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Correlation between ^{95}Mo NMR chemical shifts and rate constants of oxygen atom transfer reactions of various *cis*-dioxobis(dithiocarbamato)molybdenum(VI) complexes with PPh_3

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Abstract

The ^{95}Mo NMR properties of *cis*-dioxomolybdenum(VI) complexes with various dithiocarbamates $[MoO_2(R_2dtc)_2]$ (R_2dtc^-: dithiocarbamates, $R=CH_3$, C_2H_5, i-C_3H_7, i-C_4H_9, C_6H_5, $C_6H_5CH_2$) have been investigated. The chemical shifts varied from $\delta=151$ ($R=CH_3$) to $\delta=216$ ($R=$i-C_3H_7) depending on the nature of the substituents on the dithiocarbamate ligands, and they were found to be in a good correlation with the rate constants for the oxygen atom transfer reaction between $[MoO_2(R_2dtc)_2]$ and triphenylphosphine in 1,2-$C_2H_4Cl_2$.

Keywords: ^{95}Mo NMR spectroscopy; Molybdenum complexes; Oxo complexes; Dithiocarbamate complexes

1. Introduction

High-valent oxomolybdenum complexes containing sulfur-donor ligands have received much attention as structural and reactivity models of the molybdenum site in oxomolybdenum enzymes [1]. Since Barral et al. reported that *cis*-dioxomolybdenum(VI) complexes with dithiocarbamate undergo an oxygen atom transfer reaction with PPh_3 [2], which is the mimic reaction catalyzed by oxomolybdenum enzymes, many types of oxomolybdenum(VI) complexes have been synthesized and the kinetic studies of the oxygen atom transfer reaction have been carried out by several workers [1]. However, further systematic study of the metal–ligand bonding of *cis*-dioxomolybdenum(VI) complexes is still required to clarify the mechanism of the oxygen atom transfer reaction.

The metal nuclear NMR spectroscopy of transition metal complexes is a useful method for the investigation of metal–ligand bondings, because it provides direct information of the electronic structure around the metal center of the complex. The influence of the ligand and coordination structure on the chemical shift has been discussed experimentally and theoretically [3]. Many problems are still left unsolved, and systematic studies are awaited.

We carried out ^{95}Mo NMR spectroscopy of *cis*-dioxomolybdenum(VI) complexes with various dithiocarbamates, $[MoO_2(R_2dtc)_2]$ (R_2dtc^-: dithiocarbamates, $R=CH_3$ (Me), C_2H_5 (Et), i-C_3H_4 (i-Pr), i-C_4H_9 (i-Bu), C_6H_5 (Ph), $C_6H_5CH_2$ (Bzyl)), and found that the shielding of the ^{95}Mo nucleus of $[MoO_2(R_2dtc)_2]$ is apparently influenced by the nature of the substituents R on the dithiocarbamate ligands, and that ^{95}Mo NMR chemical shifts correlate with the rate constants of the oxygen atom transfer reaction between $[MoO_2(R_2dtc)_2]$ and PPh_3.

2. Experimental

2.1. Materials

Sodium salts of dithiocarbamates R_2dtc^- ($R=$i-Pr, i-Bu, Bzyl, Ph) were prepared by literature methods

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[4,5]. Sodium salts of dimethyldithiocarbamate and diethyldithiocarbamate were purchased from Nacalai Tesque Inc. The complexes $[MoO_2(R_2dtc)_2]$ were prepared according to the literature methods [6,7].

2.2. ^{95}Mo NMR measurements

The ^{95}Mo NMR spectra were recorded on a Brücker AM-400FT-NMR at room temperature (296–298 K), with a pulse repetition time of 0.1 s. The pre-aqusition delay and number of the transient accumulated are 300 μs and 8000–1 017 000, respectively. The chemical shift reference is Na_2MoO_4 in H_2O/D_2O (4+1) at pH 11.

3. Results and discussion

The ^{95}Mo NMR spectrum of $[MoO_2(i\text{-}Pr_2dtc)_2]$ in $CHCl_3$ is shown in Fig. 1. The ^{95}Mo NMR spectrum of each $[MoO_2(R_2dtc)_2]$ in $CHCl_3$ exhibits only a single resonance as shown in Fig. 1. The ^{95}Mo NMR data are collected in Table 1.

The chemical shifts of $[MoO_2(Me_2dtc)_2]$ and $[MoO_2(Et_2dtc)_2]$ obtained in our work are consistent with the values ($\delta = 151$ for $[MoO_2(Me_2dtc)_2]$, $\delta = 176$ for $[MoO_2(Et_2dtc)_2]$) previously reported by Enemark and co-workers [8].

As shown in Table 1, the chemical shifts of $[MoO_2(R_2dtc)_2]$ varied from $\delta = 151$–216 depending on the nature of the substituents on the dithiocarbamates. Chemical properties of dithiocarbamate complexes are susceptible to the nature of the substituents on the dithiocarbamate ligands because of the existence of resonance forms described below [9].

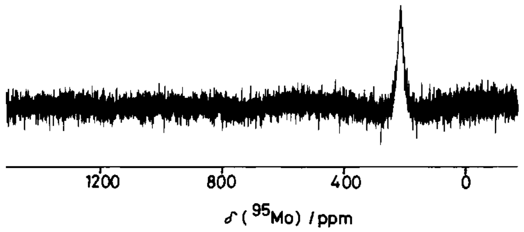
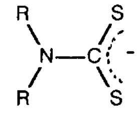
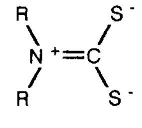


Fig. 1. ^{95}Mo NMR spectrum of $[MoO_2(i\text{-}Pr_2dtc)_2]$ in $CHCl_3/CDCl_3$ (4+1) (relative to Na_2MoO_4 in H_2O/D_2O (4+1) at pH 11).

Table 1
^{95}Mo NMR data of $[MoO_2(R_2dtc)_2]$ in $CHCl_3/CDCl_3$ (3+1 or 4+1) at room temperature and redox potentials ($E^{\circ\prime}$) of $[MoO_2(R_2dtc)_2]^{0/-1}$ processes in CH_2Cl_2 at −18 °C [11]

Complex	Chemical shift δ (^{95}Mo)	Linewidth Δ (Hz)	$E^{\circ\prime}$ (V) vs. Fc/Fc^+
$[MoO_2(i\text{-}Pr_2dtc)_2]$	216	610	−1.45
$[MoO_2(i\text{-}Bu_2dtc)_2]$	173	600	−1.42
$[MoO_2(Et_2dtc)_2]$	175	420	−1.38
$[MoO_2(Me_2dtc)_2]$	151	250	−1.34
$[MoO_2(Bzyl_2dtc)_2]$	158	850	−1.30
$[MoO_2(Ph_2dtc)_2]$	169	820	−1.29


(I)


(II)

The increase in the electron-donating ability of the R group prefers resonance form II and hence induces an increase in the electron density on the sulfur atoms bound to the metal atom.

The nuclear magnetic shielding constant (σ) is expressed by Ramsey's equation (Eq. (1)) [10]

$$\sigma = \sigma_d + \sigma_p \qquad (1)$$

where σ_d and σ_p are the diamagnetic and the temperature-independent paramagnetic shielding term, respectively. The chemical shift (δ) increases with the decrease in σ. The σ_d term is mainly contributed from the inner core atomic orbitals of the metal atom so that the increase of the electron density of the metal leads to the increase in σ_d and hence to the decrease in the chemical shift. The formal potentials ($E^{\circ\prime}$ (V) versus Fc/Fc^+ (Fc/Fc^+ = ferrocene/ferricinum)) of $[MoO_2(R_2dtc)_2]^{0/-1}$ (Table 1) [11] are associated with the redox processes around the metal center, $Mo(VI) \rightleftharpoons Mo(V)$, so that the increase in the electron density of the molybdenum atom leads to the negative shift of $E^{\circ\prime}$. Accordingly, if a dominant part of the ^{95}Mo NMR nuclear shielding is σ_d, the chemical shift should decrease with the decrease in $E^{\circ\prime}$. As shown in Table 1, such a tendency between the ^{95}Mo NMR chemical shifts of $[MoO_2(R_2dtc)_2]$ and the redox potentials of $[MoO_2(R_2dtc)_2]^{0/-1}$ processes was not observed. This indicates that σ_d does not play a dominant role for σ, or the effect is superimposed by another factor. Nakatsuji et al. demonstrated that the metal nuclear chemical shift is dominated by σ_p, and that σ_d has a minor contribution for metal complexes [3b].

The σ_p term is contributed by the valence molecular orbital. Therefore, σ_p for the metal nucleus significantly depends on the nature of the metal–ligand bonding and hence the metal chemical shift provides important information on the nature of the metal–ligand bonding. Nakatsuji et al. also demonstrated that the chemical shifts increase with an increase in the donation of electrons from the p orbitals of the ligands to the d orbitals of the metal and/or the backdonation of electrons from the metal to the ligands [3b]. Since the metal in the present complexes has d^0 electronic configuration, the ^{95}Mo NMR chemical shift is caused by the donation of electrons from the p orbitals of the ligands to the metal d orbitals. Accordingly, it is expected that the increase in the electron density of the sulfur atoms bound to the metal atom should lead to increase in electron donation from the p orbitals of the sulfur atoms to the molybdenum d orbitals and then give rise to an increase in the ^{95}Mo NMR chemical shifts. The dithiocarbamate ligand has two resonance forms as stated above. The increase in the electron-donating ability of the R group favors resonance form II and hence leads to the increase in the electron density of the sulfur atoms bound to the metal atom. Consequently, the ^{95}Mo NMR chemical shifts of $[MoO_2(R_2dtc)_2]$ should increase with the increase in electron-donating ability of the substituents on the dithiocarbamate ligands. Fig. 2 shows the correlation between the ^{95}Mo NMR chemical shifts and Taft's parameter (σ^*) [12], which reflects the electron-donating ability of the substituents on the dithiocarbamate ligands

In the case of the alkyl derivatives, as expected above, the tendency of the ^{95}Mo NMR chemical shifts to increase with the increase in the electron-donating ability of the substituents is observed. However, for the complexes with Ph and Bzyl groups, $[MoO_2(Ph_2dtc)_2]$ and $[MoO_2(Bzyl_2dtc)_2]$, the reverse tendency of the chemical shifts is observed. The phenyl group seems to stabilize the resonance form II, because of its mesomeric effect, causing the unexpected large electron density at the sulfur atoms. In fact, a similar mesomeric effect of the phenyl group is observed for the correlation between redox potentials of $[MoO_2(R_2dtc)_2]^{0/-1}$ processes and σ^*. Fig. 3 shows correlation between the formal potentials of $[MoO_2(R_2dtc)_2]^{0/-1}$ processes and σ^* of the substituents of the ligands. This indicates that the mesomeric effect of the phenyl group brings about the unexpected large electron density of the sulfur atoms.

It is interesting to note that the deviation of $[MoO_2(Ph_2dtc)_2]$ from the correlation line shown in Fig. 2 is larger than that in Fig. 3. The donation of electrons from the p orbitals of the ligand to the metal d orbital occurs through both σ and π interactions. The formal potential of $[MoO_2(R_2dtc)_2]^{0/-1}$ reflects the total charge flow from the ligands to the metal through both σ and π interactions. On the other hand, the ^{95}Mo NMR chemical shift of $[MoO_2(R_2dtc)_2]$ seems to be more sensitive to the donation of electrons through π interaction, and the Ph group of the dithiocarbamate ligand seems to enhance the π electron donation from the sulfur atom p orbitals to the metal d orbitals because of its mesomeric effect. Deviation of $[MoO_2(Ph_2dtc)_2]$ from the alkyl group correlation line, shown in Figs. 2 and 3 is due to such an enchanced π interaction between metal and ligating sulfur atoms. Though the mesomeric effect of the Bzyl group seems to be minor, the Bzyl group should also enchance π electron donation from the p orbitals of the sulfur atom to the d orbitals of the metal.

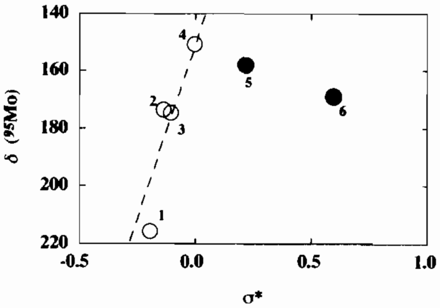


Fig. 2. Correlation between chemical shifts δ (^{95}Mo) of $[MoO_2(R_2dtc)_2]$ and Taft's constants (σ^*) of the substituents on the dithiocarbamate ligands. (1) $[MoO_2(i\text{-}Pr_2dtc)_2]$, (2) $[MoO_2(i\text{-}Bu_2dtc)_2]$, (3) $[MoO_2(Et_2dtc)_2]$, (4) $[MoO_2(Me_2dtc)_2]$, (5) $[MoO_2(Bzyl_2dtc)_2]$, (6) $[MoO_2(Ph_2dtc)_2]$.

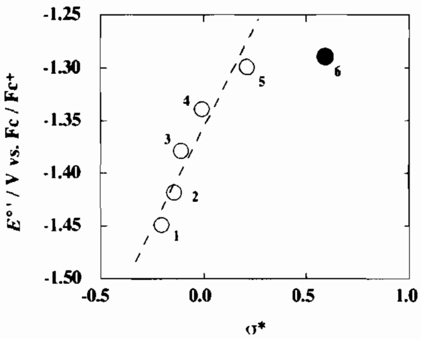


Fig. 3. Correlation between the redox potentials ($E^{\circ\prime}$ (V) vs. Fc/Fc$^+$) of $[MoO_2(R_2dtc)_2]^{0/-1}$ processes [11] and Taft's constants (σ^*) of the substituents on the dithiocarbamate ligands. (1) $[MoO_2(i\text{-}Pr_2dtc)_2]$, (2) $[MoO_2(i\text{-}Bu_2dtc)_2]$, (3) $[MoO_2(Et_2dtc)_2]$, (4) $[MoO_2(Me_2dtc)_2]$, (5) $[MoO_2(Bzyl_2dtc)_2]$, (6) $[MoO_2(Ph_2dtc)_2]$.

Consequently, the ^{95}Mo NMR chemical shift of $[MoO_2(R_2dtc)_2]$ reflects the contribution of the p electron donation (especially through π interaction) from the sulfur atoms of the dithiocarbamate ligands to the metal.

The linewidth of an NMR signal correlates with the relaxation time of the observed nucleus. From Table 1, it is found that the linewidth of $[MoO_2(R_2dtc)_2]$ increases, and consequently, the relaxation time of the ^{95}Mo nucleus decreases with increase in steric bulkiness of the dithiocarbamate ligands. Enemark and co-workers also reported that the linewidth of the ^{95}Mo NMR spectrum of $[MoO_2(R_2dtc)_2]$ increases with the length of the n-alkyl chain of the dithiocarbamate ligand [8].

The *cis*-dioxobis(dithiocarbamato)molybdenum(VI) complexes $[MoO_2(R_2dtc)_2]$ undergo an oxygen atom transfer reaction with PPh_3 (coupled reactions (2) and (3)) [2].

$$[MoO_2(R_2dtc)_2] + PPh_3 \xrightarrow{k_1} [MoO(R_2dtc)_2] + OPPh_3 \quad (2)$$

$$[MoO_2(R_2dtc)_2] + [MoO(R_2dtc)_2] \underset{}{\overset{K_d}{\rightleftharpoons}} [Mo_2O_3(R_2dtc)_4] \quad (3)$$

Reaction (2) has received a great deal of attention as the mimic reaction catalyzed by oxotransferases such as xanthineoxidase etc. [1], and some indexes for the activity of this kind of reaction have been proposed [13,14].

We previously reported that the rate constant k_1 is dependent on the nature of the substituents of the dithiocarbamate ligands [15]. The trend seems very similar to the present ^{95}Mo NMR chemical shift dependence on the substituent. Fig. 4 indicates that log k_1 decreases as the shielding of the Mo nucleus in the complex decreases

The relationship suggests that the enhancement of the donation from the dithiocarbamate ligand, a good measure of which is the ^{95}Mo nuclear shielding (vide supra), causes a substantial effect on the metal–oxo bonding, and leads to retardation of the oxygen transfer reaction. The electron releasing substituent or the group which favors the resonance form II in the dithiocarbamate ligand allows the electron flow into the metal center, especially the π electrons into the metal d orbitals, and the effect competes against the π interaction with the oxo ligand at the *cis* or *trans* position of the sulfur using the same metal orbitals, and may give rise to the decrease in the donation from the oxo ligand. A similar effect can be considered for the σ interactions. Thus, the electron density at the oxo ligand may increase to some extent eventually, when the donation of electrons from the dithiocarbamate ligand to the metal increases. Accordingly, the attack of PPh_3 on the oxo ligand, which seems to be the rate determining step of the oxygen atom transfer, becomes unfavorable with the increase in the donation of electrons (especially of π electrons) from the dithiocarbamate ligands to Mo, which is sensitively reflected in the shift of the ^{95}Mo NMR signal to a lower field.

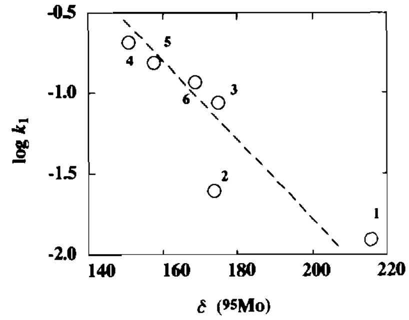


Fig. 4. Correlation between log k_1(M^{-1} s^{-1}) (k_1: the rate constants of oxygen atom transfer reactions with PPh_3 [15]) and chemical shifts δ (^{95}Mo). (1) $[MoO_2(i\text{-}Pr_2dtc)_2]$, (2) $[MoO_2(i\text{-}Bu_2dtc)_2]$, (3) $[MoO_2(Et_2dtc)_2]$, (4) $[MoO_2(Me_2dtc)_2]$, (5) $[MoO_2(Bzyl_2dtc)_2]$, (6) $[MoO_2(Ph_2dtc)_2]$.

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