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Dinuclear ruthenium and osmium complexes containing the bis(pyridin-2-yl)-1,2,4-triazolate bridge

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Abstract

The electrochemical and photophysical properties of mononuclear and dinuclear ruthenium and osmium complexes involving the ligand 3,5-bis(pyridin-2-yl)-1,2,4-triazolate (bpt^-) have been studied. The electrochemical data show that the lowest unoccupied molecular orbital (LUMO) is bpy based for all complexes. The asymmetric coordination environment (N1 and N4 of the triazole ring) causes a large splitting of the oxidation potentials for the dinuclear ruthenium complex. The presence of the different coordination sites is also reflected in the different electrochemical behaviour of the isomeric ruthenium-osmium (N1-N4 and N4-N1) complexes. The intense intervalence transition bands observed in the mixed-valence species indicate a strong interaction between the metal ions. The mixed-metal complexes exhibit efficient energy-transfer processes from the ruthenium-based ^{3}MLCT to the osmium-based ^{3}MLCT states.

1. INTRODUCTION

Ruthenium(II) complexes containing 2,2'-bipyridine (bpy) ligands and derivatives have attracted considerable attention in the last decade, because of their potential as redox-catalysts and photocatalysts [1]. Due to their kinetic inertness, a large number of well-defined dinuclear and polynuclear complexes have been described [2]. Two types of dinuclear complexes with bpy ligands have been reported:

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systems with bridges that link together a number of ligands belonging to different complexes, like bpy-R-bpy [3]) and complexes with bridges which directly coordinate two $M(bpy)_2$ moieties, such as 2,2'-bipyrimidine [4]. In this contribution, dinuclear $Ru(bpy)_2$ and $Os(bpy)_2$ complexes of the second type with bis(pyridin-2-yl)-1,2,4-triazolate (bpt^-) are discussed. Most of the data presented here has been published before [5-10].

2. RESULTS AND DISCUSSION

The preparation of all complexes reported here and experimental details has been presented in previous publications [5-10]. The structures of the mononuclear and dinuclear compounds have been elucidated by using X-ray crystallography and ^1H-NMR spectroscopy [5,7,10]. The metal centres in the mononuclear compounds are coordinated via N1 of the triazolate ligand [5,8]. The general formula of these compounds is $[M(bpy)_2(bpt)]^+$ with M=Ru (abbr. as **Ru**) or M=Os (abbr. as **Os**). The dinuclear complexes have been prepared from mononuclear compounds [5,7-9]. For example, reaction of $[Ru(bpy)_2(bpt)]^+$ with $[Os(bpy)_2Cl_2]$ afforded $[Ru(bpy)_2(bpt)Os(bpy)_2]^{3+}$ (**RuOs**, see Figure 1), whilst reaction of $[Os(bpy)_2(bpt)]^+$ with $[Ru(bpy)_2Cl_2]$ afforded $[Os(bpy)_2(bpt)Ru(bpy)_2]^{3+}$ (**OsRu**, see Figure 1). Reaction of Hbpt with excess of $[M(bpy)_2Cl_2]$, yielded $[\{M(bpy)_2\}_2(bpt)]^{3+}$ (M=Ru: **RuRu** or M=Os: **OsOs**).

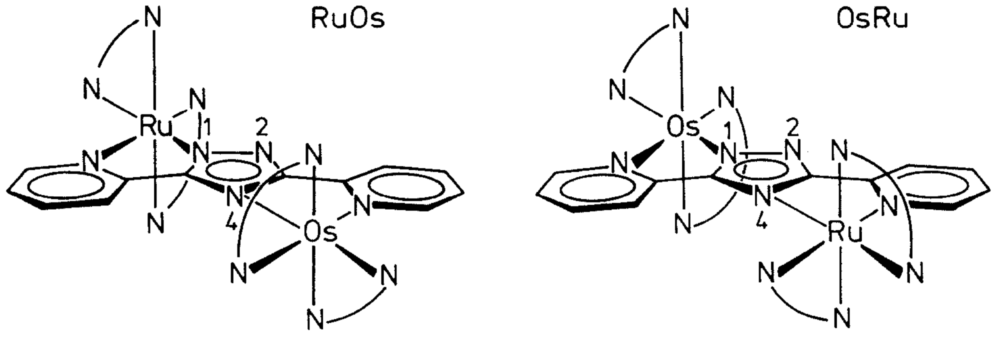

Figure 1. Structures of the two isomeric heteronuclear complexes.

2.1. Electrochemistry.

The oxidation and reduction potentials of the complexes are listed in Table 1 [5-10]. In all cases the first reduction potential is located around −1.4 V *vs.* SCE, suggesting a bpy-based reduction. The reduction potential of the dinuclear complexes is less negative than those of the mononuclear complexes, due to differences in charge of the complexes ($[\mathrm{Ru(bpy)_2(bpt)}]^+$ *vs.* $[\{\mathrm{Ru(bpy)_2}\}_2\mathrm{(bpt)}]^{3+}$). The **RuRu**, **OsRu**, and **OsOs** complexes show bielectronic reduction waves in the differential pulse polarograms, whilst the **RuOs** compound exhibits a clear splitting of the two bpy-based waves. As observed for other osmium and ruthenium complexes, the osmium-based oxidation potential is in general approximately 400 mV lower than the analogous ruthenium-based oxidation potential. Another observation is that the oxidation potentials of the **RuOs** and **OsRu** complexes are distinctly different. The N1 atom of the triazolate ligand has stronger σ-donor properties than the N4 site, which causes lower oxidation potentials for the N1-bound M(bpy)$_2$ centres. The different donor properties of the two nitrogen donors are partially responsible for the large difference in the two oxidation waves observed for the **RuRu** and **OsOs** compounds. Additionally, electrostatic effects and delocalisation through the triazolate bridge (*vide supra*) leads to a further splitting.

Table 1
Electrochemical data of the complexes, obtained in CH$_3$CN with 0.1 M TBAP (V *vs*.SCE).

Compound	Ox.pot.		Red.pot.			
Ru	0.85		−1.47		−1.72	
Os	0.49		−1.41		−1.69	
RuRu	1.04	1.34	−1.40		−1.62	−1.67
RuOs	0.73	1.20	−1.33	−1.41	−1.59	−1.69
OsRu	0.65	1.30	−1.36		−1.63	
OsOs	0.64	0.85	−1.34		−1.57	

2.2. Absorption and Emission Spectra.

The observation that the bpy ligands are reduced more easily than the bpt$^-$ ligand is confirmed by the electronic spectra. The bpt$^-$ ligand has weaker π-acceptor and stronger σ-donor properties than bpy. This leads to lower energies of the metal-to-ligand (M→bpy) charge-transfer absorption and emission bands for the mononuclear complexes compared to the $[\mathrm{M(bpy)_3}]^{2+}$ complexes (M=Ru and Os). Coordination of a second M(bpy)$_2$ moiety to bpt$^-$ leads to a blue shift of the M→bpy CT levels. The negative charge of the triazolate bridge has to be shared between two metal centres, which leads to a diminished electron density on the metal ions. This phenomenon is also reflected in the higher first oxidation of **RuRu** compared to **Ru**. This is in contrast to most polypyridine-type bridging ligands, where a stabilisation of the LUMO takes place upon formation of the dinuclear species (with consequently a red shift of the MLCT energies).

Temperature dependent lifetime measurements have been carried out on **Ru** and **RuRu** [6]. The $\ln(1/\tau)$ *vs.* $1/T$ plot shows that the mononuclear ruthenium compound is much more sensitive to melting of the solvent than the dinuclear compound. Furthermore, the mononuclear ruthenium complex does not show thermal population of an upper metal-centred excited state (^{3}MC). The photostability of the mononuclear ruthenium complex is in agreement with this observation. The dinuclear **RuRu** complex undergoes photodecomposition in CH_2Cl_2 solutions containing Cl^-, yielding **Ru** and $[Ru(bpy)_2Cl_2]$. This supports the assumption that the N1 is a stronger σ donor than the N4 site. All other complexes (**Os**, **OsOs**, **RuOs**, and **OsRu**) are photostable.

Table 2
Absorption and Luminescence Properties of the complexes.

	Absorption, 298 K[a]		Emission, 77 K		Emission, 298 K	
	λ_{max}/nm	$\epsilon_{max}/M^{-1}cm^{-1}$	λ_{max}/nm	$\tau/\mu s$	λ_{max}/nm	τ/ns
Ru	480	9900	628	2.8	678	160
RuRu	453	18500	601	3.6	648	100
Os	486	10800	750	0.25	762	55
OsOs	475	18200	742	0.34	754	33
RuOs	458	23000	726	0.67	751	30
OsRu	452	23700	730	0.59	758	28

The mixed-metal **RuOs** and **OsRu** complexes exhibit only luminescence from the lowest energy osmium-based ^{3}MLCT state [8]. The comparable emission intensities of the **OsOs**, **RuOs**, and **OsRu** complexes, suggests that an efficient energy-transfer process is present. Although the bridging bpt^- is not involved in the lowest-energy excited states, efficient energy transfer from the $Ru(bpy)_2$ moiety to the $Os(bpy)_2$ takes place.

2.3. Mixed-valence species.

The dinuclear complexes have been electrochemically oxidised to their mixed-valence states, by applying the appropriate potentials [7]. In all cases, intense absorption bands in the near-IR region have been observed at 5556 cm^{-1} for **RuRu**, 7143 cm^{-1} for **RuOs**, 8772 cm^{-1} for **OsRu**, and 8333+5000 cm^{-1} for **OsOs** [6]. These bands have been assigned to intervalence transitions (electron transfer from the M^{II} to M^{III} centre) [7]. They are not visible when the complexes are in their II-II or III-III states, confirming this assignment. Interestingly, the energies of these bands can be correlated with the oxidation potentials of the complexes [7]. For example, the difference in oxidation potential of the **RuOs** complexes is 170 mV (1400 cm^{-1}) larger than that of the **RuRu** complex, which is also reflected in the differences in optical energies of the IT bands. The large α^2 values suggests a significant electron delocalisation for the bpt^- complexes. The negatively-charged bridge has easily accessible HOMO (highest occupied molecular orbital) levels and a hole transfer mechanism *via* the HOMO seems the most reasonable explanation. This has been confirmed by synthesising the analogous $[\{Ru(bpy)_2\}_2(bpzt)]^{3+}$ complex ($bpzt^-$ = 3,5-bis(pyrazin-2-yl)-1,2,4-triazole). This ligand has a much lower-lying π^* level than bpt^- [10], but shows very similar values for the mixed-valence **RuRu** complex. Therefore, if a mechanism *via* the LUMO would be present, even larger values for α^2 are expected for the $bpzt^-$ complex. The rather strong metal-metal communication for the bpt^- complexes observed in the ground state is also reflected in the efficient energy-transfer processes observed for the mixed-metal complexes (*vide infra*).

3. CONCLUSIONS

The mononuclear and dinuclear $Ru(bpy)_2$ and $Os(bpy)_2$ complexes containing bispyridyltriazolate exhibit unusual properties. In all cases the LUMO is located on the auxiliary bpy ligands, which is reflected in the reduction potentials and photophysical behaviour. This has also been confirmed by carrying out resonance Raman spectroscopy on the **Ru** and **RuRu** complexes, where only bpy vibrations have been observed [10,11]. The non-involvement of the bpt^- ligand in the lowest energy MLCT, yields interesting properties. Going from the mononuclear to dinuclear species, the negative charge on the bridge has to be shared between two metal ions and consequently the electron density on each metal ion diminishes. This causes a blue shift of the absorption and emission MLCT bands and higher first oxidation potentials for the dinuclear compounds. Such behaviour is very rare for this type of complexes and has only been observed before for analogous complexes containing the $bis(benzimidazolate)^{2-}$ ligand [12]. In most cases, the absorption and luminescence bands move to lower energies upon dinucleation [2]. A consequence of this behaviour is that the quantum yield of the emission process diminishes ('energy-gap law').

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