

HALOGENATION REACTIONS OF NICKEL(II) COMPLEXES CONTAINING NITROGEN DONOR LIGANDS

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(Received October 25th, 1969)

SUMMARY

Chlorine and bromine react with an ethanolic suspension of several non-electrolytic nickel(II) complexes having the formula NiL_2Cl_2 , forming a number of 1/1 electrolytic complexes of the type $[\text{LH}]^+[\text{NiCl}_2\text{X}]^-$ where L = pyridine, γ -picoline, quinoline or isoquinoline and X = Cl or Br. When an excess of the ligand is added to NiL_2Cl_2 and halogenation subsequently is carried out, one molecule of the ligand also becomes bonded to the metal and compounds of the type $[\text{LH}]^+[\text{NiLCl}_3]^-$ and $[\text{LH}]^+[\text{NiLCl}_2\text{Br}]^-$ are obtained.

INTRODUCTION

Nickel exhibits all the oxidation states from 0 to 4, divalent compounds being the most common. Under appropriate conditions, divalent nickel complexes containing phosphorous and arsenic donor ligands^{1,2}, ethylenediamine³, biguanide and guanylurea⁴ have been oxidised to higher-valent states by chlorine or bromine. Several compounds having the general formula NiL_2X_2 , where L is pyridine, substituted pyridine or quinoline are known^{5,6}.

We examined the possibility of raising the nickel atom in these complexes from the divalent to trivalent state by halogenation, and although this could not be achieved, a larger number of complexes of the type $[\text{LH}]^+[\text{NiCl}_2\text{X}]^-$ and $[\text{LH}]^+[\text{NiLCl}_2\text{X}]^-$ where X = Cl^- or Br^- have been isolated and characterised.

EXPERIMENTAL

All the chemicals used were of A.R. grade. The purity of the isolated compounds was established by estimating metal and halogen. The magnetic measurements were carried out at room temperature on solid specimens using Gouy method. Electrical conductance was measured by a Toshniwal Conductivity bridge. The IR spectra were recorded on Nujol mulls using a Unicam SP-200 spectrophotometer.

The starting compounds, NiL_2Cl_2 , where L is pyridine, γ -picoline, quinoline or isoquinoline, were prepared by established methods^{5,6}.

Chlorination

Pure dry chlorine was passed through an ethanolic suspension of the respective NiL_2Cl_2 compounds. The suspension cleared gradually with the evolution of much heat. After the chlorine had been passed in for about 10 min, orange to yellow coloured compounds separated out from the clear solution and these were filtered off, washed with ethanol and dried *in vacuo*. They have the composition $[\text{LH}][\text{NiCl}_3]$.

When the chlorine was passed for about 30 min in the presence of an excess ligand, L, a similar exothermic reaction took place resulting in a deep blue solution. No solid separated even when the solution was kept for some days, except that when L was quinoline a deep blue solid separated out immediately.

Bromination

Liquid bromine was added dropwise to an ethanolic suspension of NiL_2Cl_2 with vigorous shaking, and yellow or light green compounds were isolated. As with chlorination, deep blue compounds were obtained when the solutions obtained by bromination in presence of an excess of the ligand, were allowed to stand for 2–3 days.

Mixed ligand anionic complexes

The compounds having the hetero ligand in the anionic complex *viz.*, $[\text{NiLCl}_3]^-$ and $[\text{NiLCl}_2\text{Br}]^-$ were obtained by passing the halogen through an ethanolic suspension of $[\text{NiL}_2\text{Cl}_2]$ and an excess of the ligand, or alternatively by treating the $[\text{NiCl}_3]^-$ or $[\text{NiCl}_2\text{Br}]^-$ complex with an excess of free ligand. Quinoline becomes bonded to the metal in the anionic complex $[\text{NiCl}_3]^-$ after 10 min refluxing, but the product decomposes to NiL_2Cl_2 when treated with other ligands.

The analytical, conductance, melting point and magnetic susceptibility data are recorded in Table 1.

RESULTS AND DISCUSSION

When NiL_2Cl_2 is treated with chlorine or bromine there are three possibilities:

- (1). Oxidation of the bivalent nickel to trivalent or tetravalent state.
- (2). Substitution in the pyridine ring.
- (3). Solvolysis of halogen and addition of the consequent hydrogen halides to the ligand base forming quaternary halides.

Several nickel(II) complexes containing ligands with N, P and As donor atoms have previously been shown^{1–4} to undergo oxidation of the metal on halogenation. Babaeva reported⁷ the formation of pyridinium tetrachlorocobaltate(II) from the reaction of chlorine with bis(pyridine)cobalt dichloride in methanol solution, whilst oxidation occurred when CoPy_2Br_2 was treated with bromine. Halogenation of the oxine complexes of Fe^{III} , Cr^{III} and Al^{III} resulted⁸ in attack at the 5-, 6-, and 7- positions of the 8-hydroxyquinoline thereby producing halo-substituted ligands in the complexes. Thus, one finds in the literature, instances of all the three possibilities envisaged above.

Pyridinium trichloronickelate(II), $[\text{PyH}]^+ [\text{NiCl}_3]^-$

As pointed out in the introduction, the aim of this investigation was to convert nickel(II) to higher oxidation states. An orange coloured compound with a nickel/li-

TABLE 1

ANALYSIS, MELTING POINT, MAGNETIC SUSCEPTIBILITY AND MOLAR CONDUCTANCE DATA OF ANIONIC NICKEL(II) COMPLEXES

Compound	Colour and form	Melting point (°C)	Analyses found (calcd.) (%)			μ_{eff} (BM)	Λ_M (mho)
			Ni	Cl	Br		
[PyH][NiCl ₃]	Orange red, micro-crystalline	215 dec.	23.58 (23.93)	42.70 (43.42)		3.17	
[γ -PicH][NiCl ₃]	Orange red, micro-crystalline	235 dec.	22.40 (22.64)	40.43 (41.08)		3.13	
[QH][NiCl ₃]	Yellow, micro-crystalline	170 dec.	19.38 (19.89)	35.28 (36.08)		3.17	
[IQH][NiCl ₃]	Yellow, micro-crystalline	125 dec.	19.85 (19.89)	35.92 (36.08)		3.15	
[PyH][NiCl ₂ Br]	Yellowish green, amorphous	185 dec.	20.03 (20.26)	24.22 (24.50)	27.26 (27.57)	3.24	
[γ -PicH][NiCl ₂ Br]	Yellow, micro-crystalline	200 dec.	19.23 (19.33)	23.56 (23.37)	26.76 (26.31)	3.22	
[QH][NiCl ₂ Br]	Yellow, amorphous	195 dec.	17.22 (17.29)	20.70 (20.90)	23.27 (23.53)	3.25	
[IQH][NiCl ₂ Br]	Yellow, micro-crystalline	130 dec.	17.02 (17.29)	21.01 (20.90)	23.64 (23.53)	3.25	
[QH][NiQCl ₃]	Deep blue, crystalline	230 dec.	13.41 (13.84)	25.37 (25.11)		3.49	93
[PyH][NiPyCl ₂ Br]	Deep blue, crystalline	220 dec.	15.77 (15.92)	18.98 (19.25)	21.36 (21.66)	3.49	92
[γ -PicH][Ni(γ -Pic)Cl ₂ Br]	Deep blue, crystalline	225 dec.	14.61 (14.79)	17.88 (17.86)	20.21 (20.13)	3.47	105
[QH][NiQCl ₂ Br]	Deep blue, crystalline	233 dec.	12.23 (12.53)	15.32 (15.15)	17.26 (17.07)	3.53	96

gand/chlorine ratio of 1/1/3 was obtained on reacting the pale green NiPy₂Cl₂ with chlorine, and we thought that a four-coordinated nickel(III) complex having the composition [NiPyCl₃] had been formed. But magnetic susceptibility measurements indicated the presence of 2 unpaired electrons whilst nickel(III) ion should have either one (spin-paired) or three (spin-free) unpaired spins. Furthermore, no liberation of iodine occurred when this compound was treated with potassium iodide. Thus it is clear that oxidation did not take place during chlorination. Had chlorine substitution in the pyridine ring occurred the formula of the product would have been [Ni(Py·Cl)Cl₂] and the analysis of the compound would have indicated the presence of only two halogen atoms since the ring halogen would not be liberated by the dil. HNO₃ treatment.

The compound does not also show any acidic reaction and further the IR spectrum shows conclusively the presence of the N-H stretching frequency. The compound can therefore be formulated as [PyH]⁺[NiCl₃]⁻. It should be a 1/1 electrolyte, but the ionic nature coupled with the polymeric behaviour of the anion makes the compound insoluble even in nitrobenzene and hence the conductance could not be measured, as was the case with the compounds [Me₄N][NiX₃] (X = Cl or Br) reported earlier⁹. It is interesting to note that the reaction took place only in methanolic or ethanolic media in which solvolysis is possible. When carbon tetrachlo-

TABLE 2

N-H IR ABSORPTIONS (cm^{-1}) OF NICKEL(II) COMPLEXES^a

Compound	$\delta(\text{N-H})$	$\nu(\text{N-H})$
[PyH][NiCl ₃]	1482 vs	3105 s, 3215 w, 3280 w, 3360 w, 3515 m
[γ -PicH][NiCl ₃]	1508 vs	2960 m, 3115 s, 3190 w, 3260 w
[QH][NiCl ₃]	1485 s	2860 (sh), 3145 (sh), 3390 (br)
[IQH][NiCl ₃]	1497 w	3105 (sh), 3370 (br)
[PyH][NiCl ₂ Br]	1495 s	3105 m, 3450 (br)
[γ -PicH][NiCl ₂ Br]	1493 s	2940 w, 3095 m, 3450 (br)
[QH][NiCl ₂ Br]	1490 s	3155 m, 3430 (br)
[IQH][NiCl ₂ Br]	1498 w	3105 m, 3370 s
[QH][NiQCl ₃]	1490 m	3135 m, 3430 s
[PyH][NiPyCl ₂ Br]	1476 m	2950 (sh), 3105 w, 3380 (br)
[γ -PicH][Ni(γ -Pic)Cl ₂ Br]	1508 s	3450 (br)
[QH][NiQCl ₂ Br]	1490 s	3250 (br)

^a s: strong, vs: very strong, w: weak, (br): broad, (sh): shoulder, m: medium.

ride was used as solvent no reaction took place.

The compounds obtained in this work can be grouped under two categories:

- [LH][NiCl₃] and [LH][NiCl₂Br]
- [LH][NiLCl₃] and [LH][NiLCl₂Br]

The first category compounds are orange or yellow amorphous powders having poor solubility in organic solvents and apparently possessing a three-coordinated anion. It has earlier been shown⁹ that $[\text{NiX}_3]^-$ ion undergoes polymerisation through halogen bridging thereby increasing the coordination number to six. The new compounds prepared now can also be expected to have polymeric octahedral structures. The magnetic moment for octahedral nickel(II) complexes lie in the range 2.9–3.4 BM¹⁰ and the observed moments are within this range.

The compounds belonging to the second category are deep blue crystalline compounds and are fairly soluble in acetone. The molar conductance, A_m , in acetone is round about 100 mhos indicative of a 1/1 electrolyte. The deep blue solution gradually fades on standing presumably as a result of decomposition involving splitting off the added ligand. These compounds are mixed ligand anionic complexes, and are tetrahedral monomers. The magnetic moments for tetrahedral nickel(II) complexes should be in the range 3.5–4.2 BM¹⁰ and the observed moments (Table 1) are reasonably within the range after allowing for second order orbital contribution due to hetero ligands far separated in the spectro chemical series.

When this work was in progress a similar investigation was described by Mundie and Nuttall¹¹. They concluded that pyridinium compounds were formed in the reaction of halogen with dipyridine metal halides, and reported an absorption band at 3000 cm^{-1} characteristic of the N-H stretching frequency. We have recorded the IR spectra of these compounds using both Nujol and hexachlorobutadiene as mulling agents. The bands at 1300–1600 cm^{-1} and at 2900–3500 cm^{-1} were masked in Nujol mulls due to heavy nujol absorption in this region, but with hexachlorobutadiene the $\nu(\text{N-H})$ and $\delta(\text{N-H})$ frequencies at 3000–3500 cm^{-1} and $\sim 1500 \text{ cm}^{-1}$ respectively, were clearly observable (Table 2). The presence of these N-H absorption bands is a definite indication of the formation of $[\text{LH}]^+[\text{NiCl}_2\text{X}]^-$ and $[\text{LH}]^+$ -

$[\text{NiLCl}_2\text{X}]^-$ complexes. As well as giving conductance and magnetic susceptibility data not reported by Mundie and Nuttall's work¹¹ we have also extended the investigation to γ -picoline, quinoline, and isoquinoline compounds.

ACKNOWLEDGEMENT

We thank the Ministry of Education, Government of India for the award of a Research Training Scholarship to one of us (M.K.M.).

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J. Organometal. Chem., 22 (1970) 227-231