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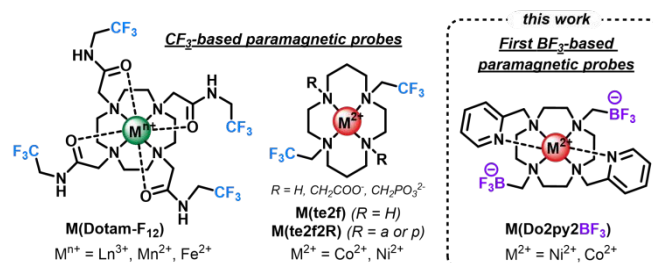
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Trifluoroborate-Appended Cyclen Complexes of Paramagnetic Transition Metals (Ni^{2+} , Co^{2+}) as Fast-Relaxing ^{19}F MRI ProbesReceived 00th January 20xx,
Accepted 00th January 20xxCharline Sire,^a Francesca Garello,^b Noémie Lalaoui,^a Nathalie Saffon Merceron,^c Nicolas Le Poul,^a Raphaël Tripier,^a Lorenzo Tei,^{*,d} and Thibault Troadec^{*,a}

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For the first time, trifluoroborate groups (BF_3s) have been investigated as sensitive probes for ^{19}F Magnetic Resonance Imaging (MRI) in paramagnetic complexes. Using a macrocyclic BF_3 -appended cyclen ligand, complexes of Ni^{2+} and Co^{2+} cations were synthesized and exhibited very fast T_1 and T_2 relaxation times that improve ^{19}F MRI detection. Notably, the cobalt complex presents the fastest ^{19}F MRI relaxation reported to date for a Co^{2+} -based probe.

^{19}F Magnetic Resonance Imaging (^{19}F MRI) is based on the natural isotope of fluorine (^{19}F , 100% natural abundance, spin $\frac{1}{2}$) that has the highest magnetic resonance sensitivity after that of ^1H . This imaging technique can be a great alternative or complement to conventional ^1H MRI, as the latter is based on the detection of endogenous water protons to provide contrast between different tissues, whereas the former enables the direct quantitative detection of an exogenous fluorinated tracer. This is permitted by the absence of fluorine from the body's soft tissues, but also comes with a relatively low overall sensitivity for ^{19}F MRI.¹ To overcome this drawback, the use of fluorinated complexes of paramagnetic cations can reduce acquisition times and provide higher ^{19}F MRI sensitivity, thanks to lower longitudinal T_1 and transversal T_2 relaxation times of the fluorine atoms due to Paramagnetic Relaxation Enhancement (PRE). The design of such probes requires a good inertness of the metal complex, a sufficient number of



Scheme 1: Selected paramagnetic CF_3 -appended ^{19}F MRI probes from literature and BF_3 -appended complexes prepared in this work.

isochronous fluorine atoms and appropriate metal-fluorine distance. With current MRI scanners technology, relaxation times of *c.a.* 1 ms are considered optimal, as lower T_1 and T_2 are too fast with respect to the MR sequences timescale. A T_2/T_1 ratio close to its theoretical maximum value of 1 is also desirable, as low values of this parameter lead to broad MR signals with low intensity.²⁻⁴ In this context, azamacrocyclic chelators, renowned for the kinetic inertness of their metal complexes and the range of coordinating and functional groups they can accommodate *via* their nitrogen atoms, have been widely studied with trifluoromethyl (CF_3) pendants. Paramagnetic lanthanide (III) complexes (from Eu^{3+} to Yb^{3+}) have first been studied in a set of cyclen ligands bearing from one to four CF_3 groups combined with amide (see example of **Dotam-F₁₂**, Scheme 1), acetate or phosphonate coordinating units.⁵⁻⁸ Such constructs can lead to efficient probes with T_1 and T_2 in the 1-10 ms range and favourable T_2/T_1 ratios (generally greater than 0.5), resulting in ^{19}F MRI detection limits in the low millimolar range. However, the coordination sphere of lanthanides, with high coordination numbers, often induces the formation of isomers exhibiting distinct ^{19}F MR chemical shifts, therefore reducing their global sensitivity.⁵ In addition, no trend has yet clearly been defined between the relaxivity, the nature of the lanthanide, and the cation-fluorine distance. Interestingly, the **Dotam-F₁₂** chelator was used to coordinate

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iron(II), with a single isomer in solution and relaxation times in the 5-10 ms, mirroring the values obtained with lanthanides.⁶ Therefore, paramagnetic transition metals were considered more recently too: first as responsive ¹⁹F MRI probes, as their redox properties can easily modulate the ¹⁹F signal MR,⁹⁻¹⁴ but also as purely sensitive tracers, as they are more abundant and less toxic *in vivo* than lanthanides.¹⁵⁻¹⁹ Cyclam-based chelators bearing acetate or phosphonate coordinating groups and CF₃ pendants (*e.g.* **te2f2R** ligands, Scheme 1) were thus studied, as they are known to form highly stable complexes with first-row transition metal cations. Satisfyingly, the corresponding nickel(II) complexes exhibit very low T₁ and T₂ (< 5 ms) and good T₂/T₁ ratios (up to 0.8). However, their solubility in water is rather poor, and isomers can again be observed.¹⁵⁻¹⁷ Cobalt(II), that has the advantage of a lower potential toxicity *in vivo*, showed slightly higher relaxation times (10-15 ms range).^{17,18} However, these studies have demonstrated a clear trend between good relaxivity and short M-F distance (within an optimal window of 4.5 to 8 Å for Ni²⁺ and Co²⁺ cations).^{5,20} We have recently presented the synthesis of the novel trifluoroborate(BF₃)-appended chelator **Do2py2BF₃** (Scheme 1) and its corresponding model zinc(II) complex. This complex could be efficiently radiolabelled with ¹⁸F, opening the way to applications in Positron Emission Tomography (PET), but also showed a promising ¹⁹F MRI signal with T₁ and T₂ values of 384 and 268 ms, respectively (T₂/T₁ = 0.70). These are lower than those of corresponding diamagnetic complexes of CF₃-appended ligands (*e.g.* T₁ = 660 ms and T₂ = 540 ms for [Co^{III}(**te2fa**)], Figure 1),¹⁸ and this model complex possesses a high kinetic inertness in solution, with the presence of only one isomer thanks to its cyclen skeleton. Therefore we anticipated that paramagnetic complexes of divalent cations with the **Do2py2BF₃** ligand could provide excellent properties as sensitive ¹⁹F MRI probes.

Herein, corresponding [Ni(**Do2py2BF₃**)] and [Co(**Do2py2BF₃**)] were thus prepared in acetonitrile from stoichiometric mixtures of H₂**Do2py2BF₃** precursor and metallic salts (Ni(ClO₄)₂ and Co(NO₃)₂), for two hours at 60 °C with excess potassium carbonate (Figure 1). Both complexes were then obtained in moderate to good yields after recrystallization from water/acetonitrile solutions (41 % for [Ni(**Do2py2BF₃**)] and 78 % for [Co(**Do2py2BF₃**)]). Single crystals were analyzed by X-Ray Diffraction (XRD), revealing similar solid-state structures for both complexes, with a MN₆ coordination sphere around the metal in a distorted trigonal prismatic geometry, and non-coordinating BF₃ groups (Figure 1, see Supporting Information for full details, Figures S7-S8). Nonetheless, slight differences were observed. The cobalt(II) complex exhibits a planar arrangement of the macrocycle nitrogen atoms and the cation lying 1.01 Å above the calculated N₄-centroid with all M-N bonds length between 2.15 and 2.31 Å. In contrast, the nickel(II) complex displays a distorted bowl-shaped geometry of the cyclen platform, with a smaller metal-centroid distance (0.91 Å) and shortening of M-N bonds with the nitrogen atoms from the pyridines (2.08 Å) and tertiary amine bearing the methylenepyridyl groups (2.12 Å). This contraction of the MN₆ coordination sphere in the case of [Ni(**Do2py2BF₃**)] results in a

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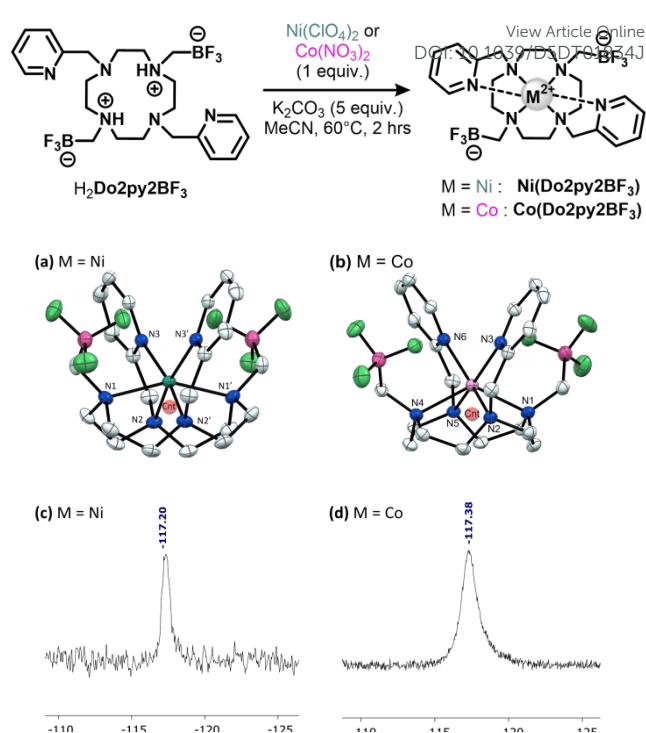


Figure 1: Synthesis (top), X-Ray diffraction structures[†] (a and b) and ¹⁹F NMR signals (c and d) of Ni(**Do2py2BF₃**) and Co(**Do2py2BF₃**). (a) and (b): Ellipsoids are drawn at 50% probability; H atoms are omitted for clarity. Cnt = calculated centroid of the 4 nitrogen atoms from cyclen; Selected bond lengths (Å): (a) centrosymmetric: Ni-N1(N1'): 2.273(3); Ni-N2(N2'): 2.121(3); Ni-N3(N3'): 2.082(2); (b) Co-N1: 2.307(2); Co-N2: 2.240(2); Co-N3: 2.156(2); Co-N4: 2.304(2); Co-N5: 2.225(2); Co-N6: 2.161(2); Ni-Cnt: 0.91; Co-Cnt: 1.01; Average M-F distances: Ni-F_{av}: 4.49; Co-F_{av}: 4.38.

slightly longer average Ni-F distance compared to [Co(**Do2py2BF₃**)] (4.49 vs. 4.38 Å), although both lie within the lower range of ideal metal-fluorine distance.

Both compounds were characterized by High-Resolution Mass Spectrometry (HR-MS) and NMR spectroscopy (see Supporting Information, Figures S1-S6). The two complexes exhibit ¹⁹F resonances at similar chemical shifts ($\delta_F = -117.2$ for Ni and $\delta_F = -117.4$ ppm for Co) in a D₂O/CD₃CN (1:1) mixture, with single signals of usual broadness for such complexes (half-width of *c.a.* 300 and 500 Hz, respectively),¹⁷ demonstrating the formation of only one isomer in solution. However, the nickel(II) complex has a poor solubility in this solvent system as well as in water or various organic solvents. Combined with the paramagnetic influence of the cation, ¹H and ¹¹B NMR spectra could therefore not be exploited. In contrast, the cobalt(II) complex was fully characterized by those means, showing a single ¹¹B resonance at $\delta_B = 43$ ppm with a strong downfield paramagnetic shift as compared to the free ligand ($\delta_B = 2$ ppm),²¹ and a classical wide distribution of broad paramagnetic ¹H signals (from $\delta_H = 249$ to -52 ppm).

The complexes were then analyzed by cyclic voltammetry in order to determine the range of potential values for which the complexes remain unchanged. In DMF, [Co(**Do2py2BF₃**)] displays a reversible reduction system at -1.66 V vs NHE, and an irreversible cathodic peak at -2.24 V (Figure S9A, Supporting Information). When scanning towards positive potential values,

the same complex exhibits an irreversible peak at +1.28 V vs NHE (at $v = 0.1$ V/s, Figure S9B), the reversibility being re-established as the scan rate increases (Figure S10B). In comparison, **[Ni(Do2py2BF₃)]** displays irreversible peaks for both oxidation and reduction reactions at +1.35 V and -1.49 V vs NHE (for $v = 0.1$ V/s), respectively (Figure S11). The irreversible character of the voltammetric signature for the Ni complex highlights the poor stability of the electrogenerated species. Interestingly, the highly negative and positive potential values found for both Co and Ni complexes evidence their high stability given the large potential range of redox inactivity. This was confirmed by measurements in aqueous media for **[Co(Do2py2BF₃)]**. Indeed, in a phosphate-based electrolyte mimicking physiological conditions (pH=7.3), no reduction peak could be detected beyond water reduction, whereas an irreversible oxidation peak was found at high potential (+1.39 V vs NHE, Figure S12). All these results strongly indicate the high stability of the Co complex and its possible use under physiological conditions.

Relaxation times of **[Ni(Do2py2BF₃)]** and **[Co(Do2py2BF₃)]** were first determined in acetonitrile/water mixtures (1:1) at 25 °C, showing very low values in the optimal range for paramagnetic ¹⁹F MRI probes, with $T_1 = 2.60$ and 1.74 ms, and $T_2 = 2.20$ and 0.75 ms, respectively (Table 1, see Supporting Information for full experimental details). Notably, these values are similar to the most efficient nickel-based probes reported to date ($T_1 = 1.80$ ms and $T_2 = 0.90$ ms for **[Ni(te2f2p)]**, Scheme 1),¹⁶ but one order of magnitude lower than the fastest-relaxing cobalt(II) complex found in literature ($T_1 = 11.9$ ms and $T_2 = 8.9$ ms for **[Co^{II}(te2f2p)]**, Scheme 1).¹⁸ The T_2/T_1 ratio is also excellent for the nickel complex (0.84 vs. 0.32 for **[Ni(te2f2p)]**)¹⁵ but somewhat lower for the cobalt one (0.43 vs. 0.78 for **[Co^{II}(te2f2p)]** and 0.68 for **[Co^{II}(te2f2a)]**). Nevertheless, this value is still appropriate to consider a use as an efficient ¹⁹F MRI contrast agent, and in the range of most previously described lanthanides complexes with multiple CF₃ pendants (e.g. 0.01 to 0.77 for **[Ln(Dotam-F₁₂)]** complexes).

MRI phantoms of **[Ni(Do2py2BF₃)]** and **[Co(Do2py2BF₃)]** were then prepared in the same solvent system (acetonitrile/water, 1:1) with at least 6 concentration points from 0 mM (control) to 42 mM (in ¹⁹F, i.e. 7.0 mM in complex, see Supporting Information for details). ¹H MRI spectra were recorded as background with a RARE sequence to detect the water signal

Table 1: Measured relaxation times for **Ni(Do2py2BF₃)** and **Co(Do2py2BF₃)**.

| Metal | medium | T (°C) | δ_F (ppm) | T_1 (ms) | T_2 (ms) |
|-------|---|--------|------------------|------------|------------|
| Ni | CH ₃ CN/H ₂ O (1:1) | 25 | -117.2 | 2.60 | 2.20 |
| Co | CH ₃ CN/H ₂ O (1:1) | 25 | -117.4 | 1.74 | 0.75 |
| | DMSO/H ₂ O (3:5) | 25 | -122.6 | 1.35 | 0.95 |
| | DMSO/H ₂ O/serum (1:1:2) | 25 | -122.6 | 1.50 | 0.52 |
| | DMSO/H ₂ O/serum (1:1:2) | 37 | -120.8 | 2.12 | 0.84 |

T_1 calculated by inversion recovery pulse sequence and T_2 with line-width with Lorentzian-shape fitting; Field: 9.4 T.

from the samples, and ¹⁹F MRI was recorded with UTE (Ultrashort Echo Time) sequence at various time points between 8 mins and 2 h 30 mins. The images revealed a detection limit, corresponding to a signal-to-noise ratio (SNR) > 2, between 5 and 10 mM ¹⁹F after only 8 minutes for the nickel complex (Figure 2 and Supporting Information, Figure S14), which is in the range of corresponding CF₃-appended nickel(II) complexes (e.g. 5.6 mM in 10 minutes for **[Ni(te2f2p)]**).¹⁶ The 5 mM sample was then clearly detected after 1 h 8 mins. In parallel, the cobalt complex could be observed at the concentration of 10 mM ¹⁹F after 34 minutes, and at 5 mM after 1h 8 mins (Figure 2 and Supporting Information, Figure S17). To the best of our knowledge, this is the first example of such low mM detection limit observed for a cobalt-based paramagnetic ¹⁹F MRI probe. Moreover, the SNR of both complexes was calculated at the various acquisition times and plotted against ¹⁹F concentration (Supporting Information, Figures S15, S18), showing a linear relationship in all cases, which confirms the stability of the ¹⁹F MRI signal in all tested conditions.

To consider future *in vivo* applications, the preservation of these relaxation parameters in biological medium is another important feature to be assessed. Unfortunately, **[Ni(Do2py2BF₃)]** showed poor solubility in other media (water, DMSO, serum), and only **[Co(Do2py2BF₃)]** could be further studied. This complex was thus solubilized in (1:1) DMSO/water and (1:1:2) DMSO/water/serum mixtures, showing a slight modification of its chemical shift ($\delta_F = -122.6$ ppm) but similar relaxation times ($T_1 = 1.35$ and 1.50 ms, $T_2 = 0.95$ ms and 0.52 ms, respectively, Table 1). Heating at 37°C in the DMSO/water/serum was finally tested as a mimic of physiological conditions, and also demonstrated the preservation of the relaxation properties ($\delta_F = -120.8$ ppm, $T_1 = 2.12$ ms, $T_2 = 0.84$ ms), which is highly encouraging to consider future use of this complex as a sensitive ¹⁹F MRI probe in biological media.

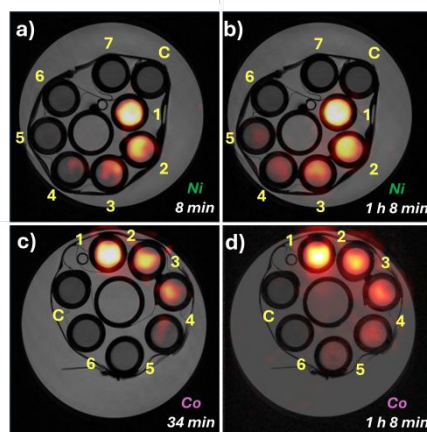


Figure 2: ¹⁹F MRI phantoms of Ni(Do2py2BF₃) at t = 8 mins (512 scans, panel a) and 1 h 8 mins (4096 scans, panel b), and of Co(Do2py2BF₃) at t = 34 mins (2048 scans, panel c) and 1 h 8 mins (4096 scans, panel d); Field : 7.0 T; solvent : CH₃CN/water (1:1); sample concentrations: 1) 42 mM, 2) 30 mM, 3) 20 mM, 4) 10 mM, 5) 5 mM, 6) 1 mM, 7) 0.1 mM, C) CH₃CN/water (1:1) (yellow labels).

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In conclusion, we have successfully prepared paramagnetic nickel(II) and cobalt(III) complexes with the BF₃-appended cyclen ligand previously described for efficient ¹⁸F-radiolabeling for PET imaging, and demonstrated their excellent properties as sensitive ¹⁹F MRI probes. This represents the first example of the use of trifluoroborate units for this purpose, and highlights the great potential and versatility of these simple functional groups for medical imaging applications. In addition, the ¹⁹F MRI properties of the two complexes are excellent when compared to well-known CF₃-appended complexes from literature, and they rely on abundant transition metals, less toxic than previously used lanthanides in such compounds. Finally, [Co(Do2py2BF₃)] is, to the best of our knowledge, the fastest-relaxing fluorinated cobalt(II) complex reported to date.

Conflicts of interest

"There are no conflicts to declare".

Data availability

The datasets supporting this article have been uploaded as part of the Electronic Supporting Information. Additional data can be provided upon reasonable request to thibault.troadec@univ-brest.fr.

Author contributions

Conceptualization and funding acquisition by TT; investigation by CS, FG, NL, NLP, NSM and TT; supervision by TT, RT, LT; original draft by TT; review and editing by all authors.

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Notes and references

‡ Supplementary crystallographic data can be obtained from The Cambridge Crystallographic Data Centre under CCDC numbers 2455805 (Ni(Do2py2BF₃)) and 2455806 (Co(Do2py2BF₃)).

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Data availability

The datasets supporting this article have been uploaded as part of the Electronic Supporting Information. Additional data can be provided upon reasonable request to thibault.trodec@univ-brest.fr.