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A ¹³C-NMR STUDY OF CIS-TI(ACAC)₂CL₂

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In this paper we report the ¹³C-NMR spectra of <u>cis</u>-Ti(acac)₂Cl₂ at variable temperatures. Previous work has shown that <u>cis</u>-disubstituted (acac)₂titanium(IV) complexes: exist in solution as nonrigid molecules (1). These compounds include both the dialkoxybis(acac)titanium and the dihalobis (acac)titanium species. Work by Fay, Lowry and Serpone (2-4) have shown that dihalobis (acac)titanium (IV) compounds rearrange via an intramolecular mechanism. In addition the dihalo- and the dialkoxybis(acac)titanium(IV) complexes undergo rapid ligand-exchange reactions which scramble both monodentate and bidentate ligands (5). Except for the diiodobis(acac)titanium (6), which exists in a dichloromethane solution in both the <u>cis</u> and <u>trans</u> forms, the other compounds of this type all have a <u>cis</u>-octahedral structure (7).

The nonrigidity of these molecules has been followed by 'H-nmr spectroscopy. Variable temperature nmr spectra show that the acetylaoetonate rings undergo rapid configurational changes which exchange, for example, the methyl groups of the acac rings, between the two nonequivalent sites of the <u>cis</u> isomer. Twisting mechanisms as well as one-bond rupture of the bidentate ligand have been suggested for these sterochemical rearrangements (3).

Typical spectra for the methyl and carbonyl carbons are shown in the figure. The methine carbon's chemical 485 shift from tetramethylsilane (TMS) was temperature independent (109.2 ppm). Examination of the spectra indicates that the methyl carbons and the carbonyl carbons of the acetylacetonate ring have different coalescence temperatures. The carbonyl carbon coalescence temperature is -5°C whereas, the methyl carbon coalescence temperature is -15°C. Chemical shifts from TMS in the nonexchanging region are methyl, 25.4 and 26.3 ppm; carbonyl, 190.1 and 193.6 ppm and in the exchanging region are methyl, 25.8 ppm and carbonyl, 191.9 ppm. The ¹H-nmr coalescence temperature of the methyl protons is reported as ~26°C (2). The peak width at half-height (±1 Hz) for the methyl, methine and carbonyl carbon resonances did not vary with concentration, indicating a unimolecular process.

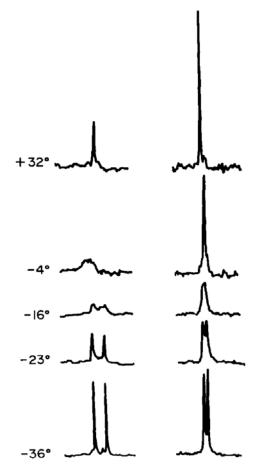


Figure: Temperature dependence of the carbonyl and methyl region of the 13C-nmr spectra for Ti(acac)2Cl2 in deuterochloroform.

The chemical shift difference (Δv) and the coalescence temperature (T_c) may be used to calculate an exchange rate, k_c , from which the activation free energy (ΔG ‡) for the exchange process may be determined (8). The sane number, 13.0 kcal., is obtained for the carbonyl and methyl carbons as well as the methyl hydrogens from proton data, indicating that all of these moieties are exchanging at the same rate. Further work on this exchange process is underway for the Ti(acac)₂X₂ and Ti(acac)₂(OR)₂ systems.

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