Bonding properties of 3,5-di-tert-butyl-1,2-benzosemiquinone radical-anionic ligand: resonance Raman spectra of $Re(CO)_4(DBSQ)$ and $Re(CO)_3(PPh_3)(DBSQ)$ complexes

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Abstract

Absorption spectra in the visible region and resonance Raman spectra of the spin-doublet $Re(CO)_{4-n}(PPh_3)_n(DBSQ)$ ($n=0,1$) complexes were measured in order to obtain information on the nature of their electronic transitions and excited states. Qualitative Raman excitation profiles measured across the visible absorption band of both complexes point to the presence of two electronic transitions. Based on the rR data, both transitions are identified as $d_\pi \rightarrow \pi^*$SOMO of the DBSQ ligand. These transitions have essentially MLCT character, with only very small amount of mixing between the metal and ligand-SOMO orbitals. The spectral assignment is also supported by the shift of the spectral band going from the tetracarbonyl to the tricarbonyl-phosphine complex and by the solvatochromism observed for the latter one. From these spectral data, the DBSQ radical-anion emerges as a ligand lacking any pronounced π-bonding properties toward the Re central atom. At best, it can be viewed as a very weak π-acceptor. This bonding picture is also supported by the EPR and IR data.

Introduction

Transition metal complexes containing chelated *ortho*-semiquinone radical-anionic ligand offer, owing to their stability, a unique possibility to investigate spectral, magnetic and chemical properties of compounds possessing a spin-doublet electronic ground state. Recently, more attention has been devoted to the electronic absorption spectra of these complexes [1–5]. Part of this interest stems from the possibility to achieve an optically-induced bistability as several combinations of the ligand and metal oxidation states are available in the same species [1]. The absorption spectra in the near-UV and visible spectral regions are usually assigned in terms of intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ as well as MLCT transitions. The π^*-orbital is the $3b_1$-SOMO of the semiquinone ligand (the symmetry labels refer to a C_{2v} point group of the idealized ligand geometry) that has a strong carbon–oxygen π-antibonding character [3, 6, 7]. However, the assignment of the absorption bands is not always unequivocal [2, 5] and virtually nothing is known about the structure of the excited states.

Resonance Raman (rR) spectroscopy is a powerful tool to investigate the nature of allowed electronic transitions and the structural changes accompanying excitation [8, 9]. However, as far as metal–dioxolene complexes are concerned, this technique has so far been applied only to bis(bipyridine)ruthenium(II) complexes [10] containing either the 3,5-di-*tert*-butyl-1,2-benzosemiquinone ligand (DBSQ) or the corresponding quinone (DBQ) and to $[Cr^{III}(semiquinone)_3]$ complexes [11, 12]. However, the presence of several chromophoric units in the coordination sphere and/or a strong interaction between the SQ ligands, respectively, complicates the spectral assignment.

We report here the electronic absorption and rR spectra of the $Re(CO)_4(DBSQ)$ (1) and $Re(CO)_3(PPh_3)(DBSQ)$ (2) complexes. This study aimed at a better understanding of the nature of the excited state of these, rather unusual, organometallic compounds with a spin-doublet ground state and on the assessment of the π-bonding properties of the DBSQ radical-anionic ligand. These complexes are quite amenable to such a combined spectroscopic study as the DBSQ is the only non-innocent ligand present and the ReDBSQ chelate ring and the DBSQ ligand itself are the only chromophores. Moreover, the dd transitions

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may well be expected to lie at relatively high energy, not interfering with the spectral bands in the visible region. The presence of CO ligands is also an advantage since IR and Raman bands corresponding to their stretching vibrations are very sensitive to the electronic properties of the central metal atom [13].

Experimental

Materials

3,5-Di-*tert*-butyl-1,2-benzoquinone, DBQ, (Aldrich) was recrystallized from n-heptane. $Re_2(CO)_{10}$ and PPh_3 were used as obtained from Strem and Merck, respectively. Benzene (Fluka) was distilled under nitrogen from sodium wire. $Re(CO)_4(DBSQ)$ was generated by photolysis of a freeze–pump–thaw degassed benzene solution of 10^{-2} M DBQ and 5×10^{-3} M $Re_2(CO)_{10}$. For the irradiation, either a 125 W medium-pressure or a 200 W high-pressure mercury lamp was used for 4 and 3 h, respectively. The 300–370 nm spectral region was selected for the photolysis by combination of the pyrex glass of the reaction vessel and an UG11 bandpass spectral filter (Oriel) to minimize the absorption by free DBQ. The solution was well stirred. Over 90% conversion was achieved. The purity of the resulting solution was checked by EPR and IR spectra which showed that no other radical and no other carbonyl complex, except for traces of unreacted $Re_2(CO)_{10}$, were present. The EPR, IR and visible absorption spectra agreed with the published data [14, 15]. The $Re(CO)_3(PPh_3)(DBSQ)$ complex was prepared by addition of a 10-fold excess of PPh_3 to the $Re(CO)_4(DBSQ)$ solution under an inert atmosphere. The purity was checked by IR and EPR spectroscopy [15, 16].

Instrumentation

Electronic absorption spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Philips PU9800 FTIR and Varian E4 instruments were used to obtain the IR and EPR spectra, respectively. The resonance Raman spectra were measured using a Dilor XY Raman spectrometer. The solutions were placed in quartz cuvettes and excited either by a SP 2016 Ar^+-laser or by a CR-590 dye laser employing Coumarine 6 or Rhodamine 6G dyes pumped by the Ar^+-laser. The intensities of the Raman lines were measured relative both to the benzene line at 1167 and at 607 cm^{-1}. Resulting Raman excitation profiles are qualitatively identical. Profiles constructed using line intensities measured relative to the 1167 cm^{-1} line are reported.

Results and discussion

Both $Re(CO)_4(DBSQ)$ (**1**) and $Re(CO)_3(PPh_3)$-(DBSQ) (**2**) exhibit quite simple absorption spectra in the visible region (Figs. 1 and 2) that consist of a single broad band centred at 506 nm ($\epsilon=5500$ M^{-1} cm^{-1}) and 578 nm (5800 M^{-1} cm^{-1}), respectively. This band is asymmetrical with a shoulder on its red side.

Typical resonance Raman (rR) spectra of **1** and **2** are shown in Fig. 3. They show the presence of the symmetrical ν_s(C–O) stretch of the DBSQ ligand as a rather strong band at 1436 cm^{-1} for **1** and at 1429 cm^{-1} for **2**. The band at 1523 (**1**) and 1521 (**2**) cm^{-1} belongs to a symmetrical stretch of the C3–C4 and C5–C6 bonds which have partial double-bond character. Rather weak bands are also observed at 1465, 1372, 1301 and 1250 cm^{-1} for **1** and at 1357, 1310, 1267 and 1253 cm^{-1} for **2**. In the region of the stretching vibrations of the carbonyl ligands, only one Raman band was

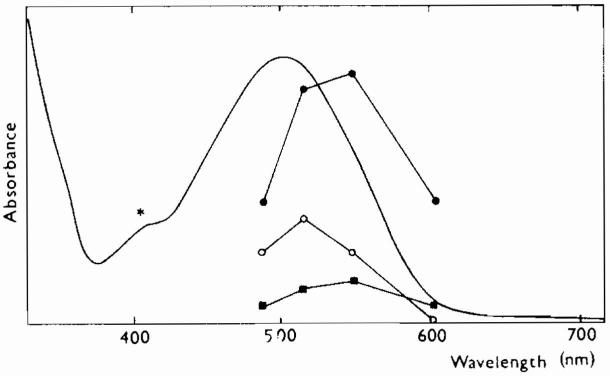

Fig. 1. Visible absorption spectrum and approximate excitation profiles of selected Raman bands of $Re(CO)_4(DBSQ)$ (**1**) in benzene solution. ●: ν_s(C–O) at 1436 cm^{-1}; ○: $\nu_s(C\equiv O)_{ax}$ at 2109 cm^{-1}; ■: ν_s(Re–O) at 553 cm^{-1}; *: traces of free DBQ.

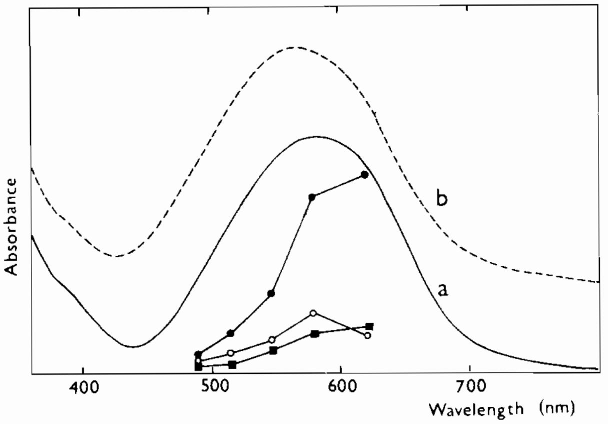

Fig. 2. Visible absorption spectrum (a) and approximate excitation profiles of selected Raman bands of $Re(CO)_3(PPh_3)(DBSQ)$ (**2**) in benzene solution. ●: ν_s(C–O) at 1429 cm^{-1}; ○: $\nu_s(C\equiv O)_{ax}$ at 2022 cm^{-1}; ■: ν_s(Re–O) at 523 cm^{-1}. Spectrum b measured in 5/1 (vol./vol.) CH_2Cl_2/C_6H_6.

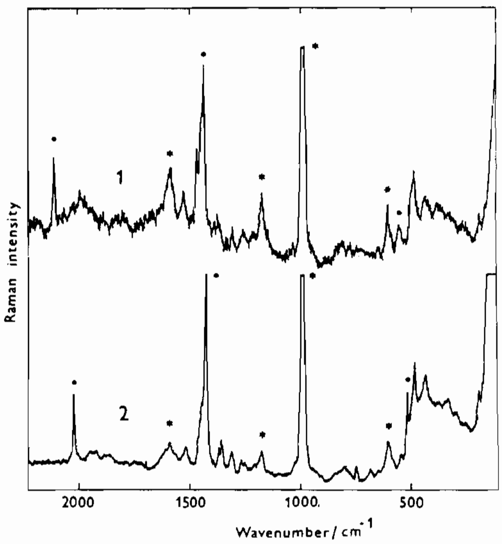

Fig. 3. Resonance Raman spectra of $Re(CO)_4(DBSQ)$ (**1**) and $Re(CO)_3(PPh_3)(DBSQ)$ (**2**) in benzene solution. Excitation at 514.5 nm (40 mW) and 579.0 nm (30 mW), respectively. *: benzene peaks; ●: peaks whose intensities were used to construct excitation profiles.

observed at 2109 (**1**) and 2022 (**2**) cm^{-1}, respectively, which belongs to the symmetrical stretching vibration of the axial (*i.e. cis* to DBSQ) carbonyl(s), $\nu_s(C{\equiv}O)_{ax}$. In accordance with data obtained for the oxalato complexes [13] and assignments of analogous rR bands of $Ru(bpy)_2(DBSQ)^+$ [10] and Fe catecholates [17], the band observed for **1** at 553 cm^{-1} and for **2** at 523 cm^{-1} is attributed to the symmetrical skeletal vibration of the ReDBSQ chelate ring. This vibration is in fact a symmetrical Re–O stretching mode partially coupled to a C1–C2 vibration and it will be further indicated as ν_s(Re–O). Other bands in the low-frequency region occur at 488 cm^{-1} for **1** and at 490 and 442 cm^{-1} for **2**. They do not have a counterpart in the rR spectra of other dioxolene complexes [10–12, 17] and are therefore tentatively assigned to M–CO stretching vibrations [13, 18, 19]. However, their assignment to a ν(Re–O) vibration coupled with the ring deformation is also plausible [13]. Taking into account the strength of the Re–CO bonds, these vibrations may well be expected in this spectral region. The bands observed at 748 and 687 cm^{-1} for **2** only may belong either to ring vibrations of DBSQ [17] or to δ-MCO deformational modes [18].

RR spectra were measured with different excitation laser lines throughout the absorption band. The ν_s(C–O), $\nu_s(C{\equiv}O)_{ax}$ and ν_s(Re–O) vibrations exhibited the most significant enhancement of intensity when the laser line came into resonance with an electronic transition. For these Raman bands, the wavelength dependence of intensity has been presented as a so called excitation profile (EP) in Figs. 1 and 2. For both complexes, the strongest rR effect is observed for ν_s(C–O) whereas $\nu_s(C{\equiv}O)_{ax}$ and, especially, ν_s(Re–O) are only weakly enhanced in intensity. The band at 488 cm^{-1} (**1**) and at 490 cm^{-1} is also weakly enhanced, its EP fully parallels that of the ν_s(Re–O). This points to its alternative assignment to a vibration involving the Re–O bonds (*vide supra*).

The interpretation of rR effects in terms of bond changes is not straightforward since the intensities depend [20] both on these changes and on the wavenumbers of the particular Raman bands:

$$\frac{I_k}{I_{k'}} = \frac{\Delta_k{}^2\omega_k{}^2}{\Delta_{k'}{}^2\omega_{k'}{}^2} \tag{1}$$

where I_k and $I_{k'}$ are the intensities of rR bands corresponding to vibrations k and k', respectively; ω_k and $\omega_{k'}$ are corresponding frequencies whereas Δ_k and $\Delta_{k'}$ are the changes in equilibrium distances between the ground and excited state potential energy curves along the normal coordinates of vibration k and k', respectively. This means that the intensities of the Raman bands belonging to $\nu_s(C{\equiv}O)_{ax}$ and ν_s(C–O) are much more sensitive even to minor bond-length changes than the intensity of the low-frequency ν_s(Re–O) Raman band which requires relatively large displacement in order to achieve the resonance enhancement. However, even if this effect is taken into account, it can be concluded that the excitation into the lowest energy electronic transition mainly affects the C–O bond of DBSQ and to a lesser extent the Re–O and carbonyl bond lengths. So, we are dealing here with a MLCT transition from Re to DBSQ, $d_\pi \rightarrow \pi^*(3b_1)$. The DBSQ SOMO ($3b_1$) is strongly π-antibonding with respect to the C–O bond of DBSQ, weakly C3–C4 and C5–C6 antibonding and weakly C1–C2 bonding [3, 6, 7]. Since the π^*-orbital is already singly occupied in the ground state, bond changes and, as a result, the rR effects will be much smaller here than for complexes such as $XRe(CO)_3$(diimine) in which the lowest π^*-orbital of the α-diimine only becomes occupied upon MLCT excitation.

The low-energy maximum in the EPs is shifted to lower energy with respect to the absorption band. This effect is not uncommon when the absorption is composed of several electronic transitions which may give rise to interference effects [8] between preresonance and rigorous resonance Raman effects. Complexes **1** and **2** both possess three different occupied d_π-orbitals of a_1, a_2 and b_1 symmetry, using the notation of the C_{2v} point group. Since the $a_1 \rightarrow 3b_1$ transition is overlap forbidden, only $a_2 \rightarrow 3b_1$ and $b_1 \rightarrow 3b_1$ will contribute to the visible absorption band and rR spectra. Due to the symmetry matching, the metal b_1 and ligand $3b_1$ orbitals can mix. As a result, a character of the $b_1 \rightarrow 3b_1$ transition can vary from purely MLCT to metal–ligand bonding-to-antibonding depending on the extent of mixing. Now, as soon as the excited state connected with this transition obtains metal–ligand π-antibonding character, ν_s(Re–O) will show a rR effect. In accordance with this, the lowest energy transition within the absorption band which has the strongest rR effect for this vibration in EP is assigned to this $b_1 \rightarrow 3b_1$ transition. The EPs show the presence of a second transition at higher energy close to the maximum of the absorption band which is assigned to the second allowed $a_2 \rightarrow 3b_1$ transition. Especially, $\nu_s(C{\equiv}O)_{ax}$ is more involved in this transition and this effect is ascribed to a decrease of the Re–$(CO)_{ax}$ π-backbonding as a result of the depopulation of the metal d_π-orbital. Apparently, this effect is more important for the $a_2 \rightarrow 3b_1$ transition. The rR effect for $\nu_s(C{\equiv}O)_{ax}$ has also been found in the rR spectra of $M(CO)_4(\alpha,\alpha'$-diimine) (M = Cr, Mo, W) and related complexes measured under MLCT excitation [21] and it has been explained by a through-space overlap between the LUMO of the diimine ligand that becomes populated in the excited state and the CO π^*-orbital [21, 22]. However, contrary to the diimine case, the $3b_1$ orbital of the DBSQ ligand is already singly occupied in the ground state of **1** and **2** and such a through-space interaction would be expected to lower significantly the $\nu_s(C{\equiv}O)_{ax}$ frequencies. However, this was found neither for **1** nor for **2** and also not for analogous Mn complexes [23]. The observed frequencies are not lower than the values typical for similar Re and Mn carbonyl complexes with innocent ligands instead of DBSQ [23]. Also, the difference between $\nu_s(C{\equiv}O)_{ax}$ frequencies corresponding to axial and equatorial CO groups in **1** (99 cm^{-1}) fits very well into the range typical for $M(CO)_4(LL)$, M = Cr, Mo, W; LL = diimines and diphosphines [24, 25]. A decrease of the $Re \rightarrow (CO)_{ax}$ back donation upon excitation caused by the depopulation of the a_2 and b_1 d_π-orbitals therefore seems to be a more plausible explanation for the $\nu_s(C{\equiv}O)_{ax}$ enhancement in this case.

The assignment of both transitions involved in the visible absorption bands as essentially MLCT ones is also supported by the red shift of the absorption band going from **1** to **2**. The substitution of the CO ligand by PPh_3 that is a stronger base and much weaker π-acceptor destabilizes the d_π-orbitals shifting the transitions to lower energy. The absorption spectrum of **2** exhibits (Fig. 2) also a solvatochromism that is typical [21] for MLCT transitions: $\lambda_{max} = 578$ and 562 nm in pure C_6H_6 and in 5/1 (vol./vol.) CH_2Cl_2/C_6H_6, respectively.

The absorption spectra of **1** and **2** do not exhibit a typical [2] low-energy absorption in the 700–1000 nm region that was proposed [3] to be diagnostic for semiquinone complexes and was assigned [1–4] to an overlap-forbidden $9a_1 \rightarrow 3b_1$ ligand localized $n \rightarrow \pi^*$ transition. If present, it may be hidden under the much more intense MLCT bands of **1** and **2**.

Conclusions

The radical *o*-semiquinone complexes **1** and **2** behave spectroscopically like analogous, though spin-singlet, carbonyl complexes of d^6 metals with ligands possessing an unoccupied π^*-orbital, *e.g.* $M(CO)_{4-n}(PR_3)_n(\alpha,\alpha'$-diimine): M = Cr, Mo, W; $n = 0,1$ [21, 22, 25]. No new bands caused by the excitation of the unpaired electron were found in the visible spectral region. As follows from the rR data, the mixing between the $3b_1$ DBSQ-localized SOMO and the metal d_π–b_1 orbital is rather limited and, consequently, the DBSQ ligand does not exert any significant π-bonding properties toward the metal. This is in full accord with EPR data that clearly point [14, 16] to a dominant localization of the unpaired electron in the electronic ground state on the DBSQ ligand with only very little delocalization over the Re atom (**1**: $a_{Re} = 28.2$ G, $a_H = 3.46$ G, $g = 2.0022$; **2**: $a_{Re} = 38.2$ G, $a_p = 25.0$ G, $g = 2.0006$) (this work). The IR $\nu(C{\equiv}O)$ frequencies of **1** (2109, 2010, 1987, 1942) are about 20 cm^{-1} lower than those of the recently described [26] analogous, albeit diamagnetic, $[Re(CO)_4(2,2'$-bipyrimidine)$]^+$ complex showing that DBSQ is a weaker π-acceptor than bpm. The crystallographic data for **2** also support [27] the rather poor π-acceptor properties of the DBSQ ligand. The excited state of both complexes may be formally viewed as d^5 Re^{II}(DBCatecholate), to some extent stabilized by a π-donation from the catecholate ligand. However, as both ground and excited states are spin-doublets, no intersystem crossing to a long-lived excited state manifold is available and the ^{2}MLCT states are expected to relax quickly to the ground state. The observed photostability of both **1** and **2** is in full accord with these conclusions.

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