Structural characterization and preliminary decomposition study of four unsymmetrically substituted nickel dithiocarbamate complexes

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ABSTRACT
Single-crystal X-ray structures of four nickel dithiocarbamate complexes, the homoleptic mixed-organic bis-dithiocarbamates Ni[S₂CN(isopropyl)(benzyl)]₂, Ni[S₂CN(ethyl)(n-butyl)]₂, and Ni[S₂CN(phenyl)(benzyl)]₂, as well as the heteroleptic mixed-ligand complex NiCl[P(phenyl)]₂[S₂CN(phenyl)(benzyl)], were determined. A slightly distorted square-planar nickel coordination environment was observed for all four complexes. The organic residues adopt conformations to minimize steric interactions. Steric effects also may determine puckering, if any, about the nickel and nitrogen atoms, both of which are planar or nearly so. A trans-influence affects the Ni-S bond distances. Nitrogens interact with the CS₂ carbons with a bond order near two; the other substituents on nitrogen display transoid conformations. There are no strong intermolecular interactions, consistent with prior observations of the volatility of nickel dithiocarbamate complexes. A preliminary thermolysis study of the homoleptic species results in production of 1:1 nickel sulfide phases, indicating the potential utility of these species as “single-source” precursors.

1. Introduction
The structure and properties of metal dithiocarbamates M(S₂CNRR')ₓ and closely related compounds [1–5] remain an important area of research [6–10]. This is due to fundamental insights into coordination chemistry to be gained from in-depth studies of dithiocarbamates [6] and wide-ranging, practical applications in agriculture [11–13], biomedicine [13–16], surface science [16, 17], and materials science [18–27].
The present and a closely related follow-on [28] study are the most recent reports from an ongoing effort to prepare new metal coordination compounds with sulfur-containing ligands (thiolates or dithiocarbamates), determine their single-crystal structures, and probe their decomposition to assess their value as (new) "single-source" precursors for solid-state, thin-film, and/or nanoparticles of sulfides [21, 29–36] for possible aerospace applications. Ideally, such precursors should be readily prepared from inexpensive starting materials, easily handled (preferably air-stable), and/or cleanly decomposed via chemical (vapor) processing to be economically viable [19–36]. In fact, these useful properties overlap quite well with the anticipated advantages to be realized by use of single-source precursors.

Our interest in this particular class of compounds concerns their use as precursors for nickel sulfide solid-state materials [18–20, 23, 25–27]. In this report, we detail the synthesis and characterization of four new Ni(II) dithiocarbamate complexes, the homoleptic unsymmetrically substituted bis-dithiocarbamates Ni[S₂CN(isopropyl)(benzyl)]₂ (1), Ni[S₂CN(ethyl)(n-buty1)]₂ (2), and Ni[S₂CN(phenyl)(benzyl)]₂ (3), together with the heteroleptic mixed-ligand complex Ni[P(phenyl)₃]Cl(S₂CN(phenyl)(benzyl)) (4). The three homoleptic dithiocarbamates are of particular interest, as their decomposition under anaerobic conditions at 400 °C results in a mass loss consistent with the formation of a 1:1 nickel sulfide phase consistent with prior literature [19, 20, 23, 25, 26].

2. Experimental

Unless otherwise indicated, chemicals and solvents were used as received. Galbraith Laboratories, Inc., Knoxville, TN, performed elemental analyses of final compounds. A Cahn TG-2131 thermogravimetric analysis (TGA) instrument was utilized with a heating rate of 5 °C/min starting at room temperature to 800 °C under flowing nitrogen [21, 32]; the mass loss was determined at 400 °C, based on prior studies [18–20, 23, 25].

Sodium N-R-N′-carbodithioate salts were prepared by the method of von Braun [37] and Delepine [38], later modified by Akerstrom [39]. Sodium hydroxide (6 g) was added slowly to distilled water (10 mL) cooled in an ice bath. With continued cooling, 0.10 mol of N-isopropyl-N-benzylamine, N-ethyl-N-butylamine, or N-phenyl-N-benzylamine [HN(R)(R′), with R, R′ = i-C₃H₇ (iPr), CH₂C₆H₅ (Bz); C₂H₅ (Et), n-C₄H₉ (n-Bu); or C₆H₅ (Ph), Bz; Aldrich, iR grade] was added slowly with rapid stirring, followed by reagent grade CS₂ (6.0 mL, 0.10 mol, Fisher Scientific). After stirring and cooling for two hours, light brown crystals were separated and dissolved in boiling distilled water (20 mL). The mixture was cooled and, after addition of absolute ethanol (5 mL), the resulting crystals were separated by filtration, washed repeatedly with petroleum ether, air-dried overnight, and used without purification.

Synthesis of unsymmetrical dithiocarbamates began with mixing aqueous solutions of nickel(II) chloride hexahydrate, NiCl₂·6H₂O (0.714 g, 3 mmol), and a sodium N-R-N′-carbodithioate salt (6 mmol). Bright green micro-crystals formed immediately and were collected on a sintered glass filter. The solid was transferred to a beaker and dissolved in CHCl₃ (50 mL). Any remaining aqueous fraction was discarded and the CHCl₃ solution was transferred to a filter flask. After addition of hexanes (50 mL), the solvent was evaporated under reduced pressure. When most of the CHCl₃ was removed, fine green crystals of product precipitated and were collected on a sintered glass filter. The wet crystals were washed with hexanes until the filtrate was colorless. The compound was dried overnight; a typical yield of dithiocarbamates was ~70%.

Results of elemental analyses and thermogravimetric analysis are reported as follows: abbreviated compound structural formula, empirical formula, color, molecular weight, analysis (%) calculated (found), and % mass remaining at 400 °C (calculated for NiS). Results for: 1 [Ni(S₂CNPrBz)] (C₂₂H₂₈N₂S₄Ni), green; 507.43; C, 52.1 (50.4); H, 5.6 (5.2); N, 5.5 (5.3); 18.4 (17.9); 2a [Ni(S₂CNETBu)] (C₁₄H₂₈N₂S₄Ni), dark green; 411.34; C, 40.9 (40.8); H, 6.9 (6.6); N, 6.8 (6.8); 21.2 (19.5); and 3 [Ni(S₂CNPhBz)] (C₂₈H₂₄N₂S₄Ni), green; 575.47; C, 58.4 (57.9); H, 4.2 (4.2); N, 4.9 (4.9); 15.2 (15.8).

Chloro(N-phenyl-N-benzylcarbodithioato)(triphenylphosphine)nickel(II), NiCl[P(C₆H₅)₃]S₂CN(C₆H₅)(CH₂C₆H₅) (4), was prepared by dissolving [Ni(S₂CNPhBz)] (0.575 g, 1.00 mmol), triphenylphosphine, PPh₃ (0.525 g, 2.0 mmol), and NiCl₂·6H₂O (0.238 g, 1.00 mmol) in boiling absolute ethanol (~20 mL). The
solution was stirred at reflux for 30 min. As the solution began to cool, a fine green precipitate settled to the bottom of the beaker. The solution was filtered through a medium sintered glass filter to remove the precipitate. The red-violet solution was allowed to cool to room temperature and then cooled further in an ice bath. After 30 min, red-violet crystals formed and n-heptane (10 mL) was added to further precipitate the complex. The solid was recovered by filtration through a medium sintered glass filter, washed with n-heptane, and air-dried overnight. Results of elemental analyses and thermogravimetric analysis are reported as follows: abbreviated compound structural formula, empirical formula, color, molecular weight, analysis (%) calculated (found), and % mass remaining at 400 °C (calculated for NiS).

Results for 4 [NiCl(S₂CNPhBz)PPh₃] (C₃₂H₂₇NS₂PClNi), violet; anal. 614.82; C, 62.5 (61.0); H, 4.4 (4.5); N, 2.3 (2.4); 22.0 (16.5). The most likely cause of the low carbon analysis for 1 and 4 is precipitation of unreacted NiCl₂·6H₂O along with the heteroleptic dithiocarbamate complexes.

Microcrystals of each compound were taken up in hot ethanol, and single crystals suitable for X-ray diffraction grew by slow evaporation of the solvent upon standing for three weeks at room temperature. Crystals of 1 were dark green equant, 2a dichroic orange prismatic, 3 dichroic green prismatic, and 4 violet prismatic. Single crystals were cemented to a quartz fiber with epoxy glue in a random orientation. X-ray intensity data were collected at 150 K on a Nonius KappaCCD X-ray diffractometer system using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Cell constants for data collection were obtained from least squares refinement, and the space groups were determined using the program XPREP. Frames were integrated with DENOZO-SMN [40]. Lorentz and polarization corrections were applied to the data. Structures were solved using the program PATTY in DIRDIF-99 [41] for 1, 2a, and 4 and by direct methods using SIR-2004 for 3 [42]. Scattering factors were taken from the international tables for crystallography [43]. Refinement was performed on an AlphaServer 2100 using SHELX-97 [44]. Crystallographic drawings were produced using ORTEP and PLUTO [45, 46]. The crystallographic information is summarized in Table 1. ORTEPs showing the atom labeling schemes are given in Figures 1–4, and cell diagrams are shown in Figure 5. Deposition numbers for crystallographic information files (CIFs) deposited with the Cambridge Crystallographic Data Center are given in Table 1.

3. Results and discussion

Single-crystal X-ray determinations for the four complexes (Table 2) allow for a comparison to the abundant literature for structures of dithiocarbamate complexes related to both homoleptic (1–3) [5, 23, 26, 47–53] and heteroleptic (4) [54–56] compounds of this study (Table 3). A structure determination for [Ni(S₂CN=CNEtBu)₂] (2b) has been reported previously [51] with a different unit cell although in the same space group, and our modification (2a) is included here for comparison. The asymmetric units of 2a and 3 comprise one half of these molecules with the metal atoms lying on inversion centers. As expected, the phenyl groups in 1, 3, and 4 are essentially planar. The butyl chain in 2a has an all-anti conformation, and the butyl and ethyl chains also are directed to opposite sides of the core structure; this should be the lowest energy conformation, minimizing steric interactions. The nickel ions necessarily reside in the plane of the ligands in 2a and 3 due to the symmetry, but they pucker slightly to lie above this plane by 0.0212(3) Å in 1 and 0.0446(5) Å in 4.

The average Ni−S bond lengths for the three homoleptic [2.2020(5)–2.2084(6) Å] and the mixed-ligand 4 [2.2110(8) Å] complexes are unexceptional. Of the three homoleptic species, the bis(isopropylbenzyl) complex (1) is the most asymmetric with a difference in Ni−S bond lengths of 0.0118(5) Å, similar to several other homoleptic unsymmetrical complexes involving mixed (aryl–alkyl or proton–alkyl) substituents (R−′R′ = “Bu-Bz, H-Pr, H-Adamantyl, Methyl-Ph) [26, 48–50]. The unsymmetrically substituted 2a and 3 with either two aliphatic or aromatic substituents have nearly symmetrical Ni−S coordination, typical of other nickel dithiocarbamates [5, 23, 47, 51–53].

The Ni−S bonding in 4 and analogous complexes [54–56] is quite asymmetric, however, with the Ni−S(1) bond trans to the electron-withdrawing chloride being shorter than the Ni−S bond trans to the phosphine by 0.0464(8) Å. This asymmetry has been observed previously for structurally related neutral compounds, including symmetrically substituted heterocyclic complexes [Ni(X)₃(S₂CNRR′)(PPh₃)]
$X = \text{Cl}, \text{Br}, \text{I}, \text{NCS}; R, R' = \text{Et}, \text{"Bu}, (\text{CH}_2)_4 \text{] [57–59]. It can be ascribed to a structural trans-effect, phosphines being stronger trans-influencing ligands than chloride as found commonly in square-planar complexes of Pd and Pt [60].}

**Figure 1.** ORTEP diagram with 30% thermal ellipsoids and atomic labeling scheme of Ni(S$_2$CNPrBz)$_2$ (1).

**Figure 2.** ORTEP diagram with 30% thermal ellipsoids and atomic labeling scheme of Ni(S$_2$CN'BuEt)$_2$ (2a).
Bond lengths involving the sp² hybridized carbons (C1 or C10) near the core of the dithiocarbamate complexes are typically 1.71(1)–1.73(2) Å for S⋯C and 1.29(1)–1.33(1) Å for N⋯C, consistent with a number of previously reported homoleptic and heteroleptic complexes [5, 23, 26, 47–59]. As expected,
the N–C(sp³) single bonds attached to the organic substituents are longer by ~0.15 Å than the N–CS₂ bond and are typical (1.47 ± 0.02 Å) for all four complexes [5]. Bond lengths near 1.3 Å found for the N–CS₂ bonds are more characteristic of N=C double bonds [61] and indicate considerable double bond character to be present between N and the CS₂ carbon in these complexes [49].
A hybridization of sp$^2$ also is consistent with the observation of small pyramidalization of the nitrogens, which are nearly planar in 2a and 3 (Table 4). The effect would be to shift electron density from nitrogen to sulfur, placing the nickel in a relatively electron-rich environment. The greatest
pyramidalization is found in 1, due possibly to the steric demands of the isopropyl group. However, since the nitrogens in 3 and 4 are similarly substituted yet pyramidalize to different degrees, other effects such as molecular packing likely contribute as well. Small pyramidalization about nitrogen is common in sp2-hybridized aromatic amines such as carbazoles and occurs with little sacrifice of energy [62].

Table 3. Average bond distances and angles for unsymmetrical Ni dithiocarbamate complexes.\textsuperscript{a,b}

| Compound |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ni(S\textsubscript{2}CNEt\textsubscript{2}Bu)\textsubscript{2} | 2.2084 | 79.28 | 1.722 | 109.9 | 85.42 | 1.321 |
| Ni(S\textsubscript{2}CNEt\textsubscript{2}Cy)\textsubscript{2} | 2.2040 | 79.29 | 1.724 | 109.4 | 85.69 | 1.319 |
| Ni(S\textsubscript{2}CNEt\textsubscript{2}PrBz)\textsubscript{2} | 2.2041 | 79.20 | 1.715 | 109.9 | 85.4 | 1.322 |
| Ni(S\textsubscript{2}CNEt\textsubscript{2}PhBz)\textsubscript{2} | 2.2020 | 79.55 | 1.720 | 110.04 | 85.20 | 1.318 |
| Ni(Cl)(PPh\textsubscript{3})(S\textsubscript{2}CNPhBz)\textsubscript{2} | 2.2224(11) | 79.02(3) | 1.730 | 107.93(11) | 86.53 | 1.309(3) |
| Ni(Cl)(PPh\textsubscript{3})(S\textsubscript{2}CNPhBz)\textsubscript{2} | 2.2205(8) | 78.05(3) | 1.716 | 107.9(2) | 87.0 | 1.316(4) |
| Ni(Cl)(PPh\textsubscript{3})(S\textsubscript{2}CNPhBz)\textsubscript{2} | 2.2218(16) | 78.38(6) | 1.713 | 108.3(3) | 86.3 | 1.329(8) |
| Ni(Cl)(PPh\textsubscript{3})(S\textsubscript{2}CNPhBz)\textsubscript{2} | 2.2087(12) | 79.13(5) | 1.717 | 107.7(2) | 87.1 | 1.325(4) |

\textsuperscript{a}Values with standard deviations are unique.
\textsuperscript{b}Temperature of data collection 293 ± 2 K or:
\textsuperscript{a}120 K.
\textsuperscript{b}150 K.
\textsuperscript{c}200 K.
\textsuperscript{d}100 K.
\textsuperscript{e}Bond trans to phosphorus.

Table 4. Distances (Å) of atoms from the specified planes.

| Cmpd. |
|-----------------|-----------------|-----------------|
| Ni from ligands | C(S\textsubscript{2}) from ligands | N from attached C |
| 1 | 0.0212(3) | 0.0221(19), 0.045(2) | 0.081(2), 0.0763(19) |
| 2a | 0 | 0.020(3) | 0.016(2) |
| 2b | 0 | 0.007(3) | 0.009(3) |
| 3 | 0 | 0.011(2) | 0.0367(16) |
| 4 | 0.0446(5) | 0.004(3) | 0.004(3) |

\textsuperscript{c}Coordinates from reference [51].

Figure 6. Transoid orientation of the alky groups (R and R') in 1–4.
Since the nitrogens are nearly planar and lie close to the plane of the inorganic core atoms, cisoid and transoid conformations are possible for the two alkyl or aryl substituents R and R′ on nitrogen in the homoleptic derivatives 1–3. The transoid geometry, in which the same organic groups are located on opposite sides of the structure, is found for all three (Figure 6). This orientation should minimize steric interactions and is expected to be lowest in energy.

The chelated S–Ni–S bond angles for the three homoleptic compounds are similar [79.28(2)–79.55(2)°], typical for homoleptic complexes reported with an average bond angle of 79.5 ± 0.4° [5, 23, 26, 47–53]. The heteroleptic 4 has a smaller bite of 78.31(12)°, within the margin of error for related mixed-ligand (pseudo)halide triphenylphosphine dithiocarbamate complexes, with an average bond angle of 78.7 ± 0.4° [54–59]. The S–C–S bond angle of 110.04° for 3 is similar to that of 1 and 2a and is typical for asymmetrically substituted homoleptic compounds [5, 23, 26, 47–53]. This angle is more than one degree smaller in 4, which like 3 also bears benzyl and phenyl organic residues, and corresponds with an S–Ni–S angle which is smaller by about the same amount, consistent with observations for other heteroleptic compounds [54–59]. The smaller bite angles about nickel and carbon in 4 are probably once again attributable to steric effects, here involving the five phenyl groups.

The Ni–S–C bond angles for 1–3 of 85.20(6)–85.68(7)° are in the midrange of 85.5 ± 0.5° observed for other homoleptic compounds [5, 23, 26, 47–53], and the slightly wider angle found in 4 of 86.5(1)° is typical of heteroleptic species [54–59]. Slight differences in the shape of the central ring of the two types of compounds could be a result of the effect of electron-withdrawing (pseudo-)halides. Bond lengths and angles outside of the core ring structure vary considerably as there are a large number of structural types, and more overarching analyses of bonding-structure correlations in dithiocarbamates and related complexes as well as potential correlations to spectroscopy have been addressed previously [1–5].

The structures reveal only weak intermolecular interactions. Putative weak intermolecular hydrogen bonds to sulfur with S···H′ distances less than the sum of the van der Waals radii (3.0 Å) are found in 1, 2a, and 4, whereas the interactions in 3 occur just beyond this distance (Table 5). The closest contacts are found in 1 (2.824 Å) and in 2a (2.631 Å), indicating that steric effects involving the phenyl groups

| Interactiona | Distances | Angles |
|--------------|-----------|--------|
| 1 Ni···H124 | 3.008     | Ni···S11···H113' 145.1 Ni···S11···H113' 89.0 S11···H113'···C113' 147.4 |
| S1···H113'  | 3.022     | C10···S11···H113' 166.7 Ni···S12···H213' 104.6 S12···H213'···C213' 148.5 |
| S2···H213'  | 2.824     | C10···S12···H213' 3.390(4) |
| C223···C223'| 3.390(4)  |        |
| 2a Ni···H14C| 3.454     | Ni···S11···H168' 173.8 Ni···S11···H168' 98.0 S11···H168'···C16 101.0 |
| S1···H168'  | 2.847     | C1···S1···H168' 159.4 Ni···S2···H15A' 151.6 S2···H15A'···C15' 107.5 |
| S2···H15A'  | 2.631     | C1···S2···H15A' 3.157 |
| 3 Ni···H24  | 3.157     | Ni···S11···H12' 134.7 Ni···S11···H12' 92.0 S11···H12'···C12' 132.9 |
| S1···H12'   | 3.019     | C1···S1···H12' 91.7 Ni···S1···H23' 111.8 S1···H23'···C23' 155.7 |
| S1···H23'   | 3.018     | C1···S1···H23' 96.2 Ni···S2···H20A' 114.5 S2···H20A'···C20' 127.3 |
| S2···H20A'  | 3.014     | C1···S2···H20A' |
| 4 Ni···H215 | 3.327     | Ni···Cl···H116' 94.0 Cl···H116'···C116' 147.2 |
| Cl···H123'  | 2.901     | Cl···H123'···C123' 165.9 |
| S2···H116'  | 2.956     | C10···S2···H116' 60.0 Ni···S2···H116' 92.9 S2···H116'···C116' 145.0 |
| C114···H121' | 2.972 | C1···S2···H215' 88.5 Ni···S2···H215' 79.8 S2···H215'···C215' 141.2 |
| C124···H233' | 2.975 |        |

aDashed lines represent intramolecular interactions, dotted lines intermolecular interactions, and primed atoms represent positions in a different molecule. van der Waals contact distances: CH 2.90, CC 3.40, SH 3.00, CIH 2.95, NIH 2.83; see: http://periodictable.com/Properties/A/VanDerWaalsRadius.al.html.
likely prevent as close an approach to the core ring in 3 and 4. Two additional weak hydrogen bonds involving Cl also are present in 4 with Cl⋯H’ distances near the sum of the van der Waals radii (2.95 Å). The interaction diagrams in Figure 7 indicate that the nickel ions have no close intermolecular contacts despite the coordination being essentially planar. Instead, the organic moieties of adjacent molecules fit hand-in-glove in the region about the open axial coordination sites. Steric effects arising from the organic groups would be present here as well and in 1 and 4 intramolecular hydrogens approach nickel (Table 5), further obstructing the coordination site about the plane of the inorganic core. However, nickel exhibits low propensity for axial coordination relative to copper and zinc in related bis(diethyl)dithiocarbamate compounds [63], which likely plays a large role in these heteroleptic analogs as well. The absence of stronger intermolecular interactions is responsible for the volatility of the nickel-containing compounds as discussed below.

Comparison of the two modifications of 2 reveals that the unit cell volume [1002.23(18) Å³] reported previously for 2b [51] is 4% larger than that [963.73(11) Å³] for the structure 2a determined here. A smaller cell is preferable as a larger volume allows for greater thermal motion and other disorder, and large temperature factors may afford bond distances smaller than the actual values [64]. Indeed, the isotropic temperature factors on the refined atoms of the published structure are about twice as large as those on corresponding atoms of 2a with the smaller volume, and 10 of the 11 unique bond distances between refined positions reported for modification 2b are smaller than those determined for 2a. More efficient packing in the smaller cell also would allow greater intermolecular interactions, decreasing volatility as discussed below. Otherwise, the structures of the two modifications are similar, with the most significant difference (over 4°) being the dihedral angle formed between the planes of the core structure and the aminoisopropyl group (Table 6).

The volatility of some nickel(II) dithiocarbamates has been reported for more than a century and more recently reviewed [65, 66]. bis(diisopropylthiocarbamato)nickel(II), for example, sublimes in vacuum almost without decomposition [38], whereas bis(diisobutylthiocarbamato)nickel(II) exhibits a single mass loss of 93% at 390 °C [67] and bis(dibutylthiocarbamato)nickel(II) also exhibits significant volatility [18]. Likewise, O’Brien and coworkers observed mass loss greater than that predicted for

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**Figure 7.** Interaction diagram showing close contacts to the core structures of (a) 1, (b) 2a, (c) 3, and (d) 4.
elemental nickel residue for symmetrically and unsymmetrically substituted Ni(S₂CNRR′)₂ complexes (R, R′ = Me, Et, nBu, Cy) [20]. Nevertheless, in the same report, low-pressure chemical vapor deposition of four homoleptic complexes resulted in the production of one or two NiS phases.

As outlined in Section 2, our preliminary TGA results also are consistent with formation of 1 : 1 NiS phases for 1–3, as mass residues are within 5% of prediction for NiS. This can be contrasted with the heteroleptic complex where a 33% differential is clearly inconsistent with production of a 1 : 1 phase. The relatively high conversions of these unsymmetrically substituted complexes, even 2a which is an isomer of bis(diisopropylidithiocarbamato)nickel(II), may result from their greater surface areas and packing efficiencies (Figure 7). We currently are completing in-depth TGA, pyrolysis, and solid-state materials studies of the thermolysis of five homoleptic nickel dithiocarbamates [28].

4. Conclusion

A slightly distorted square-planar nickel coordination environment is observed for all four unsymmetrically substituted nickel(II) dithiocarbamate complexes. Compound 1 exhibits the greatest asymmetry of the Ni–S bonds among the homoleptic compounds, and a trans-influence affects the Ni–S bond distances in 4. The organic residues adopt conformations (transoid and anti) to minimize steric interactions. Steric effects also may determine the puckering of the nickel and nitrogens, both being planar or nearly so. The nitrogens essentially form double bonds to the CS₂ carbons. The other substituents on nitrogen in 1–3 adopt transoid conformations. There are no strong intermolecular interactions, consistent with previous reports of the volatility of these compounds. Preliminary TGA results are consistent with production of 1 : 1 NiS phases, pointing to the utility of these complexes for the fabrication of solid-state materials; a more detailed study is currently underway at NASA GRC.

Supplementary material

The Cambridge Crystallographic Data Center contains the full set of supplementary crystallographic data (CIFs) for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif (see Experimental and/or Table 1 for specific deposition numbers). More complete tables of bond lengths and angles (Tables S1–S4) are included in the Supplementary information.
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No potential conflict of interest was reported by the authors.

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