Linear Trichromium Complexes with Direct Cr to Cr Contacts. 1. Compounds with $Cr_3(dipyridylamide)_4^{2+}$ Cores

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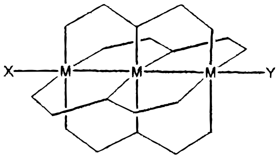
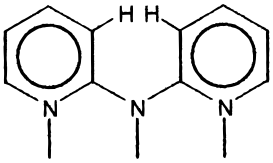
The preparation and structures of seven compounds that contain the $Cr_3(dpa)_4^{2+}$ core (dpa = the anion di(2-pyridyl)amide) are reported. The magnetic properties of several have been measured. In each case there are anionic ligands at each end of the Cr_3^{6+} chain, sometimes identical ($2Cl^-$, $2CCPh^-$), sometimes different (Cl^-, BF_4^-; Cl^-, PF_6^-). Several of these compounds have a symmetrical arrangement of the three Cr atoms, with the two Cr−Cr distances equal at ca. 2.36 Å, while others have an unsymmetrical arrangement. In the most extreme case the two Cr−Cr distances are 2.00 and 2.64 Å. The electronic structures and the remarkable flexibility of the Cr_3 arrangement are discussed.

Introduction

The utility of the anion of di(2-pyridyl)amine, dpa^-, as a ligand for supporting chains of three metal ions first became evident in 1990−1991, when the nature of the $M_3(dpa)_4X_2$ (X = Cl, Br) compounds formed by copper and nickel was revealed by X-ray crystallographic studies.[1−3] Subsequently, structurally similar compounds with M = Ru,[4] Rh,[4] Co,[5−7] and Cr,[8,9] have been reported. A general schematic representation of these compounds is found in **I**. For simplicity the ligands are depicted as planar, but actually they are twisted because of the repulsive force between adjacent hydrogen atoms, as shown in **II**. The total end-to-end twist is about 40° in each $M_3(dpa)_4X_2$ molecule. In **I** the metal atoms are shown as symmetrically arranged, that is, with the two M−M distances equal. This symmetrical disposition is the only one so far found for compounds in which X = Y = Cl, Br and the metal atoms are Cu, Ni, Ru, and Rh. On the other hand both symmetrical and unsymmetrical M_3 chains have been seen for compounds of Co and Cr.



I



II

The compounds of type **I** afford the first examples of complexes in which three metal ions are organized into a linear chain within which they are free to interact in one of two ways: (1) they may form a symmetrical array in which all valence electrons are symmetrically distributed and to some extent delocalized over the three metal atoms; (2) they may form an unsymmetrical array in which two of the metal atoms are bonded to each other, while the third is separated. At the present time, we do not know the rules that govern this seemingly simple game. In some cases (Ni, Cu, Ru, Rh) only a symmetric form has been seen, but for the last three, only one compound in one crystalline form has yet been reported. In the case of cobalt, the astonishing fact is that either a symmetric or an unsymmetric molecule can be obtained, depending on the crystal environment. We have prepared, for the first time, a series of trichromium compounds to see how they will behave.

The problem we are dealing with here is related to more broadly important questions relating to Peierls distortions (which occur in very long chains), the Renner effect, and the question of the H + H_2 reaction, in all of which cases the key question concerns the stability, or lack of it, of a linear chain of metal atoms in its most symmetrical form. The simplest such chain, of course, consists of only three atoms. It seems fair to say that, unless we understand the behavior of this simplest case, we shall not have much chance of understanding more complex ones.

It is our purpose in this paper to present a great deal of structural information as well as magnetic studies on compounds of chromium(II), i.e., compounds with a Cr_3^{6+} chain within the

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Table 1. Selected Structural Data for $Cr_2(dpa)_4L_2$ Compounds

no.	Cr−Cr distances, Å short	Cr−Cr distances, Å long	axial ligands X, Y	Cr−X, Å	Cr−Y, Å	interstitial solvent	∑Cr−Cr, Å[a]
1	1.995(1)	2.643(1)	BF_4,[b] Cl	2.374(3)	2.530(1)	$2\cdot CH_2Cl_2$	4.638(1)
2	2.008(1)	2.614(1)	PF_6,[b] Cl	2.536(4)	2.521(2)	$2\cdot CH_2Cl_2$	4.621(1)
3[c]	2.296(2)	2.414(2)	$(Cl)_2$	2.539(2)	2.525(2)	benzene	4.709(2)
	2.326(2)	2.390(2)	$(Cl)_2$	2.539(2)	2.548(2)		4.716(2)
4	2.353(2)	2.365(2)	$(Cl)_2$	2.560(2)	2.553(2)	toluene	4.717(2)
5	2.366(1) (sym)		$(Cl)_2$	2.549(2)		CH_2Cl_2	4.731(2)
6	2.365(2) (sym)		$(Cl)_2$	2.561(4)		THF	4.730(4)
7	2.415(2)	2.422(2)	$(-C\equiv C-Ph)_2$[b]	2.326(6)	2.309(6)	none	4.837(2)

[a] The values in this column are not actually the sums of the Cr−Cr distances, but rather measured distances between the terminal Cr atoms. [b] Disorder in axial ligands. [c] The asymmetric unit contains two independent molecules.

spiral wrapping of four dpa^- ligands. Since there are many similar compounds, we present in Table 1 a list of those that have been crystallographically characterized. The terminal ligands, X and Y (as in **I**), are listed, along with the solvent molecules present in the crystal, the two Cr−Cr distances found crystallographically, and a few other pertinent data.

Experimental Section

Preparation of Compounds. Methods and Materials. All operations were carried out under a nitrogen atmosphere using standard drybox techniques. Solvents were distilled prior to use from the appropriate drying agents. Chromium dichloride was purchased from Strem and used as received; Hdpa was obtained from Aldrich and purified by sublimation. $AgBF_4$ was purchased from Lancaster; $TlNO_3$ and $TlPF_6$ were purchased from Aldrich and were dried at 160 °C for 24 h before being stored in a drybox.

Physical Measurements. ^1H NMR spectra were recorded on an XL-300 NMR spectrometer; IR spectra were performed on a Perkin-Elmer 16PC FTIR spectrometer using KBr mulls. 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. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M $NBu^t_4(PF_6)$ as the supporting electrolyte. A stream of nitrogen was bubbled through the solution during measurements. *E* values were referenced to the Ag/AgCl electrode at room temperature. They were referenced to the $E_{1/2}$ of the ferrocenium/ferrocene couple, using a Bioanalytical Systems Inc. electrochemical analyzer, model 100. The scan rate was 100 mV/s at a Pt disk electrode. FAB mass spectra were acquired on a VG Analytical 70S (Manchester, U.K.) high-resolution, double-focusing, magnetic sector mass spectrometer. Elemental analyses were done by Canadian Microanalytical Co.; except for $Cr_3(dpa)_4(PF_6)_2$ they were satisfactory.

$Cr_3(dpa)_4Cl_2$. To a solution of Hdpa (0.341 g, 2.00 mmol) in 10 mL of THF at −78 °C was added MeLi (2.00 mmol). When the reaction mixture had warmed to ambient temperature, anhydrous $CrCl_2$ (0.184 g 1.50 mmol) was added. As the suspension was refluxed for 6 h, it gradually turned red and then dark green. The dark green precipitate was filtered off, and the solid was washed several times with THF. Yield: 0.40 g (87%). Green crystals of **5** were formed by slow diffusion of hexanes into a CH_2Cl_2 solution. IR (KBr mull) cm^{-1}: 1611 (vs), 1547 (s), 1480 (vs), 1376 (vs), 1152 (s), 1111 (m), 1055 (m), 1017 (s), 918 (w), 878 (m), 859 (m), 759 (s), 748 (m), 735 (s), 668 (w), 644 (m), 536 (m), 16 (m), 433 (s), 418 (s). CV (mV): anionic, −479, +97, +871; cationic, −550, +50 +782. $E_{1/2}$: $Fe(Cp)_2/Fe(Cp)_2^+$, 349. Three other crystalline forms (**3**, **4**, and **6**) were obtained by layering hexanes onto saturated solutions of $Cr_3(dpa)_4Cl_2$ in benzene, toluene, and THF, respectively.

$Cr_3(dpa)_4Cl(BF_4)\cdot 2CH_2Cl_2$, 1. To a solution of $[Cr_3(dpa)_4Cl_2]$ (0.20 g, 0.22 mmol) in 10 mL of CH_2Cl_2 was added, dropwise, a suspension of $AgBF_4$ (0.043 g, 0.22 mmol) in 8 mL of CH_2Cl_2 at room temperature. After stirring for 4 h, AgCl was removed by filtration through Celite, leaving a dark green solution that was layered with hexanes. Large block-shaped, dark-green crystals were collected after 10 days. Yield: 0.079 g (37%). IR (KBr mull, cm^{-1}): 1610 (vs), 1548 (s), 1428 (s), 1359 (s), 1310 (vs), 1285 (s), 1160 (s), 1108 (s), 1055 (m), 1020 (s), 939 (m), 881 (m), 860 (m), 766 (s), 727 (s), 698 (m), 651 (w), 539 (w), 518 (w).

$Cr_3(dpa)_4Cl(PF_6)\cdot 2CH_2Cl_2$, 2. A suspension of $[Cr_3(dpa)_4Cl_2]$ (0.10 g, 0.11 mmol) and $TlPF_6$ (ratio 1:1) in a mixture of 20 mL of MeOH and 5 mL of CH_2Cl_2 was stirred at room temperature for 18 h. Then the solvent was eliminated under vacuum, the residue extracted with toluene, and the solution layered with hexanes. Yield: 0.07 g (63%). IR (KBr mull, cm^{-1}): 1607 (vs), 1596 (vw), 1547 (m), 1311 (s), 1262 (m), 1155 (s), 1108 (m), 1108 (m), 1015 (m), 840 (s), 764 (m), 739 (m), 556 (m), 516 (m), 537 (m). MS (FAB^+, NBA): 862, $[Cr_3(dpa)_4Cl(PF_6)]^+$; 822, $[Cr_2(dpa)_4Cl]^+$; 786, $[Cr_2(dpa)_4l^+$; 743, $[Cr(dpa)_3Cl(PF_6)]^+$; 703, $[Cr_3(dpa)_3C1]^+$; 650, $[Cr_2(dpa)_3C1]^+$; 627, $[Cr_2(dpa)_2Cl(PF_6)]^+$; 481, $[Cr_2(dpa)_2Cl]^+$.

$Cr_3(dpa)_4(CCPh)_2$, 7. Addition of 1.0 M MeLi (0.57 mL, 0.57 mmol) to C_6H_4CCH (0.063 mL, 0.57 mmol) at −72 °C in 15 cm^3 of THF gave a colorless solution, which was allowed to reach room temperature; after 0.5 h, **5** (0.25 g, 0.16 mmol) was added from a solids addition tube. It was allowed to react with constant stirring for 2 h at room temperature. The color of the suspension changed from dark green to dark reddish-green. The solvent was pumped off, and the residue was extracted with CH_2Cl_2. After filtration the solution was layered with hexanes. Green crystals of **7** formed after several days. Yield (as crystals): 0.118 g (41.2%). MS: (FAB^+, NBA matrix, *m/z*) 871, $[Cr_3(dpa)_3(CCPh)_2]^+ - 2H$; 766, $[Cr(dpa)_3(CCPh)_2]^+$; 729 $[Cr(dpa)_4]^+$; 615, $[Cr_2(dpa)_3]^+$; 529, $[Cr_3(dpa)(CCPh)_2]^+$; 392, $[Cr(dpa)_2]^+$. IR (KBr mull, cm^{-1}): 2045 (m), 1605 (vs), 1467 (vs), 1414 (vs), 1363 (vs), 1310 (s), 1280 (s), 1194 (m), 1152 (vs), 1053 (m), 1013 (vs), 878 (m), 854 (m), 769 (s), 697 (m), 642 (m). CV: anionic, −536, +36, +739; cationic, −632, +42, +889. $E_{1/2}$: $Fe(Cp)_2/Fe(Cp)_2^+$, 334.

X-ray Structure Determination. All but one of the X-ray data sets were collected on a Nonius FAST area detector diffractometer at −60 °C using a Mo sealed-tube source ($\bar{\lambda}$ = 0.710 73 Å). The data for **6** were collected at 22 °C on a Rigaku AFC5R diffractometer with a Cu rotating-anode source ($\bar{\lambda}$ = 1.541 84 Å). The procedures and methods used for the FAST[10] and AFC5R[11] diffractometers in our laboratory have been described previously. The structures were solved using the direct-methods program SHELXS-86,[12] and were refined with the program SHELXL-93.[13] For compounds **1**, **2** and **7** the hydrogen atoms were freely refined, but for the others, they were introduced in idealized positions. A brief summary of crystal and refinement data for all seven structures is given in Table 2. Complete crystallographic details for all of the completed structures are included in the Supporting Information.

Results and Discussion

Syntheses. At low temperature, reaction of $CrCl_2$ and Lidpa in THF, using a molar ratio of 3:4, produces the red quadruply

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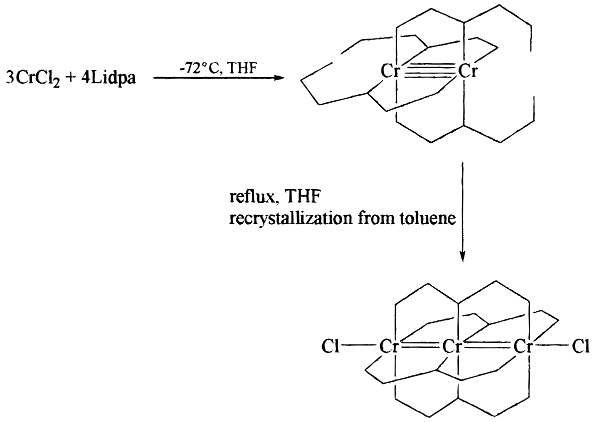
Table 2. Crystallographic Data for Compounds **1**−**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
empirical formula	$C_{42}H_{36}BCl_5Cr_3F_4N_{12}$	$C_{42}H_{36}Cl_5Cr_3F_6N_{12}P$	$C_{46}H_{38}C1_2Cr_3N_{12}$	$C_{47}H_{40}C1_2Cr_3N_{12}$	$C_{41}H_{34}C1_4Cr_3N_{12}$	$C_{44}H_{40}C1_2Cr_3N_{12}O$	$C_{56}H_{42}Cr_3N_{12}$
fw	1128.89	1187.05	985.78	999.81	992.60	979.78	1039.02
space group	$C2/c$	$C2/c$	$Pna2_1$	$Pca2_1$	$Pnn2$	$P\bar{4}n2$	$P2_1/c$
a, Å	19.114(2)	19.126(3)	18.634(5)	18.475(2)	12.996(2)	14.414(2)	16.849(5)
b, Å	16.746(1)	16.962(1)	29.36(2)	14.965(4)	14.1381(8)	14.414(2)	15.460(7)
c, Å	15.655(1)	15.515(1)	16.142(3)	16.4690(13)	11.3306(13)	10.5850(10)	20.479(3)
β, deg	110.92 (1)	109.80(1)	90	90	90	90	110.96(3)
V, Å^3	4680.7 (6)	4735.6(9)	8830(6)	4553.3(13)	2081.9(4)	2199.2(5)	4982(3)
Z	4	4	8	4	2	2	4
calcd density, g/cm^3	1.602	1.665	1.483	1.458	1.583	1.480	1.385
μ, mm^{-1}	1.033	1.063	0.895	0.869	1.074	7.525	0.694
no. of data/ restraints/ params	2984/6/401	2967/0/406	13980/1/1130	5861/1/577	2641/8/285	1766/0/149	6437/0/754
R indices $[I > 2\sigma(I)]^{a,b}$	R1 = 0.035, wR2=0.090	R1 = 0.047, wR2=0.124	R1 = 0.054, wR2=0.119	R1 = 0.050, wR2=0.113	R1 = 0.044, wR2=0.109	R1 = 0.072, wR2=0.147	R1 = 0.070, wR2=0.164
R indices (all data)	R1 = 0.038, wR2=0.092	R1 = 0.051, wR2=0.128	R1 = 0.070, wR2=0.137	R1 = 0.063, wR2=0.124	R1 = 0.053, wR2=0.118	R1 = 0.145, wR2=0.188	R1 = 0.099, wR2=0.197
GOF	1.093	1.143	1.137	1.063	1.11	1.077	1.081

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

bonded compound $Cr_2(dpa)_4$. It has been reported[9] that two of the four dpa ligands have pyridyl groups dangling on one end of the Cr_2^{4+} unit while the other two are dangling on the other end. However, by refluxing this mixture, in which there remains unreacted $CrCl_2$, a remarkable slippage of two dpa ligands occurs while a third chromium atom is incorporated as shown schematically:



This reaction takes place in high yield and, depending on the crystallization conditions, various green-colored solvates can be isolated, e.g., compounds **3**−**6**. In each one there is a chlorine atom axially coordinated to each terminal chromium atom.

Partial or complete substitution of the chlorine atoms has been accomplished, with various degrees of difficulty, with anions, X^-, such as BF_4^-, PF_6^-, and $C{\equiv}CPh^-$:

$$Cr_3(dpa)_4Cl_2 + (2-n)X^- \rightarrow Cr_3(dpa)_4Cl_nX_{2-n} + (2-n)Cl^-$$
$$n = 0, 1$$

For X $=BF_4^-$ and PF_6^-, substitution of one axial chlorine atom proceeds smoothly to give **1** and **2** when 1:1 molar ratios of $Cr_3(dpa)_4Cl_2$ and $AgBF_4$ or $TlPF_6$ are mixed at room temperature in CH_2Cl_2 or mixtures of CH_2Cl_2/MeOH. Further substitution is not easily done. For example, if the ratio of $Cr_3(dpa)_4Cl_2$ to $TlPF_6$ is 1:2, mixtures of $Cr_3(dpa)_4ClPF_6$ and $Cr_3(dpa)_4(PF_6)_2$ are obtained. Crystals of the latter compound have been isolated, but because there were crystallographic difficulties, this structure is not reported here.

If the amount of $AgBF_4$ is increased beyond the 1:1 ratio, further substitution does not take place. Instead a one-electron oxidation of the Cr_3^{6+} unit occurs. The product of the reaction as well as other Cr_3^{7+} compounds will be fully described in a future paper.

We were able to isolate a green acetylide-substituted compound from the following reaction:

$$Cr_3(dpa)_4Cl_2 + 2LiC{\equiv}CPh \xrightarrow{THF} Cr_3(dpa)_4(C_2Ph)_2 + 2LiCl$$

This reaction is difficult to optimize. Crystallization always produced a mixture of crystals of the starting material and those of the diacetylide product, **7**. The identity of the two products in the mixture was established by measuring the unit cell of various crystals and by cyclic voltammetry. Many attempts to obtain analytically pure samples were unsuccessful.

X-ray Structures. Except for the variability in distances between the Cr atoms and in the identity of the axial ligands, the molecular structures of the $Cr_3(dpa)_4L_2$ compounds have much in common. All of the Cr−N distances for the central metal atom lie within the narrow range 1.99−2.04 Å, and the Cr−N distances for the terminal metal atoms range from 2.06 to 2.14 Å. The Cr−Cr−N and N−Cr−N angles vary as expected with the variation in Cr−Cr distances, and the overall twist (the torsion angle defined for one dpa ligand as $N-Cr_{terminal}\cdots Cr_{terminal}-N$) ranges from 37.7° to 43.9°. A drawing of **1** is shown in Figure 1; this structure is typical for the unsymmetrical isomers. Figure 2 shows one of the symmetrical isomers, **5**, and is oriented to emphasize the spiral nature of the ligand set.

The metal−metal separations in these compounds clearly fall into two categories. We had postulated that some combination of terminal ligands might give rise to metal−metal separations that were intermediate between the purely unsymmetrical and the symmetrical motifs, but have not yet observed this. The presence of two different terminal ligands clearly favors the unsymmetrical arrangement. The distance between the two terminal Cr atoms is also characteristic for each structure type, with a value of about 4.63 Å for the unsymmetrical structures and 4.72 Å for the symmetrical ones having Cl terminal groups (see Table 1). The symmetrical structure with $-C{\equiv}C-Ph$ end groups, **7**, is obviously strongly affected by the covalent character of the Cr−C bonds, such that the Cr−Cr separations are significantly longer and the overall Cr−Cr−Cr distance is 4.837(2) Å. The structure of **7** is shown in Figure 3.

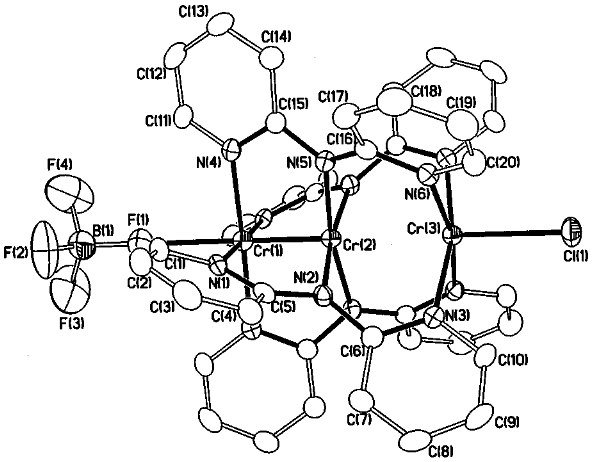


Figure 1. The structure of $Cr_3(dpa)_4ClBF_4$, **1**, drawn with 45% probability ellipsoids and with H atoms removed. Unlabeled atoms are those generated by a 2-fold axis that includes the Cr atoms, Cl(1), F(1), and B(1). Only one of the two orientations of the BF_4 group is shown.

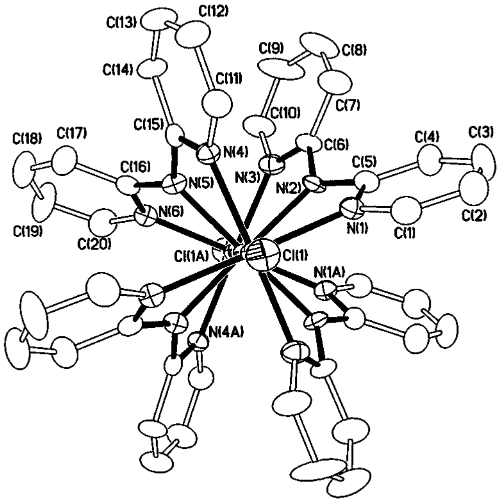


Figure 2. Near-axial view of the symmetric isomer of $Cr_3(dpa)_4Cl_2$ as found in compound **5**. A crystallographic 2-fold axis runs approximately horizontal across the page in this view. The atoms are drawn as 50% probability ellipsoids, and H atoms are not shown.

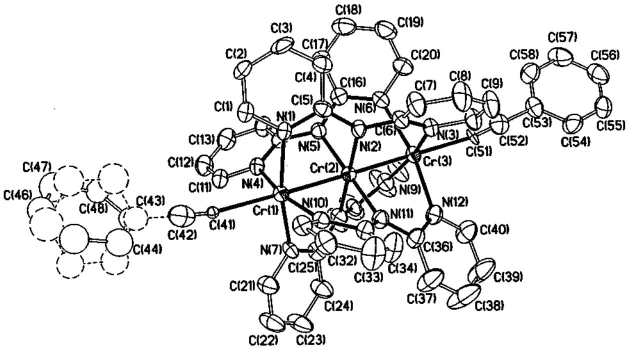


Figure 3. Structure of $Cr_3(dpa)_4(CCPh)_2$, **7**, shown with 40% probability ellipsoids and indicating the disorder in one of the CCPh groups.

Magnetic Measurements. The magnetic behavior of two compounds, one symmetrical and the other unsymmetrical, has been measured. Complete results are available in the Supporting Information. We show in Figures 4 and 5 only the plots of μ_{eff} (in μ_B) for each one. Both compounds followed the Curie law within experimental error from 15 to 300 K.

For the symmetrical compound, $Cr_3(dpa)_4Cl_2{\cdot}CH_2Cl_2$, **5**, the experimental points were fitted very closely by employing $g = 2.08$ and a diamagnetic correction of 6×10^{-4} cgs mol^{-1}. The value of μ_{eff}, which is constant from 20 to 300 K, is 5.1 μ_B. This corresponds to a ground state with four unpaired electrons and a small amount of orbital angular momentum.

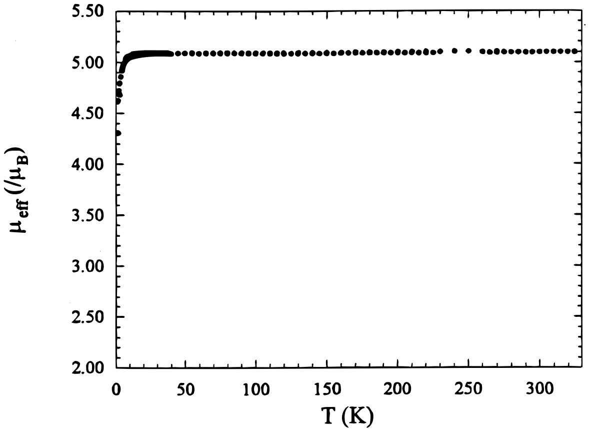


Figure 4. Plot of μ_{eff} (in μ_B) vs *T* for $Cr_3(dpa)_4Cl_2{\cdot}CH_2Cl_2$.

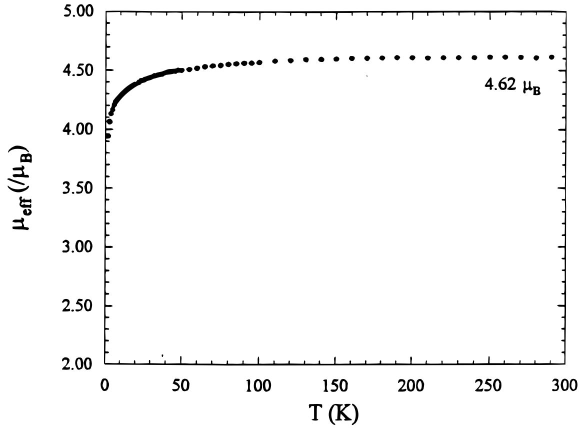


Figure 5. Plot of μ_{eff} (in μ_B) vs *T* for $Cr_3(dpa)_4Cl(PF_6){\cdot}CH_2Cl_2$.

For the unsymmetrical compound, $Cr_3(dpa)_4Cl(PF_6){\cdot}2CH_2Cl_2$, **2**, in which the Cr−Cr distances are 2.008 and 2.614 Å, the fit to the experimental data was obtained with $g = 1.88$ and a diamagnetic correction of 15×10^{-4} cgs mol^{-1}. The value of μ_{eff} is approximately constant from 100 to 300 K at 4.62 μ_B. In view of the short distance between two of the chromium atoms, we assume them to be quadruply bonded and attribute the paramagnetism entirely to the remaining Cr^{II}. The magnetic moment is consistent with the four unpaired electrons expected, although why the actual value is a little below that expected (ca. 4.9 μ_B) is not known.

The magnetic results show that there are four unpaired electrons in the Cr_3^{6+} chain whether it is completely symmetrical or extremely unsymmetrical. Thus, at no point along the entire range of structures is there a spin-state change that might cause a discontinuity. At the same time the distribution of electron spin-density must change from a symmetrical one to one in which the unpaired spins are essentially localized on one terminal chromium ion. This poses a very interesting problem for theoretical treatment.

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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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