



Bis(κ^2 S,S'-di(isopropyl)dithiocarbamato)nickel(II): Anagostic C–H \cdots Ni interactions and physical properties



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ABSTRACT

The molecular structure of bis(κ^2 S,S'-di(isopropyl)dithiocarbamato)nickel(II) has been examined by single crystal X-ray diffraction. The data reveal a C–H \cdots Ni anagostic interaction arising from the interaction of two non-equivalent molecules within the crystal. Thermal analysis data show that the complex decomposes at ~ 330 °C. The structure of the resultant NiS material was examined using scanning electron microscopy and energy dispersive X-ray spectroscopy which revealed NiS nanowires.

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1. Introduction

Dithiocarbamate complexes have attracted a significant amount of attention due to their ease of synthesis, their ability to coordinate to a range of transition and main block elements, and their interesting and useful properties [1–3]. The combination of various metal centres with the sizeable range of substituted dithiocarbamate ligands has yielded complexes with applications such as anti-neoplastic agents [4], rescue agents in cisplatin therapy [5], bio-analytical agents [6] as well as single source precursors of metal sulfide nanoparticles [7]. Dithiocarbamate complexes have also been investigated for the development of new sensors, IR detectors and solar cell technologies [8]. Substitution of the dithiocarbamate ligand gives rise to a range of electronic and steric effects across associated complexes. Some synthetic efforts have focused on optimising ligand design to allow for altered thermal properties required for nanoparticle synthesis [9]. Thus, dithiocarbamate complexes containing heterocyclic [10], alkyl [11] and phenyl [12] ligands have been pursued as single source nanoparticle

precursors.

In the context of structural interactions and possible applications of metal dithiocarbamate complexes, we have revisited the synthesis and spectroscopic characterisation of bis(κ^2 S,S'-di(isopropyl)dithiocarbamato)nickel(II) and herein report a packing polymorph of the title compound showing anagostic interactions. There are few reported structural determinations for di(isopropyl)dithiocarbamato (i-PrDTC) complexes with the only examples being Au(i-Pr₂DTC)₂, Pb(i-Pr₂DTC)₂, Hg(i-Pr₂DTC)₂ and Ni(i-Pr₂DTC)₂ [13–16].

2. Experimental

2.1. Reagents and instruments

Chemicals and solvents used in synthetic procedures were analytical or reagent grade and purchased from Sigma Aldrich and used as received. Millipore water (18.4 M Ω cm⁻¹) was used in synthetic procedures. FT-IR spectra of single crystals were recorded using an Agilent Cary 630 FTIR spectrometer fitted with a ZnSe ATR accessory. Each spectrum was collected using 16 scans, with a resolution of 4 cm⁻¹ over the range of 4000–700 cm⁻¹.

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Proton and carbon nuclear magnetic resonance spectroscopy was performed using an Agilent Technologies NMR instrument operating at 500.3 MHz (for ^1H experiments) and 125.7 MHz (for ^{13}C experiments) at 25 °C. ^1H experiments were acquired using 16 scans with a 0.01 s relaxation delay and a pulse angle of 60°. For ^{13}C experiments, 300 scans with a 1.00 s relaxation delay and a pulse angle of 45° were used. The title compound was dissolved in deuterated chloroform and the solvent residual chemical shifts of 7.26 ppm (for ^1H experiments) and 77.0 ppm (for ^{13}C experiments) were used to calibrate the spectra. Compound **1** was dissolved in deuterated methanol and the solvent residual chemical shifts of 3.31 ppm (for ^1H experiments) and 49.0 ppm (for ^{13}C experiments) were used to calibrate the spectra. High resolution mass spectra were acquired using an Agilent 6510 Q-TOF with a mobile phase of 65% acetonitrile, 35% water.

UV–Vis spectra of CHCl_3 solutions ($8.3 \times 10^{-5} \text{ mol L}^{-1}$) were recorded using an Agilent 8453 spectrometer. The spectra were collected from 190 to 1100 nm using a resolution of 1 nm. A Thermal Advantage SDT-Q600 thermal analyser was used to obtain TG, DTG and DSC data simultaneously using alumina crucibles. Experiments were conducted using a flow of nitrogen gas (150 ml min^{-1}) and a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ over a temperature range of 25–500 °C. Residues from TGA experiments were imaged using a Zeiss Supra 55VP SEM and a Zeiss EVO LS15 SEM fitted with a Bruker Nano EDX detector was used for EDX microanalysis.

2.2. Crystallographic analysis

Suitable single crystals of **2** (Scheme 1) were selected under a polarizing microscope (Leica M165Z), mounted on a MicroMount (MiTeGen, USA) consisting of a thin polymer tip with a wicking aperture. The X-ray diffraction measurements were carried out on a Bruker Kappa-II CCD diffractometer at 150 K using an μs Incoatec Microfocus Source with Mo- $K\alpha$ radiation ($\lambda = 0.710723 \text{ \AA}$). The single crystal, mounted on the goniometer using cryo loops for intensity measurements, was coated with paraffin oil and then quickly transferred to the cold stream using an Oxford Cryo stream attachment. Symmetry related absorption corrections using the program SADABS [17] were applied and the data were corrected for Lorentz and polarisation effects using Bruker APEX2 software [18]. The structure was solved by direct methods and the full-matrix least-squares refinement was carried out using Shelxl [19] in Olex2 [20]. The non-hydrogen atoms were refined anisotropically. The molecular graphic was generated using Olex2 [20]. Packing diagrams were generated using the program Mercury [21].

2.3. Synthesis

Synthesis of sodium di(isopropyl)dithiocarbamate (1): Compound **1** (Scheme 1) was prepared using an adaptation of the method of Shinobu et al. [22] An aqueous solution of sodium hydroxide (4.00 g in 10 mL) was cooled with stirring to 0 °C. Diisopropylamine (10 mL) was added followed by diethyl ether (120 mL). The solution was maintained at 5 °C whilst carbon disulfide (10 mL in 5 mL of ethanol) was added dropwise. A precipitate formed immediately

upon addition and the resultant mixture was stirred for 30 min. The crude product was collected by filtration and purified by recrystallisation of a saturated methanolic solution by slow diffusion of diethyl ether. The colourless crystals were collected by filtration, washed with cold diethyl ether, and dried over P_2O_5 *in vacuo*. The ligand crystallises with two waters of hydration as shown by TGA. HRMS ($\text{M} + \text{H}$)⁺ for $\text{NaNs}_2\text{C}_7\text{H}_{14}$ Calculated: 200.0538; Found: 200.0549. ^1H NMR (500.3 MHz, CD_3OD): δ 6.24 (br.s, 1H, $\text{CH}(\text{CH}_3)_2$), 3.88 (br.s, 1H, $\text{CH}(\text{CH}_3)_2$), 1.68 (br.s, 6H, $\text{CH}(\text{CH}_3)_2$), 1.17 (br.s, 6H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (125.7 MHz, CD_3OD): δ 211.2 (NCS_2), 57.5 ($\text{NC}(\text{CH}_3)_2$), 51.0 ($\text{NC}(\text{CH}_3)_2$), 21.3 ($\text{C}(\text{CH}_3)_2$), 19.8 ($\text{C}(\text{CH}_3)_2$).

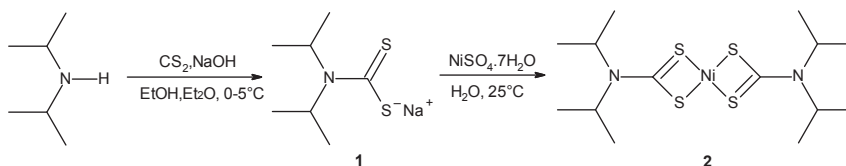
Synthesis of bis($\kappa^2\text{S,S}'$ -di(isopropyl)dithiocarbamato)nickel(II) (2): An aqueous solution of compound **1** (3.00 g, 13 mmol, in 10 mL of water) was added to an aqueous solution of nickel sulfate heptahydrate (1.46 g, 5 mmol in 8 mL of water). A dark green precipitate formed immediately upon addition. The precipitate was filtered, washed with ice cold water and then diethyl ether, and dried over P_2O_5 *in vacuo* to yield 1.77 g of **2** (86%). Crystals suitable for X-ray analysis were obtained as dark green blocks from solvent counter diffusion of diethyl ether into a chloroform solution of **2** over two days. HRMS ($\text{M} + \text{H}$)⁺ for $\text{NiN}_2\text{S}_4\text{C}_{14}\text{H}_{28}$ Calculated: 411.0562; Found: 411.0566. ^1H NMR (500.3 MHz, CDCl_3): δ 4.56 (br.s, 2H, $\text{CH}(\text{CH}_3)_2$), 1.38 (br.s, 12H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (125.7 MHz, CDCl_3): δ 205.8 (NCS_2), 50.9 ($\text{NC}(\text{CH}_3)_2$), 19.7 ($\text{C}(\text{CH}_3)_2$) UV-vis. (CHCl_3 , ϵ ($\text{L mol}^{-1} \text{ cm}^{-1}$): λ 618 (76), 490 (268), 435 (1581), 400 (5840), 330 (32100).

3. Results and discussion

3.1. X-ray crystal structure determination

Relevant crystal data, selected bond lengths and angles are given in Tables 1 and 2. Analysis of the X-ray crystal structure reveals some interesting differences compared to previously reported data for this compound [13,23]. In the current study, there are two independent molecules in the asymmetric unit (Fig. 1). There are no significant differences in bond lengths, angles or intermolecular interactions between the current and previous structural determinations. The nickel atoms, Ni1A (molecule A) and Ni1B (molecule B) are located at centrosymmetric special positions at (0,0,0.5) and (0,0.5,0.5), respectively. There are no significant differences between corresponding bond lengths and bond angles in the two independent molecules. Both NiS_4 environments are approximately square planar, however there is a significant difference in the torsion angles about the Ni–S–C–S coordination centre; 1.69 (6°) for Ni1A–S1A–C1A–S2A and 0.23 (7°) for Ni1B–S1B–C1B–S2B. The geometry about N1A is close to planar ($\text{C5A–N1A–C1A–S2A} = 0.2$ (2°)) while the geometry about N1B deviates somewhat from planarity ($\text{C5B–N1B–C1B–S2B} = -3.7$ (2°)).

The unit cell parameters of **2** determined in the current work are summarized in Table 3 together with previously reported data for comparison [13,23]. The unit cells are different with cell volumes, c axis lengths and β significantly smaller in the current study compared to the previous determinations. The differences between



Scheme 1. Synthesis of **1** and **2**.

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