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The synthesis and characterization of a new chelating benzotriazinyl radical (**Rad**<sub>2</sub>) are described. Crystallographic studies coupled with SQUID magnetometry on **Rad**<sub>2</sub> reveal the presence of discrete radical pairs which are antiferromagnetically coupled. Reaction of **Rad**<sub>2</sub> with the 3d transition metal complexes M(hfac)<sub>2</sub>·*x*H<sub>2</sub>O (hfac<sup>-</sup> = hexafluoroacetylacetonate) led to mononuclear metal complexes of general formula M(hfac)<sub>2</sub>(**Rad**<sub>2</sub>) [M = Zn(II) (1); Ni(II) (2) and Co(II) (3)] whose structures have been determined by single crystal X-ray diffraction. Compounds 1– 3 are isostructural and crystallize in the monoclinic space group  $P2_1/n$  with two molecules in the asymmetric unit. In the case of the Zn(II) complex (1) through-space intermolecular radical antiferromagnetic exchange interactions via  $\pi^* \cdots \pi^*$  contacts are observed, whereas strong intramolecular through-bond metal-radical ferromagnetic interactions [*J* = +59.3(9) cm<sup>-1</sup>] are observed for the Ni(II) complex (2). For the Co(II) complex (3), computational and magnetic studies reveal substantial zero field splitting and ferromagnetic metal-radical interactions.

# Introduction

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The development of molecule-based magnetic materials has relied heavily on magnetic exchange-coupling between paramagnetic metals centers (d- or f-based electrons) typically via diamagnetic ligands. The sign and magnitude of such magnetic super-exchange interactions for d-block metals is well understood through Goodenough-Kanamori rules.<sup>1</sup> While one and two atom bridges such as O<sup>2-</sup> and CN<sup>-</sup> prove effective exchange coupling ligands, exchange coupling via diamagnetic ligands over more extended distances is typically weak. An alternative strategy is to implement the use of bridging paramagnetic ligands where strong metal-ligand exchange can lead to high spin molecules irrespective of whether the coupling is ferro- or antiferro-magnetic.<sup>2</sup> A number of paramagnetic ligands have been explored of which nitroxide, nitronyl nitroxide, verdazyl and dithiadiazolyl radicals have been particularly well documented (Scheme 1a,b).<sup>3-6</sup> These

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ligands often give strong intramolecular metal-radical exchange  $(J_{intra}/k)$  such that the complexes' spin ground state is often fully populated at/near room temperature. Conversely through-space intermolecular exchange between molecules has been less extensively explored but is typically only evident at low temperature and often modelled using a phenomenological Weiss constant,  $\theta$  (where  $|\theta| \ll |J_{intra}/k|$ ) and typically  $|\theta|$ < 2 K. For example, Preuss' studies<sup>7</sup> on through-bond and through-space space exchange Mn(hfac)<sub>2</sub>(boadtda) revealed strong intramolecular exchange  $(J_{intra}/k = -39 \text{ K})$  and weaker through-space interactions, propagated via close S···O intermolecular contacts  $(J_{inter}/k = -$ 2.5 K). Conversely a McConnell I mechanism<sup>8a</sup> via a  $\pi \cdots \pi$  orbital overlap is proposed for through-space ferromagnetic interactions in Ni(hfac)<sub>2</sub>(boadtda).<sup>8b</sup> One approach to deconvolute contributions from intramolecular exchange, intermolecular exchange and other effects (such as residual orbital angular momentum and zero field splitting) and unambiguously probe such through-space exchange in metalradical complexes is to use complexes in which the metal ion is diamagnetic (commonly  $d^0$ , low spin  $d^6$  or  $d^{10}$ ), thereby providing a direct probe for the strength of through-space exchange.

The 1,2,4-benzotriazinyl radicals (Blatter radicals) comprise an interesting family from the viewpoint of their ease of preparation, functionalization, transformations of functional groups and robust air and moisture stability.<sup>9–12</sup> In the solid state, they tend to adopt slipped  $\pi$ -stacked structures. The magnetic properties of these radicals appear particularly

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<sup>&</sup>lt;sup>+</sup>Electronic supplementary information (ESI) available: Cyclic voltammetry, plots of M vs H/T for complexes **2** and **3**, computational details and a summary Table of crystallographic data. CCDC 1882619–1882622. *For ESI and crystallographic data in CIF or other electronic* format see DOI: 10.1039/x0xx00000x <sup>\*</sup>Both the authors have equal contribution to this work.

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sensitive to their solid state structure and exhibit a diverse range of magnetic properties including abrupt spin transitions (between paramagnetic and diamagnetic phases),13 antiferromagnetic exchange<sup>11c,g,12a,h,14</sup> and ferromagnetic  $interactions^{11b,f,15}$  depending on the subtle differences in molecular arrangement along the stacking direction. Functionalization at the C7 position of the parent Blatter radical with a trifluoromethyl<sup>11b,15b</sup> or thienyl<sup>11f</sup> group serves a dual purpose, enhancing the oxidative stability of the benzotriazinyl framework as well as favoring a 1D columnar alignment. Recently, Morgan et al. reported the coordinating Blatter radical. 1-phenyl-3-(pyrid-2-yl)-1,4-dihydro-1,2,4benzotriazin-4-yl (Rad<sub>1</sub>, Scheme 1c) with a bipyridine-like N,N'chelating pocket and its coordination complexes M(hfac)<sub>2</sub>(Rad<sub>1</sub>) (M = Mn, Fe, Co, Ni, Cu).<sup>16</sup> Magnetic studies revealed that in Rad1 the radical pairs are strongly antiferromagnetically coupled and are essentially diamagnetic below 100 K;<sup>16a</sup> Cu(II) and Ni(II) complexes showed intramolecular ferromagnetic exchange consistent with orbital orthogonality rules whereas Mn(II) and Fe(II) complexes showed antiferromagnetic exchange.<sup>16</sup>



In order to increase the robustness of the radical moiety, the current study was aimed to functionalize the parent ligating benzotriazinyl framework (Rad1) by the trifluoromethyl group (-CF<sub>3</sub>) at the C7 position (Rad<sub>2</sub>) to prevent any undesired oxidation products and to establish how such functionalization affects the solid-state structure and magnetic response. Herein, we describe the synthesis and characterization of Rad<sub>2</sub> and, despite the electron-withdrawing nature of the CF<sub>3</sub> group, we show that it can act as a chelating ligand to yield an isostructural series of *d*-block complexes of composition  $M(hfac)_2(Rad_2)$  [M = Zn(II) (1), Ni(II) (2) and Co(II) (3); hfac<sup>-</sup> = hexafluoroacetylacetonate]. The through-bond and throughspace interactions were examined through variabletemperature magnetic susceptibility measurements and theoretical calculations were carried out to probe both the metal-radical and radical…radical exchange coupling.

# **Results and Discussion**

# Synthetic considerations

The benzotriazinyl radical **Rad**<sub>2</sub> was prepared via a multistep route (Scheme 2) starting from the readily available picoline,



sodium sulfide, and 4-trifluoromethyl aniline which generated the corresponding pyridylthioamide species (A).39Reaction16f pyridylthioamide with phenyl hydrazine the gave pyridylamidrazone (B).<sup>18</sup> The ring closure and oxidation of the purified amidrazone was accomplished by a combination of Pd/C and 1,8-diazabicycloundec-7-ene in air to obtain the radical Rad<sub>2</sub>. The product was purified using column chromatography followed by recrystallization and characterized by elemental analysis, IR and EPR spectroscopy, cyclic voltammetry, magnetic measurements and single-crystal X-ray diffraction.



Scheme 2. Synthetic route of Rad2

Electrochemical studies on  $Rad_2$  reveal an oxidation and a reduction process (Figure S1, Supporting Information) comparable with other benzotriazinyls<sup>11h</sup> with a large window of redox stability (-0.85 – +0.31 V vs Fc/Fc<sup>+</sup> reference electrode) permitting it to react with a range of transition metals in common oxidation states without electron transfer. Reaction of **Rad**<sub>2</sub> with the hydrated salts M(hfac)<sub>2</sub>·xH<sub>2</sub>O (where M = Zn(II) (1), Ni(II) (2) and Co(II) (3), hfac<sup>-</sup>: hexafluoroacetylacetonate) in dichloromethane afforded complexes of general formula M(hfac)<sub>2</sub>(**Rad**<sub>2</sub>).

## **EPR studies**

EPR spectra for  $Rad_2$  and  $Zn(hfac)_2(Rad_2)$  were recorded on a Bruker EMX-MicroX-band EPR spectrometer equipped with a variable temperature unit providing access to temperatures in the range 100–300 K. The solid state EPR spectra of  $Rad_2$ revealed a strong temperature dependence (Figure 1). At high temperature (300 K) the spectrum appeared as a broad singlet with limited resolution of additional features. At 100 K there was some evidence for exchange coupling reflected in absorption to either side of the central line and some better resolution of features in the 150–200 K region. The EPR spectrum at 150 K was simulated as a single component EPR spectrum with both hyperfine coupling and zero field splitting. In general the isotropic hyperfine coupling in solution ( $a_{iso}$ ) is

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Figure 1. (a) Variable temperature solid state EPR spectra of Rad<sub>2</sub>; (b) EPR spectrum of Rad<sub>2</sub> at 150 K with simulation ( $g_x = 2.0075$ ,  $g_y = 2.0070$ ,  $g_z = 2.0055$ ;  $a_{Nz(1)} = 22$  G, 2 x  $a_{Nz(2,3)} = 14$  G, D = 0.00055 cm<sup>-1</sup>, E = 0.0001 cm<sup>-1</sup>,  $\Delta H_{pp} = 2.8$  G (Gaussian)); (c) EPR spectrum of Rad<sub>2</sub> at 200 K with simulation ( $g_x = 2.0075$ ,  $g_y = 2.0070$ ,  $g_z = 2.0055$ ;  $a_{Nx(1)} = 6$  G,  $a_{Ny(1)} = 6$  G,  $a_{Nz(1)} = 9$  G, 2 x  $a_{Nx(2,3)} = 4.5$  G, 2 x  $a_{Ny(2,3)} = 4.5$  G,  $a_{Nz(2,3)} = 6$  G, D = 0.00007 cm<sup>-1</sup>).

related to the principal components of the hyperfine coupling  $(a_x, a_y \text{ and } a_z)$  by Eqn. 1:

 $a_{iso} = 1/3 (a_x + a_y + a_z)$  Eqn. 1

For  $\pi$  radicals the hyperfine coupling to one component is large and the other two components which sit in the nodal plane of the singly occupied molecular orbital (SOMO) are near zero. The non-zero component of the hyperfine is then  $\sim$  3  $a_{iso}$ . As a starting point for simulating the solid state EPR spectrum of Rad<sub>2</sub>, we used the isotropic hyperfine coupling parameters forthe closely related "super stable" Blatter radical, 1,3diphenyl-7-trifluoro-methyl-1,4-dihydro-1,2,4-benzotriazin-4yl.11b This radical is identical to Rad<sub>2</sub> except that the pyridyl ring at the 3-position in Rad<sub>2</sub> is replaced by a phenyl group. Here, the solution EPR spectrum implemented three <sup>14</sup>N hyperfine coupling constants of 7.62, 4.95 and 4.56 G. The corresponding non-zero anisotropic parameters are expected to be in the region of 22.86, 14.85 and 13.68 G respectively. Refined parameters to simulate the anisotropic spectrum of  $Rad_2$  were 22.0, and 2 × 14.0 G in excellent agreement with expectation. A small additional zero field splitting term D = 0.00055 cm<sup>-1</sup> was included and provided a very good fit to all features in the EPR spectrum. EPR simulations were undertaken using PIP through the PIP4WIN interface.<sup>19</sup> On warming from 150 K to 200 K there are subtle changes to the solid state EPR spectrum of Rad2 associated with an increase in the zero field splitting parameter D and an averaging of the hyperfine coupling across the three components. The temperature evolution of the spectral resolution is likely due to the temperature dependence of the relaxation rates which are sensitive to distance and therefore coupled to thermal lattice expansion effects upon warming.<sup>20</sup>

Variable temperature solid state EPR spectra of  $Zn(hfac)_2(Rad_2)$  (Figure 2) were rather featureless but revealed the emergence of a weak absorption slightly to low field of the central resonance, consistent with the presence of thermal population of excited high spin states. In contrast, we were unable to observe EPR spectra for complexes 2 and 3 under the limited conditions available (100 - 300 K, X-band).



# Description of the crystal structures and molecular packing topology of the benzotriazinyl radical $(Rad_2)$ and $M(hfac)_2(Rad_2)$ (M = Zn(II) (1), Ni(II) (2) and Co(II) (3), hfac: hexafluoroacetylacetonate)

The benzotriazinyl radical Rad<sub>2</sub> crystallizes in the triclinic space group P-1 with one molecule in the asymmetric unit (Figure S2, Supporting Information). The bond lengths and bond angles are largely unexceptional and similar to the values reported for other related benzotriazinyl systems. The phenyl ring (ring I: formed by C21, C23, C24, C25, C26) makes a dihedral angle of 56.47° with the spin-bearing triazinyl ring (ring II: formed by N1, C1, C6, N2, N3, C7) and the dihedral angle between the pyridyl ring (ring III: formed by C8, C9, C10, C11, C12, N4) and the triazinyl ring II is 8.51°. Two Rad<sub>2</sub> molecules are located about the crystallographic inversion center leading to a supramolecular dimer linked through N···H interactions (2.691 Å) (Figure 3). These interactions fix the two triazinyl rings in an essentially eclipsed configuration with a centroid--centroid distance of 3.375 Å [the degree of slippage,<sup>13a</sup> longitudinal  $(\phi_1)$ = 29.40° and latitudinal  $(\phi_2)$ = 9.12°]. This distance is substantially longer compared to the centroid--centroid distance of 3.256 Å ( $\phi_1$ = 38.01°,  $\phi_2$ = 9.39°) between two triazinyl rings in Rad<sub>1</sub>.<sup>16a</sup>

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Figure 3. Structure of Rad\_ highlighting intermolecular C-H…N (a) and  $\pi \cdots \pi$  stacking (b) interactions which generate supramolecular dimers.

Topological analysis of the molecular packing<sup>21</sup> reveals that the molecule has a CN (coordination number) of 14, a common number for neighboring molecules in molecular crystals<sup>22</sup> and the topological motif of the molecular packing can be described by a net of the **bcu-x** type (14-coordinate extended body-centered packing) as shown in Figure 4.



**Figure 4.** (a) The environment of the molecule and underlying net of molecular packing in the crystal structure of compound **Rad**<sub>2</sub>. The solid angle ( $\Omega$ ) has been used as a criterion serving as a weight factor proportional to the strength of the intermolecular contact.<sup>22</sup> The surrounding fourteen molecules are highlighted depending on the solid angle of intermolecular contact ( $\Omega \ge 9\%$  - pink;  $9\% > \Omega \ge 4\%$  - yellow;  $\Omega < 4\%$  - green). The atoms of the central molecule are colored according to the color scheme presented in the legend. Black edges present the underlying net of centers of molecules with topology **bcu-x**. (b) Uninodal underlying net of the **bcu-x** topological type describing the packing of the molecular dimers formed by **Rad**<sub>2</sub> molecules.

Aforementioned,  $\pi$ - $\pi$  dimers can be observed within the crystal packing. An alternative description of the molecular packing can be considered as the packing of these supramolecular  $\pi$ - $\pi$  dimers. The corresponding dimers are

those built from the molecules having the largest of intermolecular contacts—pair with  $\Omega = 16.9\%$ . The molecular contacts—pair with  $\Omega = 16.9\%$ . The molecular considering the topology in terms of dimers, the packing description does not change and these  $\pi$ - $\pi$  dimers similarly adopt the **bcu-x** type net (Figure 4).

To realize the difference in molecular packing, topological analysis of the molecular packing of the reported **Rad**<sub>1</sub> molecule<sup>16a</sup> has been undertaken which has a CN (coordination number) of 17. The topology of the 17-c underlying net is not contained in the Topos Topological Database (Figure 5) and this net can be described as a  $\{3^{54}.4^{73}.5^9\}$  net. **Rad**<sub>1</sub> also comprises a  $\pi$ - $\pi$  dimer motif and a topological analysis based on  $\pi$ - $\pi$  dimer repeat units generates an underlying 14T3 net of supramolecular dimers in the standard representation.



**Figure 5.** The underlying net of molecular packing and environment of the (a) molecule and (b) its dimer in the crystal structure of compound **Rad**<sub>1</sub>. Surrounding (a) seventeen molecules and (b) fourteen dimers are highlighted depending on the solid angle of intermolecular contact ( $\Omega \ge 8\%$  - pink;  $8\% > \Omega \ge 3\%$  - yellow;  $\Omega < 3\%$  - green). The atoms of the central molecule are colored according to the color scheme presented in the legend. Pink, yellow and green spheres represent the centers of (a) molecules within the 17-c uninodal underlying net and (b) dimers within the 14-c uninodal underlying net.

Crystal structures of M(hfac)<sub>2</sub>(**Rad**<sub>2</sub>) (M = Zn(II) (1) Ni(II) (2) and Co(II) (3)) are isostructural and crystallize in the monoclinic space group *P*2<sub>1</sub>/n with two molecules in the asymmetric unit which exhibit similar molecular geometries. Given the isostructural nature of the compounds, the structure of Zn(hfac)<sub>2</sub>(**Rad**<sub>2</sub>) (1) is described in detail as a representative example. In 1, each six-coordinate Zn(II) center adopts a distorted {ZnN<sub>2</sub>O<sub>4</sub>} octahedral coordination geometry that is filled by one *N*,*N'*-chelating **Rad**<sub>2</sub> moiety and two hfac ligands. The two molecules in the asymmetric unit form two similar but crystallographically different centrosymmetric dimer pairs linked through C-H···O = 2.65 Å and 2.62 Å for the two crystallographically independent molecules) and  $\pi$ ··· $\pi$ interactions (Figure 6).

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Table 1. List of non-valence contacts between molecules in structure Rad<sub>2</sub> and for ZA1/ZA2 molecules in M(hfac)<sub>2</sub>(Rad<sub>2</sub>) (M = Zn(II) (1), Ni(II) (2) and Co(II) (3))

Type of contact	Number of contacts				Surface area, Å <sup>2</sup>				Fraction of total area			
	Rad₂	1 ZA1/ZA2	2 ZA1/ZA2	3 ZA1/ZA2	Rad <sub>2</sub>	1 ZA1/ZA2	2 ZA1/ZA2	3 ZA1/ZA2	Rad₂	1 ZA1/ZA2	2 ZA1/ZA2	3 ZA1/ZA2
H-F	36	122/114	112/112	121/111	93.88	256.25/251.55	245.99/233.03	267.59/251.86	23.5	37.3/35.2	37.4/34.5	38.4/35.1
F-F	3	72/69	69/68	71/64	3.76	174.90/153.14	164.54/147.37	181.10/154.24	0.9	25.5/21.4	25.0/21.8	26.0/21.5
C-H	92	92/98	84/90	91/97	64.39	73.16/70.82	73.98/68.12	74.73/71.78	16.1	10.7/9.9	11.2/10.1	10.7/10.0
F-C	42	68/102	65/95	68/102	28.84	46.80/78.88	44.81/72.93	44.72/79.39	7.2	6.8/11.0	6.8/10.8	6.4/11.1
0-Н	-	20/20	20/20	20/20	-	41.96/39.85	38.52/38.46	38.77/37.28	-	6.1/5.6	5.9/5.7	5.6/5.2
Н-Н	67	25/33	25/33	30/40	121.00	40.64/57.72	41.37/56.87	41.01/63.36	30.3	5.9/8.1	6.3/8.4	5.9/8.8
N-C	30	33/33	32/32	28/30	14.55	15.76/16.25	15.5/15.47	14.61/14.20	3.6	2.3/2.3	2.4/2.3	2.1/2.0
C-C	50	33/36	30/37	31/34	22.52	15.35/17.13	13.40/17.84	13.67/16.77	5.6	2.2/2.4	2.0/2.6	2.0/2.3
N-H	32	21/23	22/24	22/24	48.18	14.02/15.03	14.22/14.5	14.70/15.35	12.1	2.0/2.1	2.2/2.1	2.1/2.1
F-0	-	5/9	3/9	4/8	-	2.78/6.71	2.38/5.01	2.58/5.63	-	0.4/0.9	0.4/0.7	0.4/0.8
N-N	2	2/2	2/2	2/2	1.82	2.90/2.60	2.05/2.29	2.19/2.61	0.5	0.4/0.4	0.3/0.3	0.3/0.4
N-F	4	4/8	5/9	4/10	0.48	1.87/4.83	1.53/2.89	1.71/4.90	0.1	0.3/0.7	0.2/0.4	0.2/0.7



Figure 6. Structure of  $Zn(hfac)_2(Rad_2)$  highlighting intermolecular C-H···O (a) and  $\pi \cdots \pi$ stacking (b) interactions which generate supramolecular dimers.

These  $\pi \cdots \pi$  interactions in the supramolecular dimer  $[Zn(hfac)_2(Rad_2)]_2$  are rather different from those in Rad<sub>2</sub> itself. In the latter eclipsing of the benzotriazinyl framework is observed whereas in the complexes 1-3 the molecules are now slipped so that there is overlap of the triazinyl and pyridyl rings (via an inversion centre). While the supramolecular dimer in Rad<sub>2</sub> locates the two benzotriazinyl rings over each other, in [Zn(hfac)<sub>2</sub>(Rad<sub>2</sub>)]<sub>2</sub> the benzotriazinyl ring is located over the pyridyl ring with centroid…centroid distances of 3.718 Å and 3.605 Å respectively for the two crystallographically independent supramolecular dimers. The corresponding distances are 3.729 Å & 3.622 Å in Ni(hfac)<sub>2</sub>(Rad<sub>2</sub>) (2) and 3.788 Å & 3.629 Å in Co(hfac)<sub>2</sub>(Rad<sub>2</sub>) (3).

From a topological perspective, the complete molecular packings of complexes 1-3 are similar if intermolecular contacts with solid angles more than 0.4% are considered. The packing comprises two crystallographically different molecules of the same composition which are defined as ZA1 and ZA2. ZA1 has intermolecular contacts with 17 molecules - eight ZA1

and nine ZA2 (Figure 7a). The second crystallographically independent molecule (ZA2) is surrounded by 15 molecules (nine ZA1 and six ZA2) (Figure 7b). In total, the 15,17coordinated net is of a previously unknown topological type with point symbol for net (3<sup>40</sup>.4<sup>57</sup>.5<sup>8</sup>)(3<sup>47</sup>.4<sup>70</sup>.5<sup>19</sup>) (Figure 7c).



Figure 7. The environment of molecules ZA1 (a) and ZA2 (b) in the crystal structure of compound  $Zn(hfac)_2(Rad_2)$  (2) is shown as a representative example. Surrounding ZA1 and ZA2 molecules are highlighted by pink and yellow, respectively. The atoms of the central molecule are colored according to the color scheme presented in the legend. (c) The underlying net of molecular packing in 2. Orange and purple balls represent centroids of two non-equivalent ZA1 and ZA2 molecules, respectively.

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Furthermore, the role of intermolecular interactions in the solid-state packing of  $Rad_2$  and complexes 1-3 has been probed in a quantitative fashion by means of Voronoi-Dirichlet polyhedral analysis using the Dirichlet routine within ToposPro.<sup>21c</sup> The non-valence interactions governing the crystal packings in Rad<sub>2</sub> and complexes 1–3 are listed in Table 1. For Rad<sub>2</sub>, despite the presence of only three fluorine atoms, numerous interatomic contacts of types F…H, F…F, and F…C are present. In total, they comprise 31.6% of the total surface area of interatomic contacts. However, the contacts N···N, C···C and N···C, responsible for  $\pi$ - $\pi$  stacking, are also strong since they are responsible for intermolecular interactions (Table 1) with large solid angles. In the case of complexes 1-3, the fluorine atoms again produce the most numerous interatomic contacts of types F···H, F···Fand F···C between molecules (Table 1). The N…N, C…C and N…C contacts responsible for  $\pi$ - $\pi$  stacking, appear to be less important in these three structures.

# **Magnetic studies**

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In **Rad**<sub>2</sub>, the room temperature value of  $\chi_M T \simeq 0.363$  cm<sup>3</sup>mol<sup>-1</sup>K is consistent with an S =  $\frac{1}{2}$  radical with the decrease in  $\chi_M T$ upon cooling reflecting weak antiferromagnetic exchange coupling between spins (Figure 8). A plot of  $1/\chi$  vs T in the high temperature region (T > 50 K) reflected Curie-Weiss behavior with  $C = 0.379 \text{ cm}^3 \text{mol}^{-1} \text{K}$  (consistent with that expected for an S =  $\frac{1}{2}$  radical of 0.375 cm<sup>3</sup>mol<sup>-1</sup>K) and  $\theta$  = -9.4 K. The Weiss constant is indicative of weak antiferromagnetic interactions between spins. The structure of Rad<sub>2</sub> comprises a supramolecular dimer in which triazinyl rings are associated in a face-to-face  $\pi$ - $\pi$  interaction. Assuming this is the dominant exchange pathway (z = 1) then application of the mean field model ( $\theta = 2zJS(S+1)/3k$ ) affords  $J/k \sim -8$  K. A subsequent single parameter fit to the Bleaney-Bowers model<sup>23</sup> for an S =  $\frac{1}{2}$ dimer (Eqn. 2) with fixed g value (2.006) afforded J/k = -13(1)К.

$$\hat{H} = -2J\hat{S}_1\hat{S}_2$$
 Eqn. 2

The weak antiferromagnetic nature of the exchange coupling in **Rad**<sub>2</sub> contrasts with **Rad**<sub>1</sub> which was reported to be diamagnetic below 100 K.<sup>16a</sup> This can be attributed to the CF<sub>3</sub> group which weakens the  $\pi$ ··· $\pi$  stacking between the spinbearing triazinyl rings, leading to reduced orbital overlap and a resultant decrease in exchange coupling.





 $\hat{H} = -2J_1\hat{S}_1\hat{S}_2 - 2J_2\hat{S}_3\hat{S}_4$  Eqn. 3

The large variation in *J* between the two crystallographically independent dimers reflects sensitivity in orbital overlap, a phenomenon previously seen for  $\pi$ -stacked radicals.<sup>13a</sup> The formation of supramolecular dimers with a singlet ground state and thermally accessible triplet is also reflected in the emergence of additional features in the EPR spectrum above 120 K, consistent with a thermally accessible spin triplet (*vide supra*). It is clear from these studies that through-space exchange coupling through the presence of  $\pi^{*\cdots}\pi^{*}$ interactions mediated by McConnell I mechanism<sup>8a</sup> between paramagnetic ligands is likely at the origin of the observed exchange coupling.



The  $\chi_M T$  value for the Ni(II) complex (**2**) is 1.97 cm<sup>3</sup>mol<sup>-1</sup>K at room temperature (Figure 10) which is slightly larger than the calculated spin only value of one radical and one Ni(II) ion (1.8 cm<sup>3</sup>mol<sup>-1</sup>K). Upon decreasing the temperature  $\chi_M T$  increases up to 2.24 cm<sup>3</sup>mol<sup>-1</sup>K at 60K which suggests strong ferromagnetic interaction between the radical and the metal centre. Further cooling leads to a reduction in  $\chi_M T$  of 1.24 cm<sup>3</sup>mol<sup>-1</sup>K at 2 K which could arise from zero field splitting (ZFS) effects or intermolecular antiferromagnetic exchange to neighbouring molecules. In addition, the field dependence of magnetization was measured by varying dc field from 0 – 7 T at

The magnetism of Zn(hfac)<sub>2</sub>(Rad<sub>2</sub>) (1) revealed Curie Weiss behaviour with  $C = 0.379 \text{ cm}^3 \text{mol}^{-1}\text{K}$  (consistent with  $379 \text{ m}^{-2}$ spin and g = 2.00) and  $\theta$  = -6.4 K consistent with weak antiferromagnetic interactions between  $Zn(hfac)_2(Rad_2)$ molecules (Figure 9). The onset of a significant downturn in  $\chi_M T$  upon cooling below 50 K is indicative of antiferromagnetic interactions in **1**. Given the mononuclear nature of the  $S = \frac{1}{2}$ Zn(II) benzotriazinyl complex (1), this behavior is attributed to through-space intermolecular interactions between radicals. The structure of 1 reveals each radical forms a single nearest neighbor  $\pi$ - $\pi$  contact between radical ligands. However, initial attempts to model the magnetism of 1 as a simple exchange coupled dimer (Eqn. 2) failed to fit the data across the entire temperature range. Use of a Bleaney-Bowers model<sup>23</sup> for each of the two independent dimmers (Eqn. 3) provided an improved fit to the data with g = 2.006 (fixed) and two different J values;  $J_1 = -2$  K and  $J_2 = -38$  K.

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2 K, 4 K, 6 K, 8 K, and 10 K (Figure S3, Supporting Information). At low field and temperature (2 K) the magnetization increases slowly to a value of 2.9  $\mu_B$  at the highest applied field without saturation. For a well-isolated magnetic ground state, the M vs H/T curves at these different temperatures should be superimposable. This is not the case for complex **2**, reflecting the presence of low lying excited states. A fit of the experimental susceptibility to an isotropic exchange Hamiltonian (Eqn. 4) with the radical g-factor fixed at 2.006 and taking into account a generic mean field term to model either ZFS or intermolecular exchange was performed within PHI.<sup>24</sup>

$$\hat{H} = -2J\hat{S}_{Ni}\hat{S}_{Rad2}$$
 Eqn. 4

This afforded  $J = +59.3(9) \text{ cm}^{-1}$ ,  $g_{Ni} = 2.326(2)$  and a mean field exchange term,  $zJ' = -0.178(6) \text{ cm}^{-1}$ . The g value is not dissimilar to values for other octahedral Ni<sup>2+</sup> ions (typical g values in the vicinity of 2.25).<sup>25</sup> The positive J value is consistent with ferromagnetic exchange between radical and Ni<sup>2+</sup> ions based on the orbital orthogonality of the ligand  $\pi$ -system and the metal eg set (Figure 10, inset).<sup>26</sup> The small value of zJ' is consistent with small ZFS effects or weak intermolecular exchange.



**Figure 10.** Temperature dependence of  $\chi_M T$  for Ni(hfac)<sub>2</sub>(**Rad**<sub>2</sub>) (**2**) [Red line is the best fit to the experimental data (circles) using the Hamiltonian described in the text]. Inset: Mutually orthogonal nature of the Ni  $d_{z^2}$  and  $d_{x^2,y^2}$  orbitals and the N  $\pi$  system.

The magnetism of high spin octahedral cobalt(II) complexes is complex due to unquenched orbital angular momentum associated with the <sup>4</sup>T term, leading to significant anisotropy in g-tensor and an Ising-like spin.<sup>27</sup> For  $\pi$ -based radicals coordinated to the  $t_{2g}5e_g^2$  Co(II) configuration the interaction of the radical with the metal  $\pi$ -type ( $t_{2g}$ ) set is expected to be antiferromagnetic whereas the metals'  $\sigma$ -type ( $e_g$ ) electrons are mutually orthogonal like Ni(II) and are anticipated to propagate a ferromagnetic term. Typically the presence of a non-zero overlap integral is predicted to generate a net antiferromagnetic interaction between Co(II) and the radical ligand.<sup>28</sup> However, several studies have commented upon the unexpectedly small antiferromagnetic exchange for Co(II) semiquinone derivatives<sup>29</sup> while Hendrickson and co-workers reported a net ferromagnetic interaction in otherclesemie quinone radical complexes.<sup>30</sup> Work by PPeuse and Alexander respectively described a net ferromagnetic exchange coupling for both dithiadiazolyl and verdazyl radicals coordinated to  $Co(II)^{31}$ , reflecting the complexity of the situation.

The magnetic susceptibility of the cobalt benzotriazinyl radical complex **3** is 3.52 cm<sup>3</sup> mol<sup>-1</sup>K at room temperature (Figure 11) increasing up to 3.74 cm<sup>3</sup> mol<sup>-1</sup>K upon cooling to 70 K before decreasing again to 0.79  $\mbox{cm}^3\mbox{ mol}^{-1}\mbox{K}$  at 2.0 K. The high temperature behaviour is consistent with ferromagnetic interactions between radical and Co(II) centers, while the decrease at low temperature could be due to depopulation effects within the  $S_T = 2$  ground spin state or intermolecular exchange coupling. Additionally, the field dependence of the magnetization plot (Figure S4, Supporting Information) shows the magnetization does not saturate even at low temperature and a large applied field, again indicating the presence of lowlying excited states. To extract useful parameters for the magnetism of 3, we implemented a Hamiltonian (Eqn. 5) to take into account intramolecular exchange  $(J_a)$  between the radical and Co(II) and an additional intermolecular exchange term  $(J_{b})$  to take into account through-space radical-radical exchange. Additional D and E parameters were included to take into account zero field splitting effects for Co(II):

$$\begin{aligned} \hat{H} &= -2J_{a} \Big[ S_{\text{Co}(1)} S_{\text{rad}(1)} + S_{\text{Co}(2)} S_{\text{rad}(2)} \Big] - 2J_{b} \Big[ S_{\text{rad}(1)} S_{\text{rad}(2)} \Big] + \\ D \sum_{i=1}^{2} \left( S_{iz}^{2} - \frac{1}{3} S_{i}^{2} \right) + E \sum_{i=1}^{2} (S_{x}^{2} - S_{y}^{2}) + \\ \mu_{B} \cdot B \cdot \left( \sum_{i=1}^{2} S_{i} \right) \cdot g_{\text{Co}} + \\ \mu_{B} \cdot B \cdot \left( \sum_{i=1}^{2} S_{i} \right) \cdot g_{\text{rad}} \end{aligned}$$
Eqn. 5

Given the large number of variables, we undertook a series of computational studies to find an initial set of parameters from which to undertake fitting of the experimental data. We performed density functional theory (DFT) and ab initio calculations followed by CASSCF+RASSI-SO+SINGLE ANISO method by MOLCAS 8.2 software package (Supporting Information).<sup>32</sup> The exchange coupling constant was calculated using the method of Yamaguchi.33 The DFT calculations afforded  $J_a$  (+72.7 cm<sup>-1</sup>) and  $J_b$  (-3.1 cm<sup>-1</sup>). In addition, the CASSCF+RASSI-SO+SINGLE\_ANISO calculations yielded g = 2.3 and D = +33.7 cm<sup>-1</sup> and E = -4.5 cm<sup>-1</sup> for the Co<sup>II</sup> ion. The simulated  $\chi_m T$  vs T data for **3** using these computed values clearly replicate well the salient features of the magnetic data (blue). Subsequent curve-fitting of the both temperature dependence of the experimental magnetic data and the M vs H data within PHI, using these computed values as the starting point for refinement gave refined values in good agreement with computation. The best fit (red line) gives  $J_a = +71 \text{ cm}^{-1}$ ,  $J_b$ = -3.01 cm<sup>-1</sup>, D = +21 cm<sup>-1</sup>, E = -4.5 cm<sup>-1</sup> and  $g_{Co}$ = 2.3 while  $g_{rad}$ was fixed at 2.0. The large and positive D and g > 2 values obtained for Co(II) are comparable with data reported for other octahedral Co(II) ions.<sup>34</sup> Additional ac susceptibility data were measured on complex 3 but no frequency dependence of the ac response was observed in the out-of-phase signal in either zero field or with an external applied field of 2000 Oe, reflecting the absence of slow relaxation phenomena in 3.



**Figure 11.** Temperature dependence of  $\chi_M T$  for Co(hfac)<sub>2</sub>(**Rad**<sub>2</sub>) (**3**). The blue line is the computed temperature dependence, based on computed values, while the red line is the best fit using optimized parameters (see text).

# **Theoretical calculations**

To gain insight into the magnetic exchange coupling between radicals in Rad<sub>2</sub> and between metal and radical in complexes 1 and 2, we performed density functional theory (DFT) calculations in combination with broken symmetry (BS) approach to obtain information on both metal-radical  $(J_a)$  and radical-radical (J<sub>b</sub>) exchange couplings within the ORCA 4.0 software package.35 Calculations implemented the hybrid functional B3LYP with TZVP basis set for Zn and Ni and 6-311G\* for other atoms. The tight SCF convergence criteria were employed throughout the calculation. For the S =  $\frac{1}{2}$ radical **Rad<sub>2</sub>** and the zinc complex **1**, the exchange couplings via the  $\pi \cdots \pi$  interaction between nearest-neighbour benzotriazinyl radicals (Figures 3 and 6b respectively) were computed using the method of Yamaguchi<sup>33</sup> where the exchange coupling is determined from the energies (E) and expectation values (<S<sup>2</sup>>) of the triplet and broken symmetry singlet states:

$$J = \frac{-(E_T - E_{BSS})}{\langle S^2 \rangle_T - \langle S^2 \rangle_{BSS}}$$
 Eqn. 6

For the benzotriazinyl radical Rad<sub>2</sub>, there is substantial positive ( $\alpha$ ) spin density on the triazinyl ring and the superposition of these areas of positive spin density (Figure 12b) on neighbouring molecules is expected to lead to an antiferromagnetic through-space coupling based on the McConnell I mechanism.8ª These were confirmed by DFT calculations based on single point calculations based on the crystallographic coordinates for Rad2 which predict a substantial antiferromagnetic interaction (J = -89 cm<sup>-1</sup> or J/k-128 K) within the  $\pi$ -stacked dimer, consistent with that predicted based on the simple orbital overlap model described above. While the computed exchange coupling clearly reflects the correct sign of J, it over-estimates the value of J in relation to the experimental fit to the magnetic data (J/k = -13 K). It is important to mention here that discrepancies between J values derived from fitting the experimental magnetic susceptibility and theoretical calculation is a persistent problem in the family of Page 8 of 12

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benzotriazinyl radicals.<sup>12d,f</sup> As the calculations<sub>/ie</sub>are<sub>ic</sub>bighly sensitive on the choice of basis Set: 19409/functional, multiconfigurational approaches are required to accurately reproduce the value of J.<sup>12f,36</sup> However, multiconfigurational approaches are extremely computationally demanding and often qualtitative models have been used for a basic understanding.<sup>12f</sup>



Figure 12. (a) SOMO of the Blatter radical Rad<sub>2</sub>; (b) side view of spin density distribution of the radical pairs as calculated using UB3LYP/6-311+G (blue =  $\alpha$ ; green =  $\beta$ )

For the Zn(II) complex (1) the Weiss constant ( $\theta$  = -6.4 K) was consistent with weak antiferromagnetic exchange. From the mean field approximation<sup>23</sup> (Eqn. 7), the average nearest neighbour exchange coupling can be estimated as J/k = -12.8 cm<sup>-1</sup> (z = number of nearest-neighbour exchange interactions):

$$\theta = 2zJS(S+1)/3k$$
 Eqn. 7

For each crystallographically independent molecule of **1**, the nearest neighbour  $\pi \cdots \pi$  interactions between coordinated **Rad<sub>2</sub>** ligands was identified and the exchange couplings for the two pairs were computed. The calculated coupling constant  $J_1$  was -2.9 cm<sup>-1</sup> (-4.1 K) for the pair of zinc(II) complex molecules with a centroid···centroid distance of 3.718 Å whereas  $J_2$  was found around -3.5 cm<sup>-1</sup> (-5.1 K) with a centroid···centroid distance of 3.605 Å. These computed exchange couplings are in qualitative agreement with the experimental observation of two different antiferromagnetic exchange couplings, albeit under-estimating the strength of the interaction. An examination of the spin density distribution within one of the two crystallographically independent complexes reflects the superposition of positive ( $\alpha$ ) spin density between triazinyl and pyridyl rings (Figure 13).



Figure 13. Side view of spin density distribution in molecule pair in complex 1 (blue =  $\alpha$ ; green =  $\beta$ )

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In the case of the Ni(II) complex **2**, a ferromagnetic metalradical exchange coupling was computed ( $J_a = +116 \text{ cm}^{-1}$ ) which was in qualitative agreement with the estimate of *J* from fitting of the experimental data (+59 cm<sup>-1</sup>). The radical---radical exchange coupling constant was estimated by replacing paramagnetic Ni(II) by diamagnetic Zn(II) and computing the corresponding intermolecular exchange coupling between nearest-neighbour radicals. This was found to be very weakly antiferromagnetic ( $J_b = -3.1 \text{ cm}^{-1} = -4.4 \text{ K}$ ), comparable with that computed for the isostructural zinc complex, **1**, albeit a little larger than the mean field term extracted from modelling of the magnetic data.

# Conclusions

In summary, a new benzotriazinyl radical  $(Rad_2)$  and three neutral mononuclear metal complexes of general formula  $M(hfac)_2(Rad_2)$  (where M = Zn(II) (1), Ni(II) (2) and Co(II) (3); hfac<sup>-</sup>= hexafluoroacetylacetonate) have been prepared and chacterized by single crystal X-ray diffraction. These three complexes are isomorphous and the Zn(II) complex (1) allows unambiguous determination of the radical-radical magnetic exchange coupling (antiferromagnetic), whereas both the Ni(II) and Co(II) complexes (2 and 3) afforded ferromagnetic metalradical exchange coupling. Further work is continuing to pursue other paramagnetic metal complexes in which both through-bond metal-ligand and through space ligand-ligand exchange coupling may give rise to long range magnetic order.

# **Experimental section**

# Materials and methods

All chemicals and solvents were of reagent grade, commercially available and used as received. Elemental Micro vario Cube elemental analyzer was used for elemental analysis of the complexes. FT-IR spectra (4000–400 cm<sup>-1</sup>) were performed on KBr pellets with a Perkin Elmer Spectrum BX spectrometer. The magnetic data of all compounds were carried out using a Quantum Design SQUID MPMS3 magnetometer in an applied static dc field of 1000 Oe in the range 2–300 K. The experimental data were corrected for diamagnetism based on Pascal's constants as well as a diamagnetic contribution for sample holder.

# Preparation of N-(4-(trifluoromethyl)phenyl)pyridine-2carbothioamide (A)

The procedure utilized the literature procedure<sup>17</sup> but using 4trifluoromethyl aniline used instead of 3,5-dichloroaniline. The compound was purified by repeated recrystallization from methanol. Yield 60 %. FT-IR (KBr pellet, 400–4000 cm<sup>-1</sup>): 3474 (w), 3162 (m), 3050 (w), 1908 (w), 1670 (w), 1618 (m), 1591 (m), 1536 (s), 1439 (s), 1364 (m), 1329 (m), 1282 (w), 1229 (w), 1190(m), 1150 (m), 1108 (m), 1067 (m), 1042 (w), 993 (w), 837 (s), 765 (s), 738 (w), 686 (w), 621 (m), 589 (m), 509 (m). Elem. Anal. Calcd (%): C, 55.31; H, 3.21; N, 9.92; S, 11.36 Found (%): C, 55.45; H, 3.10; N, 10.02; S, 11.44. LR-LCMS (%): 282:04 [M]<sup>+</sup> (100%), 283 [M+H]<sup>+</sup> (14%).

# Preparation of (trifluoromethyl)phenyl)picolinohydrazonamide (B)

N'-phenyl-N-(4-

Compound **B** was synthesized according to the literature procedure.<sup>18</sup> Compound A (10 mmol) was dispersed in absolute ethanol (10 ml) and heated to boiling on an oil bath. Subsequently phenyl hydrazine (10 mmol) was added dropwise to the boiling solution with constant stirring. Evolution of hydrogen sulphide occurred. Reaction was continued for 1 hour to obtain a clear orange liquid, which was then cooled in an ice bath to afford a pale yellow solid. The solid was separated by filtration and washed with cold ethanol to obtain B as yellow crystals. Yield 30 %. FT-IR (KBr pellet, 400–4000 cm<sup>-1</sup>): 3372 (s), 3205 (m), 3099 (w), 3052 (w), 3021 (w), 2943 (w), 2646 (w), 2570 (w), 2338 (w), 1984 (w), 1926 (w), 1884 (w), 1773 (w), 1708(w), 1602 (m), 1581(w), 1485 (m), 1432 (m), 1408 (w), 1324 (s), 1245 (s), 1162 (s), 1104 (s), 1063 (s), 996 (m), 885 (m), 826 (s), 784 (s), 744 (s), 694 (s), 659(w), 695 (w), 587 (s), 488(s). Elem. Anal. Calcd (%): C, 64.04; H, 4.24; N, 15.72. Found (%): C, 63.95; H, 4.29; N, 15.68. LR-LCMS: m/z (%): 356.20 [M]<sup>+</sup> (100%), 357.13 [M+H]<sup>+</sup> (20%), 358.22 [M+2]<sup>+</sup> (5%).

# Preparation of 1-phenyl-3-(pyridin-2-yl)-7-(trifluoromethyl)-1,4-dihydrobenzo[e][1,2,4]triazine (Rad<sub>2</sub>)

A slightly modified version of the literature procedure was employed. B (435 mg, 1.22 mmol) was dissolved in dichloromethane (20 ml) followed by addition of 1,8diazabicycloundec-7-ene (230 mg, 1.53 mmol) and 10% Pd/C (20 mg). The reaction mixture was stirred at room until thin layer chromatography temperature (1:4 hexane:dichloromethane) showed the absence of starting material and the presence of a new fast-running dark compound. The reaction contents were filtered through a celite bed and solvents were evaporated under reduced pressure and the residue purified by flash chromatography (dichloromethane) followed by recrystallization from a hexane:dichloromethane mixture at -30 °C to afford brown needle-shaped crystals of Rad<sub>2</sub>. Yield: 220 mg (51 %), m.p.150 °C. FT-IR (KBr pellet, 400–4000 cm<sup>-1</sup>): 3061 (m), 2924 (w), 1743 (w), 1651 (m), 1590 (s), 1520 (m), 1486 (s), 1416 (s), 1366 (w), 1322 (s), 1276 (w), 1166 (s), 1102 (s), 1069(m), 1032 (w), 997 (w), 902 (m), 874 (m), 806 (w), 788 (w), 753 (m), 787 (s), 695 (m), 640 (m), 497 (w), 454 (w). Elem. Anal. Calcd (%): C, 64.59; H, 3.42; N, 15.86. Found (%): C, 63.67; H, 3.47; N, 15.81. LR-LCMS: m/z (%): 353.20 [M]<sup>+</sup> (40%), 354.10 [M+H]<sup>+</sup> (100%), 355.10 [M+2]<sup>+</sup> (30%).

# Preparation of $M(hfac)_2(Rad_2)$ (M= Zn(II) (1), Ni(II) (2) and Co(II) (3)

In a typical synthesis, a solution of benzotriazinyl radical  $Rad_2$  (5.30 mg, 0.015 mmol) in dichloromethane (10 mL) was slowly added to an equimolar solution of  $Zn(hfac)_2 \cdot 2H_2O$  (7.7 mg, 0.015 mmol) in dichloromethane (10 mL). An immediate color

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change was observed from brown to purple and the reaction mixture was stirred at room temperature for 1 h. The corresponding complex was obtained as purple powder by evaporation and was recrystallized by slow diffusion of pentane into a chloroform solution to yield large crystals of  $Zn(hfac)_2(Rad_2)$ .

The preparation of **2** and **3** followed a similar procedure using M(hfac)<sub>2</sub>·xH<sub>2</sub>O, assuming x ~ 0 based on Karl-Fischer titration (x < 2%); quantities implemented: Co(hfac)<sub>2</sub> (0.015 mmol, 7.1 mg) and Ni(hfac)<sub>2</sub> (0.015 mmol, 7.1 mg).

Zn(hfac)<sub>2</sub>(**Rad**<sub>2</sub>) (**1**). Purple crystals, Yield: 32%; FT-IR (KBr pellet, 400–4000 cm<sup>-1</sup>): 1657 (s), 1649 (s), 1614 (w), 1599 (w), 1570 (m), 1560 (m), 1529 (m), 1485 (s), 1429 (w), 1417 (w), 1392 (w), 1342 (w), 1324 (w), 1284 (w), 1261 (s), 1209 (s), 1147 (s), 1094 (w), 1074 (w), 1051 (w), 1022 (w), 999 (w), 950 (w), 908 (w), 894 (w), 842 (w), 796 (m), 760 (m), 751 (m), 742 (w), 736 (w), 691 (w), 668 (m), 651 (w), 636 (w), 622 (w), 585 (m), 526 (w), 508 (w). Elem. Anal. Calcd (%) for  $C_{29}H_{14}F_{15}N_4O_4Zn$ : C, 41.82; H, 1.69; N, 6.73. Found (%): C, 41.78; H, 1.73; N, 6.79.

Ni(hfac)<sub>2</sub>(**Rad**<sub>2</sub>) (**2**). Purple crystals, Yield: 28%; FT-IR (KBr pellet, 400–4000 cm<sup>-1</sup>): 1651 (s), 1641 (s), 1601 (w), 1593 (w), 1568 (m), 1554 (m), 1525 (m), 1489(s), 1427 (w), 1417 (w), 1395 (w) 1344 (w), 1319 (w), 1286 (w), 1254 (s), 1214 (s), 1153 (s), 1099 (w), 1077 (w), 1042 (w), 1030 (w), 990 (w), 943 (w), 911 (w), 896 (w), 846 (w), 799 (m), 763 (m), 752 (m), 745 (w), 737 (w), 687(w), 669 (m), 651 (w), 636 (w), 626 (w), 589 (m), 528 (w), 510 (w). Anal. Calcd (%) for  $C_{29}H_{14}F_{15}N_4O_4Ni: C, 42.16; H, 1.71; N, 6.78.$  Found (%): C, 42.12; H, 1.68; N, 6.82.

Co(hfac)<sub>2</sub>(**Rad**<sub>2</sub>) (**3**). Purple crystals, Yield: 35%; FT-IR (KBr pellet, 400–4000 cm<sup>-1</sup>): 1651 (s), 1639 (s), 1588 (w), 1570 (m), 1553 (m), 1528 (w), 1505 (m), 1487 (s), 1455 (m), 1491 (s), 1362 (m), 1339 (w), 1321(w) 1286 (m), 1258 (s), 1206 (s), 1158 (m), 1146 (s), 1102 (w), 1074 (w), 1059 (w), 1025(w), 998 (w), 947 (w), 909 (w), 895 (w), 842 (w), 799 (m), 763 (w), 750 (m), 737 (w), 686 (w), 664 (m), 653 (w), 638 (w), 624 (w), 586 (m), 530 (w), 510 (w). Anal. Calcd (%) for  $C_{29}H_{14}F_{15}N_4O_4Co: C, 42.15;$  H, 1.71; N, 6.78. Found (%): C, 42.10; H, 1.77; N, 6.76.

# X-ray crystallography

Intensity data were collected on a Bruker APEX-II CCD diffractometer using a graphite monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Integration and scaling of intensity data were accomplished using the program SAINT<sup>37</sup> and absorption corrections were applied by multi-scan method implemented in SADABS.<sup>38</sup> Olex2<sup>39</sup> was used as the graphical interface and the structures were solved with the ShelXT<sup>40</sup> structure solution program using intrinsic phasing. The models were refined with ShelXL<sup>40</sup> with full matrix least squares minimisation on  $F^2$ . All non-hydrogen atoms were refined anisotropically. The dataset of complex Zn(hfac)<sub>2</sub>(**Rad**<sub>2</sub>) (**1**) was twinned with a minor twinning component of 0.128(2). The hklf5 file against which this structure was refined was obtained by using TwinRotMat followed by hklf5 generate which are

available from PLATON.<sup>41</sup> Moreover, in the  $V_{iev}$  Complexes  $M(hfac)_2(Rad_2)$  (1-3) there are minor disorder  $M/SOMP^{12}CF_3$  groups which was treated using standard techniques. Complete lists of the applied restraints, the original diffraction file as well as the model itself are embedded in the deposited CIF files. Crystallographic data and refinement details for  $Rad_2$  and complexes  $M(hfac)_2(Rad_2)$  have been summerized in Table S1 (Supporting Information).

# Conflicts of interest

There are no conflicts to declare.

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A new benzotriazinyl radical, 1-phenyl-3-(pyridin-2-yl)-7-(trifluoromethyl)-1,4-dihydrobenzo[e][1,2,4]triazine ( $Rad_2$ ) and three isomorphous metal complexes of general formula M(hfac)<sub>2</sub>( $Rad_2$ ) (where M= Zn(II) (1), Ni(II) (2) and Co(II) (3); hfac<sup>-</sup> = hexafluoroacetylacetonate) have been isolated as stable crystalline solids and fully characterized, including by single crystal X-ray diffraction. The Zn(II) complex allows unambiguous determination of the radical<sup>--</sup>radical magnetic exchange coupling (antiferromagnetic), whereas both the Ni(II) and Co(II) complexes afforded ferromagnetic metal-radical exchange coupling.