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Synthesis, characterization and spectroscopic properties of 1,2-diiminetricarbonylrhenium(I)chloride complexes with *o*-benzoquinone diimines as ligands

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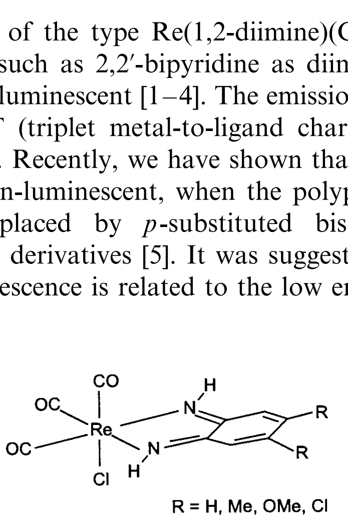
Abstract

The novel organometallic complexes Re(BQDI–R)$(CO)_3Cl$ with BQDI–R = 4,5-substituted *o*-benzoquinone diimines (R = H, Me, OMe, Cl) have been prepared and characterized by elemental analysis, IR, MS and ^{1}H-NMR spectroscopic methods. Their electronic spectra display a long-wavelength absorption band which can be ascribed to a metal-to-ligand charge transfer (MLCT) transition from Re(I) to the low-lying π*-orbitals of the *o*-benzoquinone diimine ligand, even though a significant degree of metal–ligand orbital mixing is occurring. The energy of this absorption band correlates very well with the nature of the substituents R in the 4,5-position of BQDI–R. In solvent series of decreasing polarity, the MLCT absorption maximum is shifted to longer wavelengths (negative solvatochromism). None of the Re(BQDI–R)$(CO)_3Cl$ complexes studied is photoluminescent at 298 or 77 K. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rhenium complexes; Charge transfer; Quinones; Diimines; Substituent effects; Solvatochromism

1. Introduction

Complexes of the type Re(1,2-diimine)$(CO)_3Cl$ with polypyridyls such as 2,2′-bipyridine as diimine ligands are generally luminescent [1–4]. The emission originates from ^{3}MLCT (triplet metal-to-ligand charge transfer) excited states. Recently, we have shown that such complexes are non-luminescent, when the polypyridine ligands are replaced by *p*-substituted bis(arylimino)-acenaphthene derivatives [5]. It was suggested that this lack of luminescence is related to the low energy of the corresponding MLCT states. Accordingly, it should be of considerable interest to examine other Re(1,2-diimine)$(CO)_3Cl$ complexes with long-wavelength MLCT transitions. Promising candidates for this purpose are *o*-benzoquinone diimines which can provide π* orbitals at rather low energies [6,7]. We explored this possibility and selected the following complexes for the present study (Scheme 1).



Scheme 1. Structural formula of the Re(BQDI–R)$(CO)_3Cl$ complexes.

In these compounds the π-electron system of the diimine moiety is extended by two conjugated double bonds in the six-membered ring, which in turn are directly affected by the substituents R. Inductive as well as mesomeric effects can be exploited to modify the π* orbitals of the *o*-bezoquinone diimine ligands. Therefore, the influence of the substituents R on the MLCT energies is another intriguing aspect of this investigation. The results obtained in this context may be of general significance. Charge transfer tuning of this type could be applied to other metal complexes in order to obtain desired properties such as light absorption in various spectral regions. Our present work was facilitated by previous reports on benzoquinone diimine complexes with other transition metals [7–11].

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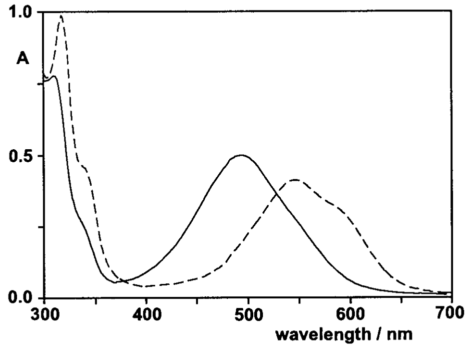

Fig. 1. Electronic absorption spectra of Re(BQDI–OMe)$(CO)_3Cl$ in methanol (—), $c = 4.1 \times 10^{-4}$ M, and toluene (- - -), $c = 2.9 \times 10^{-4}$ M.

2. Results and discussion

The compounds Re(BQDI–R)$(CO)_3Cl$ with R = H, Me, OMe and Cl are obtained as deeply colored red or blue solids, which are soluble in a variety of organic solvents. The occurrence of three CO stretching vibrations in the IR spectral region between 2030 and 1870 cm^{-1} is consistent with a facial (*fac*) arrangement of three carbonyl ligands. Accordingly, the *o*-benzoquinone diimines function as bidentate ligands, resulting in regular pseudooctahedral d^6 complexes of the *fac*-Re(1,2-diimine)$(CO)_3Cl$ type.

2.1. Spectroscopic properties

The absorption spectra of the complexes (Fig. 1, Table 1) display long-wavelength bands with maxima occurring between 500 and 700 nm, which are ascribed to metal-to-ligand charge transfer (MLCT) transitions in analogy to many other Re(1,2-diimine)$(CO)_3Cl$ compounds. This assignment is further confirmed by significant solvent polarity effects on the optical properties in the visible spectral region. The low MLCT energies observed are in accordance with the large π-accepting strength that can be expected for the quinoide BQDI–R ligands [7]. While luminescence is one of the prominent features of Re(1,2-diimine)$(CO)_3Cl$ complexes with polypiridyl derivatives as acceptor ligands [2], no authentic emission could be detected for the *o*-benzoquinone diimine complexes both at 298 and 77 K. In general, the emission quantum yields for this type of coordination compounds decrease with decreasing energy of the emitting MLCT states (energy gap law [12]). The same arguments may be applied to explain the lack of luminescence observed in the Re(BQDI–R)$(CO)_3Cl$ series, since their charge transfer states are situated at rather low energies. However, it cannot be excluded that further effects also contribute to the efficient radiationless deactivation of the photoexcited molecules. Some possible pathways including a potential role of the chloride ligand have been discussed recently in more detail for related rhenium(I) compounds [5].

2.2. Solvatochromism

The colors of the Re(BQDI–R)$(CO)_3Cl$ complexes are solvent dependent. Generally, the visible absorption bands of these compounds underlie a bathochromic shift with decreasing solvent polarity (Fig. 1). This negative solvatochromism is related directly to the charge transfer character of the corresponding electronic transitions. The solvatochromic shifts usually become smaller with an increasing π-acceptor strength of the diimine ligand as a consequence of stronger mixing between metal dπ and ligand π* orbitals by π back bonding. A quantitative analysis of these effects for the *o*-benzoquinone diimine complexes (Fig. 2) shows that the extent of charge transfer in the MLCT transition decreases in the series Re(BQDI–R)$(CO)_3Cl$ with R = OMe > Me ≥ H > Cl. The different slopes displayed in Fig. 2 decrease in the same order from 2700 to 1800, 1700 and 1000 cm^{-1}, respectively. A comparison with the MLCT band of the frequently studied compound Re(bpy)$(CO)_3Cl$ (bpy = 2,2′-bipyridyl), which gives a slope of about 3100 cm^{-1}, indicates that the BQDI–R complexes display a larger degree of electronic delocalization between rhenium and the diimine ligand than polypyridine type derivatives.

2.3. Substituent effects

In a certain solvent environment, the MLCT energies of the Re(BQDI–R)$(CO)_3Cl$ complexes are dependent on the nature of the substituents R (Fig. 3), and decrease in the series R = OMe > Me ≥ H > Cl. This

Table 1
UV–vis spectroscopic data of the Re(BQDI–R)$(CO)_3Cl$ complexes in acetonitrile solution at 298 K

R	λ_{max} (nm) (ε (l (mol cm)$^{-1}$) [a]				
H	690 sh (1100)	620 sh (1900)	538 (4000)	304 sh (3000)	
Me		526 (1300)	340 sh (1600)	310 sh (1800)	262 (23 000)
OMe		503 (1300)	313 (2400)	274 (3600)	211 (15 000)
Cl	640 sh (3800)	565 (11 100)	324 (4300)	313 (4300)	246 sh (15 200)

[a] sh = shoulder.

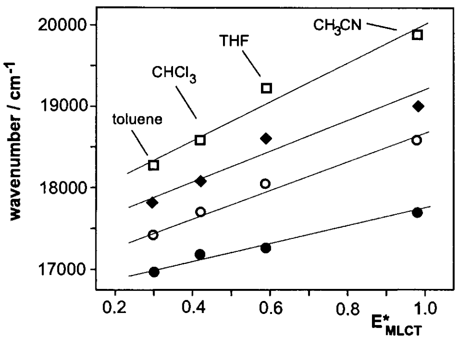

Fig. 2. Correlation between the solvent parameter E^*_{MLCT} [13] and the energy of the metal-to-ligand charge transfer transition of the Re(BQDI–R)(CO)$_3$Cl complexes (○, R = H; ◆, Me; □, OMe; ●, Cl).

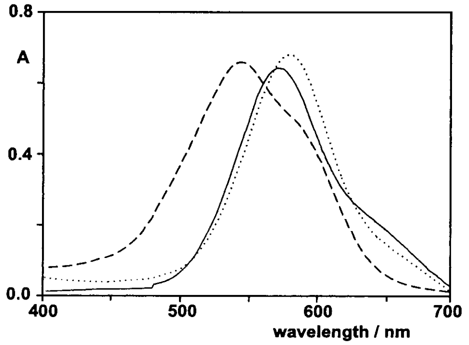

Fig. 3. Visible absorption bands of the compounds Re(BQDI–R)(CO)$_3$Cl with R = H (—), $c = 1.5 \times 10^{-4}$ M, R = Cl (···), $c = 6.0 \times 10^{-5}$ M, and R = OMe (- - -), $c = 4.7 \times 10^{-4}$ M in benzene solution.

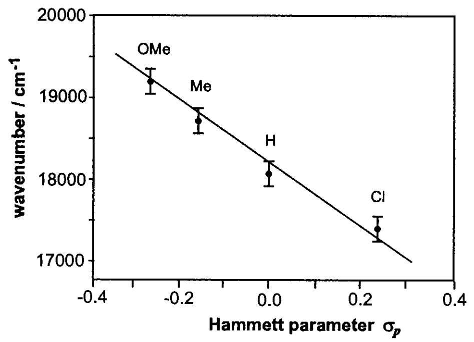

Fig. 4. Substituent effects on the MLCT absorption maxima of the Re(BQDI–R)(CO)$_3$Cl complexes dissolved in ethylacetate.

dependency reflects the electron-donating or withdrawing properties of the substituents. A reasonably linear relationship between the charge transfer energies and the Hammett parameter σ_p [14] is obtained for the complexes of the BQDI–R series (Fig. 4). The slope of the plot corresponds to $-(3600 \pm 300)$ cm^{-1} with a correlation coefficient of $R = 0.995$. This indicates a rather strong influence of the various 4,5-substituents on the electronic structures of the *o*-benzoquinone diimine complexes, which in turn can be exploited for controlling their spectroscopic properties. In this context it is interesting to point out that a substitution of the parent *o*-benzoquinone diimine ligand with the electron-donating methoxy groups prevents a delocalization of electron density from the low-valent rhenium(I) central metal to the quinoide ligand system very efficiently. Thus, the optical properties of the Re(BQDI–OMe)(CO)$_3$Cl complex preserve a rather high degree of charge transfer character. Since in a given coordination compound, the electron distribution and therefore also the formal oxidation levels of the metal and the ligand itself depend critically on the extent of orbital-mixing [7,8], these findings should also be helpful for the study of other metal complexes carrying quinoide ligand systems.

3. Experimental

3.1. Materials and methods

The starting materials Re(CO)$_5$Cl, *o*-phenylenediamine, 4,5-dimethyl-*o*-phenylenediamine and 4,5-dichloro-*o*-phenylenediamine were purchased from Aldrich and used without further purification. 4,5-Dimethoxy-*o*-phenylenediamine was prepared in two steps from 1,2-dimethoxy-4,5-dinitrobenzene following the literature method [15,16]. Preferably spectrograde solvents were used. Electronic absorption spectra were recorded at 298 K in 1-cm quartz cells on a Kontron Uvikon 932 double-beam spectrophotometer. IR spectra were measured on a Beckman Acculab 6 spectrometer. ^{1}H-NMR data were recorded with a Bruker AC 250 (250 MHz) spectrometer with TMS added as internal standard. Mass spectra were obtained using Finnigan MAT 95 and Varian MAT 311 instruments. luminescence properties were investigated with a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier.

3.2. Preparation and characterization of the *o*-benzoquinone diimine complexes

Synthesis of the title compounds Re(BQDI–R)(CO)$_3$Cl was achieved according to the general procedure described below. A suspension of Re(CO)$_5$Cl (181 mg, 0.50 mmol), an equilmolar amount of the corresponding *o*-phenylenediamine and 1 ml triethylamine in 20 ml of toluene was refluxed for 20 min. Subsequently, a stream of air was bubbled through the reaction mixture under vigorous stirring. During this period, the initially yellowish–brown suspensions turned red (R = H, Me, OMe) or blue (R = Cl). The precipitates formed were collected by filtration and dried under vacuum. Further purification of the crude products was carried out under argon protection by column chromatography on silica gel (60 mesh) using ethyl acetate (R = H, Me, OMe) or ethanol as eluents (R = Cl). When the solvent was concentrated under reduced pressure and 50 ml of *n*-hexane were added, the metal complexes precipitated as microcrystalline solids.

3.2.1. *Re(BQDI–H)(CO)$_3$Cl*

Yield 149 mg (0.36 mmol, 72%). IR (KBr): $\nu = 2030$, 1930, 1880 cm^{-1} (CO). ^{1}H-NMR (DMSO-d^6): $\delta =$ 13.43 (s, 2H), 7.10 (m, 2H), 6.14 (m, 2H). MS (FD$^+$, CH_2Cl_2): m/z (%) = 410 (45.4), 412 (100.0), 414 (44.4). $C_9H_6ClN_2O_3Re$ (411.82): Anal. Calc.: C, 26.25; H, 1.47; N, 6.80; Found: C, 27.45; H, 2.12; N, 6.73%.

3.2.2. *Re(BQDI–Me)(CO)$_3$Cl*

Yield 93 mg (0.21 mmol, 42%). IR (KBr): $\nu = 2030$, 1930, 1890 cm^{-1} (CO). MS (FD$^+$, CH_2Cl_2): m/z (%) = 440 (42.6), 442 (100.0), 444 (22.2). $C_{11}H_{10}ClN_2O_3Re$ (439.94): Anal. Calc.: C, 30.04; H, 2.29; N, 6.37; Found: C, 30.33; H, 2.58; N, 6.80%.

3.2.3. *Re(BQDI–OMe)(CO)$_3$Cl*

Yield 177 mg (0.37 mmol, 75%). IR (KBr): $\nu = 2030$, 1950, 1890 cm^{-1} (CO). ^{1}H-NMR (CD_2Cl_2): $\delta = 10.21$ (s, 2H), 6.10 (s, 2H), 3.89 (s, 6H). MS (FD$^+$, CH_2Cl_2): m/z (%) = 470 (29.4), 472 (95.2), 474 (100.0), 476 (27.0). $C_{11}H_{10}ClN_2O_5Re$ (471.87): Anal. Calc.: C, 28.00; H, 2.14; N, 5.94; Found: C, 28.79; H, 2.17; N, 6.87%.

3.2.4. *Re(BQDI-Cl)(CO)$_3$Cl*

Yield 153 mg (0.32 mmol, 64%). IR (KBr): $\nu = 2030$, 1940, 1870 cm^{-1} (CO). ^{1}H-NMR (CD_2Cl_2): $\delta = 10.63$ (s, 2H), 6.80 (s, 2H). MS (FD$^+$, acetone): m/z (%) = 478 (1.8), 480 (45.1), 482 (100.0), 484 (71.1), 486 (21.1). $C_9H_4Cl_3N_2O_3Re$ (480.71): Anal. Calc.: C, 25.08; H, 1.91; N, 5.32; Found: C, 24.89; H, 5.53; N, 5.89%.

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