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Cis-Dicyanobis(2,2′-bipyridine)ruthenium(II) as a Nitrile Ligand. Formation of Adducts with Platinum(II) Complexes

C. BARTOCCI, C. A. BIGNOZZI, F. SCANDOLA

Istituto Chimico dell'Università, Centro di Studio sulla Fotochimica e Reattività degli Stati Eccitati dei Composti di Coordinazione del C.N.R., 44100 Ferrara, Italy

R. RUMIN and P.COURTOT

Laboratoire de Photochimie, Electrochimie et Chimie Moléculaire (LA 322 du C.N.R.S.) de l'Université de Bretagne Occidentale, 6 avenue Le Gorgeu, 29283 Brest, France

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Cis-Dicyanobis(2,2′-bipyridine)ruthenium(II), Ru(bpy)$_2$(CN)$_2$, is a well characterized red-orange complex [1], with an absorption spectrum (Fig. 1a) exhibiting a prominent d–π* ruthenium-to-bipyridine charge transfer abosrption band. The position of this band is extremely sensitive to medium polarity (blue shift with increasing polarity), in agreement with the polar nature of the transition. Ru(bpy)$_2$(CN)$_2$ has a relatively long-lived and strongly emitting (Fig. 1b) d–π* triplet state [2], which makes this complex an interesting energy- and electron-transfer sensitizer [3,4].

When DMF solutions of Ru(bpy)$_2$(CN)$_2$ were mixed with DMF solutions of several Pt(II) complexes of the PtCl$_2$(Un)L type (where Un was C$_2$H$_4$ or (CH$_3$)$_2$S and L was 4-methylpyridine, py^4, or Cl$^-$, in the *cis* or *trans* configurations),* pronounced blue shifts were observed in the absorption spectra, corresponding to a change in color of the solution from orange to yellow. As an example, the spectrum obtained with *trans*-PtCl$_2$(C$_2$H$_4$)py^4 is shown in Fig. 1a. The wavelengths of the maxima obtained with the various Pt(II) complexes are shown in Table I. The rate at which the spectral shift was completed after mixing varied widely from one complex to another, going from almost instantaneous for *trans*-PtCl$_2$(C$_2$H$_4$)py^4 and [PtCl$_3$(C$_2$H$_4$)]$^-$ to very slow for *cis*-PtCl$_2$(DMS)py^4.

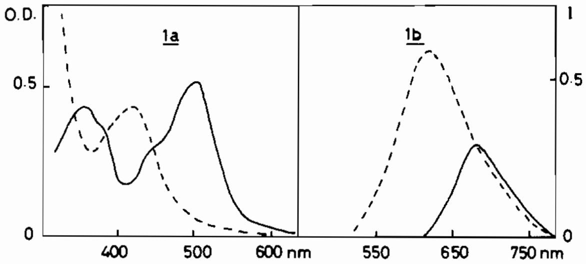

Fig. 1. (a) Absorption spectra of a 5 × 10^{-5} *M* DMF solution of Ru(bpy)$_2$(CN)$_2$ (——), and of a DMF solution containing Ru(bpy)$_2$(CN)$_2$ 5 × 10^{-5} *M* and *trans*-PtCl$_2$(C$_2$H$_4$)py^4 6.6 × 10^{-5} *M* (------); (b) Emission spectra of the same two solutions (excitation wavelength, 448 nm, Arbitrary units).

Kinetic measurements* were carried out for *cis*-PtCl$_2$(C$_2$H$_4$)py^4, indicating that the process was first order in both Pt(II) and Ru(II) complexes, with a bimolecular rate constant $k = 10.6$ M^{-1} sec^{-1}. The stability of the adduct formed in solution also varied widely, depending on the Pt(II) complex used and on the solvent. A quantitative determination* carried out for the adduct between *cis*-PtCl$_2$(C$_2$H$_4$)py^4 and Ru(bpy)$_2$(CN)$_2$ gave an 'apparent' stability constant in DMF of 1.5 × 10^4 M^{-1} or 5.2 × 10^7 M^{-2} depending on whether a single adduct with 1:1 or 1:2 Ru:Pt ratio is assumed. In less coordinating solvents, *e.g.*, CHCl$_3$, the stability increased.

Blue shifts similar to those observed in absorption were obtained in the emission spectra (Fig. 1b and Table I) together with an enhancement of the emission intensity**. Also, the emission lifetimes† were observed to undergo a general increase (Table I).

As far as the chemical changes responsible for the observed spectral shifts are concerned, the most plausible hypothesis is that of bridge formation between Ru(II) and Pt(II) through the cyanide

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*Ru(bpy)$_2$(CN)$_2$ and Zeise's Salt, K[PtCl$_3$(C$_2$H$_4$)], were prepared according to standard methods [1, 5]. *Cis*- and *trans*-dichloro(ethylene)(4-methylpyridine)platinum(II), PtCl$_2$(C$_2$H$_4$)py^4, and *cis*- and *trans*-dichloro(dimethylsulphyde)(4-methylpyridine)platinum(II), PtCl$_2$(DMS)py^4, were available from previous studies [6]. All the other chemicals were reagent or spectral grade.

*Since isobestic points were not strictly maintained in the spectral variations, both 1:1 and 1:2 Ru:Pt adducts are likely to be formed in solution; since at 530 nm the only absorbing species is Ru(bpy)$_2$(CN)$_2$, measurements at this wavelength allow the calculation of rate constants and 'apparent' stability constants.

**The emission spectra were measured with a Perkin Elmer MPF3 spectrofluorimeter equipped with a R-955 Hamamatsu tube.

†The emission lifetimes were measured with a J. K. system 2000 ruby laser.

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TABLE I. Spectroscopic Data for DMF Solutions Containing $Ru(bpy)_2(CN)_2$ and Platinum Complexes of the $PtCl_2(Un)L$ Type.

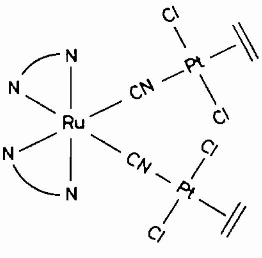
Pt(II) complex	Absorption λ_{max}, nm	Emission[a] λ_{max}, nm	Lifetimes[a] ns
—[b]	505	680	205
cis-$PtCl_2(C_2H_4)py$[4] [c]	460	620	668
trans-$PtCl_2(C_2H_4)py$[4] [c]	456	620	998
cis-$PtCl_2(DMS)py$[4] [d]	420	620	618
trans-$PtCl_2(DMS)py$[4] [d]	470	620	655
$PtCl_3(C_2H_4)^-$ [e]	450	620	640

[a]Deaerated solutions. [b]Data for $Ru(bpy)_2(CN)_2$. [c]5×10^{-5} *M* $Ru(bpy)_2(CN)_2$, 5×10^{-4} *M* Pt(II) complex. [d]5×10^{-5} *M* $Ru(bpy)_2(CN)_2$, 5×10^{-3} *M* Pt(II) complex. [e]5×10^{-5} *M* solution of the solid isolated adduct (see text).

ligands. This hypothesis is based on the following available information. Complexes of the $M(bpy)_2(CN)_2$ type are known to behave as Lewis bases, undergoing protonation at the cyanide nitrogen (M = Fe(II), Ru(II), Os(II)) [7, 8] and giving rise to adducts with typical Lewis acids such as boron halides (M = Fe(II)) [9]. On the other hand, complexes of the $PtCl_2(Un)L$ type have been shown by Orchin [10] to undergo facile L substitution by organic nitriles.

This working hypothesis has been confirmed by the isolation* of the trinuclear adduct $Ru(bpy)_2(CN)_2[PtCl_2(C_2H_4)]_2$. This complex exhibits CN stretching frequencies at 2092 and 2117 cm^{-1}, which are shifted with respect to those of $Ru(bpy)_2(CN)_2$ (2052 and 2072 cm^{-1}), indicating the bridged coordination of the CN groups [9, 10]. The Pt–Cl stretching appears as a single frequency (338 cm^{-1}), suggesting a *trans* configuration at Pt(II) [10].

These data indicate a schematic structure for the complex of the type:



When dissolved in DMF, the trinuclear complex undergoes some dissociation into mononuclear species (as shown by spectral changes), presumably due to Pt–NC bridge splitting by the solvent.

From the photophysical point of view it is interesting to note that the adduct formation with Pt(II) does not substantially modify the properties of the $Ru(bpy)_2(CN)_2$ chromophore. In particular, contrary to what happens in the postulated interaction of this chromophore with Cu^{2+}_{aq} [2], the excited state lifetime is appreciably enhanced [11]. This result seems to open new perspectives for the design of bimetallic complexes exhibiting interesting properties as photosensitizers.

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*$Ru(bpy)_2(CN)_2[PtCl_2(C_2H_4)]_2$ can be prepared by mixing methanolic solutions of Zeise's Salt and $Ru(bpy)_2(CN)_2$ in a two-to-one molar ratio. The polynuclear product precipitates immediately as a yellow-orange solid which can be filtered and washed with methanol. It can be noticed that the same product precipitates even if the molar ratio of the mononuclear reactants is lower than two, leaving in solution the unreacted $Ru(bpy)_2(CN)_2$. *Anal.* Calcd: C, 29.6; H, 2.27; Cl, 13.4; N, 7.96; Pt, 37; Ru, 9.6. Found: C, 30.7; H, 2.26; Cl, 11.4; N, 8.78; Pt, 32; Ru, 8.8.

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11 Similar lifetime enhancements have been reported to occur when Ag^+ ions are complexed with $Ru(bpy)_2(CN)_2$ (M. G. Kinnaird and D. G. Whitten, *Chem. Phys. Letts.*, *88*, 275 (1982)).