A Novel Hetero-oligomer Containing One Ruthenium(II) and Three Platinum(II) Metal Centres Bridged by 2,3-Bis(2-pyridyl)quinoxaline

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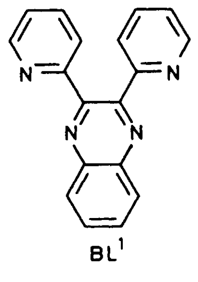
The hetero-oligonuclear complex, $[\mathrm{Ru(BL^1)_3(PtCl_2)_3](PF_6)_2}$, where BL¹ is 2,3-bis(2-pyridyl)quinoxaline, has been synthesized and its properties have been determined by visible–u.v. spectroscopy and electrochemical methods; in the complex, ruthenium(II) acts as the central atom and is bridged to the platinum(II) centres by the BL¹ ligand.

A homo-oligomer complex, $[\mathrm{Ru(BL^1)_3\{Ru(bpy)_2\}_3](PF_6)_8}$, which contains four ruthenium(II) centres, has recently been synthesized in our laboratories. The synthesis was patterned after the one reported by Hunziker and Ludi[1] for the preparation of $[\mathrm{Ru(bpm)_3\{Ru(bpy)_2\}_3](PF_6)_8}$, where bpy is 2,2′-bipyridine and bpm is 2,2′-bipyrimidine. However, in our case, rather than bipyrimidine, we used the bridging ligand 2,3-bis(2-pyridyl)quinoxaline.

As a step forward in our efforts to prepare multielectron transfer agents, we have also prepared the novel hetero-oligonuclear analogue, $[\mathrm{Ru(BL^1)_3(PtCl_2)_3](PF_6)_2}$. The synthesis and visible–u.v. and electrochemical properties of this complex are the focus of this communication.

The preparation was effected in the dark. *cis*-$[\mathrm{Pt(dmso)_2Cl_2}]$[2] (0.4 mmol) (dmso = dimethyl sulphoxide) was added to an $\mathrm{N_2}$-degassed solution containing methanol (100 ml) and $[\mathrm{Ru(BL^1)_3](PF_6)_2}$[3] (0.1 mmol) and the resulting suspension was refluxed for 8 h. After about 1 h, a red solution formed which gradually changed to deep purple. As the solution continued to reflux, a purple solid precipitated. The solution was cooled in a refrigerator for about 6 h and the solid was collected by filtration. It was recrystallized in 73% yield from 1 : 1 acetone–methylene chloride. The elemental analysis, and spectral and electrochemical data strongly support co-ordination of three platinum(II) centres with the remote nitrogen donor atoms of the BL¹ ligands in $\mathrm{Ru(BL^1)_3}^{2+}$, thereby producing the hetero-oligonuclear complex, $[\mathrm{Ru(BL^1)_3(PtCl_2)_3](PF_6)_2{\cdot}3H_2O}$.

The complex is soluble and stable in polar organic solvents. Its visible–u.v. spectrum and electrochemical properties were determined in propylene carbonate. The visible spectrum of $[\mathrm{Ru(BL^1)_3(PtCl_2)_3}]^{2+}$ is compared to spectra for $[\mathrm{Ru(BL^1)_3}]^{2+}$ and $[\mathrm{Ru(BL^1)_3\{Ru(bpy)_2\}_3}]^{8+}$ in Figure 1. The absorption spectrum of $[\mathrm{Ru(BL^1)_3}]^{2+}$ shows a band centred at 502 nm (ε 1.45×10^4 dm³ mol⁻¹ cm⁻¹) that has been assigned as a $d_\pi \rightarrow \pi^*$ (BL¹) transition.[3,4] Upon formation of the oligomer complexes, the absorption maximum shifts to the red. The absorption maximum for $[\mathrm{Ru(BL^1)_3(PtCl_2)_3}]^{2+}$ is located at 553 nm (ε 2.7×10^4); that for $[\mathrm{Ru(BL^1)_3\{Ru(bpy\}_2)_3}]^{8+}$ is centred at 622 nm (ε 4.1×10^4). It is clear from the data that the effect of platinum(II) is similar to that of ruthenium(II). Since ruthenium(II) co-ordinates to both remote nitrogen donors of the BL¹ ligand,[4] it follows that platinum(II) also does.



BL¹

The unique electrochemical feature that substantiates the $[\mathrm{Ru(BL^1)_3(PtCl_2)_3}]^{2+}$ formulation is related to the observed reductions. The free BL¹ ligand is reduced at −1.56 V *vs.* saturated standard calomel electrode (S.S.C.E.).[3] Upon co-ordination to ruthenium(II), it is reduced at a more positive potential. The reductions of $[\mathrm{Ru(BL^1)_3}]^{2+}$, for example, are observed at −0.60, −0.78 and −1.04 V *vs.* S.C.C.E. and were assigned as given in equations (1)—(3).[3]

$$[\mathrm{Ru^{2+}(BL^1)_3}]^{2+} + e^- \leftrightarrows [\mathrm{Ru^{2+}(BL^1)_2}(\overset{-}{\mathrm{BL}^1})] \quad (1)$$

$$[\mathrm{Ru^{2+}(BL^1)_2}(\overset{-}{\mathrm{BL}^1})]^+ + e^- \leftrightarrows [\mathrm{Ru^{2+}(BL^1)}(\overset{-}{\mathrm{BL}^1})(\overset{-}{\mathrm{BL}^1})] \quad (2)$$

$$[\mathrm{Ru^{2+}(BL_1)}(\overset{-}{\mathrm{BL}^1})(\overset{-}{\mathrm{BL}^1})] + e^- \leftrightarrows [\mathrm{Ru^{2+}}(\overset{-}{\mathrm{BL}^1})(\overset{-}{\mathrm{BL}^1})(\overset{-}{\mathrm{BL}^1})]^- \quad (3)$$

In the homonuclear oligomer complex, $[\mathrm{Ru(BL^1)_3\{Ru(bpy)_2\}_3}]^{8+}$, these potentials were shifted to more positive values, *i.e.* −0.27, −0.41, and −0.82 V, respectively, and were further shifted to −0.07, −0.24, and −0.79 V *vs.* S.S.C.E, respectively, for $[\mathrm{Ru(BL^1)_3(PtCl_2)_3}]^{2+}$. The more positive ligand reduction potentials for the platinum(II) complex compared to the ruthenium(II) homonuclear oligomer are related to π backbonding properties, since both metal centres have similar charges and, hence, a similar electrostatic influence on the energy of the ligand π^* level. Apparently, the d_π levels of platinum(II) are too different in energy from the π^* ligand levels to overlap appreciably. Thus the π^* ligand levels remain stabilized in the presence of platinum(II), whereas they are destabilized when co-ordinated to ruthenium(II) by π backbonding of the d_π metal orbitals with the π^* orbitals of the ligands.[5,6]

In summary, $[\mathrm{Ru(BL^1)_3(PtCl_2)_3}]^{2+}$ is a novel hetero-oligonuclear complex derived from two different metal ions

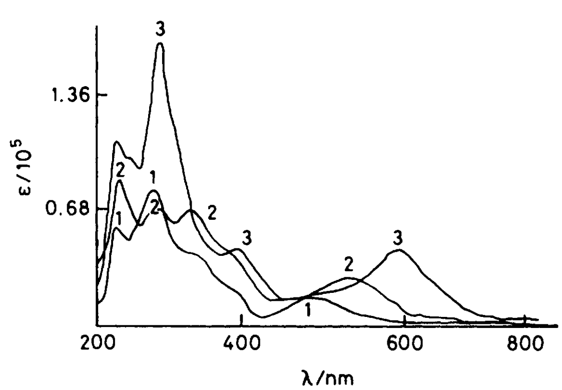


Figure 1. A visible–u.v. spectral comparison of (1) $[\mathrm{Ru(BL^1)_3](PF_6)}$; (2) $[\mathrm{Ru(BL^1)_3(PtCl_2)_3](PF_6)_2}$; and (3) $[\mathrm{Ru(BL^1)_3\{Ru(bpy\}_2)_3](PF_6)_8}$. The spectra were obtained in propylene carbonate with a Perkin-Elmer Lambda Array 3840 spectrophotometer.

incorporated into the same molecule and stabilized by 'bidentate' chelating co-ordination sites. The ability to synthesize complexes of this type suggests the possibility of designing molecules with a large number of different metal centres which may have applications in the study of multielectron transfer catalysis and intramolecular donor–acceptor complexes, where one metal centre is the donor and the other is the acceptor. Platinum(II), for example, is known to undergo oxidative addition reactions with HX producing hydrido species, which may react with hydrogen ions in solution producing H_2 upon photoinitiation at the coupled ruthenium(II) centre. Other likely possibilities involve substrate binding to one of the open co-ordination sites of platinum(II) followed by photoexcitation and transfer of two electrons from a substrate such as an alcohol to platinum resulting in the two electron reduction of platinum and the two electron oxidation of the alcohol to an aldehyde or ketone.

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