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Benzotriazole as a structural component in chelating and bridging heterocyclic ligands; ruthenium, palladium, copper and silver complexes

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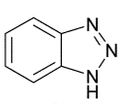
The coordination chemistry of five N,N′-bidentate ligands that contain a 1-substituted benzotriazole subunit has been studied. Spectroscopic and electrochemical studies of their chelated ruthenium bis(2,2′-bipyridine) complexes have shown that the benzotriazole group is a relatively electron rich component. X-Ray crystal structures are reported for one-dimensional polymeric copper and silver complexes of di(benzotriazol-1-yl)methane, mononuclear and dinuclear copper and silver complexes of 1-(2-pyridyl)benzotriazole (in which the ligand displays chelating, monodentate and bridging modes of coordination, respectively), bridged binuclear palladium, copper and silver complexes of 1-(2-pyridylmethyl)benzotriazole and a tetranuclear copper complex of 1-(1-isoquinolyl)benzotriazole.

Introduction

Over the last century, 2,2′-bipyridine has been extensively used as the classical N,N′-bidentate ligand in coordination, analytical and organometallic chemistry.[1] Numerous related bis-heterocyclic ligands have been synthesised that contain other heteroaromatic ring systems.[2] For example, π-deficient azines, such as pyrazines and pyridazines, and their benzo-analogues, such as quinolines and quinoxalines, have been incorporated into chelating bidentate ligands. π-Excessive azoles have also been extensively used, with pyrazoles, imidazoles, thiazoles and their benzo-analogues having proved particularly popular.[2]

We are currently engaged in the synthesis of new heterocyclic ligands that incorporate less commonly encountered ring systems. Previously, we have reported a number of chelating ligands which contain tetrazole, furoxan, benzisoxazole, oxadiazole, thiadiazole and dioxadiazine groups.[3] Benzotriazole (**1**) is extensively used as a synthetic auxiliary in organic chemistry,[4] and is also a versatile ligand in coordination chemistry.[5] For example, the deprotonated benzotriazolate anion can coordinate up to three metal centres *via* its three nitrogen donors.[5,6] Particular emphasis has been placed on copper complexes of **1**, due to the importance of benzotriazole as a corrosion inhibitor.[6,7] Surprisingly, however, benzotriazole has been virtually ignored as a component in N,N′-chelating ligands. Bi- and tribenzotriazolylborate anions have been reported,[8] and N,O-chelating ligands based on 1-(2-hydroxyphenyl)benzotriazole have been well studied because of the importance of such compounds as UV photostabilisers.[9]

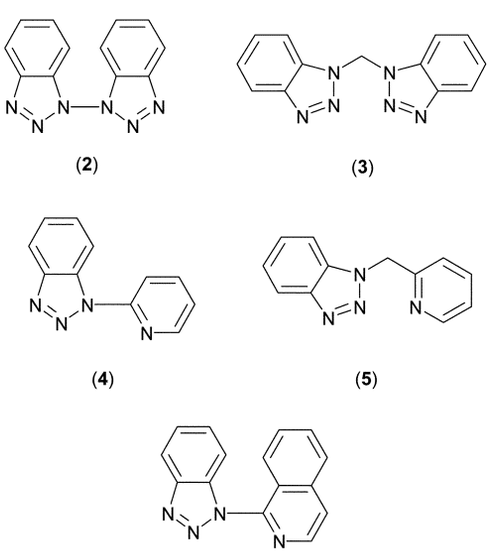


(**1**)

We now report studies of the coordination chemistry of five ligands that contain 1-substituted benzotriazole subunits. Each of these ligands is potentially capable of coordinating to a metal ion with formation of a five- or six-membered chelate ring. Such chelate ring formation represents a convergent mode of coordination.[10] However, by virtue of the fact that each benzotriazole has two nitrogen atoms capable of coordination, these ligands can also act as divergent, *i.e.* bridging, ligands. In this mode of coordination, they can be employed as building blocks for the construction of metallosupramolecular species. We describe examples of both these modes of coordination.

Results and discussion

The ligands employed in this study are shown in Chart 1, drawn in conformations that serve to emphasise their potential to act as chelating ligands using the N2-nitrogens as donors. However, each of these ligands is also capable of coordination through the less sterically encumbered N3-nitrogen atom. 1,1′-Bibenzotriazole (**2**) was prepared by cyclisation of a 2,2′-azobenzene bisdiazonium salt, as previously reported.[11] The other ligands (**3**–**6**) were prepared by nucleophilic substitution reactions of benzotriazole with diiodomethane,[12] 2-bromopyridine,[13] 2-chloromethylpyridine[14] and 1-chloroisoquinoline, respectively. In order to explore the chemistry of these ligands, we selected four metal ions as representative subjects for coordination. Ruthenium(II) and palladium(II) were chosen as examples of stereoregular octahedral and square planar metals, respectively. Copper(II) and silver(I) were selected as examples of metals that have more flexible coordination numbers and geometries.



(**2**) (**3**) (**4**) (**5**) (**6**)

Chart 1

Ruthenium complexes

A vast amount of literature has been reported on the ruthenium(II) complexes of chelating heterocyclic ligands.[15] Spectro-

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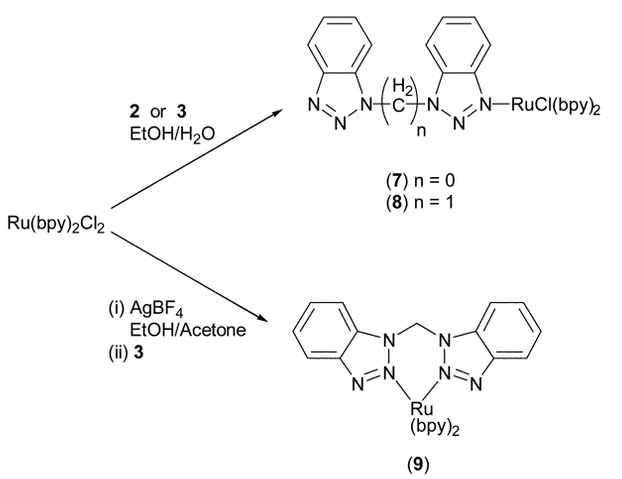
Table 1 ^{1}H NMR Chemical shifts[a] and coordination induced shifts[b] for ligands **2**–**6** and their ruthenium(II) complexes

	H4	H5	H6	H7	H3′	H4′	H5′	H6′	H7′	H8′	CH_2
2	8.34	7.70	7.78	7.53		8.34	7.70	7.78	7.53		
7	9.12	7.65	7.78	7.57		8.36	7.70	7.80	7.53		
CIS	*+0.78*	*−0.05*	*0*	*+0.04*		*+0.02*	*0*	*+0.02*	*0*		
3	8.05	7.46	7.67	8.00		8.05	7.46	7.67	8.00		7.43
8	8.88	7.47	7.71	8.07		8.10	7.45	7.68	7.78		7.57
CIS	*+0.83*	*+0.01*	*+0.04*	*+0.07*		*+0.05*	*−0.01*	*+0.01*	*−0.22*		*+0.14*
3	8.05	7.47	7.67	8.00							7.57
9	7.84	7.51	7.76	8.04							7.43
CIS	*−0.21*	*+0.04*	*+0.09*	*+0.04*							*−0.14*
4	8.16	7.56	7.72	8.69	8.30	8.09	7.47	8.68			
10	8.05	7.71	7.91	8.40	8.57	8.32	7.51	7.84			
CIS	*−0.11*	*+0.15*	*+0.19*	*−0.29*	*+0.27*	*+0.23*	*+0.04*	*−0.84*			
5	8.08	7.37	7.45	7.57	7.25	7.62	7.23	8.53			6.04
11	7.80	7.51	7.71	8.00	8.00	7.97	7.25	7.70			5.91/6.13
CIS	*−0.28*	*+0.14*	*+0.26*	*+0.43*	*+0.75*	*+0.35*	*+0.02*	*−0.83*			*−0.13/+0.09*
13	8.84	7.40	7.57	7.72	6.97	7.72	7.32	8.42			5.72
CIS	*+0.76*	*+0.03*	*+0.12*	*+0.15*	*−0.28*	*+0.10*	*+0.09*	*−0.11*			*−0.32*
6	8.24	7.60	7.71	8.03	8.62	8.05	8.17	7.94	7.79	8.39	
12	8.04	7.70	7.81	8.07	7.60	7.94	8.25	8.10	8.08	8.58	
CIS	*−0.20*	*+0.10*	*+0.10*	*+0.04*	*−1.02*	*−0.11*	*+0.08*	*+0.16*	*+0.29*	*+0.19*	

[a] For CD_3CN solutions, except for **9** and **12** in CD_2Cl_2. [b] CIS = ($\delta_{complex} - \delta_{ligand}$).

scopic and electrochemical studies of such compounds provide useful insight into the nature of the metal–ligand interactions.[15,16] In order to gain information about the nature of interactions with benzotriazole-containing ligands, bis(2,2′-bipyridine)ruthenium(II) complexes of each of the ligands **2**–**6** were prepared and studied.

Under the standard conditions used to prepare $Ru(bpy)_2L^{2+}$ complexes of chelating ligands (L),[17] reactions of 1,1′-bibenzotriazole (**2**) and di(benzotriazol-1-yl)methane (**3**) with $Ru(bpy)_2Cl_2$ gave, instead, the complexes **7** and **8**, respectively, in good yields when isolated as the hexafluorophosphate salts (Scheme 1). The composition of these products followed from their



Scheme 1

elemental analyses and FAB mass spectra. Thus, the ligands act as monodentate donors with coordination through the less hindered N3-nitrogens. The site of coordination was deduced from the ^{1}H NMR spectra. Table 1 lists the ^{1}H NMR chemical shifts for each of the ligands and their ruthenium complexes, in d_3-acetonitrile, along with the coordination-induced shifts (CIS = $\delta_{complex} - \delta_{ligand}$) in italics. The complexes **7** and **8** lack internal symmetry and hence give rise to 24 aromatic signals in the ^{1}H NMR spectra. Using procedures previously described,[18] complete assignments (see Experimental section) of these spectra were achieved by a series of 1D-TOSCY and difference NOE experiments. From Table 1 it can be seen that in complexes **7** and **8** only one signal (H4) experiences a large CIS value. This is consistent only with coordination of the ligands through the N3-nitrogens, wherein the adjacent H4-protons experience a significant downfield shift (*ca.* 0.8 ppm) due to the proximate chloro substituent.

In order to enforce chelation of the ligands, the $Ru(bpy)_2Cl_2$ precursor was treated with silver tetrafluoroborate before addition of the ligand. This strategy led to a reasonable yield of the desired complex **9** (Scheme 1), but all such attempts to prepare the corresponding complex of **2** were in vain. Owing to the C_2 symmetry present in complex **9**, the ^{1}H NMR spectrum is considerably less complex, showing only 12 aromatic resonances, which were readily assigned to the three individual four proton spin systems by 1D-TOSCY experiments. In this complex the H4 protons show negative CIS values (Table 1), since they now lie over the shielding face of nearby pyridine rings.[19] The methylene protons of the ligand gave rise to a singlet, implying that there is rapid interconversion, on the NMR time-scale, between boat conformations of the chelate ring.

In contrast to the above results, the three ligands **4**–**6** containing a π-deficient azine ring each reacted with $Ru(bpy)_2Cl_2$, under the standard conditions, to give good yields of the chelated complexes **10**–**12** (Chart 2). In the case of reaction of 1-(2-pyridylmethyl)benzotriazole (**5**) a small amount of the monodentate complex $[Ru(bpy)_2(\mathbf{5})Cl]PF_6$ (**13**) was also formed and separated by column chromatography. In complex **13**,

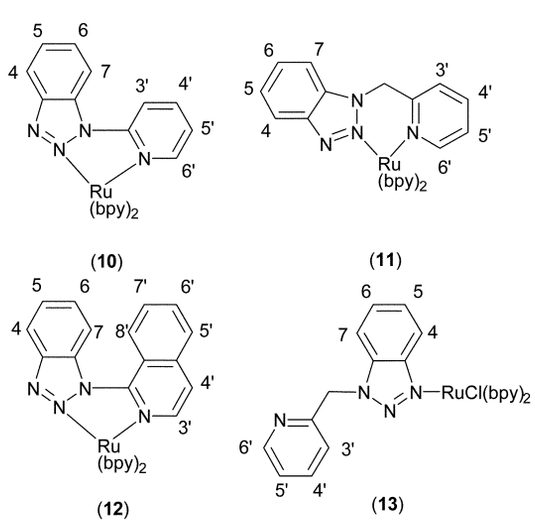


Chart 2

Table 2 Visible absorption maxima[a] and redox potentials[b] for the ruthenium complexes

	λ_{max} (ε)	E_{ox}	E_{red1}	E_{red2}	E_{red3}	$\delta E_{ox-red1}$
$Ru(bpy)_3^{2+}$	452 (13 600)	+1.26	−1.33	−1.51	−1.77	2.59
9[d]	420 (9 800)	+1.50	−1.45	−1.60	–	2.99
10	423 (16 300)	+1.53	−1.39	−1.60	–	2.92
11	426 (11 300)	+1.30	−1.43	−1.64	−2.00[c]	2.73
12[d]	429 (16 200)	+1.47	−1.34	−1.72[c]	−1.93[c]	2.81

[a] In nm (M^{-1} cm^{-1}). [b] In volts *vs.* SCE in acetonitrile. [c] Irreversible reduction. [d] In dichloromethane.

coordination *via* N3 was clearly apparent from the positive CIS value for H4.

Owing to the lack of internal symmetry, the ^{1}H NMR spectra for the chelated complexes **10**–**12** were more complex than those with the symmetrical ligands. Thus, the complexes **10** and **11** each gave rise to 24 aromatic signals, while **12** showed 26 signals. Despite this complexity, the individual spin systems were readily assigned by combinations of 1D- and 2D-NMR experiments. For example, Fig. 1 shows the ^{1}H NMR spectrum of **11**, in which the methylene protons occur as an AB quartet, along with two difference NOE spectra corresponding to irradiation of the downfield equatorial hydrogen and the upfield axial proton, respectively. These NOE spectra identify the nearby H7 and H3′ signals, which coincidentally overlap at 8.00 ppm, and the H6 proton of the nearby bpy ring, respectively. Subsequent 1D-TOCSY experiments, and other difference NOE spectra, led to a full assignment of this highly congested spectrum.

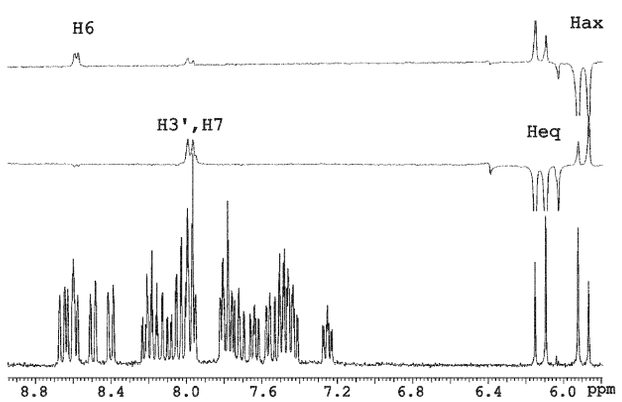


Fig. 1 ^{1}H NMR and difference NOE spectra of complex **11**.

As shown in Table 1, the protons adjacent to the nitrogen donors show large upfield shifts upon coordination, due to through-space anisotropic shielding by nearby pyridine rings. Other protons show downfield shifts of varying magnitude, some of which will be due to transfer of electron density from the ligand to the metal upon coordination.[19] However, the largest of these are experienced by protons close to the site linking the two rings. These we attribute to chelation-induced conformational changes resulting from coordination to the metal,[19] since in each case the conformation of the free ligand in solution will be very different from that shown in Chart 1. For example, N,N′-bis-heterocycles generally exist in a conformation with an *s-trans* arrangement about the inter-ring bond.[20] However, upon chelation to a metal centre this arrangement is necessarily *s-cis*. Interestingly, there was no evidence for the formation of diastereoisomeric forms for the isoquinolinyl complex **12**, as is the case in the corresponding complex of 1,1′-biisoquinoline.[21] Presumably the barrier to atropisomerism of the complexed ligand is lowered by the presence of the five-membered heterocyclic ring.

In order to gain more detailed insight into the nature of the metal-ligand interactions, electronic absorption spectra and electrochemical parameters were recorded for the chelated complexes. Table 2 lists the positions of the visible absorption maxima and redox potentials, along with the corresponding values for $Ru(bpy)_3^{2+}$. Each of the complexes **9**–**12** absorbs at higher energy than $Ru(bpy)_3^{2+}$, indicating a higher energy gap between the metal based HOMO and the ligand based LUMO. The origin of this is evident from the electrochemical data, which shows that each complex is both more difficult to oxidize and more difficult to reduce than $Ru(bpy)_3^{2+}$. In each case oxidation potentials suggest that the metal is more electron deficient than in $Ru(bpy)_3^{2+}$. We believe that the first two reductions observed correspond to reduction of the ancillary bpy ligands, rather than of the electron rich benzotriazole-containing ligands, in each case.

Palladium complexes

Having demonstrated that each of these ligands can be made to chelate to octahedral ruthenium(II) centres, their square planar palladium complexes were investigated. Each ligand readily reacted with one equivalent of palladium(II) chloride to give good yields of products. Each of these was determined, by elemental analysis, to have 1 : 1 metal : ligand stoichiometry. However, this does not allow a distinction between chelating-mononuclear, bridging-binuclear or bridging-polymeric structural possibilities.

Complex **14**, obtained from ligand **5**, furnished crystals suitable for X-ray structure determination by diffusion of methanol into a DMF solution of the complex. Fig. 2 shows a perspective view, along with selected interatomic distances and angles, of this structure. The complex is in fact a M_2L_2 dimeric complex, within which each ligand bridges two palladium atoms, with N3-coordination of the benzotriazole rings. This leads to a 14-membered dimetallocyclic ring with a Pd–Pd separation of 6.739(1) Å. Within the complex each of the ligands has its two constituent heterocyclic rings approximately orthogonal, but the conformations of the two ligands differ by a 180° rotation

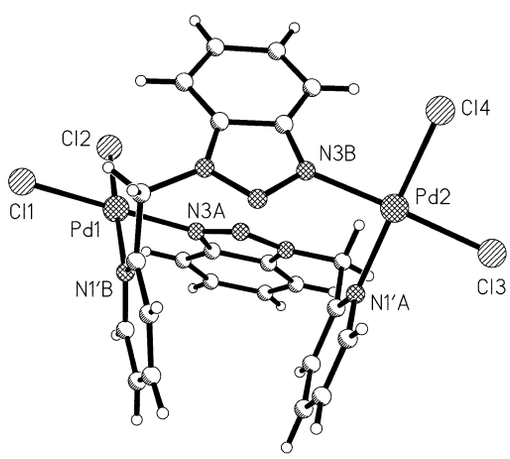


Fig. 2 Perspective view of the X-ray crystal structure of **14**. The methanol solvate molecule is not shown. Selected interatomic distances (Å) and angles (°): Pd1–N3A 2.050(7), Pd1–N1′B 2.063(7), Pd1–Cl1 2.314(2), Pd1–Cl2 2.310(2); N3A–Pd1–N1′B 87.8(3), Cl1–Pd1–Cl2 91.6(1), Pd2–N3B 2.044(7), Pd2–N1′A 2.049(6), Pd2–Cl3 2.299(2), Pd2–Cl4 2.297(3), N1′A–Pd2–N3B 88.9(3), Cl3–Pd2–Cl4 91.5(1).

of the pyridyl ring. As a result, the overall shape of the complex has an 'armchair' topology.

Copper complexes

Copper(II) is one of the most well studied transition metals for coordination of nitrogen heterocycles.[22] It forms complexes of various nuclearities within which the metal adopts a range of coordination numbers with various regular or distorted geometries. In view of the interest in the copper(II) complexes of benzotriazole (**1**),[7] we decided to prepare and structurally characterise copper(II) complexes of the above ligands.

Reactions of **2** and **3** with one equivalent of copper(II) chloride gave complexes with a 1 : 1 metal : ligand stoichiometry. Crystals of the latter complex (**15**) were suitable for X-ray structure determination. Fig. 3 shows a perspective view and selected atom labelling of the structure of **15**, which crystallizes in the triclinic space group $P\bar{1}$. The complex is a one-dimensional polymer with the $CuCl_2$ unit coordinated to two benzotriazole groups, each *via* the N3-nitrogen. Thus the ligand acts in a divergent (*i.e.* bridging) coordination mode. The coordination geometry is highly distorted tetrahedral with large N–Cu–N and Cl–Cu–Cl angles. As shown in Fig. 3, the structure extends into polymeric chains that propagate along the *b* axis.

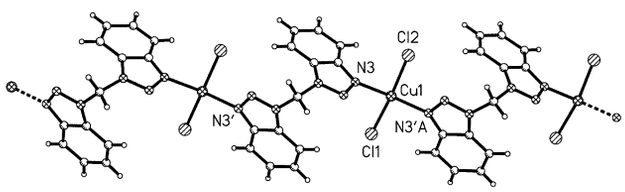


Fig. 3 Perspective view of the extended structure of **15**. N3′A is related to N3′ by the translation x, $1 + y$, z. Selected interatomic distances (Å) and angles (°): Cu1–N3 2.000(2), Cu1–N3′A 2.021(3), Cu1–Cl2 2.2137(9), Cu1–Cl1 2.2335(9); N3–Cu1–N3′A 149.3(1), N3–Cu1–Cl1 91.39(8), N3–Cu1–Cl2 94.72(8), Cl1–Cu1–N3′A 96.1(1), Cl2–Cu1–N3′A 93.2(1), Cl2–Cu1–Cl1 150.66(4).

Reaction of ligand **4** with one equivalent of copper(II) nitrate gave a complex (**16**) with a 1 : 2 metal : ligand stoichiometry. Fig. 4 shows a perspective view of the structure of **16**, which crystallizes in the monoclinic space group $P2_1/n$. The copper atom lies on a crystallographic centre of inversion and is coordinated to two chelating ligands and to two methanol molecules. The geometry of the copper shows the typical tetragonal elongation of the axial oxygen substituents (Fig. 4). The nitrate counter-ions are involved in bifurcated hydrogen bonds to the coordinated methanol OH groups. Structurally similar complexes have been reported from the reactions of copper nitrate with 4-(2-pyridyl)-1,2,3-triazolo[1,5-*a*]pyridine[23] and 3-(2-pyridyl)-1,2-benzisoxazole.[3c]

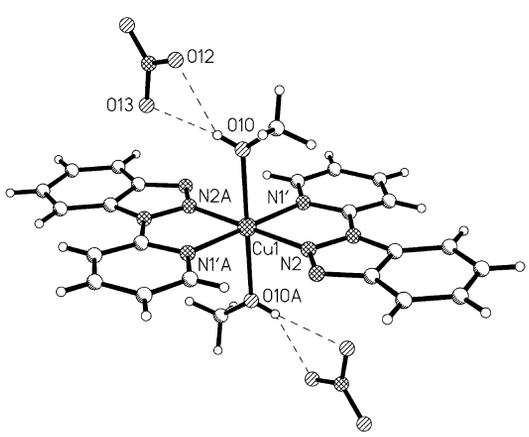


Fig. 4 Perspective view of the X-ray crystal structure of **16**. Atoms XA are related to atoms X by the transformation $-x$, $-y$, $1 - z$. Selected interatomic distances (Å) and angles (°): Cu1–N1′ 2.034(2), Cu1–N2 2.047(2), Cu1–O10 2.298(2); N1′–Cu1–N2 78.91(7), N1′–Cu1–O10 90.23(8), N2–Cu1–O10 91.71(8).

Reaction of the same ligand (**4**) with copper(II) chloride gave, in good yield, a product which elemental analysis revealed to have a 1 : 1 metal : ligand stoichiometry. However, recrystallization of this material from DMF furnished large green crystals of a reorganised complex (**17**) with 1 : 2 M : L stoichiometry. The X-ray crystal structure of **17** is shown in Fig. 5. In contrast to the chelate complex formed with copper(II) nitrate, the ligand acts as a monodentate donor in **17**. Interestingly, coordination is through the N3-nitrogen of the benzotriazole ring, in preference to the pyridine donor. The complex is binuclear and crystallizes about a centre of inversion with asymmetrically bridging chlorides. The geometry of the copper atoms is approximately square pyramidal, with a τ value[24] of 0.15, and with the longer bond to the bridging chloride occupying the apical position. The two coordinated ligands are arranged in a *trans* coplanar arrangement with respect to the copper atom and, in both cases, have an *s-trans* conformation about the inter-ring bond. However, the conformations do differ slightly: in one ligand the two rings are almost coplanar [4.6(1)°], while the other independent ligand has the pyridine ring ring rotated 13.0(1)° out of the plane of its attached benzotriazole ring.

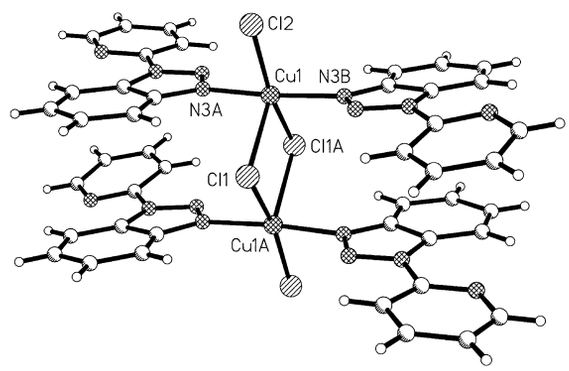


Fig. 5 Perspective view of the X–ray structure of complex **17**. Cu1A and Cl1A are related to Cu1 and Cl1 by the transformation $1 - x$, $1 - y$, $1 - z$. Selected bond lengths (Å) and angles (°): Cu1–N3A 2.0453(13), Cu1–N3B 2.0535(13), Cu1–Cl2 2.2690(7), Cu1–Cl1A 2.3107(6), Cu1–Cl1 2.6739(7); N3A–Cu1–N3B 173.29(5), N3A–Cu1–Cl2 88.85(4), N3B–Cu1–Cl2 91.12(4), N3A–Cu1–Cl1A 89.35(4), N3B–Cu1–Cl1A 88.84(4), Cl2–Cu1–Cl1A 164.059(17), N3A–Cu1–Cl1 96.82(4), N3B–Cu1–Cl1 89.70(4), Cl2–Cu1–Cl1 104.133(17), Cl1A–Cu1–Cl1 91.808(16), Cu1A–Cl1–Cu1 88.192(16).

Similar reaction of the methylene-expanded analogue **5** with copper(II) chloride gave a complex in 85% yield, that provided good quality crystals by diffusion of methanol into a DMF solution of the complex. The structure of this complex (**18**) is shown in Fig. 6. It is an M_2L_2 metallodimer, which crystallizes about a crystallographic centre of inversion. The ligand acts in a divergent manner, bridging two coppers through the pyridine and N3-benzotriazole nitrogens. The coordination geometry of the copper atom is somewhat unusual and provides clear evidence for an additional interaction with a fifth donor, *viz* the N2 nitrogen of the benzotriazole ring. This weaker interaction [Cu(1)–N(2) 2.529(2) Å] is shown as a dashed line in Fig. 6. Thus, in this complex the ligand makes use of all available donors and simultaneously acts as a chelating and bridging ligand.

Reaction of ligand **6** with copper(II) chloride gave a tan product in 89% yield, which, upon recrystallization from nitromethane, furnished small orange plates suitable for X-ray analysis. This complex (**19**) crystallizes in the monoclinic space group *C*2/*c*. Fig. 7 shows the contents of the asymmetric unit except for the nitromethane solvate molecules. The complex has a central Cu_4Cl_6 cluster encapsulating an oxo anion. Each

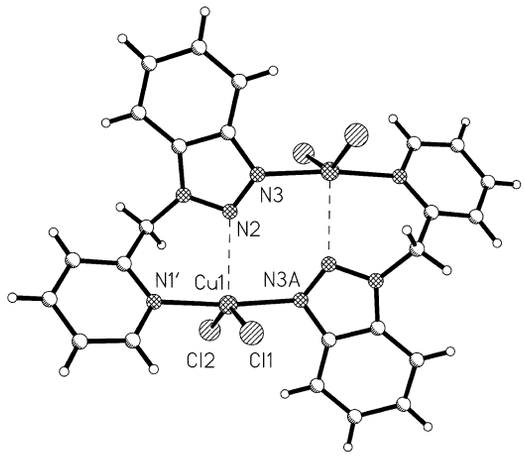


Fig. 6 Perspective view of the X-ray structure of complex **18**. N3A is related to N3 by the transformation $1 - x$, $1 - y$, $2 - z$. Selected bond lengths (Å) and angles (°): Cu1–N3A 2.0181(16), Cu1–N1′ 2.0408(16), Cu1–Cl2 2.2511(8), Cu1–Cl1 2.2823(7); N3A–Cu1–N1′ 172.80(6), N3A–Cu1–Cl2 94.14(5), N1′–Cu1–Cl2 91.53(5), N3A–Cu1–Cl1 86.63(5), N1′–Cu1–Cl1 91.53(5), Cl2–Cu1–Cl1 142.91(2).

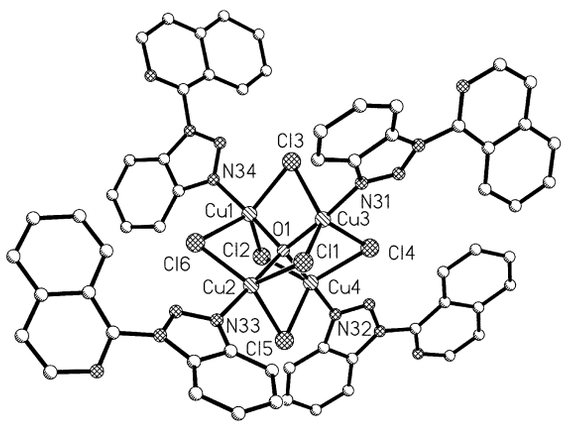


Fig. 7 Perspective view of the X-ray structure of complex **19**. Hydrogen atoms and nitromethane solvate molecules are not shown for clarity. Selected bond lengths (Å): Cu1–O1 1.913(4), Cu1–N34 1.984(5), Cu1–Cl3 2.358(2), Cu1–Cl2 2.406(2), Cu1–Cl6 2.449(2), Cu2–O1 1.908(4), Cu2–N33 1.980(5), Cu2–Cl6 2.363(2), Cu2–Cl5 2.385(2), Cu2–Cl1 2.470(2), Cu3–O1 1.915(4), Cu3–N31 1.970(5), Cu3–Cl1 2.357(2), Cu3–Cl3 2.434(2), Cu3–Cl4 2.438(2), Cu4–O1 1.901(4), Cu4–N32 1.971(5), Cu4–Cl4 2.376(2), Cu4–Cl5 2.443(2), Cu4–Cl2 2.456(2).

copper atom is coordinated to three bridging chlorine atoms, the central oxygen atom and a ligand of **6**, which once again selectively coordinates through the N3-nitrogen of the benzotriazole ring. Each of the four crystallographically independent molecules of **6** has a *trans* arrangement about the inter-ring bond, but differs in the angles between the planes of the two rings of the ligand [varying between 11 and 59°]. Such Cu_4Cl_6O clusters are relatively common.[25] One that bears a structural resemblance to **19**, is the related complex containing coordinated benzimidazole.[26]

Thus, 1-substituted benzotriazole containing ligands are capable of acting as both chelating (*via* N2) and bridging (*via* N3) ligands with copper(II). Interestingly, each of the ligands **3**–**6** gave complexes of different stiochiometry upon reaction with copper(II) chloride, *viz* $(ML)_n$, M_2L_4, M_2L_2 and M_4L_4, respectively.

Silver complexes

Silver(I) has proved very popular in recent years as a component for the construction of diverse metallosupramolecular architectures.[27] We have previously isolated a number of topologically novel structures from reactions of heterocyclic ligands with silver(I) nitrate.[28] In continuation of this work, we have now reacted each of the ligands **2**–**6** with silver salts.

Reactions of the ligands **3**–**5** with one equivalent of silver nitrate each resulted in the formation, in good yield, of complexes that were suitable for X-ray structure determination. Fig. 8 shows the extended structure of the complex (**20**) formed from ligand **3**. It crystallizes in the triclinic space group $P\bar{1}$, with the silver atom coordinated, in a distorted trigonal environment, to two ligands *via* N3 of the benzotriazole and to an acetonitrile molecule. Two oxygens of the nitrate counter-ion also make weak contacts [2.610(2) and 2.691(2) Å] with the silver atom. Thus **3** acts as a bridging ligand with the formation of a one-dimensional polymer, which propagates along the *a* axis (Fig. 8). The conformation of the ligand and the chain-like structure are similar to those observed in the corresponding copper complex **15**.

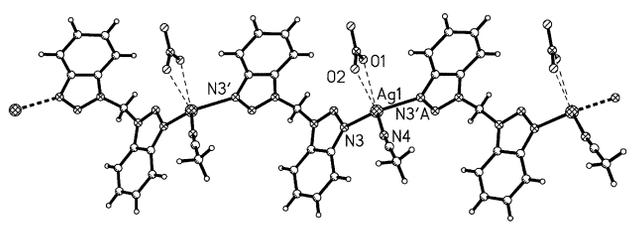


Fig. 8 Perspective view of the extended polymeric structure of **20**. N3′A is related to N3′ by the transformation $1 + x$, y, z. Selected interatomic distances (Å) and angles (°): Ag1–N3 2.255(2), Ag1–N3′A 2.311(2), Ag1–N4 2.288(2), Ag1–O1 2.691(2), Ag1–O2 2.610(2); N3–Ag1–N4 117.84(8), N3–Ag1–N3′A 124.93(7), N4–Ag1–N3′A 104.04(8).

The silver nitrate complex (**21**) of the ligand **4** is a cyclic M_2L_2 dimer (Fig. 9). It crystallizes in the triclinic space group $P\bar{1}$ about a crystallographic centre of inversion. The ligand coordinates *via* the pyridyl and N3 nitrogens to bridge two silver atoms which have a separation of 4.592(1) Å. The resulting 12-membered dimetallocyclic ring deviates from planarity as a result of a 34.1(1)° twist about the bond linking the two heterocyclic rings of the ligand. This twisting occurs to relieve steric interactions between the hydrogen atoms attached to C7 and C3′. The nitrate anions exhibits monodentate coordination to the silver atoms, which have distorted T-shaped geometry.

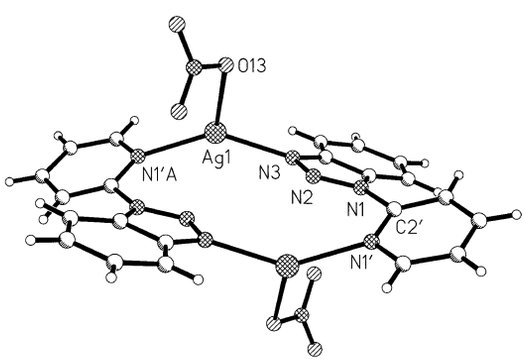


Fig. 9 Perspective view of the X-ray crystal structure of **21**. N1′A is related to N1′ by the transformation $1 - x$, $1 - y$, $-z$. Selected interatomic distances (Å) and angles (°): Ag1–N3 2.240(2), Ag1–N1′A 2.273(2), Ag1–O13 2.590(2), N1–N2 1.358(3), N2–N3 1.306(3), N1–C2′ 1.438(3); N3–Ag1–N1′A 143.18(7), N3–Ag1–O13 98.34(8), N1′A–Ag1–O13 113.97(7).

The corresponding complex (**22**) of the methylene-extended ligand **5** is also a cyclic dimer (Fig. 10). It crystallizes in the monoclinic space group *C*2/*c* about a crystallographic centre of inversion, with a separation between the silver atoms of 4.942(1) Å. In this case the 14-membered dimetallocyclic ring is far from planar as a consequence of the introduction of the tetrahedral methylene groups. Once again, the silver atom has

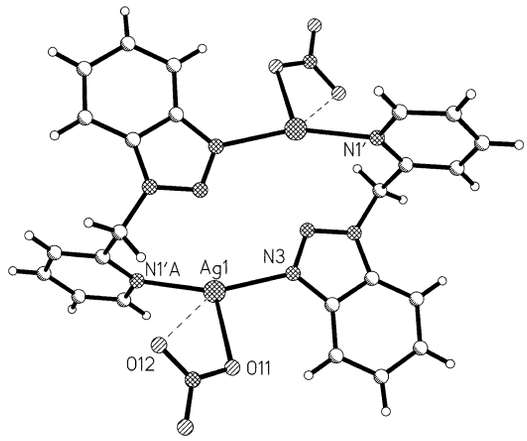


Fig. 10 Perspective view of the X-ray crystal structure of **22**. N1′A is related to N1′ by the transformation 0.5 − *x*, 1.5 − *y*, −*z*. Selected interatomic distances (Å) and angles (°): Ag1–N3 2.222(2), Ag1A–N1′ 2.228(2), Ag1–O11 2.527(2); N3–Ag1–N1′A 152.96(8), N3–Ag1–O11 92.11(7), N1′A–Ag1–O11 114.87(7).

distorted T-shaped geometry but this time also weakly interacts with a second oxygen atom of the nitrate [Ag1–O12 2.693(2) Å]. Such cyclic dinuclear complexes have been reported for a number of silver complexes of heterocyclic ligands in recent years.[27,28]

Conclusion

In this study, we have shown that the benzotriazole moiety is a useful component for incorporation into bis-heterocyclic ligands. Due to the availablity of two different nitrogen donors for coordination, 1-heteroaryl substituted benzotriazoles can act as either chelating or bridging ligands depending on the metal, the heterocyclic substituent and the reaction conditions. We are currently exploring the extension of this work to multidentate ligands containing greater numbers of benzotriazole substituents.

Experimental

General procedures and ligand syntheses

NMR spectra were recorded on a Varian Unity 300 spectrometer with a 3 mm probe and operating at 300 MHz and 75 MHz for ^{1}H and ^{13}C, respectively. ^{1}H NMR spectra recorded in $CDCl_3$ and CH_2Cl_2 were referenced relative to internal standard Me_4Si and those recorded in d_3-acetonitrile were referenced against the solvent signal at 2.0 ppm. ^{13}C NMR spectra recorded in $CDCl_3$ and acetonitrile were referenced against the solvent signals at 77.0 and 117.7 ppm, respectively. When required, ^{1}H NOE, 1D TOCSY, COSY, GHSQC and GHMBC experiments were performed using the standard pulse sequences available with the Unity 300 system. Unless otherwise stated the value for the chemical shift is given as the centre of the multiplet. Individual protons within a ring were assigned on the basis of their chemical shifts and the following typical ^3J coupling patterns for pyridine protons: H3 (d, J = 8 Hz), H4 (t, J = 8 Hz), H5 (dd, J = 8, 5 Hz), H6 (d, J = 5 Hz). Where possible, for the ^{1}H NMR spectra of the ruthenium complexes, the individual spin systems were identified by 1D-TOCSY experiments. The signals for the four pyridine rings of the ancillary 2,2′-bipyridine ligands are labelled A–D below.

UV–visible spectra were recorded on a GBC spectrophotometer for *ca.* 0.1 mmol solutions in acetonitrile. Cyclic voltametric measurements were made on a PAR Model 175 Universal Programmer coupled to a PAR Model 173 potentiostat. Measurements were made of acetonitrile solutions containing *ca.* 1 mmol of complex and 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, using a scan rate of 100 mV s^{-1} and a glassy carbon electrode (area 0.07 cm^{-2}), with a platinum wire as the auxiliary electrode. Ferrocene was used as an internal standard and potentials are given *vs.* the saturated calomel electrode [E^0(Fc/Fc$^+$) = 0.31 V *vs* SCE].

Mass spectra (EI and FAB) were recorded using a Kratos MS80RFA mass spectrometer with a Mach 3 data system. Electron impact (EI) spectra were obtained at 70 eV with a source temperature of 250 °C. Fast atom bombardment (FAB) spectra were acquired in a nitrobenzyl alcohol matrix using an Iontech ZN11NF FAB gun operated at 8 kV and 2 mA. Melting points were determined using an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by the Campbell Microanalytical laboratory at the University of Otago.

Ligands **2**[11] and **4**[13] were prepared by literature procedures. Ligands **3**[12] and **5**[14] are both known compounds, which we prepared by phase-transfer catalysed[29] alkylation reactions of benzotriazole with diiodomethane and 2-chloromethylpyridine, respectively. Ru(bpy)$_2$Cl$_2$·2H$_2$O was prepared by the literature procedure.[30]

1-(1-Isoquinolyl)benzotriazole (6). 1-Chloroisoquinoline (0.42 g, 2.5 mmol) and benzotriazole (Bt) (0.61 g, 5.3 mmol) were refluxed in dry toluene (2 ml) under an atmosphere of N_2 for 19 h. The reaction mixture was then suspended in *ca*. 30 ml of ethyl acetate and washed with 5% aqueous KOH to remove the unreacted benzotriazole. Evaporation of the solvent under reduced pressure yielded a white solid. Recrystallization from benzene gave pure **6**. Mp 151–152 °C; yield 0.44 g (70%) (Found: C, 73.07; H, 3.92; N, 22.92. Calc. for $C_{15}H_{10}N_4$: C, 73.15; H, 4.09; N, 22.75%). EI mass spectrum: calc. *m*/*z* for $C_{15}H_{10}N_4$ 246.0906; found 246.0904. *m*/*z* 246.1 (M^+, 23%), 218.1 ($M^+ - N_2$, 100%), 128.1 ($M^+ - C_6H_4N_3$, 53%). ^{1}H NMR ($CDCl_3$) δ: H3′, 8.58; H4′, 7.80; H5′, 7.99; H6′, 7.81; H7′, 7.71; H8′, 8.60; H4, 8.21; H5, 7.49; H6, 7.61; H7, 8.08. ^{13}C NMR ($CDCl_3$) δ: C1′, 148.18; C3′, 140.66; C4′, 121.95; C4A′, 138.87; C5′, 126.95; C6′, 131.14; C7′, 128.78; C8′, 126.25; C8A′, 122.84; C3A, 145.93; C4, 119.87; C5, 124.88; C6, 128.86; C7, 112.89; C7A, 133.37.

Ruthenium complexes

Complex 7. Ligand **2** (24.0 mg, 0.10 mmol) and Ru(bpy)$_2$Cl$_2$·2H$_2$O (52.9 mg, 0.10 mmol) were refluxed in 3 : 1 EtOH–H$_2$O (8 ml) for 48 h. After cooling, the reaction mixture was concentrated to dryness *in vacuo*. The residue was redissolved in the minimum of water, filtered to remove unreacted ligand, and the product precipitated by the addition of an aqueous solution of NH_4PF_6. Yield 69.6 mg (82%) (Found: C, 44.86; H, 3.05; N, 16.39. Calc. for $C_{32}H_{24}N_{10}ClF_6PRu.1½H_2O$: C, 44.84; H, 3.00; N, 16.33%). FAB mass spectrum: calc. *m*/*z* for $C_{32}H_{24}N_{10}ClRu^+$ ([(bpy)$_2$Ru(**2**)Cl]$^+$) 685.0908; found 685.0917. λ_{max} (CH_3CN): 479 nm, ε 8650 M^{-1} cm^{-1}. ^{1}H NMR (CD_3CN) δ: bpy(A) H3, 8.35; H4, 8.12; H5, 7.80; H6, 10.18; bpy(B) H3, 8.21; H4, 7.75; H5, 7.08; H6, 7.87; bpy(C) H3, 8.45; H4, 7.80; H5, 7.30; H6, 7.77; bpy(D) H3, 8.58; H4, 8.16; H5, 7.63; H6, 9.04; Bt H4, 9.12; H5, 7.65; H6, 7.78; H7, 7.57; H4′, 8.36; H5′, 7.70; H6′, 7.80; H7′, 7.53.

Complex 8. Ligand **3** (17.0 mg, 0.11 mmol) and Ru(bpy)$_2$Cl$_2$·2H$_2$O (32.1 mg, 0.11 mmol) were refluxed in 3 : 1 EtOH–H$_2$O (8 ml) for 6 h. The product was isolated, as above. Yield 44.0 mg (82%) (Found: C, 45.90; H, 2.93; N, 15.93. Calc. for $C_{33}H_{26}N_{10}ClF_6PRu.H_2O$: C, 45.98; H, 3.27; N, 16.24%). FAB mass spectrum: calc. *m*/*z* for $C_{33}H_{26}N_{10}ClRu^+$ ([(bpy)$_2$Ru(**3**)Cl]$^+$) 699.1056; found 699.1074. λ_{max} (CH_3CN): 471 nm, ε 7000 M^{-1} cm^{-1}. ^{1}H NMR (CD_3CN) δ: bpy(A) H3, 8.34; H4, 8.04; H5, 7.67; H6, 10.07; bpy(B) H3, 8.24; H4, 7.84; H5, 7.19; H6, 7.86; bpy(C) H3, 8.41; H4, 7.88; H5, 7.24; H6 7.71; bpy(D) H3, 8.53;

H4, 8.10; H5, 7.41; H6, 8.67; Bt H4, 8.88; H5, 7.46; H6, 7.71; H7, 8.07; H4′, 8.10; H5′, 7.68; H6′, 7.45; H7′, 7.78; CH_2, 7.57.

Complex 9. $AgBF_4$ (34.1 mg, 0.175 mmol) and $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (45.1 mg, 0.087 mmol) in deaerated 1 : 1 ethanol–acetone (12 ml) was stirred at 35–40 °C for 90 min. After filtering to remove precipitated AgCl, ligand **3** (25.0 mg, 0.10 mmol) was added as a solid, the solution was again deaerated by bubbling argon through the solution and the mixture stirred at 40 °C for 5 h. The resulting solution was concentrated to dryness *in vacuo*, and the residue was chromatographed on alumina. Yield 31 mg (47%) (Found: C, 47.63; H, 3.17; N, 16.56. Calc. for $C_{33}H_{26}N_{10}B_2F_8Ru$: C, 47.34; H, 3.13; N, 16.72%). FAB mass spectrum: calc. *m/z* for $C_{33}H_{26}N_{10}BF_4Ru^+$ ($[(bpy)_2Ru(\mathbf{3})](BF_4)^+$) 751.1442; found 751.1415. λ_{max} (CH_3CN): 368, 420 (sh) nm, ε 9 800 M^{-1} cm^{-1}. E^0 (CH_2Cl_2) Ru^{2+}/Ru^{3+} 1.50 V, $E^{1/2}$ 60 mV; E^0_{red} −1.45 V, $E^{1/2}$ 60 mV; E^0_{red} −1.60 V; $E^{1/2}$ 70 mV. ^1H NMR (CD_2Cl_2) δ: 8.48, bpy H3; 8.17, bpy H4; 7.57, bpy H5; 8.27, bpy H6; 8.43, bpy H3′; 8.12, bpy H4′; 7.49, bpy H5′; 7.84, bpy H6′; 7.84, H4; 7.51, H5; 7.76, H6; 8.04, H7; 7.43, CH_2.

Complex 10. Ligand **4** (11.4 mg, 0.06 mmol) and $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (30.2 mg, 0.06 mmol) in 3 : 1 EtOH–H_2O (8 ml) were refluxed for 4 h. The product was isolated, as above for complex **7**. Yield 46.1 mg (88%) (Found: C, 41.30; H, 2.70; N, 12.40. Calc. for $C_{31}H_{24}N_8F_{12}P_2Ru$: C, 41.39; H, 2.69; N, 12.46%). FAB mass spectrum: calc. *m/z* for $C_{31}H_{24}N_8F_6PRu^+$ ($[(bpy)_2Ru(\mathbf{4})](PF_6)^+$) 755.0818; found 755.0809. λ_{max} (CH_3CN): 423 nm, ε 16 300 M^{-1} cm^{-1}. E^0 (CH_3CN) Ru^{2+}/Ru^{3+} 1.53 V, $E^{1/2}$ 75 mV; E^0_{red} −1.39 V, $E^{1/2}$ 80 mV; E^0_{red} −1.60 V; $E^{1/2}$ 95 mV. ^1H NMR (CD_3CN) δ: 7.43, bpy H5; 7.48, H5′ and 2 × bpy H5; 7.55, bpy H5; 7.71, H5; 7.83, H6′ and bpy H6; 7.90, H6 and 3 × bpy H6; 8.05, H4; 8.16, 3 × bpy H4; 8.21, bpy H4; 8.32, H4′; 8.40, H7; 8.57, H3′ and 2 × bpy H3; 8.59, bpy H3; 8.62, bpy H3.

Complexes 11 and 13. Ligand **5** (13.0 mg, 0.062 mmol) and $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (32.1 mg, 0.062 mmol) in 3 : 1 EtOH–H_2O (8 ml) were refluxed for 5 h. The product was isolated, as above for complex **7**. Chromatography on alumina (1 × 7 cm), with 100 : 1 CH_2Cl_2–MeOH as eluant, cleanly separated a small dark red fraction of complex **13** then a larger orange fraction of complex **11**. Complex **11**: Yield 44 mg (77%) (Found: C, 41.21; H, 2.93; N, 12.09. Calc. for $C_{32}H_{26}N_8F_{12}P_2Ru \cdot H_2O$: C, 41.30; H, 3.03; N, 12.04%). FAB mass spectrum: calc. *m/z* for $C_{32}H_{26}N_8F_6PRu^+$ ($[(bpy)_2Ru(\mathbf{5})](PF_6)^+$) 769.0967; found 769.0957. λ_{max} (CH_3CN) 426 nm, ε 11 300 M^{-1} cm^{-1}. E^0 (CH_3CN) Ru^{2+}/Ru^{3+} 1.30 V, $E^{1/2}$ 75 mV; E^0_{red} −1.43 V, $E^{1/2}$ 70 mV; E^0_{red} −1.64 V; $E^{1/2}$ 70 mV. ^1H NMR (CD_3CN) δ: bpy(A) H3, 8.50; H4, 8.19; H5, 7.64; H6, 8.58; bpy(B) H3, 8.40; H4, 8.05; H5, 7.43; H6, 7.77; bpy(C) H3, 8.66; H4, 8.20; H5, 7.49; H6, 7.96; bpy(D) H3, 8.62; H4, 8.13; H5, 7.46; H6, 7.81; py H3′, 8.00; H4′, 7.97; H5′, 7.25; H6′, 7.70; Bt H4, 7.80; H5, 7.51; H6, 7.71; H7, 8.00; CH_2, H_{eq} 6.13, H_{ax} 5.91. Complex **13**: Yield 7.2 mg (14%) (Found: C, 47.97; H, 3.21; N, 14.04. Calc. for $C_{32}H_{26}N_8ClF_6PRu$: C, 47.80; H, 3.26; N, 13.93%). FAB mass spectrum: calc. *m/z* for $C_{32}H_{26}N_8ClRu^+$ ($[(bpy)_2Ru(\mathbf{5})Cl]^+$ 659.1028; found 659.1012. λ_{max} (CH_3CN) 494 nm, ε 5600 M^{-1} cm^{-1}. ^1H NMR (CD_3CN) δ: bpy(A) H3, 8.28; H4, 8.01; H5, 7.71; H6, 10.19; bpy(B) H3, 8.14; H4, 7.72; H5, 7.11; H6, 7.87; bpy(C) H3, 8.42; H4, 7.86; H5, 7.23; bpy H6, 7.79; bpy(D) H3, 8.53; H4, 8.09; H5, 7.56; H6, 8.90; py H3′, 6.97; H4′, 7.72; H5′, 7.32; H6′, 8.42; Bt H4, 8.84; H5, 7.40; H6, 7.57; H7, 7.72; CH_2, 5.72.

Complex 12. Ligand **6** (20.0 mg, 0.06 mmol) and $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (42.0 mg, 0.06 mmol) in 3 : 1 EtOH–H_2O (8 ml) were refluxed for 15 h. The product was isolated, as above for complex **7**. Yield 67.0 mg (87%) (Found: C, 44.12; H, 2.49; N, 11.59. Calc. for $C_{35}H_{26}N_8F_{12}P_2Ru$: C, 44.27; H, 2.76; N, 11.80%). FAB mass spectrum: calc. *m/z* for $C_{35}H_{26}N_8F_6PRu^+$ ($[(bpy)_2Ru(\mathbf{6})](PF_6)^+$) 805.0975; found 805.0966. λ_{max} (CH_3CN) 429 nm, ε 16 200 M^{-1} cm^{-1}. E^0 (CH_3CN) Ru^{2+}/Ru^{3+} 1.47 V, $E^{1/2}$ 80 mV; E^0_{red} −1.34 V, $E^{1/2}$ 80 mV; E^0_{red} −1.72 V (irreversible); E^0_{red} −1.93 V (irreversible). ^{13}C NMR (CD_2Cl_2) δ: 113.90; 119.42; 124.30; 124.67; 124.71; 124.96; 127.26; 127.56; 127.84; 128.20; 128.25; 129.88; 130.24; 133.73; 138.90; 138.98; 139.16; 141.25; 152.31; 152.58; 152.87; 153.10. ^1H NMR (CD_2Cl_2) δ: bpy(A) H3, 8.57; H4, 8.12; H5, 7.34; H6, 7.90; bpy(B) H3, 8.56; H4, 8.10; H5, 7.37; H6, 8.03; bpy(C) H3, 8.58; H4, 8.19; H5, 7.50; H6, 7.82; bpy(D) H3, 8.62; H4, 8.22; H5, 7.55; H6, 7.88; isq H3′, 7.60; H4′, 7.94; H5′, 8.25; H6′, 8.10; H7′, 8.08; H8′, 8.58; Bt H4, 8.04; H5, 7.70; H6, 7.81; H7, 8.07.

Palladium complex

Complex 14. Ligand **5** (52 mg, 0.25 mmol) dissolved in MeOH (2 ml) was added to $PdCl_2$ (44 mg, 0.25 mmol) dissolved in hot aqueous 2 M HCl (3 ml). A yellow solid precipitated immediately and was collected by filtration and recrystallized from $MeNO_2$. Crystals suitable for structure determination were grown from vapour diffusion of MeOH into a DMF solution of the complex. Mp 250–260 °C; yield 94 mg (98%) (Found: C, 37.15; H, 3.29; N, 13.82; Cl, 17.27. Calc. for $C_{24}H_{20}N_8Cl_4Pd_2 \cdot MeOH$: C, 37.20; H, 3.00; N, 13.88; Cl, 17.57%). FAB mass spectrum: calc. *m/z* for $C_{24}H_{20}N_8Cl_3Pd_2^+$ $[(\mathbf{5})_2Pd_2Cl_3^+$, 100%] 738.8965; found 738.8947.

Copper complexes

Complex 15. Ligand **3** (50 mg, 0.20 mmol) dissolved in warm MeOH (3 ml) was added to $CuCl_2 \cdot 2H_2O$ (28 mg, 0.20 mmol) dissolved in MeOH (1 ml). Green crystals suitable for X-ray structure determination grew from slow evaporation of this solution. Mp 240–250 °C; yield 60 mg (86%) (Found: C, 40.90; H, 2.52; N, 21.93; Cl, 18.34. Calc. for $C_{13}H_{10}N_6Cl_2Cu$: C, 40.59; H, 2.62; N, 21.84; Cl, 18.43%).

Complex 16. Ligand **4** (40 mg, 0.20 mmol) dissolved in MeOH (2 ml) was added to $Cu(NO_3)_2 \cdot 3H_2O$ (49 mg, 0.20 mmol) dissolved in MeOH (1 ml). Green crystals suitable for X-ray structure determination grew from slow evaporation of this solution. Mp 223–225 °C; yield 65 mg (60%) (Found: C, 44.01; H, 3.38; N, 22.32. Calc. for $C_{22}H_{16}N_{10}O_6Cu \cdot MeOH \cdot H_2O$: C, 43.85; H, 3.52; N, 22.23%). FAB mass spectrum: calc. *m/z* for $C_{22}H_{16}N_8Cu^+$ $[(\mathbf{4})_2Cu^+$, 100%] 455.0802; found 455.0796.

Complex 17. Ligand **4** (87.2 mg, 0.45 mmol) was dissolved in MeOH (3 ml) and added to $CuCl_2 \cdot 2H_2O$ (76.1 mg, 0.45 mmol) dissolved in MeOH (1 ml). The green precipitate that formed was collected by filtration and washed well with MeOH. Mp 271–274 °C; yield 122.9 mg (84%) (Found: C, 40.53; H, 2.26; N, 17.07; Cl, 21.01. Calc. for $C_{11}H_8N_4Cl_2Cu$: C, 40.13; H, 2.45; N, 17.03; Cl, 21.26%). Recrystallization from DMF afforded large green crystals suitable for X-ray analysis (Found: C, 50.15; H, 3.00; N, 21.41; Cl, 13.69. Calc. for $C_{22}H_{16}N_8Cl_2Cu$: C, 50.28; H, 3.07; N, 21.34; Cl, 13.32%).

Complex 18. Ligand **5** (56.2 mg, 0.268 mmol) was dissolved in MeOH (2 ml) and added to $CuCl_2 \cdot 2H_2O$ (45.6 mg, 0.267 mmol) dissolved in MeOH (1 ml). The green precipitate that formed was collected by filtration and washed well with MeOH. Yield 92.2 mg (85%). Recrystallization by diffusion of methanol into a DMF solution of the complex afforded crystals suitable for X-ray structure determination (Found: C, 41.74; H, 3.02; N, 15.98; Cl, 20.36. Calc. for $C_{24}H_{20}N_8Cl_4Cu_2$: C, 41.81; H, 2.92; N, 16.25; Cl, 20.57%).

Complex 19. $CuCl_2 \cdot 2H_2O$ (22.9 mg, 0.13 mmol) dissolved in 1 : 1 chloroform/methanol (1 ml) was added to ligand **6** (33.0 mg, 0.13 mmol) dissolved in chloroform (2 ml) and the resulting solution swirled. After 1 day a yellow solid had formed and this was filtered off. Vapour diffusion of diethyl ether into the filtrate precipitated more tan solid. Yield 45.4 mg (89%)

Table 3 Crystal data and X-ray experimental details for **14**–**22**

Compound	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
Data collection device	P4s	P4s	P4s	CCD	CCD	CCD	P4s	CCD	P4s
Empirical formula	$C_{25}H_{24}Cl_4N_8OPd_2$	$C_{13}H_{10}Cl_2CuN_6$	$C_{24}H_{24}CuN_{10}O_8$	$C_{44}H_{32}Cl_4Cu_2N_{16}$	$C_{24}H_{20}Cl_4Cu_2N_8$	$C_{62.5}H_{47.5}Cl_6Cu_4N_{18.5}O_6$	$C_{15}H_{13}AgN_8O_3$	$C_{11}H_8AgN_5O_3$	$C_{24}H_{20}Ag_2N_{10}O_6$
Formula weight	807.12	384.71	644.07	1053.74	689.36	1620.55	461.20	366.09	760.24
T/K	153(2)	163(2)	153(2)	163(2)	168(2)	163(2)	163(2)	168(2)	168(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$
Unit cell dimensions:									
a/Å	10.820(2)	8.554(1)	7.720(1)	10.161(3)	8.390(2)	42.585(19)	9.212(1)	8.308(2)	16.252(2)
b/Å	15.273(2)	9.250(1)	12.016(1)	10.464(3)	21.467(6)	13.589(6)	9.307(1)	8.675(2)	11.020(2)
c/Å	17.715(3)	10.322(1)	14.921(2)	11.130(3)	8.328(2)	24.550(11)	11.849(1)	9.664(3)	14.709(2)
α/°	90	88.79(1)	90	103.268(3)	90	90	92.28(1)	102.377(4)	90
β/°	97.21(1)	72.78(1)	103.14(1)	107.246(3)	119.217(8)	109.214(7)	105.92(1)	109.288(3)	96.98(1)
γ/°	90	65.83(1)	90	91.123(3)	90	90	115.69(1)	107.132(3)	90
V/Å^3	2904.3(8)	707.01(13)	1347.9(3)	1095.1(5)	1309.0(6)	13415(10)	865.5(2)	589.5(3)	2614.8(7)
Z	4	2	2	1	2	8	2	2	4
D/Mg m^{-3}	1.846	1.807	1.587	1.598	1.749	1.605	1.770	2.063	1.931
μ/mm^{-1}	1.642	1.926	0.879	1.270	2.065	1.556	1.082	1.726	1.560
F(000)	1592	386	662	534	692	6544	460	360	1504
Crystal size/mm^3	0.69 × 0.05 × 0.03	0.41 × 0.33 × 0.14	0.62 × 0.44 × 0.31	0.47 × 0.45 × 0.41	0.55 × 0.28 × 0.11	0.28 × 0.24 × 0.04	0.74 × 0.27 × 0.11	0.55 × 0.25 × 0.11	0.55 × 0.34 × 0.25
θ range for data collection/°	2.48–22.50	2.08–26.00	2.20–27.00	2.40–26.30	2.78–26.44	2.03–22.50	2.47–28.00	2.36–26.48	2.24–27.00
Reflections collected	4282	3558	3157	13315	16369	60290	4400	7588	2963
Independent reflections [R(int)]	3789 [0.1881]	2719 [0.0209]	2941 [0.0240]	4319 [0.0199]	2663 [0.0211]	8759 [0.1007]	4150 [0.0171]	2387 [0.0245]	2865 [0.0209]
Observed reflections [$I > 2\sigma(I)$]	1931	2010	2007	4125	2483	5735	3561	2206	2365
Data/restraints/parameters	3789/18/361	2719/0/199	2941/0/200	4319/0/298	2663/0/172	8759/395/884	4150/0/245	2387/0/181	2865/0/190
R_1 [$I > 2\sigma(I)$]	0.0418	0.0330	0.0373	0.0240	0.0225	0.0495	0.0281	0.0222	0.0250
wR_2 (all data)	0.0558	0.0770	0.0893	0.0651	0.0579	0.1306	0.0693	0.0562	0.0609

(Found: C, 47.05; H, 2.58; N, 14.61; Cl, 18.47. Calc. for $C_{15}H_{10}N_4Cl_2Cu$: C, 47.32; H, 2.65; N, 14.71; Cl, 18.63%). This material was recrystallized from nitromethane to give thin orange plate-like crystals of **19**.

Silver complexes

Complex 20. Ligand **3** (35 mg, 0.14 mmol) dissolved in warm MeOH (3 ml) was added to $AgNO_3$ (24 mg, 0.14 mmol) dissolved in warm MeOH (3 ml). A white solid formed immediately and was collected by filtration. Recrystallization from acetonitrile gave colourless crystals suitable for X-ray structure determination. Mp 253–255 °C; yield 48.4 mg (84%) (Found: C, 39.19; H, 2.57; N, 24.22. Calc. for $C_{13}H_{10}N_7O_3Ag.MeCN$: C, 39.07; H, 2.84; N, 24.30%).

Complex 21. Ligand **4** (40 mg, 0.20 mmol) dissolved in MeOH (3 ml) was added to $AgNO_3$ (35 mg, 0.20 mmol) dissolved in hot MeOH (2 ml). Colourless crystals suitable for structure determination grew from slow evaporation of this solution. Mp 228–229 °C; yield 57 mg (77%) (Found: C, 36.13; H, 1.99; N, 19.23. Calc. for $C_{22}H_{16}N_{10}O_6Ag_2$: C, 36.09; H, 2.20; N, 19.13%).

Complex 22. Ligand **5** (48 mg, 0.23 mmol) dissolved in MeOH (2 ml) was added to $AgNO_3$ (39 mg, 0.23 mmol) dissolved in hot MeOH (2 ml). A white solid precipitated immediately and was collected by filtration. recrystallization from MeCN gave colourless crystals suitable for X-ray structure determination. Mp 225–227 °C; yield 64 mg (73%) (Found: C, 38.10; H, 2.84; N, 18.28. Calc. for $C_{24}H_{20}N_{10}O_6Ag_2$: C, 37.91; H, 2.65; N, 18.42%).

X-Ray crystallography

The crystal data and details of the data collections and refinements for the nine structures are listed in Table 3. Measurements were made with either a Siemens P4s four-circle diffractometer or a SMART CCD area detector using graphite-monochromatized Mo-Kα (λ = 0.71073Å) radiation, as listed in Table 3. The structures were solved by direct methods using SHELXS[31] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-97.[32] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier atoms. The functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + aP^2 + bP]^{-1}$, where $P = [\max(F_o)^2 + 2F_c^2]/3$.

CCDC reference numbers 190038–190046.

See http://www.rsc.org/suppdata/dt/b2/b206990c/ for crystallographic data in CIF or other electronic format.

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