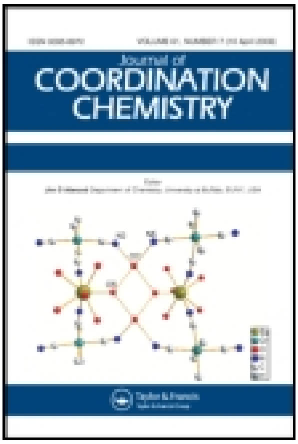

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Synthesis and spectroscopic characterization of bis(N-alkyldithiocarbamato)nickel(II) complexes: crystal structures of [Ni(S_2CNH(n-Pr))$_2$] and [Ni(S_2CNH(i-Pr))$_2$]

Subhash C. Bajia [a] & Anurag Mishra [b]

[a] Department of Pure and Applied Chemistry , M.D.S. University , Ajmer - 305 009, Rajasthan, India

[b] Department of Chemistry , University of Ulsan , Ulsan 680-749, Republic of Korea

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Synthesis and spectroscopic characterization of *bis*(*N*-alkyldithiocarbamato)nickel(II) complexes: crystal structures of [Ni(S_2CNH(*n*-Pr))$_2$] and [Ni(S_2CNH(*i*-Pr))$_2$]

SUBHASH C. BAJIA*† and ANURAG MISHRA‡

†Department of Pure and Applied Chemistry, M.D.S. University, Ajmer – 305 009, Rajasthan, India
‡Department of Chemistry, University of Ulsan, Ulsan 680-749, Republic of Korea

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Bis(*N*-alkyldithiocarbamato)nickel(II) complexes (**1–5**) [Ni(S_2CNHR)$_2$] (where R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu) were synthesized by the reaction of $NiCl_2 \cdot 6H_2O$ and the corresponding sodium salt of *N*-alkyldithiocarbamate in 1 : 2 molar ratio in aqueous medium. These *bis*(*N*-alkyldithiocarbamato)nickel(II) complexes (**1–5**) were characterized by elemental analysis, UV-Visible, IR, and $^1H/^{13}C$-NMR spectroscopy. The crystallographic investigation of [Ni(S_2CNH(*n*-Pr))$_2$] (**3**) and [Ni(S_2CNH(*i*-Pr))$_2$] (**4**) revealed distorted square-planar geometry around nickel(II). The dithiocarbamates have anisobidentate coordination with nickel and the dithiocarbamates are *trans*.

Keywords: Dithiocarbamate; Nickel(II) complex; Bidentate coordination

1. Introduction

Dithiolate ligands (*N*,*N*′-dialkyldithiocarbamates and *N*-alkyldithiocarbamates) exhibit remarkable diversities in their bonding/coordination possibilities with nickel(II) [1–4]. Dithiocarbamate salts have interesting biological applications, including anti-alkylation [5, 6] and anti-HIV [7, 8]. Attention has been focused on nickel dithiocarbamate complexes for the large variety of the reactions in which they are involved as catalysts, and are used for the preparation of semi-conducting metal sulfide thin films by single-source MOCVD techniques [3, 4].

A number of *bis*(*N*,*N*′-dialkyldithiocarbamato)nickel(II) complexes have been synthesized, several of them, such as [Ni(S_2CNHRR′)$_2$] [3, 4], [Ni(S_2CN(Et)$_2$)$_2$] [9], [Ni(S_2CN(*n*-Pr)$_2$)$_2$] [10], and [Ni(S_2CN(*i*-Pr)$_2$)$_2$] [11], have been characterized by single-crystal X-ray diffraction.

Binuclear nickel(II) dithiocarbamate has been synthesized using bridging ligands [12]. Mixed ligand nickel(II) dithiocarbamate complexes, such as [Ni(L)RNCS_2] (where R = Et_2, C_5H_{10} and L = dimethylglyoxime and oxine) [13] and bridged heterobimetallic dithiocarbamate complex [Ni(Zn(S_2CNEt_2)$_3$)$_2$], were reported. Less attention has been

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*Corresponding author. Email: subhashbajia@gmail.com

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paid to coordination chemistry of *N*-alkyldithiocarbamate with transition metals. Preliminary studies have been carried out on reactions of *N*-alkyldithiocarbamates such as NaS_2CNH_2 [14], NaS_2CNHMe [15], and *cis*-NaS_2CNH(*i*-Pr) [16] with nickel. We report herein the results of the synthesis and spectroscopic characterization of *bis*(*N*-alkyldithiocarbamato)nickel(II) complexes (**1–5**) and the determination of the molecular structure of [Ni(S_2CNH(*n*-Pr))$_2$] and [Ni(S_2CNH(*i*-Pr))$_2$] by single-crystal X-ray diffraction.

2. Experimental

2.1. *Chemicals and methods*

All chemicals (Emerk) were used after purification. Solvents were dried using standard method. $NiCl_2 \cdot 6H_2O$ (Emerk) was used as received. Elemental analysis (C, H, and N) was carried out on a Vario El III Elemental analyzer. Electronic spectra from 200 to 1100 nm were recorded on a Systronic 2201 double-beam UV-Visible spectrophotometer in dichloromethane (DCM). IR spectra (4000–300 cm^{-1}) were recorded on an ABBomen FTLA-2000 spectrophotometer using KBr discs. ^1H- and ^{13}C-NMR spectra were recorded on a Bruker DRX-300 spectrometer in $CDCl_3$ using TMS as an internal standard.

2.2. *Synthesis*

2.2.1. Synthesis of sodium salts of *N*-alkyldithiocarbamates. Sodium salts of the *N*-alkyldithiocarbamates were prepared by the reported method [17]. *N*-alkyl amine (30 mmol) in 30 mL methanol was cooled in an ice bath and carbon disulfide (30 mmol) was added dropwise with constant stirring, a light yellow precipitate was obtained. To this reaction mixture, NaOH (30 mmol) dissolved in a minimum of water was added dropwise with constant stirring. The precipitate dissolved and stirring was continued for 3 h. The reaction mixture was allowed to stand overnight at room temperature. Needle-shaped crystals of the sodium salt of *N*-alkyldithiocarbamates were obtained. The compound was filtered, washed with methanol and diethyl ether, and dried under vacuum.

2.2.2. Synthesis of *bis*(*N*-alkyldithiocarbamato)nickel(II) (1–5). *Bis*(*N*-alkyldithiocarbamato)nickel(II) complexes were prepared by the reaction of $NiCl_2 \cdot 6H_2O$ and NaS_2CNHR. The aqueous solution of the sodium salt (0.1 mol) was added to the aqueous solution of $NiCl_2 \cdot 6H_2O$ (0.05 mol) with constant stirring for 1 h. Light green precipitate was obtained, collected by filtration, washed with water, and dried. These complexes were recrystallized from DCM.

2.2.2.1. *[Ni(S_2CNHMe)$_2$] (**1**).* Aqueous solution of $NiCl_2 \cdot 6H_2O$ (0.237 g, 1.0 mmol) was added to the aqueous solution of NaS_2CNHCH_3 (0.258 g, 2.0 mmol) with constant stirring for 1 h. The light green precipitate was filtered and dried. Yield: 0.235 g (87%); Calcd for $C_4H_8N_2S_4Ni$: C, 17.72; H, 2.97; and N, 10.33. Found: C, 17.68; H, 2.92; and

N, 10.24. UV-Vis of 0.007 mol L^{-1} DCM solution λ_{max} (nm) (ε_{max} (mol^{-1} L cm^{-1})); 622 (200), 410 (96); IR KBr (υ_{max} cm^{-1}): 3482 m (N–H), 1515s (C–N), 982s (C–S), and 672, 360 m (Ni–S); ^{1}H-NMR (300 MHz CDCl$_3$): δ(ppm), 3.5 (s, 6H, CH$_3$).

2.2.2.2. *[Ni(S$_2$CNHEt)$_2$] (2).* Prepared as for **1**. Yield: 0.235 g (89%); Calcd for $C_6H_{12}N_2S_4Ni$: C, 24.09; H, 4.04; and N, 9.36. Found: C, 24.01; H, 4.0; and N, 9.30. UV-Vis of 0.006 mol L^{-1} DCM solution λ_{max} (nm) (ε_{max} (mol^{-1} L cm^{-1})); 636 (156), 425 (105); IR KBr (υ_{max} cm^{-1}): 3392s (N–H), 1520s (C–N), 1040s (C–S), 665, and 400s (Ni–S); ^{1}H-NMR (300 MHz, CDCl$_3$): δ(ppm), 1.2–1.5 (t, $J = 7.1$ Hz, 6H, CH$_3$), and 3.49–3.54 (m, $J = 7.2$ Hz, 4H, CH$_2$).

2.2.2.3. *[Ni(S$_2$CNH(n-Pr))$_2$] (3).* Prepared as for **1**. Yield: 0.267 g (91%); Calcd for $C_8H_{16}N_2S_4Ni$: C, 29.37; H, 4.93; and N, 8.56. Found: C, 29.33; H, 4.82; and N, 8.51. UV-Vis of 0.006 mol L^{-1} DCM solution λ_{max} (nm) (ε_{max} (mol^{-1} L cm^{-1})); 672 (252), 422 (148); IR KBr (υ_{max} cm^{-1}): 3455s (N–H), 1495s (C–N), 1000s (C–S), 650, 412s (Ni–S); ^{1}H-NMR (300 MHz, CDCl$_3$): δ(ppm) 0.85–0.90 (t, 6H, CH$_3$), 1.31–1.56 (m, 4H, CH$_2$), and 3.45–3.54 (m, 4H, NCH$_2$); ^{13}C-NMR (300 MHz): δ(ppm) 10.9 (CH$_3$), 20.2 (**CH$_2$**CH$_3$), 57.8 (**CH$_2$**NH), and 200.2 (N**CS$_2$**).

2.2.2.4. *[Ni(S$_2$CNH(i-Pr))$_2$] (**4**).* Prepared as for **1**. Yield: 0.165 g (86%); Calcd for $C_8H_{16}N_2S_4Ni$: C, 29.37; H, 4.93; and N, 8.56. Found: C, 29.30; H, 4.85; and N, 8.49. UV-Vis of 0.005 mol L^{-1} DCM solution λ_{max} (nm) (ε_{max} (mol^{-1} L cm^{-1})); 660 (204), 445 (109); IR KBr (υ_{max} cm^{-1}): 3510s (N–H), 1512s (C–N), 981s (C–S), 621, and 405s (Ni–S); ^{1}H-NMR (300 MHz, CDCl$_3$): δ(ppm) 1.67–1.18 (d, 6H, CH$_3$) and 4.1–4.19 (d, 2H, CH).

2.2.2.5. *[Ni(S$_2$CNH(n-Bu))$_2$] (5).* Prepared as for **1**. Yield: 0.319 g (89%); Calcd for $C_{10}H_{20}N_2S_4Ni$: C, 33.81; H, 5.68; and N, 7.88. Found: C, 33.78; H, 5.62; and N, 7.84. UV-Vis of 0.005 mol L^{-1} DCM solution λ_{max} (nm) (ε_{max} (mol^{-1} L cm^{-1})); 688 (178), 453 (116); IR KBr (υ_{max} cm^{-1}): 3460 (N–H), 1496s (C–N), 1010s (C–S), and 650, 392s (Ni–S); ^{1}H-NMR (300 MHz, CDCl$_3$): δ(ppm) 0.93 (s, 6H, CH$_3$), 1.36 (s, 4H, CH$_2$), 1.60 (s, 4H, CH$_2$), and 3.40 (s, 4H, CH$_2$).

All these complexes are soluble in common organic solvents, such as benzene and DCM, and were characterized by elemental analysis, UV-Visible, IR, and ^{1}H-NMR spectroscopic techniques. Molecular structures of *trans* [Ni(S$_2$CNH(*n*-Pr))$_2$] (**3**) and [Ni(S$_2$CNH(*i*-Pr))$_2$] (**4**) were determined by single-crystal X-ray diffraction.

2.3. *Crystal structure determination and structure refinement*

Diffraction experiments were performed on Bruker Smart and Siemens Smart CCD diffractometers for [Ni(S$_2$CNH(*n*-Pr))$_2$] (**3**) and [Ni(S$_2$CNH(*i*-Pr))$_2$] (**4**), respectively. The diffraction data were collected at 123 K for **3** and 296 K for **4** using graphite-monochromated Mo-Kα radiation. Cell refinement gave cell constants corresponding to orthorhombic for **3** and monoclinic for **4**. Crystal data and structure refinements for both complexes are given in table 1. The structures were solved by direct methods [18] and refined using the WinGX version [19] of SHELX-97 [20]. All non-hydrogen atoms were treated anisotropically.

Table 1. Crystal and experimental data for **3** and **4**.

Empirical formula	$C_8H_{16}N_2S_4Ni$	$C_8H_{16}N_2S_4Ni$
Formula weight	327.18	327.18
Temperature (K)	296(2)	123(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	*Pbca*
Unit cell dimensions (Å, °)		
a	9.4951(6)	7.9033(6)
b	7.8180(4)	11.2063(6)
c	9.9938(6)	15.7351(5)
β	106.297(2)	–
Volume ($Å^3$), Z	712.06(7), 2	1393.6(1), 4
Calculated density ($g\,cm^{-3}$)	1.526	1.559
Crystal size (mm^3)	$0.26 \times 0.18 \times 0.01$	$0.23 \times 0.19 \times 0.15$
Absorption coefficient (mm^{-1})	1.921	1.963
$F(000)$	340	680
θ range for data collection (°)	3.36–30.41	3.41–25.00
Index ranges	$-7 \le h \le 13$;	$-8 \le h \le 9$;
	$-11 \le k \le 0$;	$-13 \le k \le 13$;
	$-12 \le l \le 13$	$-17 \le l \le 18$
Reflections collected	5869	5746
Independent reflections	2106 [$R_{int} = 0.0189$]	1224 [$R_{int} = 0.0326$]
Maximum and minimum transmission	0.9810 and 0.6350	0.7572 and 0.6609
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2106/0/74	1224/0/76
Goodness-of-fit on F^2	1.074	1.076
Final R indices [$F^2 > 4\sigma(F^2)$]	$R_1 = 0.0314$, $wR_2 = 0.0729$	$R_1 = 0.0319$, $wR_2 = 0.0756$
R indices (all data)	$R_1 = 0.0480$, $wR_2 = 0.0905$	$R_1 = 0.0423$, $wR_2 = 0.0790$
Largest difference peak and hole (e $Å^{-3}$)	0.455 and −0.259	0.322 and −0.278
Structure determination	Direct methods (SHELXS-97)	Direct methods (SHELXS-97)
Refinement	Full-matrix least-squares (SHELXL-97)	Full-matrix least-squares (SHELXL-97)

3. Results and discussion

Complexes **1**–**5** were synthesized by the reaction of $NiCl_2 \cdot 6H_2O$ and NaS_2CNHR in 1 : 2 molar ratio in aqueous solution with constant stirring for 1 h, giving light green precipitate.

$$NiCl_2 \cdot 6H_2O + 2RNCS_2Na \rightarrow [Ni(S_2CNHR)_2] + 2NaCl$$

(where R = Me (**1**), Et (**2**), *n*-Pr (**3**), *i*-Pr (**4**), *n*-Bu (**5**)).

3.1. *IR spectra*

IR absorption bands at 1496–1520 cm^{-1} are intermediates between ν(C=N) (1691–1640 cm^{-1}) and ν(C–N) (1360–1250 cm^{-1}), indicating partial double bond character of the CN bond [21] (figure 1). Absorbances at 1050–950 cm^{-1} are diagnostic in deciding the coordination pattern of dithiocarbamate [17]. In this investigation, a single band is observed at 981–1040 cm^{-1}, characteristic for bidentate dithiocarbamate. The ν(Ni–S)

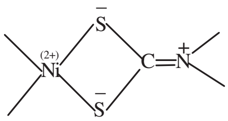

Figure 1. Partial double bond character in C–N bond.

absorptions are observed at 360–412 cm^{-1}, shifting to higher frequencies with higher alkyl group, but the butyl group has lower values.

3.2. *^{1}H-NMR*

NMR spectroscopy was used to characterize the metal complexes. Complexes **1–5** showed no NH protons, perhaps from solvent ($CDCl_3$) exchange. Methyl protons of **2–4** showed signal at 0.9–1.5 ppm, while **1** was at 3.5 ppm. Upfield shift for methyl protons, while downfield for methylene protons, were found from methyl to butyl dithiocarbamate complexes. The hydrogen on carbon adjacent to the nitrogen showed signals from 3.4 to 4.5 ppm and shifted upfield with higher alkyl groups. Complex **3** was characterized by ^{13}C-NMR spectroscopy. The methyl and methylene carbons are found at 10.9–20.2 ppm, while the methylene carbon near NH is at 57.8 ppm. The NCS_2 carbon was at 200.2 ppm.

3.3. *Electronic spectra*

Electronic absorption spectra of the **1–5** exhibit two d–d transitions in the regions 622–668 and 410–453 nm corresponding to $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively. The absorption pattern suggests square-planar coordination of nickel(II) [22]. On going from Me to Bu, the absorption shifted to higher wavenumber due to increasing inductive effect of the alkyl group.

3.4. *Molecular structure of [Ni(S$_2$CNH(n-Pr))$_2$] (3) and [Ni(S$_2$CNH(i-Pr))$_2$] (4)*

Complexes **3** and **4** were crystallized as monoclinic and orthorhombic space groups $P2_1/n$ and *Pbca*, respectively. The ORTEP diagrams (figure 2 for **3** and figure 3 for **4**) illustrate that nickel is essentially distorted square-planar with two bidentate dithiocarbamates. The nickel lies on the inversion center, implying the presence of non-equivalent alkyl group, and thus *trans* configuration. The second half of the molecule is generated by two successive operations: first, rotation along the twofold axis followed by reflection through the molecular plane (or *vice versa*), further suggesting that the molecule is *trans*. The point symmetry of the NiS_4 core in **3** is D_{2h}.

The average Ni–S distances of 2.2012(6) Å for **3** and 2.1942(8) Å for **4** are similar to the average Ni–S bond distances of *cis* [Ni(S$_2$CNH(*i*–Pr))$_2$] (2.212(4) Å) and [Ni(S$_2$CN(*i*–Pr)$_2$)$_2$] (2.203 Å). The average S–C bond distances are 1.719(2) Å in **3** and 1.719(3) Å in **4**, in good agreement with *cis* [Ni(S$_2$CNH(*i*–Pr))$_2$], suggesting the presence of S–C(sp^2) bond. The N(1)–C(2) bond length, 1.461(3) Å for **3** and 1.477(4) Å for **4**

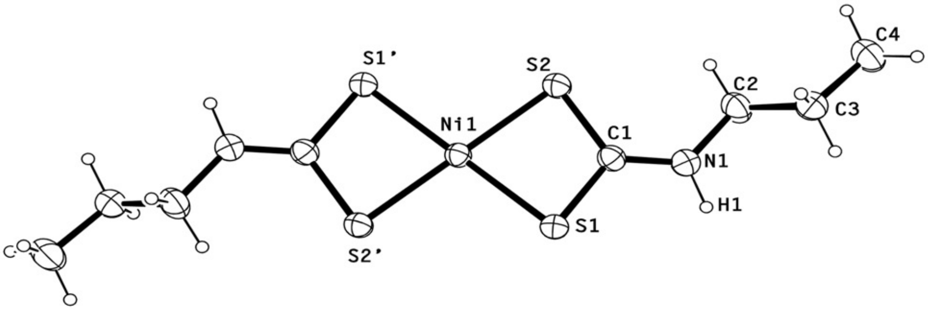

Figure 2. ORTEP plot of **3**.

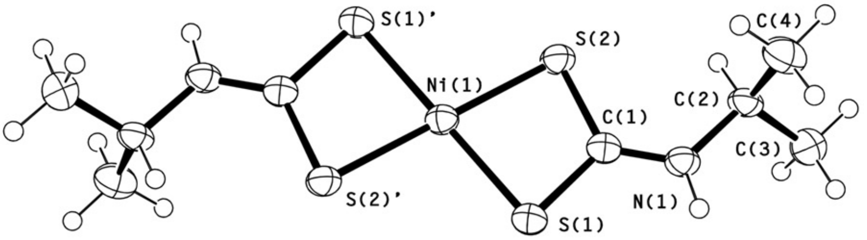

Figure 3. ORTEP plot of **4**.

Table 2. Bond lengths (Å) and angles (°) for **3** and **4**.

Bond and angles	Ni{S_2CNH(*n*-Pr)}$_2$	Ni{S_2CNH(*i*-Pr)}$_2$
Ni(1)–S(1)	2.1962(6)	2.1913(8)
Ni(1)–S(2)	2.2062(6)	2.1971(8)
N(1)–C(2)	1.461(3)	1.477(4)
S(1)–C(1)	1.716(2)	1.721(3)
S(2)–C(1)	1.722(2)	1.718(3)
S(1)–C(1)–S(2)	110.7(1)	110.64
S(1)–Ni(1)–S(2)	79.94(2)	79.76(3)
S(2)–C(1)–N(1)	125.9(2)	126.37
S(1)–C(1)–N(1)	123.4(2)	122.96
S(1)–Ni(1)–S(2)′	100.06(2)	100.24(3)
S(1)–Ni(1)–S(1)′	180.0	180.0

(table 2), are shorter than the C–N single bond, suggesting double-bond character; the structure shown in figure 1 is the contributing resonating form.

In the NiS_2C ring, the Ni–S–C, S–Ni–S, and S–C–S bond angles, 84.43°, 79.94°, and 110.7° for **3** and 85.15(1)°, 79.76(3)°, and 109.8(2)° for **4**, have good agreement with *cis* [Ni(S_2CNH(*i*-Pr))$_2$] and other complexes [18]. These angles correspond to distortion from exact square-planar geometry. The *trans* configuration is further suggested by the distances of N1(x, $-1+y$, z) and N1($1-x$, $-y$, $1-z$) 0.1093 and −0.1093 Å, respectively, from the least squares plane NiS4C2. The distance from the plane suggests that one nitrogen is above and the other below the molecular plane. Hydrogen bonding is thus significant in providing stability of the *trans* form. The tetrahedral angles around the central carbon of isopropyl N(1)–C(2)–C(3), N(1)–C(2)–C(4), and C(3)–C(2)–C(4) are 109.8(3)°, 109.9(3)°, and 112.3(3)°. Intramolecular S ⋯ H [S(1) ⋯ H(1), 2.74; S(2) ⋯ H(2), 2.70°Å] for **4** are shorter than the estimated van der Waal's distance (3.005 Å); hydrogen bonding is thus significant in providing stability in the *trans* form.

4. Conclusions

The preparation and spectroscopic characterization of *bis*(*N*-alkyldithiocarbamato) nickel(II) complexes (**1–5**) are presented. IR, UV-Visible, and NMR suggest the coordination of dithiocarbamate moieties with nickel. The molecular structure of $[Ni(S_2CNH(n\text{-}Pr))_2]$ and $[Ni(S_2CNH(i\text{-}Pr))_2]$ reveals distorted square-planar geometry around nickel(II) and shows *trans* position of dithiocarbamate moieties in the complexes. The distorted square planar geometry was further confirmed by UV-Visible spectroscopic data.

Supplementary data

CCDC numbers 788057 and 785662 contain the supplementary crystallographic data for $[Ni(S_2CNH(n\text{-}Pr))_2]$ and $[Ni(S_2CNH(i\text{-}Pr))_2]$, respectively. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 2EZ, UK [Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk].

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