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Characterization of the Chromium(III) Product from the Reaction Between $CrCl_2$ and 2,2'-Bipyridine Under Slow Oxidation

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Transition metal polypyridyl complexes have recently been investigated intensively as potential photosensitizers in photochemical systems for the conversion and storage of solar energy. Much of the work has been fully and critically reviewed [1, 2]. Of particular interest, chromium(III) polypyridyl complexes have provided the photochemist with some interesting insights into excited state behaviour [3] and solution medium effects on the photophysics of excited states [4]. Many such studies have utilized the bright yellow $[Cr(bpy)_3](ClO_4)_3\cdot\frac{1}{2}H_2O$ compound, normally prepared [5] by addition of an oxygen-free, perchloric acid solution of Cr^{2+}_{aq} to a deoxygenated aqueous suspension of 2,2'-bipyridine (bpy). The resulting black suspension of $[Cr(bpy)_3](ClO_4)_2$ is then oxidized until the black solid becomes yellow. However, depending on the experimental conditions, a pink product is obtained that we have often taken to be $Cr(bpy)_2(H_2O)_2^{3+}$.

Related to our findings, Waind and Murray [6] have noted that oxidation of $Cr(bpy)_3^{2+}$ with $Co(NH_3)_6^{3+}$ produces $Cr(bpy)_2(H_2O)_2^{3+}$ or its conjugate bases. Inskeep and Bjerrum [7] have directly synthesized this diaquo species; visible absorption spectra showed bands at ~490 nm (E ~ 40) which upon addition of base red-shifts to ~520 nm (ϵ ~ 40). Slow oxidation (1 hr) of the $Cr(bpy)_3^{2+}$ black suspension by molecular oxygen also forms $Cr(bpy)_2(H_2O)_2^{3+}$ as a side product [5], often reaching 20–30% of total yield [8]. Lee and co-workers [9] have closely investigated the effects of the rate of oxidation of the related $Cr(phen)_3^{2+}$ (phen = 1,10-phenanthroline) by various oxidants (iodine, chlorine, bromine, potassium dichromate, and 30% hydrogen peroxide) and have demonstrated that the preparation of the $Cr^{III}(phen)_3^{3+}$ complex is very sensitive to the mode of oxidation. For example, dropwise addition of an ethanolic solution of iodine to the chromium(II) complex yields little or none of $Cr(phen)_3^{3+}$; rapid addition of iodine in excess, however, leads to good yields [9] of this complex. Apparently, during slow oxidation, the labile $Cr(phen)_3^{2+}$ forms $Cr(phen)_2(H_2O)_2^{2+}$ which then catalyzes the hydrolysis of $Cr(phen)_3^{3+}$ by means of a rapid electron transfer reaction [5, 9]. Interestingly, $Cr(bpy)_3^{3+}$, $Cr(phen)_3^{3+}$, and their substituted derivatives thermally [10, 11] and photochemically [12, 13] aquate in aqueous solution to yield the diaquo or dihydroxo species, depending on pH; also, aquation is hydroxide ion catalyzed in basic solutions [11]. No evidence for the involvement of a chromium(II) species has been found in aqueous solutions [10, 11] (contrast with the photosolvolysis in DMF media where such an intermediate has been implicated [14]).

As part of our systematic studies into the nature and behaviour of transition metal polypyridyl complexes, we have characterized the pink product originating from the reaction between the blue $CrCl_2$ and 2,2'-bipyridine. Here we wish to present our preliminary findings of an X-ray structural, and spectroscopic study.

The compound was obtained as the perchlorate salt from the reaction between chromous chloride and 2,2'-bipyridine under conditions in which the Cr(II) product was slowly oxidized. All materials were of reagent grade quality. A crystal with dimensions 0.5 × 0.4 × 0.3 mm was chosen for the X-ray studies: space group $P\bar{1}$; $a = 8.723(4)$, $b = 11.371(4)$, $c = 13.876(7)$ Å, $\alpha = 84.58(4)$, $\beta = 81.30(4)$, $\gamma = 108.28(3)^\circ$; Z = 2 for $[Cr(bpy)_2(H_2O)Cl](ClO_4)_2\cdot 2H_2O$; $D_c = 1.69$ g cm^{-3}, $D_m = 1.67$ g cm^{-3} (by flotation); 3319 reflections were collected of which 2509 reflections with $I > 3\sigma(I)$ were used to solve the structure by statistical methods and Fourier techniques. Block-diagonal matrix, least-squares refinement of all non-hydrogen atoms with anisotropic thermal parameters, and of all aromatic hydrogen atoms with isotropic thermal parameters reduced the final discrepancy index to 5.8%.

The structure of the $[Cr(bpy)_2(H_2O)Cl]^{2+}$ cation is illustrated in Fig. 1; the two water molecules and the ClO_4^- anions have been omitted for clarity. The molecular geometry about chromium consists of two N-chelated bipyridyl ligands, and a Cl group and a H_2O molecule in a *cis* position. The cation is *not* the expected, and long assumed diaquo species. The chromium–nitrogen [N(1), N(3), N(4)] distances are 2.037 ± 0.005 Å, except the Cr–N(2) distance in the bond *trans* to the Cl group which is slightly longer at 2.059(5) Å. This probably arises from a small *trans* influence by the Cl [15]. The Cr–Cl and Cr–O(9) (water) bond distances are 2.259(2) and 1.975(4) Å,

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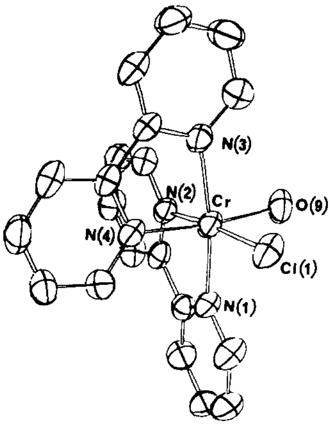

Fig. 1. Geometry of the *cis*-$[Cr(bpy)_2(H_2O)Cl]^{2+}$ cation.

respectively; C–N distances are 1.34 ± 0.01 Å and C–C distances are 1.37 ± 0.03 Å. Intraligand N–Cr–N bond angles are 79.0(2) and 79.6(2)°, comparable to the corresponding angles found in $Cu(bpy)_3^{2+}$ [16]. The two water molecules are hydrogen bonded to the bound water [17]; O(9)–O(water) distances are 2.67 and 2.64 Å. There are six ClO_4^- units about the $[Cr(bpy)_2(H_2O)Cl]^{2+}$ cation within 3.3 Å of a non-hydrogen atom. One of these has oxygens wedged in the pocket defined by the two bpy ligands, reminiscent of ion pairs in the solid state [18].

The visible absorption spectrum ($\lambda > 450$ nm) of $[Cr(bpy)_2(OH)Cl]^+$ in basic (0.01 *M* OH^-) aqueous solutions reveals a broad band at 550 nm ($\epsilon = 65$) which sharpens and blue-shifts to 520 nm ($\epsilon = 56$) in acid media (0.01 *M* HCl) for $[Cr(bpy)_2(H_2O)Cl]^{2+}$. By comparison, the $[Cr(bpy)_2(OH)_2]^+$ complex has the corresponding band at 518 nm ($\epsilon = 49$) and $[Cr(bpy)_2(H_2O)_2]^{3+}$ at 492 nm ($\epsilon = 48$) [10]. Our spectral observations for the chloroaquo complex are consistent with expectations since Cl affords a weaker ligand field than either H_2O or OH^- and thus d–d transitions occur at lower energies. As a further verification that the product from the reaction is the chloroaquo and not the diaquo complex, we determined the pK_a. The potentiometric titration of the compound in 1.0 *M* $NaNO_3$ solution gives a curve typical of a monobasic acid with a $pK_a = 4.6$ (error ~ 0.2). We also verified, by the same procedure, the pK's of $[Cr(phen)_2(H_2O)_2]^{3+}$ [19]; we find $pK_1 = 3.0$ and $pK_2 = 6.0$ (error ~ 0.2) in 1.0 *M* $NaNO_3$ solution in good agreement with 3.5 and 6.1 reported by Inskeep and Bjerrum [7] in 0.1 *M* $NaNO_3$ solution.

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