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# Enhancing the Magnetic Anisotropy of Cyano-Ligated Chromium(II) and Chromium(III) Complexes via Heavy Halide Ligand Effects

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A method of increasing the axial zero-field splitting parameter for transition metal complexes of utility in the assembly of magnetic clusters is demonstrated through the use of heavy atoms as auxiliary ligands. The octahedral complexes $[\mathrm{Cr(dmpe)_2(CN)X}]^+$ (dmpe = 1,2-bis(dimethylphosphino)ethane, X = Cl, Br, I) and $\mathrm{Cr(dmpe)_2(CN)X}$ (X = Cl, I) are synthesized and structurally characterized. Variable-field magnetization measurements show the magnitude of *D* for these complexes to increase significantly as the halide ligand varies from chloride to iodide, ranging from 0.11 $\mathrm{cm^{-1}}$ for $[\mathrm{Cr(dmpe)_2(CN)Cl}]^+$ to 6.26 $\mathrm{cm^{-1}}$ for $\mathrm{Cr(dmpe)_2(CN)I}$.

Since the initial demonstration of magnetic bistability in $\mathrm{Mn_{12}O_{12}(CH_3CO_2)_{16}(H_2O)_4}$,[1] there has been considerable interest in the possibility of generating molecular clusters with higher blocking temperatures for a variety of potential applications.[2] Such molecules, known as single-molecule magnets, exhibit a magnetic relaxation barrier, $U$, generated by action of a negative axial zero-field splitting, $D$, on a high-spin ground state, $S$. As $U = S^2|D|$ (for integer $S$), a variety of approaches have been developed for attempting to generate clusters with a very high $S$ value[3] or a large magnetic anisotropy $|D|$.[4] Among these, the synthesis of high-nuclearity metal-cyanide coordination clusters presents a promising strategy, wherein the substitutions of the metal can provide a means of manipulating $S$ and $D$.[5] To date, however, the largest relaxation barrier that has been measured for a cyano-bridged cluster is just $U_{\mathrm{eff}} = 33\ \mathrm{cm^{-1}}$.[6] A key to enhancing these barriers may lie in the synthesis of new high-anisotropy molecular building units for use in cluster assembly. Ultimately, if a sufficiently large barrier can be realized, single-molecule magnets could potentially find applications in areas such as high density information storage, quantum computing, and molecular spintronics.[2]

In a number of cases, the incorporation of second- and third-row transition metal centers has been shown to generate a large magnetic anisotropy within cyano-bridged clusters through spin−orbit coupling.[5b,c,6,7] This approach can be challenging, however, owing to their often sluggish ligand substitution kinetics and difficulties with controlling the coordination geometry to achieve high-anisotropy electron configurations.[8] An alternative strategy is to instill magnetic anisotropy within first-row transition metal building units through the spin−orbit coupling imparted by ligands with heavy donor atoms. This would allow one to exploit the synthetic and structural predictability of first-row transition metal complexes while also delivering a large single-ion anisotropy. In particular, the presence of heavy halide ligands has been shown to increase axial zero-field splitting for transition metal complexes. For example, magnetic susceptibility measurements performed on $[\mathrm{ReX_6}]^{2-}$ (X = Cl, Br) and high-field

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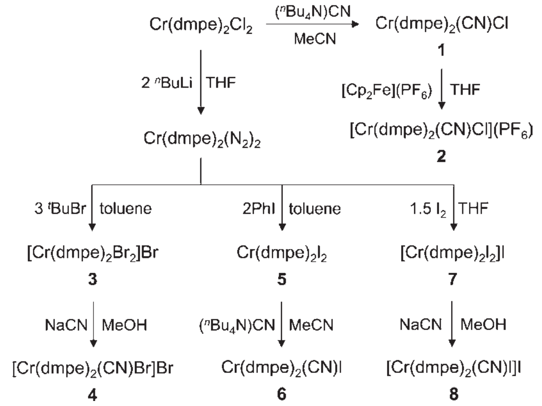
**Scheme 1.** Synthesis of $[Cr(dmpe)_2(CN)X]^{1+/0}$ Complexes



EPR studies of Tp*NiX (Tp* = hydrotris(3,5-dimethylpyrazole)borate; X = Cl, Br, I) and $(tpa)MnX_2$ (tpa = tris-2-picolylamine; X = Cl, Br, I) have shown the complexes with the heavier halide ligands to exhibit $D$ values of significantly greater magnitude.[9] Here, we demonstrate that this effect can extend to octahedral $Cr^{II}$ and $Cr^{III}$ complexes rendered suitable for use as cluster building units through the appendage of a terminal cyanide ligand.

Octahedral chromium complexes featuring a halide ligand placed *trans* to a cyanide ligand were synthesized with the use of two 1,2-bis(dimethylphosphino)ethane (dmpe) auxiliary ligands. Complexes of the form $Cr(dmpe)_2(CN)X$ (X = Cl, I) and $[Cr(dmpe)_2(CN)X]^+$ (X = Cl, Br, I) were generated, starting from $Cr(dmpe)_2Cl_2$,[10] as outlined in Scheme 1. Although some of these complexes have been reported previously, here we employ different synthetic routes with improved yields and structurally characterize compounds **1**−**8** for the first time. The complex $Cr(dmpe)_2(CN)Cl$ (**1**) was isolated from the reaction of $Cr(dmpe)_2Cl_2$ with $(^nBu_4N)CN$ and was subsequently converted into $[Cr(dmpe)_2(CN)Cl](PF_6)$ (**2**) via chemical oxidation with $[Cp_2Fe](PF_6)$.[11] Repeating the reaction with $[Cp_2Fe](BPh_4)$ afforded the analogous compound $[Cr(dmpe)_2(CN)Cl](BPh_4)$ (**2′**). In an attempt to access the $Cr^{II}$ iodo and bromo complexes, $Cr(dmpe)_2Cl_2$ was reduced to $Cr(dmpe)_2(N_2)_2$ using 2 equiv of *n*-butyllithium.[12] Oxidation of $Cr(dmpe)_2(N_2)_2$ with 2 equiv of iodobenzene then afforded $Cr(dmpe)_2I_2$ (**5**),[13] while analogous reactions employing bromobenzene or *t*-butylbromide were found to yield $[Cr(dmpe)_2Br_2]Br$ (**3**).[11] Further oxidation of $Cr(dmpe)_2(N_2)_2$ to $[Cr(dmpe)_2I_2]I$ (**7**) can be accomplished using 1.5 equiv of $I_2$.[11] Reaction of $(^nBu_4N)CN$ with $Cr(dmpe)_2I_2$ or NaCN with $[Cr(dmpe)_2X_2]X$ (X = Br,[11] I) affords the mixed cyanide-halide compounds $Cr(dmpe)_2(CN)I$ (**6**) and $[Cr(dmpe)_2(CN)X](X)$ (**4** and **8**) in high yield.

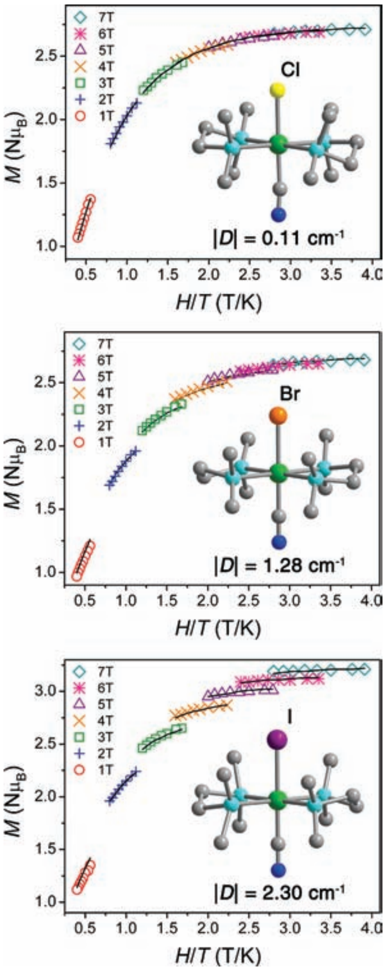


**Figure 1.** Structures and reduced magnetization data for the octahedral complexes $[Cr(dmpe)_2(CN)X]^+$ (X = Cl, Br, I), as observed in **2**, **4**, and **8**. Green, purple, orange, yellow, light blue, blue, and gray spheres represent Cr, I, Br, Cl, P, N, and C atoms, respectively; H atoms are omitted for clarity. Solid lines represent fits to the data (see text for details).

Compounds **1**, **2′**, and **3**−**8** were characterized by single crystal X-ray analysis. In each of the mixed cyanide−halide structures, the cyanide and halide ligands were equally disordered between the two *trans* positions. In most of the structures, disorder was also evident in the dmpe ligand. For the complexes $[Cr(dmpe)_2X_2]^+$, the mean Cr−X distance increases from 2.293(4) Å for X = Cl[14] to 2.457(2) Å for X = Br to 2.662(5) Å for X = I. This trend is conserved in the structures of the $[Cr(dmpe)_2(CN)X]^+$ complexes, which display a mean Cr−X distance of 2.452(2) Å for X = Cl and Cr−X distances of 2.552(3) Å for X = Br and 2.663(2) Å for X = I. We note, however, that too much emphasis cannot be placed on the bond distances which are influenced by the disorder in the structure. Analogous trends are apparent for the structures of the $Cr(dmpe)_2(CN)X$ complexes, with a mean Cr−Cl distance of 2.436(9) and a Cr−I distance of 2.733(1) Å.

Magnetic susceptibility measurements were performed on finely ground polycrystalline powders of compounds **1**, **2**, **4**, **6**, and **8** suspended in eicosane. At room temperature, the

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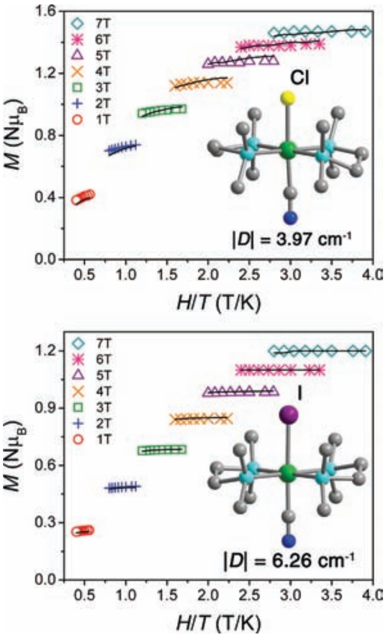

**Figure 2.** Structures and reduced magnetization data for the octahedral complexes $Cr(dmpe)_2(CN)X$ (X = Cl, I), as observed in **1** and **6**. Purple, green, yellow, light blue, blue, and gray spheres represent I, Cr, Cl, P, N, and C atoms, respectively; H atoms are omitted for clarity. Solid lines represent fits to the data (see text for details).

compounds exhibit effective magnetic moments close to the expected spin-only moments of 3.87 and 2.83 $\mu_B$ for isolated $Cr^{III}$ ($S = {}^3/_2$) and low-spin $Cr^{II}$ ($S = 1$) centers, respectively, as given in Table 1. Magnetization data collected at applied fields between 1 and 7 T and temperatures below 5 K were fit using ANISOFIT 2.0[5b] to extract the axial zero-field splitting parameters and $g$ values, as listed in Table 1. Since, in general, the sign of $D$ is not reliably obtained from such measurements, we report here only its magnitude.

The magnetization data for the $Cr^{III}$ complexes are depicted in Figure 1. Typically, an octahedrally coordinated metal center with a $t_{2g}^3$ configuration has an essentially spherical electron distribution, leading to a $D$ value near zero. This situation is borne out in the data for $[Cr(dmpe)_2(CN)Cl]^+$, wherein the isofield lines show little deviation from the Brillouin function for an $S = {}^3/_2$ ground state, leading to $|D| = 0.11\ cm^{-1}$. Importantly, replacement of the chloride ligand with bromide or iodide results in an increasing separation between isofield lines, corresponding to anisotropy parameters of $|D| = 1.28$ and $2.30\ cm^{-1}$, respectively. Thus, the simple substitution of a single halide ligand can lead to increases in the axial zero-field splitting by more than an order of magnitude. To the best of our knowledge, the value obtained for $[Cr(dmpe)_2(CN)I]^+$ is the largest yet observed for a pseudooctahedral $Cr^{III}$ complex.[15]

As shown in Figure 2, the magnetization data for the $Cr^{II}$ complexes indicate even greater anisotropy. Here, the electronic structure stems from the $t_{2g}^4$ configuration of a low-spin octahedral complex, which carries with it first-order orbital angular momentum. Accordingly, even the chloride complex $Cr(dmpe)_2(CN)Cl$ exhibits a large zero-field splitting, with $|D| = 3.97\ cm^{-1}$. Nevertheless, a substantial gain in anisotropy is again achieved through the substitution of chloride with iodide, resulting in $|D| = 6.26\ cm^{-1}$ for $Cr(dmpe)_2(CN)I$.

**Table 1.** Magnetic Parameters for Compounds Containing the Octahedral Complexes $[Cr(dmpe)_2(CN)X]^+$ (X = Cl, Br, I) and $Cr(dmpe)_2(CN)X$ (X = Cl, I)

| compound | $\mu_{eff}$ $(\mu_B)^a$ | $g$ | $\lvert D\rvert$ $(cm^{-1})$ |
|---|---|---|---|
| $[Cr(dmpe)_2(CN)Cl](PF_6)$ (**2**) | 3.64 | 1.82 | 0.11 |
| $[Cr(dmpe)_2(CN)Br]Br$ (**4**) | 3.69 | 1.84 | 1.28 |
| $[Cr(dmpe)_2(CN)I]I$ (**8**) | 3.87 | 1.82 | 2.30 |
| $Cr(dmpe)_2(CN)Cl$ (**1**) | 2.79 | 1.66 | 3.97 |
| $Cr(dmpe)_2(CN)I$ (**6**) | 2.67 | 1.61 | 6.26 |

[a] At 298 K.

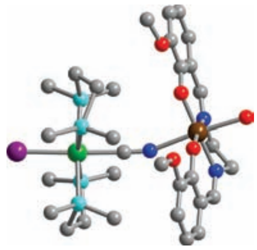

**Figure 3.** Structure of the cyano-bridged cluster $[(H_2O)(salen(OMe)_2)Mn(\mu\text{-}NC)Cr(dmpe)_2I]^{2+}$, as observed in **9**. Purple, brown, green, light blue, red, blue, and gray spheres represent I, Mn, Cr, P, O, N, and C atoms, respectively; H atoms are omitted for clarity.

The mixed cyanide-halide complexes characterized here should be of utility in the assembly of cyano-bridged coordination clusters. In particular, reactions with metal complexes of the type $[L_x^{cap}M(solvent)_y]^{n+}$ (where $L^{cap}$ represents a capping ligand) can be expected to give star-like clusters of formula $\{L_x^{cap}M[(\mu\text{-}NC)Cr(dmpe)_2X]_y\}^{n+/(n+y)+}$. Of greatest interest for this purpose will be the high-anisotropy iodo complexes $[Cr(dmpe)_2(CN)I]^+$ ($S = {}^3/_2$) and $Cr(dmpe)_2(CN)I$ ($S = 1$). As an initial example demonstrating cluster formation, the former species was found to react with $[(salen(OMe)_2)Mn(H_2O)](ClO_4)$ ($H_2salen(OMe)_2$ = *N*,*N′*-bis(3-methoxysalicylidene)ethyl-enediamine) to afford $[(H_2O)(salen(OMe)_2)Mn(\mu\text{-}NC)Cr(dmpe)_2I](ClO_4)_2$ (**9**). This compound features the cyano-bridged cluster depicted in Figure 3. The formation of a cyanide bridge precludes the halide/cyanide disorder seen in the crystal structures of the monomeric complexes and is evidence that the crystallographic disorder is not a manifestation of the cocrystallization of $[Cr(dmpe)_2X_2]^{0/1+}$ and $[Cr(dmpe)_2(CN)_2]^{0/1+}$. Although this molecule is expected to have a ground state of just $S = 1/2$ owing to antiferromagnetic coupling, related reactions can be anticipated to yield high-spin, high-anisotropy clusters and, potentially, single-molecule magnets with high relaxation barriers.

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**Supporting Information Available:** Complete experimental details (PDF) and X-ray crystallographic files for **1**−**9** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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