Recent Advances in Cyanoscorpionate Chemistry: Complexes with Co(II), Mn(II), and Ni(II)(cyclam).

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Abstract. In the past, electronic and magnetic materials have been atom based materials made up of metals or metal-oxides. Functionally, these atom based materials are extremely efficient, however, they are very expensive to synthesize, very heavy, and possess limited flexibility. These properties limit the applications of traditional atom based materials where expense, weight, and flexibility are issues. Molecule based materials contain individual molecules which are inexpensively synthesized and made from predominantly light weight carbon, hydrogen, nitrogen, and oxygen. Coordination polymers containing transition metal centers with organic ligands can provide both electronic and magnetic properties as well as allow for light-weight and flexible molecule based materials. We have been investigating the synthesis of cyanoscorpionate ligands as components of coordination polymers. Over the last several years, our group has been investigating trispyrazolylborate (Tp) ligands containing the CN substituent in the 4-position of the pyrazole ring. The cyano group has a strong electron-withdrawing character, as well as the ability to coordinate to the metal. This allows the scorpionate to form various coordination polymers in which two cyanoscorpionate complexes are bound to the metal ion through the cyano group. In this paper we present recent work in this field, including the synthesis and structural characterization of complexes in which the cyano groups are coordinated to a central metal atom. These complexes represent the first step towards the synthesis of two-component coordination polymers involving this ligand class.

Introduction

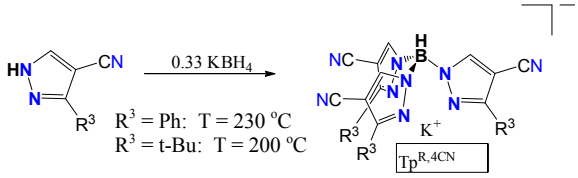
Polypyrazolylborate, or scorpionate, ligands have been a a very popular class of inorganic ligands for the past four decades. The ease with which these ligands can be synthesized with various substitients, allows for a wide variety of steric and electronic properties.[1] Scorpionate ligands containing strong electron withdrawing ligands have not been the focus of many studies, however over the last several years, our group has been investigating trispyrazolylborate ligands containing the CN substituent in the 4-position of the pyrazole ring. The cyano group has a strong electron-withdrawing character, as well as the ability to coordinate to the metal. This allows the scorpionate to form various coordination polymers in which two cyanoscorpionate complexes are bound to the metal ion through the cyano groups,

as well as complexes in which the pyrazole is only coordinated to the metal through the pyrazole N atoms.[2]

Results and Discussion

Synthesis of pyrazole & scorpionates

The syntheses of 3-R-4-cyanopyrazole (R=Ph, *t*-Bu) were achieved by a modification of Tupper and Bray's method[3]. The potassium salt of $Tp^{t\text{-}Bu,4CN}$ was synthesized by combining 4 equivalents of 3-*t*-butyl-4-cyanopyrazole with potassium borohydride and heating above the melting point of the pyrazole.



Copper polymers

Previously, a one dimensional Cu(I) coordination polymers was synthesized with $Tp^{t\text{-}Bu,4CN}$. This polymer was crystallographically characterized and showed the Cu coordinated to the three pyrazole N atoms of one Tp and the N of the cyano group from another Tp. This was the first conformation of the cyanoscorpioinate's ability to form coordination polymers. We have now isolated a $Tp^{t\text{-}Bu,4CN}$Cu(I) polymer with the same structure as the one previously synthesized, except for an acetonitrile which is crystallized in the lattice (Figure 1). This is a very good indication that there is some type of

channel within the lattice which was not previously recognized.

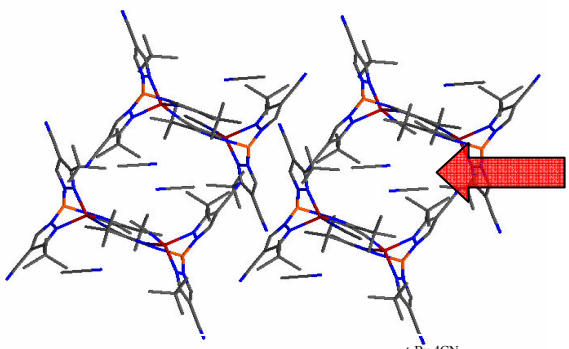


Figure 1: A Mercury drawing of the $\{Tp^{t\text{-}Bu,4CN}Cu\}_n$ with the arrow showing the channel containing the acetonitrile.

New Co(II), Mn(II), and Ni(cyclam) structures

Co^{2+}, Mn^{2+}, and $Ni(cyclam)^{2+}$ (cyclam=1,4,8,11-Tetra-azacyclotetradecane) were reacted with $Tp^{t\text{-}Bu,4CN}$ in a 1:2 ratio which produced new octahedral metal complexes (Figure 2). Unlike the previously synthesized sandwich complexes, the crystal structures showed that none of the pyrazole nitrogens are coordinated to the metal. In all three structures, the only Tp N that is coordinated is that of the CN group, with two Tp anions coordinated *trans* to each other around the metal center. This leaves the Tp pyrazole nitrogens open for another metal to coordinate, which could to lead to heterometallic complexes as well as new coordination polymers.

Conclusion

The new Cu polymer revealed a channel within the lattice. This channel provides evidence for the possibility of two- and three-dimensional polymers comprised of $Tp^{t\text{-}Bu,4CN}$ metal complexes as small molecule carriers. New $Tp^{t\text{-}Bu,4CN}$ metal complexes with Co^{2+}, Mn^{2+}, and $Ni(cyclam)^{2+}$ were synthesized with the crystal structures revealing the only coordinated N atoms were those of the CN group, leaving the Tp open for other metal coordination. This type of motif is the first step in synthesizing two- and three-dimensional polymers with useful structural as well as electronic properties.

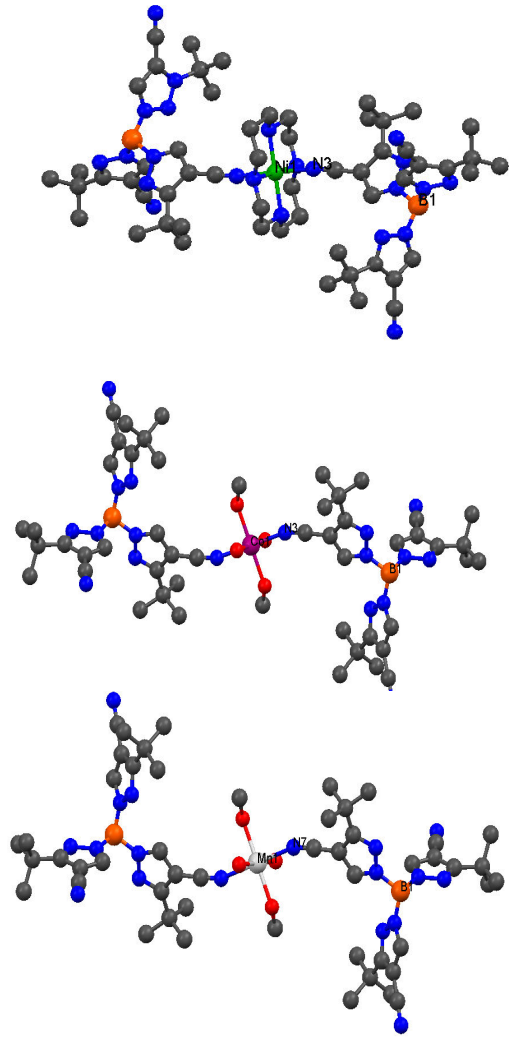


Figure 2: Structures of $(Tp^{t\text{-}Bu,4CN})_2Ni(cyclam)$, $(Tp^{t\text{-}Bu,4CN})_2Co(MeOH)_2(H_2O)_2$ and $(Tp^{t\text{-}Bu,4CN})_2Co(MeOH)_2(H_2O)_2$, respectively. H atoms have been left out for convenience.

References

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