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Preparation of Ruthenium(II) Complexes of the Tetradentate Ligand 1,2-Bis(2,2′-bipyridyl-6-yl)ethane (*o*-bpy). Synthons for Trans Metal-to-Ligand Charge Transfer Excited States

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Introduction

The photochemistry of the *cis*-Ru(bpy)$_2{}^{2+}$ moiety has a long history.[1] The preparative chemistry and excited state properties of numerous complexes containing this grouping have been explored and exploited in a variety of contexts, especially those involving the conversion of light to chemical or electrical energy;[2] a promising approach combines oligomeric complexes of the *cis*-Ru(bpy)$_2{}^{2+}$ unit[3] with semiconductor surfaces. These molecular arrays exhibit three unique design features: the ability to act as antenna fragments via directional energy transfer, directional electron transfer along the oligomer, and rapid charge injection into the semiconductor.[3a,d] All are important components for an artificial photosynthetic scheme. Unfortunately the *cis*-Ru(bpy)$_2{}^{2+}$ unit forms a "zigzag" polymer so that exploitation of the directionality of electron or energy transfer cannot be fully realized. Preparations based on *trans*-Ru(chelate)$_2{}^{2+}$ systems should alleviate these problems by allowing the synthesis of linear systems of unlimited extent.

The synthesis of the tetradentate ligand 1,2-bis(2,2′-bipyridyl-6-yl)ethane (*o*-bpy) and the characterization of perchlorate salt of its copper(II) complex have been reported by Rillema, Hatfield, and co-workers.[4] The use of this ligand in the chemistry of ruthenium seemed attractive to us because the tetradentate ligand retains many of the electronic features associated with the presence of two 2,2′-bipyridine (bpy) units while providing the kinetic inertness associated with tetradentate ligands. Moreover, since the ligand is capable of occupying the four sites of a distorted square planar copper(II) complex,[4] the longer metal−ligand bond lengths normally anticipated for a ruthenium(II) complex might allow the ligand to occupy four equatorial sites in a trans-octahedral structure.

We report here the synthesis and excited state properties of various trans ruthenium complexes, all of which are synthons for new complexes containing trans metal-to-ligand charge transfer (MLCT) excited states. These complexes are ideal precursors for trans oligomers where the bridging ligand can be varied. Since trans complexes derived from bpy or phen are relatively rare[5] and are usually unstable relative to their cis analogues, our approach to the synthesis of trans MLCT excited states is to use polydentate or macrocyclic ligands that enforce the trans geometry.

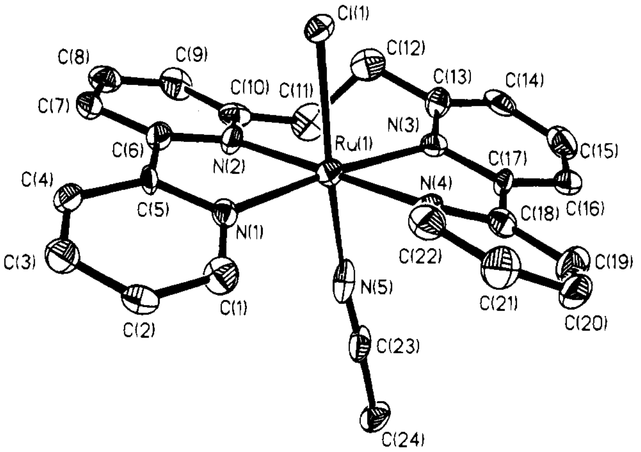

Figure 1. View of the structure of the cation [*trans*-Ru(*o*-bpy)(CH$_3$CN)Cl]$^+$ in the crystals of the hexafluorophosphate salt (**2**).

The syntheses of the Ru(II) complexes involved the direct reaction of the ligand with RuCl$_3$·3H$_2$O at 190 °C to give [*trans*-Ru(*o*-bpy)Cl$_2$]·2H$_2$O (**1**). A 100 mg sample of **1** was treated with acetonitrile and NH$_4$PF$_6$ in ethylene glycol to give the monocationic complex [*trans*-Ru(*o*-bpy)(CH$_3$CN)(Cl)]PF$_6$·0.5CH$_3$CN (**2**) (yield 75%), while another 100 mg portion of **1** was refluxed in acetonitrile followed by treatment with NH$_4$PF$_6$ to give the dicationic complex [*trans*-Ru(*o*-bpy)(CH$_3$CN)$_2$](PF$_6$)$_2$ (**3**) (yield 80%). Reaction of complex **3** with NaCN in hot ethylene glycol leads to [*trans*-Ru(*o*-bpy)(CN)$_2$][7] (**4**) (yield 40%).

The structure of [*trans*-Ru(*o*-bpy)(CH$_3$CN)(Cl)]$^+$ is shown in Figure 1. The cation adopts a six-coordinate geometry with four cis bpy nitrogen atoms [N(1), N(2), N(3), N(4)] and trans chloride and acetonitrile nitrogen atoms [N(5)]. As in the Cu(II) complex, the Ru−N bonds of 2.033(16) and 2.057(17) Å to the "open" side of the ligand [N(1) and N(4), respectively] are shorter than those of 2.113(17) Å to the "closed" side [N(2) and N(3)]. The Ru−N(5) bond length of 1.986(18) Å indicates a very tightly bound acetonitrile unit. The four bpy nitrogen atoms are not rigorously coplanar, the two bpy units being tilted at a dihedral angle of 7.7°. The torsion angles around the nominally single bonds C(10)−C(11) and C(11)−C(12) in the ligand backbone are −70.2 and 118.8°, respectively. The bond angles involving the five-membered chelation, [N(1)−Ru−N(2) and N(3)−Ru−N(4)] are 75.9(7) and 76.9(7)°, respectively, slightly smaller than the value of 81.6(2)° reported for the copper complex.[4]

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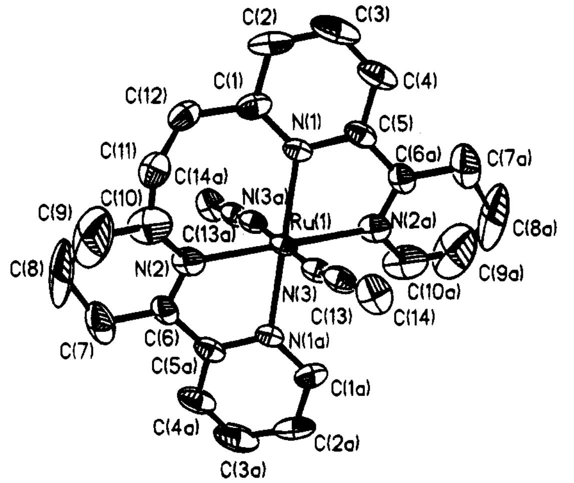

Figure 2. View of the structure of the cation [*trans*-Ru(*o*-bpy)(CH_3-$CN)_2]^{2+}$ in the crystals of the hexafluorophosphate salt (**3**). Only one of the two statically-disordered models is shown (see text).

The structure of the [Ru(*o*-bpy)($CH_3CN)_2]^{2+}$ dication in **3** is depicted in Figure 2, where only one of the two disordered models is shown; the disorder results from the presence of a crystallographic inversion center at Ru. The dication also adopts a six-coordinate geometry, the coordination being provided by the four bpy nitrogen atoms [N(1), N(2), N(1a), N(2a)] and two trans acetonitrile nitrogen atoms [N(3), N(3a)]. The metal–ligand bond lengths Ru—N(1) and Ru—N(2) are 2.090(5) and 2.090(7) Å, respectively, while the metal–acetonitrile distance Ru—N(3) is 2.018(6) Å. In the present complex the *chemically* nonequivalent nitrogen atoms [N(1), N(1a)] are *crystallographically* equivalent donors, so the observed bond lengths do not discriminate between the internal and external nitrogen atoms.

The trans nature of the dicyano complex **4** is proved by infrared spectroscopy, where only a single infrared absorption at 2062 cm^{-1} (assignable to the asymmetric CN stretch) is observed.

All the trans complexes are highly colored and exhibit MLCT transition bands. The MLCT transition maxima (λ_{max}) in CH_2Cl_2: complex **2**, 446 nm; complex **3**, 458 nm; complex **4**, 514 nm, complex **1**, 533 nm (in MeOH). Cyclic voltammetry studies show a quasi-reversible $Ru^{III/II}$ couple at $E_{1/2} = 0.56$ and 0.87 V for complexes **1** and **2**, respectively, a reversible couple at $E_{1/2} = 1.27$ V for complex **3**, and an irreversible couple at 0.75 V for complex **4**. (All potentials are referred to Ag/AgCl). For [*trans*-Ru(*o*-bpy)$(CN)_2$] compared to [*cis*-Ru$(bpy)_2(CN)_2$],[3c] the redox potential is displaced to lower values. This is probably due to both the better electron-donating ability of an alkyl-substituted bpy donor[7] and the inherent electronic difference between the trans and cis geometries.[8] Peaks due to the reduction of the *o*-bpy ligand are also found in the negative potential range.

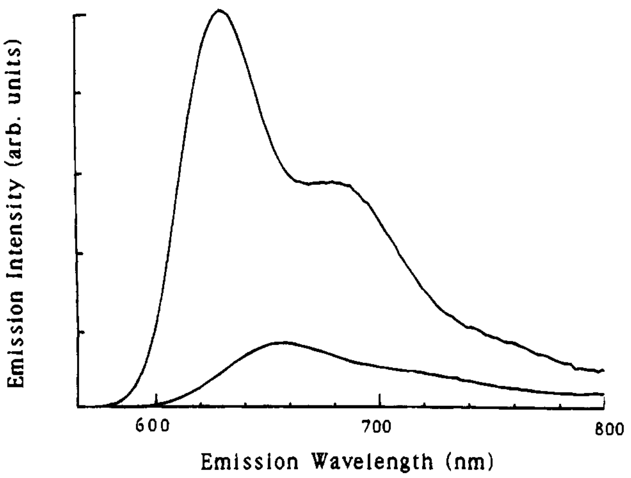

Figure 3. Emission spectra of [*trans*-Ru(*o*-bpy)$(CN)_2$] in a polycarbonate matrix at 77 K (top) and in CH_2Cl_2 solution at 295 K (bottom). Excitation wavelength was 450 nm.

At room temperature complex **4** exhibits a pronounced deep red luminescence (CH_2Cl_2 solution). Figure 3 shows the emission spectrum at room temperature and at 77 K in a polycarbonate matrix. Of note is the structured emission with a vibronic progression (629, 679, 742 nm) having a spacing of 1200 cm^{-1}, a value indicative of the participation of C—C and/or C—N modes.[9] Structure is also discernible in the room-temperature CH_2Cl_2 spectrum. Like [*cis*-Ru$(bpy)_2(CN)_2$], the complex exhibits an emission blue shift upon cooling from room to liquid nitrogen temperature.[3c] The excited state lifetime and quantum yield are $\tau = 0.20$ μs and $\phi = 0.06$ in CH_2Cl_2 (22 °C). These compare with $\tau = 0.24$ (CH_3CN)[3c] and $\tau = 0.54$ ($CHCl_3$) and $\phi = 0.06$ ($CHCl_3$)[10] for [*cis*-Ru$(bpy)_2(CN)_2$] at room temperature.

By selective preparation techniques, *e.g.* controlling the ratio, temperature, and stoichiometry of reaction between [*trans*-Ru-(*o*-bpy)$(CH_3CN)_2]^{2+}$ and [*trans*-Ru(*o*-bpy)$(CN)_2$], oligomers of different compositions and chain lengths should be capable of preparation.

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Supplementary Material Available: Tables of crystallographic experimental details, atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, anisotropic displacement coefficients, and hydrogen atom parameters for complexes **2** and **3** (14 pages). For ordering information, consult any current masthead page. Listings of observed and calculated structure factors for both structures are available from the authors.

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