2-[(Dimethylamino)methyl]phenyl Compounds of Chromium(III) and Dichromium(II) by Reaction of 2-Lithio-*N*,*N*-dimethylbenzylamine with Dichromium(II) Tetraacetate

F. Albert Cotton* and Graham N. Mott

Department of Chemistry, Texas A&M University, College Station, Texas 77843

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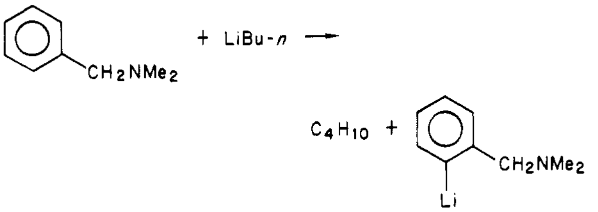
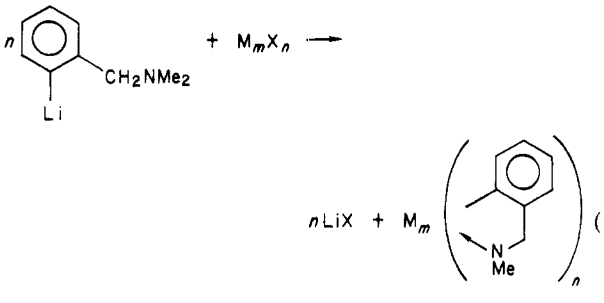
The reaction of $Cr_2(O_2CCH_3)_4$ with $Li(C_6H_4\text{-}o\text{-}CH_2NMe_2)$, Li(LL), gives several products depending on conditions. When a 1:4 ratio is used, the major product is orange, air-stable $Cr(LL)_3$, **1**. With a 1:2 ratio, dark-red, air-sensitive $Cr_4(LL)_4(O_2CCH_3)_2O$, **2**, was obtained. Both compounds were characterized by X-ray crystallography. Compound 1 crystallizes in space group $R3$ with $Z = 3$ and hexagonal unit cell dimensions of $a = 12.462$ (2) Å, $c = 13.212$ (2) Å, $V = 1777.0$ (7) Å^3. The $Cr(LL)_3$ molecule is a tris-chelate species with a *fac* arrangement of ligands to give C_3 symmetry. The important dimensions are Cr–C = 2.075 (5) Å; Cr–N = 2.356 (4) Å; ∠N–Cr–N′ = 96.8 (1)°; ∠C–Cr–C′ = 93.9 (2)°; ∠N–Cr–C = 77.2 (2)° (in chelate ring); ∠N–Cr–C = 92.9 (2)° (not in chelate ring). Contrary to an earlier report 1 appears to be stable in air for at least several months. Compound 2 crystallizes in space group $P\bar{1}$ with $Z = 2$ and unit cell dimensions of $a = 10.363$ (2) Å; $b = 23.096$ (4) Å, $c = 9.490$ (1) Å, $\alpha = 95.17$ (2)°, $\beta = 101.13$ (1)°, $\gamma = 82.07$ (2)°, $V = 2202$ (1) Å^3. The tetranuclear molecule, which is the asymmetric unit, consists of two $Cr_2(LL)_2$ units arranged so the Cr atoms form a bisphenoid with an oxygen atom at its center and two opposite slant edges bridged by acetate groups. The Cr–Cr distances are 2.544 (2) and 2.554 (2) Å, and the Cr–O(central) distances are 1.986, 2.015, 1.997, and 2.020 Å, each with an esd of 0.006. The molecule has essentially D_2 symmetry, though this is not rigorous. The Cr–Cr bonds make angles of ca. 53° to the mean Cr–C–N–O–O planes, and a simple formulation of the electronic structure is not apparent.

Introduction

The bidentate organoligand 2-[(dimethylamino)methyl]phenyl may be introduced by using the lithium reagent 2-lithio-*N*,*N*-dimethylbenzylamine, which is itself conveniently prepared by lithiation of *N*,*N*-dimethylbenzylamine, as shown in reactions 1a and 1b. The ligand is unusually interesting because its ability to form metal–carbon bonds is buttressed by the associated metal–nitrogen bond, whereby a chelate ring will normally be expected. Manzer[1,2] has reported several compounds containing this ligand.



(1a)



(1b)

We became interested in the possibility of using this and some other, similar ligands to prepare organometallic compounds of multiply bonded dimetal units. Among the ones we have investigated is the Cr_2^{4+} unit, as it is available for reaction in dichromium tetraacetate, $Cr_2(O_2CCH_3)_4$. We have found that several reaction products may be obtained, none of which is a simple substitution product of the type $Cr_2(C_6H_4\text{-}o\text{-}CH_2NMe_2)_n(O_2CCH_3)_{4-n}$. In one case we have obtained the previously made[2] $Cr(C_6H_4\text{-}o\text{-}CH_2NMe_2)_3$; we have characterized this compound, 1, crystallographically. Under somewhat different reaction conditions we have isolated (and structurally characterized) an unprecedented type of compound, 2, in which two dichromium(II) units are attached to a central oxygen atom.

Experimental Section

All reactions, manipulations, and crystallizations were performed under an atmosphere of dry argon. All solvents were dried and deoxygenated prior to use. The phenyllithium reagent $LiC_6H_4\text{-}o\text{-}CH_2NMe_2$ was prepared by the method by Manzer.[2]

Preparation of $Cr(C_6H_4\text{-}o\text{-}CH_2NMe_2)_3$, 1. $LiC_6H_4\text{-}o\text{-}CH_2NMe_2$ (0.56 g, 4 mmol) was dissolved in 20 mL of THF. To this rapidly stirred pale yellow solution was added 0.34 g (1 mmol) of anhydrous chromium(II) acetate and the darkening mixture stirred overnight. After filtration through Celite the dark orange solution was placed in a tubular flask. Bright orange cubic crystals (0.22 g) were obtained by placing a layer of hexane (20 mL) over the THF filtrate and allowing the layers to mix by slow diffusion over a period of 5 days. The elemental composition of the isolated crystals was shown by X-ray crystallography (vide infra) not to be the desired chromium(II) chelate complex $Cr_2(C_6H_4\text{-}o\text{-}CH_2NMe_2)_4$ but that of the air-stable, monomeric octahedral chromium(III) complex $Cr(C_6H_4\text{-}o\text{-}CH_2NMe_2)_3$ previously obtained by Manzer from the reaction between chromium(III) chloride and $Li(C_6H_4\text{-}o\text{-}CH_2NMe_2)$.[2] The remaining THF/hexane solution was extremely air sensitive and may contain the dinuclear complex; however, a number of attempts to obtain useful crystalline material have failed. Despite very careful repetitions under extremely anaerobic conditions the monomeric chromium(III) complex has been the major product in this reaction and the only one obtainable in crystalline form.

Preparation of $Cr_4(C_6H_4\text{-}o\text{-}CH_2NMe_2)_4(CH_3COO)_2O$, 2. $LiC_6H_4\text{-}o\text{-}CH_2NMe_2$ (0.28 g, 2 mmol) was dissolved in 20 mL of THF. Chromium(II) acetate (0.34 g, 1 mmol) was added, and the solution stirred at room temperature overnight. The amorphous precipitate of lithium acetate was removed by filtration, and the resulting filtrate was cooled to −10 °C for 1 week. A large amount

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(1) Manzer, L. E.; Guggenberger, L. J. *J. Organometal. Chem.* **1977**, *139*, C34.

(2) Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068.

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Table I. Crystallographic Data and Enraf-Nonius CAD-4 Data Collection Parameters

formula	$CrC_{27}H_{36}N_3$, 1	$Cr_4C_{40}H_{54}O_5N_4$, 2
space group	$R3$	$P\bar{1}$
M_r	454.60	878.88
a, Å	12.462 (2)	10.363 (2)
b, Å	12.462 (2)	23.096 (4)
c, Å	13.212 (2)	9.490 (1)
α, deg	90.0	95.17 (2)
β, deg	90.0	101.13 (1)
γ, deg	120.0	82.07 (2)
V	1777.0 (7)	2202 (1)
Z	3	2
d_{calcd}, g/cm^3	1.274	1.325
crystal size, mm	0.20 × 0.20 × 0.20	0.40 × 0.30 × 0.25
crystal decomposition, %	0	41.6
X-ray exposure time, h	7	44
μ(Mo Kα), cm^{-1}	5.241	10.456
radiation	graphite monochromated Mo Kα (χ = 0.71073 Å)	
scan type	ω–2θ	ω–2θ
scan width ($\Delta\omega$), deg	0.50 + 0.35 tan θ	0.50 + 0.35 tan θ
maximum counting time, s	30	30
collection range	$+h, +k, \pm l; 0 \leqslant 2\theta \leqslant 50°$	$+h, \pm k, \pm l; 0 \leqslant 2\theta \leqslant 50°$
no. of unique data	711	6281
no. of data $I > 3\sigma(I)$	561	2713
p	0.05	0.05
no. of variables	93	478
R_1 [a]	0.030	0.077
R_2 [a]	0.036	0.097
esd	0.982	2.500
largest shift [b]	0.02	0.07
largest peak [c]	0.35	1.18

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [b] Largest parameter shift in final refinement cycle. [c] Largest peak in a final difference Fourier, e/Å^3.

(ca. 0.2 g) of very air-sensitive, dark red crystalline material was observed after this time. By close inspection under degassed Nujol, a crystal of the size and quality useful for X-ray diffraction study was located. Again, the elemental composition of the sole isolated product was not that of the desired complex, $Cr_2(C_6H_4\text{-}o\text{-}CH_2NMe_2)_2(CH_3COO)_2$, but, as shown by X-ray crystallography, that of a remarkable new type of compound, $[Cr_2(C_6H_4\text{-}o\text{-}CH_2NMe_2)_2]_2(\mu\text{-}CH_3CO_2)_2(\mu_4\text{-}O)$, 2.

X-ray Data Collection and Structure Determination. For both crystals the intensity data were collected at room temperature on an Enraf-Nonius CAD-4 automated diffractometer to 2θ = 50° by using the ω–2θ method and a scan range determined by $\Delta\omega = (0.50 + 0.35 \tan\theta)°$ with a 25% extension at either end for background determination. Standard data-collection procedures have been previously summarized,[3] and the pertinent crystallographic parameters for both crystals are listed in Table I. Data were processed and all calculations required to solve and refine the structures were carried out on a PDP 11/60 computer at the Molecular Structure Corporation, College Station, TX. Tables of observed and calculated structure factors for both compounds are available as supplementary material.

Structure of $Cr(C_6H_4\text{-}o\text{-}CH_2NMe_2)_3$, 1. An orange crystal, approximately cubic (0.2 mm), was used for data collection. Automatic location and centering of 25 reflections (11° ≤ 2θ ≤ 37°) indicated a trigonal system with the cell parameters listed in Table I, and systematic absences suggested space groups $R3$ or $R\bar{3}$. The volume of the unit cell gave an indication that the expected formula, $Cr_2(C_6H_4\text{-}o\text{-}CH_2NMe_2)_4$, was not correct and implied $Cr(C_6H_4\text{-}o\text{-}CH_2NMe_2)_3$, with $Z = 3$. Moreover, the absence of any plausible Cr–Cr vector in the Patterson map also favored a mononuclear formula. The structure was solved and refined in the acentric space group $R3$, and with the Cr atom and all the nonhydrogen ligand atoms isotropically refined, residuals of R_1 = 0.069 and R_2 = 0.087 were reached. The other enantiomorph was then tested, and it gave R_1 = 0.064 and R_2 = 0.079. Refinement was therefore continued with the second choice of enantiomorph and anisotropic thermal parameters. After a few cycles, hydrogen atoms were introduced at calculated positions with fixed thermal parameters; the hydrogen atoms, with positions reset after each cycle, were included in all subsequent cycles but not themselves refined. Refinement converged with R_1 = 0.030 and R_2 = 0.036, and there were no anomalies in the final difference map. An attempt was also made to carry out refinement of a disordered model in $R\bar{3}$, but this gave vastly inferior results.

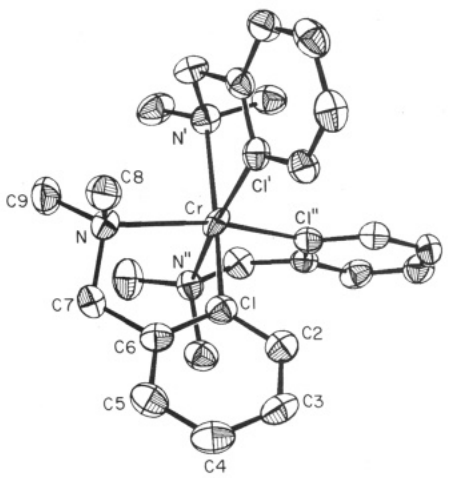

Figure 1. The *fac*-$Cr(C_6H_4CH_2NMe_2)_3$ molecule, 1, showing the atom labeling scheme. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 40% of its electron density.

Structure of $Cr_4(C_6H_4\text{-}o\text{-}CH_2NMe_2)_4(CH_3CO_2)_2O$, 2. The crystal was placed in a capillary tube which was then sealed with epoxy cement. Unfortunately this crystal decomposed considerably because of oxidation; since no other good crystal could be found the data were corrected for decay, which appeared to be a linear function of time, and used.

The volume of the unit cell was not inconsistent with the presence of four of the expected $Cr_2(C_6H_4\text{-}o\text{-}CH_2NMe_2)_2(CH_3CO_2)_2$ molecules, and the Patterson map showed two plausible Cr–Cr vectors. The positions of four independent chromium atoms were determined by using the direct-methods program MULTAN, and after four cycles of least-squares refinement of these four atoms we had R_1 = 0.38 and R_2 = 0.46. Subsequent difference Fourier maps, however, led to recognition that pairs of dinuclear units were joined by a single atom which refined best as an oxygen atom. The structure was then refined to convergence with isotropic temperature factors for all 53 nonhydrogen atoms, giving R_1 = 0.16 and R_2 = 0.20. Subsequent anisotropic refinement produced R_1 = 0.077 and R_2 = 0.097. A final difference synthesis revealed no additional chemical features in the unit cell.

Results

$Cr(C_6H_4\text{-}o\text{-}CH_2NMe_2)_3$, 1. This compound is apparently the same one previously prepared[2] by the reaction of $Li(C_6H_4\text{-}o\text{-}CH_2NMe_2)$ with $CrCl_3$. However, we find the compound to be far more stable toward air than previously reported (1 h). Samples of ours that have been exposed to air for 3 months in this laboratory have shown no visible sign of decomposition. We have also found that the substance is not attacked by ethanolic KOH, in air.

In the crystal, the molecules reside on sites of C_3 (3) symmetry. The atomic positional and thermal parameters are listed in Table II, and the bond distances and angles are listed in Table III. As shown in Figure 1, which gives a perspective view of the molecule and defines the atom labeling, the molecule is a typical distorted octahedral, tris-chelate complex, with the facial arrangement of ligands. The bond angle, within the chelate ring, ∠N–Cr–C,

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[3] Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr(C_6H_4\text{-}o\text{-}CH_2N(CH_3)_2)_3$[a,b]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	0.0000 (0)	0.0000 (0)	0.0000 (0)	2.23 (2)	2.23 (2)	1.92 (3)	2.23 (2)	0	0
N	0.0427 (3)	−0.1374 (3)	0.0902 (3)	2.9 (1)	3.0 (1)	2.5 (1)	1.53 (8)	−0.3 (1)	0.1 (1)
C(1)	−0.0920 (3)	−0.1621 (3)	−0.0842 (3)	2.0 (1)	2.9 (1)	2.7 (2)	1.13 (9)	0.2 (1)	−0.0 (1)
C(2)	−0.1336 (3)	−0.1785 (3)	−0.1848 (3)	2.6 (1)	3.1 (1)	3.0 (2)	1.58 (9)	0.2 (1)	0.0 (1)
C(3)	−0.1919 (3)	−0.2917 (4)	−0.2322 (3)	2.6 (1)	3.9 (2)	2.9 (2)	1.4 (1)	−0.6 (1)	−1.1 (1)
C(4)	−0.2112 (3)	−0.3969 (4)	−0.1820 (4)	2.9 (1)	3.4 (1)	4.4 (2)	1.4 (1)	−0.2 (2)	−1.2 (2)
C(5)	−0.1703 (4)	−0.3859 (4)	−0.0812 (4)	3.2 (1)	2.7 (1)	4.2 (2)	1 4 (1)	0.6 (1)	−0.2 (1)
C(6)	−0.1117 (3)	−0.2701 (3)	−0.0359 (3)	2.0 (1)	2.6 (1)	3.3 (2)	1.26 (8)	0.1 (1)	−0.3 (1)
C(7)	−0.0737 (4)	−0.2594 (3)	0.0748 (3)	3.4 (1)	2.5 (1)	3.3 (2)	1.4 (1)	−0.0 (1)	0.6 (1)
C(8)	0.0676 (4)	−0.1243 (4)	0.2008 (3)	5.5 (2)	3.6 (2)	2.9 (2)	1.9 (1)	−0.6 (2)	0.5 (1)
C(9)	0.1443 (4)	−0.1469 (4)	0.0401 (4)	3.3 (1)	3.1 (1)	4.0 (2)	1.85 (9)	−0.1 (1)	0.2 (1)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(2)	−0.1207 (0)	−0.1077 (0)	−0.2220 (0)	5.0000 (0)	H8A	0.1410 (0)	−0.0479 (0)	0.2140 (0)	5.0000 (0)
H(3)	−0.2193 (0)	−0.2976 (0)	−0.3001 (0)	5.0000 (0)	H8B	−0.0002 (0)	−0.1259 (0)	0.2352 (0)	5.0000 (0)
H(4)	−0.2514 (0)	−0.4752 (0)	−0.2148 (0)	5.0000 (0)	H8C	0.0778 (0)	−0.1908 (0)	0.2240 (0)	5.0000 (0)
H(5)	−0.1826 (0)	−0.4569 (0)	−0.0448 (0)	5.0000 (0)	H9A	0.2200 (0)	−0.0711 (0)	0.0482 (0)	5.0000 (0)
H(7A)	−0.0592 (0)	−0.3251 (0)	0.0918 (0)	5.0000 (0)	H9B	0.1515 (0)	−0.2124 (0)	0.0700 (0)	5.0000 (0)
H(7B)	−0.1377 (0)	−0.2634 (0)	0.1165 (0)	5.0000 (0)	H9C	0.1264 (0)	−0.1633 (0)	−0.0300 (0)	5.0000 (0)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25(B_{11}h^2a^2 + B_{22}k^2b^2 + B_{33}l^2c^2 + 2B_{12}hkab + 2B_{13}hlac + 2B_{23}klbc)]$ where a, b, and c are reciprocal lattice constants. [b] Estimated standard deviations in the least significant digits are shown in parentheses.

Table III. Bond Distances (Angstroms) and Bond Angles (Degrees) in $Cr(C_6H_4\text{-}o\text{-}CH_2NMe_2)_3$, 1

Cr-N	2.355 (4)	N-Cr-N′	98.7 (2)	Cr-C(1)-C(2)	129.2 (4)
Cr-C(1)	2.078 (5)	-C(1)	77.2 (2)	Cr-C(1)-C(6)	116.0 (4)
N-C(7)	1.500 (6)	-C(1)′	92.9 (2)	C(2)-C(1)-C(6)	114.7 (4)
N-C(8)	1.487 (7)	-C(1)″	169.2 (2)	C(1)-C(2)-C(3)	123.3 (4)
N-C(9)	1.485 (8)	C(1)-Cr-C(1)′	94.0 (2)	C(2)-C(3)-C(4)	120.5 (4)
C(1)-C(2)	1.404 (8)	Cr-N-C(7)	102.2 (2)	C(3)-C(4)-C(5)	118.8 (4)
C(1)-C(6)	1.397 (8)	Cr-N-C(8)	121.9 (4)	C(4)-C(5)-C(6)	119.0 (4)
C(2)-C(3)	1.373 (7)	Cr-N-C(9)	110.1 (3)	C(1)-C(6)-C(5)	123.8 (4)
C(3)-C(4)	1.378 (8)	C(7)-N-C(8)	106.7 (4)	C(1)-C(6)-C(7)	117.0 (4)
C(4)-C(5)	1.408 (8)	C(7)-N-C(9)	106.9 (4)	C(5)-C(6)-C(7)	119.1 (4)
C(5)-C(6)	1.386 (7)	C(8)-N-C(9)	107.9 (4)	N-C(7)-C(6)	108.7 (4)
C(6)-C(7)	1.522 (7)				

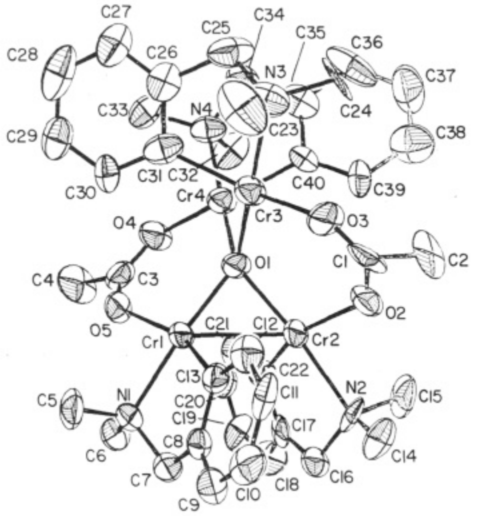

Figure 2. The entire $Cr_4(C_6H_4CH_2NMe_2)_4(CH_3CO_2)_2O$, **2**, molecule showing the numbering scheme for all atoms, each of which is represented by its ellipsoid of thermal vibration, scaled to enclose 40% of the electron density.

is small, 77.2 (2)°, while the other angles at the metal atom are all larger. The five-membered chelate ring has an envelope conformation with the nitrogen atom being appreciably out of the mean plane from which the other four atoms, Cr–C–C–C, deviate only slightly.

$Cr_4(C_6H_4\text{-}o\text{-}CH_2NMe_2)_4(CH_3CO_2)_2O$, 2 (Figure 2). The atomic positional and thermal parameters for this compound are listed in Table IV and the intramolecular distances and angles in Table V. Although there is no rigorous crystallographic symmetry imposed, the molecule has very nearly D_2 symmetry. The three C_2 rotation axes intersect at the position of the central, μ_4-O, oxygen atom (Figure 3). One axis forms a perpendicular bisector of both Cr–Cr bonds, i.e., Cr(1)–Cr(2) and Cr(3)–Cr(4). Another is defined by the C–C bonds of the two acetate groups. The third is, of course, perpendicular to both of these and bisects the Cr(1)–O(1)–Cr(4) and Cr(2)–O(1)–Cr(3) angles. Thus, effectively, all four chromium atoms are equivalent. They are, however, grouped into two bonded pairs, viz., Cr(1)–Cr(2) and Cr(3)–Cr(4), with essentially equal internuclear distances of 2.544 (2) Å and

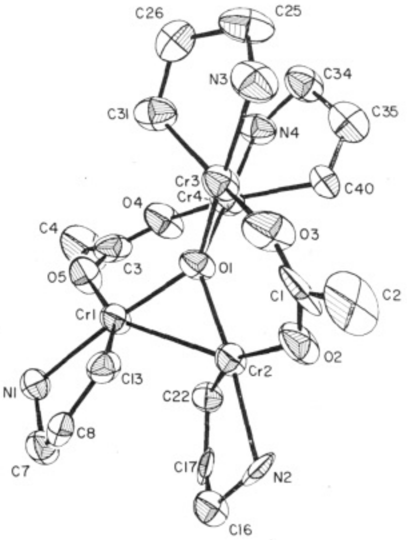

Figure 3. A view of only the central portion of the molecule of compound **2**.

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_4(C_6H_4\text{-}o\text{-}CH_2N(CH_3)_2)_4(CH_3COO)_2O$[a,b]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	0.5243 (2)	0.1689 (1)	0.2652 (3)	2.1 (1)	2.9 (1)	4.9 (1)	−0.35 (9)	0.3 (1)	−0.50 (9)
Cr(2)	0.7565 (2)	0.1761 (1)	0.2230 (3)	2.0 (1)	3.0 (1)	5.2 (1)	−0.16 (9)	0.2 (1)	−0.0 (1)
Cr(3)	0.7067 (3)	0.2727 (1)	0.5163 (3)	2.9 (1)	3.4 (1)	4.6 (1)	−0.4 (1)	−0.3 (1)	−0.2 (1)
Cr(4)	0.5603 (3)	0.3174 (1)	0.2947 (3)	3.0 (1)	2.8 (1)	4.5 (1)	0.1 (1)	0.1 (1)	−0.33 (9)
O(1)	0.6358 (9)	0.2333 (4)	0.327 (1)	2.4 (5)	2.4 (4)	4.9 (5)	0.3 (4)	−0.2 (4)	−0.4 (4)
O(2)	0.9383 (10)	0.1839 (4)	0.351 (1)	2.9 (5)	4.1 (5)	8.1 (6)	−1.1 (4)	−0.7 (5)	−1.3 (5)
O(3)	0.8914 (10)	0.2273 (4)	0.559 (1)	3.0 (5)	4.1 (5)	8.7 (7)	1.4 (5)	−0.7 (5)	−1.4 (5)
O(4)	0.3760 (10)	0.3057 (4)	0.180 (1)	2.8 (5)	3.8 (5)	7.7 (6)	0.0 (4)	−1.1 (5)	−0.7 (5)
O(5)	0.3415 (9)	0.2153 (4)	0.205 (1)	2.1 (5)	2.9 (4)	8.0 (6)	0.3 (4)	0.5 (5)	0.6 (4)
N(1)	0.418 (1)	0.0948 (5)	0.186 (1)	3.0 (6)	3.7 (5)	3.9 (6)	−1.2 (5)	0.6 (5)	−0.6 (5)
N(2)	0.871 (1)	0.1082 (5)	0.102 (1)	3.4 (6)	3.8 (5)	5.5 (6)	1.4 (5)	3.6 (5)	1.5 (5)
N(3)	0.781 (1)	0.3233 (5)	0.715 (1)	6.7 (8)	5.2 (6)	3.1 (6)	−1.6 (6)	−0.5 (6)	0.2 (5)
N(4)	0.485 (1)	0.4102 (5)	0.282 (1)	5.9 (8)	2.8 (5)	3.7 (6)	−0.2 (5)	0.7 (5)	0.4 (5)
C(1)	0.966 (2)	0.2003 (6)	0.486 (2)	3.9 (9)	1.4 (6)	10 (1)	−1.3 (6)	−1.9 (9)	0.2 (7)
C(2)	1.112 (2)	0.1845 (9)	0.561 (2)	1.1 (8)	9 (1)	14 (2)	−0.8 (8)	−3 (1)	−2 (1)
C(3)	0.308 (2)	0.2628 (6)	0.162 (2)	2.7 (8)	4.9 (8)	5.5 (8)	0.5 (7)	0.6 (7)	−1.6 (7)
C(4)	0.165 (2)	0.2747 (8)	0.067 (2)	2.5 (9)	7 (1)	12 (1)	−0.0 (9)	−3 (1)	−0 (1)
C(5)	0.336 (2)	0.0849 (7)	0.294 (2)	3.9 (8)	7.9 (9)	4.7 (8)	−2.2 (7)	2.5 (6)	−0.7 (7)
C(6)	0.332 (1)	0.1016 (6)	0.041 (2)	2.8 (8)	5.1 (8)	4.1 (7)	−0.9 (7)	−0.6 (7)	−0.1 (6)
C(7)	0.522 (1)	0.0423 (6)	0.173 (2)	3.1 (8)	2.9 (6)	5.5 (8)	−0.2 (6)	0.7 (7)	0.2 (6)
C(8)	0.631 (1)	0.0441 (6)	0.304 (1)	3.1 (7)	3.8 (6)	3.7 (7)	−1.1 (6)	1.6 (6)	−0.1 (6)
C(9)	0.696 (1)	−0.0079 (6)	0.357 (2)	3.1 (8)	3.9 (7)	5.1 (8)	−0.4 (6)	0.6 (7)	1.4 (6)
C(10)	0.801 (2)	−0.0060 (7)	0.470 (2)	6.2 (9)	4.7 (7)	5.3 (8)	−0.5 (7)	3.6 (7)	1.1 (6)
C(11)	0.832 (1)	0.0486 (7)	0.540 (2)	2.5 (7)	6.3 (8)	5.6 (8)	1.0 (7)	2.2 (6)	2.4 (7)
C(12)	0.760 (2)	0.1023 (7)	0.485 (2)	3.9 (8)	5.3 (8)	3.7 (7)	−0.6 (7)	0.7 (7)	0.4 (6)
C(13)	0.657 (1)	0.1019 (6)	0.361 (1)	2.5 (7)	4.0 (7)	3.4 (7)	−0.4 (6)	0.6 (6)	−0.5 (6)
C(14)	0.966 (2)	0.0649 (6)	0.197 (2)	3.7 (8)	5.1 (8)	4.6 (8)	1.8 (7)	1.1 (7)	2.1 (6)
C(15)	0.955 (2)	0.1402 (7)	0.032 (2)	4.5 (8)	6.4 (9)	9 (1)	−0.4 (8)	4.6 (7)	2.1 (8)
C(16)	0.775 (1)	0.0752 (6)	−0.005 (2)	2.3 (7)	3.6 (7)	4.8 (8)	−0.3 (6)	−0.6 (7)	0.1 (6)
C(17)	0.665 (1)	0.1212 (6)	−0.065 (1)	3.1 (7)	5.1 (7)	4.2 (7)	−2.1 (6)	2.3 (6)	0.2 (6)
C(18)	0.598 (2)	0.1159 (7)	−0.211 (2)	9 (1)	6.7 (9)	3.4 (7)	−2.3 (8)	3.4 (7)	−0.6 (7)
C(19)	0.496 (2)	0.1560 (7)	−0.272 (2)	3.2 (9)	6.8 (9)	4.4 (8)	1.2 (8)	−0.7 (7)	1.3 (7)
C(20)	0.462 (2)	0.2046 (7)	−0.187 (2)	3.2 (8)	6.3 (8)	4.0 (7)	−0.4 (7)	0.3 (7)	0.9 (7)
C(21)	0.526 (1)	0.2127 (6)	−0.044 (2)	3.0 (8)	4.9 (7)	5.2 (8)	−0.6 (7)	1.3 (7)	0.8 (7)
C(22)	0.629 (1)	0.1715 (6)	0.026 (2)	3.5 (8)	2.6 (6)	5.1 (8)	−0.1 (6)	1.3 (6)	0.2 (6)
C(23)	0.784 (2)	0.2805 (8)	0.837 (2)	8 (1)	8 (1)	6 (1)	−3.4 (9)	−0.4 (9)	3.1 (8)
C(24)	0.917 (2)	0.3412 (8)	0.720 (2)	3.5 (8)	10 (1)	6 (1)	−5.4 (7)	−0.5 (8)	−1.5 (8)
C(25)	0.686 (2)	0.3777 (6)	0.723 (2)	6 (1)	4.0 (7)	4.8 (8)	1.1 (8)	−0.7 (8)	−0.9 (7)
C(26)	0.538 (2)	0.3605 (6)	0.676 (2)	4.3 (9)	5.0 (8)	3.8 (7)	0.3 (7)	0.6 (7)	1.4 (6)
C(27)	0.440 (2)	0.3886 (8)	0.739 (2)	5 (1)	7 (1)	4.6 (8)	0.6 (9)	1.5 (7)	0.7 (8)
C(28)	0.312 (2)	0.3732 (8)	0.692 (2)	6 (1)	9 (1)	6.9 (9)	2.2 (9)	3.5 (8)	3.9 (8)
C(29)	0.291 (2)	0.3259 (7)	0.585 (2)	4.9 (9)	6.1 (8)	4.9 (8)	−0.0 (8)	2.2 (7)	2.1 (7)
C(30)	0.391 (1)	0.2979 (6)	0.522 (2)	2.3 (7)	4.7 (7)	4.9 (8)	−0.3 (6)	0.6 (6)	1.5 (6)
C(31)	0.520 (2)	0.3130 (6)	0.564 (2)	6 (1)	3.2 (7)	3.9 (7)	0.5 (7)	0.9 (7)	0.4 (6)
C(32)	0.484 (2)	0.4238 (7)	0.125 (2)	6 (1)	6.9 (9)	3.6 (7)	1.4 (9)	1.0 (7)	1.4 (7)
C(33)	0.345 (2)	0.4266 (7)	0.321 (2)	4.2 (9)	4.3 (8)	8 (1)	1.7 (8)	1.9 (8)	−0.3 (8)
C(34)	0.583 (2)	0.4437 (6)	0.383 (2)	3.7 (9)	4.3 (7)	5.6 (9)	−0.4 (7)	−0.5 (7)	−0.5 (7)
C(35)	0.720 (2)	0.4150 (6)	0.374 (1)	6 (1)	4.3 (7)	3.3 (7)	−1.1 (7)	−0.8 (7)	1.4 (6)
C(36)	0.831 (2)	0.4478 (7)	0.401 (2)	12 (1)	6.1 (8)	7 (1)	−6.5 (7)	−1 (1)	1.4 (8)
C(37)	0.961 (2)	0.4201 (9)	0.387 (2)	4 (1)	9 (1)	11 (1)	−1.3 (9)	0 (1)	1 (1)
C(38)	0.977 (2)	0.3638 (7)	0.347 (2)	9 (1)	5.1 (8)	7 (1)	−1.6 (9)	2.0 (9)	1.2 (8)
C(39)	0.867 (1)	0.3314 (7)	0.321 (2)	2.0 (7)	5.9 (8)	5.5 (8)	−0.5 (7)	0.5 (7)	0.6 (7)
C(40)	0.740 (1)	0.3545 (6)	0.334 (1)	3.6 (8)	3.0 (6)	3.7 (7)	−1.3 (6)	0.2 (6)	0.0 (6)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25(B_{11}h^2a^2 + B_{22}k^2b^2 + B_{33}l^2c^2 + 2B_{12}hkab + 2B_{13}hlac + 2B_{23}klbc)]$ where a, b, and c are reciprocal lattice constants. [b] Estimated standard deviations in the least significant digits are shown in parentheses.

2.554 (2) Å, respectively. The other four Cr to Cr distances, lying along the long edges of the bisphenoid, have an average value of 3.38 Å, and presumably no bonds exist in these positions.

Each chromium atom is surrounded by a distorted square array of ligand atoms. In the chelate rings the nitrogen atoms lie trans to the μ_4-O atom, O(1), and the N–Cr–C angles are all acute, with a mean value of 80.1 ± 0.8°. The chelate rings are, as in 1, nonplanar. As shown in Table VI, the chromium atoms are only slightly (0.10–0.13 Å) out of the coordination planes.

While the bisphenoid of chromium atoms with the μ_4-O atom at its center is probably the most immediately obvious feature of the structure, another interesting description of it is obtained by looking along the twofold symmetry axis defined by the acetate carbon atoms, C(1), C(2), C(3), and C(4). In this way it may be seen that all of the atoms lie in or close to one of two planes. In Table VII these two major planes are defined by the two sets of atoms, Cr(1)–O(1)–Cr(4) and Cr(2)–O(1)–Cr(3), and the deviations of all other atoms (six) bonded to the metal atoms from each plane are listed. The dihedral angle between these two major planes is 54.7°. Figure 4 presents a stereoview that emphasizes this feature.

Discussion

$Cr(C_6H_4\text{-}o\text{-}CH_2NMe_2)_3$, 1. The formation of this compound in reasonable yield using the chromium(II) compound $Cr_2(O_2CCH_3)_4$ as starting material was unexpected. The reaction has been repeated several times, with essentially the same results, under conditions normally considered to be rigorously anaerobic. It seems to us very

Table V. A List of Bond Distances (Angstroms) and Bond Angles (Degrees) for Compound 2

Distances

Cr(1)-Cr(2)	2.544 (2)	O(2)-C(1)	1.29 (2)	C(1)-C(2)	1.55 (2)	C(21)-C(22)	1.43 (1)
-O(1)	1.986 (6)	O(3)-C(1)	1.22 (2)	C(3)-C(4)	1.58 (2)	C(25)-C(26)	1.60 (2)
-O(5)	2.049 (7)	O(4)-C(3)	1.28 (1)	C(7)-C(8)	1.51 (2)	C(26)-C(27)	1.34 (2)
-N(1)	2.164 (7)	O(5)-C(3)	1.19 (1)	C(8)-C(9)	1.38 (2)	C(26)-C(31)	1.46 (1)
-C(13)	2.08 (1)	N(1)-C(5)	1.51 (1)	C(8)-C(13)	1.44 (1)	C(27)-C(28)	1.40 (2)
Cr(2)-O(1)	2.015 (6)	-C(6)	1.49 (2)	C(9)-C(10)	1.37 (2)	C(28)-C(29)	1.43 (2)
-O(2)	2.055 (8)	-C(7)	1.52 (1)	C(10)-C(11)	1.42 (2)	C(29)-C(30)	1.36 (1)
-N(2)	2.208 (7)	N(2)-C(14)	1.53 (2)	C(11)-C(12)	1.44 (1)	C(30)-C(31)	1.40 (1)
-C(22)	2.08 (1)	-C(15)	1.49 (2)	C(12)-C(13)	1.43 (2)	C(34)-C(35)	1.50 (2)
Cr(3)-Cr(4)	2.554 (2)	-C(16)	1.51 (1)	C(16)-C(17)	1.51 (1)	C(35)-C(36)	1.43 (2)
-O(1)	1.997 (6)	N(3)-C(23)	1.58 (1)	C(17)-C(18)	1.43 (2)	C(35)-C(40)	1.41 (2)
-O(3)	2.037 (8)	-C(24)	1.52 (1)	C(17)-C(22)	1.43 (2)	C(36)-C(37)	1.44 (2)
-N(3)	2.192 (8)	-C(25)	1.49 (2)	C(18)-C(19)	1.37 (2)	C(37)-C(38)	1.32 (2)
-C(31)	2.141 (1)	N(4)-C(32)	1.55 (1)	C(19)-C(20)	1.37 (2)	C(38)-C(39)	1.42 (2)
Cr(4)-O(1)	2.020 (6)	-C(33)	1.55 (1)	C(20)-C(21)	1.39 (1)	C(39)-C(40)	1.38 (1)
-O(4)	2.047 (8)	-C(34)	1.50 (1)				
-N(4)	2.182 (7)						
-C(40)	2.11 (1)						

Angles

Cr(2)-Cr(1)-O(1)	51.0 (2)	C(6)-N(1)-C(7)	108.0 (8)	O(1)-Cr(4)-O(4)	100.0 (3)	Cr(1)-C(13)-C(8)	114.1 (7)
Cr(2)-Cr(1)-O(5)	134.7 (2)	Cr(2)-N(2)-C(14)	113.8 (7)	-N(4)	174.6 (3)	-C(12)	131.5 (7)
Cr(2)-Cr(1)-N(1)	123.3 (2)	-C(15)	105.7 (6)	-C(40)	98.4 (3)	C(8)-C(13)-C(12)	113.7 (8)
Cr(2)-Cr(1)-C(13)	69.7 (3)	-C(16)	108.5 (6)	O(4)-Cr(4)-N(4)	83.5 (3)	N(2)-C(16)-C(17)	105.4 (8)
O(1)-Cr(1)-O(5)	101.1 (3)	C(14)-N(2)-C(15)	106.3 (9)	-C(40)	153.5 (4)	C(16)-C(17)-C(18)	121.1 (9)
O(1)-Cr(1)-N(1)	174.2 (3)	-C(16)	109.3 (8)	N(4)-Cr(4)-C(40)	79.6 (4)	-C(22)	119.2 (9)
-C(13)	97.5 (3)	C(15)-N(2)-C(16)	113.3 (8)	Cr(1)-O(1)-Cr(2)	79.0 (2)	Cr(2)-C(22)-C(17)	113.0 (8)
O(5)-Cr(1)-N(1)	82.8 (3)	Cr(3)-N(3)-C(23)	103.7 (6)	-Cr(3)	134.4 (4)	-C(21)	132.1 (8)
-C(13)	155.5 (4)	-C(24)	113.3 (7)	-Cr(4)	120.8 (3)	C(17)-C(22)-C(21)	114 (1)
N(1)-Cr(1)-C(13)	80.0 (4)	-C(25)	107.1 (7)	Cr(2)-O(1)-Cr(3)	120.3 (3)	N(3)-C(25)-C(26)	108.3 (9)
Cr(1)-Cr(2)-O(1)	50.0 (2)	C(23)-N(3)-C(24)	110.9 (9)	-Cr(4)	131.7 (4)	C(25)-C(26)-C(27)	121 (1)
-O(2)	135.9 (3)	-C(25)	114.1 (1)	Cr(3)-O(1)-Cr(4)	79.0 (2)	-C(31)	116.1 (9)
-N(2)	124.0 (3)	C(24)-N(3)-C(25)	108.1 (9)	Cr(4)-N(4)-C(34)	107.0 (6)	C(27)-C(26)-C(31)	123 (1)
-C(22)	71.0 (3)	Cr(4)-N(4)-C(32)	105.2 (6)	C(32)-N(4)-C(33)	111.1 (8)	C(26)-C(27)-C(28)	119 (1)
O(1)-Cr(2)-O(2)	101.7 (3)	-C(33)	114.1 (6)	-C(34)	109.5 (8)	C(27)-C(28)-C(29)	119 (1)
-N(2)	174.0 (3)	C(18)-C(17)-C(22)	119.7 (9)	C(33)-N(4)-C(34)	109.7 (8)	C(28)-C(29)-C(30)	121 (1)
-C(22)	97.2 (4)	C(17)-C(18)-C(19)	124 (1)	O(2)-C(1)-O(3)	127 (1)	C(29)-C(30)-C(31)	120 (1)
O(2)-Cr(2)-N(2)	83.5 (3)	C(18)-C(19)-C(20)	117 (1)	-C(2)	116 (1)	Cr(3)-C(31)-C(26)	110.9 (7)
-C(22)	153.1 (4)	C(19)-C(20)-C(21)	121 (1)	O(3)-C(1)-C(2)	117 (1)	-C(30)	132.2 (8)
N(2)-Cr(2)-C(22)	78.9 (4)	C(20)-C(21)-C(22)	124 (1)	O(4)-C(3)-O(5)	127 (1)	C(26)-C(31)-C(30)	116 (1)
Cr(4)-Cr(3)-O(1)	50.9 (2)	O(3)-Cr(3)-C(31)	155.8 (4)	-C(4)	115 (1)	N(4)-C(34)-C(35)	108.6 (9)
-O(3)	135.2 (3)	N(3)-Cr(3)-C(31)	81.7 (4)	O(5)-C(3)-C(4)	118 (1)	C(34)-C(35)-C(36)	121 (1)
-N(3)	124.2 (3)	Cr(3)-Cr(4)-O(1)	50.1 (2)	N(1)-C(7)-C(8)	108.7 (8)	C(34)-C(35)-C(40)	119 (1)
Cr(2)-O(2)-C(1)	129.2 (9)	-O(4)	134.2 (2)	C(7)-C(8)-C(9)	119.2 (9)	C(36)-C(35)-C(40)	119 (1)
Cr(3)-O(3)-C(1)	134.5 (9)	-N(4)	124.5 (2)	-C(13)	115.0 (9)	C(35)-C(36)-C(37)	121 (1)
Cr(4)-O(4)-C(3)	133.1 (7)	-C(40)	72.3 (3)	C(9)-C(8)-C(13)	125.8 (9)	C(36)-C(37)-C(38)	119 (2)
Cr(1)-O(5)-C(3)	132.6 (8)	Cr(4)-Cr(3)-C(31)	69.1 (3)	C(8)-C(9)-C(10)	119 (1)	C(37)-C(38)-C(39)	120 (1)
Cr(1)-N(1)-C(5)	108.4 (6)	O(1)-Cr(3)-O(3)	100.3 (3)	C(9)-C(10)-C(11)	120 (1)	C(38)-C(39)-C(40)	125 (1)
-C(6)	114.0 (6)	O(1)-Cr(3)-N(3)	175.0 (3)	C(10)-C(11)-C(12)	119.6 (9)	Cr(4)-C(40)-C(35)	111.6 (8)
-C(7)	106.4 (6)	O(1)-Cr(3)-C(31)	96.9 (3)	C(11)-C(12)-C(13)	121.5 (9)	-C(39)	132.2 (8)
C(5)-N(1)-C(6)	109.9 (8)	O(3)-Cr(3)-N(3)	82.5 (4)			C(35)-C(40)-C(39)	116 (1)
-C(7)	110.0 (7)						

Table VI. Some Planes and the Relation of Certain Atoms and Bond Directions to Them for Compound 2

plane	distance (Å) from plane of
1, O(1)-O(2)-N(2)-C(22)	Cr(2), −0.138
∠ Cr(1)-Cr(2) makes with plane 1 = 54.3°	
2, O(1)-O(5)-N(1)-C(13)	Cr(1), 0.104
∠ Cr(2)-Cr(1) makes with plane 2 = 53.0°	
3, O(1)-O(4)-N(4)-C(40)	Cr(4), −0.131
∠ Cr(3)-Cr(4) makes with plane 3 = 53.4°	
4, O(1)-O(3)-N(3)-C(31)	Cr(3), 0.116
∠ Cr(4)-Cr(3) makes with plane 4 = 53.7°	

Table VII. Two Additional Planes[a] Illustrating the Geometric Relationship between the Pairs of Cr^{II} Complexes in Compound 2

plane	distance (Å) from plane of
1, Cr(1)-O(1)-Cr(4)	O(5), −0.264
	N(1), 0.179
	C(13), −0.304
	C(40), 0.500
	N(4), −0.170
	O(4), 0.183
2, Cr(2)-O(1)-Cr(3)	N(3), 0.175
	C(31), 0.295
	O(3), −0.319
	N(2), −0.136
	C(22), 0.469
	O(2), 0.212

[a] Angle between planes 54.7°.

unlikely that oxidation is caused by oxygen from the atmosphere. In fact, when a small amount of oxygen was intentionally admitted on one occasion, the reaction mixture turned green, and none of the tris-chelate compound was obtained. It is possible that a disproportionation reaction occurs in which the Cr^{I} forms arene complexes, but we have, as yet, no evidence on this.

As we have already mentioned, this compound has been reported before[2] but only briefly described. It was said to decompose in air in less than 1 h,[2] whereas we have observed that the beautiful pseudocubic orange crystals can be left in laboratory air for at least 3 months and/or treated with water or base without any sign of decompo-

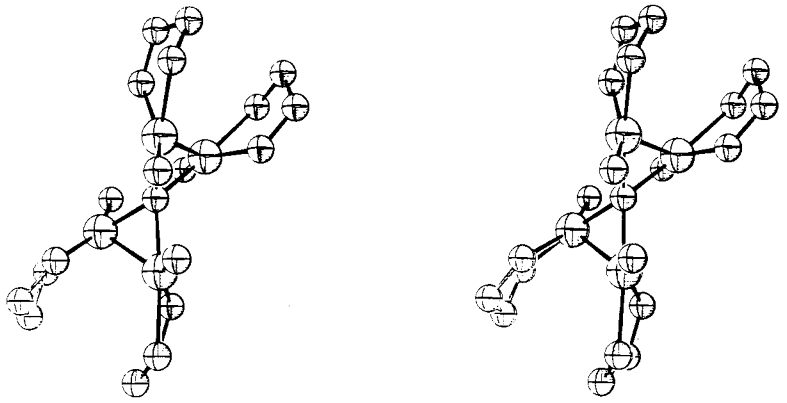

Figure 4. A stereoscopic view of the central portion of the molecule of compound 2. The acetate carbon atoms have been omitted for clarity.

sition. In even more striking contrast to our observation is the report[4] that $Cr(C_6H_4\text{-}o\text{-}CH_2NEt_2)_3$ is highly reactive toward both air and water.

It is true that many tris(organo)chromium(III) compounds are reactive toward air and water, and thermodynamically such reactions are almost certainly favored in all cases. Nonetheless, those previously known compounds with three chelating ligands have all been reported to exhibit kinetic stability except for the diethyl compound just mentioned. Possibly the inclusion of traces of reactive impurities instigated the reported reactivity. On the other hand, the steric requirements of the ethyl groups may be so great as to favor reactivity through initial unimolecular Cr–N bond dissociation.

Still another possibility, though we think it is unlikely, is that the more reactive $Cr(C_6H_4\text{-}o\text{-}CH_2NR_2)_3$ compounds contain the meridional isomer rather than the facial one. It is not inconceivable that syntheses from $CrCl_3$ and from $Cr_2(O_2CCH_3)_4$ could lead to different isomers. However, for R = Me the color is orange in each case, and this probably means that the isomer is also the same in each case.

The Cr–C distance in 1 is comparable to those found in other organochromium(III) compounds, where values from ca. 2.01 to ca. 2.11 Å have been reported.[4] The Cr–N distance, however, is extraordinarily long. Previously reported Cr–N and Cr–O distances have been around 2.15 Å, whereas in the present case we have a length of 2.356 (4) Å. In compound 2 reported here the Cr–N bond lengths are in the range 2.15–2.20 Å. Two possible explanations for this come to mind. Perhaps Cr–C bonds exert a powerful trans effect. Alternatively, nonbonded repulsions between the three mutually cis $N(CH_3)_2$ groups may be lessened by the lengthening of the Cr–N bonds. We prefer the latter, since in compound 2 described in this paper we have a Cr–O bond trans to the same type of carbon atom and that Cr–O bond length, 2.04 Å, is not unusually long.

$Cr_4(C_6H_4\text{-}o\text{-}CH_2NMe_2)_4(O_2CCH_3)_2O$, 2. Certain features of this molecule are rare and others unique. We may begin the discussion with the central oxygen atom, and mention first that we can only speculate as to its origin. As we noted in discussing compound 1, the preparative reactions are run under conditions that would normally be described as strictly anaerobic. Obviously, we cannot conclusively rule out the possibility that adventitious oxygen (O_2) is the source of this central oxygen atom, but it seems to us very unlikely. The preparation is quite reproducible, and, if even traces of O_2 are deliberately admitted, a destructive oxidation process reduces the yield of 2 to zero. We assume, therefore, that the central oxygen atom originates in the acetate ions, but we cannot offer any detailed mechanism for this.

Structurally, a μ_4-O atom is a rarity, especially in discrete molecules.[5] The Cr–O(1) bonds have a mean length of 2.00 ± 0.01 Å, which is slightly shorter than those to the acetate oxygen atoms, which average 2.047 ± 0.005 Å.

The truly astonishing feature of this structure is the geometric relationship between the pairs of planar Cr^{II} complexes that are bonded to each other. The two planes have only one atom in common, O(1), and the dihedral angle between them is that between the two major molecular planes described under Results, namely, 54.7°. The bond between the chromium atoms makes an angle of about 53° with each of these planes and makes acute angles with the Cr–O(1) and Cr–C bonds of about 50° and 70°, respectively.

With the Cr–Cr bond having such a direction relative to the ligand atoms, it is not clear how to formulate that bond in terms of d-orbital overlaps. Its mean length, 2.549 Å, is comparble to that found in $Cr_2(O_2CCF_3)_4(Et_2O)_2$, in which an extremely stretched and weak quadruple (σ, 2π, δ) interaction has been contemplated.[6] On the other hand, a bond of lower multiplicity, but more strength per component, would also be consistent with the Cr–Cr distance.

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Registry No. 1, 79171-80-5; 2, 79121-11-2; chromium(II) acetate, 15020-15-2; $LiC_6H_4\text{-}o\text{-}CH_2NMe_2$, 27171-81-9.

Supplementary Material Available: Tables of structure factors (15 pages). For ordering information see any current masthead page.

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(4) Sneeden, R. P. A. "Organochromium Compounds"; Academic Press: New York, 1975.

(5) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 154.

(6) Cotton, F. A.; Extine, M. W.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 176.