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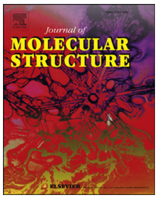

Synthesis, spectral, structural and computational studies on NiS_4 and NiS_2NP chromophores: Anagostic and C–H···π (chelate) interactions in $[Ni(dtc)(PPh_3)(NCS)]$ (dtc = N-(2-phenylethyl)-N-(4-methoxybenzyl)- dithiocarbamate and N-(2-phenylethyl)-N-(4-chlorobenzyl)dithiocarbamate)

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ABSTRACT

Bis(N-(2-phenylethyl)-N-substituted benzyldithiocarbamato-S,S′)nickel(II) (**1**–**6**) and (N-(2-phenylethyl)-N-substituted benzyldithiocarbamato-S,S′)(thiocyanato-N) (triphenylphosphine)nickel(II) (**7**–**12**) [substituted benzyl = $2HO–C_6H_4–CH_2–$ **(1,7)**, $3HO–C_6H_4–CH_2–$ **(2,8)**, $4HO–C_6H_4–CH_2–$ **(3,9)**, $4CH_3O–C_6H_4–CH_2–$ **(4,10)**, $4F–C_6H_4–CH_2–$ **(5,11)**, $4Cl–C_6H_4–CH_2–$ **(6,12)**] complexes have been synthesized and characterized by elemental analysis, IR, UV–Vis and NMR (^1H and ^{13}C) spectroscopy. In the case of heteroleptic complexes **7**–**12**, the shift in $\nu_{C\text{-}N}$ values to higher wavenumber and the NCS_2 carbon signals are shifted to downfield compared to the homoleptic complexes indicating the increasing strength of thioureide $\nu_{C\text{-}N}$ bond due to the presence of π-accepting triphenylphosphine ligand in heteroleptic complexes. Electronic spectral studies on all the complexes (**1**–**12**) suggest square planar geometry around the nickel(II). Structures of **10** and **12** have been elucidated by X-ray crystallography. The dithiocarbamate anions in **10** and **12** chelate to the nickel atom. Both the structures reveal C–H···Ni intramolecular anagostic interaction. C–H···π (chelate) is observed in complexes **10**. Supramolecular frame works are stabilised by C–H···S, C–H···π and C–H···Cl non-covalent interaction. The molecular geometry, HOMO-LUMO in the ground state and MEP have been calculated for **10** and **12** using Hartree-Fock (HF) method with LANL2DZ basic set. Molecular electrostatic potential diagram of complexes **10** and **12** support the partial double bond character of C–N (thioureide) bond in dithiocarbamate ligands.

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1. Introduction

The importance of coordination chemistry has now become broad and the applications of coordination compounds to the scientific world are tremendous [1]. Several donor atoms like oxygen, sulfur, nitrogen, phosphorous were reported earlier by many pioneer workers in this field. Metal-dithiocarbamate complexes are the most widely studied. Because of the metal binding property and their chelates vital role to biological, agricultural and industrial field etc [2]. Dithiolate Ni(II) complexes, containing a coordination NiS_4 unit, are widely applied in analytical chemistry, organic synthesis and biology. Dithiocarbamate ligands are used to extract metals [3] and their complexes serve as precursors of metal-sulfides in modern electronics [4–11]. Metal dithiocarbamate complexes have numerous applications in the chemical, agricultural and pharmaceutical industry, mainly because of their metal-binding and antioxidant properties [12,13]. A number of bis(dithiocarbamate)nickel(II), $[Ni(dtc)_2]$ and $[Ni(dtc)(NCS)(PPh_3)]$ complexes have been synthesized, several of them have been characterized by single crystal X-ray diffraction [14,15]. Non-covalent interactions are fundamental for supramolecular

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chemistry, drug design, protein folding, crystal engineering and other areas of molecular science. The crystal engineering of molecules is concerned with intriguing architectures and utilitarian consideration. Non-covalent interactions, such as conventional X–H•••Y and non-conventional C–H•••X (X or Y = F, Cl, O, N, S) hydrogen bonding, C–H•••π, π•••π, π(chelate)•••π (chelate), π(aryl) •••π (chelate), C–H•••π (chelate) and X–H•••M (X = O, N, C) metal assisted anagostic, agostic and hydrogen bonding interactions, often play crucial roles in the molecular recognition processes and organization of the supramolecular networks [16–30]. Our aim is to study the non-covalent interactions in homoleptic and heteroleptic Ni(II) complexes involving functionalized dithiocarbamate complexes. In this paper, we report the synthesis and characterization of some Ni(II) complexes containing N-(2-phenylethyl)-N-substituted benzyl dithiocarbamates. In addition, Single crystal X-ray structural analysis and computational studies on (N-(2-phenylethyl)-N-4-methoxy benzyldithiocarbamato-S,S′)(thiocyanato-N)(triphenylphosphine)nickel(II) (**10**) and (N-(2-phenylethyl)-N-4-chlorobenzyldithiocarbamato-S,S′)(thiocyanato-N)(triphenylphosphine)nickel(II) (**12**) are also presented.

2. Experimental

2.1. Materials and instrumentation

All reagents and solvents were commercially available high grade materials (Merck/sd Fine/Himedia) and used as received. FT-IR spectra were recorded on a SHIMADZU FT-IR spectrophotometer (range 400–4000 cm^{-1}) as KBr pellets. ^1H NMR spectra were recorded on Bruker 400 MHz and ^{13}C NMR spectra on Bruker 100 MHz in $CDCl_3$ and DMSO-d_6 as a solvent and tetramethylsilane (TMS) as an internal standard. For compounds **1**–**3** dissolved in DMSO-d_6, the two signals of DMSO and water arose at 2.5 and 3.4 ppm, respectively. SHIMADZU UV-1650 PC double beam UV–visible spectrophotometer was used for recording the electronic spectra of the complexes. The spectra were recorded in acetonitrile, chloroform and the pure solvents were used as the reference.

2.2. Syntheses of nickel(II) complexes

2.2.1. Preparation of bis(N-(2-phenylethyl)-N-substituted benzyldithiocarbamato-S,S′)nickel(II)

2-phenylethylamine (4.6 mmol) in methanol was added to substituted benzaldehyde (2-OH, 3-OH, 4-OH, 4-OCH_3, 4-F and 4-Cl) (5.1 mmol) in methanol and the solution was stirred continuously for 2 h. The colourless oil formed on evaporation of the solvent. The product was dissolved in methanol-dichloromethane solvent mixture (1:1, 20 mL) and sodium borohydride (13.8 mmol) was added slowly and stirred continuously for 2 h under ice cold condition (5 °C). Further, the mixture was stirred for 20 h at room temperature. After evaporation of the solvent, the resulting viscous liquid product was washed with water and the product was extracted with dichloromethane. Evaporation of the organic layer yielded N-(2-phenylethyl)-N-substituted benzylamine as pale yellow oil. N-(2-phenylethyl)-N-substituted benzylamine (4 mmol) and carbon disulfide (4.0 mmol) were dissolved in ethanol (20 mL) and stirred for 30 min. Nickel chloride hexahydrate (2.0 mmol) was dissolved in 10 mL of water and added to the solution with constant stirring. The complexes formed were filtered off, dried and recrystallized from acetonitrile (Scheme 1).

2.2.2. Preparation of (N-(2-phenylethyl)-N-substituted benzyldithiocarbamato-S,S′)(thiocyanato-N)(triphenylphosphine) nickel(II)

Bis(N-(2-phenylethyl)-N-substituted benzyldithiocarbamato-S,S′)nickel(II) (1.0 mmol), PPh_3 (2.0 mmol), $NiCl_2\cdot 6H_2O$ (1.0 mmol) and NH_4SCN (2.0 mmol) were dissolved in chloroform-methanol solvent mixture (3:2, 50 mL) and heated to reflux for 3 h. The solution obtained was filtered off. Purple-red solid formed after 5 days. It was filtered off and recrystallized from chloroform (Scheme 1).

*2.2.2.1. bis(N-(2-phenylethyl)-N-(2-hydroxybenzyl)dithiocarbamato-S,S′)nickel(II) (**1**).* Yield 78%, mp 230–231 °C. IR (KBr, cm^{-1}): ν = 3453 (ν_{OH}); 1510 (ν_{C-N}); 1026 (ν_{C-S}). UV–Vis (CH_3CN, nm): λ = 621, 478, 394, 337, 285, 250. ^1H NMR (400 MHz, DMSO, ppm):δ = 2.83 (b, 4H, ($C_6H_5-C\boldsymbol{H_2}-CH_2-N$)); 3.68 (b, 4H, $C_6H_5-CH_2-C\boldsymbol{H_2}-N$); 4.71 (s, 4H, $2HO-C_6H_4-C\boldsymbol{H_2}-N$); 6.83–7.30 (aromatic protons); 9.99 (s, 2H, $2\boldsymbol{H}O-C_6H_4-CH_2-N$). ^{13}C NMR (100 MHz, DMSO, ppm): δ = 32.5 ($C_6H_5-\boldsymbol{C}H_2-CH_2-N$); 47.4 ($C_6H_5-CH_2-\boldsymbol{C}H_2-N$); 50.4 ($2HO-C_6H_4-\boldsymbol{C}H_2-N$); *ipso carbon*; 155.5 (Ar–2OH); 115.3–137.5 (other aromatic carbons); 205.2 ($N\boldsymbol{C}S_2$); Anal. Calcd. for Chemical Formula: $C_{32}H_{32}N_2NiO_2S_4$ (%): Elemental Analysis: C, 57.92; H, 4.86; N, 4.22; Found: C, 57.13; H, 4.61; N, 4.07.

*2.2.2.2. bis(N-(2-phenylethyl)-N-(3-hydroxybenzyl)dithiocarbamato-S,S′)nickel(II) (**2**).* Yield 66%, mp 156–158 °C. IR (KBr, cm^{-1}):ν = 3370 (ν_{OH}); 1501 (ν_{C-N}); 1022 (ν_{C-S}). UV–Vis (CH_3CN, nm): λ = 618, 479, 394, 330, 283, 250. ^1H NMR (400 MHz, DMSO, ppm):δ = 2.84 (b, 4H, ($C_6H_5-C\boldsymbol{H_2}-CH_2-N$)); 3.65 (b, 4H, ($C_6H_5-CH_2-C\boldsymbol{H_2}-N$)); 4.71 (s, 4H,$3HO-C_6H_4-C\boldsymbol{H_2}-N$); 6.74–7.31 (aromatic protons); 9.64 (s, 2H,$3\boldsymbol{H}O-C_6H_4-CH_2-N$); ^{13}C NMR (100 MHz, DMSO, ppm): δ = 32.4 ($C_6H_5-\boldsymbol{C}H_2-CH_2-N$); 50.2 ($C_6H_5-CH_2-\boldsymbol{C}H_2-N$); 51.8 ($3HO-C_6H_4-\boldsymbol{C}H_2-N$); *ipso carbon*;157.7 (Ar–3OH); 114.6–137.5 (other aromatic carbons); 205.7 ($N\boldsymbol{C}S_2$); Anal. Calcd. for Chemical Formula: $C_{32}H_{32}N_2NiO_2S_4$ (%): Elemental Analysis: C, 57.92; H, 4.86; N, 4.22; Found: C, 57.94; H, 4.69; N, 4.07.

*2.2.2.3. bis(N-(2-phenylethyl)-N-(4-hydroxybenzyl)dithiocarbamato-S,S′)nickel(II) (**3**).* Yield 75%, mp 176–178 °C. IR (KBr, cm^{-1}): ν = 3360 (ν_{OH}); 1503 (ν_{C-N}); 1020 (ν_{C-S}). UV–Vis (CH_3CN, nm): λ = 618, 478, 435, 393, 313, 275, 252, 246. ^1H NMR (400 MHz, DMSO, ppm):δ = 2.79 (b, 4H, ($C_6H_5-C\boldsymbol{H_2}-CH_2-N$)); 3.61 (b, 4H, ($C_6H_5-CH_2-C\boldsymbol{H_2}-N$)); 4.67 (s, 4H,$4HO-C_6H_4-C\boldsymbol{H_2}-N$); 6.79–7.30 (aromatic protons); 9.64 (s, 2H,$4\boldsymbol{H}O-C_6H_4-CH_2-N$); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 32.4 ($C_6H_5-\boldsymbol{C}H_2-CH_2-N$); 49.8 ($C_6H_5-CH_2-\boldsymbol{C}H_2-N$); 51.5 ($4HO-C_6H_4-\boldsymbol{C}H_2-N$); *ipso carbon*; 157.4 (Ar–4OH); 115.4–137.5 (other aromatic carbons); 204.9 ($N\boldsymbol{C}S_2$); Anal. Calcd. for Chemical Formula: $C_{32}H_{32}N_2NiO_2S_4$ (%): Elemental Analysis: C, 57.92; H, 4.86; N, 4.22; Found: C, 57.37; H, 4.87; N, 4.11.

*2.2.2.4. bis(N-(2-phenylethyl)-N-(4-methoxybenzyl)dithiocarbamato-S,S′)nickel(II) (**4**).* Yield 81%, mp 182–184 °C. IR (KBr, cm^{-1}): ν = 1506 (ν_{C-N}); 1022 (ν_{C-S}). UV–Vis ($CHCl_3$, nm): λ = 629, 502, 393, 328, 261. ^1H NMR (400 MHz, $CDCl_3$, ppm):δ = 2.88 (b, 4H, ($C_6H_5-C\boldsymbol{H_2}-CH_2-N$)); 3.65 (b, 4H, ($C_6H_5-CH_2-C\boldsymbol{H_2}-N$)); 3.81 (s, 3H,$4C\boldsymbol{H_3}O-C_6H_4-CH_2-N$); 4.58 (s, 4H,$4CH_3O-C_6H_4-C\boldsymbol{H_2}-N$); 6.87–7.30 (aromatic protons); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 33.4 ($C_6H_5-\boldsymbol{C}H_2-CH_2-N$); 50.1 ($C_6H_5-CH_2-\boldsymbol{C}H_2-N$); 52.3 ($4CH_3O-C_6H_4-\boldsymbol{C}H_2-N$); 55.4 ($4CH_3O-C_6H_4-\boldsymbol{C}H_2-N$); *ipso carbon*; 159.7 (Ar–$4OCH_3$); 114.3–137.7 (other aromatic carbons); 207.9 ($N\boldsymbol{C}S_2$); Anal. Calcd. for Chemical Formula: $C_{34}H_{36}N_2NiO_2S_4$ (%): Elemental Analysis: C, 59.04; H, 5.25; N, 4.05; Found: C, 58.46; H, 4.99; N, 4.00.

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