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Synthesis and structural characterization of binuclear (η^6-benzene)ruthenium(II) complexes with one or two bridging N-donor ligands

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Abstract

Reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with pyrazole (Hpz) in appropriate molar ratio at room temperature in H_2O/CH_3OH yields the products $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)(\mu\text{-}pz)_2Ru(\eta^6\text{-}C_6H_6)]Cl$ (**1a**) and $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)_2(\mu\text{-}pz)Ru(\eta^6\text{-}C_6H_6)]Cl$ (**2a**), the structures of which were established by an X-ray study. Analogous binuclear complexes **3a** and **4a** were prepared with 4-methylpyrazole (4MepzH). The facile Cl^-/OH^- exchange in these complexes has been studied by ^1H NMR spectroscopy at elevated temperatures. The hydroxo-bridged complexes $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OH)(\mu\text{-}pz)_2Ru(\eta^6\text{-}C_6H_6)]Cl$ (**1b**) and $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OH)_2(\mu\text{-}pz)Ru(\eta^6\text{-}C_6H_6)]Cl$ (**2c**) were also be prepared directly from $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and pyrazole by refluxing in H_2O/CH_3OH solution. Reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with 6-azauracil ($6auraH_2$) in H_2O/CH_3OH solution at room temperature yields $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OH)_2(\mu\text{-}6auraH)Ru(\eta^6\text{-}C_6H_6)]Cl$ (**6**), the crystal structure of which is reported. A chloro-bridged binuclear complex could not be prepared; the analogous reaction in methanol alone gives $[(\eta^6\text{-}C_6H_6)Ru\text{-}Cl_2(6auraH_2)]$ (**7**).

Introduction

The reactions of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with pyrazole (Hpz) or 3,5-dimethylpyrazole (Me_2Hpz) in methanol at room temperature have been reported to give the mononuclear cations $[(\eta^6\text{-}C_6H_6)RuCl(R_2Hpz)_2]^+$ (R = H, Me) [1]. The complex $[(\eta^6\text{-}C_6H_6)RuCl_2(Me_2Hpz)]$ was obtained by refluxing $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with Me_2Hpz in benzene [1]. In contrast, the binuclear pyrazolate-bridged cations $[(\eta^6\text{-arene})Ru(\mu\text{-}OH)(\mu\text{-}pz)_2Ru(\eta^6\text{-arene})]^+$ (arene = *p*-cymene or hexamethylbenzene), which can be isolated as their BPh_4 salts, may be prepared by the reaction of the tri-μ-hydroxo complexes $[\{(\eta^6\text{-arene})Ru\}_2(\mu\text{-}OH)_3]BPh_4$ [2] with pyrazole in a 1 : 3 molar ratio in refluxing acetone [3]. An X-ray structural study of the *p*-cymene complex confirmed the bridging mode for the pyrazolate ligands, and established C_2 crystallographic symmetry for the binuclear cations. Interestingly, addition of $[\{(\eta^6\text{-arene})Ru\}_2(\mu\text{-}OMe)_3]BPh_4$ (arene = *p*-cymene or hexamethylbenzene) [2] to pyrazole in the same molar ratio [1 : 3], followed by refluxing in methanol, led only to the substitution of one methoxo-bridge. The resulting binuclear complexes

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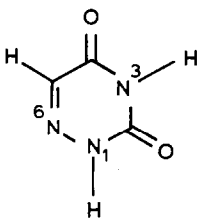
$[(\eta^6\text{-arene})Ru(\mu\text{-}OMe)_2(\mu\text{-pz})Ru(\eta^6\text{-arene})]BPh_4$ were characterized by IR and ^1H NMR spectroscopy [3].

In light of these findings we were interested in finding out whether analogous chloro-bridged complexes containing either one or two μ-pyrazolate ligands could be prepared. A second feature of interest was the question of how the maximum number of bridging N-donor ligands in such binuclear complexes is controlled by steric and/or electronic factors.

We therefore studied the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with the following potentially bridging N-donor ligands: pyrazole (Hpz), 3-methylpyrazole (3MeHpz), 4-methylpyrazole (4MeHpz) and 6-azauracil (6auraH$_2$).



Treatment of aqueous solutions of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with an excess of NaOH followed by the addition of $NaBPh_4$ yields $[(\eta^6\text{-}C_6H_6)Ru(OH)(\mu\text{-}OH)_2Ru(H_2O)(\eta^6\text{-}C_6H_6)]BPh_4$ as major and the tetranuclear complex $[\{(\eta^6\text{-}C_6H_6)Ru\}_4(OH)_4(\mu_4\text{-}O)][BPh_4]_2$ as minor product [2,4]. We thus chose to study the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with the above N-donor ligands in either H_2O/CH_3OH or CH_3OH solution, in the expectation that these conditions might allow isolation of either hydroxo- or chloro-bridged species. In the case of 3-methylpyrazole we were interested in establishing whether the presence of a methyl substituent in the 3-position adjacent to the potentially bridging ring nitrogen atom N2 would prevent the formation of binuclear complexes. In the case of the methylmercury(II) cation $[MeHg]^+$ we previously demonstrated that N6 of 6auraH$_2$ is a potential metal-binding site [5]. A bridging N1,N6 coordination mode would necessarily require the Ru atoms in a binuclear complex to be much closer than in an analogous pyrazolate-bridged species, so that steric interactions, for example between benzene protons and O2 of 6auraH$_2$, might be expected to limit the number of bridging 6auraH ligands.

Experimental

IR spectra were recorded with 1% KBr discs on a Perkin–Elmer 297 spectrometer. ^1H NMR spectra were recorded on a Bruker AM 400 spectrometer at 20 °C; δ values are given in ppm. Elemental analyses were performed with a Perkin–Elmer 2400. $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ was prepared as described previously [6] from $RuCl_3 \cdot 3H_2O$, which was a gift from Degussa AG. The pyrazole derivatives and 6-azauracil were purchased from Sigma Chemie GmbH and used as received.

*Preparation of $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)(\mu\text{-}B)_2Ru(\eta^6\text{-}C_6H_6)]Cl$ (B = pz (**1a**), B = 4Mepz (**3a**)) and $[(\eta^6\text{-}C_6H_6)RuCl_2(3MeHpz)]$ (**5**)*

In a typical preparation a solution of 27 mg (0.4 mmol) of pyrazole in 7 ml of methanol was added to a solution of 100 mg (0.2 mmol) of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ in 25

ml of H_2O. The mixture was stirred for 12 h and then reduced in volume until precipitation commenced. After addition of 2 ml of methanol the solution was set aside at 4 °C to yield red prismatic crystals of **1a**, which were filtered off and dried *in vacuo* (Yield 95 mg, 85%). **3a** and **5** were prepared under analogous conditions (yields respectively 71 and 66%). Reaction in methanol in the same molar ratio yielded the same products.

1a · $\frac{1}{2}H_2O$: Found: C, 38.0; H, 3.2; N, 9.9; $M = 572.4$. $C_{18}H_{18}N_4Cl_2Ru_2 \cdot \frac{1}{2}H_2O$ calcd.: C, 37.77; H, 3.35; N, 9.79%. ^1H NMR (D_2O, Tms–CD_2CD_2COONa): δ 5.96 (s, 12H, C_6H_6); 6.35 (s, 2H, Hpz-H4); 8.17 (s, 4H, Hpz-H3/5).

3a: Found: C, 40.0; H, 3.7; N, 9.3; M 591.5. $C_{20}H_{22}N_4Cl_2Ru_2$ calcd.: C, 40.61; H, 3.75; N, 9.40%. ^1H NMR (D_2O, Tms–CD_2CD_2COONa): δ 2.05 (s, 6H, 4Mepz-CH_3); 5.92 (s, 12H, C_6H_6); 8.00 (s, 4H, 4Mepz-H3/5).

5: Found: C, 36.5; H, 3.78; N, 8.4; $M = 332.2$. $C_{10}H_{12}N_2Cl_2Ru$ calcd.: C, 36.16; H, 3.64; N, 8.43%. ^1H NMR (D_2O, Tms–CD_2CD_2COONa): δ 2.33 (s, 3H, 3Mepz-CH_3); 5.98 (s, 6H, C_6H_6); 6.32 (1s, 1H, 3Mepz-H4); 7.83 (s, 1H, 3Mepz-H5).

*Preparation of $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)_2(\mu\text{-}B)Ru(\eta^6\text{-}C_6H_6)]Cl$ (B = pz (**2a**), B = 4Mepz (**4a**))*

In a typical preparation 14 mg (0.2 mmol) of pyrazole in 7 ml of methanol was added to a solution of 100 mg (0.2 mmol) of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ in 25 ml of H_2O. After 12 h stirring the volume was reduced until precipitation commenced. After addition of 2 ml of methanol the solution was set aside at 4 °C to yield red crystals of **2a** which were filtered off and dried *in vacuo* (yield 72 mg, 67%). **4a** was prepared under analogous conditions (yield 58%). Reaction in methanol in the same molar ratio yields the same products.

2a · H_2O: Found: C, 33.0; H, 3.0; N, 5.1; $M = 549.8$. $C_{15}H_{15}N_2Cl_3Ru_2 \cdot H_2O$ calcd.: C, 32.77; H, 3.12; N, 5.10%. ^1H NMR (D_2O, Tms–CD_2CD_2COONa): δ 5.96 (s, 12H, C_6H_6); 6.29 (s, 1H, Hpz-H4); 8.07 (s, 4 H, Hpz-H3/5).

4a · H_2O: Found: C, 34.0; H, 3.4; N, 5.4. $M = 563.8$. $C_{16}H_{17}N_2Cl_3Ru_2 \cdot H_2O$ calcd.: C, 34.08; H, 3.40; N, 4.97%. ^1H NMR (D_2O, Tms–CD_2CD_2COONa): δ 2.02 (s, 3H, 4Mepz-CH_3); 5.73 (s, 12H, C_6H_6); 7.85 (s, 2H, 4Mepz-H3/5).

*Preparation of $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OH)(\mu\text{-}pz)_2Ru(\eta^6\text{-}C_6H_6)]Cl$ (**1b**) and $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OH)_2(\mu\text{-}pz)Ru(\eta^6\text{-}C_6H_6)]Cl$ (**2c**)*

A solution of 27 mg (0.4 mmol) of pyrazole in 7 ml of methanol was added to a solution of 100 mg (0.2 mmol) of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ in 25 ml of H_2O. The mixture was refluxed for 30 min with stirring and then reduced in volume until precipitation commenced. After addition of 2 ml methanol the solution was set aside at 4 °C to yield orange crystals of **1b**, which were filtered off and dried *in vacuo* (yield 75 mg, 68%). **2c** may be prepared under analogous conditions using 14 mg (0.2 mmol) of pyrazole and refluxing for 3 h (yield 77 mg, 72%). Alternatively **1b** and **2c** may be synthesised from the chloro-bridged complexes **1a** and **2a** by refluxing these for 3 h in H_2O.

1b · H_2O: Found: C, 38.4; H, 3.7; N, 9.9; $M = 563.0$. $C_{18}H_{19}N_4OClRu_2 \cdot H_2O$ calcd.: C, 38.40; H, 3.76; N, 9.95%. ^1H NMR (D_2O, Tms–CD_2CD_2COONa): δ 5.76 (s, 12H, C_6H_6); 6.29 (s, 2H, Hpz-H4); 8.08 (s, 4H, Hpz-H3/5).

2c · $3H_2O$: Found: C, 32.4; H, 3.9; N, 5.1; $M = 549.0$. $C_{15}H_{17}N_2O_2Ru_2Cl \cdot 3H_2O$ calcd.: C, 32.82; H, 4.22; N, 5.10%. ^1H NMR (D_2O, Tms–CD_2CD_2COONa): δ 5.58 (s, 12H, C_6H_6); 6.52 (s, 1H, Hpz-H4); 8.34 (s, 2H, Hpz-H3/5).

Preparation of [(η^6-C_6H_6)Ru(μ-OH)$_2$(μ-6auraH)Ru(η^6-C_6H_6)]Cl (6) and [(η^6-C_6H_6)-RuCl$_2$(6auraH$_2$)] (7)

A solution of 90 mg (0.8 mmol) of 6-azauracil (6auraH$_2$) in 10 ml methanol was added to a solution of 200 mg (0.4 mmol) of [(η^6-C_6H_6)RuCl$_2$]$_2$ in 20 ml of H_2O. The mixture was stirred for 12 h, then reduced in volume to 5 ml and set aside at 4°C to yield red prismatic crystals of **6** which were filtered off and dried *in vacuo* (yield 266 mg, 62%). **7** was prepared under similar conditions (2 : 1 molar ratio) but in the absence of H_2O. Reaction in methanol alone in the presence of NaOMe also yielded **7**.

6: Found: C, 32.9; H, 2.7; N, 7.6; $M = 539.9$. $C_{15}H_{16}N_3O_4ClRu_2$ calcd.: C, 33.37; H, 2.99; N, 7.78%. ^{1}H NMR (D_2O, Tms–CD_2CD_2COONa): δ 5.70 (s, 6H, C_6H_6); 5.73 (s, 6H, C_6H_6); 7.50 (s, 1H, C5-H); 8.78 (s, N3-H).

7: Found: C, 29.5; H, 2.5; N, 11.5; $M = 363.2$. $C_9H_8N_3O_2Cl_2Ru$ calcd.: C, 29.76; H, 2.49; N, 11.57%. ^{1}H NMR (D_2O, Tms–CD_2CD_2COONa): δ 6.06 (s, 6H, C_6H_6); 7.51 (s, 1H, C5-H).

*X-Ray structural analyses of **1a**, **2a**, **5** and **6***

Suitable crystals for X-ray structural analyses were obtained from H_2O/CH_3OH solutions. Crystal and refinement data are summarized in Table 1. Unit cell constants were obtained from a least-squares fit to the settings of 25 reflections centered on an Enraf–Nonius CAD4 diffractometer. Intensity data were collected on the diffractometer at varied scan rates using Mo-K_α radiation. Three selected reflections were monitored at regular intervals during data collection; no significant decreases in intensity were observed. Empirical absorption corrections were performed for all data sets.

The structures were solved by Patterson and difference syntheses and refined by full-matrix least-squares. The asymmetric unit of **2a** contains disordered water and

Table 1

Crystal and refinement data

	1a	**2a**	**5**	**6**
Space group	$P2_1/n$	$C2/c$	$P2_1/c$	$P2_1/n$
a (Å)	11.640(3)	20.564(2)	6.378(1)	6.871(2)
b (Å)	12.086(2)	8.771(1)	19.354(1)	15.517(1)
c (Å)	12.877(3)	20.500(3)	10.038(1)	19.253(3)
β (°)	91.70(5)	108.61(1)	107.53(4)	93.71(2)
V (Å^3)	1811(1)	3504(1)	1182(3)	2048(1)
Z	4	8	4	4
D_c (g·cm^{-3})	2.00	2.11	1.87	1.98
Radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
μ (cm^{-1})	18.0	21.6	17.3	16.3
Scan type	ω	ω	ω	ω
$2\theta_{max}$ (°)	50	50	50	50
Reflections measured	2978	3062	2008	3572
Reflections observed	2430	2273	1633	3141
Rejection criterion	$F_o^2 < 2\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$
R	0.033	0.031	0.034	0.022
R_w	0.032	0.031	0.034	0.023
p	0.014	0.014	0.014	0.014

Table 2

Atom position parameters with equivalent isotropic temperature factors ($Å^2 \cdot 10^3$)

Atom	x	y	z	U_{eq}
1a				
Ru1	0.1621(1)	0.1751(1)	0.0315(1)	24(1)
Ru2	0.3186(1)	0.0018(1)	−0.1483(1)	23(1)
Cl1	0.2191(2)	0.5936(2)	0.0480(2)	59(1)
Cl2	0.2421(1)	−0.0071(1)	0.0225(1)	32(1)
N11	0.1652(4)	0.0827(4)	−0.1888(4)	26(3)
N12	0.1048(4)	0.1439(4)	−0.1199(4)	27(3)
N21	0.3134(4)	0.2251(4)	−0.0391(3)	25(3)
N22	0.3720(4)	0.1599(4)	−0.1039(3)	26(3)
C41	0.2826(6)	−0.1475(6)	−0.2411(6)	48(4)
C42	0.3324(8)	−0.1773(6)	−0.1464(6)	59(5)
C43	0.4408(8)	−0.1314(7)	−0.1152(6)	62(5)
C44	0.4916(6)	−0.0555(7)	−0.1763(8)	59(5)
C45	0.4396(7)	−0.0242(6)	−0.2715(6)	54(5)
C46	0.3369(7)	−0.0688(6)	−0.3022(5)	46(4)
C13	0.0073(5)	0.1767(5)	−0.1694(5)	34(3)
C14	0.0034(5)	0.1362(5)	−0.2685(5)	37(4)
C15	0.1046(5)	0.0790(5)	−0.2786(4)	30(3)
C31	0.0493(9)	0.3108(8)	0.0665(6)	69(6)
C32	−0.0110(6)	0.2133(9)	0.0782(6)	63(6)
C33	0.0311(8)	0.1310(7)	0.1405(7)	62(5)
C34	0.1347(8)	0.1427(8)	0.1942(5)	60(5)
C35	0.1947(6)	0.2413(10)	0.1873(6)	64(6)
C36	0.1532(10)	0.3237(7)	0.1233(9)	77(7)
C23	0.4663(5)	0.2160(5)	−0.1323(5)	31(3)
C24	0.4693(5)	0.3175(5)	−0.0847(5)	33(3)
C25	0.3717(5)	0.3219(5)	−0.0271(4)	27(3)
2a				
Ru1	0.1638(1)	0.0160(1)	0.4351(1)	29(1)
Ru2	0.1334(1)	0.0138(1)	0.5913(1)	32(1)
Cl1	0.2346(1)	0.0247(2)	0.5546(1)	36(1)
Cl2	0.0924(1)	−0.1323(2)	0.4858(1)	41(1)
Cl3	0.1276(1)	0.5038(2)	0.7537(1)	69(1)
N1	0.1169(2)	0.2004(5)	0.4645(2)	33(2)
N2	0.1044(2)	0.1986(5)	0.5259(2)	34(2)
O200	0.5000	0.2137(7)	0.7500	65(4)
O100	0.5000	0.1898(12)	0.2500	187(11)
C100	0.4836(11)	0.1226(21)	0.1642(9)	98(12)
C5	0.0963(3)	0.3356(6)	0.4347(3)	41(3)
C4	0.0705(3)	0.4235(7)	0.4763(3)	49(3)
C3	0.0764(3)	0.3318(6)	0.5331(3)	43(3)
C11	0.1872(3)	0.1387(3)	0.3550(2)	52(4)
C12	0.1258(3)	0.0596(3)	0.3265(2)	47(3)
C13	0.1232(3)	−0.0971(3)	0.3370(2)	51(4)
C14	0.1819(3)	−0.1748(3)	0.3759(2)	52(4)
C15	0.2433(3)	−0.0957(3)	0.4044(2)	55(4)
C16	0.2460(3)	0.0610(3)	0.3939(2)	61(4)
C21	0.1362(3)	0.1338(4)	0.6832(2)	56(4)
C22	0.0701(3)	0.0766(4)	0.6525(2)	63(4)
C23	0.0605(3)	−0.0784(4)	0.6372(2)	70(5)
C24	0.1169(3)	−0.1761(4)	0.6525(2)	74(5)
C25	0.1829(3)	−0.1189(4)	0.6831(2)	68(5)
C26	0.1926(3)	0.0361(4)	0.6985(2)	56(4)

Table 2 (continued)

Atom	x	y	z	U_{eq}
5				
Ru1	0.0164(1)	0.3519(1)	0.8240(1)	29(1)
Cl1	−0.2386(2)	0.4471(1)	0.7983(2)	44(1)
Cl2	−0.2925(3)	0.2819(1)	0.6931(2)	49(1)
N1	0.0368(7)	0.3833(2)	0.6278(4)	35(2)
N2	−0.1493(8)	0.3874(3)	0.5167(5)	42(3)
C3	−0.1015(11)	0.4135(3)	0.4025(6)	46(3)
C4	0.1157(11)	0.4255(3)	0.4421(6)	47(3)
C5	0.1980(10)	0.4063(3)	0.5813(6)	42(3)
C31	−0.2817(12)	0.4227(4)	0.2670(7)	71(4)
C11	0.3120(10)	0.3938(3)	0.9684(10)	83(5)
C12	0.1537(10)	0.3856(5)	1.0374(7)	81(5)
C13	0.0520(10)	0.3217(3)	1.0360(7)	76(5)
C14	0.1084(10)	0.2660(3)	0.9656(7)	95(6)
C15	0.2667(10)	0.2742(3)	0.8965(7)	93(6)
C16	0.3685(10)	0.3381(3)	0.8979(7)	92(6)
6				
Ru1	0.0602(1)	0.7133(1)	0.8213(1)	21(1)
Ru2	0.2062(1)	0.7566(1)	0.9779(1)	25(1)
Cl	0.4362(2)	0.9279(1)	0.8209(1)	60(1)
Ow1	0.6401(4)	0.6489(2)	0.9208(1)	38(1)
O2	0.2991(4)	0.5712(2)	1.0579(1)	51(2)
Ow2	0.5885(5)	0.5185(2)	0.8191(2)	66(2)
Ow3	0.0337(5)	1.0217(2)	0.8223(2)	68(2)
O4	0.1769(4)	0.3771(1)	0.8863(1)	46(1)
Ow4	0.6813(4)	0.4209(2)	0.5917(1)	50(2)
O11	−0.0476(3)	0.7558(1)	0.9131(1)	25(1)
O12	0.3093(3)	0.7526(1)	0.8786(1)	26(1)
N1	0.1851(4)	0.6234(2)	0.9533(1)	24(1)
N3	0.2352(4)	0.4751(2)	0.9727(1)	29(1)
N6	0.1244(4)	0.6038(2)	0.8861(1)	23(1)
C2	0.2419(5)	0.5574(2)	0.9977(2)	28(2)
C4	0.1773(5)	0.4514(2)	0.9067(2)	32(2)
C5	0.1173(5)	0.5249(2)	0.8639(2)	30(2)
C11	0.0991(7)	0.6589(3)	0.7190(2)	55(3)
C12	0.1711(6)	0.7416(3)	0.7218(2)	53(3)
C13	0.0505(7)	0.8104(3)	0.7405(2)	51(2)
C14	−0.1375(7)	0.7929(3)	0.7576(2)	55(3)
C15	−0.2084(6)	0.7078(3)	0.7558(2)	55(3)
C16	−0.0899(8)	0.6426(3)	0.7361(2)	57(3)
C21	0.3199(8)	0.8830(3)	1.0071(2)	61(3)
C22	0.1353(7)	0.8762(3)	1.0287(2)	56(3)
C23	0.0826(6)	0.8066(3)	1.0707(2)	50(2)
C24	0.2200(6)	0.7442(2)	1.0904(2)	44(2)
C25	0.4105(6)	0.7498(3)	1.0687(2)	47(2)
C26	0.4605(6)	0.8188(3)	1.0263(2)	52(2)

methanol molecules with site occupancy factors of 0.5. Four water molecules of crystallisation are present in the asymmetric unit of **6**. Anisotropic temperature factors were used for all non-hydrogen atoms in each of the complexes. Hydrogen atom positions in **1a** and **6** were refined in the final cycles. Those for **2a** were

included at calculated sites. Only the 3-methylpyrazolate protons could be included in the refinement for **5**. The hydrogen atoms in **1a** and **2a** were assigned group isotropic temperature factors. Terminal reliability indices are listed in Table 1, where $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$ with weights given by $w = [\sigma^2(F_o) + p^2F_o^2]^{-1}$. Final difference syntheses were effectively contourless. Analytical scattering factors,

Table 3

Selected bond lengths (Å) and angles (°)

1a			
Ru1–Cl2	2.395(2)	Ru2–Cl2	2.400(1)
Ru1–N12	2.077(4)	Ru2–N22	2.087(5)
Ru1–N21	2.095(4)	Ru2–N11	2.088(5)
N11–N12	1.366(6)	N21–N22	1.354(6)
N12–Ru1–Cl12	84.4(1)	N22–Ru2–Cl2	84.7(1)
N21–Ru1–Cl2	84.9(1)	N11–Ru2–Cl2	85.0(1)
N21–Ru1–N12	84.0(2)	N11–Ru2–N22	83.7(1)
Ru1–N12–N11	123.4(3)	Ru2–N22–N21	123.0(3)
Ru1–N21–N22	123.5(3)	Ru2–N11–N12	123.0(3)
Ru1–C12–Ru2	99.1(1)		
2a			
Ru1–Cl1	2.418(1)	Ru2–Cl1	2.429(1)
Ru1–Cl2	2.429(1)	Ru2–Cl2	2.422(1)
Ru1–N1	2.069(4)	Ru2–N2	2.066(4)
N1–N2	1.363(6)		
Cl1–Ru1–Cl2	80.5(1)	Cl1–Ru2–Cl2	80.4(1)
Cl1–Ru1–N1	82.3(1)	Cl1–Ru2–N2	82.4(1)
Cl2–Ru1–N1	83.8(1)	Cl2–Ru2–N2	83.6(1)
Ru1–N1–N2	120.2(3)	Ru2–N2–N1	120.5(3)
Ru1–Cl1–Ru2	90.8(1)	Ru1–Cl2–Ru2	90.7(1)
5			
Ru1–Cl1	2.420(1)	Ru1–Cl2	2.426(1)
Ru1–N1	2.102(4)		
Cl1–Ru1–Cl2	87.6(1)	Cl1–Ru1–N1	84.8(1)
Cl2–Ru1–N1	85.6(1)		
6			
Ru1–O11	2.067(2)	Ru2–O11	2.078(2)
Ru1–O12	2.068(2)	Ru2–O12	2.082(2)
Ru1–N6	2.136(3)	Ru2–N1	2.124(3)
N1–C2	1.374(4)	C2–N3	1.365(4)
N3–C4	1.358(4)	C4–C5	1.450(5)
C5–N6	1.297(4)	N6–N1	1.368(3)
C2–O2	1.218(4)	C4–O4	1.218(4)
N6–Ru1–O11	80.0(1)	N1–Ru2–O11	79.5(1)
N6–Ru1–O12	77.9(1)	N1–Ru2–O12	77.8(1)
O11–Ru1–O12	77.3(1)	O11–Ru2–O12	76.7(1)
Ru1–O11–Ru2	100.5(1)	Ru1–O12–Ru2	100.4(1)
Ru1–N6–N1	114.5(2)	Ru2–N1–N6	116.1(2)
Ru1–N6–C5	123.9(3)	Ru2–N1–C2	125.0(2)
C2–N1–N6	118.7(3)	N1–N6–C5	121.6(3)

corrected for the real and imaginary parts of anomalous dispersion were taken from ref. [7]. Calculations were performed with SHELX-76 [8] and with local programs. Atomic coordinates are listed in Table 2 and selected bond lengths and angles in Table 3. Tables of hydrogen atom coordinates, a complete list of bond lengths and angles, and lists of structure factors are available from the authors.

Discussion

$[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ reacts with either pyrazole or 4-methylpyrazole in a 1:2 molar ratio in H_2O/CH_3OH solution or in CH_3OH alone at room temperature to yield the novel chloro-bridged binuclear complexes $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)(\mu\text{-}B)_2Ru(\eta^6\text{-}C_6H_6)]Cl$ (**1a**, B = pz; **3a**, B = 4Mepz), the structure of **1a** being established by an X-ray structural analysis (Fig. 1). If the reagents are allowed to react in a 1:1 molar ratio under similar conditions then the complexes $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)_2(\mu\text{-}B)Ru(\eta^6\text{-}C_6H_6)]Cl$ (**2a**, B = pz; **4**, B = 4Mepz) can be isolated. The presence of two chloro-bridges was confirmed by X-ray analysis for **2a** (Fig. 2). As reported by McCleverty et al., use of a 4:1 ratio of pyrazole to $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ leads to bridge cleavage, and to formation of the monomeric complex $[(\eta^6\text{-}C_6H_6)RuCl(Hpz)_2][PF_6]$ in the presence of NH_4PF_6 [1].

It is instructive to compare the dimensions of cations **1a** and **2a**. The Ru–Cl distances are significantly longer in the latter species; the average values are 2.397 for **1a** and 2.424 Å for **2a**. Along with this lengthening of the Ru–Cl bonds there is a shortening of the Ru–N(pz) bonds on going from **1a** to **2a**; average values are 2.087 for **1a** and 2.067 Å for **2a**. The weakening of the Ru–Cl bonds in **2a** is accompanied by a marked change in the bridging Ru–Cl–Ru angles in this cation in comparison to **1a**. These narrow from 99.1 in **1a** to an average value of 90.8° in **2a**. At the same time the Ru–N–N angles to the bridging pyrazolato ligands fall from an average

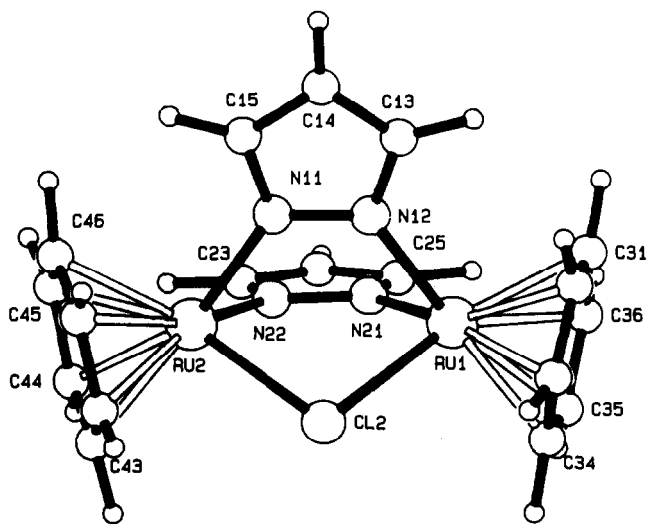


Fig. 1. Structure of the cation $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)(\mu\text{-}pz)_2(\eta^6\text{-}C_6H_6)]^+$ (**1a**).

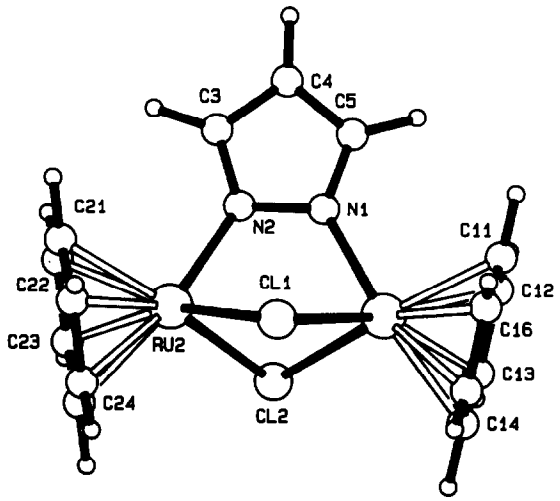


Fig. 2. Structure of the cation $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)_2(\mu\text{-}pz)(\eta^6\text{-}C_6H_6)]^+$ (**2a**).

value of 123.2 in **1a** to 120.4° in **2a**. As a result of these geometrical changes the Ru1 · · · Ru2 distance shortens from 3.649 in **1a** to 3.452 Å in **2a**.

Whereas the $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)_3Ru(\eta^6\text{-}C_6H_6)]^+$ cation is known to undergo facile bridge cleavage reactions with a variety of Lewis bases to yield monomeric complexes of the type $[(\eta^6\text{-}C_6H_6)RuClL_2]^+$ and $[(\eta^6\text{-}C_6H_6)RuCl_2L]$ ($L = C_5H_5N$, Et_2S, PR_3, etc.) [9,10], $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OH)_3Ru(\eta^6\text{-}C_6H_6)]^+$ does not react with an excess of PR_3 ($PR_3 = PPh_3$, PMe_2Ph, PEt_2Ph) in acetone even upon prolonged reflux [2]. It was therefore of interest to establish how readily substitution of the chloro-bridges in **1a**/**3a** and **2a**/**4a** by hydroxyl ions took place.

The temperature dependence of Cl^-/OH^- exchange was studied by ^1H NMR spectroscopy in D_2O solution. At temperatures below 321 K, for freshly prepared solutions only proton resonances for **1a** are observed. At higher temperatures the concentration of **1b** increases steadily, complete substitution of chloro-bridges by

$$\underset{\textbf{(1a)}}{\left[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)(\mu\text{-}pz)_2Ru(\eta^6\text{-}C_6H_6)\right]^+} \xrightarrow[-Cl^-]{+OH^-} \underset{\textbf{(1b)}}{\left[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OH)(\mu\text{-}pz)_2Ru(\eta^6\text{-}C_6H_6)\right]^+}$$

hydroxo-bridges is rapid at 346 K. The process is not reversible. After an NMR sample containing only **1b** has been cooled from 346 K to room temperature only proton resonances for this complex can be seen. A similar phenomenon is observed in the case of **3a**, leading to the rapid formation of $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OH)(\mu\text{-}4Mepz)_2Ru(\eta^6\text{-}C_6H_6)]^+$ (**3b**) at higher temperatures: ^1H NMR (346 K): δ 2.03 (s, 6H, 4Mepz-CH_3); 5.72 (s, 12H, C_6H_6); 7.90 (s, 4H, 4Mepz-H3/5). **1b** may be prepared directly from $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and pyrazole (molar ratio 1:2) in H_2O/CH_3OH solution by refluxing for 30 min. It can be assumed that an analogous synthesis of **3b** would be possible.

The stepwise substitution of the chloro-bridges in **2a** and **4a** can be monitored by ^1H NMR spectroscopy. Upon warming of a sample of **2a** to 301 K a marked

concentration of **2b** [^{1}H NMR (301 K): δ 5.76 (s, 12H, C_6H_6); 6.49 (s, 1H, Hpz-H4); 8.29 (s, 2H, Hpz-H3/5)] is also observed. At temperatures above 306 K

$$[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)_2(\mu\text{-}pz)Ru(\eta^6\text{-}C_6H_6)]^+ \qquad (\mathbf{2a})$$

$$-Cl^-\downarrow + OH^-$$

$$[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}pz)Ru(\eta^6\text{-}C_6H_6)]^+ \qquad (\mathbf{2b})$$

$$-Cl^-\downarrow + OH^-$$

$$[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OH)_2(\mu\text{-}pz)Ru(\eta^6\text{-}C_6H_6)]^+ \qquad (\mathbf{2c})$$

the concentration of **2c**, with two hydroxo-bridges, increases rapidly [**2c**: ^{1}H NMR (306 K): δ 5.58 (s, 12H, C_6H_6); 6.52 (s, 1H, Hpz-H4); 8.34 (s, 2H, Hpz-H3/5)]. Complete replacement of the chloro-bridges by hydroxo-bridges is rapid at 346 K. As in the case of **1a** this process is not reversible. When an NMR sample of **2c** is cooled from 346 K to room temperature only proton resonances for this complex are observed. **2c** was prepared by direct reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and pyrazole (molar ratio 1 : 1) in H_2O/CH_3OH solution by refluxing for 3 h.

These observations confirm that substitution of chloro-bridges in binuclear (η^6-arene)ruthenium(II) complexes by pyrazolate or hydroxyl ions occurs readily. For steric reasons the maximum number of pyrazolato-bridges is limited to two, as in **1a** and **1b**. As mentioned previously the Ru–N–N bridges angles increase on average from 120.4 in **2a** to 123.2° in **1a**. Replacement of the last chloro-bridge in **1a** by a bridging pyrazolato ligand would lead to a further increase in these angles and is thus energetically unfavourable. Reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with pyrazole in a molar ratio of 1 : 4 gives the mononuclear cation $[(\eta^6\text{-}C_6H_6)RuCl(Hpz)_2]^+$ [1].

Inspection of Figs. 1 and 2 suggests that a methyl substituent in the pyrazole 3-position adjacent to a bridging nitrogen atom N2 would come close to a benzene ligand. In order to establish whether bridging is still possible under these geometrical conditions we performed the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with 3-methylpyrazole in H_2O/CH_3OH solution. For both 1 : 1 and 1 : 2 molar ratios only the monomeric product $[(\eta^6\text{-}C_6H_6)RuCl_2(3MepzH)]$ (**5**) could be isolated. The molecular structure of **5** is depicted in Fig. 3. The terminal Ru–Cl distances in **5** (average 2.423 Å) are similar to those for the bridging chlorine atoms in **2a** (average value 2.424 Å). It may be assumed that formation of the alternative configurational isomer of **5**, $[(\eta^6\text{-}C_6H_6)RuCl_2(5MepzH)]$ (**5**), with the methyl substituent in the pyrazole 5-position adjacent to the Ru1–N1 bond, is unfavourable for steric reasons (see Fig. 3).

As a result of the geometrical requirements of a six-membered heteroaromatic ring system, an N1,N6-bridging coordination mode for 6-azauracil ($6auraH_2$) would necessarily require the Ru atoms in a binuclear complex to be much closer than in an analogous pyrazolate-bridged species. Reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with 6-azauracil (molar ratio 1 : 2) in H_2O/CH_3OH solution gives the binuclear complex $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OH)_2(\mu\text{-}6auraH)Ru(\eta^6\text{-}C_6H_6)]Cl$ (**6**). Reaction in methanol solution alone yields the mononuclear species $[(\eta^6\text{-}C_6H_6)RuCl_2(6auraH_2)]$ (**7**). The structure of cation **6** is depicted in Fig. 4. The Ru–N–N angles to the bridging 6-azauracilato ligand are respectively 116.1(2) and 114.5(2)°. The average of those

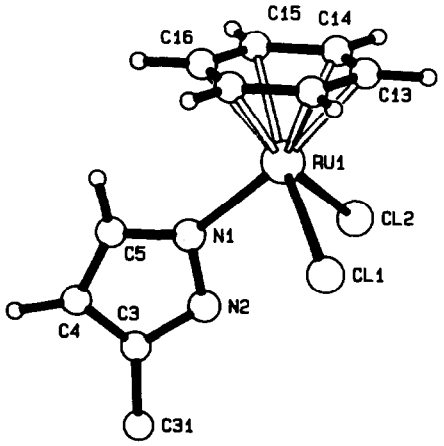


Fig. 3. Structure of $[(\eta^6\text{-}C_6H_6)RuCl_2(3MepzH)]$ (**5**).

bridging angles is 5.1°, smaller than in **2a**, which contains one bridging pyrazolato ligand. As a result the Ru1 ··· Ru2 distance shortens from 3.451 Å in **2a** to 3.187 Å in **6**. The distances between Ru and the bridging hydroxyl ligands (2.067–2.082 Å) are on average 0.346 Å shorter than the Ru–Cl distances in **2a**. The hypothetical binuclear cation $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)_2(\mu\text{-}6aura)Ru(\eta^6\text{-}C_6H_6)]^+$, which would require markedly wider Ru–N–N bridging angles and close steric contacts between O2 and the neighbouring benzene protons, is energetically unfavourable compared to **6**. For similar reason a binuclear cation containing two bridging 6-azauracilato ligands cannot be prepared.

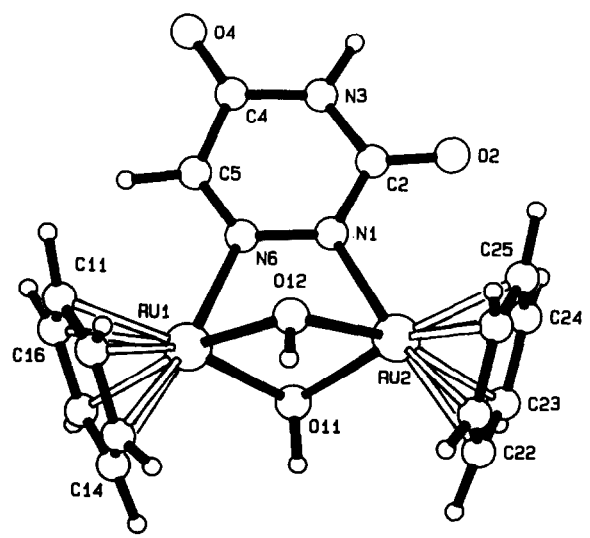


Fig. 4. Structure of the cation $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OH)_2(\mu\text{-}6auraH)Ru(\eta^6\text{-}C_6H_6)]Cl$ (**6**).

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