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## Theoretical Study on the Metal NMR Chemical Shift. Molybdenum Complexes

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The  $^{95}\text{Mo}$  NMR chemical shift of the molybdenum complexes  $\text{MoO}_{4-n}\text{X}_n^{2-}$  ( $\text{X} = \text{S}, \text{Se}; n = 0-4$ ) is studied theoretically with the ab initio molecular orbital method. The calculated results are in quite good agreement with experiments, showing the reliability of the method used in this series of studies. The Mo chemical shift mainly reflects the change in the valence 4d orbitals of molybdenum caused by ligand substitution. A perturbation theoretical analysis reveals that this change is dictated by the stabilization of the unoccupied 4d $\sigma^*$  and 4d $\pi^*$  orbitals by the participation of the ligand orbitals. We then predict that the Mo chemical shift will increase as the softness of the ligand increases. This trend is somewhat similar to that of the Mn chemical shift studied previously. We further predict inverse proportionality between the magnetically allowed d-d transition energy and the Mo chemical shift.

### Introduction

In this series of articles,<sup>1,2</sup> we are studying metal NMR chemical shifts with the ab initio molecular orbital method. The purpose is as follows: (1) to establish a reliable method of calculating metal NMR chemical shifts, which is useful for an assignment of experimental spectra; (2) to clarify electronic mechanisms and origins of metal chemical shifts and thereby to serve to understand and predict a trend in the observed chemical shifts.

We have studied so far the metal chemical shifts of the complexes of the metals Cu, Ag, Zn, Cd, Sn, Ti, and Mn.<sup>1,2</sup> The calculated values were in fairly good agreement with experiment. The predominant term is the paramagnetic term. The electronic mechanism of the chemical shifts is somewhat different between the d<sup>10</sup>s<sup>1-2</sup>p<sup>0</sup> (Cu, Ag, Zn, Cd, Sn) and d<sup>5</sup> (Mn) metals. For the d<sup>10</sup> metal complexes, two mechanisms are important. One is the *d mechanism*, which is due to a hole in the metal d orbitals produced by electron-withdrawing ligands, and the other is the *p mechanism*, which is due to an electron in the outer valence p orbitals of the metal donated from ligands. For Zn and Cd complexes, the origin is the p mechanism, so that the chemical shift increases as the electron-donating ability of the ligand increases. For Cu complexes, it is the d mechanism, so that the chemical shift increases as the electron-withdrawing ability of a ligand increases. For Ag complexes, the two mechanisms are competitive. The difference in these mechanisms originates from the difference in the atomic energy levels of these metals. On the other hand, for the Mn complexes with half-filled d orbitals, the d contribution, arising from the d-d transitions in a perturbation theoretic view, is dominant. The effect of the ligand on the occupied and unoccupied d orbitals is controlled by the  $\pi$ -donating ability and/or the hardness of the ligand.

Molybdenum chemistry is of considerable interest, particularly in its catalytic and bioinorganic aspects. For example, nitrogenase, which fixes nitrogen in the atmosphere as ammonia, consists of a  $\text{MoS}_4^{2-}$  moiety.  $^{95}\text{Mo}$  NMR is thus utilized in various fields and much data have been accumulated.<sup>3-5</sup> However, there seems to be no systematic theoretical study that is quantitatively reliable

Table I. Geometrical Parameters Used in the Present Calculations

$r(\text{Mo-O})$	1.83 Å <sup>a</sup>	$r(\text{Mo-Se})$	2.27 Å <sup>b</sup>
$r(\text{Mo-S})$	2.15 Å <sup>a</sup>	bond angle	109.47°

<sup>a</sup>Reference 11. <sup>b</sup>Optimized in this study.

and serves at the same time to understand the trends in observed chemical shifts. We study in this paper the  $^{95}\text{Mo}$  chemical shift of some mononuclear molybdenum complexes with the ab initio molecular orbital method adopted in this series of studies.<sup>1</sup> We are especially interested in the role of the d electrons of molybdenum since their importance is expected from the half-filled nature of the atomic ground state. This expectation is based on the previous results for the Mn complexes.<sup>1b</sup>

### Method

Molybdenum complexes studied here are the six complexes  $\text{MoO}_{4-n}\text{S}_n^{2-}$  ( $n = 0-4$ ) and  $\text{MoSe}_4^{2-}$ . The experimental data of the chemical shifts for these complexes are reported in water and  $\text{CH}_3\text{CN}$  solution by Lutz et al.<sup>4</sup> and by Gheller et al.<sup>5</sup> As they mentioned, the effect of replacing a hard ligand (oxygen) with a softer one (sulfur and selenium) is quite interesting in that it causes a regular change in the chemical shift.

The chemical shift is a difference between the magnetic shielding constants of a complex and a reference.

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

The magnetic shielding constant can be divided into two terms, a diamagnetic term  $\sigma^{\text{dia}}$  and a paramagnetic term  $\sigma^{\text{para}}$

$$\sigma = \sigma^{\text{dia}} + \sigma^{\text{para}} \quad (2)$$

where  $\sigma^{\text{dia}}$  and  $\sigma^{\text{para}}$  are the first- and second-order terms, respectively, in the perturbation theory. We calculate here chemical shifts by the finite perturbation method,<sup>6</sup> which has been shown to be more reliable than the conventional sum-over-state perturbation method.<sup>7</sup> We use the HONDOG program<sup>8</sup> modified for this purpose. More details were described in our previous paper.<sup>1a</sup>

The basis set of calculations are (16s10p7d)/[6s4p3d] plus diffuse p functions ( $\zeta = 0.083, 0.026$ ) for molybdenum and (6s3p)/[3s2p] for oxygen, both being due to Huzinaga et al.<sup>9</sup> For sulfur and selenium ligands, the effective core potential (ECP) and the valence basis set (3s3p)/[2s2p] of Wadt and Hay<sup>10</sup> are used. These basis sets are all of double- $\zeta$  quality. The adaptability of the ECP method for ligands will be discussed in the Appendix in comparison with all-electron calculations.

Table I summarizes the bond lengths used in this study. The Mo-O and Mo-S distances are from experiments<sup>11</sup> and the Mo-Se distance is optimized for  $\text{MoSe}_4^{2-}$  in the present ab initio calculations. The change

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**Table II.** Diamagnetic and Paramagnetic Contributions (ppm) to the  $^{95}\text{Mo}$  Magnetic Shielding Constant and Their Breakdown into Core and Valence MO Contributions

molecule	$\sigma^{\text{dia}}$				$\sigma^{\text{para}}$				$\sigma^{\text{tot}}$		exptl <sup>a</sup> shift
	core	valence	tot.	shift	core	valence	tot.	shift	tot.	shift	
$\text{MoO}_4^{2-}$	3968	195	4163	0	-172	-5429	-5601	0	-1438	0	0
$\text{MoO}_3\text{S}^{2-}$	3958	190	4148	15	-34	-6236	-6269	668	-2121	683	497
$\text{MoO}_2\text{S}_2^{2-}$	3948	185	4132	31	122	-6933	-6810	1209	-2801	1367	1066
$\text{MoOS}_3^{2-}$	3938	180	4117	46	306	-7728	-7422	1821	-3305	1867	1654
$\text{MoS}_4^{2-}$	3928	175	4102	60	505	-8443	-7938	2337	-3835	2397	2258
$\text{MoSe}_4^{2-}$	3928	169	4097	66	668	-9820	-9152	3550	-5055	3616	3339

<sup>a</sup>Reference 5.**Table III.** AO Contribution to the Diamagnetic Term of the Mo Shielding Constant (ppm)

molecule	molybdenum				ligand				$\sigma^{\text{dia}}$
	s	p	d	tot.	O	S	Se	tot.	
$\text{MoO}_4^{2-}$	1967	1454	562	3983	45			180	4163
$\text{MoO}_3\text{S}^{2-}$	1968	1454	564	3986	45	27		161	4147
$\text{MoO}_2\text{S}_2^{2-}$	1969	1454	566	3989	44	27		143	4132
$\text{MoOS}_3^{2-}$	1970	1454	569	3992	44	27		125	4117
$\text{MoS}_4^{2-}$	1970	1454	571	3996		27		107	4103
$\text{MoSe}_4^{2-}$	1969	1455	574	3998			25	99	4097

in the bond length in the mixed-ligand complex is neglected. All the bond angles are assumed to be tetrahedral.

### Comparison between Theoretical and Experimental Values

The results of calculations for the  $^{95}\text{Mo}$  magnetic shielding constants  $\sigma$  are summarized in Table II. Figure 1 shows the correlation between the theoretical and experimental<sup>5</sup> values of the chemical shift. The reference compound is  $\text{MoO}_4^{2-}$ . The plus sign in the chemical shift denotes that it is a downfield shift as is understood from the definition of  $\delta$  given by eq 1.

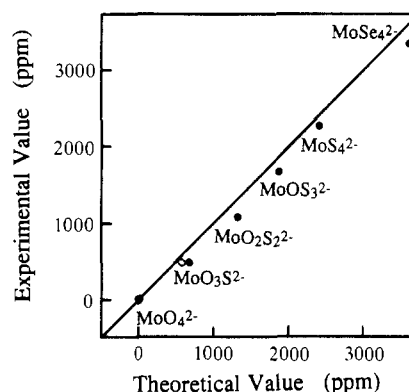
We see that the theoretical values are in quite good agreement with the experimental ones. The present theory tends to overestimate the experimental values, though the difference is at most 140–300 ppm. We therefore conclude that the method used in this study is reliable for the calculation of Mo chemical shifts. Largest and second largest deviations are for  $\text{MoO}_2\text{S}_2^{2-}$  and  $\text{MoSe}_4^{2-}$ , respectively. Two reasons are considered for this deviation. One is the geometry and the other is the use of the ECP method for the S and Se ligands. For  $\text{MoO}_2\text{S}_2^{2-}$ , the assumption of the tetrahedral geometry may be wrong, and for  $\text{MoSe}_4^{2-}$ , the optimized geometry due to the present SCF calculations may include some amount of error. The use of the ECP method for the ligands, S and Se, causes an overestimate of the chemical shift, as shown in the Appendix. For  $\text{MoO}_3\text{S}^{2-}$ , the Mo chemical shift calculated with and without the ECP approximation for the S atom is 683 ppm and 591 ppm, respectively, in comparison with the experimental value, 497 ppm. The open circle in Figure 1 shows the result of the all-electron calculation.

It is worth noting that the present calculations are performed only within the Hartree–Fock level of approximations and that the electron correlation and the relativistic effect for the Mo atom are completely neglected. A good correlation between theory and experiment, shown in Figure 1, suggests that these effects are small or more probably cancel each other. Furthermore, we expect that the solvent effect should be similar among the complexes treated here. The theoretical result indicates a regular change in the electronic structure as the ligand O is replaced by S, because of an almost equal interval in Figure 1.

### Analysis of the Magnetic Shielding Constants

The calculated magnetic shielding constants  $\sigma$  of the complexes are collected in Table II, where each of them is divided into diamagnetic  $\sigma^{\text{dia}}$  and paramagnetic  $\sigma^{\text{para}}$  terms. Though the absolute values of  $\sigma^{\text{dia}}$  and  $\sigma^{\text{para}}$  are comparable, the chemical shift is dominantly due to  $\sigma^{\text{para}}$  as easily seen from the shift value.

In Table II, the terms of  $\sigma^{\text{dia}}$  and  $\sigma^{\text{para}}$  are further analyzed into the contributions of the core and valence MO's. For the diamagnetic term, the core MO contributions are dominant but they are almost constant. For the paramagnetic term, the main contribution is from the valence MO's, and this contribution changes



**Figure 1.** Comparison between theory and experiments for the  $^{95}\text{Mo}$  chemical shift. The open circle is the result obtained without using the ECP method for the sulfur ligand. (See Appendix.)

in the same way as the chemical shift. We therefore conclude that the change in the valence MO caused by a ligand substitution is the dominant factor of the molybdenum chemical shift.

Following eqs 10a and 10b of our previous paper,<sup>1a</sup> we break down the terms  $\sigma^{\text{dia}}$  and  $\sigma^{\text{para}}$  into the AO contributions like the Mulliken population analysis. Table III shows the Mo AO contributions and the ligand contributions to the diamagnetic term. It brings us to the same conclusion as our previous one.<sup>1</sup> Each component is almost constant despite of the substitution of the ligand; namely, a Pascal-rule-like formula<sup>1</sup> is satisfied for the diamagnetic term.

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

The free atom term calculated in this study is 3991 ppm, which is very close to the value 4000.64 ppm calculated independently for the Mo atom.<sup>12</sup> This equation is derivable from the Flygare–Goodisman formalism<sup>13</sup> in fixing the geometry, so that  $\sigma^{\text{dia}}$  is determined solely by a structural factor.

Table IV summarizes the AO analysis for  $\sigma^{\text{para}}$ . The contribution of the Mo s AO is not shown because it is identically zero, for the s AO does not have angular momentum. The p AO contribution is small, and the ligand contribution is almost negligible. The dominant contribution is from the d electrons, as expected from the half-filled d electron configuration of the molybdenum atom. We thus conclude that the change in the valence d orbitals of the molybdenum caused by the ligand sub-

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Table IV. AO Contribution to the Paramagnetic Term of the Mo Shielding Constant (ppm)

molecule	molybdenum			ligand				$\sigma^{\text{para}}$
	p	d	tot.	O	S	Se	tot.	
MoO <sub>4</sub> <sup>2-</sup>	703	4862	5565	8.9			35	5601
MoO <sub>3</sub> S <sup>2-</sup>	679	5566	6264	8.7	1.1		26	6269
MoO <sub>2</sub> S <sub>2</sub> <sup>2-</sup>	661	6127	6793	8.0	0.8		18	6810
MoOS <sub>3</sub> <sup>2-</sup>	671	6746	7413	7.7	0.5		9	7422
MoS <sub>4</sub> <sup>2-</sup>	700	7236	7936		0.4		2	7938
MoSe <sub>4</sub> <sup>2-</sup>	656	8489	9145			1.5	6	9151

stitution is the origin of the Mo chemical shift of the molybdenum complexes.

### Perturbation Theoretical Consideration and Expected Trends in Chemical Shift

We here consider the origin of the Mo chemical shift in more detail on the basis of the sum-over-state perturbation formula. We want to get a predictive picture of the electronic mechanism of the Mo chemical shift. According to the sum-over-state perturbation theory, the paramagnetic term  $\sigma^{\text{para}}$  is represented as

$$\sigma^{\text{para}}_{iu} = -\frac{\mu_0 e^2}{8\pi m^2} \sum_n \left[ \frac{\langle 0 | \sum_k r_k^{-3} L_{ki} | n \rangle \langle n | \sum_k L_{ku} | 0 \rangle + \langle 0 | \sum_k L_{ku} | n \rangle \langle n | \sum_k r_k^{-3} L_{ki} | 0 \rangle}{E_n - E_0} \right] \quad (4)$$

where  $|0\rangle$  and  $|n\rangle$  denote the ground- and excited-state wave functions, respectively, and  $E_0$  and  $E_n$  their energies. The subscripts  $i$  and  $u$  stand for directions, and  $r$  and  $L$  denote the distance from the origin and the angular momentum operator around the origin, i.e., the Mo nucleus. This equation consists of two terms: one is the integral term in the numerator, which depends on the electron distribution of the system, and the other is the excitation energy in the denominator. We examine which is more important as follows.

The integral term is examined in the following approximation; since the angular momentum operator is a one-electron operator, we consider, as  $|n\rangle$ , only one-electron excited configurations generated from the Hartree-Fock ground state. Then, eq 4 reduces to

$$\sigma^{\text{para}}_{iu} = -\frac{\mu_0 e^2}{8\pi m^2} \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \left[ \frac{\langle \varphi_i | \sum_k r_k^{-3} L_{ki} | \varphi_j \rangle \langle \varphi_j | \sum_k L_{ku} | \varphi_i \rangle + \langle \varphi_i | \sum_k L_{ku} | \varphi_j \rangle \langle \varphi_j | \sum_k r_k^{-3} L_{ki} | \varphi_i \rangle}{E_{i \rightarrow j} - E_0} \right] \quad (5)$$

where  $\varphi_i$  is the  $i$ th molecular orbital. The subscripts  $i$  and  $j$  run over occupied and unoccupied MO's, respectively. When we expand  $\varphi_i$  as a linear combination of atomic orbitals  $\chi_{\mu}$ , eq 5 becomes

$$\sigma^{\text{para}}_{iu} = -\frac{\mu_0 e^2}{8\pi m^2} \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \sum_{\mu\nu\lambda\rho} [C_{\mu i}^* C_{\nu i} C_{\rho j}^* C_{\lambda j}] \langle \chi_{\mu} | r^{-3} L_{i\lambda} | \chi_{\lambda} \rangle \times \langle \chi_{\rho} | L_{\rho\nu} | \chi_{\nu} \rangle + C_{\nu i}^* C_{\mu i} C_{\rho j}^* C_{\lambda j} \langle \chi_{\nu} | L_{\nu\mu} | \chi_{\mu} \rangle \langle \chi_{\lambda} | r^{-3} L_{i\lambda} | \chi_{\mu} \rangle / (E_{i \rightarrow j} - E_0) \quad (6)$$

In eq 4, the summation must be taken to all the one-electron excited configurations and in eq 6 to all the occupied and unoccupied orbitals. However, for molecules of  $T_d$  symmetry, only the excited states having  $T_1$  symmetry give nonzero contributions. As we already know that the valence d contribution is predominant for the Mo chemical shift, it is assured that the most important excitations are from the occupied  $4d\sigma$  and  $4d\pi$  orbitals to the unoccupied  $4d\sigma^*$  and  $4d\pi^*$  orbitals. We, therefore, have examined the magnitude of the numerator of eq 6, using the coefficients of these MO's obtained in the present calculations. The results indicate that the differences in the numerator among the Mo complexes studied here are not large. We therefore conclude that the numerator of the above equation does not explain the large change in the Mo chemical shift studied here.

We next examine the excitation energy term in the denominator. The orbital energy diagram of the Mo complexes is shown in Figure 2, where the MO's whose natures are the same are connected by dotted lines. Though most MO's do not shift much

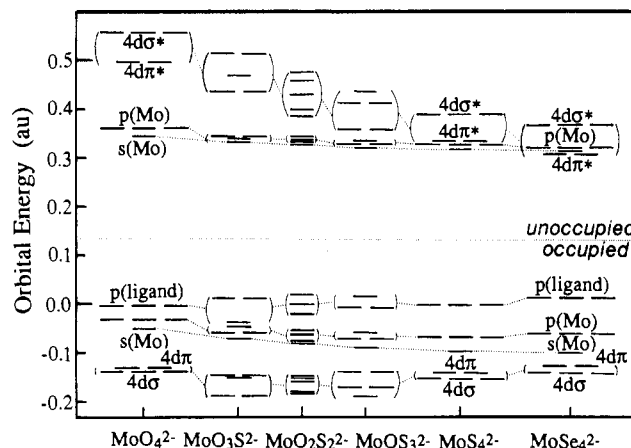


Figure 2. Orbital energy diagrams for the Mo complexes.

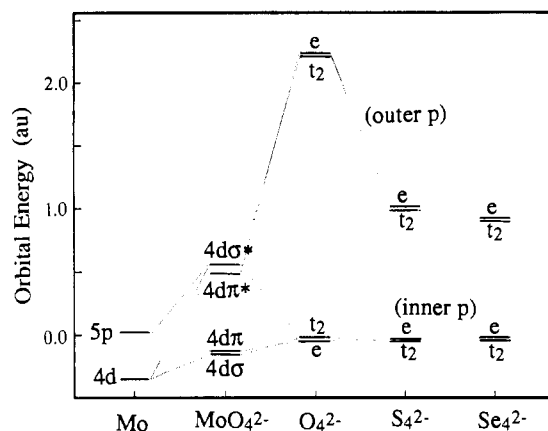


Figure 3. Orbital correlation diagram for the MoL<sub>4</sub><sup>2-</sup> complexes (L = O, S, Se).

along with the change in the ligand, the  $4d\sigma^*$  and  $4d\pi^*$  MO's in the unoccupied region are largely and regularly stabilized in replacing oxygen (hard ligand) with sulfur or selenium (soft ligand). This leads to a decrease in the energies of the excitations from the  $4d\sigma$  and  $4d\pi$  MO's to the  $4d\sigma^*$  and  $4d\pi^*$  MO's. Since the energy denominator of eq 4 thus decreases with increasing softness of the ligand, the Mo chemical shift increases with increasing softness of the ligand. Here, we come to the next question: Why are the  $4d\sigma^*$  and  $4d\pi^*$  MO's stabilized as the softness of the ligand increases?

To investigate the nature of the  $4d\sigma^*$  and  $4d\pi^*$  MO's, we show in Figure 3 the correlation diagram between the AO's of the Mo atom and the MO's of the O<sub>4</sub><sup>2-</sup> ligand (supermolecule) to form the MO's of the complex MoO<sub>4</sub><sup>2-</sup>. In addition, the MO's of the S<sub>4</sub><sup>2-</sup> and Se<sub>4</sub><sup>2-</sup> ligands are also shown in this figure. The structure of the ligand supermolecule is the same as that of the complex MoL<sub>4</sub><sup>2-</sup> except that the Mo atom is missing. In Figure 3, we have shown only those MO's that are pertinent to the following consideration.

We see that the  $4d\sigma^*$  and  $4d\pi^*$  MO's consist of the Mo 4d orbitals and the two kinds of p orbitals of the ligands, which consist of the inner and outer p GTO's of the double- $\zeta$  basis. In the supermolecule, the unoccupied t<sub>2</sub> and e orbitals (outer p orbitals) are greatly stabilized as the ligand becomes softer, though the

**Table V.** Comparison of the All-Electron (AE) and ECP Methods for Sulfur in the Calculation of the Mo Magnetic Shielding Constants of  $\text{MoO}_3\text{S}^{2-}$  (ppm)

	$\sigma^{\text{dia}}$			core	$\sigma^{\text{para}}$		$\sigma$		$\sigma^{\text{expt}}$ shift
	core	valence	tot.		valence	tot.	tot.	shift	
ECP (1)	3958	190	4148	-34	-6236	-6269	-2121	683	497
AE (2)	4002	190	4191	-30	-6190	-6220	-2029	591	497
2 - 1	44	0	43	4	46	49	92	-92	

**Table VI.** Comparison of the All-Electron (AE) and ECP Methods for Sulfur in the AO Contributions to the Diamagnetic Term of the Mo Shielding Constant of  $\text{MoO}_3\text{S}^{2-}$  (ppm)

	molybdenum				ligand			$\sigma^{\text{dia}}$ tot.
	s	p	d	tot.	O	S	tot.	
ECP (1)	1967	1454	564	3986	45	27	161	4147
AE (2)	1966	1454	565	3985	45	72	205	4191
2 - 1	-1	0	1	-1	0	45	44	44

occupied  $t_2$  and e orbitals (inner p orbitals) scarcely change in orbital energy. The outer p orbitals come to interact with the  $4d\sigma^*$  and  $4d\pi^*$  orbitals and stabilize these MO's, as the ligand is changed from O to S and Se. We have confirmed that the weight of the outer p orbital in the  $4d\sigma^*$  and  $4d\pi^*$  MO's increases as the ligand is substituted from O to S and to Se. Thus, we conclude that the stabilization of the  $4d\sigma^*$  and  $4d\pi^*$  MO's is caused by the participation of the outer p orbitals of the ligand.

As seen from Figure 3, the energy difference between the inner and outer p orbitals decreases as the softness increases. This is natural since the softness is parallel to the easiness in the response for a given perturbation such as chemical reactions. Such response should become easier as the HOMO-LUMO separation becomes smaller.

We note that the outer p orbitals mentioned above are mainly composed of the more diffuse p orbitals within the split valence basis set. It is not the Rydberg ( $n + 1$ )p orbital since we did not use any Rydberg basis set. It should be noted, however, that the Rydberg excitation energy for the excitation  $np(\text{valence}) \rightarrow (n + 1)p(\text{Rydberg})$  decreases as increasing softness of the ligands: 10.74 eV for O, 7.87 eV for S, and 7.35 eV for Se.<sup>14</sup> This is the same trend as that seen in Figure 3.

On the basis of the above analysis, we predict that the Mo chemical shift of these molybdenum complexes should be inversely proportional to the energy of the excitations from the  $4d\sigma$  and  $4d\pi$  MO's to the  $4d\sigma^*$  and  $4d\pi^*$  MO's. For the complexes of  $T_d$  symmetry, however, the optically allowed transition is not allowed for the magnetic transition under consideration. Though some low-lying spectra are observed<sup>15</sup> for the molybdenum complexes studied here, the inverse proportionality is not observed against the chemical shift. We have investigated the magnetically allowed d-d transitions of these complexes by using a reliable ab initio theory for excited states.<sup>16</sup>

Jameson and Mason described in their review<sup>17</sup> that the chemical shifts of these molybdenum complexes may be understood in terms of  $(\sigma + \pi) \rightarrow \pi^*$  charge circulation. This view would have something in common with the present theoretical conclusion, though their reasoning seems to be entirely different from the present one. Freeman et al.<sup>18</sup> have observed, for some Co complexes, a good correlation between the lowest excitation energy in the experimental spectra and the chemical shift.<sup>19</sup> This is reasonable because the d-d transition is lowest in these complexes.

**Table VII.** Comparison of All-Electron (AE) and ECP Methods for Sulfur in the AO Contributions to the Paramagnetic Term of the Mo Shielding Constant of  $\text{MoO}_3\text{S}^{2-}$  (ppm)

	molybdenum			ligand			$\sigma^{\text{para}}$ tot.
	p	d	tot.	O	S	tot.	
ECP (1)	-677	-5566	-6243	-9	-1	-26	-6269
AE (2)	-659	-5534	-6193	-9	-1	-26	-6220
2 - 1	20	32	50	0	0	0	49

### Concluding Remarks

The present theoretical study for the Mo NMR chemical shifts in the complexes,  $\text{MoO}_{4-n}\text{X}_n^{2-}$  ( $n = 0-4$ ; X = S, Se) has led to the conclusions summarized as follows.

(1) The ab initio molecular orbital method used here is reliable to investigate the Mo NMR chemical shift. It reproduces the experimental results fairly well (Figure 1).

(2) The paramagnetic term is the dominant factor of the chemical shift (Table II).

(3) The change in the valence d orbitals of the molybdenum caused by the ligand substitution is reflected in the chemical shift of these complexes (Tables II and IV).

(4) The excitations from the  $4d\sigma$  and  $4d\pi$  MO's to the  $4d\sigma^*$  and  $4d\pi^*$  MO's are the most important terms in the sum-over-state perturbation formula of the chemical shift.

(5) The softer a ligand is, the more stabilized are the  $4d\sigma^*$  and  $4d\pi^*$  MO's and the smaller is the excitation energy from the  $4d\sigma$  and  $4d\pi$  MO's to the  $4d\sigma^*$  and  $4d\pi^*$  MO's. This change leads to an increase in the chemical shift.

(6) The stabilization of the  $4d\sigma^*$  and  $4d\pi^*$  MO's is due to the stabilization and the mixing of the outer p orbitals of the ligands. As the ligand becomes softer, its outer p orbitals are stabilized, so that the Mo chemical shift increases.

(7) We expect an inverse parallelism between these d-d\* excitation energies and the Mo chemical shift. Since the transitions  $t_2(4d\sigma) \rightarrow t_2(4d\sigma^*)$ ,  $t_2(4d\sigma) \rightarrow e(4d\pi^*)$ , and  $e(4d\pi) \rightarrow t_2(4d\sigma^*)$  involve optically allowed transitions as well, we await an experimental confirmation of the inverse linearity.

After submission of this manuscript, the letter by Combariza et al.<sup>20</sup> has appeared. They have reported ab initio calculations of the chemical shifts of the same Mo complexes as studied here except for  $\text{MoSe}_4^{2-}$ . Their calculations are due to the LORG method<sup>21</sup> with the use of the basis sets and geometries somewhat different from the present ones.

**Acknowledgment.** We thank Prof. J. H. Enemark for his kind communication of a large number of experimental data on the Mo chemical shift.<sup>3</sup> The calculation was performed with FACOM M780 and HITAC M680H computers at the Data Processing Center of Kyoto University and the Institute for Molecular Science, respectively. This study has partially been supported by a Grant in Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan, and by the Kurata Foundation.

### Appendix

In this study, we have adopted the effective core potential (ECP) approximation for the heavier ligands S and Se. Here, we examine the order of the error caused by this approximation by comparing it with the all-electron (AE) calculations. The AE basis set for sulfur atom is composed of the valence AO set used in the ECP

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method<sup>10</sup> and the core AO set taken from Huzinaga's (9s6p)/[3s2p] basis.<sup>9</sup> Tables V-VII show the comparative results for MoO<sub>3</sub>S<sup>2-</sup>. The analyses are the same as those in Tables II-IV.

The Mo chemical shift of MoO<sub>3</sub>S<sup>2-</sup> is 683 ppm by the ECP approximation and 591 ppm by the AE calculation in comparison with the experimental value 497 ppm. The error is 92 ppm in which 43 ppm is due to  $\sigma^{\text{dia}}$  and 49 ppm to  $\sigma^{\text{para}}$ . In  $\sigma^{\text{dia}}$ , the error

is entirely due to the sulfur ligand contribution  $\sigma_s$  in eq 3. In  $\sigma^{\text{para}}$ , the error is included in the Mo p and d AO contributions. Though the AE calculation gives a better agreement with the experimental value, the error, 92 ppm, is small in comparison with the range of the chemical shifts, ~3000 ppm, studied in this paper. We therefore conclude that the ECP approximation adopted here causes little effect on the results of the present study.

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## Kinetics of Oxidation of Tetracyanonickelate(II) by Chlorine Monoxide, Chlorine, and Hypochlorous Acid and Kinetics of Chlorine Monoxide Formation

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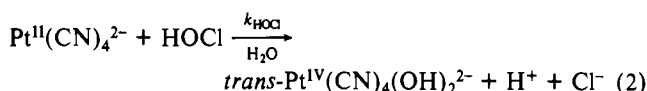
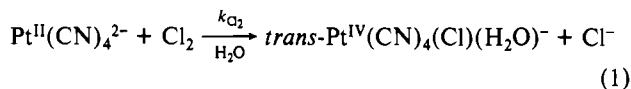
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Oxidation of Ni<sup>II</sup>(CN)<sub>4</sub><sup>2-</sup> by aqueous chlorine proceeds by three parallel pathways via Cl<sub>2</sub>O, Cl<sub>2</sub>, and HOCl to yield *trans*-Ni<sup>III</sup>(CN)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup>:  $d[\text{Ni(III)}]/dt = 2(k_{\text{Cl}_2\text{O}}[\text{Cl}_2\text{O}] + k_{\text{Cl}_2}[\text{Cl}_2] + k_{\text{HOCl}}[\text{HOCl}]][\text{Ni}^{\text{II}}(\text{CN})_4^{2-}]$ . The values of the second-order rate constants (M<sup>-1</sup> s<sup>-1</sup>; 25.0 °C;  $\mu = 0.10$  M) for oxidations by Cl<sub>2</sub>O, Cl<sub>2</sub>, and HOCl are  $1.3 \times 10^7$ ,  $3.2 \times 10^5$ , and 0.5, respectively. The proposed mechanism involves the formation of a nickel(IV) intermediate by Cl<sup>+</sup> transfer to nickel(II) in the rate-determining step. This is followed by a rapid electron transfer between the nickel(IV) intermediate and Ni<sup>II</sup>(CN)<sub>4</sub><sup>2-</sup> to give the final nickel(III) product. When the Cl<sub>2</sub>O path predominates and higher concentrations of Ni<sup>II</sup>(CN)<sub>4</sub><sup>2-</sup> are used, the formation of Cl<sub>2</sub>O (catalyzed by acetic acid) becomes rate limiting:  $d[\text{Cl}_2\text{O}]/dt = (k_2 + k_3[\text{HOAc}])[\text{HOCl}]^2$  where  $k_2$  is 0.12 M<sup>-1</sup> s<sup>-1</sup> and  $k_3$  is 280 M<sup>-2</sup> s<sup>-1</sup>. Under these conditions the direct HOCl oxidation of Ni<sup>II</sup>(CN)<sub>4</sub><sup>2-</sup> also contributes to the appearance of nickel(III).

### Introduction

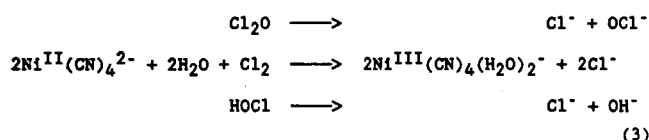
*trans*-Ni<sup>III</sup>(CN)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> can be formed by either chemical or electrochemical oxidation of Ni<sup>II</sup>(CN)<sub>4</sub><sup>2-</sup> in aqueous solution.<sup>1</sup> The Ni(III) complex is more stable in acidic than in basic solution. However, its rate of decomposition in acid increases in the presence of HCN,<sup>2</sup> and the HCN concentration in turn depends on the rate of dissociation<sup>3,4</sup> of Ni<sup>II</sup>(CN)<sub>4</sub><sup>2-</sup>. Hence, the rate of decomposition of Ni(III) depends on the efficiency of the Ni<sup>II</sup>(CN)<sub>4</sub><sup>2-</sup> oxidation. Electrochemical oxidation using bulk electrolysis gives poor oxidation efficiency ( $\approx 50\%$ ). In contrast, chemical oxidation using aqueous chlorine<sup>2</sup> gives quantitative oxidation of Ni(II) to Ni(III), and it also destroys any free HCN or CN<sup>-</sup> in the solution.<sup>5,6</sup>

A variety of oxidation reactions between metal-ligand complexes and chlorine species have been studied<sup>7-9</sup> and reviewed.<sup>10</sup> Part of the focus of these studies was to determine whether the mechanism involved a one- or two-electron oxidation. One such study is the oxidation of Pt<sup>II</sup>(CN)<sub>4</sub><sup>2-</sup> by chlorine (Cl<sub>2</sub>) and by hypochlorous acid (HOCl) to form the platinum(IV) complexes in eqs 1 and 2, where the value of  $k_{\text{Cl}_2}$  is  $1.08 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup> and



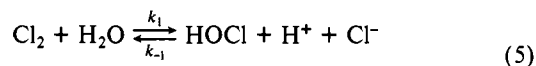
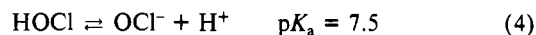
the value of  $k_{\text{HOCl}}$  is  $97.9$  M<sup>-1</sup> s<sup>-1</sup> ( $\mu = 1.0$  M at 25.0 °C).<sup>9</sup> Since Pt<sup>II</sup>(CN)<sub>4</sub><sup>2-</sup> and Ni<sup>II</sup>(CN)<sub>4</sub><sup>2-</sup> are similar low-spin d<sup>8</sup> complexes,

it is of interest to compare the oxidation kinetics of their reactions with Cl<sub>2</sub> and HOCl. In the present work, we find that chlorine monoxide (Cl<sub>2</sub>O) is even more effective than Cl<sub>2</sub> or HOCl in the oxidation of Ni<sup>II</sup>(CN)<sub>4</sub><sup>2-</sup> to *trans*-Ni<sup>III</sup>(CN)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup>, and three parallel paths occur (eq 3). The reaction rates are first order

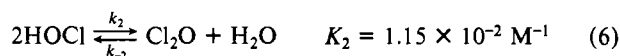


in Ni<sup>II</sup>(CN)<sub>4</sub><sup>2-</sup> and first order in each of the chlorine species. The pathway that predominates depends on the concentration of chlorine species, the Cl<sup>-</sup> concentration, and the solution acidity. In the proposed mechanism, all three pathways involve a two-step process with formation of a highly reactive intermediate in the rate-determining step. This intermediate may be either a nickel(IV) complex or a \*Cl radical. However, thermodynamic considerations and the similarity of the kinetic results to those of an analogous study of Pt<sup>II</sup>(CN)<sub>4</sub><sup>2-</sup> oxidation suggest that the nickel(IV) intermediate is more probable.

**Chlorine Equilibria.** The major equilibria of aqueous chlorine species are given in eqs 4-6. The decomposition reactions of OCl<sup>-</sup> and HOCl to form ClO<sub>2</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup> are too slow<sup>11,12</sup> to interfere with studies of the Ni<sup>II</sup>(CN)<sub>4</sub><sup>2-</sup> and aqueous chlorine reactions.



$$K_1 = 7.2 \times 10^{-4} \text{ M}^2$$



The pK<sub>a</sub> value for the dissociation of HOCl is 7.5 ( $\mu = 0$  M at 25 °C).<sup>13</sup> Equation 5 has been investigated in detail by using relaxation,<sup>14</sup> stopped-flow,<sup>9</sup> and continuous-flow techniques.<sup>15,16</sup>

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