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# Important role of CH–π interaction in linkage isomers of bis(2,2′-bipyridine)ruthenium(II) complexes with pyrimidine-2-thione and related ligands

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Nine ruthenium(II) complexes containing pyrimidine-2-thione and related ligands were prepared and characterized by elemental analysis, UV/VIS and $^1H$ and $^{13}C$ NMR spectra: $[Ru(L\text{-}N,S)(bipy)_2]ClO_4$ [$H_nL$ = Hpymt (pyrimidine-2-thione), Hmpymt (4-methylpyrimidine-2-thione), Hdmpymt (4,6-dimethylpyrimidine-2-thione), Hapymt (4-aminopyrimidine-2-thione), Hdapymt (4,6-diaminopyrimidine-2-thione), $H_2$tuc (2,3-dihydro-2-thioxo-1*H*-pyrimidin-4-one, 2-thiouracil), 5-$H_2$mtuc (5-methyl-2-thiouracil), 6-$H_2$mtuc (6-methyl-2-thiouracil) or 6-$H_2$ptuc (6-propyl-2-thiouracil); bipy = 2,2′-bipyridine]. Two linkage isomers, adjacent and remote, exist for all the complexes with unsymmetrical ligands except for apymt. The crystal structure of $[Ru(mpymt)(bipy)_2]ClO_4$ was determined. The mpymt ligand co-ordinates through the $S^2/N^3$ donors and the complex adopts an adjacent linkage form where the 4-methyl group lies just over one of the bipy chelate rings irrespective of steric hindrance. The CH–π attractive interaction between the 4- or 6-alkyl group of the thione ligand and the π system of bipy affects the isomer ratios in a striking manner.

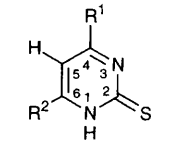
Pyrimidine-2-thione (Hpymt) acts as a bidentate-N,S ligand. For the bis(ethylenediamine)cobalt(III) complexes with an unsymmetrical $C^4$-substituted pymt ligand two linkage isomers are possible: a remote isomer with the $C^4$ substituent group away from the two en chelates and an adjacent isomer with this group near to them. Our recent investigations reveal that the substituent group (X) at $C^4$ plays an essential role in the stereochemistry. 2-Thiouracil ($H_2$tuc = 2,3-dihydro-2-thioxo-1*H*-pyrimidin-4-one, X = O)[1] and 2,4-dithiouracil ($H_2$dtuc, X = S)[2] adopt an adjacent form, whereas 4-methylpyrimidine-2-thione (Hmpymt, X = $CH_3$)[3] and 4-aminopyrimidine-2-thione (Hapymt, X = $NH_2$)[4] adopt a remote form. The existence of a strong intramolecular hydrogen bond was confirmed in the former adjacent complexes.

Here we describe the preparation of nine bis(2,2′-bipyridine)ruthenium(II) complexes containing five pyrimidine-2-thione (Hpymt, Hmpymt, Hdmpymt = 4,6-dimethylpyrimidine-2-thione, Hapymt and Hdapymt = 4,6-diaminopyrimidine-2-thione) and four 2-thiouracil ligands ($H_2$tuc, 5-$H_2$mtuc = 5-methyl-2-thiouracil, 6-$H_2$mtuc = 6-methyl-2-thiouracil and 6-$H_2$ptuc = 6-propyl-2-thiouracil). It is very interesting to compare stereochemistries of the $d^6$ complexes of ruthenium(II) and cobalt(III). The stereochemistry of bis(2,2′-bipyridine)ruthenium(II) type complexes is expected to be significantly different from that of bis(ethylenediamine)cobalt(III) type complexes because the co-ordination environment provided by bipyridine differs significantly from that by ethylenediamine. The complexes were characterized by elemental analysis, UV/VIS, $^1H$ and $^{13}C$ NMR spectra and X-ray analysis. Some preliminary results of this work have been reported elsewhere.[5]

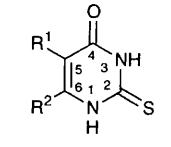
## Experimental

### Preparation of complexes

All of the thiones (Aldrich) were used without further purification. The starting material *cis*-$[RuCl_2(bipy)_2]\cdot 0.5H_2O$ was prepared according to the literature.[6] Analytical data showed this complex to be a hemihydrate not a dihydrate[6] [Found (Calc.): C, 48.70 (48.70); H, 3.40 (3.45); N, 11.35 (11.35)%].



| | $R^1$ | $R^2$ |
|---|---|---|
| Hpymt | H | H |
| Hmpymt | $CH_3$ | H |
| Hdmpymt | $CH_3$ | $CH_3$ |
| Hapymt | $NH_2$ | H |
| Hdapymt | $NH_2$ | $NH_2$ |



| | $R^1$ | $R^2$ |
|---|---|---|
| $H_2$tuc | H | H |
| 5-$H_2$mtuc | $CH_3$ | H |
| 6-$H_2$mtuc | H | $CH_3$ |
| 6-$H_2$ptuc | H | *n*-$C_3H_7$ |

The general preparation method was as follows. The pyrimidine-2-thione (0.5 mmol) was suspended in 50% aqueous methanol (50 $cm^3$) and adjusted to pH 8–9 by adding aqueous NaOH. To the above solution was added *cis*-$[RuCl_2(bipy)_2]\cdot 0.5H_2O$ (0.25 g, 0.5 mmol) and the mixture was refluxed for 2–4 h to give a brownish purple solution. Addition of $NaClO_4$ and evaporation gave a brown perchlorate salt which was recrystallized from water and methanol. The yields were 70–90%. The compounds $H_2$tuc, 5-$H_2$mtuc, 6-$H_2$mtuc and 6-$H_2$ptuc, were used without neutralizing with NaOH. The elemental analyses of the complexes are collected in Table 1.

**CAUTION:** In general, perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great care. The present ones ignite in a Bunsen-burner flame but present no hazard in solutions and in normal treatment of the solids.

### Crystallography

The mixed linkage isomers of $[Ru(mpymt)(bipy)_2]ClO_4$ were dissolved in methanol–water, and crystals were grown in a short-neck Kjeldahl flask at room temperature in 1 month. Dark red cubic crystals of an adjacent isomer were obtained first. Further prolonged crystallization resulted in the contamination of these crystals with microcrystals of a remote isomer.

**Crystal data.** $C_{25}H_{21}ClN_6O_4RuS$, $M = 638.06$, monoclinic, space group $C2/c$ (no. 15), $a = 24.313(4)$, $b = 13.645(3)$, $c = 17.282(3)$ Å, $\beta = 112.59(1)°$, $U = 5293(1)$ Å$^3$, $Z = 8$, $D_c = 1.601$ g cm$^{-3}$, $F(000) = 2576$, red crystal, 0.25 × 0.20 × 0.30 mm, $\mu$(Mo-K$\alpha$) = 8.16 cm$^{-1}$.

**Data collection and processing.** Rigaku AFC5R diffractometer, $\omega$–2$\theta$ mode with $\omega$-scan width = $(1.78 + 0.30 \tan\theta)°$, $\omega$-scan speed 16.0° min$^{-1}$, graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.710\,69$ Å); 8192 reflections measured ($1.5 \leqslant \theta \leqslant 30.0°$, $h$ 0–34, $k$ 0–19, $l$ −24 to +24), 8017 unique [merging $R = 0.038$ after absorption correction (maximum, minimum transmission factors = 1.00, 0.947)], giving 3424 with $|F_o|^2 > 3\sigma(|F_o|^2)$. Linear and approximately isotropic crystal decay, *ca.* −0.28%, corrected during processing.

**Structure analysis and refinement.** Direct method followed by normal heavy-atom procedures. The final cycle of full-matrix least squares was based on 3424 observed reflections [$|F_o|^2 > 3\sigma(|F_o|^2)$] and 427 variable parameters. All hydrogens were isotropically refined. The final values of $R$ and $R'$ {$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1/\sigma^2|F_o|$} were 0.052 and 0.058, respectively. All calculations were performed using the TEXSAN [7] crystallographic software package.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/66.

### Measurements

The UV/VIS absorption spectra were measured in acetonitrile with a Hitachi 330 spectrophotometer and proton and $^{13}C$ NMR spectra with JEOL JNM-GSX-270 and GSX-400 spectrometers in $(CD_3)_2SO$. The X-ray crystal analysis was made by the X-ray Diffraction Service of the Department of Chemistry.

## Results and Discussion

### Preparation and characterization of complexes

The complexes $[RuL(bipy)_2]^+$ were prepared in good yields by refluxing *cis*-$[RuCl_2(bipy)_2]$, pyrimidine-2-thione ligand HL and NaOH (mole ratio = 1:1:1) in water–methanol. The 2-thiouracil derivatives $H_2L$, were used without neutralizing by NaOH. The easy formation of the complexes strongly supports the four-membered N,S co-ordination by the thione ligands. Elemental analyses (Table 1) indicate that the complexes have the composition $[Ru(L \text{ or } HL)(bipy)_2]ClO_4$.

A typical UV/VIS absorption spectrum is shown in Fig. 1 and data are listed in Table 1. All complexes show similar spectra. There are mainly five components at 500–520, *ca.* 470, 335–345, *ca.* 293 and *ca.* 245 nm. The first peak is assignable to a Ru $4d_\pi \longrightarrow$ pymt $\pi^*$ metal-to-ligand charge-transfer (m.l.c.t.) transition and the second and third peaks to Ru $4d_\pi \longrightarrow$ bipy $\pi^*$ m.l.c.t. transition according to the literature.[8] The quinoline-8-thiolato complex $[Ru(SC_9H_6N\text{-}N,S)(bipy)_2]^+$, which forms a five-membered N,S-chelate ring, show similar visible bands: 501 (9700), 457 (9200) and 345 nm (7800 dm$^3$ mol$^{-1}$ cm$^{-1}$).[8] For the present complexes, however, the absorption intensity of the third peak is commonly higher than that of the first. The first peak of $[Ru(6\text{-}Hmtuc)(bipy)_2]^+$ appears at a considerably longer wavelength (559 nm) compared with those of the other complexes but the reason is not clear so far.

The sharp peak at 280–290 nm is assigned to a bipyridine intraligand $\pi \longrightarrow \pi^*$ transition because this band was observed for all the complexes with bipyridine.[8] For sulfur-containing bis(ethylenediamine)cobalt(III) complexes, the intense sulfur $\sigma \longrightarrow$ Co $d_\sigma$ ligand-to-metal (l.m.) c.t. bands have been observed at 280–290 nm.[1-4] However, such bands are completely overlapped by the more intense bipy bands of the present $[Ru(L\text{-}N,S)(bipy)_2]^+$ complexes.

In the $^{13}C$ NMR spectrum of $[Ru(dmpymt)(bipy)_2]^+$, twenty six signals, six [δ 182.5 ($C^2$), 166.8 and 165.5 ($C^4$ and $C^6$), 114.5 ($C^5$) and 23.2 and 19.8 ($CH_3$)] in the dmpymt chemical shift region and twenty (δ 158.04–123.3) in the bipy region, were observed. The result is consistent with the formulation $[Ru(dmpymt\text{-}N,S)(bipy)_2]^+$.

### Assignment of linkage isomers

Two linkage isomers, adjacent and remote, are possible depending upon the disposition of the $C^4$ substituent group of the pyrimidine ring. Since adjacent and remote are defined by the $C^4$ substituent group, it should be noted that the 4-alkyl group is away from the two bipy chelates in a remote isomer of the pymt system (pymt, mpymt, dmpymt, apymt and dapymt) but the 6-alkyl group is near to them in the same remote isomer of the tuc system (Htuc, 5-Hmtuc, 6-Hmtuc and 6-Hptuc) as shown in Fig. 2. The existence of the linkage isomers and their isomer ratio were determined from $^1H$ NMR spectroscopy (Table 2). Since pymt, dmpymt and dapymt are symmetrical ligands, there are no such isomers for these complexes.

There are two amino groups in $[Ru(dapymt)(bipy)_2]^+$ and the two signals appear at δ 6.24 and 4.37. The upfield signal of δ 4.37 is assigned to the amine in an adjacent position because the amino group is located just above one bipy and hence shows a significant upfield shift due to the ring-current effect of bipy, whereas the signal at δ 6.24 is assigned to the amine in a remote position because it is located away from the two bipy rings and shows the usual chemical shift value. Since there is no such ring-current effect in $[Co(dapymt)(en)_2]^{2+}$, the two amine signals have similar chemical shifts (δ 6.60 and 5.80). The above spectral pattern is applicable to the assignment of the linkage isomer of $[Ru(apymt)(bipy)_2]^+$ which shows only one amine signal at δ 6.88. This indicates that only one linkage isomer exists and is the remote form.

The complex $[Ru(dmpymt)(bipy)_2]^+$ shows two methyl signals at δ 2.29 and 1.28. In this case, the signal of δ 1.28 is assigned to the methyl group at an adjacent position which undergoes a significant upfield shift due to the ring-current

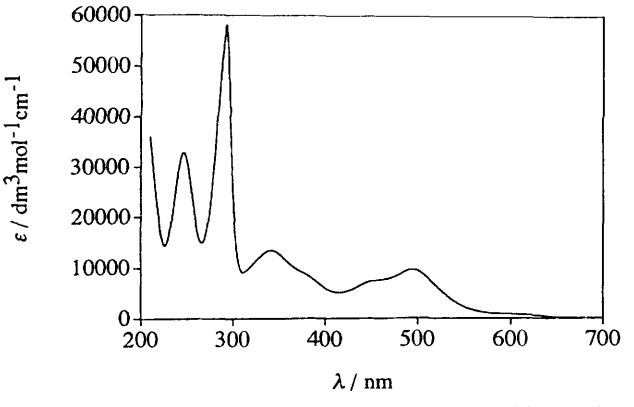



**Fig. 1** The UV/VIS absorption spectrum of $[Ru(pymt)(bipy)_2]ClO_4$

**Table 1** Elemental analyses and UV/VIS absorption spectral data for the complexes

| Complex | Analysis (%)[a] C | H | N | UV/VIS, $\lambda_{max}$ ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) |
|---|---|---|---|---|
| $[Ru(pymt)(bipy)_2]ClO_4 \cdot 0.5H_2O$ | 45.85 (45.55) | 3.15 (3.20) | 13.45 (13.30) | 497 (9 640), 450 (sh) (7 400), 380 (sh) (8 600), 341 (13 500), 293 (56 900), 245 (32 600) |
| $[Ru(mpymt)(bipy)_2]ClO_4$ | 46.65 (47.05) | 3.45 (3.30) | 13.10 (13.15) | 500 (8 170), 455 (sh) (6 300), 370 (sh) (8 900), 338 (11 700), 293 (51 400), 245 (30 200) |
| $[Ru(dmpymt)(bipy)_2]ClO_4 \cdot H_2O$[b] | 46.80 (46.60) | 3.85 (3.75) | 12.40 (12.55) | 506 (9 040), 460 (sh) (6 500), 375 (sh) (9 000), 338 (13 500), 293 (55 500), 245 (31 800) |
| $[Ru(apymt)(bipy)_2]ClO_4 \cdot 1.5H_2O$ | 42.95 (43.30) | 3.35 (3.50) | 14.60 (14.70) | 519 (10 400), 470 (sh) (6 800), 385 (sh) (8 400), 344 (15 300), 294 (61 400), 243 (35 000) |
| $[Ru(dapymt)(bipy)_2]ClO_4 \cdot 2H_2O$ | 41.90 (41.75) | 3.50 (3.65) | 16.35 (16.25) | 522 (9 450), 470 (sh) (5 900), 370 (sh) (8 300), 332 (11 900), 295 (56 100), 246 (35 100) |
| $[Ru(Htuc)(bipy)_2]ClO_4 \cdot 1.5H_2O$[b] | 43.00 (43.20) | 3.20 (3.30) | 12.50 (12.60) | 504 (8 660), 455 (sh) (5 700), 345 (10 800), 292 (54 600), 243 (28 400) |
| $[Ru(5\text{-}Hmtuc)(bipy)_2]ClO_4 \cdot 2H_2O$[b] | 43.40 (43.50) | 3.35 (3.65) | 12.10 (12.20) | 508 (8 550), 460 (sh) (5 700), 342 (11 300), 292 (54 500), 243 (29 700) |
| $[Ru(6\text{-}Hmtuc)(bipy)_2]ClO_4 \cdot 1.5H_2O$[b] | 43.65 (44.10) | 3.35 (3.55) | 12.30 (12.35) | 559 (9 730), 495 (sh) (6 300), 350 (11 800), 295 (51 400), 245 (33 200) |
| $[Ru(6\text{-}Hptuc)(bipy)_2]ClO_4 \cdot H_2O$[b] | 46.30 (46.30) | 3.65 (3.90) | 12.15 (12.00) | 506 (8 780), 455 (sh) (5 600), 344 (11 400), 294 (57 100), 244 (29 500) |

[a] Calculated values in parentheses. [b] The data are recorded for mixtures of the two linkage isomers.

**Table 2** Proton NMR spectral data[a]

| Complex | Linkage isomer | Pyrimidine-2-thionate Position 4 | Position 5 | Position 6 | NH | Bipyridine |
|---|---|---|---|---|---|---|
| $[Ru(pymt)(bipy)_2]ClO_4$ | | 8.31 (q, 1 H) | 6.76 (t, 1 H) | 7.48 (q, 1 H) | | 7.30–9.64 |
| $[Ru(mpymt)(bipy)_2]ClO_4$ | Adjacent (80%) | 1.33 (s, 3 H) | 6.71 (d, 1 H) | 8.20 (d, 1 H) | | 7.27–9.68 |
| | Remote (20%) | 2.32 (s, 3 H) | 6.66 (d, 1 H) | 7.79 (d, 1 H) | | |
| $[Ru(dmpymt)(bipy)_2]ClO_4$ | | 2.29 (s, 3 H) | 6.61 (s, 1 H) | 1.28 (s, 3 H) | | 7.30–9.72 |
| $[Ru(apymt)(bipy)_2]ClO_4$ | Remote (100%) | 6.88 (s, 2 H) | 5.83 (d, 1 H) | 6.63 (d, 1 H) | | 7.24–9.78 |
| $[Ru(dapymt)(bipy)_2]ClO_4$ | | 6.24 (s, 2 H) | 5.02 (s, 1 H) | 4.37 (s, 2 H) | | 7.21–9.87 |
| $[Ru(Htuc)(bipy)_2]ClO_4$ | Adjacent (70%) | | 5.44 (d, 1 H) | 7.42 (q, 1 H) | 12.4 | 7.22–9.67 |
| | Remote (30%) | | 5.70 (d, 1 H) | 6.52 (d, 1 H) | 12.8 | |
| $[Ru(5\text{-}Hmtuc)(bipy)_2]ClO_4$ | Adjacent (65%)[b] | | 1.59 (s, 3 H) | | 12.3 | 7.22–9.70 |
| | Remote (35%) | | 1.64 (s, 3 H) | 6.48 (s, 1 H) | 12.7 | |
| $[Ru(6\text{-}Hmtuc)(bipy)_2]ClO_4$ | Adjacent (50%) | | 5.30 (s, 1 H) | 2.02 (s, 3 H) | 12.4 | 7.21–9.72 |
| | Remote (50%) | | 5.61 (s, 1 H) | 0.98 (s, 3 H) | 12.6 | |
| $[Ru(6\text{-}Hptuc)(bipy)_2]ClO_4$ | Adjacent (40%) | | 5.29 (s, 1 H) | 0.24–1.51[c] | 12.3 | 7.22–9.72 |
| | Remote (60%) | | 5.59 (s, 1 H) | 0.85–2.27[d] | 12.6 | |

[a] Chemical shift (δ) downfield relative to $SiMe_4$ in $(CD_3)_2SO$. [b] The signal at position 6 is hidden by the bipy signals of δ 7.22–9.70. [c] δ 0.24 (t, 3 H, $CH_3$), 0.73 (m, 2 H, $CH_2CH_2CH_3$) and 1.51 (t, 2 H, $CH_2CH_2CH_3$). [d] δ 0.85 (t, 3 H, $CH_3$), 1.28 (m, 2 H, $CH_2CH_2CH_3$) and 2.27 (t, 2 H, $CH_2CH_2CH_3$).

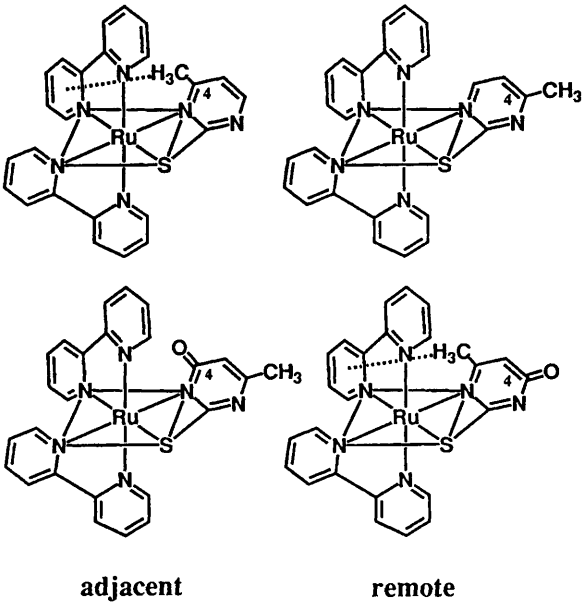



**Fig. 2** Two linkage isomers of $[Ru(mpymt)(bipy)_2]ClO_4$ (above) and $[Ru(6\text{-}Hmtuc)(bipy)_2]ClO_4$ (below). The terms adjacent and remote are defined by the $C^4$ substituent group

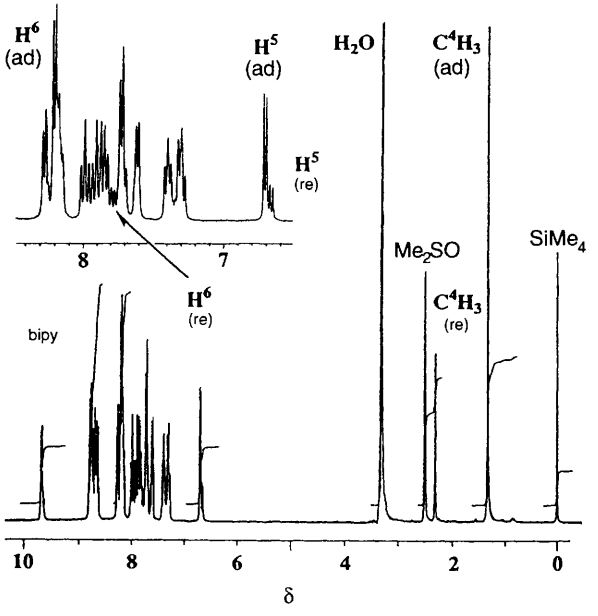



**Fig. 3** Proton NMR spectrum of $[Ru(mpymt)(bipy)_2]^+$; ad = adjacent, re = remote

effect of bipy,[9] whereas the signal at δ 2.28 is assigned to the methyl group in a remote position. Since there is no such ring-current effect in $[Co(dmpymt)(en)_2]^{2+}$ the two methyl signals have similar chemical shifts (δ 2.51 and 2.35). In the $^1H$ NMR spectrum of $[Ru(mpymt)(bipy)_2]^+$ (Fig. 3), two methyl signals appear at δ 2.32 and 1.33 which correspond to those of $[Ru(dmpymt)(bipy)_2]^+$: the ratio is 20% for δ 2.32 to 80% for δ 1.33 based on signal intensities. This result means that two linkage isomers exist in $[Ru(mpymt)(bipy)_2]^+$, 20% remote and 80% adjacent.

Since all the ligands are unsymmetric in the tuc system linkage isomers are expected. The oxygen atom occupies the 4 position and therefore the chemical shift due to a 6-proton or -alkyl group is applicable. In $[Ru(Htuc)(bipy)_2]^+$, two $H^5$ doublets were observed at similar positions [δ 5.44 (intensity 30%) and 5.70 (70%)] because of the absence of a ring-current effect. A weak doublet at δ 6.52 (30%) was assigned to the corresponding $H^6$ signal of a remote isomer ($N^1/S^2$ co-ordination) because $N^1$ is deprotonated upon co-ordination. The $H^6$ signal of the adjacent isomer ($S^2/N^3$ co-ordination) is a broad quartet at δ 7.42 in the bipy region, resulting from $H^5$ and $N^1H$ coupling. Since the 6-proton in the remote isomer is expected to be at higher field than that in the adjacent isomer the above assignment is reasonable. Thus, the adjacent isomer is dominant in $[Ru(Htuc)(bipy)_2]^+$. A similar preference of the $S^2/N^3$ co-ordination mode for tuc, which may be ascribed to an electronic effect, has been reported also in molybdenum and tungsten complexes.[10]

For $[Ru(5\text{-}Hmtuc)(bipy)_2]^+$ the linkage isomeric ratio was almost the same as that for $[Ru(Htuc)(bipy)_2]^+$. Two methyl signals appear at δ 1.59 (65%) and 1.64 (35%) due to adjacent and remote isomers. The alkyl group at the 5 position showed no eminent upfield shift for both isomers and hence has almost no effect on the linkage isomer distribution. On the other hand, the situation is considerably different in $[Ru(6\text{-}Hmtuc)(bipy)_2]^+$ and $[Ru(6\text{-}Hptuc)(bipy)_2]^+$. Two methyl signals with almost equal intensities were observed at δ 0.98 and 2.02 for $[Ru(6\text{-}Hmtuc)(bipy)_2]^+$ (Fig. 4). The first (50%) is assigned to a remote isomer and the second (50%) to an adjacent isomer. The proportion of the remote form is further increased to 60% in $[Ru(6\text{-}Hptuc)(bipy)_2]^+$. These results

indicate the important role of the 6-alkyl groups in the linkage isomer distribution.

### Crystal structure of the adjacent form of [Ru(mpymt)(bipy)$_2$]-ClO$_4$

The complex [Ru(mpymt)(bipy)$_2$]$^+$ is composed of 20% of a remote isomer and 80% of an adjacent isomer. Careful fractional crystallization of the complex from methanol–water gave a pure adjacent isomer as the first crystals, the structure of which was confirmed by the $^1$H NMR spectrum. Fig. 5 shows the numbered ORTEP[11] drawing of this complex ion, bond distances and angles are listed in Table 3. The mpymt ligand co-ordinates through the 2-sulfur and 3-nitrogen donors and adopts the adjacent linkage form irrespective of the steric hindrance. A distorted-octahedral structure is found for this complex: the N(21)–Ru–N(41) angle is 175.5(2)°, whereas the S–Ru–N(51) and N(3)–Ru–N(31) angles are 169.2(2) and 166.7(2)°, respectively. The bite angle S–Ru–N(3) is 68.2(2)°, similar to 66.6(2) and 67.7(2)° in *cis*(*P*)-[Ru(pyt)$_2$(PPh$_3$)$_2$][12] (pyt = pyridine-2-thionate) but considerably smaller than 72.4(1)° in [Co(mpymt)(en)$_2$]$^{2+}$.[3]

The Ru–S and Ru–N(3) lengths 2.408(2) and 2.103(6) Å, respectively, are in good agreement with 2.434(2) and 2.437(2) Å, and 2.115(6) and 2.132(7) Å, respectively, in *cis*(*P*)-[Ru(pyt)$_2$-(PPh$_3$)$_2$].[12] The four C–N [1.321(9), 1.33(1), 1.336(9) and 1.336(9) Å] and two C–C [1.36(1) and 1.39(1) Å] bond lengths of the mpymt ligand do not deviate much from the 1.340(2) and 1.393(2) Å, respectively, of pyrimidine itself,[13] and are also very similar to the values in [Co(mpymt)(en)$_2$]$^{2+}$. The result agrees well with our previous investigations on cobalt(III) complexes containing pymt, mpymt and dmpymt which adopt mainly the delocalized resonance structure for the pyrimidine ring.[1,3]

The S–C(2) bond length 1.711(8) Å of [Ru(mpymt)-(bipy)$_2$]ClO$_4$ is considerably longer than 1.679(1) Å of pymt.[13] Hence the double-bond character is probably altered much by co-ordination. However this C–S bond lengthening upon co-ordination is not so eminent as seen in cobalt(III) complexes: the S–C distance is 1.732(4) in [Co(mpymt-*N*,*S*)(en)$_2$][ClO$_4$]$_2$,[3] 1.738(7) in [Co(tuc-*N*,*S*)(en)$_2$]ClO$_4$[2] and 1.742(7) Å in [Co(apymt-*N*,*S*)(en)$_2$][ClO$_4$]$_2$.[4]

The Ru–N(51) bond length *trans* to sulfur is 2.063(6) Å, and the average of Ru–N(21) and Ru–N(41) *cis* to sulfur is 2.057 Å. The difference between *trans* and *cis* bond lengths is negligible in this complex.

In this complex an interaction between C(7) and the π system of bipy is expected. Fig. 6 shows a stereoview which demonstrates that the methyl group lies just over one of the pyridine rings. The non-bonded distances are C(7) · · · N(51) 3.28(1), C(7) · · · C(56) 3.61(2) and C(7) · · · C(52) 3.64(2) Å. The distance between the least-squares plane defined by atoms N(51) and C(52)–C(56) and H(7b) is 2.65 and H(7c) is 2.81 Å. These values are considerably shorter than the sums (*ca.* 2.9 Å) of van der Waals radii of the benzene (1.7 Å, *i.e.* half of the π-electron thickness) or adenine (1.6–1.8 Å)[14] and the hydrogen atom (1.2 Å).

### Role of CH–π interaction in linkage isomerism

The linkage isomer ratios of the present ruthenium(II) complexes [RuL(bipy)$_2$]$^+$ are collected in Table 4 as well as those of the corresponding cobalt(III) complexes [CoL(en)$_2$]$^{2+}$. In a case of apymt only a remote isomer exists in both complexes. Since there is no attractive interaction between the amino group and the en or bipy ligand, a remote isomer is more favourable than an adjacent isomer from a steric viewpoint.

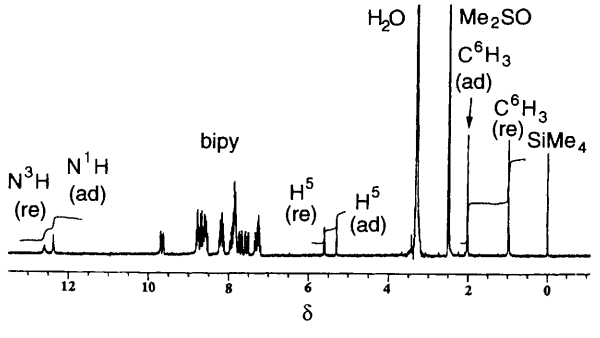



**Fig. 4** Proton NMR spectrum of [Ru(6-Hmtuc)(bipy)$_2$]$^+$

**Table 3** Selected bond distances (Å) and angles (°) for [Ru(mpymt)-(bipy)$_2$]ClO$_4$

| | | | |
|---|---|---|---|
| Ru–S | 2.408(2) | Ru–N(31) | 2.039(5) |
| Ru–N(3) | 2.103(6) | Ru–N(41) | 2.065(5) |
| Ru–N(21) | 2.044(6) | Ru–N(51) | 2.063(6) |
| S–C(2) | 1.711(8) | N(1)–C(2) | 1.321(9) |
| N(1)–C(6) | 1.33(1) | N(3)–C(2) | 1.367(9) |
| N(3)–C(4) | 1.336(9) | C(4)–C(5) | 1.39(1) |
| C(5)–C(6) | 1.36(1) | C(4)–C(7) | 1.49(2) |
| C(7)–H(7a) | 0.9(1) | C(7)–H(7b) | 1.14(9) |
| C(7)–H(7c) | 1.2(1) | | |
| | | | |
| S–Ru–N(3) | 68.2(2) | Ru–S–C(2) | 80.4(3) |
| S–C(2)–N(3) | 110.8(5) | Ru–N(3)–C(2) | 100.6(4) |
| C(2)–N(1)–C(6) | 116.9(9) | N(1)–C(2)–N(3) | 124.2(7) |
| N(1)–C(6)–C(5) | 122(1) | C(2)–N(3)–C(4) | 118.9(7) |
| N(3)–C(4)–C(5) | 118(1) | C(4)–C(5)–C(6) | 120(1) |
| N(3)–C(4)–C(7) | 118.0(9) | C(5)–C(4)–C(7) | 124(1) |
| S–Ru–N(51) | 169.2(2) | N(41)–Ru–N(51) | 78.5(2) |
| N(3)–Ru–N(31) | 166.7(2) | N(21)–Ru–N(31) | 79.2(2) |
| N(21)–Ru–N(41) | 175.5(2) | | |

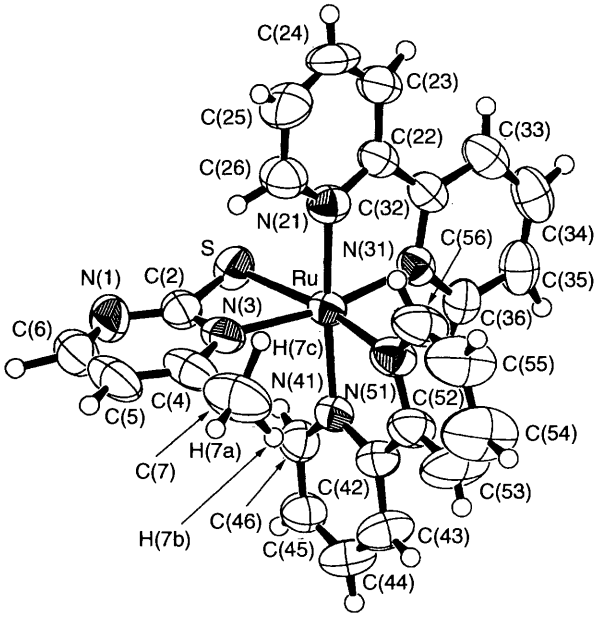



**Fig. 5** An ORTEP drawing of [Ru(mpymt)(bipy)$_2$]ClO$_4$ with thermal ellipsoids drawn at the 50% probability level

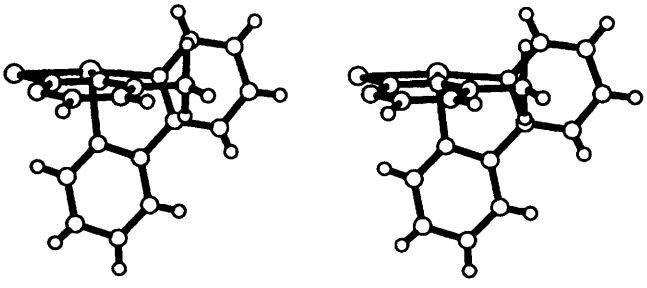


**Fig. 6** A stereoview of the CH–π interaction in [Ru(mpymt)-(bipy)$_2$]ClO$_4$

**Table 4** Proportions (%) of linkage isomers in $[RuL(bipy)_2]^+$ and $[CoL(en)_2]^{2+}$

| | Ruthenium(II) | | Cobalt(III) | |
|---|---|---|---|---|
| L | Adjacent | Remote | Adjacent | Remote |
| apymt | 0 | 100 | 0 | 100 |
| mpymt | 80 | 20 | 0 | 100 |
| Htuc | 70 | 30 | 100 | 0 |
| 5-Hmtuc | 65 | 35 | 100 | 0 |
| 6-Hmtuc | 50 | 50 | 100 | 0 |
| 6-Hptuc | 40 | 60 | | |

The dominant isomer changes drastically in the mpymt system. In $[Co(mpymt)(en)_2]^{2+}$ a remote isomer is formed stereoselectively. It is reasonable to consider that the 4-methyl group lies away from the en chelate ring to minimize the steric repulsion. However, the main isomer is the adjacent form in $[Ru(mpymt)(bipy)_2]^+$. These facts indicate that an attractive interaction exists between the methyl group and the bipy ligand. Such an attractive interaction between an alkyl group and a π system is called a CH–π interaction and was first advocated by Nishio;[15] since then many experimental facts supporting this hypothesis have been collected from many scientific fields. Okawa[16] has reviewed examples in co-ordination compounds. Thus, the drastic change in the main linkage isomer in $[Co(mpymt)(en)_2]^{2+}$ and $[Ru(mpymt)(bipy)_2]^+$ is attributed to the existence of a CH–π interaction in the latter complex. Recently we have reported the effect of a similar intramolecular interligand interaction on stereoselectivities in *mer*-$[Co(mpymt)_3]$.[17]

In the Htuc system the adjacent isomer is dominant in $[Ru(Htuc)(bipy)_2]^+$ as well as $[Co(tuc)(en)_2]^{2+}$. This means that the $S^2/N^3$ mode of co-ordination is preferred to the $N^1/S^2$ mode. It would be very interesting to know how the introduction of alkyl groups at position 5 or 6 affects the linkage isomer ratio. Since changes in isomeric ratios were not observed for the corresponding cobalt(III) series the electronic effect of introducing the alkyl group is negligible. The complex in $[Ru(5\text{-}Hmtuc)(bipy)_2]^+$ comprises 65% adjacent isomer and 35% remote. The ratio is almost the same as that in the Htuc system and thus the 5-methyl group has almost no effect on the ratio. On the other hand, the linkage isomers are formed in equal amounts in $[Ru(6\text{-}Hmtuc)(bipy)_2]^+$ and the remote form becomes dominant (60%) in $[Ru(6\text{-}Hptuc)(bipy)_2]^+$. These results indicate that there is a CH–π interaction between the 6-alkyl groups and the π system of bipy and therefore the proportion of the remote isomer increases remarkedly in the Htuc series as in $[Ru(mpymt)(bipy)_2]^+$.

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