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Geraldo M. de Lima [a] , Daniele C. Menezes [a] , Jacqueline A.F. Dos
Santos [a] , James L. Wardell [a] , Carlos A.L. Filgueiras [a] , Antônio F.
De C. Alcântara [a] , Solange M.S.V. Wardell [b] & Nivaldo L. Speziali [c]

[a] Departamento de Química , ICEx, Universidade Federal de Minas
Gerais , 31270-901 Belo Horizonte , MG , Brazil

[b] CHEMSOL , 1 Harcourt Road, Aberdeen AB15 5NY , Scotland , UK

[c] Departamento de Física , ICEx, Universidade Federal de Minas
Gerais , 31270-901 Belo Horizonte , MG , Brazil
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Cyclization of *N*-alkyldithiocarbamates in alkaline media, a counter example of well-known chemistry – an experimental and theoretical study

GERALDO M. DE LIMA*†, DANIELE C. MENEZES†, JACQUELINE
A.F. DOS SANTOS†, JAMES L. WARDELL†, CARLOS A.L. FILGUEIRAS†,
ANTÔNIO F. DE C. ALCÂNTARA†, SOLANGE M.S.V. WARDELL‡ and
NIVALDO L. SPEZIALI§

†Departamento de Química, ICEx, Universidade Federal de Minas Gerais,
31270-901 Belo Horizonte, MG, Brazil
‡CHEMSOL, 1 Harcourt Road, Aberdeen AB15 5NY, Scotland, UK
§Departamento de Física, ICEx, Universidade Federal de Minas Gerais,
31270-901 Belo Horizonte, MG, Brazil

In strong alkaline media, the reaction of 2-(*tert*-butylamino)ethanol (**3**: R = Bu^t) with CS$_2$ at 0°C produced a cyclic dithiocarbamate, 3-*tert*-butylthiazolidine-2-thione (**1**: R = Bu^t), rather than alkaline metal or ammonium salts of [S$_2$CN(Bu^t)CH$_2$CH$_2$OH]$^-$. This is in contrast to isolation of stable alkaline metal or ammonium salts of [S$_2$CN(R)CH$_2$CH$_2$OH]$^-$ (R = Me, Et, Pr, or CH$_2$CH$_2$OH) obtained in analogous reactions. The use of Ni(OAc)$_2$, both as a source of Ni(II) and a weaker base, in a one-pot reaction with (**3**: R = Bu^t) and CS$_2$, successfully gave the first reported metal complex of [S$_2$CN(Bu^t)CH$_2$CH$_2$OH]$^-$, namely [Ni{S$_2$CN(Bu^t)CH$_2$CH$_2$OH}$_2$] (**2**: R = Bu^t). Compounds **1** and **2** have been fully characterized by infrared and NMR spectroscopies, and by X-ray crystallography. DFT calculations on the cyclization and stabilities of [S$_2$CN(R)CH$_2$CH$_2$OH]$^-$ (R = Pr and Bu^t) have been carried out.

Keywords: Nickel(II) complexes; Cyclization; Dithiocarbamate complexes; DFT theoretical calculations; Spectroscopic studies

1. Introduction

Dithiocarbamates, [S$_2$CNRR′]$^-$, have found extensive use in coordination chemistry [1, 2]. Their wide range of applications in industry, agriculture, and medicine has generated a large collection of data, including crystallographic results, on their metal complexes [3]. The majority of the complexes studied have simple R and R′ groups, methyl, ethyl, and phenyl. Complexes with dithiocarbamates having functional substituted organic groups, such as R and or R′ equal to CH$_2$CH$_2$OH, are increasingly

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*Corresponding author. Email: gmlima@ufmg.br

being studied, with crystal structures reported for a number of metal complexes including those of alkali metals [4], copper [5, 6], nickel [7–10], zinc [11], mercury [12], and antimony [13]. Clearly the extra structural aspects generated by such functional groups [3, 4] have encouraged further interest in these compounds.

Generally in nickel(II) dithiocarbamates, $[Ni(S_2CNRR')_2]$, nickel has a square planar geometry defined by the S4 donor set derived from two chelating dithiocarbamates [2, 8]. Usually there is little, if any, strong intermolecular interactions between molecules, unless some functional group, such as a substituent capable of hydrogen bonding, is present within the R and R′ groups. Thus, a 3-D crystalline arrangement mediated by N–H$\cdots$S hydrogen bonds was established in $[Ni(S_2CNH_2)_2]$ [14, 15]. Similarly, extensive intermolecular hydrogen bonding of the type O–H$\cdots$O is found in the crystal structures of $[Ni\{S_2CN(R)CH_2CH_2OH\}_2]$ (**2**: R = Me) [16], (**2**: R = CH_2CH_2OH) [16, 17], and (**2**: R = Pr) [9].

The usual preparation of dithiocarbamate complexes involves isolation of an ammonium or alkali-metal dithiocarbamate salt, from reaction of CS_2 and HS_2CNRR' in an appropriate basic medium at low-temperature, and a subsequent reaction, if required, with a metal halide. While a number of investigations of dithiocarbamate complexes, $M[S_2CN(R)CH_2CH_2OH]$ (R = Me, Et, Pr, or CH_2CH_2OH, but not Bu^t), have been made, there has been no report of the formation of a cyclic dithiocarbamate, 2-R-1,3-thiazolidine-2-thione, **1**, during the initial reaction between $HN(R)CH_2CH_2OH$ (**3**) and CS_2 in basic media at the low-temperatures normally used. Cyclic dithiocarbamates (**1**, R = alkyl aryl, etc.) have been previously reported, but usually their formation requires more stringent conditions, e.g., on heating or in the presence of acids [18–20], especially with specific reagents [21].

In continuation of our studies on dithiocarbamates [22–25], we report the unexpected formation of a cyclic dithiocarbamate, (**1**: R = Bu^t), from reaction of CS_2 and (**3**: R = Bu^t) in a mixed Et_2O/aqueous KOH medium at 0°C. In addition, we also report the synthesis and characterization of the first metallic dithiocarbamate complex containing $[S_2CN(Bu^t)CH_2CH_2OH]^-$, the nickel compound, (**2**: R = Bu^t). The conditions, in particular the base used, for formation of **1** and **2** have been systematically studied. As there appears a clear difference between the stability or reactivity of $[S_2CN(Bu^t)CH_2CH_2OH)]^-$ in strong base, on one hand, and $[S_2CN(R)CH_2CH_2OH]^-$ (e.g., R = Me, Et, Pr) on the other, a DFT study has been carried out on the difference in stability and reactivity.

2. Experimental

2.1. *Materials and techniques*

All starting materials were purchased from Aldrich, Merck, or Synth and used as received. Infrared (IR) spectra were recorded from 4000 to 400 cm^{-1} with samples in KBr pellets using a Perkin-Elmer 283B spectrometer. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer PE-2400 CHN-analysis using tin sample-tubes.

^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 solution with a Bruker DRX 400 AVANCE spectrometer using tetramethylsilane as the internal standard.

2.2. *Syntheses*

3-tert-Butylthiazolidine-2-thione (**1**: R = Bu^t). 2-(*tert*-Butylamino)ethanol (**3**: R = Bu^t) (10.53 g, 0.09 mol) was added to Et$_2$O at 0°C, followed by carbon disulfide (6.84 g, 0.09 mol). After stirring for 5 min, KOH (5.04 g, 0.09 mol), dissolved in a minimal amount of H$_2$O, was slowly added until a white, crystalline solid formed. After keeping the reaction mixture at room temperature for 30 min, the solid was collected, washed with Et$_2$O, and recrystallized from EtOH. Yield 65%; m.p.: 70–71°C. IR (KBr; film; cm^{-1}) ν: 1462 (ν$_{C-N}$), 1165 (asym ν$_{C=S}$), 971 (sym ν$_{C=S}$); ^{1}H NMR (400 MHz; CDCl$_3$; ppm) δ$_H$ 1.24 (s; H-2′), 3.02 (t, *J* = 5.4 Hz; H-1), 3.68 (t, *J* = 4.9 Hz; H-1); ^{13}C NMR (100 MHz; CDCl$_3$; ppm) δ$_C$ 27.54 (C-2′), 27.73 (C-1′), 57.60 (C-1), 61.18 (C-2), 195.8 (C-3). Analysis for C$_7$H$_{13}$NS$_2$ (Calcd %): C, 47.12; H, 7.40; N, 7.64; (found %): C, 48.00; H, 7.42; N, 8.00.

[Ni{S$_2$CN(Bu^t)CH$_2$CH$_2$OH}$_2$] (**2**: R = Bu^t). Carbon disulfide (0.59 g, 0.013 mol) and a suspension of Ni(OAc)$_2$·4H$_2$O (2.06 g, 0.0083 mol) in cold ether were successively added, with care, to a solution of (**3**: R = Bu^t) (1.94 g, 0.013 mol) in cold ether at −10°C. After stirring for 2 h at room temperature, the dark brownish green residue was collected and recrystallized from MeOH. Yield 74%; m.p.: 132–135°C (decomp.); IR (KBr; film; cm^{-1}) ν: 1411 (ν$_{C-N}$), 1082 (asym ν$_{C=S}$), 989 (sym ν$_{C=S}$), and 452 (ν$_{Ni-S}$); ^{1}H NMR (400 MHz; CDCl$_3$; ppm) δ$_H$ 0.95 (s; H–2′), 1.31 (OH), and 3.49–3.77 (H-1); ^{13}C NMR (100 MHz; CDCl$_3$; ppm) δ$_C$ 12.3 (C-2′), 28.5 (C-1′), 51.6 (C-2), 52.3 (C-1), 210.6 (C-1″). Analysis for C$_{14}$H$_{28}$N$_2$S$_4$O$_2$Ni (Calcd %): C, 37.95; H, 6.32; N, 6.32; Ni, 13.26; (found %): C, 38.8; H, 6.69; N, 6.88; Ni, 13.01.

[Na][S$_2$CN(Pr)CH$_2$CH$_2$OH] (**4**). Carbon disulfide (6.84 g, 0.09 mol) was slowly added to a solution of (**3**: R = Pr) (9.27 g, 0.09 mol) in Et$_2$O (20 mL). After 1 min under stirring, NaOH (3.6 g, 0.09 mol) was added until a white precipitate was obtained. The solid was collected and recrystallized from Et$_2$O–water. Yield 78%; m.p.: 197–199°C; IR (KBr; film; cm^{-1}) ν: 462 (ν$_{C-N}$), 1047 (asym ν$_{C=S}$), and 974 (sym ν$_{C=S}$); ^{1}H NMR (400 MHz; CDCl$_3$; ppm) δ$_H$ 0.88 (t, *J* = 7.3 Hz; H-3′), 1.63–1.82 (m; H-2′), 3.88–4.00 (m; H-2 and H-1′), and 4.19 (t, *J* = 6.2 Hz; H-1); ^{13}C NMR (100 MHz; CDCl$_3$; ppm): δ$_C$ 11.0 (C-3′), 20.2 (C-2′), 55.9 (C-1′), 57.9 (C-2), 59.7 (C-1), and 209.4 (C-1″). Analysis for C$_6$H$_{12}$NS$_2$ONa (Calcd %): C, 35.98; H, 5.98; N, 6.87; (found %): C, 35.82; H, 5.78; N, 6.97.

[Ni{S$_2$CNPr)CH$_2$CH$_2$OH}$_2$] (**2**: R = Pr). NiCl$_2$·6H$_2$O (1.00 g, 0.391 mmol), dissolved in a minimal amount of water, was added to a solution of **4** (3.10 g, 0.0154 mol) in cold EtOH. After stirring for 1.5 h at room temperature, green solid was filtered off and recrystallized from MeOH. Yield 90%; m.p.: 181–182°C; IR (KBr; film; cm^{-1}) ν: 1406 (ν$_{C-N}$), 1070 (asym ν$_{C=S}$), 993 (sym ν$_{C=S}$), and 457 (ν$_{Ni-S}$); ^{1}H NMR (400 MHz; CDCl$_3$; ppm) δ$_H$ 0.89 (t, H-3′), 1.57–1.72 (m; H-2′), 1.22 (broad signal; OH), 3.56–3.74 (m; H-2 and H-1′), and 3.89 (t, H-1′); ^{13}C NMR (100 MHz; CDCl$_3$; ppm) δ$_C$ 11.7 (C-3′), 21.1 (C-2′), 51.6 (C-2), 52.3 (C-2), 60.4 (C-1), and 208.4 (C-1″). Analysis for C$_{12}$H$_{24}$NiN$_2$O$_2$S$_4$ (Calcd %): C, 34.70; H, 5.80; N, 7.22; Ni, 14.15; (found %): C, 34.73; H, 5.78; N, 6.75; Ni, 13.99.

2.3. *Crystallography*

The data for (**1**: R = Bu^t) were collected on a Enraf-Nonius AD4 diffractometer with Mo-Kα radiation at 298(2) K. The structure was solved by SIR-92 [26]. The refinements

were carried out using SHELXL-97 [27], minimizing on the weighted R factor $wR2$. All non-H atoms were refined anisotropically. The data for (**2**: R = Bu^t) were obtained at 120(2) K with Mo-Kα radiation by means of the Bruker-Nonius 95mm with area detector diffractometer of the EPSRC crystallographic service at the University of Southampton, UK. Data collection was carried out under control of the program COLLECT [28] and data reduction and unit cell refinement were achieved with the COLLECT and DENZO [29] programs. Correction for absorption was achieved by a semi-empirical method based upon variation of equivalent reflections with SADABS 2007/2 [30]. The programs ORTEP-3 for Windows [31] and MERCURY [32] were used in the preparation of the figures. SHELXL-97 [27] and PLATON [33] were used in the calculation of molecular geometry. The structures were solved by direct methods using SHELXS-97 [27] and fully refined by means of the program SHELXL-97 [27]. The hydroxyl-hydrogen of O1B–H1B was located from a difference map and refined with O–H constrained to 0.820(2). All other hydrogen atoms were placed in calculated positions. Crystal data and structure refinement details are listed in table 1.

Table 1. Crystal data and refinement details for **1** (R = Bu^t) and **2** (R = Bu^t).

Compound	**1** (R = Bu^t)	**2** (R = Bu^t)
Empirical formula	$C_7H_{13}NS_2$	$C_{14}H_{28}N_2NiO_2S_4$
Formula weight	175.30	443.33
Temperature (K)	273(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	$Cmc2_1$	P-1
Unit cell dimensions (Å, °)		
a	20.673(3)	12.3288(6)
b	11.9353(15)	12.9005(6)
c	11.303(3)	14.1829(5)
α		90
β	90	112.794(2)
γ		90
Volume (Å^3), Z	2788.7(10), 12	2079.59(16), 4
Calculated density (Mg m^{-3})	1.253	1.416
Absorption coefficient (mm^{-1})	0.504	1.343
$F(000)$	1128	936
Crystal size (mm^3)	$0.30 \times 0.25 \times 0.20$	$0.10 \times 0.10 \times 0.01$
θ range for data collection (°)	1.97–26.00	3.12–27.49
Index ranges	$-25 \leq h \leq 12$	$-15 \leq h \leq 15$
	$0 \leq k \leq 13$	$-16 \leq k \leq 16$
	$-13 \leq l \leq 0$	$-18 \leq l \leq 18$
Reflections collected	1884	24,498
Independent reflections	1426 [R(int) = 0.0595]	4244 [R(int) = 0.0432]
Reflections observed ($>2\sigma$)	2480	3662
Data completeness	0.96	0.93
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1426/1/148	4244/0/195
Goodness-of-fit on F^2	0.867	1.079
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.053$, $wR_2 = 0.126$	$R_1 = 0.042$, $wR_2 = 0.090$
R indices (all data)	$R_1 = 0.100$, $wR_2 = 0.155$	$R_1 = 0.053$, $wR_2 = 0.096$
Largest difference peak and hole (e Å^{-3})	0.259 and -0.264	0.666 and -1.030

2.4. *Theoretical calculations*

Theoretical studies were carried out using the software package GAUSSIAN03 [34]. DFT geometry optimizations were performed using the geometries previously obtained by the PM3 semi-empirical method [35]. BLYP functional with standard Pople's split valence 6-31G* basis set [36] was used in the DFT calculations. The optimized geometries were characterized as true minima on the potential energy surface (PES) when all harmonic frequencies were real.

Calculations on the reaction pathway of the cyclization reactions of $[S_2CN(Pr)CH_2CH_2OH]^-$ and $[S_2CN(Bu^t)CH_2CH_2OH)]^-$ were carried out. The electronic-nuclear energies (E) were calculated using the HF/6-31G** method. Transition states of all structures were calculated using the Gaussian keywords (OPT = Calcfc, TS) at the same level of theory (HF/6-31G**). Geometries were considered as transition states when only one harmonic frequency was negative.

3. Results and discussion

3.1. *Syntheses*

Metal dithiocarbamates are usually prepared by reactions of secondary amines and carbon disulfide in strong alkaline media, such as aqueous NaOH, KOH, or NH$_4$OH. As reported [37], similar reactions with **3** (R = Me, Et, Pr, or CH$_2$CH$_2$OH) proceeded readily to give reasonable yields of the corresponding alkali-metal or ammonium dithiocarbamate salts, M[S$_2$CN(R)CH$_2$CH$_2$OH]. When an analogous reaction was attempted, in this study, using **3** (R = Bu^t), the product was the cyclic organic dithiocarbamate, (**1**: R = Bu^t), rather than M[S$_2$CN(Bu^t)CH$_2$CH$_2$OH]. The formation of (**1**: R = Bu^t) is considered to result from an intramolecular nucleophilic attack by the thiolate moiety on the C-2, with consequent elimination of the hydroxyl group, as shown in scheme 1.

The strong basic characters of KOH, NaOH, etc. were the problem; in the presence of strong bases, [S$_2$CN(Bu^t)CH$_2$CH$_2$OH]$^-$ was clearly too reactive and readily cyclized to **1** (R = Bu^t). After consideration of alternative conditions to obtain metal salts of [S$_2$CN(Bu^t)CH$_2$CH$_2$OH]$^-$, especially the nickel salt, the best route to **2** (R = Bu^t) was found to be the use of nickel(II) acetate, both as a base and as a source of nickel, in a one-pot synthesis directly with CS$_2$ and **3** (R = Bu^t). The basicity of Ni(II) acetate is considerably less than alkali-metal hydroxides, but is still sufficient to remove the proton from **3** (R = Bu^t).

We also confirmed that the reaction of HN(Pr)CH$_2$CH$_2$OH with CS$_2$ in Et$_2$O and aqueous NaOH at 0°C does proceed readily to [Na][S$_2$CN(Pr)CH$_2$CH$_2$OH] **4**, which on reaction with NiCl$_2$ gave **2** (R = Pr).

3.2. *IR spectroscopy*

IR spectra of dithiocarbamate complexes exhibit stretching frequencies, ν_{asym}–ν_{sym} for the C–S, in the 1100–970 cm^{-1} range. Using the difference in frequencies, $\Delta\nu_{CSS}$ (ν_{asym}–ν_{sym}), as an indicator of the coordination mode of $^-S_2C-$ [38], it is apparent that
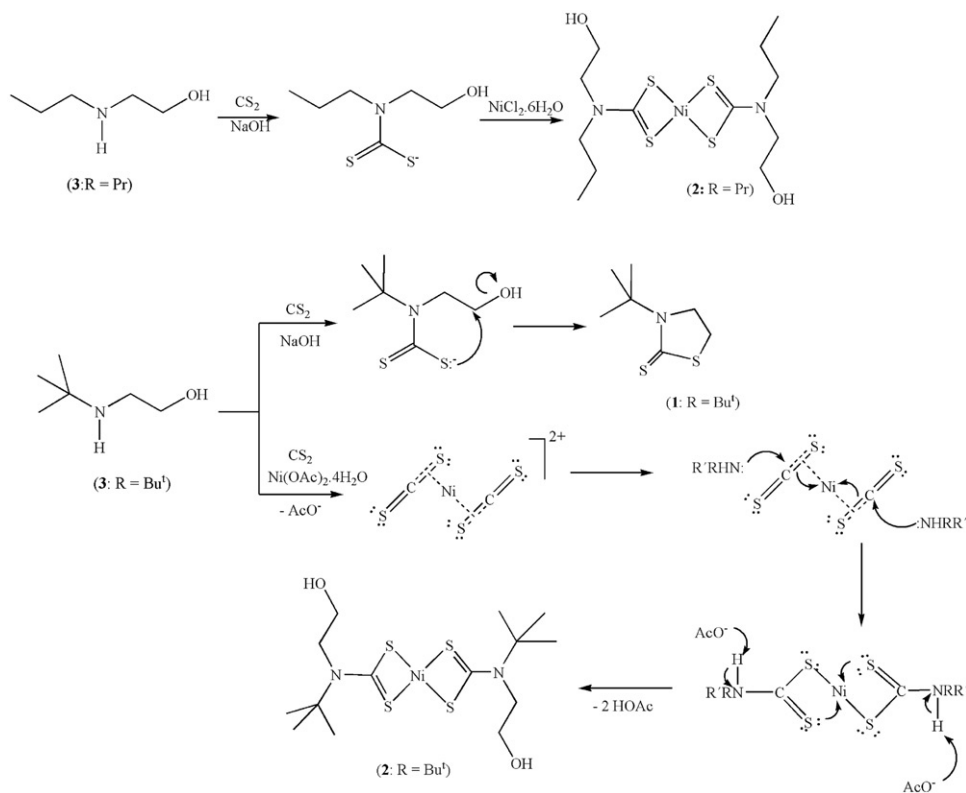
Scheme 1.   Reactions of **3** (R = Pr or Bu^t) with CS$_2$ in basic media, with nickel salts.

bidentate S$_2$C exists in **2** (R = Bu^t): $\Delta\nu_{CSS}$ ($\nu_{asym}-\nu_{sym}$) = 93 cm^{-1} [1082–989 cm^{-1}]. The Ni–S stretching frequency, ν_{Ni-S} = 452 cm^{-1}, is typical for nickel(II) dithiocarbarmate complexes.

3.3. *NMR spectroscopy*

The ^{1}H and ^{13}C NMR signals observed for the ligands did not change much on complexation. The existence of sharp NMR resonances indicates a square-planar geometry, where nickel is bonded to four sulfurs, rendering a diamagnetic d^8 electronic configuration, as found for all complexes **2** (R = Bu^t an Pr).

3.4. *X-ray crystallographic results*

3.4.1. The molecular structure of (1: R = Bu^t).   This had been previously reported [39]. However, very little information of the structure is available from the brief structural description. Furthermore, polymorphic forms of thiazolidine-2-thione derivatives have been reported in the literature [e.g., 40]. Thus as our sample of (**1**: R = Bu^t) had been obtained by a different and milder route than that used for the preparation of the
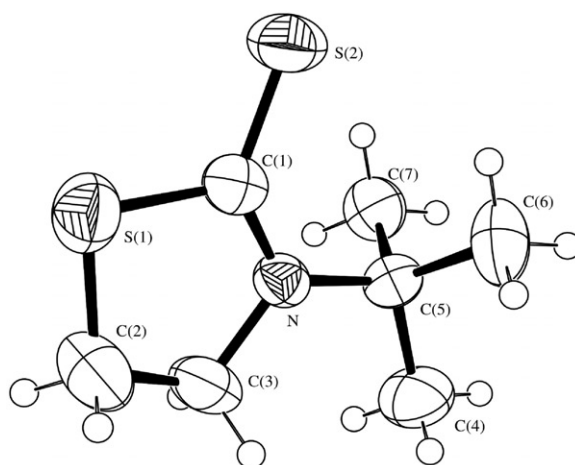
Figure 1. Atom arrangements and numbering scheme for the non-disordered molecule, molecule A, of **1** (R = Bu^t). Probability ellipsoids are drawn at the 50% level.

Table 2. Selected geometric parameters (Å, °) for **1** (R = Bu^t).

Molecule 1		Molecule 2	
Bond lengths			
N–C(1)	1.323(8)	N′–C(1′)	1.334(12)
N–C(3)	1.472(9)	N′–C(3′)	1.463(14)
S(2)–C(1)	1.665(7)	S(2′)–C(1′)	1.666(11)
S(1)–C(1)	1.754(7)	S(1′)–C(1′)	1.745(10)
S(1)–C(2)	1.767(10)	S(1′)–C(2′)	1.800(17)
N–C(5)	1.507(8)	N′–C(5′)	1.518(11)
Bond angles			
S(2)–C(1)–S(1)	116.9(4)	S(2′)–C(1′)–S(1′)	118.5(6)
N–C(1)–S(2)	131.0(5)	N′–C(1′)–S(2′)	129.7(8)
N–C(1–S(1)	112.1(5)	N′–C(1′)–S(1′)	111.8(8)

sample studied in the previous structure determination, we decided to carry out a full characterization, including X-ray diffraction. Our structure solution indicated the same phase as that previously reported. However, we point out that the asymmetric unit contains two independent molecules, molecules 1 and 2, one of which, molecule 2, is disordered, with equal populations over two sites for C(2). Only the ordered molecule, for which the ring atoms are very near planar, is shown in figure 1; the disordered molecule is numbered with an additional prime, i.e., S(1) in molecule 1 becomes S(1′) in molecule 2, with the disordered site having two designations, C(2′) and C(2″), each of which are equidistant, by 0.75 Å, from the plane through the other ring atoms, S(1′), C(1′), N′, C(3′). Thus the disordered rings have envelope shapes with flaps at the disordered carbon sites.

Selected geometric parameters are listed in table 2. The C=S bond lengths, 1.665(7) [S(2)–C(1)] and 1.666(11) Å [S(2′)–C(1′)], are in the expected region for C=S; C–S bond lengths between 1.725(3)–1.733(3) Å were found in **2** (R = Bu^t). The S(2)–C(1)–S(1) and S(2′)–C(1′)–S(1′) angles, 116.9(4)° and 118.5(6)°, are similar to those found in **2** (R = Bu^t).
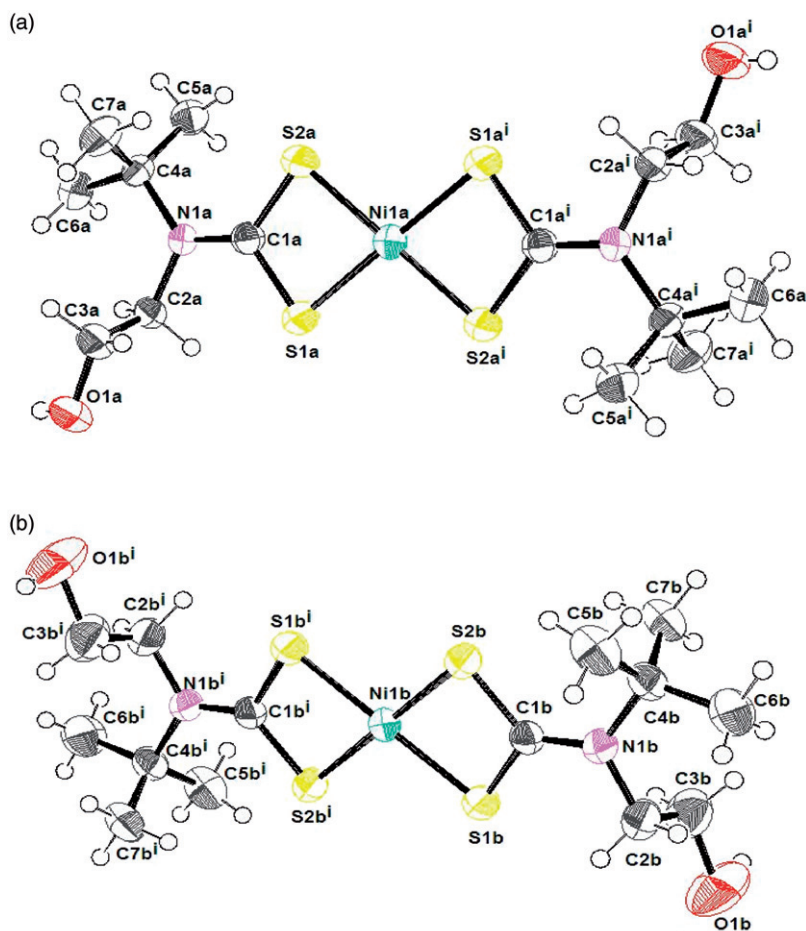
Figure 2. Atom-numbering scheme and arrangements for the two independent and centrosymmetric molecules, A and B, of **2** (R = Bu^t). Probability ellipsoids are drawn at the 50% level. (a) Symmetry operation: $^i = -x, -y+1, -z+1$. (b) Symmetry operation: $^i = -x-1, -y+1, -z+1$.

3.4.2. The molecular structure of 2 (R = Bu^t). The asymmetric unit of **2** (R = Bu^t) comprises two half complex and similar molecules, A and B, each disposed about a centre of inversion. The atom arrangements and numbering schemes for the two centrosymmetric molecules are shown in figure 2. The geometries about Ni are square planar, defined by four sulfurs in each independent molecule and thus is similar to those found generally in nickel(II) bis(dithiocarbamate) complexes [8]. The major distortion from ideal square-planar geometry arises from small chelate angles of the thiocarbamate ligands. Each of the two dithiocarbamate ligands in each independent molecule is near symmetrically chelated to nickel, with Ni–S bond lengths in the narrow range 2.1894(7)–2.1930(8) Å (see table 3). This is reflected in the C–S distances which vary little, in the range 1.725(3)–1.733(3) Å. A similar arrangement around Ni is also found in **2** (R = Pr) [9].

The presence of *tert*-butyl protons in **2** (R = Bu^t) allows the formation of weak C–H–S intramolecular hydrogen bonds in both molecules, A and B, of **2** (R = Bu^t).

Table 3. Selected geometric parameters (Å, °) for **2** (R = Bu^t).

Molecule A		Molecule B	
(a) Bond lengths[a]			
Ni(1A)–S(1A)	2.1907(9)	Ni(1B)–S(1B)	2.1889(8)
Ni(1A)–S(2A)	2.1918(8)	Ni(1B)–S(2B)	2.1925(8)
N(1A)–C(1A)	1.318(3)	N(1B)–C(1B)	1.324(4)
N(1A)–C(2A)	1.483(3)	N(1B)–C(2B)	1.484(4)
N(1A)–C(4A)	1.534(3)	N(1B)–C(4B)	1.532(4)
S(1A)–C(1A)	1.735(3)	S(1B)–C(1B)	1.725(3)
S(2A)–C(1A)	1.730(3)	S(2B)–C(1B)	1.724(3)
(b) Bond angles[a]			
S(1A)–Ni(1A)–S(1A^i)	180	S(1B)–Ni(1B)–S(1B^{ii})	180
S(2A)–Ni(1A)–S(2A^i)	180	S(2B)–Ni(1B)–S(2B^{ii})	180
S(1A)–Ni(1A)–S(2A^i)	101.29(3)	S(1B)–Ni(1B)–S(2B^{ii})	101.32(3)
S(1A)–Ni(1A)–S(2A)	78.71(3)	S(1B)–Ni(1B)–S(2B)	78.68(3)
C(1A)–N(1A)–C(2A)	116.6(2)	C(1B)–N(1B)–C(2B)	116.7(2)
C(1A)–N(1A)–C(4A)	123.2(2)	C(1B)–N(1B)–C(4B)	123.4(2)
C(2A)–N(1A)–C(4A)	119.9(2)	C(2B)–N(1B)–C(4B)	119.7(2)

(c) Hydrogen-bonds[b]				
D–H⋯A	D–H	H⋯A	D⋯A	D–H⋯A
O(1A)–H(1A)⋯O(1B^i)	0.82	1.94	2.753(5)	172
C(2A)–H(2A1)⋯S(1A)	0.97	2.51	2.965(3)	109
C(5A)–H(5A1)⋯S(2A)	0.96	2.49	3.148(4)	125
C(7A)–H(7A3)⋯S(2A)	0.96	2.79	3.445(3)	126
C(2B)–H(2B1)⋯S(1B)	0.97	2.51	2.961(4)	108
C(5B)–H(5B3)⋯S(2B)	0.96	2.54	3.185(4)	124
C(7B)–H(7B3)⋯S(2B)	0.96	2.71	3.385(4)	128

(d) C–H⋯π interactions[c]					
C–H⋯Cg	H⋯Cg	H$_{perp}$	γ	∠C–H⋯Cg	C⋯Cg
C(6A)–H(6A1)⋯Cg(3^{ii})	2.98	2.94	9.35	166	3.915(3)
C(6A)–H(6A1)⋯Cg(4)	2.98	2.94	9.35	166	3.915(3)

[a]Symmetry code: ^{i} = −x, −y + 1, −z + 1; ^{ii} = −x − 1, −y + 1, −z + 1.
[b]Symmetry code: ^{i} −1/2 − x, 1/2 + y, 3/2 − z.
[c]Cg(3) and Cg(4) are the centroids of the rings defined by Ni(1B), S(1B), C(1B), (S2B) and by Ni(1B), S(1B′), C(1B′), S(2B′), respectively. Gamma is the angle at H between the vectors H⋯Cg and H$_{perp}$. Symmetry code: ^{ii} −1 − x, 1 − y, 1 − z.

Two views of the packing arrangements are shown in figures 3 and 4. The hydroxyl groups of four molecules are grouped together, best seen in figure 3. Table 3 lists the hydrogen bonds and other interactions found in **2** (R = Bu^t). A similar arrangement of four close hydroxyl groups was found in **2** (R = Pr); however, there are significant differences between the packing of the structures of **2** (R = Bu^t and R = Pr), arising from differences in bulk of the two R groups. Unlike in **2** (R = Pr), there are no C–H⋯S intermolecular hydrogen bonds in **2** (R = Bu^t). However, as in **2** (R = Pr), there are C–H⋯π interactions involving NiS$_2$C rings [9 and the references therein]. In **2** (R = Bu^t), these interactions, with longer H⋯C separations than in **2** (R = Pr), involve the methyl hydrogen atoms of molecule A with NiS$_2$C rings of molecule B, with C–H⋯C angles somewhat short of 180°.

3.5. *Theoretical results*

Figure 5 shows HF/6-31G** electronic-nuclear energies calculated for reactants [S$_2$CN(R)CH$_2$CH$_2$OH]$^-$ (R = Pr and Bu^t), the corresponding cyclic products and
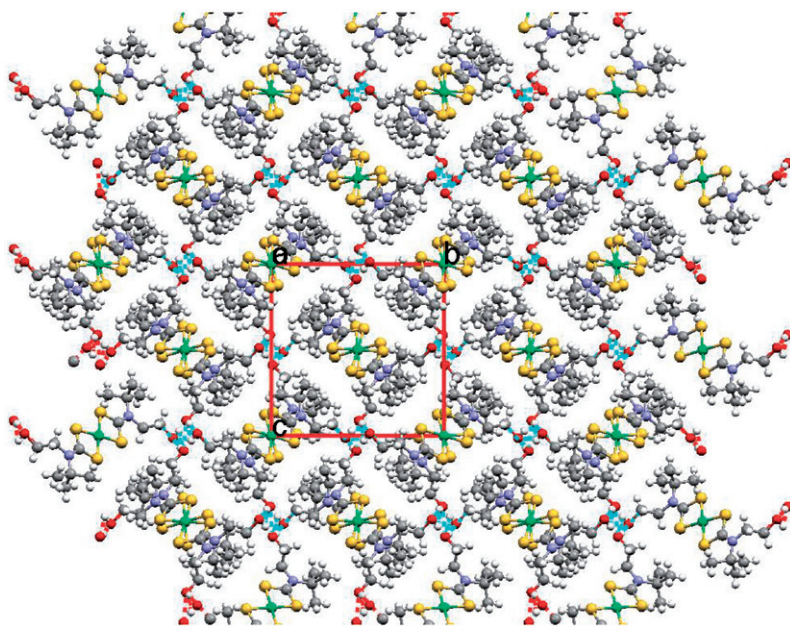
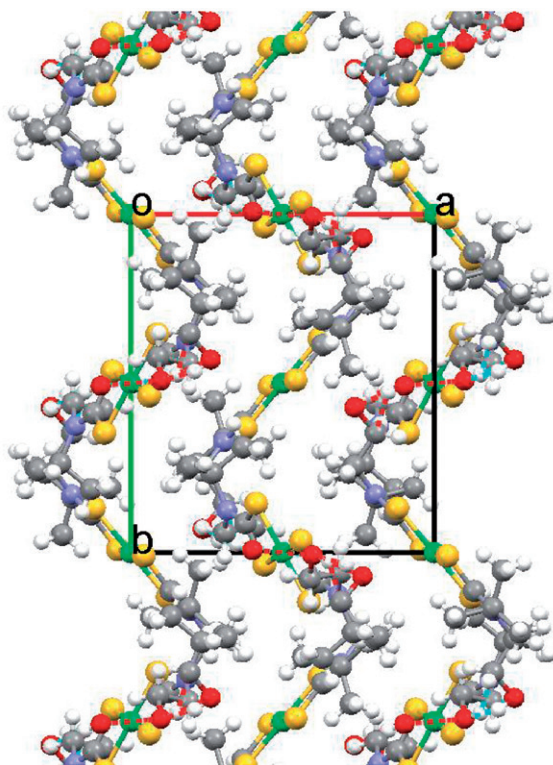Figure 3.   Packing of **2** (R = Bu^t), viewed down the *a*-axis.

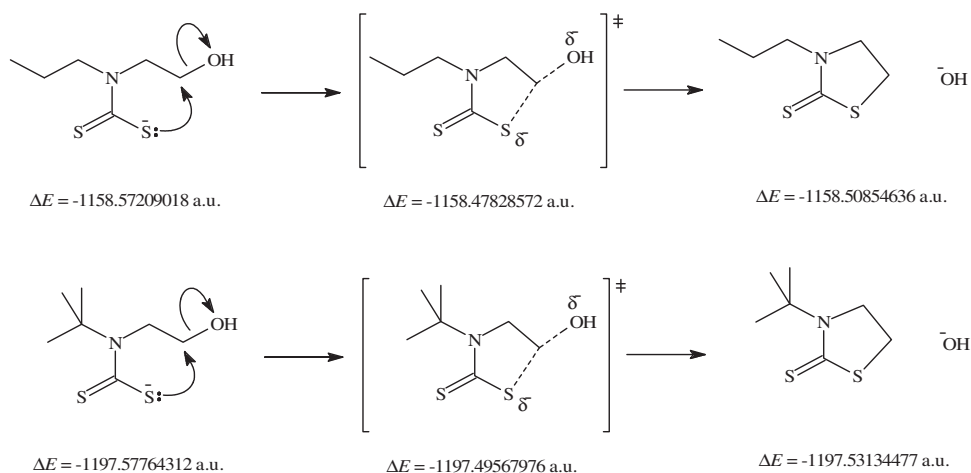Figure 4.   Packing of **2** (R = Bu^t), viewed down the *c*-axis.

$\Delta E = -1158.57209018$ a.u. $\Delta E = -1158.47828572$ a.u. $\Delta E = -1158.50854636$ a.u.

$\Delta E = -1197.57764312$ a.u. $\Delta E = -1197.49567976$ a.u. $\Delta E = -1197.53134477$ a.u.

Figure 5.   HF/6-31G** Electronic-nuclear energies calculated for the proposed pathway for the cyclization of $[S_2CN(R)CH_2CH_2OH]^-$; geometries optimized in the gaseous phase without consideration of intermolecular interactions.

transition states. Calculations were based on reaction pathways involving intramolecular nucleophilic attack of the thiolate on the carbon bearing the hydroxyl group leading to elimination of the hydroxyl. The results revealed that the cyclic products for both dithiocarbamates, $(S_2CN(R)CH_2CH_2OH)^-$, are not thermodynamically assisted. However, the formation of **1** ($R = Bu^t$) ($\Delta E = 29.05 \, kcal \, mol^{-1}$) is less disfavored than the formation of **1** ($R = Pr$) ($\Delta E = 39.87 \, kcal \, mol^{-1}$).

The transition state of both reaction paths presents only one negative harmonic frequency ($\nu - 39.59$ and $-662.15 \, cm^{-1}$, respectively). The activation energies indicate that formation of **1** ($R = Bu^t$) ($\Delta E = 51.53 \, kcal \, mol^{-1}$) is kinetically favored in relation to formation of **1** ($R = Pr$) ($\Delta E = 58.86 \, kcal \, mol^{-1}$). Thus theoretical results showed that formation of **1** ($R = Bu^t$) is kinetically and thermodynamically preferred compared to **1** ($R = Pr$).

4. Conclusions

The reaction of **3** ($R = Bu^t$) and CS_2 in strong alkaline media has yielded the cyclic dithiocarbamate (**1**: $R = Bu^t$) rather than alkaline or ammonium salts of $[S_2CN(Bu^t)CH_2CH_2OH]^-$. The complex (**2**: $R = Bu^t$) was however obtained in a one-pot reaction between **3** ($R = Bu^t$), CS_2 and $[Ni(OAc)_2]$. Confirmation that $[Na][S_2CN(Pr)CH_2CH_2OH]$ could be isolated from reactions between **3** ($R = Pr$) and CS_2 in aqueous NaOH indicates clearly the stability/reactivity differences between $[S_2CN(Bu^t)CH_2CH_2OH]^-$ and $[S_2CN(Pr)CH_2CH_2OH]^-$. Theoretical calculations indicated that the cyclization of $[S_2CN(R)CH_2CH_2OH]^-$ to **1** is not thermodynamically favorable but that formation of 3-*tert*-butylthiazolidine-2-thione is kinetically favorable.

Supplementary material

Crystallographic data are available on request from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 802095 and 802094 for compounds (**1**: R = Bu^t) and (**2**: R = Bu^t), respectively. The authors thank the EPRSC X-ray crystallography Service, based at the University of Southampton, for the data collection for (**2**: R = Bu^t).

Acknowledgments

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