

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 $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}]^+$ ($\text{dmpe} = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}$ ($\text{X} = \text{Cl}, \text{I}$) 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 cm^{-1} for $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{Cl}]^+$ to 6.26 cm^{-1} for $\text{Cr}(\text{dmpe})_2(\text{CN})\text{I}$.

Since the initial demonstration of magnetic bistability in $\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{CO}_2)_{16}(\text{H}_2\text{O})_4$,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 value³ 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 $U_{\text{eff}} = 33 \text{ cm}^{-1}$.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 $[\text{ReX}_6]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) and high-field

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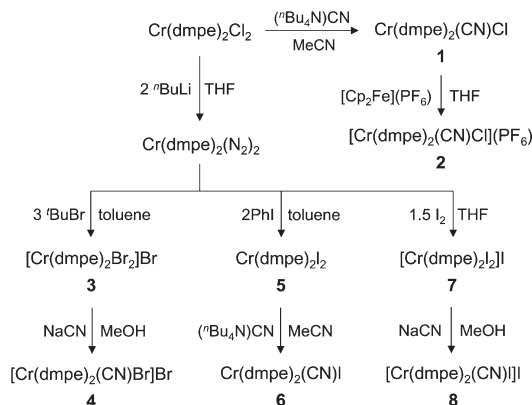
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Scheme 1. Synthesis of $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}]^{1+/0}$ Complexes

EPR studies of Tp^*NiX (Tp^* = hydrotris(3,5-dimethylpyrazole)borate; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $(\text{tpa})\text{MnX}_2$ (tpa = tris-2-picolylamine; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) 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 $\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}$ ($\text{X} = \text{Cl}, \text{I}$) and $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}]^+$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were generated, starting from $\text{Cr}(\text{dmpe})_2\text{Cl}_2$,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 $\text{Cr}(\text{dmpe})_2(\text{CN})\text{Cl}$ (**1**) was isolated from the reaction of $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ with $(n\text{Bu}_4\text{N})\text{CN}$ and was subsequently converted into $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{Cl}](\text{PF}_6)$ (**2**) via chemical oxidation with $[\text{Cp}_2\text{Fe}](\text{PF}_6)$.¹¹ Repeating the reaction with $[\text{Cp}_2\text{Fe}](\text{BPh}_4)$ afforded the analogous compound $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{Cl}](\text{BPh}_4)$ (**2'**). In an attempt to access the Cr^{II} iodo and bromo complexes, $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ was reduced to $\text{Cr}(\text{dmpe})_2(\text{N}_2)_2$ using 2 equiv of *n*-butyllithium.¹² Oxidation of $\text{Cr}(\text{dmpe})_2(\text{N}_2)_2$ with 2 equiv of iodobenzene then afforded $\text{Cr}(\text{dmpe})_2\text{I}_2$ (**5**),¹³ while analogous reactions employing bromobenzene or *t*-butylbromide were found to yield $[\text{Cr}(\text{dmpe})_2\text{Br}_2]\text{Br}$ (**3**).¹¹ Further oxidation of $\text{Cr}(\text{dmpe})_2(\text{N}_2)_2$ to $[\text{Cr}(\text{dmpe})_2\text{I}_2]\text{I}$ (**7**) can be accomplished using 1.5 equiv of I_2 .¹¹ Reaction of $(n\text{Bu}_4\text{N})\text{CN}$ with $\text{Cr}(\text{dmpe})_2\text{I}_2$ or NaCN with $[\text{Cr}(\text{dmpe})_2\text{X}_2]\text{X}$ ($\text{X} = \text{Br}, \text{I}$) affords the mixed

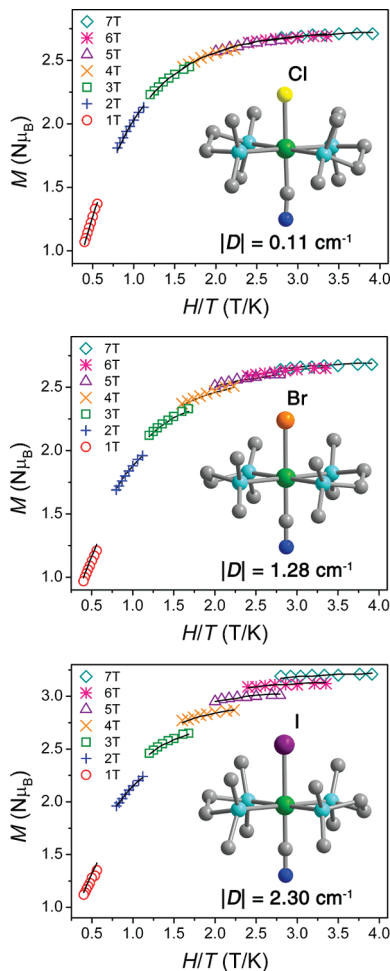


Figure 1. Structures and reduced magnetization data for the octahedral complexes $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}]^+$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), as observed in **2**, **4**, and **8**. Green, purple, orange, yellow, light blue, blue, and gray spheres represent Cr, I, 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).

cyanide-halide compounds $\text{Cr}(\text{dmpe})_2(\text{CN})\text{I}$ (**6**) and $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}](\text{X})$ (**4** and **8**) in high yield.

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 $[\text{Cr}(\text{dmpe})_2\text{X}_2]^+$, the mean Cr–X distance increases from 2.293(4) Å for $\text{X} = \text{Cl}$ ¹⁴ to 2.457(2) Å for $\text{X} = \text{Br}$ to 2.662(5) Å for $\text{X} = \text{I}$. This trend is conserved in the structures of the $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}]^+$ complexes, which display a mean Cr–X distance of 2.452(2) Å for $\text{X} = \text{Cl}$ and Cr–X distances of 2.552(3) Å for $\text{X} = \text{Br}$ and 2.663(2) Å for $\text{X} = \text{I}$. 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 $\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}$ 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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(13) The reaction between $\text{Cr}(\text{dmpe})_3$ and excess MeI was reported to give $\text{Cr}(\text{dmpe})_2\text{I}_2$; however, the product was not crystallographically characterized, and the green color of the solid suggests that it is actually $[\text{Cr}(\text{dmpe})_2\text{I}_2]\text{I}$. As isolated here, $\text{Cr}(\text{dmpe})_2\text{I}_2$ is a brown compound. (a) Cloke, F. G. N.; Fyne, P. J.; Gibson, V. C.; Green, M. L. H.; Ledoux, M. J.; Perutz, R. N.; Dix, A.; Gourdon, A.; Prout, K. *J. Organomet. Chem.* **1984**, *277*, 61. (b) Halepoto, D. M.; Holt, D. G. L.; Larkworthy, L. F.; Povey, D. C.; Smith, G. W.; Leigh, G. J. *Polyhedron* **1989**, *8*, 1821.

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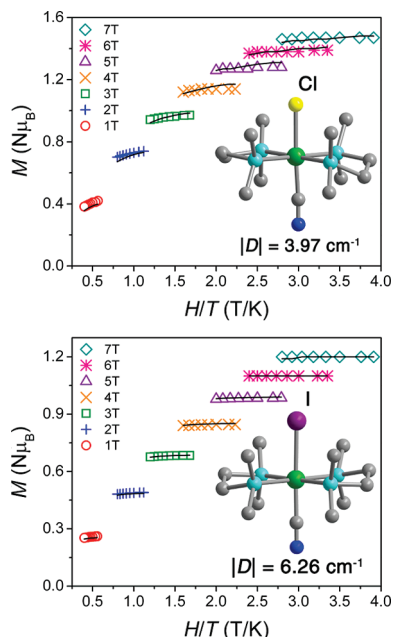


Figure 2. Structures and reduced magnetization data for the octahedral complexes $\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}$ ($\text{X} = \text{Cl}$, I), as observed in **1** and **6**. Purple, green, yellow, light blue, blue, and gray spheres represent I, Cr, Cl, P, N, and C atoms, respectively; H 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 $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{Cl}]^+$, wherein the isofield lines show little deviation from the Brillouin function for an $S = 3/2$ ground state, leading to $|D| = 0.11 \text{ cm}^{-1}$. 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 $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{I}]^+$ 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

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

compound	μ_{eff} (μ_B) ^a	g	$ D $ (cm^{-1})
$[\text{Cr}(\text{dmpe})_2(\text{CN})\text{Cl}](\text{PF}_6)$ (2)	3.64	1.82	0.11
$[\text{Cr}(\text{dmpe})_2(\text{CN})\text{Br}]\text{Br}$ (4)	3.69	1.84	1.28
$[\text{Cr}(\text{dmpe})_2(\text{CN})\text{I}]\text{I}$ (8)	3.87	1.82	2.30
$\text{Cr}(\text{dmpe})_2(\text{CN})\text{Cl}$ (1)	2.79	1.66	3.97
$\text{Cr}(\text{dmpe})_2(\text{CN})\text{I}$ (6)	2.67	1.61	6.26

^a At 298 K.

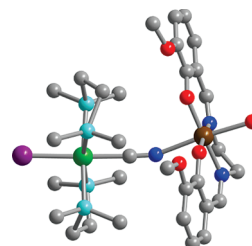


Figure 3. Structure of the cyano-bridged cluster $[(\text{H}_2\text{O})(\text{salen}(\text{OMe})_2)\text{Mn}(\mu\text{-NC})\text{Cr}(\text{dmpe})_2\text{I}]_2^{2+}$, as observed in **9**. Purple, brown, green, light blue, red, blue, and gray spheres represent I, Mn, Cr, P, O, N, and C atoms, respectively;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

complex $\text{Cr}(\text{dmpe})_2(\text{CN})\text{Cl}$ exhibits a large zero-field splitting, with $|D| = 3.97 \text{ cm}^{-1}$. Nevertheless, a substantial gain in anisotropy is again achieved through the substitution of chloride with iodide, resulting in $|D| = 6.26 \text{ cm}^{-1}$ for $\text{Cr}(\text{dmpe})_2(\text{CN})\text{I}$.

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 $[\text{L}_x^{\text{cap}}\text{M}(\text{solvent})_y]^{n+}$ (where L^{cap} represents a capping ligand) can be expected to give star-like clusters of formula $\{\text{L}_x^{\text{cap}}\text{M}[(\mu\text{-NC})\text{Cr}(\text{dmpe})_2\text{X}]_y\}^{n+/(n+y)+}$. Of greatest interest for this purpose will be the high-anisotropy iodo complexes $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{I}]^+$ ($S = 3/2$) and $\text{Cr}(\text{dmpe})_2(\text{CN})\text{I}$ ($S = 1$). As an initial example demonstrating cluster formation, the former species was found to react with $[(\text{salen}(\text{OMe})_2)\text{Mn}(\text{H}_2\text{O})](\text{ClO}_4)$ ($\text{H}_2\text{salen}(\text{OMe})_2 = N,N'$ -bis(3-methoxysalicylidene)ethyl-enediamine) to afford $[(\text{H}_2\text{O})(\text{salen}(\text{OMe})_2)\text{Mn}(\mu\text{-NC})\text{Cr}(\text{dmpe})_2\text{I}](\text{ClO}_4)_2$ (**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 $[\text{Cr}(\text{dmpe})_2\text{X}_2]^{0/1+}$ and $[\text{Cr}(\text{dmpe})_2(\text{CN})_2]^{0/1+}$. 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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