Energy transfer pathways in dinuclear heteroleptic polypyridyl complexes

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Published in:
Inorganic Chemistry

DOI:
10.1021/ic049896p

Publication date:
2004

Supplementary information for manuscript ic049896p

Ligand synthesis. *Synthesis of 1,3-bis(5-(2-pyridyl)-4H-1,2,4-triazol-3-yl)benzene (H_2mL).*

This synthesis involved four steps.

First step. Synthesis of 2-pyridylamidrazone. 2-cyanopyridine (22g, 0.21 mol) and excess hydrazine hydrate (15 g, 0.3 mol) were mixed in a minimum amount of ethanol and allowed to stir overnight. The pale yellow needle-like crystals were filtered, washed with diethyl ether and air dried. Yield = 26.8g (94%). M.P.= 96-98 ° C (lit. 95-96 ° C)[i] ^{1}H-NMR [$CDCl_3$]: δ (ppm): 7.24 (1H, dd, pyridyl H_5, J = 6Hz), 7.67 (1H, dd, pyridyl H_4, J = 7.8Hz), 8.00 (1H, d, pyridyl H_3, J = 7.8Hz), 8.50 (1H, d, pyridyl H_6, J = 6Hz), 4.63 (2H, s, broad H_{NH}), 5.42 (2H, s, H_{NH2}). ^{13}C-NMR [$CDCl_3$]: δ(ppm): 119.90, 123.90, 136.50, 148.10, 148.80, 150.97.

Second Step. Preparation of Isophthaloyl dichloride. To a solution of isophthalic acid (16.61 g, 0.1 mol) and DMF (1 cm^3), thionyl chloride (30 cm^3, 0.4 mol) was added under a nitrogen atmosphere. The reaction mixture was then heated to reflux temperature for 30 min, by which time a deep yellow solution had formed. After cooling, any excess thionyl chloride was removed by distillation, and upon cooling of the remaining solution, white crystals formed. These were collected under vacuum and washed with hexane. Yield = 9.2g (50%). M.P.= 40-42 ° C (lit. 43-44 ° C)[ii]

^{1}H-NMR [$CDCl_3$]: δ (ppm): 8.86 (1H, s, phenyl H_2), 8.43 (2H, d, phenyl H_4,H_6, J = 7.9Hz), 7.74 (1H, t, phenyl H_5, J = 7.9Hz) ^{13}C-NMR [$CDCl_3$]: δ (ppm): 130.23, 134.08, 134.70, 137.30, 167.56.

Third step. Preparation of N,N'-Isophthaloyl-bis((2-pyridyl)hydrazidine).

2-Pyridylamidrazone (6.8 g, 0.05 mol) was dissolved in a minimum amount of dry THF and 10 cm^3 triethylamine under a nitrogen atmosphere. To this was added dropwise, under N_2, with constant stirring, a solution of isophthaloyl dichloride (5.08 g, 0.025 mol) in THF, while maintaining the reaction mixture at 0° C. The reaction mixture was then

reduced to approx. 25 cm^3 volume and an equivolume of water added. The yellow product was filtered, washed with water, hot methanol and diethyl ether and dried under vacuum and in the oven at 60 °C. Yield = 7.2g (72%) M.P= 268-270 °C (lit. 278-279 °C dec.) ^{1}H-NMR [$(CD_3)_2SO$]: δ (ppm): 8.42 (1H, s, phenyl H_2), 8.20 (2H, d, pyridyl H_3, J = 7.9Hz), 7.60 (1H, t, phenyl H_5, J = 7.4Hz), 8.02 (1H, d, phenyl H_4,H_6, J = 7.4Hz), 7.91 (1H, dd, pyridyl H_4, J = 7.9Hz), 7.49 (1H, dd, pyridyl H_5, J = 5Hz), 8.60 (1H, d, pyridyl H_6, J= 5Hz), 7.02 (3H, s, H_{NH}), 10.30 (1H, s, H_{NH}). ^{13}C-NMR [$CDCl_3$]: δ (ppm): 120.85, 124.87, 126.85, 128.28, 130.27, 134.45, 136.99, 147.94, 148.16, 150.60, 162.78.

Fourth step. Cyclization of N,N'-Isophthaloyl-bis((2-pyridyl)hydrazidine) to form H_2mL.
N,N'-Isophthaloyl-bis((2-pyridyl)hydrazidine) (7.00 g, 0.017 mol) was suspended in a minimum volume (~30 cm^3) of ethylene glycol and heated under reflux temperature for 2 hours. A white crystalline precipitate was obtained upon cooling of the solution. Further precipitation of the product was induced by the addition of a small amount of water to the mother liquor. The ligand was titriated with boiling methanol, filtered and dried in the oven overnight. Completion of cyclization was confirmed by the disappearance of the C=O stretch at 1630 cm^{-1} in the IR spectrum. Yield = 2.8g (44%) M.P = 320-322 °C ^{1}H-NMR [$(CD_3)_2SO$]: δ (ppm): 8.88 (1H, s, phenyl H_2), 8.16 (2H,d, phenyl H_4,H_6, J = 7.9Hz), 7.65 (1H,t, phenyl H_5, J = 7.9Hz), 8.23 (1H, d, pyridyl H_3, J = 7.9Hz), 8.02 (1H, dd, pyridyl H_4, J = 7.9Hz), 7.55ppm (1H, dd, pyridyl H_5, J = 6Hz), 8.72 (1H, d, pyridyl H_6, J = 5Hz), 14.90 (1H, s (broad), H_{NH}). ^{13}C-NMR [$(CD_3)_2SO$]: δ (ppm): 121.53, 123.38, 123.62, 125.06, 126.58, 129.41, 131.40, 137.80, 146.31, 149.52, 149.72. Elem. Anal. Calcd. for $C_{20}H_{14}N_8$ = C: 65.56; H: 3.85; N: 30.59 %. Found: C: 65.39; H: 3.76; N: 30.57 %.

Synthesis of 1,4-bis(5-(2-pyridyl)-4H-1,2,4-triazol-3-yl)benzene (H_2pL).
Preparation of N,N'-Terephthaloyl-bis((2-pyridyl)hydrazidine). This compound was prepared as outlined above for the *N,N*'-isophthaloyl-intermediate except that a solution of terephthaloyl dichloride (5.08 g, 0.025 mol) was added to the 2-pyridylamidrazone

solution (6.8 g, 0.05 mol). Yield = 6.00g (60%). M.P. > 300 °C. ^{1}H-NMR [$(CD_3)_2SO$]: δ (ppm): 8.00 (2H, s, phenyl H), 8.19 (1H, d, pyridyl H_3, J = 7.9Hz), 7.72 (1H, dd, pyridyl H_4, J = 7.9Hz), 7.51 (1H, dd, pyridyl H_5, J = 4.9Hz), 8.62 (1H, d, pyridyl H_6, J = 4.4Hz), 7.03 (2H, s, H_{NH}), 10.30 (1H, s (broad), H_{NH}). ^{13}C-NMR [$(CD_3)_2SO$]: δ (ppm): 120.89, 125.01, 127.57, 127.96, 137.09, 148.24, 148.44, 150.30, 161.72.

Cyclization of N,N'-Terephthaloyl-bis((2-pyridyl)hydrazidine) to form H_2pL.

This was carried out as previously described for H_2mL. Yield = 1.40 g (57%) M.P. > 300 °C ^{1}H-NMR [$(CD_3)_2SO$]: δ (ppm): 8.23 (2H, s, phenyl H), 8.19 (1H, d, pyridyl H_3 J = 7.9Hz), 8.02(1H, dd, pyridyl H_4, J = 7.9Hz), 7.54 (1H, dd, pyridyl H_5, J = 6Hz), 8.72 (1H, d, pyridyl H_6, J = 5Hz), 14.50 (1H, s (broad), H_{NH}) . ^{13}C-NMR [$(CD_3)_2SO$]: δ (ppm): 121.52, 123.21, 125.11, 126.40, 126.81, 127.45, 137.88, 149.69, 150.41. Elem. Anal. Calcd. for $C_{20}H_{14}N_8$ = C: 65.56; H: 3.85; N: 30.59 %. Found: C: 65.83; H: 3.94; N: 30.28 %.

Table S1 *^{1}H-NMR data for the complexes with H_2mL in CD_3CN, (f) and (b) refer to the free and bound pyridyltriazole arms, respectively.*

Complex	**H_2mL Resonances**				
	H3	**H4**	**H5**	**H6**	**Phenyl**
mRu *(f)*	8.24	7.78	7.18	8.53	8.68 (s), 7.44 (t),
(b)	8.05	7.90	7.12	7.49	7.88 (d)
mOs[a] *(f)*	8.19	8.00	7.48	8.74	8.65 (s), 7.55 (t),
(b)	8.05	7.86	7.19	7.65	8.14 (d)
mRuRu	8.09	7.88	7.12	7.48	8.37 (s), 7.29 (t), 7.85 (d)
mRuRu[a]	8.17	7.96	7.25	7.77	8.35 (s), 7.34 (t), 7.83 (d)
mOsOs	8.10	7.72	7.03	7.37	8.41 (s), 7.32 (t), 7.86 (d)
mRuOs	8.01[b]	7.88[b]	7.14[b]	7.49[b]	8.38 (s), 7.64 (t),
	7.95[c]	7.74[c]	7.06[c]	7.39[c]	7.88 (d)
bpy rings	8.31-8.45	7.62-8.00	7.15-7.40	7.70-7.85	

[a] Measured in $(CD_3)_2(SO)$; [c] Osmium bound to pyridyltriazole arm

Table S2 *^{1}H-NMR data for the complexes with H_2pL, as measured in CD_3CN, unless otherwise indicated.. (f) and (b) refer to the free and bound pyridyltriazole arms, respectively.*

Complex	**H_2pL Resonances**				
	H3	**H4**	**H5**	**H6**	**Phenyl**
pRu *(f)*	8.16	8.10	7.47	8.63	7.95
(b)	8.32	7.97	7.25	7.58	
pOs *(f)*	8.18	7.95	7.48	8.68	7.76-7.77
(b)	8.04	7.75	7.06	7.41	
pRuRu	8.11	7.82	7.11	7.48	7.90
pRuRu[a]	8.12	7.96	7.25	7.69	7.85
pOsOs	8.10	7.72	7.05	7.39	7.90
pRuOs	8.13[b]	7.83[b]	7.13[b]	7.50[b]	7.90
	8.11[c]	7.75[c]	7.05[c]	7.39[c]	
bpy rings	8.31-8.45	7.62-8.00	7.15-7.40	7.70-7.85	

[a] Measured in $(CD_3)_2(SO)$, [b] Ruthenium bound to pyridyltriazole arm;[c] Osmium bound to pyridyltriazole arm.

Table S3 *UV/Vis/NIR absorption data for the fully oxidized complexes of H_2mL and H_2pL in their protonated and deprotonated forms. All measurements carried out using CH_3CN with 0.1 M TEAP. Solutions were acidified using $HClO_4$.*

Complex	M(III) absorption bands/ nm (ε/$M^{-1}cm^{-1}$,$\nu_{1/2}$/cm^{-1})
mRu	530 (3094, 3499); 923 (3698, 3541)
mRuH	520 (2310, 5323); 850 (2140, 5191)
mOs	734 (2123, 4078); 1680 (222); 2320 (1235)
mOsH	573 (1395); 1674 (119); 2310 (800)
mRuRu	525 (8115, 3643); 927 (7540, 3945)
mRuRuH	500 (3210); 755 (3816, 5610)
mOsOs	730 (4183, 4003); 1700 (550); 2320 (2578)
mOsOsH	566 (2463, 5319)
mRuOs	741 (2369, 4170); 930 (4625, 3471); 1685 (300); 2315 (1581)
mRuOsH	706 (1871, 4272); 912 (3994, 3996); 530 (4376); 1750 (259); 2328 (1659)
pRu	578 (2743, 3418); 978 (5114, 3200)
pRuH	550 (2608, 4293); 900 (2643, 4355)
pOs	770 (3027, 4055); 1650 (548); 2271 (1370)
pOsH	624 (1278, 4623); 1678 (165); 2305 (850)
pRuRu	535 (5242); 998 (8733, 3988)
pRuRuH	537 (2593); 870 (3048, 6210)
pOsOs	800 (6593, 2654); 1700 (420); 2343 (3390)
pOsOsH	740 (2302, 4080); 1709 (224); 2320 (1531)
pRuOs	560 (3398); 782 (2808, 4760); 1018 (7883, 4058); 1691 (358); 2316 (2050)
pRuOsH	772 (1877, 1305); 942 (6292, 1689); 1816 (245); 2319 (1603)
$[Ru(bpy)_2(pptr)]^{2+}$	920 (4523, 3118)

Table S4 *pKa values for the coordinated triazole rings in the complexes.*

Complex	pKa±0.1
mRu	3.3
mOs	3.0
mRuRu	3.5
mOsOs	3.1
mRuOs	3.2
pRu	3.6
pOs	3.3
pRuRu	3.6
pOsOs	3.4
pRuOs	3.4
H_2mL	9.5
H_2pL	9.1

i F.H. Case*, J. Org. Chem*., 1965, 30, 931.
ii Aldrich Catalogue Handbook of Fine Chemicals 1992-1993.