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A Ruthenium(II)/Platinum(II) Binuclear Complex Bridged by 2,2′-Bipyrimidine

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Few heterobinuclear complexes of coordination compounds have been reported and those have generally been linked together via a single coordination site with an ambidentate ligand such as CN^-. Reports of ruthenium(II)/platinum(II) complexes are even rarer. Scandola and coworkers recently reported the existence of complexes between $Ru(bpy)_2(CN)_2$, where bpy is 2,2′-bipyridine, and a number of platinum(II) olefin complexes [1] and also between $Ru(bpy)_2(CN)_2$ and the $Pt(diene)^{2+}$ moiety [2]. The ruthenium(II)/platinum(II) complexes derived from the olefins were unstable in solution; the ones containing the $Pt(diene)^{2+}$ were more stable, but dissociated to an extent of about 2%.

In our work, we are interested in synthesizing stable multielectron transfer agents for redox catalysis applications. As a step in this direction, we have recently synthesized a ruthenium(II)/platinum(II) complex bridged by 2,2′-bipyrimidine. The bipyrimidine acts as a bidentate bridging ligand which adds stability to the heterobinuclear complex.

The preparation was effected in the dark. After mixing deoxygenated methanol solutions of $[Ru(bpy)_2(bpm)](ClO_4)_2$ [3], where bpm is 2,2′-bipyrimidine, and *cis*-$[Pt(DMSO)_2Cl_2]$ [4] together in stoichiometric amounts and refluxing under nitrogen for 12 h, a dark green precipitate was obtained. The pure product, $[Ru(bpy)_2(bpm)PtCl_2](ClO_4)_2$ was isolated in 90% yield after filtering, washing with methanol, ethyl ether and vacuum drying for 4 h. The elemental analyses[≠], spectrum (Fig. 1) and electrochemical data (Table I) strongly support coordination of platinum(II) at the remote nitrogen centers of $[Ru(bpy)_2(bpm)]^{2+}$ producing the new heterobinuclear complex drawn below:

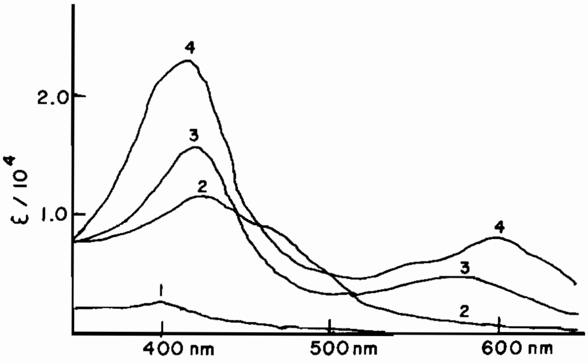

Fig. 1. A comparison of the absorption spectra of $[Pt(bpm)Cl_2]$ (1), $[Ru(bpy)_2(bpm)](ClO_4)_2$ (2), $[Ru(bpy)_2(bpm)PtCl_2](ClO_4)$ (3) and $[Ru(bpy)_2]_2(bpm)(ClO_4)_4$ (4) in propylene carbonate. Spectra were obtained with a Perkin-Elmer Lambda Array 3840 diode-array visible–UV spectrophotometer.

TABLE I. Electrochemical Data for Mononuclear and Binuclear Complexes of Ruthenium(II) and Platinum(II)

Complex	Oxidations[a]		Reductions[a]		References
	$E_{1/2}(2)$ (V)	$E_{1/2}(1)$ (V)	$E_{1/2}(1)$ (V)	$E_{1/2}(2)$ (V)	
$[Ru(bpy)_2(bpym)](ClO_4)_2$		1.36	−1.01	−1.45	b
$[Ru(bpy)_2]_2(bpym)(ClO_4)_4$	1.69	1.53	−0.41	−1.08	b
$[Ru(bpy)_2(bpym)PtCl_2](ClO_4)_2$		1.35	−0.34	−1.01	c
$[Pt(bpym)Cl_2]$			−0.88		c
$[Ru(bpy)_3]^{2+}$		1.27	−1.31	−1.50	b

[a] Potential measurements were determined by cyclic voltammetry at a Pt electrode and referenced to a saturated sodium calomel electrode (SSCE) in (b) 0.1 M TEAP–CH_3CN or (c) 0.1 M TEAP–propylene carbonate at 20 ± 1 °C. The estimated error is ±0.01 V. The difference between $E_{P_{ox}}$ and $E_{P_{red}}$ varied from 60–80 mv which is indicative of a one electron transfer process. The solvent window of propylene carbonate precludes obtaining data at a more negative potential than 1.5 V. Cyclic voltammograms were obtained with a PAR 174A polarographic analyzer adapted for cyclic voltammetry with a super cycle and were recorded on an IBM Model 7424 x-y Recorder. [b] Ref. 3. [c] This work.

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[≠] *Anal.* Calc. for $C_{28}H_{22}N_8O_8Cl_4RuPt$: C, 32.45; H, 2.14; N, 10.81; Cl, 13.68. Found: C, 32.22; H, 2.22; N, 10.76; Cl, 13.60%.

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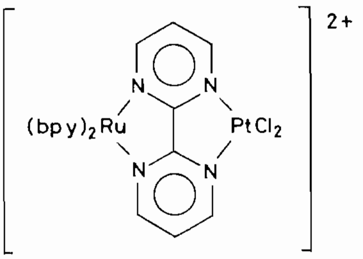

The compound was dissolved in propylene carbonate and its visible spectrum and electrochemical properties were investigated. The resulting complex is stable in solution; there is no evidence for dissociation to give mononuclear species.

A comparison of the visible spectra of $[Pt(bpm)Cl_2]$, $[Ru(bpy)_2(bpm)]^{2+}$, $[(bpy)_2Ru(bpm)Ru(bpy)_2]^{4+}$ and $[(bpy)_2Ru(bpm)PtCl_2]^{2+}$ is given in Fig. 1. The absorption spectra of the mononuclear precursor complexes show a weak absorbance at 396 nm ($\epsilon = 2.1 \times 10^3$ M^{-1} cm^{-1}) for $[Pt(bpm)Cl_2]$ and a more pronounced energy manifold centered near 426 nm for $[Ru(bpy)_2(bpm)]^{2+}$. The absorbance at 484 nm for $[Ru(bpy)_2(bpm)]^{2+}$ most likely is related to a $d\pi \rightarrow \pi^*$ (bpm) transition and the one at 426 nm to $d\pi \rightarrow \pi^*$ (bpy). Upon coordination to a second metal center, the absorption maxima shift to the red. The absorption maximum for the ruthenium(II)/platinum(II) complex is found at 571 nm; the one for the ruthenium(II)/ruthenium(II) species is at 594 nm. It is clear from the data that the effect of platinum(II) is similar to that of ruthenium(II). Since the second ruthenium(II) coordinates to both remote nitrogen donors of the bipyrimidine ligand, it follows that platinum(II) also does. It is also clear that the origin of the optical transition is from the $d\pi$ levels of ruthenium(II) to the π^* orbitals of the bipyridimide ligand. It is also interesting to note that the absorption coefficient for the homobinuclear complex is 8.2×10^3 M^{-1} at 594 nm, whereas that of the heterobinuclear complex is about one-half the value, or 4.4×10^3 M^{-1} cm^{-1} at 571 nm. This is reasonable given the fact that there are two ruthenium(II) centers in the homonuclear complex whereas there is only one in the heterobinuclear complex.

Antother unique feature exhibited by the ruthenium(II)/platinum(II) complex is related to the $Ru^{3+/2+}$ redox couple. According to the data in Table I, the $Ru^{3+/2+}$ potentials of $[Ru(bpy)_2(bpm)]^{2+}$ and $[(bpy)_2Ru(bpm)PtCl_2]^{2+}$ are the same in contrast to $[(bpy)_2Ru(bpm)Ru(bpy)_2]^{4+}$, where the presence of the second ruthenium center is noted by (a) a shift to a higher $E_{1/2}$ value for the first ruthenium(II) oxidation ($E_{1/2} = 1.53$) compared to the mononuclear analogue ($E_{1/2} = 1.36$) and (b) the presence of a second oxidation of the other ruthenium(II) center more positive at $E_{1/2} = 1.69$ V *vs.* SSCE. The behavior of the homobinuclear complex is consistent with formation of the mixed-valent [2, 3] complex after the first oxidation followed by formation of the [3, 3] form after the second oxidation [5]. In contrast, there appears to be little communication between metal centers in $[(bpy)_2Ru(bpm)PtCl_2]^{2+}$; the $Ru^{3+/2+}$ redox potential is not shifted as in $[((bpy)_2bpm]^{4+}$.

The second unique electrochemical feature is related to the observed reductions which are ligand centered for ruthenium(II) heterocycles. For free ligands 2,2′-bipyrimidine and 2,2′-bipyridine, ligand reductions occur at −1.99[‡] and −2.21 V [6] *vs.* SSCE, respectively. The same pattern is found upon coordination; the bipyrimidine ligand is reduced at more positive potential than bipyridine. In $[Ru(bpy)_2(bpm)]^{2+}$, for example, the reductions at −1.01 V and −1.45 V *vs.* SSCE were assigned [3] as given in eqns. (1) and (2).

$$[Ru(bpy)(bpy)(bpm)]^{2+} + e^- \rightleftarrows [Ru(bpy)(bpy)(bpm^-)]^+ \qquad (1)$$

$$[Ru(bpy)(bpy)(bpm^-)]^+ + e^- \rightleftarrows [Ru(bpy)(bpy^-)(bpm^-)] \qquad (2)$$

It is interesting to note that $[Pt(bpm)Cl_2]$ is reduced 0.13 V more positive than $[Ru(bpy)_2(bpm)]^{2+}$. Similarly, $[(bpy)_2Ru(bpm)PtCl_2]^{2+}$ is reduced about 0.1 V more positive than $[(bpy)_2Ru(bpm)Ru(bpy)_2]^{4+}$. The accepted explanation for positive shifts in reduction potentials as one moves from the free ligand, to mononuclear complexes, to binuclear species is related to the interaction of the ligand π^* energy levels with the charged metal ion [5]. The energy lowering is on the order of 0.5 V/positive charge. In the case of ruthenium(II) the $d\pi$ energy levels are of the appropriate energy to backbond with the ligand π^* energy levels destabilizing them and stabilizing the $d\pi$ system [7]. The electrochemical data found for platinum(II) heterocycles suggest that little backbonding occurs between the filled $d\pi$ levels of platinum(II) and the π^* orbitals on the ligands. This is manifested by the more positive ligand reduction potentials and the near constant redox potential for the $Ru^{3+/2+}$ couple in $[(bpy)_2Ru(bpm)PtCl_2]^{2+}$ compared to $[(bpy)_2Ru(bpm)]^{2+}$.

In summary, the $[(bpy)_2Ru(bpm)PtCl_2]^{2+}$ is unique due to the fact that two different metal centers are bridged by a 'bidentate' bridging ligand. The ability to synthesize complexes of this type suggests the possibility of designing molecules with a large number of different metal centers and explor-

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[‡] Measured by K. Goldsby, The University of North Carolina at Chapel Hill, in 0.10 M tetraethylamonium perchlorate-acetonitrile solution at an Ag electrode. The reduction was irreversible.

ing their electronic interactions in a fundamental way and also utilizing such complexes for multielectron transfer catalysis.

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