g, 0.5 mmol) in an ice bath. Ni(dppe)Cl₂ (0.132 g, 0.25 mmol) in chloroform (10 mL) was added drop wise to the reaction mixture. The yellowish solution turned deep red after the addition. Stirring was continued for about 4 h followed by evaporation of solvent under reduced pressure. The red solid obtained was dissolved in chloroform and kept for crystallization. Small rectangular plates were obtained after 3 days. Yield: (62%). M.P. 192 °C. Anal. Calc. for C₄₀H₃₄Ni₁O₂P₂S₂: C, 65.68; H, 4.69. Found: C, 65.73; H, 4.58%. IR(KBr pellet, cm⁻¹): 1653 ν (C=O), 1197 ν (Ph–C), 920 ν (C–S), 690 δ (SCO).





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2.2.2. Synthesis of $[Ni(en)(SCOPh)_2]$ (2)

A methanolic solution (10 mL) of thiobenzoic acid (59 µL, 0.5 mmol) was added to a methanolic solution (10 mL) of sodium hydroxide (0.020 g, 0.5 mmol) in an ice bath. To this a solution of Ni(en)₂Cl₂ (0.061 g, 0.25 mmol) (in 10 mL methanol) was added drop wise. A bright green precipitate started to form during the addition. After complete addition the reaction mixture was stirred for further 1 h. The precipitate was then filtered, washed with 5 mL methanol and dried under vacuum. Green crystals were obtained upon recrystallization from its chloroform solution. Yield: 0.081 g (72%). M.P. 120 °C (dec). Anal. Calc. for C₁₆H₁₈Ni₁N₂O₂S₂: C, 48.88; H, 4.61; N, 7.13. Found: C, 48.69; H, 4.58; N, 7.19%. IR(KBr pellet, cm⁻¹) 1588 v(C=O),1225 v(Ph-C), 967 v(C–S), 693 δ (SCO).

2.2.3. Synthesis of $[Ni(opda)(SCOPh)_2]$ (3)

Methanolic solution (10 mL) of thiobenzoic acid (59 µL, 0.5 mmol) was added to a methanolic solution (10 mL) of sodium hydroxide (0.020 g, 0.5 mmol) in an ice bath. The resulting solution was then added to a suspension of NiCl₂(opda) (0.059 g, 0.25 mmol) in methanol (10 mL). The reaction mixture was stirred for 2 h. The precipitate was filtered, washed with methanol and vacuum dried. Recrystallization from a chloroform solution yielded green thin rod like crystals. Yield: 0.073 g (66%). M.P. 160 °C (dec). *Anal.* Calc. for C₂₀H₁₈Ni₁N₂O₂S₂: C, 54.45; H, 4.11; N, 6.35. Found: C, 54.37; H, 4.15; N, 4.06%. IR(KBr pellet) 1570 ν (C=O),1224 ν (Ph–C), 968 ν (C–S), 690 δ (SCO).

2.2.4. Synthesis of [Ni₂(SCOPh)₄]·EtOH (4)

An ethanolic solution (10 mL) of thiobenzoic acid (117 µL, 1.0 mmol) was added drop wise to a solution of sodium hydroxide (0.040 g, 1.0 mmol) in the same solvent (10 mL) in an ice bath. NiCl₂·6H₂O (0.119 g, 0.5 mmol) dissolved in 10 mL ethanol was then added drop wise to the thiobenzoate solution. A red precipitate appeared soon after the addition was started. After stirring further for 2 h the red precipitate was filtered and dried under vacuum. Recrystallized from hot ethanol. Yield: 0.110 g (62%). M.P. 130 °C (dec). Anal. Calc. for C₃₀H₂₆Ni₂O₅S₄: C, 50.59; H, 3.68. Found: C, 50.51; H, 3.63%. IR(KBr pellet) 1583 ν (C=O),1217 ν (Ph–C), 958 ν (C–S), 689 δ (SCO).

2.2.5. Synhesis of [Ni₂(SCOPh)₄]·CNCH₃ (5)

A procedure similar to that described for the synthesis of 4 was adopted, the only change made being the use of anhydrous NiCl₂ in place of NiCl₂·6H₂O and acetonitrile as solvent. An almost clear red brown solution was obtained which was filtered and solvent was evaporated under vacuum leaving a dark red solid residue. Thin red coloured crystals were obtained by recrystallization from hot acetonitrile. Yield: 0.108 g (60%) M.P. 135 °C (dec). *Anal.* Calc. for $C_{30}H_{24}Ni_2N_1O_4S_4$: C, 50.88; H, 3.42; N, 1.98. Found: C, 50.81; H, 3.40; N, 2.02%. IR(KBr pellet) 2317 ν (C=N), 1601 ν (C=O),1219 ν (Ph–C), 959 ν (C–S), 687 δ (SCO).

2.3. X-ray data collection and structure refinement

Single crystal X-ray data were collected on a Xcalibur Oxford EOS diffractometer using graphite monochromated Mo K α radiation (λ = 0.7107 Å). Data collections were carried out at room temperature (293 K). The structures were solved and refined by SHELX set of software [12] using WINGX (ver. 1.80.05) [13] platform. Nonhydrogen atoms were refined anisotropically while the hydrogen atoms were placed at the calculated positions using SHELX default parameters. Restraints such as DELU, DFIX, ISOR and EADP have been applied while refining the structures (particularly in the case of complex **5**) where disordered atoms were present. A summary of crystallographic data and structure solutions are given in Table 1.

2.4. Magnetic measurements

Vibrating sample magnetic moment measurement was conducted on a EV-7 VSM ADE-DMS-Magnetic instrument within the field range of -15000 to +15000 Oe at room temperature. Variable-temperature magnetic susceptibilities were measured with a Quantum Design MPMS XL sourd magnetometer in applied magnetic field of 0.5 Tesla. Measurements were performed in the temperature range of 5–300 K.

2.5. Density functional calculations

TDDFT [14] and NBO calculations [15] were performed using the atomic coordinates obtained from X-ray crystallographic results. The calculations were performed at B3LYP [16] level using 6-31G^{**} as basis set for all the atoms. All the calculations were carried out using GAUSSIAN 03 program package [17].

3. Results and discussion

3.1. Synthesis of complexes

Thiobenzoate complexes of Ni(II) were synthesized using Ni(dppe)Cl₂, Ni(en)₂Cl₂, Ni(opda)Cl₂, Ni(H₂O)₆Cl₂ and anhydrous NiCl₂ as precursors. Synthetic routes for all the five complexes are shown in Scheme 1. The complex **4** was already synthesized way back in 1970 [18]. For **1–3** the solvent used was methanol while it was ethanol and acetonitrile for **4** and **5** respectively.

Complexes **1** and **2** were highly soluble in chloroform while complex **3** was moderately soluble in chloroform. **4** and **5** when dried were sparingly soluble in ethanol and acetonitrile. The compounds in solid state were found to be quiet stable and no apparent decomposition occurred in several months on keeping under ambient conditions. In the IR spectra of these complexes strong bands due to C=O, Ph–C, C–S stretching vibrations were observed which are characteristic for thiobenzoate ligands. These IR bands are important signals for analysing the bonding modes of the thiobenzoate ligands [19]. Generally the nitrile stretching band for acetonitrile appears at 2254 cm⁻¹, however on coordination this band is known to show a blue shift [20]. In the case of complex **5** the nitrile stretch appears at 2317 cm⁻¹.

3.2. Structural description of complexes

All the complexes synthesized were characterized by single crystal X-ray diffraction technique. Complex **1** was crystallized in orthorhombic system with $Pna2_1$ space group. The molecular structure of the complex is depicted in Fig. 1 along with the selected bond lengths and angles. The geometry around the nickel atom is square planar. Ni(II) is bonded to two phosphorus belonging to the *bis*(diphenylphosphino)ethane ligand and other two bonds are formed with sulfur atoms of the two thiocarboxylate groups. Ni(II) is slightly displaced off (by 0.026 Å) the plane constituted by P1, P2, S1 and S2 atoms. The Ni \cdots O distances are too long to have any bonding interactions between these two atoms.

Complex **2** crystallized in orthorhombic crystal system with *Pbcn* space group. Recently, a similar complex, Ni(TMEDA) thiobenzoate has been reported to crystallize in monoclinic system with $P2_1/c$ space group [21] the molecular structure of the complex is presented in the Fig. 2 along with the selected bond lengths and angles. Ni(II) is bonded to the nitrogen atoms of the ethylenediamine ligand, four other bonds are formed with the two oxygen atoms and two sulfur atoms of the two thiocarboxylate ligands. A twofold symmetry axis passes through the molecular center (Ni^{II}). The geometry around Ni(II) is slightly distorted from the

Table 1Crystallographic data collection and structure refinement for 1–5.

	1	2	3	4	5
Empirical formula	C40H34NiO2P2S2	C16H18N2NiO2S2	C20H18N2NiO2S2	C60H50Ni4O10S8	C62H46N3Ni4O8S8
M (g mol ⁻¹)	731.44	393.15	441.19	1422.32	1452.34
<i>T</i> (K)	293	293	293	293	293
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic	Triclinic
Space group	Pna21	Pbcn	Pbcn	ΡĪ	ΡĪ
a (Å)	15.807(5)	22.302(2)	20.8925(10)	10.410(5)	11.3557(19)
b (Å)	20.327(6)	8.1017(8)	10.2027(5)	11.634(5)	11.4121(18)
c (Å)	10.982(4)	9.9292(9)	9.7637(4)	12.696(5)	13.654(3)
α (°)				91.321(3)	105.029(16)
β (°)				92.830(5)	112.497(18)
γ (°)				92.867(6)	91.289(13)
V (Å ³)	3529(2)	1794.1(3)	2081.23(17)	1533.3(12)	1564.1(6)
Ζ	4	4	4	1	1
$\rho_{\rm calcd.} ({\rm g}{\rm cm}^{-1})$	1.377	1.456	1.408	1.540	1.542
$\mu (\mathrm{mm}^{-1})$	0.793	1.323	1.149	1.538	1.509
F(000)	1520	816			
Datas/restraints/parameters					
Goodness of fit (GOF) on F^2	1.006	1.098	1.032	0.955	0.985
$R_1, wR_2 [I > 2\sigma(I)]$	0.0755, 0.1340	0.0881, 0.1294	0.0396, 0.0737	0.0595, 0.1083	0.0500, 0.0635
Largest difference peak/hole (e $Å^{-3}$)	0.746/-0.515	0.556/-0.591	0.265/-0.313	0.791/-0.729	0.400/-0.518



Scheme 1. Synthesis of complexes 1-5.



Fig. 1. Thermal ellipsoid (at 30% probability level) of complex 1. For clarity hydrogen atoms are omitted. Selected metric data: Bond lengths (Å): Ni1–S1 2.230(2), Ni1–S2 2.237(2), Ni1–P1 2.158(2), Ni1–P2 2.150(2). Bond angles (deg): S1Ni1S2 95.10(8), S2Ni1P1 90.66(8), P1Ni1P2 86.66(8), P2Ni1S1 88.01(8).



Fig. 2. Thermal ellipsoid (at 30% probability level) of complex **2**. For clarity hydrogen atoms are omitted. Selected metric data: Bond lengths (Å): Ni1–N1 2.062(4), Ni1–O1 2.121(3), Ni1–S1 2.448(11). Bond angles (deg): O1Ni1S1 67.61(8), S1Ni1N1 100.39(12), N1Ni1N1¹ 83.7(2), N1¹Ni1S1¹ 94.39(13), S1¹Ni1O1 91.81(15).

regular octahedron possibly because of the small bite angles (67.62°) subtended by the thiocarboxylate ligands. The two S atoms are *trans* while the two O atoms are *cis* to each other. The chelate rings formed by the coordination of the two thiocarboxylate ligands are however, almost perpendicular to each other making an interplanar angle of 87.70°. The Ni–O and Ni–S distances are slightly longer than the sum of the respective atomic radii (by 0.21 and 0.25 Å respectively) while the Ni–N distances (2.068 Å) are nearer to the sum of their covalent radii (1.89 Å).

Complex **3** also crystallized in orthorhombic system with *Pbcn* space group. Molecular structure and numbering scheme are shown in Fig. 3 along with the selected bond lengths and angles. The molecular core, $NiN_2O_2S_2$ is structurally comparable to that of **2**. Recently, bis(o-phenylenediamine)nickel(II) carboxylate, $[Ni(opda)_2(OAc)_2]$ has been characterized structurally [22]. The Ni–O bond lengths are 2.126(5) Å while the Ni–N distances are 2.082(7) and 2.099(6) Å which are comparable to the corresponding bond lengths in **3**. The notable difference is the mode of binding of the ligands which are monodentate in $[Ni(opda)_2(OAc)_2]$ (for carboxylate) while bidentate in **3** (for thiocarboxylate).



Fig. 3. Thermal ellipsoid (at 30% probability level) of complex **3.** For clarity hydrogen atoms are omitted. Selected metric data: Bond lengths (Å): Ni1–O1 2.1026(19), Ni1–S1 2.4552(8), Ni1–N1 2.067(2). Bond angles (deg): O1Ni1S1 67.76(6), S1Ni1N1 93.10(8), N1Ni1N1ⁱ 84.48(13), O1ⁱNi1O1 91.80(11).



Fig. 4. Thermal ellipsoid (at 30% probability level) of complex **4.** For clarity hydrogen atoms are omitted. Selected metric data: Bond lengths (Å): Ni1–Ni2 2.5012(12), Ni1–01 2.009(3), Ni1–02 2.037(3), Ni1–03 2.004(3), Ni1–04 2.064(3), Ni1–05 2.054(3), Ni2–S1 2.2221(16), Ni2–S2 2.2281(16), Ni3–S3 2.2317(16), Ni2–S4 2.2255(17). Bond angles (deg): Ni2Ni101 90.17(9), Ni2Ni102 87.70(10), Ni2Ni103 90.14(10), Ni2Ni104 90.07(9), Ni2Ni105 178.40(10), O1Ni102 90.38(4), O1Ni103 179.68(13), O1Ni104 90.63(13), O1Ni105 88.47(13), O2Ni103 89.71(13), O2Ni104 177.56(14), O2Ni105 91.45(13), O3Ni104 89.28(13), O3Ni105 91.22(13), O4Ni105 90.79(12), Ni1Ni251 88.38(4), Ni1Ni252 89.34(5), Ni1Ni253 88.64(5), Ni1Ni252 91.20(5), S1Ni253 89.18(5), S1Ni254 178.43(6), S2Ni2S4 89.35(6), S3Ni2S4 89.26(5).

Complexes **4** and **5** crystallized in triclinic crystal system with $P\bar{1}$ space group. Figs. 4 and 5 depict the molecular structures of **4** and **5** respectively along with the selected bond lengths and angles. The complexes **4** and **5** are structurally similar to each other in every aspect other than the coordinated solvent which is ethanol in **4** and acetonitrile in **5**. Further, the unit cell of **5** contains a disordered molecule of solvent acetonitrile in the lattice.

Solid state structures of **4** and **5** revealed the existence of a dimeric assembly of dinuclear (two Ni atoms) complexes. The two dinuclear units are joined to each other by bridging through S atoms (Fig. 6). Two molecules of ethanol are coordinated to two Ni(II) centres of the dimer from opposite sides. Each dinuclear unit has a four bladed paddlewheel structure and the coordinated ethanol appears like a shaft. Coordination environment of the two Ni of a monomeric unit are distinctly different from each other. Ni1 is



Fig. 5. Thermal ellipsoid (at 30% probability level) of complex **5.** For clarity hydrogen atoms are omitted. Selected metric data: Bond lengths (Å): Ni1–Ni2 2.5083(18), Ni1–N1 2.055(7), Ni1–O1 2.036(4), Ni1–O2 2.022(4), Ni1–O3 2.044(5), Ni1–O4 2.009(4), Ni2–S1 2.208(2), Ni2–S2 2.232(2), Ni2–S3 2.224(2), Ni2–S4 2.210(2). Bond angles (deg): N1N11Ni2 174.95(19), N1Ni101 90.5(2), N1Ni102 87.0(2), N1Ni103 91.7(2), N1Ni104 94.0(2), Ni2Ni101 89.22(14), Ni2Ni102 87.98(14), Ni2Ni103 88.48(15), Ni2Ni104 91.03(15), O1Ni102 91.67(18), O1Ni103 177.4(2), O1Ni104 90.79(19), O2Ni103 87.10(18), O2Ni104 177.3(2), O3Ni104 90.40(19), Ni1Ni2S1 89.22(7), N11Ni2S2 89.94(8), Ni1Ni2S3 90.44(7), Ni1Ni2S4 89.04(7), S1Ni2S2 89.20(8), S1Ni2S3 179.61(11), S1Ni2S4 90.37(8), S2Ni2S3 90.70(7), S2Ni2S4 178.21(10), S3Ni2S4 89.75(8).



Fig. 6. The dimeric (tetranuclear) structure of **4** which is supposed to be due to the interaction of Ni1 of one unit with S1 of other unit.

surrounded by five oxygens (four from the thiocarboxylates and one from ethanol) while Ni2 is coordinated by five sulfurs. Though the bridging, Ni2–S1 bond is longer [2.811(2) Å] than the other Ni– S bonds yet it is significantly shorter than the sum of van der Waals radii of the two atoms (3.26 Å). The sixth coordination site of Ni1 is occupied by Ni2 and *vice versa*. Thus, the geometry around each Ni(II) centre is octahedral. Notably, the distance between the two nickel atoms, 2.500(1) Å is very close to the Ni–Ni single bond length (2.42 Å). Very recently, the structure of a nickel(II) carboxylate, Ni₂(O₂CPh)₄(NITpPy)₂ has been reported [23]. In this complex



Fig. 7. Selected molecular orbitals for 1 (orbital contour value = 0.05).



Fig. 8. The M (H) curve at room temperature for complex 4.

the two Ni(II) are bridged by four benzoate ligands forming a paddle wheel type of cage and the Ni–Ni distance is 2.645(4) Å. Antiferromagnetic coupling has been observed in this complex at lower temperatures. A few other dinuclear carboxylates have also been reported earlier [8(c)] in which the Ni–Ni distances vary between 2.70 and 2.75 Å which are significantly longer than the Ni–Ni distance in **4** and **5**. The Ni–Ni distance in dithiocarboxylate complex, Ni₂(S₂CCH₂Ph)₄ is also slightly larger being 2.551(3) Å [24].

3.3. Electronic absorption spectra

The electronic absorption spectra of compounds **1** and **2** were recorded in chloroform solutions whereas those of 3, 4 and 5 were recorded in DMSO (Fig. S1–S5; Supplementary data). For complex **1** only one prominent band centered on 467 nm was observed. For complex **2** one prominent band centered at 630 nm was observed. The complex **3** exhibited three bands of which two peaks were centered at 778 and 552 nm. A third one centered at 306 nm is due to charge transfer (LLCT). For complex **4** a broad band centered at

660 nm was observed. For complex **5** a broad band around 730 nm was obtained.

The broad nature of the spectral bands often poses a problem for their unambiguous assignment. Time dependent density functional calculations are quiet useful to understand the spectral features. However, these calculations are limited to molecules with a closed shell. TD DFT calculations were performed on complex **1** as it is the only molecule having a closed electronic shell. The results revealed presence of three bands in the visible region at 507, 472 and 463 nm. All the three bands have merged in a single broad band centered at 467 nm in the experimentally observed spectrum. Bands below 400 nm are generally associated with the ligand to metal or ligand to ligand charge transfers. Fig. 7 shows the orbitals involved in transitions for the above given respective bands.

3.4. Magnetic studies

The complexes **4** and **5** were binuclear nickel complexes and in both of them the Ni–Ni distance is in covalent bonding range. VSM magnetic moment measurements were conducted for complex **4** at



Fig. 9. Molar and inverse magnetic susceptibilities of complex 4 as a function of temperature.



Fig. 10. The effective magnetic moment of complex 4 in Bohr magnetons as a function of temperature.

room temperature varying field from -15000 Oe to +15000 Oe. Though a magnetic moment of $4.89 \ \mu\text{B}$ is expected for a system of two Ni(II) atoms (with 4 unpaired electrons) the experimentally observed value at the maximum field was found to be only 2.66 μB revealing the presence of only two unpaired electrons in the dinuclear unit.

Fig. 8 represents the M (H) curve for complex **4**. The curve clearly shows that the magnetisation (M) depends linearly on magnetic field (H) at room temperature which is an indication of the complex being paramagnetic in behaviour at room temperature. Although at very low fields region an "S" shaped M (H) curve is obtained. The enlarged view of "S" shaped curve however depicts hysteresis with very little coercivity (Hc) ~66 Oe and remanence magnetisation (Mr) ~1.313 × 10⁻³ emu/g. The hysteresis curve is shown in the inset of Fig. 8. The observed low magnetic moment (2.66 µB per dinuclear unit possessing two Ni(II) centers) is indicative of the existence of an electron pair bond between two Ni centers. It may be noted that Ni–Ni bonds are not generally expected in such systems [25]. This fact prompted us to perform detailed magnetic study for the complex **4**. In that context

we performed sound magnetic measurements for a temperature range of 5-300 K at a field of 0.5 T. A plot of molar magnetic susceptibility and inverse magnetic susceptibility for the complex 4 in the solid state as a function of temperature is shown in Fig. 9. The value of molar susceptibility is 0.0030 emu/mol at 300 K which increases smoothly till 75 K as temperature is reduced and then rises sharply reaches a maximum of 0.035 emu/ mol at around 9.8 K and then again dips down as further temperature is reduced reaching a value of 0.032 emu/mol at 5 K. Fig. 10 shows the plot of effective magnetic moment as a function of temperature. At 300 K, the effective magnetic moment μ_{eff} = 2.49 μ B which reaches a maximum of about 2.55 μ B at around 154 K. From 52 K onwards μ_{eff} falls down very sharply to a minimum of 1.07 µB at 5 K. To a plot of inverse of molar susceptibility versus temperature (Fig. 11) linear fit was applied to the Curie–Weiss law which gave a θ value of –2.8 K. The value of I calculated from the equation $J/2k = \theta$ is -3.91 cm^{-1} . The value of I was also obtained using theoretical equation of R. L. Carlin [26] by plotting a graph between molar susceptibility and temperature (Fig. 12), using the following equation.



Fig. 11. Inverse magnetic susceptibility as a function of temperature along with the fit to Curie–Weiss law.



Fig. 12. Molar magnetic susceptibility as a function of temperature along with the fit to R. L. Carlin equation.

$$\begin{split} \chi_m &= Ng^2\beta^2/kT\cdot exp(2J/kT) + 5exp(6J/kT)/1 + 3exp(2J/kT) \\ &+ 5exp(6J/kT) \end{split}$$

The best fitting for the experimental data gives a value of g = 2.24 and J = -3.76 cm⁻¹ the latter is indicative of a weak antiferromagnetic coupling in the system. Here χ_m , C, T, θ , k, N, β , g have their usual meanings.

3.5. Density functional calculations

The antiferromagnetic coupling in the carboxylate complexes have been explained by Bencini et al. who proposed $d_{z^2}-d_{z^2}$ (σ bonding) and $d_{x^2-y^2}-d_{x^2-y^2}$ (δ bonding) between two Ni centers [27]. Absence of a direct Ni–Ni bond in these complexes was however, suggested by the fact that the M–M distances are significantly longer than the same in Ni₂(S₂CCH₂Ph)₄. Rakitin et al. proposed the possibility of two super exchange channels, the σ path $(d_{x^2-y^2}-\sigma_o-\sigma_c-\sigma_o-d_{x^2-y^2})$ and the π path $(d_{xy}-\pi_o-\pi_c-\pi_o-d_{xy})$ [28]. Computations at B3LYP level using 6-31G** basis set were carried out to understand the nature of bonding in 4 and 5. The atomic coordinates obtained from X-ray diffraction measurements were used for the computations. As mentioned (in Section 3.4) above the Ni1-Ni2 distance in 4 is 2.500 Å which is comparable to the Ni-Ni single bond length. It is normally expected that a M-M bond will not be stable enough to hold two square planar Ni units as 16 electrons (from the two Ni centers) will fill four bonding and four antibonding molecular orbitals equally. One may thus argue that the close proximity of the two Ni atoms is dictated by the bite span of the thiocarboxylate ligands. However, In our recent studies on heterobimetallic thiocarboxylate complexes we have seen that the thiocarboxylate ligands can span to quite a larger extent if there is no M–M bonding [7]. An important question came forth to start DFT calculations on 4. Should the Ni atoms be considered as spin paired or with (one or two) unpaired spins. Single point energy calculation on the molecule with different electronic configurations revealed that the one with 1 unpaired electron on each Ni(II) is most stable. (However, the energy of molecule with a



Fig. 13. $d_{z^2} - d_{z^2}$ orbital overlap between two nickel atoms in complex **4**.

configuration having two unpaired electrons (in each Ni^{II}) is higher by only 11.8 kcal/mol which is rather small and in solution a change in its configuration cannot be ruled out.) Since this is consistent with the results of magnetic measurements we selected the configuration with two unpaired spins per dimeric unit of 4 for our calculations. NBO calculations revealed a Wiberg bond index of 0.17 between the two metals. A metal-metal bond subsists due to the overlap of the d_{7^2} orbitals of two neighbouring nickel atoms as shown in Fig. 13. Further, second order perturbations lead to strong bonding interactions between the two centres. Electron transfer from Lp* of Ni1 which is basically 4s orbital (with occupancy 0.26) to Lp^{*} of Ni2 results in a stabilization of 75.11 kcal mol⁻¹. In addition, there are several other electron transfers from some bonding MOs to suitable vacant MOs of which also cause sufficient stabilization. For example, Ni1-S3 bonding MO (formed by the overlap of 3p orbital of S3 and an spd hybrid orbital (36% s, 8.8% *p* and 54.8% *d*) of Ni1 acts as a donor while the 4s orbital of Ni2 acts as an acceptor and the electron transfer lowers 44.95 kcal of energy per mole.

4. Conclusion

We have synthesised five thiobenzoate complexes of Ni(II), [Ni(dppe)(SCOPh)₂] (1), [Ni(en) (SCOPh)₂] (2), [Ni(opda)(SCOPh)₂] (3), [Ni₂(SCOPh)₄]·EtOH (4), [Ni₂(SCOPh)₄]·CH₃CN (5). Bonding mode of thiobenzoate ligands and geometry of Ni(II) centers were observed to change depending on the nature of co-ligand(s) present. In case of 1 a square planar arrangement of the donor atoms exists whereas in case of 2 and 3 thiobenzoate ligands bind bidentately giving octahedral environment around the metal atom. Complexes 4 and 5 showed short Ni–Ni distances owing to Ni–Ni bonding which is also revealed by magnetic susceptibility studies.

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Appendix A. Supplementary material

CCDC 888478 (1), 888476 (2), 888475 (3), 888479 (4), 888477 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Electronic absorption spectra of all the complexes are 286 given in Figures S1-S5. Supplementary data associated with this article can be found, in the online version, at http:// dx.doi.org/10.1016/j.ica.2013.11.037.

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