Linear tri- and tetra-chromium(II) chains supported by four bis(2-pyridyl)formamidinium ligands

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Reactions of bis(2-pyridyl)formamidinium ion, DpyF$^-$, with $CrCl_2$ lead to $[Cr_3(DpyF)_4][PF_6]_2$ and $[Cr_4(DpyF)_4Cl_2]Cl_2$, both of which are structurally characterized by X-ray crystallography; the latter contains two Cr–Cr quadruple bonds even though no such bonds were preformed in the starting material ($CrCl_2$).

In our continuing study of compounds with linear chains of metal atoms,[1–3] we have employed the anion of bis(2-pyridyl)formamidine, DpyF$^-$, as a ligand and carried out reactions of the lithium salt with $CrCl_2$ under various conditions, whereby we have obtained[†] three new and interesting compounds, $[Cr_3(DpyF)_4][PF_6]_2\cdot 4MeCN\cdot 2Et_2O$ (**1**$\cdot$4MeCN$\cdot$2Et$_2$O), $[Cr_4(DpyF)_4Cl_2]Cl_2\cdot 5(Me_2CO)$ (**2**$\cdot$5Me$_2$CO) and a different solvate of **2**, namely, **2**$\cdot$4MeOH. The crystal structures of all three have been determined[‡].

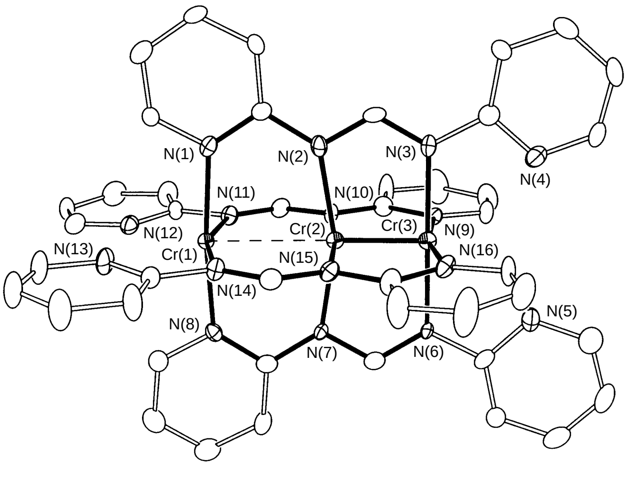


Fig. 1 Perspective view of the cation of **1**. Relevant distances (Å) and angles (°): Cr(1)–Cr(2) 2.738(7), Cr(2)–Cr(3) 1.949(7), Cr(1)–N(1) 2.054(5), Cr(1)–N(11) 2.092(6), Cr(1)–N(14) 2.074(6), Cr(2)–N(2) 2.086(5), Cr(2)–N(7) 2.102(5), Cr(2)–N(10) 2.070(5), Cr(2)–N(15) 2.068(5), Cr(3)–N(3) 2.062(5), Cr(3)–N(6) 2.031(5), Cr(3)–N(9) 2.057(5), Cr(3)–N(16) 2.078(6); Cr(1)–Cr(2)–Cr(3) 179.2(2), N(1)–Cr(1)–N(11) 88.2(2), N(2)–Cr(2)–N(10) 89.7(2), N(3)–Cr(3)–N(9) 90.4(2).

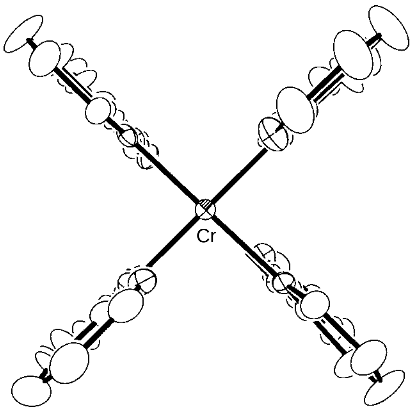
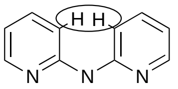
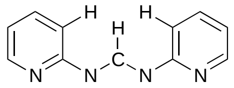


Fig. 2 The $[Cr_3(DpyF)_4]^{2+}$ cation of **1** viewed down the Cr–Cr–Cr direction

The structure of the trinuclear compound **1** is shown in Fig. 1; the Cr_3 chain is not symmetrical and can be qualitatively described as having one pair of chromium atoms quadruply bonded, Cr(2)–Cr(3) 1.949(7) Å, with the third chromium atom not significantly bonded to the central one, Cr(1)–Cr(2) 2.738(7) Å. In comparing the structure of **1** with those previously reported[2] for chromium with dpa$^-$ [dpa$^-$ = anion of bis(2-pyridyl)amine], the most obvious qualitative difference is that the central Cr_3N_{12} core in **1** is essentially untwisted, as shown in Fig. 2, whereas in the dpa compounds there is an overall twist of about 45°. Compound **1** is the first such linear, trinuclear species of any metal[§] that is non-helical. The twist in all of the dpa$^-$ compounds is clearly due to the H···H repulsion indicated in **I** while in **II** it is clear that there is no basis for a ligand-imposed twist.



I



II

As already reported[2] the Cr_3 chains in $Cr_3(dpa)_4X(Y)$ units may be symmetrical (X = Y = Cl, Cr–Cr 2.36 Å) or unsymmetrical (X = Cl, Y = BF$_4$, Cr–Cr 2.64, 2.00 Å) depending on the axial ligands. In **1** there are no axial ligands. The nearest structural comparison we can make with **1** is the structure of $Cr_3(dpa)_4Cl(BF_4)$ **3**.

To the question of whether absence of helicity is of importance to the electronic structure of the Cr_3^{6+} unit we can offer at least a partial answer at this time. The Cr_3 chain of **1**, like that in **3**, is unsymmetrical. In addition, the Cr–Cr distances in **1**, 1.949(7) and 2.738(7) Å are very similar to those in **3**, 1.995(1) and 2.643(1) Å. In these respects there is no indication that helicity in itself has a qualitative effect on the bonding in the metal atom chain. For the dpa compounds, the structure seems to be tunable, from symmetrical to unsymmetrical, by changing the axial ligands from Cl, Cl to Cl, BF$_4$. In the case of **1** there are no axial ligands, and thus the unsymmetrical character seems to be inherent in the $[Cr_3(DpyF)_4]^{2+}$ chain.

The cation in **2** is shown in Fig. 3; there are only slight differences between the dimensions in the two crystalline forms. There must, of course, be non-equivalent M–M distances in all M_n chains with $n > 3$. In this case the difference between the central and the outer Cr–Cr distances is very large, *ca.* 2.73 Å *vs. ca.* 2.01 Å. It seems reasonable to describe the bonding to a first, and probably good, approximation by saying that there are two Cr–Cr quadruple bonds and little if any bonding between the two inner chromium atoms. The short Cr–Cr distance may be compared to that in the compound $Cr_2(map)_4$[4] (map = anion of 2-amino-6-methylpyridine), where it is 1.870(3) Å. It seems reasonable to attribute the greater length of

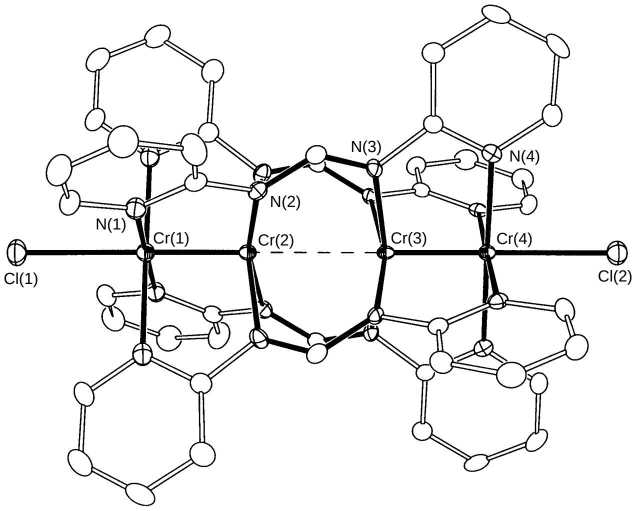


Fig. 3 Perspective view of the cation of **2**·4MeOH. Relevant distances (Å) and angles (°): Cr(1)–Cr(2) 2.013(2), Cr(2)–Cr(3) 2.726(2), Cr(3)–Cr(4) 2.001(2), Cr(1)–N(1) 2.134(4), Cr(2)–N(2) 2.036(3), Cr(3)–N(3) 2.034(4), Cr(4)–N(4) 2.135(4), Cr(1)–Cl(1) 2.545(2), Cr(4)–Cl(2) 2.564(2); Cr(2)–Cr(1)–N(1) 89.7(1), Cr(1)–Cr(2)–N(2) 97.2(1), N(2)–Cr(2)–Cr(3) 82.8(1), Cr(4)–Cr(3)–N(3) 97.3(1), N(3)–Cr(3)–Cr(2) 82.7(1), Cr(3)–Cr(4)–N(4) 90.2(1).

the bonds in **2** to the presence of the axial Cl$^-$ ligands, whereas in Cr$_2$(map)$_4$ there are no axial interactions.

The observed preference of the chain of three Cr^{2+} ions to form one quadruple bond and the chain of four Cr^{2+} ions to form two separate quadruple bonds rather than to give more delocalized, and therefore evenly spaced arrangements raises the question of how general this tendency may be. It is already known, for both Cr$_3$ and Co$_3$ compounds of dpa$^-$ that symmetrical and unsymmetrical structures both occur. In the Cr$_4$ case, the short–long–short structure makes all the metal chain electrons (MCEs) bonding electrons over short distances where d–d overlaps are very good.¶ It can be hypothesized that in other cases of four metal atoms, especially where MCE counts are higher, more delocalized configurations might be favored. Studies are in progress to examine this.

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Footnotes and References

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† Preparation of [Cr$_3$(DPyF)$_4$][PF$_6$]$_2$ **1** and [Cr$_4$(DPyF)$_4$Cl$_2$]Cl$_2$ **2**. Bis(2-pyridyl)formamidine was prepared by condensation of 2-aminopyridine with triethylorthoformate at 170 °C.[5] An solution of LiDpyF was made by adding 4.0 ml of 1.0 M methyllithium to a solution of HDpyF (0.795 g, 4.0 mmol) in THF (40 ml) at −60 °C. When the LiDpyF solution warmed to ambient temperature, it was transferred to a round-bottom flask containing CrCl$_2$ (0.528 g, 4.3 mmol). A red suspension was obtained after stirring the mixture for 6 h. At this stage, TlPF$_6$ (0.70 g, 2.0 mmol) was added to the suspension. A green solid was produced when it was heated to reflux temperature for 12 h and then cooled to room temp. The supernatant liquid was removed with a syringe and the green solid was washed with THF (15 ml) and CH$_2$Cl$_2$ (2 × 20 ml). Extraction with acetone gave a green solution. After layering with hexanes, red crystals of **2**·5Me$_2$CO were isolated. Yield 0.11 g, 7.7%. The remaining solid was only partially soluble in acetonitrile. After filtration, slow diffusion of diethyl ether into the filtrate changed the color of the solution from green to reddish and gave orange crystals of **1**·4MeCN·2Et$_2$O, yield 0.44 g, 28%. The remaining solid, which was not soluble in acetone or in acetonitrile, was dissolved in dimethyl sulfoxide to give an emerald green solution. Layering with benzene precipitated a green powder. After filtration, this was washed with diethyl ether and dried under vacuum to yield 0.64 g of green material. Red crystals of **2**·4MeOH were obtained by diffusion of diethyl ether (20 ml) into a saturated green methanol solution (25 ml) of the green powder. The combined yields for **2** are 64%. Crystals of **1** can be redissolved in acetonitrile to produce an orange solution. Red crystals of **2** are not soluble in acetonitrile but can be redissolved in methanol to give a green solution. Compound **1** is paramagnetic, μ_{obs} 4.6 μ_B; **2** is diamagnetic, ^{1}H NMR (CD$_3$OD, 300 MHz): δ 9.76 (s, 4 H, methine NCHN), 9.48 (d, 8 H, pyridyl CH), 7.83 (m, 16 H, pyridyl CH), 7.09 (t, 8 H, pyridyl CH). UV–VIS (λ/nm): 528, 620 (sh) for **1** in MeCN; 384(sh), 462, 616 for **2** in MeOH.

‡ *Crystal data*: [Cr$_3$(DpyF)$_4$][PF$_6$]$_2$·4MeCN·2Et$_2$O, **1**·4MeCN·2Et$_2$O: orange crystal, C$_{60}$H$_{68}$Cr$_3$F$_{12}$N$_{20}$O$_2$P$_2$, M = 1547.28, monoclinic, space group $P2_1/c$, a = 15.006(4), b = 14.993(2), c = 31.238(9) Å. β = 99.79(1)°, U = 6926(3) Å^3, Z = 4, D_c = 1.484 g cm^{-3}, λ = 0.71073 Å, μ(Mo-Kα) 0.599 mm^{-1}. Intensity data were collected on a CAD4 diffractometer at −100 °C. A ψ-scan absorption correction was made. A total number of 8966 independent reflections were measured, of which 4352 were observed [$I \geq 2\sigma(I)$]. The structure was solved by direct methods using SHELXTL and refined using SHELXL-97. During structural refinement, it was found that the chromium atoms were disordered. The final positions of the metal atoms clearly indicate a short Cr–Cr quadruple bond and a long, non-bonded Cr–Cr interaction. The disorder arises since the ligand framework is essentially symmetric, and the short–long bond pair can sit either way in the ligand environment. In the final refinement cycles, the relative occupancy of the two metal-atom groups was refined, and converged with the major orientation having an occupancy of 0.52(1). Final full-matrix least-squares refinement on F^2 of positional and anisotropic thermal parameters for all non-hydrogen atoms converged to R_1 = 0.181, wR_2 = 0.118 for all data; and R_1 = 0.056, wR_2 = 0.102 for data with $I \geq 2\sigma(I)$.

[Cr$_4$(DPyF)$_4$Cl$_2$]Cl$_2$·5Me$_2$CO, **2**·5Me$_2$CO: red crystal, C$_{59}$H$_{66}$Cl$_4$Cr$_4$N$_{16}$O$_5$, M = 1429.08, monoclinic, space group $C2/c$, a = 32.988(4), b = 9.269(1), c = 26.183(7) Å, β = 127.50(1)°, U = 6351(2) Å^3, Z = 4, D_c = 1.491 g cm^{-3}, λ = 0.71073 Å, μ(Mo-Kα) 0.896 mm^{-1}. Intensity data were collected on a FAST area detector system at −60 °C. A total number of 4145 independent reflections were measured, of which 3660 were observed [$I \geq 2\sigma(I)$]. The structure was solved by direct methods using SHELXTL. Full-matrix least-squares refinement on F^2 of positional and anisotropic thermal parameters for all non-hydrogen atoms converged to R_1 = 0.049, wR_2 = 0.111 for all data; and R_1 = 0.041, wR_2 = 0.103 for data with $I \geq 2\sigma(I)$.

[Cr$_4$(DPyF)$_4$Cl$_2$]Cl$_2$·4MeOH, **2**·4MeOH: red crystal, C$_{48}$H$_{52}$Cl$_4$Cr$_4$N$_{16}$O$_4$, M = 1266.86, tetragonal, space group $P4/n$, a = 12.8063(7), c = 16.326(2) Å, U = 2677.5(4) Å^3, Z = 2, D_c = 1.571 gcm^{-3}, λ = 0.71073 Å, μ(Mo-Kα) 1.050 mm^{-1}. Intensity data were collected on a FAST area detector system at −60 °C. A total number of 1767 independent reflections were measured, of which 1647 were observed [$I \geq 2\sigma(I)$]. The structure was solved by direct methods using SHELXTL. During structural refinement, it was found the crystal twinned along the (110) plane. The occupancy of both components were refined and the major component contributed to 59.5% of the structure. Final refinement converged to R_1 = 0.044 and wR_2 = 0.108 for all data, and R_1 = 0.040 and wR_2 = 0.103 for data with $I \geq 2\sigma(I)$. CCDC 182/652.

§ M$_3$(dpa)$_4$X$_2$ compounds, all of which are helical, have been reported for M = Cr,[2] Co,[3] Ni, Cu and Ru. Full references are found in ref. 3.

¶ Compounds containing two quadruply bonded M$_2^{4+}$ units (M = Mo and W), end-to-end, are also known.[6] In these cases the quadruply bonded dimetal units were already present in the starting material.

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