Polybipyridine Ligands derived from Acyclic and Macrocyclic Polyamines; Synthesis and Metal Binding Studies

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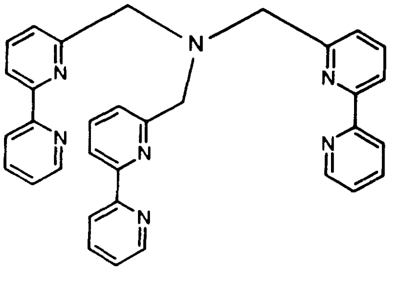
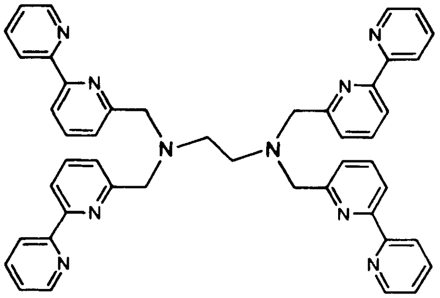
A novel series of ligand bearing three to six pendant 2,2′-bipyridine groups attached to acyclic (tripode, tetrapode) and macrocyclic (cyclam, hexacyclen) polyamines has been synthesized and shown to form metal complexes, in particular of polynuclear type.

The 2,2′-bipyridine group (bpy) has been very extensively studied in recent years for its rich co-ordination chemistry of metal ions and for the photochemical properties of its complexes.[1] These attractive features also prompted the introduction of the bpy unit into macropolycyclic structures,[2—6] thus yielding ligands susceptible to yield photoactive metal complexes, in particular inclusion complexes of cryptate type which combine the features of polycyclic structures with the properties conferred by bpy groups.[4,5]

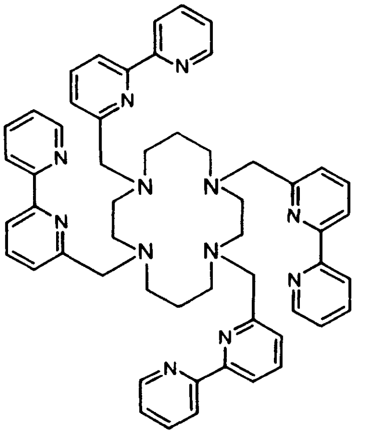
Less highly connected (*e.g.* acyclic or branched) polydentate complexing agents allow binding properties and structural flexibility to be associated, and are well suited for the preparation of polymetallic complexes, which are of much interest for their potential multiredox and catalytic features.



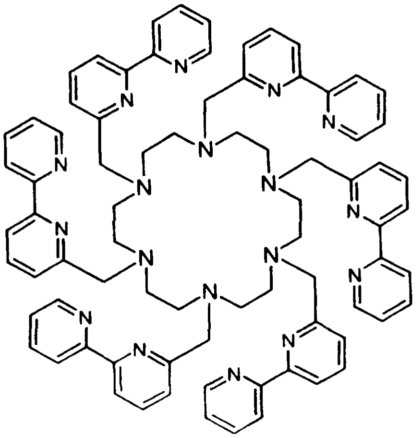
L_1



L_2



L_3



L_4

Table 1. Electronic charge transfer absorption spectra and redox potentials of the complexes of tripodal ligand L_1 and their bipyridine analogues.

Compound	$\lambda_{max.}$/nm ($\varepsilon_{max.}$)[a]	$E_{1/2}$/V *vs.* S.C.E.[b]
$[\{Ru(bpy)_2\}_3(L_1)]^{6+}$	446 (33 000)	+1.36, −1.20, −1.41, −1.68
$[Ru(L_1)]^{2+}$	462 (9600)	+0.64, −1.24, −1.42, −1.69
$[Ru(bpy)_3]^{2+}$ [c]	452 (14 600)	+1.21, −1.23, −1.42, −1.64
$[Fe(L_1)]^{2+}$	502 (1150)	+0.72, −1.31
$[Fe(bpy)_3]^{2+}$ [d]	520 (8050)	+0.96, —
$[\{Re(CO)_3Cl\}_3(L_1)]$	360 (6490)	+1.37[f], −1.44
$Re(bpy)(CO)_3Cl$ [e]	385 (3100)	+1.30[f], −1.37

[a] Electronic absorption spectra were measured in MeCN for the Ru and Re complexes and in H_2O for the Fe species. [b] Redox potentials were determined in dimethylformamide or MeCN using respectively a mercury or a platinum electrode and KPF_6 (0.1 M) as supporting electrolyte (S.C.E. = standard calomel electrode). [c] V. Balzani, F. Bolletta, M. T. Gandolfi, and M. Maestri, *Top. Curr. Chem.*, 1978, **75**, 1, and references therein. [d] W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, 1954, **54**, 959. [e] J. C. Luong, L. Nadjo, and M. S Wrighton, *J. Am. Chem. Soc.*, 1978, **100**, 5790. [f] Irreversible metal-localized oxidation.

In particular a number of polypyridine ligands of acyclic[7] or branched macrocyclic[8] types have been synthesized and their metal complexes have been studied.

We now report the efficient synthesis and some complexation properties of a class of multibranched ligands in which several bpy groups are attached to acyclic and macrocyclic polyamines: tripode L_1, tetrapode L_2, and two branched macrocycles, tetrapode L_3 and hexapode L_4 in which bpy side chains are attached to the frameworks of cyclam, [14]-N_4, and of hexacyclen, [18]-N_6.

Our interest in such ligands was also prompted by the role of ruthenium and rhenium bipyridine complexes in photochemical processes such as water reduction, water oxidation, and carbon dioxide reduction.[9]

Ligands L_1—L_4 have been obtained in a straightforward manner. Monofunctionalization of 6-methyl-2,2′-bipyridine[10] gave 6-(bromomethyl)-2,2′-bipyridine[11] which was treated with acyclic primary amines such as 6-(aminomethyl)-2,2′-bipyridine[12] and ethylenediamine, or with polyaza macrocycles, such as cyclam and hexacyclen, giving ligands L_1—L_4. In a typical experiment, 6-(aminomethyl)-2,2′-bipyridine (1 equiv.) and sodium hydroxide (2 equiv.) were dissolved in water–methanol and added dropwise to a methanolic solution of 6-(bromomethyl)-2,2′-bipyridine at room temperature. During the course of the reaction tripode L_1 precipitated and the pH of the solution decreased. Tripode L_1 was obtained as a white product in 80% yield after recrystallization (CH_2Cl_2, hexane; m.p. 142 °C). The other ligands were obtained in a similar fashion: L_2 (80% yield; m.p. 139 °C), L_3 (75% yield; m.p. 105 °C), and L_4 (40% yield; glass).† This method appears generally applicable and should allow the preparation of a variety of polybipyridine ligands by per-methylbipyridination of acyclic or cyclic polyamines.

At present, the complexation properties of mainly L_1 have been explored and may serve to illustrate some binding features of L_1—L_4.

Depending on the nature of the metallic precursor, mononuclear or trinuclear complexes could be prepared (Figure 1 and Table 1). When L_1 was allowed to react with 3 equiv. of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ in MeOH, $[\{Ru(bpy)_2\}_3(L_1)](PF_6)_6$ was isolated in 65% yield. Reaction with 3 equiv. of $Re(CO)_5Cl$ in hot toluene yielded quantitatively $[\{Re(CO)_3Cl\}_3(L_1)]$ [ν(CO) 2020, 1915, and 1890 cm^{-1}]. Both complexes were isolated as a mixture of stereoisomers. Reaction of tripod L_1 with ruthenium blue,[13] followed by chromatography and recrystallization, gave $[Ru(L_1)](PF_6)_2$ (55% yield). Similarly $[Fe(L_1)]SO_4{\cdot}3H_2O$ was obtained by reaction of tripod L_1 with $FeSO_4{\cdot}7H_2O$ in aqueous ethanol (90%). One may expect that in these complexes the metal ion is hexa-co-ordinated to the three bipyridine units of the ligand L_1, in line with the known chemistry of such binding groups. The structure of the Fe^{II}

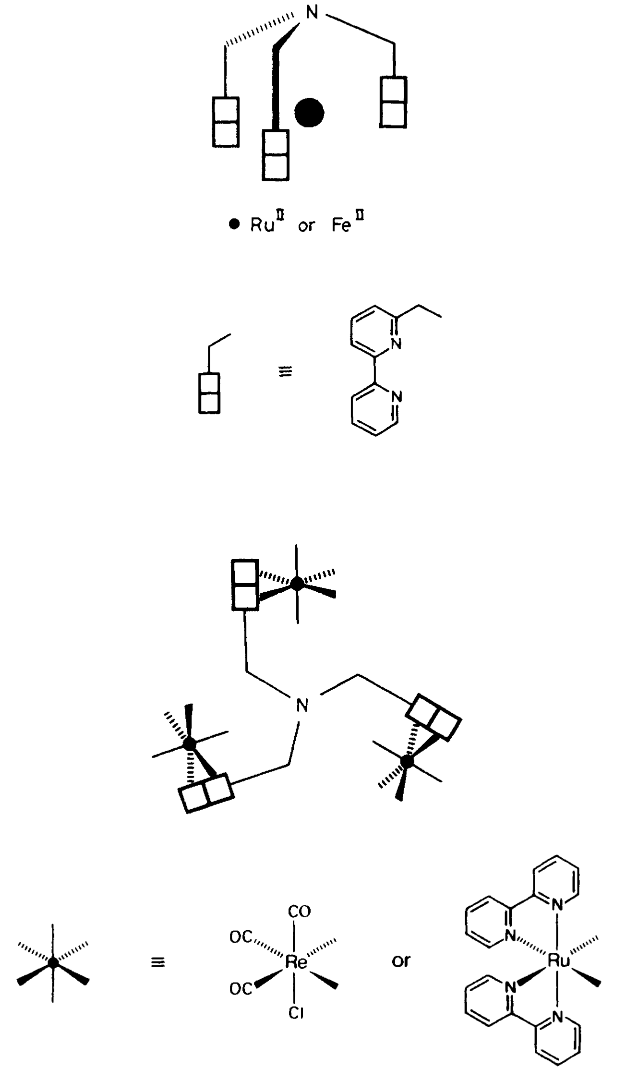


Figure 1. Schematic representation of metal complexes formed by the tripodal ligand L_1: mononuclear Ru^{II} or Fe^{II} complexes (top); trinuclear $Re(CO)_3Cl$ or $Ru(bpy)_2^{2+}$ (bottom).

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† All new compounds have n.m.r. spectra (^1H, ^{13}C), mass spectral, and microanalytical data in agreement with their structure.

complex has been confirmed by *X*-ray crystallography which indicates also participation of the apical nitrogen.[14]

Cyclic voltammetry experiments showed that the two trinuclear complexes have redox potentials similar to those reported for $Ru(bpy)_3{}^{2+}$ and $Re(bpy)(CO)_3Cl$ (Table 1). The mononuclear species presented interesting features. $[Ru(L_1)]^{2+}$ is about 600 mV easier to oxidize than its $[Ru(bpy)_3]^{2+}$ analogue, but its reduction potentials are close to those of the trinuclear species. $[Fe(L_1)]^{2+}$ presents one reversible reduction wave, whereas no reversible reduction could be detected with its $[Fe(bpy)_3]^{2+}$ analogue. The constrained tris-bipyridine ligand L_1 thus produces a marked stabilization of the Ru^{III} and Fe^{III} oxidation states with respect to those of the corresponding tris-bpy complexes and allows species such as $[Fe(L_1)]^+$ to be prepared which are not obtainable with free bpy as ligand.

The trinuclear complexes are fluorescent in MeCN solution at room temperature: $[\{Ru(bpy)_2\}_3(L_1)]^{6+}$, $\lambda_{em.}$ 610 nm; $[\{Re(CO)_3Cl\}_3(L_1)]$, $\lambda_{em.}$ 598 nm, when excited in their metal-to-ligand charge-transfer absorption band. However, no luminescence could be detected for the mononuclear complex $[Ru(L_1)]^{2+}$ at room temperature in H_2O, MeOH, MeCN, or CH_2Cl_2 solutions. Even in a methanol glass at 80 K there is still no luminescence between 600 and 900 nm.‡ Steric hindrance at the ruthenium centre,[15] distortion of the co-ordination octahedron, as well as a rapid internal quenching by the electron pair of the apical nitrogen atom might cause the lack of luminescence.

The metal binding properties of ligands L_1—L_4 are being explored further, in particular with respect to their ability to form polynuclear complexes of potential use for the catalysis of multielectronic reactions such as the oxidation of water or the reduction of carbon dioxide. The synthesis of these polybipyridine ligands and of related molecules should make available a great variety of novel transition metal complexes of interest for their structural, thermodynamic, electrochemical, photochemical, and catalytic properties.

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References

1 W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 135; K. Kalyanasundaram, *Coord. Chem. Rev.*, 1982, **46**, 159.

2 E. Buhleier, W. Wehner, and F. Vögtle, *Chem. Ber.*, 1978, **111**, 200; S. Grammenudi and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1122.

3 J.-M. Lehn, in 'Frontiers of Chemistry' (IUPAC), ed. K. J. Laidler, Pergamon, New York, 1982, p. 265; I. Bidd, A. D. Hamilton, J. M. Lehn, and J. L. Sessler, unpublished results.

4 J. C. Rodriguez-Ubis, B. Alpha, D. Plancherel, and J.-M. Lehn, *Helv. Chim. Acta*, 1984, **67**, 2264.

5 B. Alpha, J.-M. Lehn, and G. Mathis, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 266.

6 V. K. Majestic and G. R. Newkome, *Top. Curr. Chem.*, 1982, **106**, 79.

7 G. Anderegg and F. Wenk, *Helv. Chim. Acta*, 1967, **50**, 2330; G. Anderegg, E. Hubmann, N. G. Podder, and F. Wenk, *ibid.*, 1977, **60**, 123; M. M. Taqui-Khan and A. E. Martell, *Inorg. Chem.*, 1975, **14**, 676; K. D. Karlin, P. L. Dahlstrom, S. N. Cozzette, P. M. Scensny, and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1981, 881; K. D. Karlin, J. C. Hayes, S. Juen, J. P. Hutchinson, and J. Zubieta, *Inorg. Chem.*, 1982, **21**, 4106; K. D. Karlin, M. S. Haka, R. W. Cruse, and Y. Gultneh, *J. Am. Chem. Soc.*, 1985, **107**, 5828; H. Toftlund, K. S. Murray, P. R. Zwack, L. F. Taylor, and O. P. Anderson, *J. Chem. Soc., Chem. Commun.*, 1986, 191; A. F. Tai, L. D. Margerum and J. S. Valentine, *J. Am. Chem. Soc.*, 1986, **108**, 5006. For quinoline end groups, see F. Vögtle, *Angew. Chem.*, 1979, **91**, 813.

8 N. W. Alcock, K. P. Balakrishnan, and P. Moore, *J. Chem. Soc., Chem. Commun.*, 1985, 1731; E. Kimura, T. Koike, H. Nada, and Y. Iitaka, *ibid.*, 1986, 1322; L. Christiansen, D. N. Hendrickson, H. Toftlund, S. R. Wilson, and C.-L. Xie, *Inorg. Chem.*, 1986, **25**, 2813; N. W. Alcock, K. P. Balakrishnan, and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1986, 1743; K. V. Damu, M. S. Shaikjee, J. P. Michael, A. S. Howard, and R. D. Hancock, *Inorg. Chem.*, 1986, **25**, 3879; K. Wieghardt, E. Schoffmann, B. Nuber, and J. Weiss, *ibid.*, 1986, **25**, 4877.

9 M. Kirch, J.-M. Lehn, and J. P. Sauvage, *Helv. Chim. Acta*, 1979, **62**, 1345; J.-M. Lehn, J. P. Sauvage, and R. Ziessel, *Nouv. J. Chim.*, 1979, **3**, 423; R. Ziessel, J. Hawecker, and J.-M. Lehn, *Helv. Chim. Acta*, 1986, **69**, 1065; J. Hawecker, J.-M. Lehn, and R. Ziessel, *ibid.*, 1986, **69**, 1990.

10 Th. Kauffmann, J. Konig, and A. Waltermann, *Chem. Ber.*, 1976, **109**, 3864.

11 G. R. Newkome, V. K. Gupta, and F. R. Fronczek, *Inorg. Chem.*, 1983, **22**, 171.

12 6-(Aminomethyl)-2,2′-bipyridine is prepared starting from 6-(bromomethyl)-2,2′-bipyridine and hexamethylenetetramine, followed by hydrolysis in hydrochloric acid, by analogy with the synthesis of 2-bromoallylamine: A. T. Bottini, V. Dev, and J. Klink, *Org. Synth.*, 1963, **43**, 6.

13 D. Rose and G. Wilkinson, *J. Chem. Soc. A.*, 1970, 1791.

14 J. Guilhem and C. Pascard, unpublished results.

15 R. H. Fabien, D. M. Klassen, and R. W. Sontag, *Inorg. Chem.*, 1980, **19**, 1977.

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