

**The Myth of Cyanide Always Being a Strong-Field Ligand: Synthesis and Structural Characterization of Homoleptic  $S = 2$  Pentacyanochromate(II),  $[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$ , and Nonacyanodichromate(II),  $[\text{Cr}_2^{\text{II}}(\text{CN})_9]^{5-}$ \*\***

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Dedicated to Harry B. Gray

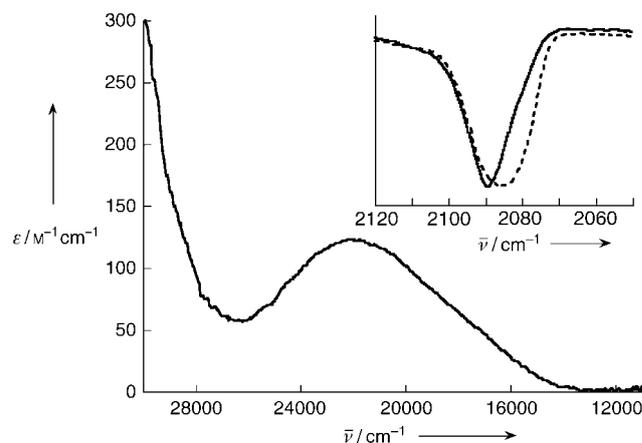
Crystal field theory has provided detailed insight into the structure, spectroscopic, and magnetic properties of transi-

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tion-metal coordination complexes since its inception. The empirical genesis of the spectrochemical series, which identifies strong  $\pi$ -acceptor ligands as strong-field ligands, is understood on the basis of molecular orbital theory. Cyanide is deeply entrenched as being a strong-field ligand, as revealed by low-spin ground states for its homoleptic complexes: for example,  $[\text{M}(\text{CN})_6]^{n-}$  ( $n = 2, 3, 4$ )<sup>[1]</sup> and  $[\text{M}^{\text{II}}(\text{CN})_5]^{3-}$  ( $\text{M} = \text{Co}, \text{Ni}$ ).<sup>[2]</sup> Furthermore, they do not violate the  $18e^-$  rule by exceeding 18 electrons about the metal center M. The only high-spin example is the unusual  $13e^- S = 5/2$  complex  $[\text{Mn}^{\text{II}}(\text{CN})_4]^{2-}$ ,<sup>[3]</sup> which being tetrahedral has a substantially reduced crystal-field stabilization energy,  $\Delta$ , of  $4/9$  the value expected for the  $17e^- S = 1/2$  complex  $[\text{Mn}^{\text{II}}(\text{CN})_6]^{4-}$ . As part of our ongoing studies toward molecule-based magnets,<sup>[4]</sup> we sought to prepare Prussian blue structured magnets based upon  $[\text{Cr}^{\text{II}}(\text{CN})_6]^{4-}$  for comparison with those derived from  $[\text{Cr}^{\text{III}}(\text{CN})_6]^{3-}$ , which magnetically order at temperatures as high as  $100^\circ\text{C}$  (approximately).<sup>[5]</sup>

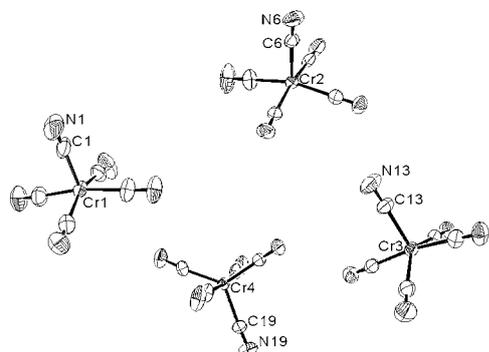
$\text{K}_4[\text{Cr}^{\text{II}}(\text{CN})_6]$  has been prepared from aqueous media, but owing to the lability of the  $d^4 \text{Cr}^{\text{II}}$  state, excess cyanide is required in solution. Despite undergoing a Jahn–Teller distortion,  $16e^- \text{K}_4[\text{Cr}^{\text{II}}(\text{CN})_6]$  is low-spin  $S = 1$ . Owing to the need for excess cyanide, aqueous routes to Prussian blue structured materials would be unproductive, so we sought a nonaqueous source of  $[\text{Cr}^{\text{II}}(\text{CN})_6]^{4-}$  and targeted  $(\text{NEt}_4)_4-[\text{Cr}^{\text{II}}(\text{CN})_6]$ . The reaction of either  $\text{Cr}_2^{\text{II}}(\text{OAc})_4$ <sup>[6]</sup> or  $[\text{Cr}^{\text{II}}(\text{MeCN})_4(\text{BF}_4)_2]$ <sup>[7]</sup> with as much as a twofold excess of  $\text{NEt}_4\text{CN}$  in MeCN led to dark purple block crystals of composition  $(\text{NEt}_4)_3[\text{Cr}^{\text{II}}(\text{CN})_5] \cdot \text{MeCN} \cdot 1/8 \text{THF}$  (**1**). In the solid state **1** exhibits a broad  $\nu_{\text{C}\equiv\text{N}}$  absorption at  $2086 \text{cm}^{-1}$  (half-width at half height:  $9.2 \text{cm}^{-1}$ , see Figure 1). This is comparable to  $2080 \text{cm}^{-1}$  reported for  $[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ ,<sup>[8]</sup> but differs from the absorptions at  $2095 (\text{m})$ ,  $2111 (\text{vs})$ , and  $2123 \text{cm}^{-1} (\text{vs})$  reported for  $[\text{Ni}^{\text{II}}(\text{CN})_5]^{3-}$ ,<sup>[9]</sup> and is higher in energy than the broad  $\nu_{\text{C}\equiv\text{N}}$  absorption at  $2020 \text{cm}^{-1}$  observed for  $\text{K}_4[\text{Cr}^{\text{II}}(\text{CN})_6]$ .<sup>[10]</sup> The electronic spectrum ( $5000\text{--}30000 \text{cm}^{-1}$ ) of a solution of  $(\text{NEt}_4)_3[\text{Cr}^{\text{II}}(\text{CN})_5]$  ( $1.30 \text{mM}$ ) in MeCN comprises an absorption at  $22120 \text{cm}^{-1}$  ( $\lambda = 452 \text{nm}$ ,  $\epsilon = 122 \text{M}^{-1} \text{cm}^{-1}$ ; Figure 1). However, **1** does not obey Beer's



**Figure 1.** Electronic absorption spectrum of  $(\text{NEt}_4)_3[\text{Cr}^{\text{II}}(\text{CN})_5]$  ( $1.30 \text{mM}$  in MeCN). Inset:  $\nu_{\text{C}\equiv\text{N}}$  vibrational spectra of  $(\text{NEt}_4)_3-[\text{Cr}^{\text{II}}(\text{CN})_5]$  (----) and  $(\text{NEt}_4)_3[\text{Cr}^{\text{II}}(\text{CN})_5][\text{Cr}_2^{\text{II}}(\text{CN})_9]$  (—) in KBr.

law, as the electronic absorption spectrum of the solution changes as a function of cyanide concentration (the details of this equilibrium are under investigation).

The asymmetric unit cell<sup>[11]</sup> contains four  $[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$  units (Figure 2), twelve  $\text{Et}_4\text{N}^+$  cations, as well as four



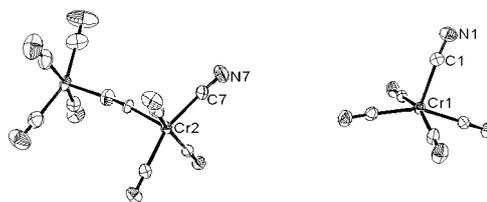
**Figure 2.** ORTEP labeling diagram of  $(\text{NEt}_4)_3[\text{Cr}^{\text{II}}(\text{CN})_5] \cdot \text{MeCN} \cdot \frac{1}{8} \text{THF}$  (**1**; 50% probability level; cations and solvent molecules are omitted for clarity).

molecules of MeCN and half a molecule of THF of solvation, which arises from the diffusion of THF into a solution of **1** in MeCN to obtain the crystals. Each  $\text{Cr}^{\text{II}}$  center is pentacoordinate, with both square-pyramidal and distorted trigonal bipyramid structures present. The low barrier for interconversion between the limiting square-pyramidal and trigonal bipyramid five-coordinate structures leads to the formation of several local structures,<sup>[12]</sup> as has been reported for  $[\text{Ni}^{\text{II}}(\text{CN})_5]^{3-}$  even within the same unit cell.<sup>[13]</sup> For the square-pyramidal structures the apical Cr–C bond lengths range from 2.229(5) to 2.238(6) Å (av 2.23 Å) and the basal Cr–C bond lengths range from 2.110(7) to 2.135(5) Å (av 2.12 Å). The  $C_{\text{apical}}\text{--Cr--}C_{\text{basal}}$  angle ranges from 93.6(2) to 108.2(3)° (av 99.0°), and the *trans*  $C_{\text{basal}}\text{--Cr--}C_{\text{basal}}$  angle ranges from 155.9(2) to 166.9(2)° (av 161.9°). The Cr atom lies 0.33 Å above the plane formed by the four basal carbon atoms. These values are similar to those found for  $[\text{M}^{\text{II}}(\text{CN})_5]^{3-}$  (M = Co, Ni; see Table 1),<sup>[14]</sup> except that the Cr–C bonds are the longest, as expected for an early first-row transition metal. In the distorted trigonal bipyramidal structure the axial Cr–C bond lengths range from 2.094(6) to 2.118(6) Å (av 2.11 Å) while the equatorial Cr–C bond lengths range from 2.113(6)

to 2.188(5) Å (av 2.15 Å). The axial Cr–C bonds are shorter than the equatorial Cr–C bonds, as reported for the distorted trigonal bipyramidal  $[\text{Ni}^{\text{II}}(\text{CN})_5]^{3-}$  structure.<sup>[13]</sup>

Owing to formation of solely the pentacyanide complex even in the presence of excess cyanide ion, the reaction was carried out with 5 equivalents of  $\text{CN}^-$  per  $\text{Cr}^{\text{II}}$  ion, and dark brown needlelike crystals of  $(\text{NEt}_4)_8[\text{Cr}^{\text{II}}(\text{CN})_5][\text{Cr}_2^{\text{II}}(\text{CN})_9] \cdot 2\text{MeCN}$  (**2**) were isolated. In the solid state **2** exhibits a broad  $\nu_{\text{C}\equiv\text{N}}$  absorption at 2090  $\text{cm}^{-1}$  (half-width at half height: 6.9  $\text{cm}^{-1}$ ), which is comparable to that observed for  $(\text{NEt}_4)_3[\text{Cr}^{\text{II}}(\text{CN})_5]$  (Figure 1). Furthermore, similar to  $(\text{NEt}_4)_3[\text{Cr}^{\text{II}}(\text{CN})_5]$ , **2** also does not obey Beer's law (the details of this equilibrium are also under investigation).

The asymmetric unit cell<sup>[15]</sup> of **2** contains one  $[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$  unit, one  $[\text{Cr}_2^{\text{II}}(\text{CN})_9]^{5-}$  unit (see Figure 3), eight  $\text{Et}_4\text{N}^+$



**Figure 3.** ORTEP labeling diagram of  $(\text{NEt}_4)_8[\text{Cr}^{\text{II}}(\text{CN})_5][\text{Cr}_2^{\text{II}}(\text{CN})_9] \cdot 2\text{MeCN}$  (**2**; 50% probability level; cations and solvent molecules are omitted for clarity).

cations, and two molecules of MeCN of solvation. Each  $\text{Cr}^{\text{II}}$  center is pentacoordinate, with a distorted square-pyramidal local  $C_{4v}$  symmetry. The Cr center in the distorted square-pyramidal  $[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$  unit lies 0.40 Å above the plane formed by the four basal carbon atoms, and the apical Cr–C bond length is 2.23 Å, while the average basal Cr–C bond length is 2.12 Å.  $[\text{Cr}_2^{\text{II}}(\text{CN})_9]^{5-}$  is composed of two square-pyramidal  $[\text{Cr}^{\text{II}}(\text{CN})_4]^{2-}$  moieties bridged by a cyanide ion. The bridging cyanide is disordered, with average Cr–C and Cr–N bond lengths of 2.20 Å observed. The Cr center lies 0.37 Å above the plane formed by the four basal carbon atoms, and the basal Cr–C bond length is 2.13 Å on average. To the best of our knowledge, this structural motif has not been previously reported.

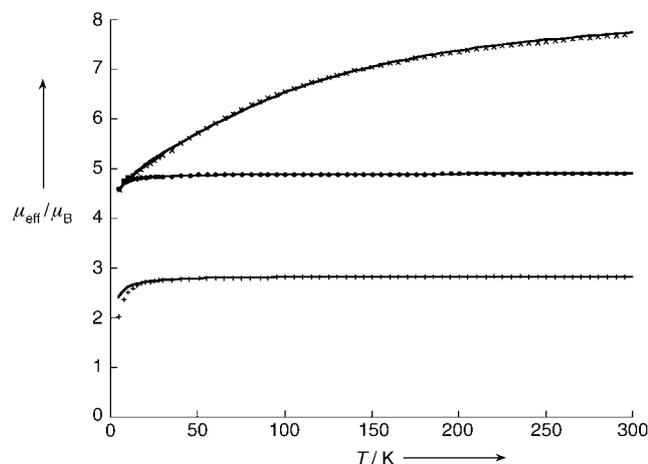
The magnetic susceptibility,  $\chi$ , was measured for both  $(\text{NEt}_4)_3[\text{Cr}^{\text{II}}(\text{CN})_5]$  and  $(\text{NEt}_4)_8[\text{Cr}^{\text{II}}(\text{CN})_5][\text{Cr}_2^{\text{II}}(\text{CN})_9]$  from 5 to 300 K.  $(\text{NEt}_4)_3[\text{Cr}^{\text{II}}(\text{CN})_5]$  has an effective room temper-

**Table 1:** Comparison of geometries of  $d^4$ ,  $d^7$ , and  $d^8$  square-pyramidal, distorted square-pyramidal, and distorted trigonal bipyramid  $[\text{M}^{\text{II}}(\text{CN})_5]^{3-}$  (M = Cr, Co, Ni) structures.

	$[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$ ( <b>1</b> )	$[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$ ( <b>2</b> )	$[\text{Cr}_2^{\text{II}}(\text{CN})_9]^{5-}$ ( <b>2</b> )	$[\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$ <sup>[14]</sup>	$[\text{Ni}^{\text{II}}(\text{CN})_5]^{3-}$ <sup>[14]</sup>
$d^n$	4	4	4	7	8
$S$	2	2	[a]	1/2	0
$M\text{--}C_{\text{apical}}$ [Å]	2.23	2.23	2.20	2.010	2.140
$M\text{--}C_{\text{basal}}$ [Å] (av)	2.12	2.12	2.13	1.894	1.890
<i>trans</i> $C_{\text{basal}}\text{--}M\text{--}C_{\text{basal}}$ [°] (av)	161.9	157.8	158.9	164.7	161.5
$C_{\text{apical}}\text{--}M\text{--}C_{\text{basal}}$ [°] (av)	98.96	100.7	100.5	97.60	99.00
deviation (M–basal plane) [Å]	0.33	0.40	0.37	0.25	0.30
$M\text{--}C_{\text{axial}}$ [Å]	2.11	–	–	–	1.84 <sup>[13a]</sup>
$M\text{--}C_{\text{equatorial}}$ [Å]	2.15	–	–	–	1.94 <sup>[13a]</sup>

[a] Singlet ground state, nonet excited state.

ature magnetic moment,  $\mu_{\text{eff}} = (8\chi T)^{1/2}$ , of  $4.90 \mu_{\text{B}}$  (corrected for temperature-independent paramagnetism (TIP); see Figure 4). This value significantly exceeds the expected spin-only moment of  $2.83 \mu_{\text{B}}$  for  $S=1$  low-spin  $\text{Cr}^{\text{II}}$ , but it is in



**Figure 4.** Temperature dependence of the effective magnetic moment,  $\mu_{\text{eff}} = (8\chi T)^{1/2}$ , of  $\text{K}_4[\text{Cr}^{\text{II}}(\text{CN})_6]$  (+),  $(\text{NEt}_4)_3[\text{Cr}^{\text{II}}(\text{CN})_5]$  (●), and  $(\text{NEt}_4)_8[\text{Cr}^{\text{II}}(\text{CN})_5][\text{Cr}_2^{\text{II}}(\text{CN})_9]$  (×). The solid lines are fits, as discussed in the text.

excellent agreement with the expected spin-only value of  $4.90 \mu_{\text{B}}$  for  $S=2$  high-spin  $\text{Cr}^{\text{II}}$ . Above 5 K,  $\chi(T)$  could be fitted to the Curie–Weiss expression,  $\chi \propto (T-\theta)^{-1}$ , with  $g=2.00$ ,  $\theta=-0.79$  K, and a TIP value of  $50 \times 10^{-6} \text{ emu mol}^{-1}$ . In contrast, the room temperature  $\mu_{\text{eff}}$  value for  $\text{K}_4[\text{Cr}^{\text{II}}(\text{CN})_6]$  is  $2.82 \mu_{\text{B}}$  (corrected for TIP). Above 5 K,  $\chi(T)$  could also be fitted to the Curie–Weiss expression with  $g=2.00$ ,  $\theta=-1.9$  K, and a TIP value of  $150 \times 10^{-6} \text{ emu mol}^{-1}$  (Figure 4). The room temperature  $\mu_{\text{eff}}$  value is consistent with the low-spin  $S=1$  ground state previously reported.<sup>[16]</sup> Hence,  $[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$  is a rare example of a high-spin homoleptic cyanide complex.

The magnetic behavior of  $(\text{NEt}_4)_8[\text{Cr}^{\text{II}}(\text{CN})_5][\text{Cr}_2^{\text{II}}(\text{CN})_9]$  is more complex (Figure 4) as a result of contributions from  $[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$  and dinuclear  $[\text{Cr}_2^{\text{II}}(\text{CN})_9]^{5-}$ . The observed data can be modeled with an  $S=2$  Curie–Weiss expression and a Bleaney–Bower-like  $S=2$  term,<sup>[17]</sup> with  $g=2.00$ ,  $J/k=-19.1$  K,  $\theta=-0.79$  K, and a TIP value of  $150 \times 10^{-6} \text{ emu mol}^{-1}$ . Hence, **2** exhibits moderate intradimer anti-ferromagnetic coupling of  $-19.1$  K ( $-13.3 \text{ cm}^{-1}$ ), and the nonet excited state lies  $266 \text{ cm}^{-1}$  ( $0.76 \text{ kcal mol}^{-1}$ ) above the singlet ground state.

Formation of  $[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$  and  $[\text{Cr}_2^{\text{II}}(\text{CN})_9]^{5-}$ , but not the sought  $(\text{NEt}_4)_4[\text{Cr}^{\text{II}}(\text{CN})_6]$ , is quite surprising as  $\text{K}_4[\text{Cr}^{\text{II}}(\text{CN})_6]$  as well as  $\text{Na}_4[\text{Cr}^{\text{II}}(\text{CN})_6]$  are known low-spin octahedral compounds.<sup>[10,18]</sup> Furthermore, why does  $(\text{NEt}_4)_3[\text{Cr}^{\text{II}}(\text{CN})_5]$ , but not  $(\text{NEt}_4)_4[\text{Cr}^{\text{II}}(\text{CN})_6]$ , form in the presence of excess cyanide? We attribute the formation of  $[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$  to the initial formation of  $[\text{Cr}^{\text{II}}(\text{CN})_6]^{4-}$ , which is expected to have a reduced  $\Delta(\text{Cr}^{\text{II}})$  value with respect to  $\Delta(\text{Cr}^{\text{III}})$  and which makes a high-spin state more accessible. High-spin  $t_{2g}^3 e_g^1 [\text{Cr}^{\text{II}}(\text{CN})_6]^{4-}$  would have an electron in an antibonding orbital that weakens the  $\text{Cr}^{\text{II}}\text{--C}$  bonds and destabilizes the system, and when the large tetranegative charge is consid-

ered—although,  $(\text{NEt}_4)_4[\text{Fe}^{\text{II}}(\text{CN})_6]$  is known to have a shorter  $\text{M}\text{--C}$  bond<sup>[19]</sup>—loss of a cyanide ion is favored to form the observed  $[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$  species. Presumably  $\text{A}_4[\text{Cr}^{\text{II}}(\text{CN})_6]$  ( $\text{A}=\text{Na}, \text{K}$ ) is stabilized through electrostatic interactions between the alkali-metal cation (and water molecules) and the nitrogen centers of the cyanide units.

### Experimental Section

**1:** In a DryBox ( $<0.5$  ppm  $\text{O}_2$ ),  $\text{Cr}_2^{\text{II}}(\text{OAc})_4$  (274.8 mg, 0.8078 mmol) was dissolved in deoxygenated MeCN (50 mL) to give an orange–red solution, which was then added dropwise to a stirring colorless solution of  $\text{NEt}_4\text{CN}$  (1.510 g, 9.563 mmol) in MeCN (50 mL). After stirring for 30 min, the dark purple solution was filtered and concentrated to 20 mL under reduced pressure. Dark purple crystalline blocks were obtained by diffusion of THF (yield: 62%) and characterized by single-crystal X-ray diffraction. The crystallographic sample was maintained in contact with the mother liquor to prevent solvent loss. Thermogravimetric analysis showed the sample was stable up to  $160^\circ\text{C}$  and could be desolvated at lower temperatures (i.e. heating at  $110^\circ\text{C}$  under reduced pressure) to form the desolvated  $(\text{NEt}_4)_3[\text{Cr}^{\text{II}}(\text{CN})_5]$ . Selected IR data (KBr):  $\tilde{\nu}=2986$  (s), 2950 (m), 2892 (w), 2086 (s), 1488 (s), 1461 (s), 1396 (s), 1375 (w), 1311 (w), 1186 (m), 1175 (s), 1080 (w), 1055 (w), 1035 (m), 1005 (s),  $787 \text{ cm}^{-1}$  (s).

**2:**  $\text{Cr}_2^{\text{II}}(\text{OAc})_4$  (55.94 mg, 0.1644 mmol) dissolved in MeCN (20 mL) was added dropwise to a solution of  $\text{NEt}_4\text{CN}$  (256.3 mg, 1.640 mmol) in MeCN (20 mL). After stirring for 30 min, the reddish purple solution was filtered and concentrated to 15 mL under reduced pressure. Brown needlelike crystals were obtained by diffusion of THF (yield: 24%) and characterized by single-crystal X-ray diffraction. The crystallographic sample was maintained in contact with the mother liquor to prevent solvent loss. Selected IR data (KBr):  $\tilde{\nu}=2986$  (s), 2949 (m), 2894 (w), 2248 (w), 2090 (s), 1484 (s), 1461 (s), 1396 (s), 1377 (w), 1310 (w), 1185 (m), 1175 (s), 1080 (w), 1057 (w), 1036 (m), 1005 (s),  $789 \text{ cm}^{-1}$  (s).

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- [11] Crystal data for  $(\text{NEt}_4)_3[\text{Cr}^{\text{II}}(\text{CN})_5]\cdot\text{MeCN}\cdot\frac{1}{8}\text{THF}$  (**1**):  $\text{C}_{126}\text{H}_{256}\text{Cr}_4\text{N}_{36}\text{O}_{0.5}$  triclinic, space group:  $P\bar{1}$ ,  $a=17.8172(3)$  Å,

$b = 20.8318(6) \text{ \AA}$ ,  $c = 21.5756(5) \text{ \AA}$ ,  $\alpha = 87.6399(9)^\circ$ ,  $\beta = 84.4486(13)^\circ$ ,  $\gamma = 71.9031(14)^\circ$ ,  $V = 7575.7(3) \text{ \AA}^3$ ,  $Z = 2$ ,  $T = 150 \text{ K}$ ,  $\rho_{\text{calcd}} = 1.092 \text{ Mg m}^{-3}$ . The structure was solved by a combination of direct methods and heavy atoms using SIR 97. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients  $U(\text{H}) = 1.2U(\text{C})$  or  $1.5U(\text{C}_{\text{Me}})$ , and their coordinates were allowed to ride on their respective carbons using SHELXL97. The asymmetric unit contains four  $[\text{Cr}(\text{CN})_5]^{3-}$  and twelve  $[\text{NEt}_4]^+$  units, as well as four molecules of acetonitrile and half a molecule of tetrahydrofuran. Most of the cations and half of the acetonitrile units exhibit orientation disorder (50:50). Only one anion,  $[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$ , of the asymmetric unit exhibits orientation disorder in one of the cyanide ligands (C18–N18 and C18'–N18') on atom Cr4 (50:50). This is not surprising as both square-pyramidal and distorted trigonal bipyramid structures are present in the unit cell. The weighting scheme employed was  $w = 1/[\sigma^2(F_o^2) + (0.1366P)^2 + 10.5826P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ . The refinement converged to  $R1 = 0.0842$ ,  $wR2 = 0.218$ , and  $S = 1.036$  for 16467 reflections with  $1 > 2\sigma(I)$ , and  $R1 = 0.1396$ ,  $wR2 = 0.2649$ , and  $S = 1.036$  for 26638 unique reflections and 1831 parameters. The maximum  $\Delta/\sigma$  value in the final cycle of the least-squares treatment was zero, and the residual peaks on the final difference-Fourier map ranged from  $-0.504$  to  $1.677 \text{ e}^- \text{ \AA}^{-3}$ .

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[15] Crystal data for  $(\text{NEt}_4)_8[\text{Cr}^{\text{II}}(\text{CN})_5][\text{Cr}_2^{\text{II}}(\text{CN})_9] \cdot 2 \text{ MeCN}$  (**2**):  $\text{C}_{82}\text{H}_{166}\text{Cr}_3\text{N}_{24}$  triclinic, space group:  $P\bar{1}$ ,  $a = 10.2618(2) \text{ \AA}$ ,  $b = 22.4902(5) \text{ \AA}$ ,  $c = 23.4526(4) \text{ \AA}$ ,  $\alpha = 114.5636(8)^\circ$ ,  $\beta = 90.3961(11)^\circ$ ,  $\gamma = 101.8783(10)^\circ$ ,  $V = 4791.3(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $T = 150 \text{ K}$ ,  $\rho_{\text{calcd}} = 1.140 \text{ Mg m}^{-3}$ . The structure was solved by a combination of direct methods and heavy atoms using SIR 97.

All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients  $U(\text{H}) = 1.2U(\text{C})$  or  $1.5U(\text{C}_{\text{Me}})$ , and their coordinates were allowed to ride on their respective carbons using SHELXL97. There are two distinctly different anions,  $[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$  and  $[\text{Cr}_2^{\text{II}}(\text{CN})_9]^{5-}$ . Three out of the eight  $(\text{NEt}_4)^+$  cations exhibit unequal (67:33) orientation disorder. The asymmetric unit contains two noncoordinating molecules of acetonitrile. The weighting scheme employed was  $w = 1/[\sigma^2(F_o^2) + (0.0944P)^2 + 4.5597P]$  where  $P = (F_o^2 + 2F_c^2)/3$ . The refinement converged to  $R1 = 0.0671$ ,  $wR2 = 0.1662$ , and  $S = 1.019$  for 14333 reflections with  $1 > 2\sigma(I)$ , and  $R1 = 0.1131$ ,  $wR2 = 0.1971$ , and  $S = 1.019$  for 21857 unique reflections and 1138 parameters. The maximum  $\Delta/\sigma$  value in the final cycle of the least-squares treatment was zero, and the residual peaks on the final difference-Fourier map ranged from  $-0.595$  to  $1.286 \text{ e}^- \text{ \AA}^{-3}$ . CCDC-253631 (**1**) and 257172 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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[17] C. J. O'Connor, *Prog. Inorg. Chem.* **1982**, *29*, 203. The equation used for this binuclear spin 2–2 system is ( $\mathbf{H} = -2JS_1S_2$ ):

$$\chi = \frac{Ng^2\mu_B^2}{k(T-\theta)} \left[ \frac{2e^{kT} + 10e^{kT} + 28e^{kT} + 60e^{kT}}{(1+3e^{kT} + 5e^{kT} + 7e^{kT} + 9e^{kT})} + 2 \right],$$

with  $T$  = temperature,  $N$  = Avogadro's number,  $k$  = Boltzmann's constant,  $\mu_B$  = Bohr Magnetron,  $\theta$  = Weiss constant,  $J$  = coupling constant, and  $S$  = spin state.

[18] When the reaction was carried out in deoxygenated water in the presence of excess cyanide ion, the complex  $[\text{Cr}^{\text{II}}(\text{CN})_5]^{3-}$  formed ( $\nu_{\text{C}\equiv\text{N}} = 2089 \text{ cm}^{-1}$ ; half-width at half height:  $9.4 \text{ cm}^{-1}$ ).

[19] J. C. Eppich, K. J. Nelson, A. M. Arif, unpublished results.