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Spectroscopic and theoretical evidence for a strong electron-donor effect of the oxo ligand in chlorodicyclopentadienyloxoniobium(V) complexes

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Abstract

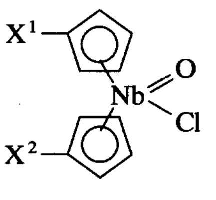
The infrared and ^{13}C NMR spectras of 1,1′-disubstituted chlorodicyclopentadienyloxoniobium(V) complex have been recorded and their features correlated with structural and substituent effects. Optimized MMX force field and EHT methods have been used to calculate the optimal geometry and charge densities and these have been correlated with corresponding spectral data. In all correlations a reverse substituent effect was observed, leading to the conclusion that the oxo ligand in chlorodicyclopentadienyloxoniobium(V) complexes exhibits a strong electron-donor effect supported by a through-space interaction between the oxygen atom and the cyclopentadienyl rings.

Key words: Niobium; Cyclopentadienyl; Oxide; Nuclear magnetic resonance; Infrared spectroscopy; Extended Hückel calculations

1. Introduction

Chlorodicyclopentadienyloxoniobium(V) complexes were first synthesized several years ago; the infrared spectra of some of their trimethylsilyl derivatives were interpreted only recently [1], but no exact assignment of ^{13}C NMR spectra as made. The chlorodicyclopentadienyloxoniobium(V) system has not up to now been investigated by quantum chemical theoretical methods.

The main goal of the present work was to examine the infrared and ^{13}C NMR spectral data, and suggest a theoretical interpretation for them, for a series of disubstituted chlorodicyclopentadienyloxoniobium(V) complexes **I–VI** [2–4].



I: $X^1 = X^2 = C(CH_3)_3$
II: $X^1 = X^2 = CH(CH_3)_2$
III: $X^1 = CH_3$,
$X^2 = CH_2CH_2CH_2CH_3$
IV: $X^1 = X^2 = CH_3$
V: $X^1 = X^2 = CH_2C_6H_5$
VI: $X^1 = X^2 = H$

2. Results and discussion

The most important infrared and ^{13}C NMR data for disubstituted chlorodicyclopentadienyloxoniobium(V) complexes (**I–VI**) are given in Table 1.

The compounds exhibit in the range 884–858 cm^{-1} a strong absorption band arising from the Nb=O

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stretching vibrational mode, a range similar to that for ν(Nb=O) vibrations observed for some trimethylsilyl derivatives of chlorodicyclopentadienyloxoniobium(V) complexes in the solid state [1]. It follows from data in Table 1 that the ν(Nb=O) vibration in compounds **I–VI** is sensitive to solvent, the change in frequency of 3–13 cm^{-1} being observed on going from CCl_4 to $CHCl_3$. This vibration also shows significant influence of substituent, the variation in series I–VI being 17 and 19 cm^{-1} in CCl_4 and $CHCl_3$, respectively. Attempts to correlate the ν(Nb=O) frequencies with Hammett σ_p or σ_m substituent constants or with Brown-Okamoto σ_p^+ values were unsuccessful. However good linear correlations are obtained with the sum of the Taft inductive constants for substituents X^1 and X^2: $\Sigma\sigma^*(X) = \sigma^*(X^1) + \sigma^*(X^2)$ for all the disubstituted compounds **I–V**. The statistical data are as follows:

$$\nu(\text{Nb=O}) = -9.9\Sigma\sigma^*(X) + 877.6 \quad \text{in } CCl_4 \qquad (1)$$

$$r = 0.943;\ s = 0.9$$

$$\nu(\text{Nb=O}) = -16.8\Sigma\sigma^*(X) + 865.5 \quad \text{in } CHCl_3 \qquad (2)$$

$$r = 0.962;\ s = 2.2$$

The fact that the ν(Nb=O) frequencies correlate with Taft inductive σ^* constants, but not with Hammett σ values is a reflection of the back-donating effect of the oxygen ligand as discussed later. It is evident from the negative values of the slopes of ν(Nb=O) *vs.* $\Sigma\sigma^*$(R) correlations (see also Fig. 1) that the groups X^1 and X^2 attached to the cyclopentadienyl rings exhibit a substituent effect on the ν(Nb=O) frequencies that is the opposite of that expected, since the polarity of the Nb=O group should be similar to that of a C=O group, for which a normal substituent effect (positive slopes of ν(C=O) *vs.* substituent constants) is always found. The presence of this reversed substituent effect is clear also from the comparison of solid state infrared data for 1,1'-bis-(dimethylsilyl)-chlorodicyclopentadienyloxoniobium (ν(Nb=O) = 865 cm^{-1}, $\sigma^*(X) = -1.44$) with those for the corresponding 1,1',3,3'-tetrakis-(dimethylsilyl) derivative (ν(Nb=O) = 875 cm^{-1}, $\sigma^*(X) = -2.88$) [1]. It follows from the above results that the oxo ligand in chlorodicyclopentadienyloxoniobium complexes(V) exhibits a strong electron-donor (or a so-called back-donating [5]) effect on the substituted cyclopentadienyl rings, and this gives rise to the reverse substituent effect. This conclusion was supported by the stability of Nb^V as well as the increase in the energy of the LUMO during the one-electron irreversible cathodic reduction of some bis-(dimethylsilyl)-chlorodicyclopentadienyloxoniobium(V) complexes [1].

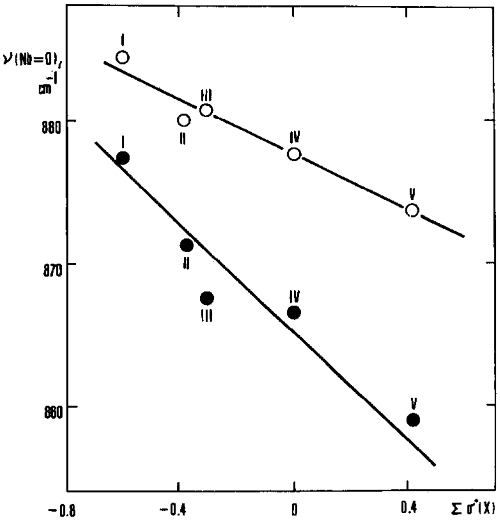

Fig. 1. Plot of ν(Nb=O) against the sum of σ^*(X) inductive substituent constants for the disubstituted chlorodicyclopentadienyloxoniobium(V) complexes (I–V): ○, in CCl_4; ●, in $CHCl_3$

It follows from Table 1 that in the ^{13}C NMR spectrum of the unsubstituted parent compound VI all the =CH– carbon atoms of the cyclopentadienyl rings give signals at very similar chemical shifts, except in the case of the C^2 atom, for which the δ value is significantly shifted downfield. This is in a very good accord with the fact that the electron-donor (back-donating) effect of the oxygen ligand is transferred most efficiently to the closest carbon atom. The above effect is very clearly pronounced also in the case of disubstituted derivatives I–V, for which, moreover, the chemical shifts for the signals from the *ipso* carbons $=C\langle$ (C^1) are strongly shifted upfield. Figure 2 shows that the chemical shifts for both carbon atoms C^1 and C^2 of

TABLE 1. Infrared and ^{13}C NMR data for disubstituted chlorodicyclopentadienyloxoniobium(V) complexes (I–VI)

Compound	ν(Nb=O), cm^{-1}		δ, ppm/d_6-DMSO				
	CCl_4	$CHCl_3$	C^1	C^2	C^3	C^4	C^5
I	884.4	877.6	144.54	101.88	112.88	113.83	114.91
II	880.0	871.4	141.65	103.60	112.42	113.13	113.73
III	880.8	–	–	–	–	–	–
IV	877.6	866.5	131.85	106.00	112.40	113.03	116.29
V	873.6	858.8	139.68	105.45	113.16	113.40	115.65
VI	868.8	865.6	133.39	114.65	133.39	132.21	132.21

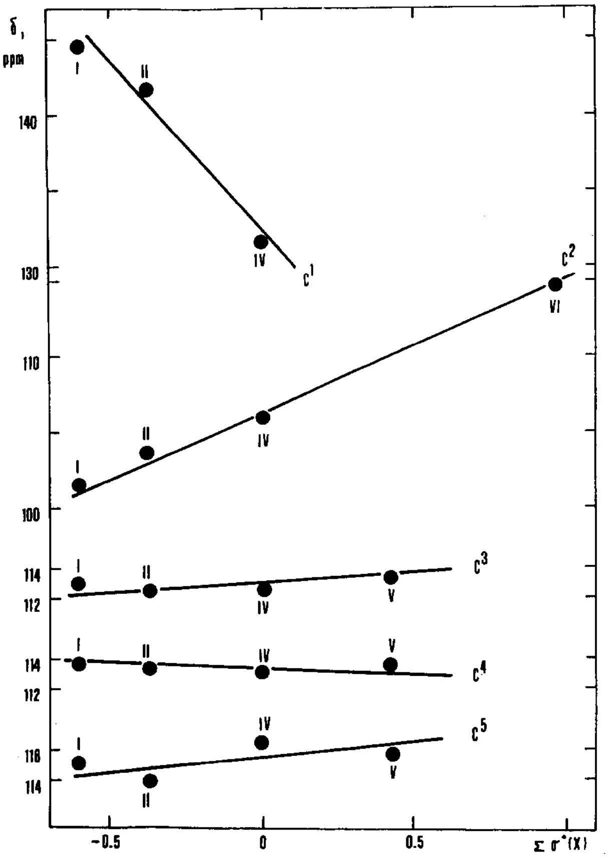

Fig. 2. Plot of $\delta(^{13}C$ NMR) values against the sum of $\sigma^*(X)$ inductive substituent constants for the disubstituted chlorodicyclopentadienyloxoniobium(V) complexes (I–VI)

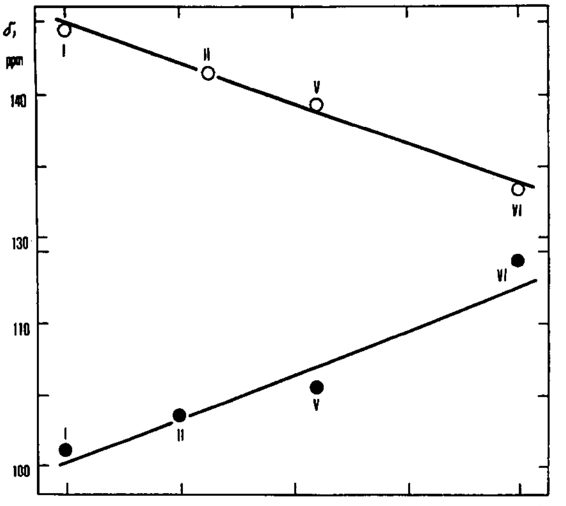

Fig. 3. Plot of $\delta(^{13}C$ NMR) values against the sum of Swain-Lupton $\mathcal{F}(X)$ and $\mathcal{R}(X)$ substituent constants for the disubstituted chlorodicyclopentadienyloxoniobium(V) complexes (I–VI): ○, for C^1; ●, for C^2.

cyclopentadienyl rings can be related to the sum of inductive effects of substituents X^1 and X^2. In both cases the δ *vs.* $\Sigma\sigma^*(X)$ correlations are reversed with respect to similar substituent effects for the corresponding C^4 and C^1 carbon-13 chemical shifts in 4-substituted acetophenones [6]. Efficient transmission of substituent effects to the *ipso* carbon atom (C^1) is rather common, but in the case of the C^2 atom the shift reflects the electron-donor properties of the oxo ligand. On the other hand the chemical shifts for the remaining cyclopentadienyl ring carbon atoms C^3, C^4 and C^5 are only slightly influenced by substituents X^1 and X^2, but in all cases the negative and positive signs of δ *vs.* $\sigma^*(X)$ correlations alternate, as is common for aromatic hydrocarbon systems. For both C^1 and C^2 chemical shifts somewhat better correlations are obtained when $\mathcal{F}$ and $\mathcal{R}$ constants of the Swain-Lupton two-parametric equation are used (see Fig. 3), where $\Sigma\mathcal{F}(X) = \mathcal{F}(X^1) + \mathcal{F}(X^2)$ and $\Sigma\mathcal{R}(X) = \mathcal{R}(X^1) + \mathcal{R}(X^2)$. This suggests that both the field (including inductive) and resonance effects are important in the charge transmission.

Theoretical calculations were performed for geometries optimized by MMX force field implemented in a PCMODEL program [7]. The above force field was parametrized in order to reproduce correctly the geometry of organometallic complexes [8]. The charges on individual atoms and reduced overlap populations were calculated by the Extended Hückel Method (EHT) [9] by use of a CACAO program [10]. The calculated charge densities and important interatomic distances determining the geometry of the basic molecule for

TABLE 2. Theoretical parameters for disubstituted chlorodicyclopentadienyloxoniobium(V) complexes (I–VI)

Compound	q							r, nm				
	Nb	O	C^1	C^2	C^3	C^4	C^5	$C^1 \cdots O$	$C^2 \cdots O$	$C^3 \cdots O$	$C^4 \cdots O$	$C^5 \cdots O$
I	1.085	−1.368	0.157	0.051	0.050	0.011	0.001	0.3211	0.2607	0.2867	0.3706	0.3543
II	1.097	−1.372	0.148	0.051	0.049	0.022	0.017	0.3201	0.2611	0.2924	0.3615	0.3754
III	1.000	−1.366	0.156	0.041	0.063	0.032	−0.015	0.3107	0.2657	0.3090	0.3683	0.3683
IV	1.128	−1.372	0.144	0.052	0.052	0.025	0.028	0.3161	0.2611	0.2990	0.3669	0.3762
V	1.133	−1.395	0.154	0.012	0.111	0.011	0.004	0.2853	0.2667	0.3394	0.3632	0.3900
VI	1.155	−1.371	0.056	0.077	0.040	0.054	0.047	0.3264	0.2634	0.2918	0.3638	0.3818

derivatives **I–VI** are listed in Table 2, and the geometry of the 1,1′-dimethyl derivative **IV** is illustrated in Fig. 4. The differences between the charge densities on the niobium and oxygen atoms q(Nb) − q(O), which give the best measure of the electronic nature of the Nb=O bond, correlate satisfactorily with Nb=O infrared stretching frequencies measured in both CCl_4 and $CHCl_3$:

$$\nu(\mathrm{Nb{=}O}) = -128.1[q(\mathrm{Nb}) - q(\mathrm{O})] + 1197.3 \quad \text{in } CCl_4 \qquad (3)$$

r = 0.973; s = 1.1

$$\nu(\mathrm{Nb{=}O}) = -207.8[q(\mathrm{Nb}) - q(\mathrm{O})] + 1384.4 \quad \text{in } CHCl_3 \qquad (4)$$

r = 0.917; s = 3.2

The signs of the straight lines (Fig. 5) indicate once again that a reverse substituent effect operates as a result of the electron-donor properties of the oxo ligand. The relatively small differences between the charge densities of carbon atoms in the series **I–VI** do not allow meaningful correlations to be made between the carbon-13 chemical shifts and theoretical parameters. Nevertheless, the calculated interatomic distances $r(C \cdots O)$ allowed correct assignment of carbon-13 chemical shifts and their substituent dependence. Thus the $r(C^2 \cdots O)$ distances are much shorter than the others, and this is the cause of the significant decrease in the δ values for the C^2 atom and their pronounced dependence on the substituent for all derivatives **I–VI**, and indicates that the back-donating effect of the oxygen ligand is also transmitted to this atom by a through-space mechanism (field effect).

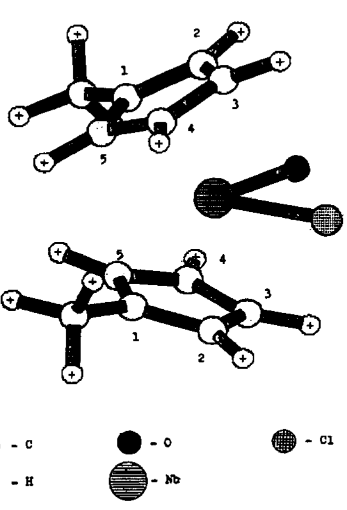

Fig. 4. Geometry of the chlorodicyclopentadienyloxoniobium(V) complex **IV** ($X^1 = X^2 = CH_3$)

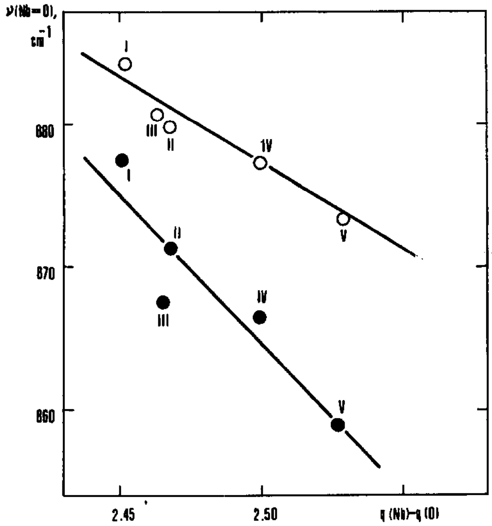

Fig. 5. Plot of ν(Nb=O) against the difference between the q(Nb) and q(O) charge densities for the disubstituted chlorodicyclopentadienyloxoniobium(V) complexes

We conclude on the basis of the above results that infrared and ^{13}C NMR spectral data and the results of theoretical calculations provide clear evidence for an electron-donor effect (by both σ- and π-mechanisms) for the oxo ligand in chlorodicyclopentadienyloxoniobium(V) complexes.

3. Experimental section

The infrared spectra were recorded on a Zeiss M 80 spectrometer for dilute solutions of compounds in CCl_4 and $CHCl_3$ and for KBr cells of thickness 0.1 or 1 mm. The peak positions were determined with an accuracy of ± 0.2 cm^{-1}.

The ^{13}C NMR spectra were measured at 25°C on a Varian VXR 300 instrument operating at 75.424 MHz. Solutions in d_6-DMSO were used, with tetramethylsilane as an internal standard. In addition to ^{13}C NMR techniques, DQ COSY and HETCOR 2D NMR methods and the SINEPT method were used in order to assign the signals of the carbon-13 atoms.

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