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ARTICLE

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Sodium Congener of the Classical Lithium Methylchromate Dimer: Synthetic, X-ray Crystallographic, and Magnetic Studies of $Me_8Cr_2[Na(OEt_2)]_4$

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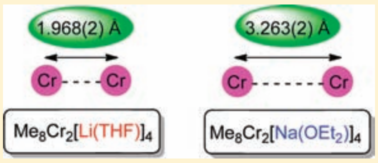
Supporting Information



ABSTRACT: One of the milestone structures in the development of transition-metal complexes with metal−metal bonds of multiple bond order was the lithium methylchromate dimer $Me_8Cr_2[Li(donor)]_4$ (donor = THF or Et_2O). Using a simple salt metathesis reaction mixing this compound with sodium *tert*-butoxide, the sodium congener $Me_8Cr_2[Na(OEt_2)]_4$ has been synthesized as a green crystalline compound and isolated in 51% yield. Its solid-state structure was determined by single-crystal X-ray diffraction. Exhibiting exact crystallographic C_{4h} symmetry, this heavier alkali-metal chromate structure is also dimeric, formally comprising a $(Me_8Cr_4)^{4-}$ tetranionic core with four peripheral Na^+ cations carrying supporting ether ligands. Its salient feature is the long Cr···Cr distance of 3.263(2) Å, which is remarkably elongated compared to that in the lithium THF-solvated congener [1.968(2) Å]. With respect to the methyl C atoms, the Cr coordination is distorted-square-planar. Each Na^+ interacts with four methyl C atoms, and there are also some short Na···H(C) contacts. Unlike for lithium chromate, no NMR spectroscopic data could be obtained for sodium chromate. The paramagnetic character of sodium chromate was confirmed by variable-temperature magnetization measurements, which indicated antiferromagnetic behavior.

INTRODUCTION

Following decades of study, metal−metal bonds, especially of high multiple bond order, still attract special interest and debate. The chemistry of the early transition metal chromium has played a pivotal role in the development of this research.[1] Power's report of the first stable compound with a metal−metal quintuple bond in the chromium terphenyl Ar′CrCrAr′ [where Ar′ = C_6H_3-2,6-$(C_6H_3$-2,6-*i*-$Pr_2)_2$][2] is a recent example that has stimulated much activity in the area.[3] A key requirement for high multiple bond orders between two low-valent Cr atoms appears to be ligands that bridge the two metal centers and thus support their close internuclear separation. Having recently started to investigate alkali-metal chromate chemistry in the context of alkali-metal-mediated metalation,[4] we were drawn back to the roots of chromium metal−metal bond development with Krause's milestone 1970 report of the methylchromate $Me_8Cr_2[Li(THF)]_4$ (where THF = tetrahydrofuran).[5] Because of its (then) super-short Cr−Cr distance [1.980 Å; later better refined to 1.968(2) Å],[6] it was initially proposed to denote a quadruple Cr−Cr bond, unusual for its lack of bridging three-center chelating ligands. The etherate $Me_8Cr_2[Li(OEt_2)]_4$ adopts the same dimeric structure. Gambarotta has since questioned this interpretation by comparing the dimers to the monomeric tetramethylethylenediamine (TMEDA) derivative $Me_4Cr[Li(TMEDA)]_2$, arguing that Li···H(Me) agostic interactions might be the primary attractive force behind the construction of the dimeric arrangement with a short Cr−Cr distance an enforced artifact.[6,7] The striking difference between the structures upon substitution of Li(THF) or $Li(OEt_2)$ by Li(TMEDA) shows the strong influence that the solvated alkali-metal cation can exert on the bonding (or at least the coordinative) situation of the transition metal. For that reason, we thought it would be interesting to study a sodium congener of the lithium methylchromate dimers, which, to the best of our knowledge, has never been synthesized previously. Thus, we report here the synthesis and successful X-ray crystallographic characterization of the sodium methylchromate etherate complex $Me_8Cr_2[Na(OEt_2)]_4$ (**1**). The magnetic properties of paramagnetic **1** have also been examined by variable-temperature magnetic susceptibility measurements.

EXPERIMENTAL SECTION

General Information. All reactions and manipulations were carried out in an atmosphere of dry pure argon gas using standard Schlenk and glovebox techniques. Diethyl ether was distilled from

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Table 1. Crystallographic Data for 1

compound	**1**
molecular formula	$C_{24}H_{64}Cr_2Na_4O_4$
M_r	612.7
cryst syst	tetragonal
space group	$I4/m$
a (Å)	14.5304(7)
c (Å)	8.7463(14)
V (Å^3)	1846.6(3)
Z	2
D_{calcd} (g cm^{-3})	1.102
reflns measd	2343
unique reflns	859
R_{int}	0.0279
obsd reflns [$I > 2\sigma(I)$]	629
R (F, obsd reflns)	0.0394
R_w (F^2, all data)	0.1091
GOF (F^2)	0.926
ρ_{min}, ρ_{max} (e Å^{-3})	0.25, −0.33

sodium benzophenone. $CrCl_2$ and NaO^tBu were purchased from Aldrich and used as received. Despite several attempts, satisfactory elemental analyses of compound **1** could not be obtained because of its highly air- and moisture-sensitive nature.

Synthesis of $Me_8Cr_2[Na(OEt_2)]_4$ (1). A slurry of 0.98 g of $CrCl_2$ (8 mmol) in 80 mL of ether was cooled below −30 °C, and the dropwise addition of MeLi (20 mL, 32 mmol of a 1.6 M solution in ether) produced a yellow suspension. This mixture was stirred for 5 h while slowly warming to 0 °C. The precipitated LiCl was then removed by filtration and washed with 10 mL of ether while maintaining the temperature of the filtrate at 0 °C. Upon the addition of 1.54 g (16 mmol) of NaO^tBu, a green solution was obtained. This solution was stirred for 1 h at 0 °C before being concentrated in vacuo and stored overnight at −27 °C. A crop of emerald-green crystals of **1** could then be isolated in 51% yield (1.25 g). ***Caution!*** *Note that these crystals are highly pyrophoric in contact with air.*

Magnetic Studies. Magnetic susceptibility data for polycrystalline samples of the complex were collected in the temperature range 2−300 K in an applied magnetic field of 1 T with a SQUID magnetometer (MPMS-7, Quantum Design). Experimental susceptibility data were corrected for underlying diamagnetism using Pascal's constants. The temperature-dependent magnetic contribution of the glass container was experimentally determined and subtracted from the measured susceptibility data.

X-ray Structure Determination. Data for compound **1** were collected on an Oxford Diffraction Xcalibur diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 123(2) K. The unit cell parameters and other experimental details of the data collection and structure refinement are listed in Table 1. The structure was solved using *SHELXS-97*[8] and refined to convergence on all independent F^2 values by the full-matrix least-squares method using the *SHELXL-97* and *SHELXTL* program systems.[8] One ethyl arm of the crystallographically unique ether ligand lying on a mirror plane is ordered, while disorder of the terminal methyl group of the second arm could be resolved and refined satisfactorily using constrained H atoms and restraints on both the geometry and displacement parameters of non-H atoms. It was possible to locate and freely refine the H atoms of the unique metal-bridging methyl group, thus providing an unbiased geometry for this key group in the structure. CCDC-820958 contains the supplementary crystallographic data for this paper and can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

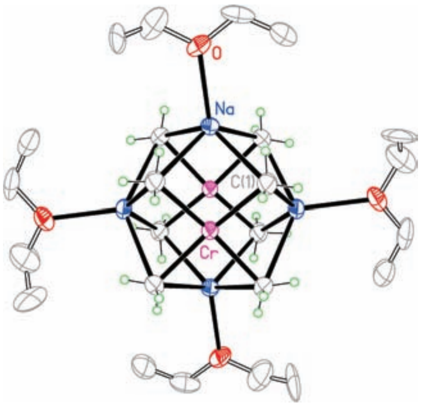


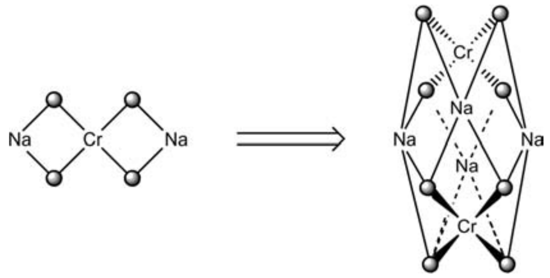
Figure 1. Molecular structure of **1** showing selected atom labeling. Minor disorder and ether H atoms have been omitted for clarity, and ellipsoids are at the 40% probability level. Selected bond lengths (Å) and angles (deg): Cr···Cr′ 3.263(2), Cr−C 2.195(3), Na−C 2.726(4), Na−C′ 2.673(4), Na−O 2.358(3); Na−C−Na′ 82.36(12), Na−C−Cr 74.15(11), Na′−C−Cr 75.28(11). A prime denotes a symmetry-generated atom.

■ RESULTS AND DISCUSSION

Synthesis and X-ray Crystallographic Characterization. A literature procedure[6] was followed to prepare an ether solution of the lithium methylchromate $Me_8Cr_2[Li(OEt_2)]_4$. When a metathesis method commonly employed to convert alkyllithium compounds to alkylsodium compounds was applied, this solution was charged with sodium *tert*-butoxide (4 mol equiv) to generate lithium *tert*-butoxide, which remained dissolved, while emerald-green crystals of **1** grew from the solution and were isolated in a yield of 51%.

X-ray crystallography (see the Experimental Section for technical details) established the dimeric molecular constitution of **1** (Figure 1). The full molecule possesses exact crystallographic C_{4h} symmetry, while its central core disregarding the ethyl arms on the ether ligands is essentially D_{4h}. Four components (one-quarter of a Cr atom, half of a Na atom, one methyl ligand, and half of an ether ligand) comprise the asymmetric unit, with the other components being equivalent to them by symmetry. Of these, Cr lies on the 4-fold rotation axis, Na lies on the mirror plane, and the ether ligand also lies on this mirror plane, with disorder across the plane being resolved for one of the two ethyl arms. Embedded in the core of the molecule, the Cr atom bonds to four methyl ligands to generate a $(Me_8Cr_2)^{4-}$ tetraanion (at least formally), which is charge-balanced by four Na^+ cations at the periphery of the structure, each of which bridges four methyl groups with the fifth, an exo sodium coordination site filled by an ether ligand. Lying out of the exact plane of four methyl C atoms by 0.362 Å, the Cr atom is displaced inward toward its symmetry equivalent at a Cr···Cr distance of 3.263(2) Å. With respect to the methyl C atoms, the coordination geometry of Cr can be described as distorted-square-planar (the C−Cr−C bond angles are 161°) or distorted-square-pyramidal if the Cr···Cr contact is included. The Na^+ coordination is square-pyramidal (with an apical O atom and four basal C atoms). H atoms have been idealized and constrained on the ether ligands, but they are completely freely refined (both their positions and displacement parameters) for the core methyl ligands. Bridging to three (one Cr and two Na) atoms, the methyl ligand is oriented approximately eclipsed with the Cr−C and Na−C bonds, meaning that

Scheme 1. **Depiction of How Aggregation of Mononuclear Chromate Units Allows for Maximization of the Number of Electrostatic Na−Me Interactions**



the metal···H(C) distances are approximately minimized rather than maximized; this is suggestive of an agostic interaction[9] (the shortest such distances are Cr···H1B 2.43 Å, Na···H1C 2.36 Å, and Na···H1A 2.38 Å). Note that these distances are direct measurements from the refinement, with no adjustment to correct for the expected real C−H bond lengths; the refined corresponding C−H distances are 0.85, 1.00, and 0.90 Å, all with uncertainties of about 0.03 Å, so these are quite reasonable for free refinement in such a metal-containing structure; and the orientation of the methyl group can be confidently accepted as essentially correct.

What this replacement of Li(THF) in Krause's analogous dimer for $Na(OEt_2)$ in **1** has done is to elongate considerably the Cr···Cr distance by 1.295 Å [i.e., from 1.968(2) to 3.263(2) Å], so that any Cr···Cr interaction, if present, must be weakened correspondingly, assuming the classical binominal bond length/bond strength correlation. However, Edema and Gambarotta have pointed out the surprisingly passive influence that divalent chromium can exert on its dinuclear structures, with ligand features (alkali metal cation, donor atom, and geometry) playing a more dominant role.[10] In the context of **1**, it could be said that qualitatively its structure is arranged to maximize the number of cation (sodium)−anion (methyl) interactions (four per sodium) starting from a more covalent square-planar $(Me_4Cr)^{2-}$ chromate building block. Were this combination to remain monomeric (Scheme 1) akin to $Me_4Cr[Li(TMEDA)]_2$, each sodium cation could engage only two methyl anions, with weakly bound neutral ether ligands acting as coordination fillers. The displacement of the Cr atoms toward each other in the formation of the dimer of **1** destroys the perfect square planarity of the $(Me_4Cr)^{2-}$ building block. Because perfect square planarity would not seemingly affect the number of cation−anion contacts, one is tempted to speculate on the existence of a Cr−Cr interaction despite the long distance involved [3.263(2) Å], noting that it is considerably shorter than that [3.622(1) Å] in the structurally related phenoxide dimer $(PhO)_8Cr_2[Na(THF)]_4$.[11] Following Gambarotta's detailed study of dinuclear structures of divalent chromium, it would appear to be inappropriate to place much value on a comparison between two chromates with distinctly different anions (Me vs PhO) and different solvating ligands (ether vs THF).

As Gambarotta reported[6] the NMR spectrum of $Me_8Cr_2[Li(THF)]_4$ in a C_6D_6 solution (the highly polar nature of the methyl group was evident from the chemical shift of −0.35 ppm observed), we likewise attempted to obtain NMR spectra of **1**. Its poor solubility in a C_6D_6 solution necessitated the addition of C_4D_8O−THF, but no satisfactory spectrum could be obtained, consistent with **1** being paramagnetic. Accordingly, we then turned to magnetic studies.

MAGNETIC STUDIES

To investigate the inherent paramagnetism indicated by the nonresolved NMR signals, previously described for related carboxylate[12,13] and carbamate[13] bridged chromium(II) dinuclear species, the magnetic properties of **1** have been explored by variable-temperature magnetization measurements on a powdered sample (see the Experimental Section). The overall characteristic of the temperature-dependent data measured in the temperature range 2−300 K in an applied field of 1 T clearly indicates an antiferromagnetic exchange interaction of the two Cr ions with spin $S_1 = S_2 = 2$, with a singlet state being lowest in energy (see the Supporting Information). A residual low value of 0.14 emu K mol^{-1} in χT at 2 K most probably indicates a small fraction of 2−3% chromium(III) species arising from decomposition. No satisfactory simulation of the data is possible, assuming a simple Heisenberg model. The temperature dependence of the magnetic moment observed presumably arises from low-lying triplet states admixing into the ground state due to a small $S-T$ energy gap expected also from the large Cr−Cr distance of 3.263 Å.

SUMMARY

The molecular structure of the newly synthesized sodium methylchromate **1** shows interesting differences from that of the previously reported lithium methylchromate $Me_8Cr_2[Li(THF)]_4$. Although both are dimeric, the former has a longer Cr···Cr separation than the latter, so it would be wrong to interpret these structures as simple contacted ion pairs with $(Me_8Cr_2)^{4-}$ tetraanions and alkali-metal countercations. Moreover, the former shows a degree of paramagnetism, while the latter is essentially diamagnetic. Magnetic measurements of sodium chromate clearly show antiferromagnetic behavior, although as yet we have not been able to find a good model that fits the experimental data satisfactorily. We plan to investigate this intriguing molecule through future multiconfigurational theoretical studies.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** X-ray crystallographic data in CIF format and plots of magnetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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