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Derivatives of luminescent metal–polypyridyl complexes with pendant adenine or thymine groups: building blocks for supramolecular assemblies based on hydrogen bonding†

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Alkylation of adenine or thymine with 5-bromomethyl-2,2′-bipyridine afforded bipya and bipyt, in which a 2,2′-bipyridyl (bipy) is attached to the N^9 position of adenine or the N^1 position of thymine *via* a CH_2 spacer. Attachment of the bipy site of bipya to $[Ru(bipy)_2Cl_2]$ or $[Ru(dbbipy)_2Cl_2]$ [dbbipy = 4,4′-bis(*tert*-butyl)-2,2′-bipyridine] gave the complexes $[Ru(bipy)_2(bipya)][PF_6]_2$ and $[Ru(dbbipy)_2(bipya)][PF_6]_2$ (Ru-Ade) respectively, in which an adenine fragment is pendant from the $\{Ru(bipy)_3\}^{2+}$ core. Attachment of the bipy site of bipyt to $[Os(dbbipy)_2Cl_2]$ and $[Re(CO)_5Cl]$ afforded $[Os(dbbipy)(bipyt)][PF_6]_2$ (Os-Thy) and $[Re(bipyt)(CO)_3Cl]$ (Re-Thy) respectively, in which the $\{Os(bipy)_3\}^{2+}$ and $\{Re(bipy)(CO)_3Cl\}$ cores have pendant thymine groups. Recrystallisation of $[Ru(bipy)_2(bipya)][PF_6]_2$ from wet MeCN resulted in partial protonation to give $[\{Ru(bipy)_2(bipya)\}\{Ru(bipy)_2(Hbipya)\}][PF_6]_5\cdot 4MeCN$ in which $[Ru(bipy)_2(bipya)]^{2+}$ and protonated $[Ru(bipy)_2(Hbipya)]^{3+}$ complex cations are associated by a Watson–Crick type hydrogen-bonding interaction between the adenine groups across an inversion centre. Similarly, in $[Os(dbbipy)_2(bipyt)][PF_6]_2\cdot Me_2CO$ there are two $[Os(dbbipy)_2(bipyt)]^{2+}$ complex cations associated *via* a centrosymmetric thymine–thymine hydrogen-bonding interaction across an inversion centre. In contrast, in $[Ru(dbbipy)_2(bipya)][PF_6]_2\cdot 2MeCN$ the $[Ru(dbbipy)_2(bipya)]^{2+}$ complex cations are associated *via* a Hoogsteen-type hydrogen-bonding interaction to give a one-dimensional 'ribbon-like' chain of hydrogen bonds. The electrochemical, UV/VIS spectroscopic and luminescence properties of the complexes are very similar to those of the parent unsubstituted complexes, indicating that the adenine or thymine substituents do not perturb the desirable properties of the complex cores. By monitoring the chemical shift of the thymine NH proton, NMR titrations allowed estimation of the association constants of the complementary Ru-Ade/Os-Thy pair in CD_3CN and CD_2Cl_2 as 60 and 123 $dm^3\ mol^{-1}$ respectively, and that of the Ru-Ade/Re-Thy pair in CD_3CN as 17.9 $dm^3\ mol^{-1}$. At the very low concentrations used for luminescence studies, these association constants are much too low to allow significant formation of hydrogen-bonded associates in mixtures of complementary complexes such as Ru-Ade/Os-Thy and Ru-Ade/Re-Thy. The requirements for observing energy-transfer across hydrogen-bonded bridges in associates of this type are discussed.

The study of high-nuclearity complexes containing several luminescent metal–polypyridyl chromophores is of particular interest for attempts to prepare light-harvesting molecules which can perform a useful function (photochemical molecular devices).[1] In such molecules the interacting fragments are generally linked by covalent bonds, which makes it possible to control both the structural properties (spatial arrangement of the chromophores, metal–metal separations) and the electronic properties (pathways for metal–metal interactions) of the complex by appropriate choice of bridging ligand.[1–3] A limitation of this approach is the availability of suitable bridging ligands. An alternative would be to rely on the self-assembly of mononuclear building blocks, since it has recently been demonstrated by a variety of groups that architecturally sophisticated, high-nuclearity complexes can be prepared if there is a suitable complementarity built in to the component parts.[4,5] Hydrogen bonding between suitable mononuclear components could be a suitable way of self-assembling photochemical molecular devices if appropriate building blocks can be prepared with appropriate hydrogen-bonding groups attached.

Hydrogen bonding has been extensively used in the area of (primarily organic) self-assembly, host–guest chemistry and molecular recognition, and this very wide area is exemplified by the work of (amongst others) Whitesides,[6] Hamilton,[7] Desiraju[8] and Lehn.[9] More recently the groups of Mingos[10] and others[11] have extended these principles to the study of metal complexes with hydrogen-bonding groups on their peripheries, with a view to controlling the three-dimensional arrangement of metal complex fragments in crystals and using metal complexes for molecular recognition of appropriate substrates. The recent observations that magnetic[12] and photophysical[13] interactions between metal centres can be propagated through hydrogen bonds makes the use of hydrogen bonding to control self-assembly in metal complexes particularly appealing, since the hydrogen bonds can both control the assembly of the components and then provide a pathway for transmitting interactions between them.

We describe here our initial studies in this area, in which we have prepared derivatives of 2,2′-bipyridine (bipy) which are functionalised with the hydrogen-bonding nucleotide bases adenine and thymine. Others have recently used adenine and thymine as complementary components in supramolecular chemistry to direct self-assembly processes.[14] These bipyridyl/nucleobase ligands have been used to prepare luminescent complexes of Re^{I}, Ru^{II} and Os^{II} which contain mutually complementary peripheral hydrogen-bonding sites. The crystal structures of these complexes, and solution NMR studies, have been used to evaluate the extent to which they associate in the

† *Non-SI unit employed*: eV ≈ 1.60×10^{-19} J.

solid state and in solution. A preliminary account of some of this work has been published.[15]

Experimental

General details

Proton NMR spectra were recorded on JEOL GX270 or Lambda 300 spectrometers, fast atom bombardment (FAB) mass spectra on a VG Autospec instrument, with 3-nitrobenzyl alcohol as matrix, electrospray mass spectra with MeCN solutions of the complexes on a VG Quattro instrument, using cone voltages of typically 25 V. Electrochemical measurements were made with a PC-controlled EG&G/PAR 273A potentiostat, using platinum-bead working and auxiliary electrodes, and a saturated calomel reference electrode (SCE). The measurements were performed using acetonitrile distilled over calcium hydride, with 0.1 mol dm^{-3} $[NBu^n_4][PF_6]$ as supporting electrolyte. Ferrocene was added at the end of each experiment as an internal reference, and all redox potentials are quoted *vs.* the ferrocene–ferrocenium couple.

Association processes driven by the complementary adenine (Ade) and thymine (Thy) groups appended to the Ru-, Os- and Re-based chromophores (see below) were investigated *via* ^{1}H NMR spectroscopy by observing the signal of the thymine NH proton. In CD_2Cl_2 this occurs at about δ 8 and is obscured by other signals; in CD_3CN, however, it occurs near δ 9 and is easy to observe. In order to evaluate the association constant, K_A, for the equilibrium (1) where *X* and *Y* denote the equilibrium

$$X + Y \rightleftharpoons X{\cdot}Y \qquad (1)$$

concentration for the interacting partners X, Y (see below) we have analysed with standard fitting procedures the NMR titration results by following the approach described by Wilcox,[16] and by using equation (2). Here, δ_{obs} is the observed proton

$$\delta_{obs} = \delta_u + \frac{\Delta\delta}{2X_o}\left[K_d + Y_o + X_o - \sqrt{(K_d + Y_o + X_o)^2 - 4Y_oX_o}\right] \qquad (2)$$

chemical shift at the employed concentrations X_o and Y_o (the latter is varied) of the interacting partners; δ_u is the chemical shift for the unbound proton, Δδ is the difference in chemical shift for the bound and unbound protons and $K_d = 1/K_A$.

The UV/VIS absorption spectra were obtained on Perkin-Elmer Lambda 2 or 5 instruments. Room-temperature luminescence experiments were performed in acetonitrile and dichloromethane (from Romil). Luminescence spectra were obtained from a Spex Fluorolog II spectrofluorimeter and uncorrected luminescence band maxima are used throughout the text unless otherwise stated. The luminescence intensity profile was corrected either by using software provided by the manufacturer or by testing the phototube response with a calibrated 45 W quartz–halogen tungsten-filament lamp (Optronic Laboratories). Luminescence quantum yields, φ_s, were evaluated by comparing areas under the corrected luminescence spectra on an energy scale and by using equation (3) where *A* is the absorb-

$$\varphi_s = \varphi_r \frac{A_r}{A_s}\frac{n_s^2}{n_r^2}\frac{\text{Area}_s}{\text{Area}_r} \qquad (3)$$

ance, *n* the refractive index of the solvent employed, and s and r stand for sample and reference, respectively. The reference compound was $[Ru(bipy)_3]^{2+}$ in air-equilibrated water (φ_r = 0.028).[17] The experimental uncertainty in the band maximum for absorption and luminescence spectra is 2 nm. Luminescence lifetimes were obtained with an IBH single-photon-counting apparatus (N_2 lamp, excitation at 337 nm). The uncertainty on the evaluated lifetimes is 8%. In order to study intercomponent photoinduced energy transfer we followed an approach outlined previously.[18] This is based on the fact that selective excitation of the component expected to act as a donor is not possible in the present cases. Thus, one selects an excitation wavelength so as to excite statistically both the donor and acceptor components in a predetermined ratio. This allows one to monitor the occurrence of energy transfer by looking at the luminescence quenching of the donor and luminescence sensitisation of the acceptor.

Adenine, thymine, 4-*tert*-butylpyridine and bipy were obtained from Aldrich and used as received. Ruthenium trichloride and osmium trichloride were generously provided on loan by Johnson Matthey. The compounds $[Ru(bipy)_2Cl_2]{\cdot}2H_2O$,[19] 4,4′-di-*tert*-butyl-2,2′-bipyridine (dbbipy)[20] and 5-bromomethyl-2,2′-bipyridine (bmbipy)[21] were prepared by the literature methods. The compounds $[M(dbbipy)_2Cl_2]$ (M = Ru or Os) were prepared according to the methods used for $[M(bipy)_2Cl_2]$ (M = Ru or Os)[19,22] but using dbbipy in place of bipy; due to their high solubilities, these compounds did not crystallise from the reaction mixtures but were extracted into CH_2Cl_2 and purified by chromatography on alumina with CH_2Cl_2–MeOH (95:5, v/v). The compound $[Re(CO)_5Cl]$ was purchased from Alfa.

Syntheses

bipya. A mixture of adenine (135 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) and KI (*ca.* 30 mg, a catalytic amount) in dry Me_2SO (15 cm^3) was stirred under N_2 for 10 min. 5-Bromomethyl-2,2′-bipyridine (610 mg, 2.45 mmol) was then added and the cloudy yellow mixture was stirred under N_2 at room temperature for 2.5 h. Water (100 cm^3) was then added and the suspension extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$) and the solvent removed *in vacuo* to give a yellow solid. Addition of a small amount of CH_2Cl_2 (5 cm^3) dissolved the unchanged bmbipy but did not significantly dissolve the much less soluble product; filtration of the suspension, washing the solid with a little CH_2Cl_2 and drying afforded bipya (142 mg, 47%). Electron impact (EI) mass spectrum: m/z = 303 (M^+). ^{1}H NMR [300 MHz, $(CD_3)_2SO$] δ 5.49 (2 H, s, CH_2), 7.28 (2 H, br s, adenine NH_2), 7.43 (1 H, ddd, bipy $H^{5'}$), 7.84 (1 H, dd, bipy H^4), 7.92 (1 H, td, bipy $H^{4'}$), 8.15 (1 H, s, adenine H^2), 8.34 (3 H, m, bipy H^3/$H^{3'}$ and adenine H^8), 8.65 (1 H, m, bipy $H^{6'}$) and 8.71 (1 H, m, bipy H^6).

bipyt. A mixture of thymine (504 mg, 4 mmol), K_2CO_3 (276 mg, 2 mmol) and KI (*ca.* 30 mg, a catalytic amount) in dry Me_2SO (10 cm^3) was stirred under N_2 for 10 min. A solution of bmbipy (200 mg, 0.8 mmol) in dry Me_2SO (2 cm^3) was then added slowly *via* a syringe and the reaction mixture was stirred under N_2 at room temperature for 3 h. Water (100 cm^3) was then added and the suspension extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$) and the solvent removed *in vacuo* to give an off-white solid. As above, soluble impurities were removed by suspending the solid in CH_2Cl_2 (5 cm^3) followed by filtration, washing with CH_2Cl_2 and drying to give bipyt (88 mg, 37%). EI mass spectrum: m/z = 294 (M^+). ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ 1.71 (3 H, s, CH_3), 4.88 (2 H, s, CH_2), 7.39 (1 H, ddd, bipy $H^{5'}$), 7.68 (1 H, s, thymine H^2), 7.81 (1 H, dd, bipy H^4), 7.89 (1 H, td, bipy $H^{4'}$), 8.31 (2 H, m, bipy H^3/$H^{3'}$), 8.61 (2 H, m, bipy H^6/$H^{6'}$) and 11.33 (1 H, s, thymine NH).

$[Ru(bipy)_2(bipya)][PF_6]_2$, $[Ru(dbbipy)_2(bipya)][PF_6]_2$ and $[Os(dbbipy)_2(bipyt)][PF_6]_2$. These compounds were all prepared in the usual way by reaction of $[Ru(bipy)_2Cl_2]$ or $[M(dbbipy)_2Cl_2]$ (M = Ru or Os) with a 10% molar excess of the appropriate ligand (bipya or bipyt) in ethylene glycol at reflux for 1 h. After cooling, addition of aqueous KPF_6 precipitated the complexes as orange (Ru) or dark green (Os) powders which were filtered off, washed with water and dried. The compound $[Ru(bipy)_2(bipya)][PF_6]_2$ was purified by chromatography on a

Table 1 Crystallographic data for $[Ru(dbbipy)_2(bipya)][PF_6]_2\cdot 2MeCN$ and $[Os(dbbipy)_2(bipyt)][PF_6]_2\cdot Me_2CO$

	$[Ru(dbbipy)_2(bipya)][PF_6]_2\cdot 2MeCN$	$[Os(dbbipy)_2(bipyt)][PF_6]_2\cdot Me_2CO$
Formula	$C_{56}H_{67}F_{12}N_{13}P_2Ru$	$C_{55}H_{68}F_{12}N_8O_3OsP_2$
M	1313.24	1369.31
System, space group	Orthorhombic, $Pca2_1$	Triclinic, $P\bar{1}$
a/Å	40.630(3)	12.730(2)
b/Å	11.705(2)	14.716(2)
c/Å	12.598(2)	16.482(3)
α/°		96.05(1)
β/°		95.03(1)
γ/°		98.00(1)
U/Å^3	5991(2)	3024.1(8)
Z	4	2
D_c/g cm^{-3}	1.456	1.504
μ/mm^{-1}	0.402	2.246
F(000)	2704	1384
Crystal size/mm	0.30 × 0.20 × 0.15	0.40 × 0.20 × 0.05
2θ Range for data collection/°	5–50	4–50
Reflections collected: total, independent (R_{int})	27 568, 10 236 (0.060)	14 445, 10 273 (0.043)
Data, restraints, parameters	10 234, 349, 865	10 271, 0, 748
Final $R1$, $wR2$ [a,b]	0.087, 0.194	0.052, 0.126
Weighting factors [b]	0.0419, 27.8136	0.0257, 20.2263
Largest peak, hole/e Å^{-3}	+0.839, −1.730	+1.519, −0.898

[a] Structure was refined on F_o^2 using all data; the value of $R1$ is given for comparison with older refinements based on F_o with a typical threshold of $F \geqslant 4\sigma(F)$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

preparative-scale silica plate (Merck article 1.057 17) using MeCN–water–saturated aqueous KNO_3 (14 : 2 : 1, v/v) as eluent; the major orange band was scraped off, and the complex soaked out of it using the elution solvent. Concentration *in vacuo* and addition of aqueous KPF_6 precipitated the pure complex which was filtered off and dried. The much more soluble complexes containing dbbipy ancillary ligands were purified by chromatography on preparative-scale alumina plates (Merck article 5726) using CH_2Cl_2–MeOH (97 : 3, v/v) as eluent. Yields in all cases were 40–50%.

$[Ru(bipy)_2(bipya)][PF_6]_2$: Electrospray (ES) mass spectrum: m/z 861.5, $[M - PF_6]^+$; 358.1, $[M - 2PF_6]^{2+}$ (Found: C, 42.4; H, 2.7; N, 15.5. Calc. for $C_{36}H_{29}F_{12}N_{11}P_2Ru$: C, 42.9; H, 2.9; N, 15.3%).

$[Ru(dbbipy)_2(bipya)][PF_6]_2$: ES mass spectrum: m/z 1086.5, $[M - PF_6]^+$; 470.8, $[M - 2PF_6]^{2+}$; and 314, $[M + H - 2PF_6]^{3+}$ (Found: C, 50.2; H, 5.2; N, 12.4. Calc. for $C_{52}H_{61}F_{12}N_{11}P_2Ru$: C, 50.7; H, 5.0; N, 12.5%).

$[Os(dbbipy)_2(bipyt)][PF_6]_2$: ES mass spectrum: m/z 1167.7, $[M - PF_6]^+$; and 511.1, $[M - 2PF_6]^{2+}$ (Found: C, 47.9; H, 5.1; N, 8.8. Calc. for $C_{52}H_{61}F_{12}N_8O_2OsP_2$: C, 47.6; H, 4.8; N, 8.6%).

[Re(bipyt)(CO)$_3$Cl]. A mixture of $[Re(CO)_5Cl]$ (111 mg, 0.3 mmol) and bipyt (89 mg, 0.3 mmol) in dry toluene (10 cm^3) was heated to reflux with stirring under N_2 for 2 h. The yellow reaction mixture was then cooled to 5 °C overnight, after which the yellow precipitate was filtered off, washed with CH_2Cl_2 and dried. FAB mass spectrum: m/z 623 (M + Na$^+$); 600 (M); and 565 (M − Cl) (Found: C, 37.6; H, 2.3; N, 9.2. Calc. for $C_{19}H_{14}ClN_4O_3Re$: C, 38.0; H, 2.4; N, 9.3%).

Crystallography

The compounds $[Ru(dbbipy)_2(bipya)][PF_6]_2$ and $[Os(dbbipy)_2(bipyt)][PF_6]_2$ were crystallised by diffusion of ether vapour into concentrated solutions of them in acetonitrile or acetone respectively. Crystals were mounted on a brass pin in a stream of N_2 at −100 °C on the diffractometer as quickly as possible to prevent decomposition due to loss of lattice solvent.

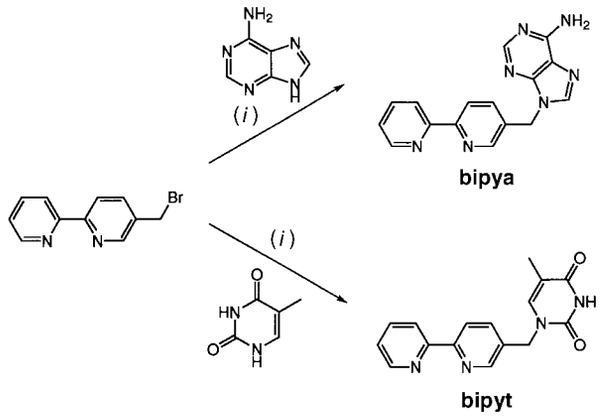
Data were collected using a Siemens SMART three-circle diffractometer with a CCD area detector (graphite-monochromatised Mo-Kα X-radiation, $\bar{\lambda} = 0.710\,73$ Å). They were corrected for Lorentz-polarisation effects, and for absorption by an empirical method based on multiple measurements of equivalent data. Details of the crystal parameters, data collection and refinement are in Table 1. The structures were solved by conventional heavy-atom or direct methods (SHELXTL)[23] and refined by the full-matrix least-squares method on all F^2 data (SHELXTL)[23] using a Silicon Graphics Indigo R4000 computer. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters.

Details of the crystal structure study on $[\{Ru(bipy)_2(bipya)\}\{Ru(bipy)_2(Hbipya)\}][PF_6]_5\cdot 4MeCN$ were published in the initial communication[15] and are not reproduced here.

For $[Ru(dbbipy)_2(bipya)][PF_6]_2\cdot 2MeCN$ there was disorder present involving two of the *tert*-butyl groups [C(17)–C(19) and C(47)–C(49)]. These were both disordered over two positions with different torsion angles between the *tert*-butyl groups and the pyridyl ring (a 'propeller'-like disorder). For C(17)–C(19) the site occupation factors for the two orientations were 0.56 and 0.44, for C(47)–C(49) they were 0.36 and 0.64. One of the two acetonitrile molecules was also disordered over two positions by a rotation about the central carbon atom: *i.e.* the central carbon atom was fixed (site occupation factor 1.00), but the terminal carbon [C(6)] and nitrogen [N(4)] were disordered with site occupation factors of 0.50 between the two sites. The second acetonitrile molecule was well behaved. The space group is chiral, and the absolute structure parameter was −0.20(6). To ensure stable refinement, restraints were applied as follows. Each disordered *tert*-butyl group was restrained to have similar C–C bond lengths and interbond angles for the two disordered components. For the hexafluorophosphate counter ions the P–F (bonded) and F···F (non-bonded) separations were restrained to be similar.

For $[Os(dbbipy)_2(bipyt)][PF_6]_2\cdot Me_2CO$ the asymmetric unit contains (as well as the complex dication) one complete $[PF_6]^-$ anion and two half-anions which are located on crystallographic inversion centres. The acetone molecule was well behaved.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1977, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/357.



Scheme 1 (*i*) K_2CO_3, Me_2SO, KI (catalytic amount)

Table 2 Selected bond lengths (Å) and angles (°) for [{Ru(bipy)$_2$-(bipya)}{Ru(bipy)$_2$(Hbipya)}][PF$_6$]$_5$·4MeCN

Ru(1)–N(41)	2.054(13)	Ru(1)–N(11)	2.069(11)
Ru(1)–N(61)	2.057(12)	Ru(1)–N(21)	2.073(12)
Ru(1)–N(31)	2.062(11)	Ru(1)–N(51)	2.075(12)
N(41)–Ru(1)–N(61)	173.0(5)	N(41)–Ru(1)–N(31)	78.8(5)
N(61)–Ru(1)–N(31)	98.8(5)	N(41)–Ru(1)–N(11)	96.6(5)
N(61)–Ru(1)–N(11)	86.5(5)	N(31)–Ru(1)–N(11)	172.6(5)
N(41)–Ru(1)–N(21)	89.5(5)	N(61)–Ru(1)–N(21)	97.2(5)
N(31)–Ru(1)–N(21)	95.4(5)	N(11)–Ru(1)–N(21)	78.6(5)
N(41)–Ru(1)–N(51)	94.4(5)	N(61)–Ru(1)–N(51)	79.1(5)
N(31)–Ru(1)–N(51)	92.4(5)	N(11)–Ru(1)–N(51)	93.8(5)
N(21)–Ru(1)–N(51)	171.8(6)	C(65)–C(70)–N(71)	114.6(13)

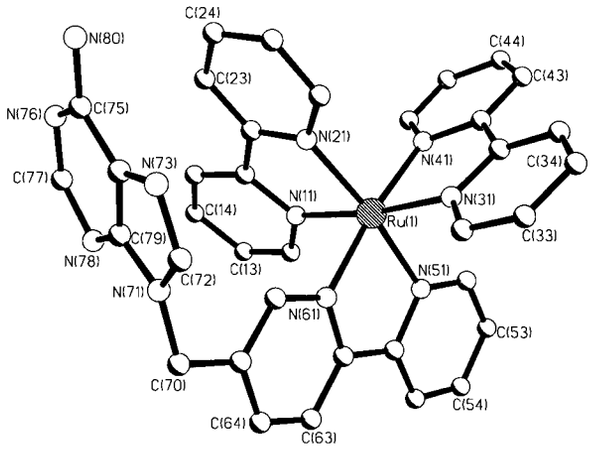


Fig. 1 Crystal structure of the complex cation of [{Ru(bipy)$_2$-(bipya)}{Ru(bipy)$_2$(Hbipya)}][PF$_6$]$_5$·4MeCN

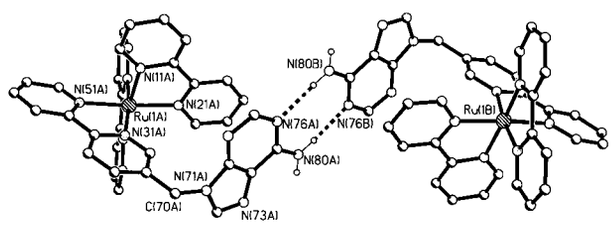


Fig. 2 Association by hydrogen bonding of two metal complex cations of [{Ru(bipy)$_2$(bipya)}{Ru(bipy)$_2$(Hbipya)}][PF$_6$]$_5$·4MeCN across an inversion centre

Results and Discussion

Ligand syntheses

Nature uses the adenine/thymine double hydrogen bond and the cytosine/guanine triple hydrogen bond to link together the two strands of duplex DNA.[24] In addition to their hydrogen-bonding capability, these bases are synthetically appealing because of the ease with which they can be functionalised by alkylation.[25] We found that reaction of adenine or thymine with bmbipy in Me_2SO using K_2CO_3 as base gave reasonable yields of bipya and bipyt in a simple one-pot reaction (Scheme 1). For bipya we used an excess of the electrophile bmbipy; for bipyt however this invariably led to double alkylation of the thymine core, and to prevent this we used a large excess of thymine relative to bmbipy. In both cases addition of a catalytic amount of KI helped considerably, allowing shorter reaction times and lower reaction temperatures. The improvement afforded by addition of KI is striking: in our original communication[15] when we had not used KI in the syntheses the preparations required elevated temperatures and gave mixtures of alkylated products which required chromatographic separation. The spectroscopic properties of the ligands, and the crystal structures of their complexes (see below), confirmed that, as required, alkylation occurred exclusively at the N^9 position of adenine and the N^1 position of thymine. We note that Constable and Fallahpour[26] have recently prepared a ligand in which a thymine residue is attached *via* the N^1 position to a 2,2′:6′,2″-terpyridyl binding site, and investigated the interactions of its ruthenium(II) complex with an adenosine derivative.

Synthesis and crystal structure of [Ru(bipy)$_2$(bipya)][PF$_6$]$_2$

Initially we prepared [Ru(bipy)$_2$(bipya)][PF$_6$]$_2$, in which the photoactive {Ru(bipy)$_3$}$^{2+}$ core bears a pendant adenine residue, by reaction of bipya with [Ru(bipy)$_2$Cl$_2$]·2H$_2$O in the normal way. Elemental analysis and ES mass spectra confirmed the formulation of the complex, and the ^{1}H NMR spectrum, although not fully assigned due to the large number of overlapping signals in the aromatic region, indicated the correct number of proton environments. A significant feature of the spectra is that the signals for the CH_2 spacers of the bipya ligand have become inequivalent (diastereotopic) on coordination of the ligand to a chiral tris-chelate metal complex. This signal is therefore an AB-type multiplet, rather than the singlet that was observed in the spectrum of free bipya.

Crystallisation from MeCN–diethyl ether showed that partial protonation of the pendant base occurs in the crystalline material, which is formulated [{Ru(bipy)$_2$(bipya)}{Ru(bipy)$_2$-(Hbipya)}][PF$_6$]$_5$·4MeCN. Full details of the structural determination of this complex have already been given in the preliminary communication and so are not reproduced here; the structure of the complex cation is shown in Fig. 1. The coordination environment around the ruthenium atom, and the bond lengths and angles within the adenine moiety, are all normal (Table 2). The unit cell contains two complex cations related by an inversion centre, four lattice acetonitrile molecules, and *five* hexafluorophosphate anions rather than the expected four, of which one is located on an inversion centre. It appears that one of the two complexes has scavenged an additional proton during recrystallisation, which must be attached to one of the basic positions of the pendant adenine group. That this had not occurred before crystallisation is evident from the electrospray mass spectrum of the initially prepared material, which showed no evidence of a triply charged cation, and from the elemental analysis. The extra proton is effectively disordered between the two complex units within the unit cell and could not be located crystallographically.

The most interesting feature of the complex is that the pendant bases (one adenine and one protonated adenine) undergo self-association by hydrogen bonding across an inversion centre (Fig. 2). The Ru···Ru distance is 15.60 Å. The hydrogen-

bonding interaction is a Watson–Crick (as opposed to Hoogsteen) type, involving the N^{10}-amino group [N(80) according to the crystallographic labelling scheme] and atom N^1 of the six-membered ring [N(76)]. The N(76A)···N(80B) separation is 3.052 Å, which is rather long for Watson–Crick base pairing (the normal range is 2.8–2.95 Å),[24] possibly due to electrostatic repulsion between the positively charged complexes. The two adenine fragments are essentially coplanar. This association is unexpected because free adenine does not undergo self-pairing by hydrogen bonding in this way. The crystal structure of 9-methyladenine, for example, shows that a Hoogsteen-type association occurs with intermolecular N(1)···N(10) (2.97 Å) and N(7)···N(10) (3.06 Å) hydrogen bonds leading to the formation of an extended two-dimensional 'ribbon'.[27] In solution, the extended aromatic systems of adenine associate by π stacking rather than hydrogen bonding with an association constant of 15 ± 2 $dm^3\ mol^{-1}$,[28] and the propensity of adenine to become involved in π-stacking interactions is a controlling factor in the structures of ternary metal complexes which contain adenine fragments in addition to other aromatic ligands.[28,29]

The unusual occurrence of the Watson–Crick hydrogen bonding in this complex is probably related to the presence of one additional proton per adenine–adenine pair. The order of protonation of the basic sites in 9-substituted adenines usually follows the sequence $N^1 > N^7 > N^3$,[30] so that monoprotonated adenines are generally protonated at N^1 in the solid state.[31] However the difference in basicity between N^1 and N^7 is slight and there is experimental[30] and theoretical[32] evidence to suggest that in solution the N^1-protonated form is in equilibrium with the N^7-protonated form. If N^1 is protonated it can no longer act as a hydrogen-bond acceptor, and in N^1-protonated adenine derivatives Hoogsteen pairing involving N^7 and the amino group (N^{10}) occurs instead.[31] The fact that we observe in this complex a Watson–Crick interaction involving the N^1 and N^{10} atoms therefore means that the protonation site is likely to be the N^7 position [N(73) according to the crystallographic labelling scheme], or possibly N^3 [N(78)], but not N^1 [N(76)]. Indirect evidence for this is also provided by the structure of $[Ru(dbbipy)_2(bipya)][PF_6]_2$ (see below) which has no extra protons and has a completely different pattern of intermolecular hydrogen bonding.

This structure shows that, in the absence of competing solvent interactions, hydrogen bonding can become the dominant intermolecular interaction between these metal–polypridyl complexes, which is encouraging from the point of view of controlling the formation of hydrogen-bonded aggregates in the solid state. From the point of view of hydrogen-bonding interactions in solution however it was apparent that this complex would not be suitable. It is insoluble in chlorinated solvents, only moderately soluble in MeCN and acetone, and requires very polar solvents such as Me_2SO or dimethylformamide to dissolve significant quantities. Maximisation of hydrogen bonding requires the use of low-polarity solvents which do not compete for hydrogen-bonding sites. We therefore switched our attention to the preparation of more soluble complexes.

Syntheses and crystal structures of $[Ru(dbbipy)_2(bipya)][PF_6]_2$ and $[Os(dbbipy)_2(bipyt)][PF_6]_2$

In order to solubilise the complexes we used dbbipy in place of bipy as the ancillary ligands. This required preparation of $[M(dbbipy)_2Cl_2]$ (M = Ru or Os) as starting materials. These could be prepared in exactly the same way as the parent $[M(bipy)_2Cl_2]$ complexes, with the exception that they did not crystallise from the reaction mixtures due to their higher solubilities and so were purified by chromatography. Their formulations were confirmed by FAB mass spectrometry and by the subsequent crystal structures described below. These complexes are both highly soluble in CH_2Cl_2 as well as more polar solvents.

Table 3 Selected bond lengths (Å) and angles (°) for $[Ru(dbbipy)_2(bipya)][PF_6]_2 \cdot 2MeCN$

Ru–N(10)	2.046(8)	Ru–N(40)	2.066(7)
Ru–N(20)	2.055(8)	Ru–N(50)	2.078(8)
Ru–N(30)	2.065(8)	Ru–N(60)	2.074(7)
N(10)–Ru–N(20)	78.0(3)	N(30)–Ru–N(60)	171.1(3)
N(10)–Ru–N(30)	95.1(3)	N(40)–Ru–N(60)	94.6(3)
N(20)–Ru–N(30)	87.6(3)	N(10)–Ru–N(50)	95.5(3)
N(10)–Ru–N(40)	173.0(3)	N(20)–Ru–N(50)	173.1(3)
N(20)–Ru–N(40)	98.1(3)	N(30)–Ru–N(50)	95.3(3)
N(30)–Ru–N(40)	78.7(3)	N(40)–Ru–N(50)	88.5(3)
N(10)–Ru–N(60)	91.9(3)	N(60)–Ru–N(50)	78.6(3)
N(20)–Ru–N(60)	99.2(3)	N(70)–C(66)–C(62)	113.2(12)

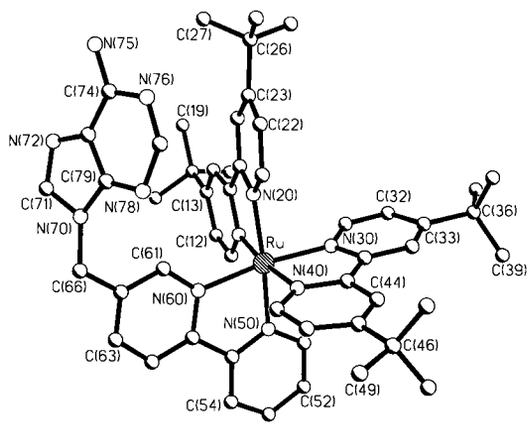


Fig. 3 Crystal structure of the complex cation of $[Ru(dbbipy)_2(bipya)][PF_6]_2 \cdot 2MeCN$

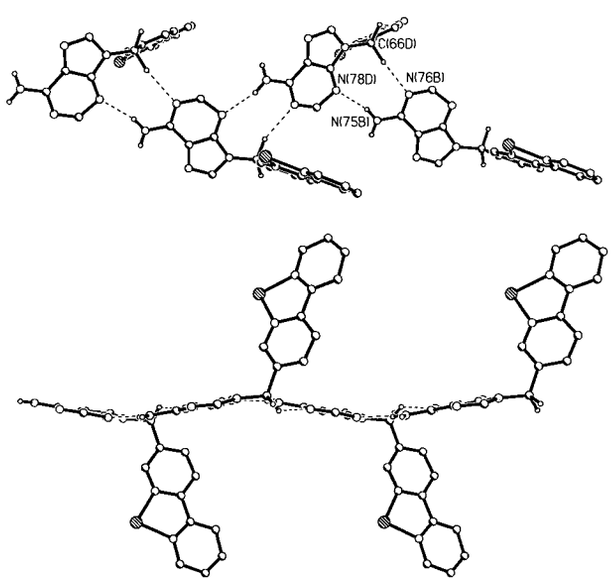


Fig. 4 Two views of the association by hydrogen bonding of the metal complex cations in $[Ru(dbbipy)_2(bipya)][PF_6]_2 \cdot 2MeCN$, showing formation of a hydrogen-bonded 'ribbon'. Ancillary dbbipy ligands are omitted for clarity

Reaction of the appropriate $[M(dbbipy)_2Cl_2]$ with bipya (M = Ru) or bipyt (M = Os) afforded, after the usual work-up and purification procedures, $[Ru(dbbipy)_2(bipya)][PF_6]_2$ and $[Os(dbbipy)_2(bipyt)][PF_6]_2$ respectively. Elemental analyses and ES mass spectra confirmed the formulations, and again the ^1H NMR spectra in CD_2Cl_2 showed the correct number of proton environments, with the CH_2 protons of the bipya or bipyt becoming diastereotopic and giving an AB-type multiplet on co-ordination to a chiral metal centre.

Table 4 Selected bond lengths (Å) and angles (°) for $[Os(dbbipy)_2(bipyt)][PF_6]_2 \cdot Me_2CO$

Os–N(11)	2.068(6)	Os–N(41)	2.058(6)
Os–N(21)	2.062(5)	Os–N(51)	2.061(6)
Os–N(31)	2.065(6)	Os–N(61)	2.069(5)
N(21)–Os–N(11)	77.7(2)	N(31)–Os–N(11)	89.9(2)
N(41)–Os–N(11)	97.0(2)	N(51)–Os–N(11)	96.0(2)
N(41)–Os–N(51)	97.4(2)	N(51)–Os–N(21)	88.4(2)
N(41)–Os–N(21)	172.5(2)	N(41)–Os–N(31)	78.3(2)
N(51)–Os–N(31)	173.2(2)	N(21)–Os–N(31)	96.3(2)
N(41)–Os–N(61)	87.1(2)	N(51)–Os–N(61)	78.7(2)
N(21)–Os–N(61)	98.7(2)	N(31)–Os–N(61)	95.7(2)
N(11)–Os–N(61)	173.7(2)	C(63)–C(67)–N(71)	110.9(6)

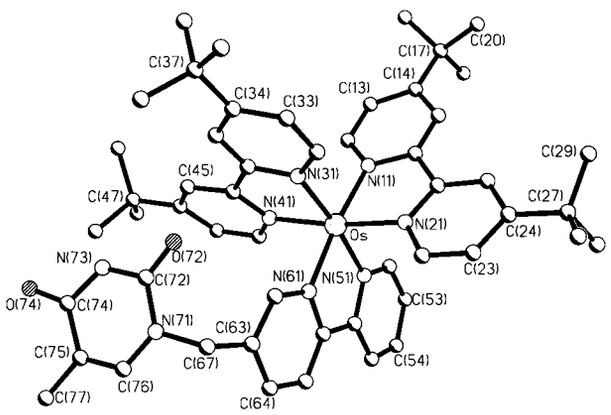


Fig. 5 Crystal structure of the complex cation of $[Os(dbbipy)_2(bipyt)][PF_6]_2 \cdot Me_2CO$

The crystal structure of the cation of $[Ru(dbbipy)_2(bipya)][PF_6]_2 \cdot 2MeCN$ is shown in Fig. 3. The structure of the individual complex units is as expected with no unusual features (Table 3). The pattern of intermolecular hydrogen bonding is, however, completely different from that of the previous example, and is shown in Fig. 4. Each pendant adenine group is involved in two pairs of hydrogen bonds, to two neighbouring adenine groups, resulting in the formation of a hydrogen-bonded ribbon of adenine moieties running through the crystal. The stronger of these hydrogen bonds is between the amino group [N(75) according to the crystallographic numbering scheme] and the adenine N^3 [N(78)] of the adjacent molecule, with the N···N separation being 2.943 Å, an entirely typical value for such an interaction.[24] The weaker interaction is between the adenine N^1 [N(76) according to the crystallographic numbering scheme] and one of the hydrogen atoms of the CH_2 fragment [C(66)] of an adjacent molecule, with the N···C separation being 3.520 Å. It is interesting that the adenine N^7 atom [N(72)] is not involved in hydrogen bonding, as it is in the structure of 9-methyladenine. However it is likely that a dominant controlling feature in the formation of this hydrogen-bonding ribbon is the requirement to maximise the separation between the positively charged metal complex units, which explains why the bipy fragments (which are of course co-ordinated to ruthenium) are disposed alternately above and below the ribbon. The separations between adjacent ruthenium atoms on the same side of the ribbon is 12.598 Å; between a pair of ruthenium atoms on alternate sides of the ribbon the separation is 13.037 Å. The relatively minor energy difference between different patterns of hydrogen bonding is likely to take second place to electrostatic repulsion effects.

The crystal structure of the cation of $[Os(dbbipy)_2(bipyt)][PF_6]_2 \cdot Me_2CO$ is shown in Fig. 5. The structure of the individual complex units is again as expected and there is nothing unusual about the structural parameters of the $\{Os(bipy)_3\}^{2+}$ core (Table 4). Two molecules are associated

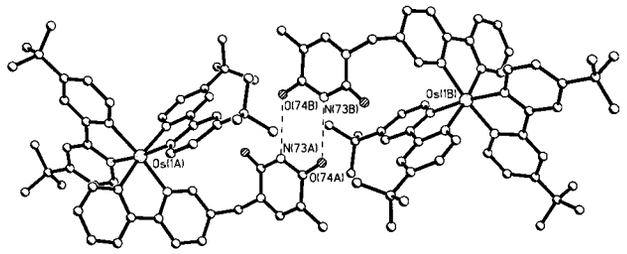


Fig. 6 Association by hydrogen bonding of two metal complex cations of $[Os(dbbipy)_2(bipyt)][PF_6]_2 \cdot Me_2CO$ across an inversion centre

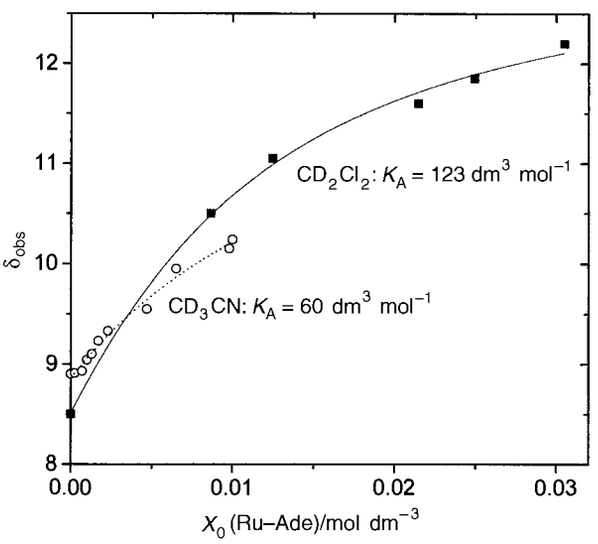


Fig. 7 Proton NMR titration of Os-Thy with Ru-Ade. The starting concentration of Os-Thy was 6.93×10^{-3} mol dm^{-3} in CD_2Cl_2 and 1×10^{-3} mol dm^{-3} in CD_3CN

across an inversion centre *via* a thymine–thymine double hydrogen bond involving N(73) and O(74) (Fig. 6); the N(73A)···O(74B) separation is 2.944 Å which lies within the normal range for Watson–Crick hydrogen bonding. This interaction is similar to that observed in the crystal structure of free thymine (as well as other uracil derivatives), in which the intermolecular N···O distances are 2.81 and 2.84 Å.[33] The slight lengthening of the intermolecular contacts may again be ascribed to electrostatic repulsion between the dicationic complex units.

Solution studies on the complexes

In order to examine the extent of association of complementary complexes in solution we performed NMR titrations. To start with we examined the $[Ru(dbbipy)_2(bipya)][PF_6]_2$–$[Os(dbbipy)_2(bipyt)][PF_6]_2$ pair (hereafter abbreviated as Ru-Ade and Os-Thy). The thymine NH proton provides a convenient NMR probe as it has a high chemical shift and therefore stands out from the mass of overlapping signals in the aromatic region, and its signal also shifts substantially when involved in hydrogen-bonding interactions.[13] Accordingly we used a fixed amount of Os-Thy in the NMR sample, added Ru-Ade in several portions, and measured the chemical shift of the thymine NH proton after each addition. We did this in both CD_3CN and CD_2Cl_2, and the results are shown in Fig. 7. From these, approximate association constant values K_A of 60 dm^3 mol^{-1} in CD_3CN and 123 dm^3 mol^{-1} in CD_2Cl_2 could be obtained. The higher value in the less polar solvent is of course to be expected, and vindicates our use of complexes with solubilising *tert*-butyl substituents. However in absolute terms these values are not sufficiently high to get a substantial amount of association in the dilute solutions necessary for luminescence studies (see below). We also performed an NMR titration (Fig. 8) with the pair Ru-Ade and [Re(bipyt)(CO)$_3$Cl] (Re-Thy) in CD_3CN (Re-

Table 5 Absorption and emission properties of the complexes[a]

	Ground-state absorption maxima			Luminescence properties[b]		
Complex	λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})			λ_{max}[c]/nm	φ[d]	τ/ns
Ru-Ade	288 (78.7)	458 (13.4)		626	4.8×10^{-2}	500
Os-Thy	292 (66.0)	491 (10.2)	586 (3.0)	750	2.9×10^{-3}	35
Re-Thy	295 (18.0)	390 (2.8)		614	3.0×10^{-3}	30

[a] Room temperature, CH_2Cl_2 solvent. [b] Air-equilibrated samples. [c] Uncorrected band maxima. [d] See text, equation (3).

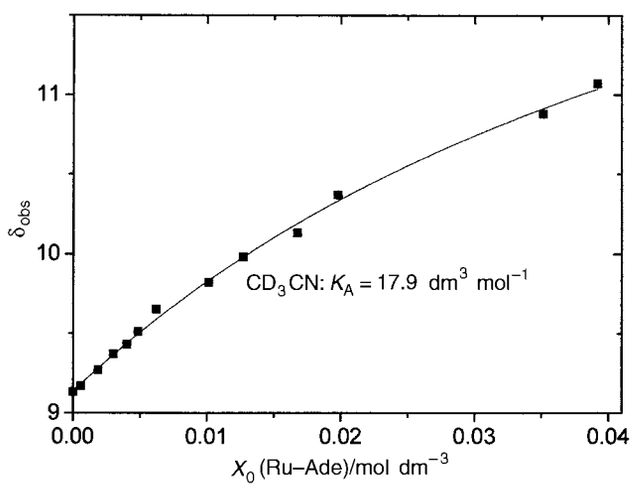


Fig. 8 Proton NMR titration of 1.95×10^{-3} mol dm^{-3} Re-Thy with Ru-Ade in CD_2Cl_2

Thy is only sparingly soluble in CH_2Cl_2; although this level of solubility was sufficient for luminescence studies, it was not enough to allow the NMR titration to be performed in CD_2Cl_2). In this case, the Ru-Ade·Re-Thy association is expected not to be influenced by electrostatic repulsion since Re-Thy is electrically neutral, in contrast to the Ru-Ade/Os-Thy pair in which both components carry a 2+ charge. However, analysis of the results in Fig. 8 indicates that the extent of association between these complementary components is again small, $K_A = 17.9$ dm^3 mol^{-1}, suggesting that intercentre electrostatic interactions are not significant.

The ground-state absorption maxima and the luminescence properties for the Ru-Ade, Os-Thy and Re-Thy complexes dissolved in CH_2Cl_2 are listed in Table 5. Comparison with the analogous values for the parent complexes $[Ru(bipy)_3]^{2+}$ (ref. 34) and $[Os(bipy)_3]^{2+}$ (ref. 35) in various solvents and [Re(bipy)$(CO)_3$Cl] in CH_2Cl_2[36,37] indicates that the presence of *tert*-butyl substituents and the pendant adenine or thymine groups only cause small changes with respect to the properties exhibited by the parent complexes. In particular, one should notice that the pendant adenine and thymine groups do not act as quenchers of the luminescence of the metal-based chromophores. Similarly, the potentials of the Ru^{II}–Ru^{III} and Os^{II}–Os^{III} couples of Ru-Ade and Os-Thy are identical to those of the parent $[M(bipy)_3]^{2+}$ complexes. Attachment of the hydrogen-bonding substituents has therefore not damaged the desirable electrochemical and spectroscopic properties of the complex cores.

From the luminescence band maxima reported in Table 5 it is predicted that both Ru ⟶ Os and Re ⟶ Ru energy-transfer steps are energetically feasible, even if in the latter case this appears only slightly exoergonic (see below). Concerning the mechanism of energy transfer we have drawn the following conclusions. According to the Förster (dipole–dipole)[38] treatment, for Re ⟶ Ru and Ru ⟶ Os energy transfer, the calculated critical transfer distance (*i.e.* the intercentre distance for which the intrinsic deactivation rate of the donor equals the energy transfer rate) is $R_0 \approx 7$ and >20 Å, respectively. Thus for Re ⟶ Ru energy transfer (*e.g.* in a Re-Thy·Ru-Ade associated pair, in which the metal–metal separation will be much greater than 7 Å) R_0 is too small and this type of (through-space) mechanism is expected to play a minor role.

According to a general approach that describes the Dexter[39] type of energy transfer as a double electron transfer and which parallels that for non-adiabatic electron transfer,[40] the energy-transfer rate constant may be expressed as in equation (4) where

$$k_{en} = \nu_N \kappa_N \kappa_E \quad (4)$$

ν_N is a frequency factor, κ_E an electronic factor related to the through-bond intercentre electronic coupling, and κ_N a nuclear factor related to both the driving force (ΔG°) and the intramolecular reorganisation energy (λ) for the energy-transfer step, equation (5).

$$\kappa_N = \exp[-(\Delta G^\circ + \lambda)^2/4\lambda kT] \quad (5)$$

It is interesting to discuss the role of the electronic and nuclear factors in the present cases. It is known that for polypyridine complexes of Ru and Os involved in photoinduced energy transfer the intramolecular reorganization energy λ_{Ru} (ref. 41) and λ_{Os} (ref. 18) is *ca.* 0.1 eV, whereas for a typical Re$(CO)_3$L chromophore (L is a bidentate ligand) λ_{Re} is larger, possibly amounting to *ca.* 0.2–0.3 eV.[36] Judging from the band maxima of Table 5,‡ this suggests that for the Ru-Ade·Thy-Os associated pair a fast, nearly activationless Ru ⟶ Os energy transfer may occur because $-\Delta G^\circ \approx 0.3$ eV and $\lambda \approx 0.2$ eV.[41] On the contrary, for the Ru-Ade·Thy-Re associated pair the nuclear factor might be rather unfavourable, $-\Delta G^\circ \approx 0$ eV and $\lambda \approx 0.3$–0.4 eV. As for the electronic factor, it is significant that electron transfer across a hydrogen bond roughly corresponds to that over two standard covalent bonds[42] so that one expects that through-bond energy transfer could also be effectively mediated by hydrogen bonds. In summary, for the present cases consideration of the intercentre distance ($d_{MM} > 15$ Å) and of the role of the electronic and nuclear factors suggests that both through-space (Förster) and through-bond (Dexter) Ru ⟶ Os energy transfer can take place n the Ru-Ade·Thy-Os associate; on the contrary, predictions based on both mechanisms do not lend support for Re ⟶ Ru energy transfer in Ru-Ade·Thy-Re.

In order to monitor the occurrence of photoinduced energy transfer, we studied the luminescent behaviour of Ru-Ade/Os-Thy and Ru-Ade/Re-Thy mixtures in acetonitrile and dichloromethane solvents; the component concentrations employed were varied in the range 10^{-3}–10^{-5} mol dm^{-3}. As discussed

‡ The use of energy levels calculated from room-temperature band maxima only provides rough estimates for G°. Better values can be obtained by employing the $E_{0\text{-}0}$ spectroscopic energies. To this aim we have performed a one-mode analysis of the corrected luminescence intensity profile on an energy (cm^{-1}) scale, according to a procedure described in ref. 36 and by using a fitting program provided by Professor T. J. Meyer. Calculated $E_{0\text{-}0}$ values were 1.96, 1.61 and 1.93 eV for the Ru-Ade, Os-Thy and Re-Thy complexes, respectively.

above, the association constants were too small to allow production of significant amounts of Ru-Ade·Thy-Os or Ru-Ade·Thy-Re associates at such low concentrations, and the detected luminescence properties proved to be in all cases those of the unbound components. These results are consistent with the fact that association processes driven by double hydrogen bonding are usually characterised by $K_A \ll 1000$ dm^3 mol^{-1}.[14,26] For typical component concentrations of 10^{-4} mol dm^{-3} this gives to an associate concentration of $\ll 10^{-5}$ mol dm^{-3}. In contrast, a compositional ratio between the associate and the parent unbound components of over 1:10 should be obtained in order to detect successfully intercomponent energy transfer by the spectroscopic methods we use.

The luminescence results of Table 5 show that by appending purine and pyrimidine nucleotides to polypyridine complexes of Ru, Os or Re good luminophores are still obtained. As a consequence we are extending our investigations to include complexes with appended cytosine and guanine bases. These bases exhibit a complementary ability to associate *via* triple hydrogen bonds that is expected to result in $K_A > 1000$ dm^3 mol^{-1};[13,43] this should afford substantially higher amounts of associated components and allow intercomponent photoinduced processes, within hydrogen-bonded associates, to be investigated.

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