

# Metal–nitron complexes: spin trapping and solution characterization †

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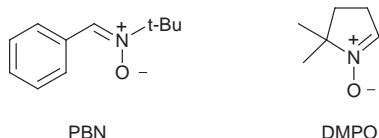
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Complexes of Cu<sup>II</sup>, Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup> and Fe<sup>II</sup> hexafluoroacetylacetonates (hfac) with spin trapping nitrones, the bidentate *N-tert-butyl-α-(2-pyridyl)nitron* (2-PyBN) and the monodentate 2,5,5-trimethyl-1-pyrroline-*N*-oxide (M<sub>3</sub>PO), were studied by NMR, conductivity and vapor pressure osmometry (VPO). Complexes with the bidentate 2-PyBN exist predominantly as neutral monomers in CH<sub>2</sub>Cl<sub>2</sub>, though their crystalline forms are neutral M(2-PyBN)(hfac)<sub>2</sub> for Cu **1** and ionic [M(2-PyBN)<sub>2</sub>hfac][M(hfac)<sub>3</sub>] for Mn **2**, Co **3**, Ni **4** or Fe **5**. Complexes of the monodentate M<sub>3</sub>PO, dimeric [M(M<sub>3</sub>PO)(hfac)<sub>2</sub>]<sub>2</sub> in the solid state for M = Mn **6**, Co **7** and Ni **8**, exist in CH<sub>2</sub>Cl<sub>2</sub> as a dimer for **6** and an equilibrium mixture of monomers and dimers for **7** and **8**. In the presence of phenyl radicals, generated by irradiation of phenylazotriphenylmethane, **2** and **4** gave spin adducts whose EPR spectra were the same as the metal nitroxide (aminoxyl) complexes prepared independently as crystalline materials. These EPR spectra were also the same as those taken from a typical nitron spin trapping experiment carried out in the presence of Mn<sup>II</sup> or Ni<sup>II</sup> metal ions, thereby showing the importance of the present study in interpreting EPR spectra of spin adducts in metal-containing systems. Spin trapping by **6** gave EPR spectra consistent with formation of Mn(hfac)<sub>2</sub> and Mn(aminoxyl)<sub>2</sub>(hfac)<sub>2</sub>. The nature of the metal ion–nitroxide interactions in these spin adducts and other metal nitroxides was investigated by measuring magnetic moment values in solution by NMR methods.

## Introduction

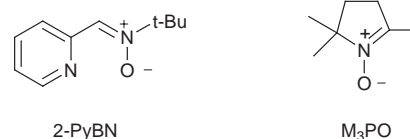
Nitrones are known to trap radicals forming relatively stable nitroxides (aminoxyls) whose EPR spectra can be used for radical characterization. Nitrones such as *N*-(benzylidene)-*tert*-butylamine *N*-oxide [*α*-phenyl-*N-tert*-butylnitron (PBN)] and 5,5-dimethyl-3,4-dihydropyrrole *N*-oxide (DMPO) are among the most commonly used spin traps including detection of reactive radicals in biological systems.<sup>1</sup> Both organic<sup>2,3</sup> and inorganic<sup>4,5</sup> radicals have been trapped by nitrones.



In some studies, the role of metals in the presence of spin traps has at least been mentioned. For example, the presence of Fe<sup>II</sup> in Fenton-type reactions has been found to be crucial in the generation of hydroxyl radicals in biological spin trapping applications.<sup>6,7</sup> An induced nucleophilic attack by water on DMPO in the presence of Fe<sup>III</sup><sup>8</sup> or Cu<sup>II</sup><sup>9</sup> to form a DMPO–OH spin adduct was attributed<sup>8</sup> to coordination of the metal to DMPO. A different mechanism was reported<sup>10</sup> for Ti<sup>IV</sup> in which formation of the DMPO–OH spin adduct involves participation of dissolved oxygen. Recently, a biologically relevant oxidation process involving reaction of Cr<sup>V</sup> with DMPO and PBN was reported.<sup>11</sup> Formation of the hydroxyl radical adduct of DMPO at pH 7.4 results from a direct oxidative mechanism, while product analysis of the reaction of Cr<sup>V</sup> with PBN revealed cleavage of the imine moiety of the nitron to form benzaldehyde.

Despite the fact that many spin trapping applications occur in the presence of metal ions, the effect of metals on this process

has not been systematically studied. For this reason we recently synthesized and characterized several complexes of metal hexafluoroacetylacetonates M(hfac)<sub>2</sub> with representative spin trapping nitrones, the bidentate *N*-(2-pyridylmethylene)-*tert*-butylamine *N*-oxide [*N-tert*-butyl-*α*-(2-pyridyl)nitron (2-PyBN)] and the monodentate 2,5,5-trimethyl-3,4-dihydropyrrole *N*-oxide (M<sub>3</sub>PO). These nitrones were chosen to provide less labile complexes thereby simplifying interpretation of spin trapping results. In all cases, CH<sub>2</sub>Cl<sub>2</sub> solutions of neutral M(hfac)<sub>2</sub> and the nitron were mixed. However, the crystals which separated showed a range of bonding types from crystal structure determinations: a molecular complex M(2-PyBN)(hfac)<sub>2</sub> for M<sup>II</sup> = Cu **1**, crystalline salts [M(2-PyBN)<sub>2</sub>hfac][M(hfac)<sub>3</sub>] for M<sup>II</sup> = Mn **2**, Co **3**, Ni **4** or Fe **5**, and oxygen bridged dimers [M(M<sub>3</sub>PO)(hfac)<sub>2</sub>]<sub>2</sub> for M<sup>II</sup> = Mn **6**, Co **7** and Ni **8**.<sup>12</sup>



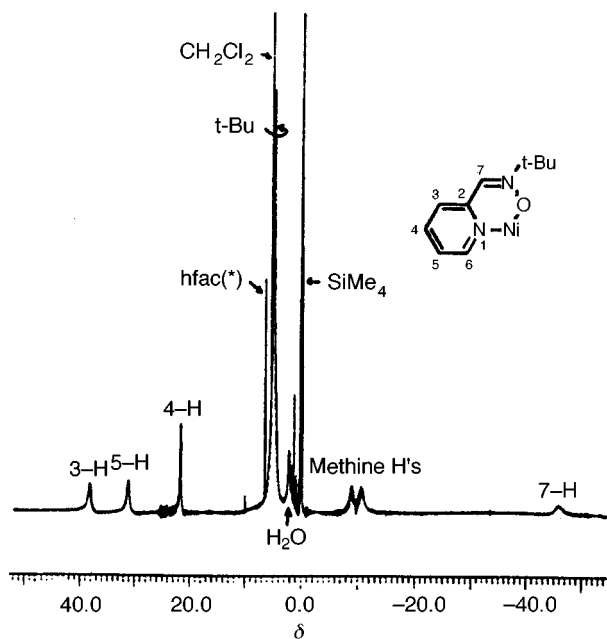
We now report our results with these metal complexes as spin traps for phenyl radicals provided by irradiation of phenylazotriphenylmethane (PAT). Although there is considerable literature on metal–nitroxide (aminoxyl) complexes,<sup>13,14</sup> to our knowledge there are no spin-trapping studies done on nitrones bound to metals. Various techniques, such as conductivity, vapor pressure osmometry (VPO), <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy, were employed to determine the forms of these metal–nitron complexes in solution.

## Results and discussion

### Spectroscopy of 2-PyBN complexes

<sup>1</sup>H NMR spectra for **1** and **2** show a broad peak at *ca.* δ 4.3 assigned to *N*-Bu<sup>†</sup> near a paramagnetic center. With increasing

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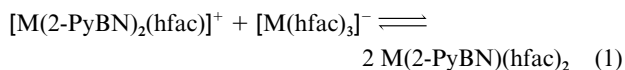
**Fig. 1**  $^1\text{H}$  NMR of  $\text{Ni}(2\text{-PyBN})(\text{hfac})_2$  in  $\text{CD}_2\text{Cl}_2$ . The sharp peak at  $\delta$  6.45 is due to free protonated hfac. The reported  $^1\text{H}$  NMR chemical shift of CH in  $\text{CF}_3\text{C}(\text{OH})\text{CHC}(\text{O})\text{CF}_3$  is  $\delta$  6.42 (s) in  $\text{CD}_2\text{Cl}_2$ .<sup>22</sup>

excess of 2-PyBN no new peak is observed, but the broad *N*-Bu<sup>t</sup> peak moves toward the chemical shift of *N*-Bu<sup>t</sup> of free 2-PyBN, thereby indicating fast exchange between complexed and free 2-PyBN for these complexes. However, the spectra for **3** and **4** remain unperturbed even in the presence of a large excess of 2-PyBN, demonstrating slow chemical exchange on the NMR time scale for the Co and Ni complexes.

$^1\text{H}$  NMR spectra of **3** and **4** show isotropic shifts for 2-PyBN hydrogens in  $\text{CDCl}_3$  and  $\text{CD}_2\text{Cl}_2$  as can be seen in Fig. 1 for the case of **4**. The large downfield shifts of pyridyl H's for both complexes are indicative of  $\sigma$  spin delocalization<sup>15,16</sup> and consistent with  $\text{Ni}^{\text{II}}$  induced proton contact shifts as reported for a variety of amines.<sup>17,18</sup> However, the upfield shift of iminyl H's (7-H) for both complexes indicates some  $\pi$  spin delocalization. VIS and NIR spectra of each of the complexes in  $\text{CH}_2\text{Cl}_2$  gave absorption bands consistent with octahedral geometry around the metal ions.<sup>12</sup>

#### Predominant form of 2-PyBN complexes in solution

The possibility that the ionic form of the complex is in equilibrium with the neutral form in solution was considered [eqn. (1)], since complex salts crystallized from  $\text{CH}_2\text{Cl}_2$  solutions of



the neutral  $\text{M}(\text{hfac})_2$  and 2-PyBN for **2–5**. Comparison of IR spectra of the complexes in the solid state and in solution was not helpful, since there are only insignificant differences in absorbance maxima in Nujol mulls, KBr and  $\text{CH}_2\text{Cl}_2$  solution. Also, the IR spectrum of **1** in the solid state is similar in profile to those of complex salts so that positions of absorbances cannot be used to distinguish these two types of complexes. In an attempt to displace postulated equilibrium (1) for the Co system,  $\text{Na}[\text{Co}(\text{hfac})_3]$  was added to a solution of **3** in  $\text{CDCl}_3$  containing 18-crown-6. However, for molar ratios of 1:0.5, 1:1 and 1:2 ( $\text{Na}[\text{Co}(\text{hfac})_3]$ – $[\text{Co}(2\text{-PyBN})_2(\text{hfac})][\text{Co}(\text{hfac})_3]$ ) only negligible (<0.1 ppm) perturbations in  $^1\text{H}$  NMR chemical shifts were observed for the coordinated 2-PyBN and hfac.

Conductivity measurements in 1,2-dichloroethane indicate that these complexes have a substantial amount of a covalent

**Table 1** Molar conductances<sup>a</sup>  $\Lambda$  of nitron complexes and model compounds in 1,2-dichloroethane at 24 °C for various concentrations (M)

$\text{Cu}(2\text{-PyBN})(\text{hfac})_2$ and $[\text{M}(2\text{-PyBN})_2(\text{hfac})][\text{M}(\text{hfac})_3]$					
$\text{M} \times 10^4$	<b>1</b> (Cu)	<b>2</b> (Mn)	<b>3</b> (Co)	<b>4</b> (Ni)	<b>5</b> (Fe)
15.00	0.52	1.99	2.25	2.91	1.59
10.00	0.52	2.13	2.22	3.08	1.62
7.50	0.50	2.13	2.32	3.19	1.57
5.00	0.55	2.22	2.37	3.40	1.62
$[\text{M}(\text{M}_3\text{PO})(\text{hfac})_2]_2$					
$\text{M} \times 10^4$	<b>6</b> (Mn)	<b>7</b> (Co)	<b>8</b> (Ni)		
14.60	0.47	0.79	0.71		
9.76	0.53	0.88	0.88		
7.32	0.58	0.93	0.99		
4.88	0.66	1.03	1.18		
Model Compounds					
$\text{M} \times 10^4$	$\text{Cu}(\text{hfac})_2$	$\text{Bu}_4\text{NClO}_4$	<b>9</b>		
19.50	—	—	17.85		
15.00	0.02	21.31	22.47		
10.00	0.04	23.90	25.10		
7.50	0.03	26.73	26.93		
5.00	0.03	29.47	29.60		

<sup>a</sup> In  $\text{S cm}^2 \text{mol}^{-1}$ .

**Table 2** Molecular weights of metal nitron complexes by vapor pressure osmometry

Metal complexes	Molecular weight ( $\text{g mol}^{-1}$ )		
	Calc. for monomer	Obsd. by VPO <sup>a</sup>	Calc. for dimer
$[\text{M}(2\text{-PyBN})(\text{hfac})_2]$			
<b>1</b> (Cu)	655	647(0) <sup>d</sup>	1310
<b>2</b> (Mn)	647	642(7)	1294
<b>3</b> (Co)	652	708(26)	1303
<b>4</b> (Ni)	651	688(3)	1302
<b>5</b> (Fe)	648	673(11)	1296
$[\text{M}(\text{M}_3\text{PO})(\text{hfac})_2]_2$			
<b>6</b> (Mn)	597	1189(45)	1193
<b>7</b> (Co) <sup>b</sup>	600	826(7)	1200
<b>8</b> (Ni)	600	915(6)	1200
$\text{Mn}(\text{TEMPO})_2(\text{hfac})_2$ <sup>c</sup>	625	583(26)	1250

<sup>a</sup> As  $\text{CH}_2\text{Cl}_2$  solutions. <sup>b</sup> As MeCN solution. <sup>c</sup> TEMPO = 2,2,5,5-tetra-methylpiperidine-*N*-oxyl. <sup>d</sup> Error limits are in parentheses.

form in that solvent. Molar conductance values are shown in Table 1 for **1–8**, as well as for  $\text{Cu}(\text{hfac})_2$  and  $\text{Bu}_4\text{NClO}_4$  which served as model compounds for a neutral complex and salt, respectively. Values for all nitron complexes are similar, despite the fact that **2–5** are ionic in the solid state, while **1** and **6–8** are neutral. The fact that these  $\Lambda$  values are intermediate to  $\text{Bu}_4\text{NClO}_4$  and  $\text{Cu}(\text{hfac})_2$  suggests that some ionic and neutral forms are present in 1,2-dichloroethane, as represented by eqn. (1) for **2–5**. The possibility that all nitron complexes exist as ions in 1,2-dichloroethane but have lower  $\Lambda$  than  $\text{Bu}_4\text{NClO}_4$  due to ion-pairing was examined by measuring  $\Lambda$  of  $[\text{Co}(\text{bipy})(\text{acac})_2][\text{Co}(\text{NO}_2)_2(\text{acac})_2]$  **9**. This salt was chosen because of its similarity in size to complex salt **3** and inertness of  $\text{Co}^{\text{III}}$  to ligand exchange which would rule out formation of neutral species. However,  $\Lambda$  for **9**, in general agreement with  $\Lambda_0$  reported for other complex salts,<sup>19–21</sup> was similar to that for  $\text{Bu}_4\text{NClO}_4$  (see Table 1). It is therefore unlikely that lower  $\Lambda$  values for nitron complexes are due to extensive ion pairing, relative to the model compounds.

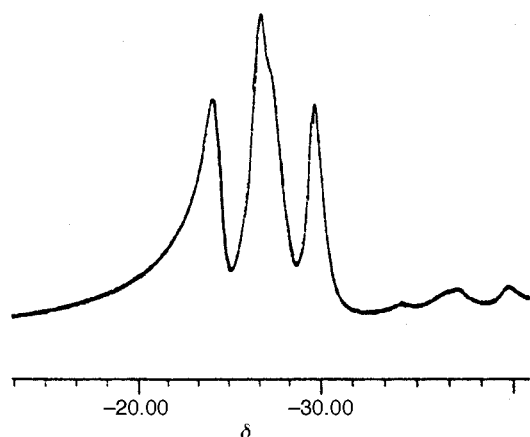
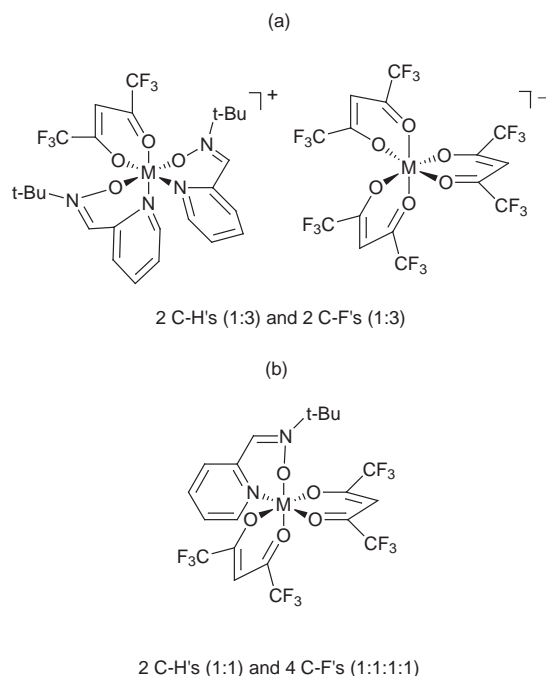


Fig. 2  $^{19}\text{F}$  NMR of  $\text{Ni}(2\text{-PyBN})(\text{hfac})_2$  in  $\text{CD}_2\text{Cl}_2$  relative to  $\text{CFCl}_3$ .

In more conclusive experiments, molecular weight determinations by VPO showed that **1–5** exist predominantly as monomers in  $\text{CH}_2\text{Cl}_2$ . As shown in Table 2, observed molecular weights were within 10% of values calculated for the neutral complex. Slightly higher values for **3–5** may indicate the presence of small amounts of complex salts consistent with *A* studies.

In the case of **4** NMR spectra prove that this complex exists as the neutral monomeric form in  $\text{CH}_2\text{Cl}_2$ . The  $^1\text{H}$  NMR spectrum of the ionic form of **4** should show 1 hfac H and 2 equivalent sets of pyridyl H's for  $[\text{M}(2\text{-PyBN})_2(\text{hfac})]^+$  and 3 equivalent hfac H's for  $[\text{M}(\text{hfac})_3]^-$  (see Scheme 1a). Instead,



Scheme 1 Predicted  $^1\text{H}$  and  $^{19}\text{F}$  NMR resonances for hfac ligands in (a) complex salt and (b) neutral monomer forms.

only 1 equivalent set of pyridyl H's and 2 hfac H's were evident as shown in Fig. 1 for **4**, consistent with the monomeric form (Scheme 1b). Also, the  $^{19}\text{F}$  NMR spectrum of **4** in  $\text{CD}_2\text{Cl}_2$  has an apparent triplet at  $\delta$   $-20$  to  $-32$  which is actually 4 broad signals (peak width *ca.* 1 ppm) of equal integrations with two overlapping peaks in the center (see Fig. 2). This result is in agreement with only the monomeric form, since the ionic form would have given only two signals with integrations of 1:3 (Scheme 1a). For other complexes NMR results were not conclusive. The relaxation time for Mn is so short that only broad signals were observed for **2**. Both complexes **3** and **5** gave one

Table 3 Magnetic moments of various metal–nitron complexes by NMR<sup>a</sup>

Complex (monomeric form)	Monomer $\mu_B^b$ per metal	Dimer $\mu_B^c$ per 2 metals
<b>1</b>	1.77(1)	
<b>2</b>	5.87(0)	8.31(0)
<b>3</b>	4.60(5)	6.50(7)
<b>4</b>	2.98(7)	4.2(1)
<b>5</b>	5.10(3)	7.22(4)
<b>6</b>	5.75(6)	8.13(8)
<b>7</b>	4.61(2)	6.52(3)
<b>8</b>	2.88(3)	4.08(4)
<b>10</b>	2.2(3)	
<b>11</b>	4.9(1)	
<b>12</b>	3.6(1)	
<b>13</b>	1.92(3) <sup>d</sup>	
$\text{Cr}(\text{acac})_3$	3.75 <sup>e</sup>	

<sup>a</sup> In  $\text{CH}_2\text{Cl}_2$  at ambient temperature. <sup>b</sup> Assuming that the weighed sample is monomeric. <sup>c</sup> Assuming that the weighed sample is dimeric. <sup>d</sup> In benzene. <sup>e</sup> Lit.,<sup>23</sup> value 3.7 in  $\text{CHCl}_3$ .

broad peak for hfac hydrogens which may be due to overlapping signals and therefore not useful to distinguish molecular and complex salt forms.

### Solution properties of $\text{M}-\text{M}_3\text{PO}$ complexes

VPO gave an experimental molecular weight of 1189(45)  $\text{g mol}^{-1}$  for **6** in  $\text{CH}_2\text{Cl}_2$  which agrees with a calculated value of 1193  $\text{g mol}^{-1}$  for a dimer (see Table 2). Such a result is not surprising, since nitronyl oxygen bridged dimers in the solid state were reported<sup>12</sup> for **6–8**. However, for **7** and **8**, observed molecular weights of 826(7)  $\text{g mol}^{-1}$  and 915(6)  $\text{g mol}^{-1}$ , respectively, were lower than expected for a dimeric form (1200  $\text{g mol}^{-1}$  both). These lower molecular weights may be due to dissociation of ligands in solution.

VIS and NIR spectra of **7** and **8** in  $\text{CH}_2\text{Cl}_2$  gave absorption peaks indicating octahedral geometry around metal atoms.<sup>12</sup> These  $\lambda_{\text{max}}$  are similar to those found in spectra of 1:1 complexes of the monodentate *N*-( $\alpha$ -methylbenzylidene)methylamine *N*-oxide ( $\alpha$ -phenyl- $\alpha$ ,*N*-dimethylnitron) with  $\text{Co}(\text{acac})_2$  and  $\text{Ni}(\text{acac})_2$ .<sup>15</sup> It therefore seems likely that these reported complexes may also be dimeric octahedral complexes rather than monomeric pentacoordinated ones.

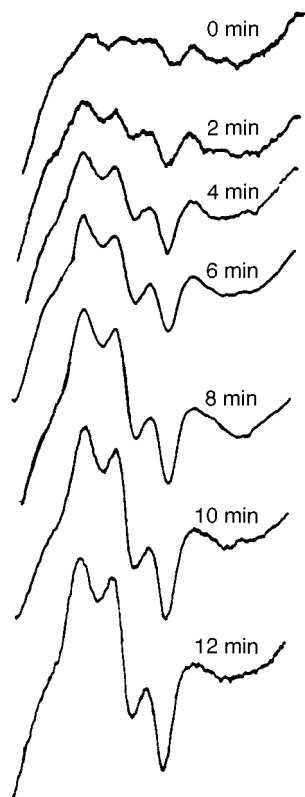
### EPR and magnetic moments of metal–nitron complexes

EPR spectra of **1–8** in  $\text{CH}_2\text{Cl}_2$ –toluene were taken prior to radical generation to characterize the behavior of the metal nitron complexes themselves. At 115 K, complex **1** gave  $g_{\parallel} = 2.335$ ,  $A_{\parallel} = 140$  G,  $g_{\perp} = 2.072$  for  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  ( $I = 3/2$ ), while **2** showed a characteristic 6-line spectrum with  $g_{\text{central}} = 2.004$ ,  $A_{\text{ave. ca.}} 100$  G for  $^{55}\text{Mn}$  ( $I = 5/2$ ). However, no EPR signals were observed for **3**, **4** or **5** either at room temperature or as frozen solutions. For  $\text{M}_3\text{PO}$  complexes, **6** gave a broad signal at 115 K centered around  $g = 2.004$ , but no signals were observed under the same conditions for **7** and **8**.

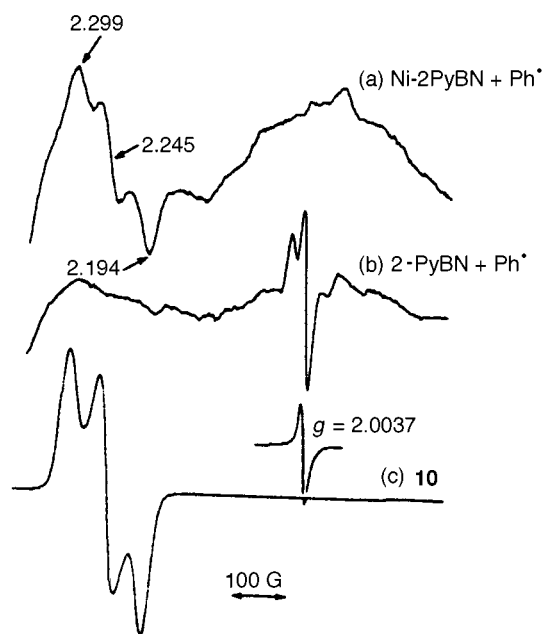
Magnetic moments for **1–8** were calculated from NMR shifts of  $\text{CH}_2\text{Cl}_2$  at room temperature and are given in Table 3. The first column results from assuming a monomeric complex, with the last assuming a dimer. These values are consistent with high spin ground state systems for all complexes using the spin only formula  $\mu = 2[S(S + 1)]^{1/2}$ .

### Spin trapping

Phenyl radicals generated from PAT by irradiation in  $\text{CH}_2\text{Cl}_2$  at room temperature were trapped by 2-PyBN and  $\text{M}_3\text{PO}$  to give the expected spin adducts. EPR spectra at room temperature showed signals which grew rapidly during irradiation with the



**Fig. 3** X-Band EPR spectra (115 K) in 80:20  $\text{CH}_2\text{Cl}_2$ -toluene glass of 30 mM  $\text{Ni}(2\text{-PyBN})(\text{hfac})_2$  with 20 mM PAT during 12 min of irradiation. Spectrometer settings: microwave frequency, 9.01 GHz; microwave power, 10 mW; modulation frequency, 100 KHz; modulation amplitude, 4 G.

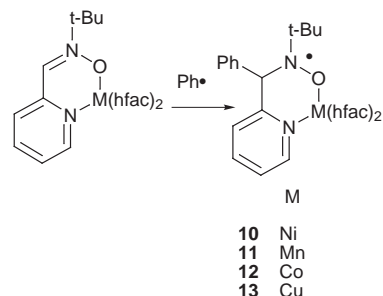


**Fig. 4** X-Band EPR spectra (115 K) in 80:20  $\text{CH}_2\text{Cl}_2$ -toluene glass: (a) 30 mM  $\text{Ni}(2\text{-PyBN})(\text{hfac})_2$  with 10 mM PAT after 15 min of irradiation; (b) 30 mM 2-PyBN with 10 mM PAT after 15 min of irradiation; (c) ca. 3.0 mM independently prepared Ni-nitroxide **10**. Spectrometer settings: microwave frequency, 9.01 GHz; microwave power, 10 mW; modulation frequency, 100 KHz; modulation amplitude, 4 G.

following  $g$  and hyperfine splitting constant values:  $g = 2.008$ ,  $A_N = 14.94$  G,  $A_H = 2.74$  G for the spin adduct of 2-PyBN and  $g = 2.006$ ,  $A_N = 14.32$  G for that of  $\text{M}_3\text{PO}$ .

**By complexes of bidentate 2-PyBN.** When  $\text{Ni}(2\text{-PyBN})(\text{hfac})_2$  was subjected to spin trapping conditions (irradiation in the

presence of PAT), a relatively rapid growth of peaks was observed (see Fig. 3). The new spectrum (Fig. 4a), with rhombic  $g$ -tensors at  $g_1 = 2.299(0)$ ,  $g_2 = 2.245(3)$  and  $g_3 = 2.194(0)$ , is different from the spin adduct of uncomplexed 2-PyBN (Fig. 4b) and cannot be due to the combinations  $\text{Ni}(\text{hfac})_2/\text{PAT}/\text{h}\nu$  (no signals) or  $\text{Ni}(2\text{-PyBN})(\text{hfac})_2/\text{h}\nu$  (no signals) as shown by blank experiments with different reaction components. The spectrum can be explained by formation of spin adduct **10** as indicated in Scheme 2.



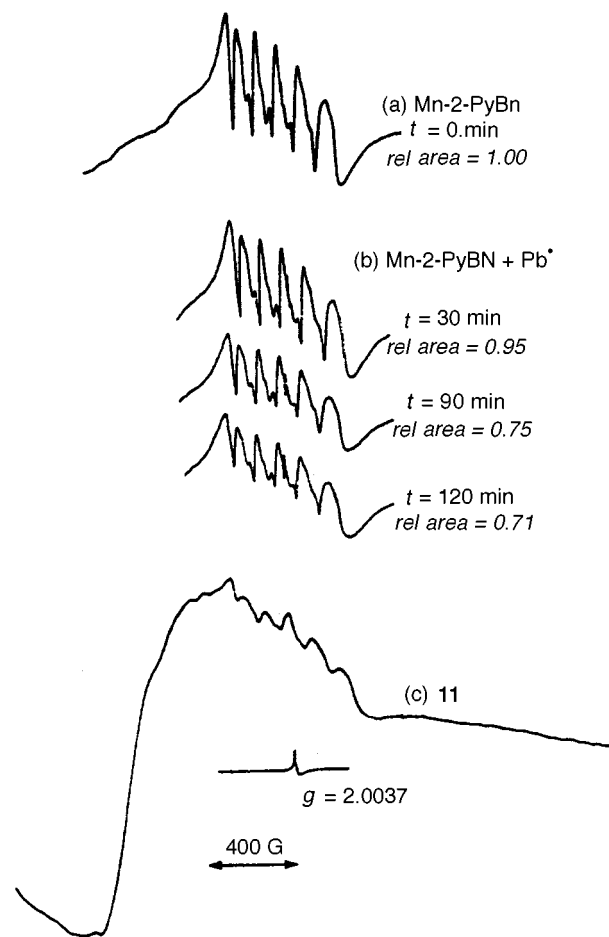
**Scheme 2** Formation of spin adducts from a metal-nitron complex.

To confirm this assignment, metal nitroxide **10** was prepared independently by addition of  $\text{Ni}(\text{hfac})_2$  to the nitroxide freshly prepared by oxidation of the hydroxylamine with  $\text{Ag}_2\text{O}$ .<sup>24</sup> The crystal structure of **10** revealed an octahedral 1:1 complex having the nitroxide as a bidentate ligand.<sup>24</sup> An interesting point concerns the oxidation state of Ni in this complex, as one could imagine this as  $\text{Ni}^{\text{III}}$  complexed to a negatively-charged hydroxyaminato ligand *via* electron transfer from  $\text{Ni}^{\text{II}}$  to the nitroxide. However, the crystal structure shows clearly that the ligand is a nitroxide by characteristic bond lengths and the planar geometry about the nitronyl nitrogen. The EPR spectrum of this independently prepared **10** (Fig. 4c) was the same as that obtained from the spin trapping reaction (Fig. 4a).

The frozen solution spectrum of Fig. 4c agrees with an  $S = 1/2$  system. If the coupling between  $\text{Ni}^{\text{II}}$  ( $S = 1$ ) and the radical in **10** is antiferromagnetic, the ground state must be  $S = 1/2$ . The  $g$  values of the pair are expected to be given by  $g = 4/3g_{\text{Ni}} - 1/3g_{\text{rad}}$ .<sup>25</sup> Using these equations for each observed  $g$  and  $g_{\text{rad}} = 2.00$ , the  $g_{\text{Ni}}$  values are calculated as  $g_{1,\text{Ni}} = 2.22$ ,  $g_{2,\text{Ni}} = 2.19$  and  $g_{3,\text{Ni}} = 2.15$  in agreement with the  $g$  values expected for octahedral  $\text{Ni}^{\text{II}}$ . Consistent with antiferromagnetic coupling is a lower  $\mu_B$  for **10** compared to  $\text{Ni}(2\text{-PyBN})(\text{hfac})_2$  (2.2 vs. 2.98 from Table 3).

The present results are in agreement with extensive studies by Gatteschi and co-workers who found that  $\text{Ni}^{\text{II}}$ -nitroxide spin interactions are generally antiferromagnetic in nature.<sup>13</sup> For example, the closely related  $\text{Ni}(\text{NIT2-Py})(\text{hfac})_2$  where NIT2-Py is 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl 3-oxide, has a Kramers' doublet ground state, giving principal  $g$ -values of  $g = 2.17$  and 2.20.<sup>26</sup> The reported EPR spectrum is similar to that observed for the present  $\text{Ni}(2\text{-PyBN})$  spin adduct. In addition, the reported<sup>26</sup> magnetic moment for solid  $\text{Ni}(\text{NIT2-Py})(\text{hfac})_2$  is consistent with  $S = 1/2$  at room temperature.

When  $\text{Mn}(2\text{-PyBN})(\text{hfac})_2$  as a 1 mM solution was irradiated in the presence of 4.6 mM PAT, EPR signals due to  $\text{Mn}(2\text{-PyBN})(\text{hfac})_2$  decrease as shown in Fig. 5b. The decrease in intensities is relatively much faster than for irradiation of  $\text{Mn}(2\text{-PyBN})(\text{hfac})_2$  alone or  $\text{Mn}(\text{hfac})_2/\text{PAT}/\text{h}\nu$  at the same concentrations. This result can be taken as evidence for the formation of metal-nitroxide spin adduct **11**, since the Mn nitroxide prepared independently gave the same diminished spectrum (Fig. 5c). The crystal structure of **11** also showed this is to be an octahedral 1:1 complex with a planar geometry around the nitronyl nitrogen<sup>24</sup> again demonstrating a  $\text{M}^{\text{II}}$ -nitroxide complex.

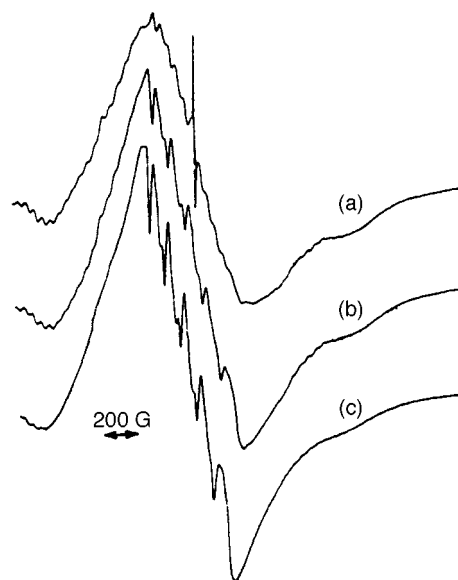


**Fig. 5** X-Band EPR spectra (115 K) in 80:20  $\text{CH}_2\text{Cl}_2$ -toluene glass: (a) 1 mM  $\text{Mn}(2\text{-PyBN})(\text{hfac})_2$  before irradiation (relative gain = 250); (b) 1 mM  $\text{Mn}(2\text{-PyBN})(\text{hfac})_2$  with 4.6 mM PAT during 2 h of irradiation; (c) ca. 0.05 mM independently prepared Mn-nitroxide **11**. Spectrometer settings: microwave frequency, 9.01 GHz; microwave power, 10 mW; modulation frequency, 100 KHz; modulation amplitude, 4 G. (The broad feature at the lower field is due to the background signal which can be observed in other spectra with low sample concentration.)

The EPR spectrum of **11** can also be interpreted in terms of antiferromagnetic coupling. In this case, however, such coupling of  $\text{Mn}(d^5)$  electrons with the nitroxide electron leads to  $S = 2$ , and EPR transitions for systems with an even number of unpaired electrons are generally not observed in this region of the microwave. Confirmation of an antiferromagnetic interaction between Mn and nitroxide unpaired electrons is indicated by the lower  $\mu_B$  for **11** compared to  $\text{Mn}(2\text{-PyBN})(\text{hfac})_2$  (4.9 vs. 5.87 from Table 3).  $\text{Mn}(\text{NIT}2\text{-Py})(\text{hfac})_2$ , like most Mn-nitroxides,<sup>13</sup> exhibits antiferromagnetic coupling. The  $\chi T$  value of this complex at 300 K corresponds to  $S = 2$ , which would predict a weak transition consistent with the present result for **11**.

With  $\text{Cu}(2\text{-PyBN})(\text{hfac})_2$  under spin trapping conditions, no significant change in spectral profile was observed, either at room temperature or at 115 K. Since independently prepared Cu-nitroxide **13** has an entirely different spectral profile, it appears that  $\text{Cu}(2\text{-PyBN})(\text{hfac})_2$  is inert toward phenyl radical. In the case of  $\text{Fe}(2\text{-PyBN})(\text{hfac})_2$ , the complex itself is EPR silent and no signals developed during the spin trapping conditions employed.

For  $\text{Co}(2\text{-PyBN})(\text{hfac})_2$  it was not possible to determine whether spin trapping occurred. The complex itself did not show EPR signals even at 115 K, presumably due to strong spin-orbit coupling interactions. Also, no EPR signals could be observed at 115 K under spin trapping conditions. Even NMR methods did not provide enough information on formation of



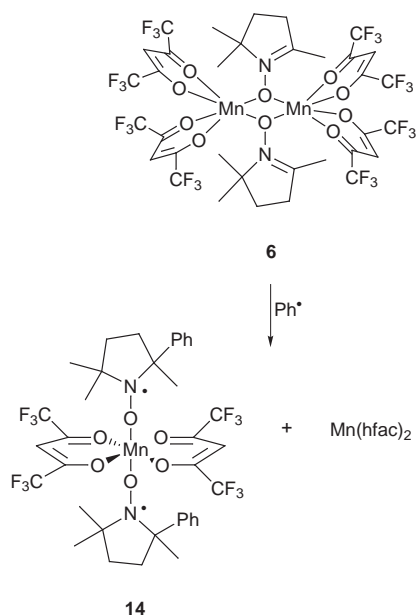
**Fig. 6** X-Band EPR spectra (115 K) in 80:20  $\text{CH}_2\text{Cl}_2$ -toluene glass of 3.5 mM  $[\text{Mn}(\text{M}_3\text{PO})(\text{hfac})_2]_2$  with 12 mM PAT during (a) 0 min; (b) 30 min; and (c) 90 min of irradiation. Spectrometer settings: microwave frequency, 9.01 GHz; microwave power, 10 mW; modulation frequency, 100 KHz; modulation amplitude, 4 G.

a spin adduct probably due to its lower sensitivity, since only small amounts of spin adduct are ever formed. It is possible that antiferromagnetically coupled spins between  $\text{Co}^{\text{II}}$  and nitroxide produce a total  $S = 1$ , so only the singlet level remains as the lowest energy level and the EPR transition cannot be observed. In fact, no signals were observed with the independently prepared **12**. The magnetic moment of **12** at ambient temperature was much smaller ( $3.6 \mu_B$ ) compared to the nitron complex  $\text{Co}(2\text{-PyBN})(\text{hfac})_2$  ( $4.60 \mu_B$ ), another indication of antiferromagnetic coupling between the spin adduct and metal center.

In an experiment important for conventional spin trapping in the presence of metal ions, spin adducts were generated in a typical manner by thermal decomposition of PAT at 80 °C in the presence of 2-PyBN. To this mixture was then added  $\text{M}(\text{hfac})_2$  ( $\text{M} = \text{Mn}$  or  $\text{Ni}$ ). EPR spectra recorded after metal complexation with the spin adducts were similar to those obtained for the  $\text{M}-2\text{-PyBN}$  complexes subjected to spin trapping conditions (see Fig. 4a in the case of Ni). In these cases, observed spectra are thus not characteristic of the spin adduct itself but of the metal-nitroxide complex.

**By complexes of monodentate  $\text{M}_3\text{PO}$ .** For  $[\text{Mn}(\text{M}_3\text{PO})(\text{hfac})_2]_2$ , which exists exclusively as the dimer in  $\text{CH}_2\text{Cl}_2$  by VPO, the broad EPR signal became better resolved after irradiation as shown in Fig. 6. A possible explanation is that the dimeric  $[\text{Mn}(\text{M}_3\text{PO})(\text{hfac})_2]_2$  decomposes during spin trapping to form  $\text{Mn}(\text{hfac})_2$  and Mn-nitroxide **14** as indicated in Scheme 3. The overall profile of the observed spectrum during spin trapping appears to be an overlap of these products and unreacted starting material. To model the EPR spectrum of **14**,  $\text{Mn}(\text{TEMPO})_2(\text{hfac})_2$ , where TEMPO is 2,2,6,6-tetramethylpiperidine-*N*-oxyl, was prepared from equimolar amounts of TEMPO and  $\text{Mn}(\text{hfac})_2$ .<sup>27</sup> The EPR spectrum of  $\text{Mn}(\text{TEMPO})_2(\text{hfac})_2$  was broad (Fig. 7a) with poorly resolved hyperfine structure as also reported for  $\text{Mn}(\text{proxyl})_2(\text{hfac})_2$ ,<sup>28</sup> [where proxyl = 2,2,5,5-tetramethylpyrrolidine-*N*-oxyl] but  $\text{Mn}(\text{hfac})_2$  alone gave much better resolved hyperfine splittings (Fig. 7b).

In agreement with a monomeric form of metal nitroxide **14**,  $\text{Mn}(\text{TEMPO})_2(\text{hfac})_2$  is monomeric both in solution (by VPO, Table 2) and in the solid state (crystal structure<sup>27</sup>). Moreover, the complex  $\text{Mn}(\text{proxyl})_2(\text{hfac})_2$ , a compound which has a



Scheme 3 Possible spin trapping products of the dimer **6**.

closer structure to **14**, is monomeric in the solid state.<sup>27</sup> Several nitronyl nitroxides can form dimers, as reported for complexes of Ni(hfac)<sub>2</sub> and Co(hfac)<sub>2</sub> with 2-ethyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (NITet) with strong antiferromagnetic coupling between the spins of the metal and the nitroxide.<sup>29</sup> However, this ligand contains a nitrone functionality, and no dimeric structures of simple nitroxides have been reported.<sup>30</sup>

For other M–M<sub>3</sub>PO complexes under spin trapping conditions, no EPR signal developed for [Co(M<sub>3</sub>PO)(hfac)<sub>2</sub>]<sub>2</sub> and [Ni(M<sub>3</sub>PO)(hfac)<sub>2</sub>]<sub>2</sub> even at 115 K. This was also the case for the (μ-oxo)diiron(III) complex [Fe(M<sub>3</sub>PO)(hfac)<sub>2</sub>]<sub>2</sub>(μ-O) which was formed by air oxidation in Fe(hfac)<sub>2</sub>/M<sub>3</sub>PO system.<sup>12</sup>

## Experimental

### Physical measurements

<sup>1</sup>H NMR spectra of all complexes were taken on a Nicolet 270 MHz spectrometer in CDCl<sub>3</sub> (Aldrich) solutions unless otherwise indicated. Chemical shifts are reported in ppm relative to tetramethylsilane. <sup>19</sup>F NMR spectra were obtained on a Bruker (Aspect 3000) 300 MHz spectrometer using a <sup>19</sup>F operating frequency of 282.4 MHz and chemical shifts were relative to CFCl<sub>3</sub>. Infrared spectra were recorded on a MIDAC FTIR as KBr pellets, Nujol mulls, thin films on NaCl and CH<sub>2</sub>Cl<sub>2</sub> solutions. UV/VIS spectra and NIR spectra were taken on Hewlett-Packard 8451A and Hitachi μ-3501 spectrophotometers as CH<sub>2</sub>Cl<sub>2</sub> solutions, respectively. Conductivity measurements were made with a VWR Model 604 digital conductivity meter on solutions in anhydrous 1,2-dichloroethane (99.8%, Aldrich, conductivity 6.0 × 10<sup>-9</sup> S cm<sup>-1</sup> at 24 °C). Molecular weight determinations in CH<sub>2</sub>Cl<sub>2</sub> (unless otherwise noted) were done by vapor pressure osmometry by Galbraith Laboratories, Inc.

For EPR spectra the CH<sub>2</sub>Cl<sub>2</sub> solvent (HPLC Grade, Fischer) was dried by refluxing over P<sub>2</sub>O<sub>5</sub> or CaH<sub>2</sub>, distilled and stored over molecular sieves Type 4A, and toluene was dried by storing over Type 4A molecular sieves. After degassing by bubbling argon through solutions for 30 min, X-band EPR spectra were recorded on a Varian E-4 spectrometer. A CH<sub>2</sub>Cl<sub>2</sub>–toluene (80:20) mixture was chosen as the solvent system because of the inertness of CH<sub>2</sub>Cl<sub>2</sub> under spin trapping conditions and its ability to form a glass at 115 K in the presence of small amounts of toluene. Spectra were referenced relative to diphenylpicrylhydrazyl (*g* = 2.0037). <sup>1</sup>H NMR spectra were

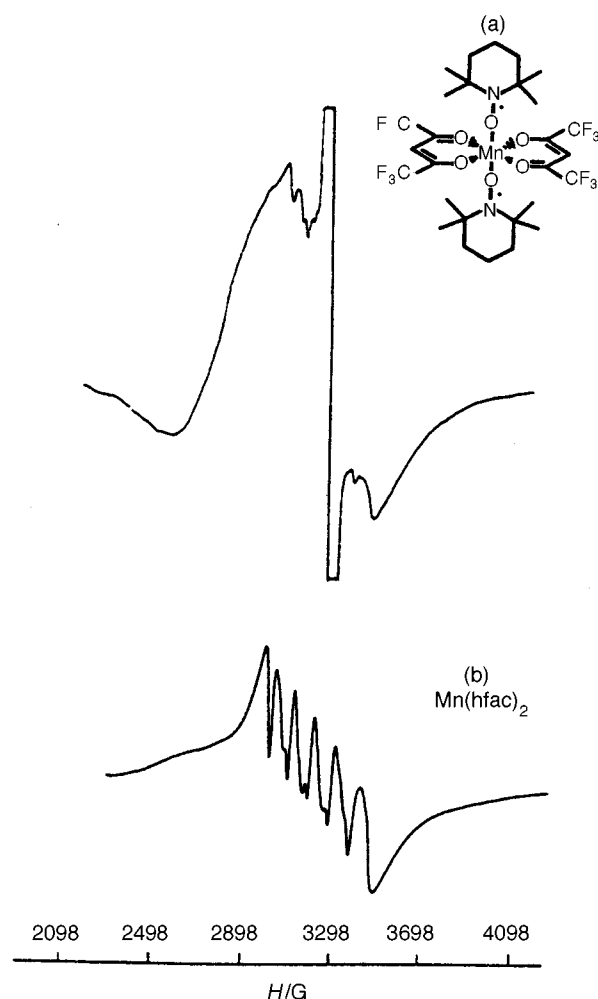


Fig. 7 X-Band EPR spectrum (115 K) in 80:20 CH<sub>2</sub>Cl<sub>2</sub>–toluene glass of (a) ca. 1 mM Mn(TEMPO)<sub>2</sub>(hfac)<sub>2</sub> with the center assigned to the uncoordinated nitroxide. (b) ca. 1 mM Mn(hfac)<sub>2</sub>. Spectrometer settings: microwave frequency, 9.01 GHz; microwave power, 10 mW; modulation frequency, 100 KHz; modulation amplitude, 4 G.

recorded on a Nicolet 270 MHz spectrometer with SiMe<sub>4</sub> as an internal standard. Magnetic moments of each of the complexes were determined at 22–24 °C using the Evans method.<sup>31</sup>

### Materials

Phenylazotriphenylmethane (PAT),<sup>32</sup> Na[Co(NO<sub>2</sub>)<sub>2</sub>(acac)<sub>2</sub>]<sup>33</sup> and [Co(acac)<sub>2</sub>(bipy)]I<sup>34</sup> were synthesized according to literature methods. *N*-*tert*-Butyl-*α*-(2-pyridyl)nitron (2-PyBN)<sup>12</sup> was prepared by oxidation of 2(*tert*-butylaminomethyl)pyridine<sup>35</sup> with Na<sub>2</sub>WO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>.<sup>36</sup> 2,5,5-Trimethyl-3,4-dihydropyrrole *N*-oxide (M<sub>3</sub>PO) was prepared as described elsewhere<sup>12</sup> by reductive cyclization<sup>37</sup> of 5-methyl-5-nitro-2-hexanone.

**Metal–nitron complexes.** Complexes were prepared by adding an equimolar amount of nitron to a stirred solution of the metal hexafluoroacetylacetonate M(hfac)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> (for 2-PyBN) or in CH<sub>2</sub>Cl<sub>2</sub>–heptane (for M<sub>3</sub>PO). Detailed procedures, characterizations, satisfactory elemental analysis and crystal structure determinations of each of the nitron metal complexes are described elsewhere.<sup>12</sup>

### [Co(acac)<sub>2</sub>(bipy)][Co(NO<sub>2</sub>)<sub>2</sub>(acac)<sub>2</sub>] **9**

Complex salt **9** was prepared by first converting [Co(acac)<sub>2</sub>(bipy)]I to the acetate by stirring a solution of 0.030 g (0.056 mmol) in 50 mL of water with 9.3 mg (0.056 mmol) of silver

acetate at 40 °C. The cloudy solution was refrigerated overnight and centrifuged for 1 h. The yellow AgI precipitate was separated, and to the supernatant was added 0.021 g (0.056 mmol) of Na[Co(NO<sub>2</sub>)<sub>2</sub>(acac)<sub>2</sub>] in 50 mL of water. After addition of 20 mL of ethanol, more AgI was removed by filtration. Evaporation of solvent under vacuum gave a red solid which was recrystallized from water–ethanol and dried over P<sub>2</sub>O<sub>5</sub> under vacuum (0.1 Torr). The procedure was repeated on the filtrate from the first filtration yielding powder of [Co(acac)<sub>2</sub>(bipy)]-[Co(NO<sub>2</sub>)<sub>2</sub>(acac)<sub>2</sub>] **9** (0.034 g, 80%), mp 162–163 °C; δ<sub>H</sub> (CDCl<sub>3</sub>) 1.87 (6H, s, CH<sub>3</sub>), 1.99 (12H, s, CH<sub>3</sub>), 2.34 (6H, s, CH<sub>3</sub>), 5.45 (2H, s, CH), 5.57 (2H, s, CH), pyridyl H's: 7.59 (2H, t), 8.14 (2H, d), 8.34 (2H, br s), 9.0 (2H, br s).

### Na[Co(hfac)<sub>3</sub>]

The procedure was similar to the preparation of Na[Co(acac)<sub>3</sub>]<sup>38</sup> but with 1,1,1,5,5,5-hexafluoroacetylacetone (Aldrich) used for the 1,3-diketone. A 9 mL methanol solution of 1.58 g (6.67 mmol) of cobalt(II) chloride hexahydrate (Baker) was added dropwise with stirring to a 13 mL methanolic solution of 0.8 g (0.020 mol) NaOH and 5.0 g (0.020 mol) of the diketone. The solution was concentrated by evaporation at room temperature, and the fine red powder which formed was isolated by filtration, washed thoroughly with ice cold methanol (*ca.* 10 mL), then with diethyl ether and air dried. Na[Co(hfac)<sub>3</sub>] is insoluble in CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> (unless in the presence of *cis*-dicyclohexano-18-crown-6) but soluble in methanol (4.0 g, 85%), mp 146–147 °C (Found: C, 22.54; H, 1.70. NaCoC<sub>15</sub>H<sub>3</sub>F<sub>18</sub>O<sub>6</sub>·5H<sub>2</sub>O requires C, 22.72; H, 1.65%); δ<sub>H</sub> (CDCl<sub>3</sub> + *cis*-dicyclohexano-18-crown-6) –16.9 (1H, s), –20.8 (1H, br s).

**Metal–nitroxide complexes.** Crystals of **10–13** were prepared as described previously<sup>24</sup> from M(hfac)<sub>2</sub> and a solution of *N-tert*-butyl-(2-pyridyl)phenylmethaniminoxyl freshly prepared by Ag<sub>2</sub>O oxidation of its hydroxylamine.<sup>39</sup> Satisfactory elemental analyses and crystal structure determinations of **10–13** were obtained.<sup>24</sup> The same procedure was followed for **13**, but the crystalline product in this case showed the presence of free ligand in the NMR and did not give a satisfactory analysis.

### Spin trapping

In a typical spin trapping experiment (unless otherwise noted) 1 mL of a CH<sub>2</sub>Cl<sub>2</sub>–toluene (80:20) solution 30 mM in nitron and 10 mM in PAT was made and 0.1 mL transferred to an EPR quartz tube (tube length, 250 mm; outer diameter, 4 mm). Irradiation was carried out with a Spectroline short-wave lamp (Fischer) with an average intensity of 4500 μW cm<sup>-2</sup> and wavelength of 254 nm. The lamp was positioned 11 cm from the tube in the sample cavity at 25 °C, and spectra were taken over 1 h.

For spin trapping by a metal complex, solutions were prepared and irradiated as above. However, after 15 min of irradiation, the solution was frozen in the EPR tube and its EPR spectrum taken at 115 K. The solution was thawed and the process repeated after 15 min irradiation intervals for a total of 1 h of irradiation. An alternative procedure involved surrounding the lamp with EPR tubes containing equal amounts of the spin-trapping solution. All tubes were positioned 11 cm away from the centre and irradiated. A tube was removed every 2 min, frozen and an EPR spectrum taken. For blank experiments, each Mn(hfac)<sub>2</sub> was irradiated in the presence of PAT under the same conditions as above. No changes in EPR spectra were observed except for the case of Mn(hfac)<sub>2</sub> for which signals diminish slightly with time, but very much slower than for Mn(2-PyBN)(hfac)<sub>2</sub>. Thermal decomposition of PAT occurs slowly at room temperature, since in the absence of light, small EPR signals developed in the presence of 2-PyBN and M<sub>3</sub>PO but do not grow with time.

### Conclusion

Although complexes of the bidentate nitron 2-PyBN with Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup> and Fe<sup>II</sup> are complex salts in the solid state, these complexes, like that of Cu<sup>II</sup>, exist predominantly as neutral complexes in CH<sub>2</sub>Cl<sub>2</sub>. Complexes of the monodentate M<sub>3</sub>PO with Mn<sup>II</sup>, Co<sup>II</sup> and Ni<sup>II</sup> on the other hand, generally exist as a mixture of monomers and dimers in that solvent.

For the 2-PyBN complexes studied, spin adducts with phenyl radical were formed for Ni<sup>II</sup> and Mn<sup>II</sup> on the basis of changes in the EPR spectra during spin trapping and correspond to those of independently prepared M<sup>II</sup> nitroxides. Under the conditions used, the Cu<sup>II</sup> complex was inert toward phenyl radical, an observation for which we have no explanation at the present time. Results for Co<sup>II</sup> were inconclusive, and the Fe<sup>II</sup> complex was EPR silent in the complex alone and under spin trapping conditions. For M<sub>3</sub>PO complexes, generation of phenyl radicals in the presence of [Mn(M<sub>3</sub>PO)(hfac)<sub>2</sub>]<sub>2</sub> gave an EPR spectrum consistent with the formation of a spin adduct and Mn(hfac)<sub>2</sub>, but results for Co<sup>II</sup>, Ni<sup>II</sup> and the (μ-oxo)diiron(III) complex were inconclusive.

Typically, many spin trapping experiments are carried out in the presence of metal ions. Such an experiment was simulated by forming the spin adduct of 2-PyBN with phenyl radical with no metals present. When Ni(hfac)<sub>2</sub> or Mn(hfac)<sub>2</sub> was then added, the same EPR spectrum was obtained as that for phenyl trapping by M(2-PyBN)(hfac)<sub>2</sub>. This result suggests that spin trapping experiments in the presence of metal ions may give spectra that represent metal complexes of the spin adducts rather than the spin adducts themselves.

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