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Synthesis and Characterization of Nickel(II) N-Alkyliminodithiocarbonato Complexes Obtained via Deprotonation of N-Alkyldithiocarbamato Complexes

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Recent results from our laboratory have demonstrated [1] that dithiocarbamates, with an electron-withdrawing group and a proton on the nitrogen atom, may lose the proton to form dithiocarbimates. In particular our studies have shown that reacting bis(N-monosubstituted-dithiocarbamato)-platinum(II) and palladium(II) complexes with excess tertiary phosphine and with nucleophilic attack by anionic $RHNCS_2^-$ on a coordinated bidentate dithioligand, can occur to give the novel N-alkyliminodithiocarbonato complexes (dithiocarbimates). Fackler and Coucouvanis [2, 3] came to a similar conclusion in the case of Ni(II) N-phenyldithiocarbamate, as they have pointed out that Lewis bases can not only interact with the metal but may also remove a proton on the nitrogen atom to form the anionic nickel(II) dithiocarbimate.

As an extension of our previous work [4] in the area of O-atom transfer reactions of the $Ni(NO_2)(S_2CNHR)(PBu_3^n)$ complexes to CO, a study of the deprotonation reactions of analogous compounds was undertaken. To date, such a study has not been performed for any nickel(II) nitro- or halo-dithiocarbamate complexes, and it is of interest to compare their behaviour towards strong bases with that previously found in the platinum and palladium complexes. The results of our attempts to find a synthetic route to Ni(II) N-alkyliminodithiocarbonato complexes, as well as the study of some protonation reactions of these complexes, are reported in this paper.

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 spectra were obtained on a Cary 17DX spectrophotometer using freshly prepared CH_2Cl_2 and THF solutions. Mass spectra were measured on a RMU-6L Hitachi Perkin-Elmer mass spectrometer with ionisation source of T-2p type operating at 70 eV. Magnetic susceptibility measurements in the solid state were made by the Faraday technique using $Hg[Co(SCN)_4]$ as the calibrant. Molecular weights were determined using a Perkin-Elmer molecular weight apparatus Model 115 in $CHCl_3$ solutions. The elemental analysis of carbon, nitrogen and hydrogen was performed on a Perkin-Elmer 240B Elemental Analyser.

Preparation of the Complexes

Nitro(N-alkyldithiocarbamato)tri-n-butylphosphinenickel(II)

Complexes of type $Ni(NO_2)(S_2CNHR)(PBu_3^n)$ were prepared according to a published method [4].

Bromo(N-alkyldithiocarbamato)triphenylphosphinenickel(II)

Complexes of type $NiBr(S_2CNHR)(PPh_3)$ were prepared as described elsewhere [5].

Bis[(N-alkyliminodithiocarbonato)tri-n-butylphosphinenickel(II)]

1 mmol of the appropriate $Ni(NO_2)(S_2CNHR)(PBu_3^n)$ complex was dissolved in methanol–acetone and treated with an aqueous solution containing an excess of $(CH_3)_3N$ or NH_3. The orange precipitate was filtered off, washed with water and methanol, and air-dried (60–70% yield). *Bis[(N-alkyliminodithiocarbonato)triphenylphosphinenickel(II)]* were prepared in the same way using $NiBr(S_2CNHR)(PPh_3)$. These complexes were protonated as follows. The appropriate $Ni(S_2C{=}NR)(PPh_3)_2$ complex (1 mmol) in benzene (30 ml) was treated with CF_3COOH (1 mmol) and the mixture was left at room temperature under continuous magnetic stirring. After a period of 2 h a greenish product was formed which was filtered off, washed with diethyl ether and dried under vacuum. The complex was recrystallised from acetone. The same compound was also formed when the reaction was carried out with $CH_2ClCOOH$, HCOOH or $(COOH)_2$.

Results and Discussion

The compounds of formula $Ni(S_2C{=}NR)(PPh_3)_2$ (R = Me, Et, Pr^i, Bu^t, Ph, *p*-ClPh, *p*-MePh and *p*-MeOPh) were obtained by treating an acetone solution of the appropriate $NiX(S_2CNHR)(PPh_3)$ complex (X = Cl, Br) with an aqueous solution of

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TABLE I. Analytical Data[a], Melting Points (°C)[b], Magnetic Data[c], and Relevant IR Frequencies ($\mathrm{cm^{-1}}$) of some Ni(II) Dithiocarbimate Complexes with their Assignments (KBr discs).[d]

Compound	M.P.	%C	%N	%H	%Ni	$\mu_{\mathrm{eff}}^{\mathrm{cor}}$/(BM)	ν(C=N)	ν(C–S)
$\mathrm{Ni(S_2C{=}NMe)(PBu_3^n)_2}$	161–163[d]	45.75 (45.90)	3.79 (3.82)	8.12 (8.19)	16.00 (16.04)	1.06	1550vs	905m
$\mathrm{Ni(S_2C{=}NMe)(PPh_3)_2}$	169–171[d]	56.18 (56.33)	3.25 (3.28)	4.29 (4.22)	13.60 (13.78)	2.13	1565vs	912m
$\mathrm{Ni(S_2C{=}NEt)(PBu_3^n)_2}$	149–151[d]	47.12 (47.36)	3.60 (3.68)	8.36 (8.42)	15.52 (15.45)	1.35	1550vs	910m
$\mathrm{Ni(S_2C{=}NEt)(PPh_3)_2}$	148–150[d]	57.18 (57.27)	3.13 (3.18)	4.50 (4.54)	13.31 (13.34)	2.33	1550vs	918m
$\mathrm{Ni(S_2C{=}NPr^i)(PBu_3^n)_2}$	127–129[d]	48.85 (48.73)	3.51 (3.55)	8.78 (8.88)	14.75 (14.89)	1.92	1540vs	908s
$\mathrm{Ni(S_2C{=}NPr^i)(PPh_3)_2}$	110–112[d]	58.20 (58.14)	3.12 (3.08)	4.81 (4.84)	12.82 (12.93)	2.06	1532vs	925m
$\mathrm{Ni(S_2C{=}NBu^t)(PBu_3^n)_2}$	100–102[d]	49.88 (50.00)	3.40 (3.43)	9.70 (9.64)	14.40 (14.39)	1.72	1535vs	910s
$\mathrm{Ni(S_2C{=}NBu^t)(PPh_3)_2}$	112–114[d]	58.91 (58.97)	2.98 (2.99)	5.10 (5.12)	12.60 (12.54)	1.90	1528vs	920m
$\mathrm{Ni(S_2C{=}NPh)(PBu_3^n)_2}$	155–157[d]	53.57 (53.27)	3.29 (3.27)	7.69 (7.75)	13.80 (13.71)		1492vs	910s
$\mathrm{Ni(S_2C{=}NPh)(PPh_3)_2}$	167–169[d]	61.45 (61.47)	2.81 (2.86)	4.02 (4.01)	12.10 (12.03)		1510vs	928m
$\mathrm{Ni[S_2C{=}N(\mathit{p}\text{-}ClPh)](PBu_3^n)_2}$	140–142[d]	49.55 (49.24)	3.00 (3.02)	6.66 (6.69)	12.65 (12.68)		1488vs	902s
$\mathrm{Ni[S_2C{=}N(\mathit{p}\text{-}ClPh)](PPh_3)_2}$	163–165[d]	57.21 (57.36)	2.65 (2.67)	3.59 (3.63)	11.18 (11.22)		1500vs	930m
$\mathrm{Ni[S_2C{=}N(\mathit{p}\text{-}MePh)](PBu_3^n)_2}$	135–137[d]	52.10 (52.37)	3.09 (3.16)	8.12 (8.08)	13.21 (13.28)		1495vs	905s
$\mathrm{Ni[S_2C{=}N(\mathit{p}\text{-}MePh)](PPh_3)_2}$	166–168[d]	62.06 (62.15)	2.82 (2.78)	4.34 (4.38)	11.49 (11.69)		1500vs	925m
$\mathrm{Ni[S_2C{=}N(\mathit{p}\text{-}MeOPh)](PBu_3^n)_2}$	142–144[d]	52.33 (52.63)	2.96 (3.07)	7.35 (7.45)	12.90 (12.81)		1490vs	920s
$\mathrm{Ni[S_2C{=}N(\mathit{p}\text{-}MeOPh)](PPh_3)_2}$	169–171[d]	60.29 (60.23)	2.78 (2.70)	4.27 (4.24)	11.40 (11.33)		1505vs	926m

[a] Figures in parentheses are the calculated values. [b] d = decomposition. [c] Temperature ≅220 °C. [d] vs = very strong, s = strong, m = medium.

$\mathrm{(CH_3)_3N}$ or $\mathrm{NH_3}$. Similarly, the $\mathrm{Ni(S_2C{=}NR)(PBu_3^n)_2}$ complexes were prepared by the action of the base on $\mathrm{Ni(NO_2)(S_2CNHR)(PBu_3^n)}$.

All the compounds are stable as solids and in solution. They are readily soluble in THF, benzene and methylene chloride, but are sparingly soluble in ethanol, ether and hexane. Analyses and decomposition temperatures are given in Table I. The low values of the molar conductivity in anhydrous acetone (2–10 $\mathrm{ohm^{-1}\ cm^2\ mol^{-1}}$) indicate the non-electrolytic character of the complexes, while molecular weight measurements in chloroform show them to be dimeric. Protonation of these compounds with trifluoroacetic acid in benzene affords green crystalline complexes formulated as $\mathrm{Ni(S_2CNHR)_2}$. This result is consistent with the evidence presented elsewhere [1] on the electrophilic reactions of alkyliminodithiocarbonato ligands.

The infrared spectra of the various dithiocarbimate complexes (Table I) clearly show the absence of the N–H stretch which is present in the parent dithiocarbamate complexes [4, 5]. The strong band found between 1490 and 1560 $\mathrm{cm^{-1}}$ in these complexes was assigned to the C=N stretch [1, 6]. The position of this band is affected by the ability of the ligand to mesomerically shift π-electron density onto the sulfur atoms [3, 7, 8]. By protonation of the complexes the ν(C=N) band is shifted to lower frequencies and its position is the same with the $\nu(\mathrm{C\overset{..}{-}N})$ band of the corresponding bis(N-alkyldithiocarbamato)nickel(II) complexes. Furthermore a new broad band in the 3300 $\mathrm{cm^{-1}}$ region appeared, also characteristic of the N-alkyldithiocarbamato complexes. The band in the region of 900–930 $\mathrm{cm^{-1}}$ is attributed to the stretching vibration of the C–S bonds. This band is shifted to lower frequencies relative to the $\nu(\mathrm{C\overset{..}{-}S})$ band of the corresponding dithiocarbamato ligands. Finally, the Ni–S stretching frequencies were observed in the 300–400 $\mathrm{cm^{-1}}$ region

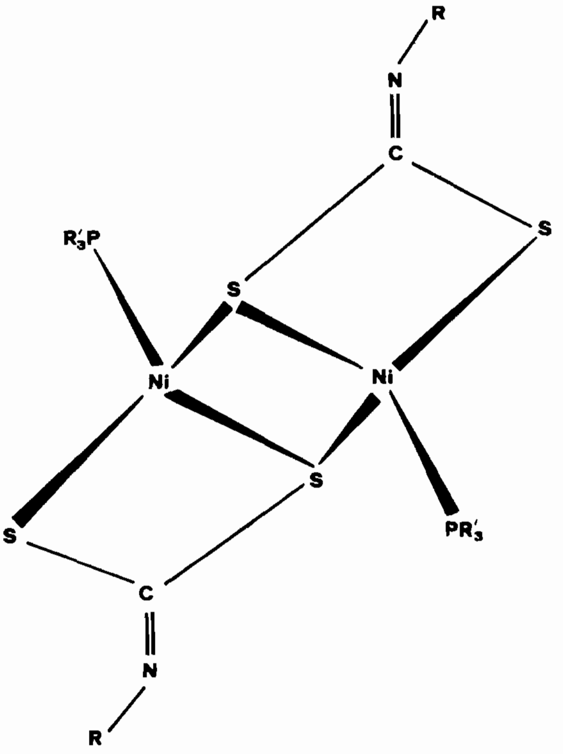
TABLE II. Electronic Spectra of some Ni(II) Dithiocarbimate Complexes in THF.

Compound	Band I	Band II	Band III	Band IV	Band V	Band VI
$Ni(S_2C{=}NMe)(PBu_3^n)_2$	40.5[a](4.54)[b]		32.3(4.62)	26.5sh(4.32)	23.7 (3.58)	20.9(3.45)
$Ni(S_2C{=}NMe)(PPh_3)_2$	40.2 (4.62)	36.9 (4.49)	31.2(4.41)	26.2 (3.95)	23.6sh(3.78)	20.8(3.70)
$Ni(S_2C{=}NEt)(PBu_3^n)_2$	40.5 (4.52)		31.6(4.60)	26.2sh(4.30)	23.7 (3.60)	20.7(3.50)
$Ni(S_2C{=}NEt)(PPh_3)_2$	40.3 (4.60)	37.0 (4.48)	31.2(4.40)	26.2 (3.94)	23.6sh(3.76)	20.6(3.69)
$Ni(S_2C{=}NPr^i)(PBu_3^n)_2$	40.5 (4.45)		31.7(4.53)	26.0sh(4.23)	23.6 (3.41)	20.6(3.36)
$Ni(S_2C{=}NPr^i)(PPh_3)_2$	40.2 (4.59)	36.9 (4.48)	31.1(4.38)	26.0 (3.93)	23.5sh(3.75)	20.4(3.68)
$Ni(S_2C{=}NBu^t)(PBu_3^n)_2$	40.3 (4.48)		31.4(4.56)	26.0sh(4.31)	23.5 (3.53)	20.7(3.46)
$Ni(S_2C{=}NBu^t)(PPh_3)_2$	40.3 (4.56)	37.0 (4.46)	31.2(4.34)	26.2 (3.91)	23.6sh(3.71)	20.8(3.65)
$Ni(S_2C{=}NPh)(PBu_3^n)_2$	38.7 (4.52)	37.7sh[c](4.49)	31.1(4.51)	26.0 (4.18)	23.2 (3.90)	20.4(3.70)
$Ni(S_2C{=}NPh)(PPh_3)_2$	39.1 (4.45)	37.0sh (4.38)	30.8(4.47)	26.1 (3.92)	23.5 (3.93)	20.9(3.56)
$Ni[S_2C{=}N(p\text{-}ClPh)](PBu_3^n)_2$	39.8 (4.51)	37.3sh (4.49)	31.3(4.51)	26.2sh(4.16)	23.1 (3.90)	20.5(3.71)
$Ni[S_2C{=}N(p\text{-}ClPh)](PPh_3)_2$	38.9 (4.42)	37.0 (4.35)	30.6(4.28)	26.1 (3.90)	23.3 (3.92)	20.8(3.53)
$Ni[S_2C{=}N(p\text{-}MePh)](PBu_3^n)_2$	39.5 (4.49)	37.3sh (4.48)	31.3(4.49)	26.0sh(4.13)	23.2 (3.81)	20.3(3.66)
$Ni[S_2C{=}N(p\text{-}MePh)](PPh_3)_2$	39.4 (4.46)	37.0sh (4.38)	30.6(4.31)	26.1 (3.90)	23.7 (3.93)	20.8(3.56)
$Ni[S_2C{=}N(p\text{-}MeOPh)](PBu_3^n)_2$	39.2 (4.49)	37.0sh (4.48)	31.7(4.48)	26.0 (4.12)	23.9 (3.88)	20.9(3.67)
$Ni[S_2C{=}N(p\text{-}MeOPh)](PPh_3)_2$	38.9 (4.45)	36.9 (4.37)	30.7(4.30)	26.0 (3.91)	23.9 (3.92)	20.8(3.54)

[a] ν/kK. [b] $\log \epsilon_{mol}$. [c] sh = shoulder.

indicating the coordination of the gem-disulfide ligands.

The magnetic properties of the compounds of interest (Table I) appear to be strongly dependent on the nature of the substituents in the amine group, as well as the phosphine group. The dimeric aryldithiocarbimato complexes are diamagnetic and are presumably of square-planar stereochemistry. On the other hand, the dimeric alkyldithiocarbimato complexes are paramagnetic and exhibit room-temperature magnetic moments lower than those expected for tetrahedral ligand field. However, it seems reasonable to assume that there is a change in structure from tetrahedral to square-planar as alkyl groups in the dithiocarbimato ligands are replaced by phenyl. We may further suggest that effects which strengthen the ligand field around the metal atom will tend to favor the diamagnetic (square-planar) form relative to the paramagnetic (tetrahedral) form. Similar effects have been observed in other series of nickel complexes [9], and equilibria between square-planar and tetrahedral forms have been demonstrated for a variety of N-substituted salicylaldimine complexes of nickel(II), either in solution or in the melt [10, 11]. Moreover, the low values for the moments strongly suggest weak magnetic exchange interactions between the two nickel centers, propagated through bridging sulfur donor atoms of the dithiocarbimato ligands according to the following structure:



The magnetic exchange interactions in these molecular magnetic systems are further supported from the dependence of the room-temperature magnetic data on the magnetic field strengths. The low magnetic moments observed both at low and high field strengths, as well as the slight decrease of the moments as the magnetic field decreases, are indicative of the operation of antiferromagntism in these compounds. These observations show that our binuclear d^8-d^8 system displays the singlet (antiferromagnetism) ground state.

The absorption maxima and the extinction coefficients of the bands observed in the electronic spectra of the compounds under investigation are shown in Table II. The most intense band I is due to an intraligand $\pi^* \leftarrow \pi$ transition located on the N=C–S group [12, 13]. This band shows an hypsochromic shift relative to the corresponding band of the N-alkyldithiocarbamato ligand due to the localisation of the π-electron system in the dithiocarbimato ligand. Band II is also due to an intraligand $\pi^* \leftarrow \pi$ transition located on the phenyl group. Band III is attributed to a $\pi^* \leftarrow n$ transition located on the sulfur atoms [14]. Bands IV, V and VI are due to a charge transfer (CT) transitions which could be either of the L → M or L ← M type. Finally, spectra obtained in the solid state (Nujol mulls) showed an absorption band in the region 800–1000 mμ due to the tetrahedral species which may be assigned to the $^3A_{2g} \leftarrow {}^3T_{1g}(F)$ transition [15].

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