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# Diastereoisomerism and inter-metallic electronic communication: synthesis and structural analysis of a fully conjugated macrocyclic exo-ditopic ligand bearing two 2,2′-bipyridine units and of its binuclear osmium diastereoisomers

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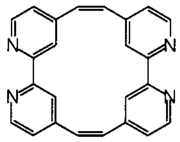
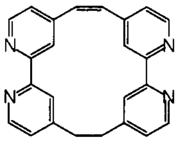
**The synthesis of a new macrocyclic exo-ditopic ligand bearing two, 2,2′-bipyridine units interconnected at the 4 and 4′ positions by two –CH=CH– spacers was achieved, and its Os(II) homobinuclear diastereomeric complexes were prepared, separated and characterised in the solid state by X-ray diffraction on single crystals; the two stereoisomers showed almost identical electrochemical and UV–VIS characteristics and rather weak metal–metal interactions.**

Inter-metallic electronic communication in di- or poly-nuclear transition metal complexes is currently under active investigation.[1] Often, this challenging problem is further complicated by stereoisomerism which occurs when metals with octahedral coordination geometry and chelating ligands are used.[2] The role of diastereoisomerism on the physical properties of metal complexes has recently been elegantly discussed.[3] The combination of Ru(II) and/or Os(II) and bipyridine containing ligands has been shown to exhibit interesting photochemical and electrochemical properties. In order to study intramolecular short- and long-range electron or energy transfer, a variety of homo- and hetero-bincuclear complexes bearing oligopyridine ligands have been prepared.[3,4]

We believed that compound **1** might be of interest for studying both inter-metallic communication between metal centers through conjugation and the effect of diastereoisomerism on such a process. The design of **1** was based on two 2,2′-bipyridine units doubly interconnected at the 4 and 4′ positions by two π systems (CH=CH). The choice of 4 and 4′ positions for interconnecting the two chelate moieties was based on electronic and geometric reasons. For some time now, we have been involved in the design and synthesis of exo-bis-bidentate ligands based on two 2,2′-bipyridine units interconnected at the 4 and 4′ positions by two alkyl[5] as well as two silyl[6] spacers.



**1**



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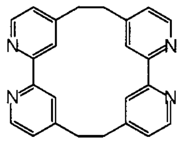

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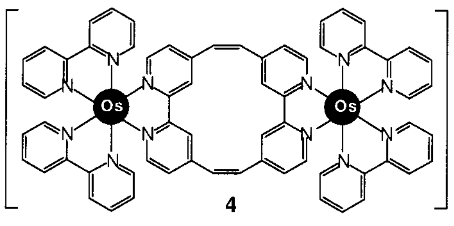

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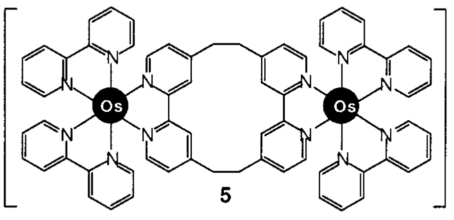

**5**

Here, we report the first synthesis and solid state structural analysis of compound **1** and of its binuclear Os(II) diastereoisomeric complexes **4** as well as the redox behavior of separated and structurally characterised *rac*-**4** (Δ,Δ;Λ,Λ) and *meso*-**4** (Δ,Λ) diastereoisomers.

The synthesis of ligand **1** was based on the dehydrogenation of the previously reported compound **3**.[5a] Thus, treatment of **3** with 2.5 equiv. of DDQ[7] in bromobenzene at 132 °C for 20 h, afforded a mixture of the starting material **3** (20%), the partially oxidized compound **2** (10–15%) and the desired compound **1** (30% isolated yield). Attempts to increase the yield by changing the reaction conditions such as the DDQ/**3** ratio, temperature or reaction time failed. Owing to the rather close $R_f$ values for compounds **1**–**3**, the separation had to be performed carefully and was achieved by column chromatography ($Al_2O_3$, AcOEt–$CHCl_3$–EtOH = 60:39:1). The pure compound **1** was further recrystallised from $CH_2Cl_2$–hexane. In addition to NMR spectroscopy, compound **1** was also characterised by X-ray diffraction on single crystals.

Using the ligand **1**, the synthesis of binuclear Os(II) diastereomeric complexes **4** with $PF_6^-$ as the counter anion was achieved in 62% yield upon refluxing a mixture of **1** and Os(2,2′-bipy)$_2$Cl$_2$ in butanol–water (2:1) for 24 h under an argon atmosphere. The dark green solid thus obtained after evaporation was then dissolved in water, and upon addition of $KPF_6$ and heating at 40 °C for 3 min, the binuclear Os(II) complexes **4** were recovered by filtration as a 4:6 mixture of *meso*- and *rac*-**4** stereoisomers. Diastereoisomeric separation of *rac*- and *meso*-**4** was achieved by column chromatography (Sephadex SP C25, 0.1 M sodium *O,O*′-dibenzoyl-L-tartrate in $H_2O$) following reported procedures.[8] Single crystals of both stereoisomers were obtained after two weeks by the slow diffusion of benzene into a nitromethane solution containing the complex at 6–8 °C. For comparison purposes, homobinuclear Os(II) diastereomeric complexes **5** using the ligand **3** were also prepared and separated.

In the solid state, the structure of *meso*-**4** was studied by X-ray diffraction on a single crystal† (Fig. 1). In addition to *meso*-**4**, 4$PF_6^-$, 2$C_6H_6$, 2$MeNO_2$ and 2$H_2O$ molecules were present in the solid state. In marked contrast with the free ligand **3**, both bipy units in the complex adopt a *cisoid* conformation with NCCN dihedral angles of −2 and 4° allowing, as expected, the chelation of Os(II) cations. The macrocycle is not planar but rather adopts a bent conformation with CCCC dihedral angles around the ethylene spacers of 3.9 and 7.6°. For both Os(II) centers, the coordination sphere is composed of six nitrogen atoms amongst which four are belonging to the two auxiliary bipy units, and the remaining two are part of the macrocyclic ligand **1**. The coordination geometry around each Os(II) was

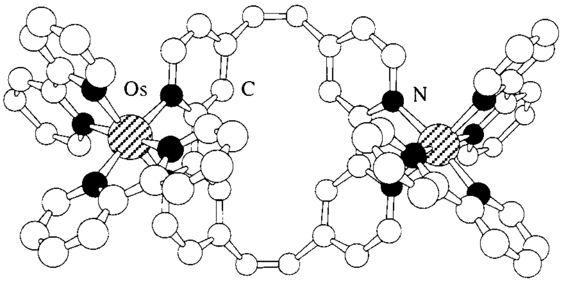

**Fig. 1** X-Ray crystal structure of the *meso*-**4** Os(II) binuclear complex obtained with ligand **1**. For the sake of clarity, anions, solvent molecules and H atoms are not represented (for distances and angles see text).

almost octahedral with an average Os–N distance of *ca.* 2.05 Å. The two Os(II) centres are separated by a distance of 9.368 Å.

The structure of *rac*-**4** was also studied by X-ray diffraction on a single crystal† (Fig. 2). In this case, in addition to *rac*-**4**, $4PF_6^-$, $C_6H_6$ and $2MeNO_2$ molecules were found to be present in the crystal. As before, both bipy units in the complex adopt a *cisoid* conformation with NCCN dihedral angles of −9.4 allowing the coordination of Os(II) cations in the chelate mode. The macrocycle is again not planar but adopts a bent shape with a CCCC dihedral angle around the ethylene spacers of 4.7°. Again, both Os(II) centers are coordinated to six nitrogen atoms with an average Os–N distance of *ca.* 2.05 Å and in almost octahedral geometry. Interestingly, the two Os(II) centers are separated by a distance of 8.177 Å.

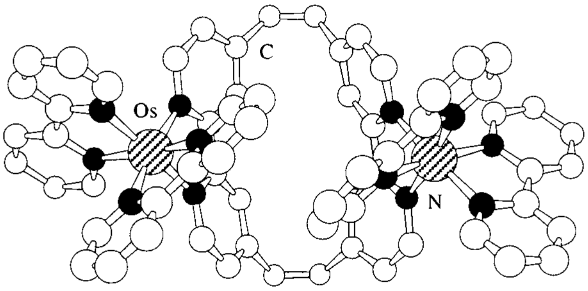

**Fig. 2** X-Ray structure of the *rac*-**4** Os(II) binuclear complex obtained with ligand **1**. For the sake of clarity, anions, solvent molecules and H atoms are not represented (for distances and angles see text).

The electrochemical behaviour of *meso*-**4**, *rac*-**4** and **5** as a mixture of stereoisomers was studied by cyclic voltametry (CV) at 1 mM concentration under argon (MeCN, 25 °C, 0.1 M $NBu_4PF_6$, Pt disk, ferrocene as internal reference, potential values are given with respect to SCE). Although the Os–Os distances for the *meso*-**4** (9.368 Å) and the *rac*-**4** (8.177 Å) stereoisomers are substantially different, for both complexes, only one reversible di-electronic oxidative wave at 0.84 and 0.87 V were observed, respectively. For **5** also a single wave was observed at 0.83 V. Attempts to separate the observed waves into two mono-electronic components using differential pulsed voltametry were unsuccessful. Interestingly, the $\Delta E_p$ values of 90 and 88 mV observed for *meso*- and *rac*-**4**, respectively, were significantly higher than the $\Delta E_p$ of 70 mV obtained for **5** or the expected value of 59 mV for a reversible process. This observation indicates a weak but nevertheless existing electronic communication between the two Os(II) centers. The rather weak nature of the communication may be rationalised on the basis of structural information obtained in the solid state. Indeed, because of the strength imposed by the rather short spacers that leads to the bent conformation of the macrocyclic portion of ligand **1** in the complexes **4**, the conjugation between the two bipyridine units through the ethylene bridges may be significantly weakened.

In conclusion, using the conjugated macrocyclic exo-ligand **1** based on the interconnection of two 2,2′-bipyridine units by two ethylene spacers at the 4 and 4′ positions, two diastereoisomeric binuclear Os(II) complexes **4** were synthesised, separated and structurally characterised in the crystalline phase. Both *meso*- and *rac*-**4** isomers showed identical electrochemical characteristics and rather weak metal–metal interactions. The photochemical behaviour of both **4** and **5** as well as their heterobinuclear Ru(II)Os(II) complexes are under current investigation. The formation of coordination networks using compound **1** is also currently under study.

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## Notes and references

† *meso*-**4** (brown crystals, 173 K): $C_{64}H_{48}N_{12}Os_2 \cdot 4PF_6 \cdot 2C_6H_6 \cdot 2CH_3NO_2 \cdot 2H_2O$, $M$ = 2259.78, triclinic, space group $P\bar{1}$, $a$ = 15.9680(4), $b$ = 15.8640(9), $c$ = 20.9420(7) Å, $\alpha$ = 80.74(3), $\beta$ = 67.57(3), $\gamma$ = 77.10(2), $U$ = 4762.9(5) Å$^3$, $Z$ = 2, $D_c$ = 1.58 g cm$^{-3}$, Mo-K$\alpha$ radiation, KappaCCD, $\mu$ = 2.834 mm$^{-1}$, 13822 data with $I > 3\sigma(I)$, $R$ = 0.061, $R_w$ = 0.076.

*rac*-**4** (brown crystals, 173 K): $C_{64}H_{48}N_{12}Os_2 \cdot 4PF_6 \cdot C_6H_6 \cdot 2CH_3NO_2$, $M$ = 2145.63, orthorhombic, space group *Pbcn*, $a$ = 26.3232(7), $b$ = 13.9495(2), $c$ = 21.4335(7) Å, $U$ = 7870.3(6) Å$^3$, $Z$ = 4, $D_c$ = 1.81 g cm$^{-3}$, Mo-K$\alpha$ radiation, KappaCCD, $\mu$ = 3.423 mm$^{-1}$, 7843 data with $I > 3\sigma(I)$, $R$ = 0.031, $R_w$ = 0.053. CCDC 182/1419.

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