Anionically Substituted 1,1′,1″-Methylidynetris[1*H*-pyrazole] Ligands for the Formation of Neutral Lanthanide Complexes in Water: Synthesis, Characterization, and Photophysical Properties

by **Loïc J. Charbonnière*** and **Raymond Ziessel***

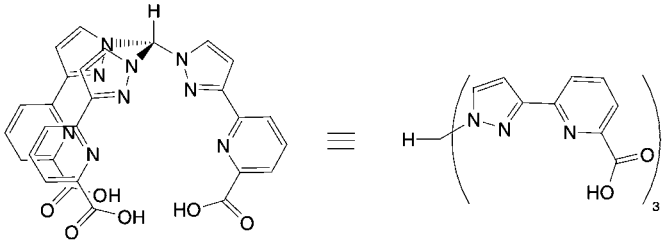
Laboratoire de Chimie Moléculaire, associé au CNRS, Ecole de Chimie, Polymères et Matériaux, 25 rue Becquerel, F-67087 Strasbourg Cedex 02
(e-mail: charbonn@chimie.u-strasbg.fr)

The six-step synthesis of the new podand-type ligand 6,6′,6″-[methylidenetri(1*H*-pyrazole-1,3-diyl)]tris-[pyridine-2-carboxylic acid] (LH_3) is described. Reaction of LH_3 with $LnCl_3 \cdot 6\,H_2O$ (Ln = Eu, Gd, Tb) in MeOH resulted in the isolation of $[LnL] \cdot HCl$ complexes characterized by elemental analysis, mass and IR spectroscopy. Photophysical studies of the Eu and Tb complexes in aqueous solutions revealed the characteristic luminescence features of the metal atoms, indicative of an efficient ligand-to-metal energy-transfer process. Determination of the luminescence quantum yields in H_2O showed the Tb complex to be highly luminescent ($\phi = 15\%$), while, for the Eu complex, the quantum efficiency was only 2%. Excited-state-lifetime measurements in H_2O and D_2O evidenced the presence of *ca.* three H_2O molecules in the first coordination sphere of the complexes. Investigation of the Gd complex allowed the determination of the ligand-centered triplet state and showed the ligand to be well suited for energy transfer to the metal. The luminescence properties of the complexes are described, and the properties of the ligand as a suitable complexation pocket is questioned.

Introduction. – Lanthanide complexes are currently finding a wide range of applications in numerous fields of analytical sciences. While their magnetic properties are particularly interesting for nuclear-magnetic-resonance imaging (MRI) with gadolinium [1] or europium [2] complexes, they also display unique photophysical properties [3] that make them excellent targets for applications in fields such as fluoroimmunoassays [4], time-resolved microscopy [5], or luminescent sensors [6]. The use of these complexes as luminescent probes has boosted the search for highly luminescent, H_2O-soluble and stable compounds with particular emphasis for europium and terbium cations. Two main strategies have been developed to combine luminescence efficiency and H_2O stability. The former one consisted of highly pre-organized architectures that encapsulated the metal cation in cryptand-like molecules in which the metal was embedded in a confined volume [7]. Although this approach is expected to ensure the kinetic and thermodynamic stability of the complexes, it does not always allow for efficient shielding of the metal toward solvent molecules, and it sometimes suffers from low-yield multistep synthetic protocols for the obtention of the macrobicyclic ligands. The second approach takes advantage of the introduction of anionic functions grafted on heteroaromatic moieties to stabilize the compounds through multiple electrostatic interactions with the triply charged lanthanide cations. In addition, chelating arms can be easily introduced in podand-type scaffolds [8] or macrocyclic architectures [9] to bring a primary mode of pre-organization.

As a coordination number of 9 is often found for lanthanide complexes, the introduction of three tridentate chelating arms have encountered great success, and

very elegant C_3-symmetric complexes have been obtained such as dinuclear triple helices [10] that are perfectly stable and luminescent in H_2O solutions. In this context, we envisaged that a 1,1′,1″-methylidynetris[1*H*-pyrazole] base should be an adequate cornerstone for the construction of such a C_3-symmetric complex. Further introduction of pyridine rings at the 3-position of the pyrazole rings are expected to lead to highly luminescent complexes, especially in the case of terbium complexes [11]. Finally, addition of a carboxylate function at the 2-position of the pyridine rings should increase the stability of the complex by introduction of three negatively charged functions leading to a potentially tris-tridentate ligand. In this paper, we describe the synthesis of an LH_3 ligand that combines all these features and of the complexes formed with europium, gadolinium, and terbium ions, together with their photophysical properties in H_2O solution.

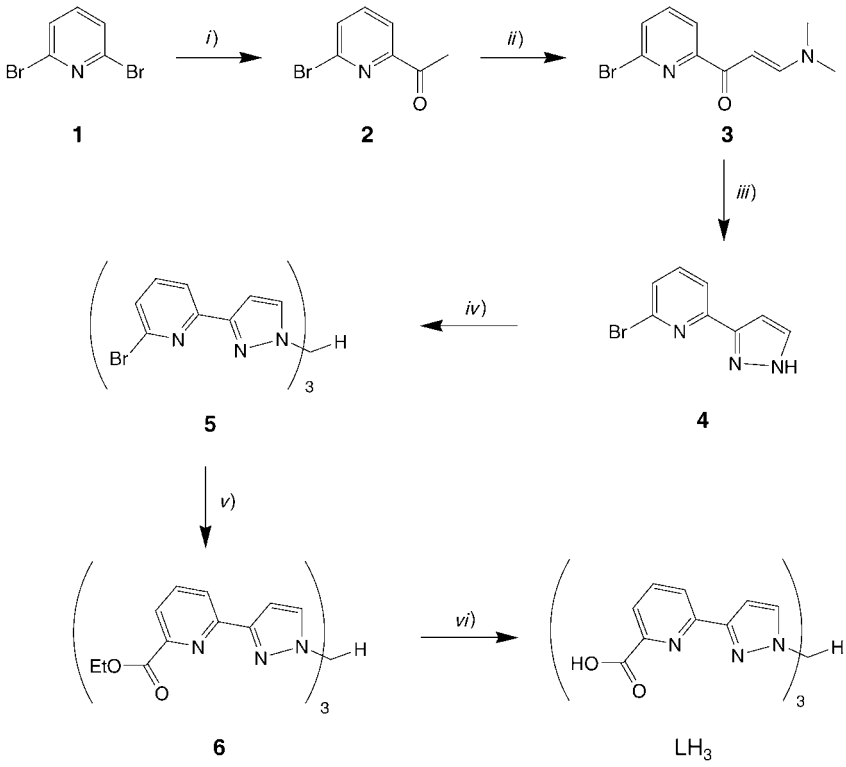


LH_3

Results and Discussion. – *Synthesis of the Ligand.* Ligand LH_3 was obtained according to the synthetic methodology depicted in *Scheme 1*. Commercially available 2,6-dibromopyridine was first transformed to 1-(6-bromopyridin-2-yl)ethanone (**2**) following the procedure developed by *Holm* and co-workers [12]. Upon reaction with a slight excess of dimethylformamide dimethyl acetal at 100°, compound **3** was obtained in 77% yield. The condensation of **3** with hydrazine in hot MeOH afforded the pyrazolylpyridine **4** in quantitative yield. The transformation to the methylidynetris-[pyrazole] precursor **5** was achieved according to a procedure described in [13] with minor modifications. Derivate **4** was first reacted in H_2O with Na_2CO_3, resulting in an exothermal reaction. After cooling, $CHCl_3$ was added to the solution, together with a phase-transfer catalyst, and the reaction mixture was refluxed. At the end of this first step, conventional aqueous workup allowed the isolation of **5**, besides some starting material and an isomer of **5** of σ symmetry. At this stage, **5** and its isomer should not be separated as the procedure is tedious and impairs the overall yield. Thus, the mixture was dissolved in dry toluene and heated in the presence of catalytic amounts of CF_3COOH, which totally converted the isomeric compounds into **5** and made the purification by column chromatography less difficult, yielding the targeted compound **5** in 38% overall yield.

The Br-atoms on the pyridine rings were next transformed in 68% yield into carboxylate functions by an alkoxycarbonylation procedure, by using $[PdCl_2(PPh_3)_2]$ as catalyst under a stream of CO, in a hot mixture of EtOH and Et_3N [14]. After saponification of the ester functions with NaOH and acidification of the mixture, LH_3 was obtained as a dihydrochloride salt in 88%.

Scheme.



i) BuLi, THF, −78°, MeC(O)NMe_2, [12]. *ii*) $Me_2NCH(OMe)_2$, 100°, 2 h; 77%. *iii*) $H_2NNH_2 \cdot H_2O$, MeOH, 80°, 45 min, quant. *iv*) H_2O, Na_2CO_3, $CHCl_3$, $Bz(Et)_3NCl$, reflux, 19 h, then PhMe, CF_3COOH, 110°, 24 h; 38%. *v*) [$Pd(PPh_3)_2Cl_2$], EtOH, Et_3N, CO (1 atm), 70°, 15 h; 68%. *vi*) NaOH, EtOH, H_2O, 70°, 3 h; then conc. HCl; 88%.

Synthesis of the Complexes. The Eu, Gd, and Tb complexes were obtained in very good yields by dissolving equimolar amounts of the ligand and hydrated chloride salts of the lanthanide cations, followed by precipitation of the complexes with acetone. The elemental analyses of all three complexes were very similar and corresponded to a one-ligand-to-one-metal stoichiometry completed by one molecule of HCl. The FAB-MS spectra (positive-ion mode) of each complex revealed the $[Ln(L)]+H]^+$ species to be the major peak, with, in the case of the Eu complex, the expected isotopic distribution. Interestingly, in the ESI-MS of the Tb complex, the major species corresponded to $[[Ln(L)]+Na]^+$, and no peak corresponding to the protonated species was observed in contrast to the FAB-MS. This result pointed to an easy displacement of the H^+ by a Na^+ ion in diluted solutions, disregarding the possibility of strong intramolecular H-bonding in the complex, as previously highlighted in similar structures [15]. The IR spectra of all complexes were also very similar, pointing to an isostructural series. The spectra established the presence of the ligand with absorption bands characteristic of the C=O vibrations around 1630–1633 cm^{-1}, which were shifted by *ca.* 90 cm^{-1} to lower energy

when compared to the protonated ligand, suggesting that the acidic function was deprotonated in the complex and strongly interacting with the lanthanide cation [16].

Photophysical Properties. The UV/VIS absorption spectrum of the ligand LH_3 in basic aqueous solution (pH 9.6) displays two strong absorption bands in the UV domain at 254 and 285 nm that, according to their molar absorption coefficients, are attributed to $\pi \rightarrow \pi^*$ transitions centered on the aromatic moieties, with a probable contribution from $n \rightarrow \pi^*$ transitions. Upon excitation in the low-energy tail of the spectrum, a broad and structured emission spectrum is observed in the 320–450 nm region, with maxima at 324 and 349 nm and a shoulder around 380 nm (*i.e.*, 30860, 28650, and 26250 cm^{-1} resp.; see *Fig. 1*). When a 10-μs delay is inserted before integration of the emitted signal, all the luminescence vanishes, thus pointing to a fluorescence signal arising from $^1\pi\pi^*$ and $^1n\pi^*$ transitions of the aromatic moieties. This is further confirmed by the excitation spectra (λ_{em} 347 nm), which corresponds well to the absorption spectrum of deprotonated LH_3 (*Fig. 1*).

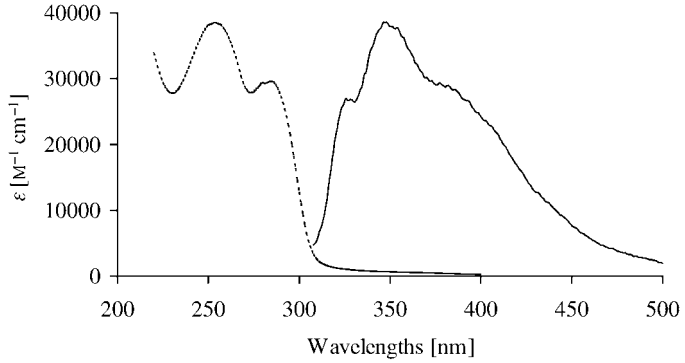


Fig. 1. *UV/VIS Absorption* (···) *and fluorescence* (—) *spectra of the ligand* LH_3 *in basic aqueous solution* (pH 9.6)

The UV/VIS absorption spectrum of the Gd complex displays features similar to those of the free ligand at pH 9.6 (see *Table*). The coordination of the metal atom has only a weak influence when compared to the basic form of the ligand, except for what concerns the intensity of the transitions which are smaller in the complex. Upon excitation at 292 nm, a broad emission band arises in the emission spectrum, with a maximum at 343 nm and a pronounced shoulder at 329 nm. In this case, too, the excitation spectrum closely matches the absorption spectrum, suggesting that this emission arises from the $^1\pi\pi^*$ and $^1n\pi^*$ transitions of the aromatic moieties. Introduction of a 10- to 40-μs delay before integration of the emitted signal results in the loss of the luminescence at 343 nm. Concomitantly, a broad structureless emission band can then be observed around 435 nm (23000 cm^{-1}). On the bases of its energy level and long-living excited state, this emission is attributed to the $^3\pi\pi^*$ level centered on the aromatic moieties, in good agreement with values reported for other pyrazolylpyridine ligands [7c][11]. Taking the maximum of the fluorescence band as the energy level of the singlet state (29150 cm^{-1}) gives a rough estimate of the energy difference between the singlet and the triplet states of 6150 cm^{-1}, a value above

Table. *Photophysical Properties of the Ligand LH_3 and Its Lanthanide Complexes [Ln(L)] · HCl in Water*

	Absorption[a])	Emission[b])					
	λ_{max} [nm] (ε [м$^{-1}$ cm^{-1}])	$^1\pi \rightarrow \pi^*$ (λ_{max})	$^3\pi \rightarrow \pi^*$ (λ_{max})	Ln* (λ_{max})	τ_{H2O} [ms] τ_{D2O} [ms]	Φ_{H2O} [%] Φ_{D2O} [%]	q
LH_3 [c])	285 (29600)	349					
	254 (38650)						
[Eu(L)]·HCl	291 (22390)			619[d])	0.28	2	3.1[e])
	250 (32450)				2.12	23	
[Gd(L)]·HCl	292 (22200)	343	435				
	250 (30100)						
[Tb(L)]·HCl	291 (22500)			548[f])	1.00	15	2.7[g])
	252 (33100)				2.54	80	

[a]) Concentration ranging from 4.3 to $7.3 \cdot 10^{-5}$ м. [b]) Concentration ranging from 4.3 to $7.3 \cdot 10^{-6}$ м. [c]) pH 9.6. [d]) Corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition on Eu^{3+}. [e]) Calculated according to [18]. [f]) Corresponding to the $^5D_4 \rightarrow {}^7F_5$ transition on Tb^{3+}. [g]) Calculated according to [21].

5000 cm^{-1} postulated to be the lower limit for an efficient singlet-to-triplet intersystem crossing [17].

The UV/VIS absorption spectrum of the Eu complex is very similar to that of the Gd complex (see *Table*). Upon excitation at 291 nm, the emission spectrum shows the typical metal-centered emission of Eu^{3+} with emission bands at 581, 595, 619, 652, and *ca.* 695 nm attributed to $^5D_0 \rightarrow {}^7F_J$ ($J = 0-4$) transitions (*Fig. 2*). The corresponding excitation spectrum (λ_{em} 620 nm) perfectly matches the absorption spectrum, unravelling an efficient ligand-to-metal energy-transfer process in the complex. The decays of the emission intensity of the complex in H_2O and D_2O (see *Table*) perfectly fit mono-exponential functions. According to the empirical formula developed by *Horrocks* and *Supkowski* [18], the apparent hydration state is 3.1, with an estimated standard error of 0.1 H_2O molecules. This clearly demonstrates that the Eu-atom is not well shielded from the solvent molecules, with *ca.* three H_2O molecules in the first coordination sphere of the metal. This result is quite surprising when considering the fact that the ligand presents nine coordinating heteroatoms, which should perfectly fit the coordination number of the Eu-atom. The probable origin of the presence of H_2O molecules is to be found in the diverging binding vectors of the three coordinating arms of L, as previously observed in the X-ray crystal structures of similar complexes constructed from 3,3′,3″-trisubstituted 1,1′,1′-methylidynetris[1*H*-pyrazole] (see, *e.g.*, [19]) or tris(3-substituted 1*H*-pyrazole-κN^1)hydroborate [11a][20] ligands. The slightly distorted sp^3 geometry of the capping C-atom of L prevents the chelating arms from fully folding up around the metal atom, and the face of the metal atom opposite to this C-atom is probably 'naked' and accessible to H_2O molecules. Despite this high number of H_2O molecules, the emission quantum yields of the Eu complex in H_2O or D_2O remain interesting with values of 2 and 23%, respectively.

The absorption properties of an aqueous solution of the Tb complex are very similar to those observed for the Eu and Gd complexes. Upon excitation at 291 nm, the emission spectrum displays the characteristic features of Tb^{3+} emission with narrow emission bands at 492, 548, 588, and 623 nm attributed to the $^5D_4 \rightarrow {}^7F_J$ ($J = 6-3$)

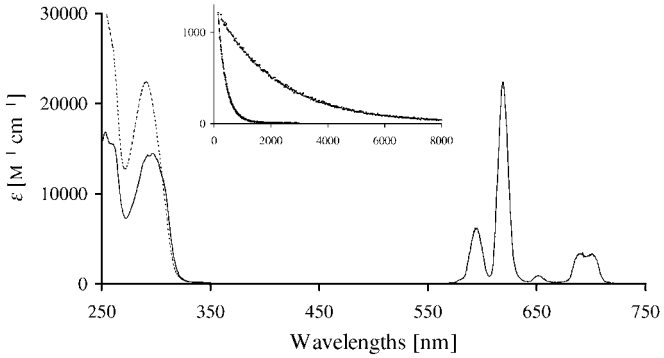


Fig. 2. *UV/VIS Absorption* (···), *excitation* (—, left) *and emission* (—, right) *spectra of [EuL] · HCl in water.* Inset: luminescence decay in H_2O and D_2O (abcissa in μs).

transitions (*Fig. 3*). The perfect match of the absorption and excitation spectra again reveals energy transfer from the ligand to the complex. Measured excited-state lifetimes for the Tb complex in H_2O and D_2O give values of 1.00 and 2.54 ms, respectively. By using the relationship developed by *Parker* and co-workers [21] for Tb complexes, the calculated hydration number is 2.7. For the Tb complex, too, *ca.* three H_2O molecules are coordinated in the first coordination sphere of the metal. The measured quantum yields are far better for the Tb complex (see *Table*). These values perfectly match the results of *Mukkala* and co-workers, who showed that good energy transfer can occur when the triplet state of the ligand (23000 cm^{-1}) is situated far enough above the $^5D_4$ level of Tb^{3+} (20800 cm^{-1}) to avoid back energy transfer ($\Delta E >$ 1850 cm^{-1}) at room temperature. In the case of the Eu complex, the lower quantum yield cannot be explained only by the quenching due to proximate H_2O molecules. A less-efficient ligand-to-metal energy transfer and a plausible ligand-to-europium electron-transfer quenching mechanism should be kept in mind [22].

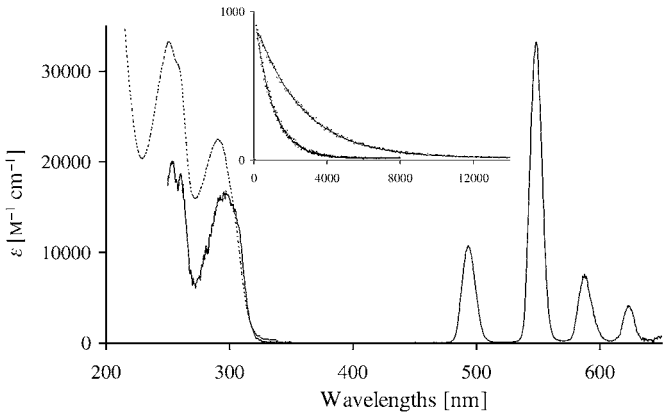


Fig. 3. *UV/VIS Absorption* (···), *excitation* (—, left) *and emission* (—, right) *spectra of [TbL] · HCl in H_2O.* Inset: luminescence decay in H_2O and D_2O (abcissa in μs).

In conclusion, we have synthesized a new podand-type ligand based on tridentate pyrazolylpyridinecarboxylate arms. This ligand efficiently coordinates to lanthanide cations in H_2O solutions to form 1:1 metal-to-ligand complexes. The luminescence properties displayed by the Eu and Tb complexes are appealing, particularly for the Tb complex, but the complexation pocket offered by the ligand is too large to shield efficiently the metal atoms from the solvent molecules. The diverging directionality imposed by the central C-atom prevents a good folding of the chelating arms, leaving free coordination sites on the cations. These sites are filled by three H_2O molecules that largely quenched the metal-centered luminescence by vibronic deactivation processes. To improve the folding of the chelating arms, a methodology is currently under study in which methylene bridges will be introduced between the central C-atom and the chelating arms.

This work was supported by the *CNRS* and the *Conseil Général d'Alsace*. *L. C.* thanks the French *Ministère de la Recherche* for financial support (*ACI Jeunes Chercheurs* n° 4116).

Experimental Part

General. Solvents and raw materials were of anal. grade and were used as received. An exception was MeCN, which was filtered over activated alumina (*Merck*) and distilled from P_2O_5 under Ar immediately prior to use. The 1-(6-bromopyridin-2-yl)ethanone (**2**) was synthesized according to [12]. CC = Column chromatography. Absorption spectra: *Uvikon 933* spectrophotometer; 1-cm pathlength quartz cells. FT-IR Spectra: *Nicolet-210* spectrometer; KBr pellets; in cm^{-1}. NMR Spectra: *Bruker AC-200* spectrometer at 200 (^1H) and 50 MHz (^{13}C); perdeuterated solvents as internal standards; δ in ppm, J in Hz. Fast-atom-bombardment (FAB) MS: positive mode; nitrobenzyl alcohol as matrix; in *m/z* (rel. %). Fluorescence and corrected excitation spectra: *Perkin-Elmer LS 50* spectrofluorimeter equipped with a *Hamamatsu R928* photomultiplier tube for emission in the red part of the spectra. Luminescence quantum yields (uncertainty ± 15%) were measured relative to *Rhodamine 6G* in MeOH ($\phi = 0.86$; [23]) for the Tb complex and $[Ru(bipy)_3]Cl_2$ in air-equilibrated dist. H_2O ($\phi = 0.028$, [24]) for the Eu complex as standard. The emission spectra were then recorded in the phosphorescence mode with a delay time of 0 μs and an integration time of 20 ms for the Eu and 40 ms for the Tb complex. Correction for the wavelength dependence of the excitation intensity and the photomultiplier response were realized by the instrumental setup. When necessary, corrections were introduced for refractive index of the solvents [25]. Excited-state lifetimes were measured on a *PTI-Quantamaster* instrument by monitoring the emission at 620 and 545 nm, respectively, for the Eu and Tb complex. The decay curves were the average of five measurements with 500 channels on timescales at least greater than five lifetimes. The decays were fitted with mono- and bi-exponential functions with the software-implemented curve fitting program, and the fitting parameters showed excellent agreement with single exponential decays in all cases.

1-(6-Bromopyridin-2-yl)-3-(dimethylamino)prop-2-en-1-one (**3**). In a *Schlenck* tube under Ar, **2** (900 mg, 4.46 mmol) and dimethylformamide dimethyl acetal (590 mg, 4.96 mmol) were heated for 2 h at 100°. After cooling the mixture to r.t., the resulting solid was sonicated with Et_2O (20 ml). After filtration, a first fraction of **3** (510 mg) was obtained as a yellow solid. Vacuum evaporation of the mother liquor followed by crystallization of the oily residue with CH_2Cl_2 gave a second crop of **3** (417 mg; overall 77%). ^1H-NMR ($CDCl_3$): 2.99 (*s*, 3 H); 3.17 (*s*, 3 H); 6.37 (*d*, $^3J = 12.5$, 1 H); 7.52 (*d*, $^3J = 7.5$, 1 H); 7.63 (*t*, $^3J = 7.5$, 1 H); 7.88 (*d*, $^3J = 12.5$, 1 H); 8.08 (*d*, $^3J = 7.5$, 1 H). ^{13}C-NMR ($CDCl_3$): 37.6; 45.3; 91.1; 120.9; 129.9; 139.1; 140.8; 155.2; 157.5; 185.0. ESI-MS: 254.9754 (95, $[M+H]^+$), 256.9742 (100, $[M+H]^+$). Anal. calc. for $C_{10}H_{11}BrN_2O$: C 42.89, H 2.70, N 18.75; found: C 42.73, H 2.62, N 18.64.

2-Bromo-6-(1H-pyrazol-1-yl)pyridine (**4**). A soln. of **3** (496 mg, 1.84 mmol) and hydrazine hydrate (360 μl, 7.4 mmol) in MeOH (10 ml) in a *Schlenck* tube was heated to 80° for 45 min. After evaporation, the residue was dissolved in CH_2Cl_2/MeOH 98:2 (10 ml), the soln. filtered over a 1-cm-thick layer of silica gel, and the silica gel was further washed with CH_2Cl_2/MeOH 98:2 (100 ml). Evaporation and drying under vacuum gave 410 mg (quant.) of **4**. Pale yellow oily residue. ^1H-NMR ($CDCl_3$): 6.80 (*d*, $^3J = 2.0$, 1 H); 7.31 (*d*, $^3J = 7.5$, 1 H); 7.49 (*t*, $^3J = 8.0$, 1 H); 7.69 (*d*, $^3J = 7.5$, 1 H); 7.75 (*m*, $^3J = 2.0$, 1 H); 12.37 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$): 104.0; 118.9; 126.6; 134.1 (br.); 139.0; 141.7; 146.3 (br.); 151.6. FAB-MS: 224.3 (100, $[M+H]^+$), 226.3 (98, $[M+H]^+$).

*2,2′,2″-[Methylidynetri(1*H*-pyrazol-1,3-diyl)]tris[6-bromopyridine]* (**5**). To a vigorously stirred suspension of **4** (1.0 g, 4.5 mmol) and triethyl(benzyl)ammonium chloride (120 mg, 0.53 mmol) in H_2O (10 ml), Na_2CO_3 (3.0 g, 28 mmol) was slowly added by portions. After the exothermic reaction had ceased, $CHCl_3$ (15 ml) containing triethyl(benzyl)ammonium chloride (120 mg, 0.053 mmol) was added, and the mixture was refluxed for 19 h. The aq. phase was extracted twice with CH_2Cl_2 (75 ml), and the combined org. phase dried (Na_2SO_4) and evaporated. The solid was dissolved in dry toluene (35 ml) containing 3 drops of CF_3COOH, and the soln. was heated to 110° for 24 h in a *Schlenck* tube under Ar. After cooling, the soln. was washed with 5% $NaHCO_3$ soln. (30 ml) and H_2O (20 ml). The H_2O layer was extracted with CH_2Cl_2 (50 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the residue purified by CC (SiO_2, CH_2Cl_2): **5** (391 mg, 38%). White solid. R_f 0.54 (SiO_2, CH_2Cl_2). ^{1}H-NMR ($CDCl_3$): 7.07 (*d*, ^3J = 3, 3 H); 7.42 (*dd*, ^3J = 8.0, ^4J = 1.0, 3 H); 7.57 (*t*, ^3J = 7.5, 3 H); 7.65 (*d*, ^3J = 2.5, 3 H); 7.93 (*dd*, ^3J = 7.5, ^4J = 1.0, 3 H); 8.52 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 84.0; 107.0; 119.2; 127.5; 131.1; 139.0; 141.8; 152.4; 152.9. FAB-MS: 682.3 (100, M^+), 684.3 (100, M^+). Anal. calc. for $C_{25}H_{16}Br_3N_9$: C 44.02, H 2.36, N 18.48; found: C 43.78, H 2.09, N 18.21.

*Triethyl 6,6′,6″-[Methylidynetri(1*H*-pyrazol-1,3-diyl)]tris[pyridine-2-carboxylate]* (**6**). To a soln. of **5** (206 mg, 0.30 mmol) in CH_2Cl_2 (4 ml), EtOH (15 ml), Et_3N (10 ml), and $[Pd(PPh_3)_2Cl_2]$ (32 mg, 0.045 mmol) were added. The soln. was heated to 70°, and CO was allowed to bubble into the soln. for 15 h. The soln. was cooled, evaporated, and co-evaporated with MeOH (2 × 20 ml), and the residue was purified by CC (SiO_2, CH_2Cl_2/MeOH 100:0 → 99:1): **7** (137 mg, 68%). Pale yellow solid. R_f 0.26 (SiO_2, CH_2Cl_2/MeOH 99:1). ^{1}H-NMR ($CDCl_3$): 1.45 (*t*, ^3J = 7.0, 9 H); 4.47 (*q*, ^3J = 7.0, 6 H); 7.18 (*d*, ^3J = 2.5, 3 H); 7.69 (*d*, ^3J = 2.5, 3 H); 7.85 (*t*, ^3J = 8.0, 3 H); 8.05 (*dd*, ^3J = 8.0, ^4J = 1.0, 3 H); 8.15 (*dd*, ^3J = 8.0, ^4J = 1.0, 3 H); 8.58 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 14.4; 61.9; 84.1; 107.0; 123.7; 124.4; 131.1; 137.6; 148.2; 151.7; 153.6; 165.3. ES-MS: 662.2 (18, $[M + M^+]$), 684.2 (100, $[M + Na^+]$). Anal. calc. for $C_{34}H_{31}N_9O_6$: C 61.72, H 4.72, N 19.05; found: C 61.46, H 4.56, N 18.74.

*6,6′,6″-[Methylidynetri(1*H*-pyrazol-1,3-diyl)]tris[pyridine-2-carboxylic acid]* (**LH_3**). To a soln. of **6** (132 mg, 0.20 mmol) in EtOH (5 ml) was added H_2O (10 ml) containing NaOH (48 mg, 1.2 mmol). The soln. was heated to 70° for 3 h and then concentrated to 3 ml. Conc. HCl soln. was slowly added until pH 2. A white solid precipitated, which was separated by centrifugation and dried under reduced pressure: $LH_3 \cdot 2$ HCl (114 mg, 88%). IR: 2972, 2926, 2890, 1720, 1587, 1447, 1341, 1248, 18083, 1050. ^{1}H-NMR ((D_6) DMSO): 7.19 (*d*, ^3J = 2.5, 3 H); 7.99–8.10 (*m*, 6 H); 8.15–8.20 (*m*, 3 H); 8.22 (*d*, ^3J = 2.5, 3 H), 9.35 (*s*, 1 H). ^{13}C-NMR ((D_6)acetone): 84.4; 107.6; 124.3; 126.8; 133.2; 139.8; 147.9; 151.7; 153.5; 165.6. FAB-MS: 578.3 (100, $[M + H]^+$), 533.2 (15, $[M - CO_2 + H]^+$). Anal. calc. for $C_{28}H_{19}N_9O_6 \cdot 2$ HCl: C 51.71, H 3.25, N 19.38; found: C 51.59, H 3.16, N 19.29.

Lanthanide Complexes with LH_3. Typical Procedure. $LH_3 \cdot 2$ HCl (1 equiv.) was dissolved in a MeOH soln. of $LnCl_3 \cdot 6\ H_2O$ (1 equiv.). The soln. was agitated at r.t. for 30 min and evaporated. The solid was dissolved in a minimum of MeOH, and acetone was slowly added to the soln., resulting in the precipitation of the complex, which was isolated by centrifugation and dried under reduce pressure.

*{6,6′,6″-[Methylidynetri(1*H*-pyrazol-1,3-diyl)]tris[pyridine-2-carboxylato]}europium Hydrochloride Dihydrate* ($[Eu(L)] \cdot HCl \cdot 2\ H_2O$). Yield 88%. IR: 2972, 2926, 2886, 1630, 1600, 1461, 1401, 1255, 1083, 1050. FAB-MS (pos.): 726.3 (80), 727.3 (30), 728.3 (100), 729.2 (30); calc. for ($[[Eu(L)] + H]^+$): 726 (86), 727 (30), 728 (100), 729 (34). Anal. calc. for $C_{28}H_{16}EuN_9O_6 \cdot HCl \cdot 2\ H_2O$: C 42.09, H 2.65, N 15.78; found: C 41.97, H 2.72, N 15.64.

*{6,6′,6″-[Methylidynetri(1*H*-pyrazol-1,3-diyl)tris[pyridine-2-carboxylato]}gadolinium Hydrochloride Hydrate* ($[Gd(L)] \cdot HCl \cdot H_2O$). Yield 92%. IR: 2972, 2923, 2880, 1633, 1594, 1527, 1454, 1408, 1382, 1084, 1040. FAB-MS (pos.): 732.4 (80, ($[[Gd(L)] + H]^+$). Anal. calc. for $C_{28}H_{16}GdN_9O_6 \cdot HCl \cdot H_2O$: C 42.78, H 2.44, N 16.03; found: C 41.65, H 2.64, N 15.87.

*{6,6′,6″-[Methylidynetri(1*H*-pyrazol-1,3-diyl)tris[pyridine-2-carboxylato]}terbium Hydrochloride Hydrate* ($[Tb(L) \cdot HCl \cdot H_2O$). Yield 88%. IR: 2972, 2926, 2893, 1633, 1594, 1528, 1455, 1402, 1250, 1090, 1045. FAB-MS (pos.): 734.5 (100 $[[Tb(L)] + H]^+$). ESI-MS: 756.3 ($[[Tb(L)] + Na]^+$). Anal. calc. for $C_{28}H_{16}N_9O_6Tb \cdot HCl \cdot H_2O$: C 42.68, H 2.43, N 16.00; found: C 42.51, H 2.59, N 15.76.

REFERENCES

[1] P. Caravan, J. J. Ellison, T. J. McMurry, R. B. Laufer, *Chem. Rev.* **1999**, *99*, 2293; C. Piguet, J.-C. G. Bünzli, *Chem. Soc. Rev.* **1999**, *28*, 347.

[2] S. Zhang, P. Winter, K. Wu, A. D. Sherry, *J. Am. Chem. Soc.* **2001**, *123*, 1517.

[3] J.-C. G. Bünzli, in 'Lanthanide Probes in Life, Chemical and Earth Sciences', Eds. G. R. Choppin, J.-C. G. Bünzli, Elsevier, Amsterdam, 1989, p. 219.
[4] E. F. Gudgin Dickson, A. Pollak, E. P. Diamandis, *J. Photochem. Photobiol. B: Biol.* **1995**, *27*, 3; I. Hemmilä, S. Webb, *Drug Discovery Today*, **1997**, *2*, 273; V. W.-W. Yam, K. K.-W. Lo, *Coord. Chem. Rev.* **1998**, *184*, 157.
[5] G. Marriott, R. M. Clegg, D. J. Arndt-Jovin, T. M. Jovin, *Biophys. J.* **1991**, *60*, 1374; A. Beeby, S. W. Botchway, I. M. Clarkson, S. Faulkner, A. W. Parker, D. Parker, J. A. G. Williams, *J. Photochem. Photobiol. B: Biol.* **2000**, *57*, 83.
[6] H. Tsukube, S. Shinoda, *Chem. Rev.*, **2002**, *102*, 2389; D. Parker, *Coord. Chem. Rev.*, **2000**, *205*, 109; O. S. Wolfbeis, A. Dürkop, M. Wu, Z. Lin, *Angew. Chem. Int. Ed.*, **2002**, *41*, 4495; T. Gunnlaugsson, D. A. McDonaill, D. Parker, *J. Am. Chem. Soc.*, **2001**, *123*, 12866; L. J. Charbonnière, R. Ziessel, M. Montalti, L. Prodi, N. Zaccheroni, C. Boehme, G. Wippf, *J. Am. Chem. Soc.* **2002**, *124*, 7779.
[7] B. Alpha, J.-M. Lehn, G. Mathis, *Angew. Chem., Int. Ed.*, **1987**, *26*, 266; G. Mathis, *Clin. Chem.* **1993**, *39*, 1953; C. Galaup, J. Azéma, P. Tisnès, C. Picard, P. Ramos, O. Juanes, E. Brunet, J. C. Rodrigues-Ubis, *Helv. Chim. Acta* **2002**, *85*, 1613.
[8] Y. Bretonnière, M. Mazzanti, J. Pécaut, F. A. Dunand, A. Merbach, *Chem. Commun.* **2001**, 621; L. J. Charbonnière, N. Weibel, R. F. Ziessel, S*ynthesis* **2002**, *8*, 1101.
[9] H. Takalo, I. Hemmilä, T. Sutela, M. Latva, *Helv. Chim. Acta* **1994**, *295*, 27; L. Charbonnière, R. Ziessel, M. Guardigli, A. Roda, N. Sabbatini, M. Cesario, *J. Am. Chem. Soc.*, **2001**, *123*, 2436.
[10] C. Platas-Iglesias, C. Piguet, N. André, J.-C. G. Bünzli, *J. Chem. Soc. Dalton Trans.* **2001**, 3084; M. Elhabiri, R. Scopelliti, J.-C. G. Bünzli, C. Piguet, *J. Am. Chem. Soc.* **1999**, *121*, 10747; M. Elhabiri, R. Scopelliti, J.-C. G. Bünzli, C. Piguet, *Chem. Commun.* **1998**, 2347; J. J. Lessmann, W. D. Horrocks Jr., *Inorg. Chem.* **2000**, *39*, 3114.
[11] a) N. Armaroli, G. Accorsi, F. Barigelletti, S. M. Couchman, J. S. Fleming, N. C. Harden, J. C. Jeffery, K. L. V. Mann, J. A. McCleverty, L. H. Rees, S. R. Starling, M. D. Ward, *Inorg. Chem.* **1999**, *38*, 5769; b) N. Armaroli, F. Barigelletti, M. D. Ward, J. A. McCleverty, *Chem. Phys. Lett.*, **1997**, *276*, 435; c) M. Latva, H. Takalo, V.-M. Mukkala, C. Matachescu, J. C. Rodriguez-Ubis, J. Kankare, *J. Lumin.* **1997**, *75*, 149; d) J. C. Rodrigues-Ubis, R. Sedano, G. Barroso, O. Juanes, E. Brunet, *Helv. Chim. Acta* **1997**, *80*, 86.
[12] J. E. Parks, B. E. Wagner, R. H. Holm, *J. Organomet. Chem.* **1973**, *56*, 53.
[13] D. L. Reger, T. C. Grattan, K. J. Brown, C. A. Little, J. J. S. Lamba, A. L. Rheingold, R. D. Sommer, *J. Organomet. Chem.* **2000**, *607*, 120.
[14] A. El Ghayoury, R. Ziessel, *J. Org. Chem.* **2000**, *65*, 7757.
[15] F. Renaud, C. Piguet, G. Bernardinelli, J.-C. G. Bünzli, G. Hopfgartner, *J. Am. Chem. Soc.* **1999**, *121*, 9326; F. Renaud, C. Piguet, G. Bernardinelli, G. Hopfgartner, J.-C. G. Bünzli, *Chem. Commun.* **1999**, 457.
[16] R. M. Silverstein, G. C. Bassler, 'Identification Spectrométrique des Composes Organiques', Masson et Cie/Gauthier-Villars, Paris, 1968.
[17] F. J. Steemers, W. Verboom, D. N. Reinhoudt, E. B. Van der Tol, J. W. Verhoeven, *J. Am. Chem. Soc.*, **1995**, *117*, 9408.
[18] R. M. Supkowski, W. D. Horrocks Jr., *Inorg. Chim. Acta* **2002**, *340*, 44.
[19] D. L. Reger, J. E. Collins, *Inorg. Chem.*, **1997**, *36*, 345; D. L. Reger, J. E. Collins, S. M. Myers, A. L. Reingold, L. M. Liable-Sands, *Inorg. Chem.*, **1997**, *36*, 345.
[20] Z. R. Reeves, K. L. V. Man, J. C. Jeffery, J. A. McCleverty, M. D. Ward, F. Barigelletti, N. Armaroli, *J. Chem. Soc., Dalton Trans.* **1999**, 349; A. Beeby, B. P. Burton-Pye, S. Faulkner, G. R. Motson, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **2002**, 1923; P. L. Jones, A. J. Amoroso, J. C. Jeffery, J. A. McCleverty, E. Psillakis, L. H. Rees, M. D. Ward, *Inorg. Chem.* **1997**, *36*, 10.
[21] A. Beeby, I. M. Clarckson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. De Sousa, J. A. Gareth Williams, M. Woods, *J. Chem. Soc., Perkin Trans. 2* **1999**, 493.
[22] J.-C. G. Bünzli, P. Froidevaux, J. M. Harrowfield, *Inorg. Chem.* **1993**, *32*, 3306; J.-C. G. Bünzli, F. Ihringer, *Inorg. Chim. Acta*, **1996**, *246*, 195; L. J. Charbonnière, C. Balsiger, K. J. Schenk, J.-C. G. Bünzli, *J. Chem. Soc., Dalton Trans.* **1998**, 505.
[23] J. Olmsted III, *J. Phys. Chem.* **1979**, *83*, 2581.
[24] K. Nakamura, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.
[25] B. Valeur, 'Molecular Fluorescence', Wiley-VCH Verlag GmbH, Weinheim, 2002.

Received May 28, 2003