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Photochemical behavior of the dichlorobis(dimethylsulfoxide)bis-(*t*-butylpyridine)ruthenium(II) complex

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Abstract

The photochemical behavior of the *cis, cis, trans*-[$RuCl_2(dmso)_2(tbpy)_2$] (tbpy = 4-*t*-butylpyridine, dmso = dimethyl sulfoxide) has been investigated by means of electronic, FTIR and ^{1}H NMR spectroscopy, cyclic voltammetry and reversed-phase HPLC techniques. Excitation at the charge-transfer and ligand field bands in the near-UV region leads to the selective labilization of the dimethyl sulfoxide ligands, forming the corresponding acetonitrile complexes with complete retention of configuration. No evidence of parallel geometric or linkage isomerization processes has been found. The reactive excited state is consistent with a ^{3}LF state around 19,000 cm^{-1}.

Keywords: Ruthenium-sulfoxides; Dimethyl sulfoxide; Photodissociation

1. Introduction

Ruthenium–sulfoxide complexes have been extensively investigated in the last two decades [1] because of their interesting properties and usefulness, particularly in catalysis [2] and transition metal chemotherapy [3]. A typical example is the *cis*-[$RuCl_2(S\text{-}dmso)_3(O\text{-}dmso)$] complex (S,O-dmso = S or O bound dimethyl sulfoxide). This species has been prepared by thermal reactions, constituting an important reagent for the synthesis of ruthenium complexes. The corresponding *trans*-[$RuCl_2(S\text{-}dmso)_4$] derivative results from the photoisomerization of the starting compound. Both isomers exhibit pronounced antitumor activity, similarly to the *cis*-[$Pt(NH_3)_2Cl_2$] complex. They strongly bind to guanine bases and seem to inhibit the restriction enzymes that recognize DNA sequences containing two or more adjacent guanines [3]. Mixed derivatives with biological bases and *N*-heterocyclic ligands such as nitroimidazole have also been employed in radiosensitizing measurements [4].

Recent reports from this laboratory have focused on the synthesis and characterization of a series of [$RuCl_2(S\text{-}dmso)_2L_2$] compounds, where L = *N*-heterocyclic bases [5–7], starting from the *cis*-[$RuCl_2(S\text{-}dmso)_3(O\text{-}dmso)$] complex. This type of complex admits five geometrical isomers involving distinct *cis* or *trans* configurations for the Cl, dmso and L ligands, i.e., the all *cis* (*ccc*), all *trans* (*ttt*), and the mixed *cct*, *ctc* and *tcc* isomers, respectively. In the case of the 4-*t*-butylpyridine (tbpy) derivative, the most stable isomers have been isolated and characterized as the *ccc* and *cct* species [8].

In spite of the frequent use of photochemical methods in the synthesis of ruthenium-sulfoxide complexes, little is known about the photoreactivity of the mixed ligand species. In the course of our previous work [8] we observed that the *cct*-[$RuCl_2(dmso)_2(tbpy)_2$] complex undergoes dramatic colour changes when exposed to UV or sun light, in contrast to the *ccc* isomer. The photochemistry involved is not obvious, since in addition to photoredox processes, this type of complex can undergo geometrical and/or S-to-O (dmso) linkage photoisomerization processes, as well as, concurrent or selective photolabilization of the Cl^-, dmso and tbpy ligands. Now, in order to elucidate the photochemical behavior of this complex, we employed combined techniques, such as electronic, vibrational and NMR spectroscopy, chromatography and cyclic voltammetry, capable of monitoring the redox properties and the electronic structure of the species involved, as well as the presence of free ligands in solution. Organic sensitizers were also used, in order to characterize the reactive excited states involved in the photochemical process.

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2. Experimental details

The *cct*-[$RuCl_2$(S-dmso)$_2$(tbpy)$_2$] complex was synthesized and characterized previously [8]. Acetonitrile, HPLC grade, (Carlo Erba) was dried over molecular sieves.

Electronic absorption spectra were recorded on a Hewlett-Packard model 8453 spectrophotometer. Infrared spectra of the complex were recorded on a FTIR-Midac spectrophotometer. ^1H NMR spectra (in $CDCl_3$ vs. TMS) were recorded on a Bruker AC-200 spectrometer. High-performance liquid chromatography (HPLC) measurements were carried out using a Zorbax RP C-8 column (isocratic elution with 60:40 methanol–water, flow rate 1.25 cm^3 min^{-1}) and a CG model 480-C instrument equipped with diode-array detection. Electrochemical measurements were performed using an EG and G Princeton Applied Research model 173 potentiostat, using the conventional three electrode arrangement. A platinum working electrode was employed *versus* an Ag/$AgNO_3$ (0.010 mol dm^{-3}) reference electrode, in acetonitrile containing 0.10 mol dm^{-3} tetraethylammonium perchlorate.

Monochromatic irradiations at 270, 365 and 430 nm were carried out by using an Applied Photophysics system equipped with a 150 W xenon lamp source. Ferrioxalate actinometry was used for light intensity measurements. The ruthenium complex solutions, typically 1×10^{-4} mol dm^{-3}, in argon saturated acetonitrile, were always freshly prepared and kept in the dark. Photolysis were carried out at room temperature, using 4.00 cm pathlength quartz cells, under constant stirring. The quantum yields were determined from the decay of the absorbance of the starting complex at the isosbestic point for the primary and second photoproducts, i.e., $\lambda=278$ nm ($\varepsilon=2.5\times10^{-3}$ cm^{-1} mol^{-1} dm^3). Sensitization studies were carried out using rhodamine-6G (Sigma) and biacetyl (Aldrich), in acetonitrile solutions.

3. Results and discussion

The *cct*-[$RuCl_2$(S-dmso)$_2$(tbpy)$_2$] complex exhibits a C_{2v} microsymmetry, where the metal d_π orbitals transform according to the b_1, b_2 and a_2 representations, and the lowest unoccupied π^* orbitals of the tbpy ligand form the basis of two representations, namely, b_1 and a_1, or ψ and χ, respectively.

The electronic spectrum (Fig. 1) consists of two relatively strong bands at 270, and 316 nm, respectively, which have been previously ascribed to ruthenium-to-tbpy ($d_\pi{}^{-}p_\pi$) charge transfer transitions [8]. According to symmetry and orbital overlap considerations, these two bands are consistent with the $d_\pi(b_1)-L_\pi(b_1)^*$, and $d_\pi(b_1)-L_\pi(a_1)^*$ transitions, or MLCT(1) and MLCT(2), respectively. A third band can be detected at 430 nm, exhibiting a much smaller intensity [8]. Although the possibility of a weak charge-transfer transition can not be ruled out, its assignment as a ligand field transition is most plausible. In fact, the small intensity is coherent with a ligand field transition, as determined by the Laporte prohibition, and its location in the region of the $^1A_{1g}-{}^1T_{1g}$ ligand field transition for hexacoordinated ruthenium(II) complexes, (e.g., 529, 390 and 370 nm, respectively [9], for $[Ru(H_2O)_6]^{2+}$, $[Ru(NH_3)_6]^{2+}$, and $[Ru(en)_3]^{2+}$), is rather suggestive. This band is observed at 315 nm (31,700 cm^{-1}) in the starting *cis*-[$RuCl_2$(dmso)$_4$] complex [10], reflecting the strong ligand field strength of the S-bound dimethyl sulfoxide ligand. In the case of the *cct* isomer, it should be noticed that the ligand field strength of pyridine is comparable to that of ammonia, whereas chloride ions and S-dmso are about 1.7 times weaker and 1.3 times stronger, respectively, than NH_3 [9,11,12]. The smaller ligand field strength of chloride is compensated by the higher field strength of dmso ligands, and as a consequence, the average ligand field environment around the metal ion results comparable with that for the $[Ru(NH_3)_6]^{2+}$ complex. The absorption band at 430 nm is indeed very close to that corresponding to the first spin-allowed transition ($^1T_{1g}$) in ruthenium(II)–amines [13].

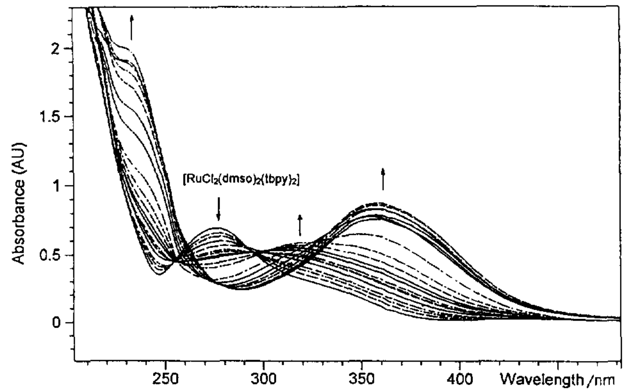

Fig. 1. Absorption spectra of the *cct*-[$RuCl_2$(S-dmso)$_2$(tbpy)$_2$] complex in acetonitrile, showing the successive changes, after irradiation at 270 nm.

The colour of the acetonitrile solutions of the *cct*-[$RuCl_2$(S-dmso)$_2$(tbpy)$_2$] complex changed from practically colorless to deep yellow, after a few minutes of exposition to UV or sun light, indicating the occurrence of light induced processes. Upon irradiation at three different wavelengths (270, 365 and 430 nm) the intensity of the absorption band around 270 nm decreased and a new band appeared around 315 nm, as shown in Fig. 1. The process is well behaved, exhibiting isosbestic points at 255 and 295 nm; however, after prolonged irradiation a consecutive photochemical reaction takes place, converting the initial products absorbing at 315 nm, to new species absorbing at 358 nm, with an isosbestic point at 278 nm.

Determinations of the quantum yields for the first process led essentially to the same value for all the wavelengths employed, e.g., 0.13 (±0.02) mol $einstein^{-1}$. These results are consistent with the participation of a single reactive excited state, generated via internal conversion and intersystem crossing mechanisms involving the ^{1}MLCT and ^{1}LF states.

The electronic spectrum of the product absorbing at 315 nm was rather similar to that of the *ccc*-[$RuCl_2$(S-dmso)$_2$(tbpy)$_2$] complex [8], and the possibility of photoisomerization was strongly considered at this point. In order to confirm this hypothesis, the photochemical process was also monitored by means of HPLC, ^{1}H NMR and FTIR techniques.

The chromatogram of a methanol solution of the *cct*-[RuCl$_2$(S-dmso)$_2$(tbpy)$_2$] isomer stored in the dark showed only one peak with retention time (T_R) of 1680 s. After irradiation at $\lambda = 430$ nm, the intensity of this peak decreased while two new peaks with retention times of 1400 s and 140 s appeared. The first peak was due to the photoproduct absorbing at 315 nm, while the second one having the lowest T_R coincided with that of the non-coordinated dimethyl sulfoxide, indicating the occurrence of dissociation of the sulfur ligand.

The ^{1}H NMR spectra of the CDCl$_3$ solution [8] exhibited a new peak at 2.62 ppm (vs. TMS) after irradiation, corresponding to the resonance signal of the free dimethyl sulfoxide ligand. This result was also indicative of preferential photolabilization of the dmso ligand from the complex.

The FTIR spectroscopy also provided support to this observation. The sulfoxide molecules coordinated to the ruthenium(II) by the sulfur atom are responsible for a strong band at 1080 cm^{-1} in the vibrational spectra, corresponding to the ν(SO) frequency [8]. After a solution of the *cct* complex in CDCl$_3$ was irradiated, the intensity of the ν(SO) vibrational peak decreased, as expected for the dissociation of the sulfoxide ligand.

In this way, the photoisomerization hypothesis was ruled out. In order to determine the nature of the dissociation products, the photolysis was also monitored electrochemically, as illustrated in Fig. 2.

The voltammogram of the starting *cct*-[RuCl$_2$(S-dmso)$_2$(tbpy)$_2$] complex exhibited a reversible monoelectronic wave corresponding to the Ru$^{III/II}$ redox couple at $E = 1.12$ V (vs. SHE), in acetonitrile [8]. After irradiation, the initial electrochemical waves were gradually replaced by new reversible ones, at $E = 0.87$ V, associated with the primary photodissociation product.

High redox potential values have been observed for ruthenium(II)–sulfoxide complexes due to the contribution of the Ru$^{II} \rightarrow$ S-dmso π-backdonation to the HOMO stabilization [7]. Therefore, analogously to the spectrochemical series, the E° values are also related to the binding properties of the ligands, and can be rationalized in terms of the E_L parameters [14], according to the equation:

$$E^\circ = S_M \Sigma E_L + I_M$$

The angular and linear coefficients of the E° vs. E_L correlations, e.g., S_M and I_M, depend upon the nature and stereochemistry of the metal complexes [14], allowing the differentiation of two isomeric species. The literature values of E_L for the Cl$^-$, tbpy, CH$_3$CN and dmso ligands were -0.24, 0.23, 0.34 and 0.47, respectively [14]. In acetonitrile solutions, the photodissociation of a ligand would lead to the rapid coordination of the solvent molecule. Therefore, considering the relative E_L values, the observed decrease of E_o can only be explained in terms of the replacement of a dmso ligand by an acetonitrile molecule, since any other possibility would increase the redox potentials. The possibility of occurring a parallel isomerization reaction can also be eliminated, since the *ccc*-isomer [8] exhibits a higher redox potential ($E_o = 1.27$ V) in comparison with the *cct* analogue ($E_o = 1.12$ V).

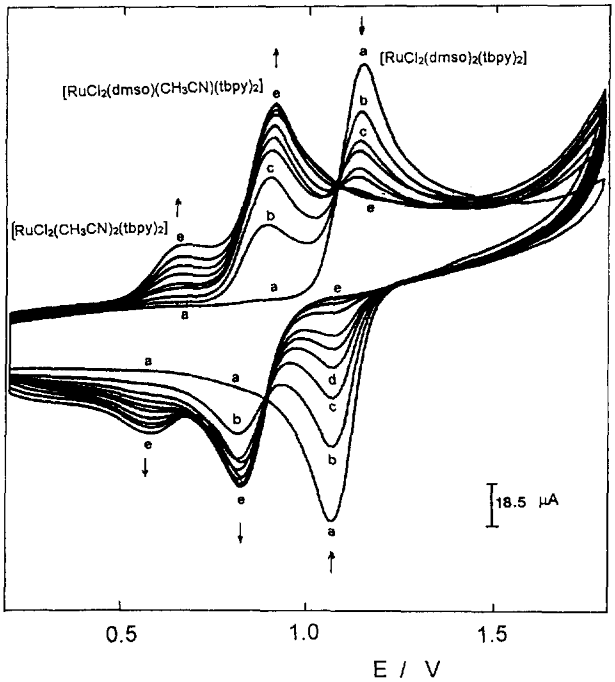

Fig. 2. Cyclic voltammograms of a solution of the *cct*-[RuCl$_2$(S-dmso)$_2$(tbpy)$_2$] in acetonitrile, (a) before irradiation; and after (b) 2 min; (c) 4 min; (d) 6 min; (e) 30 min of irradiation at 270 nm.

As observed spectrophotometrically, the primary product of the photoreaction ($E^\circ = 0.87$ V vs. SHE) undergoes further photolysis leading to a second product exhibiting $E^\circ = 0.62$ V. Based on similar arguments, the second photochemical step can be ascribed to the photodissociation of the second S-dmso ligand from the complex.

Therefore, the overall photoprocess can be represented by the following reactions:

$$[\mathrm{RuCl_2(S\text{-}dmso)_2(tbpy)_2}] + \mathrm{CH_3CN} \xrightarrow{h\nu} [\mathrm{RuCl_2(S\text{-}dmso)(CH_3CN)(tbpy)_2}] + \mathrm{dmso}$$

$$[\mathrm{RuCl_2(S\text{-}dmso)(CH_3CN)(tbpy)_2}] + \mathrm{CH_3CN} \xrightarrow{h\nu} [\mathrm{RuCl_2(CH_3CN)_2(tbpy)_2}] + \mathrm{dmso}$$

The correlations of the redox potentials and E_L parameters in the series of the *cct* and *ccc* [RuCl$_2$(dmso)$_2$L$_2$] complexes have been previously investigated [7]. The two series of complexes exhibit distinct correlations, as shown in Fig. 3. This fact allows the differentiation of the species derived from the *cct* and *ccc* isomers, providing a useful way to evaluate

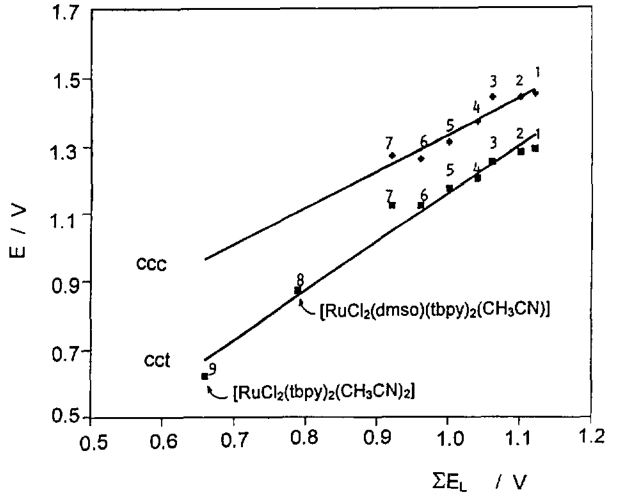

Fig. 3. Electrochemical correlations for the *ccc* and *cct* isomers of the $[RuCl_2(S\text{-}dmso)_2L_2]$ complex [7], where L = pyrazine (1), 4-cyanopyridine (2), 4-acetylpyridine (3), 4-carboxymethylpyridine (4), 4,4′-bipyridine (5), pyridine (6) and 4-*t*-butylpyridine (7); including the photoisomerization products (8, 9).

the geometry of the photosubstitution products. As one can see in Fig. 3, the $[RuCl_2(dmso)(CH_3CN)(tbpy)]$ and $[RuCl_2(CH_3CN)_2(tbpy)_2]$ species follow the electrochemical correlation for the *cct* isomer, indicating that the photolabilization proceeds with a complete retention of stereochemistry.

It should be noticed that the observed quantum yields ($\phi_{dmso} = 0.13$) are relatively high in comparison with those usually observed for ligand photolabilization in other photochemically active ruthenium complexes [15–17]. Photodissociation is a process centered on the metal ion and is usually associated with low lying ligand field states. In order to probe the reactive states, the use of sensitizers such as rhodamine 6-G and biacetyl was attempted, as recently reported in the literature [17]. Rhodamine 6-G absorbs at 510 nm, and displays a fluorescence emission at 554 nm, in acetonitrile solutions. The energy of the thermally equilibrated emitting level, E_{oo}, was estimated from the overlap of the normalized absorption and emission bands, as 19,800 cm^{-1}. Biacetyl displays two overlapping fluorescence and phosphorescence bands at 490 and 506 nm, respectively, complicating the evaluation of the E_{oo} level. For this reason, E_{oo} was assumed as the energy of the lowest triplet level, e.g., 18,800 cm^{-1}.

The fluorescence emission of rhodamine 6-G in acetonitrile solutions was not affected by the presence of 0.4–0.8 mmol dm^{-3} *cct*-$[RuCl_2(S\text{-}dmso)_2(tbpy)_2]$, indicating that the energy of the reactive state is lower than 19,800 cm^{-1}. In contrast, the phosphorescence emission of biacetyl was strongly quenched by the complex, according to a Stern–Volmer constant of 280 mol^{-1} dm^{-3}. Therefore, the reactive excited state should be located in the range of 18,800–19,800 cm^{-1}.

For a typical octahedral complex, the energy of the lowest $^1T_{1g}$ and $^3T_{1g}$ levels are given in terms of the D_q and Racah parameters [9,11], by

$$E(^1T_{1g}) = 10D_q - C + 86\,B^2/(10D_q)$$

$$E(^3T_{1g}) = 10D_q - 3C + 50\,B^2/(10D_q)$$

where $C \approx 4B$. Assuming $E(^1T_{1g}) = E(^1LF) = 23{,}200\ cm^{-1}$, and $B = 450\ cm^{-1}$ (for the $[Ru(NH_3)_6]^{2+}$ complex) one can calculate $10D_q = 24{,}300\ cm^{-1}$. In this way, the estimated energy for the $^3T_{1g} = {}^3LF$ level would be 19,300 cm^{-1}. Therefore, one can speculate that for an observed ^1LF level around 430 nm (23,200 cm^{-1}) the corresponding ^3LF level would fall near 19,300 cm^{-1}, i.e., within the interval determined by the use of the sensitizers.

4. Conclusions

The photolysis of the *cct*-$[RuCl_2(S\text{-}dmso)_2(tbpy)_2]$ complex leads to the selective labilization of the dimethyl sulfoxide ligands, forming the corresponding substituted complexes with acetonitrile. According to the electrochemical correlations, the photosubstitution reactions proceed with complete retention of configuration, with no evidence of parallel geometric or linkage isomerization processes. The reactive excited state is consistent with a ^3LF state around 19,000 cm^{-1}.

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