Alcoholysis of Nickel(II)methoxide: Synthesis and Characterization of $Ni(OCH_3)(OCH_2CCl_3)$

S. L. CHADHA* and VIJAY SHARMA

Department of Chemistry, Panjab University, Chandigarh-160014, India

(Received May 29, 1986)

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), $Ni(OCH_3)(OCH_2CCl_3)$.

The reaction of $Ni(OCH_3)_2$ [3] with an excess of 2,2,2-trichloroethanol yields a dark green solid, the analysis of which corresponded to $Ni(OCH_3)(OCH_2CCl_3)$. This compound is insoluble in non-polar solvents and is, therefore, likely to be polymeric in the solid form, probably through $-OCH_3$ bridging. Its magnetic moment at 298 K is 4.08 BM and it shows bands at 7.6 and 15.4×10^3 cm^{-1} in its reflectance spectra. These data are characteristic of a tetrahedral geometry [4, 5] for this compound. In polymeric $Ni(OCH_3)_2$ there is an average of one terminal and one bridging Ni–OCH_3 bond [3], and it seems very likely that the former is knocked out by the $-OCH_2CCl_3$ 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

$$[Ni(OCH_3)^b(OCH_3)^t]_n + HOCH_2CCl_3 \longrightarrow [Ni(OCH_3)^b(OCH_2CCl_3)^t]_n + CH_3OH$$

The infrared spectrum of this compound shows bands due to $\nu(C-O)^b$, $\nu(C-O)^t$ [8], $\nu(C-Cl)$ [9], $\nu(Ni-O)$ [10, 11] and $\nu(Ni-O-Ni)$ [10, 11]. The ^1H NMR spectrum in pyridine at room temperature gives a slightly broad singlet at $\delta = 4.6$ ppm which suggests an exchange between $-OCH_3$ and $-OCH_2CCl_3$ groups; at low temperatures (−11 °C), the spectrum shows four singlets at $\delta = 4.09$, 4.58, 5.06 and 5.25 ppm, apart from the signals for the pyridine ring.

The mass spectrum of $Ni(OCH_3)(OCH_2CCl_3)$ shows the molecular ion (m/e) peak for the monomeric 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.

TABLE I. m/e Values for $Ni(OCH_3)(OCH_2CCl_3)$ (Dimer)

Peak position	Assignment
357	$Cl_3CH_2CO-Ni(O,CH_3)(O,CH_3)-Ni-OCH_2$
	↓ $(-NiOCH_3)$ $(-OCH_2)$
238	$Cl_3CH_2CO-Ni-OCH_3$ (M^+)
	↓ $(-HCl)$ $(-O)$
185	$Cl_2CHCO-Ni-CH_3$
	↓ $(-HCl)$
149	$ClCCO-Ni-CH_3$

Experimental

All manipulations were done on vacuum line or under O_2 free dry N_2.

To a known weight of $Ni(OCH_3)_2$ 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 CCl_4 and dried under vacuum.

Anal. Calc. for $Ni(OCH_3)(OCH_2CCl_3)$: 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, 1090-vs ($C-O^t$), 1015m ($C-O^b$), 1000, 810, 780s (C–Cl), 715, 600 (C–Cl), 415 (Ni–O), 370 (Ni–O→Ni). Reaction of $Ni(OCH_3)_2$/$Ni(OCH_3)(OCH_2CCl_3)$ with fresh 2,2,2-trichloroethanol and for a prolonged period did not yield any other product.

References

1 B. P. Baranwal and R. C. Mehrotra, *Aust. J. Chem., 33*, 31 (1980).

0020-1693/86/$3.50

2 D. C. Bradley, R. C. Mehrotra and P. Gaur, 'Metal Alkoxides', Academic Press, London, 1978.
3 C. H. Brubaker and M. Wicholas, *J. Inorg. Nucl. Chem., 27*, 59 (1965).
4 B. N. Figgis, 'Introduction to Ligand Fields', Wiley, New York, 1966.
5 B. N. Figgis and J. Lewis, in F. A. Cotton (ed.), 'Progress in Inorganic Chemistry', Vol. 6, Interscience, New York, 1964, p. 62.
6 K. J. Cavell, J. A. Connor, G. Pilcher, M. A. Ribeiro de Silva, M. D. M. C. Ribeiro de Silva, H. A. Sbinner, Y. Virmani and M. T. Zafaran-Moattar, *J. Chem. Soc., Faraday Trans., 77*, 1585 (1981).
7 R. L. Martin and G. Winter, *Nature (London), 188*, 313 (1960).
8 S. L. Chadha, V. Sharma, C. Mohini, S. P. Taneja and D. Raj, *Z. Anorg. Allg. Chem.*, in press.
9 J. Travert and J. C. Lavelley, *Spectrochim. Acta, Part A, 32*, 637 (1976).
10 A. G. Kruger and G. Winter, *Aust. J. Chem., 23*, I (1970).
11 R. W. Adams, R. L. Martin and G. Winter, *Aust. J. Chem., 20*, 773 (1967).