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Spectroscopic and Electrochemical Properties of Rh(I) Complexes Containing Diene (Norbornadiene or Cyclooctadiene) and Diimine (Bipyrimidine) Type Ligands

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Abstract

Some spectroscopic and electrochemical properties of the complexes Rh(nbd)(bpym)$^+$, Rh(cod)(bpym)$^+$, [Rh(nbd)]$_2$(bpym)$^{2+}$ and [Rh(cod)]$_2$(bpym)$^{2+}$ are reported; nbd = bicyclo[2,2,1]heptadiene (norbornadiene), cod = 1,5-cyclooctadiene, and bpym = 2,2'-bipyrimidine. In all cases the lowest excited states are of metal-to-ligand charge transfer (Rh → bpym) nature and first reduction involves the bpym ligand. Comparison of spectroscopic and electrochemical data for related mononuclear and dinuclear complexes indicates that the energy levels of the metal centered and ligand centered orbitals involved in the lowest energy metal-to-ligand transition and in the first oxidation and reduction processes are very similar for the two cases. However, while the mononuclear complexes are found to luminesce at 77 K, the dinuclear complexes are not luminescent. The interaction between the two metal centers is regarded as a possible cause of this behavior.

Introduction

The study of the interactions occurring between metal centers in polynuclear (polymetallic) complexes is a rapidly expanding research field [1–3]. The final goals are related to applications in the field of the interconversion of light and chemical energy, with particular emphasis on multiphoton and/or multielectron processes [4, 5].

Particularly useful units to build polynuclear complexes are the Ru(L)$_2$$^{2+}$ species (L = bipyridine type ligands), now well characterized from a spectroscopic and electrochemical viewpoint [1–5]. Such units can absorb light in the visible region and originate Ru → L metal-to-ligand charge transfer (MLCT) states, which exhibit a rich excited state chemistry owing to the presence of separate sites for oxidation and reduction processes [6].

It seems interesting to compare the behavior of d^6 metal centers, e.g. Ru(II), with that of electron richer d^8 metal centers, as for instance Rh(I) or Ir(I). Basic arguments suggest that for d^8 centres the energy separation between (metal centered) occupied and (ligand centered) unoccupied orbitals should dramatically reduce, possibly compromising the key feature of having spatially separate centers for the reduction and oxidation. In view of possible applications of complexes containing d^8 centers, it is therefore worth establishing the nature and energy position of the orbitals involved in the spectroscopic and electrochemical processes.

For complexes of the type Rh(dien)L$^+$, where dien = nbd or cod; L = bpy, phen and bpz, it was found that reduction occurred at L and light absorption resulted in Rh → L CT excited state formation [7, 8]; nbd = bicyclo[2,2,1]heptadiene (norbornadiene), cod = 1,5-cyclooctadiene, bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline and bpz = 2,2'-bipyrazine. On the basis of the above arguments, those Rh(I) complexes therefore satisfy some basic requirements in order to be employed as excited state reactants.

We report here on the spectroscopic and electrochemical properties of some complexes of the type Rh(dien)(bpym)$^+$, previously synthesized in one of our laboratories [9]; bpym = 2,2'-bipyrimidine. The molecular structure of the mononuclear complex containing the norbornadiene ancillary ligand is shown below.

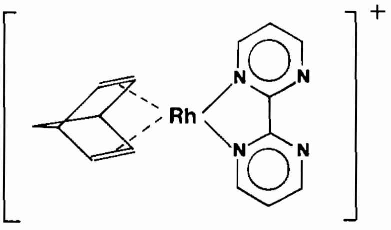

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TABLE 1. Spectroscopy and photophysics

	Absorption[a], 298 K λ (nm) (ε (M^{-1} cm^{-1}))	Emission[b], 77 K		Reference
		λ (nm)	τ (μs)	
Rh(cod)(bpym)$^+$	482 (500), 342 (3600)	650	0.32	
[Rh(cod)]$_2$(bpym)$^{2+}$	477 (580), 343 (4800)			
Rh(nbd)(bpym)$^+$	478 (800), 325 (4100)	655	0.37	
[Rh(nbd)]$_2$(bpym)$^{2+}$ [c]				
Rh(cod)(bpz)$^+$	485 (976)	709	0.60	8

[a]Solvent AN. [b]Solvent EtOH–MeOH (4:1 vol./vol.). [c]Not soluble in AN.

The bpym ligand has the lowest unoccupied molecular orbital (LUMO) level close in energy to that of bpz (see below), and one expects Rh(dien)(bpym)$^+$ complexes to exhibit spectroscopic and electrochemical properties similar to those of the analogous bpz complexes. Furthermore, as the bpym ligand is able to coordinate an additional Rh(I) center, we have examined the behavior of some [Rh(dien)]$_2$(bpym)$^{2+}$ complexes in order to probe metal–metal interactions as well as the role of the intervening ligand.

Experimental

Preparation and characterization of the investigated complexes were reported in a previous paper [9]. All the employed solvents were of the best grade commercially available.

The absorption spectra were recorded with a Perkin-Elmer λ$_5$ or Kontron Uvikon 860 spectrophotometer. Uncorrected emission spectra were obtained with a Perkin-Elmer MPF-44B spectrofluorometer equipped with a Hamamatsu R928 tube.

For the luminescence lifetime measurements a N_2 laser from Lamda Physik was employed as a pulsed source (full width at half maximum was *c.* 3.5 ns). The decay of the emission intensity was analysed according to a single exponential law. The estimated error on the lifetime is $\leq$10%.

Electrochemical experiments were carried out by using a Pt working electrode versus SCE, at room temperature and in acetonitrile (AN) solvent. The potential window explored was +1.6 to −1.6 V and the scan rate was 0.1 V s^{-1}. The equipment was a 273 Par multipurpose unit.

Results and Discussion

The spectroscopic properties of the examined complexes are reported in Table 1, together with those of Rh(cod)(bpz)$^+$ [8], which will serve for comparison purposes. The absorptions of AN solutions of the Rh(nbd)(bpym)$^+$ and Rh(cod)(bpym)$^+$ mononuclear and of the [Rh(cod)]$_2$(bpym)$^{2+}$ dinuclear complexes exhibit quite similar features and profiles, consisting of weak bands ($\epsilon = 5-10 \times 10^2$ M^{-1} cm^{-1}) in the visible region and stronger bands ($\epsilon = 4-5 \times 10^3$ M^{-1} cm^{-1}) in the UV region. The [Rh(nbd)]$_2$(bpym)$^{2+}$ complex was not soluble in AN. Figure 1 shows the absorption spectrum for the Rh(nbd)(bpym)$^+$ complex.

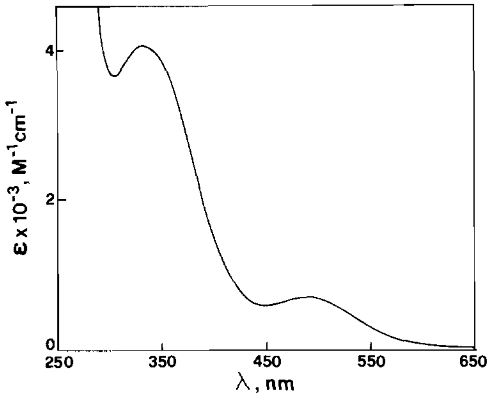

Fig. 1. Room temperature absorption spectrum of Rh(nbd)(bpym)$^+$ in AN.

The luminescence of the complexes was studied in EtOH–MeOH (4:1 vol./vol.) where all four complexes are soluble. The emissions of the mononuclear complexes at 77 K are characterized by broad spectra and lifetimes on the μs scale, Table 1. No emission was detected for the dinuclear complexes.

For the case of Rh(cod)(bpz)$^+$, the lowest energy absorption band and the 77 K emission band were ascribed to the Rh → bpz metal-to-ligand charge transfer transitions, the ancillary cod ligand not being involved [8]. For the Rh(nbd)(bpym)$^+$ and Rh(cod)(bpym)$^+$ complexes, the close similarity of the spectroscopic and photophysical properties with respect to those obtained for Rh(cod)(bpz)$^+$ (Table 1), allows us to conclude that the lowest excited state is of Rh(I) → bpym CT nature.

Electrochemical data for the complexes Rh(nbd)(bpym)$^+$, Rh(cod)(bpym)$^+$ and [Rh(cod)]$_2$(bpym)$^{2+}$ are reported in Table 2, together with data useful for comparison purposes. A previous report concerning

TABLE 2. Electrochemistry[a]

	$E_{1/2}^{(\mathrm{ox})}$ (V)	$E_{1/2}^{(\mathrm{red})}$ (V)	Reference
$\mathrm{Rh(cod)(bpym)^+}$	+0.96	−0.83, −0.90	
$\mathrm{[Rh(cod)]_2(bpym)^{2+}}$	+1.0, +1.42	−0.82[b]	
$\mathrm{Rh(nbd)(bpym)^+}$	+1.1	−0.83, −0.91	
$\mathrm{[Rh(nbd)]_2(bpym)^{2+}}$	c		
$\mathrm{Rh(cod)(bpz)^+}$		−0.72, −1.26	7
bpz		−1.70	10
bpym		−1.80	10
$\mathrm{Ru(bpy)_2(bpz)^{2+}}$		−0.89	11
$\mathrm{Ru(bpy)_2(bpym)^{2+}}$		−1.02	12

[a]Measurements at 298 K in 0.1 M TEAP in AN at a Pt working electrode vs. SCE. [b]Two waves. [c]Not soluble in AN.

$\mathrm{Rh(cod)(bpz)^+}$ [7] indicated that first and second reductions involve the bpz ligand. First reduction for bpz and bpym free ligands takes place at −1.70 and −1.80 V, respectively and at −0.89 and −1.02 V, respectively when the ligands are attached to a $\mathrm{Ru(bpy)_2^{2+}}$ unit, Table 2 [10–12]. EHMO calculations gave −10.47 and −9.94 eV, respectively for the LUMO energy and −9.91 and −9.46 eV, respectively for the second lowest unoccupied molecular orbital (SLUMO) energy, pointing to a LUMO–SLUMO energy separation of 0.5–0.6 eV in both cases [13]. On these bases, for the complexes of Table 2, it seems reasonable to assume that first and second reduction processes involving the bpym ligand occur at potentials less negative than −1.6 V. In particular, for the examined complexes, we assume that the two reduction waves detected at potentials less negative than −1.0 V are bpym centered.

Notice that for $\mathrm{[Rh(cod)]_2(bpym)^{2+}}$, the first and second reductions take place at similar potentials with respect to the related $\mathrm{Rh(cod)(bpym)^+}$ complex, suggesting that addition of the second metal center does not cause significant stabilization of the bpym bridging orbitals. For $\mathrm{[Rh(cod)]_2(bpym)^{2+}}$, the first oxidation ($E_{1/2}^{(1)} = +1.0$ V) occurs at a slightly more positive potential than for the case of Rh(cod)-$\mathrm{(bpym)^+}$ (0.96 V), as expected on the basis of electrostatic arguments. For the same complex, the second oxidation takes place at $E_{1/2}^{(2)} = +1.42$ V. For Ru(II)–polynuclear complexes it is well known that $\Delta E_{1/2} = E_{1/2}^{(2)} - E_{1/2}^{(1)}$ is related to the amount of communication between the two metal centers, as allowed by the electronic and geometric properties of the intervening ligand [3]. Our results suggest that the two Rh(I) centers of $\mathrm{[Rh(cod)]_2(bpym)^{2+}}$ interact effectively, as expected because the two metal centers are fixed at a distance of 6–7 Å by the (aromatic) bpym bridge.

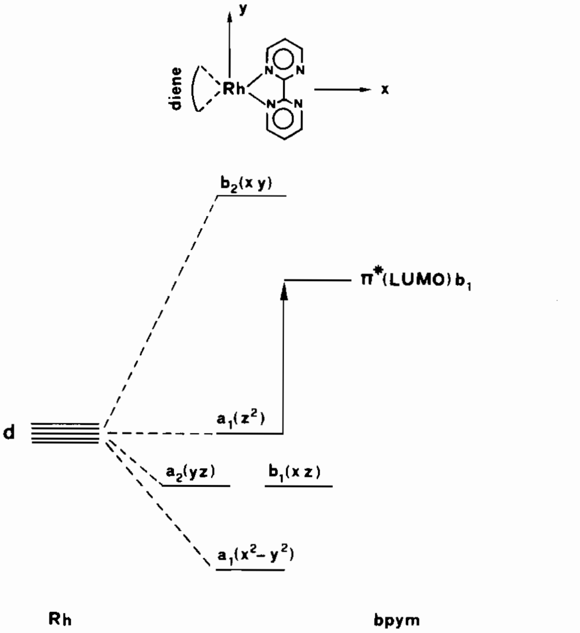

Fig. 2. Orbital labelling for a $\mathrm{Rh(diene)(bpym)^+}$ complex according to a C_{2v} description. The indicated $a_1 \rightarrow b_1$ ($^1A_1 \rightarrow {}^1B_1$) transition is polarized perpendicularly to the metal–bpym axis.

The energy level diagram of Fig. 2 shows a simplified description of the metal and ligand orbitals involved in the lowest energy MLCT optical transition and in the electrochemical processes for the mononuclear case (Tables 1 and 2). According to previous suggestions [8, 14, 15] the dinuclear case, not drawn, could be described by using the same C_{2v} description and allowing the interaction of relevant metal orbitals.

As seen above, the lowest energy MLCT transitions as well as the first oxidation and reduction processes for the mononuclear and the dinuclear cases are quite similar suggesting that the involved metal centered and ligand centered orbitals are practically unaffected by the metal–metal interaction. This conclusion points to some inconsistency with respect to that drawn on the basis of $\Delta E_{1/2} = E_{1/2}^{(2)} - E_{1/2}^{(1)}$.

On the basis of energy and symmetry arguments summarized in Fig. 2, the absorption band in the visible region ($\epsilon \sim 5-10 \times 10^2\ M^{-1}\ cm^{-1}$) is ascribed to a ^{1}MLCT transition polarized perpendicularly to the metal–bpym axis. This transition is expected to be weak because polarization and transfer of electron density do not share the same direction [16].

An explanation for the poor luminescence exhibited by the examined complexes could be based on the role played by MLCT and metal centered (MC, of d → d origin) excited states. As it is well known, for example, for the complexes of the Ru(II)–polypyridine family [6], MC states are effective channels for depopulation (through non-radiative and/or photochemical paths) of MLCT excited states responsible for the luminescence. The fact that the complexes $Rh(nbd)(bpym)^+$ and $Rh(cod)(bpym)^+$ emit at 77 K but not at room temperature indicates that the MLCT and MC states are close enough in energy so that effective thermal population of the latter takes place at the higher temperature. For $[Rh(nbd)]_2(bpym)^{2+}$ and $[Rh(cod)]_2(bpym)^{2+}$ the electron density on the bpym ligand is shared by two metal centers so that one expects a decrease of the ligand strength due to this ligand. In this case the MC energy levels move to lower energy with respect to the case of the related mononuclear complexes and effective deactivation of the emitting MLCT excited states apparently takes place even at 77 K.

Acknowledgements

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