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Accepted version. *Inorganic and Nuclear Chemistry Letters*, Vol. 13, No. 10 (1977): 485-487. DOI. © 1997 Published by Elsevier Ltd. Used with permission.

Chemistry Faculty Research and Publications/College of Arts and Sciences

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A ^{13}C -NMR STUDY OF CIS-TI(ACAC) $_2$ CL $_2$

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In this paper we report the ^{13}C -NMR spectra of cis-Ti(acac) $_2$ Cl $_2$ at variable temperatures. Previous work has shown that cis-disubstituted (acac) $_2$ titanium(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 cis and trans forms, the other compounds of this type all have a cis-octahedral structure (7).

The nonrigidity of these molecules has been followed by ^1H -nmr spectroscopy. Variable temperature nmr spectra show that the acetylacetonate rings undergo rapid configurational changes which exchange, for example, the methyl groups of the acac rings, between the two nonequivalent sites of the cis isomer. Twisting mechanisms as well as one-bond rupture of the bidentate ligand have been suggested for these stereochemical rearrangements (3).

Typical spectra for the methyl and carbonyl carbons are shown in the figure. The methine carbon's chemical 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 $\sim 26^\circ\text{C}$ (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 ^{13}C -nmr spectra for $\text{Ti}(\text{acac})_2\text{Cl}_2$ in deuteriochloroform.

The chemical shift difference ($\Delta\nu$) and the coalescence temperature (T_c) may be used to calculate an exchange rate, k_c , from which the activation free energy (ΔG^\ddagger) for the exchange process may be determined (8). The same 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 $\text{Ti}(\text{acac})_2\text{X}_2$ and $\text{Ti}(\text{acac})_2(\text{OR})_2$ systems.

We thank the Marquette University Committee on Research for support of this project.

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