

Communications to the Editor

Compounds with Linear, Bonded Trichromium Chains

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Received June 17, 1997

Beginning with the first observations, in 1990, that the anion of bis(2-pyridyl)amine (dpa⁻) can support the formation of directly bonded, linear chains of metal atoms,¹ studies of such compounds have been pursued in other laboratories, including our own. We now report that compounds with chains of chromium atoms can be obtained and that they have interesting structural and redox properties.

The chemistry is summarized in Scheme 1.² Reaction of CrCl₂ with dpa⁻ in a molar ratio of 3 to 4 produces first a red suspension which then changes to green. After LiCl is removed, the solution affords green blocked-shaped crystals of Cr₃(dpa)₄Cl₂·CH₂Cl₂, **1**·CH₂Cl₂,³ the structure of which is shown in Figure 1. It consists of a linear Cr₃⁶⁺ chain ligated by a spiral set of dipyriddy anions; each terminal Cr atom is also bonded to a Cl anion. Because the central Cr atom resides on a crystallographic 2-fold axis, the metal atom chain is symmetrical and the Cr–Cr distances are each 2.36(1) Å (Figure 2). This type of symmetrical arrangement has also been observed for analogous complexes of Co,⁴ Ni,⁵ Cu,⁶ Ru, and Rh.⁷

The room temperature magnetic susceptibility measurements for **1** show the presence of two unpaired electrons, which is consistent with an electronic structure of $\sigma_b^2\pi_b^4\delta_b^2\delta_n^2\pi_n^2$ (where subscripts *b* and *n* signify bonding and nonbonding, respectively). This configuration is the same as that predicted by a Fenske–Hall calculation and corresponds to the presence of two Cr–Cr double bonds.

Compound **1** reacts smoothly with 1 equiv of AgBF₄,⁸ causing the replacement of one chloride ion by a tetrafluoroborate anion. The resulting compound, **2**, forms green, blocked-shaped crystals containing Cr₃(dpa)₄Cl(BF₄) molecules. The striking feature of this molecule is that although the ligand arrangement remains

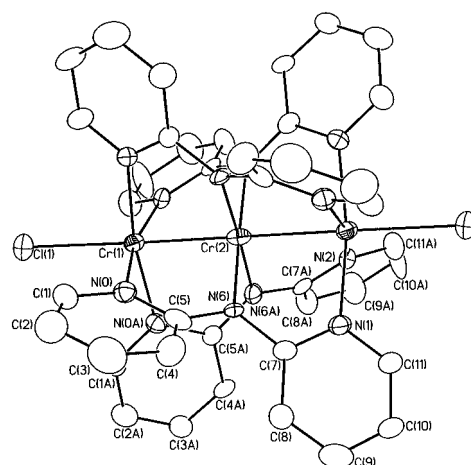
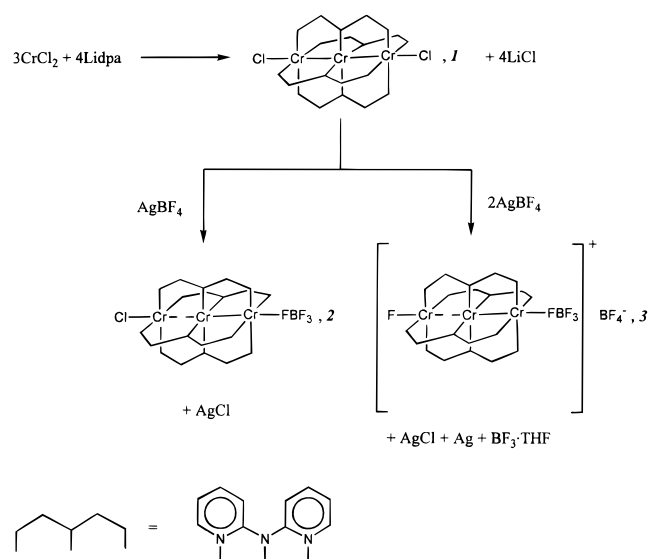


Figure 1. A drawing of the molecular structure of [Cr₃(dpa)₄Cl₂] in **1**·CH₂Cl₂. Ellipsoids are drawn at the 50% probability level. The hydrogen atoms have been omitted for clarity.

Scheme 1



almost unchanged, the Cr₃ chain is now highly unsymmetrical. The shorter distance of 1.9952(8) Å is reminiscent of those found in the dichromium complexes bridged by N,N- or N,O-containing ligands (e.g., formamidinates and 2-oxopyridinates).⁹ The separation of 2.6427(8) Å found between Cr(1) and Cr(2) is too long to be considered a bonding interaction. Consequently, the complex can be considered as composed of a quadruply bonded dichromium(II) unit attached to a square pyramidal Cl–Cr–N₄ unit.

When **1** reacts with 2 equiv of AgBF₄ instead of 1 equiv (which produced **2**), the additional amount of AgBF₄ does not react simply to substitute the second Cl atom. Instead, a redox reaction takes place and one of the terminal chromium atoms is oxidized to produce green plate-like crystals of [Cr₃(dpa)₄–

[†] Texas A&M University.[‡] University of Costa Rica.(1) Wu, L.-P.; Field, P.; Morrissey, T.; Murphy, C.; Nagle, P.; Hathaway, B.; Simmons, C.; Thornton, P. *J. Chem. Soc., Dalton Trans.* **1990**, 3835.

(2) Elemental analyses for all compounds were satisfactory.

(3) Compound **1** was prepared from a solution of Hdpa (0.341 g, 2.00 mmol) in 10 mL THF at –78 °C to which was added MeLi (2.00 mmol). When the reaction mixture had warmed to ambient temperature, anhydrous CrCl₂ (0.184 g, 1.50 mmol) was added. The suspension was refluxed for 6 h, while it gradually turned to red and then to dark green. A dark green precipitate was filtered under nitrogen, and was washed several times with THF. Yield: 0.40 g (87%). The product was recrystallized by slow diffusion of hexanes into a CH₂Cl₂ solution. IR (KBr mull) cm⁻¹: 1611vs, 1547s, 1480vs (br), 1376vs (br), 1152s, 1111m, 1055m, 1017s, 918w, 878m, 859m, 759s, 748m, 735s, 668w, 644m, 536m, 516m, 433s, 418s. The magnetic susceptibility corresponds to 2.84 μ_B. (The Evans method was used for all magnetic susceptibility measurements.) Crystal data for **1**·CH₂Cl₂: dimensions 0.2 × 0.2 × 0.18 mm, orthorhombic, space group *Pnn2*, *a* = 12.996(2), *b* = 14.1381(8), and *c* = 11.3306(13) Å, *V* = 2081.9(4) Å³, *Z* = 2, *T* = –60 °C, *D*_{calcd} 1.663 g/cm³, *μ*(Mo Kα) 1.172 mm⁻¹; 2644 unique data were used to refine the 276 parameters of the model, giving final residuals based on *F*_o² of 0.160 (all data) and 0.150 [for *I* > 2σ(*I*)] and those based on *F*_o of 0.064 (all data) and 0.056 [for *I* > 2σ(*I*)]. Molecules of disordered interstitial CH₂Cl₂ were located in the crystal.

(4) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., *IV Chem. Commun.* **1997**, 421.(5) Aduldecha, S.; Hathaway, B. *J. Chem. Soc., Dalton Trans.* **1991**, 993.(6) Pyrka, G. J.; El-Mekki, M.; Pinkerton, A. A. *J. Chem. Soc., Chem. Commun.* **1991**, 84.(7) Sheu, J.-T.; Lin, C.-C.; Chao, I.; Wang, C.-C.; Peng, S.-M. *Chem. Commun.* **1996**, 315.

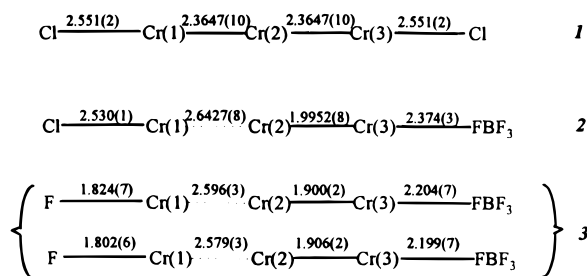


Figure 2. Interatomic separations (Å) along the linear $\text{XCr}_3\text{X}'$ units.

$\text{F}(\text{BF}_4)](\text{BF}_4) \cdot 2\text{CH}_2\text{Cl}_2 \cdot \text{C}_6\text{H}_{14}$, $\mathbf{3} \cdot 2\text{CH}_2\text{Cl}_2 \cdot \text{C}_6\text{H}_{14}$.¹⁰ In this remarkable compound which contains two crystallographically independent molecules, very dissimilar Cr–Cr distances are found. The short distances of 1.900(2) and 1.906(2) Å are clearly consistent with the presence of a quadruple bond between two adjacent chromium atoms while the third chromium atom of each independent molecule, which is separated from the central metal atom by 2.596(3) or 2.579(3) Å, is simply a square pyramidal unit¹¹ with no metal–metal bonding interaction. This is consistent with the measured magnetism of $4.4 \mu_{\text{B}}$ which indicates that the molecule has three unpaired electrons. These can be assigned to the Cr^{3+} (d^3) species; the quadruply bonded fragment would not be expected to contribute to the paramagnetism of the molecule.

The presence of the F ion in **3** can be explained by considering the dissociation of the BF_4^- anion in THF to give F^- and $\text{BF}_3 \cdot \text{THF}$.

In view of the localized quadruple bonds found in **2** and **3**, we examined the possibility that the symmetrical Cr–Cr distances (with no quadruple bonds) found in **1** might be an artifact of the diffraction experiment and could be due to crystallographic disorder in which an unsymmetrical Cr_3 chain is randomly oriented in both directions. However, this hypoth-

(8) Compound **2** was prepared by stirring a solution of **1** (0.200 g, 0.22 mmol) in 10 mL of CH_2Cl_2 to which 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 4 h of stirring, AgCl was removed by filtration through Celite, leaving a clear dark green solution that was layered with hexanes. After 10 days, large block-shaped, dark green crystals were collected. Yield: 0.079 g (37%). IR (KBr mull) cm^{-1} : 1610vs, 1548s, 1428s (br), 1359s (br), 1310vs, 1285s, 1160s, 1108s, 1055m, 1020s, 939m, 881m, 860m, 766s, 727s, 698m, 651w, 539w, 518w. The magnetic susceptibility, μ_{eff} , of $3.29 \mu_{\text{B}}$ corresponds to 2.5 unpaired electrons. This value could be explained by an in-solution equilibrium between the asymmetric species $\text{Cr}^{\text{II}} \cdots \text{Cr}^{\text{II}} - \text{Cr}^{\text{II}}$ (4 unpaired electrons) and the symmetric one $\text{Cr}^{\text{II}} - \text{Cr}^{\text{II}} - \text{Cr}^{\text{II}}$ (2 unpaired electrons, as in **1**); further studies in the solid state are being carried out. Crystal data for $\mathbf{2} \cdot \text{CH}_2\text{Cl}_2$: dimensions $0.4 \times 0.3 \times 0.3$ mm, monoclinic, space group $C2/c$, $a = 19.114(2)$, $b = 16.746(1)$, and $c = 15.655(1)$ Å, $\beta = 110.92(1)^\circ$, $V = 4680.7(6)$ Å³, $Z = 4$, $T = -60$ °C; 2948 reflections were used to refine the model, R_1 (on F_o): 0.038 (all data), 0.035 ($I > 2\sigma(I)$); wR_2 0.091 (all data), 0.088 ($I > 2\sigma(I)$). The BF_4^- anion is disordered and was modeled with each of the three F-atoms not linked to Cr(3) disordered over two positions. A molecule of CH_2Cl_2 is also statically disordered in two positions sharing a common central carbon atom.

(9) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, 1993.

esis can be readily eliminated. Given that the end-to-end length of the Cr_3 chain is 4.73 Å, if there were one short (say 2.00 Å) and one long (2.73 Å) internal distance, the apparent separation of the two central Cr/2 atoms would be 0.73 Å. This distance is so large that resolved peaks should be observed in the electron density maps at Cr(2), but none are seen. Furthermore, the displacement parameters are normal for all atoms. As a final proof that the Cr_3 chain in $\mathbf{1} \cdot \text{CH}_2\text{Cl}_2$ is truly symmetrical, we have introduced the disordered model of $\text{Cr}-\text{Cr}/2-\text{Cr}/2-\text{Cr}$ with distances of 2.00, 0.73, and 2.00 Å and refined it. The result was that the two Cr/2 atoms rapidly coalesced at the central position.¹²

The rather remarkable phenomenon that is exemplified by compounds **1** and **2** is that simply by changing from an identical pair of axial anions (Cl^- , Cl^-) to a dissimilar pair (Cl^- , BF_4^-) the structural and electronic character of the Cr_3 chain is drastically changed from a symmetrical one with Cr–Cr bond orders of 2 and 2 to a grossly unsymmetrical one with Cr–Cr bond orders of 0 and 4. We are not aware of any precedent for such a phenomenon.

Acknowledgment. We are grateful to the Vicerrectoría de Investigación U.C.R. (project 115-87-516) and the Department of Chemistry for support of work at the University of Costa Rica and to the National Science Foundation for support of work at Texas A&M University. The authors thank Dr. X. Feng for helpful discussions.

Supporting Information Available: Tables of crystallographic data including diffractometer and refinement data, final coordinates, bond lengths, bond angles, and anisotropic displacement parameters (42 pages). See any current masthead page for ordering and Internet access instructions.

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(10) Compound **3** was prepared similarly to **2**, but with a 1:2 ratio of $\text{Cr}_3(\text{dpa})_4\text{Cl}_2$ to AgBF_4 . To the solvent, CH_2Cl_2 , was added two drops of THF. The product was isolated as large, plate-like dark green crystals. Yield: 0.15 g (66%). IR (KBr mull) cm^{-1} : 1608s, 1587s, 1550m, 1470vs, 1428vs, 1359s, 1287m, 1266m, 1242w, 1158m, 1119m, 1055w, 1021m, 924s, 883m, 859w, 766m, 741m, 649w, 537w, 517w. The magnetic susceptibility at 22 °C corresponds to $4.4 \mu_{\text{B}}$. Crystal data for $\mathbf{3} \cdot 2\text{CH}_2\text{Cl}_2 \cdot \text{C}_6\text{H}_{14}$: dimensions $0.6 \times 0.2 \times 0.05$ mm, orthorhombic, space group $Pna2_1$, $a = 23.878(1)$, $b = 29.488(1)$, and $c = 14.244(2)$ Å, $V = 10029(1)$ Å³, $T = -60$ °C; 12827 independent reflections, 1342 parameters refined, R_1 (on F_o) 0.103 (all data), 0.079 ($I > 2\sigma(I)$); wR_2 (on F_o^2) 0.235 (all data), 0.203 ($I > 2\sigma(I)$); Flack's parameter $-0.05(6)$. Two crystallographically independent, but chemically similar molecules are present. Molecules of disordered CH_2Cl_2 and hexane were found in the interstices of the crystal.

(11) This represents, to our knowledge, only the second example of a high-spin square pyramidal $\text{Cr}^{\text{III}}\text{N}_4\text{X}$ unit. The first one was $\text{Cr}(\text{tmtaa})\text{Cl}$ where tmtaa is the dianion of a tetrazamacrocyclic. See: Cotton, F. A.; Czuchajowska, J.; Falvello, L. R.; Feng, X. *Inorg. Chim. Acta* **1990**, *172*, 135.

(12) **Note Added in Proof:** The converse situation has been encountered in a recently determined structure in which an unsymmetrical Cr_3 chain was indeed disordered so as to appear, initially as a symmetrical complex. In this case, however, all three Cr atoms in the symmetrical model displayed extremely elongated displacement ellipsoids. When each was split and the model refined, the atoms did *not* coalesce into a single position. Diffraction data can clearly recognize a disordered model when that situation exists.