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# Complexes of ruthenium(III) and chromium(III) with a new tetradentate $N_2O_2$ -donor ligand: crystal structures, redox properties and spectroelectrochemistry

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#### Abstract

Reaction of 3-(2-methoxyphenyl)pyrazole with 1,2-bis(bromomethyl)benzene under phase-transfer conditions, followed by demethylation of the methoxyphenyl units with BBr<sub>3</sub>, affords the new ligand H<sub>2</sub>L in which two bidentate chelating units (pyrazolyl-phenol) are separated by a *o*-xylyl spacer. Reaction of H<sub>2</sub>L with [M(acac)<sub>3</sub>] (M = Cr, Ru) afforded in each case two mononuclear products [M(L)(acac)] and [M(L)(HL)]. Crystal structure determinations of [M(L)(acac)] for both M = Cr and Ru show that the complexes have similar structures, with the ligand L<sup>2-</sup> folded such that it coordinates as a tetradentate chelate in a *cis*-N<sub>2</sub>,*cis*-O<sub>2</sub> manner with the remaining two coordination sites at the metal occupied by the acac ligand. Neither complex [M(L)(HL)] formed X-ray quality crystals but we assume a similar mononuclear structure in which one L<sup>2-</sup> is coordinated as a tetradentate chelate, and the second (HL)<sup>-</sup> is coordinated via one bidentate *N*,*O*-binding site with the second site pendant and remaining protonated. [Ru(L)(acac)] undergoes reversible oxidation to Ru(IV) and an irreversible reduction to Ru(II); in contrast, for [Ru(L)(HL)] the Ru(III)–Ru(IV) and Ru(II)–Ru(III) couples are both reversible. A UV–Vis–NIR spectroelectrochemical study of [Ru(L)(HL)] was accordingly carried out, and shows that in the Ru(IV) state the spectrum develops intense, low-energy charge-transfer transitions in the near-IR region. © 2001 Elsevier Science Ltd. All rights reserved.

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#### 1. Introduction

Ligands containing two bidentate compartment separated by a spacer group have been extensively used in self-assembly recently [1]. In particular, formation of dinuclear triple helicates with stoichiometry  $M_2L_3$  [2], and edge-bridged tetrahedral cages of stoichiometry  $M_4L_6$  [3,4], arise from reaction of these ligands (having four donor atoms) with labile metal ions having a preference for octahedral geometry, such that a ratio of 1.5 ligands for each metal ion is required to satisfy both the coordination preference of each metal ion and the tendency of a polydentate ligand to use all of its donor atoms.

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We have recently investigated the coordination behaviour of ligand  $L^1$  (Scheme 1) which contains two pyrazolyl-pyridine termini separated by an *o*-xylyl spacer, and found that this ligand can bridge two metal ions to result in either dinuclear helicates [with Cu(I)]



Scheme 1.

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Fig. 1. Crystal structure of Me<sub>2</sub>L<sup>1</sup>.

[5] or tetrahedral cages [with Co(II)] [4]. However, it is also capable of coordination to a single metal ion as a tetradentate chelate, giving simpler mononuclear complexes [5], and in the dinuclear complex [{(L<sup>1</sup>)Ni} ( $\mu$ -L<sup>1</sup>){Ni(L<sup>1</sup>)]<sup>4+</sup> both terminal (tetradentate) and bridging (bis-bidentate) coordination modes were observed [4].

In seeking to extend our studies on potentially bridging ligands of this type we wished to prepare a ligand having a similar architecture but a different donor set. To that end we report in this paper the synthesis and some coordination chemistry with the new ligand H<sub>2</sub>L (Scheme 1) which contains two potentially *N*,*O*-chelating sites, based on pyrazolyl-phenolate units, linked by an *o*-xylyl spacer. The harder donor set of these ligands compared to L<sup>1</sup> is expected to result in stabilisation of metal complexes in higher oxidation states, and we describe our initial studies of the coordination behaviour of H<sub>2</sub>L with Cr(III) and Ru(III).

#### 2. Results and discussion

#### 2.1. Ligand synthesis

The synthesis of the new ligand H<sub>2</sub>L follows the general method used to prepare L<sup>1</sup>, viz. preparation of a pyrazole with a suitable substituent (here, 2methoxyphenyl) attached, followed by reaction of 2 equiv. of the pyrazole with 1,2-bis(bromomethyl)benzene under phase-transfer conditions [5]. The only variation required in this method for its use in the synthesis of H<sub>2</sub>L is that the phenols are protected as their methyl ethers during synthesis of the backbone, and then deprotection at the end with BBr<sub>3</sub> liberates the two pyrazolyl-phenol sites. The appropriate 3-(2methoxyphenyl)pyrazole has been described by us before, when it was used to make a tris(pyrazolyl)borate [6], and reaction of this with 1,2-bis(bromomethyl)benzene afforded the protected precursor Me<sub>2</sub>L in 55% yield. In addition to characterisation by standard methods (see Section 3) it gave X-ray quality crystals from  $CH_2Cl_2-Et_2O$  and the crystal structure is shown in Fig. 1. The steric bulk of the methoxy group results in a substantial twist between the pyrazolyl and adjacent methoxyphenyl rings (torsion angles of 31 and 47°). Deprotection of Me<sub>2</sub>L with BBr<sub>3</sub> afforded H<sub>2</sub>L in 89% yield; in its <sup>1</sup>H NMR spectrum a broad singlet at 10.64 ppm is characteristic of the phenol protons which each form an O-H···N hydrogen-bonding interaction with the adjacent pyrazolyl ring, as we have observed with a variety of pyridine-phenol chelating ligands [7].

# 2.2. Preparation and characterisation of complexes with Cr(III) and Ru(III)

Complexes with Cr(III) and Ru(III) were prepared by reaction of  $H_2L$  with the appropriate  $[M^{III}(acac)_3]$  in a 3:2 stoichiometry, in ethylene glycol at higher temperatures. Under these conditions the acidic protons of the phenol donors protonate the anionic acac ligands to form neutral Hacac which evaporates from the reaction mixture [8].

The reaction with  $[Cr(acac)_3]$  afforded a clear, dark green solution. TLC examination revealed the presence of two principal products and several trace products. Extraction of the reaction mixture with CH<sub>2</sub>Cl<sub>2</sub> and purification by column chromatography allowed isolation of the two main products, one in much higher yield than the other. On the basis of their electron-impact mass spectra these were readily identified as the mononuclear complexes [Cr(L)(acac)] (major product) and [Cr(L)(HL)] (minor product). Assuming the usual octahedral coordination, the former of these must have  $L^{2-}$  coordinated as a tetradentate chelate, whereas the latter will have one tetradentate chelating ligand  $L^{2-}$ and one 'hypodentate' (HL)<sup>-</sup> which is acting as only a bidentate, mono-anionic ligand through one bidentate binding site with the other bidentate site pendant. [Cr(L)(acac)] formed X-ray quality crystals by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution, and the structure is shown in Fig. 2. The ligand  $L^{2-}$  is folded such that it coordinates as a tetradentate chelate in a cis-N<sub>2</sub>, cis-O<sub>2</sub> manner with the remaining two coordination sites occupied by the acac ligand. The pyrazolyl-phenolate units form six-membered chelate rings with the Cr(III) centre, with torsion angles of 21° between rings 1 and 2, and 19° between rings 3 and 4 [where ring 1 contains atoms N(11)–C(15), and so on]. The bond distances are unremarkable.

Reaction of  $H_2L$  with  $[Ru(acac)_3]$  in a similar way afforded a dark blue solution from which two products were isolated after chromatographic purification. These were identified by mass spectrometry and elemental analysis as [Ru(L)(acac)] (major product) and [Ru(L)(HL)] (minor product). The crystal structure of [Ru(L)(acac)] is shown in Fig. 3; it is very similar to the Cr(III) analogue described above, with torsion angles of 25 and 22° within each bidentate pyrazolyl-phenolate unit [involving rings 1/2 and 3/4 respectively, following the notation used for the Cr(III) analogue]. Again,  $L^{2-}$  is folded and acting as a tetradentate chelate with a *cis*-N<sub>2</sub>,*cis*-O<sub>2</sub> coordination mode, and unremarkable bond distances which are all slightly longer in the Ru(III) complex than in the Cr(III) complex.

It is presumably the kinetic inertness of these metal ions that prevents formation of higher oligomers such as the tetrahedral  $(metal)_4(ligand)_6$  cages that we observed with ligand L<sup>1</sup>. As mentioned earlier, the pyridine-based ligand L<sup>1</sup> can adopt either bridging or terminal binding modes [4,5], but since the metal ions to which it was coordinated [e.g. Ni(II), Co(II), Cu(I)] were labile, the most thermodynamically stable struc-



Fig. 2. Crystal structure of [Cr(L)(acac)].



Fig. 3. Crystal structure of [Ru(L)(acac)].

ture could form in each case even if the initially-formed complex was not ideal. In these Ru(III) and Cr(III) complexes however, initial formation of a complex in which 1 equiv. of  $L^{2-}$  is acting as a tetradentate chelate effectively prevents formation of higher nuclearity cage structures. The largest structures that are likely to form in significant amounts under these conditions are therefore the dinuclear complexes [LM<sup>III</sup>( $\mu$ -L)M<sup>III</sup>L], and it is clear that [Cr(L)(HL)] and [Ru(L)(HL)] are 'en route' to this and would form such complexes by reaction of the pendant bidentate site with a second equivalent of [ML(acac)] (M = Cr, Ru respectively). However, no significant amounts of such dinuclear complexes could be detected.

Interestingly, the residue left at the top of the column after chromatographic separation of [Ru(L)(HL)] and [Ru(L)(acac)] was examined by FAB mass spectrometry and revealed the presence of higher oligomers: weak peaks at m/z 2506 and 1984 can be assigned as  $\{Ru_4L_5\}$ and  $\{Ru_3L_4\}$  species respectively, suggesting that formation of cages with stoichiometry  $\{Ru_4L_6\}$  might be accessible under sufficiently forcing conditions. However, these fractions were present in only tiny amounts and could not be separated chromatographically.

### 2.3. Redox and spectroscopic properties

The Cr(III) complexes showed no significant redox behaviour, with only irreversible processes at extreme negative potentials. This is not surprising: the redox chemistry of Cr(III) complexes is often associated with ligand-centred processes, as in the three reductions of  $[Cr(bipy)_3]^{3+}$  [9], or with Cr(III)–Cr(II) couples if the donor set will stabilise the Co(II) state. In these complexes however, there are no reducible ligands and a hard donor set.

Both Ru(III) complexes however are redox active (Fig. 4). [Ru(L)(acac)] in CH<sub>2</sub>Cl<sub>2</sub> shows a reversible Ru(III)–Ru(IV) couple at + 0.20 V versus Fc/Fc<sup>+</sup>, and an irreversible process which we assume to be a Ru(II)–Ru(III) couple at approximately - 1.4 V versus Fc/Fc<sup>+</sup>. In contrast, for [Ru(L)(HL)] both Ru(III)–Ru(IV) and Ru(II)–Ru(III) couples are fully reversible, and occur at + 0.14 and - 1.47 V, respectively versus Fc/Fc<sup>+</sup>. Despite the difference in donor sets—N<sub>2</sub>O<sub>4</sub> for [Ru(L)(acac)] and N<sub>3</sub>O<sub>3</sub> for [Ru(L)(HL)]—the potentials for reversible oxidation to Ru(IV) are very similar. The value of + 0.14 V versus Fc/Fc<sup>+</sup> for this redox process in [Ru(L)(HL)] is also identical to that of [Ru<sup>III</sup>(no)<sub>3</sub>] [Hno = 2-(2-hydroxyphenyl)pyridine] which has a (pyridine)<sub>3</sub>(phenolate)<sub>3</sub> donor set [8a].

Because of the reversibility of both Ru(III)–Ru(IV) and Ru(II)–Ru(III) processes of [Ru(L)(HL)] we carried out a UV–Vis–NIR spectroelectrochemical study (CH<sub>2</sub>Cl<sub>2</sub>, -30 °C) to determine the electronic spectra in all three accessible oxidation states; the results are in



Fig. 4. Cyclic voltammograms of (a) [Ru(L)(acac)]; and (b) [Ru(L)(HL)] in CH<sub>2</sub>Cl<sub>2</sub> at a Pt-bead electrode (scan rate, 0.2 V s<sup>-1</sup>).



Fig. 5. Results of the spectroelectrochemical study on [Ru(L)(HL)](CH<sub>2</sub>Cl<sub>2</sub>, 243 K). (a) Spectra recorded during reduction of Ru(III) to Ru(II); (b) spectra recorded during oxidation of Ru(III) to Ru(IV). In (b), the discontinuity (\*) at 860 nm arises from the detector change.

Fig. 5. In the starting Ru(III) state the lowest-energy feature, at 575 nm, may be assigned as phenolate  $\rightarrow$ Ru(III) ligand-to-metal charge-transfer (LMCT) by analogy with related complexes [8]. On reduction to the Ru(II) state, this LMCT transition collapses and is replaced by a transition at higher energy (440 nm) which we tentatively ascribe to a Ru(II)  $\rightarrow$  pyrazolyl( $\pi^*$ ) MLCT process, by analogy with the much more wellknown Ru(II) complexes with pyridine-based ligands [10].

On oxidation of the metal to the Ru(IV) state, the phenolate  $\rightarrow$  Ru(III) LMCT at 575 nm is replaced by a series of intense lower-energy transitions: the most intense is at 860 nm, and lower-intensity bands are visible at approximately 1100 and 1550 nm. We assign the intense 860 nm transition to a phenolate  $\rightarrow Ru(IV)$ LMCT process. Compared to the Ru(III) complex, this transition is more intense as the metal is more electrondeficient, and is red-shifted because the metal  $d(\pi)$ manifold will be lowered in energy on oxidation. Exactly similar behaviour is seen in e.g. a series of oxo-Mo(V) complexes with phenolate ligands, in which oxidation to Mo(VI) results in the phenolate  $\rightarrow$  Mo LMCT process being increased in intensity and lowered in energy for the same reasons [11]. The nature of the two lower-energy transitions is less obvious. They could have  $pyrazolyl \rightarrow Ru(IV)$  LMCT character, or could arise because the  $d(\pi)$  orbital set is not degenerate; with a low-spin d<sup>4</sup> configuration there are two holes in the  $d(\pi)$  orbital set such that for each donor atom two LMCT transitions at different energies are possible.

Whatever their exact assignment however, it is apparent that these intense, low-energy transitions-which span much of the near-IR region-are relevant to our current work on near-IR electrochromic dyes [11,12]. Materials which can be switched electrochemically between transparent and strongly absorbing in this region of the spectrum are of possible technological interest for at least two reasons: (i) they could be used in 'smart windows' to filter out the part of the solar spectrum which is felt as heat; and (ii) they could be used for switching data transmission along silica fibre-optic cables which operate in the near-IR region [13]. To date we have concentrated on systems based on rutheniumdioxolene [12] and tris(pyrazolyl)borato-oxo-Mo(V) chromophores [11] which show strong, low-energy charge-transfer transitions in some oxidation states but not others. This new work indicates that charge-transfer transitions in simple Ru(IV) complexes are also worth further study in this respect.

#### 3. Experimental

#### 3.1. General details

3-(2-Methoxyphenyl)pyrazole was prepared according to the previously described route [6]. Other starting materials and reagents were obtained from the usual commercial sources (Aldrich, Avocado, Lancaster) and used as received. The following instruments were used for routine spectroscopic analyses: <sup>1</sup>H NMR spectra, a JEOL Lambda 300 MHz spectrometer; EI and FAB mass spectra, a VG-Autospec instrument; X-band EPR spectra, a Bruker ESP-300E spectrometer. Instrumentation used for electrochemical measurements, and for the spectroelectrochemical study with an OTTLE cell, has been described before [14].

## 3.2. Synthesis of $H_2L$

A two-phase mixture of 3-(2-methoxyphenyl)pyrazole (3.13 g, 18 mmol), 1,2-bis-(bromomethyl)benzene (2.25 g, 8.5 mmol), toluene (150 cm<sup>3</sup>) "Bu<sub>4</sub>NOH (25 drops of 40% aqueous solution) and aqueous NaOH (10 molar concentration, 35 cm<sup>3</sup>) was heated to 85 °C and stirred vigorously at this temperature for 24 h. After cooling, the yellow-orange organic phase was separated, washed with water, and dried over MgSO4. Filtration and removal of the solvent afforded a brown solid. Purification by column chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub>) afforded pure Me<sub>2</sub>L as a white solid (2.22 g, 55%). EIMS: m/z 450 ( $M^+$ ), 276 { $M^+ - [3-(2$ methoxyphenyl)pyrazole]}. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.96 (2H, dd, J = 7.6, 1.9 Hz; anisyl H<sup>3</sup>), 7.27–7.31 (6H, m; anisyl H<sup>5</sup>, phenyl, and pyrazolyl H<sup>5</sup>), 7.15 (2H, m; phenyl), 6.91-7.03 (4H, m; anisyl H<sup>4</sup> and  $H^{6}$ ), 6.79 (2H, d, J = 2.7 Hz; pyrazolyl  $H^{4}$ ), 5.46 (4H, s; CH<sub>2</sub>), 3.89 (6H, s; OMe). Anal. Found: C, 74.6; H, 5.7; N, 12.2. Calc. C, 74.7; H, 5.8; N, 12.4%.

Deprotection of  $Me_2L$  was carried out as follows. To a solution of  $Me_2L$  (1.94 g, 4.3 mmol) in dry  $CH_2Cl_2$ (30 cm<sup>3</sup>) under  $N_2$  was added BBr<sub>3</sub> (10.8 g, 4 cm<sup>3</sup>, 10 equiv.) and the mixture was stirred at 30 °C for 5 h. After this period, aqueous NaOH (pH 9) was carefully added dropwise to afford a white precipitate and a yellow aqueous phase. This mixture was extracted with several portions of  $CH_2Cl_2$ , which were combined, 5.33 (4H, s; CH<sub>2</sub>). Anal. Found: C, 73.7; H, 5.4; N,

13.1. Calc. C, 73.9; H, 5.2; N, 13.3%.

# 3.3. Syntheses of complexes

A mixture of  $H_2L$  and  $[M(acac)_3]$  (M = Cr, Ru; 0.67 equiv. with respect to  $H_2L$ ) in ethylene glycol was heated to 170 °C (M = Cr) or 140 °C (M = Ru) whilst bubbling a stream of N<sub>2</sub> slowly through the mixture; this was maintained for 6 h. For M = Cr the reaction mixture became dark green after 20 min; for M = Ru a dark blue-violet colour was observed. After allowing the reaction mixture to cool to room temperature (r.t.), excess water was added and the mixture was extracted with several portions of CH<sub>2</sub>Cl<sub>2</sub> which were combined, dried (MgSO<sub>4</sub>) and evaporated to dryness. Purification by column chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub> containing 1–1.5% added MeOH) afforded two main products in each case whose characterisation data are as follows.

[Cr(L)(acac)] (dark green): EIMS: m/z 571 (80%,  $M^+$ ), 472 (100%,  $M^+$  – acac). Found: C, 53.7; H, 4.3; N, 7.2. Calc. for [Cr(L)(acac)]·2CH<sub>2</sub>Cl<sub>2</sub>: C, 53.4; H, 4.3; N, 7.6%.

Table	1

Crystallographic dat	a for the	three	crystal	structures
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Compound	Me <sub>2</sub> L	[Cr(L)(acac)]·2CH <sub>2</sub> Cl <sub>2</sub>	[Ru(L)(acac)]·CH <sub>2</sub> Cl <sub>2</sub>
Chemical formula	$C_{28}H_{26}N_4O_2$	C <sub>33</sub> H <sub>31</sub> Cl <sub>4</sub> CrN <sub>4</sub> O <sub>4</sub>	$C_{31}H_{29}Cl_2N_4O_4Ru$
Formula weight	450.53	741.42	705.56
System, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
a (Å)	7.9949(19)	8.853(4)	10.392(5)
b (Å)	12.330(3)	15.325(7)	13.312(6)
c (Å)	23.989(6)	24.741(8)	21.454(8)
$\beta(\circ)$	91.37(3)	90.07(2)	90.38(4)
$V(Å^3)$	2364.2(10)	3357(2)	2968(2)
Z	4	4	4
$D_{\text{cale}}$ (Mg m <sup>-3</sup> )	1.266	1.467	1.579
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.081	0.703	0.753
Crystal size (mm)	$0.4 \times 0.3 \times 0.2$	$0.3 \times 0.2 \times 0.2$	$0.5 \times 0.2 \times 0.05$
Reflections collected: total, independent, $R_{int}$	12557, 4156, 0.0307	21199, 7651, 0.0496	12032, 5997, 0.0776
Data, restraints, parameters	4156, 0, 317	7651, 0, 415	5997, 0, 390
Final $R_1$ , $wR_2^{a,b}$	0.0423, 0.1145	0.0474, 0.1277	0.0471, 0.0970
Largest residuals (e $Å^{-3}$ )	+0.204, -0.258	+0.625, -0.578	+0.464, -0.542

<sup>a</sup> Structure was refined on  $F_o^2$  using all data; the value of  $R_1$  is given for comparison with older refinements based on  $F_o$  with a typical threshold of  $F \ge 4\sigma(F)$ .

<sup>b</sup>  $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]^{1/2}$  where  $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$  and  $P = [\max(F_o^2, 0) + 2F_c^2] / 3$ .

Table 2 Selected inter-atomic lengths (Å) and angles (°) for  $[Cr(L)(acac)] \cdot 2CH_2Cl_2$  and  $Ru(L)(acac)] \cdot CH_2Cl_2$ 

Bond lengths			
Cr(1)–O(42)	1.921(2)	Ru(1)–O(42)	1.983(3)
Cr(1)–O(22)	1.931(2)	Ru(1)-O(22)	2.008(3)
Cr(1)-O(62)	1.963(2)	Ru(1)-O(64)	2.015(3)
Cr(1)-O(64)	1.964(2)	Ru(1)–O(62)	2.028(3)
Cr(1)–N(31)	2.087(2)	Ru(1)–N(11)	2.061(4)
Cr(1)–N(11)	2.100(2)	Ru(1)–N(31)	2.077(4)
Bond angles			
O(42)–Cr(1)–O(22)	91.30(9)	O(42)-Ru(1)-O(22)	93.58(14)
O(42)–Cr(1)–O(62)	92.19(9)	O(42)-Ru(1)-O(64)	84.20(14)
O(22)–Cr(1)–O(62)	176.50(8)	O(22)-Ru(1)-O(64)	88.05(14)
O(42)-Cr(1)-O(64)	91.36(8)	O(42)-Ru(1)-O(62)	89.39(14)
O(22)-Cr(1)-O(64)	90.31(9)	O(22)-Ru(1)-O(62)	176.71(14)
O(62)-Cr(1)-O(64)	89.30(9)	O(64)-Ru(1)-O(62)	93.66(13)
O(42)-Cr(1)-N(31)	84.77(9)	O(42)-Ru(1)-N(11)	171.19(14)
O(22)-Cr(1)-N(31)	96.71(9)	O(22)-Ru(1)-N(11)	83.71(16)
O(62)–Cr(1)–N(31)	83.92(9)	O(64)-Ru(1)-N(11)	87.33(14)
O(64)-Cr(1)-N(31)	172.05(9)	O(62)-Ru(1)-N(11)	93.56(16)
O(42)-Cr(1)-N(11)	173.65(9)	O(42)-Ru(1)-N(31)	86.96(15)
O(22)-Cr(1)-N(11)	83.14(9)	O(22)-Ru(1)-N(31)	94.31(15)
O(62)–Cr(1)–N(11)	93.36(9)	O(64)-Ru(1)-N(31)	170.97(15)
O(64)–Cr(1)–N(11)	85.63(9)	O(62)-Ru(1)-N(31)	84.43(15)
N(31)-Cr(1)-N(11)	98.88(9)	N(11)-Ru(1)-N(31)	101.58(16)

[Cr(L)(HL)] (grass green): FABMS: m/z 894 (100%,  $M^+$ ), 916 (80%,  $M + Na^+$ ). Found: C, 67.6; H, 5.0; N, 12.0. Calc. for [Cr(L)(HL)]·0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 67.3; H, 4.5; N, 12.0%.

[Ru(L)(acac)] (blue-green): EIMS: m/z 621 (100%,  $M^+$ ), 521 (10%,  $M^+$  – acac). Found: C, 54.9; H, 4.4; N, 7.3. Calc. for [Ru(L)(acac)]·CH<sub>2</sub>Cl<sub>2</sub>: C, 54.4; H, 4.3; N, 7.9%. EPR (CH<sub>2</sub>Cl<sub>2</sub>-thf glass, 105 K):  $g_1 = 2.413$  (positive-going signal),  $g_2 = 2.106$  (inflexion),  $g_3 = 1.818$  (negative-going signal).

[Ru(L)(HL)] (blue-violet): FABMS: m/z 943 (100%,  $M^+$ ), 966 (15%,  $M + \text{Na}^+$ ). Found: C, 64.0; H, 4.8; N, 11.0. Calc. for [Ru(L)(HL)]·0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 64.0; H, 4.3; N, 11.4%. EPR (CH<sub>2</sub>Cl<sub>2</sub>-thf glass, 105 K):  $g_1 = 2.291$  (positive-going signal),  $g_2 = 2.161$  (inflexion),  $g_3 = 1.862$  (negative-going signal).

#### 3.4. X-ray crystallography

Suitable crystals were quickly transferred from the mother liquor to a stream of cold  $N_2$  (173 K) on a Siemens SMART diffractometer fitted with a CCD-type area detector. In all cases a full sphere of data was collected at 173 K using graphite-monochromatised Mo K $\alpha$  radiation. Empirical absorption corrections were applied using SADABS [15], and structure solution and refinement was performed with the SHELX suite of programs [16]. Table 1 contains a summary of the crystal parameters, data collection and refinement details; selected bond distances for the structures are

collected in Table 2. None of the structural determinations presented any significant problems.

#### 4. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 167121–167123. 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; email: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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