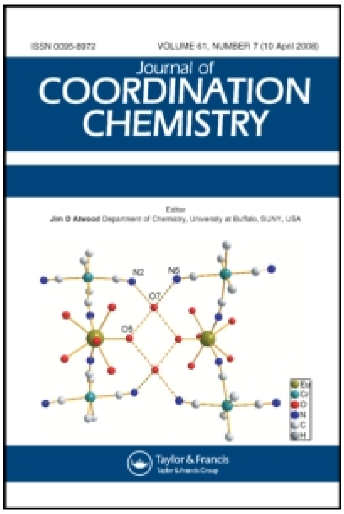

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AN UNUSUAL RUTHENIUM(II) COMPLEX OF 2-(2-PYRIDYL)BENZOTHIAZOLE

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AN UNUSUAL RUTHENIUM(II) COMPLEX OF 2-(2-PYRIDYL)BENZOTHIAZOLE

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The ligand 2-(2-pyridyl)benzothiazole (L) can act both as an $N-N$ and an $N-S$ chelating donor. The latter coordination mode is expected to be preferred when it is involved in coordination to Ru(II) which is a soft acceptor centre. However, in the title compound, chlorobis(acetonitrile)triphenylphosphino-2-(2-pyridyl)benzothiazole-*N,N*-ruthenium(II) chloride, $[Ru(L)(PPh_3)(CH_3CN)_2Cl]Cl$, the ligand acts in *N,N*-bidentate manner and the Ru(II) ion is found to be present in an N_4PCl coordination environment. PPh_3 and Cl are *trans* to each other and the two CH_3CN ligands occupy *cis* positions facing the *NN* donor atoms of ligand L.

Keywords: Ruthenium; 2-(2-pyridyl)benzothiazole; Crystal structure

INTRODUCTION

As a part of our continued interest [1–7] in the chemistry of ruthenium ligated to various types of $N-S$ donors we ventured to design, prepare and characterise mononuclear ruthenium complexes containing one $N-S$ chelating donor along with other weakly coordinating monodentate ligands

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which may be used as precursors of a wide variety of mixed chelates. In order to prepare such a Ru(II) complex of an $N-S$ chelating donor along with monodentate donors like Cl, PPh_3, *etc.*, we reacted 2-(2-pyridyl) benzothiazoline (L_1H) with $Ru(PPh_3)_3Cl_2$ in refluxing dichloromethane and isolated two different products, (1) and (2). The former was a brown complex identified as $Ru(L_1)(PPh_3)Cl$. The chocolate coloured complex (2), $[Ru(L_1)(PPh_3)_2Cl]$, was dissolved in hot acetonitrile, cooled and ether allowed to diffuse in slowly in a sealed tube. After two weeks needle-shaped crystals were isolated. These were characterized by elemental analysis, magnetic susceptibility, and conductance measurement as $[Ru(L)(PPh_3)(CH_3CN)_2Cl]Cl$, where L = 2-(2-pyridyl)benzothiazole. We report here the crystal structure of this complex.

EXPERIMENTAL

Preparation of the Complex

Solid $Ru(PPh_3)_3Cl_2$ (240 mg, 0.25 mmol) was refluxed in CH_2Cl_2 (20 cm^3) with solid 2-(2-pyridyl)benzothiazoline (54 mg, 0.25 mmol) for 5 h. After cooling, excess petroleum ether (60 – 80°) was added and the mixture was kept overnight in a refrigerator. The brown coloured residue was filtered, washed with petroleum ether, dried over anhydrous $CaCl_2$ and characterized as $[Ru(L_1)(PPh_3)Cl]$. The filtrate was allowed to evaporate, leaving a chocolate coloured residue, identified as $[Ru(L_1)(PPh_3)_2Cl]$. It was dissolved in acetonitrile and filtered. That filtrate was put in a long glass tube and diethyl ether was carefully added to the top. The tube was sealed and kept at room temperature. Slow diffusion of ether into the acetonitrile solution (15 days) of the complex yielded needle-shaped crystals. *Analysis*: calculated for $Ru(L)(PPh_3)(CH_3CN)_2Cl]Cl$ (%): C, 56.02; H, 3.98; N, 7.69. Found: C, 56.10; H, 3.96; N, 7.66. Conductance in CH_3CN (Λ_M): 148 ohm^{-1}.

X-ray Crystallography

A single crystal of the complex suitable for X-ray data collection was mounted on an Enraf-Nonius diffractometer equipped with a graphite monochromator. MoKα ($\lambda = 0.71073$ Å) radiation was employed. Unit cell parameters and the crystal orientation matrix were determined by least-squares refinement of the setting angles of 25 reflections. The crystal and instrument stabilities were monitored with a set of 3 standard reflections measured every 97 reflections; in all cases no significant variations were found. Some 11,192 reflections were measured ($h - 17$ to 1, $k - 19$ to 18, $l - 20$ to 20) and which, after data reduction ($R_{int} = 0.0346$), gave 9819 unique reflections. The data were corrected for Lorentz and polarization effects. An empirical absorption correction based on ψ-scans was also applied resulting in transmission factors ranging from 0.67 to 0.89. Crystal data are summarized in Table I.

The structure was solved in the centrosymmetric space group $P1$ by the Patterson method followed by successive Fourier syntheses and refined through least-squares calculations based on F^2. The solution of the crystal structure reveals that the asymmetric unit consists of two molecules of the complex. During refinement, the crystal structure was found to be disordered. The ligand L is disordered over two positions about a two-fold axis passing through Ru1 and the mid point of the C29–C30 bond for molecule **1** [for molecule **2**, Ru2 and C59–C60] with site occupancy factors 0.75/0.25 in molecule **1** and 0.6/0.4 in **2**. The anion Cl^- was also disordered over four sites in molecule **1** with occupancy factors 0.25/0.25/0.25/0.25 and over two sites with occupancy factor 0.6/0.4 in **2**. The site occupancy factors were determined from peak heights in a Fourier map and were kept fixed in subsequent refinement.

As a result of disorder, the data to parameter ratio was low (8.3). This was partially compensated by full-matrix block refinements of **1** and **2** and their disordered counterparts cyclically. The pyridine and phenyl moieties of

TABLE I Crystal data and structure refinement details for $[Ru(L)(PPh_3)(CH_3CN)_2Cl]Cl$

Empirical formula	$C_{34}H_{29}Cl_2N_4P_1Ru_1S_1$
Formula weight	728.61
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P1$
a (Å)	14.634(4)
b (Å)	16.315(4)
c (Å)	17.184(5)
α (°)	82.63(5)
β (°)	75.50(5)
γ (°)	71.07(5)
Volume (Å^3)	3752.3(18)
Z	4
ρ_{calc} (mg mm^{-3})	1.290
μ (mm^{-1})	0.685
$R(F)$	0.0830
$R_w(F)$	0.2380
GOF (F^2)	1.068

TABLE II Final coordinates for the non-hydrogen

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Ru1	0.2853(1)	0.4953(1)	0.8779(1)	Ru2	0.7608(1)	0.9101(1)	0.5908(1)
P1	0.3325(2)	0.4711(2)	0.7426(2)	P2	0.8166(2)	0.7633(2)	0.6205(2)
Cl1	0.2351(2)	0.5200(3)	1.0216(2)	Cl2	0.7049(3)	1.0665(2)	0.5550(3)
C1	0.3445(8)	0.5602(7)	0.6653(6)	C35	0.8284(10)	0.7237(9)	0.7241(7)
C2	0.3266(10)	0.6423(9)	0.6879(8)	C36	0.7807(11)	0.7741(11)	0.7876(9)
C3	0.3378(10)	0.7089(10)	0.6280(9)	C37	0.7850(17)	0.7415(17)	0.8679(11)
C4	0.3659(9)	0.6917(10)	0.5484(9)	C38	0.8400(20)	0.6637(19)	0.8784(13)
C5	0.3835(9)	0.6060(10)	0.5297(8)	C39	0.8891(18)	0.6133(14)	0.8153(14)
C6	0.3749(8)	0.5423(8)	0.5867(6)	C40	0.8818(14)	0.6409(11)	0.7407(10)
C7	0.4559(8)	0.3942(9)	0.7136(7)	C41	0.7385(8)	0.7039(8)	0.6024(8)
C8	0.5342(9)	0.4266(10)	0.7101(7)	C42	0.7339(8)	0.6922(8)	0.5242(8)
C9	0.6319(10)	0.3698(14)	0.6945(8)	C43	0.6690(11)	0.6512(9)	0.5136(10)
C10	0.6489(13)	0.2833(14)	0.6820(10)	C44	0.6105(12)	0.6212(10)	0.5761(11)
C11	0.5709(13)	0.2582(11)	0.6822(11)	C45	0.6103(12)	0.6362(13)	0.6514(12)
C12	0.4780(10)	0.3086(9)	0.6973(10)	C46	0.6747(11)	0.6771(10)	0.6639(9)
C13	0.2453(9)	0.4297(9)	0.7113(7)	C47	0.9424(8)	0.7083(8)	0.5641(7)
C14	0.2356(10)	0.3505(9)	0.7424(8)	C48	1.0173(9)	0.7348(9)	0.5791(9)
C15	0.1581(11)	0.3235(11)	0.7261(10)	C49	1.1141(10)	0.6986(11)	0.5415(11)
C16	0.0948(12)	0.3772(12)	0.6828(10)	C50	1.1386(11)	0.6369(13)	0.4914(11)
C17	0.1038(10)	0.4549(11)	0.6531(9)	C51	1.0663(11)	0.6058(11)	0.4780(10)
C18	0.1781(9)	0.4829(9)	0.6670(7)	C52	0.9669(10)	0.6436(10)	0.5140(8)
N1	0.1712(9)	0.4511(8)	0.8958(6)	N5	0.8888(8)	0.9044(7)	0.5122(7)
C19	0.1072(14)	0.4253(10)	0.9124(9)	C53	0.9616(11)	0.9034(9)	0.4697(9)
C20	0.0229(12)	0.3872(13)	0.9300(12)	C54	1.0584(13)	0.8979(13)	0.4170(13)
N2	0.1882(8)	0.6112(8)	0.8589(7)	N6	0.8241(10)	0.9361(8)	0.6730(8)
C21	0.1279(13)	0.6699(12)	0.8468(10)	C55	0.8570(14)	0.9503(11)	0.7160(11)
C22	0.0497(14)	0.7508(12)	0.8284(18)	C56	0.9022(19)	0.9691(15)	0.7768(14)
C29	0.4860(8)	0.4483(8)	0.8934(7)	C63	0.5683(10)	0.8994(9)	0.6010(13)
Cl1A	0.2777(17)	0.0341(17)	0.0552(15)	S2	0.4456(4)	0.9017(4)	0.6553(6)
Cl1B	0.8163(19)	0.8306(13)	0.0492(17)	N7	0.6190(11)	0.9184(10)	0.6508(13)
Cl1C	0.8038(23)	0.8221(17)	0.1000(18)	C57	0.5574(10)	0.9455(12)	0.7270(10)
Cl1D	0.1865(28)	0.7168(20)	0.0648(21)	C58	0.5865(12)	0.9777(14)	0.7848(14)

S1	0.5927(3)	0.4649(3)	0.8996(3)	C59	0.5227(18)	0.9977(14)	0.8594(12)
N3	0.4130(8)	0.5170(9)	0.8789(7)	C60	0.4299(16)	0.9856(13)	0.8762(10)
C23	0.4398(7)	0.5900(7)	0.8783(6)	C61	0.4008(10)	0.9534(12)	0.8185(13)
C24	0.3821(6)	0.6756(8)	0.8694(7)	C62	0.4646(10)	0.9333(11)	0.7439(11)
C25	0.4221(9)	0.7427(6)	0.8665(8)	N8	0.7022(9)	0.8882(8)	0.4971(8)
C26	0.5198(9)	0.7242(8)	0.8726(7)	C64	0.6050(9)	0.8863(9)	0.5245(8)
C27	0.5775(6)	0.6386(9)	0.8815(7)	C65	0.5517(9)	0.8797(10)	0.4703(12)
C28	0.5375(7)	0.5715(7)	0.8844(6)	C66	0.5956(14)	0.8749(9)	0.3886(11)
N4	0.3764(6)	0.3673(6)	0.9029(6)	C67	0.6927(15)	0.8768(9)	0.3612(8)
C30	0.4720(7)	0.3658(6)	0.9027(6)	C68	0.7460(9)	0.8834(9)	0.4154(9)
C31	0.5424(6)	0.2878(8)	0.9165(8)	S2A	0.4882(8)	0.8874(7)	0.5381(9)
C32	0.5172(8)	0.2112(6)	0.9306(8)	N7A	0.6650(19)	0.9040(17)	0.5295(22)
C33	0.4216(10)	0.2126(6)	0.9307(8)	C57A	0.6553(22)	0.8946(14)	0.4605(18)
C34	0.3513(7)	0.2907(7)	0.9169(7)	C58A	0.7332(17)	0.8995(16)	0.3962(25)
S1A	0.5960(11)	0.3690(9)	0.9137(9)	C59A	0.7284(20)	0.8892(18)	0.3184(21)
N3A	0.4081(26)	0.4200(22)	0.9007(21)	C60A	0.6457(27)	0.8740(17)	0.3049(15)
C23A	0.4417(21)	0.3360(16)	0.9124(19)	C61A	0.5678(20)	0.8690(17)	0.3691(20)
C24A	0.3736(19)	0.2902(21)	0.9248(21)	C62A	0.5725(17)	0.8793(16)	0.4469(17)
C25A	0.4030(31)	0.2012(21)	0.9421(28)	N8A	0.6229(16)	0.9379(18)	0.6956(19)
C26A	0.5005(35)	0.1579(16)	0.9470(34)	C64A	0.5532(22)	0.9176(20)	0.6659(15)
C27A	0.5686(24)	0.2037(24)	0.9346(31)	C65A	0.4608(19)	0.9216(21)	0.7151(20)
C28A	0.5392(19)	0.2927(24)	0.9173(23)	C66A	0.4381(16)	0.9459(22)	0.7940(19)
N4A	0.3939(17)	0.5838(16)	0.8652(17)	C67A	0.5077(22)	0.9662(20)	0.8237(15)
C30A	0.4871(19)	0.5344(13)	0.8768(19)	C68A	0.6001(19)	0.9622(17)	0.7745(19)
C31A	0.5540(16)	0.5750(18)	0.8851(20)	Cl2A	0.7941(7)	0.1085(6)	0.2274(6)
C32A	0.5277(20)	0.6650(19)	0.8818(21)	Cl2B	0.1246(12)	0.9079(11)	0.6124(10)
C33A	0.4345(22)	0.7145(13)	0.8703(21)				
C34A	0.3676(16)	0.6739(15)	0.8620(18)				

TABLE III Bond lengths (Å) and bond angles (°) for $[Ru(L)(PPh_3)(CH_3CN)_2Cl]Cl$

Ru(1)–N(1)	1.97(13)	Ru(1)–N(2)	2.01(12)
Ru(1)–N(3)	2.02(11)	Ru(1)–N(3A)	1.92(3)
Ru(1)–N(4)	2.14(8)	Ru(1)–P(1)	2.30(3)
Ru(1)–N(4A)	2.43(2)	Ru(1)–Cl(1)	2.44(4)
P(1)–C(7)	1.82(12)	P(1)–C(13)	1.84(12)
P(1)–C(1)	1.86(12)	N(1)–C(19)	1.11(2)
N(2)–C(21)	1.11(2)	N(3)–C(29)	1.32(2)
C(29)–C(30)	1.41(2)	N(4)–C(30)	1.39
Ru(2)–N(5)	2.00(12)	Ru(2)–N(6)	2.02(14)
Ru(2)–N(7)	2.04(14)	Ru(2)–N(7A)	1.99(3)
Ru(2)–N(8)	2.12(11)	Ru(2)–N(8A)	2.31(2)
Ru(2)–P(2)	2.30(3)	Ru(2)–Cl(2)	2.46(4)
P(2)–C(41)	1.82(11)	P(2)–C(47)	1.84(12)
P(2)–C(35)	1.84(13)	N(5)–C(53)	1.13(2)
N(6)–C(55)	1.06(2)	N(7)–C(63)	1.38(3)
C(63)–C(64)	1.31(2)	N(8)–C(64)	1.39
N(1)–Ru(1)–N(3)	166.2(5)	N(2)–Ru(1)–N(3)	106.9(5)
N(1)–Ru(1)–N(3A)	119.5(11)	N(2)–Ru(1)–N(3A)	154.3(11)
N(1)–Ru(1)–N(2)	84.9(5)	N(1)–Ru(1)–N(4)	89.6(4)
N(1)–Ru(1)–N(4A)	165.6(7)	N(2)–Ru(1)–N(4)	174.4(4)
N(2)–Ru(1)–N(4A)	81.9(7)	N(3)–Ru(1)–N(4)	78.4(5)
N(3A)–Ru(1)–N(4A)	72.9(12)	N(1)–Ru(1)–P(1)	93.9(3)
N(2)–Ru(1)–P(1)	91.7(4)	N(3)–Ru(1)–P(1)	93.0(3)
N(4)–Ru(1)–P(1)	89.9(3)	N(3A)–Ru(1)–P(1)	94.2(10)
N(4A)–Ru(1)–P(1)	92.3(7)	P(1)–Ru(1)–Cl(1)	179.6(2)
N(1)–Ru(1)–C1(1)	85.9(3)	N(2)–Ru(1)–Cl(1)	88.5(4)
N(3)–Ru(1)–Cl(1)	87.3(3)	N(4)–Ru(1)–Cl(1)	89.9(3)
N(3A)–Ru(1)–Cl(1)	85.7(10)	N(4A)–Ru(1)–Cl(1)	88.0(7)
Ru(1)–N(1)–C(19)	174.2(13)	Ru(1)–N(2)–C(21)	171.8(13)
N(5)–Ru(2)–N(7)	168.5(7)	N(5)–Ru(1)–N(8)	89.6(5)
N(5)–Ru(2)–N(8A)	167.0(9)	N(5)–Ru(2)–N(7A)	107.6(11)
N(6)–Ru(2)–N(8)	175.1(5)	N(6)–Ru(2)–N(7A)	164.2(10)
N(6)–Ru(2)–N(7)	104.9(7)	N(6)–Ru(2)–N(8A)	82.5(9)
N(5)–Ru(2)–N(6)	86.1(5)	N(7)–Ru(2)–N(8)	79.2(7)
N(7A)–Ru(2)–N(8A)	83.0(13)	N(5)–Ru(2)–P(2)	90.6(3)
N(6)–Ru(2)–P(2)	91.8(4)	N(7)–Ru(2)–P(2)	92.6(5)
N(8)–Ru(2)–P(2)	90.7(3)	N(7A)–Ru(2)–P(2)	95.8(8)
N(8A)–Ru(2)–P(2)	95.9(7)	P(2)–Ru(2)–Cl(2)	178.2(14)
N(5)–Ru(2)–Cl(2)	87.7(3)	N(6)–Ru(2)–Cl(2)	88.8(4)
N(7)–Ru(2)–Cl(2)	89.0(5)	N(8)–Ru(2)–Cl(2)	88.6(4)
N(7A)–Ru(2)–Cl(2)	84.1(8)	N(8A)–Ru(2)–Cl(2)	85.9(7)
Ru(2)–N(5)–C(53)	177.3(12)	Ru(2)–N(6)–C(55)	179.5(2)

ligand L were constrained to have idealized hexagonal geometry. All non-hydrogen atoms except the disordered ligand atoms of **1** with site occupancy factor 0.25 were modelled using anisotropic thermal parameters. Hydrogen atoms were constrained to ride on the respective carbon atom (C–H 0.96 Å) with an isotropic displacement parameter equal to that of the parent atom. At convergence (maximum parameter shift/esd 0.087), the final residuals were $R1 = 0.083$, $wR2 = 0.238$[9] for 7883 reflections with $I > 2\sigma(I)$, goodness of fit = 1.068. Final difference Fourier maps showed maximum and minimum peak heights of 1.557 eÅ^{-3} and -0.709 eÅ^{-3}, respectively. The largest, being at a distance 0.907 Å from Ru1, has no chemical significance. All calculations were carried out using SHELXS86 [8], SHELXL93 [9], PARST [10] and ZORTEP [11] programs. Final fractional coordinates, selected bond distances and bond angles for the complex are listed in Tables II and III.

RESULTS AND DISCUSSION

A ZORTEP view of the complex with atom numbering scheme is shown in Figures 1a to 1d. The study reveals that molecules **1** and **2** and their disordered counterparts have the same molecular structure, consisting of $[RuL(PPh_3)(CH_3CN)_2Cl]^+$ and Cl^- ions. The ligand, monoanionic is

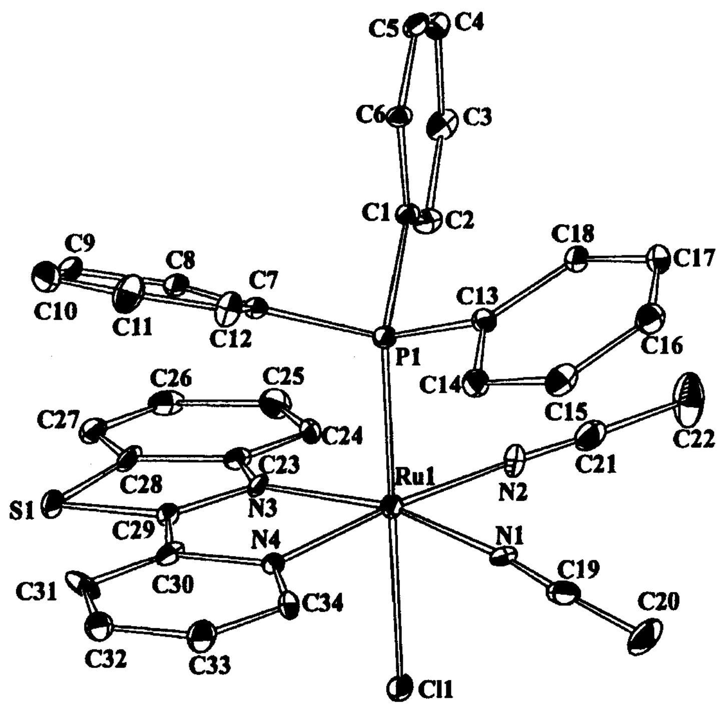

FIGURE 1(a) A ZORTEP view of the molecular structure of the complex cation (**Molecule 1**) in one orientation of the disordered ligand.

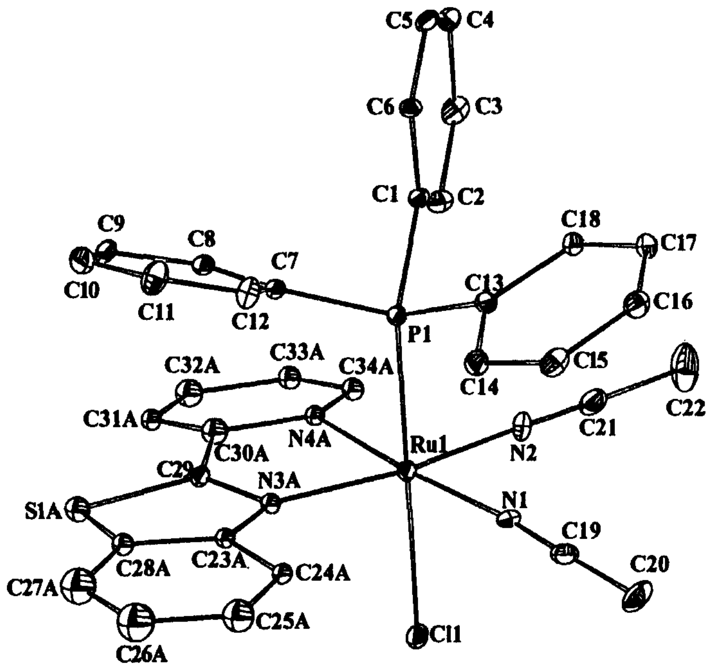

FIGURE 1(b) A ZORTEP view of the molecular structure of the complex cation (**Molecule 1A**) in another orientation of the disordered ligand.

attached to Ru(II) in chelating bidentate fashion. The coordination polyhedron around the metal is best described as a distorted octahedron. The two nitrogen atoms (N1, N2 for 1 and N5, N6 for 2) of acetonitrile ligands and two nitrogen atoms (N3, N4/N3A, N4A for **1** and **1A**; N7, N8/N7A, N8A for **2** and **2A**) of the ligand L define the equatorial plane. Phosphorous (P1 for **1** and P2 for **2**) and chlorine atoms. (Cl1 for **1**; Cl2 for **2**) are in axial positions [P1–Ru–Cl1 179.6(2)° **1**; P2–Ru–Cl2 178.21(1)° **2**]. The P–Ru–Cl axis is nearly orthogonal to the equatorial plane (angle range from 85.7(10)° to 94.2(10)° for molecule **1**; 84.1(8) to 95.8(8)° for molecule **2**]. The ligand L is essentially planar and the acetonitrile moieties are almost linear. Back donation from the Ru(II) centre to the empty orbitals of the coordinated acetonitrile ligand is *cis*, reflected in shorter Ru–N bond lengths (Ru1–N1 1.967 Å, Ru1–N2 2.011 Å, Ru1–N3 2.015 Å, Ru1–N4 2.139 Å). The Ru1–N2 bond length is quite short compared to Ru1–N4 due to the greater *trans* influence of N2 of acetonitrile (N2–Ru1–N4 174.3(4)°; N1–Ru1–N3 166.2(5)°). The crystal packing is dominated by an extensive intermolecular hydrogen bonding network.

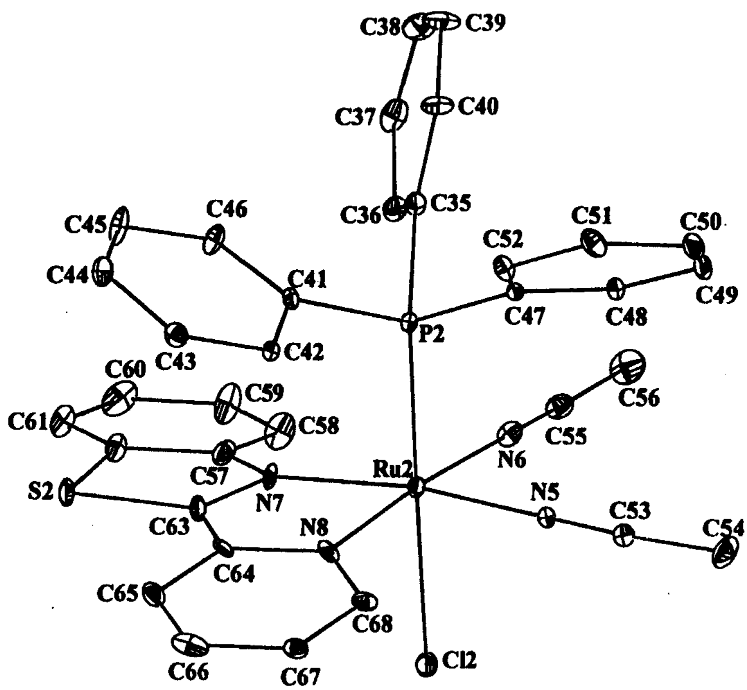

FIGURE 1(c) A ZORTEP view of the molecular structure of the complex cation (**Molecule 2**) in one orientation of the disordered ligand.

The most interesting feature of the structure is that here the ligand does not act as a *N–S* donor although it is well known that in related complexes strong Ru–S σ-bonding results from the overlap of a vacant ruthenium *d*-orbital with a sulfur sp orbital. A probable explanation of this phenomenon is offered later.

It is known that pyridine-2-aldehyde and 2-acetyl pyridine react with 2-aminothiophenol to form 2-(2-pyridyl)benzothiazoline $(L_1H)^1$ and 2-methyl-2-(2-pyridyl)benzothiazoline $(L_2H)^2$ respectively [12, 13]. It is reported that in presence of a suitable metal ion or a base both the above ligands are transformed into the corresponding Schiff bases and are found to form classical Schiff base complexes as tridentate *NNS* donors, coordinating through the deprotonated thiolate sulfur, the azomethine and the pyridine ring nitrogen atoms [3, 4]. Reaction of L_1H with $Ru(PPh_3)_2X_2$ (X = Cl, Br) in refluxing noncoordinating solvents C_6H_6/CH_2Cl_2 produces Ru(II) complexes of general formula $Ru(L_1)(PPh_3)_2X$ and $Ru(L_1)(PPh_3)X$ (X = Cl, Br), the ligand acting in its usual *NNS* donor mode [13]. Coordination of the soft thiolate sulfur to the soft Ru(II) acceptor centre is quite expected. The

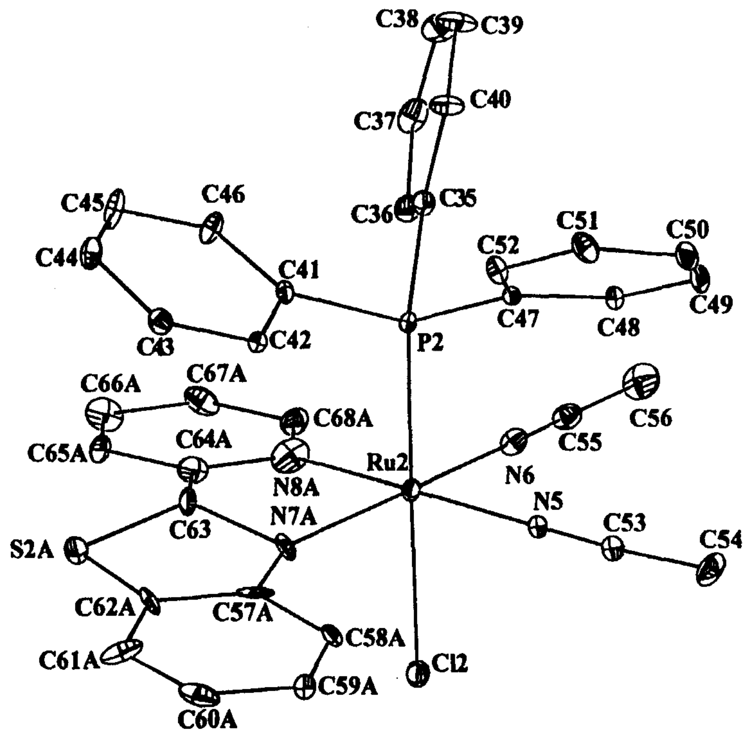

FIGURE 1(d) A ZORTEP view of the molecular structure of the complex cation (**Molecule 2A**) in another orientation of the disordered ligand.

methyl analogue L_2H is also reported to be behave in exactly the same manner [13]. However, when $[Ru(L_1)(PPh_3)_2Cl]$ is dissolved in hot acetonitrile and the solution is left undisturbed in contact with diethylether for about 2 weeks, needle-shaped, brown crystals of formula $[Ru(L)(PPh_3)(CH_3CN)_2Cl]Cl$ are obtained. Structure determination reveals that in this complex the Schiff base form of the ligand, present in the original complex $Ru(L_1)(PPh_3)Cl$, has undergone cyclisation into the corresponding thiazole derivative and has coordinated to the Ru(II) centre through the two nitrogen atoms belonging to the pyridine and the thiazole moieties acting as a bidentate $N-N$ donor ligand. The re-cyclisation of the coordinated Schiff base to the corresponding thiazole is probably promoted by the bringing of the thiolato sulfur and the carbon atom of the C=N moiety in the Ru(II) complex in a position suitable for such a ring closure process.

Transformation of the coordinated Schiff base of a related ligand into the corresponding thiazole was previously noted [14]. In that complex

$[Fe^{III}(HBT)_2Br]$ (HBT = monoanion of the Schiff base of 2-aminothiophenol with salicylaldehyde) the cyclised ligand coordinated to the Fe(III) centre through its phenolate oxygen and the thiazole ring nitrogen. Hard-hard N–O coordination is quite expected for Fe(III), centre which is a fairly hard acceptor. However, the present case is rather unusual because the soft acceptor Ru(II) generally exhibits preference towards the mixed hard-soft *N–S* mode of coordination to the hard *N–N* donor set. Coordination of the 2-(2-pyridyl) benzothiazole ligand to the soft acceptor Ru(II) through its nitrogen atoms is rather uncommon. This apparently anomalous behaviour may be accounted for in the following way.

The sulfur atom of the benzothiazole part of the re-cyclised ligand is a much weaker donor compared to the thiolate sulfur atom of the Schiff base form. The ligand in the *N–N* donor form possesses much higher ligand field strength compared to the *N–S* donor mode much like bithiazole which coordinates to Ru(II)as a *N–N* donor in preference to the *N–S* donor mode. The diimine moiety of the ligand in the *N–N* donor form can behave like the diimine moiety of bpy, in the same manner as is found in the case of $Ru(btz)_3^{2+}$ (btz = *N–N* donor form of bithiazole) [15] and thus effective π-back bonding from metal to ligand is possible. Back donation of electron density from the π-donor Ru(II) centre to the empty orbitals of the PPh_3 moiety and the two coordinated CH_3CN ligands can make the Ru(II) centre a comparatively harder acceptor and may tilt its preference to the hard *N–N* donor. The effect of such back-donation is reflected in the shorter Ru–P bond lengths (2.299(3) and 2.303) in this complex compared to Ru–P bond lengths of other Ru(II) complexes [7, 16, 17] containing coordinated PPh_3 (2.342 in $[Ru(L)(PPh_3)(bpy)](ClO_4)_2$; 2.332 and 2.319 in $Ru(py2\text{-thiolato})(PPh_3)_2$; 2.416 and 2.419 in $Ru(PPh_3)_2(DBSQ)Cl_2$; Rul–N1 = 1.967 Å; Rul–N2 = 2.011 Å; Rul–N3 = 2.015 Å; and Rul–N4 = 2.139 Å). The unusually shorter $Ru-N(2)(CH_3CN)$ lengths observed [18, 19] support this contention.

Supplementary Material

Full lists of crystallographic data are available from the author upon request.

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