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# Reactivity of $[\{(\eta^6\text{-arene})RuCl(\mu\text{-}Cl)\}_2]$ towards some potentially bidentate ligands. Molecular structure of $[(\eta^6\text{-}p\text{-cymene})RuCl(taz)]PF_6$ ($p$-cymene $= p\text{-}MeC_6H_4CH\text{-}Me_2$; taz = 2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine)

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## Abstract

Reactions of $[\{(\eta^6\text{-arene})RuCl(\mu\text{-}Cl)\}_2]$ [arene = benzene or $p$-cymene ($p$-isopropyltoluene)] have been carried out with 4-cyanopyridine (4-CNpy), $o$-aminophenol (oap), $o$-phenylenediamine (opda), $p$-phenylenediamine (ppda) and 2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine (taz). The isolated complexes are of the types $[(\eta^6\text{-}C_6H_6)RuCl_2L]$ [L = 4-CNpy (Ia) or oap (IIa)], $[(\eta^6\text{-}C_6H_6)RuClL_2]Cl$ [L = oap (IIIa); $L_2$ (bidentate) = opda (IVa) or taz (VIa)] or $[\{(\eta^6\text{-}C_6H_6)Cl_2Ru\}_2(\mu\text{-ppda})]$ (VIIIa). Complexes IVa and VIa undergo anion exchange with $KPF_6$ to give the corresponding hexafluorophosphates (Va and VIIa). The $p$-cymene analogues (Ib–VIIIb) have been obtained. Conductance measurements, thermogravimetry and spectroscopic (IR and $^1H$ and $^{13}C$ NMR) methods have been used to study the new compounds. The structure of VIIb was determined by X-ray diffraction methods. The ruthenium atom of the cation of VIIb is coordinated by the 4-amino (Ru–N = 2.140(2) Å) and 3-thioxo (Ru–S = 2.354(1) Å) groups of the triazine and a chloride ligand (Ru–Cl = 2.394(1) Å). The $\eta^6$-$p$-cymene ring completes the hexacoordination.

*Key words:* Ruthenium; Arene

## 1. Introduction

The reaction of $[\{(\eta^6\text{-arene})RuCl(\mu\text{-}Cl)\}_2]$ towards neutral mono- and bi-dentate ligands have been widely studied and recently reviewed [1]. Cleavage of the chloride bridges of $[\{Ru(\eta^6\text{-arene})Cl\}_2(\mu\text{-}Cl)_2]$ with various monodentate ligands (L) gives monomeric compounds [2–10] $[(\eta^6\text{-arene})RuCl_2L]$ and further halide substitution may afford the cationic derivatives $[(\eta^6\text{-arene})RuClL_2]^+$ [2,3,6,7,11–13], depending on L and the solvent used. With potentially bidentate ligands (LL) complexes of the types $[(\eta^6\text{-arene})RuCl(LL)]^+$ and $[\{(\eta^6\text{-arene})RuCl_2\}_2(\mu\text{-LL})]$ are formed similarly [11,14,16].

In this paper we present the results obtained from the reaction between $[\{\eta^6\text{-arene})RuCl(\mu\text{-}Cl)\}_2]$ (arene = benzene or $p$-cymene) and 4-cyanopyridine, $o$-aminophenol, $o$- and $p$-phenylenediamine, and 4-amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1, 2,4-triazine. They are all potentially bidentate ligands with little or no ability to back-accept electron density from the metal. Similar reactions with the isoelectronic $[\{\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)\}_2]$ have been reported [17].

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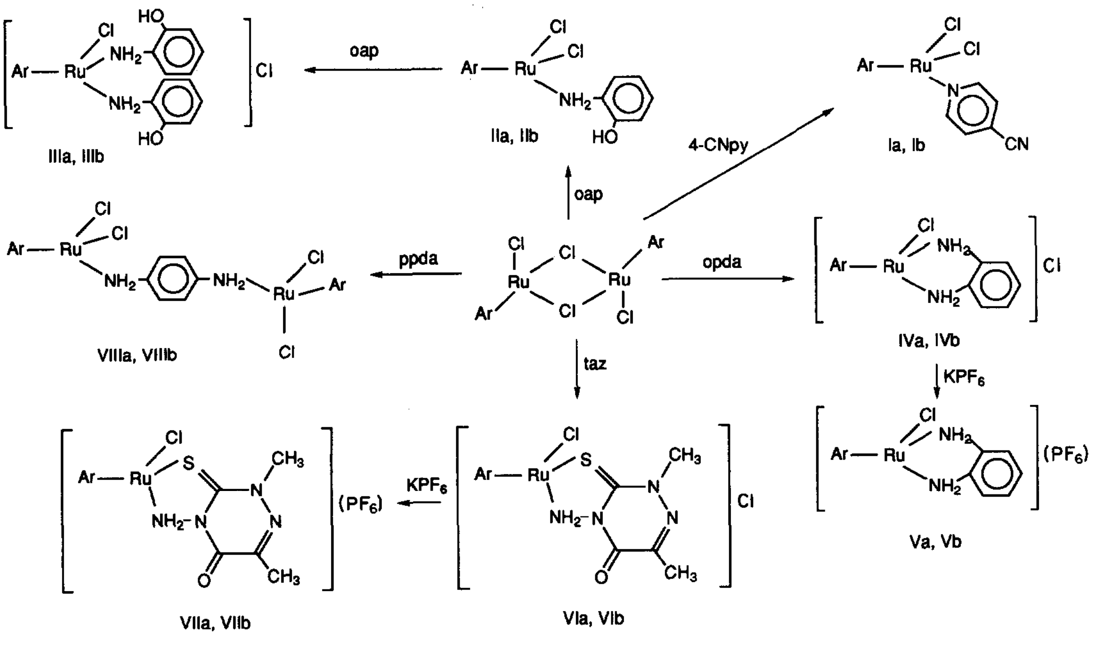
## 2. Results and discussion

In dichloromethane the complexes $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = benzene or *p*-cymene) react with the Lewis bases mentioned above to form the complexes shown in Scheme 1. All the ruthenium compounds isolated are air-stable solids which gave satisfactory partial elemental analyses and their colours, yields and conductance data are listed in Table 1. The oap and 4-CNpy are monodentate donors but further chloride substitution takes place only with oap to give the cationic derivatives IIIa and IIIb. Attempts to prepare complexes containing bridging 4-CNpy were fruitless, though the isolation of complexes of the type $[(CO)(PPh_3)_2(4\text{-NCpy})HRuNCC_5H_4NRuL_2(\eta^5\text{-}C_5H_5)]^+$ was reported recently [18]. Opda and taz behave as chelating bidentate donors but the ppda complexes VIIIa and VIIIb are neutral, with the diamine bridging two $(\eta^6\text{-arene})Cl_2Ru$ fragments.

Some IR data are collected in Table 2. Complexes Ia and Ib exhibit an $\nu$(CN) absorption around 2240 $cm^{-1}$ compared to 2242 $cm^{-1}$ in the corresponding free 4-CNpy, implying the non-coordination of the CN group. The bonding through the pyridine nitrogen is also shown by the shifts to higher wavenumbers of the bands having contributions from $\nu$(C–C) and $\nu$(C–N) of the pyridine molecule [19] which are found at *ca.* 1605m, 1540m and 1410m $cm^{-1}$ in the spectra of Ia and Ib. The IR spectra of complexes II–VIII show the bands attributed to $\nu$(NH) of the coordinated amino groups, which appear at lower ($\Delta\nu > 100$ $cm^{-1}$) wavenumbers than in the spectra of the free donors.

The absence of absorptions from the 3400–3300 $cm^{-1}$ range for the ppda complexes VIIIa and VIIIb indicate that both amino groups are bonded to ruthenium. The important IR bands of uncoordinated taz are found at 3320, 3220 (NH stretch), 1665 (C=O stretch), and 1380 (the thioamide band II) [20,21]. As can be seen in Table 2, the 4-$NH_2$ nitrogen of taz is involved in coordination, but the C=O stretching vibration is shifted to higher wavenumber, indicating that the carbonyl group remains uncoordinated and that the free carbonyl oxygen is likely to be hydrogen bonded. The presence of a band (or a shoulder on the strong band at 1375 $cm^{-1}$ arising from the methyl deformation mode) at *ca.* 1340 $cm^{-1}$ in the spectra of complexes VI and VII is attributed to coordination of taz through the sulfur atom of the thiocarbonyl group [21], so the triazine is a bidentate N,S-donor.

This has been confirmed by a single-crystal X-ray diffraction study of VIIb. The IR spectrum of IVa shows the presence of water of hydration and its thermogravimetric curve indicates that one $H_2O$ molecule is lost at *ca.* 147°C to give the stable, anhydrous compound. A broad, strong band at 840 $cm^{-1}$ in the spectra of complexes Va, Vb, VIIa, and VIIb demon-



Scheme 1.

TABLE 1. Analytical data, yields, colours and conductivities for the ruthenium complexes

| Complex | Colour | Yield (%) | Analysis (%) [a] | | | M.P. [b] (°C) | $\Lambda_M$ [c] |
|---|---|---|---|---|---|---|---|
| | | | C | H | N | | |
| Ia | yellow | 70 | 40.51 | 2.90 | 7.86 | 144 | 0 [d] |
| | | | (40.65) | (2.82) | (7.90) | | |
| Ib | orange | 77 | 46.90 | 4.37 | 6.45 | 126 | 0 [e] |
| | | | (46.84) | (4.42) | (6.83) | | |
| IIa | light brown | 75 | 40.35 | 3.86 | 3.95 | 154 | 13 [d] |
| | | | (40.11) | (3.62) | (3.90) | | |
| IIb | orange | 60 | 46.31 | 5.00 | 3.49 | 168 | 1 [e] |
| | | | (46.25) | (5.06) | (3.37) | | |
| IIIa | yellow | 80 | 46.48 | 4.52 | 6.39 | 145 | 29 [d] |
| | | | (46.12) | (4.27) | (5.98) | | |
| IIIb | yellow | 75 | 50.09 | 5.51 | 5.47 | 118 | 20 [d] |
| | | | (50.34) | (5.34) | (5.34) | | |
| IVa [f] | yellow brown | 80 | 38.25 | 4.33 | 7.57 | 172 | 32 [d] |
| | | | (38.31) | (4.29) | (7.45) | | |
| IVb | yellow | 75 | 46.42 | 5.49 | 6.68 | 191 | 31 [d] |
| | | | (46.38) | (5.35) | (6.76) | | |
| Va | brown | 75 | 30.16 | 3.18 | 5.70 | 196 | 106 [e] |
| | | | (30.20) | (2.94) | (5.87) | | 33 [d] |
| Vb | red brown | 70 | 36.80 | 4.11 | 5.32 | 178 | 123 [e] |
| | | | (36.03) | (4.13) | (5.25) | | 30 [d] |
| VIa | yellow | 66 | 31.12 | 3.37 | 13.11 | 166 | 50 [d] |
| | | | (31.26) | (3.31) | (13.26) | | |
| VIb | yellow orange | 80 | 37.58 | 4.62 | 11.60 | 137 | 34 [d] |
| | | | (37.62) | (4.60) | (11.70) | | |
| VIIa | brown | 60 | 24.86 | 2.69 | 10.32 | 168 | 41 [d] |
| | | | (24.41) | (2.59) | (10.35) | | |
| VIIb | orange | 78 | 30.70 | 3.81 | 9.42 | 137 | 39 [d] |
| | | | (30.15) | (3.68) | (9.38) | | |
| VIIIa | light brown | 75 | 35.62 | 3.32 | 4.54 | 173 | 7 [d] |
| | | | (35.51) | (3.29) | (4.60) | | |
| VIIIb | orange | 75 | 42.62 | 5.18 | 4.29 | 219 | 5 [d] |
| | | | (43.30) | (5.00) | (3.88) | | |

[a] Calculated values in parentheses. [b] Decomposition temperatures from the thermogravimetric curves. [c] $Ohm^{-1}\ cm^2\ mol^{-1}$ ($c \approx 5 \times 10^{-4}$ M). [d] In dimethyl sulfoxide. [e] In acetone. [f] The yield and the analytical data are for the monohydrated complex.

strates the presence of the $PF_6$ anion. One or two bands at 310–270 $cm^{-1}$ in the spectra of all the complexes are attributed to $\nu$(Ru–Cl) [9].

Complexes Ia, IIa, IIIa, and IIIb are soluble only in donor solvents such as dimethyl sulfoxide but the $^1H$ NMR spectra of the solutions show that there is displacement of neutral ligands by solvent according to eqns. (1) and (2). Thus, the spectra consist of

$$[\eta^6\text{-}C_6H_6)RuCl_2L] + S \longrightarrow [(\eta^6\text{-}C_6H_6)RuCl_2S] + L$$

$$(L = 4\text{-CNpy or oap; } S = (CD_3)_2SO) \qquad (1)$$

$$[(\eta^6\text{-arene})RuClL_2]Cl + S \longrightarrow [(\eta^6\text{-arene})RuCl_2S] + 2L$$

$$(\text{arene} = \text{benzene or } p\text{-cymene; } L = \text{oap; } S = (CD_3)_2SO) \qquad (2)$$

the signals of uncoordinated L and those arising from the ruthenium-dmso complex [5.96 (s, $C_6H_6$) for Ia, IIa, and IIIa); 5.78 (s, $H_A + H_B$), 2.82 (spt, $CHMe_2$), 2.07 (s, Me), and 1.17 (d, $CHMe_2$, $J = 6.8$ Hz) for IIIb]. However, when the spectrum of a recently prepared solution of Ia in dmso-$d_6$ was recorded quickly, a mixture of Ia (5%; $^1H$ NMR data in Table 3) and the dmso complex (95%) could be detected. Complexes Ia and IIa are non-electrolytes in dmso solution. The corresponding data for IIIa and IIIb given in Table 1 are those obtained from freshly prepared solutions, but both values are low for 1 : 1 electrolytes [22]. Furthermore, when the solutions of IIIa and IIIb were left for *ca.* 30 min they became non-conducting which is consistent with the dissociation process described above (eqn. 2). Complexes Ib and IIb are soluble in acetone and in this solvent they are non-electrolytes. The $^1H$ and $^{13}C$ NMR data in Table 3 indicate that in acetone-$d_6$ the 4-CNpy or oap remain within the coordination sphere of ruthenium.

Complexes IVa and IVb are soluble only in dimethyl sulfoxide but the hexafluorophosphate salts Va and Vb are also soluble in acetone and the four compounds behave as 1 : 1 electrolytes. The $^1H$ NMR spectra show

TABLE 2. Some relevant IR data ($cm^{-1}$; Nujol mulls) for the ruthenium complexes

| Complex | $\nu$(N–H) | $\nu$(Ru–Cl) | Others |
|---|---|---|---|
| Ia | | 280sh, 270s | 2230m $\nu$(C≡N) |
| Ib | | 280br,m | 2240w $\nu$(C≡N) |
| IIa | 3200vs,br | 285sh, 280s | |
| IIb | 3250s, 3210s, 312s | 280s, 270m | |
| IIIa | 3280s, 3160s, 3130m | 300m, 280sh | 3320sh $\nu$(OH) |
| IIIb | 3290s, 3120br,s | 290m | 3320sh $\nu$(OH) |
| IVa [a] | 3140s,br | 305s, 285m | 3470m,br, 3420m,br, $\nu$(OH), 1620m, $\delta$(HOH) |
| IVb | 3170s,br | 310s, 290m | |
| Va | 3300vs, 3170vs, 3120s | 290s | 840s,br ($PF_6$-) |
| Vb | 3310s, 3220s, 3125m | 285sh, 270m | 840s,br ($PF_6$-) |
| VIa | 3090s | 295s | 1715vs $\nu$(C=O), 1345sh $\nu$(C=S) |
| VIb | 3170m,br | 280m, 275sh | 1720vs $\nu$(C=O), 1350sh $\nu$(C=S) |
| VIIa | 3250m, 3180m,br | 285m | 1700s $\nu$(C=O), 1340s $\nu$(C=S), 845vs,br ($PF_6$-) |
| VIIb | 3240m, 3130m | 290m | 1715vs $\nu$(C=O), 1330m $\nu$(C=S), 845vs,br ($PF_6$-) |
| VIIIa | 3260m, 3190m, 3120m | 290s, 280sh | |
| VIIIb | 3300m, 3160m, 3080s | 275m,br | |

[a] Data for the monohydrated complex.

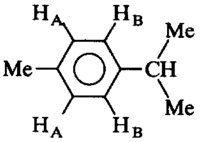
TABLE 3. NMR data [a,b] for the ruthenium complexes (*J* in Hz)

| Complex | $^1$H $\delta$ (SiMe$_4$) | $^{13}$C{$^1$H} $\delta$ (SiMe$_4$) |
|---|---|---|
| Ia [c] | 9.20 (d, 2H, 2- and 6-H of 4-CNpy, *J* 6.5) | |
| | 7.95 (d, 2H, 3- and 5-H of 4-CNpy, *J* 6.5) | |
| | 5.77 (s, 6H, $C_6H_6$) | |
| Ib [d] | 9.38 (m, 2H, 2- and 6-H of 4CNpy) | 157.07 ($C^{2,6}$, 4-CNpy) |
| | 7.63 (m, 2H, 3- and 5-H of 4CNpy) | 126.70 ($C^{3,5}$, 4-CNpy) |
| | 5.55 (d, 2H, $H_{A/B}$, *J* 6) | 122.17 ($C^4$, 4-CNpy) |
| | 5.35 (d, 2H, $H_{B/A}$, *J* 6) | 116.62 (CN) |
| | 3.06 (sp, 1H, C*H* Me$_2$) | 103.88 (*C*-$^i$Pr) |
| | 2.20 (s, 3H, Me) | 98.25 (*C*-Me) |
| | 1.39 (d, 6H, CH*Me*$_2$) | 84.17 ($C_B$) |
| | | 83.07 ($C_A$) |
| | | 31.45 (*CH* Me$_2$) |
| | | 22.41 (CH*Me*$_2$) |
| | | 18.08 (Me) |
| IIb [d] | 9.14 (s, br, 1H, OH) | 148.67 (C-OH) |
| | 7.48–6.88 (m, 4H, oap) | 134.81 (C-$NH_2$) |
| | 5.14 (d, 2H, $H_{A/B}$, *J* 6.1) | 126.53 (oap) |
| | 4.98 (d, 2H, $H_{B/A}$, *J* 6.1) | 122.29 (oap) |
| | 4.87 (s, br, 2H, $NH_2$) | 120.89 (oap) |
| | 2.81 (sp, 1H, C*H*Me$_2$) | 117.13 (oap) |
| | 2.05 (s, 3H, Me) | 103.78 (C-$^i$Pr) |
| | 1.20 (d, 6H, CH*Me*$_2$) | 95.46 (*C*-Me) |
| | | 82.88 ($C_B$) |
| | | 79.93 ($C_A$) |
| | | 31.28 (C*H* Me$_2$) |
| | | 22.08 (CH*Me*$_2$) |
| | | 18.41 (Me) |
| IVa [c] | 8.64 (d, 2H, $NH_2$, *J* 12.6) | 139.84 ($CNH_2$) |
| | 7.20 (m, 4H, opda) | 126.83 ($C^{3,6}$, opda) |
| | 6.41 (d, 2H, $NH_2$, *J* 12.6) | 126.11 ($C^{4,5}$, opda) |
| | 5.94 (s, 6H, $C_6H_6$) | 83.08 ($C_6H_6$) |
| IVb [c] | 8.51 (d, 2H, $NH_2$, *J* 12.6) | 140.08 ($CNH_2$) |
| | 7.20 (m, 4H, opda) | 126.60 ($C^{3,6}$, opda) |
| | 6.13 (d, 2H, $NH_2$, *J* 12.6) | 126.12 ($C^{4,5}$, opda) |
| | 5.86 (d, 2H, $H_{A/B}$, *J* 5.7) | 102.96 (*C*-$^i$Pr) |
| | 5.60 (d, 2H, $H_{B/A}$, *J* 5.7) | 96.21 (*C*-Me) |
| | 2.96 (sp, 1H, C*H* Me$_2$, *J* 6.8) | 82.00 ($C_B$) |
| | 2.21 (s, 3H, Me) | 80.31 ($C_A$) |
| | 1.13 (d, 6H, CH*Me*$_2$, *J* 6.8) | 30.04 (*CH* Me$_2$) |
| | | 22.48 (CH*Me*$_2$) |
| | | 18.18 (Me) |
| Va [d] | 8.22 (d, 2H, $NH_2$, *J* 12.1) | 139.86 ($CNH_2$) |
| | 7.34 (m, 4H, opda) | 128.55 ($C^{3,6}$, opda) |
| | 5.97 (s, 6H, $C_6H_6$) | 127.04 ($C^{4,5}$, opda) |
| | 5.77 (d, 2H, $NH_2$, *J* 12.1) | 84.39 ($C_6H_6$) |
| Vb [d] | 7.91 (d, 2H, $NH_2$, *J* 12.1) | 139.83 ($CNH_2$) |
| | 7.42 (m, 2H, 3- and 6-H of opda) | 128.47 ($C^{3,6}$, opda) |
| | 7.24 (m, 2H, 4- and 5-H of opda) | 126.84 ($C^{4,5}$, opda) |
| | 5.93 (d, 2H, $H_{A/B}$, *J* 6.4) | 104.45 (*C*-$^i$Pr) |
| | 5.71 (d, 2H, $H_{B/A}$, *J* 6.4) | 99.66 (*C*-Me) |
| | 5.65 (d, 2H, $NH_2$, *J* 12.1) | 83.06 ($C_B$) |
| | 3.00 (sp, 1H, C*H* Me$_2$, *J* 6.5) | 81.70 ($C_A$) |
| | 2.29 (s, 3H, Me) | 31.46 (C*H* Me$_2$) |
| | 1.21 (d, 6H, CH*Me*$_2$, *J* 6.5) | 22.42 (CH*Me*$_2$) |
| | | 18.54 (Me) |

TABLE 3. (continued)

| Complex | $^1$H $\delta$ (SiMe$_4$) | $^{13}$C{$^1$H} $\delta$ (SiMe$_4$) |
|---|---|---|
| VIa [c] | 10.89 (d, br, 1H, $NH_2$, $J \approx 8.4$) | |
| | 9.30 (d, br, 1H, $NH_2$, $J \approx 8.4$) | |
| | 6.03 (s, 6H, $C_6H_6$) | |
| | 3.89 (s, 3H, 2-Me of taz) | |
| | 2.30 (s, 3H, 6-Me of taz) | |
| VIb [c,e] | 10.86 (d, br, 2H, $NH_2$) | |
| | 9.16 (d, br, 2H, $NH_2$) | |
| | 5.99 (br, 2H, $H_{A/B}$) | |
| | 5.89 (br, 2H, $H_{B/A}$) | |
| | 5.75 (br, 2H, $H_{A/B}$) | |
| | 5.63 (br, 2H, $H_{B/A}$) | |
| | 3.92 (br, 6H, 2-Me of taz) | |
| | 2.80 (sp, br, 2H, C*H* Me$_2$) | |
| | 2.26 (br, 6H, 6-Me of taz) | |
| | 2.18 (br, 6H, Me) | |
| | 1.22 (br, 12H, CH*Me*$_2$) | |
| VIIa [c] | 10.70 (d, 1H, $NH_2$, *J* 8.6 Hz) | |
| | 9.20 (d, 1H, $NH_2$, *J* 8.6 Hz) | |
| | 5.98 (s, 6H, $C_6H_6$) | |
| | 3.88 (s, 3H, 2-Me of taz) | |
| | 2.30 (s, 3H, 6-Me of taz) | |
| VIIb [c,e] | 10.43 (d, br, 2H, $NH_2$, $J \approx 8.6$) | |
| | 9.10 (d, br, 2H, $NH_2$, $J \approx 8.6$) | |
| | 6.02 (br, 2H, $H_{A/B}$) | |
| | 5.88 (br, 2H, $H_{B/A}$) | |
| | 5.70 (br, 2H, $H_{A/B}$) | |
| | 5.53 (br, 2H, $H_{B/A}$) | |
| | 3.93 (br, 6H, 2-Me of taz) | |
| | 2.77 (sp, br, 2H, *CH* Me$_2$) | |
| | 2.16 (s, 6H, 6-Me of taz) | |
| | 2.08 (s, 6H, Me) | |
| | 1.20 (pseudo t, 12H, CH*Me*$_2$, *J* 5.9, *J'* 7.0) | |

[a] Abbreviations: s = singlet, d = doublet, t = triplet, sp = septet, m = multiplet, br = broad. [b] Labelling of the *p*-cymene protons:



[c] In $(CD_3)_2SO$. [d] In $(CD_3)_2CO$. [e] See text.

that the hydrogen atoms of each amino group are diasterotopic pairs because chelation of the opda prevents rotation about the Ru–N bond. The single resonance for the $H_2N$-bonded carbon atoms of the opda also confirms that the diamine is bidentate.

The molar conductivities of freshly prepared solutions (Table 1) of complexes VIb and VIIb in dimethyl sulfoxide correspond to 1:1 electrolytes but those of VIa and VIIa are higher than the expected values for 1:1 electrolytes. However, *ca.* 30 min after the preparation of the solutions, the conductivities were higher than the initial values. For example, the conductivity of a solution of VIIa in dimethyl sulfoxide increases from 41 ohm$^{-1}$ cm$^2$ mol$^{-1}$ to a steady value of 68 ohm$^{-1}$

cm$^2$ mol$^{-1}$. These results suggest that slow replacement of Cl$^-$ by dmso takes place, according to eqn. 3.

$$[(\eta^6\text{-arene})RuCl(taz)] + X^- \xrightleftharpoons{\text{dmso}} [(\eta^6\text{-arene})Ru(dmso)(taz)]^{2+}(Cl^-, X^-)$$

$$(\text{arene} = \text{benzene or } p\text{-cymene}; X = Cl \text{ or } PF_6) \quad (3)$$

The $^1$H NMR data are consistent with this. In all cases the triazine is bound to the ruthenium atom [$^1$H NMR data for taz in dimethyl sulfoxide-$d_6$: $\delta$ 6.58 (s, 2H, NH$_2$), 3.87 (s, 3H, 2-Me) and 2.20 (s, 3H, 6-Me)] and the 4-NH$_2$ hydrogen atom pairs are diasterotopic. The $^1$H spectrum of complex VIa indicates that there are two ruthenium complexes in the solution, in the approximate ratio 10%:90%. The former is believed to be complex VIa ($^1$H NMR data in Table 3) and the latter is assigned to $[\eta^6\text{-}C_6H_6)Ru(taz)(dmso\text{-}d_6)]^{2+}$ [$^1$H NMR, $\delta$ 10.89 (d, br, 1H, NH$_2$, $J = 8.4$ Hz), 9.21 (d, br, 1H, NH$_2$, $J = 8.4$ Hz), 5.95 (s, 6H, C$_6$H$_6$), 3.91 (s, 3H, 2-Me of taz), 2.25 (s, 3H, 6-Me of taz)]. The spectrum of complex VIIa exhibits only one set of resonance signals (Table 3) that are probably due to the dication arising from the replacement of Cl$^-$ by dmso. The $^1$H NMR data of the $p$-cymene derivatives VIb and VIIb in Table 3 suggest the presence of an equimolecular mixture of the monocationic and dicationic species of eqn. (3). The structures VIb and VIIb would be expected to exhibit double aromatic and isopropyl methyl proton resonances (two AB systems and two doublets respectively) because the three ligands forming the three legs of the piano-stool arrangement around the ruthenium atom are different [23–24].

Complexes VIIIa and VIIIb are non-electrolytes in dimethyl sulfoxide solution but the $^1$H NMR spectra (in dmso-$d_6$) suggest the presence of three different complexes in the solution, but no reliable assignment could be made.

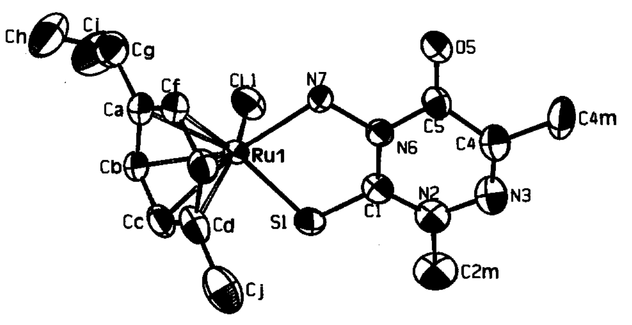


Fig. 1. Molecular structure of the cation of complex $[(\eta^6\text{-}p\text{-cymene})RuCl(taz)]PF_6$ (VIIb).

TABLE 4. Fractional atomic coordinates (×10$^4$) with the equivalent temperature factors

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Ru1 | −61.7(0.3) | 1965.2(0.2) | 2083.2(0.2) | 2.72 |
| Cl1 | 2821(1) | 2185(1) | 1606(1) | 4.45 |
| S1 | 757(1) | 756(1) | 2932(1) | 3.76 |
| C1 | 1989(3) | 1863(2) | 4328(2) | 2.81 |
| N2 | 2568(3) | 1588(2) | 5187(2) | 3.39 |
| C2m | 2439(6) | 336(4) | 4944(4) | 5.24 |
| N3 | 3345(3) | 2429(2) | 6361(2) | 3.62 |
| C4 | 3704(3) | 3576(3) | 6664(2) | 3.25 |
| C4m | 4523(5) | 4495(4) | 7932(3) | 4.47 |
| C5 | 3364(3) | 4026(2) | 5790(2) | 2.95 |
| O5 | 3808(3) | 5087(2) | 5987(2) | 3.98 |
| N6 | 2400(3) | 3081(2) | 4649(2) | 2.62 |
| N7 | 1816(3) | 3430(2) | 3757(2) | 2.94 |
| Ca | −1356(4) | 2448(3) | 728(2) | 3.48 |
| Cb | −1773(4) | 1146(3) | 241(2) | 3.50 |
| Cc | −2627(4) | 470(3) | 765(3) | 3.70 |
| Cd | −3088(4) | 1052(3) | 1820(2) | 3.61 |
| Ce | −2619(4) | 2330(3) | 2327(3) | 3.53 |
| Cf | −1774(4) | 3015(3) | 1786(3) | 3.55 |
| Cg | −552(5) | 3202(3) | 149(3) | 4.71 |
| Ch | −2129(8) | 3500(5) | −424(4) | 6.53 |
| Ci | 371(9) | 2589(5) | −751(5) | 7.08 |
| Cj | −4016(5) | 323(4) | 2376(3) | 5.05 |
| P1 | 1731(1) | 6683(1) | 4000(1) | 3.17 |
| F1 | 2311(3) | 5577(2) | 3224(2) | 5.09 |
| F2 | 692(3) | 5836(2) | 4529(2) | 5.01 |
| F3 | −171(3) | 6156(2) | 2963(2) | 5.41 |
| F4 | 1119(3) | 7755(2) | 4782(2) | 5.42 |
| F5 | 2749(3) | 7514(2) | 3479(2) | 5.51 |
| F6 | 3636(3) | 7187(2) | 5028(2) | 5.21 |
| H21 | 1107(37) | −332(30) | 4427(30) | 5.09 |
| H22 | 3007(50) | 387(35) | 5650(25) | 5.09 |
| H23 | 3006(51) | 97(36) | 4343(29) | 5.09 |
| H41 | 4617(66) | 3991(40) | 8317(39) | 7.94 |
| H42 | 3556(57) | 4828(42) | 8230(40) | 7.94 |
| H43 | 5555(51) | 5119(38) | 8039(44) | 7.94 |
| H71 | 3019(40) | 3739(34) | 3644(33) | 5.09 |
| H72 | 1553(52) | 4126(28) | 4155(30) | 5.09 |
| Hb | −1273(49) | 664(32) | −408(27) | 5.09 |
| Hc | −2747(48) | −415(24) | 450(31) | 5.09 |
| He | −2932(51) | 2710(32) | 3036(25) | 5.09 |
| Hf | −1434(50) | 3882(23) | 2151(30) | 5.09 |
| Hg | 506(42) | 3968(27) | 777(27) | 5.09 |
| Hh1 | −1633(63) | 4034(39) | −789(40) | 7.94 |
| Hh2 | −2993(61) | 2708(33) | −1152(32) | 7.94 |
| Hh3 | −2796(64) | 3976(44) | 95(38) | 7.94 |
| Hi1 | 1014(62) | 3140(38) | −1044(41) | 7.94 |
| Hi2 | 1576(51) | 2462(46) | −410(42) | 7.94 |
| Hi3 | −578(57) | 1869(35) | −1488(32) | 7.94 |
| Hj1 | −3670(66) | −446(34) | 2180(42) | 7.94 |
| Hj2 | −5378(38) | 5(45) | 2178(42) | 7.94 |
| Hj3 | −3616(65) | 726(43) | 3216(24) | 7.94 |

Figure 1 shows a view of the cation of complex VIIb, together with the atom labelling used. Fractional atomic coordinates and selected bond lengths and angles are presented in Tables 4 and 5, respectively. The geometry about the ruthenium atom is that of a distorted octahedron. Each ruthenium is coordinated by a *fac*-Cl, N, S set involving the 4-amino (Ru1–N7 = 2.140(2) Å)

TABLE 5. Selected bond lengths (Å) and angles (°) with their e.s.d.'s

| | | | |
|---|---|---|---|
| Ru1–Cl1 | 2.394(1) | Ca–Cb | 1.433(4) |
| Ru1–S1 | 2.354(1) | Ca–Cf | 1.410(4) |
| Ru1–N7 | 2.140(2) | Cd–Cj | 1.497(4) |
| Ru1–Ca | 2.238(3) | Cb–Cc | 1.395(4) |
| Ru1–Cb | 2.180(3) | Cc–Cd | 1.429(4) |
| Ru1–Cc | 2.182(3) | Cd–Ce | 1.398(4) |
| Ru1–Cd | 2.225(3) | Ce–Cf | 1.418(4) |
| Ru1–Ce | 2.194(3) | Cd–Cj | 1.497(4) |
| Ru1–Cf | 2.195(3) | Ca–Cg | 1.508(4) |
| | | Cg–Ch | 1.527(6) |
| | | Cg–Ci | 1.526(6) |
| | | C1–S1 | 1.687(3) |
| | | C1–N6 | 1.358(3) |
| | | N6–N7 | 1.435(3) |
| S1–Ru1–Cl1 | 86.8(1) | Cf–Ca–Cb | 116.8(3) |
| N7–Ru1–Cl1 | 81.2(1) | Cg–Ca–Cb | 123.0(3) |
| N7–Ru1–S1 | 81.7(1) | Cg–Ca–Cf | 120.2(3) |
| C1–S1–Ru1 | 100.1(1) | Cc–Cb–Ca | 121.2(3) |
| N6–C1–S1 | 122.2(2) | Cd–Cc–Cb | 121.4(3) |
| N7–N6–C1 | 118.4(2) | Ce–Cd–Cc | 117.8(3) |
| Ru1–N7–N6 | 116.3(1) | Cj–Cd–Cc | 121.3(3) |
| | | Cj–Cd–Ce | 121.0(3) |
| | | Cf–Ce–Cd | 120.8(3) |
| | | Cd–Cf–Ca | 122.0(3) |
| | | Ch–Cg–Ca | 107.9(3) |
| | | Ci–Cg–Ca | 114.4(3) |
| | | Ci–Cg–Ch | 110.8(3) |

and 3-thioxo (Ru1–S1 = 2.354(1) Å) substituents on the triazine ring and a chloride (Ru1–Cl1 = 2.394(1) Å). The $\eta^6$-*p*-cymene ring completes the hexacoordination. The C1–S1 distance (1.687(3) Å) supports the double-bond character of the 3-thioxo group [25]. The Ru1–S1–C1 angle (100.1°) is slightly higher than that found (96.15°) in the previously reported $[Ni(triazine)_2(H_2O)_2]^{2+}$ [21] but the bite angle at ruthenium (N1–Ru1–S1 = 81.7°) is slightly smaller than the corresponding angle in the nickel complex (83.2°).

The $\eta^6$-*p*-cymene ring is planar (carbon atom deviations from the mean plane defined by Ca, Cb, Cc, Cd, Ce and Cf atoms lie between −0.016 and 0.013 Å; r.m.s.d., 1.12%). The ring centroid is 1.689 Å from the ruthenium atom and the Ru–C distances lie in the range 2.180–2.238 Å. Similar distances have been observed in other ($\eta^6$-*p*-cymene)ruthenium(II) complexes [5,26]. The C–C bond length alternation which has been observed in $\eta^6$-arene coordinated to transition metals is also apparent in complex VIIb. The isopropyl group is not coplanar with the aromatic ring plane. The dihedral angle between the plane defined by Cg, Ch and Ci and the aromatic ring plane is 69.2°. The 2-carbon atom of the isopropyl group lies in the same plane as the aromatic ring (deviation, −0.096 Å), but the Ch and Ci atoms do not (deviations, −1.519 and 0.307 Å, respectively). The methyl carbon Cj is on the aromatic ring plane (deviation, −0.035 Å).

## 3. Experimental section

All the manipulations were carried out under dinitrogen. The solvents were dried by conventional methods. The amines were commercial grade chemicals and $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ (arene = benzene or *p*-cymene) were prepared by published methods [27,28]. 4-Amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine was synthesized as described elsewhere [29] and was recrystallized from ethanol. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AC 200E instrument. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer as Nujol mulls. The C, H, and N analyses were obtained with a Perkin-Elmer 240C microanalyzer. Thermal decomposition studies were carried out on a Mettler TG-50 thermobalance. Conductivities were measured with a Crison 525 conductimeter.

### *3.1. Synthesis of the complexes*

#### *3.1.1. Complexes Ia, IIa, IIIa, IIIb, IVa, IVb, and VIa*

These were prepared according to the following procedure. To a dichloromethane (10 ml) solution of $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ (0.20 mmol) was added the appropriate donor (0.42 mmol for Ia, IIa, IVa, IVb, VIa; or 0.84 mmol for IIIa and IIIb). The resulting suspension was stirred for 1 h and the solid was separated by filtration, repeatedly washed with dichloromethane and air-dried.

#### *3.1.2. Complexes Ib, IIb, and VIb*

The donor (0.42 mmol) was added to a solution of $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ (0.20 mmol) in dichloromethane (10 ml). After stirring the solution for 1 h, it was vacuum-concentrated and subsequent addition of diethyl ether caused the formation of a microcrystalline solid which was filtered off, washed with dichloromethane and air-dried. Analytical samples of Ib and VIb were obtained by recrystallization from acetone-diethyl ether.

#### *3.1.3. Complexes VIIIa and VIIIb*

The diamine (0.20 mmol) was added to a dichloromethane (10 ml) solution of $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ (0.20 mmol). The resulting suspension (VIIIa) was stirred for 1 h and then filtered to give a solid which was washed with methanol and air dried. For VIIIb the solution resulting from the addition of the amine was stirred for 1 h, then vacuum-concentrated and set aside at 4°C overnight. The crystals were recovered by filtration, washed with methanol and air-dried.

### 3.1.4. Complexes Va, Vb and VIIb

To an ethanol (5 ml) solution of the corresponding chloride salt (IVa, IVb or VIb, respectively; 0.25 mmol) was added $KPF_6$ (0.25 mmol). The mixture was stirred for 5 min and then water (1.5 ml) was added slowly. The solution darkened immediately and was stirred for 1 h. Partial evaporation of the solvent and subsequent addition of diethyl ether caused the formation of a precipitate which was filtered off and air-dried. All three complexes were recrystallized from acetone-diethyl ether.

### 3.1.5. Complex VIIa

This compound precipitated directly on addition of $KPF_6$ (0.25 mmol) to a solution of VIa (0.25 mmol) in ethanol (5 ml). After stirring the mixture for 1 h, the solid was filtered off and air-dried. It was recrystallized from acetone-diethyl ether.

### 3.2. Crystal structure determination of $[(\eta^6\text{-}p\text{-cymene})RuCl(taz)]PF_6$

A suitable crystal of $C_{15}H_{22}RuClSON_4 \cdot PF_6$ (M = 587.9) of dimensions 0.42 × 0.15 × 0.10 mm was used for X-ray crystal structure determination. Cell parameters were $a = 7.747(1)$, $b = 12.658(2)$, $c = 12.930(2)$ Å, $\alpha = 113.24(1)$, $\beta = 99.93(1)$, $\gamma = 105.10(1)°$, $V = 1070(1)$ Å$^3$ which were obtained by least squares refinement of 25 high-angle reflections on an Enraf-Nonius CAD4 diffractometer. Crystals are triclinic with space group $P\bar{1}$, $Z = 2$, $D_c = 1.83$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 10.8 cm$^{-1}$. Mo K$\alpha$ radiation monochromatized by reflection from a graphite crystal was used for data collection. Using the $\omega$-$2\theta$ technique, 4091 reflections were collected ($2\theta < 50°$), of which 3759 were unique and all considered as observed. The range of $hkl$ was $-9 \le h \le 9$, $-15 \le k \le 15$, $0 \le l \le 15$. The standard reflection decay was 0.75%. Lorentz, polarization and empirical absorption corrections were applied (max. and min. transmission correction factors 0.9997 and 0.9700).

The structure was solved by using the RANTAN option in the MULTAN 11/84 program [30]. A subsequent weighted Fourier synthesis gave the positions of almost all the non-hydrogen atoms. Full-matrix refinement on $F$ was carried out with the SHELX76 least-squares program [31] using anisotropic thermal parameters for non-H atoms. H atoms were located by difference Fourier synthesis and refined with two global isotropic temperature factors (for methyl and non-methyl hydrogens). The refinement process converged at $R = 0.031$, $R_w = 0.034$ with $w = 1/(\sigma^2(F) + 0.005466\ F^2)$. Scattering factors were taken from International Tables for X-Ray Crystallography [32] except for those of H-atoms [33]. Maximum and minimum final difference Fourier map peaks were 0.63 (near Ru atom) and $-0.47$ eÅ$^{-3}$.

Additional material available from the authors or the Cambridge Crystallographic Data Centre comprises tables of anisotropic thermal parameters, bond distances and bond angles. Structure factors are available from the authors.

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