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Synthesis, crystal structure and luminescence properties of a europium(III) complex with a new planar aromatic tridentate N_3 ligand

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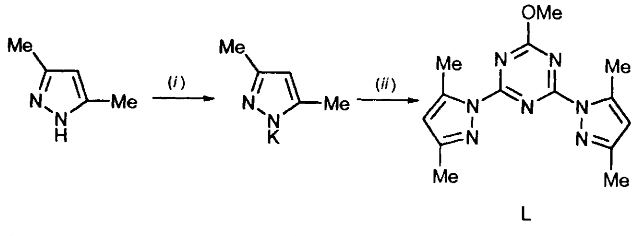
The new planar aromatic tridentate nitrogen ligand 2,4-bis(3,5-dimethylpyrazol-1-yl)-6-methoxy-1,3,5-triazine (L) has been synthesized and the crystal structure of $[EuL(NO_3)_3(H_2O)]\cdot L$ revealed a mononuclear structure with a ten-co-ordinate metal centre; π–π stacking and hydrogen bonding between the co-ordinated and unco-ordinated L molecules sensitized Eu^{III} luminescence.

The terpyridine-like ligands have attracted considerable interest in recent years for their extensive co-ordination chemistry with metal ions.[1] The terpyridine-like chromophores can form photo- and redox-active complexes with transition-metal ions (*e.g.* Ru^{III} or Cu^{II}) as catalysts,[2] or highly luminescent complexes with lanthanoid ions (*e.g.* Eu^{III} or Tb^{III}) as highly sensitive probes for the detection of protein and DNA samples.[3] In particular, terpyridine-like ligands self-assemble with Ln^{III} ions to produce stable mononuclear triple-stranded helicates as supramolecular light-conversion devices.[4] The difficulties in the synthesis of terpyridine derivatives limit the use of their complexes as building blocks for extended helical supramolecular structures,[5] although a number of terpyridine analogues have been explored.[6] Recently we have developed an alternative approach based on 2,4-bis(pyrazol-1-yl)-1,3,5-triazine, which is general and convenient for the synthesis of various terpyridine-like ligands. We describe here the synthesis of 2,4-bis(3,5-dimethylpyrazol-1-yl)-6-methoxy-1,3,5-triazine (L) and report the crystal structure and luminescence properties of its Eu^{III} complex.

The synthesis of L is outlined in Scheme 1.† Reaction of the potassium salt of 3,5-dimethylpyrazole with 2,4-dichloro-6-methoxy-1,3,5-triazine in anhydrous dioxane gave L in high yield. Dropwise addition of $Eu(NO_3)_3\cdot 6H_2O$ to methanolic L afforded a clear, colourless solution, from which transparent crystals of $[EuL(NO_3)_3(H_2O)]\cdot L$ **1** deposited upon slow evaporation. Recrystallization of the complex from methanol afforded X-ray quality crystals whose fast-atom-bombardment mass spectrum (m/z = 300 and 452) suggested the formation of a complex in a 1 : 1 metal : ligand ratio ([EuL] = 452, L = 299) and one unco-ordinated L. The crystal structure‡ of complex **1** (Fig. 1) revealed neutral $[EuL(NO_3)_3(H_2O)]$ and unco-ordinated L molecules, where Eu^{III} is ten-co-ordinated by three nitrogen atoms of L, six oxygen atoms of three bidentate NO_3^- groups and one water molecule. The ligand L is virtually planar with only small dihedral angles between the triazine and pyrazolyl rings ($\leq 6°$), and adopting a *cis–cis* conformation leading to a planar meridional co-ordination of the Eu^{III} atom which lies approximately in a basal plane defined by three co-ordinated nitrogen atoms of L and the O(8) atom of a nitrate group. The ligand L is bound to the Eu^{III} atom in an approximately symmetrical fashion with the Eu–N bond lengths in the range 2.575(6)–2.627(7) Å. The Eu–O distances in **1** fall in the range 2.423(6)–2.545(6) Å with the shortest one involving the aqua ligand. As illustrated in Fig. 2 the co-ordinated and unco-ordinated ligands are packed in AABB parallel layers running along the $(\frac{1}{2},0,\frac{1}{2})$ direction, producing slipped stacks of the aromatic ligands with zigzag arrangement. There are two kinds of intermolecular interactions observed between neighbouring molecules; besides intermolecular hydrogen bonding between the unco-ordinated L and the aqua ligand [O · · · N 2.822(10) and 2.924(9) Å], stacking interactions are found between the co-ordinated and unco-ordinated L molecules (3.1 Å) and between the two neighbouring co-ordinated L (3.6 Å).

Europium(III) complexes are of special interest for their luminescence properties, since luminescence from Eu^{III} can be



Scheme 1 Reagents and conditions: (*i*) K, dioxane, 60 °C; (*ii*) 2,4-dichloro-6-methoxy-1,3,5-triazine, 80 °C, 5 h

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† Potassium (0.8 g, 20 mmol) was added to a solution of 3,5-dimethylpyrazole (2.2 g, 23 mmol) in ahydrous dioxane (100 cm^3) at 60 °C under nitrogen gas and the mixture was stirred until the metal dissolved. The resulting suspension of potassium salt was cooled to 0–5 °C, and a solution of 2,4-dichloro-6-methoxy-1,3,5-triazine (1.8 g, 10 mmol) in dioxane (100 cm^3) was added dropwise with vigorous stirring. The mixture was stirred at room temperature for 1 h and at 80 °C for 5 h. The precipitate was filtered off after cooling, and the filtrate evaporated. The residue was recrystallized from aqueous ethanol to give L as colourless needles (2.5 g, 83%), m.p. 86–87 °C. IR (KBr): 1602, 1553, 1356, 1016, 811 and 751 cm^{-1}. Mass spectrum (EI) (m/z): 300 (M + 1). ^1H NMR ($CDCl_3$): δ 6.08 (s, 2 H), 3.49 (s, 3 H), 2.74 (s, 6 H), 2.34 (s, 6 H) (Found: C, 56.1; H, 5.7; N, 32.7. Calc.: C, 56.2; H, 5.7; N, 32.8%).

‡ Crystal data. **1**, $C_{28}H_{36}EuN_{17}O_{12}$, colourless polyhedron, M = 954.7, monoclinic, space group $P2_1/n$, a = 16.893(3), b = 12.410(3), c = 18.494(2) Å, β = 103.20(1)°, U = 3775(2) $Å^3$, Z = 4, D_c = 1.680 g cm^{-3}, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 1.811 mm^{-1}. 7157 Independent reflections were collected at 294 K on an Enraf-Nonius CAD4 diffractometer with $2\theta_{max}$ = 52°. The structure was solved by direct methods and refined by full-matrix least squares on all F^2 data using SHELXL 93.[7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters. Refinement converged at $R1$ = 0.0755, $wR2$ = 0.2173. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/26.

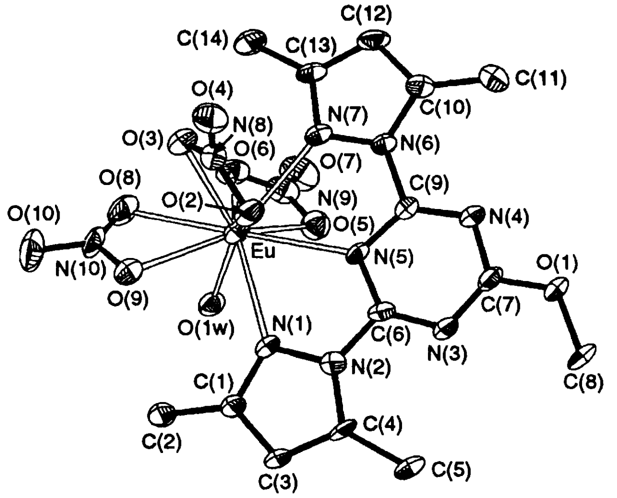

Fig. 1 Molecular structure of [$EuL(NO_3)_3(H_2O)$] in **1**. Selected bond lengths (Å): Eu–O(1w) 2.423(6), Eu–O(6) 2.451(6), Eu–O(2) 2.466(6), Eu–O(9) 2.483(7), Eu–O(8) 2.527(6), Eu–O(5) 2.540(7), Eu–O(3) 2.545(6), Eu–N(5) 2.575(6), Eu–N(1) 2.601(6) and Eu–N(7) 2.627(7)

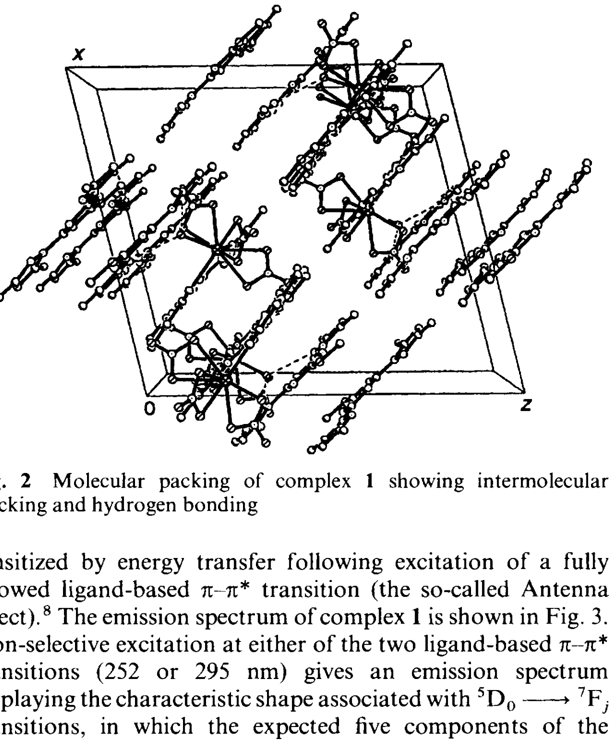

Fig. 2 Molecular packing of complex **1** showing intermolecular stacking and hydrogen bonding

sensitized by energy transfer following excitation of a fully allowed ligand-based π–π* transition (the so-called Antenna effect).[8] The emission spectrum of complex **1** is shown in Fig. 3. Non-selective excitation at either of the two ligand-based π–π* transitions (252 or 295 nm) gives an emission spectrum displaying the characteristic shape associated with $^5D_0 \longrightarrow {}^7F_j$ transitions, in which the expected five components of the $^5D_0 \longrightarrow {}^7F_{0-4}$ transitions are well resolved. The observed $^5D_0 \longrightarrow {}^7F_0$ and the intense hypersensitive $^5D_0 \longrightarrow {}^7F_2$ (τ = 0.74 ms) transition reflect a low site symmetry of Eu^{III}, in agreement with the crystal structure. The most important observation is that there are no ligand emission bands at 376 and 456 nm in the spectrum of crystalline **1**, as shown in Fig. 3. This is indicative of intermolecular energy transfer from uncoordinated L to the central Eu^{III}, which might arise from the peculiar packing and hydrogen bonding found in the crystal, since π–π overlaps and hydrogen-bonding interactions favour energy-migration processes.[9] Investigation into the detailed energy-transfer mechanism in complex **1** is in progress.

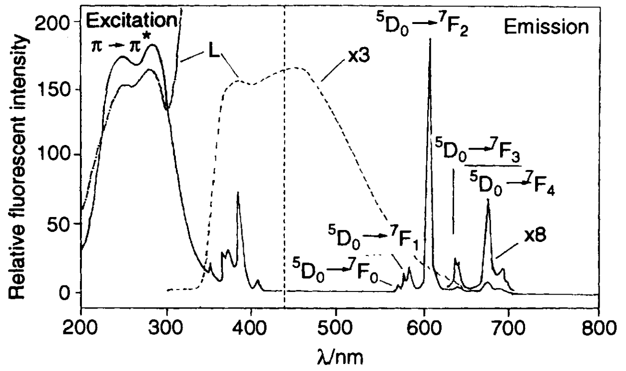

Fig. 3 Luminescence spectrum of microcrystalline **1** at 295 K

Acknowledgements

This work was supported by the National Commission of Science and Technology of China.

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Received 8*th January* 1996; *Communication* 6/00167J