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Carbodithioato Derivatives of Weak Nitrogenous Nucleophiles
II. Non-direct Syntheses and Structural Studies of Ni(II) *N*-Carbodithioates with Substituted Ureas, Carbamic Esters and Sulfonamides

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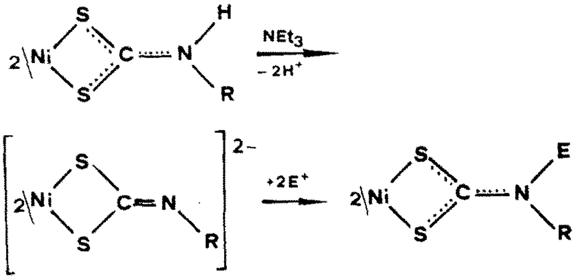
Abstract

In a sequence to our earlier reports on electrophilic substitution reactions of Ni(II) *N*-alkyldithiocarbamates, we here report the isolation of nickel(II) complexes of the type Ni$[S_2CN(E)R]_2$, (E = electrophile), and their characterization by chemical analysis, as well as magnetic and spectral studies. A thorough inspection of the spectroscopic and magnetic data of the novel compounds clearly indicates the bidentate bonding mode of the carbodithioato ligands in the complexes and their square-planar configuration. Therefore, all new compounds have broadly similar structures, involving the square-planar NiS_4 chromophore.

Introduction

We recently reported [1] that treatment of the square-planar Ni(II) *N*-alkyldithiocarbamates, $Ni(S_2CNHR)_2$, with acetic anhydride or benzoyl chloride in the presence of triethylamine results in the formation of the novel nickel(II) amide *N*-carbodithioates of the general type Ni$[S_2CN(COR')R]_2$, where R = Me, Et, Bu^i, Bz, Ph, *p*-MePh or *p*-ClPh, and R' = Me or Ph. The direct synthesis of such ligands by the reaction of the corresponding weak nitrogenous base or other nucleophiles with carbon disulfide in alkaline media is difficult, even impossible to afford, although some examples concerning the formation of *N*-formyl and *N*-methyl *N*-formyl dithiocarbamates and their thioformyl analogues have already been published [2–6]. However, no reports on their corresponding coordination compounds with transition metals have been found by us to date. Therefore, the nickel(II) complexes of the aforesaid carbodithioato ligands are probably some of the first examples in the pure chemistry of the dithiocarbamates which may be considered as derivatives of weak nitrogenous bases. The mechanism of these electrophilic substitution reactions at the level of the frontier molecular orbital approach of chemical reactivity has been fully investigated by EHMO-SCCC calculations [1, 7]. According to these theoretical investigations the acylation reaction of the bis(*N*-alkyldithiocarbamato)nickel(II) complexes in the presence of triethylamine as a deprotonating agent, proceeds via an S_E1 mechanism, involving as a transition state the $[Ni(S_2C{=}NR)_2]^{2-}$ complexes. It is readily apparent from this reactivity pattern that by using a wide diversity of electrophiles (E^+), new classes of carbodithioato complexes, not available by other methods, may be synthesized according to the following general scheme



Taking advantage of this reactivity pattern, convenient, straightforward routes to carbodithioato derivatives of weak nitrogenous bases, such as secondary amides [1], ureas, carbamic esters and sulfonamides, have emerged. Consequently, the results of our investigations on the synthesis and structural studies of some novel nickel(II) carbodithioates of the general formula Ni$[S_2CN(E)R]_2$, where E = CONHPh, $CONPh_2$, COOEt or $ArSO_2$, are reported in the present paper. The complexes have been isolated in the solid state and structures have been assigned tentatively on the basis of their elemental analysis, as well as their spectral and magnetic properties.

Experimental

Physical Measurements

Infrared spectra were recorded in the 4000–250 cm^{-1} region on a Perkin-Elmer 467 spectrophotometer using KBr pellets or Nujol mulls. Electronic

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spectra were obtained on a Cary 17DX spectrophotometer using dimethylformamide (DMF) solutions at 25 °C. Magnetic susceptibility measurements in the solid state were done by the Faraday technique using $Hg[Co(SCN)_4]$ as the calibrant. Conductivity measurements were done on a WTW conductivity bridge using 10^{-3} M solutions in DMF. Molecular weights were determined using a Perkin-Elmer molecular weight apparatus Model 115. Melting points were determined with a Büchi apparatus and are uncorrected. The elemental analysis of carbon, nitrogen and hydrogen was performed on a Perkin-Elmer 240B Elemental Analyzer. Nickel was determined according to published methods [8].

Starting Materials

All solvents were of reagent grade and were used without further purification in synthetic work. The bis(*N*-alkyldithiocarbamato)nickel(II) complexes were obtained from the reaction between nickel chloride and the appropriate dithiocarbamate salt in water–ethanol (1:1) solution [9]. The *N*-alkyldithiocarbamate salts were prepared and recrystallized as previously reported [10]. All the other reagents were obtained commercially.

Preparation of the Complexes

The $Ni[S_2CN(E)R]_2$ complexes ($E = CONPh_2$, COOEt, $PhSO_2$, p-$MePhSO_2$) were prepared according to the following synthetic route. A solution of 5 mmol of the appropriate $Ni(S_2CNHR)_2$ in 100 ml of acetone was treated with 10 mmol of triethylamine and 10 mmol of the appropriate precursor of the corresponding electrophile, e.g. Ph_2NCOCl, ClCOOEt, $PhSO_2Cl$ or p-$MePhSO_2Cl$ and the mixture was left for 1 h at room temperature under continuous magnetic stirring. The solid material formed was further separated on addition of 100 ml of water. The precipitate was filtered off, washed several times with water and dried over $CaCl_2$ under vacuum. The complexes were recrystallized from acetone solutions. The yields in this procedure were about 70%.

The $Ni[S_2CN(CONHPh)Me]_2$ complex was prepared according to the following method. A solution of 5 mmol of the $Ni(S_2CNHMe)_2$ complex in 100 ml of acetone–benzene was treated with 10 mmol of PhNCO, and the reaction mixture was stirred for 1 h at room temperature. The solution was condensed to a small volume, causing a microcrystalline solid to separate. The resulting solid material was filtered off, washed several times with water and dried over $CaCl_2$ under vacuum. Recrystallization was carried out by dissolving the complex in acetone and reprecipitating with water. The yield in this procedure was about 70%.

Results and Discussion

Reaction of acetone solutions of bis(*N*-alkyldithiocarbamato)nickel(II) complexes, $[Ni(S_2CNHR)_2]$,

TABLE 1. Analytical data for the new Ni(II) carbodithioates

Compound[a]	Melting point (°C)	C (%)	N (%)	H (%)	Ni (%)	Molecular weight
$Ni[S_2CN(PhHNCO)Me]_2$	186–188d[b]	39.88 (39.94)[c]	10.43 (10.35)	3.43 (3.35)	10.43 (10.35)	550 (541.3)
$Ni[S_2CN(Ph_2NCO)Me]_2$	86–88d	50.53 (50.49)	7.76 (7.85)	6.58 (6.50)	7.76 (7.85)	705 (713.7)
$Ni[S_2CN(COOEt)Me]_2$	179–181d	28.76 (28.92)	6.86 (6.75)	3.73 (3.88)	6.86 (6.75)	427 (415.2)
$Ni[S_2CN(COOEt)Bu^n]_2$	67–69	39.06 (38.48)	5.58 (5.61)	5.41 (5.65)	5.58 (5.61)	530 (499.4)
$Ni[S_2CN(COOEt)Bz]_2$	177–179	46.44 (46.57)	4.49 (4.81)	4.22 (4.26)	4.94 (4.81)	549 (567.4)
$Ni[S_2CN(PhSO_2)Me]_2$	203–205d	34.67 (34.85)	5.15 (5.08)	2.84 (2.92)	5.15 (5.08)	563 (551.4)
$Ni[S_2CN(p\text{-}MePhSO_2)Me]_2$	215–217d	37.42 (37.31)	5.07 (4.83)	3.51 (3.48)	5.07 (4.83)	587 (579.5)
$Ni[S_2CN(p\text{-}MePhSO_2)Bu^n]_2$	208–210d	43.52 (43.44)	4.18 (4.23)	4.78 (4.86)	4.18 (4.23)	670 (663.6)
$Ni[S_2CN(p\text{-}MePhSO_2)Bz]_2$	221–223d	49.05 (49.52)	3.78 (3.83)	3.78 (3.86)	3.78 (3.83)	740 (732.7)

[a] Abbreviations used throughout: Me = methyl, Bu^n = n-butyl, Ph = phenyl, Bz = benzyl, *p*-MePh = *p*-methylphenyl. [b] d = decomposition. [c] Figures in parentheses are the calculated values.

TABLE 2. Relevant IR frequencies (cm^{-1}) of the investigated compounds and their assignments (KBr discs)[a]

Compound	ν(C=O)	ν(C=N)	$\nu_{as}(SO_2)$	$\nu_s(SO_2)$	ν(S–N)	ν(CSS)	ν(Ni–S)
$Ni[S_2CN(PhHNCO)Me]_2$	1687vs	1537s				965m	385m
$Ni[S_2CN(Ph_2NCO)Me]_2$	1720vs	1550s				1003m	380m
$Ni[S_2CN(COOEt)Me]_2$	1731vs	1433m				982w	393w
$Ni[S_2CN(COOEt)Bu^n]_2$	1738vs	1455m				965w	397w
$Ni[S_2CN(COOEt)Br]_2$	1742vs	1442m				989m	393w
$Ni[S_2CN(PhSO_2)Me]_2$		1447m	1367vs	1169vs	1038vs	988w	392w
$Ni[S_2CN(p\text{-}MePhSO_2)Me]_2$		1428m	1373vs	1168vs	1038vs	948m	382w
$Ni[S_2CN(p\text{-}MePhSO_2)Bu^n]_2$		1450m	1360vs	1168vs	1052vs	974w	385m
$Ni[S_2CN(p\text{-}MePhSO_2)Bz]_2$		1430m	1355vs	1173vs	1087vs	963w	380w

[a] vs = very strong, s = strong, m = medium, w = weak.

with the appropriate precursor of the corresponding electrophile (E^+) in the presence of triethylamine (1:2:2 molar ratios) resulted in the formation of solid compounds of stoichiometry $Ni[S_2CN(E)R]_2$ (E = CONHPh, $CONPh_2$, COOEt or $ArSO_2$). Obviously, in the case of the $Ni[S_2CN(CONHPh)Me]_2$ complex, the presence of triethylamine as deprotonating agent was unnecessary. The above formulations have been further corroborated on the basis of spectral properties of these compounds.

All the complexes are microcrystalline solids, quite stable both in solid and solution state. They are moderately soluble in most of the common organic solvents, such as chloroform, acetone and methylene chloride, but insoluble in ethanol, diethyl ether, carbon tetrachloride and water. The low values of the molar conductivity in DMF indicate the non-electrolyte character of the complexes, whereas their monomeric nature was established by osmometric molecular weight measurements. Moreover, they are diamagnetic, as would be expected for d^8 planar species. Data from elemental analyses, decomposition temperatures, and molecular weights of the new compounds are given in Table 1.

The frequencies (cm^{-1}) of the most relevant absorption bands in the IR spectra of the studied compounds and their tentative assignments are presented in Table 2. The spectra of the $Ni(S_2CNHR)_2$ complexes show one broad band in the 3300–3200 cm^{-1} region due to the N–H stretching frequency [11]. In contrast, no such band appears in the spectra of the $Ni[S_2CN(E)R]_2$ complexes, as a consequence of deprotonation of the S_2CNHR system. Moreover, the strong band found between 1730–1680 cm^{-1} in most of the complexes was assigned to the C=O stretch, thereby indicating the electrophilic substitution of the *N*-alkyldithiocarbamato ligands. On the other hand, sulfonamides show two strong bands at the frequencies near 1160 and 1350 cm^{-1}, which are due to the symmetric and antisymmetric vibrations of the sulphonyl group [12]. They also show one absorption band near 1050 cm^{-1} which may be identified with the S–N frequency. The ν(C=N) and ν(CSS) stretching frequencies fall in the range 1590–1460 and 1010–

TABLE 3. Electronic spectral data of the Ni(II) carbodithioates for DMF solutions

Compound	Band I L(π^*) ← L(π) M(d) ← L(π)	Band II L(π^*) ← M(d)	Band III L(π^*) ← M(d)	Band IV L(π^*) ← M(d) M(d) ← M(d)	Band V M(d) ← M(d)
$Ni[S_2CN(PhHNCO)Me]_2$	30.8[a] (4.54)[b]	26.8 (3.73)	23.8sh[c] (3.22)	21.1 (2.29)	15.8 (1.87)
$Ni[S_2CN(Ph_2NCO)Me]_2$	30.9 (4.08)	26.3 (3.28)	24.1sh (2.91)	20.7 (2.19)	15.7sh (1.88)
$Ni[S_2CN(COOEt)Me]_2$	31.0 (4.60)	26.7sh (3.73)	21.8 (3.97)	20.2sh (3.40) 18.9sh (3.14)	15.8sh (1.87)
$Ni[S_2CN(COOEt)Bu^n]_2$	30.9 (4.77)	26.5sh (3.72)	21.6 (3.99)	20.1sh (3.53) 18.7sh (3.17)	
$Ni[S_2CN(COOEt)Bz]_2$	30.6 (4.73)	27.3sh (3.71)	21.6 (3.96)	20.1sh (3.55) 18.5sh (3.11)	
$Ni[S_2CN(PhSO_2)Me]_2$	30.5 (3.90)	26.0sh (3.15)	22.3 (3.31)	19.5sh (3.07)	16.3sh (2.05)
$Ni[S_2CN(p\text{-}MePhSO_2)Me]_2$	30.7 (3.98)	26.1sh (3.18)	22.3 (3.56)	19.5sh (2.86)	16.5sh (2.03)
$Ni[S_2CN(p\text{-}MePhSO_2)Bu^n]_2$	30.6 (4.33)	25.8sh (3.38)	22.3 (3.68)	19.7sh (3.14)	16.4sh (2.08)
$Ni[S_2CN(p\text{-}MePhSO_2)Bz]_2$	30.5 (4.00)	25.6sh (3.35)	22.1 (3.74)	19.7sh (3.25)	16.1sh (2.13)

[a] ν (kK). [b] log ϵ_{mol}. [c] sh = shoulder.

970 cm^{-1}, respectively [13, 14]. The presence of only one strong band in the region where ν(CSS) lies, strongly supports chelation of the dithiocarbamates, a doublet being expected in the region 1000 ± 70 cm^{-1} in the unchelated dithiocarbamates [15]. Finally, single peaks have been observed in the range 400–380 cm^{-1}, which are likely to be due to metal–sulphur modes according to the observed values for the dithiocarbamates of the nickel triad metals [13, 16].

The IR data, the diamagnetic nature of the complexes under investigation and their stoichiometry allowed us to suggest a square-planar configuration. This conclusion is consistent with an X-ray crystal structure determination [17] of one derivative of this series, namely the $Ni[S_2CN(COMe)Bz]_2$.

The electronic spectra of the studied compounds are complicated, exhibiting a number of overlapping intense bands in the ultraviolet and visible region. This complicated nature of the spectra prevents any simple classification and rationalization in terms of the ligand-field model. This is a general problem encountered in any ligand-field interpretation of the electronic spectra of many nickel(II) dithiocarbamates. However, in a previous paper [1] we have attempted to interpret the electronic spectrum of the $Ni[S_2CN(COMe)Bz]_2$ complex by means of EHMO-SCCC quantum-chemical calculations. Assignments were made by associating the observed bands with the transitions they most nearly matched in energy. Furthermore, it is evident that the spectra of the complexes under investigation are similar to those of the corresponding Ni(II) amide *N*-carbodithioates. Therefore, it is reasonable to invoke the same assignments of the bands for the $Ni[S_2CN(E)R]_2$ complexes as well. Their electronic spectral data and the assignments of the absorption bands are listed in Table 3.

As can be seen from Table 3, band I at *c.* 30 kK can be assigned as a mixture of LMCT and L–L transitions. This fact is quite in line with the contradictory assignments of that band in nickel(II) dithiocarbamates [18, 19]. The bands II and III, in the region 21–27 kK, include all the calculated excitations of the $L(\pi^*) \leftarrow M(d)$ type and are reasonably assigned to MLCT transitions, in accordance with the results of previously published electronic spectral data on nickel(II) dithiocarbamato complexes [9, 18]. Finally, the low intensity bands IV and V are assigned to the $^1B_{3g} \leftarrow {}^1A_g$ and $^1B_{1g} \leftarrow {}^1A_g$ LF excitations. For the former band a mixing with one $L(\pi^*) \leftarrow M(d)$ type excitation cannot be excluded, particularly when this band has high intensity. However, this is not the case for the $Ni[S_2CN(COOEt)R]_2$ complexes where both the $L(\pi^*) \leftarrow M(d)$ and $^1B_{3g} \leftarrow {}^1A_g$ bands are well separated, whereas the low energy $^1B_{1g} \leftarrow {}^1A_g$ LF band is not observed. Finally, the other two expected high energy LF transitions for the quadratic NiS_4 chromophore (D_{2h}) were impossible to observe, since the intense CT bands are extended up to the ligand-field part of the spectra, obscuring the weaker d–d transitions.

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