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Electronic Origin of ^{95}Mo NMR Chemical Shifts in Molybdenum Complexes. Relationship between Excitation Energy and Chemical Shift

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From the previous ab initio theoretical study on the electronic origin of the ^{95}Mo NMR chemical shifts of the complexes $MoO_{4-n}S_n^{2-}$ (n = 0–4) and $MoSe_4^{2-}$, it became clear that the d–d* excitations are the dominant factors in the perturbation theoretic point of view (Nakatsuji, H.; Sugimoto, M. *Inorg. Chem.* **1990**, *29*, 1221). This suggests an inverse proportionality between the Mo chemical shifts and the excitation energies. In the present paper, this relationship is examined by calculating the magnetically allowed excitation energies by the SAC–CI (symmetry-adapted cluster–configuration interaction) theory. The results show a nice linear relationship between the Mo chemical shifts and the energies of the excitations from the 4dσ MO to the 4dπ* MO. This result quantitatively supports the previously reported mechanism of the Mo chemical shifts.

Introduction

Recently we have studied the electronic origin of the ^{95}Mo NMR chemical shifts of the molybdenum complexes $MoO_{4-n}S_n^{2-}$ (n = 0–4) and $MoSe_4^{2-}$,[1] by an ab initio finite perturbation method.[2] We have found that the paramagnetic term σ^{para} dominates the Mo chemical shifts rather than the diamagnetic term σ^{dia} and that the chemical shifts depend on the energies of the excitations from the 4dσ and 4dπ MOs to the 4dσ* and 4dπ* MOs, i.e., d–d* transitions. Consequently, the result seems to suggest that the chemical shift δ is inversely proportional to the d–d* excitation energy (ΔE)

$$\delta = A(1/\Delta E_{ref} - 1/\Delta E) = \alpha + \beta/\Delta E \qquad (1)$$

Here we assume that only one state mainly contributes to the magnetic shielding constants σ and that A is roughly constant among the complexes. The validity of the second assumption has been checked in the previous paper.[1]

This mechanism of the Mo chemical shift is basically due to the half-filled nature of the d subshell of the Mo atom ($d^5s^1p^0$). The mechanism of the Mn chemical shifts in $Mn(CO)_5X$ (X = H, CN, CH_3, Cl) was similar[3] because of the similar electronic configuration of the manganese atom ($d^5s^2p^0$). For the metals Cu, Ag, Zn, and Cd with the configurations $d^{10}s^{1-2}p^0$, different mechanisms have been elucidated as the electronic origin of the metal chemical shifts.[4] Combariza et al. have also recently reported ab initio calculations of the Mo chemical shifts.[5]

In this paper we theoretically examine the ΔE dependence of the Mo chemical shifts, namely whether the relationship of eq 1 holds or not, using the symmetry-adapted cluster–configuration interaction (SAC–CI) theory.[6,7] The SAC–CI theory has been shown to give excited states to a considerable accuracy within a reasonable amount of computations because of several theoretical reasons.[6-8] Since only magnetically allowed transitions can contribute to chemical shifts and since, in higher symmetry molecules, they are electric dipole forbidden and so not always observed in experiments,[9] we here calculate them by a reliable theoretical method for excited states.[10]

Computational Details

We calculate a number of excited states by the SAC–CI theory,[6,7] including the optically allowed and magnetically allowed states.[10] The basis sets used in this calculation are as follows: the relativistic effective core potential (ECP) with the valence (3s3p4d)/[3s2p3d] set for molybdenum and the ECP with the valence (3s3p)/[2s2p] sets for sulfur and selenium, all due to Wadt and Hay.[11] For oxygen, we use Huzinaga's (9s5p)/[3s2p] set.[12] The basis sets for molybdenum and oxygen are different from those used previously.[1] In the chemical shift calculations, the use of the ECP method for the Mo atom should be avoided since the ECP orbitals are quite different from all-electron orbitals in the core region, therefore causing a serious error.[4] However, in the calculation of excited states, the ECP method is preferable, since it includes, to some extent, the relativistic effects. For oxygen the present basis set is the same as that used in the calculation of the excited and ionized states of RuO_4 and OsO_4.[13]

In the SAC–CI calculations we take 12 occupied and 31 unoccupied MOs as active orbitals, and the dimensions of the Hamiltonian matrices to be diagonalized are 3000–8500 after configuration selection. More details of the SAC–CI calculations are described in ref 10, where we show the results for a number of low-lying excited states of the molybdenum complexes. The reliability of the calculated excitation energies is estimated from the average discrepancy from the experimental values, which is 0.20–0.32 eV in these molybdenum complexes.[10]

Electronic Origin of the ^{95}Mo Chemical Shift

We qualitatively showed in our previous paper[1] that in the molybdates $MoO_{4-n}S_n^{2-}$ (n = 0–4) and $MoSe_4^{2-}$ the chemical shifts arise from the variations in the energies of the excitations from the 4dσ and 4dπ MOs to the 4dσ* and 4dπ* MOs, i.e., d–d* transitions. This is based on the two facts: One is that the valence MOs, which mainly consist of the molybdenum 4d orbitals, contribute predominantly to the Mo chemical shifts. The other is that the energy levels of the 4dσ* and 4dπ* MOs are considerably affected by the ligand substitution, though those of the other MOs are not.

The paramagnetic term which was shown to be important for the Mo chemical shifts[1] is expressed in the perturbation theoretic form as

$$\sigma^{para}_{Mtu} = -\frac{e^2}{4m^2c^2}\sum_{n\neq 0}[\langle 0|\sum_j r_{Mj}{}^{-3}L_{Mjt}|n\rangle\langle n|\sum_j L_{ju}|0\rangle + \langle 0|\sum_j L_{ju}|n\rangle\langle n|\sum_j r_{Mj}{}^{-3}L_{Mjt}|0\rangle]/(E_n - E_0) \qquad (2)$$

where $|0\rangle$ and $|n\rangle$ denote the ground and the excited states, re-

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(1) Nakatsuji, H.; Sugimoto, M. *Inorg. Chem.* **1990**, *29*, 1221.

(2) (a) Cohen, H. D.; Roothaan, C. C. J. *J. Chem. Phys.* **1965**, *43*, 534. (b) Cohen, H. D. *Ibid.* **1965**, *43*, 3558; **1966**, *45*, 10. (c) Pople, J. A.; McIver, J. W.; Ostlund, N. S. *Chem. Phys. Lett.* **1967**, *1*, 465; *J. Chem. Phys.* **1968**, *49*, 2960. (d) Ditchfield, R.; Miller, D. R.; Pople, J. A. *Ibid.* **1970**, *53*, 613.

(3) Kanda, K.; Nakatsuji, H.; Yonezawa, T. *J. Am. Chem. Soc.* **1984**, *106*, 5888.

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(5) Combariza, J. E.; Enemark, J. H.; Barfield, M.; Facelli, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 7619. Since it was mentioned in this paper that the calculated magnetic shielding constant of CuCl in our previous paper[4] was almost certainly incorrect, we have recalculated it recently and obtained the same value as that reported in ref 4. So, we think that the value obtained by Combariza et al. is incorrect.

(6) Nakatsuji, H.; Hirao, K. *J. Chem. Phys.* **1978**, *68*, 2053.

(7) (a) Nakatsuji, H. *Chem. Phys. Lett.* **1978**, *59*, 362. (b) Nakatsuji, H. *Ibid.* **1979**, *67*, 329.

(8) Nakatsuji, H. *Theor. Chim. Acta* **1987**, *71*, 201.

(9) It is well-known that, e.g. in octahedral Co(III) complexes, d–d transitions to T_{1g} and T_{2g} states are successfully observed though they are originally electric dipole forbidden. In the case of MoS_4^{2-} and $MoSe_4^{2-}$, some observed peaks have also been assigned to the magnetically allowed transitions.

(10) Nakatsuji, H.; Saito, S. *J. Chem. Phys.*, in press.

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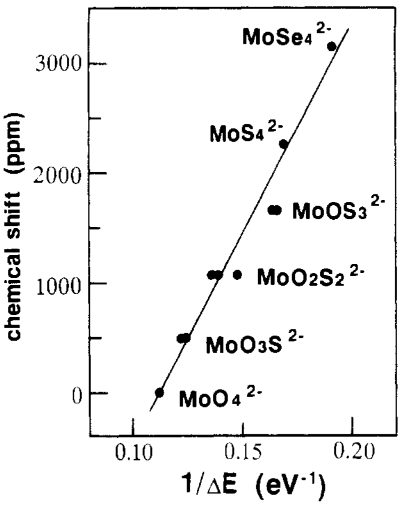

Figure 1. Relationship between the inverse of the lowest *magnetically allowed* d–d* excitation energies ΔE and the chemical shifts. The chemical shifts are the experimental values due to Gheller et al.[14] and the excitation energies are the SAC–CI theoretical values for the $4d\sigma \rightarrow 4d\pi^*$ transitions with the T_1 (T_d), $A_2 + E(C_{3v})$, and $A_2 + B_1 + B_2$ (C_{2v}) symmetries. The correlation factor is 0.987 in the least-squares fitting.[18]

spectively, L_{jt} is the angular momentum operator of the jth electron in the t direction, and the subscript M denotes the nucleus under consideration, which is here molybdenum. The summation is taken over all the excited states including continuous states. On the other hand, the electronic transition probability from the i state to the f state in the electromagnetic field is proportional to

$$P_{i\rightarrow f} = \left|\left\langle f\left|\frac{e}{m}\sum_j e^{i\mathbf{k}\cdot\mathbf{r}}(\mathbf{e}_{\mathbf{k},\gamma}\cdot\mathbf{p}_j)\right|i\right\rangle\right|^2 \qquad (3)$$

where $\mathbf{k}$ is a wave vector and $\mathbf{e}_{\mathbf{k},\gamma}$ is a unit vector that is orthogonal to $\mathbf{k}$. When we expand $e^{i\mathbf{k}\cdot\mathbf{r}}$ into the Taylor series

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i\mathbf{k}\cdot\mathbf{r} + ... \qquad (4)$$

and consider the case when $\mathbf{k}$ and $e_{\mathbf{k},\gamma}$ are parallel to the x and y axes, respectively, we obtain

$$\left\langle f\left|\frac{e}{m}\sum_j e^{i\mathbf{k}\cdot\mathbf{r}}(\mathbf{e}_{\mathbf{k},\gamma}\cdot\mathbf{p}_j)\right|i\right\rangle = \frac{i(E_f - E_i)}{\hbar}\langle f|\sum_j ey_j|i\rangle - \frac{ke(E_f - E_i)}{2\hbar}\langle f|\sum_j x_j y_j|i\rangle + \frac{ike}{2m}\langle f|\sum_j L_{jz}|i\rangle + ... \qquad (5)$$

where E_i and E_f are the energies of the i and f states, respectively. The first term represents the well-known electric dipole transition moment as observed in the usual experiments, and the second and third terms are related to electric quadruple and magnetic dipole transitions, respectively. Since the selection rule for the last term is identical with that of the numerator of eq 2, we understand that the magnetically allowed transitions from the ground state contribute to the chemical shift.

In the case of the T_d molecules (MoO_4^{2-}, MoS_4^{2-}, $MoSe_4^{2-}$), the excitations to the $^1T_1$ states are magnetically allowed because L_j belongs to the T_1 symmetry. The operator r belongs to the T_2 symmetry, so that the magnetically allowed transition is optically forbidden unless we consider vibronic coupling. For molecules with lower symmetries such as MoO_3S^{2-}, $MoOS_3^{2-}$ (C_{3v}), and $MoO_2S_2^{2-}$ (C_{2v}), the T_1 state splits into $A_2 + E$ (C_{3v}) and $A_2 + B_1 + B_2$ (C_{2v}) states, respectively, all of which are magnetically allowed.

The excited states contributing to the Mo chemical shift should therefore satisfy the following criteria: (i) the nature of the transition is mainly d–d*; (ii) the excitation from the ground state is magnetically allowed. In addition, we assume (iii) the excitation energy is as low as possible.

From the present calculations, the excitation satisfying conditions i–iii has been found to be that from the $4d\sigma$ MO to the $4d\pi^*$ MO. Although our calculations cover the excitation energy region up to 7.30 eV for $MoSe_4^{2-}$, for example, there are no other states whose main configurations consist of magnetically allowed d–d* transitions. In Figure 1, we show a plot of the experimental Mo chemical shifts δ observed by Gheller et al.[14] against $1/\Delta E$ of the energies ΔE calculated for the $4d\sigma \rightarrow 4d\pi^*$ excitations. For the molecules with lower symmetry, MoO_3S^{2-}, $MoOS_3^{2-}$, and $MoO_2S_2^{2-}$, the transition energies are for the transitions to the A_2 and E states for C_{3v} and to the A_2, B_1, and B_2 states for C_{2v}.[15] We summarize in Table I the calculated excitation energies ΔE and the observed chemical shifts.[14]

Table I. Observed Chemical Shifts and Magnetically Allowed $4d\sigma \rightarrow 4d\pi^*$ Excitation Energies Calculated by the SAC–CI Method

	theoret excitation energy,[a] eV	obsd chem shift,[b] ppm
MoO_4^{2-}	8.99 (T_1)	0
MoO_3S^{2-}	8.13 (A_2), 8.16 (E)	497
$MoO_2S_2^{2-}$	6.80 (B_2), 7.21 (B_1), 7.36 (A_2)	1066
$MoOS_3^{2-}$	6.05 (E), 6.08 (A_2)	1654
MoS_4^{2-}	5.95 (T_1)	2258
$MoSe_4^{2-}$	5.23 (T_1)	3145

[a] The symmetry of the excited state is shown in parentheses. [b] Reference 14.

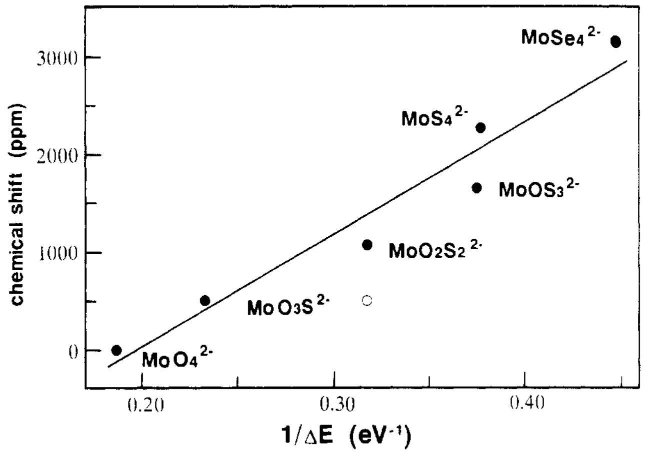

Figure 2. Relationship between the inverse of the lowest *optically allowed* transition energies ΔE and the chemical shifts. The energies and the chemical shifts were obtained experimentally by Müller et al.[17] and Gheller et al.,[14] respectively. The symmetries of the excited states are as follows: T_2 (MoO_4^{2-}, MoS_4^{2-}, $MoSe_4^{2-}$), A_1 or E (MoO_3S^{2-}), B_2 ($MoO_2S_2^{2-}$), E ($MoOS_3^{2-}$). The correlation factor is 0.972 in the least-squares fitting. The open circle corresponds to the observed first peak of 3.15 eV for MoO_3S^{2-} (See text and refs 10 and 17.)

Figure 1 clearly shows a nice linear relationship between the chemical shift δ and the inverse of the magnetically allowed $4d\sigma \rightarrow 4d\pi^*$ transition energy. This justifies the validity of the mechanism of the Mo chemical shift proposed in ref 1. The origin of the Mo chemical shift is attributed to the variations in the excitation energy of the magnetically allowed d–d* transition. Although eq 2 involves all the transitions with T_1 symmetry, the $4d\sigma \rightarrow 4d\pi^*$ transition is most important for the Mo chemical shifts.

Referring to Table I, we note that these d–d* transitions are rather high in energy. For example, in $MoSe_4^{2-}$, there are more than 15 excited states that are lower in energy than this T_1 state. Since the oxidation number of the central molybdenum atom of this complex is +6, many states corresponding to the electron-transfer excitations from the ligands to the molybdenum exist in the lower energy region.

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(15) The E states of C_{3v} molecules and the B_1 and B_2 states of C_{2v} molecules are both optically and magnetically allowed for the transitions from the totally symmetric ground state. For MoO_3S^{2-}, $MoOS_3^{2-}$, and $MoO_2S_2^{2-}$, these states under consideration are 3–4 eV higher than the lowest optically allowed states.[10]

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Although a linear relationship has been shown between chemical shifts and *lowest* excitation energies for octahedral Co(III) complexes,[16] we must note that chemical shifts are not always determined by lowest excited states. In Figure 2, we plot the Mo chemical shifts against the inverse of the lowest optically allowed transition energies observed by Müller et al.[17] Since these excitations do not correspond to the magnetically allowed transitions and since the nature of the excitations is not the d–d* excitation but the intramolecular CT transition,[10] the linearity is not so good as that in Figure 1. Actually, the correlation factors for Figures 1 and 2 in the least-squares fitting are 0.987 and 0.972, respectively.[18]

For MoO_3S^{2-}, we have pointed out[10] that the peak of the lowest excitation is not the first peak at 3.15 eV but the second one at 4.30 eV in the experimental spectra.[17] The SAC–CI calculations have given no peak near 3.15 eV for MoO_3S^{2-}, though they give fairly good agreements with the experimental spectra for the other molybdenum complexes.[10] We have shown[10] that the experimental spectra of MoO_3S^{2-} can be explained as a result of an overlap of the spectra of $MoO_2S_2^{2-}$ onto that of MoO_3S^{2-}. In addition to these results, Figure 2 provides additional evidence supporting the above conclusion; the open circle, corresponding to the observed first peak at 3.15 eV, deviates too much from the rough linear relation that the other complexes show.

The rough linear relation observed in Figure 2 is explained as follows. As studied in detail in ref 10, the lowest optically allowed transitions of the $MoO_{4-n}S_n^{2-}$ and $MoSe_4^{2-}$ complexes are the electron-transfer excitations from the ligands to the d* orbital. Since the occupied ligand levels are rather constant,[1,10] the lowest transitions reflect the level of the d* orbital, which is more sensitive to the ligand substitution. Since this d* orbital is common to the magnetically allowed d–d* transition, a rough parallelism arises between the lowest optically allowed and magnetically allowed transitions.

Summary

In this paper, we have calculated the lowest *magnetically allowed* $d\sigma$–$d\pi^*$ transition energies of the six molybdates $MoO_{4-n}S_n^{2-}$ ($n = 0$–4) and $MoSe_4^{2-}$ by the SAC–CI theory and discussed the relationship between the Mo chemical shift and the d–d* transition energy.

The nature of the excited states contributing to the chemical shifts should be magnetic dipole allowed, e.g., the excitation to $^1T_1$ states for T_d molecules. The excitation most important to the Mo chemical shift is shown to be $4d\sigma \rightarrow 4d\pi^*$. We have obtained a nice linear relationship by plotting the experimental chemical shifts against the reciprocal of the excitation energies. This confirms the validity of the origin of the ^{95}Mo NMR chemical shifts previously proposed.

Acknowledgment. The calculations were performed by the HITAC M680H and S820/80 computers at the Computer Center of the Institute for Molecular Science. This study was partially supported by Grant-in-Aids for Scientific Research from the Ministry of Education, Science, and Culture of Japan and by the Kurata Foundation.

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[18] The correlation factor in Figure 1 has been calculated by averaging the energies shown in Table I for the complexes MoO_3S^{2-}, $MoO_2S_2^{2-}$, and $MoOS_3^{2-}$.

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Electron-Impact and Flash-Vacuum Pyrolysis of Trivalent and Pentavalent Phosphorus Azides: Generation of Original Unsaturated Mono-, Di-, and Tricoordinated Phosphorus Cations

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Contrary to most azides, $[(i\text{-}Pr)_2N]_2P(S)N_3$ (**1**) and $[(i\text{-}Pr)_2N]_2PN_3$ (**4**) do not lose nitrogen subsequent to ionization. Instead, the loss of one azide radical appears to be more favorable, reflecting the capability of phosphorus to stabilize a positive charge. Simple cleavage reactions are the privileged decompositions of the molecular ions of $\mathbf{4}^{\bullet+}$, not only within the ion source but also within the field-free regions for metastable $\mathbf{4}^{\bullet+}$. Besides the unconventional dicoordinated divalent ($>P^+$) or tetravalent ($-P^+{\equiv}N$) phosphonium ions formed in these processes, original monocoordinated phosphonium $P^+{=}N-$ ions are also observed. A prominent rearrangement reaction differentiates the behavior of $\mathbf{1}^{\bullet+}$: immonium ions h are produced at low internal energy by loss of a phosphorus-containing radical, pointing out the stabilizing effect of sulfur. A similar conclusion arises from a flash-vacuum pyrolysis (FVP) study of **1** and **4**: formation of $(i\text{-}Pr)_2N{-}P{=}S$ (**6**) is observed at ca. 400–500 °C during the pyrolysis of **1**, while no significant phosphorus-containing product could be unambiguously identified for **4**. In both cases, diisopropylamine (**7**) and *N*-isopropyldimethylimine (**8**) were the main pyrolysis products. These results were derived from tandem mass spectrometry (MS/MS) experiments.

Introduction

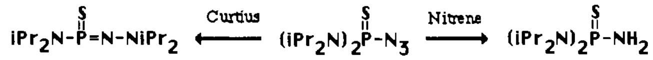
Much work has been devoted to organic azides[1] since the discovery of the Curtius reaction in 1890.[2] Thermolytic, photolytic, or acid-promoted rearrangement of aliphatic, aromatic, or heteroaromatic azides afford the corresponding carbon–nitrogen double-bonded compounds. Similarly, it has been shown that the Curtius rearrangement is effective for group 13 (B), group 14 (Si, Ge), and group 15 (P) azides (Scheme I).[3]

In addition to this behavior, competitive nitrene-type reactions sometimes occur, such as hydrogen abstraction or CH insertion.

Scheme I

$$R_nMN_3 \xrightarrow[\text{or } h\nu \text{ or } H^+]{\Delta} R_{n-1}M{=}N{-}R + N_2$$

Scheme II



$$\underset{\mathbf{2}}{iPr_2N{-}\overset{\overset{\displaystyle S}{\|}}{P}{=}N{-}NiPr_2} \xleftarrow{\text{Curtius}} \underset{\mathbf{1}}{(iPr_2N)_2\overset{\overset{\displaystyle S}{\|}}{P}{-}N_3} \xrightarrow{\text{Nitrene}} \underset{\mathbf{3}}{(iPr_2N)_2\overset{\overset{\displaystyle S}{\|}}{P}{-}NH_2}$$

Moreover, the phosphorus atom is an interesting model to study the scope and limitation of such rearrangements because of the

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