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The Use of Optical Electronegativities
to Assign Electronic Spectra of Semiquinone Complexes

By

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in

Chemical Physical Letters

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The use of Optical Electronegativities to Assign Electronic Spectra of Semiquinone Complexes

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Abstract

Semiquinone complexes of a wide range of transition metals show ligand to metal charge transfer transitions in their electronic spectra. Using the optical electronegativity approach it has been shown that these assignments are consistent with one another. The optical electronegativity of 3,5-di-t-butylsemiquinone is found to vary from 1.2 to 1.5, depending on the metal ion. In cases where the optical electronegativity appears to lie outside these limits alternative assignments are discussed. Optical electronegativities for 2,2'-bipyridine, 2,2'-bipyrazine and 2-picolinic acid N-oxide are also reported.

Introduction

➤ Catechols, semiquinones and quinones, known as dioxolenes, are non-innocent ligands, related to one another by one-electron transfers. These ligands are of interest for their biological importance, redox and magnetic properties, [1-4]. Although their complexes usually display rich electronic spectra few detailed studies and assignments of these spectra have been reported [5-10].

The spectra of dioxolene complexes are often dominated by charge transfer and intraligand transitions [5-10]. The visible spectra of

catechol and quinone complexes are relatively easy to assign, as they tend to show ligand to metal charge transfer (LMCT) and metal to ligand charge transfer (MLCT) respectively. The spectra of semiquinone complexes are more complicated because of several internal ligand transitions in the near-ultraviolet to near-infrared (NIR) region [11,12] and the possibility of either MLCT or LMCT transitions.

We investigate here the use of optical electronegativities because the usual methods for assigning CT transitions [13] cannot always be applied for semiquinone complexes. For example, CT and interligand transitions may shift in parallel when ligand substituents are changed and shifts are sometimes small and may be misleading [5,7-9,14]. Correlations with redox potentials can also be used to identify CT transitions [15,16] but the relevant redox potentials are generally unavailable for semiquinone complexes.

The concept of optical electronegativity was introduced by Jørgensen as a means of rationalising the LMCT spectra of metal complexes [17,18]. It has been used fairly extensively for LMCT [19-39], and generalised to include MLCT spectra of various pyridine N-oxide complexes [40-42]. This paper extends the optical electronegativity database for MLCT to include 2,2'-bipyridine (bpy), 2,2'-bipyrazine (bpz) and 3,5-di-*t*-butylsemiquinone (DTBSq). This provides an insight into the use of optical electronegativities for non-innocent ligands and enables us to make new assignments and show that, in most cases, previously suggested assignments are consistent with one another. Our discussion is restricted to complexes of DTBSq because of the large amount of data available for this ligand.

Theory and Background

Optical electronegativities

The optical electronegativity approach [17,43] assumes that the energy of a CT transition is proportional to the difference in electronegativity between the donor and acceptor orbitals involved in the transition. A correction is made for the change in spin-pairing energy (Δ SPE) occurring on the metal ion, and the constant $30,000 \text{ cm}^{-1}$ is used to relate the electronegativities to the Pauling electronegativity scale. For a MLCT transition (in cm^{-1}) [17,43]:

$$\nu_{\text{CT}}' = 30,000[\chi_{\text{M}} - \chi_{\text{L}}] \quad (1)$$

$$\text{where } \nu_{\text{CT}}' = \nu_{\text{CT}}(\text{obsd}) - \Delta\text{SPE} \quad (2)$$

χ_{M} and χ_{L} are the optical electronegativities of the metal and ligand respectively. χ_{M} is taken as the energy of the (presumed) non-bonding t_{2g} orbitals in an octahedral complex and a correction of $10Dq$ is included in equation 2 for transitions involving the e_g orbitals. π -bonding effects on the t_{2g} orbitals are not taken into account.

The optical electronegativity is assumed in principle to be constant for a metal ion in a particular oxidation state and stereochemistry, though variations have been found for complexes containing the strongly π -donating oxo group [17]. Hollebne also found a dependence of χ_{M} of copper on χ_{L} in a series of pseudo-halide complexes [21].

Spectra of semiquinone complexes

The transitions expected in semiquinone complexes (see Table 1) have been discussed by Benelli et al. who have compared the spectra of mono-semiquinone complexes of Cr, Co, Ni and Zn with both DTBSq and tetrachlorosemiquinone (TC1Sq) and an innocent cis-bound aza-macrocycle

as the co-ligand [8-10]. Two intraligand transitions to the semiquinone singly occupied molecular orbital (SOMO) are expected, a weak band around 13000 cm^{-1} ($n-\pi^*$) and a stronger band around 28000 cm^{-1} ($\pi-\pi^*$). Other intense visible region transitions in the Ni, Cr and Co complexes were assigned as MLCT, based on the absence of corresponding bands in the spectra of the Zn analogues and the free ligand, and the shift to lower energy of these bands upon substitution of DTBSq by the more electron-withdrawing TClSq.

Detailed assignments of the spectra of ruthenium mixed ligand bpy-dioxolene species have also been made [5-7]. These typically show MLCT to both semiquinone and bpy with most of the intraligand transitions being obscured.

LMCT assignments have been suggested for Fe^{III} and Co^{III} semiquinone complexes [49,52,56]. Such transitions are expected at higher energy than those in similar catecholate species. LMCT from catechol to metal normally occurs in the visible region only in complexes where the metal is readily reducible (e.g. V^{IV} , Mn^{IV} , Fe^{III} , Mo^{VI} , Re^{VI} [57-61], not in Cr^{III} , Rh^{III} , most M^{II} , etc. [9,62,63]). In complexes of metals which have a filled t_{2g} set (Co^{III} , Ni^{II} etc.) the lowest energy LMCT transition would be $\pi^* \rightarrow \sigma^*$ in nature, and therefore relatively weak.

Calculations

Few optical electronegativity values are available for M^{II} . We have recalculated some χ_{M} values from the data of Byers et al. [40] for picolinic acid N-oxide complexes, using Jørgensen's method [17,43], with $\chi_{\text{M}}(\text{Ni}) = 2.1$ as a standard (Table 2). Reasonable agreement is found with gas-phase values reported by Jørgensen [64]. A value of χ_{M} for

χ_M of 1.7 was obtained by extrapolation from Jørgensen's values for Ru^{IV} and Ru^{III} [17]. These values of χ_M and the literature value for Cr^{III} [17] were then used to calculate χ_L for bpy and bpz in complexes in which the MLCT assignments are secure, to check the consistency of the results for MLCT transitions. Consistent values of χ_L for bpy and bpz in the various complexes are obtained. Some variation in $\chi_L(\text{bpy})$ might be expected in parallel with the bpy/bpy^- reduction potential which depends strongly upon the metal oxidation state [71].

$\chi_L(\text{DTBSq})$ was then calculated for the underlined transitions in Table 1, assuming they correspond to MLCT to the semiquinone SOMO ($3b_1$ in the free ligand). The assignments are those in the literature, or, where data were previously unassigned, the most prominent band in the visible region was chosen (apart from the $n-\pi^*$ band around 700 nm). For example, in the chromium complexes the intense band around 500 nm was chosen, consistent with the assignment of Benelli et al. for the mono-DTBSq complex [10]. This band seems to be characteristic of Cr-semiquinone species and shifts consistently, albeit a small amount, to the red with increasing charge on the complex, as expected for MLCT. In many cases it is a double band, probably due to splitting of the t_{2g} orbitals.

Calculated values of $\chi_L(\text{DTBSq})$ for most complexes lie in the range 1.2-1.5 electronegativity units (Table 3). In the case where transitions to both bpy and DTBSq are observed in the same molecule $\Delta\chi_L(\text{bpy} - \text{DTBSq})$ can be obtained directly from the difference in transition energy without calculation of the spin pairing contributions or knowledge of χ_M . Differences of ~ 0.3 are obtained for the ruthenium species which show CT to both bpy and DTBSq and also for $\text{Cr}(\text{bpy})(\text{DTBCat})(\text{DTBSq})$ if the band at 27600 cm^{-1} is assigned as

Cr → bpy.

Discussion

The values of $\chi_L(\text{DTBSq})$ are consistently higher than those of bpy, as expected for the easily reduced semiquinone ligand. The variation from 1.2 to 1.5 is not unreasonable, given the variation in values for bpy and the large variation (>1 V) in the reduction potential of DTBSq in its complexes (Table 3) as a function of metal oxidation state. There are various possible sources of error, such as the estimation of the Racah parameter, B. Errors in B are unlikely to be more than ± 200 cm^{-1} which gives a maximum error of ± 0.1 (for high spin d^5) and considerably less for most metal ions. There are also some uncertainties in the values of χ_M which we have minimised by checking against bpy and bpz.

χ_M for Mn^{II} is questionable because of uncertainty in the assignment. The relatively high intensity suggests that the transition is from the t_{2g} orbitals (a transition from the e_g would then be expected at roughly the same energy as the $n-\pi^*$ band), whereas the value of χ_M for Mn^{II} was calculated assuming the transition in the picolinic acid complex was from the e_g set, in agreement with the assignments of the original authors [40].

The data in Table 3 appear to show some variation in $\chi_L(\text{DTBSq})$ for series of complexes of the same metal ion, e.g. Cr^{III} . Most of this variation is probably due to variation in χ_M , and may result from differences in π -bonding abilities of the other ligands. Any real variation in $\chi_L(\text{DTBSq})$ for a given metal ion is a secondary effect (therefore smaller), caused by changes in χ_M . Thus the variations in χ_M and χ_L for a particular metal ion cannot be deconvoluted and it is more

reasonable to assume that χ_L is constant. For example, for Cr^{III} , if $\chi_L(\text{DTBSq})$ remains constant at ~ 1.4 $\chi_M(\text{Cr}^{\text{III}})$ decreases from 1.95 to 1.75 as the charge on the complex becomes more negative. These values of χ_M are well within the range given in the literature and the decrease is in the expected direction, the metal becoming less electronegative as more charge is donated by the ligands. Similarly for the other metals χ_L can be assumed constant for complexes of a given ion without assuming any undue variation in χ_M .

As expected, results for the Fe^{III} complexes are inconsistent with those of the other metals if the transitions are assumed to be MLCT. It is likely that the transitions are intraligand and LMCT transitions, in agreement with previous assignments [49,56].

Other complexes which give relatively extreme values of $\chi_L(\text{DTBSq})$ are those of Co^{III} , Rh^{III} and Ni^{II} . The transitions in the Ni-CTH complexes shift in the direction expected for MLCT when DTBSq is compared to TClSq and are too intense for d-d bands. There are no other transitions in the visible region (where the transition must lie) which could be assigned to $\text{Ni} \rightarrow \text{DTBSq}$.

Similarly for the Rh^{III} complexes, there are no reasonable alternative assignments. There are no other bands in the visible region that could be the expected MLCT band and the observed band at 20000 cm^{-1} in $\text{Rh}(\text{DTBSq})_3$ is much too intense (it is very broad) and too low in energy for a d-d transition [55]. The band in $[\text{Rh}(\text{bpy})_2(\text{DTBSq})]^{2+}$ occurs at lower energy than any band of comparable intensity in the corresponding DTBCat species and is therefore unlikely to be an LMCT or d-d transition [54]. It is possible that the value of χ_M for Rh may be slightly too high; in general second row transition metals have lower values than first row metals in the same group, whereas Jørgensen's

values for Co^{III} and Rh^{III} are the same [17]. A decrease in χ_{M} of 0.1 would decrease χ_{L} to 1.35-1.45 which would agree well with the rest of the data.

Both $[\text{Co}^{\text{III}}\text{CTH}(\text{DTBSq})]^{2+}$ and its TClSq analogue show two main bands in the 18000-30000 cm^{-1} region [8]. The higher is assigned as $\pi-\pi^*$ and the lower to MLCT; both shift to the red when TClSq replaces DTBSq . The so-called $\pi-\pi^*$ band is noticeably more prominent in the Co complexes than in the analogous Ni and Zn complexes [8,9]. A plausible alternative assignment for the ~ 19000 cm^{-1} band is to the lowest spin-allowed d-d transition, with its intensity increased by mixing with the nearby MLCT transition which would then be a component of the absorption around 27000 cm^{-1} . The position of the lower band is appropriate for a d-d transition in a $\text{Co}^{\text{III}}\text{O}_2\text{N}_4$ chromophore and a band of similar energy is found in the catechol analogues [8]. The prominence of the higher band is then explained since it contains both the $\pi-\pi^*$ and MLCT absorptions. The 19000 cm^{-1} (d-d) band is more intense in the TClSq complex because it lies closer to the MLCT transition than in the DTBSq species. Similar assignments are also possible for the other two Co^{III} complexes in Table 1. Using these alternative assignments, $\chi_{\text{L}}(\text{DTBSq})$ is 1.35-1.4 for the Co^{III} complexes, in agreement with data for other metals.

Values of $\chi_{\text{L}}(\text{DTBSq})$ are then:

Rh^{III}	$>$	Cr^{III}	$>$	Co^{III}	$=$	Ru^{III}	$>$	Mn^{II}	$=$	Fe^{II}	$=$	Ru^{II}	$>$	Co^{II}	$>$	Ni^{II}
1.5		1.4		1.35				1.3						1.2		1.1

showing a clear dependence on metal oxidation state. However it should be borne in mind that some of this variation may be due to variation in χ_{M} .

In general the reduction potentials for DTBSq bound to M^{III} are more

positive than those for DTBSq bound to M^{II} , in agreement with the lower values of χ_L for the latter. However, the ligand reduction potentials also depend on the charge on the complex (Table 3). Considering complexes of a given charge, it appears that there is at least a qualitative correlation between $\chi_L(\text{DTBSq})$ and the reduction potential.

Summary

The spectra of semiquinone complexes can be interpreted using the optical electronegativity method. A range of values for $\chi_L(\text{DTBSq})$ of 1.1-1.5 is found, with generally higher values for M^{III} than for M^{II} complexes. These numbers relate to the semiquinone SOMO.

Assignments of metal to ligand charge transfer transitions in complexes of Cr^{III} , Mn^{II} , Fe^{II} , Co^{II} , Co^{III} , Ni^{II} , Ru^{II} , Ru^{III} and Rh^{III} give consistent results which support some of the previous assignments and enable previously unassigned spectra and our own new data to be understood. Alternative assignments do not lead to the consistency observed here.

The fact that semiquinone is a non-innocent ligand and that some of the species are highly delocalised, i.e. the metal "oxidation state" is poorly defined [7], does not seem to be a problem. The relatively large variation in both χ_L and the ligand reduction potential is probably due more to the small size of the aromatic system in these ligands (compared to bpy or a phthalocyanine for example) than to non-innocence.

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Table 1. Visible-NIR electronic spectra of semiquinone complexes

Complex ^{a, b}	$\lambda_{\max}/\text{cm}^{-1}$ ($10^{-3}\epsilon/\text{M}^{-1}\text{cm}^{-1}$) ^c			Ref.
	M \rightarrow Sq	n \rightarrow π^*	Other	
Metal(II)				
Mn ₄ (DTBSq) ₈	<u>24400</u> (4.5)	13200(2.5)		44
t-Mn(py) ₂ (DTBSq) ₂	<u>23600</u>	12800		44
Fe(bpy)(DTBSq) ₂ ^d	<u>15600</u>			45
Co ₄ (DTBSq) ₈ ^e		13200(2.5)	26300(4.8)	44
Co(bpy)(DTBSq) ₂	<u>18200</u> (2.0)	13000(2.7)		44
Ni ₄ (DTBSq) ₈	<u>23300</u> (4.5)	13700(2.5)		44
Ni(bpy)(DTBSq) ₂	<u>23300</u> (4.3)	13100(2.5)		44
[Ni(CTH)(DTBSq)] ⁺	<u>21200</u> (1.3)	13000(0.46)		9
[Zn(CTH)(DTBSq)] ⁺		13000(0.39)	26600(1.5) ^f	9
[Ru(bpy) ₂ (DTBSq)] ⁺	<u>11850</u> (15)		28750(13) ^{f, g}	5
	8350(0.74)		20250(9.1) ^g	
Ru(bpy)(DTBSq) ₂	<u>10500</u> (12.1)	16500(11.6)	26700(5.7) ^{f, g}	7
	8 ^f 10(6.1)		19800(3.1) ^g	
[Ru(DTBSq) ₃] ⁻	<u>10750</u> (17)	16200(2.5)		46
Metal(III)				
[Cr(CTH)(DTBSq)] ²⁺	<u>22800</u> (4.5)	11500(0.5)	25000(3.7) ^f	10
			14850(3.1) ^h	
[Cr(DTBQ)(DTBSq) ₂] ⁺	<u>21100</u> (6.5)	13100(2.0)	23800(5.2) ^f	47
	19300(4.8)		14700(2.5) ^h	
[Cr(bpy)(DTBSq) ₂] ⁺	<u>20400</u> (7.2)		23800(5.0) ^f	44, 47
	19200(4.7)		14300(2.5) ^h	

Cr(DTBSq) ₃	<u>18000</u> (18)	12900(4.2)	27300(6.2) ^f	47-49
Cr(bpy)(DTBCat)(DTBSq)	<u>18900</u> (6.5)	11500(2.3) ^h	27600(4.8) ^f 14800(2.3) ^h	47
[Cr(DTBCat)(DTBSq) ₂] ⁻	<u>17600</u> (5.1)	13700(4.1)	26200(2.5) ^f 16100(5.1)	48
[Cr(DTBCat) ₂ (DTBSq)] ²⁻		12900(4.2) ^h	22300(2.9) ^f 19200(3.2)	48
Fe(bpy)(DTBCat)(DTBSq)		13000	27700, ^f 18500 ^j	45
Fe(DTBSq) ₃		15400(17) ^j	26600(22) ^{f,j} 23300(10) ^j	49, 50
Fe ₄ (DTBCat) ₄ (DTBSq) ₄		14700(10) ^j	25500(14) ^{f,j}	50
[Co(CTH)(DTBSq)] ²⁺	<u>18100</u> (0.98)	12000(0.17)	26000(1.5) ^f	8
[Co(trien)(DTBSq)] ^{2+k}	<u>19500</u> (1.3)		27800(1.1) ^f	51
Co(bpy)(DTBCat)(DTBSq)	<u>16400</u>	13000	27800, ^f 7690	52
Ru(DTBSq) ₃ (hexane) ^l	<u>17900</u> (12)	12000(9.4)	8170(4.7)	46, 53
[Rh(bpy) ₂ (DTBSq)] ²⁺	<u>23400</u> (2.1)	11000	29100(1.8) ^f	54
Rh(DTBSq) ₃	<u>20300</u> (6.2)	10700(6.5)		55

 a) py = pyridine, CTH = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-cyclotetradecane, DTBQ = 3,5-di-t-butylquinone, DTBCat = 3,5-di-t-butylcatechol.

b) For solvents and conditions see original literature. Note that there are some wide variations in ϵ for different reports of the same complex.

c) Only main bands and well-defined shoulders whose assignment is clear are reported.

d) Solvent dependent, reported in toluene. Band may also contain Fe \rightarrow bpy transition.

e) No band consistent with MLCT is reported.

- f) Internal ligand $\pi \rightarrow \pi^*$ transition.
- g) $M \rightarrow \text{bpy } \pi^*$ transition; in Ru complexes bands around 20,000 cm^{-1} are to the bpy LUMO and bands around 28,000 cm^{-1} are to the next highest bpy π^* level and overlap the sq $\pi \rightarrow \pi^*$ transition.
- h) May be an intensity-enhanced spin forbidden d-d transition, see Ref. 10.
- i) May be intervalence DTBCat \rightarrow DTBSq, or contain a component of this.
- j) Probably has LMCT component.
- k) Probably 6-coordinate in solution, with coordinated solvent molecule.
- l) Solvent dependent, reported in hexane. Assignment tentative as "oxidation state" is uncertain.

Table 2. Optical electronegativity data for picolinic acid N-oxide, 2,2'-bipyridine and 2,2'-bipyrazine complexes

Complex	MLCT/cm ⁻¹	B ^a /cm ⁻¹	χ _M	χ _L	Ref.
Mn(picO) ₂ (H ₂ O) ₂ ^b	24700	835	1.6 ^c	1.02 ^c	41
Fe(picO) ₂ (H ₂ O) ₂	21000	800	2.2(HS) ^c	1.02 ^c	41
Co(picO) ₂ (H ₂ O) ₂	23800	770	2.15 ^c	1.02 ^c	41
Ni(picO) ₂ (H ₂ O) ₂	24400	900	2.1	1.02 ^c	41
[Cr(bpy) ₃] ³⁺	29000	495	1.85	1.05	65
[Fe(bpy) ₃] ²⁺	19200	600	1.75(LS) ^d	1.0	66
[Ni(bpy) ₃] ²⁺	26000	800	2.1	1.0	67
[Ru(bpy) ₃] ²⁺	22300	350	1.7	0.9	68
[Cr(bpz)(H ₂ O) ₄] ³⁺	27940	650	1.85	1.1	69
[Fe(bpz) ₃] ²⁺	19700	600	1.75(LS) ^d	1.0	69
[Co(bpz) ₃] ²⁺	26400	750	2.15	0.95	69
[Ni(bpz) ₃] ²⁺	27600	800	2.1	0.95	69
[Ru(bpz) ₃] ²⁺	22700	350	1.7	0.9	70

a) Data from Refs. 40 and 13, Ch. 5 and 9 (estimated where data unavailable).

b) Transition is assumed to be from the e_g orbitals; a value of 8000 cm⁻¹ is used for 10Dq, as in Ref. 40.

c) Recalculated from data in Ref. 40, using Jørgensen's method [17,43] and χ_M(Ni^{II}) = 2.1 as a standard.

d) Calculated from data for bpy and bpz.

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HS = high spin; LS = low spin.

Table 3. Optical electronegativity data for DTBSq complexes.

Complex	$\lambda_{\text{max}}/\text{cm}^{-1}$	$\chi_{\text{M}}^{\text{b}}$	χ_{L}	$E(\text{L}/\text{L}^-)^{\text{c}}/\text{V}$	Ref.
<u>Metal(II)</u>					
$\text{Mn}_4(\text{DTBSq})_8$	850	1.6	1.3 ^d		
$t\text{-Mn}(\text{py})_2(\text{DTBSq})_2$	850	1.6	1.35 ^d		
$\text{Fe}(\text{bpy})(\text{DTBSq})_2$	600	2.2(\text{HS})	1.3		
$\text{Co}(\text{bpy})(\text{DTBSq})_2$	800	2.15	1.2		
$\text{Ni}_4(\text{DTBSq})_8$	800	2.1	1.05		
$\text{Ni}(\text{bpy})(\text{DTBSq})_2$	800	2.1	1.05		
$[\text{Ni}(\text{CTH})(\text{DTBSq})]^+$	800	2.1	1.15	-0.64	9
$[\text{Ru}(\text{bpy})_2(\text{DTBSq})]^+$	350	1.7	1.25	-0.49	5
$\text{Ru}(\text{bpy})(\text{DTBSq})_2$	350	1.7	1.3	-0.82 ^e	7
$[\text{Ru}(\text{DTBSq})_3]^-$	350	1.7	1.3	-0.64	46
<u>Metal(III)</u>					
$[\text{Cr}(\text{CTH})(\text{DTBSq})]^{2+}$	600	1.85	1.3	0.21	10
$[\text{Cr}(\text{DTBQ})(\text{DTBSq})_2]^+$	500	1.85	1.3		
$[\text{Cr}(\text{bpy})(\text{DTBSq})_2]^+$	500	1.85	1.35	0.2	47
$\text{Cr}(\text{DTBSq})_3$	500	1.85	1.4	0.21	72
$\text{Cr}(\text{bpy})(\text{DTBCat})(\text{DTBSq})$	600	1.85	1.4	-0.3	47
$[\text{Cr}(\text{DTBCat})(\text{DTBSq})_2]^-$	700	1.85	1.5	-0.72	72
$[\text{Co}(\text{CTH})(\text{DTBSq})]^{2+}$	550	2.3	1.6	0.34	8
$[\text{Co}(\text{trien})(\text{DTBSq})]^{2+}$	550	2.3	1.55	0.12	51
$\text{Co}(\text{bpy})(\text{DTBCat})(\text{DTBSq})$	550	2.3	1.65		
$\text{Ru}(\text{DTBSq})_3$	300	2.05	1.35		
$[\text{Rh}(\text{bpy})_2(\text{DTBSq})]^{2+}$	400	2.3	1.45	0.32	54

Rh(DTBSq) _g	400	2.3	1.55	-0.13	55
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a) Data from Ref. 13, Ch. 5 and 9 (estimated where data unavailable).

b) Data from Table II and Ref. 17.

c) DTBSq/DTBCat reduction potential vs. SCE.

d) Transition assumed to be from the t_{2g} orbitals because the intensity is comparable to other $t_{2g} \rightarrow S_q$ transitions. If it is from the e_g set χ_L is 0.3 units lower.

e) Not a simple DTBSq/DTBCat reduction - see ref. 7.