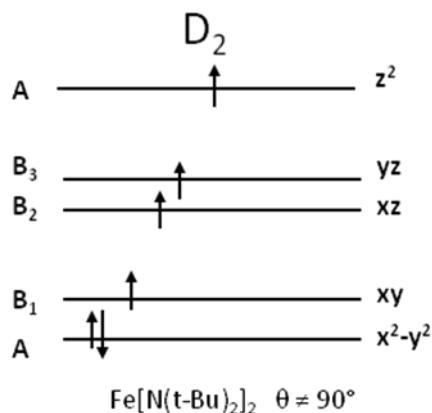


The lowest known coordination number for a transition metal is two. Compounds that exhibit such a low coordination number are rare with only twenty-one such complexes having been reported. The few known two-coordinate complexes have often displayed interesting reactivity, structural features, and physical properties.<sup>1-11</sup> While a variety of ligand types have been used to synthesize two-coordinate complex, by far the most common is the amido ligand. Amido ligands have the advantage of possessing two substituents on the nitrogen atom makes it relatively easy to engineer a ligand with sufficient bulk to stabilize a two-coordinate complex.

This group has investigated the unusually bulky di(*tert*-butyl)amido ligand for the synthesis of new two-coordinate complexes. Lappert has reported two main group complexes of di(*tert*-butyl)amide<sup>12</sup> but until Potratz, working in this group, reported the synthesis of the iron(II) complex  $\text{Fe}[\text{N}(\text{t-Bu})_2]_2$  and the chromium(III) complex  $\text{Cr}[\text{N}(\text{t-Bu})_2]_2$  no transition metal complexes of di(*tert*-butyl)amide had been reported.<sup>13</sup>

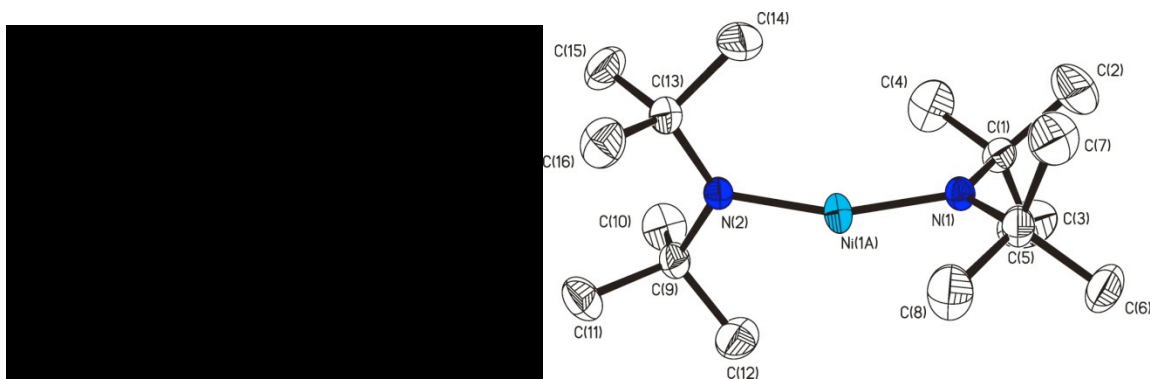
The linear  $\text{Fe}[\text{N}(\text{t-Bu})_2]_2$  was found to have a large magnetic moment of  $5.55 \mu_{\text{B}}$  indicating significant unquenched orbital angular momentum. The orbital contribution to the magnetic moment is not entirely quenched because the nearly degenerate  $xy$  and  $x^2-y^2$  orbitals (Figure 1) are nonbonding in nature so the molecule does not distort in either a Jahn-Teller or Renner-Teller fashion. Applied Mössbauer spectroscopy revealed an internal hyperfine field of ( $H_{\text{INT}}$ ) 105 T. This  $H_{\text{INT}}$  is unusually large with only one other compound haven been reported with a larger value<sup>11</sup> and being over 20 T higher than the next closest.<sup>14</sup> Then orbital contribution to the hyperfine field is  $\sim 155$  T.

Treatment of  $\text{MnBr}_2(\text{THF})_2$  with two equivalents of  $\text{LiN}(\text{t-Bu})_2$  followed by sublimation results in the linear  $\text{Mn}[\text{N}(\text{t-Bu})_2]_2$  as a pale yellow solid. The N-Mn-N bond angle is  $179.30(5)^\circ$  and the  $\text{NR}_2$  planes describe a dihedral angle of  $80.0(1)^\circ$ . The magnetic moment of  $5.53 \mu_{\text{B}}$  is consistent with the expected  $S = 3/2$ .



**Figure 1.** The d-orbital splitting for Fe[N(t-Bu)<sub>2</sub>]<sub>2</sub>. The xy and x<sup>2</sup>-y<sup>2</sup> orbitals are nearly degenerate.

Likewise treatment of CoBr<sub>2</sub>(DME) and NiBr<sub>2</sub>(DME) with two equivalents of LiN(t-Bu)<sub>2</sub> results in the two coordinate Co[N(t-Bu)<sub>2</sub>]<sub>2</sub> and Ni[N(t-Bu)<sub>2</sub>]<sub>2</sub> respectively. The blue Ni<sup>II</sup> complex is bent with a N-Ni-N bond angle of 160.9(2)° (Figure 2). The magnetic moment of Ni[N(t-Bu)<sub>2</sub>]<sub>2</sub> was found to be 2.88 μ<sub>B</sub>. This moment is indicative of a two-coordinate high-spin d<sup>8</sup> complex with completely quenched orbital angular momentum. The dark red Co[N(t-Bu)<sub>2</sub>]<sub>2</sub>, with its expected d-electron configuration of (xy, x<sup>2</sup>-y<sup>2</sup>)<sup>4</sup>(xz,yz)<sup>1</sup>(z<sup>2</sup>)<sup>1</sup>, is surprisingly bent with a N-Co-N angle of 159.2(2)° (Figure 2). The magnetic moment of 5.24 μ<sub>B</sub> for the Co<sup>II</sup> is significantly larger than the spin only value of 3.87 μ<sub>B</sub>. Larger than expected magnetic moments for cobalt compounds is common as a result of mixing with excited states.<sup>15</sup>

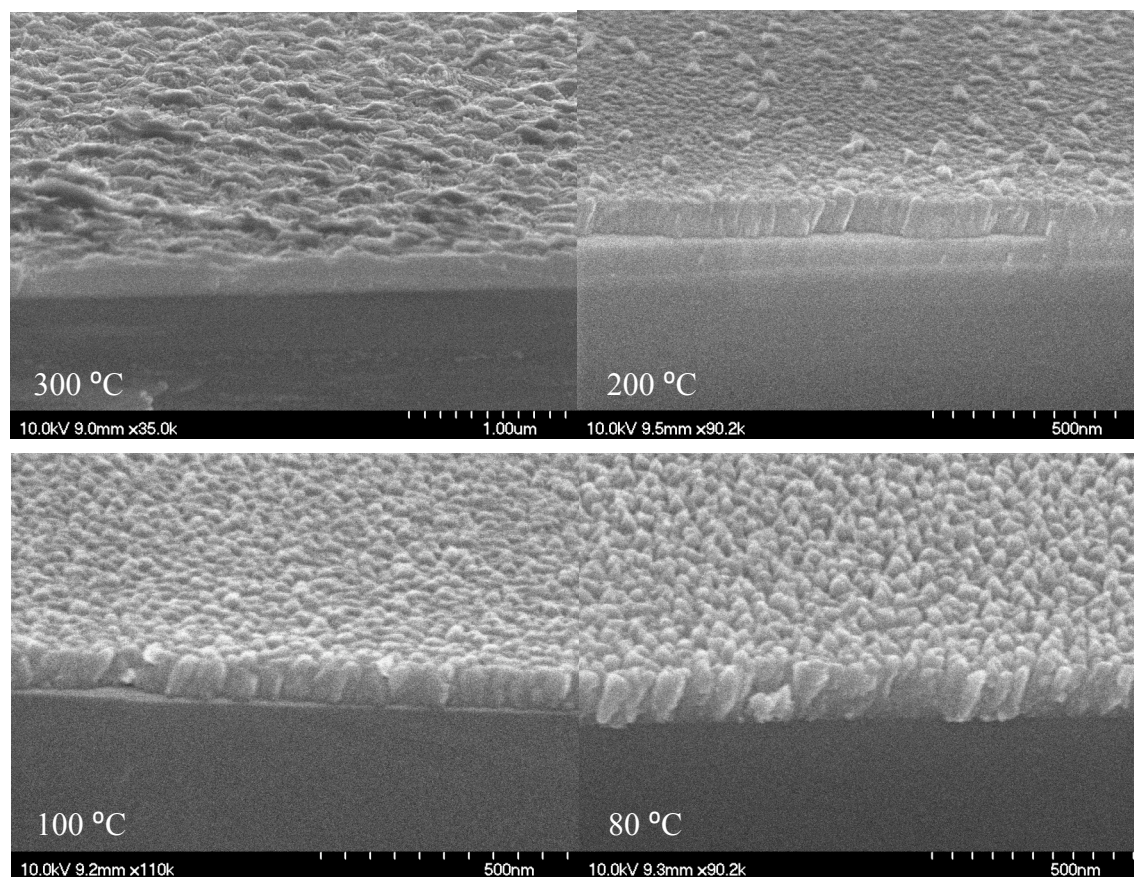


**Figure 2.** Molecular structure of Co[N(t-Bu)<sub>2</sub>]<sub>2</sub> (right) and Ni[N(t-Bu)<sub>2</sub>]<sub>2</sub> (left). The 30% probability density surfaces are shown; hydrogen atoms are omitted for clarity.

Metal nitrides have a wide range of applications and can be found being used in wear-resistant tool coatings,<sup>16</sup> Josephson junctions,<sup>17</sup> solar-control coatings,<sup>18</sup> and magnetic recording media<sup>19</sup> to name a few. Chemical vapor deposition (CVD) is one of the leading techniques for depositing thin films of these materials. Surprisingly however the literature is devoid of attempts to grow thin films of manganese nitrides through CVD techniques. The volatile  $\text{Mn}[\text{N}(\text{t-Bu})_2]_2$  is a good candidate for growth of thin films of manganese nitrides through CVD.

When the precursor container was heated to 40 °C and a  $\text{N}_2$  with a flow rate of 10 sccm was used it was possible to grow thin films on Si(100) at a substrate temperature of 300 °C. These films grew at the extremely slow growth rate of 0.1 nm/min. The films had a globular morphology when examined by Scanning Tunneling Microscopy (SEM) and Auger Electron Spectroscopy (AES) revealed a composition of 52 at. % Mn, 33 at. % C and 15 at. % O.

It was possible to improve the composition and growth rate of the films by using 4.3 sccm of anhydrous ammonia as a coreactant. Films grown at 300 °C under these conditions had a growth rate over 50 times faster at 5.3 nm/min. The stoichiometry of these films also improved with the carbon concentration decreasing to 15 at. % and the nitrogen concentration increasing to 14 at. %. At lower temperatures the carbon concentration dropped below detection limits with compositions of Mn = 65 %, N = 26 %, C < 1 %, O = 9 % as detected by AES. Growth rates decreased with temperature but films grown at 80 °C still had a growth rate of 2.1 nm/min! All films grown in the presence of ammonia had columnar morphologies (Figure 3). This columnar structure is believed to have allowed fast diffusion pathways for oxygen during exposure to air before analysis. Air exposure is likely the primary source of oxygen in all the films grown in the presence of ammonia.



**Figure 3.** Comparison of films grown from  $\text{Mn}[\text{N}(\text{t-Bu})_2]_2$  and ammonia on Si(100) at different temperatures. The flow rates of the carrier gas and  $\text{NH}_3$  were 10 and 4.3 sccm respectively.

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