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Conformational properties of Eu(III) complexes of 3,3′; 5,3″-polymethylene bridged derivatives of 2,2′; 6,2″-terpyridine

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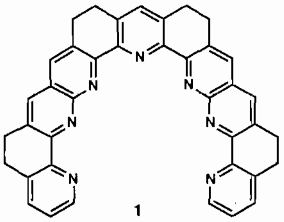
Abstract

The complex $[Eu(tpy)_3](ClO_4)_3$, where tpy = 2,2′; 6,2″-terpyridine, has been prepared and reexamined. The complex appears to be stable in acetonitrile solution with respect to decomplexation of the ligands but the addition of water does cause partial replacement of tpy. Analogous complexes have been prepared with 3,3′; 5,3″-polymethylene bridged derivatives of tpy having two or three carbons in the bridge. The bridging enforces a *cisoid* geometry of the ligand and prohibits its replacement by added water. An X-ray determination was carried out for $[Eu(\mathbf{3b})_3](ClO_4)_3$, where **3b** = 3,3′; 5,3″-dimethylene tpy, which crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.908(4)$, $b = 15.768(5)$, $c = 29.513(9)$ Å, $\beta = 93.60(2)°$, $\mu = 13.5$ cm^{-1} and $Z = 4$. The complex forms a tricapped trigonal prism with each of the ligands adopting the same *dl* conformation. Variable temperature NMR analysis of the bridged ligand complexes indicates that conformational inversion of the bound ligand is not a concerted process and barriers for inversion of individual methylene units can be estimated from coalescence of the signals from the geminal methylene protons. The luminescence properties of the bridged tpy complexes are similar to the parent unbridged system.

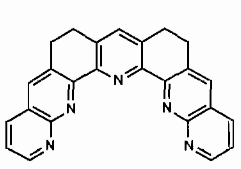
Introduction

There has been recent interest in the energy transfer luminescence of europium(III) cryptates derived from macrobicyclic polypyridine ligands [1]. This luminescence is believed to involve absorption of light by the polypyridine residues of the crypt, energy transfer from the π,π^* excited states of these polypyridines to the excited state levels of the Eu(III), and finally the emission of long wavelength visible light from the lanthanide ion. This unusual and quite impressive room temperature emission has been attributed to protection of the encryptated europium ions from competing radiationless deactivation by the surrounding solvent molecules.

Our interest in polyaza cavity shaped ligands suggested that the same type of protection could be afforded to a lanthanide ion by a large cavity-shaped ligand. We have studied the complexation of **1** with ruthenium(II) and found that it binds in a 2:1 fashion to form an octahedral system using the central tridentate binding sites on two orthogonal ligands [2]. We anticipated that this species might also coordinate with Eu(III) in a 2:1 fashion, taking advantage of the larger ionic radius of the lanthanide and its increased coordination number to accommodate the higher denticity of **1**.

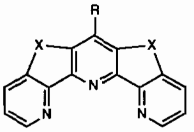


1

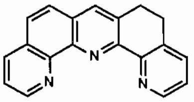


2

To test this hypothesis we first examined ligand **2** which was more readily available and showed better solubility characteristics [3]. Upon treatment of **2** with Eu(III) perchlorate only unreacted materials were recovered. We suspected that the europium ion might be more demanding than anticipated in its coordination geometry and proceeded to study the next lower homolog of the ligand, **3b**. This paper will describe our findings for coordination of europium(III) with **3a–e**, **4** and the conformational properties of the resulting complexes.



3a X = H, H; R = H
b X = CH_2CH_2, R = H
c X = $(CH_2)_3$, R = H
d X = $(CH_2)_4$, R = H
e X = CH_2CH_2, R = *p*-tolyl



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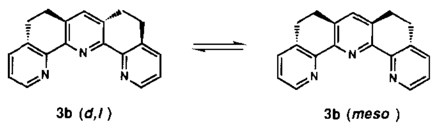
In earlier work we have examined the ruthenium(II) complexation of *bis*-polymethylene bridged derivatives of 2,2′; 6,2′-terpyridine (**3b–d**) [4]. The conformation of the free ligand is strongly influenced by the length of the polymethylene bridge which causes twisting about the 2,2′ and 6,2″ bonds. The dihedral angle (ϕ) between two adjacent pyridine rings is calculated to be 18° for **3b**, 45° for **3c**, and 58° for **3d** (calculated using the programs given in ref. 5; these dihedral angles differ from those estimated in ref. 4).

Each bridge may be considered as a chiral center which leads to the potential existence of two diastereomers for these molecules. When the twist angle has the same sign for both interpyridine bonds, the molecule exists in a partially helical *dl* conformation while opposite signs of thc twist angle would providc a mirror plane leading to a *meso* conformation. Ruthenium(II) is not overly demanding in its coordination geometry and hence complexes of the type RuL_2^{2+} form readily with L = **3b–d** and for **3b, c** the ligand remains conformationally mobile in the bound state. It is interesting to note that a crystal structure analysis of the ruthenium(II) complex where L = **3d** shows both conformers of the ligand to be present [4].



3b (*d,l*) 3b (*meso*)

From the perspective of tridentate coordination, europium(III) may be considered as being homologous to ruthenium in its formation of EuL_3^{3+} type complexes. This paper will use X-ray and NMR analysis to examine the conformational properties of such species.

Experimental

Nuclear magnetic resonance spectra were recorded on a General Electric QE-300 spectrometer at 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR. Variable temperature NMR experiments were run on a Nicolet NT-300 at 300 MHz for ^1H NMR. Chemical shifts are reported in ppm downfield from Me_4Si. Emission spectra were obtained on a Perkin-Elmer LS-50 luminescence spectrometer using a Hamamatsu R928 photomultiplier tube. The ligand **3a** was obtained from GFS Chemicals and the ligands **3b–e** were prepared according to published procedures [3, 6]. The synthesis of ligand **4** will be described separately [7]. Elemental analyses were carried out by Canadian Microanalytical Service Ltd, Delta, BC.

[Eu(3a)₃](ClO₄)₃ [8]

A solution of 41 mg (0.073 mmol) of $Eu(ClO_4)_3 \cdot 6H_2O$ in 3 ml of ethanol was added dropwise to a refluxing solution of 72 mg (0.31 mmol) of 2,2′; 6,2″-terpyridine (**3a**) in 4 ml of ethanol. Reflux was continued for 3 h under argon. A white precipitate formed, which was filtered and vacuum dried to afford 62.4 mg (75%) of [Eu(**3a**)₃](ClO_4)₃: m.p. > 300 °C; ^1H NMR (300 MHz, CD_3CN) δ 16.14 (broad, s, 2H, $H_{6'}$, $H_{6''}$), 6.91 (t, J = 7.8 Hz, 2H, $H_{4'}$, $H_{4''}$), 6.14 (d, J = 6.6 Hz, 2H, $H_{5'}$, $H_{5''}$), 5.07 (t, J = 7.9 Hz, 1H, H_4), 2.38 (d, J = 8 Hz, 2H, H_3, H_5), 2.21 (d, J = 8.4 Hz, 2H, $H_{3'}$, $H_{3''}$); ^{13}C NMR (CD_3CN) 190.4 ($C_{6'}$, $C_{6''}$), 157.2 (C_2, C_6 or $C_{2'}$, $C_{2''}$), 154.9 (C_2, C_6 or $C_{2'}$, $C_{2''}$), 151.1 (C_4), 150.1 ($C_{4'}$, $C_{4''}$), 110.3 ($C_{5'}$, $C_{5''}$), 96.5 ($C_{3'}$, $C_{3''}$), 91.3 (C_3, C_5).

[Eu(3b)₃](ClO₄)₃

Following the same procedure as described for [Eu(**3a**)₃](ClO_4)₃, 25 mg (0.0877 mmol) of 3,3′; 5,3″-bis(dimethylene)-2,2′; 6,2″-terpyridine (**3b**) were treated with 11.4 mg (0.0202 mmol) of $Eu(ClO_4)_3 \cdot 6H_2O$ to afford 21.5 mg (81%) of [Eu(**3b**)₃](ClO_4)₃ as a dark yellow precipitate. A small amount was recrystallized from CH_3CN/toluene (1:4): m.p. > 300 °C; ^1H NMR (300 MHz, CD_3CN) δ 14.9 (broad s, 2H, $H_{6'}$, $H_{6''}$), 6.75 (d, J = 7.7 Hz, 2H, $H_{4'}$, $H_{4''}$), 5.99 (d, J = 6.9 Hz, 2H, $H_{5'}$, $H_{5''}$), 4.46 (s, 1H, H_4), 0.26 (broad s, 8H, CH_2). *Anal.* Calc. for $EuC_{57}H_{45}N_9O_{12}Cl_3 \cdot 1.5H_2O$: C, 51.33; H, 3.60; N, 9.46. Found: C, 51.23; H, 3.59; N, 9.45%.

[Eu(3c)₃](ClO₄)₃

Following the same procedure as described for [Eu(**3a**)₃](ClO_4)₃, 37 mg (0.118 mmol) of 3,3′; 5,3″-bis(trimethylene)-2,2′; 6,2″-terpyridine (**3c**) were treated with 15.4 mg (0.0274 mmol) of $Eu(ClO_4)_3 \cdot 6H_2O$ to afford 23.6 mg (62%) of [Eu(**3c**)₃](ClO_4)₃ as a white precipitate. A small amount was recrystallized from CH_3CN/toluene (1:9): m.p. > 300 °C; ^1H NMR (300 MHz, CD_3CN) δ 11.82 (broad s, 2H, $H_{6'}$, $H_{6''}$), 7.01 (d, J = 7.7 Hz, 2H, $H_{4'}$, $H_{4''}$), 5.82 (s, 1H, H_4), 5.56 (d, J = 6.8 Hz, 2H, $H_{5'}$, $H_{5''}$), 1.64 (broad m, 2H, CH_2), 1.45 (broad m, 2H, CH_2), 1.15 (broad m, 2H, CH_2), 0.58 (broad m, 2H, CH_2), 0.40 (broad m, 2H, CH_2), −0.96 (broad m, 2H, CH_2). *Anal.* Calc. for $EuC_{63}H_{57}N_9O_{12}Cl_3 \cdot 2H_2O$: C, 53.03; H, 4.28; N, 8.84. Found: C, 53.12; H, 4.27; N, 8.23%.

[Eu(3e)₃](ClO₄)₃

Following the same procedure as described for [Eu(**3a**)₃](ClO_4)₃, 26 mg (0.0693 mmol) of 3,3′; 5,3″-bis(dimethylene)-4-*p*-tolyl-2,2′; 6,2″-terpyridine (**3e**) were treated with 9.16 mg (0.0162 mmol) of

$Eu(ClO_4)_3 \cdot 6H_2O$ to afford 21.7 mg (85%) of $[Eu(\mathbf{3e})_3](ClO_4)_3$ as a pale yellow precipitate. A small amount was recrystallized from CH_3CN/toluene (1:1): m.p. > 300 °C; ^1H NMR (300 MHz, CD_3CN) δ 15.39 (broad s, 2H, $H_{6'}$, $H_{6''}$), 6.94 (d, $J = 7.8$ Hz, 2H, $H_{4'}$, $H_{4''}$), 6.62 (d, $J = 7.7$ Hz, 2H, H_7), 5.94 (d, $J = 7.8$ Hz, 2H, $H_{5'}$, $H_{5''}$), 5.91 (d, $J = 8.1$ Hz, 2H, H_8), 2.12 (s, 3H, CH_3), 0.88 (broad s, 2H, CH_2), 0.51 (broad s, 2H, CH_2), −0.59 (broad s, 4H, CH_2). *Anal.* Calc. for $EuC_{78}H_{63}N_9O_{12}Cl_3 \cdot 2H_2O$: C, 58.08; H, 4.16; N, 7.82. Found: C, 57.95; H, 4.06; N, 7.51%.

$[Eu(4)_3](ClO_4)_3$

Following the same procedure as described for $[Eu(\mathbf{3a})_3](ClO_4)_3$, 22 mg (0.0777 mmol) of 5,6-dihydroquino[8,7-*b*]-1,10-phenanthroline (**4**) were treated with 10.2 mg (0.0181 mmol) of $Eu(ClO_4)_3 \cdot 6H_2O$ to afford 19.8 mg (84%) of $[Eu(\mathbf{4})_3](ClO_4)_3$ as a pale yellow precipitate. A small amount was recrystallized from CH_3CN/toluene (1/4): m.p. > 300 °C; ^1H NMR (300 MHz, CD_3CN)* δ 13.28 (broad s, 2H, H_2, H_{12}), 7.84 (d, $J = 8.2$ Hz, 1H, H_4), 6.90 (d, $J = 7.7$ Hz, 1H, H_3), 6.78 (broad s, 1H, H_6), 5.93 (broad s, 1H, H_5), 5.86 (d, $J = 8.9$ Hz, 1H, H_{10}), 5.41 (s, 1H, H_7), 4.98 (d, $J = 8.8$ Hz, 1H, H_{11}), 1.18 (broad s, 2H, CH_2), 0.58 (broad s, 2H, CH_2). *Anal.* Calc. for $EuC_{57}H_{39}N_9O_{12}Cl_3 \cdot 2H_2O$: C, 51.22; H, 3.22; N, 9.43. Found: C, 51.08; H, 3.14; N, 8.84%.

X-ray determination of $[Eu(3b)_3](ClO_4)_3$

A lemon yellow irregular fragment having approximate dimensions 0.56×0.45×0.38 mm was cut from a large prismatic wedge and mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. Since samples of the material were known to slowly decompose when removed from the mother liquor, a thin coat of epoxy was applied to the crystal to retard possible solvent loss. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 1. The Laue symmetry was determined to be 2/*m*, from the systematic absences noted the space group unambiguously was shown to be $P2_1/c$. Intensities were measured using the omega scan technique, with the scan rate depending on the count obtained in rapid prescans of each reflection. Two standard reflections were monitored after every two hours or every 100 data collected, and these showed no significant variation. In reducing the data, Lorentz and polarization corrections were applied, however no correction for absorption was made due to the small absorption coefficient.

TABLE 1. Crystallographic data for $[Eu(\mathbf{3b})_3](ClO_4)_3$

Chemical formula	$[C_{57}H_{45}N_9Eu^{3+}] \cdot 3(ClO_4^-) \cdot C_2H_3N$
Formula weight	1347.48
Cell constants	
a (Å)	11.908(4)
b (Å)	15.768(5)
c (Å)	29.513(9)
β (°)	93.60(2)
V (Å^3)	5531
Space group	$P2_1/c$, monoclinic
Formula units per cell, Z	4
Density, ρ (g cm^{-3})	1.62
Absorption coefficient, μ (cm^{-1})	13.5
Radiation (Mo Kα), λ (Å)	0.71073
R[a]	0.044
R_w[a]	0.043

[a] $R = S||F_o| - |F_c||/S|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, with $w = \sigma(F)^{-2}$.

The structure was solved by interpretation of the Patterson map, which revealed the position of the Eu atom. The remaining atoms were located in subsequent Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens attached to carbon were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor. One of the perchlorate anions is massively disordered over two general sites, each site having two distinct molecular orientations present. Thus four rigid body perchlorates were refined, each having a population factor of 25% (based on analysis of thermal parameters). A single variable isotropic temperature factor was refined for all of the atoms involved. Additionally, at both of the disordered anion sites some residual electron density was found which roughly corresponded to the shape of acetonitrile. Apparently each site is occupied half the time by an anion and half the time by solvent, which explains the observed decomposition of the crystals upon removal from the solvent. The acetonitrile also seems to be disordered at the two general sites and was also refined as rigid bodies having 25% population factors. Only three orientations could be clearly distinguished, however it is assumed that a fourth site is also present. After all shift/e.s.d. ratios were less than 0.5 (excluding the rigid groups) convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement (excluding rigid groups), and the final difference density map showed a maximum peak of about 1.1 e/Å^3 located near C14. All calculations were made

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*Proton numbering begins with a peripheral nitrogen on the 1,10-phenanthroline moiety and proceeds around the outer edge of the molecule with each non-bridgehead position being assigned a sequential number.

using Nicolet's SHELXTL PLUS (1985) series of crystallographic programs [9].

Results and discussion

Synthesis and characterization

The synthesis of the ligands **3b–e** has been described previously [3, 6] and the synthesis of **4** will be described separately [7]. The complexes were prepared according to the procedure of Durham *et al.* [8] by treating a four-fold equivalent of the terpyridine with $Eu(ClO_4)_3 \cdot 6H_2O$ in refluxing absolute ethanol. In the case of **3d** only unreacted starting materials were obtained, indicating that the ligand was too distorted to coordinate effectively.

As will be discussed later, NMR provides a very sensitive probe of the structure of europium terpyridine complexes, however, it does not allow one to distinguish unambiguously between systems having one, two or three ligands chelated with the metal. Such a distinction is better provided by the elemental analyses which were uniformly consistent with a 3:1 ligand-to-metal ratio.

Structure of [Eu(3b)₃](ClO₄)₃

The crystal structure of tris(2,2′; 6,2″-terpyridyl)europium(III) perchlorate has been reported by Hursthouse and co-workers [10]. The complex is nine-coordinate and the coordination polyhedron approximates a tricapped trigonal prism. The most serious distortion from idealized D_3 symmetry is caused by non-planarity of the tpy ligands. The dihedral angles between neighboring pyridine rings range from 12 to 26° which are considerably larger than the dihedral angles found for $Ru(tpy)_2^{2+}$. The angles in $[Eu(tpy)_3](ClO_4)_3$ are in the range of what we expect for our bridged tpy derivatives **3b, c** and thus we undertook a single crystal analysis of the complex $[Eu(\mathbf{3b})_3](ClO_4)_3$ to ascertain the exact disposition of these ligands.

The crystallographic data are given in Table 1, the atomic coordinates are given in Table 2, and significant bond lengths, bond angles and torsion angles are given in Table 3. An ORTEP drawing of the complex is presented in Fig. 1. Once again the coordination polyhedron approximates a tricapped trigonal prism. The degree of distortion appears to be somewhat diminished from the corresponding complex of **3a** in that the interpyridine ring dihedral angles now vary from 13.8 to 20.0°. The sign of all the dihedral angles is the same so that the three ligands in the complex all adopt a *d,l* conformation. This approximation of helical ligand disposition exerts a torque on the tricapped prism so that the two trigonal faces are twisted about 11° out of an eclipsed geometry.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å \times 10^3$) for $[Eu(\mathbf{3b})_3](ClO_4)_3$

Atom	*x*	*y*	*z*	U_{eq}
Eu	1937(1)	2506(1)	1332(1)	30(1)
N(1)	1538(6)	947(4)	1093(2)	38(3)
C(2)	555(7)	716(5)	870(3)	41(3)
C(3)	514(8)	19(6)	583(3)	53(4)
C(4)	1478(9)	−444(6)	536(3)	56(4)
C(5)	2459(8)	−267(5)	784(3)	44(3)
C(6)	3543(8)	−754(6)	772(3)	56(4)
C(7)	4135(8)	−818(6)	1230(3)	57(4)
C(8)	4260(7)	50(5)	1454(3)	41(3)
C(9)	5141(7)	276(6)	1760(3)	48(3)
C(10)	5225(7)	1087(6)	1942(3)	41(3)
C(11)	6203(7)	1379(6)	2238(3)	55(4)
C(12)	5900(8)	2136(6)	2529(3)	61(4)
C(13)	5306(7)	2818(6)	2251(3)	44(3)
C(14)	5462(8)	3690(6)	2318(3)	52(4)
C(15)	4867(8)	4261(6)	2042(3)	55(4)
C(16)	4074(7)	3948(6)	1718(3)	46(3)
N(17)	3880(6)	2126(5)	1651(2)	39(3)
C(18)	4527(6)	2567(7)	1902(2)	40(3)
C(19)	4406(7)	1663(6)	1793(3)	40(3)
N(20)	3510(5)	1464(4)	1507(2)	32(2)
C(21)	3459(7)	662(5)	1351(3)	36(3)
C(22)	2448(7)	445(5)	1067(3)	34(3)
N(23)	−208(5)	2684(4)	1395(2)	34(2)
C(24)	−640(7)	2799(5)	1799(3)	45(3)
C(25)	−1681(8)	3152(6)	1831(3)	59(4)
C(26)	−2316(8)	3411(6)	1447(3)	64(4)
C(27)	−1876(7)	3289(6)	1032(3)	48(3)
C(28)	−2489(9)	3582(7)	588(3)	65(4)
C(29)	−2294(7)	2973(6)	211(3)	55(3)
C(30)	−1067(6)	2755(5)	184(3)	37(3)
C(31)	−594(6)	2520(6)	−211(2)	44(3)
C(32)	530(7)	2296(4)	−213(2)	37(3)
C(33)	1077(8)	2066(6)	−644(3)	57(4)
C(34)	2057(7)	1461(6)	−541(3)	57(4)
C(35)	2829(7)	1761(6)	−155(3)	43(3)
C(36)	3970(8)	1620(7)	−131(3)	63(4)
C(37)	4619(8)	1872(7)	240(3)	66(4)
C(38)	4093(7)	2233(5)	601(3)	48(3)
N(39)	2996(5)	2372(4)	595(2)	38(2)
C(40)	2380(7)	2139(5)	218(2)	34(3)
C(41)	1179(7)	2324(4)	196(2)	33(3)
N(42)	719(4)	2544(5)	590(2)	31(2)
C(43)	−376(6)	2744(4)	587(2)	33(3)
C(44)	−825(6)	2919(5)	1023(3)	36(3)
N(45)	1632(6)	4076(4)	1104(2)	40(3)
C(46)	1580(8)	4347(6)	662(3)	51(3)
C(47)	1059(9)	5081(7)	534(3)	62(4)
C(48)	592(8)	5592(6)	853(3)	60(4)
C(49)	683(7)	5373(6)	1294(3)	47(3)
C(50)	238(9)	5867(6)	1674(3)	64(4)
C(51)	939(8)	5838(6)	2101(3)	58(4)
C(52)	1283(7)	4941(5)	2229(3)	44(3)
C(53)	1553(7)	4684(5)	2671(3)	46(3)
C(54)	1893(7)	3856(5)	2759(3)	39(3)
C(55)	2166(8)	3520(6)	3233(3)	55(4)
C(56)	3033(8)	2787(6)	3234(3)	58(4)
C(57)	2622(7)	2115(6)	2894(3)	46(3)
C(58)	2739(8)	1248(6)	2961(3)	55(4)

(*continued*)

TABLE 2. (*continued*)

Atom	x	y	z	U_{eq}
C(59)	2328(8)	696(6)	2626(3)	56(4)
C(60)	1873(7)	1009(5)	2223(3)	45(3)
N(61)	1800(6)	1838(4)	2141(2)	35(2)
C(62)	2119(6)	2383(5)	2476(2)	34(3)
C(63)	1919(6)	3291(5)	2399(3)	34(3)
N(64)	1680(5)	3538(4)	1968(2)	33(2)
C(65)	1384(7)	4350(5)	1888(3)	35(3)
C(66)	1229(7)	4611(5)	1407(3)	37(3)
Cl(1)	1177(2)	8492(2)	1796(1)	59(1)
O(1)	476(7)	9170(5)	1638(3)	102(4)
O(2)	1489(8)	8012(6)	1412(3)	121(4)
O(3)	2148(6)	8819(5)	2025(3)	98(4)
O(4)	552(6)	7956(5)	2089(2)	84(3)
Cl(2)	2843(2)	5826(2)	4074(1)	60(1)
O(5)	3452(6)	6582(4)	3980(2)	76(3)
O(6)	3629(7)	5169(5)	4161(4)	140(5)
O(7)	2087(8)	5613(7)	3699(3)	144(5)
O(8)	2164(7)	5946(5)	4442(2)	89(3)
Cl(3)	4161(15)	6179(10)	1125(6)	91(2)
O(9)	3478	6052	1507	121(3)
O(10)	5179	5682	1188	121(3)
O(11)	4448	7066	1092	121(3)
O(12)	3539	5915	713	121(3)
Cl(3′)	3984(15)	6208(10)	1135(6)	91(2)
O(9′)	3354	5965	1517	121(3)
O(10′)	3980	5518	813	121(3)
O(11′)	5131	6402	1291	121(3)
O(12′)	3474	5949	919	121(3)
Cl(4)	7064(12)	5935(9)	560(4)	91(2)
O(13)	6678	6776	667	121(3)
O(14)	6850	5364	928	121(3)
O(15)	8258	5958	497	121(3)
O(16)	6471	5641	147	121(3)
Cl(4′)	6455(12)	5911(10)	681(4)	121(3)
O(13′)	6188	6705	894	121(3)
O(14′)	5884	5226	897	121(3)
O(15′)	7656	5770	729	121(3)
O(16′)	6093	5942	205	121(3)
N(67)	4349(42)	6875(30)	859(15)	120
C(68)	3957	6447	1254	120
C(69)	3655	6116	1560	120
N(70)	7588(41)	5824(31)	290(14)	120
C(71)	7356	6081	746	120
C(72)	7176	6279	1099	120
N(70′)	6978(44)	5652(35)	511(18)	120
C(71′)	5914	5719	246	120
C(72′)	5091	5770	42	120

The Eu–N bond lengths are 2.52–2.63 Å and fall within the normal range for lanthanide complexes [11]. It is noteworthy, however, that the distance from europium to the nitrogen of the central pyridine (2.52–2.55 Å) is shorter than the corresponding distance to the distal pyridines (2.59–2.63 Å). This difference may be partly attributed to the polymethylene bridges which tend to prevent serious distortion of the N–Eu–N chelation angle.

TABLE 3. Selected bond lengths, bond angles and torsion angles for $[Eu(\mathbf{3b})_3](ClO_4)_3$

Bond lengths (Å)				
Eu–(1)	2.594(7)	Eu–N(17)	2.631(7)	
Eu–N(20)	2.521(6)	Eu–N(23)	2.588(6)	
Eu–N(39)	2.589(7)	Eu–N(42)	2.550(5)	
Eu–N(45)	2.585(7)	Eu–N(61)	2.625(6)	
Eu–N(64)	2.518(6)			
Bond angles (°)				
N(1)–Eu–N(17)	126.3(2)			
N(1)–Eu–N(20)	63.8(2)			
N(17)–Eu–N(20)	62.8(2)			
N(23)–Eu–N(39)	127.2(2)			
N(23)–Eu–N(42)	63.2(2)			
N(39)–Eu–N(42)	64.0(2)			
N(45)–Eu–N(61)	127.2(2)			
N(45)–Eu–N(64)	63.5(2)			
N(61)–Eu–N(64)	64.1(2)			
Torsion angles (°)				
C10	C11	C12	C13	−49.3
C13	C18	C19	C10	−16.7
N17	C18	C19	N20	−11.8
C5	C6	C7	C8	−51.2
C8	C21	C22	C5	−21.0
N20	C21	C22	N1	−19.1
C27	C28	C29	C30	−48.7
C30	C43	C44	C27	−15.0
N42	C43	C44	N23	−14.9
C32	C33	C34	C35	−48.6
C35	C40	C41	C32	−13.4
N39	C40	C41	N42	−14.1
C49	C50	C51	C52	−48.2
C52	C65	C66	C49	−17.8
N64	C65	C66	N45	−14.2
C54	C55	C56	C57	−52.7
C57	C62	C63	C54	−19.5
N61	C62	C63	N64	−15.4

Conformational analysis by NMR

Chapman *et al.* have reported on the ^1H NMR spectrum of $[Eu(tpy)_3](ClO_4)_3$ in acetonitrile solution [12]. They observe a spectrum containing more peaks than would be expected based on the symmetrical structure dictated by the earlier X-ray analysis. They are able to dissect the spectrum into three-groups of signals which they assign to three complexes which are nine-, eight- and seven-coordinate in terpyridine nitrogens. A careful analysis of the NMR integral leads to a relative ratio of 78:16:6 (±5%) for the three different complexes. They surmise that the predominant component is the symmetrical tris-tridentate complex. The minor components they assign to a complex containing two tridentate and one bidentate tpys and a complex containing two tridentate and one monodentate tpys. They further surmise that the uncoordinated ring or rings of the bidentate and monodentate tpys are conformationally rotated into a *transoid* rather than the normally chelating *cisoid* geometry. It is suggested that

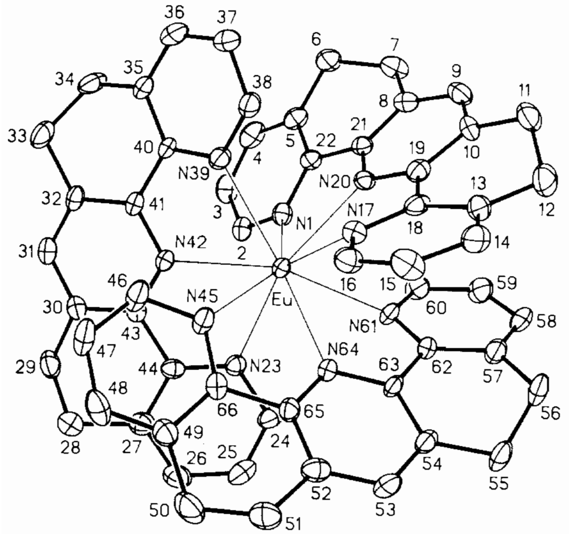
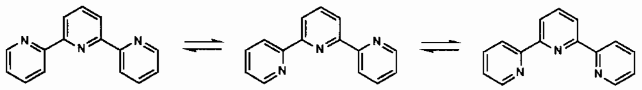


Fig. 1. View of the $[Eu(\mathbf{3b})_3]^{3+}$ cation, with labeling of key atoms. The thermal ellipsoids are 30% equiprobability envelopes, and hydrogens have been omitted for clarity.

the uncoordinated sites on europium for the eight- and seven-coordinate systems may be occupied by acetonitrile-d_3 which is the NMR solvent.



3a (*anti, anti*) 3a (*syn, anti*) 3a (*syn, syn*)

This explanation is somewhat disturbing from two perspectives. First, rotation of a distal pyridine ring into a *transoid* geometry would direct a C–H bond directly toward the metal center. Occupation of the unchelated metal coordination site by a molecule of acetonitrile would cause too much steric congestion in an already very crowded complex. We prepared the complex $[Eu(\mathbf{3a})_3](ClO_4)_3$ in the same manner as described by Durham *et al.* [8] and analyzed it by ^1H NMR. The spectrum showed only a single set of proton resonances which correspond with the major isomer described by Chapman *et al.* The NMR spectrum of the complex remained unchanged after 16 days in solution. Upon the addition of small increments of water, however, peaks immediately appeared which were very similar to those assigned to the minor isomers observed by the previous workers.

To ascertain the importance of *syn,anti* and *anti,anti* conformers in the coordination of tpy to europium, we investigated its complexation with **3b–d**. The dimethylene and trimethylene bridged terpyridines readily formed tris-complexes with Eu(III) in yields of 81% and 62%, respectively. The tetramethylene bridged system would not form a tris-complex and only unreacted starting materials were recovered. Both complexes with **3b** and **3c** remain unchanged upon the addition of water, indicating that decomplexation of the tpy by rotation about an interpyridine bond is no longer possible due to the restraint imposed by the polymethylene bridge.

Table 4 summarizes the ^1H NMR data for the ligands **3a–c, e** and their Eu(III) complexes. The $H_6/H_{6''}$ proton is the most sensitive to a dipolar shift with Eu(III) and hence is shifted downfield by 3.1–7.4 ppm upon complexation. The largest shift is observed for **3a** wherein the ligand is the least restricted and assumes the most planar *syn,syn* conformation in solution. For **3c**, which should show the highest degree of nonplanarity in the ligand, the shift is considerably less, indicating that this proton does not point directly toward the metal. This conformational effect is mirrored to a lesser extent by $H_5/H_{5''}$ which again shows the greatest upfield shift for **3c** and the smallest shift for **3a**.

The nature of the signals for the protons on the polymethylene bridges is more diagnostic of the conformational environment of the bound tpy ligand. From the X-ray analysis of $[Eu(\mathbf{3b})_3](ClO_4)_3$ we know that the dimethylene bridged ligand in the solid state assumes a *d,l* conformation. If this same conformational rigidity were retained in solution on the NMR time scale, the four protons of each dimethylene bridge would be magnetically non-equivalent and hence should give rise to distinct NMR resonances. In the top trace of Fig. 2 we observe two broad, poorly resolved signals for the methylene protons of this complex implying that the geminal positions of the bridges are equilibrating. This equilibration would be accomplished through conformational inversion of the bound ligand **3b**. As the solution is cooled, the two broad signals decoalesce so that at −40 °C four distinct signals are observed and conformational rigidity has been achieved. We estimate a coalescence temperature of about −5 °C for which a free energy of activation for the conformational inversion of 12.4 kcal/mol can be calculated [13].

For the trimethylene-bridged analogue $[Eu(\mathbf{3c})_3](ClO_4)_3$ the situation is considerably different. At +21 °C (Fig. 3) six signals are observed for the bridge protons, implying magnetic non-equivalence of all six protons on each of the bridges. As the solution is warmed, the signals begin to broaden and coalesce, but not at the same rate. The signals originally at +1.76 and +1.85 ppm coalesce first at about +50 °C (16.5 kcal/mol). The second pair, originally at +0.79 and +0.96 ppm, coalesces at about 100 °C (18.0 kcal/mol). The third pair of signals at +1.45 and −0.46 ppm move closer with increasing temperature but will not coalesce below 100 °C. This behavior suggests that at +21 °C the bound ligand **3c** is conformationally rigid in solution on the NMR time scale. At elevated temperatures conformational inversion causes the geminal protons on each bridge methylene to coalesce at

TABLE 4. ^1H NMR data for **3a–c**, **3e** and their europium complexes[a]

Ligand/complex	$H_{6',6''}$	$H_{5',5''}$	$H_{4',4''}$	H_4	$H_{3',3''}$	$H_{3,5}$	$-CH_2-$
3a	8.70(d)	7.32(t)	7.85(t)	7.96(t)	8.46(d)	8.62(d)	
$[Eu(\mathbf{3a})_3](ClO_4)_3$	16.14(s)	6.14(d)	6.91(t)	5.07(t)	2.21(d)	2.38(d)	
		$J=6.6$ Hz	$J=7.8$ Hz	$J=7.9$ Hz	$J=8.4$ Hz	$J=8.0$ Hz	
3b	8.70(dd)	7.22(dd)	7.58(dd)	7.49(s)			3.01(s)
$[Eu(\mathbf{3b})_3](ClO_4)_3$	14.9(s)	5.99(d)	6.75(d)	4.46(s)			0.26(bs)
		$J=6.9$ Hz	$J=7.7$ Hz				
3c	8.70(dd)	7.22(dd)	7.55(dd)	7.46(s)			2.27(q); 2.59(t)
$[Eu(\mathbf{3c})_3](ClO_4)_3$	11.82(s)	5.56(d)	7.01(d)	5.82(s)			1.64; 1.45; 1.15; 0.58; 0.40; −0.96 (broad m)
		$J=6.8$ Hz	$J=7.7$ Hz				
3e	8.74(dd)	7.24(dd)	7.54(dd)	CH_3 2.46 H_8 7.1 H_7 7.32			2.72(t); 2.87(t)
$[Eu(\mathbf{3e})_3](ClO_4)_3$	15.39(s)	5.94(d)	6.94(d)	CH_3 2.12			0.88; 0.51; −0.59
		$J=7.8$ Hz	$J=7.8$ Hz	H_8 5.91(d)	$J=8.1$ Hz		(broad s)
				H_7 6.62(d)			

[a] Recorded at ambient temperature in $CDCl_3$ for the ligands and in CD_3CN for the complexes. Chemical shifts are given in ppm downfield from Me_4Si.

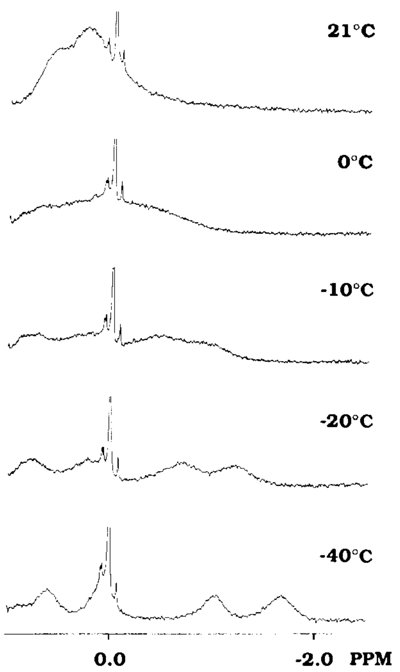


Fig. 2. Temperature dependent display of the upfield region of the 300 MHz ^1H NMR of $[Eu(\mathbf{3b})_3](ClO_4)_3$ in CD_3CN. The signal centered at 0 ppm is Me_4Si.

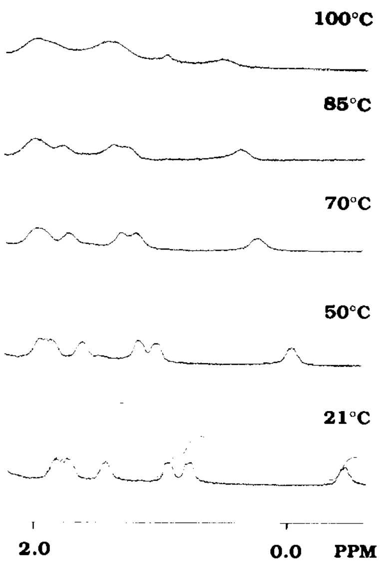


Fig. 3. Temperature dependent display of the upfield region of the 300 MHz ^1H NMR of $[Eu(\mathbf{3c})_3](ClO_4)_3$ in nitrobenzene-d_5.

different rates. We assign the two lowest field signals to the central methylene group where the greatest flexibility exists and the least difference is found in the magnetic environment of the two protons. We assign the second pair of signals (+0.90 and +0.79 ppm) to the methylene group closest to the distal pyridine of **3c** where we also expect a reasonable degree of flexibility. The methylene group closest to the central pyridine is the most inflexible. Its geminal protons would experience the greatest difference in magnetic environment and hence the 2 ppm difference in their room temperature chemical shifts.

For $[Eu(\mathbf{3e})_3](ClO_4)_3$ we find an intermediate situation (Fig. 4). Unlike the dimethylene system **3b**, the two sets of geminal protons in the bridges of **3e** coalesce at different temperatures. Four well resolved signals are observed at −36 °C. As the temperature is raised, the upfield and downfield pairs begin to coalesce such that the upfield pair merge at about +15 °C (13.7 kcal/mol) and the downfield pair merge at +35 °C (14.5

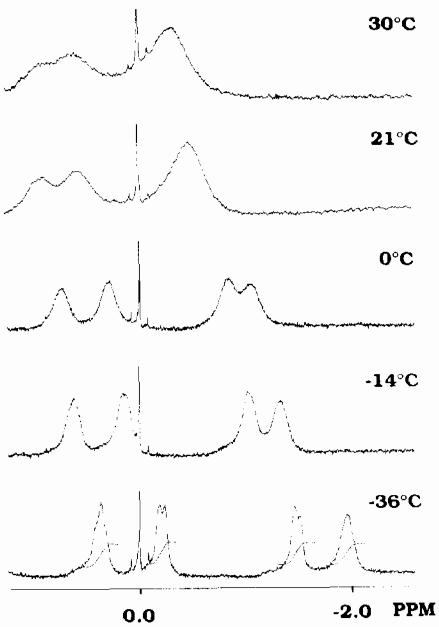


Fig. 4. Temperature dependent display of the upfield region of the 300 MHz ^{1}H NMR of [Eu(**3e**)$_3$](ClO$_4$)$_3$ in CD$_3$CN. The signal centered at 0 ppm is Me$_4$Si.

kcal/mol). The final pair of broad peaks for the complex of **3e** at +30 °C closely approximates those observed for **3b**. We assign the upper field resonances to the geminal protons on the methylene adjacent to the terminal pyridine and the lower field pair to the methylene adjacent to the central pyridine. This latter pair would experience some steric inhibition to conformational inversion from the *p*-tolyl substituent on the central ring.

The case of [Eu(**4**)$_3$](ClO$_4$) represents the extreme of conformational mobility for a bridged tpy complex. Unlike the ligands **3a–e**, **4** does not possess a symmetry axis through C4 and thus the potential exists for the formation of two isomeric tris-complexes with Eu(III). The material obtained in 84% yield from the coordination of **4** with Eu(ClO$_4$)$_3$ shows a single set of ligand resonances in its ^{1}H NMR, indicating the presence of the more symmetrical arrangement of the three ligands about the metal. The single dimethylene bridge evidenced two broad signals at 1.18 and 0.58 ppm which remain virtually unchanged upon cooling to −40 °C. The other half of the ligand is virtually planar due to the unsaturation which is now present in the other bridge. This planarity causes the dimethylene bridged half of the molecule to also prefer a more planar conformation and subsequently lowers the inversion barrier such that it falls below our available temperature range.

Several lanthanide complexes of 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid (DOTA) were examined by Desreux using variable temperature NMR [14]. He concluded that the ethano bridges of the ligand were rigid below room temperature on the NMR time scale. At elevated temperatures ring inversion of the DOTA was achieved by sequential inversion of the ethano bridges around the DOTA perimeter. The estimated inversion barrier of 15.2 kcal/mol is in good accord with our results for bridged terpyridine inversion. A more recent study, however, interprets temperature dependent changes in the NMR spectra of DOTA–lanthanide(III) complexes as being associated with movement of the pendent acetate groups independent of any rearrangement involving the cyclododecane ring [15].

Luminescence

The original premise for our investigation of europium(III) polypyridyl complexes was the hope of observing ligand to metal charge transfer followed by significant luminescence from the excited state of the metal. We were unable to prepare complexes of **1** or **2** but have examined instead the luminescence properties of the model complexes which led to the conformational study herein reported.

The emission spectra of [Eu(**3b,c,e**)$_3$](ClO$_4$)$_3$ in CH$_3$CN are illustrated in Fig. 5. Three principal bands are observed at 592, 616 and 692 nm. The energies of these bands correspond closely with what is observed for the parent complex [Eu(**3a**)$_3$](ClO$_4$)$_3$ [8, 12] indicating that the emission is metal based. The spectra were not adjusted for optical density so that the relative intensities shown in the Figure are not significant. Nevertheless, the emission of [Eu(**3c**)$_3$](ClO$_4$)$_3$ is clearly the least intense although the sample was the most concentrated. Variation of the exciting wavelength from 258 to 323 nm resulted in only a slight variation in this intensity. Therefore, one can conclude that the

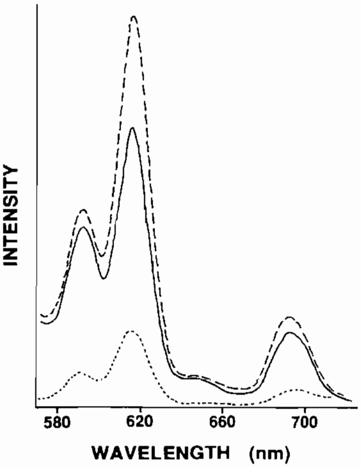


Fig. 5. Emission spectra of [Eu(L)$_3$](ClO$_4$)$_3$ in CH$_3$CN at 25 °C with excitation at 310 nm: L=**3b** (——), 1.5×10^{-4} M; L=**3c** (-----), 1.7×10^{-4} M; L=**3e** (– – –), 7×10^{-5} M.

complex with trimethylene bridged terpyridine emits less strongly than the analogous dimethylene bridged ones due to the less favorable coordination geometry of the more distorted ligand **3c**.

In summary it has been demonstrated that Eu(III) complexes such as $[Eu(\mathbf{3a})_3](ClO_4)_3$ can be stabilized with respect to ligand dissociation. This stabilization may be accomplished by appropriate polymethylene bridging between adjacent pyridine rings. NMR is a powerful tool for the study of the solution conformation of the attached ligands and temperature dependent behavior is evidenced by the coalescence of geminal bridge methylene protons. The inversion process for dimethylene and trimethylene bridges may occur such that individual methylenes in the same bridge undergo conformational change at different rates. A final conclusion of these studies is that the geometry about a tris-coordinated $Eu(tpy)^{3+}$ trication is quite congested and not amenable to the accommodation of more hindered or highly distorted tpy derivatives.

Supplementary material

Tables (26 pages) pertinent to the X-ray crystallographic determination of $[Eu(\mathbf{3b})_3](ClO_4)_3$ including data collection and processing parameters (S1), anisotropic displacement parameters (S2), bond lengths (S3), bond angles (S4), H-atom coordinates (S5), torsion angles (S6), and observed and calculated structure factors (S7) are available from R.P.T.

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