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Linear Trichromium Complexes with Direct Cr to Cr Contacts. 2. Compounds with Cr_3(dipyridylamide)$_4^{3+}$ Cores

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Seven compounds having in common a $Cr_3(dpa)_4^{3+}$ core (dpa = di(2-pyridyl)amide ion) have been prepared and all shown to have an unsymmetrical chain of three Cr atoms. This chain can be described as a pair of quadruply bonded Cr^{II} atoms to which a Cr^{III} atom is attached. No symmetrical chain has been found, contrary to a previous preliminary report. The seven compounds have been well characterized crystallographically, and their short and long Cr to Cr distances (Å, in parentheses) are: **1** $[Cr_3(dpa)_4Cl_2]Cl\cdot 2CH_2Cl_2\cdot THF$ (2.12, 2.47), **2** $[Cr_3(dpa)_4Cl_2]AlCl_4\cdot CH_2Cl_2$ (2.011, 2.555), **3** $[Cr_3(dpa)_4Cl_2]FeCl_4\cdot CH_2Cl_2$ (2.009, 2.562), **4** $[Cr_3(dpa)_4Cl_2]I_3\cdot THF\cdot 2H_2O$ (2.08, 2.49), **5** $[Cr_3(dpa)_4Cl_2]PF_6\cdot 2CH_2Cl_2$ (2.08, 2.48), **6** $[Cr_3(dpa)_4(BF_4)F]BF_4\cdot 2CH_2Cl_2$ (1.900, 2.595), **7** $[Cr_3(dpa)_4ClF]BF_4\cdot CH_2Cl_2\cdot C_6H_{14}$ (2.039, 2.507). Magnetic susceptibility measurements on **1** and **2** reveal $\mu_{eff} = 3.85 \pm 0.05\ \mu_B$ from 10 to 300 K.

Introduction

A number of trinuclear compounds of the type $M_3(dpa)_4XY$, where dpa is the anion of di-(2-pyridyl)amine, X and Y are uninegative anions, and M = Cr,[1] Co,[2] Ni,[3] Ru,[4] Rh,[4] and Cu,[5] have been reported. To date it is only for chromium and cobalt that the consequences of one-electron oxidation have been investigated. We have made brief preliminary reports[1] on a few such chromium compounds, but we now provide a detailed account of all the work completed so far, which covers five compounds containing the $[Cr_3(dpa)_4Cl_2]^+$ cation as well as compounds containing the $[Cr_3(dpa)_4F(BF_4)]^+$ and $[Cr_3(dpa)_4ClF]^+$ cations.

We previously reported[6] for the neutral species, that have $Cr_3(dpa)_4^{2+}$ cores, that the Cr_3 chains may be either symmetrical or unsymmetrical. In the work reported here we have prepared and structurally characterized compounds in which the central $Cr_3(dpa)_4^{2+}$ core has been oxidized to $Cr_3(dpa)_4^{3+}$. The purpose of this work was to see if the same variability in the Cr_3 chain would be observed for the once-oxidized species. For the reader's convenience, the seven compounds included in the present report are listed below:

1 $[Cr_3(dpa)_4Cl_2]Cl\cdot 2CH_2Cl_2\cdot THF$

2 $[Cr_3(dpa)_4Cl_2]AlCl_4\cdot CH_2Cl_2$

3 $[Cr_3(dpa)_4Cl_2]FeCl_4\cdot CH_2Cl_2$

4 $[Cr_3(dpa)_4Cl_2]I_3\cdot THF\cdot 2H_2O$

5 $[Cr_3(dpa)_4Cl_2]PF_6\cdot 2CH_2Cl_2$

6 $[Cr_3(dpa)_4(BF_4)F]BF_4\cdot 2CH_2Cl_2$

7 $[Cr_3(dpa)_4ClF]BF_4\cdot CH_2Cl_2\cdot C_6H_{14}$

Experimental Section

Materials. All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk and glovebox techniques. Solvents were purified by conventional methods and were freshly distilled under nitrogen prior to use. Anhydrous $CrCl_2$ was purchased from Strem Chemicals and used as received; I_2 and 2,2′-dipyridylamine, Hdpa, were purchased from Aldrich. The latter was purified by sublimation prior to use. The compounds $PhICl_2$, $[FeCp_2]FeCl_4$,[7] and $[FeCp_2]PF_6$[8] were prepared following published procedures. $[FeCp_2]AlCl_4$ was prepared following a procedure similar to that for $[FeCp_2]FeCl_4$; $Cr_3(dpa)_4Cl_2$ was prepared as reported previously by our group.[6]

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Physical Measurements. ^{1}H NMR spectra were recorded on an XL-300 NMR spectrometer and IR spectra on a Perkin-Elmer 16PC FTIR spectrometer using KBr mulls; FAB mass spectra were acquired on a VG Analytical 70S (Manchester, U.K.) high-resolution, double-focusing, magnetic sector mass spectrometer. Magnetic susceptibility data were collected on a Quantum Design, model MPMS, SQUID (superconducting quantum interference device) housed in the Department of Physics and Astronomy at Michigan State University. Data were collected from 2 to 300 K at a field of 2000 G. Elemental analyses of solvent-free **1**−**6** were performed by Canadian Microanalytical Services; they were satisfactory.

Preparation of [$Cr_3(dpa)_4Cl_2$]Cl·2CH_2Cl_2·THF, 1. To a solution of $Cr_3(dpa)_4Cl_2$ (0.10 g, 0.10 mmol) in 15 mL of CH_2Cl_2 was added dropwise, at −70 °C, a solution of $PhICl_2$ (0.015 g, 0.05 mmol) in 10 mL of CH_2Cl_2. After stirring for 5 min the green solution turned black. It was then allowed to reach room temperature. Stirring was continued for 2 h, after which a black powder was isolated by filtration after precipitation with hexanes. Yield: 0.070 g (67%). IR (KBr mull, cm^{-1}): 1607 (vs), 1453 (vs), 1426 (vs), 1362 (s), 1311 (s), 1263 (m), 1155 (m), 1110 (m), 1017 (m), 866 (w), 764 (s), 739 (m), 646 (w), 537 (w), 516 (w). The product was recrystallized after layering hexanes on top of a CH_2Cl_2 solution of the product which also contained a few drops of THF.

Preparation of [$Cr_3(dpa)_4Cl_2$]$AlCl_4$·CH_2Cl_2, 2. The procedure was very similar to that used for **1**, but using 0.038 g (0.10 mmol) of [$FeCp_2$]$AlCl_4$ as oxidizing agent. Yield: 0.18 g (84%). IR (KBr mull, cm^{-1}): 1619 (vs), 1458 (vs), 1360 (s), 1309 (s), 1242 (s), 1204 (m), 1150 (m), 1018 (m), 840 (w), 752 (m), 650 (m), 649 (w), 540 (w), 518 (w), 504 (w).

Preparation of [$Cr_3(dpa)_4Cl_2$]$FeCl_4$·CH_2Cl_2, 3. This was prepared similarly to **1** but using [$FeCp_2$]$FeCl_4$ as the oxidizing agent, 0.10 g (0.10 mmol) of $Cr_3(dpa)_4Cl_2$, and 0.075 g (0.10 mmol) of [$FeCp_2$]$FeCl_4$. It was isolated as large black crystals from a solution of CH_2Cl_2 layered with hexanes. Yield: 0.098 g (80.5%). IR (KBr mull, cm^{-1}): 1607 (vs), 1459 (vs), 1362 (s), 1313 (s), 1262 (m), 1154 (m), 1018 (m), 840 (m), 753 (m), 653 (m), 649 (m), 542 (w), 513 (w).

Preparation of [$Cr_3(dpa)_4Cl_2$]I_3·THF·2H_2O, 4. This was prepared similarly to **1**, but the reaction was carried out in cold THF instead of CH_2Cl_2 as solvent, and with I_2 in THF as the oxidizing agent, 0.10 g (0.10 mmol) of $Cr_3(dpa)_4Cl_2$, and 0.015 g (0.059 mmol) of I_2. Compound **4** was isolated as black crystals from a THF solution layered with hexanes. Yield: 0.13 g (91%).

Preparation of [$Cr_3(dpa)_4Cl_2$]PF_6·2CH_2Cl_2, 5. It was prepared similarly to **1** but using [$FeCp_2$]PF_6 as the oxidizing agent, 0.10 g (0.10 mmol) of $Cr_3(dpa)_4Cl_2$, and 0.075 g (0.10 mmol) of [$FeCp_2$]PF_6. The product was isolated as large black crystals from a solution of CH_2Cl_2 layered with hexanes. Yield: 0.094 g (81%). IR (KBr mull, cm^{-1}): 1608 (vs), 1466 (vs), 1428 (vs), 1365 (s), 1313 (s), 1262 (s), 1159 (s), 1019 (br, vs), 800 (vs), 741 (m), 660 (w), 649 (w), 557 (m).

Preparation of [$Cr_3(dpa)_4(BF_4)F$]BF_4·2CH_2Cl_2, 6. A stirred solution of $Cr_3(dpa)_4Cl_2$ (0.20 g, 0.21 mmol) in 10 mL of CH_2Cl_2 was added dropwise, via cannula, to a suspension of $AgBF_4$ (0.083 g, 0.44 mmol) in 8 mL of CH_2Cl_2 at room temperature. After stirring for 4 h, AgCl and Ag were removed by filtration through Celite, leaving a clear greenish-black solution that was diluted with 5 mL of THF and layered with hexanes. The product was isolated as large, platelike dark-green crystals. Yield: 0.15 g (66%). IR (KBr mull) cm^{-1}: 1608 (s), 1587 (s), 1550 (m), 1470 (vs), 1428 (vs), 1359 (s), 1287 (m), 1266 (m), 1242 (w), 1158 (m), 1119 (m), 1055 (w), 1021 (m), 924 (s), 883 (m), 59 (w), 766 (m), 741 (m), 649 (w), 537 (w), 517 (w).

Preparation of [$Cr_3(dpa)_4ClF$]BF_4·CH_2Cl_2·C_6H_{14}, 7. To a cold (−72 °C), stirred solution of 0.10 g of $Cr_3(dpa)_4Cl_2$ (0.10 mmol) in 10 mL of CH_2Cl_2 was added a suspension of cold $AgBF_4$ (0.043 g, 0.22 mol) in 10 mL of CH_2Cl_2. The mixture was allowed to react for 2 h, at low temperature, after which AgCl and Ag were removed by filtration. Crystallization was effected by diffusion of hexanes into the filtrate at −40 °C. This product was a mixture of about 65% [$Cr_3(dpa)_4ClF$]BF_4·CH_2Cl_2·C_6H_{14} with what was thought to be [$Cr_3(dpa)_4Cl_2$]BF_4·CH_2Cl_2·C_6H_{14}. However, the crystal structure of the latter was never refined satisfactorily and thus its composition remains problematical and it will not be discussed further.

Crystallographic Procedures

Data for all compounds were collected on a Nonius FAST diffractometer at −60 °C. In each case, a suitable crystal was attached to the tip of a quartz fiber with a small amount of silicone grease. Unit-cell dimensions for all crystals were obtained from an auto-indexing routine and were refined with up to 250 reflections within a 2θ range of 18−45°. Cell dimensions and Laue symmetry for all crystals were confirmed by axial photography. All data were corrected for Lorentz and polarization effects. Procedures used on this instrument have been described previously in detail.[9] For all structures, the positions of the heavy atoms and the main skeleton of the ligands were found by direct methods.[10] Subsequent cycles of least-squares refinement using SHELXL-93,[11] followed by difference Fourier syntheses, revealed the positions of the remaining non-hydrogen atoms. In some cases hydrogen atoms were located in difference Fourier maps, but all were used in idealized calculated positions. Each structure presented here contains at least one molecule of interstitial solvent, and in many cases the solvent site was disordered to some extent. For each occurrence of CH_2Cl_2 or THF, the disorder was successfully modeled so that each site contained two or sometimes three solvent molecules, each having a reasonable geometry. The single exception is for **7**, in which an area containing interstitial isomers of hexane was modeled as a collection of carbon atoms without regard for the geometry. A total of 10 centers of electron density were identified, and the positions, isotropic displacement parameters, and occupancies were allowed to refine within the restriction that the occupancies added to exactly 6.0. Other details of data collection and refinement are given in Table 1. Atomic positions, distances, angles as well as isotropic and anisotropic displacement parameters for all structures are given as Supporting Information.

Results

The chemistry involved in the preparation of these compounds was not particularly difficult for compounds **1**−**5**. The oxidation processes proceed smoothly by reacting $Cr_3(dpa)_4Cl_2$ with a halogen source or an appropriate ferrocenium salt in CH_2Cl_2. The corresponding dark-colored [$Cr_3(dpa)_4Cl_2$]$^+$ cationic species can be isolated by filtration in high yield. All unwanted products remain in solution. The interstitial water molecules found in crystals of **4** have an adventitious origin.

However, reaction of $Cr_3(dpa)_4Cl_2$ and $AgBF_4$ is more complex. Addition of 1 equiv of each substance in CH_2Cl_2, at room temperature, causes precipitation of AgCl generating the unoxidized compound $Cr_3(dpa)_4Cl(BF_4)$.[6] When the reaction is carried out at room temperature but the ratio $Cr_3(dpa)_4$:$AgBF_4$ is equal to 1:2, a one-electron oxidation process along with Cl substitution by F also occurs, giving [$Cr_3(dpa)_4(BF_4)F$]BF_4. If the latter reaction is caried out at lower temperature (−72 °C), mixtures of products are observed: one of them was structurally characterized as [$Cr_3(dpa)_4ClF$]BF_4·CH_2Cl_2·C_6H_{14}, **7**.

A summary of structural results for the seven compounds is presented in Table 2. Many additional details are available in the Supporting Information. In all the compounds the central $Cr_3(dpa)_4^{3+}$ unit is helical. The overall twist angle varies slightly

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Table 1. Crystallographic Data for Compounds **1**−**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
empirical formula	$C_{46}H_{44}Cl_7Cr_3N_{12}O$	$C_{41}H_{34}AlCl_8Cr_3N_{12}$	$C_{41}H_{34}Cl_8Cr_3FeN_{12}$	$C_{44}H_{41}Cl_2Cr_3I_3N_{12}O_{1.5}$	$C_{42}H_{36}Cl_{3.5}Cr_3F_6N_{12}P$	$C_{42}H_{36}B_2Cl_4Cr_3F_9N_{12}$	$C_{47}H_{48}BCl_3Cr_3F_5N_{12}$
fw	1185.08	1161.38	1190.25	1369.49	1133.87	1199.25	1149.1
space group	*Ibca*	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$Pna2_1$	$P2_1/n$
a, Å	16.122(1)	11.657(2)	11.670(5)	13.571(3)	11.545(2)	23.878(2)	11.499(3)
b, Å	17.151(1)	28.350(6)	28.398(4)	34.607(9)	21.426(4)	29.488(1)	20.976(1)
c, Å	37.508(2)	15.019(3)	15.031(11)	11.424(3)	20.238(4)	14.245(8)	19.862(3)
β, deg	90	104.41(3)	104.51(1)	113.108(3)	92.78(3)	90	92.804(4)
vol, Å^3	10371(1)	4807(2)	4823(4)	4935(2)	5001(2)	10030(6)	4785(2)
Z	8	4	4	4	4	8	4
T, °C	−60	−60	−60	−60	−60	−60	−60
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
calcd density, g/cm^3	1.518	1.605	1.639	1.843	1.506	1.588	1.595
μ, mm^{-1}	1.027	1.175	1.442	2.683	0.926	0.931	0.906
no. of data/ restraints/ params	3397/0/333	5794/0/604	6071/0/586	6259/3/597	6260/33/663	12823/64/1307	6258/5/664
R indices [I>2ó(I)]^{a,b}	R1 = 0.064, wR2 = 0.166	R1 = 0.054, wR2 = 0.117	R1 = 0.040, wR2 = 0.095	R1 = 0.072, wR2 = 0.150	R1 = 0.090, wR2 = 0.209	R1 = 0.068, wR2 = 0.151	R1 = 0.063, wR2 = 0.149
R indices (all data)	R1 = 0.075, wR2 = 0.185	R1 = 0.071, wR2 = 0.134	R1 = 0.045, wR2 = 0.101	R1 = 0.099, wR2 = 0.174	R1 = 0.137, wR2 = 0.268	R1 = 0.092, wR2 = 0.173	R1 = 0.069, wR2 = 0.155
GOF	1.069	1.117	1.084	1.14	1.114	1.077	1.096

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

Table 2. Summary of Important Structural Parameters for Compounds **1**−**7**

compd no.	axial ligands	anion	occupancy of major orientation	$\mathrm{Cr}\overset{4}{-}\mathrm{Cr}^{a}$ distance, Å	Cr···Cr distance, Å	axial L to Cr^{II}, Å	axial L to Cr^{III}, Å
1	Cl, Cl	Cl^-	0.5	2.12(1)	2.47(1)	unresolved	unresolved
2	Cl, Cl	$AlCl_4^-$		2.010(1)	2.555(1)	2.441(2)	2.274(2)
3	Cl, Cl	$FeCl_4^-$		2.009(1)	2.562(1)	2.446(2)	2.278(2)
4	Cl, Cl	I_3^-	0.81(3)	2.08(1) 2.09(2)	2.49(1) 2.48(2)	unresolved	unresolved
5	Cl, Cl	PF_6^-	0.69(5)	2.09(2) 2.09(2)	2.48(2) 2.48(2)	unresolved	unresolved
6^b	BF_4, F^c	BF_4^-		1.900(2) 1.903(2)	2.595(2) 2.579(2)	2.205(6) 2.193(6)	1.821(6) 1.810(5)
7	Cl, F^c	BF_4^-	0.71(1)	2.039(5) 2.066(9)	2.507(4) 2.481(9)	2.413(4) 2.381(8)	1.886(8) 1.90(2)

[a] For disordered structures with two inequivalent orientations the distances for the major orientation are listed first. [b] Two independent molecules in the asymmetric unit. [c] The F atom is attached to the Cr^{III} atom.

from one compound to another, but stays within the range 41.4−48.2°. We shall now discuss these results individually.

Compound 1. This compound has already been reported by us,[1b] but further study has shown that the previous refinement of this structure, which was incomplete, is also incorrect. The way in which this happened is worth describing because it entails the sort of problem that may be expected to recur in compounds of this kind. Figure 1a shows the molecule as initially refined, and reported to have equal Cr−Cr distances. The molecule resides on a crystallographic site of 2-fold symmetry (2-fold axis perpendicular to the Cr−Cr−Cr chain), and thus equal Cr−Cr distances seemed reasonable. However, Figure 1a shows an anomaly that was previously overlooked, namely, the large, prolate displacement ellipsoid of Cr(2). We have now shown that this prolate ellipsoid is the result of there being an *unsymmetrical* molecule on each site, with random directional orientations from site to site. When this is taken into account and the refinement conducted accordingly, the structure shown in Figure 1b is obtained. Because of the disorder the *x* and *y* coordinates (these directions being perpendicular to the 2-fold axis) are less precise and therefore Cr−Cr distances are accurate to only ±0.01 Å. However, these distances are quite different, being 2.12(1) Å for Cr(1)−Cr(2) and 2.47(1) Å for Cr(2)−Cr(1)′. Contrary to our previous description of this molecule, it is not symmetric, but distinctly unsymmetric, with a Cr−Cr quadruple bond and an isolated Cr^{III} atom. The fact that the unsymmetrical nature of the molecule does not show up in other dimensions (e.g., Cr−N and Cr−Cl distances) is due to the averaging effect of the disorder. We shall see what the differences in these distances really look like when we turn, next, to the structures of **2** and **3**.

Compounds 2 and 3. These two compounds are closely isomorphous. Compound **3** was made first, and when its structure turned out to be such a precise one, we decided to make **2** so as to have such a precise structure in a compound that could be studied magnetically as well. In both of these compounds, the Cr_3 arrangement is distinctly unsymmetric and there is no disorder, so that the Cr−Cr distances are obtained with high accuracy. Moreover, the difference between Cr(1) and Cr(3) shows very clearly in the associated metal−ligand distances. Averaging over both **2** and **3**, it is found that the Cr(1)−N distances are 0.027 Å longer than the Cr(3)−N distances, and the Cr(1)−Cl distances average 2.443 Å compared to 2.276 Å for the Cr(3)−Cl distances. This is all in good accord with Cr(1) being Cr^{II} and Cr(3) being Cr^{III}. It is also clear why, in **1**, the Cr(1)−N and Cr(3)−N distances were indistinguishable. The two Cr−Cl distances have a mean value of 2.36 ± 0.08 Å, compared with the averaged value of 2.35 Å obtained for **1**. The results reported here for **3** are exactly the same as, but more precise than, those given in the preliminary communication.[1b]

Compound 4. This compound and its structure have not been previously reported. We have here another example of a disorder, but, in contrast to that in **1**, the two orientations are

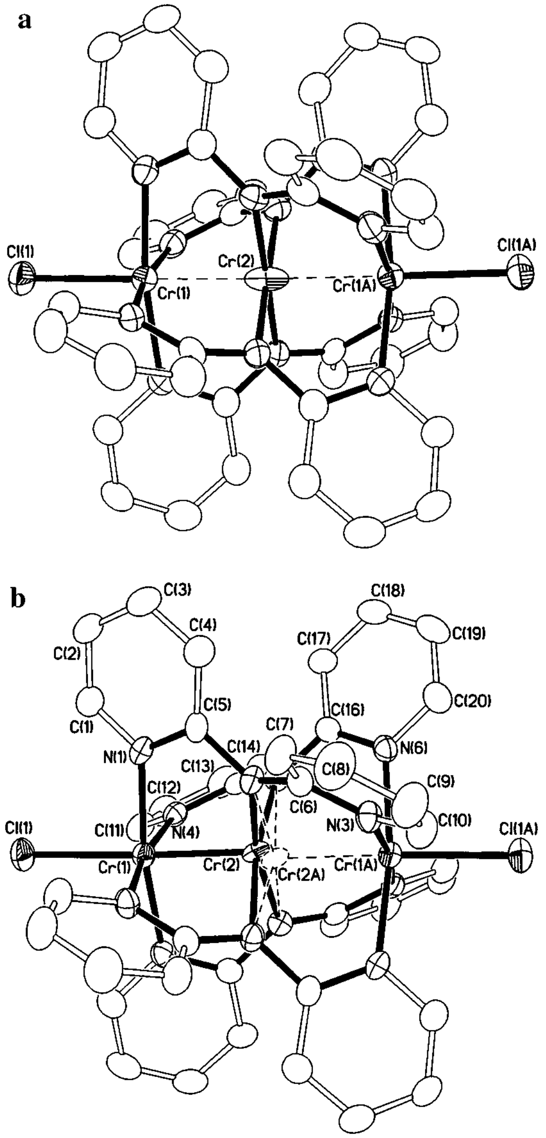

Figure 1. Views of the cation in compound **1** both (a) before and (b) after modeling of the disorder in the Cr−Cr−Cr chain. The ellipsoids are shown at the 40% probability level, and hydrogen atoms are not shown.

not equally represented. Instead, one of them (**A**) is present 80% of the time and the other (**B**) 20%. Needless to say, the accuracy with which the former was refined is superior. As shown in Figure 2, Cr(2A) is closer to Cr(1) and Cr(2B) is closer to Cr(3). For Cr(2A) the short and long distances (Å) are Cr(1)−Cr(2A), 2.08(1), and Cr(3)−Cr(2A), 2.49(1), while for Cr(2B) the distances are Cr(3)−Cr(2B), 2.09(2), and Cr(1)−Cr(2B), 2.48(2). The Cr−Cl distances also suffer from the disorder, but also reflect the dominance of the sites with Cr(2A); they are Cr(1)−Cl(1), 2.379(4) Å, and Cr(3)−Cl(2), 2.309(4) Å.

Compound 5. This compound was reported earlier[1b] and was described as only somewhat unsymmetrical with Cr−Cr distances of 2.119(3) and 2.369(3) Å. More rigorous refinement has now shown that there is a disordering of unsymmetrical molecules (68% and 32%) and that the extent of asymmetry is much greater than previously recognized. The short Cr−Cr distance is 2.09(2) Å, and the long one is 2.48(2) Å. Here, again, even though the esd's are large, they undoubtedly underestimate the actual uncertainties because of the difficulties arising from the disorder.

Compound 6. In this case there was no problem with disorder, and because of the marked difference between the two axial ligands, the molecule is, not unexpectedly, quite unsymmetrical, as shown in Figure 3. There are, in fact, two molecules in the asymmetric unit, but they are metrically almost identical. The short Cr−Cr distances are very short, 1.900(2) and 1.903(2) Å, and the longer ones are quite long, 2.595(2) and 2.579(2) Å. In this case the Cr(1)−N and Cr(3)−N distances are only slightly different with the average of the former being 0.02 Å longer than the latter, as expected for Cr^{II}−N vs Cr^{III}−N bonds. The molecular dimensions reported here are not significantly different from those given in our preliminary communication.[1a]

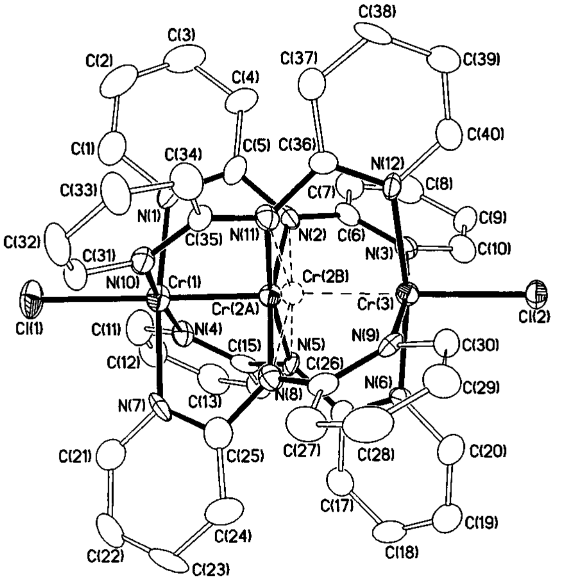

Figure 2. View of the cation in compound **4**, showing both positions of atom Cr(2). The minor (approximately 20% occupancy) position is drawn with dashed lines. The displacement ellipsoids are drawn at the 40% probability level.

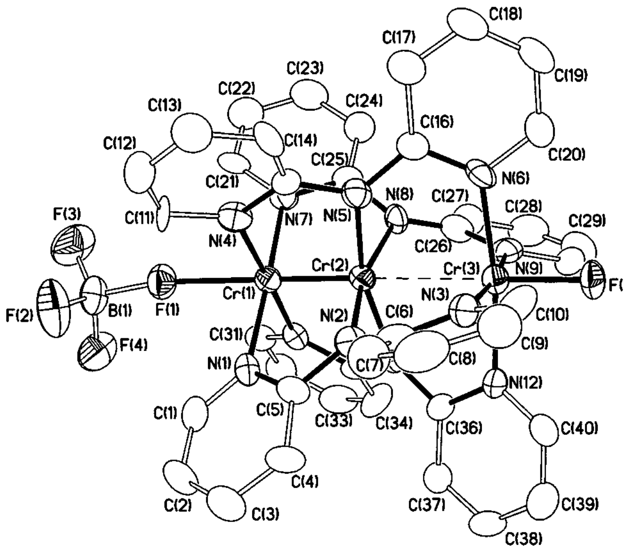

Figure 3. One of the two independent cations in compound **6**, shown with 50% probability displacement ellipsoids. The clean, almost spherical ellipsoids for the Cr atoms and the low uncertainties in the metal positions provide evidence that no disorder is present in this structure.

Compound 7. This compound also posed a tricky disorder problem. It has an unsymmetrical Cr$_3$ chain, and the order of atoms along the axis is $\mathrm{Cl{-}Cr(1)\overset{4}{-}Cr{-}{-}{-}Cr(3){-}F}$. The structure was refined with 70% of the molecules, those with Cl(1A),

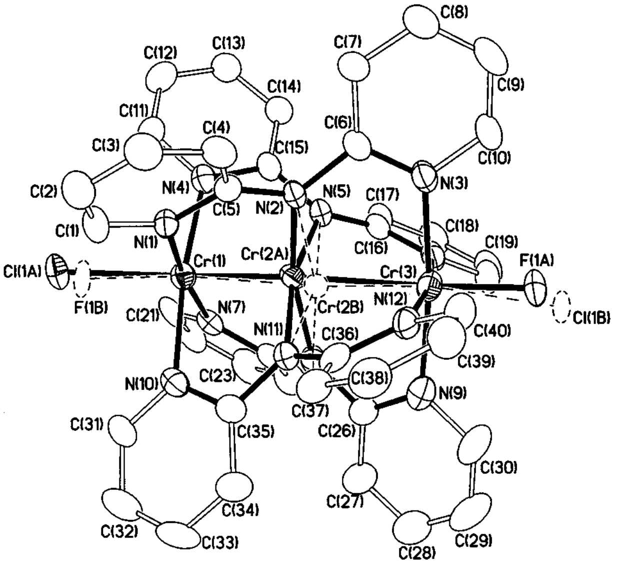

Figure 4. A representation of the cation in compound **7**, showing the disorder both in the central Cr atom and in the axial Cl and F ligands, drawn with 40% displacement ellipsoids. The occupancy of the major orientation refines to approximately 70%.

Cr(2A), and F(1A), oriented in one direction and 30%, those with Cl(1B), Cr(2B), and F(1B), oriented in the other, as shown in Figure 4. For the major molecule (70% occupancy) the following distances (Å) were obtained:

$$\mathrm{Cl(1A)}\overset{2.314(4)}{\text{———}}\mathrm{Cr(1)}\overset{2.039(5)}{\text{———}}\mathrm{Cr(2A)}\overset{2.507(4)}{\text{———}}\mathrm{Cr(3)}\overset{1.886(8)}{\text{———}}\mathrm{F(1A)}$$

Because of the disorder there are probably uncertainties in these distances that exceed those represented by the esd's. Bearing that in mind, however, these distances compare satisfactorily with those of the same nature in the other molecules. For example, the above value of the Cl to Cr$\overset{4}{-}$Cr distance is within the range of those in **1** (2.353(2)), **2** (2.441(2)), **3** (2.446(2)), **4** (2.379(4)), and **5** (2.375(4)) and the Cr−F distance is similar to that in **6** (1.821(6)).

Magnetic Measurements. The magnetic susceptibilities of compounds **1** and **2** were measured from 5 to 300 K. Both follow the Curie law very well and give essentially constant values, 3.85 ± 0.05 μ_B, of the magnetic moment from 10 to 300 K.

Discussion

The structural results, as well as the magnetic data, lead to only one conclusion as to the bonding in the seven compounds with $\mathrm{Cr_3(dpa)_4}^{3+}$ cores. The chromium atoms group themselves into a diamagnetic pair of Cr^{II} atoms that are quadruply bonded (Cr−Cr distances range from 1.90 to 2.12 Å) and a paramagnetic Cr^{III} atom ($S = {}^3/_2$) which lies at a long distance (2.47−2.59 Å) from the inner Cr^{II} atom. Indeed, if compounds **1** and **5** are excluded, the short and long Cr−Cr distances lie within even narrower ranges, viz., 1.900−2.08 and 2.49−2.59 Å. In all of these compounds except **2** and **3**, the true uncertainties in the Cr−Cr, Cr−Cl, and Cr−F distances are difficult to assess because of the effects of the disorders, so not too much should be made of apparent differences. In **1** where the two orientations are equally populated, this problem is doubtless at its worst, and thus the appearance of there being less difference between the short and long Cr−Cr distances is illusory.

The overall message of this work is that, for $\mathrm{Cr_3(dpa)_4}^{3+}$ cores, the set of Cr atoms is more stable in an unsymmetrical Cr$^{II}\overset{4}{-}$Cr^{II}---Cr^{III}) arrangement than in a symmetrical one in *all* cases. Thus, our previous suggestion, based on preliminary results, that there are a variety of $\mathrm{Cr_3(dpa)_4}^{3+}$ arrangements, ranging from symmetric to very unsymmetric, has to be, and is, withdrawn. The true situation is that all seven compounds so far examined are very similar and we see no reason to believe that any further examples would be different.

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Supporting Information Available: Crystal and structure refinement data, positional parameters, anisotropic displacement parameters, and complete listings of bond distances and angles, in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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