Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2005, 15(1), 6–8
Mendeleev Communications

Synthesis, structure and luminescence of ruthenium complexes with 6-cyano-2,2′-bipyridines

Valery N. Kozhevnikov,*[a] Dmitry N. Kozhevnikov,[a] Olga V. Shabunina,[a] Vladimir L. Rusinov,[a] Oleg N. Chupakhin,[a] Manfred Zabel[b] and Burkhard König*[b]

[a] *Department of Organic Chemistry, Urals State Technical University, 620002 Ekaterinburg, Russian Federation. Fax: +7 3432 74 0458; e-mail: dnk@htf.ustu.ru*
[b] *Institut für Organische Chemie, Universität Regensburg, D-93040 Regensburg, Germany. Fax: +49 941 943 1717; e-mail: burkhard.koenig@chemie.uni-regensburg.de*

DOI: 10.1070/MC2005v015n01ABEH002024

The crystallographic data, NMR and UV-VIS spectra and luminescence of the heteroleptic complexes $[Ru(L)(bpy)_2](PF_6)_2$ (L = 5-aryl-6-cyano-2,2′-bipyridine) are described.

2,2′-Bipyridine (bpy) derivatives are the most popular chelating ligands for binding various metal ions. Systematic variations of substituents in bpy are important tools for changing and tuning the physical properties of bpy complexes.[1,2] Special attention is paid to ruthenium bpy complexes because of their unique photophysical properties.[1] Recently,[3] we reported a method for the synthesis of 5-aryl-6-cyano-2,2′-bipyridines (cbpy) that allows wide variations of aromatic substituents. Here we report the synthesis, structure, spectral and luminescent properties of heteroleptic ruthenium complexes of 6-cyano-2,2′-bipyridines and the influence of aryl substituents on these properties.

6-Cyano-2,2′-bipyridines **1a–c** bearing 4-bromophenyl, 4-methoxyphenyl and 2-thienyl residues at the 5-position were synthesised according to a known method.[3] These ligands are appropriate for the preparation of heteroleptic cbpy–bpy_2 complexes with Ru^{II}. Thus, the reaction of ligands **1** with $(bpy)_2RuCl_2$ followed by treatment of the reaction mixture with NH_4PF_6 resulted in the formation of complexes $[Ru(bpy)_2(\mathbf{1})](PF_6)_2$ **2a–c** (Scheme 1).† The structure and composition of complexes **2**

† *General procedure for the synthesis of complexes* $[Ru(bpy)_2(\mathbf{1})](PF_6)_2$ **2a–c**. Cyanobipyridine **1a–c** (0.11 mmol) and $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (47 mg, 0.09 mmol) were refluxed for 12 h in 6 ml of a methanol–water (5:1) mixture. Water (20 ml) was added and the mixture was treated with CH_2Cl_2 (2×30 ml). A 10% aqueous NH_4PF_6 solution (2 ml) was added to the aqueous layer and the resulting mixture was extracted with CH_2Cl_2 (3×30 ml). The organic layer was dried over Na_2SO_4, the solvent was removed under reduced pressure, the residue was treated with methanol, and the crystals were filtered off.

were studied by NMR spectroscopy and FAB mass spectrometry. The solid-state structure was determined by X-ray analysis of complex **2b** (Figure 1).‡

The ^{1}H NMR spectra of complexes **2a–c** revealed clear separation of signals due to six heteroaromatic protons of ligands **1a–c**. The hydrogen atom at the 6′-position showed an expected high-field shift from δ 8.7 to 8.1 upon ruthenium coordination, as well a high-field shift from δ 7.4 to 7.2 for 5′-H, and a low-field shift of signals of 3-H protons (from δ 7.9 to 8.2) and 3′-H (from δ 8.4 to 8.6). Coordination of ligands **1** with a non-symmetric arrangement of substituents at the ruthenium centre causes different chemical surroundings for all protons of the two bpy ligands in complexes **2**. For this reason, the ^{1}H and ^{13}C NMR spectra of **2a–c** show complicated patterns of signals for bpy hydrogens and carbons.

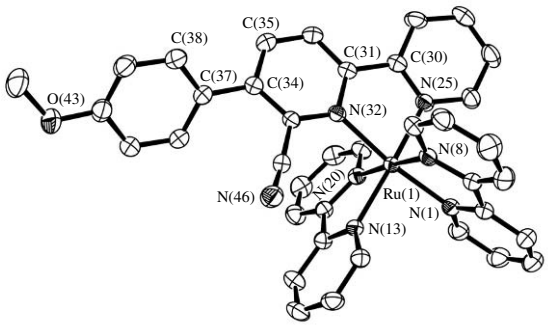
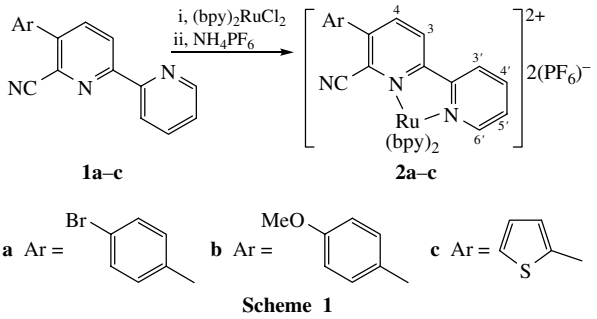


Figure 1 Crystal structure of the complex anion $[Ru(\mathbf{1b})(bpy)_2]^{2+}$. Hydrogens are omitted. Selected bonds lengths/Å: Ru(1)–N(32) 2.106(2), Ru(1)–N(25) 2.059(2), Ru(1)–N(20) 2.080(2), Ru(1)–N(13) 2.069(2), N(46)–C(45) 1.145(4). Selected angles/°: N(25)–Ru(1)–N(32) 78.11(9), N(13)–Ru(1)–N(20) 77.85(9), N(1)–Ru(1)–N(8) 78.77(9). Selected torsion angles/°: N(25)–C(30)–C(31)–N(32) 8.3(3), N(13)–C(18)–C(19)–N(20) 3.9(3), C(35)–C(34)–C(37)–C(42) 129.7(3).

Crystallographic data of **2b** (Figure 1) show ligand distortions caused by the cyano group resulting in a non-planar structure of the pyridine rings of compound **1b** and bpys next to the cyano group (the torsion angles N–C–C–N in these ligands are 8.3° and 3.9°, respectively).



Scheme 1

Table 1 summarises UV-VIS data for ruthenium complexes **2a–c**. For complexes **2**, two types of transitions were observed (Figure 2). These are MLCT transitions at 250 and 440 nm, causing the intense red colour of the complexes. Other intense bands at 285 and 330 nm are assigned to intra ligand $\pi\rightarrow\pi^*$ transitions. In general, the UV-VIS spectra of complexes **2a–c** are very similar to those of $[Ru(bpy)_3](PF_6)_2$ complexes reported previously.[4]

Complexes **2a–c** exhibited luminescence typical of such ruthenium complexes originated from an MLCT exited state. Luminescence band maxima of the test complexes are summarised in Table 1. Luminescence at room temperature was observed in acetonitrile. Emission maxima of complexes **2a–c** with cyano bipyridines were shifted by 40 nm to longer wavelengths than that of $[Ru(bpy)_3](PF_6)_2$.[4] Emission time of complexes **2a–c** at room temperature was found to be around 0.10–0.16 μs. A decrease in the temperature to 77 K caused an increase in the emission time to 5.0–5.6 μs (Table 1).

Thus, the introduction of the cyano group into a bipyridine ligand results in a 40 nm red shift of the maximum of emission, while the quantum yields remain practically unchanged. Variation of aromatic substituents in the bipyridine molecule had no influence on the luminescence of the ruthenium complexes. This can be explained by the disrupted conjugation between aryl and bipyridine moieties due to their torsion of about 50°.

This work was supported by the Russian Foundation for Basic Research (grant no. 04-03-96106) and the Fonds der Chemischen Industrie. V. N. Kozhevnikov aknowledges a postdoctoral fellowship of the Alexander von Humboldt Foundation.

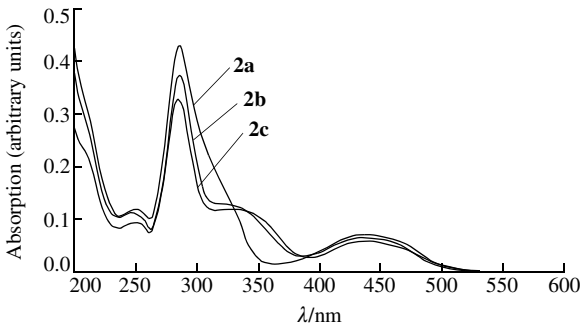


Figure 2 UV-VIS spectra of complexes **2a–c**.

‡ $[Ru(\mathbf{1a})(bpy)_2](PF_6)_2$ **2a**: ^{1}H NMR (300 MHz, CD_3CN) δ: 7.25 (ddd, 1H, 5′-H, *J* 7.6 Hz, *J* 5.9 Hz, *J* 1.0 Hz), 7.30–7.70 (m, 12H, BrC_6H_4 + 5,5′-Hbpy + 6,6′-Hbpy), 7.89 (ddd, 1H, 4′-H, *J* 7.9 Hz, *J* 7.6 Hz, *J* 1.6 Hz), 8.00–8.15 (m, 5H, 6′-H + 4,4′-Hbpy), 8.21 (d, 1H, 3-H, *J* 8.5 Hz), 8.40–8.55 (m, 4H, 3,3′-Hbpy), 8.62 (d, 1H, 3′-H, *J* 7.9 Hz), 8.71 (d, 1H, 4-H, *J* 8.5 Hz). ^{13}C NMR (75 MHz, CD_3CN) δ: 125.2, 125.4, 125.6, 125.7, 126.9, 127.5, 128.6, 128.8, 129.1, 129.2, 132.1, 132.9, 134.6, 137.0, 138.9, 139.1, 139.4, 139.6, 140.7, 148.0, 152.3, 152.8, 153.0, 153.2, 154.1, 157.0, 158.6, 159.6. FAB MS, *m/z*: 894 and 896, 374 and 376.

$[Ru(\mathbf{1b})(bpy)_2](PF_6)_2$ **2b**: ^{1}H NMR (300 MHz, CD_3CN) δ: 3.81 (s, 3H, OMe), 7.01 (m, 2H, $MeOC_6H_4$), 7.25 (ddd, 1H, 5′-H, *J* 7.6 Hz, *J* 5.8 Hz, *J* 1.0 Hz), 7.33–7.50 (m, 6H, $MeOC_6H_4$ + 5,5′-Hbpy), 7.50–7.55 (m, 1H, 6-Hbpy), 7.60–7.65 (m, 2H, 6,6′-Hbpy), 7.68 (m, 1H, 6′-Hbpy), 7.89 (ddd, 1H, 4′-H, *J* 8.0 Hz, *J* 7.6 Hz, *J* 1.6 Hz), 8.00–8.15 (m, 5H, 6′-H + 4,4′-Hbpy), 8.22 (d, 1H, 3-H, *J* 8.5 Hz), 8.40–8.55 (m, 4H, 3,3′-Hbpy), 8.60 (d, 1H, 3′-H, *J* 8.0 Hz), 8.71 (d, 1H, 4-H, *J* 8.5 Hz). ^{13}C NMR (75 MHz, CD_3CN) δ: 56.3 (MeO), 115.3, 125.2, 125.4, 125.6, 125.7, 126.6, 127.4, 128.6, 128.9, 129.0, 129.1, 131.9, 138.9, 139.1, 139.4, 139.6, 140.7, 152.3, 152.7, 152.9, 153.2, 154.1. FAB MS, *m/z*: 846, 350.

X-ray data for complex **2b** (the crystal was obtained by dissolving **2b** in acetonitrile followed by slowly evaporation) collected on a STOE-IPDS diffractometer applying a MoKα graphite monochromator ($\theta/2\theta$-scan) at 173 K. The structure was solved by direct methods (SIR-97) and refined by full-matrix anisotropic least squares (SHELXL97). The H atoms were calculated geometrically and a riding model was used for the refinement. $C_{38}H_{29}N_7ORu\cdot2(F_6P)\cdot1.5(MeCN)$, M = 1052.27, a = 8.5079(7), b = = 10.9796(9) and c = 23.6079(18) Å, α = 92.731(10)°, β = 96.947(9)°, γ = 100.336(10)°, V = 2148.1(3) Å^3, Z = 1, d_{calc} = 1.627 g cm^{-3}, μ = = 0.537 cm^{-1}, space group $P\bar{1}$, 7593 reflections measured, 6912 unique which were used in all calculations. $R(F)$ = 0.0399, GOF = 1.070. The final *wR* was 0.0986 (all data).

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 234721. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.

$[Ru(\mathbf{1c})(bpy)_2](PF_6)_2$ **2c**: ^{1}H NMR (300 MHz, CD_3CN) δ: 7.18 (dd, 1H, Thieyl, *J* 5.2 and 3.8 Hz), 7.27 (ddd, 1H, 5′-H, *J* 7.4, 5.9 and 1.4 Hz), 7.34–7.54 (m, 5H), 7.56 (dd, 1H, Thienyl, *J* 3.6 and 1.1 Hz), 7.60–7.73 (m, 4H), 7.93 (ddd, 1H, 4′-H, *J* 7.9, 7.4 and 1.4 Hz) 8.03–8.15 (m, 5H, 6′-H + 4,4′-Hbpy), 8.33 (d, 1H, 3-H, *J* 8.5 Hz), 8.41–8.50 (m, 4H, 3,3′-Hbpy), 8.60 (d, 1H, 3′-H, *J* 8.0 Hz), 8.70 (d, 1H, 4-H, *J* 8.5 Hz). ^{13}C NMR (75 MHz, CD_3CN) δ: 125.2, 125.4, 125.6, 125.7, 126.8, 127.4, 128.5, 128.58, 128.8, 129.08, 129.12, 129.6, 132.0, 132.1, 135.6, 138.9, 139.1, 139.4, 139.6, 140.4, 141.9, 152.3, 152.7, 152.9, 153.2, 154.2, 157.0, 157.7, 158.0, 158.1, 158.7, 159.0. FAB MS, *m/z*: 822, 338.

Table 1 Absorption (λ_{abs}) and emission (λ_{emis}) maxima, quantum yields (φ_{emis}) and emission life times for complexes **2a–c** (in MeCN).

Complex	λ_{abs}/nm	λ^{a}_{emis}/nm	φ_{emis} (%)	Emission life time/μs	
				at 295 K	at 77 K[b]
2a	440, 286, 249	648	2.6	0.16	5.9
2b	440, 334, 285, 248	652	1.9	0.12	5.6
2c	437, 328, 285, 249	653	2.1	0.10	5.0
$[Ru(bpy)_3](PF_6)_2$[c]	451, 287, 244	610			

[a]Recorded in MeCN at room temperature and excitation at 436 nm. [b]In butyronitrile. [c]Lit.[4]

References

1 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.

2 J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995.

3 V. N. Kozhevnikov, D. N. Kozhevnikov, T. V. Nikitina, V. L. Rusinov, O. N. Chupakhin, M. Zabel and B. Koenig, *J. Org. Chem.*, 2003, **68**, 2882.

4 A. F. Stange, S. Tokura and M. Kira, *J. Organomet. Chem.*, 2000, **612**, 117.

5 P. A. Mabrouk and M. S. Wrighton, *Inorg. Chem.*, 1986, **25**, 526.

Received: 3rd September 2004; Com. 04/2349