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Diastereoisomerically pure pyrazole-3,5-dicarboxylate-bridged dinuclear ruthenium(II) and osmium(II) complexes of 2,2'-bipyridine: structural, electrochemical and spectral studies

Sujoy Baitalik^a, Pradip Bag^a, Ulrich Flörke^b, Kamalaksha Nag^{a,*}

^a Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India ^b Anorganische und Analytische Chemie, Universität Paderborn, D-33098 Paderborn, Germany

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Abstract

Pyrazole-3,5-dicarboxylate-bridged dinuclear ruthenium(II) and osmium(II) complexes of 2,2'-bipyridine of composition $[(bpy)_2Ru(pzdc)Ru(bpy)_2](ClO_4) \cdot H_2O$ (1) and $[(bpy)_2Os(pzdc)Os(bpy)_2](ClO_4) \cdot H_2O$ (2) have been obtained in high yield and have been separated to their homochiral $(\Lambda\Lambda/\Delta\Delta)$ rac (1a, 2a) and heterochiral $(\Lambda\Delta/\Delta\Lambda)$ meso (1b, 2b) diastereoisomers. The distinctive structural features of these diastereoisomers have been characterized by 1-D and 2-D ¹H NMR spectroscopy. The X-ray crystal structure of rac-[(bpy)_2Os(pzdc)Os(bpy)_2](ClO_4) \cdot H_2O (2a) has been determined. The electrochemical and electronic spectral studies have established that there remain difference in properties and hence difference in intermetallic communication between the diastereoisomeric forms in each case.

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1. Introduction

The electrochemical, photochemical and photophysical properties of di- and oligonuclear ruthenium(II) and osmium(II) complexes in which the mononuclear polypyridine units are anchored by bridging ligands have received much attention [1-5]. The length, charge, topology and conjugation of the bridging ligands in these assemblies play important roles to regulate photoinduced intramolecular electron and energy transfer processes [6,7]. The physicochemical properties of these systems are also influenced by the stereoisomeric relationship between component species. Since most of the earlier reported studies have been carried out with mixture of diastereoisomers, lately, separation of the diastereoisomers or stereospecific synthesis of optical isomers has been the focus of interest [8-12] to address the role of chirality on the physicochemical properties.

* Corresponding author. Fax: +91-33-2473-2805.

E-mail address: ickn@mahendra.iacs.res.in (K. Nag).

We reported [13–15] spectroscopic properties and proton-coupled redox activities of mononuclear and diastereoisomerically pure diruthenium(II) polypyridine complexes with pyrazole-3,5-bis(benzimidazole) [H3pzbzim] and pyrazole-3,5-bis(benzothiazole)-[Hpzbzth] as the bridging ligands. To examine the effect of increasing anionic charge of the bridging ligand on the properties of the complexes, we have recently reported [16] homoand heterodinuclear ruthenium(II) and osmium(II) complexes derived from 2,2'(-bipyridine (bpy) and pyrazole-3,5-dicarboxylic acid [H₃pzdc]. Although the dinuclear complexes were expected to be isolated as homochiral rac $(\Lambda\Lambda/\Delta\Delta)$ and heterochiral meso $(\Lambda\Delta/\Delta\Lambda)$ diastereoisomers, we could isolate the Ru^{II}Ru^{II}, Os^{II}Os^{II} and Ru^{II}Os^{II} complexes exclusively in the rac form. To resolve this unexpected observation, we have reexamined the synthetic methods. Using modified procedures, we have now been able to obtain the homodinuclear complexes as the mixture of two diastereoisomers in high yield. The separation of these diastereoisomers into rac and meso forms has enabled us

to compare their physicochemical properties. The structure of rac-[(bpy)₂Os(pzdc)Os(bpy)₂](ClO₄) · H₂O is also reported here.



2. Experiment

2.1. Preparation of complexes

All the complexes were prepared under a nitrogen atmosphere. *Caution*: The perchlorate salts reported here are potentially explosive and, therefore, should be handled with care.

2.1.1. $[(bpy)_2Ru(pzdc)Ru(bpy)_2](ClO_4) \cdot H_2O(1)$ and separation of rac (1a) and meso (1b) diastereoisomers

A mixture of *cis*-[Ru(bpy)₂Cl₂]·2H₂O (1.04 g, 2 mmol), H₃pzdc·H₂O (0.17 g, 1 mmol) and triethylamine (0.3 g, 3 mmol) in 100 ml of 1:1 ethanol–water was heated under reflux with constant stirring for 12 h. The solution was filtered and concentrated to about 10 ml on a rotary evaporator. An aqueous solution (5 ml) of NaClO₄ (1.5 g) was slowly added to this solution when a red product deposited, which was collected by filtration. The product was dissolved in minimum volume of boiling methanol, filtered and the filtrate was kept in a refrigerator for overnight period. The microcrystalline orange red compound that deposited was filtered on a glass frit; yield 0.90 g (82%). *Anal.* Found: C, 49.0; H, 3.25; N, 12.85%. Calc. for C₄₅H₃₅N₁₀ClO₉Ru₂: C, 49.25; H, 3.2; N, 12.75.

The compound thus obtained was found to be an almost 1:1 mixture of homochiral $(\Lambda\Lambda/\Delta\Delta) rac$ (1a) and heterochiral $(\Lambda\Delta/\Delta\Lambda)$ meso (1b) diastereoisomers. The previously characterized rac form [16] was found to be relatively less soluble in methanol or ethanol as compared to the meso form. Their separation was achieved by fractional crystallization from 1:1 methanol-ethanol. Four cycles of fractionation afforded the pure diastereoisomers.

2.1.2. $[(bpy)_2Os(pzdc)Os(bpy)_2](ClO_4) \cdot H_2O(2)$ and separation of rac (2a) and meso (2b) diastrereoisomers

A mixture of *cis*-[Os(bpy)₂Cl ₂] (0.57 g, 1 mmol), H₃pzdc \cdot H₂O (0.09 g, 0.5 mmol) and triethylamine (0.15 g, 1.5 mmol) in 100 ml of 1:1 ethanol–water was heated under reflux with constant stirring for 72 h. The solution was filtered and the filtrate was reduced to about 10 ml on a rotary evaporator. This was cooled in an icebath and the dark product that deposited was filtered after 2 h. The product was dissolved in requisite amount of water, filtered and to the filtrate 1 g of NaClO₄ dissolved in 5 ml of water was slowly added. The mixture was kept at 10 °C for 6 h, after which the microcrystalline product that deposited was filtered. The product was recrystallized from methanol; yield 0.48 g (76%). *Anal.* Found: C, 42.2; H,2.85; N, 10.85%. Calc. for C₄₅H₃₅N₁₀ClO₄Os₂: C, 42.35; H, 2.75; N, 10.95.

Similar to 1, compound 2 was also found to be a mixture of rac (2a) and meso (2b) diastereoisomers in ca. 1:1 ratio. The two isomers were separated by fractional recrystallization (four times) from 1:1 methanol-ethanol in which the *meso* form again is relatively more soluble.

2.2. Physical measurements

¹H NMR (300 MHz) spectra were obtained on a Bruker Avance DPX spectrometer using DMSO-d₆ solutions. The spectral assignments were made with the assistance of COSY and taking into consideration the following typical ³J coupling patterns for bipyridine protons: H(3)[d, $J \approx 8$ Hz], H(4)[t, $J \approx 8$ Hz], H(5)[dd/t, $J \approx 8.5$ Hz], H(6)[d, $J \approx 5$ Hz]. UV–Vis absorption spectra were recorded for methanol, ethanol, acetonitrile, *N*,*N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) solutions of the complexes. Emission spectra were recorded at 77 K for 1:4 methanol–ethanol solutions (1 × 10⁻⁵ M) of the complexes.

The electrochemical measurements were performed under nitrogen using a BAS-100B electrochemistry system. Cyclic, square wave and differential pulse voltammograms were recorded in acetonitrile solution of the complexes ($\sim 1 \times 10^{-3}$ M) containing 0.1 M tetraethylammonium perchlorate as the supporting electrolyte using a platinum or glassy carbon working electrode and Ag|AgCl reference electrode. The reference electrode was separated from the bulk electrolyte by a salt bridge (acetonitrile/0.1 M[Et₄N](ClO₄)). Under the experimental condition used, the ferrocene/ferrocenium couple was observed at 365 mV.

2.3. Crystal structure determination of rac $(\Lambda\Lambda/\Delta\Lambda)[(bpy)_2Os(pzdc)Os(bpy)_2](ClO_4) \cdot H_2O(2a)$

Single crystals used for structure determination were obtained by slow evaporation of a methanol solution of **2a**. X-ray diffraction data were collected using Siemens SMART CCD diffractometer using graphite monochromated Mo K α radiation. Crystal data and details of data collection are listed in Table 1. The intensity data were corrected for Lorentz and polarization effects and semi-empirical absorption correction was made from ψ -scans. A total of 12 039 reflections were collected in the range $\theta = 2.17-27.53^{\circ}$ with $h = \pm 36$, k = -1 to 15 and Table 1

Crystallographic data for $\it rac\mathchar`-[(bpy)_2Os(pzdc)Os(bpy)_2]~(ClO_4)\cdot H_2O~(2a)$

Empirical formula	$C_{45}H_{35}ClN_{10}O_9Os_2$
Formula weight	1275.68
Crystal size (mm)	0.38 imes 0.35 imes 0.26
Crystal system	orthorhombic
Space group	$Pna2_1$
a (Å)	27.972(8)
b (Å)	12.239(6)
<i>c</i> (Å)	12.640(3)
V (Å ³)	4327(4)
Ζ	4
$D_{\text{calc}} \text{ (g cm}^{-3})$	1.958
λ (Mo Kα) (Å)	0.71073
<i>T</i> (K)	293
$\mu (\mathrm{mm}^{-1})$	5.992
F(000)	2464
Reflections measured	12 039
Unique reflections	5643
Final R indices	$R_1^{a} = 0.0451$
$[I > 2\sigma(I)]$	$wR_2^{b} = 0.0832$
R indices (all data)	$R_1 = 0.0862$
	$WR_2 = 0.1033$

^a $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$ ^b $wR_2(F^2) [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}.$

l = -16 to 1, of which 5643 independent reflections ($R_{int} = 0.0689$) were used for structure determination. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using the programs SHELXTL-PLUS [17] and SHELXL-97 [18]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (riding model) and were not refined. The refinement [$I > 2.00\sigma(I)$] converged to $R_1 = 0.0451$ and wR_2 (all data) = 0.1033. The goodness-of-fit on F_2 was 1.072 and the maximum and minimum peak on the final difference Fourier map corresponded to 1.038 and -1.021 eÅ³, respectively.

3. Results and discussion

3.1. Separation of diastereoisomers

In our earlier study [16] the complexes $[(bpy)_2Ru(pzdc)Ru(bpy)_2](ClO_4) \cdot H_2O$ and $[(bpy)_2Os$ $(pzdc)Os(bpy)_2](ClO_4) \cdot H_2O$ were obtained in 35–40% yield solely as the homochiral rac $(\Lambda\Lambda/\Delta\Delta)$ form. Since these compounds were isolated as the perchlorate salts from fairly dilute ethanol-water solution, in retrospect, it appeares that the heterochiral meso $(\Lambda\Delta/\Delta\Lambda)$ diastereoisomer remained unrecovered from the solution. The fact that the chloride salts of these dinuclear complexes are more soluble in methanol, ethanol or water as compared to the perchlorate salts has been used with advantage in the present modified syntheses. Indeed, reduction of the ethanol-water reaction solution containing the chloride salt of the complexes to a small volume, followed by precipitation of their perchlorate salt, has led to the isolation of compounds 1 and 2 in about 80% yield. The ¹H NMR spectra of 1 and 2 (Figs. 1 and 2) show that both are mixture of *rac* and *meso* diastereoisomers in about 1:1 ratio. The separation of the diastereoisomers has been accomplished by fractional recrystallization from 1:1



Fig. 1. The ¹H NMR spectra (DMSO-d₆, 300 MHz) of unseparated and separated diastereoisomers of $[(bpy)_2Ru(pzdc)Ru(bpy)_2]^+$: (a) *rac* $(\Lambda\Lambda/\Delta\Delta)$ form; (b) unseparated mixture *of rac* and *meso* forms; (c) *meso* ($\Lambda\Delta/\Delta\Lambda$) form.



Fig. 2. The ¹H NMR spectra (DMSO-d₆, 300 MHz) of unseparated and separated diastereoisomers of $[(bpy)_2Os(pzdc)Os(bpy)_2]^+$: (a) *rac* $(\Lambda\Lambda/\Delta\Delta)$ form; (b) unseparated mixture of *rac* and *meso* forms; (c) *meso* ($\Lambda\Delta/\Delta\Lambda$) form.

methanol–ethanol in which the *meso* $(\Lambda\Delta/\Delta\Lambda)$ form is relatively more soluble. As shown in Figs. 1 and 2, clean separation of the two isomers in both cases has been achieved after four recrystallization steps.

3.2. ¹H NMR spectra

The ¹H NMR of the separated pairs of the diastereoisomers la $(\Lambda\Lambda/\Delta\Delta)$ and lb $(\Lambda\Delta/\Delta\Lambda)$ and 2a $(\Lambda\Lambda/\Delta\Delta)$ and **2b** $(\Lambda\Delta/\Delta\Lambda)$ have been assigned using a combination of one- and two-dimensional techniques as reported earlier [16]. The results are summarized in Table 2. As may be seen in Figs. 1 and 2, there are significant differences in the spectral patterns displayed by the homochiral $(\Lambda\Lambda/\Delta\Delta)$ and heterochiral $(\Lambda\Delta/\Delta\Lambda)$ diastereoisomers of the diruthenium(II) and diosmium(II) complexes. Interestingly, the spectra exhibited by the rac pair la and 2a or the meso pair 1b and 2b show generally similar features but they differ in detail, signifying subtle influence of the metal centres on the chemical shifts of bpy ligand in a given stereochemical arrangement.

3.3. Crystal structure of rac- $[(bpy)_2Os(pzdc)Os(bpy)_2]$ (ClO₄) · H₂O (**2a**)

The crystal structures of the homodinuclear *rac*- $[(bpy_2Ru(pzdc)Ru(bpy)_2](ClO_4) \cdot H_2O$ (1a) and the heterdinuclear *rac*- $[(bpy_2Ru(pzdc)Os(bpy)_2](ClO_4) \cdot (3a)$ complexes have already been reported [16]. An ORTEP representation of $2a^+$ cation along with the atom labels is shown in Fig. 3. Selected bond distances and angles are given in Table 3. The stereochemical disposition of



Fig. 3. ORTEP representation of the rac-[(bpy)₂Os(pzdc)Os(bpy)₂]⁺ cation (**2a**⁺) showing the 50% probability of thermal ellipsoids.

the chelating ligands around the two osmium centres (Fig. 3) depicts homochirality, indicating it to be the *rac* $(\Lambda\Lambda/\Delta\Delta)$ diastereoisomer. The *rac* form of diruthenium (**1a**), diosmium (**2a**) and ruthenium–osmium (**3a**) complexes all crystallize in the orthorhombic space group $Pna2_1$ with four dinuclear units in the unit cell. The *meso* diastereoisomer for none these compounds could be obtained as suitable single crystals for structure determination despite many attempts.

The coordination environment around each osmium(II) in **2a** is slightly distorted octahedral with the average Os–N(bpy), Os–N(pyrazolate) and Os–O(carboxylate) distances being 2.03(2), 2.08(1) and 2.09(2) Å, respectively. The corresponding distances observed for

Table 2

¹H NMR data^a for homochiral *rac* ($\Lambda\Lambda/\Delta\Delta$) and heterochiral *meso* ($\Lambda\Delta/\Delta\Lambda$) diastereoisomers of [(bpy)₂Ru(pzdc)Ru(bpy)₂](ClO₄) · H₂O (1) and [(bpy)₂Os(pzdc)Os(bpy)₂](ClO₄) · H₂O (2)

Proton	rac la	meso 1b	rac 2a	meso 2b
pz-CH	6.85, 1H	6.82, 1H	6.84, 1H	6.82, 1H
H(3)	7.89, 2H, 8.1	7.98, 2H, 8.0	7.88, 2H, 8.0	7.94, 2H, 8.2
	8.34, 2H, 8.1	8.10, 2H, 8.1	8.35, 4H, 8.0	8.12, 2H, 8.1
	8.40, 2H, 8.1	8.49, 2H, 8.0		8.43, 2H, 8.1
	8.53, 2H, 8.2	8.69, 2H, 8.0	8.49, 2H, 8.2	8.64, 2H, 8.1
H(4)	7.34, 2H, 7.7	7.75, 2H, 7.3	6.97, 2H, 7.6	7.07, 2H, 7.7
	7.77, 2H, 7.7	7.79, 2H, 7.3	7.51, 4H, 7.7	7.52, 2H, 7.8
	7.95, 2H, 7.8	8.01, 2H, 7.7		7.68, 2H, 7.4
	8.11, 2H, 7.5	8.14, 2H, 7.6	7.80, 2H, 7.7	7.73, 2H, 7.3
H(5)	6.68, 2H, 6.7	6.61, 2H, 6.4	6.45, 2H, 6.6	6.12, 2H, 6.7
	7.08, 2H, 6.5	7.07, 2H, 6.5	6.90, 2H, 6.6	6.92, 2H, 7.0
	7.24, 2H, 6.4	7.43, 2H, 6.3	7.02, 2H, 6.5	7.32, 2H, 6.6
	7.84, 2H, 6.4	7.47, 2H, 6.8	7.72, 2H, 6.5	7.38, 2H, 6.8
H(6)	6.36, 2H, 5.6	6.81, 2H, 5.1	6.34, 2H, 5.6	6.46, 2H, 5.8
	6.63, 2H, 5.6	6.98, 4H, 5.4	6.40, 2H, 5.5	6.94, 2H, 5.9
	7.00, 2H, 5.3		6.62, 2H, 5.5	7.92, 2H, 5.9
	8.77, 2H, 5.4	8.18, 2H, 5.2	8.53, 2H, 5.6	7.98, 2H, 5.6

^a For ¹H NMR data, respectively: chemical shift (ppm), number of protons, J (Hz).

Table 3 Selected bond distances (Å) and angles (°) for *rac*-[(bpy)₂Os(pzdc)Os(bpy)₂]⁺(C1O₄) \cdot H₂O (**2a**)

Bond distances			
Os(1)–N(11)	2.026(12)	Os(2)–N(31)	2.012(13)
Os(1)–N(21)	2.034(11)	Os(2)–N(41)	2.014(9)
Os(1)–N(22)	2.043(10)	Os(2)–N(42)	2.048(11)
Os(1)–N(12)	2.048(11)	Os(2)–N(32)	2.055(12)
Os(1)–N(51)	2.094(11)	Os(2)–N(52)	2.073(12)
$Os(1) \cdot \cdot \cdot Os(2)$	4.662(2)		
Bond angles			
N(11)-Os(1)-N(21)	88.4(5)	N(31)–Os(2)–N(41)	82.3(5)
N(11)-Os(1)-N(22)	100.7(5)	N(31)–Os(2)–N(42)	100.5(5)
N(21)-Os(1)-N(22)	77.7(5)	N(41)–Os(2)–N(42)	78.5(5)
N(11)-Os(1)-N(12)	79.9(5)	N(31)–Os(2)–N(41)	82.3(5)
N(21)–Os(1)–N(12)	98.7(5)	N(31)–Os(2)–N(42)	100.5(5)
N(22)–Os(1)–N(12)	176.2(5)	N(42)–Os(2)–N(32)	177.9(5)
N(11)-Os(1)-O(51)	82.9(5)	N(31)–Os(2)–O(53)	89.1(4)
N(21)–Os(1)–O(51)	168.5(5)	N(41)–Os(2)–0(53)	167.8(5)
N(22)–Os(1)–O(51)	96.5(5)	N(42)–Os(2)–O(53)	94.6(4)
N(12)-Os(1)-O(51)	87.2(5)	N(32)–Os(2)–O(53)	86.9(4)
N(11)-Os(1)-N(51)	159.6(5)	N(31)–Os(2)–N(52)	166.3(4)
N(21)–Os(1)–N(51)	111.8(5)	N(41)–Os(2)–N(52)	110.4(5)
N(22)-Os(1)-N(51)	87.3(4)	N(42)–Os(2)–N(52)	87.5(5)
N(12)-Os(1)-N(51)	93.4(5)	N(32)–Os(2)–N(52)	94.2(5)
O(51)–Os(1)–N(51)	77.5(4)	O(53)–Os(2)–N(52)	79.1(4)

the diruthenium(II) analogue in **la** are 2.05(1), 2.10(1) and 2.10(1) Å [16]. It is also of interest to note that the Os···Os separation of 4.662 Å in **2a** is slightly shorter compared to the Ru···Ru distance of 4.685 Å in **1a**, indicating tighter bonding in the osmium compound. The bite angles of bpy and pzdc ligands are nearly equal, 79(1)°. On the other hand, the shorter C–O distance of the free carbonyl moiety of pzdc (1.22(3) Å) relative to that of the metal-bound C–O (1.32(2) Å) is consistent with pronounced double bond character of the former.

3.4. Electrochemical studies

The electrochemical characteristics of the homo- and heterochiral diruthenium (1a and 1b) and diosmium (2a and 2b) complexes have been examined by cyclic voltammetry, square wave voltammetry and differential pulse voltammetry and the observed redox potentials are given in Table 4. As shown in Fig. 4, for each of the diastereoisomers, two fully reversible metal-centred redox couples $M^{\rm II}M^{\rm II}/M^{\rm II}M^{\rm III}$ and $M^{\rm II}M^{\rm III}/M^{\rm III}M^{\rm III}$ are observed. The separations between these two redox couples $(\Delta E_{1/2} = \hat{E}_{1/2}^2 - E_{1/2}^1)$ are 170 mV (for **1a**) and 200 mV (for **1b**) with the diruthenium diastereoisomers, while in the cases with the diosmium analogues these values are 165 mV (for 2a) and 195 mV (for 2b). Almost identical differences in redox separation for the two diastereoisomers of the two metals indicate that the metal-metal interactions in these compounds are chirality dependent. The differences in redox potentials of the rac and the meso forms of the same complex may be used to determine their comproportionation constant $(K_c = 10^{(16.92 \times \Delta E_{1/2})}$ at 298 K). The K_c values given in Table 4 indicate that the mixed-valence $(M^{II}M^{\overline{III}})$ species derived from the meso form has at least threefold greater stability compared to that of the rac form. Differences in the electrochemical properties of the diastereoisomers of some other diruthenium complexes

Table 4

	Redox 1	potentials ^a	for the	diastereoisomers	of [$\{M(bpy)_2\}$	$\frac{1}{2}(pzdc)]^+$	in	acetonitrile
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r r r r r r r r r r r r r r r r r r r	1 ((F))2)2(F				
Complex	$E_{1/2}^{1}$ (mV)	$E_{1/2}^2$ (mV)	$\Delta E_{1/2}^{\rm b}$ (V)	K _c (298 K)	
	$M^{\rm II}M^{\rm II}/M^{\rm II}M^{\rm III}$	$M^{\rm II}M^{\rm III}/M^{\rm III}M^{\rm III}$			
$[{Ru(bpy)_2}_2(pzdc)]^+$					
rac (1a)	750	920	0.170	750	
meso (1b)	710	910	0.200	2400	
$[{Os(bpy)_2}_2(pzdc)]^+$					
rac (2a)	305	470	0.165	620	
meso (2b)	300	495	0.195	1990	

^a All the potentials are referenced against Ag|AgCl electrode with $E_{1/2} = 365$ for ferrocene/ferrocenium couple. Uncertainty in $E_{1/2}$ values ± 5 mV. ^b $\Delta E_{1/2} = E_{1/2}^2 - E_{1/2}^1$.



Fig. 4. Cyclic voltammograms for the oxidation of the diastereoisomers of $[(bpy)_2Ru(pzdc)Ru(bpy)_2]^+$ (a) and $[(bpy)_2Os(pzdc)Os(bpy)_2]^+$ (b) in acetonitrile: —, *rac* form; ---, *meso* form.

have been reported [11,19–21]. However, it is not possible to predict for which of the diastereoisomers the comproportionation constant will be greater.

In the reductive mode, all the diastereoisomers (1a, 1b, 2a, 2b) exhibited two redox couples with the $E_{1/2}$ values -1.60 ± 0.05 and -2.05 ± 0.05 V. Each of these redox couples corresponds to two-electron process, indicating simultaneous transfer of one electron to two complimentary bipyridine moieties. Differential pulse voltammetry or square wave voltammetry failed to resolve the two redox couples further.

3.5. Electronic spectra

The absorption spectra of the homochiral *rac* and the heterochiral *meso* diastereoisomers of the diruthenium(II) and diosmium(II) complexes have been recorded in several solvents to find out whether any spectral difference observed between the two diastereoisomers is due to their difference in stereochemistry or due to their variation in solvation. The spectral data (in the range 300–900 nm) for the stereoisomers **1a/1b** and **2a/2b** in different solvents are given in Table 5.

The spectra obtained for **1a** and **1b** in methanol are shown in Fig. 5. It may be noted that the metal-to-ligand $\operatorname{Ru}(d\pi) \rightarrow \operatorname{bpy}(\pi^*)$ charge transfer transition observed at 512 nm for the homochiral *rac* form (**1a**) is blueshifted to 507 nm for the heterochiral *meso* form (**1b**). The spectral data given in Table 5 indicate that in other solvents also similar blue-shift of the MLCT band of the *meso* form (1b) occurs by 5-7 nm relative to the *rac* form (1a). The variation of the solvents has the effect of solvation of both the diastereoisomers almost to the same extent, as a result the relative difference in peak positions between the two stereoisomers remains more or less same in all the solvents (Table 5).

The absorption spectra of the two diastereoisomers of the diosmium(II) complex again follow the same trend. For example, the spectra of **2a** (*rac*) and **2b** (*meso*) recorded in dimethyl sulfoxide (Fig. 6) show that relative to the *rac* form, the metal-to-ligand charge transfer band of the *meso* form is shifted from 550 to 542 nm. Clearly, there is a real difference, albeit small, in the electronic transition energies between the homochiral and heterochiral diastereoisomers. In other words, the intermetallic electronic communication in polymetallic systems depends, among other things, on chiral relationships.

The luminiscence spectral behaviour of the diastereoisomers **1a** and **1b** of the diruthenium(II) complex has been examined in methanol–ethanol (1:4) glass at 77 K, The excitation of the MLCT band at 516 nm (for **1a**) and 510 nm (for **1b**) provided an emission peak at 615 nm in both the cases, indicating the same excited state behaviour of the two diastereoisomers.

4. Conclusion

The homodinuclear complexes [(bpy)₂Ru(pzdc) $Ru(bpy)_2[(ClO_4) \cdot H_2O \text{ and } [(bpy)_2Os(pzdc)Os(bpy)_2]$ $(ClO_4) \cdot H_2O$ have been synthesized in high yield as approximately 1:1 mixture of their homochiral $(\Lambda\Lambda/\Delta\Delta)$ rac and heterochiral $(\Lambda\Delta/\Delta\Lambda)$ diastereoisomers. The separation of the diastereoisomers has been accomplished by fractional recrystallization, taking into advantage of the relatively greater solubility of the meso form. The difference in spatial orientations of the bipyridine ligands in each pair of the diastereoisomers is reflected in their ¹H NMR spectra. The crystal structure of rac-[(bpy)₂Os(pzdc)Os(bpy)₂]⁺ has been determined. The diastereoisomers of both the metals show a significant difference in their metal-centred redox potentials. The separation between the two redox couples M^{II}M^{II}/ M^{II}M^{III} and M^{II}M^{III}/M^{III}M^{III} are about 170 mV for the rac form and 200 mV for the meso form in both the complexes. In terms of their comproportionation constants, these values indicate relatively stronger metalmetal interaction in the meso form compared to the rac form. The difference in physico-chemical properties of the diastereoisomers also become evident when their absorption spectra measured in different solvents are considered. For both the metal complexes, the MLCT band of the *meso* form is shifted to a lower wavelength by 5–7 nm relative to the *rac* form, again indicating small but definite dependence of metal-metal coupling on the chiral combination of the metal centres. In contrast, the

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Table 5

Electronic spectral data for diastereoisomers of diruthenium(II) and diosmium(II) complexes in different solvents

Complex	Solvent	λ_{\max} , nm (ϵ , M ⁻¹ cm ⁻¹)		
		rac	meso	
$[(bpy)_2Ru(pzdc)Ru(bpy)_2]^+$	MeOH	346(16870)	348(17780)	
		460(9450)	458(9840)	
		512(13 480)	507(13900)	
	EtOH	346(17 540)	350(19000)	
		459(9740)	462(10 300)	
		517(14 380)	511(14810)	
	MeCN	357(17 000)	358(19200)	
		474(9380)	470(10 220)	
		530(4300)	525(15430)	
	DMF	358(17420)	358(18100)	
		475(9500)	472(10140)	
		533(14 300)	529(15260)	
	DMSO	356(18 200)	356(18420)	
		474(10110)	470(10830)	
		534(15250)	527(15400)	
$[(hny) \Omega_{s}(nzd_{s})\Omega_{s}(hny)]^{+}$	МаОН	356(17,300)	360(18,100)	
$[(0py)_2Os(pzdc)Os(0py)_2]$	Ween	430(13 540)	424(13,960)	
		530(12,700)	526(13,220)	
		720b(3100)	720b(3100)	
	MeCN	362(17 360)	358(17800)	
		436(12 680)	432(12850)	
		542(12 470)	537(12120)	
		725b(3200)	725b(3200)	
	DMSO	362(17 600)	360(16950)	
		438(13 230)	432(13 360)	
		550(13 020)	542(13 230)	
		740b(3280)	740b(3200)	



Fig. 5. Absorption spectra of the diastereoisomers of [(bpy)₂Ru(pzdc)Ru(bpy)₂]⁺ in methanol: —, *meso* form; ---, *rac* form.



Fig. 6. Absorption spectra of the diastereoisomers of $[(bpy)_2Os(pzdc)Os(bpy)_2]^+$ in dimethyl sulfoxide: —, *meso* form; ---*rac* form.

luminiscent spectral behaviour of the two diastereoisomers of the diruthenium(II) complex is identical.

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