

THEORETICAL STUDY ON METAL NMR CHEMICAL SHIFTS: TITANIUM COMPLEXES

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$^{47,49}\text{Ti}$ chemical shifts for several titanium(IV) compounds have been studied theoretically by an ab initio molecular orbital method. The complexes studied here are TiF_4 , TiF_6^{2-} , TiCl_4 , TiCl_6^{2-} , TiBr_4 and $\text{Ti}(\text{OMe})_4$ (Me: methyl group). The calculated values of the titanium chemical shifts compare well with the experimental values. The "inverse" halogen dependence is shown. The d-contribution is predominant for the chemical shifts, because of the partly filled nature of the d-subshell of the titanium atom.

Titanium is an early transition-metal element, belonging to the IVb group. It has two magnetically active isotopes ^{47}Ti and ^{49}Ti , whose natural abundances are 7.3% and 5.5%, respectively. The two NMR peaks are separated by 271 ppm and the intensities are almost the same. Although titanium compounds are quite useful as catalysts in many catalytic reactions, the amount of experimental data on the $^{47,49}\text{Ti}$ nuclear magnetic shielding constant is very small [1,2]. In this communication, we report an ab initio theoretical study on the $^{47,49}\text{Ti}$ chemical shifts of the complexes, TiF_4 , TiF_6^{2-} , TiCl_4 , TiCl_6^{2-} , TiBr_4 and $\text{Ti}(\text{OMe})_4$ (Me: methyl group).

In this series of articles [3-9], we have studied theoretically the metal chemical shifts of Ag, Cu, Cd, Zn, Mn, Mo and Sn compounds, and obtained nice correlations between theory and experiment. For the

Ag, Cu, Cd, Zn and Sn atoms, the lowest electronic configurations are characterized by $d^{10}s^1p^{0-2}$ and for the Mn and Mo atoms, they are characterized by $d^5s^1p^0$. For the complexes of the former metals, p- and d-mechanisms are shown to be important as the origin of metal chemical shifts. The p-mechanism is due to the electrons in the valence p-orbitals of the metal transferred from the electron-donating ligands, and the d-mechanism is due to the holes in the valence d-subshell of the metal produced by the electron-withdrawing ligands. For the Mn and Mo compounds, the metal chemical shifts are predominantly determined by the d-d transitions in a perturbation theoretic viewpoint. This reflects the half-filled nature of the d-subshell of the metals [4,8].

The electronic configuration of the ground state of the Ti atom is $3d^24s^24p^0$. Thus, an important con-

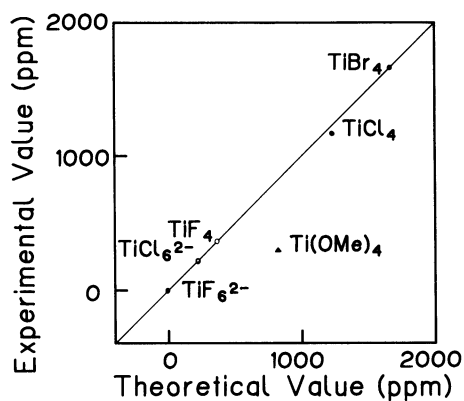
Table 1
Geometry of the titanium complexes

	Symmetry	Ti-X length (Å)			
		X=F	X=Cl	X=Br	X=OCH ₃
TiX ₄	T _d	1.754 ^{a)}	2.170 ^{a)}	2.339 ^{a)}	1.994 ^{b)}
TiX ₆ ²⁻	O _h	1.754 ^{c)}	2.170 ^{c)}	-	-

^{a)} Ref. [12].

^{b)} The Ti-O distance is taken from TiO₂-type ionic lattice [13], and the geometry of the OCH₃ group is taken from that of methanol [12].

^{c)} Assumed value.



tribution of the partly filled d-subshell to the $^{47,49}\text{Ti}$ NMR chemical shifts is expected. For many transition-metal chemical shifts, "inverse" halogen dependence is observed experimentally. This is a high-frequency shift of the metal chemical shift with a

◀ Fig. 1. The correlation between the experimental and theoretical values of the $^{47,49}\text{Ti}$ chemical shifts of the titanium complexes. For TiF_4 and TiCl_6^{2-} , the experimental values are not available so that the open circles show only the theoretical values. For $\text{Ti}(\text{OMe})_4$ (Me: methyl group), the experimental value is also not available and so we give the experimental value of $\text{Ti}(\text{O}i\text{Pr})_4$ (*i*Pr: isopropyl) as the open triangle.

Table 2

Diamagnetic and paramagnetic contributions, σ^{dia} and σ^{para} , to the Ti nuclear magnetic shielding constant σ and their analysis into core and valence MO contributions and into the contributions of the s-, p- and d-AOs of Ti and the ligand AOs (in ppm)

Compound	σ^{dia}							total	shift
	MO contribution		AO contribution						
	core	valence	Ti(s)	Ti(p)	Ti(d)	ligand			
TiCl_6^{2-}	1838	228	979	614	26	447	2066	-150	
TiF_6^{2-}	1634	282	980	613	14	309	1916	0	
TiF_4	1618	192	980	615	12	203	1810	106	
$\text{Ti}(\text{OMe})_4$	1650	270	979	610	21	310	1920	-4	
TiCl_4	1752	159	978	612	24	297	1911	5	
TiBr_4	2029	151	979	613	25	563	2180	-264	

Compound	σ^{para}						total	shift
	MO contribution		AO contribution ^{a)}					
	core	valence	Ti(p)	Ti(d)	ligand			
TiCl_6^{2-}	186	-1655	-382	-1058	-29	-1469	374	
TiF_6^{2-}	-539	-556	-528	-492	-75	-1095	0	
TiF_4	-396	-962	-538	-770	-50	-1358	263	
$\text{Ti}(\text{OMe})_4$	-665	-1246	-472	-1334	-105	-1911	816	
TiCl_4	186	-2501	-662	-1622	-31	-2315	1220	
TiBr_4	193	-3210	-698	-2208	-111	-3017	1922	

Compound	σ^{total}		Exp. shift
	total	shift	
TiCl_6^{2-}	597	224	-
TiF_6^{2-}	821	0	0
TiF_4	452	369	-
$\text{Ti}(\text{OMe})_4$	9	812	304 ^{b)}
TiCl_4	-404	1225	1177 ^{c)} , 1162 ^{d)}
TiBr_4	-837	1658	1675 ^{c)} , 1645 ^{d)}

^{a)} For the paramagnetic term, the Ti s-AO contribution vanishes identically, because the s-electron does not have an angular momentum.

^{b)} The experimental value is not available, so that the value of $\text{Ti}(\text{O}i\text{Pr})_4$ is shown [17]. ^{c)} Ref. [16]. ^{d)} Ref. [17].

systematic replacement of halogen ligands in MX_n ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$) by heavier halogens from F to I. In a previous paper [8], the "inverse" dependence is discussed for a series of complexes, $\text{MoO}_{4-n}\text{X}_n^{2-}$ ($\text{X}=\text{S}, \text{Se}; n=0-4$).

In this study, we use, as before, finite perturbation theory [3,10,11] for calculating the Ti nuclear magnetic shielding constants. The geometries of the titanium complexes used in the present calculations are summarized in table 1. The basis sets are taken from Huzinaga's book [14], and comprise (14s8p5d)/[5s3p2d] [14] plus valence p-functions with the exponent of 0.065 for the Ti atom, (10s7p)/[3s2p] for O and F atoms, (6s3p)/[3s2p] for C atom, (11s8p)/[4s3p] for Cl atom, (13s10p4d)/[5s4p1d] for Br atom and (2s)/[1s] for H atom. For SCF calculations, a modified version of the HONDOG program [15] is used.

The chemical shift $\Delta\sigma$ of the complex M is calculated relative to the reference compound, TiF_6^{2-} ,

$$\Delta\sigma_M = \sigma(\text{TiF}_6^{2-}) - \sigma(\text{M}),$$

where σ is the $^{47,49}\text{Ti}$ nuclear shielding constant. We show in fig. 1 the correlation between the present theoretical values and the experimental values [16,17] of the Ti chemical shifts. The open circles for TiF_4 and TiCl_6^{2-} show only the theoretical values, because their experimental values are not available. The open triangle for $\text{Ti}(\text{OMe})_4$ implies that the value for the similar compound $\text{Ti}(\text{O}i\text{Pr})_4$ ($i\text{Pr}$: isopropyl group) is used since the experimental value of $\text{Ti}(\text{OMe})_4$ is also not available. We see that the theoretical values compare well with the experimental ones [16,17].

We next investigate the mechanism of the titanium chemical shift. In table 2, the shielding constant is decomposed into diamagnetic and paramagnetic contributions, and they are further analyzed into core and valence MO contributions and into the Ti AO contributions and the ligand contributions. For the titanium complexes studied here, the chemical shift is dominantly determined by the paramagnetic term. The ratios between the diamagnetic and paramagnetic contributions to the chemical shifts lie in the range of 2:5 (in TiF_6^{2-} and TiCl_6^{2-}) to 1:244 (in TiCl_4). It is known that the diamagnetic term is determined only by structural factors [3,18]. For the paramagnetic term, the valence MO contribution is

Table 3

Mulliken population analysis for Ti s-, p- and d-AOs of the titanium complexes

Compound	Ti			Chemical shift
	s	p	d	
TiCl_6^{2-}	6.33	12.56	2.91	224
TiF_6^{2-}	6.40	12.44	1.34	0
TiF_4	6.34	12.27	1.20	369
$\text{Ti}(\text{OMe})_4$	6.25	11.84	2.03	812
TiCl_4	6.16	12.44	2.46	1225
TiBr_4	6.28	12.73	2.68	1658
Ti atom	8.00	12.00	2.00	528 ^{a)}

^{a)} Nuclear shielding constant of the Ti atom is calculated as 1623 ppm [19].

more important than the core MO contribution. From the AO analysis, we see that the d-orbital contribution is predominant, as expected. This reflects the partly filled nature of the titanium d-subshell. Table 3 shows the Mulliken population analysis for the s-, p- and d-AOs of Ti. Some correlations are found between the valence d-electron populations and the chemical shifts of four-coordinated and six-coordinated complexes. More details of this study will be published in a separate paper.

The calculations have been carried out with the use of the computers at the Institute for Molecular Science and at the Data Processing Center of Kyoto University. Part of this study has been supported by the Kurata Foundation and a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

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