Different Bonding Modes for 6-(2-Thienyl)-2,2′-bipyridine at Ruthenium(II); the Structural Characterisation of [Ru(HL)(HL)Cl][BF$_4$] [HL = 6-(2-Thienyl)-2,2′-bipyridine]

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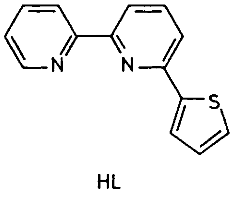
The ligand 6-(2-thienyl)-2,2′-bipyridine (HL) forms ruthenium complexes in which it acts as a terdentate *N,N,S*-donor, a bidentate *N,N*-donor, and in a deprotonated form a terdentate *N,N,C*-donor; the complex [RuCl(HL)$_2$][BF$_4$] has been structurally characterised and shown to contain both *N,N,S*- and *N,N*-bonded ligands.

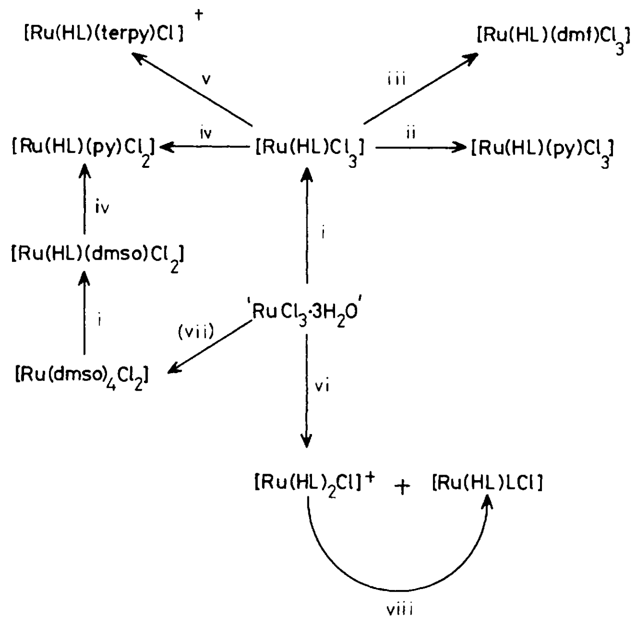
We have recently demonstrated that the potentially terdentate ligand 6-(2-thienyl)-2,2′-bipyridine (HL) adopts a range of bonding modes in square planar complexes of d^8 metals, including one in which cyclometallation of the thiophene ring at C-3 occurs.[1,2] The ligand was initially investigated with the aim of preparing *S*-bonded thiophene complexes, and in this Communication we describe the first octahedral complexes of HL. The related ligand 2-(2′-thienyl)pyridine has been shown to adopt a variety of bonding modes, but only very weak M–S interactions have been detected.[3,4]

The reaction of 'RuCl$_3$·3H$_2$O' with HL in EtOH led to the formation of the brown paramagnetic (μ_{eff} = 2.01 μ_B, 298 K) complex [RuCl$_3$(HL)] containing a terdentate *N,N,S*-bonded ligand. The reaction of [RuCl$_3$(HL)] with dimethylformamide (dmf) or pyridine (py) resulted in the formation of [RuCl$_3$(dmf)(HL)] or [RuCl$_3$(py)(HL)] respectively. These two complexes contain bidentate *N,N*-bonded HL ligands; we have structurally characterised the pyridine adduct, and demonstrated a meridional arrangement of the three chloride ligands.[5] In contrast, the reaction of [RuCl$_3$(HL)] with pyridine in the presence of Et$_3$N results in reduction and the formation of the diamagnetic ruthenium(II) complex [RuCl$_2$(py)(HL)], containing a terdentate *S,N,N*-bonded HL ligand. Other ruthenium complexes of HL are indicated in Scheme 1.

Reaction of 'RuCl$_3$·3H$_2$O' with an excess of HL yields [RuCl(HL)$_2$]Cl, which undergoes a metathesis reaction with Na[BF$_4$] to yield [RuCl(HL)$_2$][BF$_4$]. The ^{1}H n.m.r. spectrum of [RuCl(HL)$_2$]$^+$ clearly indicates that the two ligands are non-equivalent. The resonance expected for H(3) of one of thienyl rings was not observed at room temperature, and it was initially thought that the complex contained one metallated and one nonmetallated ligand. However, the corresponding H(4) proton was observed as a doublet of doublets at δ 6.47, and a double quantum filtered COSY experiment established a single observable coupling to H(5) which



HL



Scheme 1. *Reagents:* i, HL; ii, py; iii, dmf; iv, py, Et_3N; v, 2,2′; 6′, 2″-terpyridyl (terpy); vi, excess HL; vii, Ag^+.

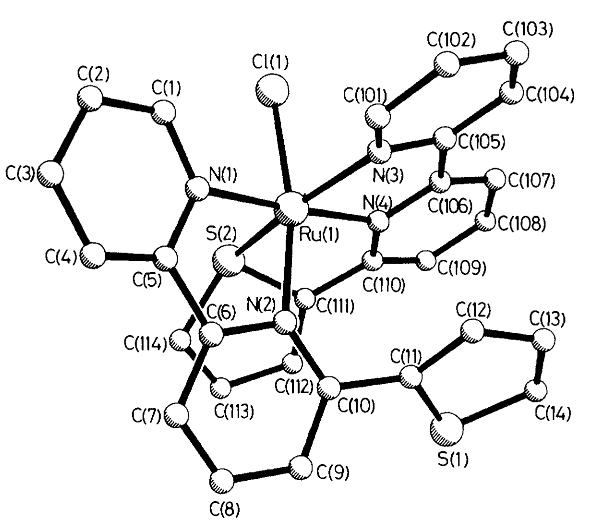


Figure 1. The crystal and molecular structure of the cation in $[RuCl(HL)_2][BF_4]\cdot CH_2Cl_2$ showing the numbering scheme adopted. Selected bond lengths (Å): Ru(1)–Cl(1) 2.390(1), Ru(1)–N(1) 2.064(5), Ru(1)–N(3) 2.024(4), Ru(1)–S(1) 2.380(2), Ru(1)–N(2) 2.116(4), Ru(1)–N(4) 2.025(4). Selected bond angles (°): N(1)–Ru(1)–N(4) 176.1(2), S(2)–Ru(1)–N(3) 159.8(1), S(2)–Ru(1)–N(4) 81.6(1), S(2)–Ru(1)–N(2) 88.4(1), S(2)–Ru(1)–N(1) 102.2(1), Ru(1)–S(2)–C(111) 94.9(2), Ru(1)–S(2)–C(114) 131.0(2).

appears as a doublet at δ 7.0; variable temperature studies indicated that a fluxional process was occurring, such that H(3) was fully coalesced at room temperature. We are currently investigating this process further.

Recrystallisation of $[RuCl(HL)_2][BF_4]$ from CH_2Cl_2 gave a crystalline solvate, $[RuCl(HL)_2][BF_4]\cdot CH_2Cl_2$,† which we have structurally characterised. The crystal and molecular structure of the cation $[RuCl(HL)_2]^+$, together with the numbering scheme adopted, is shown in Figure 1. The two HL ligands are seen to differ in the bonding mode adopted; one is a bidentate *N,N*-donor, whilst the other is a terdentate *S,N,N*-donor. The co-ordinated chloride is *trans* to the central pyridine ring of the bidentate ligand. In the bidentate ligand, the thienyl ring is twisted with respect to the adjacent pyridine to yield a dihedral angle of 45.3°, whereas in the terdentate ligand the twist angle is 35.2°. The non-co-ordinated thienyl ring is approximately coplanar with the bipyridine portion of the other ligand, with an interplanar angle of 22.3°. The co-ordinated sulphur shows a non-bonded contact with the chloride of 3.251 Å. The Ru(1)–S(2) bond is not coplanar with the S(2) thienyl ring, but forms an angle of 123.6° with it; this is consistent with a distorted tetrahedral geometry about the sulphur atom. There are no short contacts between the metal and the non-co-ordinated thiophene ring [calculated distances; Ru(1)–H(12) 3.586 and Ru(1)–H(13) 5.396 Å].

There are two other examples of structurally characterised *S*-bonded thiophene complexes, both of which are ruthenium(II) derivatives. The Ru–S distance in $[RuCl(HL)_2]^+$ of 2.380(2) Å closely resembles those of 2.343 and 2.402 Å observed in a benzothiophene complex[6] and 2.408 Å in a 2-thienylmethylcyclopentadienide compound.[7] This clearly indicates that *S*-bonding of a thiophene does not involve an inherently weak M–S interaction, and that such a bonding mode may readily be enforced by polydentate ligands.

A minor product from the reaction of '$RuCl_3\cdot 3H_2O$' with an excess of HL is the complex [Ru(HL)(L)Cl], which contains a cyclometallated L ligand. We have previously demonstrated this bonding mode in palladium(II), platinum(III), and gold(III) complexes of HL.[1] The cyclometallated complex may also be obtained in low yield by the reaction of $[RuCl(HL)_2]^+$ salts with Ag^+.

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† *Crystal data:* $C_{29}H_{22}BCl_3F_4N_4RuS_2$, red-brown blocks, $M = 782.88$, monoclinic, space group $P2_1/c$, $a = 7.576(1)$, $b = 16.072(3)$, $c = 26.083(4)$ Å, $\beta = 96.02(1)$°, $U = 3158.5$ Å^3, $Z = 4$, $D_c = 1.65$ g cm^{-3}, Mo-K_α radiation ($\lambda = 0.7107$ Å), μ(Mo-K_α) = 9.2 cm^{-1}. 6171 Reflections collected on a four-circle diffractometer with 2θ(max) 29°. The data were averaged and 4313 unique reflections with $I > 3\sigma(I)$ were used in structure solution and refinement. The structure was solved by heavy atom methods, and refined (Ru, Cl, C, N, S, B, F anisotropic) to $R = 0.0504$, $R_w = 0.0585$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

References

1 E. C. Constable, R. P. G. Henney, and T. A. Leese, *J. Organomet. Chem.*, 1988, 361, 277.
2 E. C. Constable, R. P. G. Henney, and D. A. Tocher, manuscript in preparation.
3 H. Sigel, H. Wynberg, T. J. van Bergen, and K. Kahmann, *Helv. Chim. Acta*, 1972, **55**, 610.
4 T. J. Giordano and P. G. Rasmussen, *Inorg. Chem.*, 1975, **14**, 1628.
5 E. C. Constable, R. P. G. Henney, and D. A. Tocher, unpublished results.
6 S. R. Bucknor, M. Draganjac, T. B. Rauchfuss, and C. J. Rutting, *J. Am. Chem. Soc.*, 1984, **106**, 5379.
7 M. Draganjac, C. J. Rutting, and T. B. Rauchfuss, *Organometallics*, 1985, **4**, 1909.