SUPPORTING INFORMATION

Reactions of Ar'CrCrAr' with N2O or N3(1-Ad): Complete Cleavage of the Cr-Cr Quintuple Interaction

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The supporting information contains:

1. Experimental Details
2. Details of the magnetic characterization of 1 and 2.
3. Crystallographic Data.

1. Experimental Details

General Procedures. All manipulations were carried out using modified Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres HE-43 drybox. All of the solvents were first dried by the method of Grubbs, followed by 3 A molecular sieves overnight and degassed three times (freeze-thaw) prior to use. Ar'CrCrAr' was prepared by the literature method. AdN3 was purchased from Acros Organics and used as received. N2O was purchase from Puritan Medical Products Inc. and dried over P2O5 prior to use. Melting points were recorded in glass capillaries sealed under N2 and are uncorrected. UV-vis data were recorded on a Hitachi-1200 spectrometer.

Ar'Cr(μ-O)2Cr(O)Ar' (1): About 30 mL of hexanes was added to a flask containing Ar'CrCrAr' (0.270g, 0.3mmol) at room temperature. The flask containing this deep red
solution was evacuated and quickly refilled with N$_2$O. The mixture was exposed to the N$_2$O atmosphere for about 2 hours and then sealed and stirred overnight, by which time the solution had become dark green and some precipitate had formed. The solution was filtered and dark green filtrate was concentrated to ca. 5 mL, which afforded X-ray quality dark green crystals of 1 after storage for 2 days at -18 ºC. Yield 0.097g (34.2%). This compound melts at 157-159 ºC. UV-Vis ((hexane, nm [ε, cm$^{-1}$M$^{-1}$]): 418(2000), 706(250).

Ar'Cr($\mu_2$:$\eta^1$,$\eta^3$-N$_3$(1-Ad))CrAr' (2): About 30 mL of hexanes was added to a mixture of Ar'CrCrAr' (0.270g, 0.3mmol) and N$_3$(1-Ad) (0.056g, 0.31mmol) at room temperature. The mixture was stirred for 2 days by which time the deep red solution had become dark brown and some precipitate had formed. The solution was filtered and the dark brown filtrate was concentrated to ca. 2 mL, which afforded X-ray quality dark amber crystals of 2 after storage for 2 weeks at -18 ºC. Yield 0.090g (27.8%). This compound melts at 135-138 ºC. UV-Vis ((hexane, nm [ε, cm$^{-1}$M$^{-1}$]): 438(2300) broad.

**Magnetic Studies.** The powdered samples of 1 and 2 used for magnetic measurements were sealed under N$_2$ in 3 mm diameter quartz tubing. The sample magnetization was measured using a Quantum Design MPMSXL7 superconducting quantum interference magnetometer. For each compound the sample was zero-field cooled to 2 K and the moment was measured upon warming to 320 K in an applied field of 0.01 T. Additional time was allowed between measurements at low temperature to ensure thermal equilibrium between the sealed sample and the temperature sensor. Diamagnetic corrections of −0.000336 and −0.000406 emu/mol Cr, obtained from tables.
of Pascal’s constants, have been applied to the measured susceptibility of 1 and 2 respectively.

**X-ray Crystallographic Studies.** Suitable crystals of 1-2 were selected and covered with a layer of hydrocarbon oil under a rapid flow of argon. They were mounted on a glass fiber attached to a copper pin and placed in the cold N₂ stream on the diffractometer. X-ray data were collected on a Bruker SMART 1000 diffractometer at 90(2) K using Mo K\(\alpha\) radiation (\(\lambda = 0.71073 \text{ Å}\)) or on a Bruker SMART Apex II diffractometer at 90(2) K with Mo K\(\alpha\) radiation (\(\lambda = 0.71073 \text{ Å}\)). Absorption corrections were applied using SADABS.\(^2\) The structures were solved using direct methods and refined by the full-matrix least-squares procedure in SHELX.\(^4\) All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and included in the refinement using a riding model.

2. Details of the magnetic characterization of 1 and 2.

The magnetic properties of 1, see Figure S1, indicate that it is essentially a paramagnetic complex with little if any intramolecular exchange interaction. The inverse molar magnetic susceptibility exhibits a close to linear temperature dependence between 2 and 320 K, see the inset to Figure S1; a linear fit yields a small Weiss temperature of \(-5.5\) K, a Curie constant of 0.487 mol Cr/emu K, and an effective magnetic moment of \(1.97 \mu_B\). As is shown in Figure S1, the effective magnetic moment increases linearly from \(1.81 \mu_B\) at 15 K to \(1.99 \mu_B\) at 320 K, an increase that presumably results\(^5\) from an increasing orbital contribution to the moment as a consequence of spin-orbit mixing of excited states into the ground state. Below 15 K the moment decreases to \(1.35 \mu_B\) at 2 K most likely as
a result of long range intermolecular magnetic exchange coupling or, perhaps less likely, as a result of zero-field splitting in the molecular dimer. The magnetic properties of \( \text{I} \) are fully consistent with the presence of both the \( 3d^3 \) trivalent \( \text{Cr}(2) \) ion with a distorted tetrahedral coordination environment and \( S = \frac{1}{2} \) and the \( 3d^1 \) pentavalent \( \text{Cr}(1) \) ion with \( S = \frac{1}{2} \); for the observed average effective magnetic moment of 1.97 \( \mu_B \) the average \( g \)-value is 2.27.

![Figure S1](image.png)

**Figure S1.** The temperature dependence of the effective magnetic moment of \( \text{I} \). Inset: A linear Curie-Weiss law fit of the temperature dependence of the inverse molar magnetic susceptibility of \( \text{I} \).

The magnetic properties of \( \text{II} \), see Figure S2, indicate that each of the chromium(II) ions have an \( S = 1 \) ground state. This expected ground state for the \( 3d^4 \) chromium(II) ion results from a highly distorted coordination environment that results in two unpaired and two paired electrons on each ion. This result is consistent with the Curie-Weiss law fit of the inverse molar magnetic susceptibility observed for \( \text{II} \) which is linear above 100 K.
This fit (not shown) yields a Weiss temperature of 29 K, a Curie constant of 1.095 mol Cr/emu K, and a corresponding effective magnetic moment of 2.96 μB, a moment that is far below the 4.9 to 5.2 μB moment that might be anticipated for chromium(II) ions with S = 2. Further, as is shown in the inset to Figure S2, the inverse molar susceptibility is not linear below 100 K but indicates the presence of weak intramolecular ferromagnetic interactions between the two chromium(II) ions. Thus the magnetic properties of 2 obtained between 15 and 320 K have been fit with a model corresponding to magnetic exchange between two chromium(II) ions. The result of this fit is shown by the solid line for the magnetic moment in Figure S2 and the solid line for the inverse molar magnetic susceptibility in the inset to Figure S2. The fit, which is excellent, yields a weak intramolecular ferromagnetic exchange coupling constant, J, of 7.8(7) cm⁻¹ and an average g-value of 2.40(2), values that are consistent both with the highly distorted coordination environment of each chromium(II) ion in 2 and the highly bent Cr–N–Cr superexchange pathway between the two ions. Unexpectedly, these fits required a temperature independent reduction in the observed molar magnetic susceptibility of –0.00067(6) emu/mol Cr, a small reduction that probably indicates either the loss of some of the hexane of crystallization in the sample under study, an error in the diamagnetic correction, or a small error in the mass of the sample. As is shown in Figure S2, the magnetic moment of 2 begins to decrease from 3.97 μB at 10 K to 3.48 μB at 2 K, a decrease that is probably the result of a small zero-field splitting associated with one or both of the chromium(II) ions.
Figure S2. The temperature dependence of the effective magnetic moment of 2. Inset: The temperature dependence of the inverse molar magnetic susceptibility of 2. The solid line in each plot corresponds to a 15 and 320 K fit with weak ferromagnetic exchange between the two chromium(II) ions with $S = 1$ and $J = 7.8(7)$ cm$^{-1}$. 
References:

3. SADABS, version 5.0 package; an empirical absorption correction program from the SAINTPlus NT; Bruker AXS: Madison, WI 1998.
4. SHELXL, version 5.1; Bruker AXS: Madison WI 1998.
6. The Hamiltonian used for these fits is given in the supplementary information provided with reference 4.