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# Synthesis of some Ruthenium Complexes with Mixed Diimine Ligands

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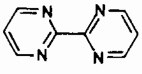
## Abstract

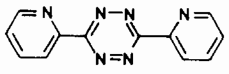
The use of $Ru(DMSO)_4Cl_2$ and $Ru(Py)_4Cl_2$ (DMSO = dimethyl sulphoxide; Py = pyridine) in synthesizing mixed ligand complexes is reported. The bidentate ligands used are of the diimine type, namely, 2,2′-bipyrimidine (bpm); 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine (dpt); 2,3-bis(2-pyridyl)-5,6-dihydropyrazine (dhp); 2,3-bis(2-pyridyl)-pyrazine (dpp); 2,3-bis-(2-pyridyl)-quinoxaline (dpq); 2,3,5,6-tetrakis(2-pyridyl)-pyrazine (tpp). Characterization of the complexes has been accomplished using elemental analysis, conductivity, IR and UV–Vis spectroscopy.

## Introduction

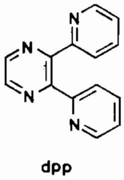
The catalytic water splitting [1–3] and solar energy conversion [3, 4] by ruthenium(II) complexes provide a strong impetus for synthesizing even more ruthenium diimine complexes. In this work we report the use of $Ru(DMSO)_4Cl_2$ and $Ru(Py)_4Cl_2$ [5] to synthesize a series of mixed ligand ruthenium(II) complexes. The reactions are relatively simple and straightforward to carry out. The polypyridyl ligands, bpm, dpq, dhp, dpp, dpt and tpp can replace two coordinated DMSO molecules when the ligand to complex ratios are 1:1. Replacement of two pyridines or two chlorines by the above ligands has also been accomplished.



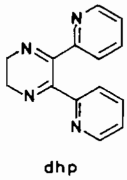
bpm



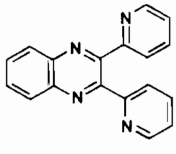
dpt



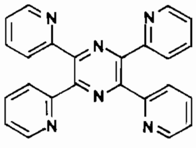
dpp



dhp



dpq



tpp

## Experimental

### Materials

DMSO (Merck) was purified by drying over sodium hydroxide pellets for several days followed by vacuum distillation. $Ru(DMSO)_4Cl_2$ and $Ru(Py)_4Cl_2$ were prepared according to the method of Evans *et al.* [5]. Bipyrimidine (Lanchester Synthesis Ltd.) was recrystallized from benzene. The procedure of Geldard and Lions [6] was used to prepare dpt which was purified by crystallization from a 1:1 $CHCl_3$/EtOH mixture. The ligands, dpq, dpp, tpp and dhp were prepared according to the method of Goodwin and Lions [7]. All solvents used were AR grade.

### Elemental Analysis

These were carried out by M.H.W. Laboratories. P.O. Box 15853, Phoenix, Arizona 85018, U.S.A.

### Physical Measurements

UV–Vis spectra were recorded with a UV-240 SHIMADZU Spectrophotometer. KBr disk IR spectra were taken on a Pye-Unicam SP3-300 spectrophotometer. Solution conductivities at 25 °C in acetonitrile were measured for $1 \times 10^{-3}$ M concentrations using a Harris conductivity meter.

### Synthesis of Complexes

#### Reactions of $Ru(DMSO)_4Cl_2$ (general procedure)

1 mmol of each of the diimine ligands and $Ru(DMSO)_4Cl_2$ were refluxed in 30 ml ethanol (3 h) or toluene (50 min). The ethanolic solutions were reduced to 15 ml volume and ether was added to precipitate the product. Toluene solutions were vacuum evaporated to dryness. The solid residue was

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TABLE I. Reactions of $Ru(DMSO)_4Cl_2$ with Diimine Ligands

| Complex | Reaction solvent | Colour of product | Yield (%) |
|---|---|---|---|
| $[Ru(DMSO)_2Cl_2bpm]\cdot 2H_2O$ | ethanol | dark brown | 74 |
| $[Ru(DMSO)_2Cl_2dpt]\cdot H_2O$ | toluene | violet | 78 |
| $[Ru(DMSO)_2Cl_2dpq]\cdot 2H_2O$ | ethanol | deep blue | 82 |
| $[Ru(DMSO)_2Cl_2dpp]\cdot H_2O$ | ethanol | blue | 86 |
| $[Ru(DMSO)_2Cl_2dhp]\cdot 2H_2O$ | ethanol | blue | 88 |

then dissolved in 10 ml of acetone and precipitated with ether. The precipitated solid was then washed with ethanol or acetone, finally with ether and then vacuum dried. All solids did not melt or decompose below 300 ℃. Table I summarizes the details of the synthesis for each complex.

### *Reactions of $Ru(Py)_4Cl_2$*

*Tetrakis(pyridine)-2,3-bis(2-pyridyl)-quinoxaline ruthenium(II) hexafluorophosphate dihydrate and bis(pyridine)-bis(2,3-bis(2-pyridyl)-quinoxaline)ruthenium(II) hexafluorophosphate trihydrate, $Ru(Py)_4(dpq)(PF_6)_2\cdot 2H_2O$ and $Ru(Py)_2(dpq)_2(PF_6)_2\cdot 3H_2O$.* $Ru(Py)_4Cl_2$ (0.124 g, $2.5 \times 10^{-4}$ mol) and dpq (0.213 g) were refluxed in 30 ml of a 50–50 mixture of $H_2O$ and 2-methoxylethylether for 2 h. The solution was filtered and vacuum distilled to a volume of 20 ml. Three successive extractions with ether were done to remove excess ligand. The product was precipitated by the addition of $NH_4PF_6$ (2 g) in 10 ml $H_2O$. The precipitate formed was filtered off, redissolved in acetone (10 ml) and precipitated upon addition of ether.

The two complexes resulting from the reaction mixture were separated by chromatography using a column packed with neutral alumina and developed by acetone. Acetone was used first to elute a wine-red impurity which was identified by fluorescence to be $Ru(dpq)_3(PF_6)_2$. $Ru(Py)_2(dpq)_2(PF_6)_2$ was eluted using 5% methanol in acetone and $Ru(Py)_4(dpq)(PF_6)_2$ was separated from an undefined impurity at the top of the column by using 20% methanol in acetone. Both complexes (in 30% yields) were precipitated by addition of ether to the eluent after it was reduced in volume to 10 ml. The two products were collected by suction and vacuum dried.

*Tetrakis(pyridine)-2,3-bis(2-pyridyl)-5,6-dihydropyrazine ruthenium(II) hexafluorophosphate monohydrate, $Ru(Py)_4dhp(PF_6)_2\cdot H_2O$.* $Ru(Py)_4Cl_2$ (0.248 g, $5 \times 10^{-4}$ mol) and dhp (0.236 g, $1 \times 10^{-3}$ mol) were refluxed in $CHCl_3$ (60 ml) for 40 h. The solution was evaporated to dryness under reduced pressure. The solid collected was redissolved in $H_2O$ (15 ml) and filtered. 3 g of $NH_4PF_6$ in 10 ml $H_2O$ were added to precipitate the complex which was collected, redissolved in a minimum amount of acetone and added to a column containing neutral alumina developed with acetone. The desired complex was separated from an undefined impurity at the top of the column by using acetone. The eluent was reduced in volume to 10 ml and the complex was precipitated with ether, collected by suction and vacuum dried. The yield was 72%.

*Tetrakis(pyridine)-2,3,5,6-tetrakis(2-pyridyl)-pyrazine ruthenium(II) hexafluorophosphate, $Ru(Py)_4tpp(PF_6)_2$.* 0.6 g ($1.5 \times 10^{-3}$ mol) of tpp in 30 ml of a mixture of 2-methoxyethylether/water (70–30) was added slowly to $Ru(Py)_4Cl_2$ ($5 \times 10^{-4}$ mol, 0.248 g) in 2-methoxyethylether (10 ml). An immediate colour change to brown took place and upon refluxing (30 min) the colour changed to olive green and then to dark blue. The solvent was evaporated to dryness under reduced pressure and then the solid dissolved in $H_2O$ (15 ml) and the product precipitated upon addition of $NH_4PF_6$ (2 g). The blue solid was collected by suction and redissolved in a minimum amount of acetone and precipitated upon addition of ether. The complex was dissolved in a minimum amount of acetone and was added to a column containing neutral alumina. The desired mononuclear complex was eluted from undefined impurities using 5% methanol in acetone. The yield was 75%.

## Results and Discussion

Table II confirms by elemental analysis the formula suggested for the compounds in 'Experimental'. The conductivity table (Table II) confirms that the DMSO complexes are non-electrolytes with the two chlorines inside the coordination sphere. The pyridine complexes indicate the 1:2 electrolytic behaviour expected from their formula [8].

The reaction of $Ru(Py)_4Cl_2$ with dpq in chloroform yields $Ru(dpq)_3^{2+}$ [9]. In 2-methoxyethylether/water, two products are formed, $Ru(Py)_4dpq^{2+}$ and $Ru(Py)_2(dpq)_2^{2+}$ with the tris complex as an impurity. All the other ligands substituted for the chlorine when equimolar ligand and complex quantities were used.

TABLE II. Elemental Analysis and Conductivity ($10^{-3}$ M in acetonitrile) of the Complexes

| Complex | $\Lambda_m$ ($ohm^{-1}\ cm^2\ mol^{-1}$) | Analysis: calculated(found) (%) | | | |
|---|---|---|---|---|---|
| | | C | H | N | S |
| $[Ru(DMSO)_2Cl_2bpm\}\cdot 2H_2O$ | 9.0 | 27.00<br>(27.69) | 3.95<br>(4.23) | 10.61<br>(10.77) | 11.66<br>(12.30) |
| $[Ru(DMSO)_2Cl_2dpq\}\cdot 2H_2O$ | 13 | 43.27<br>(43.48) | 3.92<br>(3.62) | 10.18<br>(10.14) | 5.82<br>(5.79) |
| $[Ru(DMSO)_2Cl_2dpt\}\cdot H_2O$ | 7.0 | 33.1<br>(33.1) | 3.00<br>(3.10) | 6.21<br>(6.34) | 16.57<br>(16.66) |
| $[Ru(DMSO)_2Cl_2dpp\}\cdot H_2O$ | 23 | 38.90<br>(38.22) | 3.53<br>(3.58) | 10.42<br>(10.73) | 6.44<br>(6.37) |
| $[Ru(DMSO)_2Cl_2dhp]\cdot 2H_2O$ | 6.0 | 36.31<br>(36.85) | 4.00<br>(4.20) | 10.85<br>(10.73) | 6.08<br>(6.13) |
| $[Ru(Py)_2(dpq)_2](PF_6)_2\cdot 3H_2O$ | 225 | 48.24<br>(48.33) | 3.29<br>(3.80) | 12.33<br>(11.51) | |
| $[Ru(Py)_4dpq](PF_6)_2\cdot 2H_2O$ | 242 | 45.19<br>(45.31) | 3.30<br>(3.39) | 11.10<br>(10.98) | |
| $[Ru(Py)_4dhp](PF_6)_2\cdot H_2O$ | 248 | 43.27<br>(43.32) | 3.39<br>(3.41) | 10.18<br>(10.29) | |
| $[Ru(Py)_4tpp](PF_6)_2$ | 225 | 48.22<br>(49.14) | 3.29<br>(3.31) | 12.79<br>(13.49) | |

IR and NMR studies [10, 11] on DMSO metal complexes indicate that this solvent can bind to the metal through either O or S atoms. The ratio of sulphur-bonded to oxygen-bonded DMSO in $Ru(DMSO)_4Cl_2$ has been found to be 3:1 [5]. The treatment of this complex with equimolar quantities of the ligand (L) leads to the complexes, $Ru(DMSO)_2LCl_2$ with L = bpm, dhp, dpp, dpt and dpq. The *cis* configuration of the starting material [5] is expected to be retained in the new complexes.

IR results are given in Table III. In the DMSO complexes an SO stretching peak for O-bonded DMSO (present in $Ru(DMSO)_4Cl_2$ [5]) completely disappears, while the S–O stretching (1090–1120 $cm^{-1}$) for an S-bonded DMSO is still retained. Thus, the more weakly held O-bonded DMSO is removed first during the substitution reaction. The second DMSO to be removed is necessarily an S-bonded one, thus leaving two S-bonded molecules on the metal atom. The complexes also exhibit bands that belong to the ligand L. In particular, bands roughly in the range of 1570–1615 $cm^{-1}$ [12] and 1545–1565 $cm^{-1}$ [13] are assigned to C=N and C=C stretching in the ring of the bidentate ligand respectively. In general the C=N frequency in our results increases upon complexation. Similar results for bpm have been observed recently [14]. This effect has been explained by an interplay of $\sigma$ and $\pi$ bonding effects in which $\sigma$ bonding increases the C=N bond strength by increasing the positive charge on the bonded nitrogen thus attracting $\pi$ electrons from the ring closer to the C=N fragment, while $\pi$ back donation from the metal places electronic charges into $\pi^*$ orbitals of the ring and weakens the C=N bond strength. In all cases observed here, $\sigma$ bonding seems to dominate the complexation effect on the C=N stretching frequency (C=N ($cm^{-1}$) for ligands: bpm = 1558; dhp = 1578; dpt = 1582; dpp = 1592). This applies to the IR results for the pyridine–L complexes as well. Unfortunately, an identification of C=N modes where N is not complexed has proved difficult due to the broadness and overlap of the peaks in both ligands and complexes. In addition the pyridine complexes exhibit a pyridine ring breathing [15] mode in the range of (1440–1470 $cm^{-1}$). These together with the peaks near 1050 and 750 $cm^{-1}$ further support the presence of pyridine.

The UV–Vis results in Table IV exhibit peaks in two main regions. Below 375 nm the peaks belong to ligand transitions with the high energy peaks usually typical of $\pi,\pi^*$ transitions of the uncomplexed diimine ligand in solution. Thus in $Ru(DMSO)_2Cl_2$-bpm, the 266 nm peak is the same as in bpm and is assigned as a ($\pi,\pi^*$) transition [16]. Ligand n,$\pi^*$-transitions are sometimes observed (e.g. 278 nm for $Ru(DMSO)_2Cl_2bpm$). The strong very broad bands in the visible regions for the DMSO complexes are a superposition of many MLCT (metal to ligand

TABLE III. Infra-red Spectra of the Complexes[a]

| Compound | Characteristic IR bonds (cm$^{-1}$) | Assignments |
|---|---|---|
| [Ru(DMSO)$_2$bpmCl$_2$]·2H$_2$O | 1570(s) | $\nu$(C=N) |
| | 1545(m) | $\nu$(C=C) |
| | 1403(s) | ring stretching |
| | 1090(s) | SO–S-bonded |
| | 1020(m) | pr-CH (DMSO) |
| | 680(m) | $\nu_a$(CS) |
| | 420(m) | $\delta_a$(CSO) |
| | 380 | $\delta_{as}$(CSO) |
| | 1625, 1310, 930, 720, 1190 | unassigned |
| [Ru(DMSO)$_2$dpqCl$_2$]·2H$_2$O | 1590(m) | $\nu$(C=N) |
| | 1548(m) | $\nu$(C=C) |
| | 1080(m) | $\nu$(SO–S-bonded) |
| | 1015 | pr-CH (DMSO) |
| | 676(m) | $\nu_a$(CS) |
| | 426(m) | $\delta_s$(CSO) |
| | 380(w) | $\delta_{as}$(CSO) |
| | 1620(m), 1460, 1405, 1310, 1255(m), 1145(m), 775, 600 | unassigned |
| [Ru(DMSO)$_2$dppCl$_2$]·2H$_2$O | 1620 | $\nu$(C=N) |
| | 1585(m) | $\nu$(C=N) |
| | 1550 | $\nu$(C=C) |
| | 1405 | ring stretching |
| | 1085 | $\nu$(SO–S-bonded) |
| | 1015 | pr-CH (DMSO) |
| | 670(m) | $\nu$(CS) |
| | 425(m) | $\delta$(CSO) |
| | 375(w) | $\delta_{as}$(CSO) |
| | 1455, 1350, 1233, 770, 750, 630, 560, 520 | unassigned |
| [Ru(DMSO)$_2$dptCl$_2$]·2H$_2$O | 1596(w) | $\nu$(C=N) |
| | 1550(m) | $\nu$(C=C) |
| | 1410 | ring stretching |
| | 1080 | $\nu$(SO–O-bonded) |
| | 1012 | pr-CH (DMSO) |
| | 680(m) | $\nu_a$(CS) |
| | 422(m) | $\delta_a$(CSO) |
| | 370 | $\delta_{as}$(CSO) |
| | 1380, 1310, 1250, 1145, 826, 780, 745, 475 | unassigned |
| [Ru(DMSO)$_2$dhpCl$_2$]·2H$_2$O | 1590(m) | $\nu$(C=N) |
| | 1565(m) | $\nu$(C=C) |
| | 1085(s) | $\nu$(SO–S-bonded) |
| | 1410 | ring stretching |
| | 1012 | pr-CH (DMSO) |
| | 670 | $\nu_a$(CS) |
| | 424 | $\delta_a$(CSO) |
| | 370 | $\delta_{as}$(CSO) |
| | 1450, 1340, 1240, 1150, 745, 770 | unassigned |

*(continued)*

TABLE III. *(continued)*

| Compound | Characteristic IR bonds ($cm^{-1}$) | Assignments |
|---|---|---|
| $[Ru(py)_4Cl_2]$ | 3070 | $\nu$(C–H) |
| | 1440 | ring breathing |
| | 1470 | ring breathing |
| | 1050 | ring vibration |
| | 760 | $\delta$(CH) |
| | 680 | $\delta$(CH) |
| | 1148, 1058, 995, 682 | unassigned |
| $[Ru(Py)_4dpq](PF_6)_2 \cdot 2H_2O$ | 1607 | $\nu$(C=N) (dpq) |
| | 1563 | $\nu$(C=C) (dpq) |
| | 1438 | ring breathing (Py) |
| | 1060 | ring vibration (Py) |
| | 750 | $\delta$(CH) (Py) |
| | 550, 1150, 1235, 1340, 1395 | unassigned |
| $[Ru(Py)_4dhp](PF_6)_2 \cdot H_2O$ | 1618 | $\nu$(C=N) (dhp) |
| | 1580 | $\nu$(C=C) (dhp) |
| | 1455 | ring breathing (Py) |
| | 1070 | ring vibration (Py) |
| | 830 | $PF_6$ peak |
| | 750 | $\delta$(CH) (Py) |
| | 515, 565, 602, 630, 690, 990, 1110, 1198, 1235, 1303 | unassigned |
| $[Ru(Py)_2(dpq)_2](PF_6)_2 \cdot 3H_2O$ | 1603 | $\nu$(C=N) (dpq) |
| | 1569 | $\nu$(C=C) (dpq) |
| | 1445 | ring vibration (Py) |
| | 1018 | ring vibration (Py) |
| | 828 | $PF_6$ peak |
| | 755 | $\delta$(CH) (Py) |
| | 565, 630, 690, 998, 1110, 1198, 1260, 1303, 1340 | unassigned |
| $[Ru(Py)_4tpp](PF_6)_2$ | 1620 | $\nu$(C=N) (tpp) |
| | 1590 | $\nu$(C=C) (tpp) |
| | 1445 | ring breathing (Py) |
| | 1015 | ring vibration (Py) |
| | 835 | $PF_6$ peak |
| | 755 | $\delta$(CH) (Py) |
| | 555, 690, 1090, 1189, 1245, 1400 | unassigned |

[a] The spectra was carried out using KBr pellets. s, strong; m, medium; w, weak; $\nu$, stretching, $\nu_a$, symmetric stretching; $\delta$, symmetric deformation; $\delta_{as}$, asymmetric deformation; pr, rocking.

charge transfer) bands from the metal d-orbitals to DMSO and diimine ligand orbitals. In the pyridine complexes comparison with $Ru(Py)_2(bpy)_2^{2+}$ [17] strongly indicates that the peak or shoulder at around 350 nm is due to an MLCT transition to a pyridine $\pi^*$-orbital. The higher wavelength peaks are due to MLCT transitions to diimine $\pi^*$-orbitals.

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TABLE IV. UV–Vis Spectral data for Complexes of Ru(II) in Acetonitrile[a]

| Complex | $\lambda_{max}$ (nm) | $\epsilon$ (l $mol^{-1}$ $cm^{-1}$) |
|---|---|---|
| $[Ru(DMSO)_2bpmCl_2]\cdot 2H_2O$ | 589(b) | 6950 |
| | 278(sh) | 13200 |
| | 266 | 16400 |
| $[Ru(DMSO)_2dhpCl_2]\cdot 2H_2O$ | 630(b) | 4000 |
| | 374(sh) | 60000 |
| | 277 | 100000 |
| $[Ru(DMSO)_2dpqCl_2]\cdot 2H_2O$ | 620(b) | 7250 |
| | 336(sh) | 33400 |
| | 276 | 62000 |
| $[Ru(DMSO)_2dppCl_2]\cdot H_2O$ | 595(b) | 9200 |
| | 325 | 56000 |
| | 274 | 60000 |
| $[Ru(DMSO)_2dptCl_2]\cdot 2H_2O$ | 630(b) | 5300 |
| | 480(sh) | 3370 |
| | 345(sh) | 11200 |
| | 175 | 41300 |
| $[Ru(Py)_2(dpq)_2](PF_6)_2\cdot 3H_2O$ | 570 | 6070 |
| | 490 | 7250 |
| | 360(sh) | 27000 |
| | 334 | 33000 |
| | 278 | 62900 |
| | 255 | 58000 |
| $[Ru(Py)_4dpq](PF_6)_2\cdot 2H_2O$ | 545 | 7600 |
| | 455 | 5300 |
| | 350(sh) | 27000 |
| | 286 | 32000 |
| | 252 | 33000 |
| $[Ru(Py)_4dhp](PF_6)_2\cdot H_2O$ | 502 | 7400 |
| | 350 | 18000 |
| | 316 | 26100 |
| | 245 | 26200 |
| $[Ru(Py)_4tpp](PF_6)_2$ | 603 | 8250 |
| | 476 | 4720 |
| | 350(sh) | 18900 |
| | 313 | 22000 |
| | 244 | 19300 |

[a] Concentrations were $1 \times 10^{-4}$ M in the visible region and $1 \times 10^{-5}$ M in the UV region. sh, shoulder; b, broad.

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