

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

Hemamala I. Karunadasa, Kristine D. Arquero, Louise A. Berben, and Jeffrey R. Long\*

*Department of Chemistry, University of California, Berkeley, California 94720-1460*

Received February 15, 2010

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  $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}]^+$  ( $\text{dmpe} = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$ ,  $\text{X} = \text{Cl, Br, I}$ ) and  $\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}$  ( $\text{X} = \text{Cl, I}$ ) 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  $0.11 \text{ cm}^{-1}$  for  $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{Cl}]^+$  to  $6.26 \text{ cm}^{-1}$  for  $\text{Cr}(\text{dmpe})_2(\text{CN})\text{I}$ .

Since the initial demonstration of magnetic bistability in  $\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{CO}_2)_{16}(\text{H}_2\text{O})_4$ ,<sup>1</sup> there has been considerable interest in the possibility of generating molecular clusters with higher blocking temperatures for a variety of potential applications.<sup>2</sup> 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<sup>3</sup> or a large magnetic anisotropy  $|D|$ .<sup>4</sup> 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  $D$ .<sup>5</sup> To date, however, the largest relaxation barrier that has been measured for a

cyano-bridged cluster is just  $U_{\text{eff}} = 33 \text{ cm}^{-1}$ .<sup>6</sup> 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.<sup>2</sup>

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.<sup>5b,c,6,7</sup> 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.<sup>8</sup> 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  $[\text{ReX}_6]^{2-}$  ( $\text{X} = \text{Cl, Br}$ ) and high-field

\*To whom correspondence should be addressed: E-mail: jrlong@berkeley.edu.

(1) (a) Sessoli, R.; Tsai, H. L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Foltling, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804. (b) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141.

(2) (a) Garanin, D. A.; Chudnovsky, E. M. *Phys. Rev. B* **1997**, *56*, 11102. (b) Leuenberger, M. N.; Loss, D. *Nature* **2001**, *410*, 789. (c) Stamp, P. C. E.; Gaita-Arino, A. *J. Mater. Chem.* **2009**, *19*, 1718.

(3) (a) Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hidai, M.; Fujishima, A.; Ohkoshi, S.; Hashimoto, K. *J. Am. Chem. Soc.* **2000**, *122*, 2952–2953. (b) Murugesu, M.; Habrych, M.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *J. Am. Chem. Soc.* **2004**, *126*, 4766. (c) Ako, A. M.; Hewitt, I. J.; Mereacre, V.; Clérac, R.; Wernsdorfer, W.; Anson, C. E.; Powell, A. K. *Angew. Chem., Int. Ed.* **2006**, *45*, 4926.

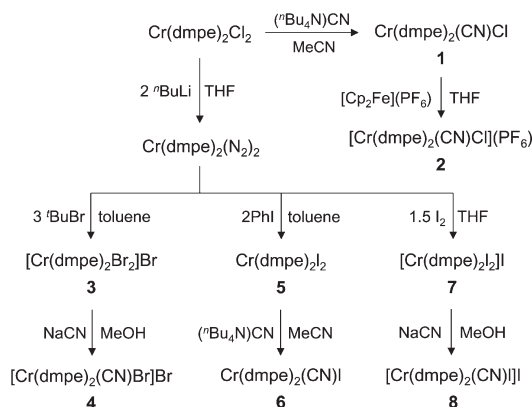
(4) (a) Gatteschi, D.; Sorace, L. *J. Solid State Chem.* **2001**, *159*, 253. (b) Oshio, H.; Nakano, M. *Chem.—Eur. J.* **2005**, *11*, 5178. (c) Milios, C. J.; Vinslava, A.; Wernsdorfer, W.; Moggach, S.; Parsons, S.; Perlepes, S. P.; Christou, G.; Brechin, E. K. *J. Am. Chem. Soc.* **2007**, *129*, 2754. (d) Cirera, J.; Ruiz, E.; Alvarez, S.; Neese, F.; Kortus, J. *Chem.—Eur. J.* **2009**, *15*, 4078.

(5) (a) Sculler, A.; Mallah, T.; Verdager, M.; Nivorozhkin, A.; Tholence, J. L.; Veillet, P. *New J. Chem.* **1996**, *20*, 1. (b) Shores, M. P.; Sokol, J. J.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 2279. (c) Sokol, J. J.; Hee, A. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 7656. (d) Berlinguette, C. P.; Vaughn, D.; Cañada-Vilalta, C.; Galán-Mascarós, J. R.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1523. (e) Marvaud, V.; Decroix, C.; Sculler, A.; Guyard-Duhayon, C.; Vaissermann, J.; Gonnet, F.; Verdager, M. *Chem.—Eur. J.* **2003**, *9*, 1677. (f) Song, Y.; Zhang, P.; Ren, X.-M.; Shen, X.-F.; Li, Y.-Z.; You, X.-Z. *J. Am. Chem. Soc.* **2005**, *127*, 3708. (g) Li, D. F.; Parkin, S.; Wang, G. B.; Yee, G. T.; Prosvirin, A. V.; Holmes, S. M. *Inorg. Chem.* **2005**, *44*, 4903. (h) Harris, T. D.; Long, J. R. *Chem. Commun.* **2007**, 1360. (i) Schelter, E. J.; Karadas, F.; Avendano, C.; Wernsdorfer, W.; Dunbar, K. *J. Am. Chem. Soc.* **2007**, *129*, 8139. (j) Glaser, T.; Heidemeier, M.; Krickemeyer, E.; Bögge, H.; Stämmler, A.; Fröhlich, R.; Bill, E.; Schnack, J. *Inorg. Chem.* **2009**, *48*, 607.

(6) (a) Lim, J. H.; Yoon, J. H.; Kim, H. C.; Hong, C. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 7424. (b) Freedman, D. E.; Jenkins, D. M.; Iavarone, A. T.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 2884.

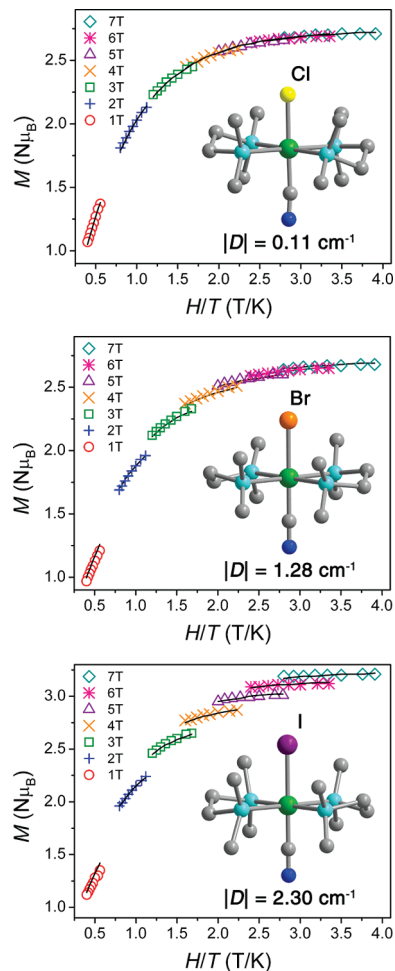
(7) (a) Schelter, E. J.; Prosvirin, A. V.; Dunbar, K. R. *J. Am. Chem. Soc.* **2004**, *126*, 15004. (b) Song, Y.; Zhang, P.; Ren, X.-M.; Shen, X.-F.; Li, Y.-Z.; You, X.-Z. *J. Am. Chem. Soc.* **2005**, *127*, 3708. (c) Yoon, J. H.; Lim, J. H.; Kim, H. C.; Hong, C. S. *Inorg. Chem.* **2006**, *45*, 9613. (d) Zhao, H.; Shatruk, M.; Prosvirin, A. V.; Dunbar, K. R. *Chem.—Eur. J.* **2007**, *13*, 6573.

(8) Karunadasa, H. I.; Long, J. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 738.

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

EPR studies of  $\text{Tp}^*\text{NiX}$  ( $\text{Tp}^*$  = hydrotris(3,5-dimethylpyrazole)borate;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and  $(\text{tpa})\text{MnX}_2$  ( $\text{tpa}$  = 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.<sup>9</sup> Here, we demonstrate that this effect can extend to octahedral  $\text{Cr}^{\text{II}}$  and  $\text{Cr}^{\text{III}}$  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  $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ ,<sup>10</sup> 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  $[\text{Cp}_2\text{Fe}](\text{PF}_6)$ .<sup>11</sup> 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  $\text{Cr}^{\text{II}}$  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.<sup>12</sup> 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),<sup>13</sup> while analogous reactions employing bromobenzene or *t*-butylbromide were found to yield  $[\text{Cr}(\text{dmpe})_2\text{Br}_2]\text{Br}$  (3).<sup>11</sup> 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  $\text{I}_2$ .<sup>11</sup> Reaction of  $(n\text{Bu}_4\text{N})\text{CN}$  with  $\text{Cr}(\text{dmpe})_2\text{I}_2$  or  $\text{NaCN}$  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  $\text{X} = \text{Cl}$ <sup>14</sup> 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

(9) (a) Busey, R. H.; Sonder, E. *J. Chem. Phys.* **1962**, *36*, 93. (b) Desrochers, P. J.; Telsner, J.; Zvyagin, S. A.; Ozarowski, A.; Krzystek, J.; Vivic, D. A. *Inorg. Chem.* **2006**, *45*, 8930. (c) Duboc, C.; Phoeung, T.; Zein, S.; Pecaut, J.; Collomb, M.-N.; Neese, F. *Inorg. Chem.* **2007**, *46*, 4905.

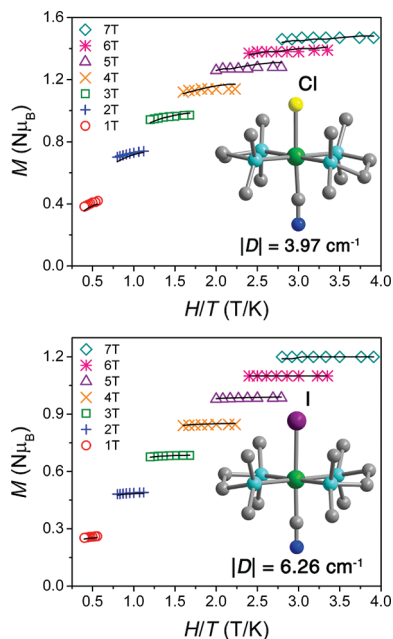
(10) Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 1339.

(11) Suzuki, T.; Kashiwabara, K.; Usami, T.; Imamura, T.; Kiki, M.; Fujita, J.; Kaizaki, S. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1055.

(12) Berben, L. A.; Kozimor, S. A. *Inorg. Chem.* **2008**, *47*, 4639.

(13) The reaction between  $\text{Cr}(\text{dmpe})_3$  and excess  $\text{MeI}$  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.

(14) Salt, J. E.; Girolami, G. S.; Wilkinson, G.; Motevalli, M.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 685.



**Figure 2.** Structures and reduced magnetization data for the octahedral complexes  $\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}$  ( $\text{X} = \text{Cl}, \text{I}$ ), 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  $2.83 \mu_{\text{B}}$  for isolated  $\text{Cr}^{\text{III}}$  ( $S = 3/2$ ) and low-spin  $\text{Cr}^{\text{II}}$  ( $S = 1$ ) 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<sup>5b</sup> 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.

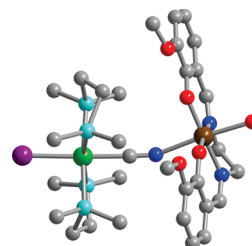
The magnetization data for the  $\text{Cr}^{\text{III}}$  complexes are depicted in Figure 1. Typically, an octahedrally coordinated metal center with a  $t_{2g}^3$  configuration has an essentially spherical electron distribution, leading to a  $D$  value near zero. This situation is borne out in the 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  $2.30 \text{ cm}^{-1}$ , 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  $\text{Cr}^{\text{III}}$  complex.<sup>15</sup>

As shown in Figure 2, the magnetization data for the  $\text{Cr}^{\text{II}}$  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  $[\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}]^+$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and  $\text{Cr}(\text{dmpe})_2(\text{CN})\text{X}$  ( $\text{X} = \text{Cl}, \text{I}$ )

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

<sup>a</sup> At 298 K.



**Figure 3.** Structure of the cyano-bridged cluster  $[(\text{H}_2\text{O})(\text{salen}(\text{OMe})_2)\text{Mn}(\mu\text{-NC})\text{Cr}(\text{dmpe})_2]^{2+}$ , 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  $\text{L}^{\text{cap}}$  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  $[\text{Cr}(\text{dmpe})_2\text{X}]^{0/1+}$  and  $[\text{Cr}(\text{dmpe})_2(\text{CN})]^{0/1+}$ . 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.

**Acknowledgment.** This research was funded by NSF Grant No. CHE-0617063. We thank Tyco Electronics for partial support of H.I.K.; Drs. F. J. Hollander, A. G. Oliver, and S. J. Teat for experimental assistance; and Dr. S. A. Kozimor for helpful discussions.

**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>.

(15) (a) Solano-Peralta, A.; Sosa-Torres, M. E.; Flores-Alamo, M.; El-Mkami, H.; Smith, G. M.; Toscano, R. A.; Nakamura, T. *Dalton Trans.* **2004**, 2444. (b) Rebilly, J.-N.; Catala, L.; Charron, G.; Rogez, G.; Riviere, E.; Guillot, R.; Thuery, P.; Barra, A.-L.; Mallah, T. *Dalton Trans.* **2006**, 2818.