DALTON
COMMUNICATION

Ruthenium(II) complex of bis(2,2′-bipyridine)(6,7-dicyano-dipyrido[3,2-*a*:2′,3′-*c*]phenazine): synthesis, structure, electrochemical and luminescence studies

Julia Rusanova,[a] Silvio Decurtins,*[a] Eduard Rusanov,[b] Helen Stoeckli-Evans,[b] Sandra Delahaye[c] and Andreas Hauser[c]

[a] *Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland. E-mail: decurtins@iac.unibe.ch*

[b] *Institut de Chimie, Université de Neuchâtel, Av. Bellevaux 51, 2007 Neuchâtel, Switzerland. E-mail: Helen.Stoeckli-Evans@unine.ch*

[c] *Départment de Chimie Physique, Sciences II, Université de Genève 30, Quai Ernest-Ansermet, 1211 Genève 4, Switzerland. E-mail: Andreas.Hauser@chiphy.unige.ch*

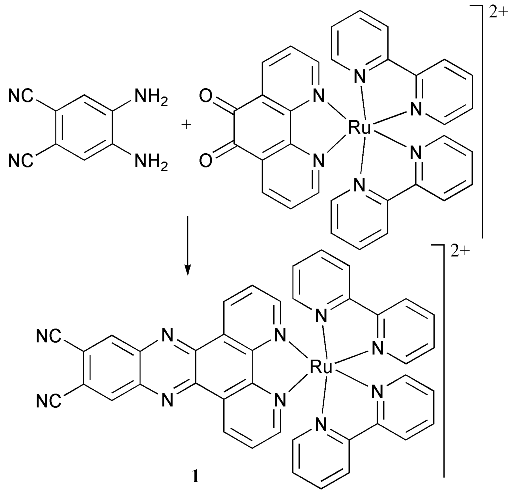
Received 3rd September 2002, Accepted 23rd October 2002
First published as an Advance Article on the web 4th November 2002

A novel ruthenium complex with a 6,7-dicyanosubstituted dppz ligand has been synthesised: its crystal structure and physico-chemical studies are reported.

There has been much interest in the study of ruthenium complexes with polypyridyl ligands due to their remarkable properties, *e.g.* their site-specific interaction with DNA.[1–3] Current research is aimed at the design and construction of new ligands and their corresponding ruthenium complexes, capable of performing useful light-induced functions.[4] In recent years, ligands derived from a modification of 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) have been employed for certain applications.[4] This work is part of our investigations in the field of construction of multicomponent systems based on phthalocyanines (Pc). We have recently focused our attention on the modification of the periphery of Pcs by constructing new building blocks, with the aim of introducing additional ligands capable of coordinating metal ions. In this way, the coordination chemistry of the central cavity of the Pc as well as the peripherial metal binding sites can be exploited for the assembly of new structural topologies with tunable optical, redox and electronic properties.[5] Here we report the synthesis and characterization, as well as the crystal structure, of a new Ru(II) complex based on a derivative of the fully conjugated and planar ligand dipyrido [3,2-*a*:2′,3′-*c*]phenazine (dppz).

The title compound $[Ru(bpy)_2dppz(CN)_2](PF_6)_2$† (**1**) was obtained by condensation of $[Ru(bpy)_2(phenO_2)](PF_6)_2$[6] and 1,2-diamino-4,5-dinitrilebenzene (Scheme 1), which were prepared with slight modifications of the reported procedures,[7] (yield after recrystallization: 65%). Crystals of **1**, suitable for single crystal X-ray diffraction analysis, were obtained by slow evaporation of a methanol solution. Chemicals and solvents utilized in this study were obtained in their highest available purity from commercial sources (Fluka, Aldrich) and used without additional purification.

The asymmetric unit of compound **1** (Fig. 1) comprises one monomeric $[Ru(bpy)_2dppz(CN)_2]^{2+}$ cation, two PF_6^- anions, one methanol and two water molecules; the latter being statistically disordered about centers of inversion, with multiplicity 0.5. The complex exhibits a distorted octahedral geometry around the metal atom with Ru–N distances in the range 2.049(5)–2.087(5) Å. Due to the chelating nature of the ligand the coordination angles depart by up to ~12° from ideal



Scheme 1 Reaction conditions: refluxing in EtOH, 15 h.

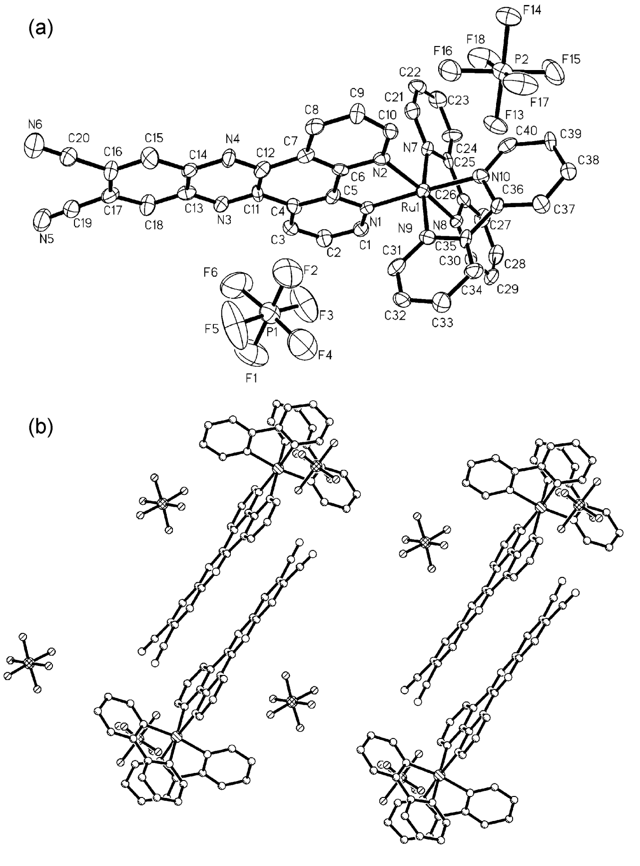


Fig. 1 The molecular structure (a) and fragment of molecular packing of **1** (b) showing the π–π stacking in dimers.

Table 1 Electrochemical data

Complex	$E_{1/2}^{\mathrm{Ox}}$/V	$E_{1/2}^{\mathrm{Red}}$/V	Ref.
dppz		−1.62	9
$[\mathrm{Ru(bpy)_3}]^{2+}$	+0.88	−1.69, −1.89, −2.14	8
$[\mathrm{Ru(bpy)_2dppz}]^{2+}$	+0.91	−1.36, −1.79, −2.00	9
$[\mathrm{Ru(bpy)_2dpq(CN)_2}]^{2+}$	+0.98	−0.94, −1.36, −1.8, −2.04, −2.21	8
$[\mathrm{Ru(bpy)_2dppz(CN)_2}]^{2+}$ (**1**)	+1.30	−0.54, −1.12	This work

[a] Redox potentials were measured in MeCN under N_2 with Pt and Ag/AgCl as working and reference electrodes, respectively. The values are referenced to Fc^+/Fc at RT; Bu_4NPF_6 as supporting electrolyte.

octahedral values, and vary from 78.7 to 99.0°. The $\mathrm{dppz(CN)_2}$ and bpy ligands are practically planar (mean atom deviations from the least-squares plane do not exceed 0.09, 0.06 and 0.03 Å, respectively). It was not possible to locate the disordered solvents hydrogen atoms, but short contacts, $\mathrm{O3(CH_3OH)} \cdots \mathrm{F5(PF_6^-)}$ 2.75(3) Å and O3 ··· O1a(H_2O) 2.66(3) Å (a = $-x, -y, -1 - z$), between heteroatoms indicate extensive hydrogen bonding. The most prominent feature of the crystal structure of **1** is the dimerisation of two complexes in a centrosymmetric pair by π–π stacking between $\mathrm{dppz(CN)_2}$ ligands, with the shortest C ··· C distances being 3.489(9) Å.

The electrochemical properties of the title compound have been studied in MeCN. The half-wave potentials are presented in Table 1 together with the values for $[\mathrm{Ru(bpy)_3}]^{2+}$, $[\mathrm{Ru(bpy)_2dppz}]^{2+}$, $[\mathrm{Ru(bpy)_2dpq(CN)_2}]^{2+}$ (dpq = dipyridoquinoxaline), as well as for dppz for comparison purposes. By analogy with similar complexes, the wave centered at $E_{1/2}$ = 1.30 V is associated with the metal-localized $\mathrm{Ru^{II/III}}$ oxidation. The potential of this wave is shifted to positive values. This trend is commonly observed in complexes containing π-acceptor ligands.[10] It could be a result of pronounced π-acceptor character due to the combined effect of the increase in conjugation and the presence of strong electron-withdrawing groups in $\mathrm{dppz(CN)_2}$ compared to $\mathrm{dpq(CN)_2}$ and dppz, respectively. The first reduction has been assigned to the $\mathrm{dppz(CN)_2}$ ligand. This reduction potential is also anodically shifted with respect to that of $[\mathrm{Ru(bpy)_3}]^{2+}$, which emphasizes the enhanced π-acceptor characteristics of $\mathrm{dppz(CN)_2}$.

The spectroscopic properties of the title complex are shown in Fig. 2. The room temperature absorption spectrum of a 10^{-4} M deareated acetonitrile solution is dominated by an intense band centered at 22400 cm^{-1} (440 nm, ε = 16400 M^{-1} cm^{-1}), which is assigned to a spin-allowed metal–ligand charge transfer (^{1}MLCT) transition. A very similar spectrum, including somewhat sharper bands at higher energy, has also been reported for the dppz derivative.[11] The prominent ^{1}MLCT absorption band has a long tail well into the red, which is due to a series of lower-energy[1,3] MLCT transitions. Fig. 2 also shows the room temperature emission spectrum excited at 457.5 nm for complex **1** in a 10^{-5} M deareated acetonitrile solution. There is a single, unstructured band centered at 16100 cm^{-1} (617 nm). The luminescence decay is perfectly single exponential with a lifetime of 910(3) ns and quantum efficiency ϕ = 0.005(1). This is very much in line with the emission from the analogous dppz complex[11] and is attributed to the well-known ^{3}MLCT emission of ruthenium(II) polypyridyl complexes. In the solid state too, there is a comparatively strong emission already at room temperature and it grows in intensity as the temperature is lowered. However, as compared to luminescence in solution, the band maximum is shifted to lower energy by 3400 cm^{-1}, that is to 12700 cm^{-1} (787 nm). This shift has to be attributed to the π–π interactions between the orbitals of the stacked $\mathrm{dppz(CN)_2}$ ligands. In the centrosymmetric arrangement of a pair of crystallographically equivalent complexes such interactions result in an important splitting of the ligand centered LUMO.[12,13] In the dimer, emission occurs from the lower energy component and thus at lower energy than in the monomer.

In conclusion, we have prepared a novel Ru(II) complex based on dppz, a heterocyclic π-system, which combines the chelating function of α-diimines with the electron transfer capacity of 1,4-diazines (pyrazines, quinolins, phenazines, *etc.*). π-Electron conjugation over the aromatic parts of this molecule allows a long-distance yet sufficiently strong electronic interaction and makes this complex very promising as a building block for the synthesis of new bulky supramolecular assemblies.

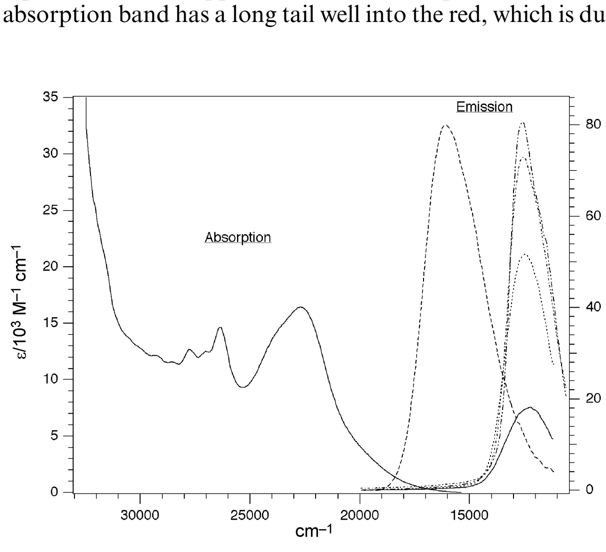


Fig. 2 Absorption (—) and emission spectrum (– – –) of complex **1** in acetonitrile. Variable temperature emission spectra of complex **1** as a microcrystalline powder (12 K: —, 101 K – – –, 191 K - - -, and 295 K · · ·). Emission spectra are corrected for the response of the experimental set-up.

Notes and references

† Selected data for $\mathrm{[Ru(bpy)_2dppz(CN)_2]\cdot(PF_6)_2\cdot H_2O\cdot 0.5CH_3OH}$: ^{1}H-NMR (DMSO-$d_6$) δ 9.59 (dd, 1H), 9.42 (s, 1H), 8.89 (m, 1H), 8.55 (d, 1H), 8.29 (dd, 1H), 8.26–8.14 (m, 1H), 8.04 (q, 1H), 7.95 (dd, 1H), 7.8 (d, 1H), 7.77–7.68 (m, 1H), 7.62–7.53 (m, 1H), 7.37 (td, 1H); MS (ES) *m/z* 373 [M − $2PF_6$]$^{2+}$, 891 [M − PF_6]$^+$; Crystal data for $\mathrm{C_{40.5}H_{28}N_{10}O_{1.5}P_2F_{12}Ru}$ **1**: M = 1069.74, monoclinic, a = 9.304(2), b = 37.034(7), c = 12.014(2) Å, β = 97.54(3)°, V = 4103.8(14) Å^3, T = 153 K, space group $P2_1/c$, Z = 4, D_c = 1.731 g cm^{-3}, μ(Mo-Kα) = 5.66 cm^{-1}, R = 0.0388 and Rw = 0.0592 for 6401 unique reflections with $I > 2\sigma(I)$. CCDC reference number 192681. See http://www.rsc.org/suppdata/dt/b2/b210440g/ for crystallographic data in CIF or other electronic format.

1 (*a*) N. Gupta, N. Grover, G. A. Neyhart, W. Liang, P. Singh and H. H. Thorp, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1048; (*b*) E. D. A. Stemp, M. R. Arkin and J. K. Barton, *J. Am. Chem. Soc.*, 1997, **119**, 2921.

2 E. J. Olson, D. Hu, A. Hörmann, A. M. Jonkman, M. R. Arkin, E. D. A. Stemp, J. K. Barton and P. F. Barbara, *J. Am. Chem. Soc.*, 1997, **119**, 11458.

3 (*a*) V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759 and references therein; (*b*) V. Balzani, F. Scandola, in *Comprehensive Supramolecular Photochemistry*, eds. J. Atwood, D. MacNicol, E. Davies, F. Vogtle and J.-M. Lehn, Pergamon Press, Oxford, UK, 1996, vol. 10, p. 687.

4 (*a*) V. Balzani, F. Barigelletti, P. Belser, S. Bernhard, L. De Cola and L. Flamigni, *J. Phys. Chem.*, 1996, **100**, 16786; (*b*) A. Gourdon and J.-P. Launay, *Inorg. Chem.*, 1998, **37**, 5336.

5 J. Rusanova, M. Pilkington and S. Decurtins, *Chem. Commun.*, 2002, 2236.

6 J. Rusanova, S. Decurtins, E. Rusanov and H. Stoeckli-Evans, *Z. Kristallogr.*, 2002, **217**, 1–4, CCDC reference number 1267/920.

7 (*a*) S. A. Mikhalenko, V. M. Derkacheva and E. A. Luk'yanets, *Russ. J. Gen. Chem.*, 1981, **51**, 1405; (*b*) E. V. Kudrik, G. P. Shaposhnikov and A. E. Balakirev, *Russ. J. Gen. Chem.*, 1999, **69**, 1321; (*c*) C. A. Goss and H. D. Abruna, *Inorg. Chem.*, 1985, **24**, 4263.

8 B. Gholamkhass, K. Koike, N. Negishi, H. Hori and K. Takeuchi, *Inorg. Chem.*, 2001, **40**, 756.

9 N. Komatsuzaki, R. Katoh, Y. Himeda, H. Sugihara, H. Arakawa and K. Kasuga, *J. Chem. Soc., Dalton Trans.*, 2000, **18**, 3053.

10 K. Kalyanasundaram, *Photochemistry of Polypyridine, Porphyrin Complexes*, Academic Press Inc., San Diego, 1992 .

11 J. Bolger, A. Gourdon, E. Ishow and J.-P. Launay, *Inorg. Chem.*, 1996, **35**, 2937.

12 V. M. Minkovski and V. H. Holding, *Inorg. Chem.*, 1989, **28**, 1529.

13 F. Wu, E. Riesgo, A. Pavalova, R. A. Kipp, R. H. Schmehl and R. P. Thummel, *Inorg. Chem.*, 1999, **38**, 5620.