

A Convenient Method of Preparing Nickel(II) Thiocyanate and its Use in Synthesis

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Summary

A convenient method for preparing nickel(II) thiocyanate is described. Some new compounds containing nickel thiocyanate and ligands, such as OPPh_3 , OAsPh_3 , bipy, Me_2NH , Et_3N or N_2H_4 are reported, together with their structures and the nature of the bond between the thiocyanate and the metal, which has been determined by physical and chemical methods.

Introduction

Compounds containing nickel(II) thiocyanate are prepared mostly by metathesis between nickel(II) chloride or nitrate with alkali metal thiocyanates⁽¹⁾. However, in such syntheses if precautions are not taken, the final product may be contaminated with starting materials. Use of nickel(II) thiocyanate for such purposes should overcome this difficulty. Methods known for preparing this compound include: treatment of a dilute thiocyanic acid solution with nickel hydroxide or carbonate, followed by evaporating the mixture at 150°C ^(2, 3); mixing and boiling aqueous solutions of ammonium thiocyanate and barium hydroxide, followed by addition of an aqueous nickel sulphate and finally concentrating^(3, 4); and metathetic preparation in ethanol followed by addition of benzene and slow concentration of the solution at atmospheric pressure with final heating to 110°C *in vacuo*⁽⁵⁾.

Here we report a very simple one step method of preparing nickel(II) thiocyanate by treating a solution of nickel(II) chloride or nitrate in acetic acid with a solution of ammonium thiocyanate in the same solvent at room temperature. The physical properties of the resulting compound have been studied in the solid state and in solution. This nickel(II) thiocyanate has been used to prepare many including new compounds containing nickel thiocyanate and other ligands.

Experimental

All the materials used were chemically pure or of Analar grade. Carbon, hydrogen and nitrogen analyses were carried out at the microanalytical laboratory IIT, Kanpur. Nickel was estimated by the standard method; volumetrically by titration with EDTA using murexide as indicator⁽⁶⁾. Solid state magnetic susceptibilities were measured by the Gouy method at room temperature using $\text{HgCo}(\text{CNS})_4$ as calibrant. I.r. spectra in solution and solid in KBr or nujol were recorded on a Perkin-Elmer 297 Infrared spectrophotometer in $4000\text{--}600\text{ cm}^{-1}$ range. Electronic spectra were recorded in MeOH or PhNO_2 , in $900\text{--}350\text{ nm}$ range on a Beckmann 26 spectrophotometer. Conductivity measurements were performed on an Elico type CM 82 T conductivity bridge in MeCN or PhNO_2 .

Nickel(II) thiocyanate

To a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (9.5 g, 0.04 mole) in H_2O (10 cm^3), diluted with glacial HOAc (100 cm^3), was added a solution of ammonium thiocyanate (7.6 g, 0.1 mole) in HOAc (20 cm^3) with constant stirring at room temperature. An instantaneous reaction took place and a yellow compound separated and the mother liquor turned almost colourless. Stirring was continued for another 2 h. The product was separated by filtration and washed with 1 : 10 $\text{H}_2\text{O} : \text{HOAc}$ 3 to 4 times and finally dried *in vacuo* over conc. H_2SO_4 . Yield, 90%.

Alternatively, the compound was prepared from $\text{Ni}(\text{NO}_3)_2$ in a similar manner, however the product so obtained was not as pure.

$[\text{Ni}(\text{OPPh}_3)_2(\text{SCN})_2]$

A melt of OPPh_3 (1 g, 0.036 mole) was made in an oil bath to 165°C , and $\text{Ni}(\text{SCN})_2$ (0.175 g, 0.01 mole) was added with constant stirring. The stirring was continued for 15 min while the mixture was maintained at *ca.* 165°C . The mixture was then cooled, powdered in an agate mortar and washed several times with PhH to remove unreacted OPPh_3 . It was finally dried *in vacuo*. Yield, 97%.

$[\text{Ni}(\text{OAsPh}_3)_2(\text{SCN})_2]$

A solution of $\text{Ni}(\text{SCN})_2$ (0.175 g, 0.01 mole) in MeOH (3 cm^3) was diluted with Me_2CO (30 cm^3) and a solution of OAsPh_3 (0.7 g, 0.022 mole) in Me_2CO (5 cm^3) was added; the mixture was boiled under reflux for 2 h. The resulting yellowish green product, $[\text{Ni}(\text{OAsPh}_3)_2(\text{SCN})_2]$, was separated by centrifugation, washed with Me_2CO and PhH and dried *in vacuo*. Yield, 88%.

$[\text{Ni}(\text{bipy})_3](\text{SCN})_2$, $[\text{Ni}(\text{Me}_2\text{NH})_4(\text{SCN})_2]$, $[\text{Ni}(\text{Et}_3\text{N})_4(\text{SCN})_2]$ and $[\text{Ni}(\text{quinoline})_4(\text{SCN})_2]$

The method was similar to that used for preparing $[\text{Ni}(\text{OAsPh}_3)_2(\text{SCN})_2]$, except that a smaller quantity of Me_2CO (15 cm^3) was used and $\text{Ni}(\text{SCN})_2$ and the ligands were taken in 1 : 3 or 1 : 4 molar ratio depending on the composition of the complex required. Yield, 80–90%.

$[\text{Ni}(\text{N}_2\text{H}_4)_2(\text{SCN})_2]$ and $[\text{Ni}(\text{en})_2(\text{SCN})_2]$

To a solution of $\text{Ni}(\text{SCN})_2$ (0.175 g, 0.01 mole) in MeOH (3 cm^3), $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ or $\text{H}_4\text{C}_2(\text{NH}_2)_2$ (0.02 mole) was added and the compound separated out immediately. It was centrifuged, washed with MeOH and dried *in vacuo*. Yield, 90%.

$[\text{Ni}(\text{PPh}_3)_2(\text{NCS})_2]$

To a suspension of $\text{Ni}(\text{SCN})_2$ (0.175 g, 0.01 mole) in *n*-BuOH (5 cm^3) a solution of PPh_3 (0.53 g, 0.02 mole) in *n*-

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Table 1. Analytical and physical data of the nickel thiocyanato complexes.

Compound	Colour	M.p. (°C)	μ_{eff} (B.M.)	Found (Calcd.)%		N	S	Ni	Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
				C	H				
Ni(SCN) ₂	yellow	240 (dec)	3.26	13.6 (13.7)		15.7 (16.0)	36.1 (36.6)	33.3 (33.6)	
Ni(OPPh ₃) ₂ (SCN) ₂	yellow	182-5	2.82	62.1 (62.4)	4.3 (4.1)	3.7 (3.8)	8.9 (8.8)	8.3 (8.0)	
Ni(OAsPh ₃) ₂ (SCN) ₂	yellowish green	240-50	3.10	55.3 (55.7)	3.5 (3.7)	3.9 (3.4)	8.3 (7.8)	7.8 (7.2)	
[Ni(bipy) ₃](SCN) ₂	light pink	> 300	-	55.6 (55.3)	3.5 (3.2)	19.4 (19.8)	10.9 (11.3)	10.6 (10.4)	218 ^{a)}
[Ni(Me ₂ NH) ₄ (NCS) ₂](NCS) ₂	green	> 320	-	33.2 (33.8)	7.5 (7.9)	24.1 (23.7)	17.7 (18.0)	16.3 (16.6)	148 ^{b)}
[Ni(Et ₃ N) ₄ (NCS) ₂](NCS) ₂	green	> 320	-	54.3 (53.9)	9.9 (10.4)	14.8 (14.5)	10.8 (11.1)	10.2 (10.1)	152 ^{b)}

a) In MeCN; b) In PhNO₂.

Table 2. Spectral data for Ni(SCN)₂ in different media.

Solvent	λ_{max} (nm) (ϵ_{max})	I.r. (cm ⁻¹)
Solid	650 ^{a)} 430	2165s ^{b)} 2120sh 765w
EtOH	727 (3.7), 662 (3.8), 398 (9.6)	
MeOH	725 (4), 660 (4.2), 390 (10), 362 (11)	2110s 2055sh
DMF	735 (5.7), 675 (6.4), 404 (16.5)	
DMSO	750br (3), 410 (8)	
Me ₂ CO	665sh (9), 615sh (10.3)	2150sh, 2105s, 2070sh, 790m
α -picoline	685 (4.4), 360	
MeCN	710sh, 610 (16), 370sh	2100s, 800m
Pyridine	775sh, 587 (7.9), 360 (18.3)	

a) Reflectance spectrum; b) In KBr or nujol.

BuOH (5 cm³) was added and the mixture was stirred at room temperature for 1 h. A dark red crystalline product separated, which was washed with Et₂O and dried *in vacuo*. Yield, 94%.

[Ni(py)₄(NCS)₂], *[Ni(DMF)₄(NCS)₂]* and *[Ni(DMSO)₄(SCN)₂]*

Ni(SCN)₂ (0.5 g) was mixed with pyridine, DMF or DMSO (5 cm³) and heated on a water bath for *ca.* 30 min, when a clear coloured solution was obtained. The product separated from the solution on cooling, and was washed with Me₂CO and dried *in vacuo*. Yield, 60-70%.

Results and Discussion

Nickel(II) thiocyanate (prepared according to the method described in the Experimental Section), was described earlier, by different authors⁽²⁻⁵⁾. Its analytical data confirm the composition to be Ni(SCN)₂ (Table 1). The i.r. spectrum in nujol

or potassium bromide shows a strong and sharp band at 2165 cm⁻¹ similar to the band observed by Flint and Goodgame⁽⁵⁾ for Ni(SCN)₂, which is assigned unambiguously to $\nu(\text{CN})$ of the bridging -SCN group. A weak band at 765 cm⁻¹ is assigned to $\nu(\text{CS})$ of the bridging thiocyanate group⁽⁵⁾. Mitchell and Williams⁽⁷⁾ reported a band at 2151 cm⁻¹ for $\nu(\text{CN})$ of the bridging -SCN group of Ni(SCN)₂. The electronic reflectance spectrum in the 900-300 nm region show bands at 650 nm and at 430 nm. The former band is identical to that reported earlier⁽⁵⁾ whilst the band at 430 nm could be due to charge-transfer band. The magnetic moment of the compound is 3.26 B.M. which is close to the value reported by Flint and Goodgame⁽⁵⁾. The structure proposed for nickel thiocyanate in the solid state consists of a tetragonal coordination sphere with four bridging sulphur atoms in the plane with nitrogen atoms in the axial positions.

The i.r. and visible spectra of nickel thiocyanate have been recorded in organic solvents in order to ascertain the coordination mode of the thiocyanato group in solution and the nature of coordination around the nickel atom. I.r. spectra of nickel thiocyanate in acetonitrile, acetone and methanol show a band at *ca.* 2100 cm⁻¹ (Table 2) which may be assigned to terminal $\nu(\text{CN})$ of the N-bonded thiocyanate. A band at *ca.* 800 cm⁻¹ in the acetonitrile or acetone solution is characteristic of the $\nu(\text{CS})$ of the N-bonded thiocyanate group⁽⁸⁾. However, an analogous band was not observed in methanol solution. I.r. studies of nickel thiocyanate in donor solvents have not been reported earlier, however, i.r. spectra of NiL₂(SCN)₂ (L = methanol or ethanol) in nujol provide evidence for a bridging thiocyanato group⁽⁵⁾.

The electronic spectra of nickel thiocyanate have been studied in different organic solvents in order to determine the nature of coordination around the metal ion. The spectra in the visible region show two bands at *ca.* 700 nm and one at *ca.* 400 nm (Table 2). The molar extinction coefficient for these bands lie in 3 to 20 range, which indicate an octahedral environment around nickel. Two bands at *ca.* 700 nm can be assigned to ${}^3A_2(\text{F}) \rightarrow {}^3T_1(\text{F})$ and at *ca.* 400 nm to ${}^3A_2(\text{F}) \rightarrow {}^3T_1(\text{P})$ transitions. Normally in a pure octahedral environment, only one band at *ca.* 700 nm should be observed, however, the lowering of symmetry to *D_{4h}*, probably due to the formation of *[Ni(L)₄(NCS)₂]* (L = methanol, ethanol,

N,N-dimethylformamide, dimethyl sulphoxide, acetone, α -picoline, acetonitrile or pyridine), the ${}^3T_1(F)$ state is split into two, one of two fold degeneracy and the other a singly degenerate state and hence two absorption bands at *ca.* 700 nm. The visible and u.v. spectra of nickel thiocyanate in methanol, ethanol and pyridine reported by Kiss and Csokan⁽⁹⁾ describes the formation of $[Ni(SCN)_2L_2]$ when no free thiocyanate ions were added and that of $[Ni(SCN)_4]^{2-}$ and $[Ni(SCN)_4L_2]^{2-}$ when an excess of free thiocyanate ions were present. We describe here the octahedral coordination around the nickel ion due to the formation of the species $NiL_4(SCN)_2$ (*L* = solvent molecule). The spectra are similar to the spectra of $NiL_4(SCN)_2$ to be discussed later.

Nickel thiocyanate has been used to prepare complexes containing oxygen, nitrogen and phosphorus donor ligands, *i.e.* triphenylphosphine oxide, triphenylarsine oxide, *N,N'*-bipyridyl, hydrazine, ethylene diamine, dimethylamine, triethylamine, *N,N*-dimethylformamide, quinoline, pyridine, dimethylsulphoxide or triphenylphosphine.

The i.r. spectra of complexes containing triphenylphosphine oxide or triphenylarsine oxide show a strong band at *ca.* 2100 cm^{-1} assignable to $\nu(CN)$ of the terminal thiocyanato group⁽⁸⁾. The terminal thiocyanate can be either S-bonded or N-bonded. We propose here only S-bonding as there is no absorption in 780–860 cm^{-1} region due to $\nu(CS)$ of the N-bonded thiocyanate⁽⁸⁾. $\nu(CS)$ of the S-bonded thiocyanato group should be observed in 690 to 740 cm^{-1} region⁽⁸⁾. There are several bands in this region due to the ligand phenyl groups, hence no absorption can be assigned unambiguously to $\nu(CS)$ of the S-bonded thiocyanate. An example of such a complex of nickel(II), *i.e.* $[Ni(OPPh_3)(SCN)Cl]_2$ having similar i.r. absorptions has been reported⁽¹⁰⁾. I.r. bands at 1185 cm^{-1} and 866 cm^{-1} in the phosphine oxide and arsine oxide complexes are assigned to $\nu(P=O)$ and $\nu(As=O)$ ⁽⁸⁾ respectively.

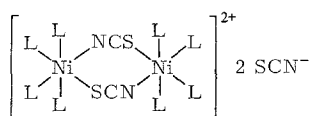
$Ni(OPPh_3)_2(SCN)_2$ and $Ni(OAsPh_3)_2(SCN)_2$ have four coordination around the nickel(II) ion. If the complexes are assumed to be monomeric, either a square planar or a distorted tetrahedral geometry is possible. For penta- or hexa-coordination, the complexes have to be either dimeric or polymeric respectively, bridging through thiocyanato groups. No evidence of bridging thiocyanato groups is available from i.r. (absence of absorption in 2100–2200 cm^{-1} region), hence penta- or hexa-coordination is not possible in these cases. Square planar complexes of nickel(II) are generally diamagnetic⁽¹¹⁾ and have magnetic moments *ca.* 3 B.M., which is slightly lower than the moments of tetrahedral nickel(II) complexes⁽¹²⁾. Thus, the possible geometry of these complexes is distorted tetrahedral, which is supported further by their electronic reflectance spectra discussed below which show bands at *ca.* 650 and 400 nm in both the cases. A band at 850 nm is also observed in the arsine oxide complex. A band similar to this in the phosphine oxide complex, if present beyond 900 nm, could not be observed due to the range of measurement of the instrument. The bands at 850 and 650 nm may be assigned to ${}^3T_1(F) \rightarrow {}^3A_2(F)$ and ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transitions respectively of a nickel(II) tetrahedral system⁽¹³⁾. The band at *ca.* 400 nm could be due to charge-transfer. The visible spectra in a non-coordinating solvent, like chloroform show only one band at *ca.* 400 nm. It seems the complexes are decomposing in chloroform. However, spectra of the complexes in a coordinating solvent like *N,N*-dimethylformamide is superimposable with the spectrum of nickel thiocyanate in that solvent. It seems that in presence of *N,N*-dimethylformamide, the phosphine oxide or the arsine oxide is liberated and an octahedral

species, such as $[Ni(DMF)_4(NCS)_2]$, is obtained in solution.

The complex containing *N,N'*-bipyridyl with composition $Ni(bipy)_3(SCN)_2$ has a molar conductance = 218 $\Omega^{-1} cm^2 mol^{-1}$, which is in the range expected for a 1:2 electrolyte in acetonitrile; hence the molecular formula, $[Ni(bipy)_3](SCN)_2$. The i.r. spectrum shows a strong band at 2045 cm^{-1} together with bands at 780 and 740 cm^{-1} . All the bands due to bipyridyl are also present. The band at 2045 cm^{-1} is assigned to $\nu(CN)$ of the ionic type of thiocyanate group, which is observed at a frequency lower than that of S-bonded or N-bonded $\nu(CN)$ ^(8, 14). The band at 740 or 780 cm^{-1} can not be assigned unambiguously to $\nu(CS)$, due to many absorptions of bipyridyl in 800–650 cm^{-1} region. The electronic spectrum shows two bands at 780 and 513 nm which may be assigned to ${}^3A_2(F) \rightarrow {}^3T_1(F)$ transition in an octahedral system. The splitting of ${}^3T_1(F)$ state may be due to the lowering in symmetry to D_3 .

A complex of composition $Ni(N_2H_4)_2(NCS)_2$ reported by Ray and Sarkar⁽¹⁵⁾ has a molar conductance of 210 $\Omega^{-1} cm^2 mol^{-1}$ in water at 24.5°C. A compound of the same composition obtained by us, is insoluble in many organic solvents and water, hence a conductance measurement and some of the physical studies in solution were not possible. The i.r. spectrum shows bands at 3320, 3300 and 3210 cm^{-1} which is assigned to $\nu(NH)$ of the hydrazine. Further a strong band at 2080 cm^{-1} and a band of medium intensity at 790 cm^{-1} may be assigned to $\nu(CN)$ and $\nu(CS)$ respectively of the N-bonded thiocyanato group⁽⁸⁾. For the ionic thiocyanato group, $\nu(CN)$ and $\nu(CS)$ should be observed at lower frequencies⁽⁸⁾. A band at 972 cm^{-1} may be assigned to $\nu(N-N)$ of the hydrazine⁽¹⁶⁾. This compound may have a polymeric structure having octahedral coordination around nickel atom. Polymerisation may be achieved by the hydrazine ligands bridging between nickel atoms and having N-bonded terminal thiocyanato group. Examples of such polymeric compounds with hydrazine are known⁽¹⁷⁾.

The complexes of dimethylamine and triethylamine are generally insoluble in most organic solvents. The i.r. spectra show a band of medium intensity at *ca.* 2105 cm^{-1} and a strong band at 2030 cm^{-1} . The band at *ca.* 2105 cm^{-1} may be assigned to $\nu(CN)$ of the bridging thiocyanato group and at 2030 cm^{-1} due to $\nu(CN)$ of the ionic thiocyanato group. Examples of $\nu(CN)$ of bridging thiocyanato occurring at 2110 cm^{-1} are known^(18, 19). The molar conductance of the compounds assuming the molecular formula $[L_4Ni(NCS)_2 NiL_4](SCN)_2$, in nitrobenzene is found to be of the order of 150 $\Omega^{-1} cm^2 mol^{-1}$, which is normally observed for 1:2 electrolyte systems. The visible spectra of these compounds in nitrobenzene show two bands at *ca.* 650 nm and one band at *ca.* 400 nm, which may be assigned to the d-d transitions of distorted octahedral systems as discussed earlier. On the basis of the above mentioned physical studies, the following dimeric structure is proposed.



L = Me_2NH or Et_3N

The complexes containing *N,N*-dimethylformamide, quinoline, pyridine, dimethylsulphoxide or ethylene diamine are similar to the reported compounds^(7, 20–23). All except the dimethylsulphoxide complex have an N-bonded thiocyanato group [*vide* infrared (Table 3)]. *N,N*-Dimethylformamide is coordinated to nickel through the oxygen atom as $\nu(C=O)$ is

shifted to 1645 cm^{-1} in the complex. Dimethylsulphoxide is coordinated to nickel in its complex is through the oxygen atom as $\nu(\text{S}=\text{O})$ is shifted towards lower frequency. All the complexes have a distorted octahedral geometry and the electronic spectra in methanol solvent are very similar, with two bands at *ca.* 700 nm and one at *ca.* 400 nm, the assignments of which could be made as above. The complex containing triphenylphosphine is a square planar N-bonded thiocyanato complex and is same as reported $[\text{Ni}(\text{PPh}_3)_2(\text{NCS})_2]$ ^(10, 12).

Table 3. Spectral data of some nickel thiocyanato complexes.

Complex	λ_{max} (nm) (ϵ_{max})	I.r. (cm^{-1})
$\text{Ni}(\text{OPPh}_3)_2(\text{SCN})_2$	660 ^{a)} 415	2100s, 1188m, 1182m
$\text{Ni}(\text{OAsPh}_3)_2(\text{SCN})_2$	850 ^{a)} , 650, 390	2097s 866m-s
$\text{Ni}(\text{bipy})_3(\text{SCN})_2$	780 (12) ^{b)} 513 (23)	2045s 780s 740m
$\text{Ni}(\text{N}_2\text{H}_4)_2(\text{NCS})_2$	—	3320, 3300 3210, 2080s 972m, 790m
$\text{Ni}(\text{Me}_2\text{NH})_4(\text{NCS})_2$	610 (5.1) ^{c)} 400 (S.6)	2104m 2030s
$\text{Ni}(\text{Et}_3\text{N})_4(\text{NCS})_2$	660 sh ^{c)} 620 (9.2) 425 (20)	2110m 2030s
$\text{Ni}(\text{en})_2(\text{NCS})_2$	880 (4.4) ^{b)} 545 (4.4)	2072s
$\text{Ni}(\text{DMF})_4(\text{NCS})_2$	735 (2.7) ^{b)} 662 (3.1) 392 (9.3)	2108s 1645s 790
$\text{Ni}(\text{Quin})_4(\text{NCS})_2$	725 (4.8) ^{b)} 660 (5.4) 397 (13)	2100s
$\text{Ni}(\text{py})_4(\text{NCS})_2$	740 sh ^{b)} 630 (5) 380 (11)	2085s 800m
$\text{Ni}(\text{DMSO})_4(\text{SCN})_2$	735 (3.4) ^{b)} 660 (4.3) 400 (10)	2090s, 1020, 995, 950
$\text{Ni}(\text{PPh}_3)_2(\text{NCS})_2$	—	2080s 865m

^{a)} Reflectance spectrum; ^{b)} in MeOH; ^{c)} in PhNO_2 .

Conclusion

A convenient method of preparing nickel(II) thiocyanate has been described. Nickel thiocyanate has been used to obtain various compounds containing nickel thiocyanate and other donor ligands, containing nitrogen, oxygen or phosphorus donor atoms. Although, most complexes of nickel(II) are known to have N-bonded thiocyanato group, some new compounds of nickel(II) containing S-bonded thiocyanato group have been prepared besides some polymeric bridging thiocyanato groups.

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