Isolation, Structure, Chemistry, and Photochemistry of cis-Bis(2,2'-bipyridyl)carbonylchlororuthenium(II) Perchlorate

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Summary The molecular structure and chemical and photochemical reactions of [Ru(bpy)₂(CO)Cl]⁺ClO₄⁻, which has been isolated from the reaction of ruthenium trichloride and 2,2'-bipyridyl(bpy) in dimethylformamide, are described.

THERE is at present great interest in the chemistry of 2,2'-bipyridyl (bpy) complexes of ruthenium, in part because their electrochemical and photochemical properties make them attractive candidates as catalysts and solar energy converters. We now report a new and unexpected synthesis and full structural and spectroscopic characterisation of [Ru(bpy)₂(CO)Cl]⁺ClO₄⁻ (I). This compound has chemical and photochemical reactivity which we show makes it a versatile reagent for preparing bis(bipyridyl)-ruthenium(II) complexes; current synthetic methods for most Ru(bpy)₂ complexes employ Ru(bpy)₂Cl₂.2H₂O as starting material.

We have prepared Ru(bpy)₂Cl₂.2H₂O, for our studies of polyvinylpyridine-bound ruthenium complexes,¹ by the convenient method reported by the North Carolina group.²,³ In this procedure commercial ruthenium trichloride is allowed to react with two moles of 2,2'-bipyridyl in refluxing dimethylformamide, most of the solvent is then removed by distillation, and the crude Ru(bpy)₂Cl₂ is precipitated by addition of acetone. The yields obtained by us and by the original authors⁴,⁵ lie in the range 60—70%. We now report that if sodium perchlorate is added to the mother
liquor remaining after the removal of Ru(bpy)$_3$Cl$_2$, then the complex cis-[Ru(bpy)$_2$(CO)Cl]ClO$_4$ may be isolated in 30—40% yield based on the ruthenium trichloride starting material. Although this complex had previously been isolated in low yield from the reaction of [RuCl$_2$(CO)-(norbornadiene)]$^-$ with 2,2'-bipyridyl,$^4$ no report of its spectroscopic and chemical properties has been published to the best of our knowledge.

The complex [Ru(bpy)$_2$(CO)Cl]ClO$_4$ (I), isolated as mentioned above, was purified by column chromatography on neutral alumina using 1:1 benzene-acetonitrile as eluant and recrystallised from benzene-acetonitrile as air-stable yellow crystals. The structure of the complex, surmised from elemental and spectroscopic analysis,$^6$ was confirmed by X-ray crystallography.$^7$ (Figure). It consists of discrete [Ru(bpy)$_2$(CO)Cl]$^+$ cations and ClO$_4^-$ anions. The geometry of the cation is normal, with the expected cis geometry of the bipyridyl rings. The Ru—N distance trans to the CO group is at 2-18(2) Å, slightly longer than those trans to N [mean value 2-10(2) Å] (cf. Ru(bpy)$_3$)$_2$, 2-056(4) Å,$^8$ [(bpy)$_2$(NO)$_2$Ru$^{III}$-O-Ru$^{III}$(NO)$_2$(bpy)$_2$]$^{2+}$, 2-08$(2)$ Å$^8$ and to Cl 2-07(1) Å, in accordance with the expected trans influence order CO>N$_{bpy}$>Cl. The C—O distance of 1-12(3) Å and Ru—C—O angle of 175(3)$^o$ are close to previously recorded values.$^7$

![Figure](link)

**Figure.** The structure of (I). Bond distances to the Ru atom are: N(1) 2-097(12), N(2) 2-066(10), N(3) 2-177(16), N(4) 2-104(15), Cl(I) 2-396(7), and C(21) 1-861(29) Å. C(21)—O(1) 1-129(22) Å, Ru—C(21) (1-174 5(2)-8). A

Discrete cis-[Ru(bpy)$_2$(CO)Cl]$^+$ cations and ClO$_4^-$ anions. The structure of the cation is normal, with the expected cis geometry of the bipyridyl rings. The Ru—N distance trans to the CO group is at 2-18(2) Å, slightly longer than those trans to N [mean value 2-10(2) Å] (cf. Ru(bpy)$_3$)$_2$, 2-056(4) Å,$^8$ [(bpy)$_2$(NO)$_2$Ru$^{III}$-O-Ru$^{III}$(NO)$_2$(bpy)$_2$]$^{2+}$, 2-08$(2)$ Å$^8$ and to Cl 2-07(1) Å, in accordance with the expected trans influence order CO>N$_{bpy}$>Cl. The C—O distance of 1-12(3) Å and Ru—C—O angle of 175(3)$^o$ are close to previously recorded values.$^7$

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† I.r. (Nujol) δ 1631 cm$^{-1}$. 1H N.m.r. multiplets in range δ 7-4-7-3, 16 inequiv. protons.

‡ Crystal data: C$_{18}$H$_{16}$Cl$_2$N$_4$O$_2$Ru, $M$ = 576-308, monoclinic, space group $C_{2h}$, $a$ = 31-77, $b$ = 11-13, $c$ = 7-24 Å, $β$ = 96°-6', $Z$ = 4, $D_x$ = 1-624 g cm$^{-3}$, $D_c$ = 1-504 g cm$^{-3}$, $\mu$(Mo-K$_\alpha$) = 7-72 cm$^{-1}$. Data were collected on a Stoe 2-circle diffractometer on a crystal mounted in a capillary in the presence of benzene-acetonitrile vapour. The structure was solved by heavy-atom methods using 2442 unique observations and refined by full-matrix least squares to $R$ = 11-7% using anisotropic temperature factors for Ru, Cl(1), and Cl(2) only. At the current stage of refinement the bipyridyl rings are treated as rigid groups, and the perchlorate group is poorly resolved with high thermal motion of the oxygen atoms. The programmes SHEX and XANADU were used for all calculations. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ The photo-induced reactions of (I) in solutions containing 2,2'-bipyridyl were investigated spectrophotometrically. In non-coordinating solvents such as nitromethane and nitropropane the product observed was [Ru(bpy)$_2$(CO)]$^{3+}$; in co-ordinating solvents such as acetonitrile or pyridine the product was the corresponding [Ru(bpy)$_2$(Cl solvent)]$^{3+}$ and in water or methanol [Ru(bpy)$_2$(Cl solvent)]$^{3+}$ was initially formed but then reacted slowly to give [Ru(bpy)$_2$(CO)]$^{3+}$. Were [Ru(bpy)$_2$(η$^5$-py)$_2$(Cl)]$^{3+}$ sufficiently stable to be formed under the conditions reported in ref. 8, it should have been possible to isolate it under the mild conditions employed above. These present observations support other findings (ref. 9) that the photolysis of [Ru(bpy)$_2$(CO)]$^{3+}$ in hydrochloric acid yields [Ru(bpy)$_2$(H$_2$O)Cl]$^{3+}$ and not [Ru(bpy)$_2$(η$^5$-py)$_2$(Cl)]$^{3+}$.