

Supplementary Material for

From model compounds to protein binding: Syntheses, characterizations and fluorescence studies of $[\text{Ru}^{\text{II}}(\text{bipy})(\text{terpy})\text{L}]^{2+}$ complexes (bipy = 2,2'-bipyridine; terpy = 2,2':6',2''-terpyridine; L = imidazole, pyrazole and derivatives, cytochrome c)

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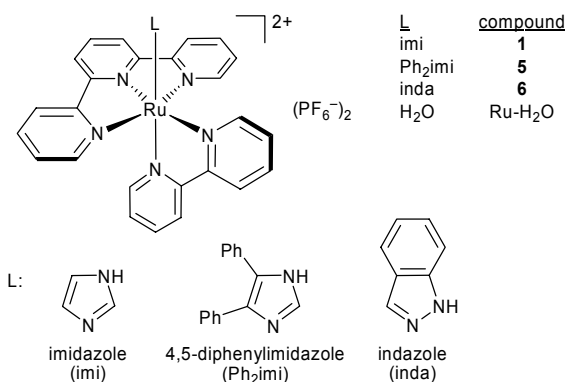
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This supplementary material contains a listing and more extensive discussion of the π - π and C-H $\cdots\pi$ stacking found in the crystal structures of the complexes $[(2,2'$ -Bipyridine)(imidazole)(2,2':6',2''-terpyridine)ruthenium(II)]bis(hexafluorophosphate), $[\text{Ru}(\text{bipy})(\text{terpy})(\text{imi})](\text{PF}_6)_2$, (**1**), $[(2,2'$ -Bipyridine)(4,5-diphenylimidazole)(2,2':6',2''-terpyridine)ruthenium(II)]bis(hexafluorophosphate)-methanol, $[\text{Ru}(\text{bipy})(\text{terpy})(\text{Ph}_2\text{imi})](\text{PF}_6)_2 \cdot \text{CH}_3\text{OH}$, (**5**·CH₃OH), $[(2,2'$ -Bipyridine)(indazole)(2,2':6',2''-terpyridine)ruthenium(II)]bis(hexafluorophosphate), $[\text{Ru}(\text{bipy})(\text{terpy})(\text{inda})](\text{PF}_6)_2$, (**6**) and $[(\text{Aqua})(2,2'$ -bipyridine)(2,2':6',2''-terpyridine)-ruthenium(II)]bis(hexafluorophosphate), $[\text{Ru}(\text{bipy})(\text{terpy})\text{H}_2\text{O}](\text{PF}_6)_2$ (Ru-H₂O).



Discussion

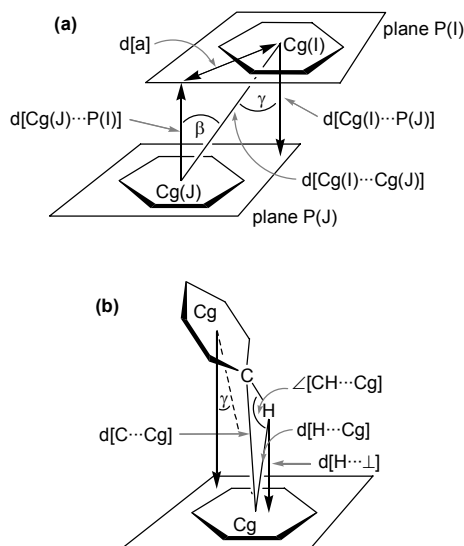
Despite the presence of ligand π -systems in the cations of compounds **1**, **5**, **6** and $[\text{Ru}(\text{bipy})(\text{terpy})\text{H}_2\text{O}](\text{PF}_6)_2$ there are only few intermolecular C-H $\cdots\pi$ ¹ or π - π interactions² evident, due to the separating action of the PF₆⁻ anions. These few non-covalent interactions are listed in Table 1. The listed π -stacking interactions can be viewed as medium to weak in that they exhibit rather long centroid-centroid distances (>4.0 Å) together with large slip angles ($\beta, \gamma > 30^\circ$) and vertical displacements ($a > 2.0$ Å) between the ring centroids. In comparison, strong π -stackings show rather short centroid-centroid contacts (<3.8 Å), small slip angles ($\beta, \gamma < 25^\circ$) and vertical displacements (<1.5 Å) which translate into a sizable

overlap of the pyridyl-plane areas.^{1,3} The intermolecular C-H $\cdots\pi$ contacts start around 2.7 Å for the (C)-H \cdots ring centroid distances (Table 1). As such, these C-H $\cdots\pi$ contacts lie at the short end of the accepted distance range for this type of contact.^{1,4} The cation of compound **5** also features intramolecular π - π stacking between one of the phenyl groups of the imidazole ligand and the terpyridine ligand (see Fig. 3 in the publication). There is also substantial intramolecular π -overlap between this phenyl ring plane and the metal chelate ring built from Ru-N1-N2-C5-C6. It has been suggested that an active electron delocalization within the metal-N-heterocyclic chelate ring could exhibit some degree of "metalloaromaticity".^{5,6} The possibility of the hydrophobic $[\text{Ru}(\text{bipy})(\text{terpy})]^{2+}$ -fragment to enter into C-H $\cdots\pi$ or π -stacking interactions with the hydrophobic grooves of the protein may be an additional aspect of its protein binding.⁷

Table 1 Distances (d/Å) and angles (°) for the π -contacts in the crystal structures ^a

compound, π - π interactions ring(I)··ring(J)	d[Cg(I)··Cg(J)] ^b	α ^c	β ^d	γ ^e	d[Cg(I)··P(J)] ^f	d[Cg(J)··P(I)] ^g	d[a] ^h
1, terpy-N2··terpy-N3 ⁱ	4.38	0.85	36.5	36.2	3.53	3.52	2.60
5, intermolecular bipy-N4··Ph-imi C29-34 ⁱⁱ intramolecular π - π interaction Ph-imi C35-40··terpy-N1	4.16	14.0	32.3	30.2	3.60	3.52	2.22
Ph-imi C35-40·· metallacycle Ru-N1-N2-C5-C6	3.75	6.4	23.8	26.1	3.37	3.43	1.51
Ph-imi C35-40··terpy-N2	3.66	9.5	31.0	25.1	3.32	3.14	1.89
	4.18	12.7	45.3	36.1	3.38	2.94	2.97
6, bipy-N4··bipy-N4 ⁱⁱⁱ	3.83	8.7	15.4	15.4	3.69	3.69	1.02
Ru-H ₂ O, terpy-N1··terpy-N3 ^{iv}	4.03	17.5	23.3	24.9	3.66	3.70	1.60
compound, CH- π interactions ligand-C-H··ring	d[H··Cg] ⁱ	d[H·· \perp] ^j	γ ^e	\angle [CH··Cg] ^k	d[C··Cg] ^l		
1, terpy-C12-H··imi ⁱ	2.77	2.73	8.91	148.2	3.59		
5, terpy-C3-H··Ph-imi C29-34 ^v terpy-C14-H··bipy-N4 ⁱ	2.74	2.67	12.6	144.6	3.54		
	3.09	2.95	17.7	155.1	3.97		
6, terpy-C8-H··inda-C ₆ ^{vi} inda-C ₆ -C30-H··inda-5-ring ^{vii}	2.90	2.86	10.3	163.1	3.81		
	2.73	2.68	11.4	160.2	3.63		
Ru-H ₂ O, bipy-C17-H··bipy-N5 ^{viii}	3.24	3.02	21.3	145.4	4.04		

^a For a graphical depiction of distances and angles in the assessment of the π -contacts, see Scheme 1. Pyridyl rings of the terpy or bipy ligands are named by their nitrogen atoms. – ^b Centroid-centroid distance. – ^c Dihedral angle between the ring planes. – ^d Angle between the centroid vector Cg(I)··Cg(J) and the normal to the plane I. – ^e Angle between the centroid vector Cg(I)··Cg(J) and the normal to the plane J. – ^f Perpendicular distance of Cg(I) on ring plane J. – ^g Perpendicular distance of Cg(J) on ring plane I. – ^h Vertical displacement between ring centroids. – ⁱ H-centroid distance. – ^j Perpendicular distance of H on ring plane. – ^k C-H-centroid angle. – ^l C-centroid distance. – Symmetry transformations: i = 1-x, 1-y, 1-z; ii = x, 1/2-y, -1/2+z; iii = -x, y, 1/2-z; iv = x, 3/2-y, -1/2+z; v = -x, 1/2+y, 1/2-z; vi = x, -1+y, z; vii = 1/2-x, 1/2+y, z; viii = x, 3/2-y, 1/2+z.


Scheme 1 Graphical presentation of the parameters used in Table 1 for the description of (a) π - π stacking and (b) CH- π interactions.

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