

A NEW BUILDING BLOCK FOR POLYNUCLEAR COMPLEXES: THE ION $[\text{Ru}(\text{bptz})(\text{CN})_4]^{2-}$ (bptz = 3,6-BIS(2-PYRIDYL)-1,2,4,5-TETRAZINE)

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Dedicated to Prof. Pedro J. Aymonino on the occasion of his 75th birthday

Abstract

The synthesis and physicochemical properties of the new mononuclear ruthenium(II) complex, of formula $\text{Na}_2[\text{Ru}(\text{bptz})(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ (bptz = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine) are reported. The IR and UV-vis spectral data, together with cyclic voltammetry measurements, indicate that the ligand bptz has a π -acceptor ability intermediate between dpp and bpz when coordinated to the tetracyanoruthenate(II) moiety (dpp = 2,3-bis(2'-pyridyl)pyrazine ; bpz = 2,2'-bipyrazine). This complex can be used as a photosensitizer, since it emits at room temperature in alcoholic solutions, and as a building block for new polynuclear complexes, such as the symmetric ion $[(\text{CN})_4\text{Ru}(\text{bptz})\text{Ru}(\text{CN})_4]^{4+}$, whose preparation and spectral properties in aqueous solutions are also described in this work.

Resumen

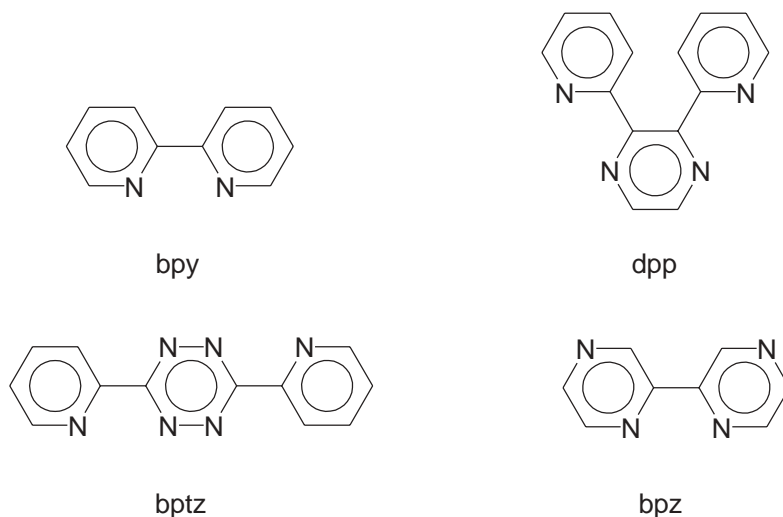
Se reportan la síntesis y las propiedades fisicoquímicas del nuevo complejo mononuclear de rutenio (II), de fórmula $\text{Na}_2[\text{Ru}(\text{bptz})(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ (bptz = 3,6-bis(2-piridil)-1,2,4,5-tetrazina). Los datos espectrales de IR y de UV-visible, junto a las medidas de voltamperometría cíclica, indican que el ligando bptz tiene una capacidad aceptora π -intermedia entre dpp y bpz cuando se coordina a un grupo tetracianorutenato(II) (dpp = 2,3-bis(2'-piridil)pirazina ; bpz = 2,2'-bipirazina). Este complejo puede ser usado como un fotosensibilizador, pues emite a temperatura ambiente en soluciones alcohólicas, y como una unidad estructural para la construcción de nuevos complejos polinucleares, tales como el ion simétrico $[(\text{CN})_4\text{Ru}(\text{bptz})\text{Ru}(\text{CN})_4]^{4+}$, cuya preparación y propiedades espectrales en soluciones acuosas se describen también en este trabajo.

Introduction

Poly(pyridine) ruthenium complexes have been extensively studied due to their relevance in connection to artificial photosynthesis [1]. The first complex of the series $[\text{Ru}(\text{L})(\text{CN})_4]^{2-}$ was prepared by Scandola *et al.* [2] by using L = bpy (bpy = 2,2'-bipyridine), as a representative example of an emissive poly(pyridine) complex with a single chromophoric unit. We later investigated the properties of ruthenium analogues with L = bpz (bpz = 2,2'-bipyrazine) [3], and

L = dpp (dpp = 2,3-bis(2'-pyridyl)pyrazine) [4], in order to establish the degree of influence of ligand size and geometry in the spectral and electrochemical properties of these systems. Now, we complete in this report the description of this class of photosensitizers by preparing the new complex $[\text{Ru}(\text{bptz})(\text{CN})_4]^{2-}$, with bptz = 3,6-bis-(2-pyridil)-1,2,4,5-tetrazine, whose physicochemical properties are analyzed in the context of the above mentioned series.

Besides, the poly(azines) bpz, dpp and bptz, unlike bpy, can be used as building blocks for polynuclear complexes. In the particular case of bptz, a symmetric species of formula $[(\text{CN})_4\text{Ru}(\text{bptz})\text{Ru}(\text{CN})_4]^+$ can be prepared and is also described in this work. Other homo- and hetero-dinuclear complexes with bptz as a bridging ligand have been reported [5-8]. The degree of electronic communication between both metallic centers in these dinuclear species, a factor important for the design of energy conversion devices [1], can be assessed from spectral and electrochemical measurements. The structures of the compared ligands are shown in Scheme 1.



Scheme 1

Experimental

Synthesis- The complex $\text{Na}_2[\text{Ru}(\text{bptz})(\text{CN})_4] \cdot 4\text{H}_2\text{O}$, **1**, was prepared by irradiating with a Pen-Ray UV-lamp ($\lambda_{\text{ex}} = 254 \text{ nm}$) a solution of 1 g of $\text{K}_4[\text{Ru}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ with 0.5 g of bptz in 30 mL of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ 1:3 v/v. After 53 hs, the caramel-colored solution was filtered to eliminate unreacted bptz; then, ethanol was added to precipitate unreacted $\text{K}_4[\text{Ru}(\text{CN})_6]$. After filtering, the solution was rotoevaporated until complete dryness; it was then re-dissolved in a minimum amount of water and chromatographed on a Sephadex G-25 column (24 x 4 cm). When eluting with water, the dinuclear species $[(\text{CN})_4\text{Ru}(\text{bptz})\text{Ru}(\text{CN})_4]^+$, **2**, was collected first; afterwards, complex **1** was eluted, reduced in volume and precipitated with acetone. It was finally washed with acetone and ether, and further purified by a second precipitation with acetone, to which excess KI was added. It was stored *in vacuo* over P_4O_{10} overnight. A fine orange precipitate was obtained, with a yield of 35 %. Anal. Calcd.: C, 32.5 ; H, 2.7 . Found: C, 32.7; H, 2.6 %.

Materials and equipments – All chemicals were analytical grade reagents and used without further purification. IR spectra were recorded on a Perkin-Elmer 983G IR

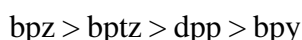
spectrophotometer as KBr pellets. UV-visible spectra were obtained by using a Shimadzu UV-160 A spectrophotometer, provided with 1-cm quartz cells. Luminescence experiments were performed with a Shimadzu RF-5301 PC spectrofluorometer. Cyclic voltammetry measurements were carried out on a BAS- Epsilon equipment, provided with vitreous carbon as a working electrode, silver wire as an auxiliary electrode and Ag/AgCl (3 M) as a reference electrode. Ar was bubbled for 15 min prior to photophysical and electrochemical measurements. Chemical analyses were done at INQUIMAE (University of Buenos Aires, Argentina), with an estimated error of $\pm 0.5\%$.

Results and Discussion

Synthesis – Complex 1 was prepared by following a photochemical technique already described for complexes of the type $\text{Na}_2[\text{Ru}(\text{CN})_4\text{L}] \cdot x\text{H}_2\text{O}$ (with $x = 2$ for $\text{L} = \text{bpy}$ [2], and $x = 4$ for $\text{L} = \text{dpp}$ and bpz [3,4]), with a slight modification in the purification procedure. In this case, gel permeation with Sephadex G-25 allowed the separation and isolation, in water, of both the mononuclear and dinuclear bptz-cyanoruthenium species. Repeated precipitation from acetone/water mixtures with added KI was necessary to achieve good elemental analyses.

IR spectroscopy - The very strong bands that appear between 2100 and 2000 cm^{-1} in the IR spectrum of 1 can be attributed to cyanide stretching vibrations ($\nu_{\text{C}\equiv\text{N}}$) and are characteristic of a tetracyanoruthenate(II) moiety with a C_{2v} symmetry [4]. The most intense peak appears at 2054 cm^{-1} , a value intermediate between that of the corresponding cyanoruthenium complexes with $\text{L} = \text{bpy}$ (2048 cm^{-1}) and $\text{L} = \text{bpz}$ (2066 cm^{-1}) [3], thus pointing to an intermediate π -acceptor ability of bptz. Bands characteristic of bptz in the low-frequency region appear at slightly higher values with respect to the free ligand values, due to coordination to Ru [9].

UV-visible spectroscopy - Figure 1 shows the UV-visible spectrum of complex 1 in water. Bands appearing between 200 and 350 nm can be assigned to π - π^* ligand-centered transitions, as expected for poly(pyridine) complexes [3]. These transitions also appear in the free ligand bptz, but they are shifted to lower energy values in the mononuclear species than in the dinuclear one, due to the lower symmetry imposed by coordination to only one metallic center. The strong increase in absorbance near 200 nm can be assigned to a $d_{\pi}(\text{Ru}) \rightarrow \pi^*(\text{CN})$ MLCT transition, while the strong band at $\lambda_{\text{max}} = 454$ nm can be attributed to a $d_{\pi}(\text{Ru}) \rightarrow \pi^*(\text{bptz})$ MLCT transition, by comparison with spectra of similar complexes [3,6]. When contrasting this latter value to other maximum absorption wavelengths for $[\text{Ru}(\text{L})(\text{CN})_4]^{2-}$ species, as shown in Table 1, the following decreasing order of π -backbonding $\text{Ru} \rightarrow \text{L}$ is disclosed:



Thus, bptz has a π -acceptor ability intermediate between bpy and bpz, in agreement with the IR results; and more precisely, between dpp and bpz. Besides, the solvent dependence for this MLCT band is the expected one for a cyanoruthenium species [3]: when the solvent AN (AN = Acceptor Number) decreases, the energy of the maximum absorption band (E_{abs}) also decreases; in CH_3CN , for example, $\lambda_{\text{max}} = 521$ nm.

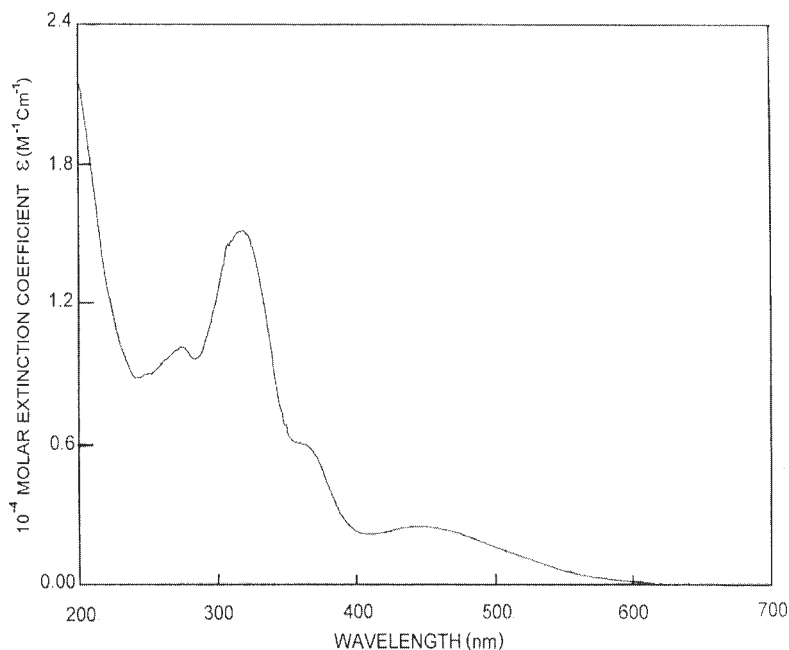


Figure 1. UV-vis spectrum of $[Ru(bptz)(CN)_4]^{2-}$, at 23 °C, in water.

Table 1. Spectral and electrochemical properties of complexes of the type $[Ru(L)(CN)_4]^{2-}$ in water (unless stated otherwise).

<i>L</i>	E_{abs}^a , eV	E_{em}^b , eV	$E_{1/2}(Ru^{III}/Ru^{II})^c$, V	Reference
Bpy	3.10	2.03	0.78	[2]
Dpp	2.77	1.91	0.80 ^d	[4]
Bptz	2.73	1.80 ^e	0.84	This work
Bpz	2.68	1.76	1.00	[3]

^a E_{abs} = energy of the absorption maximum. ^b E_{em} = energy of the emission maximum. ^c vs. SCE.
^dCorrected by solvent change. ^eIn CH_3OH/C_2H_5OH 4:1 v/v.

The dinuclear species **2**, whose UV-visible spectrum in water (as obtained by elution in the chromatographic column) is shown in Figure 2, has its absorption maximum at $\lambda_{max} = 540$ nm. The energy shift that occurs, in water, when going from the mononuclear to the dinuclear species ($\Delta E = 0.43$ eV) is almost 3 times larger than that observed in the dpp analogue ($\Delta E = 0.14$ eV, [4]) and points to the much higher electronic delocalization and lower steric restrictions imposed by the planarity of bptz that results from its coordination to a second metallic centre. A strong

electronic communication between both ruthenium centers is then disclosed, in agreement with previous findings in tetraammineruthenium(II) complexes of bptz [5]. It can therefore be predicted that the corresponding mixed-valent species, $[(\text{CN})_4\text{Ru}(\text{bptz})\text{Ru}(\text{CN})_4]^{3-}$, will be completely delocalized [10], as occurs in other metal moieties containing bptz as a bridging ligand [7]. In effect, we demonstrated in a recent work [11] on the mixed-valent chemistry of complexes of the type $[(\text{CN})_4\text{Fe}(\text{L})\text{Fe}(\text{CN})_4]^{3-}$ (with L = bptz and bpym; with bpym = 2,2'-bipyrimidine) that size and distance do not always matter: in spite of the larger size and metal-to-metal distance in bptz as compared to bpym, the mixed-valent complex with L = bptz can be described as fully delocalized. This unusual behaviour was accounted for by the higher MO coefficients at the coordinating N atoms of bptz with respect to bpym. The stability of this mixed-valent species can be further tuned by exploiting the solvent sensitivity of cyanometallates [12].

Electrochemistry - Cyclic voltammetry measurements on complex **1** in aqueous solutions gave a redox potential value $E_{1/2}[\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}] = 0.84 \text{ V}$ (vs. SCE) in the oxidative range, which is consistent with the spectral results, as shown in Table 1. When stabilizing the oxidation state (II) of ruthenium with a stronger π -accepting ligand, the redox potential is consequently increased and the complex is harder to oxidize. Red-shifts of MLCT transitions with increasing oxidation potentials have already been observed for other single chromophoric systems, such as $[\text{Re}(\text{I})(\text{R-bpy})(\text{CO})_3\text{Cl}]$ [13].

Photophysical properties - Complex **1** emits at room temperature in a solution of $\text{CH}_3\text{OH}/\text{C}_2\text{H}_5\text{OH}$ 4:1 v/v, as shown in Figure 3 (in water, the emission is almost undetectable). The value of the maximum emission wavelength $\lambda_{\text{em}} = 690 \text{ nm}$ (at $\lambda_{\text{ex}} = 460 \text{ nm}$) is coherent with the trend in absorption energies of similar complexes with poly(azines). In effect, as shown in Table 1, when the energy of the absorption maximum (E_{abs}) of the MLCT transition $d_{\pi}(\text{Ru}) \rightarrow \pi^*(\text{L})$ decreases, the emission energy maximum (E_{em}) – corresponding to the reverse process $\pi^*(\text{L}) \rightarrow d_{\pi}(\text{Ru})$ - decreases concomitantly.

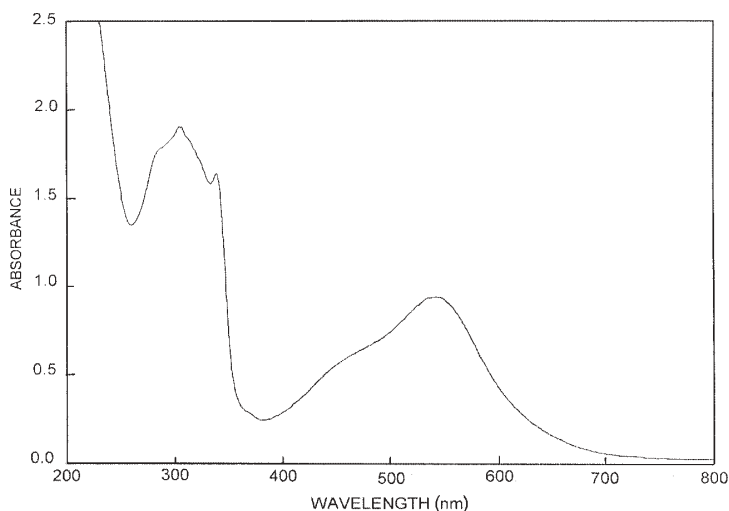


Figure 2. UV-vis spectrum of the dinuclear species $[(\text{CN})_4\text{Ru}(\text{bptz})\text{Ru}(\text{CN})_4]^{4-}$, at 23°C , in water (eluted from a chromatographic column).

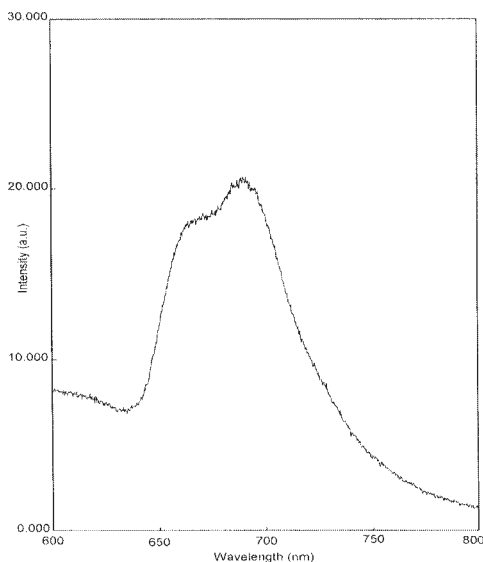


Figure 3. Emission spectrum of $[Ru(bptz)(CN)_4]^{2-}$, in CH_3OH/C_2H_5OH 4: 1 v/v, at $23\text{ }^\circ\text{C}$, and $\lambda_{ex} = 460\text{ nm}$.

Conclusions

The new mononuclear ruthenium complex described in this work, $[Ru(bptz)(CN)_4]^{2-}$, can act as a photosensitizer, as deduced by its luminescence at room temperature in alcoholic solutions. Spectral and electrochemical properties of this complex allows the classification of bptz as a ligand with π -electron-acceptor properties intermediate between dpp and bpz. In the symmetric bptz-bridged dinuclear species, $[(CN)_4Ru(bptz)Ru(CN)_4]^{4+}$, the electronic communication disclosed between both metallic centers is much stronger than in the dpp-bridged analogue, due to its lower steric constraints.

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