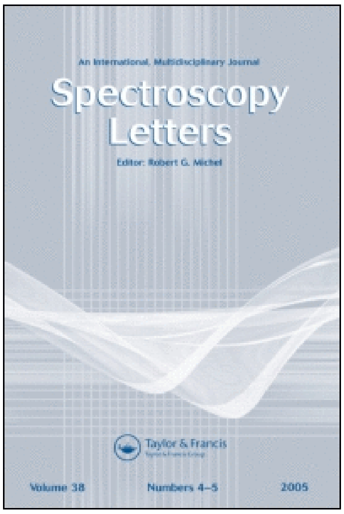


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Halochromic Properties of cis-Ru(bpy)$_2$Cl$_2$ Inorganic Solvents

Ricardo L. de Almeidaa[a]; Marcos Caroli Rezendeb[b]; Eduardo Stadlera[a]
[a] Departamento de Química, Universidade Federal de S. Catarina, S. Catarina, SC, Brasil [b] Facultad de Quimica y Biología, Universidad de Santiago de Chile, Santiago, Chile

To cite this Article de Almeidaa, Ricardo L. , Rezendeb, Marcos Caroli and Stadlera, Eduardo(1999) 'Halochromic Properties of cis-Ru(bpy)$_2$Cl$_2$ Inorganic Solvents', Spectroscopy Letters, 32: 3, 497 — 504
To link to this Article: DOI: 10.1080/00387019909350001
URL: http://dx.doi.org/10.1080/00387019909350001

SPECTROSCOPY LETTERS, 32(3), 497-504 (1999)

HALOCHROMIC PROPERTIES OF *cis*- $Ru(bpy)_2Cl_2$ IN ORGANIC SOLVENTS.

keywords: Halochromism, voltammetry, salt effect, ruthenium complex

Ricardo L. de Almeida[a] , Marcos Caroli Rezende[b] and Eduardo Stadler * [a]

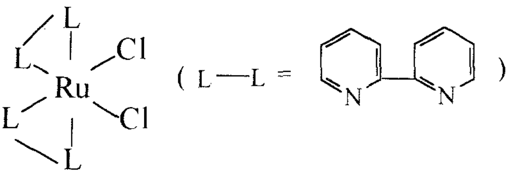
a) Departamento de Química, Universidade Federal de S. Catarina, C.P. 476, Florianópolis, S.Catarina, SC 88040-970, Brasil ; b) Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile.

Abstract: The halochromic behaviour of the title ruthenium complex in acetonitrile and dimethylformamide, in the presence of lithium, sodium and magnesium perchlorate, was studied employing parallel spectroscopic and voltammetric measurements. The results point to an association between the added cation and the chloride ligands, that depends on the nature of the cation and of the solvent, and which affects the charge density on the central ruthenium metal.

www.dekker.com

Solutions of solvatochromic dyes often exhibit the related phenomenon of halochromism, in which spectral changes are observed by the addition of electrolytes to the medium.[1-7] We have been concerned for some time with the halochromic properties of organic and inorganic compounds, trying to relate the observed effect with the structure of the dye and the nature of the added electrolyte. Thus, we have recently studied the cationic halochromism of the 1-methyl-8-oxyquinolinium betaine in organic media, which arises from metal ion-phenoxide associations.[7]

One example of a solvatochromic inorganic dye, the *cis*- $Fe(phen)_2(CN)_2$, which also exhibits halochromism, has also been the object of our studies [8]. Because of the reversible nature of its redox process, this compound provided us with the possibility of studying the dye-salt association through parallel spectroscopic and electrochemical techniques. More recently, Linert *et al.* utilized the halochromic properties of the same sensor and the analogous complex $Ru(phen)_2(CN)_2$ to build a scale of acceptor numbers for cations.[9] This report prompted us to describe our observations on another halochromic ruthenium complex, the *cis*-$Ru(bpy)_2Cl_2$, whose spectra in electrolyte organic solutions is described in the present communication, coupled with parallel voltammetric measurements of variations of its redox potential with the addition of salts.



Experimental :

The UV-visible spectra were recorded on a Hitachi U-3000 spectrophotometer. Cyclic voltammetric measurements were carried out with a

Bioanalytical CV-27 model, utilizing a Ag/AgNO$_3$ reference electrode. Au as a working electrode and a Pt wire as the auxiliary electrode.

All employed solvents were analytically pure and were further purified according to standard procedures [10], being stored over 4 A molecular sieves. Alkaline-earth-metal perchlorates prepared by treatment of the corresponding carbonate with a 70% HClO$_4$ solution, were crystallized from water. All crystallized perchlorates, including the commercially available sodium salt (Merck) were thoroughly dried at 80-90°C for 4 h under vacuum (1 mm Hg). The metal complex *cis*-Ru(bpy)$_2$ Cl$_2$ was prepared following a reported procedure[11], and afterwards dried under vacuum.

The halochromic shifts of the title compound in organic media ($c = 10^{-3}$ mol.dm^{-3}) were measured at 25°C by recording the position of its charge-transfer absorption bands around 370 and 550 nm in the presence of increasing concentrations of added metal perchlorate. The half-potentials were measured at a constant temperature (25°C) in the presence of a fixed concentration of tetrabutylammonium fluoroborate (Fluka) as the supporting electrolyte. The effect of salt addition upon the half-wave potential of *cis*-Ru(bpy)$_2$Cl$_2$ was followed by recording voltammograms of the same solution of the dye ($c = 10^{-3}$ mol.dm^{-3}) and Bu$_4$NBF$_4$ (0.1 mol.dm^{-3}) , to which were added increasing amounts of the perchlorate salts. All voltammetric measurements were carried out under argon atmosphere.

Results and Discussion:

The *cis*-Ru(bpy)$_2$ Cl$_2$ complex presents two solvent-sensitive charge-transfer absorptions in the visible. These metal-to-ligand charge-transfer (MLCT) absorptions probably arise from transitions from the metal t_{2g} to two bipyridine π^* orbitals. Thus, the energy separation between MLCT1 and MLCT2 compares well with the differences between the first two internal

Table 1 - Halochromic shifts of the two metal-to-ligand charge-transfer bands of *cis*-$Ru(bpy)_2Cl_2$ in MeCN and DMF, in the presence of sodium ,lithium and magnesium perchlorate.

	Acetonitrile						Dimethylformamide			
$M(ClO_4)_n$/ mol.dm^{-3}	$\lambda_{max}{}^{a}$ / nm			$\lambda_{max}{}^{b}$ / nm			$\lambda_{max}{}^{a}$ / nm		$\lambda_{max}{}^{b}$ / nm	
	Na^+	Li^+	Mg^{+2}	Na^+	Li^+	Mg^{+2}	Na^+	Mg^{+2}	Na^+	Mg^{+2}
0.00	374	374	374	548	548	548	382	382	562	562
0.09	373	371	364	545	542	524	381	381	560	561
0.13	371	369	361	544	537	521	380	381	559	560
0.16	371	367	360	543	535	520	379	381	558	560
0.20	371	366	358	542	532	518	379	-	557	559
0.23	371	365	357	541	531	517	379	380	557	559
0.26	370	364	355	540	530	516	378	380	556	-
0.28	370	363	355	539	529	515	377	379	555	558
0.31	369	362	-	539	528	-	377	378	554	558
0.35	368	360	355	538	526	514	376	377	553	558
0.40	367	359	352	536	-	-	375	375	550	558

(a) Corresponding to $\pi_1{}^*$(bpy) ← dπ (Ru) ;

(b) corresponding to $\pi_2{}^*$(bpy) ← dπ (Ru)

π → π* transitions.[12] The two negatively charged π–donor ligands Cl^- help stabilize the Ru(III) oxidation

The halochromic shifts of the two MLCT bands of the title ruthenium complex were measured in acetonitrile and dimethylformamide, in the presence of increasing concentrations of sodium, lithium and magnesium perchlorate. The corresponding λ_{max} variations with the salt concentration are given in Table 1.

Table 2 - Variation of the reversible half-wave redox potential of $Ru(bpy)_2Cl_2$ in acetonitrile and dimethylformamide, in the presence of increasing concentrations of metal perchlorates.

$M(ClO_4)_n$ / mol.dm^{-3}	$E_{1/2}$ / mV ^{a} Acetonitrile		Dimethylformamide	
	Na^+	Mg^{+2}	Na^+	Mg^{+2}
0.0	30.0	30.0	-	-
0.1	45.0	50.0	10.0	-
0.2	52.5	60.0	12.5	36.0
0.3	53.5	70.0	12.5	65.0
0.4	55.0	80.0	13.5	70.0
0.5	-	90.0	15.0	77.5
0.6	52.5	90.0	16.0	-
0.7	52.5	90.0	16.5	80.0
0.8	-	110.0	17.5	85.0

(a) Potentials in mV *vs* $Ag/AgNO_3$

Table 2 lists the variation of the reversible half-wave redox potential of the ruthenium complex in acetonitrile and dimethylformamide, as a function of the concentration of different metal perchlorates.

The halochromic behavior of $Ru(bpy)_2Cl_2$ in DMF and acetonitrile is similar to that of $Ru(phen)_2(CN)_2$, described by Linert *et al.* [9], and can be ascribed to an association between the chloride ligands and the cation. This is reflected by the observed hypsochromic shifts of the two MLCT bands, which increase with the concentration of the added salt. These shifts are greater in

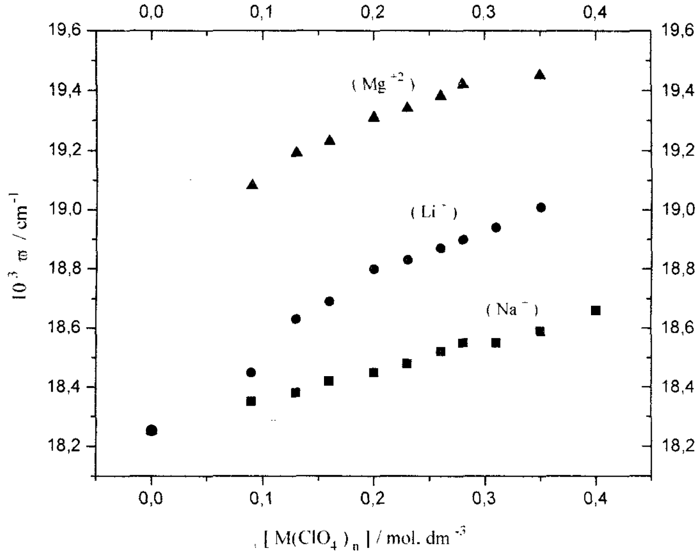


Figure 1 - Variation of the MLCT transition energies, in wavenumber values ν , of $Ru(bpy)_2Cl_2$ in acetonitrile in the presence of increasing molar concentrations of added metal perchlorate.

dilute salt solutions, tending to plateau values as more electrolyte is added (Figure 1).

Such curves reflect the fact that salt dissociation and, therefore, free cation availability, are greater in dilute solutions. As a result, the spectra of the ruthenium complex are more sensitive to the addition of a metal cation in dilute perchlorate solutions.

As regards the nature of the added cation, harder species tend to associate more strongly, bringing about larger halochromic shifts. Thus, in acetonitrile, the observed halochromic shifts increase in the order $Na^+ < Li^+ < Mg^{+2}$, reflecting the increased Lewis acidity of these species. This trend had been observed before with the sensors $Fe(phen)_2(CN)_2$ [8,9] and $Ru(phen)_2(CN)_2$ [9] and arises from the fact that association of the chloride ligands with the cationic acceptors ultimately decreases the electron density on the ruthenium metal, thereby rendering more difficult the metal-to-ligand charge-transfer process. In spectroscopic terms this corresponds to increased transition energies for the MLCT bands. The same effect finds a parallel evidence in the voltammetric measurements of Table 2. Association of the chloride ligands with a cationic acceptor leads to greater positive charge on the ruthenium metal, thus shifting the oxidation potential of the Ru(II)/Ru(III) couple to larger values.

The data of Table 1 and 2 also show that halochromic shifts depend not only on the nature of the cation but also of the solvent. This is to be expected from an effect which arises from dye-cation association. In acetonitrile (DN = 14.1 kcal.mol^{-1}) cations are less solvated than in the more donor solvent DMF (DN = 26.6 kcal.mol^{-1}). This results in stronger association and greater cation differentiation in the former than in the latter solvent. The same trends had been observed for the analogous $Ru(phen)_2(CN)_2$ sensor in different organic media [9].

In conclusion, the title ruthenium complex, like the analogues $Fe(phen)_2(CN)_2$ and $Ru(phen)_2(CN)_2$, studied by us [8] and others [9] exhibits cationic halochromism, which arises from associations of the added M^{+n} species with the chloride ligands in organic media. This salt-dye association affects the transition energies of the MLCT bands of this complex and its reversible redox potential, by decreasing the charge density upon the central ruthenium atom.

References:

1. Zanotto, S.P., Scremin M., Machado C. and Rezende M.C. **J.Phys.Org.Chem.** 1993, *6*, 637.
2. Reichardt C., Asharin-Fard S. and Schaefer G., **Chem. Ber.** 1993, *126*, 143.
3. Reichardt C., Asharin-Fard S. and Schaefer G. **Liebigs Ann. Chem.** 1993, 23.

4. Machado C., Nascimento M.G. and Rezende M.C. **J.Chem.Soc. Perkin 2** , 1994, 2539

5. Ramirez C.B., Carrasco N. and Rezende M.C. **J.Chem. Soc. Faraday Trans.** 1995, *91*, 3839.

6. Reichardt C., Blum A. , Harms K. and Schaefer G., **Liebigs Ann./ Recueil** 1997, 707.

7. Machado V.G., Nascimento M.G. and Rezende M.C. , **Spectroscopy Letters** 1998, *31*, 359.

8. Rodrigues C.A., Stadler E. and Rezende M.C. **J.Chem.Soc. Faraday Trans.** 1991, *87*, 701

9. Linert W., Jameson R.F. , Bauer G. and Taha A., **J.Coord.Chem.** 1997, 42, 211.

10. Furniss B.S. , Hannaford A.J., Smith P.W.G. and Tatchell A.R., **Vogel's Textbook of Practical Organic Chemistry,** 5 th ed., Longman, Essex, 1989.

11. Sullivan B.P., Salmon D.J. and Meyer T.J., **Inorg. Chem.** 1978, *17*, 3334

12. Johnson C.R. and Shepherd R.E. ,**Inorg. Chem.** 1983, *22*, 2439.

Date Received: October 5, 1999
Date Accepted: March 1, 1999