

A Dichromium(II,II) Compound with a Strong Antiferromagnetic Coupling but Little or No Cr–Cr Bonding

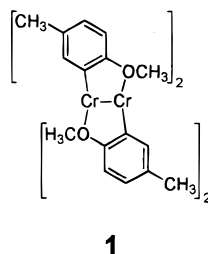
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Introduction

There is now a very extensive chemistry of compounds in which two central Cr^{II} atoms are surrounded by a set of four bridging ligands. In the vast majority, there is significant bonding between the chromium atoms, and in some cases this is very strong. For example in the dichromium compound **1**,



the metal–metal contact of 1.83 Å is the shortest known in any stable substance. However, the variability of the Cr–Cr distances is astonishing and highly dependent on its surroundings. The earliest Cr₂⁴⁺ compounds to be discovered and studied were those with four bridging carboxylate groups. In condensed phases, as solids or in solution, these typically have Cr–Cr distances in the range 2.256(4)¹ to 2.541(1) Å.² The only tetracarboxylate compounds whose Cr–Cr distances fall outside this range are gaseous Cr₂(O₂CCH₃)₄, with a metal–metal distance of 1.96 Å,³ and Cr₂(O₂CAr)₄⁴ (O₂CAr represents the anion of 2,4,6-triisopropylbenzoic acid), which has a Cr–Cr distance of 1.966(2) Å. There is now overwhelming evidence indicating that in these carboxylates, as well as in compounds with other classes of bridging ligands, axial interactions of either σ or π type⁵ are primarily responsible for the Cr–Cr bond lengthening.

Another factor that might be expected to induce lengthening of Cr–Cr bonds (and indeed M–M bonds in general) is the presence of ligands that favor the formation of divergent bonds to the metal atoms.⁶ An excellent example of such a ligand is

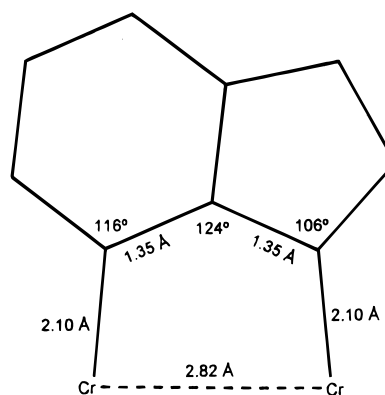
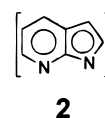
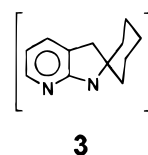


Figure 1. Calculated geometric parameters for an azin ligand for a typical Cr–N bond of 2.10 Å.

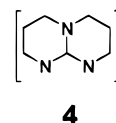
the anion of 7-azaindole, azin, **2**. For this ligand, geometric



considerations indicate that for an N–Cr bond length of 2.1 Å, the formation of unbent N–Cr bonds would require a Cr–Cr distance of 2.82 Å, as shown in Figure 1. Another example is the anion of 1',3'-dihydrospiro[cyclohexane-1,2'-[2H]imidazo-[4,5-b]pyridine], CHIP, which is shown as **3**. The CHIP ligand



may not be as rigid as **2**, but because of similar geometry, namely, fused 5- and six-membered rings, this ligand, too, will favor long metal–metal separations in a paddlewheel structure. We have reported⁷ recently that when axial coordination is absent, the compound Cr₂(CHIP)₄ has a Cr–Cr distance of 2.016(1) Å, which is 0.16 Å longer than that in Cr₂(hpp)₄⁸ (hpp is shown as **4**). In this report, it will be shown that when the



divergent geometry is coupled with strong axial coordination, the chromium–chromium separation can be elongated to as

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much as 2.688(2) Å, so far the longest in any known dichromium paddlewheel complex.

Experimental Section

All syntheses and manipulations were carried out under an atmosphere of nitrogen with standard Schlenk and glovebox techniques. The ligand 7-azaindole was purchased from Lancaster and sublimed before use, while CrCl₂ was purchased from Strem Chemicals. Methylolithium (1.0 M in THF/cumene) was purchased from Aldrich and used as received. All solvents were freshly distilled over suitable drying reagents under N₂. An infrared spectrum was obtained from KBr pellets on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Elemental analysis was performed by Canadian Microanalytical Services Ltd.

Preparation of [Li₂(DMF)₆][Cr₂(azin)₄Cl₂]. The compound Hazin (0.24 g, 2.0 mmol) was dissolved in THF (20 mL), and cooled to -78 °C. Butyllithium in hexanes (1.6 M, 1.3 mL, 2.1 mmol) was added. After reaching ambient temperature, the colorless solution of Li(azin) was transferred to another flask charged with CrCl₂ (0.12 g, 1.0 mmol). A brown suspension was obtained immediately; this was stirred at room temperature for 12 h. After filtration, a yellow solid was collected, washed with THF (3 × 10 mL) and acetone (20 mL), and dried under vacuum. The yellow solid was then extracted with dimethylformamide (DMF, 10 mL); a red solution was collected by filtration and layered with diethyl ether. Large block-shaped red crystals of [Li₂(DMF)₆][Cr₂(azin)₄Cl₂] were obtained in 5 days. Yield: 0.48 g (88%). IR (KBr pellet, cm⁻¹): 1681 (m), 1660 (vs), 1595 (m), 1552 (w), 1529 (w), 1513 (w), 1493 (w), 1462 (s), 1422 (m), 1387 (m), 1337 (s), 1283 (m), 1261 (m), 1158 (s), 1101 (m), 1064 (w), 936 (w), 914 (w), 798 (m), 767 (m), 729 (m), 676 (w), 637 (w), 584 (w), 471 (m), 409 (w). Anal. Found: C, 50.40; H, 5.56; N, 16.77. Calcd: C, 50.42; H, 5.70; N, 17.89.

Crystallographic Study

The data set was collected on a Nonius FAST area detector diffractometer with a 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 207 reflections ranging in 2θ from 18° to 41°. Laue group and centering conditions were confirmed by axial images. Data were collected using 0.2° intervals in φ for the range 0° < φ < 220° and 0.2° intervals in ω for two different regions in the range 0° < ω < 72°. In this way, nearly a full sphere of data was collected. The highly redundant data set was corrected for Lorentz and polarization effects, and for absorption using the program SORTAV.⁹

The positions of the chromium atoms, chlorine atoms, oxygen 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, except for disordered portions, were refined anisotropically. The disordered parts and all three non-methyl hydrogen atoms in DMF ligands were isotropically refined. The rest of the hydrogen atoms were placed in idealized positions, and a displacement parameter for each was set at 1.5 times (for aliphatic) or 1.2 times (for aromatic) that of the attached atom.

The structure of [Li₂(DMF)₆][Cr₂(azin)₄Cl₂] was solved in space group P1̄ with cation and anion residing on inversion centers. The anion [Cr₂(azin)₄Cl₂]²⁻ was disordered presumably because the 5- and 6-membered rings in an azin ligand are similar enough in size that molecular packing in the crystal allows each of the ligands to be oriented in either direction. Such disorder has been observed before.^{6b,7} The disordered azin ligands were successfully modeled as having two superimposed

Table 1. Crystal Data and Structure Refinement

complex	[Li ₂ (DMF) ₆][Cr ₂ (azin) ₄ Cl ₂]
chem formula	C ₄₆ H ₆₂ N ₁₄ O ₆ Cl ₂ Cr ₂ Li ₂
fw	1095.88
space group	P1̄
a, Å	10.758(2)
b, Å	11.264(1)
c, Å	12.358(2)
α, deg	85.986(8)
β, deg	71.872(8)
γ, deg	69.619(8)
V, Å ³	1332.8(3)
Z	1
data collection instrument	Nonius FAST
T, K	213(2)
radiation λ, Å	0.71073
ρ(calcd), g cm ⁻³	1.365
μ(Mo Kα), cm ⁻¹	5.67
R1 ^{a,c} /R1 ^{a,d}	0.062/0.067
wR2 ^{b,c} /wR2 ^{b,d}	0.162/0.169

^a R1 = Σ(|F_o| - |F_c|)/Σ|F_o|. ^b wR2 = [Σ[w(F_o² - F_c²)²]/Σ[w(F_o²)²]]^{1/2}, w = 1/[σ²(F_o²) + (aP)² + bP], P = [max(F_o² or 0) + 2(F_c²)/3]. ^c Denotes value of the residual considering only the reflections with I > 2σ(I). ^d Denotes value of the residual considering all the reflections.

Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) for [Li₂(DMF)₆][Cr₂(azin)₄Cl₂]

Cr(1)···Cr(1)#1 ^a	2.688(2)	Cr(1)-N(11)#1	2.108(2)
Cr(1)-Cl(1)	2.606(2)	Cr(1)-N(2)#1	1.984(9)
Cr(1)-N(1)	2.124(7)	Cr(1)-N(12)	2.085(7)
N(12)#1-Cr(1)-Cr(1)#1	86.0(1)	N(1)-Cr(1)-Cr(1)#1	86.0(1)
N(2)#1-Cr(1)-Cr(1)#1	86.1(1)	Cr(1)#1-Cr(1)-Cl(1)	178.63(4)
N(11)-Cr(1)-Cr(1)#1	85.8(1)		

^a Symmetry transformation used to generate equivalent atoms: #1 -x, -y, -z.

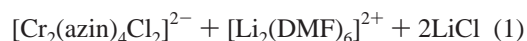
orientations; the occupancy for one of the orientations was refined as 55%, and for the other orientation, 45%.

Crystallographic data for [Li₂(DMF)₆][Cr₂(azin)₄Cl₂] are given in Table 1; selected bond distances and angles are listed in Table 2.

Magnetic Susceptibility Measurements. Variable-temperature 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. The compound is diamagnetic, χ ≈ 10⁻⁴ cgsu throughout the temperature range.

Results and Discussion

Preparation. The compound reported here was obtained by a method (eq 1) in which azin, Cr²⁺, Li⁺, Cl⁻, and DMF were all present, so that a product containing all of these was accessible. This situation differs from that obtaining in the preparation^{6c} of a related compound (eq 2). Thus, in each case, the Cr₂(azin)₄ molecule was obtained, but as the [Cr₂(azin)₄Cl₂]²⁻ ion in one case and as the Cr₂(azin)₄(DMF)₂ molecule in the other.



Structures. The structure of the [Cr₂(azin)₄Cl₂]²⁻ anion is shown in Figure 2 and that of the [Li₂(DMF)₆]²⁺ cation in Figure

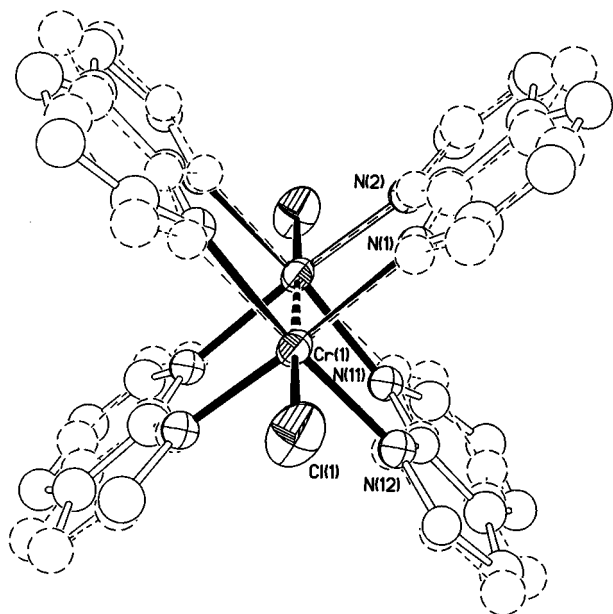


Figure 2. Structure of the $[\text{Cr}_2(\text{azin})_4\text{Cl}_2]^{2-}$ anion in $[\text{Li}_2(\text{DMF})_6][\text{Cr}_2(\text{azin})_4\text{Cl}_2]$. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms have been omitted for clarity. A second orientation of each disordered azin ligand is shown in broken lines.

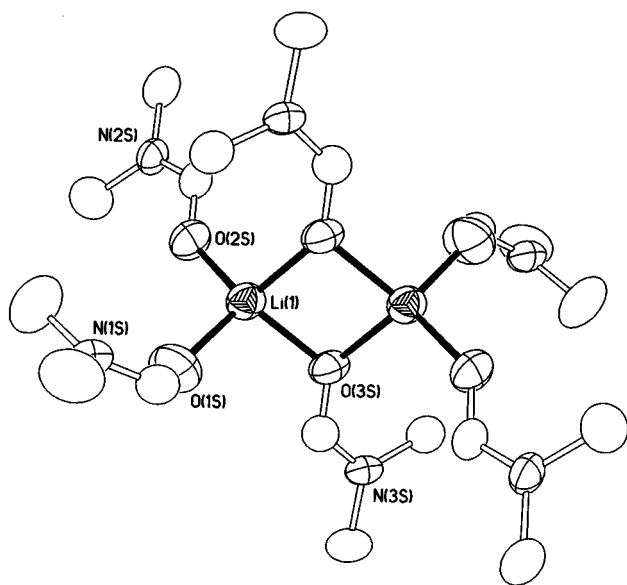


Figure 3. Structure of the $[\text{Li}_2(\text{DMF})_6]^{2+}$ cation, with displacement ellipsoids at the 50% probability level, and hydrogen atoms omitted.

3. The latter consists of two LiO_4 tetrahedra sharing an edge and has no features requiring comment. The anion displays a paddlewheel structure, but the azin ligands are disordered, as they were in the cases of $\text{W}_2(\text{azin})_4$ ^{6b} and $\text{Mo}_2(\text{azin})_4$.⁷ It is

interesting that, in the case of $\text{Cr}_2(\text{azin})_4(\text{DMF})_2$, there was no reported disorder of this kind. Because of the disorder the Cr–N distances and various angles involving the nitrogen atoms are relatively inaccurate, but the Cr–Cr and Cr–Cl distances are unaffected.

The Cr–Cr distance in the present case, 2.688(2) Å, is somewhat longer than that in $\text{Cr}_2(\text{azin})_4(\text{DMF})_2$, 2.604(2) Å. In both cases, the tendency of the azin ligand to form divergent bonds to the metal atoms, coupled with the well-known capacity of axial ligands to elongate Cr–Cr bonds,⁴ keeps the Cr atoms well separated to the extent that formation of a quadruple bond is impossible.

The significance of this compound is that while it has, qualitatively speaking, a typical paddlewheel structure, and it has no unpaired electrons, it cannot be assigned a Cr–Cr quadruple bond. The Cr to Cr distance of 2.688(2) Å is far too long to allow for the four direct orbital overlaps required to form such a bond. How, then, do we explain the diamagnetic nature of the molecule?

No simple and definitive answer can be given to this question, but we believe that a correct understanding must be within the context of the following concept. It is possible that when two metal atoms lie at an intermediate distance—i.e., too long for all possible bonding interactions to be fully established but not so long that *all* of them must be considered impossible—the best formulation of the metal–metal interaction is a mixture of both bonding and exchange coupling. This concept had already been invoked to explain the Mo–Mo interactions in $\text{Mo}_2\text{X}_9^{3-}$ species,¹⁰ where there is postulated to be a direct σ bond but only indirect coupling of the pairs of $d\pi$ electrons on the two metal atoms.

In the present case, it is likely that there is a direct σ bond, but whether there are also direct π bonds and then an indirect coupling of the δ electrons or only indirect coupling of both π and δ electrons is an open question. Whatever indirect couplings exist, they may be assumed to occur by processes of superexchange through the three-atom (N–C–N) bridges that connect the two chromium atoms. Thus, the Cr–Cr bond order is most likely 1 or possibly 3, but no direct bonding at all cannot be firmly ruled out.

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Supporting Information Available: An X-ray crystallographic file in CIF format and Figures S1 and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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