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The oxidation and subsequent co-ordination chemistries of 4′,4″-diphenyl-2,2′:6′,2″:6″,2‴-quaterpyridine

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Selective oxidation of 4′,4″-diphenyl-2,2′:6′,2″:6″,2‴-quaterpyridine leads to two new ligands which, when complexed to a trivalent lanthanide centre, yield either approximately cubic or dodecahedral complexes.

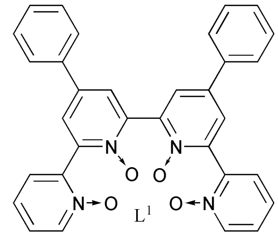
The use of polypyridine ligands to complex a variety of metals has been explored in depth by several research groups.[1] While the terpyridine unit has been used with great success in areas such as molecular electronics[2] and lanthanide luminescence,[3] longer chain ligands such as quater-, quinque- and sexipyridine have been found to give an interesting array of helical molecules with interesting structural and electronic properties.[4] In addition, the co-ordination chemistry of 2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2′′′′′-sexipyridine has been expanded to lanthanide metals and was observed to form mononuclear monohelical complexes with the europium ion.[5]

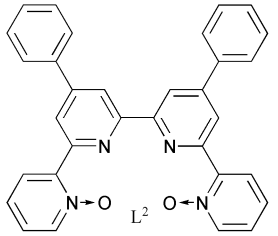
In contrast, we have been interested in the oxidative adaptation of such ligands to form the poly-N-oxide ligands.[6] Such ligands should have a greater affinity for lanthanide metals than their analogous parent pyridyl systems, due to the harder oxygen donor atom. Also, it has been noted by several groups that the inclusion of the N-oxide fragment within a europium complex often results in a higher quantum yield in the photochemistry of the resulting complex, relative to the unoxidised parent species.[7]

While such species are also of interest due to their potential use in the preparation of functionalised oligopyridines, a particular feature of interest to us is the change in the ligand's stereochemical preferences which occur upon ligand oxidation.[6] We have observed the greater flexibility of the terpyridine trisoxide in its abilty to facially co-ordinate a metal centre and were naturally interested in the change in the co-ordinating properties of longer oligomers. To this end we focussed upon the oxidation of readily synthesised 4′,4″-diphenyl-2,2′:6′,2″:6″,2‴-quaterpyridine.[8]

Attempts to oxidise this species to the tetra-oxide species using the standard procedure of 30% H_2O_2 and acetic acid gave varying ratios of starting material and bis-oxide. Even with extended reaction times and additional hydrogen peroxide, the reaction did not proceed to completion and thus stronger oxidising conditions were required. In order to avoid the use of hazardous 90% H_2O_2 or FOH,[9] the urea–hydrogen peroxide adduct and trifluoroacetic anhydride were used[10] to generate peroxytrifluoroacetic acid which resulted in the full N-oxidation of the quaterpyridine. In keeping with the oxidation of terpyridine,[11] the addition of two equivalents of MCPBA to the quaterpyridine gave the *N*,*N*‴-bis-oxide in almost quantitative yield. However, in contrast to terpyridine, addition of one or three equivalents of MCPBA yielded largely the bis-oxide or starting material.

Both the bis-oxide and tetra-oxide quaterpyridines (L^2 and L^1, respectively) † co-ordinate to a variety of metal centres. The addition of two equivalents of ligand to an aqueous solution of lanthanide perchlorate (Eu, Gd and Tb) results in the precipitation of the desired complex $[ML_2](ClO_4)_3$. ‡





Crystals of $[Gd(L^1)_2][ClO_4]_3$, **1**, and $[Tb(L^2)_2][ClO_4]_3 \cdot 2CH_3CN$, **2**, were obtained and their structures were determined by X-ray crystallography (see Fig. 1). § Both complexes consist of an eight co-ordinate lanthanide centre. While **1** has

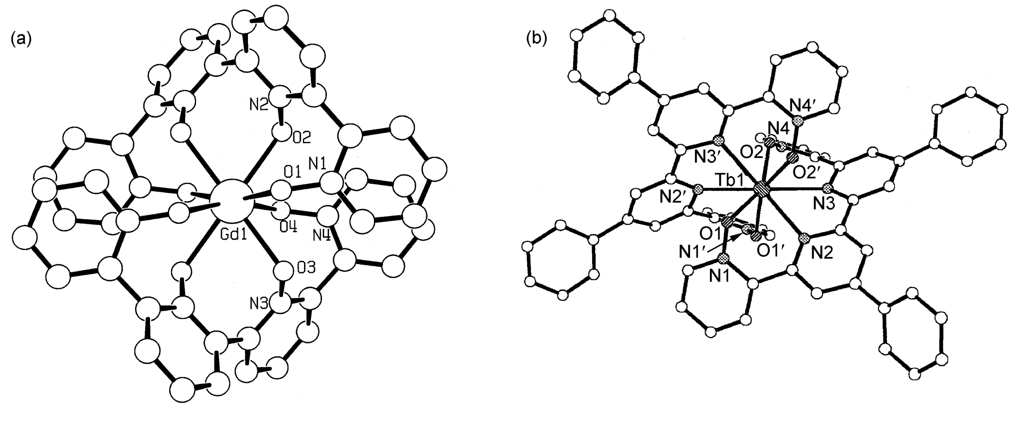


Fig. 1 Crystal structures of (a) [Gd(4′,4″-diphenyl-2,2′:6′,2″:6″,2‴-quaterpyridine-1,1′,1″,1‴-O_4)$_2$][ClO_4]$_3$ **1** (phenyl groups omitted for clarity) and (b) [Tb(4′,4″-diphenyl-2,2′:6′,2″:6″,2‴-quaterpyridine-1,1‴-O_2)$_2$][ClO_4]$_3$ **2** (anions omitted for clarity). Selected bond lengths (Å) for **1**: Gd(1)–O(1) 2.354(4), Gd(1)–O(2) 2.389(4), Gd(1)–O(3) 2.412(4), Gd(1)–O(4) 2.365(4); for **2**: Tb(1)–O(1) 2.282(5), Tb(1)–O(2) 2.253(5), Tb(1)–O(1*) 2.301(5), Tb(1)–O(2*) 2.290(5), Tb(1)–N(2) 2.544(6), Tb(1)–N(3) 2.566(5), Tb(1)–N(2*) 2.555(5), Tb(1)–N(3*) 2.489(6).

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an almost cubic structure similar to that of La(bipyridyl-*N*,*N*′-bis-oxide)$_4^{3+}$,[12] the ligand in **2** is more constricted in its binding mode and gives a less symmetrical configuration, of approximately dodecahedral geometry. The Gd–O bond lengths [av. 2.380(4) Å] are similar to those observed for europium complexes of pyridine-*N*-oxides[13] but are slightly shorter than those observed for the La(bipyridyl-*N*,*N*′-bis-oxide)$_4$ species (2.506 Å). In comparison, the terbium species exhibits slightly shorter Tb–O bonds [av. 2.282(5) Å] but the remaining Eu–N bonds are much longer (av. 2.539 Å). This lowering of symmetry from cubic to dodecahedral (C_{2v}) on going from complexes **1** to **2** is probably due to two factors and is expected to be due to the steric preferences of the ligand and not the metal. First, due to the presence of the central bipyridyl donors in L^2, these donors will have a smaller bite angle [N2–Tb–N3 63.90(19), N′–Tb–N3′ 64.3(2)°] than if these are the flexible, oxide donors [*e.g.* O3–Gd–O3′ 71.90(19), O2–Gd–O′ 71.83(17)°]. This results in the two central donors being pulled together as shown in Fig. 2a. Secondly, while the tetra-oxide is a more flexible donor, and can arrange itself in numerous ways (thus allowing the cubic geometry), the bis-oxide ligand has the central bipyridyl fragment. This makes the ligand tend towards a more linear form of co-ordination and favours the dodecahedral geometry (Fig. 2b).

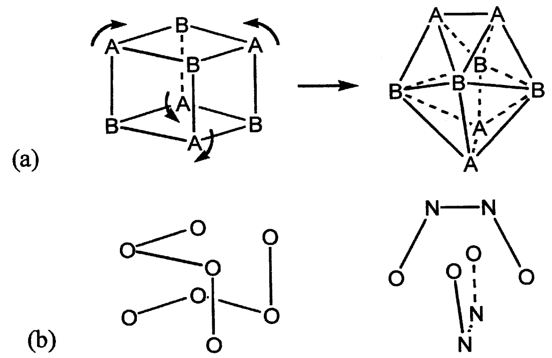

Fig. 2 (a) The distortion from cubic to dodecahedral geometry, (b) the relative positions of the two tetradentate donors.

Further studies will investigate the comparative stability and fluorescence properties of these complexes and their further functionalisation into polydentate ligands with enhanced stabilities.

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Notes and references

† 4′,4″-Diphenyl-2,2′:6′,2″:6″,2‴-quaterpyridine-1,1,1″,1‴-tetra-oxide, (L^1). Trifluoroacetic anhydride (8.4 g, 40 mmol) in acetonitrile (10 ml) was added dropwise over 10 min at 0 °C to a stirring suspension of urea–hydrogen peroxide (4.7 g, 50 mmol) in acetonitrile (25 ml). Stirring was continued at 0 °C for 30 minutes after which time a suspension of 4′,4″-diphenyl-2,2′:6′,2″:6″,2‴-quaterpyridine (1 g, 2.16 mmol) in acetonitrile was added dropwise. The suspension was allowed to rise to room temperature then refluxed at 50 °C for 48 hours. The reaction mixture was evacuated at reduced pressure to yield a yellow oil which was washed with distilled water (3 × 50 ml). The remaining oil was refluxed in ethanol (50 ml) with stirring (1 h) and allowed to cool. The white precipitate formed was collected by filtration to yield L^1 (0.4 g, 35%). δ_H (400 MHz; CDCl$_3$) 8.29 [2H, m, H_6], 8.05 [2H, d, *J* 2.9, $H_{3'}$], 7.9 [2H, d, *J* 2.7, $H_{5'}$], 7.69 [2H, m, H_3], 7.69 [4H, dd, *J* 1.4 Hz, 7.1, H_o], 7.39–7.34 [8H, m, H_{4+m+p}], 7.26 [2H, m, H_5]; IR(KBr)/cm^{-1} 1635(m), 1493(m), 1423(s), 1360(m), 1261(vs), 1230(sh), 1096(s), 1021(s), 875(m), 801(s), 766(s), 697(m), 597(m); MS *m*/*z* 527 (M + H, 75%), 511 (M + H − O, 22%), 496 (M + 2H − 2O, 19%), 465 (M + 3H − 4O, 11%).

4′,4″-Diphenyl-2,2′:6′,2″:6″,2‴-quaterpyridine-1,1‴-bis-oxide, (L^2). 60% MCPBA (1.25 g, 4.33 mmol) was added to a stirring solution of 4′,4″-diphenyl-2,2′:6′,2″:6″,2‴-quaterpyridine (1 g, 2.16 mmol) in dichloromethane (30 ml). The solution immediately turned light orange in colour, light yellow after 10 minutes and a fine white suspension was formed after 15 minutes. Stirring was continued at room temperature for 48 hours. The solvent was removed under reduced pressure and acetone (60 ml) was added to the remaining solid. After stirring at room temperature for 30 minutes the solution was left at −10 °C for 2 hours and the white precipitate formed was collected by filtration to yield L^2 (1.02 g, 96%). δ_H (400 MHz; CDCl$_3$) 9.23 [2H, d, *J* 1.5, $H_{3'}$], 8.75 [2H, d, *J* 1.5, $H_{5'}$], 8.35 [2H, dd, *J* 1.95, 6.1, $H_{3/6}$], 8.30 [2H, d, *J* 6.37, $H_{3/6}$], 7.79 [2H, d, *J* 7.09 Hz, H_o], 7.48–7.39 [8H, m, H_{4+m+p}], 7.26 [2H, m, H_5]; IR(KBr)/cm^{-1} 1610 (w), 1587(s), 1546(s), 1485(s), 1438(s), 1381(s), 1277(s), 1255(w), 1223(s), 1157(w), 1074(w), 1040(s), 880.3(s), 856(s), 754(s), 723(w), 690(s); FAB-MS (NOBA matrix) *m*/*z* 495 (M + H, 100%), 479 (M + H − O, 30%), 463 (M + H − 2O, 15%).

‡ General procedure for the synthesis of metal complexes. The metal perchlorate salt (0.5 mol equiv.) was dissolved in the minimum amount of ethanol and added to a suspension of ligand in hot ethanol (3 ml). A precipitate was formed almost immediately which was collected by filtration. Yield 70–88%. Recrystallisation of all complexes was by vapour diffusion of diethyl ether into a CH$_3$CN solution.

[Gd(PhquaterO$_4$)$_2$][ClO$_4$]$_3$ (**1**), yield 76%. (Found C, 50.74; H, 2.69; N, 7.33. $C_{64}H_{44}Cl_3N_8O_{20}Gd$ requires C, 50.95; H, 2.94; N, 7.43%); IR(KBr)/cm^{-1} 1607(s), 1497(m), 1447(m), 1415(s), 1236(s), 1226(s), 1217(s), 1091(vs), 870(s), 837(s), 770(s), 624(m); FAB-MS (NOBA matrix) *m*/*z* 1309 (M − 2ClO$_4$, 97%), 1210 (M − 3ClO$_4$, 100%).

[Tb(PhquaterO$_2$)$_2$][ClO$_4$]$_3$, (**2**), yield 85%. (Found C, 53.07; H, 2.98; N, 9.13. $C_{68}H_{50}Cl_3N_{10}O_{16}Tb$ requires C, 53.43; H, 3.30; N, 9.16%); IR(KBr)/cm^{-1} 1604(s), 1544(m), 1494(m), 1458(w), 1447(w), 1396(s), 1233(m), 1083(vs), 858(w), 811(w), 767(s), 702(w), 623(s); FAB-MS (NOBA matrix) *m*/*z* 1347 (M − ClO$_4$, 100%), 1247 (M − 2ClO$_4$, 65%).

§ Crystallographic data for **1**: $C_{64}H_{44}Cl_3GdN_8O_{20}$, monoclinic, space group *C*2/*c*, $a = 16.783(3)$, $b = 19.408(4)$, $c = 19.979(4)$ Å, $\beta = 93.93(3)°$, $U = 6492(2)$ Å^3, $Z = 4$, μ(Mo-Kα) = 1.226 mm^{-1}, 30729 reflections measured, 7535 observed reflections [$R_{int} = 0.1208$]. *R* indices (observed data), $R1 = 0.0657$, $wR2 = 0.1253$.

For **2**: $C_{68}H_{50}Cl_3N_{10}O_{16}Tb$, triclinic, space group $P\bar{1}$, $a = 15.3287(5)$, $b = 15.4120(6)$, $c = 17.7298(10)$ Å, $\alpha = 69.9040(15)$, $\beta = 65.6000(16)$, $\gamma = 66.882(2)°$, $U = 3424.9(3)$ Å^3, $Z = 2$, μ(Mo-Kα) = 1.224 mm^{-1}, 23857 reflections measured, 11870 unique [$R_{int} = 0.0946$]. *R* indices (observed data), $R1 = 0.0726$, $wR2 = 0.1125$. CCDC reference numbers 178771 and 180509. See http://www.rsc.org/suppdata/dt/b2/b203087j/ for crystallographic data in CIF or other electronic format.

1 E. C. Constable, *Prog. Inorg. Chem.*, 1994, **42**, 67.
2 J.-P. Collin, P. Laine, J.-P. Launay, J.-P. Sauvage and A. Sour, *J. Chem. Soc., Chem. Commun.*, 1993, 434; E. C. Constable, E. R. Schofield, S. Encinas, N. Armaroli, F. Barigelletti, L. Figggemeier and J. G. Vos, *Chem. Commun.*, 1999, 869.
3 H. Takalo, V. M. Mukkala, L. Merio, J. C. Rodriguez-Ubis, R. Sedano, O. Juanes and E. Brunet, *Helv. Chim. Acta*, 1997, **80**, 372; A. P. de Silva, H. Q. N. Gunaratne, T. E. Rice and S. Stewart, *Chem. Commun.*, 1997, 1891.
4 M. D. Ward and F. Barigelletti, *Coord. Chem. Rev.*, 2001, **216–7**, 127; E. C. Constable, S. M. Elder, M. J. Hannon, A. Martin, P. R. Raithby and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1996, 2423; P. K. K. Ho, K. K. Cheung and C. M. Che, *Chem. Commun.*, 1996, 1197; E. C. Constable, M. A. M. Daniels, M. G. B. Drew, D. A. Tocher, J. V. Walker and P. D. Wood, *J. Chem. Soc., Dalton Trans.*, 1993, 1947; E. C. Constable and M. D. Ward, *J. Am. Chem. Soc.*, 1990, **112**, 1256; R. Chotalia, E. C. Constable, M. Neuburger, D. R. Smith and M. Zehnder, *J. Chem. Soc., Dalton Trans.*, 1996, 4207.
5 E. C. Constable, R. Chotalia and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1992, 771.
6 A J. Amoroso, M. W. Burrows, A. A. Dickinson, C. Jones, D. J. Willock and W. T. Wong, *J. Chem. Soc., Dalton Trans.*, 2001, 225.
7 L. Prodi, M. Maestri, V. Balzani, J.-M. Lehn and C. Roth, *Chem. Phys. Lett.*, 1991, **180**, 45; J.-M. Lehn and C. Roth, *Helv. Chim. Acta*, 1991, **74**, 572; C. de Mello Donegá, S. A. Junior and G. A. de Sá, *Chem. Commun.*, 1996, 1199.
8 E. C. Constable, P. Haverson, D. R. Smith and L. A. Whall, *Tetrahedron*, 1994, **50**, 7799.
9 S. Rozen and S. Dayan, *Angew. Chem., Int. Ed.*, 1999, **38**, 3472.
10 R. Ballini, C. Marcantoni and M. Petrini, *Tetrahedron Lett.*, 1992, **33**, 4835.
11 R. P. Thummel and Y. Jahng, *J. Org. Chem.*, 1985, **50**, 3635.
12 A. R. Al-Karaghouli, R. O. Day and J. S. Wood, *Inorg. Chem.*, 1978, **17**, 3702.
13 For example: C. O. Paul-Roth, J.-M. Lehn, J. Guilhem and C. Pascard, *Helv. Chim. Acta*, 1995, **78**, 1895; P. Gawryszewska, L. Jerzykiewicz, M. Pietraszkiewicz, L. Legendziewicz and J. P. Riehl, *Inorg. Chem.*, 2000, **39**, 5365.