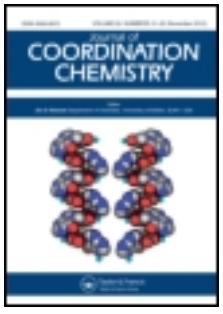

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Group 3 and lanthanide triflate-complexes with [N,N,O]-donor ligands: synthesis, characterization, and cytotoxic activity

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Group 3 and lanthanide triflate-complexes with [N,N,O]-donor ligands: synthesis, characterization, and cytotoxic activity

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Group 3 and rare-earth triflate-complexes M(OTf)$_2$(bdmpza) {M = Sc (**1^{Sc}**), Y (**1^{Y}**), La (**1^{La}**), Sm (**1^{Sm}**), Eu (**1^{Eu}**) OTf = SO_3CF_3} bearing the heteroscorpionate ligand bdmpza {bdmpza = bis(3,5-dimethyl-pyrazol-1-yl)acetate} have been synthesized and characterized, together with the yttrium and europium complexes M(OTf)(bdmpza)$_2$ {M = Y (**2^{Y}**), Eu (**2^{Eu}**)}. The photoluminescent behavior of **2^{Eu}** has been investigated. The coordination mode of the [N,N,O]-donor in these complexes has been elucidated by DFT calculations. The cytotoxic effect of selected complexes and of the free ligand toward HeLa cells has been evaluated.

Keywords: Group 3; Lanthanides; Scorpionates; Cytotoxicity

1. Introduction

Since the first examples of scandium, yttrium, lanthanum, and rare-earth metal homoleptic hydrotris(pyrazol-1-yl)borate complexes M(Tp)$_3$ were reported [1], homo- and heteroscorpionate ligands have been shown to be useful for synthesis of a wide range of stable group 3 and lanthanide derivatives [2]. As a result of the variable size of M(III), the predominant ionic bonding and the well-known oxophilicity of these metals, the coordinative unsaturation, the presence of hard donors and the ligand charge are critical factors in controlling the coordination number, the geometry, and the architecture of their complexes and isolation of well-defined molecular species. Scorpionates represent an attractive and versatile choice, with possible fine-tuning of the electronic and steric properties of these ligands and consequently control of the metal coordination sphere.

A class of scorpionate [N,N,O]-donor ligands having interesting coordinating and bio-mimetic properties toward several different metal ions is that of

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bis(pyrazol-1-yl)acetate derivatives, initially proposed by Burzlaff and co-workers [3, 4]. Otero *et al*. studied the coordination chemistry of these polydentate ligands toward scandium and yttrium, with isolation of several complexes where the coordination sphere is saturated by chloride, alkoxide, and phenanthroline ligands [5].

A field of applied coordination chemistry where group 3 and lanthanide complexes are deeply studied is that of chemotherapeutic agents. The biologic properties of these metal ions, primarily based on their similarity to calcium, have been the basis for research into potential therapeutic applications. For example, complexes of rare-earth metals with coumarin-based ligands have been examined on different cell lines and DNA cleavage studies have been carried out. Lanthanide complexes having macrocyclic monoanionic ligands containing five coordinating nitrogen atoms in the central core, the texaphyrins, have progressed into clinical trials. A series of cerium(III) complexes with bipyridine or phenanthroline ligands has shown interesting antiproliferative activity against tumor cell lines, while a lanthanum complex with 2,6-pyridine dicarboxylic acid and α-picolinic acid induce leukemia K562 tumor cell apoptosis [6]. Recently, Wang and co-workers have investigated systematically the binding of Congo Red–Sm(III) and hematoxylin–Eu(III) complexes with DNA [7].

The choice of ligand coordinating metal ions is crucial for tuning biological activity of the corresponding group 3 and rare-earth complexes. In this work, we report the synthesis and characterization of some group 3 and lanthanide triflate-complexes with the heteroscorpionate ligand bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza), together with the evaluation of the cytotoxic effect of selected complexes and the free ligand toward human cervix adenocarcinoma HeLa cells.

2. Experimental

2.1. *Materials and methods*

All manipulations were carried out under oxygen- and moisture-free atmosphere in a MBraun MB 200 glove-box with a purifying unit G-II. All reaction and NMR solvents were thoroughly deoxygenated and dried under N_2 by refluxing over suitable drying agents following common procedures [8]. Anhydrous group 3 and lanthanide triflates $M(OTf)_3$ were purchased from Strem or Aldrich and used as received. Bis(3,5-dimethylpyrazol-1-yl)acetic acid (**Hbdmpza**) was prepared following the reported procedure starting from dibromoacetic acid and 3,5-dimethylpyrazole (Aldrich) [3]. Purification of the stable products before elemental analyses was carried out by slowly cooling (from 30°C to −25°C during a week) clear solutions of the complexes. The vials or glass tubes containing the solutions were cooled in a jacketed glass vessel connected to a programmable Thermo Scientific C25P cryostat having a Phoenix II controlling unit.

CHNS elemental analyses were carried out on either a Fison EA1108 or a Thermo Scientific FLASH 2000 CHNS-O microanalyzer. Conductivity measurements were carried out at 298 K on 10^{-3} mol L^{-1} dichloromethane solutions using a Radiometer Copenhagen CDM 83 instrument. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at variable temperature on a Bruker Avance 300 or a Bruker AC 200 spectrometer using CD_2Cl_2 or $(CD_3)_2SO$ as solvents. NMR chemical shifts are reported downfield from

tetramethylsilane. The solvent signals, quoted with respect to TMS ($\delta = 0$ ppm), are used as internal references. NMR solvents were Euriso-Top products. IR spectra were recorded from 4000 to 450 cm^{-1} using a Perkin Elmer Spectrum One spectrophotometer. Samples were dispersed in KBr or nujol.

Photoluminescence emission (PL) and excitation (PLE) measurements were carried out on dichloromethane solutions of the europium complexes with a Jobin Yvon Fluorolog-3 spectrofluorometer. A Xenon arc lamp was used as continuous-spectrum source selecting the excitation wavelength by a double Czerny-Turner monochromator. A single-grating monochromator coupled to a photomultiplier tube for measurements in the visible spectral range was used as detection system. Excitation and emission spectra were corrected for instrumental functions. Time-resolved analyses were performed in multi-channel scaling modality by using a tunable pulsed Nd:YAG laser system as excitation source. The luminescent lifetimes were derived from the luminescence decay curves, fitting the data with the least-squares method by using exponential equations. The intrinsic quantum yield (Q_i) has been estimated on the basis of equation (1), where τ is the measured lifetime and τ_{rad} is obtained from equation (2).

$$Q_i = \frac{\tau}{\tau_{rad}}, \tag{1}$$

$$\frac{1}{\tau_{rad}} = 14.65n^3 \frac{I(^5D_0 \rightarrow {}^7F_J)}{I(^5D_0 \rightarrow {}^7F_1)}. \tag{2}$$

In equation (2), n indicates the refractive index of the sample and the value of pure dichloromethane, 1.4242, is assumed. $I(^5D_0 \rightarrow {}^7F_J)/I(^5D_0 \rightarrow {}^7F_1)$ is the ratio between the total integrated emission from the Eu($^5D_0$) level to the ^7F_J manifold ($J = 0$–6) and the integrated intensity of the transition $^5D_0 \rightarrow {}^7F_1$ [9].

2.2. *Synthesis of M(OTf)$_2$(bdmpza) (1^M) (M = Sc, Y, La, Sm, Eu)*

In a typical procedure, potassium *tert*-butoxide (0.112 g, 1.0 mmol) was slowly added to a solution of bis(3,5-dimethylpyrazol-1-yl)acetic acid (0.248 g, 1.0 mmol) in THF (10 mL). After 15 min the resulting solution was slowly added to 1.0 mmol of the proper anhydrous $M(OTf)_3$ triflate salt dissolved in THF (20 mL). The resulting reaction mixture was stirred overnight at room temperature. The solvent was then removed by evaporation under reduced pressure and dichloromethane (20 mL) was added. The by-product was separated by centrifugation and the solution was concentrated to *ca* 2 mL. Diethylether was slowly added producing a precipitate, which was filtered, washed with diethylether (3×5 mL), and dried under vacuum. Yield is $>75\%$ in all cases. Analytically pure samples were obtained by slow cooling of saturated dichloromethane/diethylether solutions.

2.2.1. Characterization of 1^{Sc}. Anal. Calcd for $C_{14}H_{15}F_6N_4O_8S_2Sc$ (%): C, 28.5; H, 2.56; N, 9.49; S, 10.86. Found (%): C, 28.4; H, 2.55; N, 9.50; S, 10.9. ^{1}H NMR (CD_2Cl_2, 298 K): 6.01 (s, br, 3H, *pyrazole and CH*); 2.46 (s, br, 12H, *CH$_3$*). ^{1}H NMR (CD_2Cl_2, 242 K): 6.05 (s, slightly br, 2H, *pyrazole*); 5.95 (s, 1H, *CH*); 2.60–2.10 (m, 12H, *CH$_3$*). ^{1}H NMR (CD_2Cl_2/$(CD_3)_2SO$, 298 K): 6.59 (s, 1H, *CH*); 5.63 (s, 2H, *pyrazole*); 2.02 (s, 6H,

CH$_3$); 1.94 (s, 6H, *CH*$_3$). ^{13}C {^{1}H} NMR (CD_2Cl_2/DMSO-d_6, 298 K): 165.7 *COO*, 146.4, 140.3 *non H-bonded pyrazole carbon atoms*, 105.7 *pyrazole-CH*, 73.3 *CH*, 12.7, 10.6 *CH*$_3$. IR (KBr): 1639 cm^{-1} (s) ν_{COO}, 1031 cm^{-1} (s) ν_{SO}. IR (nujol): 1633 cm^{-1} (s) ν_{COO}, 1026 cm^{-1} (s) ν_{SO}.

2.2.2. Characterization of 1^{Y}. Anal. Calcd for $C_{14}H_{15}F_6N_4O_8S_2Y$ (%): C, 26.5; H, 2.28; N, 8.83; S, 10.1. Found (%): C, 26.4; H, 2.30; N, 8.80; S, 10.0. ^{1}H NMR (CD_2Cl_2, 298 K): 6.52 (s, slightly br, 1H, *CH*); 5.94 (s, slightly br, 2H, *pyrazole*); 2.36 (s, slightly br, 12H, *CH*$_3$). ^{1}H NMR (CD_2Cl_2, 309 K): 6.55 (s, slightly br, 1H, *CH*); 5.98 (s, slightly br, 2H, *pyrazole*); 2.43 (s, 6H, *CH*$_3$); 2.39 (s, slightly br, 6H, *CH*$_3$). The methyl signals give an unresolved multiplet in the range 2.75–2.10 ppm at 193 K in CD_2Cl_2 solution. ^{1}H NMR (CD_2Cl_2/DMSO-d_6, 298 K): 6.53 (s, 1H, *CH*); 5.62 (s, 2H, *pyrazole*); 1.91 (s, 12H, *CH*$_3$). ^{13}C {^{1}H} NMR (CD_2Cl_2/DMSO-d_6, 298 K): 173.7 *COO*, 146.5, 140.4 *non H-bonded pyrazole carbon atoms*, 106.1 *pyrazole-CH*, 73.5 *CH*, 12.8, 10.6 *CH*$_3$. IR (KBr): 1644 cm^{-1} (s) ν_{COO}, 1031 cm^{-1} (s) ν_{SO}.

2.2.3. Characterization of 1^{La}. Anal. Calcd for $C_{14}H_{15}F_6LaN_4O_8S_2$ (%): C, 24.6; H, 2.21; N, 8.19; S, 9.37. Found (%): C, 24.5; H, 2.20; N, 8.20; S, 9.35. ^{1}H NMR (CD_2Cl_2, 298 K): 5.89 (s, br, 3H, *pyrazole and CH*); 2.35 (s, br, 12H, *CH*$_3$). ^{1}H NMR (CD_2Cl_2, 202 K): 5.91, 5.81 (2s, br, 3H, *pyrazole and CH*); 2.23 (s, very br, 12H, *CH*$_3$). ^{1}H NMR (CD_2Cl_2/$(CD_3)_2SO$, 298 K): 6.48 (s, 1H, *CH*); 5.62 (s, 2H, *pyrazole*); 2.00 (s, 6H, *CH*$_3$); 1.94 (s, 6H, *CH*$_3$). ^{13}C {^{1}H} NMR (CD_2Cl_2/DMSO-d_6, 298 K): 172.3 *COO*, 146.3, 140.2 *non H-bonded pyrazole carbon atoms*, 105.8 *pyrazole-CH*, 74.0 *CH*, 12.7, 10.8 *CH*$_3$. IR (KBr): 1630 cm^{-1} (s) ν_{COO}, 1032 cm^{-1} (s) ν_{SO}.

2.2.4. Characterization of 1^{Sm}. Anal. Calcd for $C_{14}H_{15}F_6LaN_4O_8S_2$ (%): C, 24.2; H, 2.17; N, 8.05; S, 9.22. Found (%): C, 24.2; H, 2.20; N, 8.00; S, 9.20. ^{1}H NMR (CD_2Cl_2/$(CD_3)_2SO$, 298 K): 6.81 (s, 1H, *CH*); 5.66 (s, 2H, *pyrazole*); 2.07 (s, 6H, *CH*$_3$); 1.65 (s, 6H, *CH*$_3$). ^{1}H NMR spectrum of **1^{Sm}** in pure CD_2Cl_2 did not furnish any easily assignable signal. ^{13}C {^{1}H} NMR (CD_2Cl_2/DMSO-d_6, 298 K): 175.9 *COO*, 146.7, 140.2 *non H-bonded pyrazole carbon atoms*, 106.0 *pyrazole-CH*, 72.8 *CH*, 12.7, 10.7 *CH*$_3$. IR (KBr): 1633 cm^{-1} (s) ν_{COO}, 1026 cm^{-1} (s) ν_{SO}.

2.2.5. Characterization of 1^{Eu}. Anal. Calcd for $C_{14}H_{15}EuF_6N_4O_8S_2$ (%): C, 24.1; H, 2.17; N, 8.03; S, 9.20. Found (%): C, 24.0; H, 2.20; N, 8.00; S, 9.15. ^{1}H NMR ($(CD_3)_2SO$, 298 K): 6.56 (s, slightly br, 1H, *CH*); 5.67 (s, slightly br, 2H, *pyrazole*); 2.44 (s, 6H, *CH*$_3$); 1.99 (s, 6H, *CH*$_3$). ^{1}H NMR spectrum of **1^{Sm}** in pure CD_2Cl_2 did not furnish any easily assignable signal. IR (KBr): 1635 cm^{-1} (s) ν_{COO}, 1032 cm^{-1} (s) ν_{SO}.

2.3. *Synthesis of M(OTf)$_2$(bdmpza) (2^M) (M = Y, Eu)*

A stoichiometric amount of potassium *tert*-butoxide (0.224 g, 2.0 mmol) was slowly added to a solution of bis(3,5-dimethylpyrazol-1-yl)acetic acid (0.496 g, 2.0 mmol) in THF (20 mL). After 15 min, the resulting solution was slowly added to a solution containing 1.0 mmol of $Y(OTf)_3$ or $Eu(OTf)_3$ dissolved in THF (20 mL). The resulting

mixture was allowed to react for 20 h under stirring at room temperature. The solvent was then evaporated under reduced pressure and the residual solid was dissolved in 30 mL of dichloromethane. After centrifuging, the solution was concentrated under reduced pressure and diethylether was slowly added until a solid started to precipitate. After cooling the mixture at −25°C the product was filtered, washed with fresh diethylether (3 × 5 mL), and dried under vacuum. Yield >70% in both cases. Analytically pure samples were obtained by slow cooling of saturated dichloromethane/diethylether solutions.

2.3.1. Characterization of 2^{Y}. Anal. Calcd for $C_{25}H_{30}F_3N_8O_7SY$ (%): C, 41.0; H, 4.13; N, 15.3; S, 4.38. Found (%): C, 39.9; H, 4.15; N, 15.2; S, 4.40. ^{1}H NMR (CD_2Cl_2/DMSO-d_6, 298 K): 6.59 (s, 1H, *CH*); 5.71 (s, 2H, *pyrazole*); 2.09 (s, 6H, CH_3); 2.02 (s, 6H, CH_3). Two very broad signals centered at 5.90 ppm and 2.47 ppm are observable in pure CD_2Cl_2 and these peaks remain unresolved also at low temperature. ^{13}C {^{1}H} NMR (CD_2Cl_2/DMSO-d_6, 298 K): 173.3 *COO*, 147.0, 140.5 *non H-bonded pyrazole carbon atoms*, 106.0 *pyrazole-CH*, 72.6 *CH*, 12.9, 10.5 CH_3. IR (KBr): 1644 cm^{-1} (s) ν_{COO}, 1032 cm^{-1} (s) ν_{SO}.

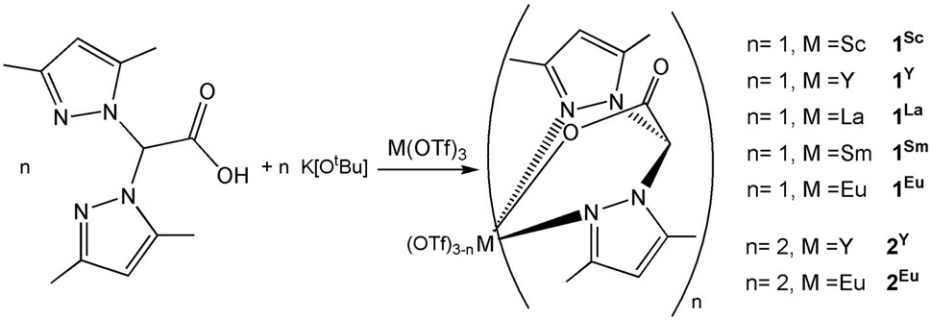
2.3.2. Characterization of 2^{Eu}. Anal. Calcd for $C_{25}H_{30}EuF_3N_8O_7S$ (%): C, 37.7; H, 3.80; N, 14.1; S, 4.03. Found (%): C, 37.5; H, 3.75; N, 14.0; S, 4.00. ^{1}H NMR ($(CD_3)_2SO$, 298 K): 6.32 (s, slightly br, 1H, *CH*); 5.63 (s, slightly br, 2H, *pyrazole*); 2.35 (s, 6H, CH_3); 1.97 (s, 6H, CH_3). ^{1}H NMR spectrum of $\mathbf{2^{Eu}}$ in pure CD_2Cl_2 did not furnish any easily assignable signal. IR (KBr): 1636 cm^{-1} (s) ν_{COO}, 1032 cm^{-1} (s) ν_{SO}. PL (CH_2Cl_2, 298 K, $\lambda_{excitation} = 310$ nm, nm): 578 ($^5D_0 \rightarrow {}^7F_0$, 2%); 589, 596 ($^5D_0 \rightarrow {}^7F_1$, 12%); 612, 618, 621sh ($^5D_0 \rightarrow {}^7F_2$, 51%); 649 ($^5D_0 \rightarrow {}^7F_3$, 3%); 698 ($^5D_0 \rightarrow {}^7F_4$, 31%). PLE ($CH_2Cl_2$, 298 K, $\lambda_{emission} = 616$ nm, nm): 362, 376, 382, 394, 464 (Eu^{3+} excitation); <340 (ligand excitation). τ (CH_2Cl_2, 298 K, $\lambda_{emission} = 616$ nm, $\lambda_{excitation} = 310$ nm, ms): 1.37. $Q_i = 48\%$.

2.4. *Computational studies*

The computational geometry optimization of $\mathbf{1^{Y}}$ was carried out using the hybrid DFT M06 functional [10], without symmetry constraints, in combination with a polarized triple-ζ quality basis set composed by the 6-311G(d,p) basis set on light atoms and the LANL2TZ(f) basis set on yttrium [11]. The "restricted" formalism was applied in the calculation. The stationary point was characterized as true minima by IR simulation [12]. The software used was Gaussian 09 [13]. The simulation was performed at CINECA (Centro Italiano di Supercalcolo, Bologna, Italy) using an IBM P6-575 workstation equipped with 64-bit IBM Power6 processors.

2.5. *Cytotoxicity assay*

HeLa (human cervix adenocarcinoma cells) were grown in Nutrient Mixture F-12 [HAM] (Sigma Chemical Co.) supplemented with 10% heat-inactivated fetal calf serum (Biological Industries). 100 U mL^{-1} penicillin, 100 μg mL^{-1} streptomycin, and



Scheme 1. Syntheses of $\mathbf{1^M}$ and $\mathbf{2^M}$.

0.25 μg mL^{-1} amphotericin B (Sigma Chemical Co.) were added to the medium. The cells were cultured at 37°C in a moist atmosphere of 5% carbon dioxide in air.

For the cytotoxicity assay, HeLa cells (3×10^4) were seeded into each well of a 24-well cell culture plate. After incubation for 24 h, the medium was replaced with an equal volume of fresh medium and various concentrations of the test agents were added. The cells were then incubated in standard conditions for a further 72 h.

A trypan blue assay was performed to determine cell viability. Cytotoxicity data were expressed as percentage of viable cells with respect to untreated cells.

3. Results and discussion

3.1. *Syntheses and characterizations of 1^M and 2^M*

The triflate-complexes M(OTf)$_2$(bdmpza) ($\mathbf{1^M}$) and M(OTf)(bdmpza)$_2$ ($\mathbf{2^M}$) were prepared by reacting the anhydrous M(OTf)$_3$ salts {M = Sc, Y, La, Sm, Eu} with the proper quantity of bis(3,5-dimethylpyrazol-1-yl)acetic acid, previously deprotonated with a stoichiometric amount of potassium *tert*-butoxide at room temperature in THF. The reactions leading to $\mathbf{1^M}$ and $\mathbf{2^M}$ are depicted in scheme 1. All the complexes were isolated in pure form and good yields after filtration of the by-products and the evaporation of the solvent. The elemental analyses are in agreement with the chemical formulae of $\mathbf{1^M}$ and $\mathbf{2^M}$. Dichloromethane solutions of all the complexes are not conductive.

The ^{1}H NMR spectra in CD_2Cl_2 show quite broad signals, even for diamagnetic scandium, yttrium, and lanthanum derivatives. The ^{1}H NMR spectra in dichloromethane are not resolved at low temperature. Addition of deuterated DMSO to the samples in all the cases leads to the spectra with sharp resonances. In particular, a singlet attributable to the methine-CH is present around 6.5 ppm, while another singlet is observable around 5.6 ppm and corresponds to the resonance of the pyrazole hydrogen in position 4. In the low-frequency region signals of the methyl groups can be detected. No signal attributable to coordinated THF molecules is present. Figure 1 shows as example the ^{1}H NMR spectra of $\mathbf{1^Y}$ at 193 K and 309 K in pure CD_2Cl_2 and the spectrum of the same complex in $CD_2Cl_2/(CD_3)_2SO$ solution at room temperature. The broad resonances observed in pure dichloromethane can be tentatively ascribed to

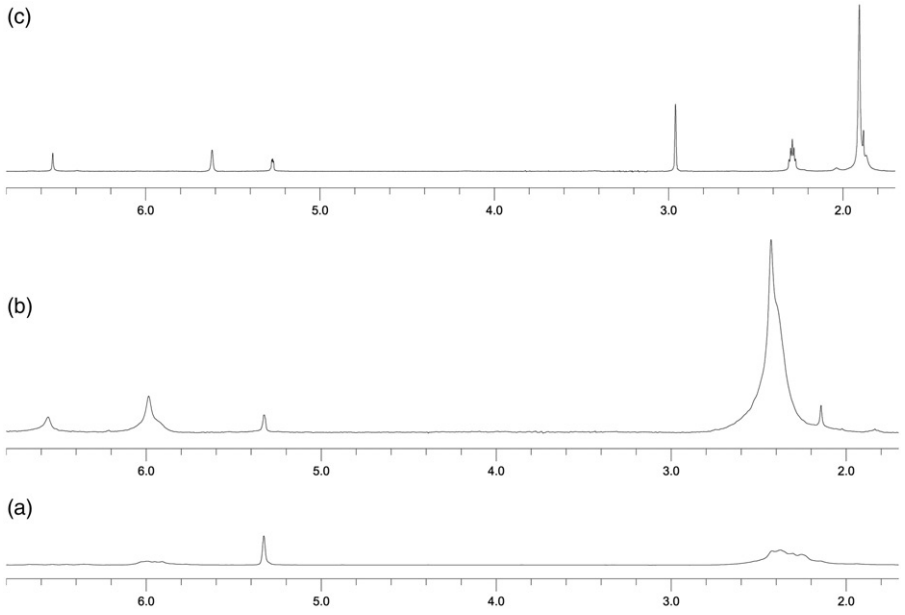


Figure 1. ^{1}H NMR spectra of $\mathbf{1^{Y}}$: (a) CD_2Cl_2 solution, 193 K; (b) CD_2Cl_2 solution, 309 K; (c) CD_2Cl_2/$(CD_3)_2SO$ solution, 298 K. The signal of $CHDCl_2$ has been used as reference.

fluxional behavior of the [N,N,O]-donor and saturation of the coordination sphere of the metal centers by DMSO can explain the strong change of the ^{1}H NMR spectra in the presence of this solvent. It is likely that DMSO, which is a good O-donor for hard Lewis acids such as group 3 and lanthanide ions [14], can partially displace the pyrazole rings from the coordination sphere. A fast equilibrium reaction where one coordinated N-donor heterocycle is displaced by DMSO has been already invoked to explain the ^{1}H NMR spectra of $Ln(Tp)_3$ (Ln = Sm, Eu, Gd, Tb, Dy, Yb; Tp = hydrotris(pyrazol-1-yl)borate) in deuterated DMSO [2s, 2t]. ^{13}C $\{^{1}H\}$ NMR spectra recorded in dichloromethane/dimethylsulfoxide solution show the carbon of the carboxylic group at 176–165 ppm, three resonances in the aromatic region attributable to pyrazole rings, a signal due to the methine carbon at 74–73 ppm, and two signals corresponding to methyl in the low-frequency region. In the presence of DMSO the pyrazole rings are therefore equivalent on the NMR timescale, and in the case of $\mathbf{2^{M}}$ derivatives both bdmpza are equivalent, as observable in the ^{1}H NMR spectra of $\mathbf{2^{Y}}$ and $\mathbf{2^{Eu}}$ reported in figure 2.

IR spectra of $\mathbf{1^{M}}$ and $\mathbf{2^{M}}$ show in all cases a strong signal around 1640 cm^{-1} attributable to COO stretch. The presence of this vibration is in agreement with monodentate coordination of the carboxylate of bdmpza. A signal around 1030 cm^{-1} is attributable to an S–O stretch of the triflate [15].

The europium derivatives $\mathbf{1^{Eu}}$ and $\mathbf{2^{Eu}}$ are white solids luminescent in the red region of the visible range upon irradiation with UV light. This emission is more intense for $\mathbf{2^{Eu}}$, whose PL in dichloromethane at room temperature has been studied. The PL spectrum of $\mathbf{2^{Eu}}$, reported in figure 3, shows typical bands associated with the transitions from the $^{5}D_0$ to the $^{7}F_J$ levels (J = 0–4) at 575–700 nm. The most intense signal is that associated with the hypersensitive $^{5}D_0 \rightarrow {}^{7}F_2$ transition centered at 616 nm. The radiative lifetime of this emission is 1.37 ms, corresponding to an intrinsic quantum yield (Q_i) of 48%.

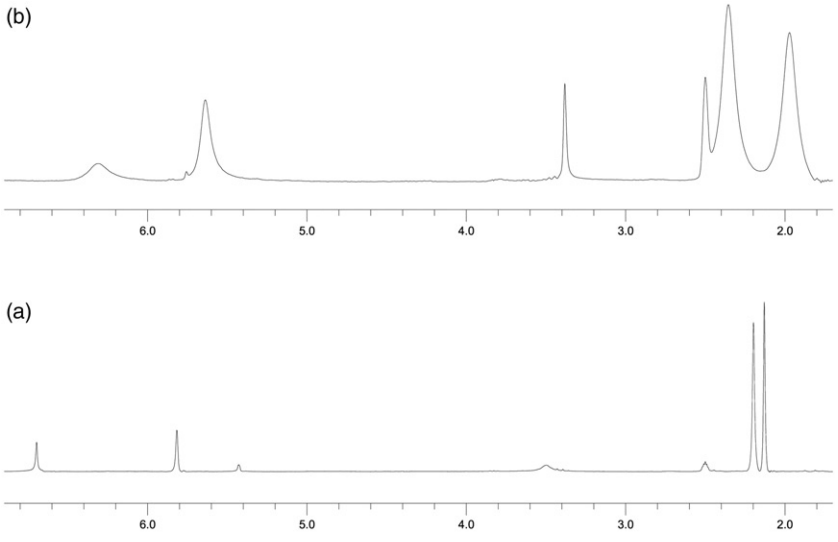


Figure 2. ^{1}H NMR spectra of $\mathbf{2}^{\mathbf{Y}}$ in $CD_2Cl_2/(CD_3)_2SO$ at 298 K (A) and of $\mathbf{2}^{\mathbf{Eu}}$ in $(CD_3)_2SO$ at 298 K (B). The signal of $(CHD_2)(CD_3)SO$ has been used as reference.

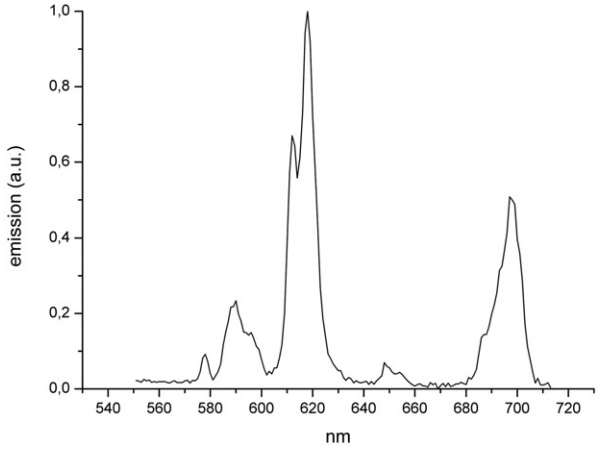


Figure 3. Normalized PL spectrum of $\mathbf{2}^{\mathbf{Eu}}$ (CH_2Cl_2, 298 K, $\lambda_{excitation} = 310$ nm).

PLE measurement (figure 4) shows that these emissions are attributable not only to direct excitation of the europium center, but to energy transfer (antenna-effect) from the coordinated bdmpza ligands to europium ions at wavelengths below 340 nm. The relatively high ratio between the $^{5}D_0 \rightarrow {}^{7}F_2$ and the $^{5}D_0 \rightarrow {}^{7}F_1$ transitions, more than four, suggests a quite low symmetry of the coordination sphere around the europium [9, 16].

3.2. *DFT calculations*

The coordination mode of the ligands in the complexes was studied by DFT calculations on $Y(OTf)_2$(bdmpza) ($\mathbf{1}^{\mathbf{Y}}$) as model compound. The optimized structure is

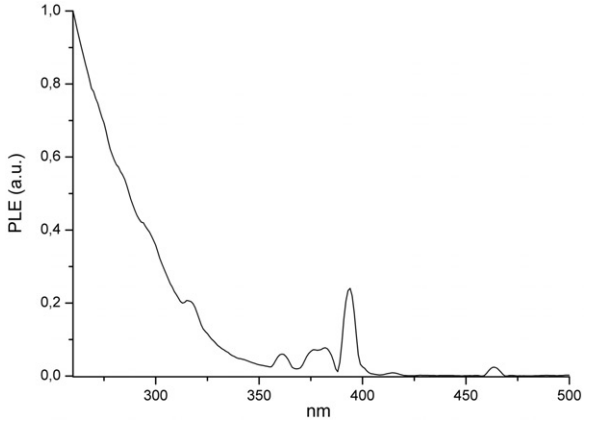


Figure 4. Normalized PLE spectrum of $\mathbf{2}^{\mathbf{Eu}}$ (CH_2Cl_2, 298 K, $\lambda_{emission} = 616$ nm).

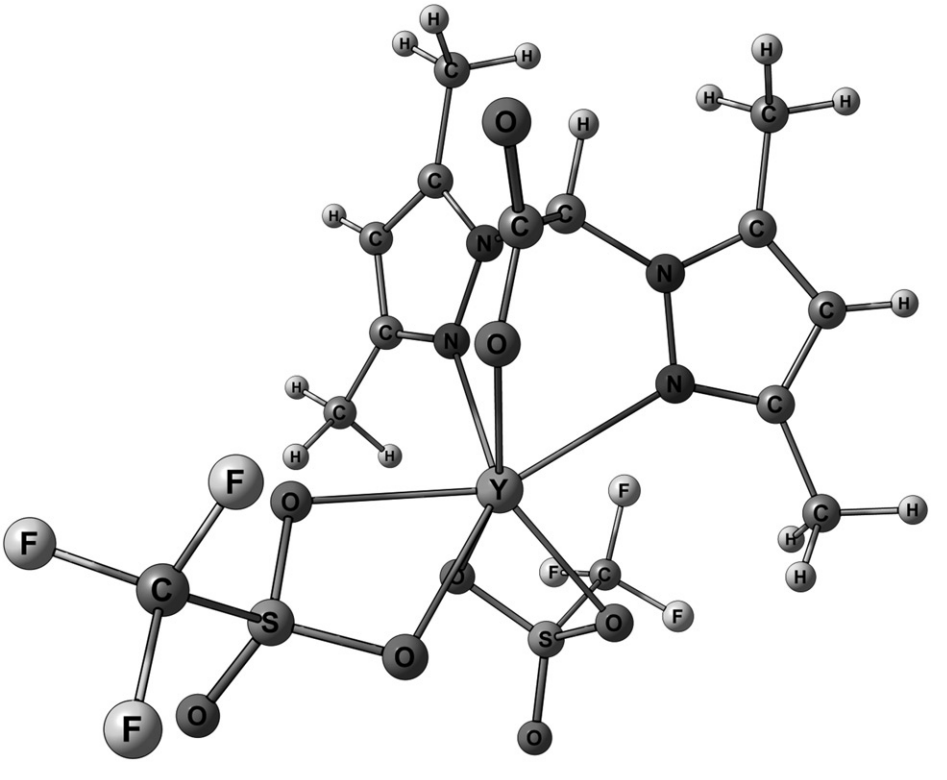


Figure 5. DFT-optimized geometry of $\mathbf{1}^{\mathbf{Y}}$.

reported in figure 5, while selected bond lengths are collected in table 1. Complex $\mathbf{1}^{\mathbf{Y}}$ is seven-coordinate and the coordination sphere around yttrium can be described as a distorted monocapped trigonal prism, where the three donors of bdmpza occupy the three vertices of a trigonal face. The inner coordination sphere of Y(III) in $\mathbf{1}^{\mathbf{Y}}$ is

Table 1. Selected calculated bond lengths (Å) for $\mathbf{1^Y}$.

Bond	Length (Å)
Y–N	2.515
Y–N	2.428
Y–O (bdmpza)	2.171
Y–O (triflate)	2.338
Y–O (triflate)	2.411
Y–O (triflate)	2.424
Y-O (triflate)	2.389

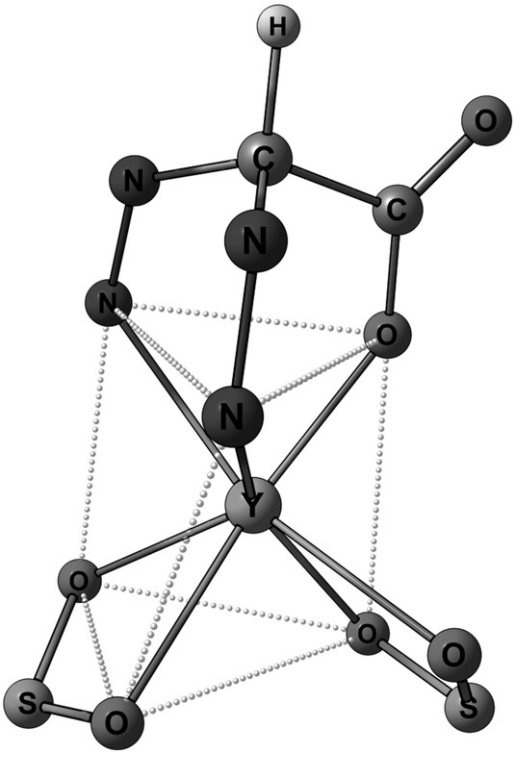


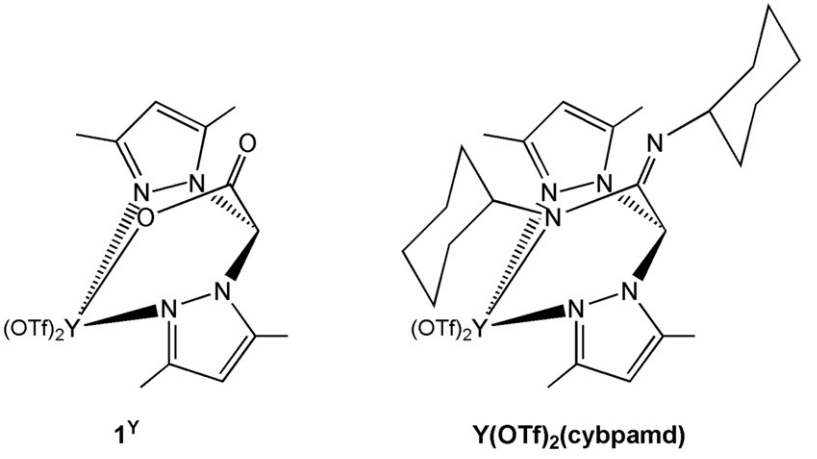
Figure 6. Fragment of the computed structure of $\mathbf{1^Y}$ highlighting the coordination sphere around the metal center.

highlighted in figure 6 for clarity. The data reported in table 1 are in agreement with an asymmetric k^3-coordination of bdmpza and an asymmetric k^2-coordination of both triflate ligands, already observed for other group 3 and lanthanide trifluoromethanosulfonato complexes [17]. A quite short Y–O bond length, 2.171 Å, is predicted between the metal center and the carboxylate, in agreement with an electrostatic contribution enforcing the interaction. The other Y–O bonds are comprised between 2.33 and 2.43 Å. The two Y–N bond lengths are 2.428 and 2.515 Å, respectively, and the longest one corresponds to the pyrazole ring *trans* to the shortest Y–O(triflate) bond, 2.338 Å.

Table 2. Effect on cell viability of test complexes and ligand.

	Concentration ($\mu mol\,L^{-1}$)			
Complex	5	10	20	50
$\mathbf{1^Y}$	84	73	64	57
$\mathbf{2^Y}$	103	100	109	95
$\mathbf{1^{Sc}}$	107	90	89	84
Hbdmpza	103	94	83	84

The values indicate the percentage of cell viability with respect to the control culture.



$\mathbf{1^Y}$ **Y(OTf)$_2$(cybpamd)**

Scheme 2. Sketches of $\mathbf{1^Y}$ and **Y(OTf)$_2$(cypbamd)**.

On the contrary, the longest Y–O(triflate) interaction, 2.424 Å, is *trans* to carboxylate in the prismatic structure.

3.3. *Cytotoxic activity*

The ability of selected complexes and free ligand to inhibit cell growth was evaluated by *in vitro* assay performed on HeLa (human cervix adenocarcinoma) cells. These cells are currently studied as potential target for several cytotoxic transition metal complexes different from platinum, for example manganese, iron, ruthenium, and gold [18]. The results, expressed as percentage of viable cells with respect to the untreated cells, are shown in table 2. The obtained data indicate for $\mathbf{1^Y}$ the capacity to reduce the percentage of viable cells of about 40% at the highest test concentration, i.e. $50\,\mu mol\,L^{-1}$, while both the other complexes and the ligand are unable to induce any significant reduction in cell viability. In the same experimental conditions, cisplatin showed an IC_{50} value, i.e. the concentration able to cause 50% of cell death with respect to the control culture, of $0.84\,\mu mol\,L^{-1}$ [19], while Gao and co-workers reported under comparable experimental conditions average IC_{50} values around 8–9 $\mu mol\,L^{-1}$ for dibenzylmalonate complexes of Mn(II) having 2,2′-bipyridine or 1,10-phenanthroline in the coordination sphere [18a].

The comparison of the activity of $\mathbf{1^Y}$ with that of the comparable yttrium triflate-complex **$Y(OTf)_2$(cybpamd)**, where cypbmad represents the [*N*,*N*,*N*′]-donor scorpionate-ligand *N*,*N*′-dicyclohexyl-2,2-bis-(3,5-dimethyl-pyrazol-1-yl)-acetamidinate, shows that the replacement of the acetamidinate moiety with carboxylate causes a strong reduction of the cytotoxic activity. The two complexes are sketched in scheme 2 for clarity. In fact, a 6 μmol L^{-1} concentration of **$Y(OTf)_2$(cybpamd)** induces the 50% of mortality in HeLa cell line [20].

4. Conclusion

Several neutral group 3 and lanthanide triflate-complexes bearing the tridentate [N,N,O]-donor heteroscorpionate ligand bis(3,5-dimethylpyrazol-1-yl)acetate have been prepared and characterized by NMR and IR spectroscopy. PL measurements have been carried out on the red-emitting europium complex $\mathbf{2^{Eu}}$. The coordination mode of the tridentate ligand has been established by comparing the spectroscopic results with DFT calculations on $\mathbf{1^Y}$. The evaluation of the cytotoxic effect for $\mathbf{1^Y}$ showed a weak capacity to inhibit human cervix adenocarcinoma cell growth, while for the other complexes and free ligand no significant effect on cells has been demonstrated. Further studies will be carried out to understand the correlation between structure and cytotoxic activity of triflate-scorpionate group 3 and lanthanide complexes.

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