

Alcoholysis of Nickel(II)methoxide: Synthesis and Characterization of Ni(OCH₃)(OCH₂CCl₃)

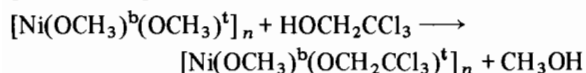
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The primary alkoxides of nickel(II) do not undergo alcoholysis reactions with other alcohols even under forcing conditions [1, 2], though these reactions readily occur for most of the other transition metal alkoxides [2]. To our knowledge, there is no report of alcoholysis of nickel(II) methoxide. We have now characterized this alcoholysis reaction and report the first example in the synthesis of methoxy(2,2,2-trichloroethoxy)nickel(II), Ni(OCH₃)(OCH₂CCl₃).

The reaction of Ni(OCH₃)₂ [3] with an excess of 2,2,2-trichloroethanol yields a dark green solid, the analysis of which corresponded to Ni(OCH₃)(OCH₂CCl₃). This compound is insoluble in non-polar solvents and is, therefore, likely to be polymeric in the solid form, probably through -OCH₃ bridging. Its magnetic moment at 298 K is 4.08 BM and it shows bands at 7.6 and 15.4 × 10³ cm⁻¹ in its reflectance spectra. These data are characteristic of a tetrahedral geometry [4, 5] for this compound. In polymeric Ni(OCH₃)₂ there is an average of one terminal and one bridging Ni-OCH₃ bond [3], and it seems very likely that the former is knocked out by the -OCH₂CCl₃ moiety. It has been estimated [6] that conversion of two M-OR^t (t = terminal) bonds into four M-OR^b (b = bridging) bonds is enthalpically favorable and consequently the driving force for the replacement of only -OR^t appears to be the unique stability of -OR^b. This is similar to the replacement of only -OR^t by -OH during the hydrolysis of [Ti(OR)₄]₃ [7]. Accordingly, the reaction may be



The infrared spectrum of this compound shows bands due to ν(C-O)^b, ν(C-O)^t [8], ν(C-Cl) [9], ν(Ni-O) [10, 11] and ν(Ni-O-Ni) [10, 11]. The ¹H NMR spectrum in pyridine at room temperature gives a slightly broad singlet at δ = 4.6 ppm which suggests an exchange between -OCH₃ and -OCH₂CCl₂ groups; at low temperatures (-11 °C), the spectrum shows four singlets at δ = 4.09, 4.58, 5.06 and 5.25 ppm, apart from the signals for the pyridine ring.

The mass spectrum of Ni(OCH₃)(OCH₂CCl₃) shows the molecular ion (m/e) peak for the mono-

TABLE I. m/e Values for Ni(OCH₃)(OCH₂CCl₃) (Dimer)

Peak position	Assignment
357	$\begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{Cl}_3\text{CH}_2\text{CO}-\text{Ni} \quad \text{Ni}-\text{OCH}_3 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CH}_3 \end{array}$
	↓ (-NiOCH ₃) ↓ (-OCH ₂)
238	Cl ₃ CH ₂ CO-Ni-OCH ₃ (M ⁺)
	↓ (-HCl) ↓ (-O)
185	Cl ₂ CHCO-Ni-CH ₃
	↓ (-HCl)
149	ClCCO-Ni-CH ₃

meric species (Table I) which conforms with the fragmentation of the polymer to yield the monomer in the vapour state. Peaks at higher m/e values are also observed and they appear to be due to the initial degradation products from the dimer/polymer.

Experimental

All manipulations were done on vacuum line or under O₂ free dry N₂.

To a known weight of Ni(OCH₃)₂ in benzene was added 2,2,2-trichloroethanol, slightly in excess of the calculated amount for a 1:2 molar ratio, and the contents were stirred for 4 h. The mixture was refluxed azeotropically using the Dean and Stark apparatus until methanol production ceased (confirmed by IR and NMR). The solid obtained was washed repeatedly with CCl₄ and dried under vacuum.

Anal. Calc. for Ni(OCH₃)(OCH₂CCl₃): C, 15.12; H, 2.1; Ni, 24.6; Cl, 44.7. Found: C, 15.0; H, 1.99; Ni, 24.5; Cl, 44.6%. Did not melt upto 260 °C but colour changed at 110 °C. IR: 1255m, 1210m, 1090vs (C-O^t), 1015m (C-O^b), 1000, 810, 780s (C-Cl), 715, 600 (C-Cl), 415 (Ni-O), 370 (Ni-O-Ni). Reaction of Ni(OCH₃)₂/Ni(OCH₃)(OCH₂CCl₃) with fresh 2,2,2-trichloroethanol and for a prolonged period did not yield any other product.

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