A Facile One-Step Synthesis of *cis*-Dichlorobis(2,2'-bipyridine)osmium(II)

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Cis-dichlorobis(2,2'-bipyridine)osmium(II) is a useful precursor for synthesizing substituted $(bpy)_2OsL_2^{2+}$ complexes, where L = phosphite, phosphine, or nitrile, and bpy = 2,2'-bipyridine [1]. The reported synthesis of *cis*-$(bpy)_2OsCl_2$, however, involves a two-step procedure starting from either K_2OsCl_6 or $(NH_4)_2OsCl_6$ [2, 3]. In addition, the published procedures require the synthesis of the $(bpy)_2Os^{3+}$ precursor. Recently, interest in the use of $(bpy)_2Ru$ and $(bpy)_2Os$ complexes as catalysts for directed electron transfer has increased [4]. Therefore, a facile synthesis of the most widely used osmium starting material, *cis*-$(bpy)_2OsCl_2$, was sought. Meyer *et al.* have demonstrated that the synthesis and purification of many $(bpy)_2OsL_2^{2+}$ and $(bpy)_2RuL_2^{2+}$ are identical [1, 5]. We have found that the synthesis of *cis*$(bpy)_2OsCl_2$ can be achieved in a single step, in a similar fashion to the synthesis of *cis*-$(bpy)_2RuCl_2$, by refluxing the commercially available $OsCl_3$ in dimethylformamide in the presence of 2,2'-bipyridine.

In a typical reaction, 0.95 g (22.4 mmol) of lithium chloride was dissolved in 25 ml of degassed dimethylformamide with gentle warming. 0.50 g $OsCl_3$ (Aldrich Chemical Co., **CAUTION! HIGHLY TOXIC**) was added to the reaction mixture under nitrogen, followed by addition of 0.53 g (3.40 mmol) of 2,2'-bipyridine (Aldrich Chemical Co.). The reaction mixture was refluxed for two hours whereupon the solution became deep purple-red in color. The solution was then cooled to room temperature, poured into 100 ml of reagent grade acetone, and then cooled to 0 °C whereupon dark mulberry-red crystals precipitated from solution after several hours. The product was isolated by suction filtration and washed thoroughly with deionized water to remove excess lithium chloride. The solid was dried *in vacuo* at room temperature over P_2O_5 for 12 hours in an Abderhalden. Yield was 0.92 g (95%). *Anal.* Calcd. for $C_{20}H_{16}N_4Cl_2Os$: C, 41.88; H, 2.81; N, 9.77. Found: C, 41.71; H, 3.02; N, 9.68%. (Robertson Laboratory, Florham Park, N.J., U.S.A.). A cyclic voltammogram of a 1.2×10^{-3} M solution of the product was recorded in acetonitrile with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte (Bioanalytical Systems CV1-B unit using a Pt disk, Pt wire, and saturated calomel as the working, auxiliary, and reference electrodes, respectively).

A cyclic voltammogram of the isolated osmium complex displayed a reversible wave (ΔE_p = 63 mV, i_{pa}/i_{pc} = 1) at $E_{1/2}$ = –0.063 V *vs.* S.C.E. (Literature value $E_{1/2}$ = –0.061 V *vs.* S.C.E., [7]). The electrochemical results, along with the results obtained from the elemental analysis, demonstrate that we have indeed synthesized *cis*-$(bpy)_2OsCl_2$. The synthetic procedure requires a shorter reaction period than is necessary for the preparation of the analogous ruthenium complex [6]. Dimethylformamide not only serves as an excellent solvent for the dissolution of the starting material, $OsCl_3$, but it also reduces Os^{3+} to Os^{2+} [2]. Addition of the lithium chloride first to the dimethylformamide solution precludes the formation of the 'tris' complex, $(bpy)_3Os^{2+}$. Although the yield (95%) in this reaction is slightly smaller than the quantitative yield reported by Sargeson *et al.*, [2], the one-step synthesis reported herein provides a quick and efficient method for the preparation of a useful coordination compound.

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