Letter

New hybrid ditopic ligands containing fused phenanthroline and crown ether units

Craig R. Rice, Ana Guerrero, Zöe R. Bell, Rowena L. Paul, Graham R. Motson, John C. Jeffery and Michael D. Ward*

School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS.
E-mail: mike.ward@bristol.ac.uk

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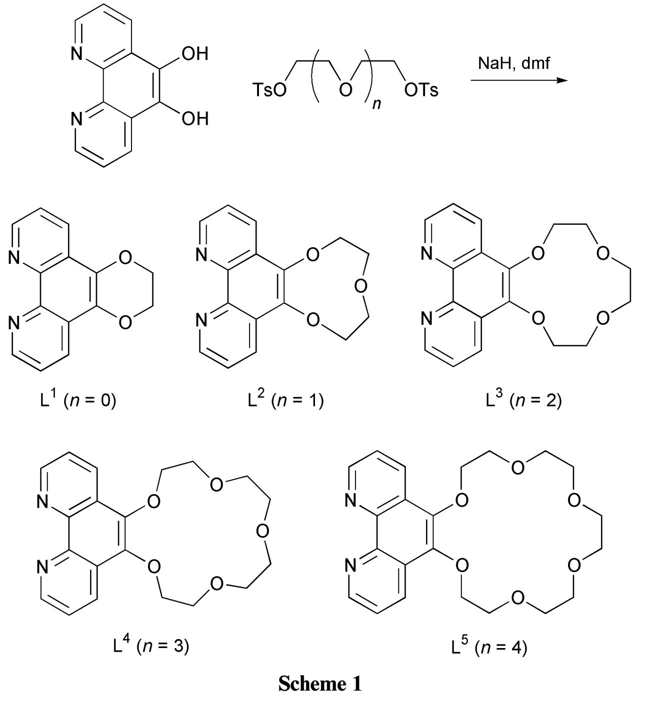
Reaction of 5,6-dihydroxy-1,10-phenanthroline with various poly(ethylene)glycol-ditosylates affords, in good yield, a series of ligands in which a phenanthroline binding site is attached to an adjacent crown ether unit; the NN chelating site may be coordinated to $\{Ru(bipy)_2\}^{2+}$ units to afford $[Ru(bipy)_3]^{2+}$ derivatives with pendant crown ether units, which can bind alkali metal ions.

Ditopic ligands which contain a macrocyclic unit attached to another metal-ion binding site have found a very wide range of applications in numerous fields.[1] Where the macrocycle is attached to a polypyridyl unit, the resulting ligands can be used to prepare luminescent or electrochemical sensors in which the luminescence and/or redox properties of a metal–polypyridyl complex core is modified by coordination of a group IA or group IIA metal ion to peripheral crown ether sites.[2–7] Amongst the many examples of this type of phenomenon, ditopic polypyridyl–crown ether ligands prepared by the groups of Beer,[2] Yam,[4,5] and Hupp[6] are particularly relevant to the work presented here. We report here the facile synthesis of a new series of ditopic phenanthroline–crown ether ligands derived from 5,6-dihydroxy-1,10-phenanthroline, in which the two metal-ion binding sites are directly fused. Attachment of the NN chelating site to a Ru(II) fragment results in a series of $[Ru(bipy)_3]^{2+}$ derivatives with a pendant crown ether fragment capable of binding group IA and IIA metal ions. The structures of some of these complexes, and preliminary metal-ion binding studies at the peripheral macrocyclic site, are presented.

The ligands L^1 to L^5 were all prepared by reaction of 5,6-dihydroxy-1,10-phenanthroline (dhp)[8] with the appropriate poly(ethyleneglycol)-di-*p*-tosylate in *N*,*N*-dimethylformamide,† using NaH as a deprotonating agent (Scheme 1); in all cases this gave reasonable yields of the 1 : 1 adducts, with no evidence for formation of 2 + 2 (or higher) adducts. For example a 2 + 2 reaction of dhp with di(ethyleneglycol)-di-*p*-tosylate would give an 18-crown-6 core with two externally-directed phenanthroline binding sites, which might be expected if there were a significant templating effect from the Na^+ ion.[9] However the only significant products were the 1 + 1 adducts in each case (Scheme 1), despite the fact that we took no precautions to use high dilution conditions. Under these conditions, the templating effect of Na^+ is clearly limited, possibly because of competing coordination by the donor solvent (dmf). The result is a homologous series of 1 : 1 macrocyclic ligands with crown ethers ranging from 9-crown-3 (L^2) to 18-crown-6 (L^5) fused to a peripheral phenanthroline unit (ligand L^1 is too small to be classed as a macrocycle). All of the new ligands were satisfactorily characterised on the basis of their ^1H NMR and mass spectra.

The well-established metal coordination properties of crown ethers with metal ions from group IA and IIA, and of bipyridine-type fragments with an extensive variety of transition metals, should ensure that this readily-available series of ligands finds wide application as bridging ligands for polynuclear complexes. Our initial studies have been with complexes of ruthenium(II). Reaction of each new ligand with $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ in ethanol at reflux for 2 h, followed by precipitation with aqueous NH_4PF_6, afforded good yields of the complexes $[Ru(bipy)_2(L^n)][PF_6]_2$ ($n = 1$ to 5), which were satisfactorily characterised by elemental analysis and electrospray mass spectrometry.‡ Whilst these generally afforded oily precipitates when attempts were made to crystallise them, metathesis of the anion to perchlorate greatly improved matters and we were able to obtain crystals of complexes $[Ru(bipy)_2(L^n)][ClO_4]_2$ ($n = 1, 3, 5$). The structures of these complex cations are shown in Fig. 1; crystallographic data are collected in Table 1.§ The structures of the $[Ru(bipy)_3]^{2+}$ core of each complex show little variation, with Ru–N distances being in the typical range for a $[Ru(bipy)_3]^{2+}$-type core (2.04–2.08 Å). Of more significance are the pendant crown ether fragments, which—as is usual for crown ethers—are more or less preorganised for metal-ion binding.[9] The ability of these cavities to act as ligands for secondary metal ions is illustrated by the structure of $[Ru(bipy)_2(L^4)\{Li(MeCN)\}][ClO_4]_3$ (Fig. 2),¶ which was prepared by recrystallising $[Ru(bipy)_2(L^4)][PF_6]_2$ from MeCN in which $LiClO_4$ was also dissolved. Apart from the unremarkable $[Ru(bipy)_3]^{2+}$ core, the Li^+ ion is six-coordinate, bonding to the pentadentate 15-crown-5



Scheme 1

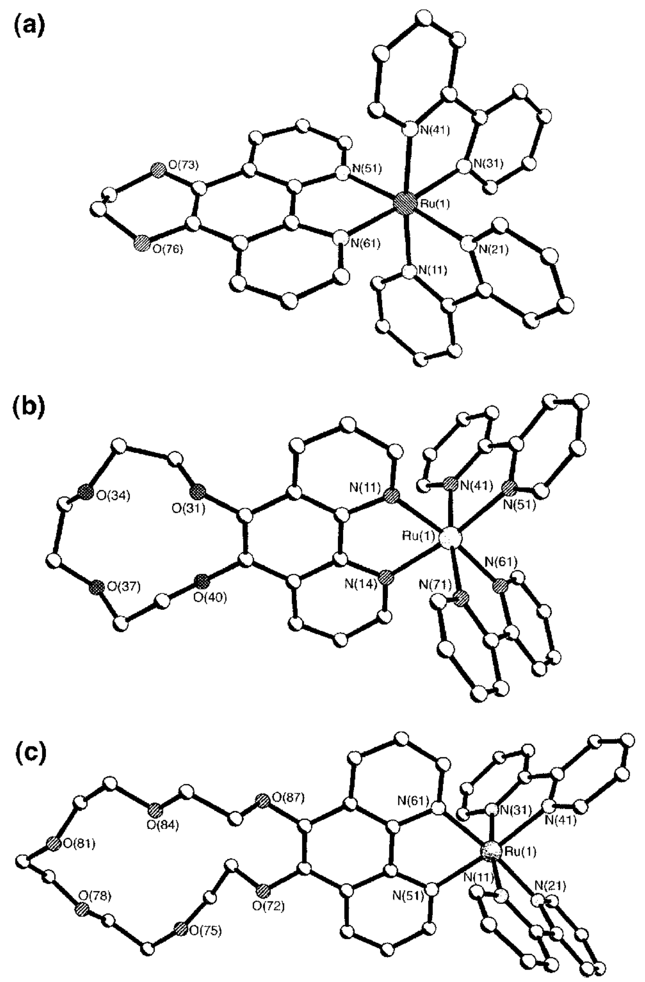


Fig. 1 Structures of the complex cations of (a) $[Ru(bipy)_2(L^1)][ClO_4]_2$, (b) $[Ru(bipy)_2(L^3)][ClO_4]_2$, and (c) $[Ru(bipy)_2(L^5)][ClO_4]_2$. The geometries of the $[Ru(bipy)_3]^{2+}$ cores are unremarkable, with all Ru–N distances lying in the normal range, 2.04–2.08 Å.

fragment and an additional molecule of MeCN. The Li^+ ion clearly has strong interactions with the acetonitrile N donor N(91) and oxygen donors O(75) and O(81) of the macrocycle, as all of these Li–ligand distances are *ca.* 2.0 Å. The interactions with O(78), O(84) and O(72) are progressively weaker with Li–O separations of 2.225(9), 2.384(9) and 2.601(9) Å, respectively. This irregularity in Li–O separations, including some rather long bonds, is characteristic of the very limited number of Li^+ complexes with 15-crown-5 and its derivatives that have been structurally characterised.[10–13] Despite the irregularity in the bond distances, the coordination geometry about the Li^+ ion may be described as approximately octahedral on the basis of the bond angles, with the 12 'right angles' falling between 79 and 97°, and the angles involving the three *trans* pairs of ligands all being over 170°.

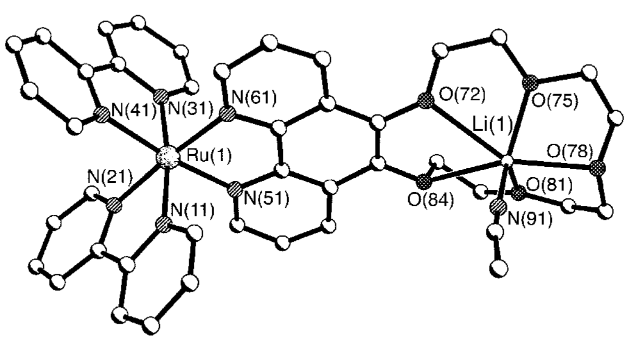


Fig. 2 Structure of the complex cation of $[Ru(bipy)_2(L^4)\{Li(MeCN)\}][ClO_4]_3$. Selected bond distances (Å) and angles (°) are as follows. Ru(1)–N(31), 2.055(4); Ru(1)–N(61), 2.063(4); Ru(1)–N(51), 2.063(3); Ru(1)–N(11), 2.064(4); Ru(1)–N(21), 2.068(4); Ru(1)–N(41), 2.070(3); Li(1)–N(91), 1.974(11); Li(1)–O(81), 1.990(9); Li(1)–O(75), 2.007(9); Li(1)–O(78), 2.225(9); Li(1)–O(84), 2.384(9); Li(1)–O(72), 2.601(9): N(91)–Li(1)–O(81), 121.8(5); N(91)–Li(1)–O(75), 122.8(5); O(81)–Li(1)–O(75), 112.1(5); N(91)–Li(1)–O(78), 95.8(4); O(81)–Li(1)–O(78), 77.0(3); O(75)–Li(1)–O(78), 78.0(3); N(91)–Li(1)–O(84), 96.7(4); O(81)–Li(1)–O(84), 71.1(3); O(75)–Li(1)–O(84), 118.5(5); O(78)–Li(1)–O(84), 147.7(4); N(91)–Li(1)–O(72), 87.5(4); O(81)–Li(1)–O(72), 130.3(5); O(75)–Li(1)–O(72), 70.5(3); O(78)–Li(1)–O(72), 144.3(4); O(84)–Li(1)–O(72), 66.0(2).

The crystal structure depicted in Fig. 2 confirms the ability of these ditopic bridging ligands to form heterodinuclear complexes and, accordingly, we were interested to see how the properties of the $[Ru(bipy)_3]^{2+}$ core would be perturbed by the presence of the additional metal ion. As a representative example we examined the redox properties of $[Ru(bipy)_2(L^5)]^{2+}$ as a function of the concentration of Ba^{2+}. We chose this because (i) Ba^{2+} is known to have a high affinity for the 18-crown-6 unit, both because of the good size match and its relatively high positive charge;[9] and (ii) the higher charge density of Ba^{2+} compared to *e.g.* Na^+ or K^+

Table 1 Crystallographic data[a]

Compound	$[Ru(bipy)_2(L^1)][ClO_4]_2 \cdot MeCN$	$[Ru(bipy)_2(L^3)][ClO_4]_2 \cdot 4MeCN$	$[Ru(bipy)_2(L^5)][ClO_4]_2 \cdot MeCN$	$[Ru(bipy)_2(L^4)\{Li(MeCN)\}][ClO_4]_3 \cdot 3MeCN$
Formula	$C_{36}H_{29}Cl_2N_7O_{10}Ru$	$C_{46}H_{46}Cl_2N_{10}O_{12}Ru$	$C_{44}H_{45}Cl_2N_7O_{14}Ru$	$C_{48}H_{50}Cl_3LiN_{10}O_{17}Ru$
FW	891.63	1102.90	1067.84	1253.34
System, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1$	Triclinic, $P\bar{1}$
a/Å	8.7139(4)	11.830(4)	12.748(4)	12.485(2)
b/Å	12.6362(5)	13.271(5)	13.181(4)	13.085(4)
c/Å	16.8896(7)	17.791(6)	13.847(4)	17.988(4)
α/°	81.778(1)	97.664(6)	90	71.249(14)
β/°	80.395(1)	92.213(6)	107.04(3)	76.915(16)
γ/°	78.851(1)	115.897(6)	90	82.05(2)
U/Å^3	1787.22(13)	2475.6(15)	2224.6(11)	2703.8(11)
Z	2	2	2	2
μ/mm^{-1}	0.659	0.496	0.550	0.518
Reflections collected:				
total, independent, R_{int}	18 754, 8108, 0.0285	25 957, 11 238, 0.0739	14 570, 9568, 0.0341	28 774, 12 322, 0.0377
Data, restraints, parameters	8108, 0, 535	11 238, 0, 611	9568, 37, 615	12 322, 3, 749
Final R_1, wR_2[c]	0.0356, 0.0932	0.0525, 0.1252	0.0550, 0.1469	0.0633, 0.1932

[a] Details in common: diffractometer, Siemens SMART using Mo-Kα radiation (0.710 73 Å); temperature of data collection, 173 K. [b] Structure was refined on F_0^2 using all data; the value of R_1 is given for comparison with older refinements based on F_0 with a typical threshold of $F \geq 4\sigma(F)$. [c] $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2]^{1/2}$ where $w^{-1} = [\sigma^2(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

would maximise the likelihood of seeing a perturbation of the properties of the $[\mathrm{Ru(bipy)_3}]^{2+}$ core.

$[\mathrm{Ru(bipy)_2(L^5)}][\mathrm{PF_6}]_2$ shows the typical redox properties of a $[\mathrm{Ru(bipy)_3}]^{2+}$ derivative, with a Ru(II)/Ru(III) couple at −0.89 V *vs.* ferrocene/ferrocenium ($\mathrm{Fc/Fc^+}$), and three ligand-centred couples at −1.74, −1.93 and −2.17 V *vs.* $\mathrm{Fc/Fc^+}$ in MeCN (the other complexes show essentially identical behaviour). On addition of $\mathrm{Ba^{2+}}$ to the solution, the ligand-centred reductions become rather broad and ill-defined, but the Ru(II)/Ru(III) couple undergoes a gradual positive shift to +0.94 V after addition of *ca.* 10 equivalents of $\mathrm{Ba^{2+}}$, a shift of 50 mV. Clearly, binding of $\mathrm{Ba^{2+}}$ at the 18-crown-6 site causes a slight electrostatic destabilisation of the Ru(III) state. The effect is rather modest, but is in the same range observed by Beer and co-workers.[2,14] and Yam and co-workers.[4,5] for related redox-responsive systems based on attachment of group 1A or IIA metal ions to pendant crown ethers. More detailed studies on this effect are in progress.

We also attempted to investigate the effects of secondary metal-ion binding on the optical spectroscopic properties of the complexes; however this was less successful. Addition of $\mathrm{Ba^{2+}}$ (up to 5 equivalents) to a sample of $[\mathrm{Ru(bipy)_2(L^5)}][\mathrm{PF_6}]_2$ resulted in no significant change of either the ^{1}MLCT absorption maximum at 451 nm, or of the ^{3}MLCT emission at 610 nm.

In conclusion, we have described a simple synthesis of a homologous series of new ligands in which a crown ether macrocycle is attached to an externally-directed phenanthroline fragment. Such ditopic ligands have clear promise for the preparation of heterodinuclear complexes in which there are electronic interactions between the two metal centres. One such complex, $[\mathrm{Ru(bipy)_2(L^5)}][\mathrm{PF_6}]_2$, shows a small but significant change in its redox behaviour in the presence of $\mathrm{Ba^{2+}}$. Studies extending the use of these ligands to other redox-active or luminescent complexes are in progress.

Acknowledgements

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Notes and references

† The following synthesis of $\mathrm{L^5}$ is typical. To a stirred solution of 5,6-dihydroxy-1,10-phenanthroline (0.26 g, 1.24 mmol) in dry DMF (8 cm^3) under $\mathrm{N_2}$ was added NaH (0.10 g of 60% mineral oil dispersion, 2.5 mmol) and the mixture was stirred for 5 min. Then, a solution of pentaethyleneglycol-ditosylate (0.67 g, 1.22 mmol) in degassed DMF (7 cm^3) was added and the mixture was stirred at 80 °C for 18 h. The solvent was then removed *in vacuo*, water (25 cm^3) was added, and the suspension was extracted with several small portions of $\mathrm{CH_2Cl_2}$ which were combined and dried over $\mathrm{MgSO_4}$, before evaporation to dryness *in vacuo* to give a brown oil. Chromatography on silica with $\mathrm{CH_2Cl_2}$–MeOH (90 : 10, v/v) afforded pure $\mathrm{L^5}$ as a yellow oil in 50% yield.

The other ligands $\mathrm{L^1}$–$\mathrm{L^4}$ were prepared in exactly the same way, but using the ditosylate of mono-, di-, tri- or tetra-ethylene glycol (1 equiv. with respect to 5,6-dihydroxy-1,10-phenanthroline), respectively. Yields were in the range 40–60% in every case. Significant characterisation data are summarised below. All NMR spectra were recorded in $\mathrm{CDCl_3}$. $\mathrm{L^1}$. EIMS: *m/z* 238 (95%, M^+), 182 (100%). ^{1}H NMR: δ 9.07 (2H, dd, *J* 4.3, 1.6; phen H^2/H^9), 8.44 (2H, dd, *J* 8.2, 1.6; phen H^4/H^7), 7.60 (2H, dd, *J* 8.2, 4.3 Hz; phen H^3/H^8), 4.54 (4H, s; $\mathrm{CH_2}$).

$\mathrm{L^2}$. EIMS: *m/z* 282 (80%, M^+), 182 (100%). ^{1}H NMR: δ 9.00 (2H, dd, *J* 4.3, 1.6; phen H^2/H^9), 8.44 (2H, dd, *J* 8.2, 1.6; phen H^4/H^7), 7.55 (2H, dd, *J* 8.2, 4.3 Hz; phen H^3/H^8), 4.52 (4H, m; $\mathrm{CH_2}$), 3.98 (4H, m; $\mathrm{CH_2}$).

$\mathrm{L^3}$. EIMS: *m/z* 326 (60%, M^+), 182 (100%). ^{1}H NMR: δ 9.12 (2H, dd, *J* 4.3, 1.6; phen H^2/H^9), 8.54 (2H, dd, *J* 8.2, 1.6; phen H^4/H^7), 7.64 (2H, dd, *J* 8.2, 4.3 Hz; phen H^3/H^8), 4.44 (4H, m; $\mathrm{CH_2}$), 4.05 (4H, m; $\mathrm{CH_2}$), 3.90 (4H, s; $\mathrm{CH_2}$).

$\mathrm{L^4}$. EIMS: *m/z* 370 (40%, M^+), 182 (100%). ^{1}H NMR: δ 9.12 (2H, dd, *J* 4.3, 1.6; phen H^2/H^9), 8.56 (2H, dd, *J* 8.2, 1.6; phen H^4/H^7), 7.62 (2H, dd, *J* 8.2, 4.3 Hz; phen H^3/H^8), 4.46 (4H, m; $\mathrm{CH_2}$), 4.10 (4H, m; $\mathrm{CH_2}$), 3.81 (8H, m; $\mathrm{CH_2}$).

$\mathrm{L^5}$. EIMS: *m/z* 414 (70%, M^+), 182 (100%). ^{1}H NMR: δ 9.11 (2H, dd, *J* 4.3, 1.6; phen H^2/H^9), 8.59 (2H, dd, *J* 8.2, 1.6; phen H^4/H^7), 7.63 (2H, dd, *J* 8.2, 4.3 Hz; phen H^3/H^8), 4.45 (4H, m; $\mathrm{CH_2}$), 4.04 (4H, m; $\mathrm{CH_2}$), 3.82 (8H, m; $\mathrm{CH_2}$), 3.72 (4H, s; $\mathrm{CH_2}$).

‡ The following synthesis of $[\mathrm{Ru(bipy)_2(L^5)}][\mathrm{PF_6}]_2$ is typical. To a solution of $\mathrm{L^5}$ (0.035 g, 0.094 mmol) in EtOH (25 cm^3) was added $[\mathrm{Ru(bipy)_2Cl_2}]\cdot 2\mathrm{H_2O}$ (0.050 g, 0.096 mmol) and the reaction mixture heated to reflux for 2 h. After this time the reaction mixture was cooled and the solvent evaporated *in vacuo*. The pure complex was obtained by column chromatography on silica, using MeCN–$\mathrm{H_2O}$–saturated aqueous $\mathrm{KNO_3}$ (10 : 2 : 1, v/v) as eluent; the major orange band was collected, concentrated *in vacuo*, and the complex precipitated by addition of aqueous $\mathrm{NH_4PF_6}$. After filtration and drying, the complex was recrystallised from MeCN–$\mathrm{Et_2O}$ to give $[\mathrm{Ru(bipy)_2(L^5)}][\mathrm{PF_6}]_2$ in 40% yield.

Complexes with the other ligands $\mathrm{L^1}$–$\mathrm{L^4}$ were prepared in a similar manner in yields of typically 40–55%. Electrospray mass spectra in MeCN showed, in every case, a strong peak corresponding to the $[\mathrm{Ru(bipy)_2(L^{\mathit{n}})}]^{2+}$ dication, as follows: $n = 1$, $m/z = 326$; $n = 2$, $m/z = 349$; $n = 3$, $m/z = 370$; $n = 4$, $m/z = 391.5$; $n = 5$, $m/z = 416$. Satisfactory elemental analyses were obtained for all of the complexes.

§ Diffraction intensity data were collected on a Siemens SMART-CCD diffractometer. The software used was SHELXS-97 for structure solution,[15] SHELXL-97 for structure refinement,[15] and SADABS for the absorption correction.[16] Details of the crystal parameters, data collection and refinement are collected in Table 1. Structure solution and refinement was generally straightforward, apart from problems associated with disordered solvent molecules/anions, which will be discussed in more detail in a subsequent full paper. CCDC reference number 440/241. See htlp: www.rsc.org/suppdata/nj/b0/b008378j/ for crystallographic files in .cif format.

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