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Stepwise synthetic strategy for the preparation of trinuclear complexes of bis(terpyridyl) bridging ligands containing aza-crown macrocyclic spacer groups

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A synthetic strategy has been devised for the preparation of the mononuclear complex $[Ru(tpy)(L^2)][PF_6]_2$ (where L^2 is a bridging ligand containing two chelating 2,2′:6′,2″-terpyridyl fragments attached *via* tolyl spacers to the N atoms of a 1,10-diaza-18-crown-6 macrocycle), which avoids the separation of a statistical mixture of mono- and di-nuclear complexes which would arise from normal synthetic methods. Reaction of 1,10-diaza-18-crown-6 with one equivalent of 4′-[4-(bromomethyl)phenyl]terpyridine afforded L^1, in which there is one terpyridyl group pendant from the macrocycle, and the second NH site of the macrocycle is not alkylated. Reaction of L^1 with $[Ru(tpy)Cl_3]$ gave mononuclear $[Ru(tpy)(L^1)][PF_6]_2$. Subsequent reaction of this with a second equivalent of 4′-[4-(bromomethyl)phenyl]-terpyridine resulted in attachment of the second (vacant) terpyridyl chelating site by alkylation of the remaining secondary amine group in the macrocycle to give $[Ru(tpy)(L^2)][PF_6]_2$. Assembly of two of these mononuclear 'complex ligands' around first-row transition-metal dications M^{2+} (M = Fe or Ni) afforded in high yield the linear trinuclear Ru–M–Ru complexes $[\{(tpy)Ru(L^2)\}_2M][PF_6]_6$, in which the two terminal $\{Ru(tpy)_2\}^{2+}$ and the central $\{M(tpy)_2\}^{2+}$ fragments are separated by diaza-18-crown-6 units. Electrospray mass spectrometry proved a very useful characterisational tool in all cases, showing a variety of charged species arising from both loss of anions and protonation of the basic amine sites in the aza-crown macrocycles: for $[\{(tpy)Ru(L^2)\}_2Fe][PF_6]_6$ for example intact complex cations were observed with charges of up to +9 (from loss of all six anions, and triple protonation). The mononuclear complexes $[Ru(tpy)(HL^1)][ClO_4]_2[PF_6]\cdot 2MeCN\cdot Et_2O\cdot H_2O$ and $[Ru(tpy)(L^2)][PF_6]_2\cdot 0.7HPF_6\cdot 0.3Et_2O\cdot MeCN\cdot 1.5H_2O$ were crystallographically characterised. Electrochemical and electronic spectroscopic studies show that the $\{Ru(tpy)_2\}^{2+}$ and $\{M(tpy)_2\}^{2+}$ components of the trinuclear complexes are essentially electronically isolated.

Introduction

Bridging ligands containing two 2,2′:6′,2″-terpyridyl chelating fragments linked by a spacer group (tpy–X–tpy) have recently been of particular interest for a variety of reasons, including: (i) the study of intramolecular photoinduced energy transfer between luminescent ruthenium(II) and osmium(II) termini as a function of the spacer group X;[1,2] (ii) the study of intervalence electron transfer as a function of the bridging pathway in homodinuclear mixed-valence complexes;[3,4] and (iii) the preparation of polynuclear complexes having predictable linear structures in which there are no problems with geometric and optical isomerism of the highly symmetric metal complex fragments.[2,4–6] We recently described the synthesis of a bridging ligand L^2 (see Scheme 1), in which two terpyridyl termini are separated by a diaza-18-crown-6 macrocyclic group, and the synthesis and crystal structure of its homodinuclear complex $[\{Ru(tpy)\}_2(\mu\text{-}H_2L^2)][PF_6]_6$.[7] Our interest in this (and related) ligands was prompted by the fact that such hybrid ligands, containing oligopyridyl and macrocyclic components, have been exploited in many areas including the development of luminescent[8] or electrochemical[9] sensors, molecular recognition[10] and photocatalysis.[11] Of particular interest to us is the possibility that incorporation of a metal ion in the macrocyclic cavity may allow access to a variety of new chromophore/quencher complexes.[12]

However, to use L^2 to make hetero-dinuclear and -polynuclear complexes requires, as with all such dinucleating bridging ligands, preparation of a mononuclear complex in which one of the terpyridyl sites is vacant, for use as a 'complex ligand'. The usual way to prepare these is to control the reaction stoichiometry, such that reaction of the dinucleating bridging ligand with one equivalent of a metal ion would afford predominantly a mononuclear complex.[1,13] Traces of the dinuclear complex and the unchanged ligand, which are inevitable by-products, can generally be removed chromatographically because the difference in charges between the species means that they separate well. However this does not always work, and in such cases (as here) an alternative strategy must be found. Denti and co-workers[14] have used a protective-group strategy for the controlled stepwise synthesis of high-nuclearity dendrimeric complexes containing both ruthenium(II) and osmium(II) chromophores, in which one of the two binding sites of the bridging ligand is blocked with a suitable protecting group, the metal ion is attached to the single vacant site, and then the protecting group is removed to liberate the second site which is now available for further co-ordination. In contrast, Constable *et al.*[5] solved this problem by attachment of a second terpyridyl fragment to a pre-formed mononuclear complex with a suitable peripheral functional group, thereby completing formation of the bridging ligand after incorporation of the first metal ion. In this paper we describe a strategy for the preparation of the mononuclear 'complex ligand' $[Ru(tpy)(L^2)][PF_6]_2$, and the use of this to prepare heterotrinuclear complexes $[\{(tpy)Ru(L^2)\}_2M][PF_6]_6$ (M = Fe or Ni) which contain three metal–bis(terpyridyl) units in a linear chain. The spectroscopic, structural and electrochemical properties of these complexes are described.

Experimental

General details

The complex $[Ru(tpy)Cl_3]$,[15] 4′-[4-(bromomethyl)phenyl]-

terpyridine[16] (Br-toltpy) and 4′-(4-methylphenyl)terpyridine (tol-tpy)[16] were prepared according to the published methods; all other reagents were commercially available and used as received. Instruments used for routine spectroscopic and electrochemical analysis have been described in previous papers.[13]

Preparations

L^1. A mixture of Br-toltpy (1.00 g, 2.48 mmol), 1,10-diaza-18-crown-6 (0.652 g, 2.48 mmol) and $^iPr_2EtN$ (2.2 cm^3, 12.4 mmol) in ethanol (80 cm^3) was heated to reflux for 2 h. After cooling, addition of a few drops of water resulted in precipitation of the bis(terpyridyl) by-product L^2 as a white powder, which was filtered off. The filtrate (containing the more soluble L^1) was evaporated to dryness and the residue purified by column chromatography on alumina (Brockmann activity III) using CH_2Cl_2 containing 1% MeOH as eluent. Compound L^1 was obtained as a pale brown oil which slowly solidified on prolonged drying. Yield: 45% of L^1, with 21% of L^2 also isolated as a by-product. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75–8.70 (4 H, m; $H^{3'}/H^{5'}$ and $H^6/H^{6''}$), 8.68 (2 H, d, J = 7.8; $H^3/H^{3''}$), 7.92–7.82 (4 H, m; $H^4/H^{4''}$ and phenyl H^2/H^6), 7.49 (2 H, d, J = 8.2; phenyl H^3/H^5), 7.36 (2 H, ddd, J = 7.5, 4.8, 1.2 Hz; $H^5/H^{5''}$), 3.76 (2 H, s; $C_6H_4CH_2N$), 3.72 (4 H, m; crown CH_2), 3.65–3.55 (12 H, m; crown CH_2), 2.93 (4 H, t; crown CH_2) and 2.83 (4 H, t; crown CH_2) (Found: C, 65.8; H, 7.2; N, 11.2. $L^1 \cdot 2H_2O$ requires C, 65.9; H, 7.3; N, 11.3%). EI-MS: m/z 583 (50, M^+) and 322 (100%, tpy–$C_6H_4CH_2$).

$[Ru(tpy)(L^1)][PF_6]_2 \cdot 2HPF_6$. A mixture of L^1 (0.200 g, 0.34 mmol), $[Ru(tpy)Cl_3]$ (0.166 g, 0.38 mmol) and *N*-methylmorpholine (a few drops) in MeOH (50 cm^3) was heated to reflux for 3 h. After cooling the mixture was filtered to remove solid by-products, and aqueous NH_4PF_6 added. Concentration *in vacuo* resulted in precipitation of the crude product, which was filtered off. Purification was by column chromatography on flash silica using MeCN–water–saturated aqueous KNO_3 (16 : 2 : 1, v/v) as eluent. The major orange band was collected and an excess of NH_4PF_6 added. Concentration *in vacuo* resulted in precipitation of the product which was filtered off and dried, and finally recrystallised by diffusion of diethyl ether vapour into a concentrated MeCN solution. Yield: 0.251 g, 50% {Found: C, 39.3; H, 3.7; N, 7.8. $[Ru(tpy)(L^1)][PF_6]_2 \cdot 2HPF_6$ requires C, 39.3; H, 3.6; N, 7.5%}. ^{1}H NMR (300 MHz, CD_3CN): δ 9.01 (2 H, s; L^1 $H^{3'}/H^{5'}$), 8.76 (2 H, d, J = 8.1; tpy $H^{3'}/H^{5'}$), 8.65 (2 H, d, J = 7.7; L^1 $H^3/H^{3''}$), 8.50 (2 H, d, J = 7.7; tpy $H^3/H^{3''}$), 8.43 (1 H, t, J = 8.1; tpy $H^{4'}$), 8.31 (2 H, d, J = 8.2; phenyl H^2/H^6), 7.86–7.98 (6 H, m; L^1 $H^4/H^{4''}$, tpy $H^4/H^{4''}$ and phenyl H^3/H^5), 7.42 (2 H, br d, J = 5.7; tpy $H^6/H^{6''}$), 7.37 (2 H, br d, J = 5.5 Hz; L^1 $H^6/H^{6''}$), 7.12–7.22 (4 H, m; L^2 $H^5/H^{5''}$ and tpy $H^5/H^{5''}$), 4.65 (2 H, s; $C_6H_4CH_2N$), 3.90 (4 H, br m; crown CH_2), 3.78 (4 H, t; crown CH_2), 3.69 (8 H, s; crown CH_2), 3.50 (4 H, br s; crown CH_2) and 3.33 (4 H, br s; crown CH_2).

$[Ru(tpy)(L^2)][PF_6]_2 \cdot HPF_6$. To a solution of $[Ru(tpy)(L^1)][PF_6]_2 \cdot 2HPF_6$ (0.246 g, 0.164 mmol) in MeCN (30 cm^3) was added a solution of Br-toltpy (0.066 g, 0.164 mmol) and $^iPr_2EtN$ (0.14 cm^3, 0.8 mmol) in CH_2Cl_2 (10 cm^3). The mixture was heated to reflux with stirring for 1.5 h, after which time a further portion of Br-toltpy (0.066 g, 0.164 mmol) dissolved in CH_2Cl_2 (10 cm^3) was added and the mixture heated to reflux for 1.5 h. After cooling, aqueous NH_4PF_6 was added and the mixture concentrated *in vacuo* until the complex precipitated, after which it was filtered off, washed with water, and dried. The crude product was dissolved in MeCN (5 cm^3) and diethyl ether added dropwise until the solution became turbid. After cooling to −20 °C overnight the supernatant solution was decanted off the precipitate of the product, which was recrystallised by diffusion of diethyl ether vapour into a concentrated MeCN solution. Yield: 0.247 g, 88% {Found: C, 49.8; H, 4.4; N, 8.8. $[Ru(tpy)(L^2)][PF_6]_2 \cdot HPF_6$ requires C, 49.8; H, 4.2; N, 9.0%}. ^{1}H NMR spectrum: see Results and discussion section.

$[\{(tpy)Ru(L^2)\}_2M][PF_6]_6 \cdot nHPF_6$. To a solution of $[Ru(tpy)(HL^2)][PF_6]_3$ (0.050 g, 29.9 μmol) in MeCN (10 cm^3) was added dropwise a solution of either $FeSO_4$ (20 μmol) in MeOH (2 cm^3), or $NiSO_4$ (20 μmol) in water (2 cm^3), as appropriate. After stirring the solution for 0.5 h, aqueous NH_4PF_6 was added and the mixture concentrated *in vacuo* until the product precipitated. The solid was filtered off, washed with water and dried, and finally recrystallised from MeCN–Et_2O as described above. Yields are approximately 90%.

M = Fe (Found: C, 44.1; H, 3.3; N, 8.3. $[\{(tpy)Ru(L^2)\}_2Fe][PF_6]_6 \cdot 3HPF_6$ requires C, 44.4; H, 3.6; N, 8.0%). ^{1}H NMR (300 MHz, CD_3CN): δ 9.20 (4 H, s; L^2 $H^{3'a}/H^{5'a}$), 9.02 (4 H, s; L^2 $H^{3'b}/H^{5'b}$), 8.77 (4 H, d, J = 8.3; tpy $H^{3'}/H^{5'}$), 8.65 (8 H, m; L^2 $H^{3a}/H^{3''a}$ and $H^{3b}/H^{3''b}$), 8.51 (4 H, d, J = 7.7; tpy $H^3/H^{3''}$), 8.42 (2 H, t, J = 8.2; tpy $H^{4'}$), 8.39 (4 H, d, J = 8.1; phenyl H^{2a}/H^{6a}), 8.28 (4 H, d, J = 8.0; phenyl H^{2b}/H^{6b}), 7.98–7.84 (20 H, m; phenyl H^{3a}/H^{5a} and H^{3b}/H^{5b}, L^2 $H^{4a}/H^{4''a}$ and $H^{4b}/H^{4''b}$, and tpy $H^4/H^{4''}$), 7.43 (4 H, d, J = 5.6; tpy $H^6/H^{6''}$), 7.37 (4 H, d, J = 5.6; L^2 $H^{6b}/H^{6''b}$), 7.23–7.05 (16 H, m; tpy $H^5/H^{5''}$, and L^2 $H^{5a}/H^{5''a}$, $H^{6a}/H^{6''a}$ and $H^{5b}/H^{5''b}$), 4.32 (8 H, br s, $C_6H_4CH^a_2N$ and $C_6H_4CH^b_2N$), 3.88 (16 H, br s, crown CH_2), 3.72 (16 H, s, crown CH_2) and 3.23 (16 H, br s, crown CH_2).

M = Ni (Found: C, 43.1; H, 3.8; N, 7.6. $[\{(tpy)Ru(L^2)\}_2Ni][PF_6]_6 \cdot 4HPF_6$ requires C, 42.7; H, 3.5; N, 7.7%). ^{1}H NMR spectrum: see Results and discussion section.

Electrospray (ES) mass spectroscopic data for all of the new complexes are summarised in Table 1.

X-Ray crystallography

Suitable crystals were quickly transferred from the mother-liquor to a stream of cold N_2 on a Siemens SMART diffractometer fitted with a CCD-type area detector. Data were collected at −100 or −150 °C using graphite-monochromatised Mo-Kα radiation. Table 2 contains a summary of the crystal parameters, data collection and refinement. The structures were solved by conventional heavy-atom or direct methods and refined by the full-matrix least-squares method on all F^2 data using the SHELXTL 5.03 package on a Silicon Graphics Indy computer.[17] Empirical absorption corrections were applied to the integrated data using SADABS.[18] Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atom.

The complex $[Ru(tpy)(L^1)][PF_6]_2 \cdot 2HPF_6$ did not on its own afford X-ray quality crystals, but addition of $BaClO_4$ to a solution of the complex in MeCN, followed by diffusion of diethyl ether vapour into the solution, afforded a few crystals of $[Ru(tpy)(HL^1)][ClO_4]_2[PF_6] \cdot 2MeCN \cdot Et_2O \cdot H_2O$. Recrystallisation of $[Ru(tpy)(L^2)][PF_6]_2 \cdot HPF_6$ in the same way from MeCN–diethyl ether afforded crystals of $[Ru(tpy)(L^2)][PF_6]_2 \cdot 0.7HPF_6 \cdot 0.3Et_2O \cdot MeCN \cdot 1.5H_2O$. In both cases the crystals were very thin plates and lost solvent rapidly on removal from the mother-liquor; they consequently diffracted poorly. The quality of the structural determinations is therefore modest ($R1$ values of 0.104 and 0.133 respectively) but the gross structures of the complexes are perfectly clear.

In $[Ru(tpy)(HL^1)][ClO_4]_2[PF_6] \cdot 2MeCN \cdot Et_2O \cdot H_2O$ all of the components except the ether molecule are well behaved and were located and refined without problems. An area containing numerous electron-density peaks in an irregular pattern was approximated as a disordered ether molecule, with three of the atoms having site occupancies of 100% and the other two being disordered over two sites with 50% occupancy in each site. Geometric restraints were applied to the ether molecule to keep

its geometry reasonable; in addition the thermal parameters of all atoms were restrained to be similar to those of their immediate neighbours.

In the structure of $[Ru(tpy)(L^2)][PF_6]_2 \cdot 0.7HPF_6 \cdot 0.3Et_2O \cdot MeCN \cdot 1.5H_2O$ the complex cation, the two entire hexafluorophosphate anions and the solvent MeCN and H_2O molecules were all well behaved. The asymmetric unit also contained a mass of electron-density peaks close together, which were approximated as a disordered mixture of another hexafluorophosphate anion (70% site occupancy), an ether molecule (30% site occupancy), and a water molecule (50% site occupancy). There is evidence for additional geometric disorder of the partial hexafluorophosphate anion but we made no attempt to model this. The largest residual electron-density peaks were associated with this disordered mixture of components. Owing to the complexity of the structure and the comparative weakness of the data, numerous restraints were used to keep the refinement stable: *viz.* (i) all aromatic rings were restrained to be flat with all C–C distances similar and all C–N distances similar; (ii) thermal parameters of all atoms were restrained to be similar to those of their immediate neighbours; (iii) geometric restraints were applied to the disordered hexafluorophosphate anion/ether molecule.

CCDC reference number 186/1129.

See http://www.rsc.org/suppdata/dt/1998/3397/ for crystallographic files in .cif format.

Results and discussion

Attempts to prepare mononuclear $[Ru(tpy)(L^2)][PF_6]_2$ by reaction of L^2 with one equivalent of $[Ru(terpy)Cl_3]$ in the normal way afforded a mixture that does contain some $[Ru(tpy)(L^2)]^{2+}$ [as shown by electrospray (ES) mass spectrometry], and also (inevitably) contains dinuclear $[\{Ru(tpy)\}_2(\mu\text{-}L^2)]^{4+}$ as well as unchanged L^2. However the mixture is not amenable to chromatographic separation: $[Ru(tpy)(L^2)]^{2+}$ adheres immovably to both silica and alumina, and use of lipophilic Sephadex did not in our hands give a very satisfactory separation between the components. Accordingly we developed a different strategy which is outlined in Scheme 1, and takes advantage of the fact that 1,10-diaza-18-crown-6 can be readily mono-*N*-alkylated, which allows an unambiguous step-by-step assembly of the mononuclear complex ligand with no difficult separations or purifications required.

$[Ru(tpy)(L^1)][PF_6]_2$

The compound L^1 was prepared by reaction of br-toltpy with 1,10-diaza-18-crown-6 in a 1:1 stoichiometry in ethanol and $^iPr_2EtN$; it contains one terpyridyl binding site, and one unchanged secondary amine site in the macrocyclic ring available for alkylation later. Assuming a statistically normal product distribution we would expect a 50% yield of L^1, 25% yield of doubly alkylated L^2 and 25% of unchanged 1,10-diaza-18-crown-6, which may be compared with our isolated yields of 45% for L^1 and 21% of L^2. Separation of L^1 from L^2 was simple because of their very different solubilities, and L^1 was readily characterised on the basis of its mass and ^1H NMR spectra.

Reaction of L^1 with $[Ru(tpy)Cl_3]$ in MeOH, in the presence of *N*-methylmorpholine to assist with reduction of Ru^{III} to Ru^{II}, afforded after chromatographic purification and recrystallisation a material analysing as $[Ru(tpy)(L^1)][PF_6]_2 \cdot 2HPF_6$, suggesting that both of the basic amine groups of the macrocycle were protonated to give a tetracation. This highlights a common problem in the characterisation of these compounds: variable degrees of protonation and the consequent presence of additional anions can make it difficult to obtain repeatable elemental analyses, and can also complicate the crystallography (see later). The ^1H NMR spectrum of the complex was fully assigned with the assistance of ^1H–^1H correlation (COSY) spectroscopy and contains all of the signals to be expected for one tpy and one L^1 ligand at shifts characteristic of $\{Ru(tpy)_2\}^{2+}$ cores. The ES mass spectrum (Table 1) showed a variety of peaks corresponding to species with various charges arising from either loss of hexafluorophosphate anions, gain of protons, or both; in particular the peak at $m/z = 605.2$, corresponding to the species $\{Ru(tpy)(H_2L^1)(PF_6)_2\}^{2+}$, confirms that double protonation of the macrocycle can occur, in agreement with the elemental analysis.

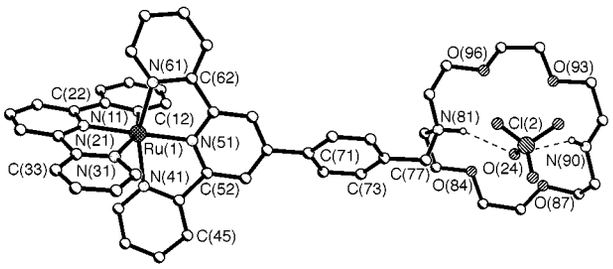
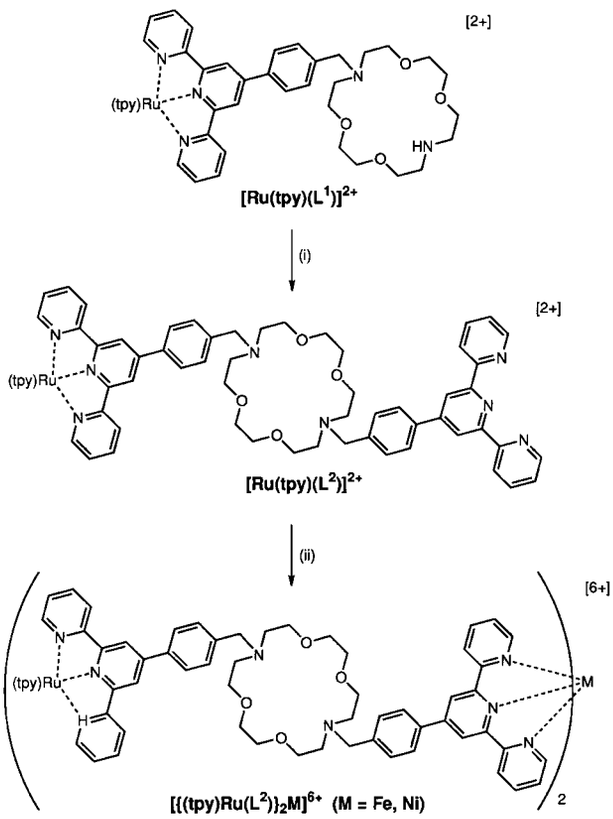


Fig. 1 Crystal structure of the cation of $[Ru(tpy)(HL^1)][ClO_4]_2[PF_6] \cdot 2MeCN \cdot Et_2O \cdot H_2O$ and the hydrogen-bonded perchlorate anion.



Scheme 1 (i) Br-toltpy, $^iPr_2EtNH$–MeCN–CH_2Cl_2, reflux; (ii) M^{2+}, MeCN.

We could not obtain X-ray quality crystals of $[Ru(tpy)(L^1)][PF_6]_2$ (in any of its protonated forms), but addition of a small amount of $Ba(ClO_4)_2$ to the recrystallisation mixture afforded a few crystals of what proved to be $[Ru(tpy)(HL^1)][ClO_4]_2[PF_6] \cdot 2MeCN \cdot Et_2O \cdot H_2O$, whose crystal structure is in Fig. 1. Owing to the small, weakly diffracting crystals, rapid solvent loss and the presence of substantial disorder involving solvent molecules, common problems in structure determinations of compounds of this sort, the level of refinement is poor, but the gross structure of the complex is quite clear. The $\{Ru(tpy)_2\}^{2+}$ core has the normal pseudo-octahedral geometry, with the bonds to the two central pyridyl rings (average 2.00 Å) being shorter than those to the four terminal pyridyl rings (average 2.08 Å). The presence of three anions means that an

Table 1 Electrospray mass spectrometric data for the complexes

Complex	*m/z**	Intensity (%)	Assignment
$[Ru(tpy)(L^1)][PF_6]_2$	1208.8 (1209.0)	10	$\{M + H^+\}^+$
	1062.9 (1063.0)	10	$\{M - [PF_6]^-\}^+$
	605.2 (605.0)	5	$\{M + 2H^+\}^{2+}$
	532.0 (532.0)	30	$\{M + H^+ - [PF_6]^-\}^{2+}$
	458.9 (459.0)	100	$\{M - 2[PF_6]^-\}^{2+}$
	306.2 (306.3)	35	$\{M + H^+ - 2[PF_6]^-\}^{3+}$
$[Ru(tpy)(L^2)][PF_6]_2$	1530.4 (1530.4)	5	$\{M + H^+\}^+$
	1384.7 (1384.4)	5	$\{M - [PF_6]^-\}^+$
	838.4 (838.7)	5	$\{M + [PF_6]^- + 3H^+\}^{2+}$
	765.6 (765.7)	25	$\{M + 2H^+\}^{2+}$
	692.5 (692.7)	15	$\{M + H^+ - [PF_6]^-\}^{2+}$
	619.4 (619.7)	10	$\{M - 2[PF_6]^-\}^{2+}$
	413.3 (413.5)	100	$\{M + H^+ - 2[PF_6]^-\}^{3+}$
$[\{(tpy)Ru(L^2)\}_2Fe][PF_6]_6$	1184.0 (1184.5)	4	$\{M + 4H^+ + [PF_6]^-\}^{3+}$
	1135.5 (1135.8)	6	$\{M + 3H^+\}^{3+}$
	1086.9 (1087.2)	6	$\{M + 2H^+ - [PF_6]^-\}^{3+}$
	1038.7 (1038.5)	6	$\{M + H^+ - 2[PF_6]^-\}^{3+}$
	990.2 (989.9)	5	$\{M - 3[PF_6]^-\}^{3+}$
	851.9 (852.1)	7	$\{M + 4H^+\}^{4+}$
	815.0 (815.6)	12	$\{M + 3H^+ - [PF_6]^-\}^{4+}$
	779.1 (779.1)	20	$\{M + 2H^+ - 2[PF_6]^-\}^{4+}$
	742.7 (742.6)	30	$\{M + H^+ - 3[PF_6]^-\}^{4+}$
	705.6 (706.1)	23	$\{M - 4[PF_6]^-\}^{4+}$
	651.8 (652.7)	4	$\{M + 4H^+ - [PF_6]^-\}^{5+}$
	623.5 (623.5)	23	$\{M + 3H^+ - 2[PF_6]^-\}^{5+}$
	594.1 (594.3)	33	$\{M + 2H^+ - 3[PF_6]^-\}^{5+}$
	564.3 (565.1)	29	$\{M + H^+ - 4[PF_6]^-\}^{5+}$
	535.9 (536.0)	15	$\{M - 5[PF_6]^-\}^{5+}$
	470.4 (471.1)	60	$\{M + 2H^+ - 4[PF_6]^-\}^{6+}$
	446.5 (446.8)	62	$\{M + H^+ - 5[PF_6]^-\}^{6+}$
	421.6 (422.5)	30	$\{M - 6[PF_6]^-\}^{6+}$
	382.8 (383.1)	100	$\{M + 2H^+ - 5[PF_6]^-\}^{7+}$
	361.7 (362.2)	57	$\{M + H^+ - 6[PF_6]^-\}^{7+}$
	316.6 (317.0)	98	$\{M + 2H^+ - 6[PF_6]^-\}^{8+}$
	281.9 (281.9)	9	$\{M + 3H^+ - 6[PF_6]^-\}^{9+}$
$[\{(tpy)Ru(L^2)\}_2Ni][PF_6]_6$	1185.5 (1185.5)	1	$\{M + 4H^+ + [PF_6]^-\}^{3+}$
	1136.9 (1136.8)	2	$\{M + 3H^+\}^{3+}$
	1088.2 (1088.1)	4	$\{M + 2H^+ - [PF_6]^-\}^{3+}$
	1039.5 (1039.5)	2	$\{M + H^+ - 2[PF_6]^-\}^{3+}$
	990.5 (990.8)	2	$\{M - 3[PF_6]^-\}^{3+}$
	779.9 (779.9)	4	$\{M + 2H^+ - 2[PF_6]^-\}^{4+}$
	743.3 (743.4)	8	$\{M + H^+ - 3[PF_6]^-\}^{4+}$
	706.6 (706.9)	11	$\{M - 4[PF_6]^-\}^{4+}$
	536.1 (536.5)	8	$\{M - 5[PF_6]^-\}^{5+}$
	470.6 (471.6)	11	$\{M + 2H^+ - 4[PF_6]^-\}^{6+}$
	422.7 (422.9)	100	$\{M - 6[PF_6]^-\}^{6+}$

* Calculated values in parentheses.

additional proton must be present on one of the two macrocyclic amine groups. This is indirectly confirmed by observation that one of the perchlorate anions is associated with the aza-crown macrocycle, having two very similar N···O contacts O(24)···N(81) (3.04 Å) and O(24)···N(90) (3.07 Å) which are entirely typical of N–H···O hydrogen bonds. Since this requires *both* amine sites to act as hydrogen-bond donors, the tertiary amine site [N(81)] must therefore be the site of protonation, consistent with the fact that tertiary amines are generally rather more basic than analogous secondary amines. Crown-ether and aza-crown-ether macrocycles are well known to bind a variety of neutral and anionic guests by hydrogen bonding,[19–21] and this association of perchlorate to the two protonated nitrogen groups is similar to the way in which thiocyanate and halide ions are associated with diaza-18-crown-16 derivatives.[20]

The electronic spectrum of the complex (Table 3) is as expected for a $\{Ru(tpy)_2\}^{2+}$ chromophore, with the principal $Ru[d(\pi)] \longrightarrow tpy(\pi^*)$ MLCT transition at 482 nm, and the usual intense ligand-centred transitions in the UV region. The CH_2 spacer separating the macrocyclic amine group from the $\{Ru(tpy)_2\}^{2+}$ core ensures that there is no significant electronic perturbation of the core by the electron-rich amine substituent.

$[Ru(tpy)(L^2)][PF_6]_2$

Reaction of $[Ru(tpy)(L^1)][PF_6]_2$ with another equivalent of br-toltpy in EtOH–^{i}Pr$_2$EtN results in alkylation of the remaining secondary amine site of the macrocycle to give $[Ru(tpy)(L^2)][PF_6]_2$, our target 'complex ligand' in which one terpyridyl terminus of L^2 is occupied by a $\{Ru(tpy)\}^{2+}$ fragment but the second is vacant. Following recrystallisation of the crude reaction mixture, this product was isolated as $[Ru(tpy)(L^2)][PF_6]_2 \cdot HPF_6$ (according to the elemental analysis) in 88% yield. The ES mass spectrum again is particularly informative, showing fragments having a variety of charges arising from protonation and/or loss of hexafluorophosphate anions. The peaks at *m/z* 765.6 and 838.4, corresponding to the fragments $\{Ru(tpy)(H_2L^2)(PF_6)_2\}^{2+}$ and $\{Ru(tpy)(H_3L^2)(PF_6)_3\}^{2+}$, show that the complex can become triply protonated (at least), twice at the macrocyclic amine sites and the third time presumably on one of the pyridyl rings of the pendant terpyridyl site. The ^{1}H NMR spectrum of this complex could not be fully assigned, even with two-dimensional techniques, because of the presence of three closely overlapping sets of signals from three terpyridyl groups all in different environments; however the number of chemically inequivalent proton environments, and the ratio of the integrals of aromatic to aliphatic protons, are both correct.

Table 2 Crystallographic data for the two crystal structures

	$[Ru(tpy)(HL^1)][ClO_4]_2[PF_6]\cdot 2MeCN\cdot Et_2O\cdot H_2O$	$[Ru(tpy)(L^2)][PF_6]_2\cdot 0.7HPF_6\cdot 0.3Et_2O\cdot MeCN\cdot 1.5H_2O$
Formula	$C_{57}H_{71}Cl_2F_6N_{10}O_{14}PRu$	$C_{74.22}H_{77.60}F_{16.17}N_{12}O_{5.81}P_{2.70}Ru$
M	1437.18	1722.46
System, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
T/K	173(2)	123(2)
a/Å	8.357(4)	11.417(4)
b/Å	17.697(5)	18.318(9)
c/Å	22.442(8)	20.444(9)
α/°	76.16(3)	76.40(3)
β/°	87.85(2)	88.87(5)
γ/°	81.87(2)	81.32(4)
U/Å^3	3190(2)	4107(3)
Z	2	2
D_c/g cm^{-3}	1.496	1.393
μ/mm^{-1}	0.443	0.336
Crystal size/mm	0.15 × 0.15 × 0.05	0.45 × 0.20 × 0.05
Reflections collected: total, independent, R_{int}	16835, 5931, 0.089	27129, 10662, 0.103
2θ Limit for data used/°	40	45
Data, restraints, parameters	5917, 263, 840	10656, 1123, 1047
Final $R1$, $wR2$ [a,b]	0.104, 0.319	0.133, 0.429
Weighting factors [b]	0.2005, 22.0741	0.2726, 0

[a] Structure was refined on F_o^2 using all data; the value of $R1$ is given for comparison with older refinements based on F_o with a typical threshold of $F \geqslant 4\sigma(F)$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{\frac{1}{2}}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 3 Electronic spectra of the complexes in MeCN

Complex	λ_{max}/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1})
$[Ru(tpy)(L^1)][PF_6]_2$	482 (23),[a] 308 (72), 281 (49), 272 (49)
$[Ru(tpy)(L^2)][PF_6]_2$	482 (21),[a] 307 (75), 280 (86), 274 (86)
$[\{(tpy)Ru(L^2)\}_2Fe][PF_6]_6$	567 (25),[b] 483 (36),[a] 307 (146), 284 (127)
$[\{(tpy)Ru(L^2)\}_2Ni][PF_6]_6$	794 (0.02),[c] 483 (36),[a] 308 (154), 284 (140)

[a] Ru-based MLCT transition. [b] Fe-based MLCT transition. [c] Ni-based d–d transition.

Recrystallisation of $[Ru(tpy)(L^2)][PF_6]_2\cdot HPF_6$ from MeCN–ether afforded very thin plates of what proved to be (approximately) $[Ru(tpy)(L^2)][PF_6]_2\cdot 0.7HPF_6\cdot 0.3Et_2O\cdot MeCN\cdot 1.5H_2O$. Again the structure determination is of poor quality because of problems associated with crystal decomposition, weak diffraction, and disorder but the gross structure of the complex cation is clear (Fig. 2). Apart from confirming the formulation of the complex there are three points to notice. First, the pendant terpyridyl fragment is approximately planar, with adjacent pyridyl rings being oriented mutually *transoid* to one another, which is the usual preferred conformation of non-co-ordinated oligopyridyl ligands in both the solid state and in solution.[22] Secondly, an electron-density peak approximately in the centre of the macrocyclic ring was refined successfully as the oxygen atom of a water molecule; crown ether ligands are well known to co-ordinate water molecules (as well as other neutral guests) by multiple hydrogen bonding.[19] Thirdly, the conformation of the complex is such that the two terpyridyl substituents on the aza-crown core are not directed away from the macrocycle in an 'extended' conformation, as we saw earlier in the structure of $[Ru(tpy)(HL^1)][ClO_4]_2[PF_6]$, but the molecule is folded such that each face of the macrocycle is partially shielded by these substituents. This 'blocking' of the faces of the macrocycle by the bulky substituents is similar to that previously seen in the structure of $[\{Ru(tpy)\}_2(\mu\text{-}H_2L^2)][PF_6]_6$, the dinuclear complex with the same ligand.[7]

The electronic spectrum of $[Ru(tpy)(L^2)][PF_6]_2$ is very similar to that of $[Ru(tpy)(L^1)][PF_6]_2$, with the exception that the ligand-centred transitions in the UV region are more intense because of the presence of the extra terpyridyl group.

Trinuclear complexes $[\{(tpy)Ru(L^2)\}_2M][PF_6]_6$ (M = Fe or Ni)

Reaction of $[Ru(tpy)(L^2)][PF_6]_2$ with iron(II) or nickel(II) salts resulted in immediate assembly of trinuclear Ru–M–Ru complexes *via* co-ordination of the pendant terpyridyl sites of two equivalents of $[Ru(tpy)(L^2)][PF_6]_2$ to a single central M^{2+} ion (M = Fe or Ni). These reactions were clean and essentially quantitative with only mechanical losses and emphasise the power of the stepwise 'complexes as ligands' approach to the preparation of high nuclearity complexes. These complexes have an obvious architectural similarity to the trinuclear Ru–M–Ru complexes (where M is a first-row transition-metal dication) prepared by Ziessel and co-workers,[2,23] in which conjugated alkynyl spacers between the $\{Ru(tpy)_2\}^{2+}$ and $\{M(tpy)_2\}^{2+}$ complex fragments results in significant electronic interactions between them.

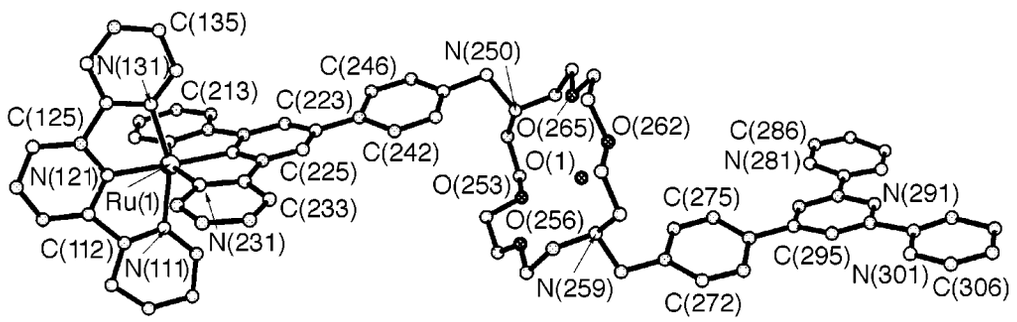


Fig. 2 Crystal structure of the cation of $[Ru(tpy)(L^2)][PF_6]_2\cdot 0.7HPF_6\cdot 0.3Et_2O\cdot MeCN\cdot 1.5H_2O$, showing the oxygen atom of the water molecule in the central cavity.

Elemental analyses of the recrystallised materials were again consistent with the presence of additional equivalents of HPF_6 arising from protonation of the macrocyclic amine sites; the Ru_2Fe complex crystallised with three extra equivalents of HPF_6, and the Ru_2Ni complex with four extra equivalents. The maximum number of additional equivalents of HPF_6 to be expected is four, one for each tertiary amine site in the complex. The ES mass spectra of both complexes (in a weakly acidic medium) showed peaks for fragments in which four extra protons are bound, such as $m/z = 851.9$ for $[\{(tpy)Ru(H_2L^2)_2\}Fe(PF_6)_6]^{4+}$ and 1185.5 for $[\{(tpy)Ru(H_2L^2)_2\}Ni(PF_6)_7]^{3+}$, and also fragments in which the complexes are mono-, di- or triprotonated: there was, as expected, no evidence for attachment of more than four additional protons. The ES mass spectra and the elemental analyses are therefore both consistent with the expected basicity of these complexes.

The ^1H NMR spectrum of $[\{(tpy)Ru(L^2)\}_2Fe][PF_6]_6$ in CD_3CN could be fully assigned with the assistance of a COSY spectrum and the spectra of appropriate mononuclear complexes for comparison purposes. There are three inequivalent terpyridyl fragments, being the terminal tpy on the Ru atoms, and the two termini of the bridging ligands (fragment a, co-ordinated to Fe; and fragment b, co-ordinated to Ru). These could be distinguished by comparison with the spectra of $[Fe(tol\text{-}tpy)_2][PF_6]_2$ and $[Ru(tpy)(L^1)][PF_6]_2$. Although there is considerable overlap of signals in the spectrum enough of the signals are clearly assignable to confirm the structure of the complex, and the relative integrals of the aromatic and aliphatic regions are correct.

Proton NMR spectroscopy of $[\{(tpy)Ru(L^2)\}_2Ni][PF_6]_6$ is complicated by the paramagnetism of the central $\{Ni(tpy)_2\}^{2+}$ fragment. A ^1H NMR spectrum of the mononuclear model complex $[Ni(tol\text{-}tpy)_2][PF_6]_2$ in CD_3CN showed signals at δ 0.65, 7.02, 11.13 and 13.46 which showed no fine structure and which became successively broader at lower fields. Greater shift to low field and increased broadening is presumably related to the proximity of the protons to the metal centre. We would expect 8 proton environments for this complex so it is clear that some of the signals are broadened to the extent that they are undetectable (or are shifted beyond the window we examined, δ −5 to +30). The spectrum of $[\{(tpy)Ru(L^2)\}_2Ni][PF_6]_6$ was a superposition of sharp, well resolved peaks for the $\{Ru(tpy)_2\}^{2+}$ fragments and the macrocyclic rings, and broad, highly shifted signals clearly associated with the $\{Ni(tpy)_2\}^{2+}$ fragment, *e.g.* at δ 11.2 and 13.5. In addition, at least one broad $\{Ni(tpy)_2\}^{2+}$-based signal overlaps with the sharp $\{Ru(tpy)_2\}^{2+}$-based resonances in the δ 7–9 region. We have accordingly made no attempt to assign this spectrum fully but just note that it contains characteristic signals for all of the component parts.

Electronic spectra of the complexes (Table 3) also confirm the presence of the two different types of chromophore. For $[\{(tpy)Ru(L^2)\}_2Fe][PF_6]_6$ the characteristic MLCT transition of the $\{Fe(tpy)_2\}^{2+}$ chromophore occurs at 567 nm, whilst for $[\{(tpy)Ru(L^2)\}_2Ni][PF_6]_6$ the lowest energy of the three d–d transitions is visible at 794 nm. These are both entirely typical wavelengths for the transitions of $\{Fe(tpy)_2\}^{2+}$ and $\{Ni(tpy)_2\}^{2+}$ chromophores,[24,25] and are essentially identical to the equivalent transitions for the model complexes $[M(tol\text{-}tpy)_2]^{2+}$ (M = Fe or Ni) under the same conditions, suggesting that the complex fragments are electronically isolated. This is confirmed by the observation that the Ru-based MLCT transitions of the trinuclear complexes $[\{(tpy)Ru(L^2)\}_2M][PF_6]_6$ are at an identical wavelength to that of the mononuclear precursor $[Ru(tpy)(L^2)][PF_6]_2$; *i.e.* attachment of a dipositive metal fragment to the pendant tpy site of $[Ru(tpy)(L^2)][PF_6]_2$ has no discernible effect on the $\{Ru(tpy)_2\}^{2+}$ core, in strong contrast to the case where there is a conjugated substituent linking the two chromophores.[23]

Cyclic and square-wave voltammetry of $[\{(tpy)Ru(L^2)\}_2Fe][PF_6]_6$ in MeCN revealed two reversible oxidation processes, at $E_{1/2}$ values of +0.72 and +0.89 V *vs.* the ferrocene–ferrocenium couple ($Fc–Fc^+$), of which the latter is twice the intensity of the former (Fig. 3). By 'reversible' is meant that the waves are clearly symmetric, with equal cathodic and anodic peak currents, and have peak–peak separations ΔE_p of *ca.* 70 mV. Both the potentials and relative intensities of these waves suggest that the first is the $Fe^{II}–Fe^{III}$ couple of the central $\{Fe(tpy)_2\}^{2+}$ core,[24,26,27] and the second corresponds to the simultaneous $Ru^{II}–Ru^{III}$ oxidations of the two terminal $\{Ru(tpy)_2\}^{2+}$ groups.[6] There is no evidence for any separation of the second wave into two components, showing that the electrostatic interaction between the two remote $\{Ru(tpy)_2\}^{2+}$ is undetectably small. Compared to the mononuclear complex $[Fe(tol\text{-}tpy)_2]^{2+}$ whose $Fe^{II}–Fe^{III}$ redox potential (measured under the same conditions) was +0.67 V *vs.* $Fc–Fc^+$, the iron(II) centre of the trinuclear complex is slightly harder to oxidise (by 50 mV), possibly as a consequence of a weak electrostatic through-space interaction with the two dipositive metal fragments adjacent to it. Also present are ligand-centred reductions at −1.65 and −1.80 V. The ΔE_p values for both are difficult to determine because (i) the waves overlap in the cyclic voltammogram, and (ii) the return wave of the second is obscured by a stripping peak following an electrode absorption process after the outward scan. These correspond to the usual ligand-centred reductions characteristic of both $\{Fe(tpy)_2\}^{2+}$ and $\{Ru(tpy)_2\}^{2+}$ groups.

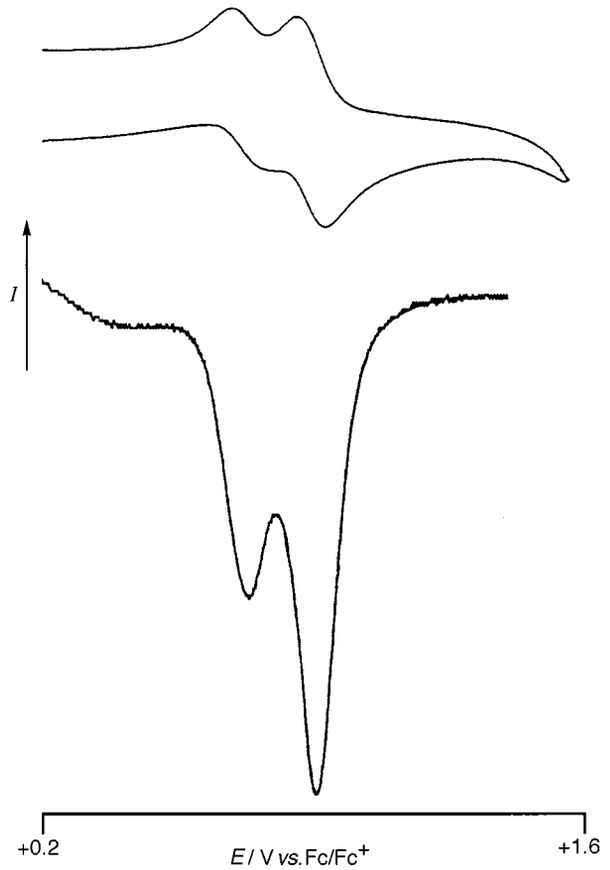


Fig. 3 Cyclic and square-wave voltammograms of $[\{(tpy)Ru(L^2)\}_2Fe][PF_6]_6$ in MeCN, showing the $Fe^{II}–Fe^{III}$ and the two coincident $Ru^{II}–Ru^{III}$ couples.

Similarly, electrochemical study of $[\{(tpy)Ru(L^2)\}_2Ni][PF_6]_6$ allows assignment of the redox processes to the individual complex fragments. A reversible wave at +0.89 V corresponds to simultaneous oxidation of both ruthenium(II) centres to Ru^{III}, whilst the reversible reduction at −1.62 V is associated with the $\{Ni(tpy)_2\}^{2+}$ fragment (whether it is a ligand-centred reduction to give a radical anion, or metal-centred to give Ni^I, is

debatable).[27,28] An additional reversible ligand-centred reduction occurred at −1.87 V. For comparison $[Ni(tol\text{-}tpy)_2][PF_6]_2$ under the same conditions showed reversible reductions at −1.60 and −2.04 V *vs.* $Fc–Fc^+$.

Conclusion

Stepwise alkylation of a 1,10-diaza-18-crown-6 unit allowed us to develop an efficient synthesis of the mononuclear 'complex ligand' $[Ru(tpy)(L^2)][PF_6]_2$, in which one terpyridyl site of the binucleating bridging ligand L^2 is co-ordinated to a $\{Ru(tpy)\}^{2+}$ fragment, but the second is free. Reaction of two equivalents of this complex with first-row transition metals (Fe^{2+}, Ni^{2+}) results in the simple assembly of linear trinuclear Ru–M–Ru complexes in which the two terminal $\{Ru(tpy)_2\}^{2+}$ and the central $\{M(tpy)_2\}^{2+}$ fragments are separated by diaza-18-crown-6 units. The electronic isolation of the metal fragments is demonstrated by their electronic spectra and electrochemical behaviour. Future work will involve the insertion of additional metals into the macrocyclic cavities.

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