

## Theoretical Study on Metal NMR Chemical Shifts. Niobium Complexes

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$^{93}\text{Nb}$  chemical shifts in 19 niobium complexes,  $\text{NbX}_{6-n}\text{Y}_n^-$  ( $n = 0-6$ ; X, Y = F, Cl, and Br), are calculated by the ab initio Hartree-Fock method. The calculated values are in very good agreement with the experimental ones. Theoretical analyses reveal that the Nb chemical shifts are dominated by the paramagnetic contributions and are due to the d-d\* transition mechanism, in which the critical factor is a variation in the excitation energy  $\Delta E$ . Based on an orbital interaction picture,  $\Delta E$  is found to depend on the overlap interactions between the Nb 4d and ligand  $np$  orbitals. It is also observed that the Nb chemical shift is related to the electronegativity of the ligand atom, the Nb net charge, and the d-electron population of the central Nb atom. The origin of this correlation is also clarified.

### Introduction

A vast amount of experimental data has accumulated in recent years for transition-metal NMR chemical shifts.<sup>1</sup> For understanding the regularities and irregularities in the observed values, the need for knowledge on the electronic origin and the mechanism of the chemical shifts is ever increasing.

In this series of studies,<sup>2-4</sup> we systematically investigate NMR chemical shifts of metal nuclei, such as Cu, Ag, Zn, Cd<sup>3a,b</sup> ( $d^{10}s^1-2p^0$ ; class I), Sn,<sup>3c</sup> Ge<sup>3d</sup> ( $d^{10}s^2p^2$ ; class II), Mn,<sup>3e</sup> Mo,<sup>3f,4</sup> Ti<sup>3g</sup> ( $d^2-5s^1-2$ ; class III). Recently, Tossel<sup>5</sup> and Barfield et al.<sup>6</sup> have also studied the metal chemical shifts in Zn and Mo complexes, respectively. We have shown that the origins are classified into three types, depending on the occupations of the valence  $nd$  and  $(n+1)p$  subshells. For the class I compounds, the d-hole or p-electron mechanism is the origin of the metal chemical shift. For the class II compounds, only the p-electron mechanism is important. For the class III compounds in which a metal has an open d subshell, the d-electron mechanism is dominant and is most clearly understood as a mixing of the magnetically allowed d-d\* transitions from the perturbation theory point of view.

We here report ab initio molecular orbital (MO) calculations of  $^{93}\text{Nb}$  NMR chemical shifts for 19 niobium complexes,  $\text{NbX}_{6-n}\text{Y}_n^-$  ( $n = 0-6$ ; X, Y = F, Cl, Br), and elucidate the electronic origin and the mechanism of the chemical shifts. The Nb chemical shifts are expected to originate from the d-d\* transition mechanism, because the Nb atom has an open d subshell as  $4d^45s^1$ . In the complexes studied here, the shifts move monotonically downfield as the ligand is substituted into a less electronegative one. We will clarify that the interaction between the Nb 4d orbital and the halogen valence  $np$  orbital determines the

electronic structures of the Nb complexes and thereby their chemical shifts. We will see the existence of the parallelism between Nb chemical shifts and some other quantities in these complexes.

### Computational Details

The Nb magnetic shielding constant  $\sigma$  and the Nb chemical shift  $\delta$  are calculated for 19 hexahalogenoniobates,  $\text{NbX}_{6-n}\text{Y}_n^-$  ( $n = 0-6$ ; X, Y = F, Cl, Br). The geometrical isomers for the compounds of  $n = 2-4$  are also investigated.

We use the finite perturbation method for calculating the paramagnetic term of a magnetic shielding constant<sup>7</sup> as in this series of studies.<sup>2,3</sup> The unperturbed Hartree-Fock wave function is calculated by the HONDO7 program.<sup>8</sup> The gauge origin is placed at the position of the Nb atom. This choice is very natural and is expected to reduce errors in such highly symmetrical molecules. This is also anticipated from the work of Snyder and Parr, who showed that the contribution of the continuum states in the sum-over-states formula grows large when the gauge origin is moved away from the position of the nucleus.<sup>9</sup>

The basis sets are all taken from the Huzinaga's book;<sup>10</sup> the Nb basis is  $(16s10p7d)/[6s3p3d]$  augmented with the two diffuse p functions ( $\zeta = 0.074, 0.023$ ) representing 5p orbitals. The basis sets for F, Cl, and Br atoms are  $(7s4p)/[2s1p]$ ,  $(10s7p)/[3s2p]$ , and  $(13s10p4d)/[4s3p1d]$ , respectively.

Our previous studies have concluded that the dominant contribution mainly comes from the metal atom concerned, and those of the ligands are negligibly small.<sup>3</sup> This suggests that the basis set for the central metal atom should be more accurate, and those for the ligands are less important. In addition, we have checked the ligand basis set dependence for the Nb magnetic shielding constants of  $\text{NbF}_6^-$  and  $\text{NbCl}_6^-$  using a split valence set augmented with a polarization d function. The results are discussed in the Appendix.

The geometries are as follows: the Nb-F, Nb-Cl, and Nb-Br lengths are assumed to be constant for all the molecules studied here and are taken from the geometries of the neutral molecules  $\text{NbF}_5$ ,  $\text{NbCl}_5$ , and  $\text{NbBr}_5$ ,<sup>11</sup> i.e.  $d(\text{Nb-F}) = 1.88 \text{ \AA}$ ,  $d(\text{Nb-Cl}) = 2.28 \text{ \AA}$ , and  $d(\text{Nb-Br}) = 2.45 \text{ \AA}$ , respectively. The bond angles

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TABLE I: Calculated Nb Magnetic Shielding Constants and Their Breakdown into Core and Valence MO Contributions (ppm)

molecule	$\sigma^{\text{dia}}$				$\sigma^{\text{para}}$				$\sigma(\text{total})$	$\delta^a$	
	core	valence	total	shift	core	valence	total	shift		calc	expt <sup>b</sup>
NbF <sub>6</sub> <sup>-</sup>	3939.3	193.2	4132.6	149.8	-477.4	-1303.8	-1781.2	-1748.0	2351.4	-1598.2	-1490
NbF <sub>5</sub> Cl <sup>-</sup>	3969.1	188.2	4157.3	125.1	-476.6	-1524.2	-2000.7	-1528.5	2156.6	-1403.4	
trans-NbF <sub>4</sub> Cl <sub>2</sub> <sup>-</sup>	3998.9	183.4	4182.2	100.2	-474.8	-1765.8	-2239.9	-1289.3	1942.3	-1189.1	
cis-NbF <sub>4</sub> Cl <sub>2</sub> <sup>-</sup>	3998.9	183.3	4182.1	100.3	-480.4	-1777.5	-2257.9	-1271.3	1924.2	-1171.0	
mer-NbF <sub>3</sub> Cl <sub>3</sub> <sup>-</sup>	4028.6	178.5	4207.1	75.3	-480.7	-2053.9	-2534.6	-994.6	1672.5	-919.3	
fac-NbF <sub>3</sub> Cl <sub>3</sub> <sup>-</sup>	4028.7	178.4	4207.1	75.3	-487.3	-2060.1	-2547.4	-981.8	1659.6	-906.4	
trans-NbF <sub>2</sub> Cl <sub>4</sub> <sup>-</sup>	4058.3	173.9	4232.2	50.2	-480.1	-2363.7	-2843.7	-685.5	1388.5	-635.3	
cis-NbF <sub>2</sub> Cl <sub>4</sub> <sup>-</sup>	4058.4	173.8	4232.1	50.3	-488.2	-2365.6	-2853.7	-675.5	1378.4	-625.2	
NbFCl <sub>5</sub> <sup>-</sup>	4088.1	169.2	4257.2	25.2	-486.6	-2696.8	-3183.5	-345.7	1073.7	-320.5	-258
NbCl <sub>6</sub> <sup>-</sup>	4117.7	164.6	4282.4	0.0	-481.8	-3047.4	-3529.2	0.0	753.2	0.0	0
NbCl <sub>5</sub> Br <sup>-</sup>	4183.3	163.2	4346.5	-64.1	-474.1	-3223.1	-3697.2	168.0	649.3	103.9	126
trans-NbCl <sub>4</sub> Br <sub>2</sub> <sup>-</sup>	4248.8	161.9	4410.7	-128.3	-465.6	-3404.9	-3870.5	341.3	540.1	213.1	246
cis-NbCl <sub>4</sub> Br <sub>2</sub> <sup>-</sup>	4248.8	161.9	4410.6	-128.2	-465.6	-3407.2	-3872.7	343.5	537.9	215.3	253
mer-NbCl <sub>3</sub> Br <sub>3</sub> <sup>-</sup>	4314.3	160.5	4474.8	-192.4	-456.3	-3597.6	-4053.8	524.6	421.0	332.2	371
fac-NbCl <sub>3</sub> Br <sub>3</sub> <sup>-</sup>	4314.3	160.5	4474.8	-192.4	-456.3	-3598.4	-4054.6	525.4	420.1	333.1	378
trans-NbCl <sub>2</sub> Br <sub>4</sub> <sup>-</sup>	4379.8	159.1	4539.0	-256.6	-446.0	-3796.9	-4242.9	713.7	296.1	457.1	492
cis-NbCl <sub>2</sub> Br <sub>4</sub> <sup>-</sup>	4379.8	159.1	4538.9	-256.5	-446.1	-3796.4	-4242.4	713.2	296.5	456.7	497
NbClBr <sub>5</sub> <sup>-</sup>	4445.4	157.8	4603.1	-320.7	-434.9	-4002.3	-4437.2	908.0	166.0	587.2	616
NbBr <sub>6</sub> <sup>-</sup>	4510.9	156.4	4667.3	-384.9	-422.7	-4215.2	-4637.9	1108.7	29.4	723.8	735

<sup>a</sup>The definition of chemical shift is  $\sigma(\text{NbCl}_6^-) - \sigma$ . A value of a positive sign means the downfield shift. <sup>b</sup>References 12 and 13.

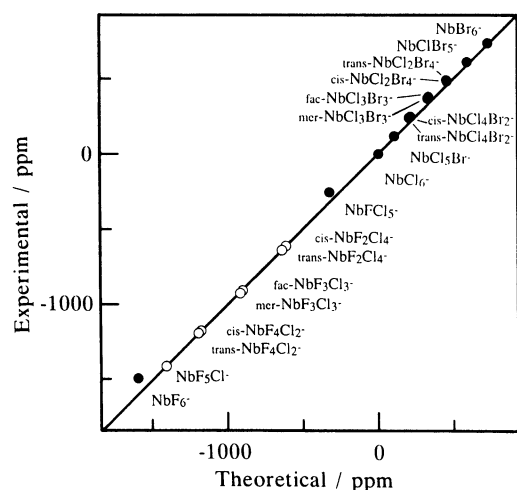


Figure 1. Correlation between the calculated and experimental values of the Nb chemical shifts in the NbX<sub>6-n</sub>Y<sub>n</sub><sup>-</sup> series (X, Y = F, Cl, Br; n = 0–6). The open circles indicate the lack of the experimental values.

are all assumed to be 90°; i.e., all complexes are octahedral or pseudooctahedral.

### Theory–Experiment Correlation and Suggested Trends

The calculated results of the Nb magnetic shielding constant  $\sigma$  and chemical shift  $\delta$  are summarized in Table I. The definition of the chemical shifts utilized here is

$$\delta = \sigma(\text{ref}) - \sigma \quad (1)$$

The reference molecule is NbCl<sub>6</sub><sup>-</sup>. The experimental values are from Tarasov et al.<sup>12</sup> for NbCl<sub>6-n</sub>Br<sub>n</sub><sup>-</sup>. For NbF<sub>6</sub><sup>-</sup> and NbFCl<sub>5</sub><sup>-</sup>, the data from Kidd and Goodfellow are converted by using the relation<sup>13</sup>

$$\delta(\text{ref:NbCl}_6^-) = \delta(\text{ref:NbF}_6^-) - 1490 \text{ ppm} \quad (2)$$

Figure 1 shows the correlation between the theoretical and experimental values of the Nb chemical shifts. The experimental values for the NbF<sub>6-n</sub>Cl<sub>n</sub><sup>-</sup> series with n = 1–4 are not available to the best of our knowledge. For the other compounds, our

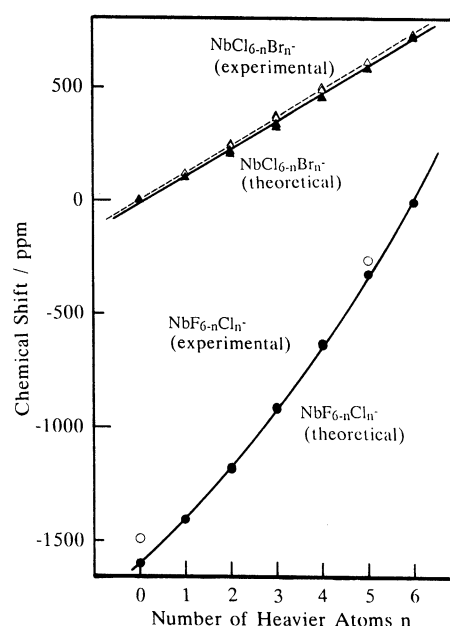


Figure 2. The dependence of the calculated and experimental Nb chemical shifts on the number of the heavier ligands.

theoretical results well reproduce the experimental values. This shows that the theoretical method used in the present study is reliable for the calculation of the Nb chemical shifts in these complexes. Relativistic and correlation effects seem to be small or to cancel for the Nb chemical shifts studied here.

For each of the compounds NbF<sub>6-n</sub>Cl<sub>n</sub><sup>-</sup> and NbCl<sub>6-n</sub>Br<sub>n</sub><sup>-</sup> with n = 2–4, there are two geometrical isomers. Our results show that the trans (meridional for n = 3) isomers have an upfield shift relative to the cis (facial) isomers except for NbCl<sub>2</sub>Br<sub>4</sub><sup>-</sup> whose cis and trans isomers have nearly equal shifts. For the NbCl<sub>6-n</sub>Br<sub>n</sub><sup>-</sup> series, this trend is in accordance with the assignment of Tarasov et al.<sup>12</sup> Our calculations indicate that the splitting between the isomers seems to become smaller as the ligand is substituted with a heavier atom.

The dependence of the experimental and theoretical chemical shifts on the number of heavier ligands n is nearly linear as depicted in Figure 2. It is interesting to see that the slopes of the two series of complexes, NbF<sub>6-n</sub>Cl<sub>n</sub><sup>-</sup> and NbCl<sub>6-n</sub>Br<sub>n</sub><sup>-</sup>, are different, implying a difference in the effects of the substitution. A smaller slope for the NbCl<sub>6-n</sub>Br<sub>n</sub><sup>-</sup> series reflects that the substitution of Cl with F brings larger effects on the electron distribution than the substitution with Br. In exaggerated terms, the theoretical plot for the NbF<sub>6-n</sub>Cl<sub>n</sub><sup>-</sup> series shows a small U-

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TABLE II: AO Contributions to the Nb Diamagnetic Term  $\sigma^{\text{dia}}$  in ppm

molecule	niobium				fluorine, bromine				chlorine			$\sigma^{\text{dia}}$ total
	s	p	d	total	s	p	d	total <sup>a</sup>	s	p	total <sup>a</sup>	
NbF <sub>6</sub> <sup>-</sup>	1916.4	1407.9	524.8	3849.1	19.5	27.7		47.2				4132.6
NbF <sub>3</sub> Cl <sup>-</sup>	1916.1	1407.8	526.1	3850.0	19.5	27.6		47.1 (ax)	24.3	47.2	71.5	4157.3
												47.2 (eq)
<i>trans</i> -NbF <sub>4</sub> Cl <sub>2</sub> <sup>-</sup>	1915.6	1407.7	527.8	3851.1	19.5	27.6		47.1	24.3	47.0	71.3	4182.2
												47.1 (ax)
<i>cis</i> -NbF <sub>4</sub> Cl <sub>2</sub> <sup>-</sup>	1915.7	1407.8	527.6	3851.0	19.5	27.6		47.1 (ax)	24.3	47.1	71.4	4182.1
<i>mer</i> -NbF <sub>3</sub> Cl <sub>3</sub> <sup>-</sup>	1915.1	1407.7	529.5	3852.3	19.6	27.5		47.0 (ax)	24.3	47.0	71.3 (ax)	4207.1
												47.1 (eq)
<i>fac</i> -NbF <sub>3</sub> Cl <sub>3</sub> <sup>-</sup>	1915.2	1407.8	529.2	3852.2	19.6	27.5		47.0	24.3	46.9	71.2 (eq)	4207.1
												47.0 (ax)
<i>trans</i> -NbF <sub>2</sub> Cl <sub>4</sub> <sup>-</sup>	1914.6	1407.6	531.6	3853.8	19.5	27.5		47.0	24.3	46.8	71.1	4232.2
												47.0 (ax)
<i>cis</i> -NbF <sub>2</sub> Cl <sub>4</sub> <sup>-</sup>	1914.7	1407.7	531.3	3853.7	19.6	27.4		47.0	24.3	46.8	71.1 (ax)	4232.1
												47.0 (eq)
NbFCl <sub>5</sub> <sup>-</sup>	1914.1	1407.7	533.5	3855.2	19.6	27.4		46.9	24.3	46.8	71.1 (ax)	4257.2
												47.0 (eq)
NbCl <sub>6</sub> <sup>-</sup>	1913.5	1407.7	535.8	3856.9	19.6	27.5		47.0	24.3	46.6	70.9	4282.4
												47.0 (ax)
NbCl <sub>5</sub> Br <sup>-</sup>	1913.2	1407.7	536.4	3857.3	30.4	66.2	38.2	134.8	24.3	46.6	70.9 (ax)	4346.5
												46.6 (eq)
<i>trans</i> -NbCl <sub>4</sub> Br <sub>2</sub> <sup>-</sup>	1913.0	1407.8	536.9	3857.7	30.4	66.2	38.2	134.7	24.3	46.6	70.9	4410.7
												46.6 (ax)
<i>cis</i> -NbCl <sub>4</sub> Br <sub>2</sub> <sup>-</sup>	1913.0	1407.8	536.9	3857.7	30.4	66.2	38.2	134.8	24.3	46.6	70.9 (ax)	4410.6
												46.6 (eq)
<i>mer</i> -NbCl <sub>3</sub> Br <sub>3</sub> <sup>-</sup>	1912.7	1407.9	537.5	3858.1	30.4	66.2	38.2	134.7 (ax)	24.3	46.6	70.8 (ax)	4474.8
												134.7 (eq)
<i>fac</i> -NbCl <sub>3</sub> Br <sub>3</sub> <sup>-</sup>	1912.7	1407.9	537.5	3858.1	30.4	66.2	38.2	134.7	24.3	46.6	70.8	4474.8
												46.6 (ax)
<i>trans</i> -NbCl <sub>2</sub> Br <sub>4</sub> <sup>-</sup>	1912.5	1407.9	538.1	3858.5	30.4	66.1	38.2	134.7	24.3	46.6	70.9	4539.0
												46.5 (ax)
<i>cis</i> -NbCl <sub>2</sub> Br <sub>4</sub> <sup>-</sup>	1912.5	1407.9	538.1	3858.5	30.4	66.1	38.2	134.7 (ax)	24.3	46.5	70.8	4538.9
												134.7 (eq)
NbClBr <sub>5</sub> <sup>-</sup>	1912.2	1408.0	538.7	3858.9	30.4	66.1	38.2	134.7 (ax)	24.3	46.5	70.8	4603.1
												134.7 (eq)
NbBr <sub>6</sub> <sup>-</sup>	1912.0	1408.1	539.3	3859.4	30.4	66.1	38.2	134.7				4667.3

<sup>a</sup>The parentheses indicate the position of a ligand; ax, axial; eq, equatorial.

shaped relationship as observed for Si and Sn chemical shifts of halogen-containing complexes.<sup>1</sup>

**Origin of the Nb Chemical Shifts**

As is well-known, a magnetic shielding constant  $\sigma$  is composed of two terms: a diamagnetic term  $\sigma^{\text{dia}}$  and a paramagnetic term  $\sigma^{\text{para}}$ , which are first-order and second-order quantities, respectively, in the perturbation theory. Table I shows the component analysis of the calculated chemical shift. We observe that the dominant contribution is from the paramagnetic term  $\sigma^{\text{para}}$  rather than the diamagnetic term  $\sigma^{\text{dia}}$ . The sign of  $\Delta\sigma^{\text{dia}}$  is even different from that of  $\Delta\sigma^{\text{para}}$  and the observed shifts. Thus,  $\Delta\sigma^{\text{para}}$  is the dominant factor for the Nb chemical shift. It corresponds to an electronic response against an external magnetic perturbation and is represented by a mixing of excited states of the unperturbed system into the ground state. Therefore, it is necessary to investigate what state mixes in this way for giving rise to the paramagnetic term.

Table I also shows the analysis of  $\sigma^{\text{dia}}$  and  $\sigma^{\text{para}}$  into core and valence MO contributions. The valence MOs are the higher 18 occupied MOs composed of the Nb 4d, 5s and ligand *np* AOs. It is observed that the variations in the valence MO contributions of the paramagnetic term result in the chemical shifts. This is natural since the variations in the electronic states due to the ligand substitution are governed by the valence electrons.

Tables II and III show the analyses of the  $\sigma^{\text{dia}}$  and  $\sigma^{\text{para}}$ , respectively, into atomic orbital (AO) contributions. The AO analysis is defined previously,<sup>3a</sup> similar to the Mulliken population analysis. For the diamagnetic term, the well-established Pascal-rule-like formula<sup>3a</sup> is also satisfied for the present Nb complexes.

$$\sigma^{\text{dia}} = \sigma^{\text{dia}}(\text{Nb atom}) + \sum n_L \sigma_L^{\text{dia}} \quad (3)$$

This relation is derivable from the Flygare-Goodisman equation<sup>16</sup> when we neglect variations of M-L bonds. Thus,  $\sigma^{\text{dia}}$  is determined solely by the structural factors. The average of the  $\sigma^{\text{dia}}$  of Nb atom is calculated to be 3855 ppm in this study, while the free

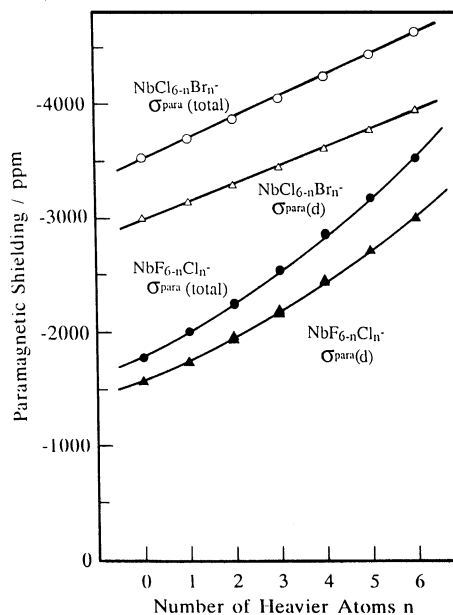


Figure 3. The dependence of the Nb paramagnetic shielding constants and their Nb d components on the number of the heavier ligands.

atom value by Malli and Froese is 3870.35 ppm.<sup>17</sup>

For  $\sigma^{\text{para}}$ , the contributions from the d orbitals of Nb are evidently the most significant. The contributions of the ligands themselves are negligibly small.

In Figure 3, we plot the dependence of  $\sigma^{\text{para}}$  and the Nb d component of  $\sigma^{\text{para}}$  on the number of heavier ligands *n*. The  $\sigma^{\text{para}}$  is clearly dominated by the d component. We also see that the dependence is almost linear. The difference in the slopes of the two series of compounds is also observed. The tendency of deviation from the linearity is also seen for NbF<sub>6-n</sub>Cl<sub>n</sub><sup>-</sup>. This is the reason why the *n* dependence of  $\delta$  shown in Figure 2 deviates from

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(17) Malli, G.; Froese, C. Int. J. Quantum Chem. 1967, 1, 95.

TABLE III: AO Contributions to the Nb Paramagnetic Term  $\sigma^{\text{para}}$  in ppm

molecule	niobium <sup>a</sup>			fluorine, bromine			chlorine			$\sigma^{\text{para}}$ total	
	p	d	total	s	p	d	total <sup>b</sup>	s	p		total <sup>b</sup>
NbF <sub>6</sub> <sup>-</sup>	-178.5	-1570.6	-1749.1	-1.9	-3.4		-5.3				-1781.2
NbF <sub>5</sub> Cl <sup>-</sup>	-231.1	-1737.8	-1968.8	-1.8	-3.3		-5.1 (ax)	-1.7	-3.7	-5.4	-2000.7
<i>trans</i> -NbF <sub>4</sub> Cl <sub>2</sub> <sup>-</sup>	-266.9	-1941.7	-2208.6	-1.8	-3.5		-5.4 (eq)	-1.5	-3.5	-5.0	-2239.9
<i>cis</i> -NbF <sub>4</sub> Cl <sub>2</sub> <sup>-</sup>	-289.9	-1936.4	-2226.3	-1.9	-3.5		-5.4 (ax)	-1.6	-3.8	-5.4	-2257.9
<i>mer</i> -NbF <sub>3</sub> Cl <sub>3</sub> <sup>-</sup>	-329.9	-2173.7	-2503.6	-1.7	-3.2		-4.9 (ax)	-1.6	-3.8	-5.4 (ax)	-2534.6
<i>fac</i> -NbF <sub>3</sub> Cl <sub>3</sub> <sup>-</sup>	-355.8	-2160.3	-2516.1	-1.8	-3.5		-5.3 (eq)	-1.5	-3.5	-5.0 (eq)	-2547.4
<i>trans</i> -NbF <sub>2</sub> Cl <sub>4</sub> <sup>-</sup>	-372.3	-2441.2	-2813.4	-1.7	-3.2		-4.9 (ax)	-1.6	-3.9	-5.5	-2843.7
<i>cis</i> -NbF <sub>2</sub> Cl <sub>4</sub> <sup>-</sup>	-400.8	-2422.3	-2823.1	-1.8	-3.5		-5.3 (eq)	-1.4	-3.5	-4.9	-2853.7
NbFCl <sub>5</sub> <sup>-</sup>	-449.3	-2704.3	-3153.6	-1.7	-3.2		-4.9 (ax)	-1.6	-3.9	-5.5 (eq)	-3183.5
NbCl <sub>6</sub> <sup>-</sup>	-502.4	-2997.7	-3500.0	-1.4	-3.5		-4.9 (eq)	-1.4	-3.5	-4.9	-3529.2
NbCl <sub>5</sub> Br <sup>-</sup>	-529.0	-3138.7	-3667.8	-3.3	-3.9	1.8	-5.5	-1.3	-3.2	-4.5 (ax)	-3697.2
<i>trans</i> -NbCl <sub>4</sub> Br <sub>2</sub> <sup>-</sup>	-553.1	-3287.7	-3840.8	-1.4	-3.5	1.8	-5.2	-1.4	-3.5	-4.8	-3870.5
<i>cis</i> -NbCl <sub>4</sub> Br <sub>2</sub> <sup>-</sup>	-556.8	-3286.3	-3843.0	-3.3	-3.9	1.8	-5.5	-1.4	-3.5	-4.9 (ax)	-3872.7
<i>mer</i> -NbCl <sub>3</sub> Br <sub>3</sub> <sup>-</sup>	-582.0	-3441.9	-4023.8	-1.3	-3.2	1.8	-5.2 (ax)	-1.3	-3.2	-4.5 (ax)	-4053.8
<i>fac</i> -NbCl <sub>3</sub> Br <sub>3</sub> <sup>-</sup>	-585.6	-3439.0	-4024.7	-3.3	-4.0	1.8	-5.5 (eq)	-1.4	-3.5	-4.8 (eq)	-4054.6
<i>trans</i> -NbCl <sub>2</sub> Br <sub>4</sub> <sup>-</sup>	-608.2	-3604.3	-4212.5	-3.3	-4.0	1.8	-5.5 (eq)	-1.3	-3.2	-4.5	-4242.9
<i>cis</i> -NbCl <sub>2</sub> Br <sub>4</sub> <sup>-</sup>	-611.9	-3600.2	-4212.1	-3.3	-3.7	1.8	-5.2 (ax)	-1.4	-3.5	-4.8	-4242.9
NbClBr <sub>5</sub> <sup>-</sup>	-639.4	-3767.1	-4406.5	-3.3	-4.0	1.8	-5.5 (ax)	-1.3	-3.2	-4.5	-4437.2
NbBr <sub>6</sub> <sup>-</sup>	-668.1	-3938.9	-4607.0	-3.2	-3.7	1.8	-5.2 (eq)	-1.3	-3.2	-4.5	-4637.9

<sup>a</sup>Nb s AO contribution is identically zero because of the lack of the angular momentum. <sup>b</sup>The parentheses indicate the position of a ligand: ax, axial; eq, equatorial.

linearity. We think that this nonlinearity is due to the same origin as the U-shaped dependence of the chemical shifts observed for Si and Sn chemical shifts.<sup>3d</sup>

From these analyses, we conclude that the valence 4d orbitals of the Nb complexes determine the Nb chemical shifts. This implies that the responsible mixing states are due to the transitions between the MOs of primarily Nb 4d orbital character, i.e., d-d transition.

The second-order perturbation theory formula for  $\sigma^{\text{para}}$  is given by

$$\sigma_{\text{Mitu}}^{\text{para}} = -\frac{e^2}{4m^2c^2n \neq 0} \sum_j \{ \langle 0 | \sum_j r_{Mj}^{-3} L_{Mj} | n \rangle \langle n | \sum_j L_{jz} | 0 \rangle + \langle 0 | \sum_j L_{jz} | n \rangle \langle n | \sum_j r_{Mj}^{-3} L_{Mj} | 0 \rangle \} / (E_n - E_0) \quad (4)$$

with standard notations. We already know that the excited states which are important in the summation are due to the d-d transition. We next consider which is more important in such terms, the numerator or the denominator.

#### Correlation with the Nb Charge and 4d Population

In this section, we investigate the relationship between the electronegativity of the ligand and the chemical shift. First of all, we show the  $n$  dependences of the net charge of niobium and of the Nb 4d population in Figure 4. More detailed analyses of the Mulliken populations are also summarized in Table IV. It is observed that, since the electronegativities reduce in the order F → Cl → Br, the net charge on Nb reduces in this order.

The important facts we note here are the following: (1) the increase in the Nb 4d population and the decrease in the Nb net charge are monotonic or almost linear, (2) the slope is larger for the NbF<sub>6-n</sub>Cl<sub>n</sub><sup>-</sup> series than for the NbCl<sub>6-n</sub>Br<sub>n</sub><sup>-</sup>, (3) the nonlinearity is larger for the NbF<sub>6-n</sub>Cl<sub>n</sub><sup>-</sup> series than for the NbCl<sub>6-n</sub>Br<sub>n</sub><sup>-</sup> series, and (4) the change in the Nb net charge is due to that of the Nb 4d electron population. These observations correspond well to the  $n$  dependence of the paramagnetic shielding constants, which also show a shallow U-shape. We note that the Cl → F substitution causes larger effects than the Br → Cl one for both the magnetic shielding constant and the charge distribution (Figures

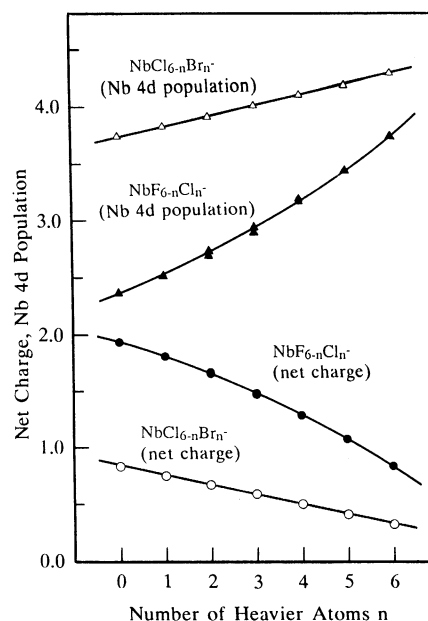


Figure 4. The  $n$  dependence of the Nb net charge and 4d population.

2-4). This is the trend frequently observed for a variety of chemical properties.

We depict in Figure 5 the dependence of  $\sigma$  and  $\sigma^{\text{para}}$  on the net charge of Nb in the complexes. The total magnetic shielding constant and the paramagnetic term almost linearly change as the net charge. This is because both the shielding constants and the net charges have very similar dependences on  $n$  as shown in Figures 3 and 4. We easily find that the slopes are different for the two series of complexes, NbF<sub>6-n</sub>Cl<sub>n</sub><sup>-</sup> and NbCl<sub>6-n</sub>Br<sub>n</sub><sup>-</sup>. It is smaller for NbF<sub>6-n</sub>Cl<sub>n</sub><sup>-</sup> than for NbCl<sub>6-n</sub>Br<sub>n</sub><sup>-</sup>. The introduction of the F atom leads to a larger change in the net charge of Nb than that of the Cl atom. The larger change in  $\sigma$  for NbF<sub>6-n</sub>Cl<sub>n</sub><sup>-</sup> than for NbCl<sub>6-n</sub>Br<sub>n</sub><sup>-</sup> is due to the same origin.

TABLE IV: Mulliken AO Population Analyses for NbX<sub>6-n</sub>Y<sub>n</sub><sup>-</sup> (X, Y = F, Cl, Br; n = 0-6)

molecule	niobium				fluorine, bromine			chlorine		
	4d	5s	5p	net charge	s <sup>a</sup>	p <sup>a</sup>	net charge <sup>b</sup>	s <sup>a</sup>	p <sup>a</sup>	net charge <sup>b</sup>
NbF <sub>6</sub> <sup>-</sup>	2.364	0.107	0.463	1.937	1.939	5.553	-0.490			
NbF <sub>5</sub> Cl <sup>-</sup>	2.514	0.069	0.478	1.819	1.942	5.527	-0.467 (ax)	1.941	5.517	-0.449
<i>trans</i> -NbF <sub>4</sub> Cl <sub>2</sub> <sup>-</sup>	2.737	0.010	0.476	1.667	1.940	5.538	-0.476 (eq)	1.944	5.472	-0.406
<i>cis</i> -NbF <sub>4</sub> Cl <sub>2</sub> <sup>-</sup>	2.692	0.025	0.503	1.672	1.941	5.524	-0.463 (ax)	1.941	5.486	-0.418
<i>mer</i> -NbF <sub>3</sub> Cl <sub>3</sub> <sup>-</sup>	2.937	-0.038	0.508	1.494	1.943	5.513	-0.455 (eq)	1.942	5.459	-0.391 (ax)
<i>fac</i> -NbF <sub>3</sub> Cl <sub>3</sub> <sup>-</sup>	2.892	-0.024	0.537	1.498	1.941	5.502	-0.444 (ax)	1.944	5.442	-0.377 (eq)
<i>trans</i> -NbF <sub>2</sub> Cl <sub>4</sub> <sup>-</sup>	3.200	-0.103	0.520	1.294	1.944	5.501	-0.443	1.942	5.458	-0.390
<i>cis</i> -NbF <sub>2</sub> Cl <sub>4</sub> <sup>-</sup>	3.158	-0.090	0.551	1.295	1.942	5.503	-0.443	1.944	5.417	-0.352
NbFCl <sub>5</sub> <sup>-</sup>	3.439	-0.159	0.572	1.072	1.944	5.491	-0.433	1.944	5.415	-0.350 (ax)
NbCl <sub>6</sub> <sup>-</sup>	3.737	-0.232	0.602	0.828	1.941	5.411	-0.342 (ax)	1.941	5.433	-0.365 (eq)
NbCl <sub>5</sub> Br <sup>-</sup>	3.827	-0.269	0.630	0.748	1.944	5.392	-0.326 (eq)	1.944	5.371	-0.305
<i>trans</i> -NbCl <sub>4</sub> Br <sub>2</sub> <sup>-</sup>	3.920	-0.306	0.655	0.667	1.945	5.363	-0.298 (ax)	1.944	5.365	-0.298 (eq)
<i>cis</i> -NbCl <sub>4</sub> Br <sub>2</sub> <sup>-</sup>	3.918	-0.307	0.659	0.666	1.944	5.359	-0.292	1.944	5.359	-0.292 (ax)
<i>mer</i> -NbCl <sub>3</sub> Br <sub>3</sub> <sup>-</sup>	4.011	-0.343	0.686	0.583	1.945	5.356	-0.292 (eq)	1.945	5.356	-0.292 (ax)
<i>fac</i> -NbCl <sub>3</sub> Br <sub>3</sub> <sup>-</sup>	4.009	-0.344	0.691	0.582	1.947	5.302	-0.242 (ax)	1.945	5.351	-0.286 (ax)
<i>trans</i> -NbCl <sub>2</sub> Br <sub>4</sub> <sup>-</sup>	4.104	-0.380	0.715	0.500	1.949	5.300	-0.241 (eq)	1.944	5.353	-0.287 (eq)
<i>cis</i> -NbCl <sub>2</sub> Br <sub>4</sub> <sup>-</sup>	4.101	-0.380	0.720	0.498	1.947	5.302	-0.242	1.945	5.351	-0.286
NbClBr <sub>5</sub> <sup>-</sup>	4.194	-0.417	0.751	0.412	1.949	5.293	-0.234	1.944	5.348	-0.281
NbBr <sub>6</sub> <sup>-</sup>	4.286	-0.454	0.783	0.325	1.949	5.295	-0.235 (eq)	1.945	5.345	-0.280
					1.947	5.289	-0.228 (ax)	1.945	5.340	-0.275
					1.949	5.286	-0.227 (eq)			
					1.948	5.280	-0.221			

<sup>a</sup>The valence s and p orbitals for each ligand. <sup>b</sup>The parentheses indicate the position of a ligand: ax, axial; eq, equatorial.

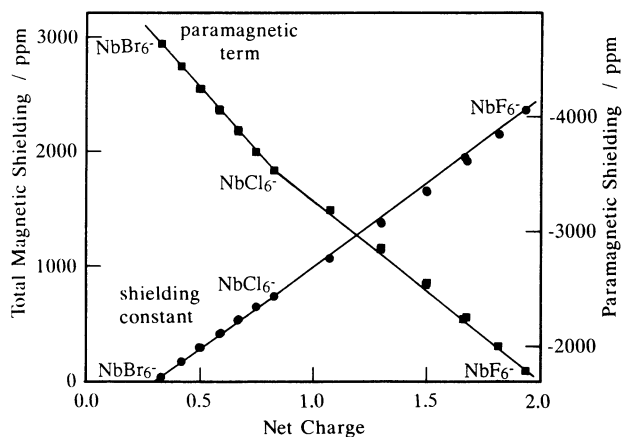


Figure 5. Correlations of the Nb total magnetic shielding constant and the paramagnetic term against the Nb net charge.

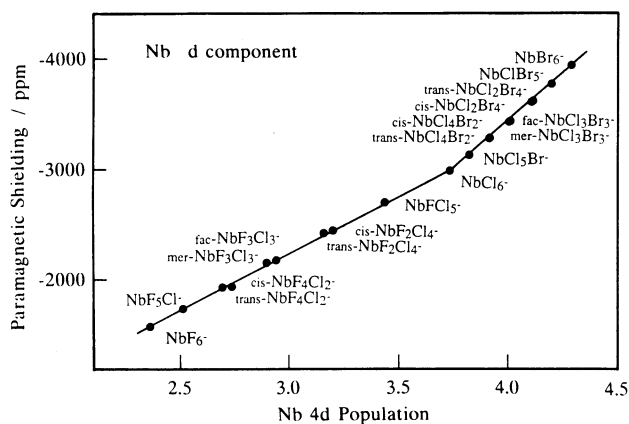


Figure 6. The dependence of the d component of the Nb paramagnetic term on the Nb 4d orbital population.

We show the relation of the Nb 4 d AO population and the Nb d AO contribution to  $\sigma^{para}$  in Figure 6. As is clearly observed,

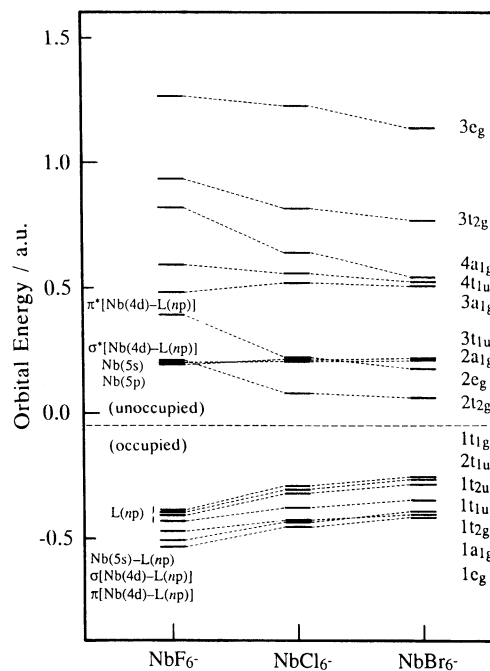


Figure 7. Orbital energy diagrams for the octahedral complexes.

the d component of the paramagnetic shielding constant increases linearly as the increase of the 4d orbital population.

**Molecular Orbital Picture of the Nb Chemical Shifts**

In the preceding two sections, we have found the following three facts: (i) The Nb chemical shifts are determined by the valence d AO contribution to the paramagnetic term. This implies that the responsible states which mix into the perturbed wave function under the magnetic field are due to the magnetically allowed d-d transition. (ii) The change in the Nb charge reflects that in the Nb 4d population. (iii) The 4d population and the d component of  $\sigma^{para}$  are linearly dependent. The clue for understanding these

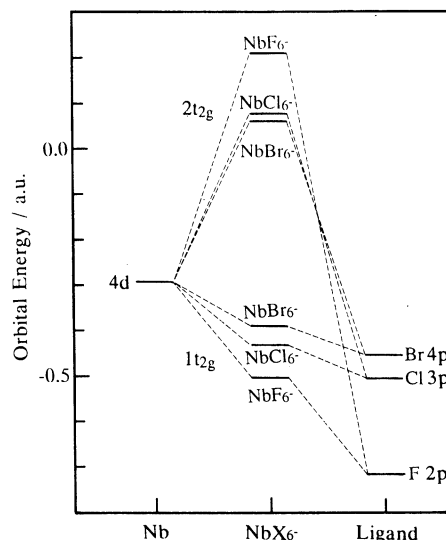
**TABLE V: Mulliken Population Component Analysis (in %) of the Occupied  $1t_{2g}$  and  $1e_g$  and Unoccupied  $2t_{2g}$  and  $2e_g$  MOs in  $NbX_6^-$  ( $X = F, Cl, Br$ )**

	$NbF_6^-$	$NbCl_6^-$	$NbBr_6^-$
$1e_g$ (occupied)			
orbital energy, au	-0.53112	-0.45332	-0.41638
Nb d	18.9	31.2	37.8
ligands	81.1	68.8	62.2
$1t_{2g}$ (occupied)			
orbital energy, au	-0.50333	-0.43218	-0.39054
Nb d	21.0	25.9	25.8
ligands	79.0	74.1	74.2
$2t_{2g}$ (unoccupied)			
orbital energy, au	0.21017	0.07991	0.06296
Nb d	83.1	76.4	75.9
ligands	16.9	23.6	24.1
$2e_g$ (unoccupied)			
orbital energy, au	0.39392	0.22084	0.17915
Nb d	77.2	62.6	56.1
ligands	22.8	37.4	43.9

facts is found from the investigations about the nature of the Nb-L bonds.

We show in Figure 7 the orbital energy levels of the octahedral complexes  $NbF_6^-$ ,  $NbCl_6^-$ , and  $NbBr_6^-$ . The symmetries and the natures of these MOs are also shown in the figure. The numbering is for valence MOs. In general notation, e.g., the  $1t_{2g}$  and  $1e_g$  MOs correspond to the  $2t_{2g}$  and  $4e_{2g}$  MOs in  $NbF_6^-$ ,  $3t_{2g}$  and  $6e_g$  in  $NbCl_6^-$ , and  $6t_{2g}$  and  $10e_g$  in  $NbBr_6^-$ .

Among the unoccupied MOs consisting of Nb d orbitals, the  $2t_{2g}$  and  $2e_g$  MOs largely change in their orbital energies. The occupied MOs which give the magnetically allowed transitions to the  $2t_{2g}$  and  $2e_g$  MOs are  $1t_{2g}$  and  $1e_g$ , both of which are the highest occupied MOs composed of the Nb 4d AO. Accordingly, it is expected that the important mixing states are those due to


**Figure 8.** Correlation diagrams of the  $1t_{2g}$  and  $2t_{2g}$  MOs with the Nb 4d and ligand  $np$  orbitals.

the transitions from the  $1t_{2g}$ ,  $1e_g$  MOs to the  $2t_{2g}$ ,  $2e_g$  MOs. Based on the approximation that the excitation energy  $\Delta E$  is parallel to the orbital energy difference, the  $\Delta E$  of this magnetically allowed transition decreases as a ligand is substituted into a less electronegative ligand. This rationalizes the trend in the observed chemical shifts, and therefore we conclude that the  $\Delta E$  is the main factor for the paramagnetic terms and the Nb chemical shifts studied here.

In our previous studies of the Mn and Mo complexes,<sup>3e,f</sup> we have shown that the Mn and Mo chemical shifts reflect the change in

**TABLE VI: Ligand Basis Set Dependence of the Energy and the Mulliken AO Population for  $NbF_6^-$  and  $NbCl_6^-$** 

molecule	ligand basis set <sup>a</sup>	total energy	niobium				fluorine, chlorine <sup>b</sup>			
			4d	5s	5p	net charge	s	p	d	net charge
$NbF_6^-$	MIN	-4346.644 040	2.364	0.107	0.463	1.937	1.939	5.553		-0.490
$NbF_6^-$	SV	-4346.821 600	1.744	0.229	0.290	2.571	1.975	5.624		-0.595
$NbF_6^-$	SVP	-4346.879 351	1.647	0.203	0.287	2.692	1.988	5.640	-0.008	-0.615
$NbCl_6^-$	MIN	-6504.682 011	3.737	0.232	0.602	0.828	1.944	5.371		-0.305
$NbCl_6^-$	SV	-6504.792 392	4.010	0.105	0.879	-0.076	1.921	5.260		-0.154
$NbCl_6^-$	SVP	-6504.940 212	3.179	0.221	0.615	0.892	1.893	5.398	0.045	-0.315

<sup>a</sup>MIN: minimal set, (7s4p)/[2s1p] for F and (10s7p)/[3s2p] for Cl. SV: split valence set, (7s4p)/[3s2p] for F and (10s7p)/[4s3p] for Cl. SVP: SV set with a polarization d function,  $\zeta = 1.496$  and 0.514 for F and Cl, respectively. <sup>b</sup>The valence AOs are indicated.

**TABLE VII: Ligand Basis Set Dependence of the AO Contributions to the Diamagnetic Term  $\sigma^{dia}$  (ppm)**

molecule	ligand basis set <sup>a</sup>	niobium				fluorine, chlorine				$\sigma^{dia}$ total
		s	p	d	total	s	p	d	total	
$NbF_6^-$	MIN	1916.4	1407.9	524.8	3849.1	19.5	27.7		47.2	4132.6
$NbF_6^-$	SV	1917.1	1408.3	520.1	3845.4	19.8	28.0		47.7	4131.8
$NbF_6^-$	SVP	1916.9	1408.4	519.0	3844.3	19.8	28.1	0.0	48.0	4132.1
$NbCl_6^-$	MIN	1913.5	1407.7	535.8	3856.9	24.3	46.6		70.9	4282.4
$NbCl_6^-$	SV	1915.4	1409.4	537.1	3861.9	24.0	46.0		70.0	4282.2
$NbCl_6^-$	SVP	1916.1	1408.1	531.1	3855.4	24.0	46.7	0.4	71.2	4282.4

<sup>a</sup>MIN: minimal set, (7s4p)/[2s1p] for F and (10s7p)/[3s2p] for Cl. SV: split valence set, (7s4p)/[3s2p] for F and (10s7p)/[4s3p] for Cl. SVP: SV set with a polarization d function,  $\zeta = 1.496$  and 0.514 for F and Cl, respectively.

**TABLE VIII: Ligand Basis Set Dependence of the AO Contributions to the Paramagnetic Term  $\sigma^{para}$  (ppm)**

molecule	ligand basis set <sup>a</sup>	niobium			fluorine, chlorine				$\sigma^{para}$ total	$\sigma^{total}$
		p	d	total	s	p	d	total		
$NbF_6^-$	MIN	-178.5	-1570.6	-1749.1	-1.9	-3.4		-5.3	-1781.2	2351.4
$NbF_6^-$	SV	-170.8	-1395.6	-1566.4	-3.6	-5.7		-9.3	-1621.9	2509.9
$NbF_6^-$	SVP	-200.3	-1302.9	-1503.2	-4.1	-14.1	-8.0	-26.2	-1660.0	2472.1
$NbCl_6^-$	MIN	-502.4	-2997.7	-3500.0	-1.4	-3.5		-4.9	-3529.2	753.2
$NbCl_6^-$	SV	-818.4	-2760.7	-3579.1	-0.4	-4.0		-4.4	-3605.5	676.7
$NbCl_6^-$	SVP	-842.7	-2523.3	-3366.0	-2.3	-11.8	-7.5	-21.7	-3496.1	786.3

<sup>a</sup>MIN: minimal set, (7s4p)/[2s1p] for F and (10s7p)/[3s2p] for Cl. SV: split valence set, (7s4p)/[3s2p] for F and (10s7p)/[4s3p] for Cl. SVP: SV set with a polarization d function,  $\zeta = 1.496$  and 0.514 for F and Cl, respectively.

the magnetically allowed d-d\* transition energy. For the Mo complexes, in particular, we have calculated these d-d\* excited states using the SAC/SAC-CI method<sup>18</sup> and confirmed that the Mo chemical shifts certainly show a linear dependence on the inverse of the 4dσ → 4dπ\* transition energy.<sup>4</sup>

The variation of the MOs concerned is understood when we consider how these orbitals are formed. Figure 8 shows the correlation diagrams for the 1t<sub>2g</sub> (occupied) and 2t<sub>2g</sub> (unoccupied) orbitals of NbX<sub>6</sub><sup>-</sup> (X = F, Cl, Br), and Nb 4d orbital, and the ligand np orbital. A similar correlation diagram is also valid for the 1e<sub>g</sub> and 2e<sub>g</sub> MO pair. The orbital energy levels of the atoms are due to the Hartree-Fock calculations for the individual atoms. We observe in this figure that, as the energy level of the ligand np orbital moves upward, the separation between the occupied bonding and the unoccupied antibonding orbitals decreases. This is probably because the interaction of the constituent orbitals is mainly dominated by the overlap rather than the orbital energy difference. Intuitively, this is reasonable since the heavier atoms have more diffuse AOs, i.e., more sparse electron distribution in the bonding region, which results in a weaker bond. As the bond is weaker, the bond length becomes larger, which again results in a smaller overlap between the Nb and ligand orbitals.

Table V shows the Mulliken orbital population for the occupied 1e<sub>g</sub> and 1t<sub>2g</sub> and the unoccupied 2e<sub>g</sub> and 2t<sub>2g</sub> orbitals of NbF<sub>6</sub><sup>-</sup>, NbCl<sub>6</sub><sup>-</sup>, and NbBr<sub>6</sub><sup>-</sup>. The Nb 4d orbital components of the 1e<sub>g</sub> and 1t<sub>2g</sub> MOs are 18.9% and 21.0%, respectively. In NbCl<sub>6</sub><sup>-</sup> they increase to 31.2% and 25.9%, and in NbBr<sub>6</sub><sup>-</sup> they are 37.8% and 25.8%, respectively. This trend is also understood from the orbital correlation diagram. The electronegative ligands has lower np orbital which makes the nature of the 1e<sub>g</sub> and 1t<sub>2g</sub> orbitals more similar to the ligand. In contrast, the unoccupied 2t<sub>2g</sub> and 2e<sub>g</sub> MOs are more localized onto the metal atom.

Therefore, Figure 8 explains the change in the d component of σ<sup>para</sup>, the Nb 4d population, and the correlation between them shown in Figure 6.

### Summary

In this paper, we have investigated the electronic origin and the mechanism of the Nb NMR chemical shifts for the 19 Nb complexes, NbX<sub>6-n</sub>Y<sub>n</sub><sup>-</sup> (n = 0-6; X, Y = F, Cl, Br) by the ab initio Hartree-Fock method. The results are summarized as follows:

1. The origin of the Nb chemical shift lies in the change of the paramagnetic term σ<sup>para</sup> of the shielding constants. Especially, the dominant contribution for the Nb chemical shift is due to the Nb 4d AO.

2. From the perturbation theory viewpoint, the most important contribution to σ<sup>para</sup> arises from the transitions from the 1t<sub>2g</sub>, 1e<sub>g</sub> MOs to the 2t<sub>2g</sub>, 2e<sub>g</sub> MOs, i.e. d-d\* transitions, induced by the external magnetic field. The change in the energy denominator ΔE is expected to be the main controlling factor causing the Nb chemical shifts. It reflects the alterations of the orbital energy levels of the bonding d and antibonding d\* orbitals, which depends on the strength of the overlap interactions between the Nb 4d and the ligand np orbitals.

(18) (a) Nakatsuji, H.; Hirao, K. *J. Chem. Phys.* **1978**, *68*, 2053. (b) Nakatsuji, H. *Chem. Phys. Lett.* **1978**, *59*, 362.

3. The d component of the paramagnetic shielding constants has a linear relation with the 4d population of the Nb atom and the Nb atomic charge. This is because the 4d population is dominated by the energy levels of the ligand np orbitals through the formation of the 1t<sub>2g</sub> and 1e<sub>g</sub> MOs by the interaction with the Nb 4d AO.

4. The Nb chemical shifts studied here show an almost linear dependence on the number of heavier ligands n, but in exaggerated terms, the dependence in the NbF<sub>6-n</sub>Cl<sub>n</sub><sup>-</sup> series is U-shaped as observed in Si and Sn compounds.

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### Appendix

In this Appendix, we examine the dependence of the Nb magnetic shielding constants and chemical shifts on the quality of the ligand basis set. We choose NbF<sub>6</sub><sup>-</sup> and NbCl<sub>6</sub><sup>-</sup> as representative molecules. The basis set of niobium is the same as that described in the text and is of split valence quality. For the fluorine atom, we examine (7s4p)/[2s1p] minimal (MIN), (7s4p)/[3s2p] split valence (SV), and (7s4p1d)/[3s2p1d] split valence plus polarization (SVP, ζ<sub>d</sub> = 1.496) sets, and for the chlorine atom, (10s7p)/[3s2p] (MIN), (10s7p)/[4s3p] (SV), and (10s7p1d)/[4s3p1d] (SVP, ζ<sub>d</sub> = 0.514). The MIN basis sets have been used in the text. In the SV basis sets, we make the most diffuse function free in the contractions.

Table VI shows the ligand basis set dependence of the energy and the Mulliken AO population. We see that the energy decreases according to the basis set quality. In NbF<sub>6</sub><sup>-</sup>, the change in the Nb net charge is monotonic, whereas in NbCl<sub>6</sub><sup>-</sup> it is not. The population of the augmented d function of the ligand atom is very small.

Tables VII and VIII show the ligand basis set dependence of σ<sup>dia</sup> and σ<sup>para</sup>, respectively. It is observed that the diamagnetic shielding constant is completely basis set independent. In contrast, the paramagnetic shielding constants are basis set dependent as shown in Table VIII. In NbF<sub>6</sub><sup>-</sup>, the changes in the d and p contributions are +168 and -22 ppm, respectively, and in NbCl<sub>6</sub><sup>-</sup>, +474 and -340 ppm, respectively. Although the paramagnetic shielding constants are thus slightly dependent on the basis set quality, the MIN set gives reasonable values compared to the SVP set. The chemical shifts are deviating at most by about 120 ppm. It is interesting to note that the difference between the MIN and SV sets is larger than that between the MIN and SVP sets. Therefore, we can safely conclude that the calculations with the MIN set for the ligands are reliable for this series of complexes.

**Registry No.** NbF<sub>6</sub><sup>-</sup>, 16918-69-7; NbF<sub>5</sub>Cl<sup>-</sup>, 32992-48-6; *trans*-NbF<sub>4</sub>Cl<sub>2</sub><sup>-</sup>, 32992-51-1; *cis*-NbF<sub>4</sub>Cl<sub>2</sub><sup>-</sup>, 32992-52-2; *mer*-NbF<sub>3</sub>Cl<sub>3</sub><sup>-</sup>, 32982-76-6; *fac*-NbF<sub>3</sub>Cl<sub>3</sub><sup>-</sup>, 32982-72-2; *trans*-NbF<sub>2</sub>Cl<sub>4</sub><sup>-</sup>, 32982-74-4; *cis*-NbF<sub>2</sub>Cl<sub>4</sub><sup>-</sup>, 32992-54-4; NbFCl<sub>5</sub><sup>-</sup>, 32982-78-8; NbCl<sub>6</sub><sup>-</sup>, 21640-06-2; NbCl<sub>5</sub>Br<sup>-</sup>, 34373-30-3; *trans*-NbCl<sub>4</sub>Br<sub>2</sub><sup>-</sup>, 68422-25-3; *cis*-NbCl<sub>4</sub>Br<sub>2</sub><sup>-</sup>, 40354-71-0; *mer*-NbCl<sub>3</sub>Br<sub>3</sub><sup>-</sup>, 68422-26-4; *fac*-NbCl<sub>3</sub>Br<sub>3</sub><sup>-</sup>, 40354-72-1; *trans*-NbCl<sub>2</sub>Br<sub>4</sub><sup>-</sup>, 68422-24-2; *cis*-NbCl<sub>2</sub>Br<sub>4</sub><sup>-</sup>, 40354-73-2; NbClBr<sub>5</sub><sup>-</sup>, 34371-96-5; NbBr<sub>6</sub><sup>-</sup>, 32965-80-3.