

$[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2(\text{P}(\text{OPh})_3)]$.¹² There is little difference in the average W-N-O bond angles between the 19-electron complex and the 18-electron $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{Cl}]$ ²⁰ complex. However, there is much discussion in the literature²⁰ about the influence of electron density on M-N-O bond angles in metal nitrosyl complexes. The major difference in structure is the substantially larger N-W-N bond angle in this 19-electron complex compared to that in the 18-electron analogue.²¹

The differences between the 18- and 19-electron structures are readily interpreted in terms of a MO calculation by Hall and co-workers.²² These authors indicate that the 19th electron will occupy an orbital that has substantial $2\pi(\text{NO})$ character. Nevertheless, in the case of $[\text{Mo}(\text{NO})_2\text{L}_2\text{Cl}_2]$, the other ligands such as Cl contribute to this MO. Two kinds of stereochemistry are observed for $\text{Mo}(\text{NO})_2\text{L}_2\text{Cl}_2$ complexes: *cis*-dinitrosyl-*cis*-dichloro ($\text{L} = \text{MeCN}, \text{py}$) and *cis*-dinitrosyl-*trans*-dichloro ($\text{L}_2 = \text{bpy}$). For the first type, the Mo-Cl bond is labilized in the 19-electron state; for the second type, the Mo-Cl bond is more stable in the 19-electron state. The key features of the chloride elimination are (i) the reduction of the $[\text{Mo}(\text{NO})_2\text{L}_2\text{Cl}_2]$ complexes to their 19-electron anions and (ii) the rapid chloro ligand exchange of the paramagnetic intermediate. The multistep reduction produces trichloro and tetrachloro complexes, which are reducible at a more negative potential than the dichloro complexes. The multiple-step

system is clearly not catalytic, but is rather of the electroactivation type.²³ The labile species " $\text{Mo}(\text{NO})_2^{+}$ ", which is a potentially efficiency catalyst such as " $\text{Fe}(\text{NO})_2^{+}$ ",¹⁰ can be generated by electroreduction. The values of the standard potential E° of the redox systems (Table I) give an estimation of the energy difference between the respective LUMO's. A decrease in the $\nu(\text{NO})$ frequencies indicates stabilization of the LUMO. The energy of the LUMO is in the following order: dicationic > monocationic > neutral > monoanionic > dianionic. Among these classes of dinitrosyl complexes, the energy of the LUMO becomes more stabilized with increasing σ -donor and decreasing π -acceptor properties of ligand L.

Registry No. 1^{2+} , 63087-71-8; 1^+ , 99948-14-8; 2^+ , 99948-22-8; 2^{2+} , 100018-91-5; 3^+ , 99948-23-9; 3^{2+} , 67158-74-1; **4**, 99948-17-1; 4^+ , 100018-92-6; 4^- , 99948-19-3; 4^{2-} , 99948-20-6; **5**, 99948-15-9; 5^+ , 100018-93-7; **6**, 99948-18-2; **6^-**, 69254-57-5; **7**, 14324-79-9; **7^-**, 99948-16-0; **8^-**, 99948-13-7; 8^{2-} , 99948-24-0; 9^{2-} , 65085-25-8; 9^{3-} , 99948-21-7; MeCN, 75-05-8; Et_4NCl , 56-34-8; Cl_2 , 7782-50-5.

Supplementary Material Available: Figures showing cyclic voltammograms of $[\text{Mo}(\text{NO})_2(\text{MeCN})_4]^{2+}$, $[\text{Mo}(\text{NO})_2(\text{bpy})(\text{MeCN})_2]^{2+}$, $[\text{Mo}(\text{NO})_2(\text{MeCN})_3\text{Cl}]^+$, $[\text{Mo}(\text{NO})_2(\text{bpy})(\text{MeCN})\text{Cl}]^+$, $[\text{Mo}(\text{NO})_2(\text{MeCN})_2\text{Cl}_2]$, and $[\text{Mo}(\text{NO})_2\text{bpyCl}_2]$ and rotating-disk electrovoltammograms of the 19-electron complexes $[\text{Mo}(\text{NO})_2(\text{MeCN})_4]^+$ and $[\text{Mo}(\text{NO})_2(\text{MeCN})_2\text{Cl}_2]$ (9 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, The Ohio State University, Columbus, Ohio 43210, and Wright State University, Dayton, Ohio 45435

Electrochemistry of Niobium(IV) and Tantalum(IV) Complexes: Ligand Additivity in d^1 Octahedral Complexes

B. E. Bursten,*^{1a,c} M. R. Green,^{1a} V. Katović,*^{1b} J. R. Kirk,^{1b} and D. Lightner, Jr.^{1b}

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The electrochemistry of the octahedral complexes $[\text{MCl}_{6-n}(\text{NCMe})_n]^{-2+n}$ ($\text{M} = \text{Nb}, \text{Ta}; n = 0, 1, 2$ (*cis*)) has been investigated by using cyclic voltammetry. The ease with which these d^1 systems are oxidized to the corresponding d^0 systems decreases with increasing substitution of chloride by acetonitrile. The electrochemical data are in good accord with the model of ligand additivity and with Fenske-Hall molecular orbital calculations on the Nb series. It is concluded that NCMe is a more stabilizing ligand than Cl, largely because the latter acts as a π donor whereas the former is a weak π acceptor.

Introduction

The continuing growth in the high-valent chemistry of the early transition metals places new demands on the experimental techniques commonly used to elucidate the nature of the metal-ligand bonding. Such complexes often exhibit featureless electronic spectra and many are paramagnetic, hindering analysis by NMR. Further, the ligands generally used to stabilize early transition metals in high oxidation states (e.g. halides, nitriles, and phosphines) are not as amenable to spectroscopic probing as those commonly found in low-valent systems, such as CO .²

A technique of paramount importance in providing information about the energetics of high-valent systems is electrochemistry. The redox potentials of such systems provide, in principle, a measure of the ligand and metal atom influences on the electron

energetics, data of great import given the attention focused on high-valent systems as potentially controllable oxidants.

We have previously advanced a model,³ called ligand additivity, which we have used to correlate the trends in the redox potentials and ionization energies of low-spin d^6 octahedral complexes. This model has been used successfully on the ligand substitution series $\text{ML}_n\text{L}'_{6-n}$ where L and L' are π -acid ligands such as CO, CNR, or PR_3 , and M is a low-valent d^6 metal atom such as Cr(0), Mo(0), Mn(I), or Re(I).³⁻⁵ The ligand additivity model not only correlates the experimental data but, in so doing, provides direct information about the relative bonding capabilities of L and L'.

As our previous research on the ligand additivity model has been limited to low-valent organometallic systems containing π -acid ligands, we were interested in determining whether the model could be extended to encompass high-valent coordination complexes containing classical donor ligands. In this paper we report a combined experimental and theoretical study of some

(1) (a) The Ohio State University. (b) Wright State University. (c) Camille and Henry Dreyfus Foundation Teacher-Scholar 1984-1989 and Fellow of the Alfred P. Sloan Foundation 1985-1987.

(2) See, for example: (a) Fowles, G. W. A.; Tidmarsh, D. J.; Walton, R. A. *Inorg. Chem.* **1969**, *8*, 631-638. (b) Luetkens, M. L., Jr.; Elcesser, W. L.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1984**, *23*, 1718-1726. (c) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 3592-3596.

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monomeric acetonitrile-substituted niobium(IV) and tantalum(IV) chlorides of the formulation $[M(\text{NCMe})_n\text{Cl}_{6-n}]^{2+n}$ ($n = 0, 1, 2$). It will be demonstrated that the redox potentials of such systems are consistent with the ligand additivity model and that the model can be used to provide a comparison of the relative ligand influences on the metal center.

Experimental Section

Electrochemical Measurements. Electrochemical measurements were made with a PAR Model 173 potentiostat-galvanostat equipped with a PAR Model 178 electrometer probe and a PAR 175 universal programmer. The cyclic voltammograms were recorded on a Houston Omni-graphic X-Y recorder.

The acetonitrile used for the electrochemical measurements was spectral-quality grade (Burdick and Jackson) and contained less than 0.03% water. It was refluxed under CaH_2 and distilled in vacuo. The supporting electrolyte, $n\text{-Bu}_4\text{NPF}_6$ (Southwestern Analytical Chemicals), was recrystallized three times from acetonitrile/ether solution and vacuum-dried before use.

A special vacuum electrochemical cell was employed in order to lower the water concentration in "dry" acetonitrile from 10^{-3} M to less than 10^{-5} M, thereby preventing the hydrolysis of the niobium and tantalum halides. The cell was equipped with a loading device for the introduction of air-sensitive samples⁶ and an Al_2O_3 column, which served to lower the water content in nonaqueous solution.⁷

In order to determine the amount of water in the organic solvent before and after purification with Al_2O_3 , 9,10-diphenylanthracene (DPA) was used as an indicator.⁸ In addition, DPA also served as an internal standard, since a Ag quasi-reference electrode was employed. The DPA^+/DPA couple ($E_{1/2} = 1.21$ V) was established by using the ferrocenium/ferrocene redox couple, which has a known $E_{1/2}$ value of 0.400 V vs. the normal hydrogen electrode (NHE).⁹ The working electrode was a Pine Instrument Co. glassy-carbon disk electrode, and the auxiliary electrode was a platinum wire. Full internal resistance compensation was employed in all experiments. All potentials are referred to the NHE.

Sample Preparation. Niobium pentachloride and tantalum pentachloride (99.9%+) were purchased from Alfa Products. Their purity was confirmed by metal and chloride analysis. $\text{cis-NbCl}_4(\text{NCMe})_2$ was prepared by the Al reduction of NbCl_5 in acetonitrile.¹⁰ The complexes $\text{MCl}_5(\text{NCMe})$ and Et_4NMCl_6 ($M = \text{Nb}$ and Ta) were prepared by established literature methods.¹⁰⁻¹² A solution of $\text{TaCl}_4(\text{NCMe})_2$ in acetonitrile was prepared by the electrochemical reduction of TaCl_5NCMe .¹³ As niobium and tantalum halides are extremely sensitive to air and moisture, the syntheses and all subsequent handlings were done in a high-vacuum manifold or in a nitrogen-atmosphere drybox.

Computational Details

Molecular orbital calculations were performed on an Amdahl 470/V8 computer system using the Fenske-Hall method.¹⁴ The molecular geometries used for $[\text{NbCl}_6]^{2-}$, $[\text{NbCl}_5(\text{NCMe})]^-$, $\text{cis-NbCl}_4(\text{NCMe})_2$, and $\text{trans-NbCl}_4(\text{NCMe})_2$ were taken from X-ray crystal structure data of $\text{cis-NbCl}_4(\text{NCMe})_2$ and the inner coordination shells were idealized to O_h , C_{4v} , C_{2v} , and D_{4h} symmetry, respectively.¹⁵ Bond lengths employed were as follows: Nb-Cl, 2.342 Å; Nb-N, 2.220 Å; N-C, 1.167 Å; C-C, 1.438 Å; C-H, 1.090 Å. The acetonitrile ligands were treated as possessing a linear Nb-N-C-C linkage. A tetrahedral value was assumed for the C-C-H angles.

All atomic basis functions were generated by using the method of Bursten, Jensen, and Fenske.¹⁶ Contracted double- ζ representations were used for the Nb 4d AO's, for the Cl 3p AO's, and for the C and N 2p

Table I. Predicted $E_{1/2}$ Values for the Series $\text{ML}_n\text{L}'_{6-n}$ Where L Is a More Stabilizing Ligand Than L'

compd	n	d ⁶		d ¹	
		x_{HOMO}^a	predicted $E_{1/2}$	x_{HOMO}^a	predicted $E_{1/2}$
ML'_6	0	0	A	0	A
MLL'_5	1	0	A + B	1	A + B + C
<i>trans</i> - $\text{ML}_2\text{L}'_4$	2	0	A + 2B	2	A + 2B + 2C
<i>cis</i> - $\text{ML}_2\text{L}'_4$	2	1	A + 2B + C	2	A + 2B + 2C
<i>mer</i> - $\text{ML}_3\text{L}'_3$	3	1	A + 3B + C	3	A + 3B + 3C
<i>fac</i> - $\text{ML}_3\text{L}'_3$	3	2	A + 3B + 2C	2	A + 3B + 2C
<i>trans</i> - $\text{ML}_4\text{L}'_2$	4	2	A + 4B + 2C	4	A + 4B + 4C
<i>cis</i> - $\text{ML}_4\text{L}'_2$	4	2	A + 4B + 2C	3	A + 4B + 3C
$\text{ML}_5\text{L}'$	5	3	A + 5B + 3C	4	A + 5B + 4C
ML_6	6	4	A + 6B + 4C	4	A + 6B + 4C

^a x_{HOMO} is the number of L ligands contributing to the HOMO of the complex.

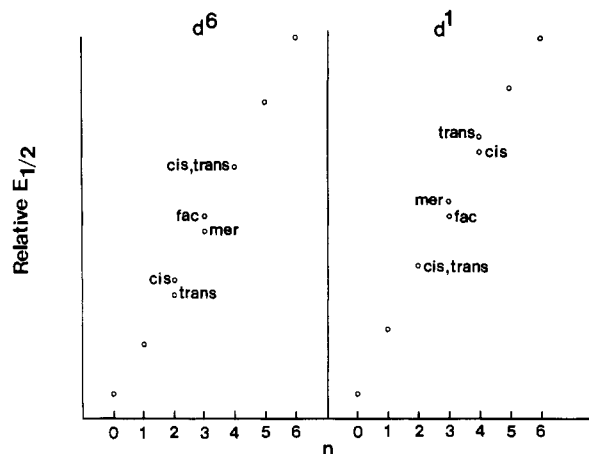


Figure 1. Predicted relative $E_{1/2}$ values vs. n for the $\text{ML}_n\text{L}'_{6-n}$ systems ($M = \text{low-spin } d^6 \text{ or } d^1$).

AO's. An exponent of 1.16 was used for the hydrogen 1s AO's.¹⁷ The basis functions for Nb were derived for the +2 oxidation state with the 5s exponent fixed at 1.9 and the 5p exponent at 1.3. In calculations involving acetonitrile, the NCMe 4a₁, 5a₁, 1e, 4e, 8a₁, 9a₁, and 10a₁ orbitals were deleted from the basis transformation set.¹⁸

Extension of the Ligand Additivity Model

Ligand additivity postulates that the orbital energies for the valence $d\pi$ orbitals of the $\text{ML}_n\text{L}'_{6-n}$ system will be given by³

$$\epsilon_i = a + bn + cx_i \quad (1)$$

wherein ϵ_i is the energy of the i th valence $d\pi$ orbital (d_{xy} , d_{xz} , d_{yz}), n is the number of ligands L in the complex, x_i is the number of ligands L with which the i th $d\pi$ orbital interacts, and a , b , and c are empirically determined parameters.

In the application of the model to electrochemical data, use is made of the empirical linear relationship between the $E_{1/2}$ value and the HOMO energy.^{19,20} The resulting ligand additivity equation becomes

$$E_{1/2} = A + Bn + Cx_{\text{HOMO}} \quad (2)$$

Table I summarizes the ligand additivity equations for the d^1 system $\text{ML}_n\text{L}'_{6-n}$ and, as well, contrasts them to those for the low-spin d^6 system. The difference between these two systems lies with the variable x_{HOMO} , which is defined as the number of ligands L with which the HOMO in the complex interacts. For low-spin d^6 complexes the HOMO is the highest energy $d\pi$ orbital; however, for d^1 complexes the HOMO is the lowest energy $d\pi$

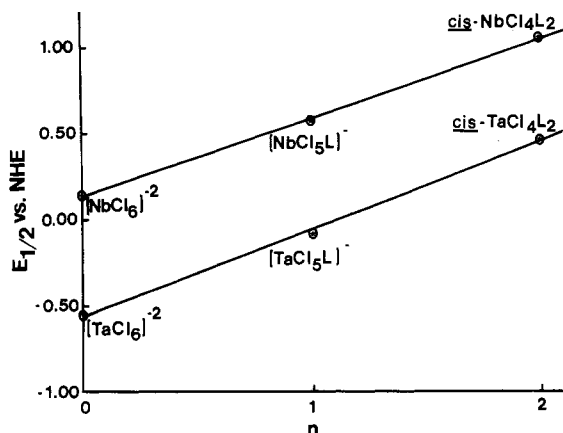
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Table II. Summary of Cyclic Voltammetric Data Obtained for a Series of Acetonitrile-Substituted Niobium and Tantalum Chlorides^a

electrode process ^b	$E_{p,c}^c$, V	$E_{p,a}^c$, V	$E_{1/2}^c$, V	ΔE_p , mV
$[\text{NbCl}_6]^- + e^- \rightarrow [\text{NbCl}_6]^{2-}$	0.11	0.17	0.14	60
$\text{NbCl}_5\text{L} + e^- \rightarrow [\text{NbCl}_5\text{L}]^-$	0.53	0.59	0.56 ^d	60
$\text{cis-}[\text{NbCl}_4\text{L}_2]^+ + e^- \rightarrow \text{cis-}[\text{NbCl}_4\text{L}_2]$	1.00	1.06	1.03 ^e	60
$[\text{TaCl}_6]^- + e^- \rightarrow [\text{TaCl}_6]^{2-}$	-0.59	-0.50	-0.55	90
$\text{TaCl}_5\text{L} + e^- \rightarrow [\text{TaCl}_5\text{L}]^-$	-0.12	-0.06	-0.09	60
$\text{cis-}[\text{TaCl}_4\text{L}_2]^+ + e^- \rightarrow \text{cis-TaCl}_4\text{L}_2$	0.40	0.48	0.44	80

^a Scan rate = 50 mV/s. All scans in NCMc with 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte. *T* = 20 °C. ^b L = NCMc. ^c Vs. NHE. ^d *T* = 5 °C. ^e Scan rate = 500 mV/s.

**Figure 2.** Plot of $E_{1/2}$ vs. n for the series $\text{MCl}_{6-n}\text{L}_n$ ($\text{M} = \text{Nb(IV)}$ or Ta(IV) ; $\text{L} = \text{NCMe}$; $n = 0, 1, 2$ (cis)).

orbital. This difference in the nature of the HOMO results in different χ_{HOMO} values for each case, thereby causing the ligand additivity equations to be different.

Plots of the predicted trend in $E_{1/2}$ values vs. n for the low-spin d^6 and d^1 systems are shown in Figure 1. Several interesting features are apparent in these graphs. First, it is evident that in both cases the $E_{1/2}$ values should exhibit isomer dependency for two values of n (for d^6 $n = 2, 3$; for d^1 $n = 3, 4$). Second, the $E_{1/2}$ values should be isomer independent in each case for one value of n (for d^6 $n = 4$; for d^1 $n = 2$). Further, it is interesting to note that for $n = 3$, the model predicts that, in the low-spin d^6 system, the *fac* isomer will have a greater $E_{1/2}$ value than the *mer* isomer, while for the d^1 system, in contrast, the model predicts the *fac* isomer to have a smaller $E_{1/2}$ value than the *mer* isomer.

Results

The electrochemical data obtained for the two series of complexes $[\text{MCl}_{6-n}(\text{NCMe})_n]^{-2+n}$ [$\text{M} = \text{Nb, Ta}$; $n = 0, 1, 2$ (cis)] are summarized in Table II. These are the only known monomeric members of these substitution series (vide infra). For the niobium complexes the cyclic voltammetric data obtained possess the characteristics of reversible one-electron-oxidation/reduction reactions ($\Delta E_p < 60$ mV). For the tantalum complexes the processes range from reversible to quasi-reversible one-electron-oxidation/reduction reactions. The results in Table II clearly show that the $\text{M(V)} \rightarrow \text{M(IV)}$ reduction processes are sensitive to the number of chloride ligands coordinated to the central metal ion. As the number of chlorides in the $[\text{M}(\text{NCMe})_n\text{Cl}_{6-n}]^{-2+n}$ series is increased from 4 to 6, it becomes increasingly more difficult to reduce the M(V) to the M(IV) complex.

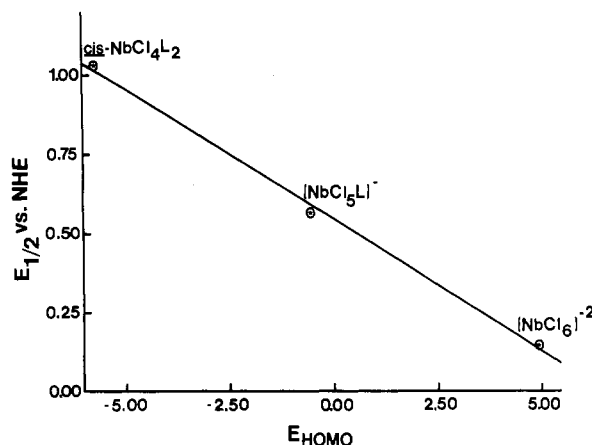
If it is assumed that $\text{L} = \text{NCMe}$ and $\text{L}' = \text{Cl}$, it is evident from Table I that a plot of $E_{1/2}$ vs. n for the series of three complexes for each metal should be linear with a slope of $B + C$. The electrochemical data is plotted vs. n in Figure 2, wherein it can be seen that the relationship is indeed linear. The slope, $B + C$, has a value of 0.445 V for $\text{M} = \text{Nb}$ and 0.495 V for $\text{M} = \text{Ta}$.

As the individual values of B and C can be used to compare the relative bonding capabilities of chloride and acetonitrile ligands, it is desirable to obtain individual values for these parameters rather than their sum. In order to accomplish this, we have carried out a series of Fenske-Hall molecular orbital calculations on the Nb series. The linear relationship between $E_{1/2}$ and ϵ_{HOMO} , in

Table III. Fenske-Hall Molecular Orbital Energies for the $d\pi$ Orbitals of $[\text{NbCl}_{6-n}(\text{NCMe})_n]^{-2+n}$ ($n = 0, 1, 2$)

complex	orbital energies, ^a eV	degeneracy	ligand additivity eq
$[\text{NbCl}_6]^{2-}$	4.92 (HOMO)	3	<i>a</i>
$[\text{NbCl}_5(\text{NCMe})]^-$	0.13 (LUMO)	1	<i>a + b</i>
	-0.55 (HOMO)	2	<i>a + b + c</i>
<i>cis</i> - $\text{NbCl}_4(\text{NCMe})_2$	-5.04 (LUMO)	2	<i>a + 2b + c</i>
	-5.70 (HOMO)	1	<i>a + 2b + 2c</i>
<i>trans</i> - $\text{NbCl}_4(\text{NCMe})_2$	-4.45 (LUMO)	1	<i>a + 2b</i>
	-5.60 (HOMO)	2	<i>a + 2b + 2c</i>

^a The Fenske-Hall method may yield positive eigenvalues for negatively charged complexes.²¹

**Figure 3.** Plot of $E_{1/2}$ vs. ϵ_{HOMO} (Fenske-Hall) for the Nb(IV) complexes $\text{NbCl}_{6-n}\text{L}_n$ ($\text{L} = \text{NCMe}$; $n = 0, 1, 2$ (cis)).

consonant with the ligand additivity equations previously developed,³ will allow us to arrive at separate B and C values from the electrochemical data. Calculations were not performed on the Ta series since the Fenske-Hall method is unable to include relativistic effects for third-row transition elements.

The results obtained from the Fenske-Hall molecular orbital calculations are summarized in Table III. The calculated orbital energies and their corresponding ligand additivity equations (constructed from eq 1) are listed. A least-squares solution of this set of simultaneous linear equations yields values for the parameters a (4.83), b (-4.65), and c (-0.61).²² The calculations include the *trans* isomer, even though it is not known to exist as a monomer.²³ It is interesting to note that in accord with the model the HOMO energies for the *cis* and *trans* isomers are nearly equal, differing by only 0.1 eV.

The empirical linear relationship between the $E_{1/2}$ value and the HOMO energy allows the electrochemical parameters B and C to be determined from the orbital energy parameters b and c . A plot of $E_{1/2}$ vs. ϵ_{HOMO} for the niobium series is shown in Figure 3. A least-squares fit of the data yields the relation²⁴

$$E_{1/2} = -0.084(\epsilon_{\text{HOMO}}) + 0.54 \quad (3)$$

(22) Root mean square deviation = 0.070 eV.

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Table IV. Mulliken Populations of the Ligand π Orbitals (e) for $[\text{NbCl}_{6-n}(\text{NCMe})_n]^{2+n}$ ($n = 0, 1, 2$)

complex	Cl $3p_x, 3p_y$ ^a	NCMe 2e ^a	NCMe 3e ^b
$[\text{NbCl}_6]^{2-}$	1.93		
$[\text{NbCl}_5(\text{NCMe})]^-$	1.91	2.00	0.05
<i>cis</i> - $\text{NbCl}_4(\text{NCMe})_2$	1.88	2.00	0.03
<i>trans</i> - $\text{NbCl}_4(\text{NCMe})_2$	1.88	2.00	0.03

^a Free ligand population = 2.00 e. ^b Free ligand population = 0.00 e.

Thus, by use of eq 1–3, it follows that $B = +0.39$ V and $C = +0.05$ V.

Comparison of the Bonding Capabilities of Chloride and Acetonitrile

The parameters B and C can be used to compare the relative donor and acceptor properties of chloride and acetonitrile as ligands.³ The parameter B (+0.39 V) is interpreted as an "electrostatic term" and accounts for the major shift in the $E_{1/2}$ value upon ligand substitution. B provides a measure of the total donor ability of chloride vs. that of acetonitrile. B is positive, thus indicating that chloride is a better overall ($\sigma + \pi$) donor of electron density than acetonitrile and, hence, that acetonitrile is a more stabilizing ligand than chloride in this system. The parameter C , on the other hand, is interpreted as a "bonding term" and is a measure of the relative ability of each ligand to energetically stabilize the complex by π interactions. Since C is positive, we can conclude that chloride has a larger destabilizing effect than NCMe upon the niobium $d\pi$ orbitals.

As it is commonly accepted that donation of electron density to a metal center destabilizes (raises in energy) all the metal orbitals, it is apparent that chloride is a better π donor than NCMe. This characterization is further supported by the Mulliken population analysis on the niobium series. As shown in Table IV the average chloride $3p_x, 3p_y$ (π donor) orbital populations indicate that electron density is being transferred from chloride to the Nb(IV) center in each complex. The amount of electron density transferred is also seen to increase as Cl is substituted by NCMe, consistent with the previous conclusion that NCMe is a weaker overall donor than Cl.

When NCMe interacts with the niobium $d\pi$ set, two sets of NCMe orbitals are involved, the 2e and 3e. The NCMe 2e is the N–C π bond, which can act as a π donor to the metal, while the 3e is the corresponding π antibond, which can act as a π acceptor from the metal. As shown in Table IV the populations of the NCMe 2e orbitals remain unchanged from their free ligand values of 2.0, indicating that NCMe is not functioning as a π donor ligand. Further, it is seen that the metal is transferring a small amount of electron density into the NCMe 3e orbitals. Thus, it is apparent that NCMe is acting as a weak π accepting ligand in this system. It is also interesting to note that the amount of

(24) It is to be noted that the values of the least-squares parameters in eq 3 will be somewhat dependent on the choice of metal atom basis functions. It is our experience on this and other systems, however, that the linearity of the fit will be independent of the basis set choice within reason. We have chosen Nb(II) functions for all of the calculations reported here as these closely match the calculated Mulliken atomic charges for Nb in these formally Nb(IV) complexes.

Table V. Summary of the Calculated Fenske–Hall Orbital Energies and Electrochemical Data vs. Their Values from the Ligand Additivity Model

complex	orbital energy, eV	
	Fenske–Hall	ligand additivity
$[\text{NbCl}_6]^{2-}$	4.92	4.83
$[\text{NbCl}_5(\text{NCMe})]^-$	0.13	0.18
	–0.55	–0.42
<i>cis</i> - $\text{NbCl}_4(\text{NCMe})_2$	–5.04	–5.07
	–5.70	–5.67
<i>trans</i> - $\text{NbCl}_4(\text{NCMe})_2$	–4.45	–4.46
	–5.60	–5.67

complex	$E_{1/2}$ (exptl), V	$E_{1/2}$ (ligand additivity), V
$[\text{NbCl}_6]^{2-}$	0.14	0.14
$[\text{NbCl}_5(\text{NCMe})]^-$	0.56	0.58
<i>cis</i> - $\text{NbCl}_4(\text{NCMe})_2$	1.03	1.02
$[\text{TaCl}_6]^{2-}$	–0.55	–0.56
$[\text{TaCl}_5(\text{NCMe})]^-$	–0.09	–0.07
<i>cis</i> - $\text{TaCl}_4(\text{NCMe})_2$	0.44	0.43

electron density accepted by the NCMe 3e decreases upon substitution of Cl by NCMe, once again reflecting that chloride is a better overall donor than NCMe.

Conclusion

For the niobium (IV) series examined in this paper the parameters B and C were found to have values of +0.39 and +0.05 V, respectively. In contrast, earlier studies we performed on the $[\text{Mn}(\text{CO})_n(\text{CNMe})_{6-n}]^+$ series yielded values for B and C of +0.38 and +0.12 V, respectively.³ This similarity in B terms is somewhat surprising. Since B is an electrostatic term, one might expect that the difference between a formally charged ligand, chloride, and an uncharged ligand, NCMe, with a high-valent metal, Nb(IV), would be greater than the difference between two neutral ligands, CO and CNMe, with a low-valent metal, Mn(I).

The difference in the C terms, on the other hand, indicates that the π -interaction differences of Cl and NCMe with Nb(IV) are, in fact, less than the π -interaction difference between CO and CNMe with Mn(I). This is somewhat surprising as well since it was not intuitively obvious that the π -interaction differences between a weak π donor ligand, chloride, and a weak π -acceptor ligand, NCMe, with a high-valent metal center would be significantly less than the π -interaction differences between two strong π -acceptor ligands, CO and CNMe, with a low-valent metal.

The validity of the extension of the ligand additivity model to the d^1 octahedral $\text{ML}_n\text{L}'_{6-n}$ system is perhaps best gauged by the ability of the model to reproduce the experimental data. A comparison of the orbital energies and $E_{1/2}$ values predicted by the ligand additivity model to the Fenske–Hall calculated orbital energies and experimentally observed $E_{1/2}$ values is presented in Table V. As shown, the model, despite its simplicity, is able to reproduce the experimental and calculational data quite well.

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