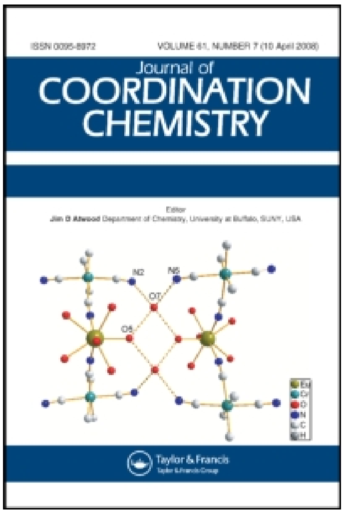

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CRYSTAL STRUCTURE AND PHOTOCHEMISTRY OF *BIS*(BIPYRIDINE)-*BIS*(4-AMINOPYRIDINE)RUTHENIUM(II)

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CRYSTAL STRUCTURE AND PHOTOCHEMISTRY OF *BIS*(BIPYRIDINE)-*BIS*(4-AMINOPYRIDINE)RUTHENIUM(II)

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The title complex, *cis*-$[Ru(bpy)_2(4\text{-}apy)_2](ClO_4)_2CH_3CN$ (where bpy = 2,2′-bipyridine, 4-apy = 4-aminopyridine), has been synthesized and characterized. An X-ray crystal structure determination established that the coordination geometry about ruthenium(II) is distorted octahedral with four nitrogen atoms from the two bpy molecules and two pyridine nitrogen atoms from apy coordinate. Time-resolved and steady-state luminescence spectra show that the emission wavelength, quantum yield and the luminescence lifetime are quite similar to those of corresponding complexes with pyridine instead of apy, which indicates that the amino group of the apy cannot quench the luminescence. Electrochemistry in CH_3CN is consistent with this result.

The complex crystallines in the monoclinic space group, $P2_1/n$ with cell parameters $a = 10.585(2)$, $b = 11.615(2)$, $c = 15.992(3)$ Å, $\beta = 99.76(3)°$ and $Z = 4$. The structure was refined by full-matrix least-squares methods to $R = 0.071$ and $R_w = 0.093$ for 4625 reflections having $F > 6\sigma(F)$.

Keywords: Ruthenium(II); crystal structure; time-resolved luminescence

INTRODUCTION

Over the past 15 years a great number of polypridine ruthenium(II) complexes have been synthesized and characterized. Most of them exhibit photophysical, photochemical and electrochemical properties appropriate for

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* Corresponding author.

playing the role of building blocks for the construction of supramolecular systems for electron transfer and energy migration, and which can be used as photochemical molecular devices (PMDs).[1–6]

Tris(2,2′-bipyridine)ruthenium, $[Ru(bpy)_3]^{2+}$, is the archetypal species and demonstrates the combined attributes of significant absorption in the visible region, relative longevity of metal-to-ligand charge transfer, interitness of the metal centre in a variety of oxidation states and rapidity of redox reactions involving the excited state (quench). The lowest excited state properties of this and related complexes are controlled by the pattern of low-lying electronic levels which are ligand-dependent.[7–9] By changing the ligand around the ruthenium centre, it is possible to "fine tune" redox and photophysical properties of the ground and excited states of polypyridinyl ruthenium(II) complexes.

The use of mixed ligand complexes is part of our continuing research to find more useful building blocks used for photo-, electro-, thermal- and magneto-functional complexes.[10,11] We report here the synthesis, characterization, crystal structure and time-resolved photochemistry of a *bis*(bipyridinyl)ruthenium(II) complex containing two 4-aminopyridine ligands.

EXPERIMENTAL

All chemicals were of reagent grade and used without further purification. *Cis*-$[Ru(bpy)_2Cl_2]2H_2O$ was prepared according to literature methods.[12]

Physical Measurements

Elemental analysis was performed on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded on a Nicolet FT-IR-170SX spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. The solution electronic spectrum was recorded on a Shimadzu 240 spectrophotometer.

Cyclic voltammetry was performed using an EG and G PAR 273 potentiostat, in conjunction with a three-electrodes cell fitted with a purge dinitrogen inlet and outlet, a platinum-wire working electrode. The potentials quoted in this work are relative to Ag/AgCl at 25°C and a platinum auxiliary electrode. Current–potential curves were displayed on an IBM computer using model 270 electrochemical analysis software. Data were recorded on a Hewlett-Packard recorder. The voltammograms of the complexes were obtained in CH_3CN with n-Bu_4NClO_4 (0.1 mol dm^{-3}) as the electrolyte and $[Ru(bpy)_3](ClO_4)_2$ (1.0×10^{-3} M) as internal reference. The current–potential curve gives two reversible redox reactions at $E_{1/2} = 1.20$ and

-1.30 V in the range -1.5 to 1.0 V with a scanning rate of 100 mV s^{-1}, assigned to the Ru(III)/Ru(II) and Ru(II)/Ru(I) redox potential's, respectively. Another irreversible redox potential at -1.45 V is assigned to the bpy or the apy ligand reactions.

Luminescence intensities were measured on a Perkin-Elmer LS50 spectrofluorometer in acetonitrile at room temperature with irradiation at 440 nm and a sample concentration of 1.0×10^{-5} M. Solutions were degassed by 3 freeze–pump–thaw cycles. Electronic absorption spectra of the solutions used in the luminescence experiments were measured before and after collection of steady-state and time-resolved data. In every case the spectra were identical before and after the experiments, indicating that sample degradation did not occur during data acquisition. Emission intensities for vacuum-degassed solutions of all four complexes were measured with respect to $[Ru(bpy)_3](ClO_4)_2$ in CH_3CN with concentration 1.0×10^{-5} M ($\lambda_{em} = 0.062$).[13] Correction was made for the difference in absorption of the sample and the actinometer solution at the excited wavelength; the quantum yield for the title complex is 0.0040.

Time-resolved emission decays were measured following excitation by an FL2002 dye laser pumped by an EMG 201 quasimolecular laser. Lasing at 450 nm was achieved by coumarin 460. Emission was monitored at right angles to the excitation by using a Hamamastsu R3896 PMT coupled to a Macpherson 272 scanning monochromator. The output of the PMT was processed by a Lecroy 7200A transient digitizer interfaced to an IBM PC. Transient decays were fitted to single-exponential functions. Figure 1 shows the decay for the title complex; the luminescence lifetime is $\tau^0 = 460$ ns.

Preparation of the Title Complex

Ethanol solutions of $[Ru(bpy)_2Cl_2] \cdot 2H_2O$ (2 mmol, 1.0 g) and 4-aminopyridine (4.2 mmol, 0.44 g) were mixed. After refluxing for 8 h, the solution was filtered, and a red-brown crystalline solid formed after adding a methanol solution containing sodium perchlorate. The product was isolated and dried under vacuum. Crystals suitable for X-ray analysis were obtained by evaporating a CH_3CN solution in air; yield, 0.12 g (73%). IR data (KBr disc, cm^{-1}): 3227, 3364, 3459 ν(N–H), 1619, 1516, 1465, 1422 ν(C=N, C=C), 1089, 931, 624 ν(Cl–O), 763 δ(C–H), 558ν(Ru–N). Electronic spectrum (nm) (CH_3CN, log(ϵ)(max): 205(4.31), 258(4.85), 288(4.5), 450(4.12). *Anal.*: calc., for $C_{34}H_{36}Cl_2N_8O_8Ru$(%): C, 47.7; H, 4.2; N, 13.1; found, C, 47.2; H, 4.0; N, 12.8.

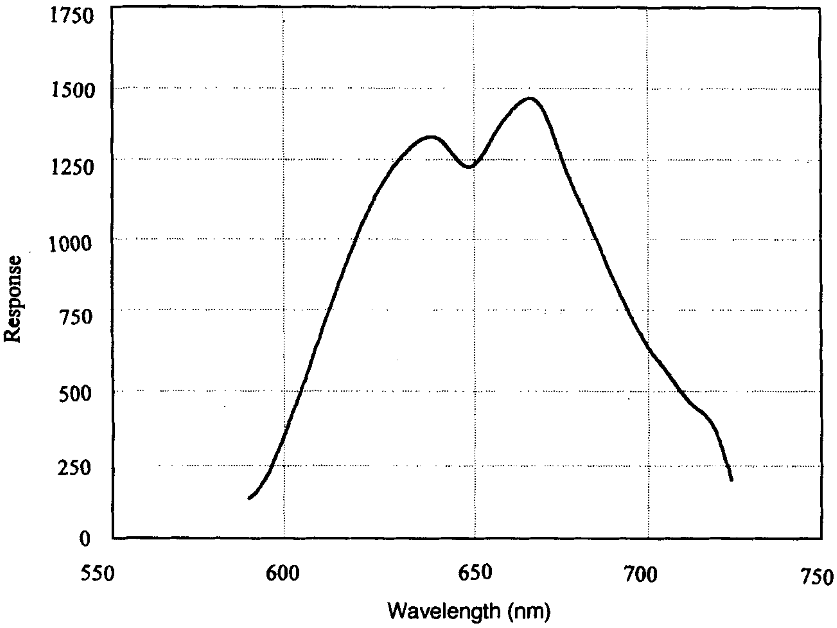

FIGURE 1 Time-resolved emission decay in CH_3CN solution at 298 K with the calculated fits; $\lambda_{ex} = 440$ nm, $\lambda_{em} = 600$ nm.

Crystallography

A single crystal with dimensions $0.20 \times 0.10 \times 0.15$ mm was mounted on a Rigaku RAXIS IIC imaging-plate diffractometer using MoKα radiation ($\lambda = 0.7109$ Å) from a rotating-anode generator operating at 50 kV and 150 mA ($2\theta_{max} = 55.20°$; 24 oscillation frames in the range 0–180°, exposure 10 min per frame). Some 6383 independent reflections were collected and 4625 observed reflections with $F > 6\sigma(F)$ were used for further computation. The title complex, *cis*-[Ru(bpy)$_2$(apy)$_2$](ClO$_4$)$_2$ · CH$_3$CN is monoclinic, space group $P2_1/n$ with cell parameters $a = 10.585(2)$, $b = 11.615(2)$, $c = 15.992(3)$, $\beta = 99.76(3)°$, $V = 1766(2)$ Å^3, $Z = 2$, $Mr = 821.2$, $Dc = 1.583$ g cm^{-3}, F(000) = 856 and $\mu = 0.659$ mm^{-1}.

Intensities were corrected for absorption using the ABSCOR program based on Fourier-coefficient fitting to intensities of symmetry-equivalent reflections.[14] The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (on F). Hydrogen atoms were placed in calculated positions (C–H = 0.96 Å), assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. The contribution of these hydrogen atoms were included in the structure factor calculations. The final R and R_w factor

TABLE I Atomic coordinates and equivalent isotropic displacement coefficients

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
Ru(1)	0.3026(1)	0.1699(1)	0.2680(1)	4.4(1)
N(1)	0.4790(1)	0.2047(1)	0.3635(1)	6.2(1)
C(1)	0.5245(1)	0.1209(1)	0.3900(1)	8.2(1)
C(2)	0.6480(1)	0.1564(1)	0.4544(1)	10.1(1)
C(3)	0.7214(1)	0.2769(1)	0.4914(1)	11.7(1)
C(4)	0.6733(1)	0.3668(1)	0.4655(1)	9.4(1)
C(5)	0.5558(1)	0.3311(1)	0.4020(1)	6.6(1)
N(2)	0.3741(1)	0.3645(1)	0.3095(1)	5.2(1)
C(6)	0.4969(1)	0.4183(1)	0.3681(1)	6.8(1)
C(7)	0.5652(1)	0.5486(1)	0.3956(1)	9.3(1)
C(8)	0.4994(1)	0.6220(1)	0.3607(1)	9.9(1)
C(9)	0.3756(1)	0.5706(1)	0.3052(1)	9.1(1)
C(10)	0.3156(1)	0.4391(1)	0.2796(1)	7.4(1)
N(3)	0.3926(1)	0.1770(1)	0.1629(1)	5.1(1)
C(11)	0.5232(1)	0.1908(1)	0.1666(1)	6.9(1)
C(12)	0.5760(1)	0.2006(1)	0.0932(1)	8.9(1)
C(13)	0.4921(1)	0.1960(1)	0.0158(1)	8.9(1)
C(14)	0.3612(1)	0.1879(1)	0.0139(1)	7.8(1)
C(15)	0.3117(1)	0.1795(1)	0.0884(1)	5.2(1)
N(4)	0.1406(1)	0.1515(1)	0.1681(1)	4.8(1)
C(16)	0.1709(1)	0.1670(1)	0.0910(1)	5.2(1)
C(17)	0.0746(1)	0.1669(1)	0.0219(1)	7.3(1)
C(18)	0.0593(1)	0.1480(1)	0.0280(1)	7.8(1)
C(19)	−0.0920(1)	0.1248(1)	0.1035(1)	7.3(1)
C(20)	0.0096(1)	0.1293(1)	0.1724(1)	5.6(1)
N(5)	0.2034(1)	0.1710(1)	0.3715(1)	5.3(1)
C(21)	0.1373(1)	0.2517(1)	0.3962(1)	6.1(1)
C(22)	0.0846(1)	0.2661(1)	0.4693(1)	6.6(1)
C(23)	0.0981(1)	0.1939(1)	0.5243(1)	6.5(1)
C(24)	0.1621(1)	0.1050(1)	0.4980(1)	7.1(1)
C(25)	0.2091(1)	0.0960(1)	0.4239(1)	6.7(1)
N(6)	0.0494(1)	0.2050(1)	0.5988(1)	9.3(1)
N(7)	0.2431(1)	−0.3000(1)	0.2261(1)	5.4(1)
C(26)	0.1162(1)	−0.1046(1)	0.2217(1)	5.7(1)
C(27)	0.0704(1)	−0.2334(1)	0.1888(1)	5.9(1)
C(28)	0.1537(1)	−0.2970(1)	0.1549(1)	5.8(1)
C(29)	0.2834(1)	−0.2218(1)	0.1579(1)	5.8(1)
C(30)	0.3236(1)	−0.0932(1)	0.1932(1)	5.4(1)
N(8)	0.1102(1)	−0.4251(1)	0.1169(1)	9.0(1)
C(31)	0.3326(1)	0.4724(1)	0.9274(1)	13.5(1)
C(32)	0.2900(1)	0.4796(1)	0.9963(1)	15.2(1)
N(9)	0.3918(1)	0.4616(1)	0.8538(1)	15.9(1)
Cl(1)	0.2751(1)	0.0777(1)	0.7476(1)	6.8(1)
O(1)	0.1558(1)	0.0009(1)	0.6799(1)	14.3(1)
O(2)	0.3709(1)	0.1343(1)	0.7047(1)	13.5(1)
O(3)	0.2250(1)	0.1617(1)	0.8050(1)	13.9(1)
O(4)	0.3240(1)	0.0055(1)	0.7942(1)	11.3(1)
Cl(2)	−0.0870(1)	−0.5486(1)	0.2877(1)	8.6(1)
O(8)	−0.1970(1)	−0.5220(1)	0.3087(1)	19.6(1)
O(5)	−0.1140(1)	−0.5650(1)	0.1921(1)	15.2(1)
O(6)	−0.1336(1)	−0.6734(1)	0.2896(1)	16.3(1)
O(7)	−0.0293(1)	−0.4657(1)	0.3298(1)	21.4(1)
O(7′)	−0.0023(1)	−0.5172(1)	0.3856(1)	15.1(1)
O(6′)	−0.0302(1)	−0.6212(1)	0.2415(1)	15.1(1)
O(5′)	−0.0654(1)	−0.4444(1)	0.2667(1)	5.0(1)

($w^{-1} = \sigma^2(F) + 0.0005F^2$) values were 0.071 and 0.093 for the observed reflections. The maximum shift/esd and largest peak in the final difference Fourier map was 0.02 and 0.89 e Å^{-3}, respectively.

All calculations were carried out on a PC 486 using the SHELXTL-PC program package.[15] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[16] Atomic coordinates for non-hydrogen atoms are listed in Table I and selected bond distances and angles are given in Table II.

TABLE II Selected bond lengths (Å) and angles (°) for the complex

Atom–atom	*Distance*	*Atom–atom*	*Distance*
Ru(1)–N(1)	2.070(1)	C(14)–C(15)	1.394(1)
Ru(1)–N(2)	2.060(1)	C(15)–C(16)	1.465(1)
Ru(1)–N(3)	2.076(1)	N(4)–C(16)	1.367(1)
Ru(1)–N(4)	2.057(1)	C(17)–C(18)	1.396(1)
Ru(1)–N(5)	2.104(1)	C(18)–C(19)	1.379(1)
Ru(1)–N(7)	2.121(1)	C(19)–C(20)	1.382(1)
N(1)–C(1)	1.326(1)	N(4)–C(20)	1.354(1)
N(1)–C(5)	1.380(1)	C(16)–C(17)	1.371(1)
C(1)–C(2)	1.404(1)	N(5)–C(21)	1.343(1)
C(2)–C(3)	1.317(1)	N(5)–C(25)	1.357(1)
C(3)–C(4)	1.401(1)	C(21)–C(22)	1.372(1)
C(4)–C(5)	1.351(1)	C(22)–C(23)	1.375(1)
C(5)–C(6)	1.490 (1)	C(23)–C(24)	1.404(1)
N(2)–C(6)	1.341(1)	C(23)–N(6)	1.367(1)
N(2)–C(10)	1.330(1)	C(24)–C(25)	1.353(1)
C(6)–C(7)	1.398(1)	N(7)–C(26)	1.359(1)
C(7)–C(8)	1.401(1)	N(7)–C(30)	1.360(1)
C(8)–C(9)	1.328(1)	C(26)–C(27)	1.366(1)
C(9)–C(10)	1.400(1)	C(27)–C(28)	1.394(1)
N(3)–C(11)	1.335(1)	C(28)–C(29)	1.391(1)
N(3)–C(15)	1.358(1)	C(28)–N(8)	1.366(1)
C(11)–C(12)	1.399(1)	C(29)–C(30)	1.369(1)
C(12)–C(13)	1.375(1)	C(31)–C(32)	1.251(1)
C(13)–C(14)	1.357(1)	C(31)–N(9)	1.419(1)

Atom–atom–atom	*Angle*	*Atom–atom–atom*	*Angle*
N(1)–Ru(1)–N(2)	80.0(1)	N(3)–C(11)–C(12)	121.2(1)
N(1)–Ru(1)–N(3)	96.4(1)	C(11)–C(12)–C(13)	119.5(1)
N(2)–Ru(1)–N(3)	87.1(1)	C(12)–C(13)–C(14)	118.9(1)
N(1)–Ru(1)–N(4)	173.3(1)	C(13)–C(14)–C(15)	120.3(1)
N(2)–Ru(1)–N(4)	95.1(1)	N(3)–C(15)–C(14)	120.6(1)
N(3)–Ru(1)–N(4)	78.7(1)	N(3)–C(15)–C(16)	115.6(1)
N(1)–Ru(1)–N(5)	86.6(1)	C(14)–C(15)–C(16)	123.7(1)
N(2)–Ru(1)–N(5)	90.6(1)	C(16)–N(4)–C(20)	117.6(1)
N(3)–Ru(1)–N(5)	175.8(1)	C(15)–C(16)–N(4)	114.5(1)
N(4)–Ru(1)–N(5)	98.1(1)	C(15)–C(16)–C(17)	123.8(1)
N(1)–Ru(1)–N(7)	96.9(1)	N(4)–C(16)–C(17)	121.7(1)
N(2)–Ru(1)–N(7)	176.0(1)	C(16)–C(17)–C(18)	120.2(1)
N(3)–Ru(1)–N(7)	90.8(1)	C(17)–C(18)–C(19)	118.2(1)
N(4)–Ru(1)–N(7)	87.8(1)	C(18)–C(19)–C(20)	119.3(1)

TABLE II (*Continued*)

Atom–atom–atom	*Angle*	*Atom–atom–atom*	*Angle*
N(5)–Ru(1)–N(7)	91.7(1)	N(4)–C(20)–C(19)	122.9(1)
C(1)–N(1)–C(5)	118.3(1)	C(21)–N(5)–C(25)	113.6(1)
N(1)–C(1)–C(2)	122.2(1)	N(5)–C(21)–C(22)	125.6(1)
C(1)–C(2)–C(3)	119.6(1)	C(21)–C(22)–C(23)	119.8(1)
C(2)–C(3)–C(4)	118.8(1)	C(22)–C(23)–C(24)	115.7(1)
C(3)–C(4)–C(5)	120.9(1)	C(22)–C(23)–N(6)	122.5(1)
N(1)–C(5)–C(4)	120.1(1)	C(24)–C(23)–N(6)	121.7(1)
N(1)–C(5)–C(6)	114.6(1)	C(23)–C(24)–C(25)	120.5(1)
C(4)–C(5)–C(6)	125.3(1)	N(5)–C(25)–C(24)	124.6(1)
C(6)–N(2)–C(10)	118.2(1)	C(26)–N(7)–C(30)	114.9(1)
C(5)–C(6)–N(2)	116.1(1)	N(7)–C(26)–C(27)	124.1(1)
C(5)–C(6)–C(7)	122.2(1)	C(26)–C(27)–C(28)	120.4(1)
N(2)–C(6)–C(7)	121.8(1)	C(27)–C(28)–C(29)	116.2(1)
C(6)–C(7)–C(8)	117.4(1)	C(27)–C(28)–N(8)	122.6(1)
C(7)–C(8)–C(9)	121.5(1)	C(29)–C(28)–N(8)	121.1(1)
C(8)–C(9)–C(10)	117.4(1)	C(28)–C(29)–C(30)	120.4(1)
N(2)–C(10)–C(9)	123.7(1)	N(7)–C(30)–C(29)	124.0(1)
C(11)–N(3)–C(15)	119.3(1)	C(32)–C(31)–N(9)	174.3(1)

DISCUSSION

Synthesis and IR Spectrum

On refluxing [Ru(bpy)$_2$Cl$_2$]·2H$_2$O with 1 : 2 mol equivalents of 4-aminopyridine in ethanol under nitrogen, the corresponding complex [Ru(bpy)$_2$(4-apy)$_2$](ClO$_4$)$_2$ was produced. Infrared spectra show N–H bands at 3227, 3346 and 3459 cm^{-1} for the amino group in 4-apy. The bands at 1619, 1516, 1465, 1422 cm^{-1} can be assigned to νC=N and ν(C=C) of 4-aminopyridine and the bipyridine group. Bands due to the ionic perchlorate groups are seen around 1089 (strong), 931 (weak) and 624 cm^{-1} (strong), which can be assigned as the IR-allowed ν_3 mode, forbidden ν_1 mode and non-degenerate ClO$_3$ symmetrical bending frequency ν^3, respectively.[17] The strong band at *ca* 763 cm^{-1} can safely be assigned to the bending vibration of C–H of the pyridine ring. The weak band at *ca* 558 cm^{-1} might be assigned to the stretching vibration of Ru–N(bpy) in the *cis*-configuration.

Electronic Spectra

The electronic spectrum is quite similar to the spectrum of Ru(bpy)$_3^{2+}$ and its derivatives. The high energy bands in the 200–350 nm region are generally assigned to $\pi \rightarrow \pi^*$ transitions. The lower energy absorptions in the 380–500 nm region are assigned to d $\rightarrow \pi^*$ transitions, which show unsymmetrical bands with a red shift compared to that in $[Ru(bpy)_3](ClO_4)_2$ in the same solution.

Visible light absorption in polypyridyl complexes of ruthenium(II) arises primarily from charge transfer transitions from filled $d\pi$ Ru(II) levels to multiple low lying π^* (ligand levels).[18] For the archetypal *tris*(bidentate) species $[Ru(bpy)_3]^{2+}$, the MLCT transitions produce excited states that are largely singlet, *e.g.*, $^1(d\pi^6) \rightarrow {}^1(d\pi^5\pi^{*1})$, but possess significant triplet character due to spin–orbit coupling. In mixed-chelate complexes, separate transitions may occur to each ligand.[19]

Descriptions of the Structure

Figure 2 shows an ORTEP plot of the ruthenium complex with the atom numbering scheme. The complex exhibits octahedral geometry with the

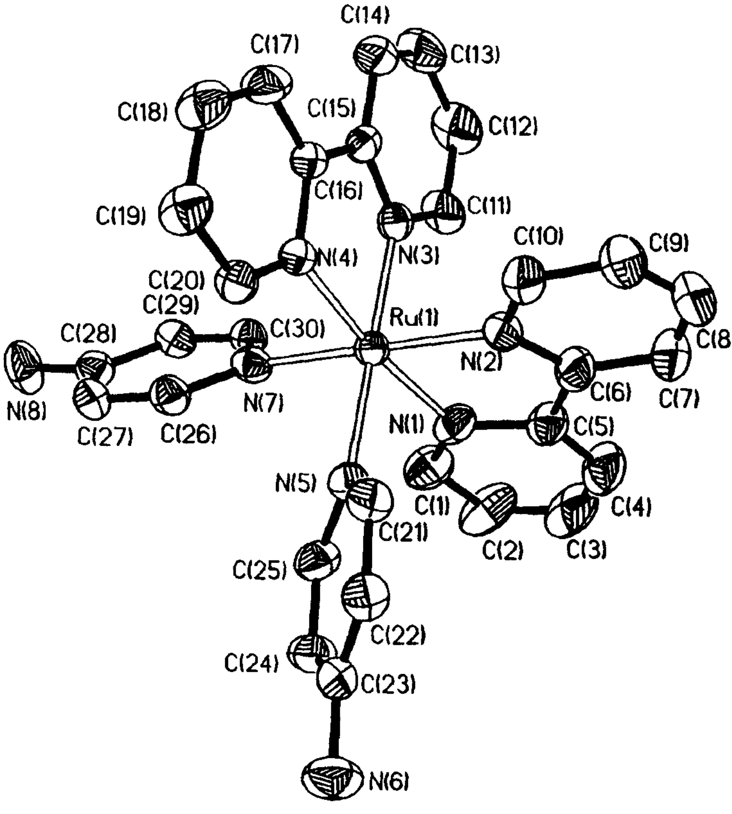

FIGURE 2 An ORTEP plot of the title complex with atom numbering scheme. The thermal ellipsoids are shown at a probability level of 30%.

ruthenium(II) ion bound to two bipyridinyl rings in *cis* configuration along with two aminopyridine ligands.

The bond lengths for 4-apy to ruthenium, Ru(1)–N(5) 2.104(1), Ru(1)–N(7) 2.121(1) Å are longer as compared to the Ru–N bond lengths observed for the bpy ligands. This could be caused by diminished back-bonding in this system.[20,21] The lengths Ru–N(bpy), 2.057(1)–2.076(1) Å, are similar to Ru–N in $[Ru(bpy)_3]^{2+}$ complexes, *e.g.*, X = ClO_4^-(2.056(3)–2.060(3) Å[22]) or PF_6^-(2.056(2) Å at 298 and 143 K[23]; 2.053(2) Å at 105 K[24]) and in $[Ru(bpy)_2L]^{2+}$, *e.g.*, L = 2,3-*bis*(2-pyridyl)quinoxaline (Ru–N, 2.06 Å[25]) $[Ru(bpy)_2L]^+$ (LH = 3-methyl-5-(pyridine-2′methyl)-1,2,4-triazole, 2.042(5), 2.060(4) Å;[26] LH = 2-(2-hydroxyphenyl)pyridine, 2.022(4)–2.049(5)[27]) and $[Ru(bpy)_2 (NH{=}CMe_2)_2]^{2+}$, 2.035(9), 2.081(9) Å.[28] The bite angles of the two bipyridine ligands are 80.0(1) and 78.7(1)° and are normal for this type of compound.

Electrochemistry

The electrochemical behaviour of polypyridyl complexes of ruthenium(II) has been rationalized in terms of a metal-based and a series of ligand-based reactions. These occur in a stepwise manner with respect to each ligand π^*-system, with the order of the reduction correlated with the ease of reduction of the uncoordinated ligands.[29–30] $E_{1/2}$ values were obtained from an average of anodic and cathodic peak potentials $[E_{1/2} = (E_{pa} + E_{pc})/2]$. By analogy with polypyridyl ruthenium electrochemical data, the assignment of these redox couples is straightforward. Cyclic voltammetry for the complex shows one reversible Ru(III)/Ru(II) oxidation wave at 1.20 V *vs* AgCl/Ag. At negative potentials the complexes show two irreversible reductions at −1.30 and −1.45 V, respectively, and which can be assigned to Ru(II)/Ru(I) and the redox potential of the ligands.

From these redox potentials and the MLCT excited state energy (2.1 eV)[31] the following excited state potentials are calculated: $E_{1/2}$[Ru(III)/*Ru(II)] = −0.90 V; $E_{1/2}$[*Ru(II)/Ru(I)] = 0.80 V. These potentials indicate that an electron acceptor with a reduction potential >−0.90 V or an electron donor with an oxidation potential < 0.80 V will quench the MLCT excited state by electron transfer. Cyclic voltammetry on the Ru(II) complex reveals that the functional group NH_2 is not redox active within the potential window −1.3 to +1.3 V. This indicates that the NH_2 functional group cannot quench the Ru MLCT excited state by a thermodynamically favourable electron transfer.

Luminescence Properties

The emission spectrum of the title complex at 298 K in CH_3CN solution (concentration 1.0×10^{-5} M; Figure 3) is characterized by a well-defined vibrational progression with spacing ν_M between the first two components ($1300\,cm^{-1}$). Emission spectra of this type are typical of MLCT excited states with bipyridine. The vibration progressions appear to be framework vibration(s);[32] the $\nu'_M = 0 \rightarrow \nu_M = 0$ emission energy is calculated as $16900\,cm^{-1}$ (600 nm) and the emission yield is 0.0040. This value is comparable to that of the corresponding ruthenium complex *cis*[Ru-$(bipy)_2(py)_2](ClO_4)_2$, $16980\,cm^{-1}$ and 0.0047 for the emission energy and quantum yield, respectively.

The emission lifetime as determined by a time-resolved method in acetonitrile is 460 nm. A rate constant (k_r) can be obtained from the life time (τ^0) and emission quantum yield φ_{em}[32] as $8.6 \times 10^3\,s^{-1}$. The emission lifetime of the title complex is slightly smaller than that of *cis*-Ru $(bipy)_2(py)_2^{2+}$. This is likely due to the pyridine group, since k_r for the two ruthenium complex is almost the same ($8.9 \times 10^3\,s^{-1}$). This indicates that the NH_2 group does not quench the Ru MLCT excited state by electron transfer, in accord with predictions based upon redox potentials of *Ru and the NH_2 group of 4-aminopyridine.

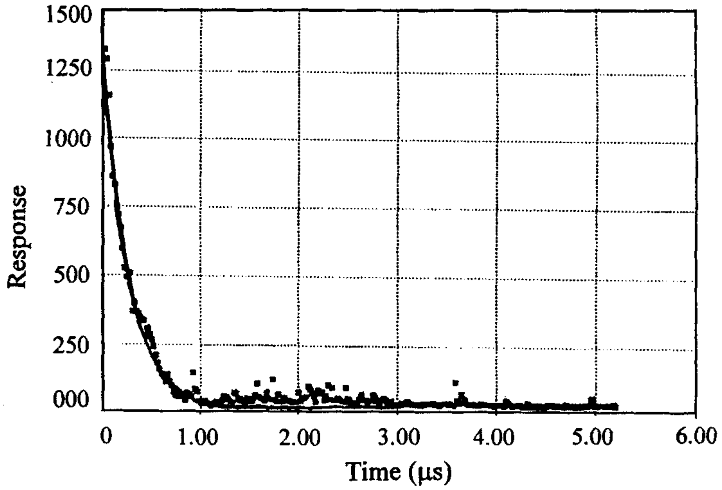

FIGURE 3 Emission spectra of the complex at 298 K in CH_3CN solution, excited at 440 nm; concentration is 1.0×10^{-5} M.

Supplementary Material

Tables of hydrogen atoms coordinates, thermal parameters, all bond distances and angles and observed and calculated structure factors are available from the authors on request.

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References

[1] G. Bruno, F. Nicol, S. Lo Schiavo, M.S. Sinicropi and G. Tresoldi, *J. Chem. Soc., Dalton Trans.*, 17 (1995).
[2] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. Von Zelewsky, *Coord. Chem. Rev.*, **88**, 85 (1988).
[3] J. Bolger, A. Bolder, G. Gourdon, E. Ishow and J.P. Launy, *J. Chem. Soc., Chem. Commun.*, 1799 (1995).
[4] P. Belser, R. Dux, M. Baak, L.L. Decola and V. Balzani, *Angew. Chem., Int. Ed. Engl.*, **34**, 1100 (1995).
[5] J.P. Collin, A. Harriman, V. Heitz, F. Odobel and J.P. Sauvage, *J. Am. Chem. Soc.*, **116**, 5679 (1994).
[6] A. Harriman, F. Odobel and J.P. Sauvage, *J. Am. Chem. Soc.*, **117**, 9461 (1995).
[7] V. Balzani and F. Scandola, *Supramolecular Photochemistry* (Horwood, Chichester, 1991).
[8] W. Bannwarth, D. Schmidt, R.L. Stallard, C. Hornung, R. Knorr and F. Miller, *Helv. Chim. Acta*, **71**, 2085 (1988).
[9] E.M. Kober, J.V. Caspar, B.P. Sullivan and T.J. Meyer, *Inorg. Chem.*, **24**, 3195 (1985).
[10] N.J. Niu, X.Z. You and C.Y. Duan, *Inorg. Chem.*, **35**, 3201 (1996).
[11] Z.L. Lu, C.Y. Duan, Y.P. Tian, X.Z. You, Z.Y. Zhou and T.M. Mak, *Polyhedron*, **16**, 187 (1997).
[12] B.P. Sullivan, D.J. Salmon and T.J. Meyer, *Inorg. Chem.*, **17**, 3334 (1978).
[13] P.A. Anderson, G.B. Deacon, K.H. Harrmann, F.R. Keene, T.J. Meyer, D.A. Reitsma, B.W. Skeleton, G.F. Strouse, N.C. Thomas, T.A. Treadway and A.H. White, *Inorg. Chem.*, **34**, 6145 (1995).
[14] J. Tanner and K.L. Krause, *The Rigaku Journal*, **11**, 4 (1994); *ibid*, **7**, 28 (1990).
[15] K.L. Krause and G.N. Phillips, *J. Appl. Cryst.*, **25**, 146 (1992).
[16] G.M. Sheldrick, in *Computational Crystallography*, Ed. D. Sayre, pp. 506–514 (Oxford University Press, New York, 1982).
[17] B.J. Hathaway, I.M. Procter, R.C. Slade and A.A.G. Tomlinson, *J. Chem. Soc. (A)*, 2219 (1969).
[18] H. Riesen and E. Krauz, *J. Chem. Phys.*, **99**, 7614 (1993).
[19] P.A. Anderson, G.F. Strouse, J.A. Treadway, F.R. Keene and T.J. Meyer, *Inorg. Chem.*, **33**, 3863 (1994).
[20] R. Hage, J.P. Turkenburg, R.A.C. de Graff, J.G. Haasnoot and J. Reeduk, *Acta Crystallogr. C.*, **45**, 381 (1989).
[21] C.R. Hecker, P.E. Fanvick and D.R. McMillin, *Inorg. Chem.*, **30**, 659 (1991).
[22] J.M. Harrowfield and A.N. Sobolev, *Aust. J. Chem.*, **47**, 763 (1994).
[23] M. Biner, H.B. Burhi, A. Ludi and C. Rohr, *J. Am. Chem. Soc.*, **114**, 5197 (1992).

[24] D.P. Rellema, D.S. Jones and H.A. Levy, *J. Chem. Soc., Chem. Commun.*, 849 (1979).

[25] D.P. Rellema, D.G. Taghdiri, D.S. Jones, C.D. Keller, L. Worl and T.J. Meyer, *Inorg. Chem.*, **26**, 578 (1987).

[26] B.G. Buchanan, J.V. Vos, M. Kaneko and W.J.M. von der Putten, *J. Chem. Soc., Dalton Trans.*, 2425 (1990).

[27] B.M. Holigan, J.C. Jeffery, M.K. Norgett, E. Schhatz and M.D.J. Ward, *J. Chem. Soc., Dalton Trans.*, 3345 (1992).

[28] K.Y. Wong, C.M. Che, C.K. Liu, W.H. Chiu, Z.Y. Zhou and T.C.W. Mak, *J. Chem. Soc., Chem. Commun.*, 754 (1992).

[29] D.P. Rillema, G. Allen, T.J. Meyer and D. Conard, *Inorg. Chem.*, **22**, 1617 (1983).

[30] M.A. Masood, B.P. Sullivan and D.J. Hodgeon, *Inorg. Chem.*, **33**, 4611 (1994).

[31] J.A. Bolger, G. Ferguson, J.P. James, C. Long, P. McArdle and J.G. Vos, *J. Chem. Soc., Dalton Trans.*, 1577 (1993).

[32] J.V. Caspar and T.J. Meyer, *Inorg. Chem.*, **22**, 2444 (1983).