Preparation and structural characterization of tetranuclear (η^6-benzene)ruthenium(II) complexes with bridging N-donor ligands

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Abstract

Reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with adenine (adeH) in a 1:2 molar ratio in aqueous solution at room temperature yields the tetrameric complex $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-adeH})\}_4]Cl_4$ (**2**), the structure of which was established by X-ray analysis. $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-6made})]_4$ (**3**) (6madeH = N^6-methyladenine) may be prepared under analogous conditions in methanol solution in the presence of NaOMe. Both the neutral adenine ligands in **2** (N1 protonation) and the N^6-methyladeninate ligands in **3** display an N7, N9 bridging mode in these tetranuclear complexes, for which crystallographic S_4 symmetry is observed. Reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with 3-aminopyrazole in a 1:1 molar ratio in H_2O/CH_3OH solution yields **4** in which $[(\eta^6\text{-}C_6H_6)Cl_2Ru(\mu\text{-3apzH})RuCl_2(\eta^6\text{-}C_6H_6)]$ (**4a**) and $[\{(\eta^6\text{-}C_6H_6)ClRu(\mu\text{-Cl})(\mu_3\text{-3apz})Ru(\eta^6\text{-}C_6H_6)\}_2]Cl_2$ (**4b**) are present in a 2:1 ratio in the same unit cell. Coordination of ruthenium atoms by the 3-amino group is observed for both species. In the dinuclear complex **4a** the second ruthenium atom is coordinated by the pyrazole nitrogen N1 with N2 protonated. 3-Aminopyrazolate anions acting as tridentate ligands coordinate three different ruthenium atoms in the centrosymmetric tetranuclear cation of **4b**. This leads to the formation of a central eight-membered metallocyclus.

Introduction

Dinuclear pyrazolate-bridged (η^6-benzene)ruthenium(II) cations $[(\eta^6\text{-benzene})Ru(\mu\text{-Cl})_2(\mu\text{-pz})Ru(\eta^6\text{-benzene})]^+$ and $[(\eta^6\text{-benzene})Ru(\mu\text{-Cl})(\mu\text{-pz})_2Ru(\eta^6\text{-benzene})]^+$ may be prepared by the reaction of $[(\eta^6\text{-benzene})RuCl_2]_2$ with pyrazole (Hpz) in appropriate molar ratio at room temperature in H_2O/CH_3OH [1]. A facile Cl^-/OH^- exchange, which may be followed by ^1H NMR spectroscopy, is observed for these complexes at elevated temperatures. The analogous dinuclear cations $[(\eta^6\text{-arene})Ru(\mu\text{-OMe})_2(\mu\text{-pz})Ru(\eta^6\text{-arene})]^+$ and $[(\eta^6\text{-arene})Ru(\mu\text{-OH})(\mu\text{-pz})_2Ru(\eta^6\text{-arene})]^+$ (arene = *p*-cymene or hexamethylbenzene), were prepared as their BPh_4 salts by the reactions of $[\{(\eta^6\text{-arene})Ru\}_2(\mu\text{-OMe})_3]BPh_4$ and $[\{(\eta^6\text{-arene})Ru\}_2(\mu\text{-OH})_3]BPh_4$ with pyrazole in a 1:3 ratio in refluxing methanol or acetone, respectively [2, 3].

Treatment of aqueous solutions of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with an excess of NaOH or Na_2CO_3 followed by 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 the major product and the tetranuclear complex $[\{(\eta^6\text{-}C_6H_6)Ru\}_4(\mu\text{-OH})_4(\mu_4\text{-O})](BPh_4)_2$ as the minor product [3, 4]. In contrast, a different tetranuclear cation with a cubane-like structure $[\{(\eta^6\text{-}C_6H_6)Ru(\mu_3\text{-OH})\}_4]^{4+}$ may be prepared by the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with Na_2CO_3 in a 1:2 molar ratio [5].

We now describe the preparation of a series of tetranuclear (η^6-benzene)ruthenium(II) complexes, which contain the following bridging N-donor ligands: im^- (imH = imidazole), adeH (adenine), $6made^-$ (6madeH = N^6-methyladenine) and $3apz^-$ (3apzH = 3-aminopyrazole). Crystal structures are presented for $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-adeH})\}_4]Cl_4$ (**2**), $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-6made})]_4$ (**3**) and **4** in which a dinuclear complex $[(\eta^6\text{-}C_6H_6)Cl_2Ru(\mu\text{-3apzH})RuCl_2(\eta^6\text{-}C_6H_6)]$ (**4a**) and a tetranuclear cation $[\{(\eta^6\text{-}C_6H_6)ClRu(\mu\text{-Cl})(\mu_3\text{-3apz})Ru(\eta^6\text{-}C_6H_6)\}_2]^{2+}$ (**4b**) are present in a 2:1 ratio in the same unit cell.

Experimental

^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. Imidazole, the adenine derivatives and 3-aminopyrazole were purchased from Sigma Chemie GmbH and used as received.

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Preparation of $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}im)]_n$ (1)

A solution of 27 mg (0.4 mmol) of imidazole in 10 ml methanol and 0.4 mmol 1 M NaOMe was added to 100 mg (0.2 mmol) of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ in 20 ml methanol. The solution was refluxed for 2 h with stirring, and then reduced in volume until precipitation commenced. After addition of 2 ml methanol the solution was set aside at −18 °C to yield red crystals of **1** which were filtered off and dried *in vacuo* (yield 74%).

1: *Anal.* Found: C, 37.5; H, 3.3; N, 9.3%; $M = 1126.8$ (for $n = 4$). Calc.: C, 38.4; H, 3.2; N 9.9%. ^{1}H NMR (D_2O, Tms-CD_2CD_2COONa): δ 5.73 (s, 24H, C_6H_6), 7.52 (s, 8H, im-H4/5), 8.77 (s, 4H, im-H2).

Preparation of $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}adeH)\}_4]Cl_4$ (2)

54 mg (0.4 mmol) of adenine were added to 100 mg (0.2 mmol) of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ in 20 ml H_2O, the solution stirred for 2 h and then reduced in volume until precipitation commenced. The orange crystals of **2** were filtered off and dried *in vacuo* (yield 92%). Suitable crystals for an X-ray analysis were obtained by recrystallization from H_2O.

2·$4H_2O$: *Anal.* Found: C, 32.3; H, 3.3; N, 17.2%; $M = 1612.9$. Calc.: C, 32.8; H, 3.3; N 17.4%. ^{1}H NMR (D_2O, Tms-CD_2CD_2COONa): δ 6.01 (s, 24H, C_6H_6), 6.30 (s, 4H, adeH-H8), 8.52 (s, 4H, adeH-H2).

Preparation of $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}6made)]_4$ (3)

A solution of 60 mg (0.4 mmol) of N^6-methyladenine in 10 ml methanol and 0.4 mmol 1 M NaOMe was added to 100 mg (0.2 mmol) of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ in 20 ml methanol. The solution was refluxed for 2 h with stirring, and then reduced in volume until precipitation commenced. After addition of 2 ml methanol the solution was set aside at −18 °C to yield red crystals of **3** which were filtered off and dried *in vacuo* (yield 88%). Suitable crystals for an X-ray analysis were obtained by recrystallization from methanol.

3: *Anal.* Found: C, 39.7; H, 3.6; N, 19.0%; $M = 1451.1$. Calc.: C, 39.7; H, 3.3; N 19.3%. ^{1}H NMR (D_2O, Tms-CD_2CD_2COONa): δ 3.24 (s, 12H, 6made-CH_3), 5.83 (s, 24H, C_6H_6), 7.41 (b, 4H, 6made-H6), 8.26 (s, 4H, 6made-H2), 9.16 (s, 4H, 6made-H8). Resonances are also observed for $[\{(\eta^6\text{-}C_6H_6)Ru(6made)(D_2O)\}]^{4+}$ (**3a**) (ratio **3**:**3a** *c.* 1.7:1): δ 3.69 (s, 12H, 6made-CH_3), 5.87 (s, 24H, C_6H_6), 7.58 (b, 4H, 6made-H6), 8.38 (s, 4H, 6made-H2), 9.19 (s, 4H, 6made-H8).

Preparation of $2[(\eta^6\text{-}C_6H_6)Cl_2Ru(\mu\text{-}3apzH)RuCl_2(\eta^6\text{-}C_6H_6)]\cdot[\{(\eta^6\text{-}C_6H_6)ClRu(\mu\text{-}Cl)(\mu_3\text{-}3apz)Ru(\eta^6\text{-}C_6H_6)\}_2]Cl_2$ (4)

A solution of 17 mg (0.2 mmol) of 3-aminopyrazole in 7 ml methanol was added to 100 mg (0.2 mmol) of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ in 25 ml H_2O. The solution was stirred for 2 h and then reduced in volume until precipitation commenced. After addition of 2 ml methanol the solution was set aside at 4 °C to yield deep red crystals of **4** which were filtered off and dried *in vacuo* (yield 83%). Suitable crystals for an X-ray analysis were obtained by recrystallization from H_2O.

4·$6H_2O$: *Anal.* Found: C, 29.9; H, 3.3; N, 7.0%; $M = 2368.3$. Calc.: C, 30.4; H, 3.3; N 7.1%. ^{1}H NMR (D_2O, Tms-CD_2CD_2COONa): δ 5.57, 5.75, 5.90, 6.05 (4s, 48H, C_6H_6), 5.95, 6.17 (2s, 4H, 3apz-H4), 7.45, 8.33 (2s, 4H, 3apz-H5).

Preparation of $[(\eta^6\text{-}C_6H_6)RuCl_2(3apzH)]$ (5)

The preparation was carried out in an analogous manner to **4** with 33 mg (0.4 mmol) of 3-aminopyrazole and 100 mg (0.2 mmol) of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$. Yield 89% for **5** (orange crystals).

5: *Anal.* Found: C, 31.3; H, 3.4; N, 11.9%; $M = 333.2$. Calc.: C, 32.4; H, 3.3; N 12.6%. ^{1}H NMR (D_2O, Tms-CD_2CD_2COONa): δ 5.93 (s, 6H, C_6H_6), 6.07 (s, 1H, 3apz-H4), 7.36 (1s, 1H, 3apz-H5).

X-ray structural analyses of 2, 3 and 4

Crystal and refinement data for **2**–**4** are summarized in Table 1. Unit cell constants were obtained from a least-squares fit to the settings for 25 reflections centered on an Enraf-Nonius CAD4 diffractometer. Intensity data were collected on the diffractometer at varied scan rates using Cu Kα radiation for **2** and Mo Kα radiation for **3** and **4**. Three selected reflections were monitored for each of the compounds 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 **2** contains 2.5 water molecules of crystallization. Two methanol molecules are present in the asymmetric unit of **3**, 1.5 water molecules in the asymmetric unit of **4**. Anisotropic temperature factors were introduced for all non-hydrogen atoms in each of the complexes. Hydrogen atom positions in **3** were refined together with group isotropic temperature factors in the final cycles. Those for **2** and **4** were included at calculated sites and assigned group isotropic temperature factors. Terminal reliability indices are listed in Table 1, where $R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$ with weights given by $w = [\sigma^2(F_o) + p^2 F_o^2]^{-1}$. Final difference syntheses were effectively contourless. Analytical scattering factors, 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. Atom coordinates are listed in Table 2 and selected bond lengths and angles in Table 3. See also 'Supplementary material'.

TABLE 1. Crystal and refinement data

Compound	**2**·10H_2O	**3**·8CH_3OH	**4**·6H_2O
Space group	$P4_2/n$	$I4_1/a$	$P2_1/n$
a (Å)	13.815(2)	20.871(2)	7.780(1)
b (Å)	13.815(2)	20.871(2)	24.135(2)
c (Å)	16.471(3)	15.610(1)	19.839(2)
β (°)	90	90	95.32(2)
V (Å^3)	3143.6(14)	6799.5(16)	3708.8(13)
Z	2	4	2
M	1721.0	1707.5	2368.3
D_c (g cm^{-3})	1.82	1.67	2.12
Radiation	Cu Kα	Mo Kα	Mo Kα
μ (cm^{-1})	116.3	10.8	21.2
Scan type	ω	ω	ω
$2\theta_{max}$ (°)	140	50	45
Reflections measured	2978	2985	5608
Reflections observed	2224	2223	2825
Rejection criterion	$F_o^2 < 3\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$
R	0.085	0.040	0.059
R_w	0.086	0.041	0.053
p	0.007	0.014	0.014

Discussion

$[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ reacts with the imidazolate anion in a 1:2 molar ratio in methanol at room temperature to yield the oligomeric imidazolate-bridged complex $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-im})]_n$ (**1**). We were unable to grow single crystals of **1** suitable for an X-ray structural analysis. However, in light of the tetranuclear structures established for the analogous adenine and N^6-methyladeninate complexes **2** and **3** in the course of this work, it seems reasonable to assume that $n=4$ in **1**. A tetranuclear dicarbonylrhodium(I) complex $[Rh(\mu\text{-}2mim)(CO)_2]_4$, containing bridging 2-methylimidazolate anions, has been reported by Oro and co-workers [9]. The observed resonance position for the C2 proton in **1** at 8.77 ppm (D_2O solution) represents a downfield shift of 1.67 ppm with respect to the free base. The C4 and C5 protons, which are magnetically equivalent, appear as a singlet at 7.52 ppm.

The nucleobase adenine contains an imidazole-like ring system, which should be capable of acting as a bridging ligand in multinuclear (η^6-benzene)ruthenium(II) complexes similar to **1**. However, the pyrimidine nitrogen atoms N1 and N3 or the exocyclic amino function (N6) are also available as potential coordination sites (see Fig. 1 for the numbering scheme in adenine derivatives). Indeed, an N3,N9 binding mode is observed for dinuclear complexes of the type $[(diene)Rh(\mu\text{-ad})]_2$ (diene = cod or nbd, adH = adenine, N^6-methyladenine or N^6,N^6-dimethyladenine) [10]. When N9 is substituted by an alkyl group or sterically unavailable (e.g. in 3-methyladenine = 3made) then N6 may be metallated. We have established respectively N1,N6 and N6,N7 binding modes for the dinuclear complexes $[(cod)Rh(\mu\text{-maade})]_2$ (maadeH = 8-aza-9-methyladenine) and $[(CO)_2Rh(\mu\text{-}3madeH_{-1})]_2$ [10].

In contrast to the dinuclear (diene)rhodium(I) complexes described above [10], N7,N9 coordination is observed for the (η^6-benzene)ruthenium(II) complexes of adenine derivatives presented in this work. Reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with adenine in aqueous solution in the absence of base yields the tetranuclear complex $[\{(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-adeH})\}_4]Cl_4$ (**2**), the structure of which was established by X-ray analysis. Figure 1 displays the bridging function of the adenine ligands in the tetranuclear cation, which displays crystallographic S_4 symmetry with a structure similar to that of **3** depicted in Fig. 2. As would be predicted, the most basic of the remaining available nitrogen atoms in the adenine ligands, namely N1 ($pK_a = 4.1$ [11]) are protonated in **2**, leading to a wide endocyclic angle C6–N1–C2 of 124(1)°. By way of comparison, the analogous angle displays a value of 118.3(5)° in **3**, in which the nitrogen atoms N1 are not protonated. As may be seen from Fig. 1 the base planes of neighbouring adenine ligands are inclined at an angle of 90.0° to one another in **2**. As a result the C8–H8 bond is directed towards an adjacent adenine ligand leading to a number of short intramolecular interactions: H8...N3a 2.72, H8...C4a 2.50, H8...N9 2.51 Å.

The ^1H NMR spectrum of **2** in D_2O solution contains only three singlets, indicating that Cl^-/D_2O ligand exchange is not of significance. As a result of the protonation of the pyrimidine nitrogen N1 the resonance for the neighbouring C2 proton (8.52 ppm) is shifted

TABLE 2. Atom positional parameters with equivalent isotropic temperature factors ($Å^2 \times 10^3$).

Atom	x/a	y/b	z/c	U_{eq}
2·10H_2O				
Ru	0.9011(1)	0.2565(1)	0.0879(1)	41(1)
Cl1	0.8407(2)	0.1279(2)	0.1747(2)	55(2)
Cl2	0.2534(3)	0.3809(3)	0.0679(2)	76(3)
N1	1.1945(9)	0.1261(8)	0.2529(6)	59(7)
N3	1.2739(8)	0.1037(9)	0.1273(7)	57(7)
N6	1.0327(9)	0.1704(10)	0.2713(6)	69(8)
N7	1.0338(7)	0.1816(7)	0.0813(6)	43(6)
N9	1.1684(7)	0.1369(7)	0.0123(6)	43(6)
C2	1.2720(10)	0.1024(11)	0.2065(9)	63(9)
C5	1.1049(9)	0.1569(8)	0.1365(7)	40(7)
C4	1.1889(9)	0.1317(9)	0.0942(7)	47(7)
C6	1.1070(10)	0.1520(10)	0.2223(8)	52(8)
C8	1.0771(9)	0.1670(8)	0.0099(7)	40(7)
C11	0.9301(9)	0.3907(7)	0.0265(6)	74(11)
C12	0.8302(9)	0.3772(7)	0.0308(6)	73(11)
C13	0.7860(9)	0.3607(7)	0.1057(6)	85(13)
C14	0.8418(9)	0.3576(7)	0.1763(6)	81(12)
C15	0.9417(9)	0.3711(7)	0.1720(6)	78(12)
C16	0.9859(9)	0.3876(7)	0.0971(6)	77(11)
O1	0.0000	0.5000	0.3203(8)	74(10)
O2	0.1162(8)	0.6449(9)	0.3964(7)	87(8)
O3	0.4973(14)	0.3780(12)	0.0623(8)	146(14)
3·8CH_3OH				
Ru	0.6482(1)	0.6636(1)	0.2360(1)	30(1)
Cl1	0.6117(1)	0.7548(1)	0.3161(1)	42(1)
N1	0.4382(3)	0.5871(3)	0.3775(3)	45(3)
N3	0.3989(2)	0.5699(3)	0.2365(3)	41(3)
N6	0.5307(3)	0.6439(3)	0.4066(3)	55(4)
N7	0.5507(2)	0.6429(2)	0.2100(3)	30(3)
N9	0.4706(2)	0.6085(2)	0.1247(3)	29(3)
C2	0.3965(3)	0.5663(3)	0.3192(4)	46(4)
C4	0.4537(3)	0.5969(3)	0.2088(4)	33(3)
C5	0.5021(3)	0.6191(3)	0.2621(4)	32(3)
C6	0.4921(3)	0.6173(3)	0.3498(4)	40(4)
C8	0.5286(3)	0.6357(3)	0.1309(4)	31(3)
C61	0.5174(5)	0.6458(6)	0.4965(5)	102(8)
C11	0.7109(5)	0.6450(5)	0.3417(6)	83(6)
C12	0.6670(4)	0.5908(4)	0.3312(6)	65(5)
C13	0.6644(3)	0.5626(4)	0.2544(6)	56(5)
C14	0.7007(4)	0.5816(4)	0.1864(5)	54(5)
C15	0.7417(4)	0.6320(3)	0.1948(6)	59(5)
C16	0.7483(4)	0.6632(4)	0.2717(7)	64(5)
O20	0.1097(3)	0.4570(4)	0.0356(4)	98(5)
O21	0.0658(4)	0.4382(4)	0.2005(4)	115(6)
C20	0.1726(5)	0.4459(7)	0.0323(7)	134(10)
C21	−0.0003(5)	0.4285(5)	0.2095(6)	95(7)
4·6H_2O				
Ru1	0.0961(2)	0.8997(1)	0.3613(1)	35(1)
Ru2	0.4103(2)	0.9095(1)	0.5217(1)	30(1)
Ru3	0.5232(2)	0.6613(1)	0.3084(1)	27(1)
Ru4	1.0657(2)	0.6489(1)	0.5596(1)	28(1)
Cl1	0.7962(7)	0.5148(2)	0.6464(3)	53(3)
Cl11	0.0276(6)	0.9965(2)	0.3764(3)	49(3)
Cl12	0.1126(6)	0.8963(2)	0.4822(3)	45(3)
Cl31	0.8343(6)	0.6617(3)	0.3113(3)	63(4)
Cl32	0.5433(7)	0.7466(2)	0.3713(3)	56(3)
Cl41	1.0516(6)	0.6683(2)	0.6777(2)	43(3)
Cl42	0.9558(7)	0.7415(2)	0.5339(3)	49(3)
Ow1	0.8767(18)	0.7517(6)	0.1994(8)	68(10)
Ow2	0.1217(17)	0.7761(6)	0.1155(8)	63(10)
Ow3	0.1755(21)	0.4785(8)	0.6917(9)	98(14)
N11	0.3519(20)	0.9283(6)	0.3696(8)	40(10)
N12	0.4395(19)	0.9448(6)	0.4276(7)	33(9)
N13	0.6782(18)	1.0086(6)	0.4568(7)	34(9)
N21	0.5728(18)	0.6230(6)	0.4033(7)	27(8)
N22	0.6653(17)	0.6472(5)	0.4545(7)	25(8)
N23	0.7995(16)	0.6269(6)	0.5677(6)	26(8)
C13	0.5710(22)	0.9767(7)	0.4084(9)	30(10)
C14	0.5623(22)	0.9792(7)	0.3390(8)	28(10)
C15	0.4239(23)	0.9482(7)	0.3158(9)	31(10)
C23	0.7027(20)	0.6119(7)	0.5056(9)	23(10)
C24	0.6363(22)	0.5613(7)	0.4869(10)	34(11)
C25	0.5562(23)	0.5716(8)	0.4215(9)	35(12)
C31	0.1662(16)	0.8465(7)	0.2852(9)	66(16)
C32	0.1140(16)	0.8143(7)	0.3380(9)	73(18)
C33	−0.0479(16)	0.8228(7)	0.3611(9)	58(15)
C34	−0.1577(16)	0.8634(7)	0.3313(9)	52(14)
C35	−0.1055(16)	0.8956(7)	0.2785(9)	58(15)
C36	0.0565(16)	0.8871(7)	0.2554(9)	69(17)
C41	0.6191(20)	0.9046(5)	0.6046(7)	46(13)
C42	0.4716(20)	0.8796(5)	0.6258(7)	61(16)
C43	0.3865(20)	0.8383(5)	0.5865(7)	78(19)
C44	0.4488(20)	0.8219(5)	0.5259(7)	73(18)
C45	0.5963(20)	0.8468(5)	0.5046(7)	63(16)
C46	0.6814(20)	0.8882(5)	0.5440(7)	55(14)
C51	0.2810(14)	0.6178(5)	0.2879(5)	35(12)
C52	0.4090(14)	0.5896(5)	0.2570(5)	43(12)
C53	0.5096(14)	0.6177(5)	0.2134(5)	47(13)
C54	0.4822(14)	0.6741(5)	0.2008(5)	53(14)
C55	0.3542(14)	0.7023(5)	0.2318(5)	47(13)
C56	0.2536(14)	0.6741(5)	0.2754(5)	47(13)
C61	1.0944(16)	0.5995(8)	0.4712(7)	65(16)
C62	1.1223(16)	0.5658(8)	0.5282(7)	65(17)
C63	1.2443(16)	0.5808(8)	0.5810(7)	54(15)
C64	1.3385(16)	0.6297(8)	0.5765(7)	50(14)
C65	1.3106(16)	0.6635(8)	0.5197(7)	60(15)
C66	1.1886(16)	0.6484(8)	0.4669(7)	59(15)

to lower field in comparison to the free base (8.22 ppm). A remarkable highfield shift from 8.17 for the free base to 6.30 ppm was registered for the C8 proton in **2** in D_2O solution. This behaviour is in contrast to the marked downfield shift observed for H2 in **1** and H8 in **3**. It is conceivable that the ring current of the neighbouring adenine ligands could be responsible for the pronounced increase in shielding experienced by H8 in **2**.

Deprotonation of the adenine nitrogen atoms N1 in **2** should lead to the formation of the neutral tetranuclear complex $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-ade})]_4$. We were able to obtain single crystals suitable for an X-ray analysis for the analogous complex $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-6made})]_4$ (**3**) by the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with N^6-methyladenine in methanol in the presence of NaOMe. The

TABLE 3. Bond distances (Å) and angles (°) to the ruthenium atoms in **2–4**

2·10H_2O			
Ru–Cl1	2.428(3)	Ru–N7	2.11(1)
Ru–N9a	2.12(1)	Ru–C11	2.15(1)
Ru–C12	2.15(1)	Ru–C13	2.16(1)
Ru–C14	2.18(1)	Ru–C15	2.18(1)
Ru–C16	2.16(1)		
3·8CH_3OH			
Ru–Cl1	2.402(2)	Ru–N7	2.120(4)
Ru–N9a	2.103(4)	Ru–C11	2.141(7)
Ru–C12	2.161(7)	Ru–C13	2.155(7)
Ru–C14	2.174(7)	Ru–C15	2.157(7)
Ru–C16	2.162(7)		
4·6H_2O			
Ru1–Cl11	2.420(5)	Ru1–Cl12	2.393(5)
Ru1–N11	2.10(1)	Ru1–C31	2.09(1)
Ru1–C32	2.12(2)	Ru1–C33	2.17(2)
Ru1–C34	2.19(1)	Ru1–C35	2.16(2)
Ru1–C36	2.12(1)	Ru2–Cl12	2.396(5)
Ru2–N12	2.08(1)	Ru2–N13a	2.14(1)
Ru2–C41	2.20(1)	Ru2–C42	2.20(1)
Ru2–C43	2.16(1)	Ru2–C44	2.14(1)
Ru2–C45	2.14(1)	Ru2–C45	2.18(1)
Ru3–Cl31	2.416(5)	Ru3–Cl32	2.404(5)
Ru3–N21	2.10(1)	Ru3–C51	2.16(1)
Ru3–C52	2.16(1)	Ru3–C53	2.16(1)
Ru3–C54	2.15(1)	Ru3–C55	2.16(1)
Ru3–C56	2.16(1)	Ru4–Cl41	2.403(5)
Ru4–Cl42	2.429(5)	Ru4–N23	2.16(1)
Ru4–C61	2.15(1)	Ru4–C62	2.16(1)
Ru4–C63	2.17(2)	Ru4–C63	2.17(1)
Ru4–C65	2.16(1)	Ru4–C66	2.15(1)

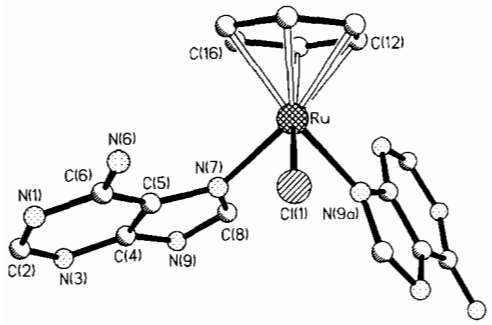

Fig. 1. Bridging function of the adenine ligands in **2** with the numbering scheme for the asymmetric unit.

structure of the complex, which also displays crystallographic S_4 symmetry is depicted in Fig. 2. As in **2**, adjacent adenine ring systems are inclined at 90.0° to one another. The following short intramolecular interactions are observed between H8 and the neighbouring N^6-methyladeninate ligand: H8...N3a 2.77, H8...C4a 2.46, H8...N9a 2.56 Å. In contrast to **2** Cl^-/D_2O ligand exchange leads to two sets of ^1H NMR resonances for complex **3** in D_2O solution. Interestingly H8 in **3** is shifted 1.09 ppm to lower field in comparison

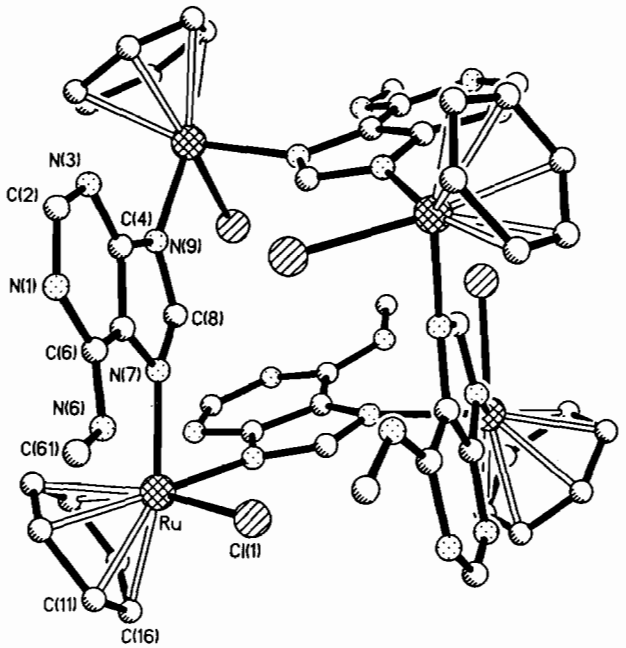

Fig. 2. The tetranuclear complex $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}6made)]_4$ (**3**).

to the free base. As discussed above an opposite shift was observed for the adenine proton H8 in **2**.

To our knowledge the N7,N9 bridging mode has not previously been observed for complexes of adenine derivatives [12]. In contrast, N3,N9 bridged dinuclear Cu(II) complexes have been reported, in which the ligand is either the adeninate anion, neutral (N7H) adenine or the (N1H, N7H) adeninium cation [13–15]. A similar binding mode has been observed for dinuclear Cd(II) and Ag(I) complexes [16, 17]. It has been postulated that Ag(I) cations form chain-like structures in dilute aqueous solution, in which adeninate anions display an N1,N9 bridging mode [18]. However, it has also been demonstrated that initial displacement of the N9 proton by CH_3Hg^+ leads to an enhancement of the donor basicities of the remaining adenine ring nitrogen atoms in the order N7 > N3 > N1. Thus, in addition to N9, N7 is coordinated in the complex $[(CH_3Hg)_2ade]NO_3\cdot 2H_2O$ [19]. Our present findings suggest that the metallation of N9 by the soft $[\eta^6\text{-}C_6H_6)Ru(II)$ fragment may likewise promote subsequent coordination at N7 rather than N1 or N3.

In 'Introduction' we have discussed the preparation of dinuclear (η^6-benzene)ruthenium(II) complexes containing one or two bridging pyrazolate ligands. It might be expected that the employment of 3-aminopyrazole instead of pyrazole as a bridging ligand might allow two such dinuclear units to be linked via a coordinating amino function. We have, therefore, studied the reaction on $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with 3-aminopyrazole (3apzH) in both a 1:2 and 1:1 molar ratio. The former ratio leads in the absence of base to the formation of

$[(\eta^6\text{-}C_6H_6)RuCl_2(3apzH)]$ (**5**), for which, in analogy to $[(\eta^6\text{-}C_6H_6)RuCl_2(3mpzH)]$ (3mpzH = 3-methylpyrazole) [1], N1 coordination of the pyrazole ring may be assumed. For the 1:1 molar ratio a red crystalline product **4** was obtained in which $[(\eta^6\text{-}C_6H_6)Cl_2Ru(\mu\text{-}3apzH)RuCl_2(\eta^6\text{-}C_6H_6)]$ (**4a**) and $[\{(\eta^6\text{-}C_6H_6)ClRu(\mu\text{-}Cl)(\mu_3\text{-}3apz)Ru(\eta^6\text{-}C_6H_6)\}_2]Cl_2$ (**4b**) are present in a 2:1 ratio in the same unit cell. **4b** displays crystallographic C_i symmetry.

The molecular structure of the dinuclear complex **4a** is depicted in Fig. 3, that of the tetranuclear cation of **4b** in Fig. 4. The 3-amino group coordinates ruthenium atoms in each of the complexes leading to torsion angles of 65.9 and 100.5° for N22–C23–N23–Ru4 and N12–C13–N13–Ru2a, respectively (symmetry position a = 1 − x, 2 − y, 1 − z). N22 of the pyrazole ring in **4a** is protonated. The Ru–N(pyrazole) distances lie in the range 2.08(1)–2.10(1) Å and are so slightly longer than those observed in the dinuclear complex $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)_2(\mu\text{-}pz)Ru(\eta^6\text{-}C_6H_6)]Cl$ (2.066(4), 2.069(4) Å [1]). In contrast to this complex the pyrazolate bridged ruthenium atoms in **4b** Ru1 and Ru2 display only one chlorine bridge. This allows a widening of the Ru–Cl–Ru angle from 90.8(1)° in the dinuclear complex to 106.5(2)° in **4b**, which is accompanied by a lengthening of the Ru...Ru distance from 3.451(1) to 3.838(1) Å. The Ru–N(amino) bond lengths of 2.16(1) and 2.15(1) Å in **4a** and **4b** are markedly longer than the Ru–N(pyrazole) bond lengths discussed above.

Reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with 3apzH in both 1:1 and 1:2 molar ratio at elevated temperature (> 60 °C) or in the presence of base (NaOMe) yields black precipitates which are insoluble in conventional organic solvents, indicating the formation of polymeric products. Further characterization of these products was not successful.

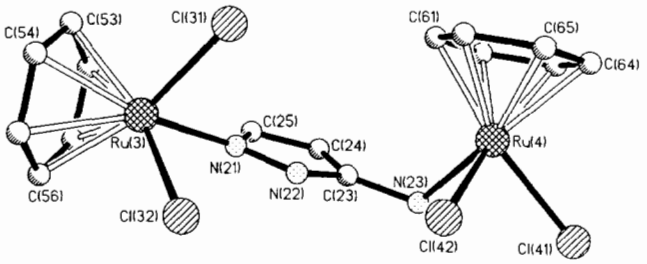

Fig. 3. Structure of $[(\eta^6\text{-}C_6H_6)Cl_2Ru(\mu\text{-}3apzH)RuCl_2(\eta^6\text{-}C_6H_6)]$ (**4a**).

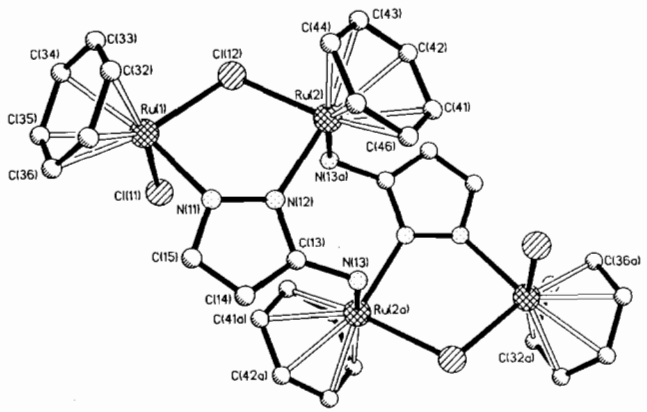

Fig. 4. Structure of $[\{(\eta^6\text{-}C_6H_6)ClRu(\mu\text{-}Cl)(\mu_3\text{-}3apz)Ru(\eta^6\text{-}C_6H_6)\}_2]^{2+}$ (**4b**).

Supplementary material

Tables of hydrogen atom coordinates, a complete list of bond lengths and angles, and lists of structure factors are available from the authors.

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