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Synthesis and structural characterization of η^6-arene-ruthenium(II) complexes of α-amino acids with coordinating side chains

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Abstract

η^6-Areneruthenium(II) complexes of the amino acids *l*-penicillamine (*l*-penH), *l*-histidine (*l*-hisH), *l*-histidine methyl ester (*l*-hisMe) and the peptide triglycine (glyglyglyH) have been prepared by reaction of these amino acids with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$. Crystal structure analyses are reported for $[(\eta^6\text{-}C_6H_6)Ru(l\text{-pen})]_2Cl_2$ (**1**), $[(\eta^6\text{-}C_6H_6)Ru(l\text{-hisMe})Cl]Cl$ (**3**) and $[(\eta^6\text{-}C_6H_6)Ru(glyglygly)Cl]$ (**4**). The amino acidate ligands are tridentate in **1**, with the deprotonated sulphur atoms adopting a bridging position between two ruthenium atoms, leading to the formation of a four-membered RuSRuS-ring. Bidentate *N*(ammine), *N*(imidazole) and *N*(ammine), *N*(peptide) binding, respectively, are exhibited by the complexes **3** and **4**. The factors influencing the observed metal binding sites and chiralities are discussed.

Introduction

Organoruthenium(II) complexes of α-amino acids of the type $[(diene)Ru(aa)_2]$ (aa = gly, *l*-ala) [1] and $[(\eta^6\text{-}C_6H_6)Ru(aa)Cl]$ (aa = gly, *d,l*-ala) [2] have been prepared. Such complexes can exhibit chirality both in the ligand and at the metal. For instance, on the basis of ^1H NMR spectroscopic studies it was inferred that two diastereomerically related pairs of enantiomers are present for $[(\eta^6\text{-}C_6H_6)Ru(d,l\text{-ala})Cl]$ in D_2O solution. In view of the the synthetic potential (e.g. asymmetric catalysis) of chiral organotransition metal templates [3] we are interested in the resolution of η^6-areneruthenium(II) complexes of *l*-amino acids. In general, a relative stabilization of one diastereomer may be achieved through preferential intramolecular hydrogen bonding or interaction with solvent molecules (or anions in

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the case of cationic species). Furthermore, steric interactions may lead to a relative destabilization of the second diastereomer. We now describe the preparation and structural characterization of η^6-C_6H_6-ruthenium(II) complexes of amino acids with coordinating side chains. We chose the potentially tridentate ligands *l*-penicillamine (*l*-pen), *l*-histidine(*l*-his) and the peptide triglycine (glyglygly). As suitable crystals of $[(\eta^6\text{-}C_6H_6)Ru(l\text{-his})Cl]Cl$ could not be grown, an X-ray structural analysis was performed on the analogous complex of *l*-histidine methyl ester (*l*-hisMe).

Results and discussion

The reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ [4,5] with *l*-penicillamine yields $[(\eta^6\text{-}C_6H_6)Ru(l\text{-pen})]_2Cl_2 \cdot H_2O$ (**1**), the structure of the cation of which is depicted in Fig. 1. The carboxyl groups are protonated at O112 and O212, and do not participate in metal binding. The C–O bond distances are respectively C11–O111 1.211(6), C11–O112 1.312(6), C21–O211 1.203(6) and C21–O212 1.322(6) Å. Both penicillaminate ligands are tridentate, with the deprotonated sulphur atoms adopting a bridging position between the two ruthenium atoms and so giving rise to an essentially planar central four-membered RuSRuS-ring. Deviations from the best least-squares plane are: Ru1 0.008, Ru2 0.009, S13 −0.009 and S23 −0.008 Å. The coordination spheres of the ruthenium atoms are completed by the amino nitrogens N12 and N22, which are involved in five-membered chelate rings, both of which display an envelope conformation with C13 and C23 displaced from the best planes of the remaining four atoms. Distances from these least-squares planes are: Ru1 −0.022, N12 0.034, C12 −0.027, S13 0.015, C13 0.661 Å; Ru2 −0.019, N22 0.029, C22 −0.023, S23 0.013, C23 0.710 Å. The adoption of this conformation minimizes steric contacts to the penicillamine methyl groups.

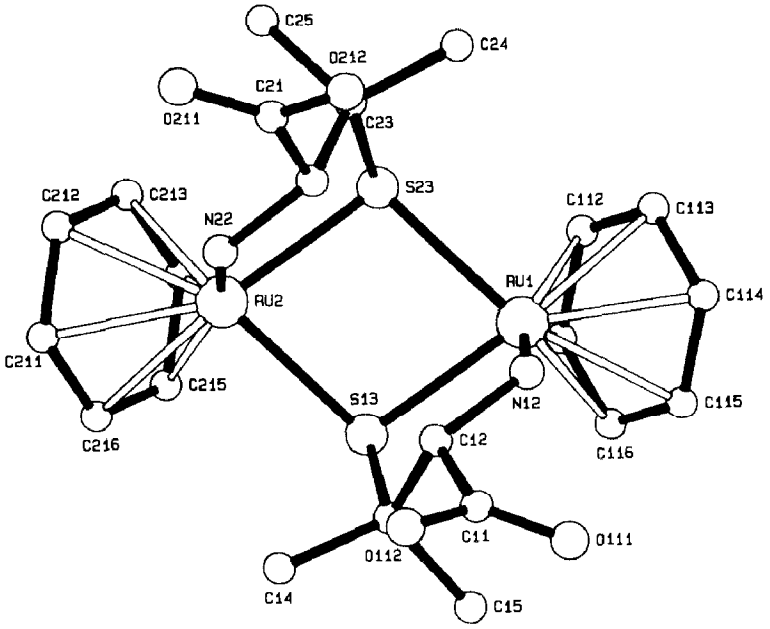

Fig. 1. Structure of the cation $[(\eta^6\text{-}C_6H_6)Ru(l\text{-pen})^+]_2$ (**1**). Hydrogen atoms have been omitted for clarity.

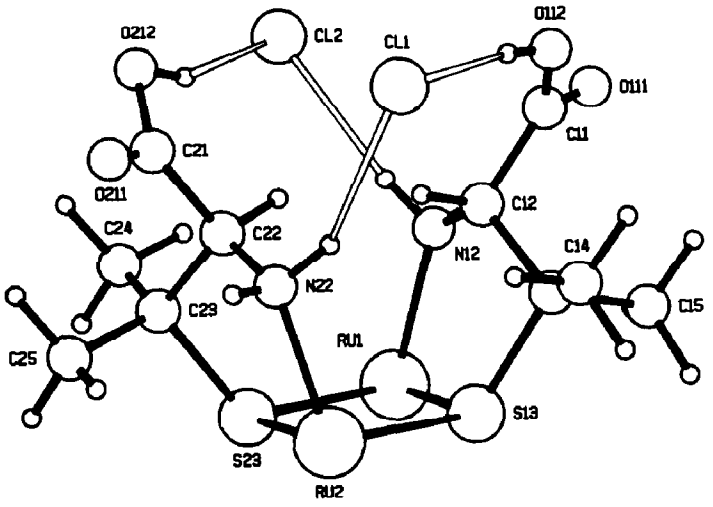

Fig. 2. Hydrogen bonding (open bonds) to the chloride ions in **1**. η^6-C_6H_6-ligands have been omitted for clarity.

As may be seen from Fig. 1, the dimeric cation in **1** exhibits an approximately C_2 symmetry. The Ru–S distances in the chelate rings (2.346(1), 2.345(1) Å) are markedly shorter than the bridging Ru–S distances in the central four-membered ring (2.416(1), 2.398(1) Å). The chiralities of the individual Ru atoms may be established by assigning a higher priority to the sulphur which participates in the chelate ring, according to the rule of Prelog [6]. A diastereomeric pair with R_{Ru}, S_S, S_S, R_{Ru} or S_{Ru}, R_S, R_S, S_{Ru} configurations (both R_C, R_C) is feasible for the *cis*-arrangement of the η^6-benzene ligands displayed by **1** in the solid state. The former configuration observed for **1** is stabilised by O–H...Cl (2.924, 2.966 Å) and N–H...Cl (3.257, 3.231 Å) hydrogen bonds to the two chloride anions, as depicted in Fig. 2. Use of models indicates that the alternative S_{Ru}, R_S, R_S, S_{Ru} configuration would lead to close steric contacts between the carboxyl groups, and would not be favourable for formation of four hydrogen bonds to the chloride anions. A *trans*-arrangement of the benzene ligands would also give rise to unfavourable steric contacts, in this case between these and amino acidate ligands, which would now be on the same side of the central four-membered ring. A diastereomeric pair with R_{Ru}, S_S, R_S, S_{Ru} and S_{Ru}, R_S, S_S, R_{Ru} configurations may be formulated for the *trans*-arrangement. The coordination mode in **1** is, to our knowledge, novel for penicillaminate ligands [7,8].

A single resonance at δ 5.92 ppm is observed for the benzene protons in the ^{1}H NMR spectrum of **1** in D_2O. The methyne protons exhibit a doublet of doublets (J 5.7 Hz), which can be attributed to spin–spin coupling with the nitrogen protons. In contrast a singlet is observed for this proton in the free ligand (present as a zwitterion), with a chemical shift (3.70 ppm) at markedly lower field than in **1** (2.67 ppm). The methyl resonance at 0.94 ppm may be assigned to C25 (axial), that at 1.49 ppm to C24 (equatorial) for the puckered five-membered chelate ring (Fig. 1). An ABX spin system is observed for the penicillaminate nitrogen and methyne protons in the CD_3OD spectrum with chemical shifts at 6.30, 6.19, and 2.72 ppm, respectively. The following coupling constants may be assigned using the Karplus-Conroy curve: ^2J 13 Hz, $^3J_{gauche}$ 5 Hz, $^3J_{trans}$ 11 Hz.

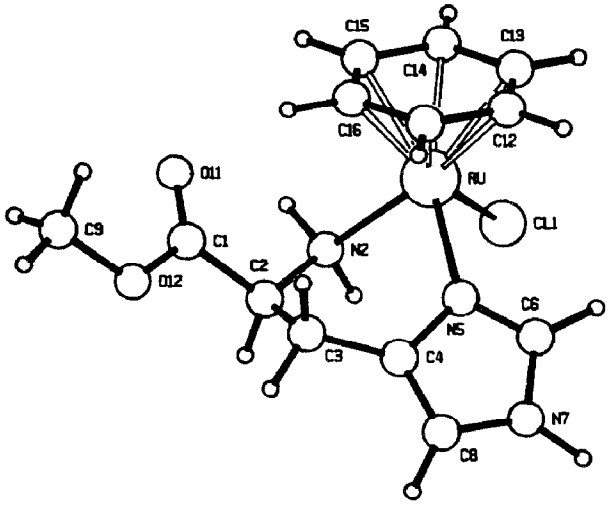

Fig. 3. Structure of the cation $[(\eta^6\text{-}C_6H_6)Ru(l\text{-hisMe})Cl]^+$ (**3**).

Reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with *l*-histidine and its methyl ester yields $[(\eta^6\text{-}C_6H_6)Ru(l\text{-his})Cl]Cl$ (**2**) and the analogous complex $[(\eta^6\text{-}C_6H_6)Ru(l\text{-hisMe})Cl]Cl$ (**3**), the structure of the cation of which is displayed in Fig. 3. Bidentate coordination of the amino acid via the amino nitrogen N2 and the imidazole nitrogen N5 is exhibited by **3**, which results in the formation of a six-membered chelate ring with a twisted-boat conformation. The following displacements are observed from the best least-squares plane through N2, C2, C4 and N5: Ru 1.014, C3 0.519, N2 −0.093, C2 0.100, C4 −0.108 and N5 0.101 Å. An S_C, S_{Ru} configuration is adopted by the cation. The S_{Ru} configuration at the central metal allows the formation of both intramolecular N2–H21...Cl1 (3.012 Å) and N2–H22...O11 (2.715 Å) hydrogen bonds. For the alternative R_{Ru} configuration only the latter interaction is possible. As has been observed for $[(NH_3)_5Ru^{III}(l\text{-his})Cl_3]$ [9] and other pentammine-ruthenium(III) complexes of nitrogen heterocycles, the Ru–N(heterocycle) distance, 2.063(6), is significantly shorter than the Ru–N(ammine) distance, 2.142(6) Å. The ruthenium(II) complex Δ,Λ-$[Ru(bipy)_2(l\text{-ala})]ClO_4 \cdot \frac{1}{2}H_2O$ exhibits a similar average Ru–N(heterocycle) bond length of 2.045 Å [10]; values of 2.07(1) and 2.13(1) Å are found for the Ru–N(*l*-ala) distances. No evidence is provided by the ^1H NMR spectrum of **3** (S_C, S_{Ru}) in D_2O for the existence of a detectable quantity of the second diastereomer (S_C, R_{Ru}) in equilibrium in aqueous solution. Sharp singlets are observed for the benzene, methyl, and histidine protons; The resonances for the amino acidate α-CH and β-CH_2 protons are shifted to higher field in the complexes **2** and **3**, that for the histidine proton H6 to lower field in comparison to the free ligands. The similar positions for the proton resonances in **2** and **3** indicate that the coordination mode in the former histidine complex is identical (i. e. *N*(ammine), *N*(imidazole)] to that in **3**. This means that the carboxyl group must be protonated in **2**, a fact which is confirmed by the ν(C=O) value of 1705 cm^{-1} in the IR spectrum of this compound.

The product of the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with the peptide triglycine, $[(\eta^6\text{-}C_6H_6)Ru(glyglygly)Cl] \cdot H_2O \cdot \frac{1}{2}CH_3OH$ (**4**), crystallises as a racemic mixture in the centrosymmetric space group $P\bar{1}$. Figure 4 depicts the enantiomer with S_{Ru}-con-

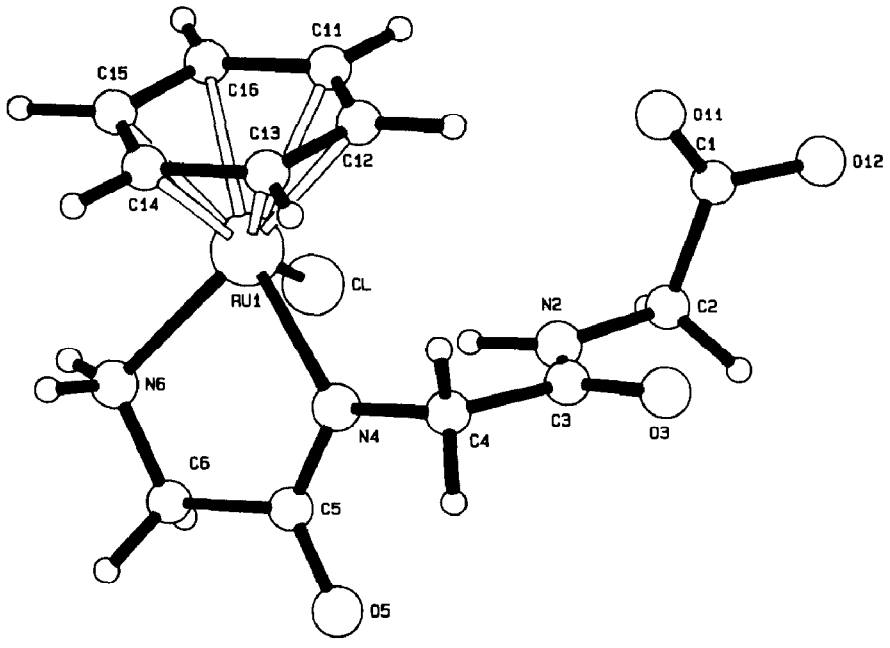

Fig. 4. Structure of the S_{Ru}-enantiomer of [(η^6-C_6H_6)Ru(glyglygly)Cl] (**4**).

figuration. Both enantiomers display an intramolecular N2–H2...Cl hydrogen bond of length 3.234 Å. There are no further intramolecular hydrogen bonds or steric interactions which would lead to a relative stabilization of one of the enantiomers. As observed for the complexes of *l*-penicillamine and *l*-histidine discussed in this work, the carboxyl group does not participate in metal binding **4**, emphasising once again the preference of ruthenium(II) for nitrogen (or sulphur) atoms as binding sites. Protonation occurs on O12, which is involved in an O12–H...O5 intermolecular hydrogen bond of length 2.566 Å to a second molecule related by a translation of 1.0 in the *z*-direction. C–O bond distances are C1–O11 1.198(10) and C1–O12 1.317(9) Å. The peptide binds ruthenium(II) through the amino nitrogen N6 and the peptide nitrogen N4, so that a five-membered chelate ring is formed. Deviations from the best least-squares plane through all five atoms of the ring are relatively small: Ru1 −0.115, N4 0.099, C5 −0.009, C6 −0.137, N6 0.163 Å. Trigonal planar coordination is exhibited by both N4 and the second peptide nitrogen N2. As expected [11], the peptide bond C4–N4 to the coordinated nitrogen N4 is with a distance of 1.305(10) Å shorter than C3–N2 to the uncoordinated peptide nitrogen N2 (1.330(10) Å).

Tridentate coordination of the peptide may be ruled out for monomeric species, as this would require that the three donor groups, the central one of which is a peptide nitrogen, would have to be coplanar with the metal atom [11]. Three potential binding modes remain, namely *O*(carboxyl),*N*(peptide), *N*(peptide),*N* (peptide) or, as observed, *N*(peptide),*N*(ammine), which allows the retention of an Ru–Cl bond. The C6-protons in the ^{1}H NMR spectrum are shifted markedly to higher field (3.19 ppm), the C4-protons to lower field (4.58 ppm) upon complexation of triglycine. Two resonances are observed, at 5.80 and 5.88 ppm, for the benzene protons. The former signal, which is larger (ratio ca. 86/14) may be

assigned to **4**, and the latter to the cation $[(\eta^6\text{-}C_6H_6)Ru(glyglygly)(D_2O)]^+$. The ready substitution of the coordinated chloride in $[(\eta^6\text{-}C_6H_6)Ru(d,l\text{-ala})Cl]$ has previously been reported by Baird [2].

The results demonstrate that a selective crystallisation of one diastereomer of η^6-areneruthenium(II) complexes of the amino acids *l*-penicillamine and *l*-histidine can be achieved. The preference of ruthenium(II) for S and N coordination sites is confirmed.

Experimental

IR spectra were recorded as 1% KBr discs on a Perkin–Elmer 297 spectrometer. ^{1}H NMR spectra were recorded on a Bruker AM 400 spectrometer for **1**, **2** and **4**, on a Bruker WP200 spectrometer for **3**, in D_2O with $(CH_3)_3SiCD_2CD_2COONa$ as internal reference. Elemental analyses were performed with a Perkin–Elmer 240 apparatus. The α-amino acids were purchased from Sigma Chemie GmbH and used as received; $RuCl_3 \cdot 3H_2O$ was a gift from Degussa AG. $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ was prepared as described in the literature [5].

Preparation of complexes 1–4

$[(\eta^6\text{-}C_6H_6)Ru(l\text{-pen})]_2Cl_2 \cdot H_2O$ (**1**). $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (100 mg, 0.2 mmol) was dissolved with heating in 20 ml of water. The solution was filtered and 60 mg (0.4 mmol) of *l*-penicillamine were added, and the volume of the solution was then reduced to 1 ml. Methanol (5 ml) was added and the solution cooled to 6 °C to give red crystals of **1** (yield 58%). **1**, Anal. Found: C, 34.8; H, 4.56; N, 3.8. $C_{22}H_{34}N_2O_5S_2Cl_2Ru$ (*M*, 743.7) calcd.: C, 35.53; H, 4.61; N, 3.77%. IR: 3600, 3450 $\nu(NH_2)$, 1733 cm^{-1} $\nu(CO)$. ^{1}H NMR (D_2O): 0.94 (s, 6H, pen CH_3), 1.49 (s, 6H, pen CH_3), 2.67 (dd, 2H, pen α-CH), 5.92 (s, 12H, C_6H_6).

$[(\eta^6\text{-}C_6H_6)Ru(l\text{-his})Cl]Cl$ **2**. $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (100 mg, 0.2 mmol) was dissolved with heating in 20 ml of water. The solution was filtered, and 62 mg (0.4 mmol) of *l*-histidine were added, and the solvent was removed in vacuum. The residual solid was dissolved in 5 ml of ethanol and the solution cooled to −5 °C to yield yellow crystals of **2** (yield 74%). **2**, Anal. Found: C, 35.5; H, 3.75; N, 10.7. $C_{12}H_{15}N_3O_2Cl_2Ru$ (*M*, 405.2) calcd.: C, 35.57; H, 3.73; N, 10.37%.. IR: 3275, 3215 $\nu(NH_2)$, 1705 cm^{-1} $\nu(CO)$, 1630–1610 $\delta(NH_2)$. ^{1}H NMR (D_2O): 3.01 (d, 2H, his β-CH_2), 3.82 (m, 1H, his α-CH), 5.94 (s, 6H, C_6H_6), 6.98 (s, 1H, his H8) 8.59 (s, 1H, his H6).

$[(\eta^6\text{-}C_6H_6)Ru(l\text{-hisMe})Cl]Cl \cdot H_2O$ (**3**). A 1 *M* solution of NaOMe in methanol (0.8 ml) and 100 mg (0.2 mmol) $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ were added to a solution of 97 mg (0.4 mmol) of *l*-histidine methyl ester hydrochloride *l*-hisMe · 2HCl. After 2–3 h stirring at room temperature the volume was reduced to yield an orange solid, which was recrystallised from methanol/water (**3**, yield 54%). **3**, Anal. Found: C, 35.9; H, 4.31; N, 9.6. $C_{13}H_{19}N_3O_3Cl_2Ru$ (*M*, 437.3) calcd.: C, 35.71; H, 4.38; N, 9.61%. IR: 3590, 3440 $\nu(NH_2)$, 1725, 1710 sh $\nu(CO)$, 1630 cm^{-1} $\delta(NH_2)$. ^{1}H NMR (D_2O): 3.01 br (2H, his-β-CH_2), 3.36 (s, 3H, OCH_3), 3.82 br (1H, his-α-CH), 5.95 (s, 6H, C_6H_6), 6.99 (s, 1H, bis H8), 8.59 (s, 1H, his H6).

$[(\eta^6\text{-}C_6H_6)Ru(glyglygly)Cl]$ (**4**). $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (100 mg, 0.2 mmol) was dissolved with heating in 20 ml of water. The solution was filtered and 76 mg (0.4 mmol) of triglycine were added. The volume was reduced, to 1 ml. 2 ml of methanol

was added, and the solution cooled to 0 °C to yield orange crystals of **4** (yield 76%). **4**, Anal. Found: C, 32.7; H, 4.12; N, 9.70%. $C_{12}H_{16}N_3O_4ClRu$ (M, 402.8) calcd.: C, 32.81; H, 3.90; N, 9.57%. IR: 3290, 3220, 3130 $\nu(NH_2) + \nu(NH)$, 1705, 1635, 1610 $\nu(CO)$ cm^{-1}. ^1H NMR (D_2O): 3.19 (s, 2H, C(6)H_2), 3.89 (s, 2H, C(2)H_2), 4.58 (s, 2H, C(4)H_2), 5.80, 5.88 (s, 6H, C_6H_6).

X-ray structural analyses of 1, 3 and 4

Suitable crystals of **1**, **3** and **4** were obtained by slow crystallisation of the complexes from methanol/water solution. **1** crystallises under these conditions as $[(\eta^6\text{-}C_6H_6)Ru(pen)]_2 \cdot H_2O$, (3) as $[(\eta^6\text{-}C_6H_6)Ru(l\text{-hisMe})Cl]Cl \cdot \frac{1}{2}CH_3OH$ and **4** as $[(\eta^6\text{-}C_6H_6)Ru(glyglygly)Cl] \cdot H_2O \cdot \frac{1}{2}CH_3OH$. 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 recorded on an Enraf–Nonius CAD4 diffractometer at varied scan rates using Mo-K_α radiation for **1** and Cu-K_α radiation for **3** and **4**. Three reflections were monitored at regular intervals during data collection; no significant decreases in intensity were observed. The structures were solved by direct methods and difference syntheses and refined by full-matrix least-squares. The asymmetric unit of **3** contains a doubly disordered methanol molecule. Site occupa-

Table 1

Crystal and refinement data

Compound	**1**	**3**	**4**
Formula	$[(\eta^6\text{-}C_6H_6)Ru(1\text{-pen})]_2\text{-}Cl_2 \cdot H_2O$	$[(\eta^6\text{-}C_6H_6)Ru(l\text{-hisMe})Cl]Cl \cdot \frac{1}{2}CH_3OH$	$[(\eta^6\text{-}C_6H_6(Ruglyglygly)Cl] \cdot H_2O \cdot \frac{1}{2}CH_3OH$
Space group	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$
a (Å)	15.243(2)	14.940(2)	10.077(2)
b (Å)	17.913(2)	15.178(3)	10.475(4)
c (Å)	9.937(2)	7.774(1)	9.638(4)
α (°)	90	90	112.46(3)
β (°)	90	90	108.86(3)
γ (°)	90	90	96.75(3)
V (Å^3)	2713(1)	1763(1)	855(1)
Z	4	4	2
D_c (g·cm^{-3})	1.82	1.58	1.70
Radiation	Mo-K_α	Cu-K_α	Cu-K_α
Crystal size (mm)	0.52×0.40×0.32	0.52×0.20×0.16	0.36×0.18×0.08
μ (cm^{-1})	14.7	103.0	93.4
Scan method	ω	θ–2θ	θ–2θ
$2\theta_{max}$ (°)	50	140	130
Reflections measured	2752	1935	2912
Reflections observed	2631	1885	2557
Rejection criterion	$F_o^2 < 2\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$
R	0.023	0.036	0.061
R_w	0.023	0.036	0.075
P	0.010	0.007	0.014

Table 2

Atom coordinates with equivalent isotropic temperature factors ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}
1				
Ru1	0.1120(1)	0.1135(1)	0.2558(1)	19(1)
Ru2	−0.1270(1)	0.0957(1)	0.2361(1)	17(1)
Cl1	−0.1608(1)	0.1727(1)	0.7104(2)	49(1)
Cl2	0.1021(1)	0.3128(1)	0.5821(2)	49(1)
O111	0.1471(2)	0.1001(2)	0.7273(4)	44(2)
O112	0.0110(3)	0.1167(3)	0.7936(4)	49(3)
C11	0.0706(4)	0.1094(3)	0.6993(5)	31(3)
C12	0.0391(3)	0.1099(3)	0.5542(5)	21(2)
N12	0.1077(3)	0.1442(3)	0.4669(4)	21(2)
C13	0.0166(3)	0.0293(3)	0.5092(5)	21(2)
S13	−0.0006(1)	0.0325(1)	0.3237(1)	19(1)
C14	−0.0679(4)	0.0003(3)	0.5731(5)	31(3)
C15	0.0913(4)	−0.0256(3)	0.5330(6)	35(3)
O212	−0.0777(3)	0.3630(2)	0.5128(5)	47(3)
O211	−0.2053(3)	0.3266(2)	0.4377(4)	43(2)
C21	−0.1279(4)	0.3148(3)	0.4478(5)	31(3)
C22	−0.0829(3)	0.2473(3)	0.3840(5)	21(2)
N22	−0.1452(3)	0.1830(2)	0.3840(4)	24(2)
C23	−0.0532(3)	0.2650(2)	0.2383(5)	25(2)
S23	−0.0151(1)	0.1762(1)	0.1646(1)	20(1)
C24	0.0238(4)	0.3194(3)	0.2350(6)	38(3)
C25	−0.1282(4)	0.2930(3)	0.1505(6)	37(3)
C111	0.1562(3)	0.0484(3)	0.0837(5)	68(5)
C112	0.1609(3)	0.1237(3)	0.0484(5)	57(4)
C113	0.2089(3)	0.1733(3)	0.1277(5)	48(4)
C114	0.2523(3)	0.1476(3)	0.2423(5)	43(3)
C115	0.2477(3)	0.0723(3)	0.2776(5)	48(4)
C116	0.1996(3)	0.0227(3)	0.1983(5)	59(4)
C211	−0.2646(2)	0.0564(2)	0.2544(3)	38(3)
C212	−0.2616(2)	0.1140(2)	0.1600(3)	38(3)
C213	−0.2039(2)	0.1097(2)	0.0514(3)	39(3)
C214	−0.1491(2)	0.0478(2)	0.0371(3)	37(3)
C215	−0.1521(2)	−0.0098(2)	0.1316(3)	38(3)
C216	−0.2098(2)	−0.0055(2)	0.2402(3)	40(3)
O3	0.5457(5)	0.2094(4)	0.1116(9)	123(3)
3				
Ru	0.8831(1)	0.9445(1)	0.7713(1)	27(1)
Cl1	0.7247(1)	0.9747(1)	0.7572(3)	36(1)
Cl2	0.6771(1)	0.7149(1)	0.1402(4)	49(1)
O11	0.9773(4)	0.8699(4)	1.2225(9)	54(4)
O12	1.0107(4)	0.7260(4)	1.1860(8)	51(4)
N2	0.8434(4)	0.8655(4)	0.9864(8)	31(3)
N5	0.8515(4)	0.8291(4)	0.6453(9)	29(3)
N7	0.7897(4)	0.7311(4)	0.4762(10)	44(4)
C1	0.9639(5)	0.8005(6)	1.1562(12)	41(5)
C2	0.8888(5)	0.7811(5)	1.0264(10)	34(4)
C3	0.9266(5)	0.7328(5)	0.8651(11)	38(4)
C4	0.8694(5)	0.7449(4)	0.7096(11)	36(4)
C6	0.8044(5)	0.8180(5)	0.5042(12)	39(4)
C8	0.8303(6)	0.6849(5)	0.6028(13)	46(5)
C9	1.0875(7)	0.7385(7)	1.3009(14)	65(6)

Table 2 (continued).

Atom	x	y	z	U_{eq}
3				
C11	1.0181(3)	0.9452(3)	0.6722(8)	49(5)
C12	0.9650(3)	0.9980(3)	0.5666(8)	50(6)
C13	0.9148(3)	1.0664(3)	0.6378(8)	41(4)
C14	0.9178(3)	1.0821(3)	0.8145(8)	43(5)
C15	0.9710(3)	1.0293(3)	0.9102(8)	45(5)
C16	1.0211(3)	0.9609(3)	0.8489(8)	43(5)
C10	0.1683(12)	0.0183(13)	0.2924(30)	66(4)
O101	0.2638(12)	0.0153(19)	0.3042(40)	66(4)
O102	0.2257(17)	0.0287(18)	0.4401(32)	66(4)
4				
Ru1	0.1891(1)	0.2815(1)	0.1162(1)	41(1)
Cl	0.1792(2)	0.0314(2)	−0.0391(3)	52(1)
O3	0.7068(6)	0.3838(7)	0.1680(7)	59(3)
O5	0.5337(6)	0.2393(7)	0.4624(7)	56(3)
O11	0.4471(7)	0.2799(8)	−0.2165(8)	64(3)
O12	0.5706(7)	0.1385(7)	−0.3277(7)	59(3)
N2	0.5044(7)	0.1959(8)	0.0340(8)	45(3)
N4	0.3998(6)	0.3079(7)	0.2758(7)	40(3)
N6	0.1485(7)	0.2045(8)	0.2764(8)	47(3)
C1	0.5131(9)	0.1916(9)	−0.2206(10)	45(3)
C2	0.5446(10)	0.1266(10)	−0.1025(10)	50(4)
C3	0.5891(9)	0.3220(10)	0.1578(10)	44(3)
C4	0.5348(8)	0.3935(9)	0.2912(9)	44(3)
C5	0.4142(8)	0.2415(9)	0.3679(10)	45(3)
C6	0.2733(9)	0.1645(10)	0.3605(11)	50(4)
C11	0.1302(10)	0.3120(8)	−0.1070(7)	79(6)
C12	0.2440(10)	0.4292(8)	0.0217(7)	71(5)
C13	0.2305(10)	0.5042(8)	0.1688(7)	70(5)
C14	0.1032(10)	0.4620(8)	0.1873(7)	84(6)
C15	−0.0105(10)	0.3448(8)	0.0586(7)	101(8)
C16	0.0030(10)	0.2698(8)	−0.0885(7)	82(6)
O1	0.9139(8)	0.5875(9)	0.4548(9)	82(2)
O2	0.0374(19)	0.8737(19)	0.5016(20)	92(5)
C22	0.1781(24)	0.8687(25)	0.5462(26)	72(6)

tion factors of 0.5 were introduced for C10, 0.25 for O101 and O102. In addition to one molecule of crystal water, the asymmetric unit of **4** also contains a disordered methanol molecule. Site occupation factors of 0.5 were employed for O2 and C22. Anisotropic temperature factors were used for all non-hydrogen atoms in **1**, **3** and **4**, with the exception of the solvate atoms. A common isotropic temperature factor was employed for the methanol C and O atoms in **3**. Hydrogen atoms were included, where possible, at calculated positions with d(C–H) 1.08 Å. The carboxyl protons H11 and H21 in **1** were located in difference syntheses and refined freely. Terminal reliability indices are listed in Table 1 where $R_w = [\Sigma w(F_0 - F_c)^2/\Sigma w F_0^2]^{1/2}$ with weights given by $w = (\sigma^2(F_0) + p^2F_0^2)^{-1}$. Final difference syntheses were effectively featureless. Analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref. 12. Calculations were performed with SHELX-76 [13] and with local programs. Full details of the X-ray analyses are available from the authors.

Table 3

Lengths (Å) of bonds to the ruthenium atoms

1			
Ru1–S13	2.346(1)	Ru2–S13	2.398(1)
Ru1–S23	2.416(1)	Ru2–S23	2.345(1)
Ru1–N12	2.169(4)	Ru2–N22	2.164(4)
Ru1–C111	2.177(3)	Ru2–C211	2.219(3)
Ru1–C112	2.199(5)	Ru2–C212	2.212(3)
Ru1–C113	2.225(5)	Ru2–C213	2.193(3)
Ru1–C114	2.228(4)	Ru2–C214	2.181(3)
Ru1–C115	2.206(5)	Ru2–C215	2.189(4)
Ru1–C116	2.180(4)	Ru2–C216	2.208(3)
3			
Ru–N2	2.142(6)	Ru–N5	2.063(6)
Ru–Cl1	2.413(2)	Ru–C11	2.159(4)
Ru–C12	2.165(5)	Ru–C13	2.174(5)
Ru–C14	2.177(5)	Ru–C15	2.172(6)
Ru–C16	2.163(5)		
4			
Ru1–N4	2.092(6)	Ru1–N6	2.118(6)
Ru1–Cl	2.441(2)	Ru1–C11	2.196(6)
Ru1–C12	2.174(8)	Ru1–C13	2.145(8)
Ru1–C14	2.138(7)	Ru1–C15	2.160(8)
Ru1–C16	2.189(7)		

Relevant atom coordinates with equivalent temperature factors are given in Table 2 and lengths of bonds to the ruthenium atoms in Table 3.

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