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Synthesis and characterisation of a series of mononuclear ruthenium(II) carbonyl complexes of heterocycle-based asymmetric bidentate ligands

Declan Mulhern^a, Yanhua Lan^b, Sally Brooker^{*,b}, John F. Gallagher^c, Helmar Görls^d, Sven Rau^d, Johannes G. Vos^{a,*}

^a National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland
 ^b Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand
 ^c National Institute for Cellular Biotechnology, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland
 ^d Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-University, 07743 Jena, Germany

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Abstract

In this contribution, the synthesis and characterisation of a series of complexes of the type $[Ru(L-L')(CO)_2Cl_2]$ are reported, where L–L' are the chelating ligands L1–L8, 2-(4H-[1,2,4]triazol-3'-yl)-pyridine (L1); 2-(4H-[1,2,4]triazol-3'-yl)-pyrazine; (L2); 2-(1-methyl-4H-[1,2,4]-triazol-3-yl)pyridine (L3); 2-(5-pyridin-2-yl-4H-[1,2,4]-triazole-3-yl)phenol (L4); 3-(5-methylphenyl)-pyridin-2-yl-1,2,4-triazole (L5); 3-(4-methylphenyl)-pyridin-2-yl-1,2,4-triazole (L6); 3-(4-methoxyphenyl)-pyridin-2-yl-1,2,4-triazole (L7); 3,6-bis[(4-methoxyphenyl)iminomethyl]pyridazine (L8). L1–L7 are triazole-based ligands, which provide two distinct bidentate coordinate modes (via N2 or N4 of the triazole) whereas L8 is pyridazine-based and contains two identical bidentate binding pockets. The products obtained are analysed using infrared and NMR spectroscopy. The X-ray and molecular structures of the complexes with the ligands L2, L6, L7 and L8 are reported. These structures are the first to be reported for triazole based ruthenium chloro and ruthenium pyridazine imine complexes. The data show that the triazole ring in L2, L6 and L7 is coordinated via the N2 atom, and that the pyridazine-based ligand L8 uses only one binding pocket hence accommodating only one ruthenium(II) centre. For all compounds the *cis*(CO)*trans*Cl conformation is obtained. The results obtained are compared with those obtained for other similar compounds.

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1. Introduction

There is at present a considerable interest in transition metal complexes based on triazole containing complexes [1,2]. Ligands based on this moiety are ideal building blocks for the preparation of multinuclear metal complexes of metals from the 1st, 2nd and 3rd row transition metals. Many of the compounds based on first row transition metals show interesting magnetic properties, while in ruthenium and osmium polypyridyl complexes the photophysical properties of both mononuclear and dinuclear compounds have been studied in detail [3]. Of particular interest in these latter studies are complexes based on pyridyl- and pyrazyltriazole type ligands. These

^{*} Corresponding author. Tel.: +353 1 7005307; fax: +353 1 7005503. *E-mail addresses:* sbrooker@alkali.otago.ac.nz (S. Brooker), Sven. Rau@uni-jena.de (S. Rau), han.vos@dcu.ie (J.G. Vos).

studies have shown that both the coordination mode of the triazole ring and its protonation are important parameters, which control, the photophysical and electrochemical properties of the compounds. It is observed that in compounds of the type $[Ru(bpy)_2(L-$ L']⁺ [4] the coordination mode of the ligands is dependent on the substitution pattern at the ring. For unsubstituted triazole ligands such as L1 and L2, a 50:50 mixture of the N2 and N4 isomers is obtained (see Fig. 1), while in the presence of a methyl or an other substituent at the C5 position only the sterically favoured N2 coordination is obtained [5]. However, for the analogous Rh(III) complexes $[Rh(bpy)_2(L-L')]^{2+}$ only one isomer, most likely the N2 bound isomer is obtained. It seems likely that in the latter type of compound electronic rather than steric considerations determine the binding mode of the the present contribution, ligands [6]. In we report on the reaction of a number of pyridyl and pyrazyltriazole type ligands L1–L7: 2-(4H-[1,2,4]triazol-3'-yl)-pyridine (L1); 2-(4H-[1,2,4]triazol-3'-yl)-pyrazine (L2); 2-(1-methyl-4H-[1,2,4]-triazol-3-yl)pyridine (L3); 2-(5-pyridin-2-yl-4H-[1,2,4]-triazole-3-yl)phenol (L4); 3-(5-methylphenyl)-pyridin-2-yl-1,2,4-triazole (L5); 3-(4-methylphenyl)-pyridin-2-yl-1,2,4-triazole (L6); 3-(4methoxyphenyl)-pyridin-2-yl-1,2,4-triazole (L7) with the precursor $[Ru^{II}(CO)_2Cl_2]_n$. Of main interest in these studies is the manner in which the triazole ring is coordinated in the absence of any steric hindrance. The reaction with the related pyridazine-based ligand 3,6-bis[(4-methoxyphenyl)iminomethyl]pyridazine (L8) is also reported as this ligand [7] and related ligands [2b] have also been proven to generate complexes with a range of interesting structures and properties. For ligand structures see Fig. 2.

2. Results and discussion

2.1. Synthesis

For the last number of years there has been a considerable interest in the synthesis and properties of complexes of the type $[Ru^{II}(L-L)(CO)_2Cl_2]$ and $[Ru^{II}(L-L)_2(CO)_2]^{2+}$. The compounds have been proposed as intermediates for the synthesis of heteroleptic ruthenium polypyridyl complexes [8] and several have shown promising behaviour as water-gas-shift reagents



Fig. 1. N2 and N4 isomers of pyridyltriazoles.





Fig. 2. Ligand structures.

and for the reduction of CO_2 [9]. There are well-defined synthetic methods for the preparation on these compounds [10-13]. In a typical experiment, 1 mmol of $[Ru^{II}(CO)_2Cl_2]_n$ was refluxed with 1.3 mmol of L1–L7 in MeOH (40 mL) for 2 h. The appearance of a precipitate meant that it was filtered hot and washed with MeOH and dried in vacuo: if a precipitate did not appear, the solution was reduced to 5 mL, filtered, and 2 drops conc. HCl added. The solution was then placed in a freezer overnight and the resulting precipitate of $[Ru(Lx)(CO)_2Cl_2]$ filtered. Satisfactory elemental analyses were obtained for all compounds. Crystals of these triazole-based complexes suitable for X-ray diffraction studies were obtained by dissolving $[Ru(CO)_2Cl_2]_n$ and L in separate aliquots of boiling MeOH, filtered, mixed and allowed to stand overnight. The resultant crystals were collected by filtration, washed with cold MeOH and dried under vacuum. Elemental analysis shows that for all of these compounds the triazole ring is protonated. This is contrary to the results obtained for the $[Ru(bpy)_2(L-L')]^+$ type compounds, where deprotonation of the triazole ring takes place spontaneously upon coordination [4]. Crystals of the analogous pyridazine-based complex $[Ru^{II}(L8)(CO)_2Cl_2]$ were successfully grown by allowing a dilute 1:1 solution of L8 and $[Ru^{II}(CO)_2Cl_2]_n$ in MeOH to react slowly at room temperature. Attempts to occupy both binding sites of L8 with metal centres, by adding either a second equivalent of $[Ru^{II}(CO)_2Cl_2]_n$, or an equivalent of [Cu^I(CH₃CN)₄]PF₆, failed. The crystals were analytically pure.

2.1.1. Spectroscopic characterisation

The spectroscopic data are listed in the experimental part. ¹H NMR spectra show only one set of signals indicating the formation of only one main product. The NMR data do however not allow for the determination of the particular isomer obtained. The infrared spectra show the presence of two CO stretching vibrations, which indicates that the CO ligands are in a *cis* arrangement. Since the chloro atoms can be *trans* or *cis* one may expect to find four isomers two with a *cis*(CO)*trans*Cl arrangement with either the triazole ring coordinated via the N2 or the N4 atom of the triazole ring and two equivalent *cis*(CO)*cis*Cl isomers. It has been shown before [9c,14] that the carbonyl stretching frequencies for these types of isomers are not significantly different therefore X-ray analysis was carried out (see Table 1).

2.1.2. Single crystal X-ray analysis

The molecular structures of four of these eight mononuclear compounds $[Ru(Lx)(CO)_2Cl_2]$, specifically the complexes of ligands L2, L6, L7 and L8, were investigated by X-ray crystallography (Fig. 3, Table 2). The single ruthenium(II) ion in each of these structures is in a slightly distorted octahedral environment, in which the donor atoms are provided by two nitrogen atoms from the heterocycle-based asymmetric bidentate ligand Lx, two carbon atoms from the two carbonyl groups and two chloride ions. In all four complexes the CO co-ligands are mutually *cis*, as anticipated from the infrared spectroscopy, and the chloride co-ligands are mutually trans. The major features of the three triazole-based compounds are that the triazole ring is protonated and that the N2 atom of the triazole ring is coordinated to the metal centre. In all three of these compounds the proton is placed on the N4 atom. In the case of the pyridazine-based compound [Ru(L8)- $(CO)_2Cl_2$, only one of the two otherwise identical bidentate binding pockets accommodates a ruthenium(II) ion.

Table 1	
Crystallographic data	for [Ru(L)(CO) ₂ Cl ₂]

In contrast to the large volume of literature relating to first row transition metal complexes of triazole or pyrazine containing ligands, relatively little attention has been given to the structures of ruthenium complexes of such ligands. To date, no structurally characterised triazole-based ruthenium chloro complexes and only six structurally characterised pyrazine-based ruthenium(II) dichloro complexes (CSD codes BAM-KIK, BAMKOQ, BAMKUW, MOLWEP, XOHTOD and XOHTUJ) [15] have been reported (CSD search version 5.25 [16]). The Ru-N_{pyrazine} distance observed for those six complexes lies in the range 2.043-2.151 A with an average Ru-N_{pyrazine} of 2.101 A [15]. In the mononuclear ruthenium(II) complexes of our triazole and pyrazine-containing ligands, L2, L6 and L7, the Ru-N_{pyrazine} distances [2.150(3), 2.163(2) and 2.143(2) Å, respectively], are at the high end of this range or in the case of $[Ru^{II}(L6)(CO)_2(CI)_2]$ it is slightly longer than the previous maximum value. Consistent with this the Ru-N_{triazole} bond lengths are shorter than the Ru-N_{pyrazine} bond lengths, by 0.05, 0.05 and 0.03 Å for the complexes of L2, L6 and L7, respectively. The Ru-Cl distance observed for the six literature complexes lies in the range 2.340–2.401 Å and the average Ru-Cl distance is 2.379 Å [15] The Ru-Cl bond lengths observed in the three triazole complexes fall within this range. These are the first triazole based ruthenium chloro complexes to be structurally characterised.

	$[Ru(L2)(CO)_2Cl_2]$	$[Ru(L6)(CO)_2Cl_2]$	$[Ru(L7)(CO)_2Cl_2]$	$[Ru(L8)(CO)_2Cl_2]$
Chemical formula	C ₈ H ₅ Cl ₂ N ₅ O ₂ Ru	C ₁₆ H ₁₅ Cl ₂ N ₅ O ₃ Ru	C ₁₅ H ₁₁ Cl ₂ N ₅ O ₃ Ru	C ₂₂ H ₁₈ Cl ₂ N ₄ O ₄ Ru
$F_{ m w}$	407.18	497.30	481.26	574.37
Colour	yellow	yellow	yellow	red
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Temperature (K)	183(2)	296(2)	294(2)	168(2)
Crystal size (mm)	$0.03 \times 0.03 \times 0.02$	$0.48 \times 0.18 \times 0.16$	0.45 imes 0.20 imes 0.08	$0.35 \times 0.11 \times 0.06$
Unit cell dimensions				
a (Å)	6.4153 (4)	11.0433 (6)	14.2089 (11)	9.303(3)
b (Å)	10.6347 (6)	10.6963 (6)	9.5634 (5)	10.354(3)
<i>c</i> (Å)	11.3683 (8)	16.7567 (10)	14.5834 (9)	13.072(4)
α (°)	71.016 (2)	90	90	70.746(4)
β (°)	80.825 (3)	97.842 (4)	115.618 (5)	72.006(4)
γ (°)	83.878 (3)	90	90	80.088
$V(\text{\AA}^3)$	722.78 (8)	1960.83 (19)	1786.9 (2)	1127.2(6)
$D_{\rm calc} \ ({\rm g \ cm^{-3}})$	1.871	1.685	1.789	1.692
<i>F</i> (000)	400	992	952	576
Ζ	2	4	4	2
Space group	P-1	$P2_1/C$	P2/n	P-1
Absorption coefficient μ (mm ⁻¹)	1.467	1.098	1.202	0.970
Absorption correction T (minimum, maximum)		0.621, 0.844	0.614, 0.910	0.91, 1.00
2θ limits (°)	2.9-27.5	1.9-26.0	2.1-28.0	2.09-26.48
Number of reflections	3273	3858	4314	14761
Number of parameters	199	254	240	300
R(F)	0.029	0.029	0.032	R_1 (4 sig) = 0.0266
$R_{w}(F)$	0.088	0.075	0.077	wR_2 (all) = 0.0577
Goodness-of-fit	1.02	1.05	1.04	0.957
Residual electron density	0.87/-0.76	0.55/-0.29	0.58/-0.40	0.36/-0.44



Fig. 3. Molecular structure and atom numbering for; top to bottom (a) $[Ru(L2)(CO)_2Cl_2]$, (b) $[Ru(L6)(CO)_2Cl_2]$, (c) $[Ru(L7)(CO)_2Cl_2]$ and (d) $[Ru(L8)(CO)_2Cl_2]$ (50% thermal ellipsoids).

To date, eleven pyridazine-containing ruthenium complexes [17] have been structurally characterised (CSD search version 5.25 [16]), only three [17b,17d] of which are ruthenium(II) (CSD codes GIDBIE, GIDBOK and LEJWOM). Of these, two complexes (GIDBIE and GIDBOK) are of the [Ru^{II}L(CO)₂Cl₂] type which is of interest here. Bruno and co-workers [12b] reported the structures of these two isomeric complexes in which L = 3,6-bis(2-pyridyl)pyridazine and the chloro ligands are mutually cis- or trans-. Both structures are of a high precision in terms of the average C-C esd's. In the cis(CO)/cisCl derivative GIDBOK, the Ru-Cl bond lengths are 2.405 and 2.431 Å (trans to N and CO, respectively) and the Ru-CO distances of 1.890 and 1.897 Å are typical. The Ru-N_{pyridazine} bond length of 2.050 A is shorter than the Ru-N_{pyridine} bond length of 2.111 Å (trans to Cl and CO, respectively). The longer Ru-Cl and Ru-N bond lengths are trans to the two carbonyl ligands. In this system the longer Ru–Cl bond is also involved in three intermolecular contacts a C-H···Cl and involving three aromatic C-H groups: however, no strong intermolecular hydrogen bonding is observed in the crystal structure. In the more symmetrical *cis*(CO)/*trans*Cl derivative GIDBIE, which has the same relative arrangements of the CO and the Cl ligands as is observed in the four complexes described here, the Ru–Cl bond lengths are 2.392 and 2.398 Å (mutually *trans* to each other) with typical Ru–CO distances of 1.882 and 1.885 Å. The Ru–N_{pyridazine} bond length is 2.085 Å and the Ru–N_{pyridine} 2.122 Å (both *trans* to CO). No strong intermolecular hydrogen bonding is observed.

To the best of our knowledge $[Ru^{II}(L8)(CO)_2(CI)_2]$ is the first structurally characterised pyridazine imine ruthenium complex. The Ru–N_{pyridazine} bond length [2.092(2) Å] in $[Ru^{II}(L8)(CO)_2(CI)_2]$ is similar to that observed in GIDBIE. However, the Ru–N_{pyridazine} bond length is somewhat shorter, and the Ru–N_{imine} bond length [2.176(2) Å] is somewhat longer, than the Ru–N_{triazole} and Ru–N_{pyrazine} bond lengths in the three triazole-based complexes [2.106(3)-2.163(2) Å]. The Ru–C and Ru–Cl distances in $[Ru^{II}(L8)(CO)_2(CI)_2]$ are very similar to those observed in GIDBIE and the complexes of the triazole-based ligands L2, L6 and L7.

Table 2 Selected bond lengths and angles for compounds [Ru(L)(CO)₂Cl₂]

	$[Ru(L2)(CO)_2Cl_2]$	$[Ru(L6)(CO)_2Cl_2]$	$[Ru(L7)(CO)_2Cl_2]$	[Ru(L8)(CO) ₂ Cl ₂]
Bond distances (Å)				
Ru–Cl(1)	2.3999(10)	2.3869(8)	2.4064(8)	2.4058(9)
Ru-Cl(2)	2.3749(10)	2.3803(9)	2.3818(9)	2.3882(10)
Ru–C(1A)	1.875(4)	1.862(3)	1.876(3)	1.886(3)
Ru–C(2A)	1.882(4)	1.871(3)	1.888(3)	1.873(3)
Ru-N(2)	2.106(3)	2.115(2)	2.109(2)	2.092(2)
Ru–N(16)	2.150(3)	2.163(2)	2.143(2)	2.176(2)
C(1A)–O(1A)	1.140(5)	1.126(4)	1.127(4)	1.132(3)
C(2A)–O(2A)	1.130(5)	1.135(4)	1.125(3)	1.122(3)
Bond angles (°)				
Cl(1)-Ru-Cl(2)	175.12(4)	175.81(3)	174.44(2)	176.62 (3)
Cl(1)-Ru-C(1A)	91.95(13)	91.45(11)	92.11(12)	92.44(8)
Cl(1)-Ru-C(2A)	91.74(13)	90.88(11)	93.51(10)	94.02(9)
Cl(1)-Ru-N(16)	89.10(8)	89.30(6)	88.57(6)	87.39(6)
Cl(1)-Ru-N(2)	89.33(9)	86.07(7)	87.24(7)	88.37(6)
Cl(2)-Ru-C(1A)	92.02(13)	92.59(11)	90.66(12)	88.97(8)
Cl(2)-Ru-C(2A)	91.09(13)	90.35(11)	91.38(10)	89.12(9)
Cl(2)-Ru-N(16)	87.67(8)	89.22(6)	86.36(6)	89.29(6)
Cl(2)-Ru-N(2)	86.39(9)	89.77(7)	89.33(7)	90.21(6)
C(1A)-Ru-C(2A)	89.91(18)	88.48(13)	88.46(13)	87.53(11)
C(1A)-Ru-N(16)	89.10(8)	95.19(11)	95.82(11)	102.84(9)
C(1A)–Ru–N(2)	173.03(15)	171.02(11)	171.89(11)	179.06(10)
C(2A)-Ru-N(16)	173.94(14)	176.32(10)	175.18(11)	169.48(9)
C(2A)-Ru-N(2)	96.90(15)	100.18(11)	99.65(10)	92.90(10)
N(16)-Ru-N(2)	77.11(12)	76.17(8)	76.09(8)	76.71(8)

The triazole compounds reported in this contribution show extensive intermolecular interactions through hydrogen bonding networks, whereas the related non-triazole compounds in the literature [9,12] do not. For example, in the two isomers of [Ru^{II}(bipy)(CO)₂-(Cl)₂] reported by Haukka and co-workers[9c], there are no strong intermolecular hydrogen bonds. For the *cis*(CO)/*cis*Cl-arrangement [9c] the Ru–Cl, Ru–N and Ru–C bond lengths are 2.411(4)/2.439(3) Å, 2.090(8)/ 2.117(8) Å and 1.899(11)/1.938(10) Å while in the *cis*-(CO)/*trans*Cl-derivative the data are as follows 2.391(5)/2.390(5) Å, 2.102(9)/2.112(12) Å and 1.817(8)/ 1.835(17) Å, respectively. However, the relatively large esd's mean that an in depth discussion is inappropriate.

In the ruthenium complex of L2 different hydrogen bond interactions can be identified. As can be seen from Fig. 3 a methanol molecule is H-bond donor to N16 of the pyrazine ring (N–O distance 2.844 Å). The C–H bond of the triazole of a different complex serves a Hbond donor to the oxygen of the methanol molecule (C–O distance 2.704 Å). This leads to the formation of a dinuclear subunit, Fig. 4. In addition to these relatively strong H-bonds a different set evolves around the chloro ligands of each ruthenium complex serves as H-bond donor to the chloro ligand of a second ruthenium complex, the distance of 3.468 Å and the N–H– Cl angle of 139.4° indicate a relatively weak interaction. The C14–H bond of the second ruthenium complex



Fig. 4. H-bond interactions between methanol and [Ru(L2)(CO)₂Cl₂].

serves in turn as H-bond donor to the chloro ligand of the first complex. This H-bond is 3.503 Å and a C–H– Cl angle of 136.8° indicates that the bonding is not very strong. This solid-state interaction leads to the formation of a three dimensional chain of H-bond bridged ruthenium complexes (see Fig. 5).

In the L6 derivative, a methanol molecule crystallises with the ruthenium complex and links the L6 derivatives



Fig. 5. Intermolecular hydrogen bonding in [Ru(L2)(CO)₂Cl₂].

into chains along the *b*-axis. The N3–H triazole forms a hydrogen bond with the methanol O–H which in turn hydrogen bonds to the pyrazine N13 atom (not involved in bonding to the Ru). The N3···O1S distance is 2.679(3) Å and the O1S··· N13[†] is 2.969(3) Å, (where † is the symmetry operation x, 1 + y, z). There are two other contacts of note namely C12–H12···Cl1ⁱ and C14–H14···Cl2ⁱⁱ, where the symmetry operators are i and ii are -x, y - 1/2, -z + 1/2 and 1 - x, y - 1/2, 1/2 - z. The interactions are depicted in Fig. 6, a PLATON packing diagram showing the aggregation of the 1:1 complex along the *b*-axis together with the flanking C–H···Cl interactions.



Fig. 6. Intermolecular interactions found in [Ru(L6)(CO)₂Cl₂].

In the L7 derivative, dimers are formed through the formation of centrosymmetric C-H···Cl interactions as depicted in the PLATON packing diagram (Fig. 7): further aggregation is achieved through pyridazinylC-H···O_{Me} and methoxyC-H···O=C interactions. The centrosymmetric N3-H3···Cl1* interaction has an N3··· Cl1* distance of 3.196(3) Å (with symmetry operation * = 1 - x, -y, -z). The Cl4-H14···O27[#] interaction has a Cl4···O27[#] distance of 3.208(3) Å and the C27-H27B···O1A[&] contact has a C27···O1A distance of 3.455(4) Å where the symmetry operations are # = x - 1, y, z and & = 1 + x, 1 + y, z.

The crystal structure of [Ru^{II}(L8)(CO)₂Cl₂], confirms the predictions based on the microanalysis and NMR results that only one of the two binding pockets of L8 is occupied. As seen above, the L8 ligand is bidentate and the two CO groups are cis to one another whilst the chloride anions are mutually trans. The ligand itself is guite flat as is indicated by the small intersection angles between the mean plane of the central pyridazine ring and those of each of the terminal benzene rings [C12 ring 22.7(1); C22 ring $7.5(2)^{\circ}$]: the bigger twist out of plane is observed for the phenyl ring which is associated with the occupied binding pocket, presumably due to steric effects. In the related GIDBIE crystal structure, the ligand is also almost flat with dihedral angles of only $4.9(1)^{\circ}$ and $13.0(1)^{\circ}$ between the central pyridazine ring and the two terminal pyridine rings[12b]. In the case of GIDBIE, the pyridine ring involved in chelation to the ruthenium atom is less twisted $[4.9(1)^{\circ}]$ away from the central pyridazine plane than the one which is not involved in coordination [13.0(1)°]. There are no strong intermolecular hydrogen bonds in the structure of $[Ru^{II}(L8)(CO)_2Cl_2]$.

3. Conclusions

One of the most important features of this work is that for all triazole-based complexes only one structural isomer was isolated and that in the pyrazinetriazole based complexes the triazole ring is coordinated via the N2 atom. Although we do not have direct evidence for this we propose that for the pyridine triazole based complexes the same coordination mode is obtained. As pointed out in the introduction metal complexes of the type $[Ru(bpy)_2(L-L')]^{n+}$, where L-L' is L1 or L2, two isomers were obtained in a 1:1 ratio, while in the presence of substituents different ratios were obtained. It is evident that for this class of compound steric consideration are the main factors, which determine the nature of the coordination isomer obtained. On the other hand for the analogous Rh(III) compounds only one isomer was obtained for all types of L-L' and in these complexes the coordination mode is most likely via N2. This suggest that there electronic factors, i.e., the fact that



Fig. 7. Intermolecular interactions observed in [Ru(L7)(CO)₂Cl₂].

there is a larger electron density present on the N2 than on the N4 atom determines the coordination mode of the ring in these electron deficient complexes. It appears that also for the compounds reported here electronic factors are important. With the absence of large coligands such as 2,2'-bipyridyl the coordination mode of the triazole ligands used in this study is not expected to be driven by steric considerations and therefore the formation of both N2 and N4 bound isomers would be expected. It seems clear that because of the presence of the strongly electron accepting CO ligands the coordination of the more electron rich N2 atom of the ring is favoured. Finally, one of the reasons for the preparation of these complexes was to investigate their potential as intermediates for the preparation of tris heteroleptic complexes. Unfortunately all compounds obtained turned out to be unreactive under a wide range of conditions.

4. Experimental

4.1. Instrumentation

¹H and ¹H COSY spectra were recorded on a Bruker AC400 (400 MHz) instrument. Peak positions are relative to residual solvent peaks. Infrared Spectra were recorded on a Perkin Elmer 2000 FTIR.

4.1.1. Crystal structure determinations of $[Ru(L)(CO)_2 Cl_2]$ where L = L2, L6, L7 and L8

All X-ray data was collected using graphite-monochromated Mo K_{α} radiation. The intensity data for the L2 compound were collected on a Nonius KappaCCD diffractometer. Data were corrected for Lorentz and polarization effects, but not for absorption: details are listed in Table 2 [18]. Intensity data for the L6 and L7 derivatives were collected on a Siemens P4 4-circle diffractometer at room temperature: absorption corrections were performed using ψ -scans (4 reflections for L6 and 3 reflections for L7, with 5° increments from 0° to 360°) and data were processed using the xscans software [19]. Data for the L8 complex were collected on a Bruker SMART area detector diffractometer: a SADABS absorption correction was performed.

All four structures were solved by direct methods (SHELXS [20]) and refined by full-matrix least-squares techniques against F_{0}^{2} (SHELXL-97 [21]). For compound $[Ru(L2)(CO)_2Cl_2]$ the hydrogen atoms of the imin-group N4 and for the C–H-groups of C1, C2 and C3 were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations for the L2 and L8 compounds. For L6 and L7 compounds the triazole H3 atom was refined with isotropic parameters and also the methanol H1S hydroxyl H atom in the L6 derivative: the ORTEP and PLATON programs were used for the molecular graphics in the L6 and L7 derivatives [22,23]. The data have been deposited on the Cambridge Structural Database.

4.2. Synthesis

All solvents were Analar grade and used without further purification. The ligands L1–L8 were available from earlier studies.

4.3. Preparation of metal complexes

4.3.1. $[Ru(CO)_2Cl_2]_n$ [24]

 $[\operatorname{RuCl}_3] \cdot xH_2O$ (5.0 g, 20.5 mmol) and paraformaldehyde (1.5 g) were added to a 90% solution of formic acid. The solution was heated at reflux for 5 h. The colour of the solution changed from red to dark green to orange. When the orange colour was obtained the reaction was cooled in an ice bath and stored in the freezer overnight (-4 °C). The solvent was removed by rotary evaporation to leave a yellow solid. This was washed with hexane and dried in vacuo. Yield 4.6 g, 20.2 mmol, 98%. IR (KBr): 2074 and 2020 cm⁻¹.

4.3.2. $[Ru(L1)(CO)_2Cl_2] \cdot H_2O$

[Ru(CO)₂Cl₂]_n (0.31 g, 1.4 mmol) was dissolved in hot MeOH (30 mL). A methanolic solution of L1 (0.20 g, 1.4 mmol in 10 mL) was added and the solution heated at reflux for 2.5 h. The solution was reduced to 5 mL, 2 drops conc. HCl added and cooled at -4 °C overnight. The resultant feathery yellow precipitate was filtered, washed with cold MeOH (5 mL) and dried in vacuo. Yield 0.13 g, 0.36 mmol, 26%. ¹H NMR (*d*₆-DMSO, 298 K) δ 9.91 (s), 9.17 (d), 8.41 (d), 8.34 (t), 7.85 (t) ppm. IR (CHCl₃)_(CO) 2075, 2000 cm⁻¹. Elemental analysis for C₉H₈Cl₂-N₄O₃Ru: *Anal.* Calc. C, 27.56; H, 2.06; N, 14.29. Found: C, 27.88; H, 1.80; N, 14.29%.

4.3.3. $[Ru(L2)(CO)_2Cl_2] \cdot MeOH$

[Ru(CO)₂Cl_{2]n} (0.30 g, 1.3 mmol) was dissolved in hot MeOH (30 mL). A methanolic solution of L2 (0.20 g, 1.35 mmol in 10 mL) was added and the solution heated at reflux for 1.5 h. The resultant red precipitate was filtered hot, washed with MeOH (10 mL) and dried in vacuo. Yield 0.20 g, 0.52 mmol, 40%. ¹H NMR (*d*₆-DMSO, 298 K) δ 10.01 (s), 9.71 (d), 9.34 (dd), 9.10 (d) ppm. IR (CHCl₃) *v*_(CO) 2072, 2011 cm⁻¹. Elemental analysis for C₉H₉Cl₂N₅O₃Ru: *Anal.* Calc. C, 26.55; H, 2.23; N, 17.20. Found: C, 26.42; H, 2.09; N, 16.94%.

4.3.4. $[Ru(L3)(CO)_2Cl_2]$

[Ru(CO)₂Cl₂]_n (0.23 g, 1.0 mmol) was dissolved in hot MeOH (30 mL). A methanolic solution of L3 (0.20 g, 1.3 mmol in 10 mL) was added and the solution heated at reflux for 1 h. The resultant feathery yellow precipitate was filtered hot, washed with MeOH (10 mL) and dried in vacuo. Yield 0.23 g, 0.6 mmol, 59%. ¹H NMR (*d*₆-DMSO, 298 K) δ 9.72 (s), 9.05 (d), 8.22 (t), 8.21 (d), 7.73 (t), 4.03 (s) ppm. IR (CHCl₃) *v*_(CO) 2072, 2012 cm⁻¹. Elemental analysis for C₁₀H₈Cl₂N₄O₂ Ru: *Anal.* Calc. C, 30.94; H, 2.08; N, 14.43. Found: C, 30.94; H ,1.96; N, 14.18%.

4.3.5. $[Ru(L4)(CO)_2Cl_2] \cdot H_2O$

[Ru(CO)₂Cl₂]_n (0.19 g, 0.83 mmol) was dissolved in hot MeOH (30 mL). A methanolic solution of L4 (0.20 g, 0.83 mmol in 10 mL) was added and the solution heated at reflux for 3 h. The resultant precipitate was filtered hot, washed with MeOH (5 mL) and dried in vacuo. Yield 0.12 g, 0.25 mmol, 31%. ¹H NMR (d_6 -DMSO, 298 K) δ 9.18 (d), 8.53 (d), 8.39 (t), 8.02 (d), 7.81 (t), 7.44 (t), 7.12 (d), 7.04 (t) ppm. IR (CHCl₃) $v_{(CO)}$ 2072, 2019 cm⁻¹. Elemental analysis for C₁₅H₁₂Cl₂N₄O₄Ru: *Anal.* Calc. C, 37.20; H, 2.50; N, 11.57. Found: C, 37.43; H, 2.36; N, 11.10%.

4.3.6. $[Ru(L5)(CO)_2Cl_2] \cdot H_2O$

[Ru(CO)₂Cl₂]_n (0.19 g, 0.83 mmol) was dissolved in hot MeOH (30 mL). A methanolic solution of L5 (0.2 g, 0.85 mmol in 10 mL) was added and the solution heated at reflux for 2 h. The solution was reduced to 5 mL, 2 drops conc. HCl added and cooled at -4 °C overnight. The resultant yellow precipitate was filtered, washed with cold MeOH (5 mL) and dried in vacuo. Yield 0.21 g, 0.46 mmol, 56%. ¹H NMR (*d*₆-DMSO, 298 K) δ 9.03 (d), 8.27 (d), 8.23 (t), 7.81 (s), 7.78 (d), 7.67 (t), 7.37 (t), 7.27 (d), 2.28 (s) ppm. IR (CHCl₃) $v_{(CO)}$ 2078, 2021 cm⁻¹. Elemental analysis for C₁₆H₁₄Cl₂N₄O₃Ru: *Anal.* Calc. C, 39.85; H, 2.93; N, 11.62. Found: C, 40.13; H, 2.99; N, 11.51%.

4.3.7. $[Ru(L6)(CO)_2Cl_2] \cdot MeOH$

[Ru(CO)₂Cl₂]_n (0.19 g, 0.83 mmol) was dissolved in hot MeOH (30 mL). A methanolic solution of L6 (0.2 g, 0.85 mmol in 10 mL) was added and the solution heated at reflux for 2 h. After cooling, 1 mL conc. HCl was added and the solution stored at -4 °C overnight. The resultant yellow precipitate was filtered, washed with cold MeOH (5 mL) and dried in vacuo. Yield 0.09 g, 0.20 mmol, 24%. ¹H NMR (*d*₆-DMSO, 298 K) δ 9.48 (s), 9.22 (d), 8.93 (d), 7.96 (d), 7.35 (d), 3.07 (s) ppm. IR (CHCl₃) *v*_(CO) 2074, 2012 cm⁻¹. Elemental analysis for C₁₆H₁₅Cl₂N₅O₃Ru: *Anal.* Calc. C, 38.64; H, 3.04; N, 14.08. Found: C, 38.41; H, 3.06; N, 13.79%.

4.3.8. $[Ru(L7)(CO)_2Cl_2] \cdot MeOH$

[Ru(CO)₂Cl₂]_n (0.20 g, 0.88 mmol) was dissolved in hot MeOH (30 mL). A methanolic solution of L7 (0.23 g, 0.90 mmol in 10 mL) was added and the solution heated at reflux for 2 h. HCl was added and the solution stored at -4 °C overnight. The resultant yellow precipitate was filtered, washed with cold MeOH (5 mL) and dried in vacuo. Yield 0.13 g, 0.28 mmol, 32%. ¹H NMR (*d*₆-DMSO, 298 K) δ 9.52 (s), 9.32 (d), 9.01 (d), 8.14 (d, 2H), 7.16 (d, 2H), 3.95 (s, 3H) ppm. IR (CHCl₃) *v*_(CO) 2077, 2020 cm⁻¹. Elemental analysis for C₁₆H₁₅-Cl₂N₅O₄Ru: *Anal.* Calc. C, 37.44; H, 2.95; N, 13.64. Found: C, 37.32; H, 2.80; N, 13.39%.

4.3.9. $[Ru(L8)(CO)_2Cl_2]$

L8⁷ (104 mg, 0.3 mmol) was dissolved in 30 mL of MeOH/CHCl₃ (2:1) with a little heating. [Ru(CO)₂Cl₂]_n (160 mg, 0.7 mmol) was dissolved in 15 mL MeOH and added in one portion. The solution was allowed reflux for 3 h, cooled and the resulting precipitate filtered. The precipitate was washed with hot MeOH (2 × 10 mL) and finally CHCl₃ (3 × 5 mL). Yield 90 mg, 0.16 mmol, (53%). ¹H NMR (d_6 -DMSO,

298 K) δ 9.20 (s), 9.11 (s), 8.86 (d), 8.71 (d), 7.76 (d), 7.68 (d), 7.23 (d), 7.08 (d), 3.87 (s), 3.84 (s) ppm. IR (KBr) $v_{(CO)}$ 2066, 1999 cm⁻¹. Elemental analysis for C₂₂H₁₈-Cl₂N₄O₄Ru: *Anal.* Calc. C, 46.00; H, 3.16; N, 9.75. Found: C, 45.76; H, 3.07; N, 9.62%.

5. Supplementary data

Crystallographic data for the crystal structure analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. (FO637,2), for [Ru(L2)(CO)₂Cl₂], CCDC no. 238930 for [Ru(L6)-(CO)₂Cl₂], CCDC no. 238931 for [Ru(L7)(CO)₂Cl₂] and CCDC no. 230603 for [Ru(L8)(CO)₂Cl₂]. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail:deposit@ccdc.cam.ac.uk).

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