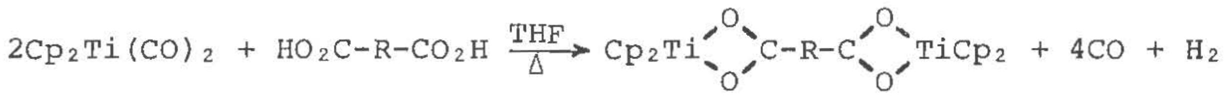
Saturated Hydrocarbon Chains as Propagators of Magnetic Exchange Interaction Between Ti(III) Metallocenes

Arrietta W. Clauss Final Seminar June 22, 1982

The study of extended organic ligands as mediators of electron transfer between two metal ions is of continuing interest.[1] In several biological electron-transport chains it is generally believed that electrons are transferred between metal ions that are separated by distances greater than 20 Å.[2] It is possible that the electrons transfer via saturated residues in the polypeptide chains. The study of magnetic exchange interactions in binuclear complexes indirectly characterizes the viability of a given organic ligand to mediate electron transfer between the two metal centers.

The present study was undertaken to ascertain whether a magnetic exchange interaction between two metal ions could be propagated by saturated hydrocarbon chains and to determine the number of carbon atoms through which an exchange interaction could be detected. Titanium(III) metallocenes bridged by the dianion of a dicarboxylic acid proved to be a convenient system to examine. The dicarboxylic acids provide an organic ligand which can be systematically varied. The presence of only one unpaired electron per Ti^{3+} ion facilitates the interpretation of the physical data. The air sensitive dimers are synthesized according to equation (1),[3,4] where R is a hydrocarbon:



$$2Cp_2Ti(CO)_2 + HO_2C\text{-}R\text{-}CO_2H \xrightarrow[\Delta]{THF} Cp_2Ti\overset{O}{\underset{O}{\;}}C\text{-}R\text{-}C\overset{O}{\underset{O}{\;}}TiCp_2 + 4CO + H_2 \qquad (1)$$

The compounds have been characterized by mass spectral, microanalytical and infrared data.

Variable temperature (4.2-300 K) magnetic susceptibility was used to characterize the exchange interaction in the solid state (see Table 1).

Table 1

$Cp_2TiO_2C\text{-}(CH_2)_n\text{-}CO_2TiCp_2$

n	$-J$ (cm^{-1})
1	2.6
2	1.6
3	0.8
4	—
6	—
8	—
10	—

Weak antiferromagnetic exchange interactions are observed in the Ti dimers bridged by the dianions of malonic (n=1), succinic (n=2) and glutaric (n=3) acids. There is a monotonic decrease in the magnitude of the antiferromagnetic exchange interaction as the number of methylene carbon atoms in the chain is increased. No interaction is observed in the binuclear Ti complexes with longer chains, n=4,6,8,10.

The monotonic decrease in the exchange parameter in the solid state suggests that the interaction is intramolecular and propagated by the carbon atoms of the bridging unit. Binuclear Ti^{3+} complexes bridged by the dianions of alkyl-substituted and cyclic dicarboxylic acids were investigated to clarify the pathway of the exchange interaction. The additional bulk of the substituents decreases the intermolecular contacts and the rigid framework of the cyclic systems ensures that the intramolecular magnetic exchange interactions are not occurring directly by contact of the $(\eta^5\text{-}C_5H_5)_2Ti$ units via a folded conformation. The presence of antiferromagnetic exchange in these complexes supports the intramolecular nature of the interaction.

Electron paramagnetic resonance (EPR) was used to characterize the exchange interaction in solution. The titanium hyperfine splitting pattern observed in the room temperature X-band EPR spectra indicates that the exchange interaction is greater than $10^{-3}cm^{-1}$.[5] Variable temperature (3-12 K) EPR studies were conducted to assess the magnitude of the exchange interaction.[6] The results are complicated by microwave power saturation of the EPR signal. Evidence for intramolecular exchange interactions is obtained for the Ti^{3+} complexes bridged by malonate (n=1), glutarate (n=3) and adipate (n=4).

Several monomeric complexes of the general formula Cp_2TiO_2CX (X=hydrocarbon) have also been studied to determine whether an intermolecular exchange can be detected in the solid state. With one exception the monomers showed no detectable exchange interaction. The benzoate derivative $Cp_2TiO_2CC_6H_5$ exhibited a significant intermolecular exchange in the solid state. Single crystal X-ray diffraction studies on two Ti dimers and the benzoate monomer have helped to identify the possible pathways for the exchange interaction.

References

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