

Dioxomolybdenum(VI) complexes: relations between oxygen transfer and ^{95}Mo NMR chemical shift

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Abstract

A relation between ^{95}Mo NMR chemical shifts, semi-empirical CNDO estimated p and d orbital electron population and oxygen transfer capacity for a number of dioxomolybdenum(VI) complexes containing the unit $[\text{Mo}^{\text{VI}}\text{O}_2]$ is discussed. The way in which the oxo ligand electronic structure could influence on its oxygen transfer capacity, i.e. intermolecular or intramolecularly is analyzed. Compounds exhibiting negative chemical shift are associated with nucleophilic attack to the oxo ligand and intermolecular oxygen transfer, while those showing a positive chemical shift are associated with intramolecular oxygen transfer.

Keywords: Oxygen atom transfer; ^{95}Mo NMR chemical shift

1. Introduction

The chemistry of molybdenum has been of considerable attention because of its biochemical role and importance both for homogeneous and heterogeneous catalysis. ^{95}Mo NMR has been utilized to characterize, provide patterns and follow reactions [1] as the chemical shift is highly sensitive to structural and electronic variations within a series of closely-related mononuclear compounds. Certain dioxomolybdenum complexes containing the *cis*- $[\text{Mo}^{\text{VI}}\text{O}_2]^{2+}$ unit, which appears to occur at the mononuclear molybdenum active sites of certain enzymes [2], catalyze oxygen atom transfer in a similar way as molybdenum containing enzymes.

The purpose of this account is to relate ^{95}Mo NMR chemical shifts and oxygen transfer capacity for a number of dioxomolybdenum(VI) complexes and, insofar as possible, to analyze them in terms of those electronic features that could control their reactivity.

2. Experimental

2.1. General materials and procedures

All reagents and chemicals obtained from commercial sources were of analytical or reagent grade purity and were used without prior purification unless otherwise noted. All solvents were thoroughly degassed prior to use by repeated evacuation followed by admission of dry nitrogen. Tetrahydrofuran (Mallinckrodt) was dried over sodium benzophenone ketyl and distilled

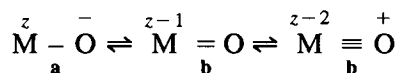
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prior to use. Dichloromethane was dried over P_2O_5 , $MoO_2(CH_2C(CH_3)_3)_2(2,2'-bipy)$ (7), and $MoO_2(CH_2C_6H_5)_2(2,2'-bipy)$ (8) [3], were prepared as described in the indicated references. $MoO_2(NCS)_2(tert-C_4H_9-2,2'-bipy)$, (1), was synthesized from $MoO_2Br_2(tert-C_4H_9-2,2'-bipy)$ adapting the method reported for the preparation of $MoO_2(NCS)_2(phen)$.

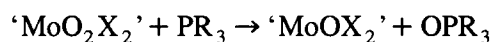
The ^{95}Mo NMR spectra were obtained on a Bruker 400 spectrometer at 26.09 MHz using a 10 mm VSP Probe. The 90° pulse was determined as 50 μs by using a 2 M sodium molybdate solution in D_2O at pH 11 which was used as the external chemical shift standard. Apart from (7) and (8), NMR data were taken from the indicated reference [1]. Reported crystallographic coordinates from X-ray data were used to define optimal geometry in the case of (1), $MoO_2(acac)_2$ (5) and $MoO_2(Etdtc)_2$ (6). $MoO_2Cl_2(tert-C_4H_9-2,2'-bipy)$ (4), geometry was simulated modifying the (Mo–Br) bond length of the dioxodibromide analogous as well as $MoO_2(*Tp)Cl$, (3), was simulated substituting the (Mo–N) bond length in (1) CNDO calculations were performed using the program GEOMO [4]. In the present work, the quantum chemical calculations were done using the CNDO (complete neglect of differential overlap) semi-empirical method at the unrestricted Hartree–Fock level. The Mo parameters are reported values [5] and the Pople and Beveridge standard parameters [6] were used for C, H, N, O, S and B.

3. Results and discussion

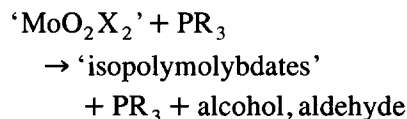
Metal–oxo bonds are usually designated as $M=O$, with recognition that bond order may vary depending on the d^n configuration, the presence and nature of trans ligands, and the coordination stereochemistry [7]. Oxo–metal bonds are described by the canonical forms (a–c)



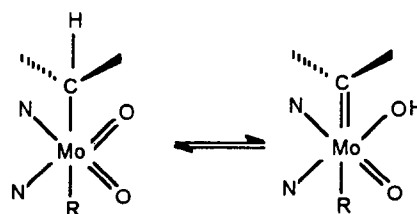
These bonds are polarized $M^{\delta+}=O^{\delta-}$ with the terminal atom being nucleophilic. Nevertheless as $M=O$ groups are stabilized at metal centers in high oxidation state (not less than 4+) with no more than 4 electrons, the metal formal charge can be considered to reduce the basicity of the oxo ligand in such a way as to survive nucleophilic attack under normally accessible experimental conditions. In fact, it has been proposed that the oxygenation of tertiary phosphines, with a number of dioxomolybdenum(VI) complexes is initiated by a nucleophilic attack to a $Mo^{VI}=O$ unit, possibly by interaction with the vacant π^* orbital. This is considered an intermolecular oxygen transfer [8].



On the other hand, a collection of dioxoalkylbipyridylmolybdenum(VI) complexes, behave in a rather different way. Phosphine oxygenation does not occur but the oxygenated organic products, like the corresponding aldehydes and alcohols, are formed instead [9]. This behaviour is observed even in the absence of a phosphine.



To justify this particular reactivity, it has been proposed that a pseudo tautomeric equilibrium involving an alkylalkylideneoxohydroxomolybdenum intermediate



may be present in those compounds where the alkyl ligand possess adequate α -hydrogens. This reactivity has been considered as an intramolecular oxygen transfer.

In this work we attempt to elucidate the manner by which oxo ligand electronic structure could influence its oxygen transfer capacity, i.e. intermolecularly or intramolecularly. ^{95}Mo NMR was chosen since the molybdenum chemical shift is sensitive to very small structural and electronic variations within a series of closely-related mononuclear compounds. We suppose that changes at the metal atom should somehow be reflected in the electrophilicity of the oxo ligands as a consequence of electronic population redistribution between molybdenum and oxygens.

For a series $[\text{MoO}_{4-n}\text{S}_n]^{2-}$ ($n = 1, 4$) using semi-empirical molecular orbital methods and ab-initio calculations, it can be demonstrated that ^{95}Mo chemical shift is mainly determined by the molybdenum p and d orbital electronic population as well as by the total electronic density [10]. Moreover p and d orbital electronic population are involved in shielding and are responsible for the molybdenum chemical shift; the contribution of p orbital population is significantly bigger, probably as a manifestation of the importance of π vs. σ bonding. An extrapolation of the linear relation obtained for these molybdates and isomolybdates to $[\text{PPN}]_2[\text{MoO}_2(\text{NCS})_4]$ permitted the estimation of a theoretical chemical shift with a value fairly close to experimental values.

In this work, total p and d orbital electronic population were estimated for certain representative neutral molybdenum(VI) complexes containing the unit $[\text{Mo}^{\text{VI}}\text{O}_2]$ using a semi-empirical molecular orbital method (CNDO). These results and the experimental ^{95}Mo chemical shift are presented in Table 1. At first sight no simple correlation is apparent between chemical shift and electronic population, either total, p or d (Figs. 1–3, respectively). Nevertheless, a tendency appears when the same compounds are regrouped into two different series, one comprising (1)–(6) while the second includes (1), (4), (7) and (8).

For the first series, (1)–(6), analysis of the calculation results shows that despite the d or-

Table 1
Semi-empirical calculated molybdenum properties and ^{95}Mo chemical shift

Molecule	Orbital occupancies			
	p	d	total	δ (ppm)
$\text{MoO}_2(\text{NCS})_2(\text{t-bpy})$, (1)	0.974	4.612	5.586	-63
$\text{MoO}_2(\text{NCS})(\text{tpb})$, (2)	1.006	5.086	6.092	-35
$\text{MoO}_2(\text{acac})$, (5)	1.058	4.612	5.670	0–17
$\text{MoO}_2\text{Cl}(\text{*Tp})$, (3)	1.010	4.512	5.522	89
$\text{MoO}_2\text{Cl}_2(\text{t-bpy})$, (4)	1.109	4.682	5.791	178
$\text{MoO}_2(\text{Et}_2\text{dtc})_2$, (6)	1.112	4.631	5.743	178
$\text{MoO}_2(\text{CH}_2\text{C}_4\text{H}_9)_2(\text{bpy})$	1.090	5.656	6.746	500
$\text{MoO}_2(\text{CH}_2\text{C}_6\text{H}_5)_2(\text{bpy})$	1.053	5.748	6.801	576

t = bpy = 4,4'-tert-C₄H₉-2,2'-bipy, *Tp = (HB(3,5-Me₂Pz)₃),
bpy = 2,2'-bipy.

bital populations are bigger than the associated p orbitals, the latter seem to be more sensitive to changes at the molybdenum coordination sphere. Thus, for this series a correlation between p orbital electronic population and the nature of the ligands, or more appropriately the ligand donor atoms, can be established (Fig. 2). The chemical shift augments mainly with the p orbital electronic population rather than with the d orbitals.

It is noteworthy that the chemical shift, δ_{M} , for molybdenum compounds is usually defined relative to an external standard, $\delta_{\text{M}} = \delta_{\text{ref}} - \delta$.

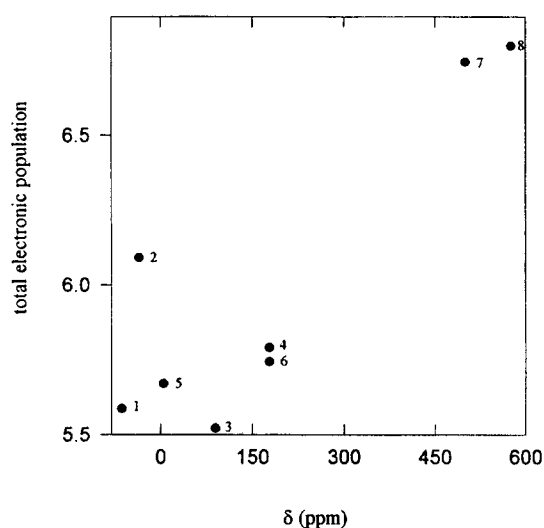


Fig. 1. Correlation between experimental ^{95}Mo chemical shift and CNDO estimated total electronic population.

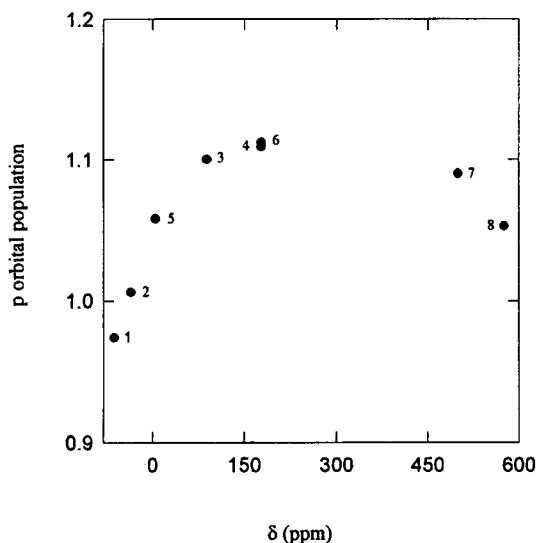


Fig. 2. Correlation between experimental ^{95}Mo chemical shift and CNDO estimated p orbital population.

Compounds which resonate at a higher frequency than the reference have positive chemical shifts, and the metal is said to be deshielded relative to that of the reference complex. A decrease in the metal chemical shift means that the shielding at the metal nucleus has increased.

Thus, it should be expected that as ancillary ligands become softer the metal atom will turn richer in electronic population and the chemical shift will increase. Then, in the case of (5) and

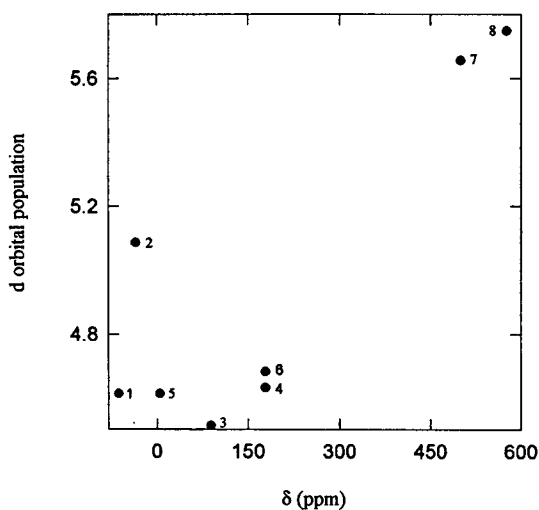


Fig. 3. Correlation between experimental ^{95}Mo chemical shift and CNDO estimated d orbital population.

(6), due to the softness of the S compared with O, a marked variation in the molybdenum electronic structure should be expected as an O-donor ligand is replaced by a S-donor ligand. In fact, the chemical shift displaces towards high fields when comparing the O- and S-ligands containing complexes as well as the p electronic population at the molybdenum increases.

In a similar way, in the case of (1), (4) and (2), (3) substitution of a thiocyanate ligand by a chloride one, results in significant displacements towards more positive (or less negative) chemical shifts together with an increase in the p orbital electronic population at the molybdenum. This can be rationalized on the basis that the π back bonding, which diminishes the molybdenum electronic density, is more favoured for the isothiocyanate containing complexes due to the hardness of the $\pi_{(\text{NCS})}^*$ bonds. In the same way, variations at the p population can be associated with the different molybdenum hybridization when π back bonding or simple σ bonding is present.

Hence, those complexes exhibiting less positive chemical shifts will be poorer in electronic population at the molybdenum and it should be expected that the oxo ligand becomes poorer as well and consequently more attractive to nucleophilic attack. Thus, according to our approach, it could be anticipated that the softer the ligand the less the oxygenation of a nucleophile will be and the more positive the chemical shift.

The above mentioned proposition can justify the fact that despite of all the $\text{Mo}^{\text{VI}}\text{O}_2$ species ever examined (6) was considered the most kinetically facile oxygen atom catalysts [11] (1), a complex containing only N-donor ligands, was recently reported as 20 times more efficient as catalyst. It is noteworthy that before the catalytic studies involving (1), oxygen atom transfer implicating complexes containing only O-donor and N-donor ligands were assumed uncommon.

For the second series, which includes only the bipyridyle derivatives, (1), (3), (7) and (8), the presence of alkyl ligands obliged us to see

their reactivity towards oxygenation in a slightly different way than the already discussed. The very positive chemical shifts observed (500–600 ppm) could be no longer justified by or correlated with the estimated p population (Fig. 2). Analysis of the calculation for the fragments Mo–NCS, Mo–Cl and Mo–alkyl, shows that again the d orbital populations are bigger than the associated p orbitals, but in contrast with the first series, the d orbitals are more sensitive to changes at the molybdenum coordination sphere and no π back bonding is present. Thus, for this series, a correlation between d orbital electronic population and the nature of the ligands should be more appropriate (Fig. 3). The chemical shift augments mainly with the d orbital electronic population rather than with the p orbital population indicating the relevance of the former orbitals to the σ bonding and to the molybdenum chemical shift. Consequently, in this series the bigger the d orbital population at the molybdenum the more positive the chemical shift. Then, those complexes exhibiting more positive chemical shifts will be richer in electronic population at the molybdenum and the oxo ligand should be expected to be consequently less susceptible to nucleophilic attack. Thus, these comparatively electron richest oxo ligands will be more attractive to an electrophilic rather than nucleophilic attack. Moreover, if the non-oxo ligands contain geometrically appropriate α -hydrogens, as in the case of alkyl derivatives, an oxygen transfer could occur, but intramolecular instead of intermolecular, and the oxygenated organic products will be formed.

In conclusion, according to our approach, dioxomolybdenum compounds exhibiting more negative chemical shift tolerate an oxygen donor nucleophilic attack with concomitant intermolecular oxygen transfer, as is the case of (1)–(6). On the contrary, compounds exhibiting more positive chemical shifts, will not be as reactive to oxygenation but to electrophilic attack instead.

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