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Linear Trichromium Complexes with the Anion of 2,6-Di(phenylimino)piperidine

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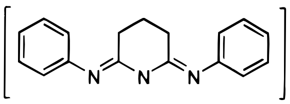
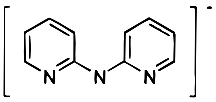
The anion of 2,6-di(phenylimino)piperidine (DPhIP) has been found to support linear chains of three metal atoms. Three new compounds, $[Cr_3(DPhIP)_4Cl]Cl\cdot 1.5CH_2Cl_2\cdot 0.5H_2O$ ($\mathbf{1}\cdot 1.5CH_2Cl_2\cdot 0.5H_2O$), $[Cr_3(DPhIP)_4(CH_3CN)](PF_6)_2\cdot H_2O\cdot 4CH_3CN$ ($\mathbf{2}\cdot H_2O\cdot 4CH_3CN$), and $[Cr_3(DPhIP)_4(F)(CH_3CN)](BF_4)_2\cdot 5CH_3CN$ ($\mathbf{3}\cdot 5CH_3CN$), have been synthesized and characterized by X-ray crystallography. Compound **1** has a linear chain of three chromium atoms arranged in an unsymmetrical fashion, with two of them forming a quadruply bonded unit (Cr−Cr distance 1.932(2) Å) and the third being a non-metal−metal-bound 5-coordinate unit (Cr···Cr distance 2.659(2) Å). The fifth coordination site is occupied by a chloride ion, and another chloride ion is located in the interstices of the crystal. The trimetal unit in compound **2** is structurally similar to that in compound **1** except that the axial ligand in **2** is a CH_3CN molecule. Compound **3** is an oxidation product prepared by reaction of **1** with $AgBF_4$. Here, a square pyramidal Cr^{III} unit, $FCrN_4$, and a Cr−Cr quadruply bonded (Cr−Cr distance 1.968(2) Å) unit, with an axially coordinated acetonitrile molecule, form the trichromium chain. The $Cr^{III}\cdots Cr^{II}$ separation of 2.594(2) Å in **3** is too long to be considered a bonding interaction.

Introduction

We recently reported[1] some dimetal and tetrametal complexes of Cr,[1a,c] Co,[1b] Mo,[1c,d] and Cu[1e] with the ligand DPhIP, which is the anion of di(phenylimino)piperidine, **I**. However, the original purpose in working with this ligand was to make linear trinuclear complexes. Previously, these linear chains were studied using the anion of 2,2′-dipyridylamine (dpa), **II**, for Cu,[2] Ru,[3] Rh,[3] Ni,[4,5] Co,[6] and Cr.[7] We felt that **I**, because of its electronic and structural differences from dpa, might lead to some new, interesting results. In this paper, we describe three trichromium compounds that do indeed differ from, but are akin to, the Cr_3 compounds previously obtained with **II**.



I



II

Experimental Section

All syntheses and manipulations were carried out under an atmosphere of nitrogen with standard Schlenk and glovebox techniques. The ligand H(DPhIP) was synthesized according to a literature method,[8] while $CrCl_2$, $TlPF_6$, and $AgBF_4$ were purchased from Strem Chemicals. All solvents were freshly distilled over suitable drying reagents under N_2. Infrared spectra were obtained from KBr pellets on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Elemental analyses were performed by Canadian Microanalytical Services Ltd.

Preparation of $[Cr_3(DPhIP)_4Cl]Cl$, 1. Compound **1** was synthesized by a reaction $CrCl_2$ (0.18 g, 1.5 mmol) with of Li(DPhIP), prepared by deprotonation of H(DPhIP) (0.53 g, 2.0 mmol) in THF (10 mL) with 1.0 M MeLi in THF (2.2 mL). The reaction mixture was heated to reflux for 6 h. The resulting yellow precipitate was collected by filtration (the greenish yellow filtrate was treated separately, as described under Results and Discussion), washed with 3 × 5 mL of THF, and

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10.1021/ic0001964 CCC: $19.00

Table 1. Crystal Data and Structure Refinement Details

	1·1.5CH_2Cl_2·0.5H_2O	**2**·4CH_3CN·H_2O	**3**·5CH_3CN
empirical formula	$C_{69.5}H_{68}N_{12}O_{0.5}Cl_5Cr_3$	$C_{78}H_{81}N_{17}OF_{12}P_2Cr_3$	$C_{80}H_{82}N_{18}F_9B_2Cr_3$
fw	1412.61	1718.54	1644.26
space group	$P2_1/c$	$P4/n$	$P4/n$
a, Å	14.2926(8)	14.1399(6)	14.1545(7)
b, Å	19.937(2)	14.1399(6)	14.1545(7)
c, Å	23.585(2)	20.8219(7)	19.873(1)
a, deg	90	90	90
β, deg	97.242(4)	90	90
γ, deg	90	90	90
V, Å^3	6667.0(9)	4163.1(3)	3981.6(4)
Z	4	2	2
diffractometer	Nonius FAST	Nonius FAST	Nonius FAST
T, K	213(2)	213(2)	213(2)
λ, Å	0.710 73	0.710 73	0.710 73
ρ(calcd), g cm^{-3}	1.407	1.371	1.372
μ(Mo Kα), cm^{-1}	7.33	5.04	4.79
$R1^{a,c}/R1^{a,d}$	0.084/0.111	0.065/0.070	0.064/0.073
$wR2^{b,c}/wR2^{b,d}$	0.196/0.231	0.198/0.208	0.163/0.177

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$. [c] Denotes value of the residual for only the reflections with $I > 2\sigma(I)$. [d] Denotes value of the residual for all reflections.

extracted with CH_2Cl_2 (15 mL). The dark-brown solution was filtered through Celite, and the filtrate was layered with hexanes. Dark-green block-shaped crystals of **1**·1.5CH_2Cl_2·0.5H_2O formed over 1 week. Crystalline yield: 0.14 g (20%). IR (KBr pellet, cm^{-1}): 1665 (w), 1589 (m, br), 1522 (vs), 1423 (s, br), 1364 (m), 1262 (m), 1219 (m), 1189 (m), 1096 (br), 1025 (s), 857 (w), 803 (s), 767 (m), 720 (w), 695 (m), 592 (w), 507 (m), 467 (w). Anal. Calc: C, 59.10; H, 4.85; N, 11.90. Found: C, 58.98; H, 4.90; N, 11.78.

Preparation of [Cr_3(DPhIP)$_4$(CH_3CN)](PF_6)$_2$, 2. The ligand H(DPhIP) (0.50 g, 1.9 mmol) was dissolved in THF (20 mL) and deprotonated with MeLi (1.0 M, 2.0 mL, 2.0 mmol). The pale yellow Li(DPhIP) solution obtained was transferred to another flask charged with $CrCl_2$ (0.20 g, 1.6 mmol) and $TlPF_6$ (0.70 g, 2.0 mmol). A large amount of gray solid appeared immediately. The gray suspension was stirred at reflux temperature for 12 h. A brown solid was collected by filtration, washed with THF (3 × 10 mL), and extracted with CH_3CN (15 mL). A red solution of **2** was collected and carefully layered with diethyl ether. Red block-shaped crystals of **2**·4CH_3CN·H_2O were obtained after 3 days. Yield: 0.55 g (67%). IR (KBr pellet, cm^{-1}): 1700 (w), 1685 (w), 1654 (w), 1637 (w), 1560 (w), 1523 (vs, br), 1508 (w), 1458 (w), 1427 (w), 1409 (s), 1367 (m), 1262 (m), 1222 (m), 1193 (m), 1099 (w), 1028 (w), 848 (vs, br), 804 (w), 763 (w), 725 (w), 696 (w), 623 (w), 558 (w), 541 (w), 508 (w), 419 (w). Anal. Calc: C, 54.51; H, 4.75; N, 13.86. Found: C, 55.88; H, 4.91; N, 13.50.

Preparation of [Cr_3(DPhIP)$_4$(F)(CH_3CN)](BF_4)$_2$, 3. Compound **3** was prepared by adding a CH_2Cl_2 (15 mL) solution of **1** (0.14 g, 0.10 mmol) to a suspension of $AgBF_4$ (0.09 g, 0.46 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred at room temperature for 2 h. The red-brown product was collected by filtration and extracted with CH_3CN. The resulting red solution was then layered with diethyl ether. Red block-shaped crystals of **3**·5CH_3CN were obtained after 2 days. Yield of crystals: 0.12 g (74%). IR (KBr pellet, cm^{-1}): 1594.6 (w), 1578.7 (w), 1561.7 (w), 1525.0 (m), 1460.0 (w), 1425.9 (m), 1404.7 (m), 1366.3 (m), 1261.5 (s), 1220.9 (w), 1191.3 (m), 1094.5 (vs), 1027.2 (vs), 856.6 (w), 804.8 (vs), 725.7 (w), 695.9 (m), 539.6 (w), 505.6 (w), 467.9 (m), 421.1 (w). Anal. Calc: C, 58.43; H, 4.69; N, 12.65. Found: C, 57.24; H, 4.73; N, 12.00.

Crystallographic Studies. All data were collected on a Nonius FAST area-detector diffractometer with each crystal mounted on the tip of a quartz fiber under a stream of nitrogen at 213 K. Cell parameters were obtained by least-squares refinement of 250 reflections ranging in 2θ from 15 to 41°. Laue groups and centering conditions were confirmed by axial images. Data were collected using 0.2° intervals in φ for the range $0° < \varphi < 220°$ and 0.2° intervals in ω for two different regions in the range $0° < \omega < 72°$. In this way, nearly a full sphere of data were collected. The highly redundant data sets were corrected for Lorentz and polarization effects and for absorption using the program SORTAV.[9]

Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) for **1**

Cr(1)···Cr(2)	2.659(2)	Cr(2)−N(5)	2.036(6)
Cr(2)−Cr(3)	1.932(2)	Cr(2)−N(8)	2.025(6)
Cr(1)−Cl(1)	2.425(2)	Cr(2)−N(11)	2.044(6)
Cr(1)−N(1)	2.125(6)	Cr(3)−N(3)	2.058(6)
Cr(1)−N(4)	2.135(7)	Cr(3)−N(6)	2.050(6)
Cr(1)−N(7)	2.125(6)	Cr(3)−N(9)	2.050(6)
Cr(1)−N(10)	2.130(6)	Cr(3)−N(12)	2.066(6)
Cr(2)−N(2)	2.041(6)		
Cr(1)−Cr(2)−Cr(3)	179.70(7)	N(7)−Cr(1)−N(4)	161.4(2)
Cl(1)−Cr(1)−Cr(2)	178.05(8)	N(10)−Cr(1)−N(4)	88.3(2)
N(1)−Cr(1)−N(7)	89.6(2)	N(1)−Cr(1)−Cl(1)	99.1(2)
N(1)−Cr(1)−N(10)	162.9(2)	N(7)−Cr(1)−Cl(1)	97.3(2)
N(7)−Cr(1)−N(10)	88.1(2)	N(10)−Cr(1)−Cl(1)	98.1(2)
N(1)−Cr(1)−N(4)	88.6(2)	N(4)−Cr(1)−Cl(1)	101.3(2)

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg) for **2**

Cr(1)−Cr(2)	1.907(2)	Cr(2)···Cr(3)	2.633(2)
Cr(1)−N(1)	2.063(3)	Cr(3)−N(3)	2.110(3)
Cr(2)−N(2)	2.051(3)	Cr(3)−N(77)	2.220(7)
Cr(1)−Cr(2)−Cr(3)	180.0	N(77)−Cr(3)−Cr(2)	180.0
N(3)−Cr(3)−N(77)	97.40(9)	C(88)−N(77)−Cr(3)	180.0

The positions of the chromium atoms, chlorine atoms, and nitrogen atoms were determined by direct methods and refined by using the program SHELXL-93. All non-hydrogen atoms were found by successive iterations of least-squares refinement followed by Fourier syntheses and, during the final cycles, were refined anisotropically. Hydrogen atoms were placed in idealized positions, and displacement parameters were set at 1.2 times those of the attached atoms.

In **1**·1.5CH_2Cl_2·0.5H_2O, three phenyl rings and two piperidyl rings were disordered and were modeled as having two orientations each; the occupancy for each orientation was optimized. In **2**·4CH_3CN·H_2O, all piperidyl rings were disordered and were modeled as having two orientations, each with an occupancy optimized by SHELXL. In **3**, the BF_4^- anion was disordered and was modeled as having two orientations, with half-occupancy for each orientation. In all three compounds studied, disordered interstitial solvent molecules were found; these were all modeled successfully.

Crystallographic data for **1**·1.5CH_2Cl_2·0.5H_2O, **2**·4CH_3CN·H_2O, and **3**·5CH_3CN are given in Table 1. Selected interatomic distances and bond angles for **1** in **1**·1.5CH_2Cl_2·0.5H_2O are given in Table 2, and those for **2** in **2**·4CH_3CN·H_2O and **3** in **3**·5CH_3CN are listed in Tables 3 and 4, respectively.

Magnetic Measurements. The magnetic susceptibility measurements were obtained on a Quantum Design MPMS-5 SQUID magnetometer

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Table 4. Selected Interatomic Distances (Å) and Bond Angles (deg) for **3**

Cr(1)−Cr(2)	1.968(2)	Cr(2)−N(2)	2.028(3)
Cr(1)−N(1)	2.102(3)	Cr(3)−F(1)	1.812(4)
Cr(1)−N(4)	2.151(6)	Cr(3)−N(3)	2.055(3)
Cr(2)···Cr(3)	2.594(2)		
Cr(1)−Cr(2)−Cr(3)	180.0	N(1)−Cr(1)−N(4)	90.76(8)
Cr(2)−Cr(1)−N(4)	180.0	F(1)−Cr(3)−N(3)	95.35(8)

(housed in the Department of Physics and Astronomy at Michigan State University). Values for compound **2** were obtained from a finely ground polycrystalline sample weighing 48.5 mg, from 2 to 300 K at 1000 G. The data were corrected for the sample holder and the experimental diamagnetic contribution 1.0×10^{-3} emu mol^{-1}. This value is in good agreement with that calculated from Pascal constants: 0.9×10^{-3} emu mol^{-1}.[10]

Results and Discussion

Synthetic Considerations. The reaction of $CrCl_2$ with a THF solution of Li(DPhIP) in a molar ratio of 3:4 at reflux temperature produced a greenish yellow solution and a yellow precipitate. The greenish yellow solution afforded long, orange prisms of $Cr_2(DPhIP)_4{\cdot}2THF$ and red blocks of $Cr_2(DPhIP)_4{\cdot}THF$, the structures of which have already been published.[1a] Recrystallization of the yellow precipitate from CH_2Cl_2/hexanes produced dark-green crystals of $\mathbf{1}{\cdot}1.5CH_2Cl_2{\cdot}0.5H_2O$. The water molecule was of adventitious origin.

One way to prepare compound **2** was to use compound **1** as a starting material, but the yield was low because the preparation for compound **1** had not been optimized. In a better procedure, compound **2** was synthesized in 67% yield by reacting a Li(DPhIP) solution in THF with a mixture of $CrCl_2$ and $TlPF_6$ at reflux temperature. Most of the product, an uncharacterized Cr^{III} impurity and the TlCl byproduct, precipitated. The solid was thoroughly washed with THF to remove the dichromium byproducts. The product, being insoluble in THF, was dissolved in CH_3CN and isolated from the filtered solution. In this way, **2** was prepared in high purity.

Compound **3** was synthesized by oxidizing **1** with $AgBF_4$ in CH_2Cl_2. This compound cannot be prepared in a way similar to that used for **2** since $CrCl_2$ will react very easily with $AgBF_4$, yielding inert Cr^{III} species. Thus, the accessibility of **3** is still limited by the availability of compound **1**.

Structural and Magnetic Studies. The structure of **1** (Figure 1) reveals a linear Cr_3^{6+} chain supported by a set of four di(phenylimino)piperidine anions. It has only one axial Cl anion; the other Cl anion lies between the cations, surrounded by a pocket of six hydrogen atoms at distances varying from 2.76 to 2.94 Å. This ligand arrangement is quite different from that of the symmetrical dpa complex,[7c] where each terminal Cr atom is bound to a Cl anion. In **1**, the Cr_3 chain is unsymmetrical, where the short distance of 1.932(2) Å (Figure 1) is comparable to those found in dichromium complexes bridged by formamidinate ligands.[11] The longer Cr(1)−Cr(2) distance of 2.659(2) Å is too long to be considered a bonding interaction.

$\mathbf{2}{\cdot}4CH_3CN{\cdot}H_2O$ crystallized with all three chromium atoms and an acetonitrile molecule aligned along a 4-fold axis. The structure (Figure 2) is very similar to that of **1** except for the axial ligand; in **1**, a chloride ion is axially coordinated to a square pyramidal Cr^{II} atom, but in **2**, a CH_3CN molecule replaces the chloride ion.

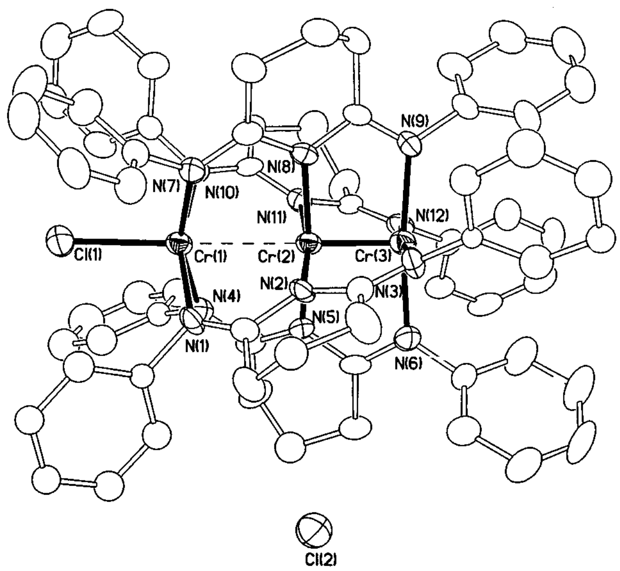

Figure 1. Diagram of the structure of compound **1**, $[Cr_3(DPhIP)_4Cl]Cl$. Displacement ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity.

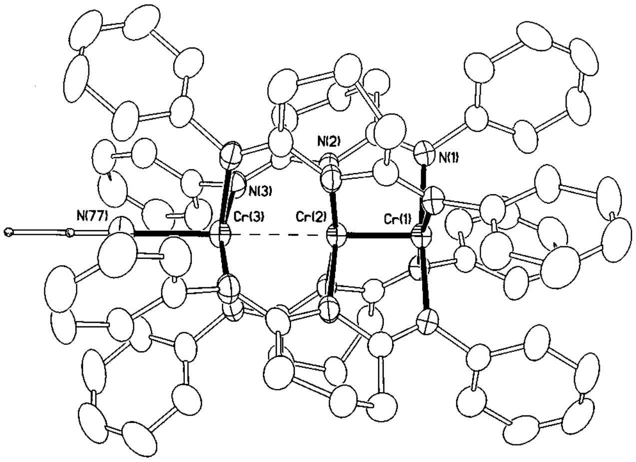

Figure 2. Diagram of the structure of the $[Cr_3(DPhIP)_4(CH_3CN)]^{2+}$ cation in **2**. Displacement ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity.

The magnetic susceptibility study reveals that **2** follows the Curie law between room temperature and 15 K (Figure 3). Below 15 K, we observe a reduction of the effective moment with a decrease in temperature due to a zero-field-splitting effect or a small antiferromagnetic interaction among the molecules of **2** ($|J| < 1$ K). The most important information obtained by the fitting of the Curie behavior (inset, Figure 3) is the Curie constant C or the effective magnetic moment μ_{eff}. The value of 2.3 emu K/mol for C (or 4.3 μ_B for μ_{eff}) is slightly lower than expected for a spin $S = 2$ ($C = 0.5S(S + 1) = 3$ or $\mu_{\mathrm{eff}} = (8C)^{1/2} = 4.9$). The g value deduced from this result is 1.75, which is comparable to those found for other unsymmetric systems such as $Cr_3(dpa)_4ClPF_6{\cdot}CH_2Cl_2$ ($g = 1.88$)[7c] and $Cr_5(tpda)_4Cl_2{\cdot}CH_2Cl_2$ ($g = 1.78$)[12] but lower than that of the symmetric compound $Cr_3(dpa)_4Cl_2{\cdot}CH_2Cl_2$ ($g = 2.08$).[7c] Thus this observed magnetic behavior is typical for an unsymmetrical chain of three Cr^{II} atoms. By analogy with the previously reported[7c] dpa system, this result confirms that there is no bonding interaction between the quadruply bonded dimetal unit and the square pyramidal Cr^{II} unit in **2**. The magnetic contribution arises from the spin of the pyramidal Cr^{II} ($S = 2$).

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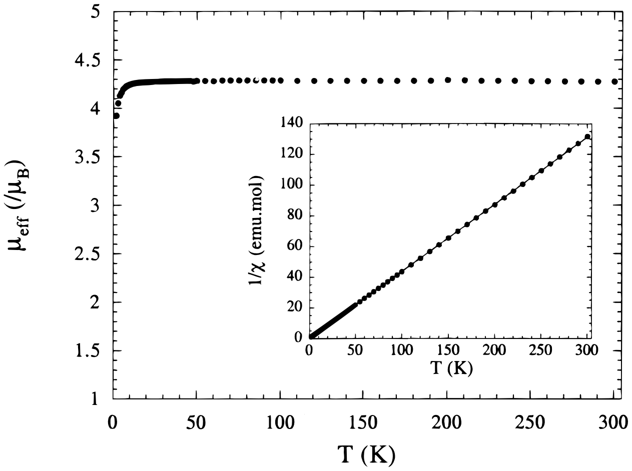

Figure 3. Thermal dependence of the effective moment (μ_{eff}) for **2** from 2 to 300 K. Inset: Reciprocal dependence of the magnetic susceptibility on temperature. The solid line was obtained by a Curie−Weiss fit.

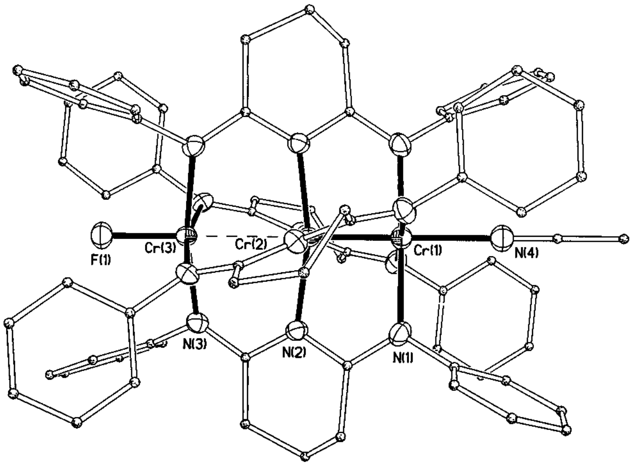

Figure 4. Diagram of the structure of the $[Cr_3(DPhIP)_4(F)(CH_3CN)]^{2+}$ cation in **3**. Thermal ellipsoids are shown at the 50% probability level, carbon atoms are drawn at an arbitrary scale, and hydrogen atoms are omitted for clarity.

3·5CH_3CN also crystallized in the *P*4/*n* space group with the Cr−Cr vectors residing on a 4-fold axis. The structure (Figure 4) consists of a square pyramidal Cr^{III} unit and a quadruply bonded dichromium unit (Cr−Cr distance 1.968(2) Å), with no metal−metal bonding interaction between the two components (Cr(2)···Cr(3) distance 2.594(2) Å). The quadruple bond is lengthened, presumably because of the axial interaction with a CH_3CN molecule. The Cr^{III}−F and Cr^{III}−N distances are comparable to those distances of Cr^{III} units found in Cr_3^{7+} dpa complexes.[7d]

In all three compounds, the DPhIP ligands are twisted. For example, the N−Cr−Cr′−N′ torsional angles for compounds **1** and **2** in the quadruply bonded portion are 16.0 and 15.2°, respectively, and in the other portion are 19.7 and 18.7°, respectively. The twisting of the DPhIP ligands is attributable to the repulsion between the four terminal phenyl groups imposed by the trichromium complex. In contrast to what happens to the phenyl groups in a formamidinate ligand,[11] the phenyl groups in a DPhIP ligand do not have freedom of rotation as a result of the repulsion between the two phenyl rings and the meta-hydrogen atoms on the piperidyl ring. Direct evidence comes from the recently synthesized compound $[Co_2(DPhIP)_3]_2(CoCl_4)$ (Co···Co distance 3.2 Å),[1b] where no ligand distortion has been found because there are only three ligands around the metal−metal vector; this ligand arrangement is not nearly as crowded at the two terminal positions as that in a $Cr_3(DPhIP)_4$ type complex. However, in $V_2(dpa)_3Cl_2$ (V···V distance 3.0 Å),[13] the dpa ligands are still twisted due to a ligand-imposed distortion[14] although there are only three dpa ligands surrounding the V···V vector in this complex.

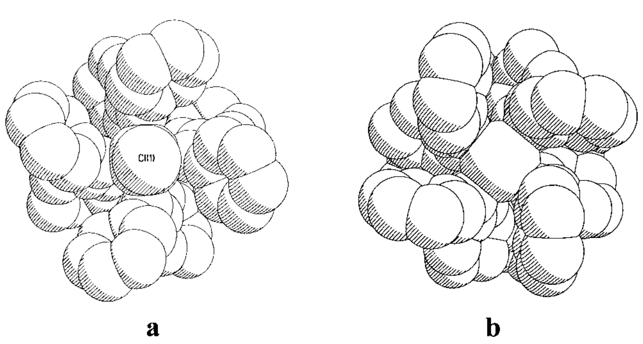

Figure 5. Space-filling models of the two ends of a $[Cr_3(DPhIP)_4Cl]^{2+}$ cation in **1** showing the reorientation of the phenyl groups because of the Cl−Cr axial coordination.

As shown in Figure 5, the orientations of the phenyl groups of the DPhIP ligands at the two terminal positions in **1** are quite different. This space-filling model shows that the axial Cl^- anion in compound **1** causes a reorientation of the adjacent terminal phenyl groups of the DPhIP ligands. At the other end, there is not enough space for another Cl^- anion. Similarly, in compound **2**, incorporation of one acetonitrile molecule at one end does not leave enough room for another axial acetonitrile ligand at the other end. However, because an F^- anion is smaller than a CH_3CN molecule, an F^- anion and a CH_3CN molecule were incorporated as ligands into compound **3** at the axial positions. In the dpa case,[7] the axial positions are more spacious and ligands as large as BF_4^- and PF_6^- can be accommodated. The DPhIP ligands might support a linear chain without axial ligands if sufficiently large anions and an appropriate solvent are used. Further experiments with this ligand and various transition metals are underway.

The results reported here for chains of three Cr^{II} atoms surrounded by four DPhIP ligands are similar to those obtained[7c] for most of the $Cr_3(dpa)_4XY$ compounds in that each Cr_3 chain consists of one quadruply bonded Cr_2 unit to which a separated 5-coordinate Cr^{2+} ion is annexed. Thus, once again, it appears that the dominant tendency of chains of Cr^{2+} atoms is to separate themselves into pairs of diamagnetic quadruply bonded Cr_2^{4+} units to which, in each case where there is an odd number of chromium atoms, a separate high-spin 5-coordinate Cr^{2+} ion is attached. In compound **3**, the situation is exactly the same as that found in all $[Cr_3(dpa)_4Cl_2]^+$ complexes,[7d] namely, that there is a Cr_2^{4+} unit with a quadruple bond and a separate high-spin 5-coordinate Cr^{3+} ion.

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Supporting Information Available: Additional ORTEP views of **1** and X-ray crystallographic files, in CIF format, for the three structures presented in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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