The First Example of a Mono-helical Complex of 2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗ : 6⁗, 2′′′′′-Sexipyridine; Preparation, Crystal and Molecular Structure of Bis(nitrato-*O,O′*) (2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗ : 6⁗,2′′′′′-sexipyridine)europium(III) Nitrate

Edwin C. Constable,*[a] **Rohit Chotalia**[a] **and Derek A. Tocher***[b]

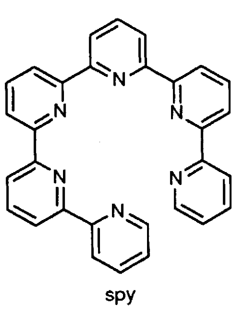
[a] *Cambridge Centre for Molecular Recognition, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*

[b] *Department of Chemistry, University College London, 20 Gordon St., London WC1H 0AJ, UK*

The hexadentate ligand 2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗ : 6⁗,2′′′′′-sexipyridine (spy) forms double-helical binuclear complexes with transition metals, but 1 : 1 complexes with lanthanides; the photoactive complex [Eu(spy)$(NO_3)_2$][NO_3] is obtained from the reaction of spy with europium(III) nitrate and has been structurally characterised as a mono-helical ten-coordinate species with a helically twisted hexadentate spy ligand.

There is considerable current interest in the factors which determine the ability of metal ions to control the configurations of organic ligands.[1] Double- and triple-helical, interlinked or knotted coordination compounds are both aesthetically satisfying and synthetically challenging, and embody all the control features needed for the assembly of larger and more complex ligand arrays.[2] We have demonstrated that the higher oligopyridines are of particular interest in this respect.[3] The potentially hexadentate ligand 2,2′ : 6′,2″ : 6″, 2‴ : 6‴,2⁗ : 6⁗,2′′′′′-sexipyridine (spy) forms double-helical binuclear complexes with first, second and third row transition metals; indeed, these are so favoured that we have developed a templated synthesis of the complex [$Ni_2(spy)_2$]$^{4+}$ from 6-bromo-2,2′ : 6′,2″-terpyridine.[4] We have now investigated the interaction of spy with lanthanide cations, and describe in this paper the formation of helical 1 : 1 complexes.

The free ligand spy is extremely insoluble, but upon heating a suspension of spy with a methanolic solution of $Eu(NO_3)_3{\cdot}5H_2O$ the ligand dissolved to give a pale yellow luminescent solution. Upon cooling, the solution deposited well-formed crystals of [Eu(spy)$(NO_3)_2$][NO_3]; alternatively the addition of [NH_4][PF_6] precipitated the off-white salt [Eu(spy)$(NO_3)_2$][PF_6]. The FAB mass spectra (3-nitrobenzyl alcohol matrix) of both of these complexes exhibit peaks at *m/z* 615/617 [Eu(spy)], 677/679 [Eu(spy)(NO_3)], 739/741 [Eu(spy)$(NO_3)_2$]. This is strongly indicative of the formation of a 1 : 1 complex, as all the double-helical binuclear complexes of spy exhibit intense (often base-peak) ions corresponding to [$M_2(spy)_2$][PF_6]$_n$ (n = 0,1). The europium complexes are paramagnetic, but we have been unable to obtain well-resolved EPR spectra for the solid products or acetonitrile glasses of solutions at 77 or 298 K. This is compatible with the $^7F_0$ ground state for europium(III).[5] A



spy

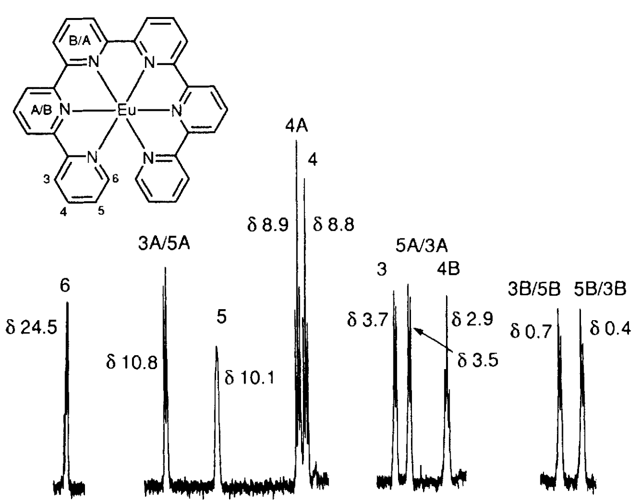


Fig. 1 ^1H NMR spectrum of CD_3CN solution of [Eu(spy)$(NO_3)_2$][NO_3] with partial assignments. The ambiguity in assignment of the AMX spin systems of the central rings is indicated in the description A/B for these rings.

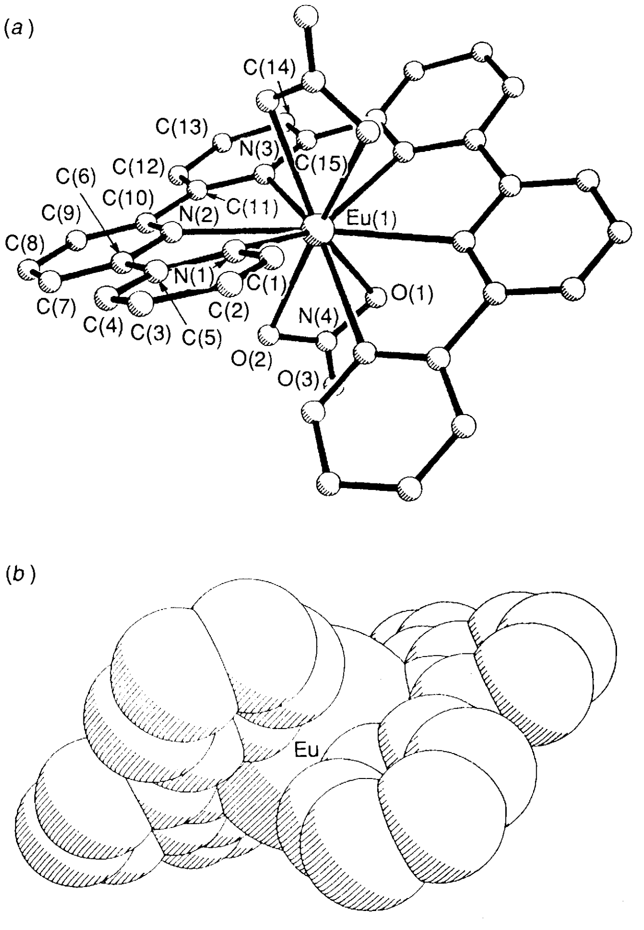


Fig. 2(*a*) The crystal and molecular structure of the $[Eu(spy)(NO_3)_2]^+$ cation in $[Eu(spy)(NO_3)(NO_3)][NO_3]$ showing the numbering scheme adopted [Eu(1)–N(1) 2.583(16), Eu(1)–N(2) 2.589(10), Eu(1)–N(3) 2.536(14), Eu(1)–O(1) 2.504(16), Eu(1)–O(2) 2.558(16) Å] and (*b*) a space-filling representation of the cation with nitrate ligands omitted

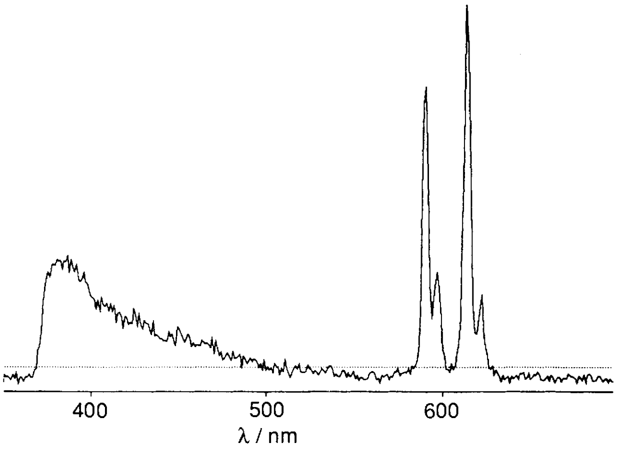


Fig. 3 Luminescence spectrum (300 nm excitation) of a fluid MeCN solution of $[Eu(spy)(NO_3)_2][PF_6]$ at 298 K

solution of $[Eu(spy)(NO_3)_2][PF_6]$ in CD_3CN exhibits a sharp and well-resolved paramagnetically shifted ^1H NMR spectrum, with resonances ranging from δ +24.5 to +0.4 (Fig. 1). The spectrum clearly exhibits a total of ten proton environments on the NMR time-scale, and suggests that the ligand is in an environment symmetrical about the central interannular C–C bond. This would be compatible with either a double-helical binulcear or C_2 symmetrical 1:1 structure. The assignments given in Fig. 1 have been made on the basis of selective homonuclear decoupling experiments; the assignment of the AMX patterns associated with the inner rings is ambiguous. The resonances for the terminal rings do not show the expected alternation associated with a contact shift mechanism, and we assume that either a pseudo-contact or mixture of mechanisms is operative.[6]

Slow cooling of the solution obtained from the reaction of spy with europium(III) nitrate in methanol gave good quality blocks of the complex $[Eu(spy)(NO_3)_2][NO_3]$; the crystal and molecular structure of one of the two enantiomers of this cation present in the unit cell is presented in Fig. 2(*a*), together with a space filling representation of the {Eu(spy)} core in Fig. 2(*b*).† The cation is mononuclear with a ten-coordinate europium centre; the spy acts as a hexadentate ligand and adopts a helical twist about an equatorial plane. The remaining four axial coordinate sites are occupied by two mutually orthogonal bidentate nitrate ligands [Eu(1)–O(1), 2.504(16) Å; Eu(1)–O(2), 2.558(16) Å]. The remaining nitrate ion does not interact with the metal and is found in a number of disordered lattice sites. The helical twisting of the spy ligand minimises the interactions which would occur between the two terminal rings of the ligand in a completely planar configuration, and is achieved by a series of individual twistings about interannular C–C bonds between adjacent pyridine rings, with the major twist being associated with the two central rings (1/2, 5.8°; 2/3, 7.6°; 3/3A, 18.8°; rings numbered according to the nitrogen atom they contain). The overall effect is for the two terminal rings to lie at 45° with respect to each other, with a centroid to centroid distance of 4.18 Å. The Eu–N(py) distances are all similar [2.536(14)–2.589(10) Å] and in the range observed for other europium(III) pyridine complexes.[7] The ten-coordinate geometry of the complex cation is not readily described in terms of any simple coordination polyhedron.

The electronic spectrum of a solution of the complex $[Eu(spy)(NO_3)_2][PF_6]$ in MeCN exhibits two sharp absorptions at 304 and 325 nm, in addition to ligand n–π* transitions in the range 200–250 nm. The complex is also luminescent in fluid solution at 298 K. Excitation within the ligand n–π* manifold (220.6 nm) results in very weak emission, but excitation at 304 nm or 350 nm results in an intense luminescence (Fig. 3). The luminescence spectrum (304 or 350 nm excitation) exhibits four major features (591, 597, 614 and 622 nm). These results are as expected for emission from the lowest lying metal centred excited state ($^5D_0$) to the various *j* levels of the ^7F_n (n = 0–6) ground state. Irradiation of a solution of $[Eu(spy)(NO_3)_2][PF_6]$ with an ultraviolet lamp results in an intense red emission. We are currently investigating a range of other lanthanide spy complexes, together with more detailed studies of the luminescent behaviour of these complexes.

We thank the SERC for grants towards the purchase of a diffractometer (D. A. T.), molecular graphics facilities (E. C. C.) and a studentship (R. C.), and the Royal Society

---

† *Crystal data*: $C_{30}H_{20}EuN_9O_9$, off-white blocks, M = 802.49, monoclinic, space group $C2/c$, a = 18.602(11), b = 15.892(8), c = 14.071(8) Å, β = 128.64(3)°, U = 3250 Å^3, Z = 4, D_c = 1.64 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å), μ(Mo-Kα) = 19.9 cm^{-1}. 3009 Reflections collected on a four-circle diffractometer with 2θ(max.) 50°. The data were averaged and 1417 unique data with $I \geqslant 3.0\sigma(I)$ were used in structure solution and refinement. The structure was solved by direct methods followed by iterative least-squares refinement and difference Fourier synthesis and refined (Eu, C, H, N, O of cation anisotropic, nitrate anion and H isotropic) to R = 0.0695, R_w = 0.0699. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

and the Isaac Newton Trust for grants enabling the purchase of spectrometers (E. C. C.).

Received, 3rd February 1992; Com. 2/00584K

References

1 H.-J. Schneider and H. Dürr, *Frontiers in Supramolecular Organic Chemistry and Photochemistry*, Verlag Chemie, Cambridge, 1991; F. Vögtle, *Supramolecular Chemistry*, Wiley, Chichester, 1991.

2 E. C. Constable, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1450.

3 See, *e.g.* E. C. Constable, *Nature*, 1990, **346**, 319; E. C. Constable, M. G. B. Drew and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1987, 1600; *Polyhedron,* 1989, **8**, 2551; C. J. Cathey, E. C. Constable, M. J. Hannon, D. A. Tocher and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1990, 621; E. C. Constable, S. M. Elder, J. A. Healy, M. D. Ward and D. A. Tocher, *J. Am. Chem. Soc.*, 1990, **112**, 4590; E. C. Constable, S. M. Elder, P. R. Raithby and M. D. Ward, *Polyhedron*, 1991, **10**, 1395; E. C. Constable, M. D. Ward and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1991, 1675; E. C. Constable, J. M. Holmes and P. R. Raithby, *Polyhedron*, 1991, **10**, 127; E. C. Constable, S. M. Elder, J. Healy and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1990, 1669; E. C. Constable, F. K. Khan, V. E. Marquez and P. R. Raithby, *Acta Crystallogr., Sect C,* in the press; E. C. Constable, S. M. Elder, J. V. Walker, P. D. Wood and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1992, 229; E. C. Constable, S. M. Elder and D. A. Tocher, *Polyhedron*, in the press; E. C. Constable, M. J. Hannon and D. A. Tocher, *Angew. Chem., Int. Ed. Engl.*, in the press; E. C. Constable, S. M. Elder, P. R. Raithby and M. D. Ward, *Polyhedron*, 1991, **12**, 1395; E. C. Constable, J. V. Walker and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1992, preceding communication; E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Chem. Commun.*, 1992, 617; E. C. Constable and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1990, 1405; E. C. Constable, A. M. W. Cargill Thompson and D. A. Tocher, *New J. Chem.*, in the press; E. C. Constable, A. M. W. Cargill Thompson and D. A. Tocher, in *Supramolecular Chemistry*, ed. V. Balzani, NATO ASI Series, Reidel, Dordrecht, 1992.

4 E. C. Constable, M. D. Ward and D. A. Tocher, *J. Am. Chem. Soc.*, 1990, **112**, 1256; E. C. Constable, M. D. Ward and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1991, 1675; E. C. Constable and R. Chotalia, *J. Chem. Soc., Chem. Commun.*, 1992, 64.

5 S. Cotton, *Lanthanides and Actinides*, Macmillan, Basingstoke, 1991.

6 F. A. Hart in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 3.

7 H. Ningh-Hai, L. Yong-Hua, S. Qi, X. Yan and S. En-Dong, *Huaxue Xuebao*, 1986, **44**, 388; R. C. Holz and L. C. Thompson, *Inorg. Chem.*, 1988, **27**, 4640; G. H. Frost, F. A. Hart, C. Heath and M. B. Hursthouse, *Chem. Commun.*, 1969, 1421.