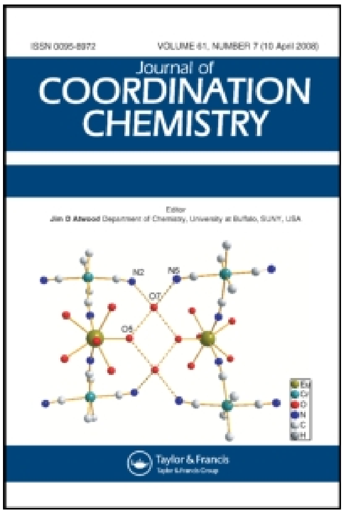

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# THE PREPARATION AND CHARACTERISATION OF SALTS OF *cis*-BIS(2,2'-BIPYRIDINE)-CHLORO(DIMETHYLSULFOXIDE)-RUTHENIUM(II) AND THE CRYSTAL STRUCTURE OF THE PERCHLORATE DIHYDRATE. PRECURSORS FOR DNA-BINDING RUTHENIUM(II) COMPLEXES

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# THE PREPARATION AND CHARACTERISATION OF SALTS OF *cis*-BIS(2,2′-BIPYRIDINE)-CHLORO(DIMETHYLSULFOXIDE)-RUTHENIUM(II) AND THE CRYSTAL STRUCTURE OF THE PERCHLORATE DIHYDRATE. PRECURSORS FOR DNA-BINDING RUTHENIUM(II) COMPLEXES

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The preparation and characterisation of salts of the complex cation *cis*-bis(2,2′-bipyridine)-chloro(dimethylsulfoxide-*S*)ruthenium(II), $[Ru(bpy)_2Cl(dmso)]^+$, is reported. The complex was prepared by the reaction of 2,2′-bipyridine with $RuCl_3 \cdot 3H_2O$ in dimethylsulfoxide. The value of this complex arises from its ability to react with suitable bidentate ligands particularly those that could act as DNA intercalators. The structure of $[Ru(bpy)_2Cl(dmso)][ClO_4] \cdot 2H_2O$ has been determined by single crystal X-ray diffraction. The complex crystallises in space group $P\bar{1}$ with $a = 8.205(3)$, $b = 10.448(4)$, $c = 16.769(6)$ Å; $\alpha = 78.99(3)°$, $\beta = 77.47(3)°$, $\gamma = 72.20(3)°$, $Z = 2$. The structure was refined by least-squares methods using 4070 observed reflections with 196 variable parameters (final $R = 0.039$).

*Keywords:* Ruthenium(II) complexes; bipyridine; dimethylsulfoxide; X-ray structure

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[*] Corresponding author.

## INTRODUCTION

Ruthenium(II) complexes containing *N*-heterocyclic ligands have been extensively studied because of their photophysical properties.[1] Much recent research has investigated the DNA-binding capacity of ruthenium(II) complexes incorporating large planar ligands.[2] Developing synthetic methods to obtain ruthenium(II) complexes containing *N*-heterocyclic ligands has become the subject of intense interest recently.

The complex $[Ru(bpy)_2Cl(dmso)]^+$ was first reported in an NMR study of $[Ru(bpy)_2Cl_2]$ in dimethylsulfoxide.[3] This complex has been found to be a superior starting material to $[Ru(bpy)_2Cl_2]$ for the preparation of complexes of the formula $[Ru(bpy)_2L]$, where L is a bidentate $\alpha$-diimine ligand.[4] In this paper, we report the preparation of $[Ru(bpy)_2Cl(dmso)]Cl$, $[Ru(bpy)_2Cl(dmso)][PF_6]\cdot H_2O$ and $[Ru(bpy)_2Cl(dmso)][ClO_4]\cdot 2H_2O$. The crystal structure of $[Ru(bpy)_2Cl(dmso)][ClO_4]\cdot 2H_2O$ has been determined by X-ray diffraction methods. The structure determination confirms that the dimethylsulfoxide molecule is *S*-bound to the ruthenium centre and that the chloro and dmso ligands are *cis* to each other.

## EXPERIMENTAL

2,2′-Bipyridine and $RuCl_3\cdot 3H_2O$ were purchased from Sigma-Aldrich Chemical Company. $^1H$ NMR spectra of the complexes **1** and **2** were recorded on a Varian 400 XL instrument and electrospray mass spectra were obtained on a Fisons Quattro-II triple-quadrupole mass spectrometer. The electrospray mass spectrum for compound **3** was obtained on a Perkin-Elmer SCIEX API 365 LC MS instrument. Elemental analyses were determined in the Microanalytical Laboratory of the School of Chemistry, University of New South Wales.

### Synthesis of *cis*-$[Ru(bpy)_2Cl(dmso\text{-}S)]Cl$ (1), *cis*-$[Ru(bpy)_2Cl(dmso\text{-}S)][PF_6]\cdot H_2O$ (2) and *cis*-$[Ru(bpy)_2Cl(dmso\text{-}S)][ClO_4]\cdot 2H_2O$ (3)

2,2′-Bipyridine (1.55 g, 10 mmol) was added to a solution of $RuCl_3\cdot 3H_2O$ (1.30 g, 5 mmol) in hot dimethylsulfoxide (60 ml, 80°C). The dark red solution was stirred whilst the temperature was maintained at 80–90°C for 15 min. The solution was allowed to cool and then filtered. The filtrate was evaporated on a hotplate to 10 ml while nitrogen was blown through the solution. The solution was cooled and poured into acetone (50 ml). After several days, the red crystals that formed were filtered off, washed with cold acetone and air dried to give the complex **1**. Yield: 0.33 g (12.3%). $^1$H NMR of the complex **1** in dmso-$d_6$: $\delta$ 10.04 (d, 1H, $J = 6.1$ Hz), 9.54 (d, 1H, $J = 6.1$ Hz), 8.85 (d, 1H, $J = 8.1$ Hz), 8.75 (d, 1H, $J = 8.5$ Hz), 8.69 (m, 2H), 8.39 (t, 1H, $J = 7.9$ Hz), 8.24 (t, 1H, $J = 7.8$ Hz), 8.05 (m, 2H), 7.97 (t, 1H, $J = 6.4$ Hz), 7.86 (t, 1H, $J = 6.4$ Hz), 7.82 (d, 1H, $J = 5.7$ Hz), 7.4 (m, 2H), 7.18 (d, 1H, $J = 6.0$ Hz), 3.17 (s, 3H), 2.14 (s, 3H). MS: 527 $[Ru(bpy)_2Cl(dmso)]^+$, 60%; 492 $[Ru(bpy)_2(dmso)]^+$, 33%; 481 $[Ru(bpy)_2Cl(CH_3OH)]^+$, 59%; 449 $[Ru(bpy)_2Cl]^+$, 100%. A solution of potassium hexafluorophosphate (5% in water) was added to the filtrate remaining after the isolation of complex **1** to precipitate the hexafluorophosphate salt. The red crystals which formed were filtered off, washed with acetone and air-dried to give complex **2**. Yield: 2.0 g (63%). *Anal.* Found: C, 38.8; H, 3.6; N, 7.9. Calcd. for $C_{22}H_{24}ClF_6N_4O_2PRuS$(%): C, 38.3; H, 3.5; N, 8.1. $^1$H NMR of the complex **2** (dmso-$d_6$): $\delta$ 10.03 (d, 1H, $J = 6.4$ Hz), 9.54 (d, 1H, $J = 6.4$ Hz), 8.82 (d, 1H, $J = 8.4$ Hz), 8.75 (d, 1H, $J = 8.4$ Hz), 8.70 (d, 1H, $J = 8.4$ Hz), 8.66 (d, 1H, $J = 8.4$ Hz), 8.39 (t, 1H, $J = 7.9$ Hz), 8.25 (t, 1H, $J = 7.9$ Hz), 8.08 (t, 1H, $J = 8.0$ Hz), 8.02 (t, 1H, $J = 8.1$ Hz), 7.97 (t, 1H, $J = 6.5$ Hz), 7.86 (t, 1H, $J = 6.5$ Hz), 7.81 (d, 1H, $J = 5.6$ Hz), 7.40 (m, 2H), 7.17 (d, 1H, $J = 5.6$ Hz), 3.17 (s, 3H), 2.14 (s, 3H). Complex **3** was isolated by addition of saturated aqueous sodium perchlorate solution to the solution remaining after the precipitation of complex **1**. MS: 527 $[Ru(bpy)_2Cl(dmso)]^+$, 15%; 492 $[Ru(bpy)_2(dmso)]^+$, 4%; 481 $[Ru(bpy)_2Cl(CH_3OH)]^+$, 100%; 449 $[Ru(bpy)_2Cl]^+$, 72%.

## Crystal Data, Data Collection, Solution and Refinement of the Structures

Crystal data and some details concerning data collection and solution and refinement of the structure are given in Table I. Reflexion data were measured with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using graphite-monochromatised molybdenum radiation ($\lambda = 0.7107$ Å). Data were corrected for absorption using the analytical method of de Meulenaer and Tompa.[5] Reflexions with $I > 3\sigma(I)$ were considered observed. The structure was determined by direct phasing and Fourier methods. Hydrogen atoms were included in calculated positions and were assigned thermal parameters equal to those of the atom to which they were bonded. Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined using full-matrix least-square methods. The perchlorate anion is disordered

TABLE I Crystal data, structure solution and refinement details for the complex

| | |
|---|---|
| Complex | $[Ru(bpy)_2Cl(dmso)][ClO_4]\cdot 2H_2O$ |
| Formula | $C_{22}H_{26}Cl_2N_4O_7RuS$ |
| Molecular weight | 662.5 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$ (Å) | 8.205(3) |
| $b$ (Å) | 10.448(4) |
| $c$ (Å) | 16.769(6) |
| $\alpha$ (°) | 78.99(3) |
| $\beta$ (°) | 77.47(3) |
| $\gamma$ (°) | 72.20(3) |
| $V$ (Å$^3$) | 1324.0(9) |
| $D_c$ (g cm$^{-3}$) | 1.66 |
| $Z$ | 2 |
| $\mu$ (cm$^{-1}$) | 9.06 |
| Radiation | MoK$\alpha$ |
| Wavelength (Å) | 0.7107 |
| Temperature (°C) | 21 |
| Crystal dimensions (mm) | 0.24 × 0.20 × 0.18 |
| Scan mode | $\theta/2\theta$ |
| $2\theta$ max (°) | 50 |
| Unique reflections | 4646 |
| Observed reflections ($I > 3\sigma(I)$) | 4070 |
| $R_{merge}$ for equivalent reflections | 0.015 |
| Transmission factors (min, max) | 0.82, 0.87 |
| $R$ | 0.039 |
| $R_w$ | 0.058 |
| Colour | Orange |
| Crystal habit | Prisms |

and the three orientations have been modelled as objects of $T_d$ symmetry, with refinable Cl–O bond lengths, with rigid-body (TLX) thermal parameters. The occupancies of the three orientations are 0.47(2), 0.25(2) and 0.28(2) for the fragments designated in the atom labelling scheme $ClO_4$, $ClO_4'$ and $ClO_4''$, respectively. Reflexion weights used were $1/[\sigma^2(F_o) + 0.0016(F_o)^2]$. The weighted residual is defined as $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography.[6] Structure solution was by SIR92[7] and refinement used RAELS.[8] ORTEP-II[9] running on a Macintosh IIcx was used for the structural diagrams and a DEC Alpha-AXP workstation was used for all calculations.

Atomic coordinates are given in Table II. Bond lengths and selected bond angles are given in Tables III and IV, respectively. Material available from the authors upon request comprises further bond angles, torsion angles, thermal parameters and observed and calculated structure factors.

TABLE II Non-hydrogen atomic parameters for $[Ru(bpy)_2Cl(dmso)][ClO_4] \cdot 2H_2O$, and equivalent isotropic thermal parameter

| *Atom* | *x/a* | *y/b* | *z/c* | $U_{eq}$ |
|---|---|---|---|---|
| Ru | 0.39002(3) | 0.33171(3) | 0.29379(2) | 0.0350(1) |
| N1A | 0.5090(4) | 0.4535(3) | 0.3321(2) | 0.0409(5) |
| N2A | 0.5564(4) | 0.1915(3) | 0.3673(2) | 0.0405(5) |
| C1A | 0.4932(6) | 0.5872(4) | 0.3077(3) | 0.0521(7) |
| C2A | 0.5692(7) | 0.6583(5) | 0.3406(3) | 0.067(1) |
| C3A | 0.6640(7) | 0.5979(5) | 0.4002(3) | 0.068(1) |
| C4A | 0.6844(6) | 0.4596(5) | 0.4268(3) | 0.0562(7) |
| C5A | 0.6071(5) | 0.3915(4) | 0.3913(2) | 0.0442(5) |
| C6A | 0.6332(5) | 0.2439(4) | 0.4109(2) | 0.0439(5) |
| C7A | 0.7366(6) | 0.1620(5) | 0.4673(3) | 0.0554(7) |
| C8A | 0.7651(6) | 0.0239(5) | 0.4759(3) | 0.066(1) |
| C9A | 0.6932(6) | −0.0299(4) | 0.4306(3) | 0.065(1) |
| C10A | 0.5871(5) | 0.0561(4) | 0.3765(3) | 0.0508(6) |
| N1B | 0.3051(4) | 0.1844(3) | 0.2618(2) | 0.0432(4) |
| N2B | 0.5691(4) | 0.2775(3) | 0.1923(2) | 0.0412(4) |
| C1B | 0.1658(6) | 0.1420(4) | 0.3023(3) | 0.0555(4) |
| C2B | 0.1245(7) | 0.0361(5) | 0.2781(3) | 0.0747(5) |
| C3B | 0.2295(8) | −0.0273(5) | 0.2128(3) | 0.0778(5) |
| C4B | 0.3703(7) | 0.0177(5) | 0.1709(3) | 0.0632(5) |
| C5B | 0.4059(5) | 0.1229(4) | 0.1966(2) | 0.0476(4) |
| C6B | 0.5561(5) | 0.1759(4) | 0.1584(2) | 0.0457(4) |
| C7B | 0.6745(6) | 0.1264(5) | 0.0907(3) | 0.0581(6) |
| C8B | 0.8110(6) | 0.1829(5) | 0.0580(3) | 0.0683(9) |
| C9B | 0.8249(6) | 0.2872(5) | 0.0934(3) | 0.0666(8) |
| C10B | 0.7025(5) | 0.3325(4) | 0.1587(2) | 0.0518(5) |
| C1 | 0.1708(1) | 0.3688(1) | 0.4174(1) | 0.0469(2) |
| SDM | 0.2076(1) | 0.4984(1) | 0.2224(1) | 0.045(3) |
| ODM | 0.1492(5) | 0.6344(3) | 0.2496(2) | 0.071(4) |
| C1DM | 0.0159(6) | 0.4563(5) | 0.2190(4) | 0.077(5) |
| C2DM | 0.2866(8) | 0.5266(6) | 0.1150(3) | 0.083(5) |
| C1 | 0.7253(7) | 0.7273(5) | 0.0590(3) | 0.054(4) |
| O1 | 0.8056(13) | 0.6259(9) | 0.0091(7) | 0.140(7) |
| O2 | 0.6286(12) | 0.8399(8) | 0.0141(6) | 0.146(7) |
| O3 | 0.8507(11) | 0.7634(11) | 0.0868(7) | 0.129(3) |
| O4 | 0.6161(15) | 0.6801(10) | 0.1261(5) | 0.144(6) |
| C1′ | 0.7103(14) | 0.7172(10) | 0.0557(6) | 0.060(4) |
| O1′ | 0.7446(24) | 0.8352(14) | 0.0110(10) | 0.114(6) |
| O2′ | 0.8571(23) | 0.6084(15) | 0.0432(13) | 0.146(8) |
| O3′ | 0.5734(23) | 0.6940(24) | 0.0296(13) | 0.197(7) |
| O4′ | 0.6659(27) | 0.7310(17) | 0.1391(6) | 0.124(4) |
| C1″ | 0.7169(12) | 0.7246(9) | 0.0449(6) | 0.060(4) |
| O1″ | 0.7317(27) | 0.7427(23) | −0.0404(6) | 0.190(7) |
| O2″ | 0.7994(24) | 0.5907(10) | 0.0719(13) | 0.164(9) |
| O3″ | 0.5424(14) | 0.7545(19) | 0.0805(13) | 0.134(6) |
| O4″ | 0.7942(19) | 0.8103(17) | 0.0675(11) | 0.095(4) |
| OW1 | 0.0690(5) | 0.7254(3) | 0.4095(2) | 0.078(1) |
| OW2 | −0.1673(7) | 0.8620(4) | 0.2391(3) | 0.118(2) |

TABLE III Bond lengths for $[\mathrm{Ru(bpy)_2Cl(dmso)}][\mathrm{ClO_4}]\cdot 2\mathrm{H_2O}$

| *(a) Coordination sphere* | | | |
|---|---|---|---|
| Bond | | Bond | |
| Ru–N1A | 2.080(3) | Ru–N2B | 2.037(3) |
| Ru–N2A | 2.085(3) | Ru–Cl | 2.438(1) |
| Ru–N1B | 2.068(3) | Ru–SDM | 2.257(1) |
| *(b) Bipyridine ligands* | | | |
| Bond | Ligand A | Ligand B | |
| N1–C1 | 1.353(5) | 1.349(5) | |
| N1–C5 | 1.355(5) | 1.358(5) | |
| N2–C6 | 1.340(5) | 1.337(5) | |
| N2–C10 | 1.343(5) | 1.356(5) | |
| C1–C2 | 1.355(6) | 1.400(6) | |
| C2–C3 | 1.341(7) | 1.378(7) | |
| C3–C4 | 1.398(6) | 1.379(7) | |
| C4–C5 | 1.366(5) | 1.383(5) | |
| C5–C6 | 1.471(5) | 1.475(5) | |
| C6–C7 | 1.394(5) | 1.391(6) | |
| C7–C8 | 1.373(6) | 1.385(7) | |
| C8–C9 | 1.343(7) | 1.381(7) | |
| C9–C10 | 1.394(6) | 1.364(6) | |
| *(c) Dimethylsulfoxide ligand* | | | |
| Bond | | Bond | |
| SDM–ODM | 1.482(3) | SDM–C2DM | 1.778(5) |
| SDM–C1DM | 1.772(5) | | |

TABLE IV Bond angles (°) for $[\mathrm{Ru(bpy)_2Cl(dmso)}][\mathrm{ClO_4}]\cdot 2\mathrm{H_2O}$

| *(a) Coordination sphere* | | | |
|---|---|---|---|
| N1A–Ru–N2A | 77.7(1) | N2A–Ru–SDM | 174.4(1) |
| N1A–Ru–N1B | 170.5(1) | N1B–Ru–N2B | 78.6(1) |
| N1A–Ru–N2B | 98.4(1) | N1B–Ru–Cl | 95.0(1) |
| N1A–Ru–Cl | 87.5(1) | N1B–Ru–SDM | 91.6(1) |
| N1A–Ru–SDM | 97.5(1) | N2B–Ru–Cl | 172.9(1) |
| N2A–Ru–N1B | 93.3(1) | N2B–Ru–SDM | 94.7(1) |
| N2A–Ru–N2B | 89.0(1) | Cl–Ru–SDM | 88.5(0) |
| N2A–Ru–Cl | 88.4(1) | | |
| *(b) Angles related to the chelate rings* | | | |
| | Ligand A | Ligand B | |
| Ru–N1–C1 | 127.7(3) | 125.6(3) | |
| Ru–N1–C5 | 115.3(2) | 115.4(2) | |
| Ru–N2–C10 | 125.8(3) | 125.4(3) | |
| Ru–N2–C6 | 115.8(2) | 116.6(2) | |
| C1–N1–C5 | 116.9(3) | 119.0(3) | |
| C6–N2–C10 | 118.4(3) | 117.9(3) | |
| N1–C5–C4 | 122.4(4) | 121.8(4) | |
| N1–C5–C6 | 115.1(3) | 114.1(3) | |
| N2–C6–C5 | 115.0(3) | 115.2(3) | |
| N2–C6–C7 | 121.5(4) | 122.0(4) | |
| C4–C5–C6 | 122.4(4) | 124.0(4) | |
| C5–C6–C7 | 123.4(4) | 122.8(4) | |
| *(c) Angles related to the dimethylsulfoxide ligand* | | | |
| Ru–SDM–ODM | 117.5(1) | ODM–SDM–C1DM | 105.9(2) |
| Ru–SDM–C1DM | 112.5(2) | ODM–SDM–C2DM | 105.1(2) |
| Ru–SDM–C2DM | 114.4(2) | C1DM–SDM–C2DM | 99.5(3) |

## RESULTS AND DISCUSSION

This paper reports a simple means of preparing salts of the complex $[Ru(bpy)_2Cl(dmso)]^+$ that have been found to be extremely useful in the preparation of complexes of the general formula $[Ru(bpy)_2L]^{2+}$, where L is a planar heterocyclic bidentate ligand.[4] These mixed-ligand complexes have been found to be able to intercalate DNA and have been extensively studied in recent years.[2] Previously the complexes $[Ru(bpy)_2L]^{2+}$ have been prepared by the reaction of the bidentate ligand with *cis*-$[Ru(bpy)_2Cl_2]$, typically in alcoholic solvents with long reflux times.[10]

The complex $[Ru(bpy)_2Cl(dmso)]^+$ has been prepared by reacting 2,2′-bipyridine (2 mol) with ruthenium(III) chloride (1 mol) in hot dimethylsulfoxide. Dimethylsulfoxide has the advantage that no other reducing agent is required to reduce ruthenium(III) to ruthenium(II). The complex has been previously reported, though not isolated, as a product formed when $[Ru(bpy)_2Cl_2]$ was heated in dimethylsulfoxide solution in the course of an NMR study on the isomerism of $[Ru(bpy)_2Cl_2]$.[3]

Several salts of *cis*-$[Ru(bpy)_2Cl(dmso)]^+$ have been isolated. The chloride is very soluble in acetone compared to the hexafluorophosphate and the perchlorate. Because of the high solubility of the chloride, the yield can be maximised by adding a concentrated solution of sodium perchlorate or hexafluorophosphate to the reaction mixture. The salts have been characterised by electrospray mass spectroscopy, $^1H$ NMR spectroscopy and microanalysis (hexafluorophosphate salt only).

As expected for the *cis* configuration 16 separate signals in the aromatic region are observed in the $^1H$ NMR spectrum. The spectrum observed agrees closely with that previously reported.[3] The dimethylsulfoxide group coordinates to the ruthenium *via* sulfur. This is indicated by the two singlet signals corresponding to the two methyl groups appearing at $\delta$ 3.17 and 2.14 ppm. The principal ions observed in the mass spectra include $[Ru(bpy)_2Cl(dmso)]^+$ at *m/z* 527 (the assignments are based on $^{102}Ru$, $^{35}Cl$ and the common isotopes of the other elements). Other ions are formed by loss of ligands from the complex (*e.g.* $[Ru(bpy)_2Cl]^+$, *m/z* 449 and $[Ru(bpy)_2(dmso)]^+$, *m/z* 492). The most abundant ion at *m/z* 481 arises through the replacement of the coordinated dimethylsulfoxide by methanol, the solvent used to introduce the complex into the mass spectrometer.

The structure determination has confirmed that the chloro and dmso ligands are *cis* to each other. In terms of the synthetic utility of this compound, the *cis* arrangement of the monodentate ligands will best allow a bidentate ligand to replace them. An ORTEP view of the complex cation is

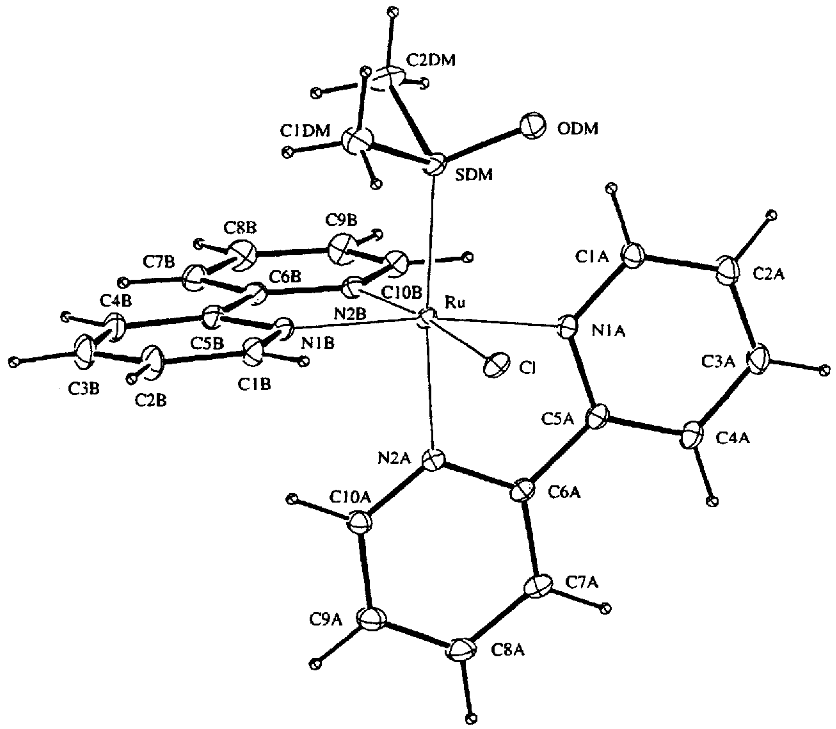

FIGURE 1 An ORTEP view of the complex cation, *cis*-$[Ru(bpy)_2Cl(dmso\text{-}S)]^+$.

given in Figure 1. The dmso ligand was found to be *S*-bound. Dimethylsulfoxide can bind through the oxygen atom or through the sulfur atom and in complexes with metals of the Fe/Ru/Os triad there are examples of *O*- and *S*-bound dmso for each metal. For iron, dmso is generally bound through the oxygen atom, particularly in iron(III) complexes, for example $[Fe(dmso)_6](NO_3)_3$,[11] and for osmium, the sulfur atom is generally directly bound to the metal centre, as in *trans*-$[Os(dmso)_4Br_2]$.[12] For ruthenium, these are several occurrences of *O*-bound dmso and there may be some indication that a *trans* influence operates, in that in *cis*-$[Ru(dmso)_4Cl_2]$ the dmso *trans* to an *S*-bound dmso is *O*-bound whereas the dmso ligands *trans* to chloro ligands are *S*-bound.[13] This suggests that dmso preferentially *S*-bonds *trans* to a hard donor and *O*-bonds *trans* to a soft donor. The analogous bromo complex *cis*-$[Ru(dmso)_4Br_2]$ also has three *S*-bound and one *O*-bound dmso ligands.[13] Interestingly, the complex *trans*-$[Ru(dmso)_4Cl_2]$ has four *S*-bound dmso ligands,[13] so it is difficult to argue for any *trans* influence based on the chemical hardness of a *trans* ligand.

The complex cation is found to closely approximate octahedral structure. The principal deviations from octahedral stereochemistry arise because of the limited bite of the bidentate ligand and the large solid angle occupied by the coordinated dmso molecule. The 'bite' angles (N1–Ru–N2) are 77.7(1)° and 78.6(1)° for ligands A and B, respectively. The angles around the Ru centre between the dmso and the ligands *cis* to dmso are all greater than 90° except for the S–Ru–Cl angle (88.5°). The Ru–N distances are as expected for ruthenium(II) complexes of heterocyclic nitrogen ligands, being similar to the bond lengths found for $[Ru(bpy)_3]^{2+}$ (2.056(2) Å).[14] For ligand A, the Ru–N bond lengths are the same, within experimental error, indicating that the *trans* influences for *S*-bound dmso and bipyridine are similar. For ligand B, it appears that there is a difference in the *trans* influences of a chloro ligand and another bipyridine in that Ru–N2B (*trans* to Cl) is shorter than Ru–N1B (*trans* to N) with both bonds being shorter than those involving ligand A. The Ru–Cl bond length is similar to that found in the complex *cis*-$[Ru(bpy)_2Cl_2]$[15] and also in other complexes with chloro and dmso ligands, such as *cis, cis, cis*-$[RuCl_2(dmso)_2$(3,5-lutidine)(1,2-dimethylimidazole)].[16] The Ru–S bond length is certainly within the range for ruthenium(II) dmso complexes.[17]

There is a hydrogen-bonding scheme, facilitated by the lattice water molecules, that links the anions and cations. Relevant dimensions are given in Table V. Since hydrogen atoms were not located on difference maps, the distances between the non-hydrogen atoms involved in the bonds are presented. Both hydrogens on the water molecules are involved in hydrogen bonds; the chloro ligand accepts two hydrogen bonds and the oxygen atom of the dimethylsulfoxide ligand accepts two hydrogen bonds. The perchlorate anion is hydrogen bound to a water molecule. One inference that can be drawn is that the hydrogen positions for OW1 must be disordered because that water molecule is apparently engaged in three hydrogen bonds.

TABLE V Hydrogen bond distances

| *Atoms* | *Distance* (Å) |
|---|---|
| OW1···Cl | 3.54 |
| $OW1^a$···Cl | 3.30 |
| OW1···ODM | 2.89 |
| OW2···ODM | 2.95 |
| OW2···$O3^b$ | 2.89 |

Equivalent positions: $^a -x, 1-y, 1-z$; $^b x-1, y, z$.

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