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Reaction of Nickel(II) Alkoxide with Ligands. Synthesis and Characterization of Complexes of $Ni(OCH_3)(OCH_2CCl_3)$ with Ligands

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Abstract

Reaction of $Ni(OCH_3)(OCH_2CCl_3)$ with some oxygen and nitrogen donor ligands results in the formation of 1:1 adducts which have been characterized from their magnetic susceptibility, reflectance, IR and mass spectral data.

Introduction

Metal alkoxides in general [1] and nickel(II) alkoxides [1, 2] in particular are known to be coordinatively saturated compounds and do not react with ligands to form complexes. In fact $Ni(OCH_3)_2$ does not undergo any reaction with ligands even under forcing conditions [3]. In a previous paper [4], we described the synthesis of a new mixed alkoxy derivative of nickel(II), $Ni(OCH_3)(OCH_2CCl_3)$. Here, we report the first example of the reaction of nickel(II) alkoxide with ligands and describe the synthesis and characterization of the complexes of $Ni(OCH_3)(OCH_2CCl_3)$ with some oxygen and nitrogen donor ligands.

Results and Discussion

The reaction of $Ni(OCH_3)(OCH_2CCl_3)$ with ligands yields solid complexes formulated as $Ni(OMe)(OCH_2CCl_3)\cdot L$ (where L = *N*-methylacetamide (NMA), dimethylacetamide (DMA), tetramethylurea (TMU), hexamethylphosphoramide (HMPA), α- and γ-picoline-*N*-oxide (α-, and γ-pic-*N*-O), pyridine (py), and α-picoline (α-pic). The analytical data of these complexes are given in Table I. The reaction of $Ni(OCH_3)(OCH_2CCl_3)$ with ligands to yield adducts undoubtedly demonstrates that complexation takes place due to the enhanced acceptor power of Ni(II) which is affected by the replacement of one

TABLE I. Analytical Data of Complexes of Methoxy(2,2,2-trichloroethoxy)nickel(II)

Compound[a]	Colour and state	Melting point[b] (°C)	Calculated (theoretical) (%)				
			Ni	Cl	C	H	N
Ni(OMe)(OR)·NMA	green solid		18.9	34.0	23.5	4.1	4.5
			(18.8)	(34.2)	(23.1)	(3.8)	(4.4)
Ni(OMe)(OR)·DMA	green solid	260	17.9	32.5	25.2	4.2	4.4
			(18.0)	(32.7)	(25.8)	(4.3)	(4.3)
Ni(OMe)(OR)·TMU	green solid	260	16.3	29.8	26.1	4.6	8.0
			(16.5)	(30.0)	(27.1)	(4.7)	(7.9)
Ni(OMe)(OR)·HMPA	green solid	260	14.2	25.3			
			(14.0)	(25.5)			
Ni(OMe)(OR)·α-pic-*N*-O	dark green solid	170^{d}	16.7	29.9	32.3	3.4	4.6
			(16.9)	(30.6)	(31.1)	(3.5)	(5.0)
Ni(OMe)(OR)·γ-pic-*N*-O	green solid		16.8	30.4	31.3	3.3	
			(16.9)	(30.6)	(31.1)	(3.4)	
Ni(OMe)(OR)·py	dark green solid	100^{d}	18.4	33.0	29.7	3.6	
			(18.5)	(33.5)	(30.2)	(3.1)	(4.4)
Ni(OMe)(OR)·α-pic	green solid	115^{d}	18.0	31.7	33.0	3.2	4.0
			(17.7)	(32.0)	(32.6)	(3.6)	(4.2)

[a] R = CH_2CCl_3. [b] d = decomposes.

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TABLE II. Magnetic Moments (room temperature) and Electronic Spectral Data of $Ni(OCH_3(OCH_2CCl_3)\cdot L$ Complexes

Compound	Temperature (K)	Magnetic moment (BM)	$^3T_1 \rightarrow {}^3A_2$ (ν_2) (cm^{-1})	$^3T_1 \rightarrow {}^3T_1(P)$ (ν_3) (cm^{-1})	10 *Dq* (cm^{-1})	*B* (cm^{-1})	β
$Ni(OMe)(OCH_2CCl_3)\cdot NMA$	304	4.142	7690	14300	4685	865	0.83
$Ni(OMe)(OCH_2CCl_3)\cdot TMU$			7400	14200	4009	761	0.73
$Ni(OMe)(OCH_2CCl_3)\cdot HMPA$			8000	14700	4329	779	0.75
$Ni(OMe)(OCH_2CCl_3)\cdot \alpha$-pic-*N*-O	298	4.160	7200	15000	3908	822	0 79
$Ni(OMe)(OCH_2CCl_3)\cdot \gamma$-pic-*N*-O	304	4.135	7700	14200	4164	753	0.72
$Ni(OMe)(OCH_2CCl_3)\cdot py$			7500	16300	4075	902	0.87
$Ni(OMe)(OCH_2CCl_3)\cdot \alpha$-pic	298	4.140	7600	15300	4122	831	0.80

$-OCH_3$ group of $Ni(OCH_3)_2$ by $-OCH_2CCl_3$; the latter having the electron-withdrawing chlorine atoms.

Infrared spectra of the complexes show the presence of two bands at 1090–1070 cm^{-1} and 1040–1000 cm^{-1} where ν(C–O) arising from the –OR group absorbs. The band around 1080 ± 10 cm^{-1} arises from the ν(C–O) of terminal –OR group whereas that around 1020 ± 20 cm^{-1} originates from the ν(C–O) of the bridging –OR group [5, 6] suggesting these complexes to be alkoxo bridged. The $-OCH_2CCl_3$ group is very likely to be in the terminal position whereas $-OCH_3$ is the bridging group. The latter is known to promote bridge formation as has been found in polymeric $Ni(OMe)_2$ [7] whereas the former may not act as bridging group on steric consideration because the 2,2,2-trichloroethoxy group has been shown to resemble the neopentyloxide group in steric effect which in turn is well known for its non-bridging behaviour [8]. This is further supported by a reaction of $Ni(OCH_3)(OCH_2CCl_3)$ or $Ni(OCH_3)(OCH_2CCl_3)\cdot L$ with 1 mole of acetylchloride, when $Ni(OCH_3)Cl$ or $Ni(OCH_3)Cl\cdot L$ are formed and enthalpically favoured [9] bridged methoxy moiety is not replaced. The spectra show the presence of bands around 540–500 cm^{-1} and 460–430 cm^{-1} assigned to the ν(Ni–O) and ν(Ni–O → Ni) stretching vibrations [10] which further supports the alkoxy bridged structures for these complexes. The spectra also show changes in ligand vibrations on complexation and these changes confirm their coordination to nickel [5, 11].

Magnetic moments of the complexes have been determined at room temperature (Table II) and the values are indicative of tetrahedral stereochemistry for nickel(II) [2]. The magnetic moment data are sensitive to geometry since square planar nickel(II) complexes are diamagnetic and the values for octahedral nickel(II) are of the order of 3.2–3.5 BM [2]. These observations get further support from the electronic spectra of the complexes showing bands corresponding to those of typical tetrahedral nickel(II) alkoxy derivatives [2]. The spectra exhibit two well defined spin-allowed transitions occurring at 7200–8000 cm^{-1} and 14200–16300 cm^{-1} assigned to $^3T_1 \rightarrow {}^3A_2(\nu_2)$ and $^3T_1 \rightarrow {}^3T_1(P)(\nu_3)$ respectively. The complexes also show transitions between 20000–25600 cm^{-1} which may be assigned as spin-forbidden transitions. These are derived from field free terms ^1O or ^1G. These transitions acquire intensity by mixing via spin orbit coupling of the upper 'singlet' states with nearly 'triplet' states of the same symmetry.

The position of observed bands, their proposed assignments, the ligand field parameter (10 *Dq*), Recah parameter (*B*) and the covalency factor (β) are given in Table II. The parameters 10 *Dq* and **B** which have been calculated by spectral fitting procedure reported by Konig [12] are found to be in accord with similar observations reported for tetrahedral nickel(II) alkoxy derivatives [2]. The values of the Recah parameter, *B* are remarkably depressed compared with the free ion value (1041 cm^{-1}) of Ni^{2+} which is indicative of an appreciable covalent character of Ni → O bonds in these complexes.

^1H NMR spectra of the complexes with pyridine, α-picoline and HMPA show the appearance of one strong slightly broad signal at $\delta = 4.35$, 4.50 and 4.4 ppm, respectively and this suggests the coalescence of all signals due to the bridging and terminal OCH_3/OCH_2CCl_3 groups [13]. The mass spectrum of the complex $Ni(OCH_3)(OCH_2CCl_3)\cdot\alpha$-picoline-*N*-oxide (Table III) gives the molecular ion peak for α-picoline *N*-oxide and monomeric alkoxide (m/e = 238) confirming the dissociation of the complexes to yield these species in the vapour phase. Another m/e peak which appears at a higher position (m/e = 368) supports that such a species comes from the dimeric complex.

Experimental

Methoxy(2,2,2-trichloroethoxy)nickel(II) was prepared as described earlier [4].

TABLE III. Mass Spectral Data for $Ni(OCH_3)(OCH_2CCl_3)\cdot$ α-picoline-*N*-oxide complex

m/e Peak	Possible assignment
368w	$Cl_3CH_2CO{-}Ni{-}\overset{CH_3}{O} \longrightarrow NiCl_2$
	$\downarrow -NiCl_2$
238w	$Cl_3CH_2CO{-}Ni{-}OCH_3$
	$\downarrow$
148s	$-OCH_2CCl_3$
	$\downarrow -C$
136s	$CCl_3 + H_2O$
120s	H_2CCl_3
109vs	Pic-O
83s	CCl_2

Preparation of Complexes

$Ni(OCH_3(OCH_2CCl_3)$ was mixed with liquid ligands/chloroform solution of solid ligands such as α-picoline-*N*-oxide and γ-picoline-*N*-oxide. The resulting mixture was stirred for 4–5 h (warmed in some cases to dissolve the alkoxide). Green coloured adducts were separated out by addition of ether/petroleum ether/dichloromethane/chloroform.

Nickel and chlorine were estimated gravimetrically [14]. C, H, N analyses were done on Elemental Analyzer M 00.1106 from the Regional Sophisticated Instrumentation Centre, Panjab University, Chandigarh. Infrared spectra were recorded as nujol mulls on a Perkin-Elmer 621 spectrophotometer. Reflectance spectra were recorded on a Hitachi specord 300 in the region 200–1400 nm. The ^1H NMR spectra of a few complexes were run on the Varian EM 390 spectrophotometer at 90 MHz on scale using TMS as reference. The mass spectrum of the compound was done on the V.G. Micromass 7075 instrument.

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