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Polymetallic Chromium Alkoxides: Synthesis and Crystal Structures of $(i\text{-PrO})_8Cr_2Na_4(THF)_4$ and $(\mu_3\text{-OPh})_{10}Cr_4(\mu_3\text{-O})_3Na_4(TMEDA)_4$

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The reaction of $(RO)_8Cr_2Na_4(THF)_4$ [R = *i*-Pr (**1a**), Ph (**1b**)] with TMEDA (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) has been studied. While the isopropyl derivative **1a** yielded the polymeric $[(i\text{-PrO})_2Cr]_n$, in the case of **1b**, the Cr(III) aggregate $(PhO)_{10}Cr_4(\mu_3\text{-O})_3Na_4(TMEDA)_4$ (**2**) was formed via an unusual oxidation reaction. Crystal data for **1a** and **2** are as follows: **1a** is monoclinic, space group $P2_1/c$ with $a = 11.979$ (1) Å, $b = 21.243$ (1) Å, $c = 12.009$ (2) Å, $\beta = 113.75$ (1)°, $V = 2796.9$ (6) Å^3, $Z = 2$; **2** is triclinic, space group $P\bar{1}$, $a = 14.332$ (1) Å, $b = 15.403$ (1) Å, $c = 26.447$ (2) Å, $\alpha = 98.24$ (1)°, $\beta = 98.71$ (1)°, $\gamma = 115.87$ (1)°, $V = 5046.7$ (8) Å^3, $Z = 2$.

Introduction

Di- and polynuclear group 6 transition-metal alkoxides have been the subject of intensive study, not only because of the interesting reactivity pattern observed with various unsaturated organic substrates[1-7] but also because they may provide versatile substrates with which to (a) mimic processes which are relevant for both homogeneous and heterogeneous catalysis[8-13] and (b) study the nature of the intermetallic interaction (metal–metal bonds, magnetic couplings, ligand-mediated superexchange, etc.).[14] In contrast to the rich chemistry of Mo and W alkoxide clusters,[1-5,9-12] the chromium analogues remain much less known, for both oxidation states +II[15-20] and +III,[21-25] and limited to few examples of low-nuclearity compounds (mainly monomers).[19,20,27-29] The probable reason for this peculiarity is that, when supported by monodentate ligands (alkoxides,[19,20] amides,[26] and aryls[27,28]), chromium displays a generally poor tendency to form metal–metal bonds capable of holding together the molecular frames.[29] Conversely, the alkali-metal cation, associated with the structure of anionic Cr(II) alkoxides, plays a fundamental role in the assembling of dimeric[19,20] and oligomeric structures.[30] Among the properties which determine this behavior, the Lewis acidity of the alkali-metal cation is the most effective.

The possibility of modifying the molecular structure of anionic transition-metal alkoxides by changing the dimensions of the alkali-metal cation has a precedent in the chemistry of anionic yttrium(III)[31] and chromium(II)[30] and main-group element alkoxides.[32] Furthermore, in the case of dimeric lithium alkoxochromates(II), the modification of the coordination sphere of the alkali-metal cation via ligation of Lewis bases has been shown to be able to determine considerable rearrangements of the molecular frame, including the cleavage of the Cr_2 core.[30] Therefore, in order to gain more information into this curious phenomenon, we felt it was important to attempt similar reactions on the corresponding sodium derivatives.

In this paper we report the first structural characterization of an aliphatic sodium alkoxochromate and an unpredictable molecular rearrangement, obtained by reaction with a chelating diamine.

Experimental Section

All operations were performed under dry nitrogen by using standard Schlenk techniques or in a nitrogen-filled drybox (Braun MB-200). $CrCl_2(THF)_2$,[33] $Mes_2Cr(THF)_2(THF)$,[34] and $(PhO)_8Cr_2Na_4(THF)_4$[20] were prepared according to published procedures. Infared spectra were recorded on a Unicam SP-300 instrument. Nujol mulls were prepared in the drybox. Elemental analyses were carried out at the Chemistry Department of the State University of Groningen. Magnetic measurements were carried out with a MB-4 Faraday balance (Oxford Instruments) interfaced with an Apple II computer and corrected for the underlying diamagnetism.[35]

$[(i\text{-PrO})_2Cr]_n$. A purple solution of $Mes_2Cr(THF)_2(THF)$ (1.28 g, 2.45 mmol) in THF (30 mL) was treated with *i*-PrOH (0.37 mL, 4.89

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Table I. Crystal and Structural Analysis Results

	1	**2**
formula	$C_{40}H_{88}O_{12}Cr_2Na_4$	$C_{90}H_{130}N_{10}O_{13}Na_4Cr_4$
fw	1914.17	1860.03
space group	$P2_1/c$	$P\bar{1}$
cryst syst	monoclinic	triclinic
Z	2	2
a, Å	11.979 (1)	14.332 (1)
b, Å	21.243 (1)	15.403 (1)
c, Å	12.009 (2)	26.447 (2)
α, deg		98.24 (1)
β, deg	113.75 (1)	98.71 (1)
γ, deg		115.87 (1)
V, Å^3	2796.9 (6)	5046.7 (8)
D_{calcd}, g cm^{-3}	1.136	1.224
μ_{calcd}, cm^{-1}	4.9	5.2
radiation (Mo Kα), Å	0.71073	0.71073
T, K	295	295
$R_F{}^a$	0.065	0.051
$R_w{}^b$	0.073	0.061

$^a R_F = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $^b R_w = [\Sigma(w||F_o| - |F_c||)/\Sigma wF_o{}^2]^{1/2}$.

mmol). The color turned deep red, and solid, purple-red $[(i\text{-PrO})_2Cr]_n$ precipitated (0.31 g, 1.8 mmol, yield 74%). Anal. Calcd (found) for $C_6H_{14}O_2Cr$: C, 41.93 (42.05); H, 8.15 (8.24); Cr, 28.89 (30.30). IR (Nujol mull, KBr, cm^{-1}): 1335 (m), 1150 (m), 1120 (s), 950 (s), 815 (m), 580 (s).

$(i\text{-PrO})_8Cr_2Na_4(THF)_4$ (1a). Method A. NaH (0.88 g, 36.7 mmol) was slowly added to a stirred solution of *i*-PrOH (2.80 mL, 37 mmol) in THF (50 mL). The color of the resulting solution turned green upon addition of $CrCl_2(THF)_2$ (1.93 g, 7.2 mmol), and the stirring was continued for 3 h. The solvent was removed in vacuo, and the solid residue was crystallized from toluene (15 mL) at −30 °C, resulting in the formation of yellow-green crystals of **2** (2.72 g, 2.8 mmol, 79% yield). Anal. Calcd (found) for $C_{40}H_{88}O_{12}Cr_2Na_4$: C, 50.21 (50.17); H, 9.27 (9.19); Cr, 10.87 (10.92); Na, 9.62 (9.56). IR (Nujol mull, KBr, cm^{-1}): 1370 (m), 1355 (m), 1315 (m), 1155 (s), 1150 (s), 1110 (m), 1080 (m), 1020 (w), 985 (s), 895 (m), 810 (s), 560 (s), 470 (m). (μ_{eff} = 3.25 μ_B).

Method B. A suspension of $[(i\text{-PrO})_2Cr]_n$ (0.63 g, 3.7 mmol) in THF (40 mL) was treated with a solution of *i*-PrONa, obtained by reacting a solution of *i*-PrOH (0.60 mL, 7.9 mmol) in THF with NaH (0.187 g, 7.8 mmol). The color turned green, and the stirring was continued for 3 h. The solution was worked up as above, yielding 1.28 g of **1** (1.32 mmol, 71%).

$(PhO)_{10}Cr_4O_3Na_4(TMEDA)_4$ (2). A suspension of $(PhO)_8Cr_2Na_4(THF)_4$ (4.36 g, 3.55 mmol) in toluene (40 mL) was treated with 60 mL of TMEDA. The color turned deep blue during 1.5 h refluxing. The resulting intense blue solution was evaporated to dryness, the residual solid was redissolved in toluene (25 mL), and a small amount of white insoluble material was filtered out. Large blue crystals of **2** precipitated upon addition of hexane (30 mL) and cooling to −30 °C (1.86 g, 1.01 mmol, 57%). Anal. Calcd (found) for $C_{90}H_{130}O_{13}N_{10}Cr_4Na_4$: C, 58.12 (57.97); H, 7.05 (6.70); N, 7.52 (7.38); Cr, 11.18 (11.04); Na, 4.94 (4.78). IR (Nujol mull, KBr, cm^{-1}): 1575 (s), 1560 (sh), 1405 (w), 1355 (w), 1305 (m), 1290 (sh), 1275 (s), 1250 (s), 1155 (s), 1130 (m), 1095 (w), 1065 (m), 1035 (w), 1020 (s), 990 (s), 945 (m), 880 (m), 870 (w), 840 (s), 825 (m), 785 (w), 760 (s), 750 (m), 730 (m), 690 (s). (μ_{eff} = 3.48 μ_B).

Reaction of 1a with TMEDA. A solution of **1a** (1.26 g, 1.32 mmol) in toluene (20 mL) was treated with an excess of TMEDA (10 mL). The color turned red, and a purple amorphous solid separated after 1 h of reflux. The solid was washed, dried, and identified by both elemental analysis and comparison of the IR spectrum with that of an analytically pure sample (0.14 g, 31% yield).

X-ray Crystallographic Studies. X-ray data were collected on an Enraf-Nonius CAD-4F (Mo Kα, Zr filtered) automatic diffractometer. Crystal data and numerical details on structure determinations are presented in Table I. Relevant bond distances and angles are reported in Table IV. Scattering factors were taken from ref 36 and corrected for anomalous dispersion.[37] The calculation of the geometrical data and the preparation of the thermal plots were carried out with the program PLATON of the EUCLID package[38] on a MicroVax-II cluster.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **1**

atom	x	y	z	U(eq), Å^2
Cr	0.08582 (9)	0.04285 (5)	0.42338 (9)	0.0558 (3)
Na1	0.1247 (2)	0.0532 (1)	0.6946 (2)	0.0689 (9)
Na2	−0.1509 (2)	0.0878 (1)	0.4462 (2)	0.070 (1)
O10	0.0630 (5)	0.1170 (2)	0.5132 (4)	0.077 (2)
O20	−0.0898 (4)	0.0414 (2)	0.6469 (4)	0.078 (2)
O30	−0.0793 (4)	0.0574 (2)	0.2938 (4)	0.079 (2)
O40	−0.02325 (4)	−0.0192 (2)	0.4292 (4)	0.072 (2)
O50	0.2415 (6)	0.0978 (3)	0.8872 (5)	0.122 (3)
O60	−0.2959 (6)	0.1728 (3)	0.3960 (6)	0.122 (3)
C11	0.099 (1)	0.1757 (5)	0.515 (1)	0.171 (8)
C12	0.154 (1)	0.2016 (5)	0.442 (1)	0.163 (7)
C13	0.076 (1)	0.2173 (5)	0.604 (1)	0.174 (7)
C21	−0.140 (1)	0.0614 (4)	0.719 (1)	0.154 (7)
C22	−0.199 (1)	0.0251 (6)	0.7744 (9)	0.140 (5)
C23	−0.122 (1)	0.1311 (4)	0.750 (1)	0.138 (6)
C31	−0.1140 (8)	0.0848 (6)	0.1867 (9)	0.140 (5)
C32	−0.040 (1)	0.1157 (5)	0.1396 (9)	0.135 (5)
C33	−0.2528 (8)	0.0870 (6)	0.1154 (8)	0.132 (5)
C41	−0.3462 (8)	−0.0325 (7)	0.398 (1)	0.178 (7)
C42	−0.3960 (9)	−0.0710 (5)	0.466 (1)	0.129 (5)
C43	−0.4344 (8)	−0.0040 (6)	0.2827 (9)	0.140 (5)
C51	0.214 (1)	0.0930 (7)	0.991 (1)	0.172 (7)
C52	0.308 (1)	0.1215 (6)	1.0924 (9)	0.139 (5)
C53	0.397 (1)	0.1474 (7)	1.046 (1)	0.157 (6)
C54	0.350 (1)	0.1318 (8)	0.922 (1)	0.216 (9)
C61	−0.396 (1)	0.1712 (6)	0.429 (1)	0.163 (7)
C62	−0.449 (2)	0.2327 (8)	0.402 (2)	0.21 (1)
C63	−0.390 (2)	0.2680 (6)	0.337 (2)	0.195 (9)
C64	−0.287 (1)	0.2316 (5)	0.343 (1)	0.178 (8)

Complex 1. Data were collected [$\omega/2\theta$ scan; $\Delta\omega = (0.90 + 0.35 \tan \theta)°$; $\theta_{max} = 27.5°$] for a yellowish crystal (0.15 × 0.38 × 1.00 mm) mounted under nitrogen in a Lindemann glass capillary. Unit cell parameters were calculated from the SET4 setting angles[39] for 25 reflections in the range $11 < \theta < 14°$. The space group was derived from the observed systematic absences. The intensities of 5922 reflections were corrected for L_p but not for absorption and merged into a unique data set of 3170 reflections with $I > 2.5\sigma(I)$. The structure was solved with standard Patterson and Fourier methods (SHELXS-86)[40] and refined on F by full-matrix least squares (SHELX-76)[41] with anisotropic thermal parameters for the non-hydrogen atoms. Both isopropoxy groups and THF molecules are partly disordered as indicated by the thermal motion ellipsoids. In view of this, no hydrogen atoms were taken into consideration in the refinements. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table II. Convergence was reached at $R = 0.065$, $R_w = 0.073$, $w = 1.0$, and $S = 1.79$. A final difference Fourier map showed no features outside the range −0.35 to +0.29 e/Å^3. Relevant bond distances and angles are given in Table IV.

Complex 2. A blue block-shaped crystal (0.58 × 0.38 × 0.28 mm) was mounted under nitrogen in a Lindemann glass capillary and transferred to an Enraf-Nonius CAD-4F diffractometer for data collection [$\omega/2\theta$ scan; $\Delta\omega = (0.60 + 0.35 \tan \theta)°$; $\theta_{max} = 24.0°$]. Unit cell parameters were determined from the SET4 setting angles[39] of 25 reflections with $9.3 < \theta < 16.3°$. Unit cell parameters were checked for the presence of higher lattice symmetry.[42] The intensities of 16482 reflections were corrected for Lp and for the instability (±4%) of the intensity control reflection during the 98 h of X-ray exposure time but not for absorption; redundant data were merged into a unique data set of 15761 reflections of which 8435 had $I \geq 2.5\sigma(I)$. The structure was solved with standard Patterson methods (SHELXS-86)[40] and a series of subsequent difference Fourier analyses. Refinement on F was carried out by full-matrix least-squares techniques (SHELX-76).[41] H atoms were introduced on calculated positions (C–H = 0.98 Å) and included in the refinement

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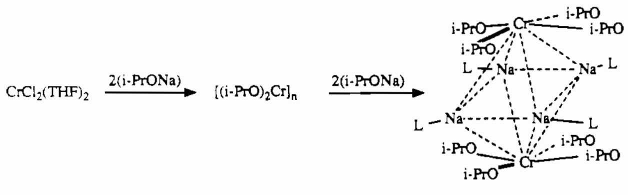
Table III. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **2**

atom	x	y	z	U(eq), Å^2
Cr1	0.08430 (6)	0.08547 (6)	0.22062 (3)	0.0393 (3)
Cr2	−0.04270 (6)	0.20214 (6)	0.19548 (3)	0.0401 (3)
Cr3	0.13666 (6)	0.27431 (6)	0.30466 (3)	0.0371 (3)
Cr4	0.03847 (7)	0.42471 (6)	0.27611 (3)	0.0420 (3)
Na1	0.1953 (2)	−0.0231 (2)	0.17832 (9)	0.0668 (9)
Na2	−0.1041 (2)	0.0389 (2)	0.28418 (9)	0.0665 (9)
Na3	−0.1957 (2)	0.3139 (2)	0.17673 (8)	0.0589 (8)
Na4	0.2331 (2)	0.4955 (2)	0.38944 (8)	0.0560 (8)
O1	0.0933 (3)	0.0606 (3)	0.1472 (1)	0.054 (1)
O2	0.2365 (3)	0.1217 (3)	0.2403 (1)	0.049 (1)
O3	0.0452 (3)	−0.0529 (3)	0.2194 (1)	0.056 (2)
O4	−0.0348 (3)	0.2555 (2)	0.2194 (1)	0.045 (1)
O5	−0.1923 (3)	0.1626 (3)	0.1574 (1)	0.052 (1)
O6	0.0036 (3)	0.3483 (2)	0.1975 (1)	0.045 (1)
O7	−0.0998 (3)	0.4264 (3)	0.2555 (2)	0.065 (2)
O8	0.0909 (3)	0.5107 (3)	0.3478 (2)	0.066 (2)
O9	0.1817 (3)	0.4152 (2)	0.2936 (1)	0.040 (1)
O10	0.1838 (3)	0.3279 (3)	0.3821 (1)	0.051 (1)
O11	0.1119 (2)	0.2278 (2)	0.2240 (1)	0.036 (1)
O12	0.0827 (3)	0.1256 (2)	0.2972 (1)	0.041 (1)
O13	−0.0676 (3)	0.0636 (2)	0.2021 (1)	0.043 (1)
N1	0.2192 (6)	−0.0970 (5)	0.0969 (2)	0.085 (3)
N2	0.2963 (5)	−0.1157 (5)	0.2033 (2)	0.078 (3)
N3	−0.1031 (5)	−0.0395 (4)	0.3600 (2)	0.071 (2)
N4	−0.2758 (4)	−0.1238 (4)	0.2604 (3)	0.075 (2)
N5	−0.2692 (5)	0.3167 (5)	0.0806 (2)	0.076 (2)
N6	−0.3858 (4)	0.2934 (5)	0.1653 (2)	0.089 (3)
N7	0.2944 (6)	0.6008 (5)	0.4821 (2)	0.090 (3)
N8	0.4381 (5)	0.5785 (5)	0.4146 (3)	0.093 (3)
C1	0.1376 (5)	0.1255 (4)	0.1178 (2)	0.046 (2)
C2	0.2371 (5)	0.2087 (4)	0.1363 (2)	0.055 (2)
C3	0.2799 (5)	0.2709 (5)	0.1039 (3)	0.070 (3)
C4	0.2251 (6)	0.2517 (5)	0.0530 (3)	0.075 (3)
C5	0.1278 (6)	0.1680 (5)	0.0342 (2)	0.069 (3)
C6	0.0836 (5)	0.1064 (4)	0.0660 (2)	0.056 (2)
C7	0.2975 (4)	0.1233 (4)	0.2850 (2)	0.046 (2)
C8	0.2606 (4)	0.0504 (4)	0.3130 (2)	0.048 (2)
C9	0.3286 (5)	0.0528 (5)	0.3571 (2)	0.064 (3)
C10	0.4311 (6)	0.1252 (5)	0.3743 (3)	0.074 (3)
C11	0.4685 (5)	0.1989 (5)	0.3474 (3)	0.073 (3)
C12	0.4023 (5)	0.1986 (4)	0.3032 (2)	0.057 (2)
C13	−0.0283 (4)	−0.1394 (4)	0.1867 (2)	0.049 (2)
C14	−0.0856 (5)	−0.1459 (4)	1.1373 (2)	0.062 (2)
C15	−0.1604 (6)	−0.2372 (5)	0.1051 (3)	0.079 (3)
C16	−0.1787 (7)	−0.3220 (5)	0.1209 (3)	0.111 (3)
C17	−0.1222 (7)	−0.3166 (5)	0.1688 (3)	0.113 (4)
C18	−0.0485 (5)	−0.2267 (5)	0.2014 (3)	0.077 (3)
C19	−0.1090 (4)	0.2302 (4)	0.3102 (2)	0.040 (2)
C20	−0.2163 (4)	0.1667 (4)	0.2864 (2)	0.055 (2)
C21	−0.2928 (5)	0.1452 (4)	0.3163 (3)	0.069 (3)
C22	−0.2649 (6)	0.1815 (5)	0.3689 (3)	0.077 (3)
C23	−0.1591 (6)	0.2421 (5)	0.3930 (3)	0.076 (3)
C24	−0.0813 (5)	0.2666 (4)	0.3646 (2)	0.059 (2)
C25	−0.2490 (4)	0.0739 (4)	0.1236 (2)	0.051 (2)
C26	−0.3234 (5)	0.0145 (5)	0.1225 (3)	0.082 (3)
C27	−0.4114 (6)	−0.0767 (7)	0.0866 (4)	0.118 (4)
C28	−0.3674 (8)	−0.1098 (6)	0.0520 (4)	0.111 (4)
C29	−0.2646 (7)	−0.0518 (6)	0.0527 (3)	0.086 (3)
C30	−0.2040 (5)	0.0399 (5)	0.0877 (2)	0.064 (3)
C31	0.0329 (4)	0.3961 (4)	0.1589 (2)	0.048 (2)
C32	0.0595 (5)	0.3549 (5)	0.1165 (3)	0.073 (3)
C33	0.0890 (7)	0.4041 (7)	0.0780 (3)	0.106 (4)
C34	0.0930 (7)	0.4975 (8)	0.0815 (4)	0.120 (5)
C35	0.0660 (6)	0.5364 (6)	0.1221 (3)	0.096 (4)
C36	0.0365 (5)	0.4872 (4)	0.1604 (2)	0.066 (3)
C37	−0.1470 (5)	0.4674 (4)	0.2827 (2)	0.050 (2)
C38	−0.2151 (5)	0.4182 (5)	0.3117 (3)	0.068 (3)
C39	−0.2703 (6)	0.4595 (7)	0.3362 (3)	0.088 (3)
C40	−0.2542 (7)	0.5511 (8)	0.3338 (4)	0.115 (4)
C41	−0.1846 (8)	0.6023 (6)	0.3066 (4)	0.114 (4)
C42	−0.1317 (6)	0.5617 (5)	0.2815 (3)	0.078 (3)
C43	0.0837 (5)	0.5901 (5)	0.3685 (2)	0.060 (2)
C44	0.0247 (5)	0.5845 (6)	0.4068 (3)	0.082 (3)
C45	0.0221 (8)	0.6672 (9)	0.4317 (3)	0.122 (5)
C46	0.071 (1)	0.7503 (9)	0.4180 (6)	0.157 (8)
C47	0.130 (1)	0.7669 (9)	0.3836 (6)	0.148 (7)
C48	0.1355 (7)	0.6805 (7)	0.3570 (3)	0.107 (4)
C49	0.2644 (4)	0.4583 (4)	0.2712 (2)	0.045 (2)
C50	0.2795 (5)	0.5408 (5)	0.2712 (2)	0.070 (3)
C51	0.3662 (7)	0.5860 (6)	0.2315 (3)	0.109 (4)
C52	0.4388 (7)	0.5492 (7)	0.2278 (3)	0.111 (4)
C53	0.4232 (6)	0.4694 (6)	0.2468 (3)	0.097 (3)
C54	0.3368 (5)	0.4694 (6)	0.2468 (3)	0.097 (3)
C55	0.1942 (4)	0.2818 (4)	0.4199 (2)	0.046 (2)
C56	0.1532 (5)	0.2897 (5)	0.4633 (2)	0.070 (3)
C57	0.1661 (6)	0.2430 (6)	0.5027 (3)	0.087 (3)
C58	0.2193 (6)	0.1878 (5)	0.4997 (3)	0.078 (3)
C59	0.2621 (5)	0.1804 (5)	0.4579 (3)	0.068 (2)
C60	0.2499 (4)	0.2274 (4)	0.4172 (2)	0.052 (2)
C61	0.1204 (8)	−0.1500 (9)	0.0613 (4)	0.207 (7)
C62	0.2871 (9)	−0.0230 (8)	0.0734 (4)	0.172 (7)
C63	0.267 (1)	−0.1560 (9)	0.1095 (4)	0.190 (8)
C64	0.3066 (9)	−0.1635 (8)	0.1546 (4)	0.144 (6)
C65	0.2373 (8)	−0.1889 (7)	0.2293 (4)	0.152 (6)
C66	0.4021 (6)	−0.0504 (7)	0.2376 (3)	0.130 (4)
C67	−0.0179 (8)	−0.0652 (7)	0.3663 (4)	0.156 (6)
C68	−0.0894 (8)	0.0293 (6)	0.4058 (4)	0.145 (5)
C69	−0.2066 (8)	−0.1274 (6)	0.3504 (3)	0.118 (4)
C70	−0.2622 (8)	−0.1739 (7)	0.2990 (5)	0.180 (6)
C71	−0.3678 (6)	−0.1118 (6)	0.2582 (5)	0.180 (6)
C72	−0.2892 (8)	−0.1830 (7)	0.2106 (4)	0.168 (6)
C73	−0.2699 (8)	0.2338 (7)	0.0488 (3)	0.136 (5)
C74	−0.2066 (8)	0.4020 (8)	0.0620 (4)	0.174 (6)
C75	−0.3763 (7)	0.3065 (8)	0.0751 (3)	0.128 (5)
C76	−0.4354 (6)	0.2563 (7)	0.1090 (3)	0.116 (4)
C77	−0.4424 (7)	0.2217 (8)	0.1934 (4)	0.1473 (5)
C78	−0.3885 (7)	0.3852 (7)	0.1862 (3)	0.143 (5)
C79	0.4596 (6)	0.4953 (7)	0.4109 (4)	0.126 (4)
C80	0.4952 (6)	0.6424 (6)	0.3832 (3)	0.122 (4)
C81	0.4710 (7)	0.6377 (8)	0.4700 (4)	0.144 (5)
C82	0.3851 (9)	0.6034 (8)	0.5014 (3)	0.143 (6)
C83	0.3008 (7)	0.6979 (5)	0.4839 (3)	0.108 (4)
C84	0.2217 (9)	0.5573 (7)	0.5158 (4)	0.155 (6)

riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; H atoms were refined with three separate common isotropic thermal parameters [U = 0.178 (6), 0.22 (1), and 0.090 (3) Å^2 for CH_3, CH_2, and CH hydrogen atoms, respectively]. Solvate molecules (located on two independent inversion symmetry sites and tentatively interpreted as TMEDA on the basis of the analytical results) could not be unambiguously located from difference Fourier maps and were taken into account in the structure factor and refinement calculations by direct Fourier transformation of the electron density in the cavity, following the BYPASS procedure.[43] Weights were introduced in the final refinement cycles; convergence was reached at R = 0.051, R_w = 0.061, $w = 1.0/[\sigma^2(F) + 0.001168F^2]$, and S = 1.99. A final difference Fourier map showed no features outside the range -0.27 to +0.39 e/Å^3. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table III. Relevant bond distances and angles are given in Table IV.

Scheme I



1a

Discussion and Results

The synthetic procedure used for the preparation of Cr(II) isopropoxides is the same one already employed for the preparation of the aromatic congeners[19,20] and is summarized in Scheme I. After preliminary formation of the polymeric $[(i\text{-PrO})_2Cr]_n$, further reaction with an excess of i-PrONa gave a green slurry

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[43] van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.

Table IV. Selected Bond Distances (Å) and Angles (deg)

1		2	
Cr···Cr′	3.739 (2)	Cr1···Cr2	3.133 (1)
Cr-O10	1.989 (5)	Cr2···Cr3	3.243 (1)
Cr-O20′	1.987 (4)	Cr2···Cr4	3.366 (1)
Cr-O30	1.987 (5)	Cr1-O1	1.959 (4)
Cr-O40′	1.992 (5)	Cr1-O13	2.020 (5)
Na2-O10	2.436 (7)	Cr2-O13	2.043 (3)
Na2-O20	2.428 (5)	Na1-O3	2.451 (5)
Na2-O30	2.402 (6)	Na2-O13	2.352 (4)
Na2-O40	2.451 (5)	Cr2-O5	2.003 (5)
Na2-O60	2.407 (7)	Cr2-O6	2.040 (3)
O10-Cr-O20′	167.3 (2)	Na2···O4	3.046 (4)
O10-Cr-O30	89.5 (2)	Na2···C19	2.963 (6)
O10-Na2-O20	85.4 (2)	Cr1-O1-Na1	84.1 (2)
O10-Na2-O30	70.7 (2)	Cr1-O13-Na2	96.3 (2)
O10-Na2-O60	116.7 (2)	Cr1-O13-Cr2	100.9 (2)
		Cr2-O4-Cr3	89.2 (2)
		Cr3-O4-Cr4	89.3 (1)
		O7-Cr4-O9	176.2 (2)
		O6-Cr4-O7	85.4 (2)

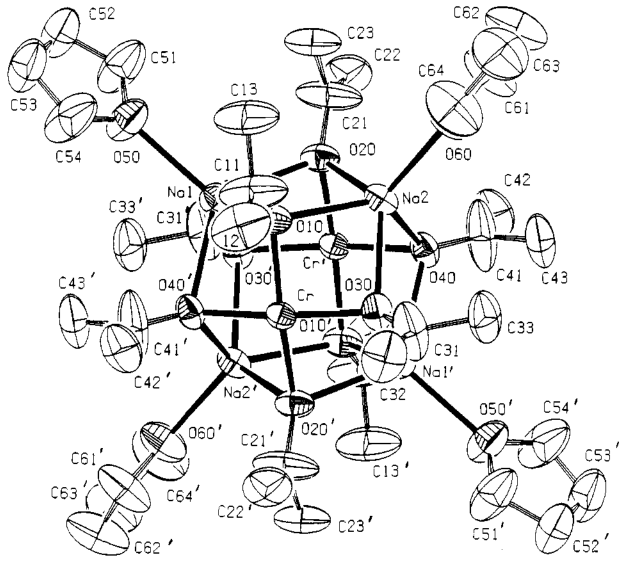


Figure 1. Thermal motion ellipsoid plot of **1** drawn at the 50% probability level.

from which greenish yellow crystals of $(i\text{-PrO})_8Cr_2Na_4(THF)_4$ were isolated in good yield (79%) after recrystallization from toluene. Unlike the case of the aryloxochromates, there is no evidence for the intermediate formation of the monomeric $(i\text{-PrO})_4CrNa_2(THF)_4$.[19,20] This is probably a result of the higher basicity of the isopropoxide oxygen atoms, which are more competitive with respect to THF for the coordination to sodium.

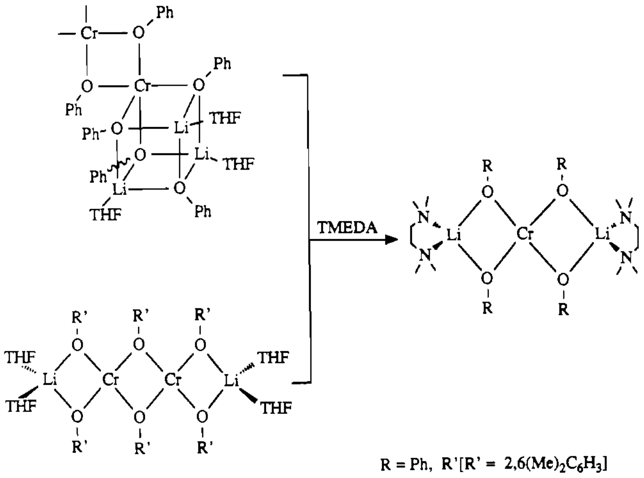
The structure of **1a** has been determined by X-ray diffraction analysis. The complex is isostructural with the previously reported Cr(II) phenoxides $(PhO)_8Cr_2Na_4L_4$.[19,20] The geometry of the molecule (Figure 1) can be described in terms of a distorted coordination octahedron, positioned on an inversion center, with the two chromium atoms occupying the apical positions and four sodium atoms defining the equatorial plane. The eight isopropoxide groups cap the triangular faces of the octahedron and are μ^3-bonded to one chromium and two sodium atoms [Cr–O10 = 1.989 (5) Å, Na1–O10 = 2.415 (5) Å, Na2–O10 = 2.436 (7) Å]. The Cr atoms are slightly outside the plane defined by the four closest oxygen atoms (distance from plane 0.21 Å), resulting in a distorted square-planar coordination geometry. The Na atoms are pentacoordinated, the fifth coordination site being occupied by one molecule of THF. Cr···Cr distance [3.739 (2) Å] is the longest yet found in this class of compounds and excludes the presence of a Cr–Cr bonding interaction.

Linear dependence of the magnetic susceptibility on $1/T$, in agreement with the Curie–Weiss law, has been found in the range 50–298 K. The value of the magnetic moment (μ_{eff} = 3.25 μ_B) of **1** is significantly lower than expected for a high-spin, d^4 electronic configuration (μ_{eff} = 4.90 μ_B calculated for spin only). Although the highly negative value of θ (θ = −85 K) might suggest the occurrence of a strong direct antiferromagnetic exchange between the two chromium atoms,[14] ligand-mediated superexchange is more likely responsible for the low magnetic moment observed in this class of compounds. In fact, within comparable Cr···Cr distances, the values of μ_{eff} seem to be strongly dependent on the nature of both the solvent coordinated to the alkali-metal cation and the nature of the alkoxide moiety (Table V). The direct influence of the nature of the alkoxide and of the coordination environment of the alkali metal in determining the magnetic properties of the complex indicates that the bridging interactions $Cr\text{–}OR\text{–}Na_2\text{–}OR\text{–}Cr$ are strong and able to provide electronic communication between the two transition metals. We tentatively suggest that a similar interaction may occur in the isomorphous and almost diamagnetic $Me_8Cr_2Li_4(THF)_4$,[44] where the presence of a supershort Cr–Cr quadrupule bond is believed to hold together the molecular frame, the role of the alkali-metal cation being regarded as purely electrostatic.

Table V. Magnetic Moments of $(RO)_8Cr_2Na_4(L)_4$

R	L	μ_{eff}, μ_B	Cr···Cr, Å	ref
Ph	pyridine	3.46	3.634	20
Ph	THF	2.84	3.622	19
β-$C_{10}H_7$	THF	2.83		20
i-Pr	THF	3.25	3.729	this work

Scheme II



The presence of the Na cation seems to be crucial for the stabilization of the anionic structure of **1a**, since the utilization of other alkali-metal cations (Li, K) afforded only the polymeric $[(i\text{-PrO})_2Cr]_n$. Incorporation of lithium in the molecular structure of anionic alkoxochromates was observed only in the case of the aromatic congeners, which showed remarkably different molecular structures (Scheme II).[30] In accordance with the fundamental role of the nature of the alkali-metal cation in determining the bonding and structure of these complexes, simple replacement of coordinated THF with TMEDA (TMEDA = N,N,N',N'-tetramethylethylenediamine) gave a major molecular rearrangement and cleavage of the $Cr_2(OR)_2$ unit (Scheme II).[30]

In an attempt to generalize the unprecedented possibility of affecting the overall molecular complexity of anionic alkoxochromates, by introducing a fairly strong Lewis base in the coordination sphere of the alkali-metal cation, we have carried out similar reactions on the sodium-containing dimers $(RO)_8Cr_2Na_4(THF)_4$. While the isopropyl derivative **1a** gave the polymeric $[(i\text{-PrO})_2Cr]_n$, the reaction of the phenyl derivative **1b** required several hours of reflux in TMEDA/toluene mixtures (2:1) to form a Cr(III) complex $(PhO)_{10}Cr_4(\mu_3\text{-O})_3Na_4(TMEDA)_4$ via a surprising oxidation reaction (Scheme III). The origin of the

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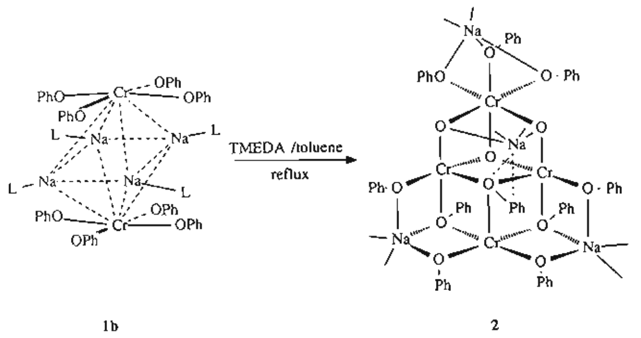
[44] (a) Krausse, J.; Mark, G.; Schodl, G. *J. Organomet. Chem.* **1970**, *21*, 159. (b) Krausse, J.; Schodl, G. *J. Organomet. Chem.* **1971**, *27*, 59.

Scheme III



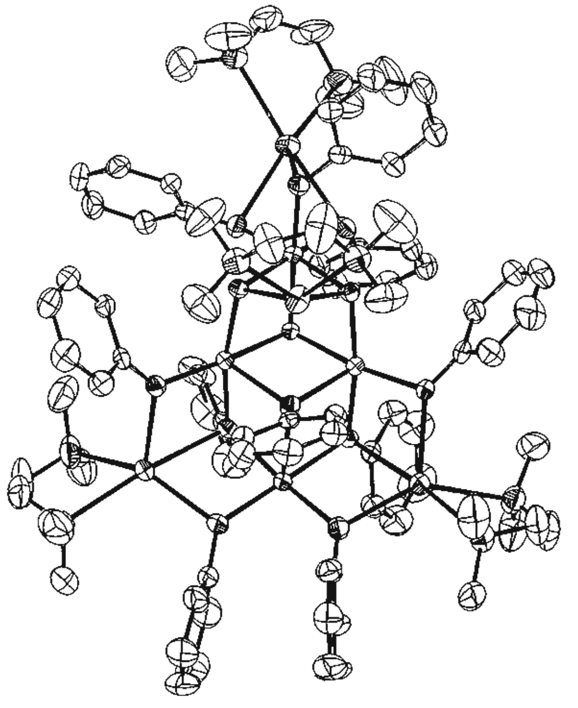


Figure 2. Thermal motion ellipsoid plot of 2 drawn at the 30% probability level.

three M_3-O groups is unclear. The IR spectrum of 2 did not show any resonance which could eventually identify the three bridging gorups as μ_3-OH. On the basis of the extreme air sensitivity of all the Cr(II) alkoxides, the reproducibility of the reaction yield, and the anhydrous reaction conditions employed, we tentatively suggest that the oxo groups are introduced in the complex via a deoxygenation reaction of either NaOPh or THF. Furthermore, similar incorporation of oxo groups has been observed in the chemistry of the extremely moisture-sensitive yttrium[31,45] and zirconium alkoxides,[46] where the enormous Lewis acidity of the transition metal is probably responsible for the deoxygenation reaction. While a very large excess of TMEDA is necessary for a complete reaction, deliberate addition of stoichiometric amounts of H_2O to either the reaction mixture or toluene solutions containing smaller amounts of TMEDA (5 equiv) led to a completely different result and formation of brown intractable material. It is quite remarkable that, under similar treatment, dimeric lithium phenoxochromates formed exclusively monomeric Cr(II) species (Scheme II).[30]

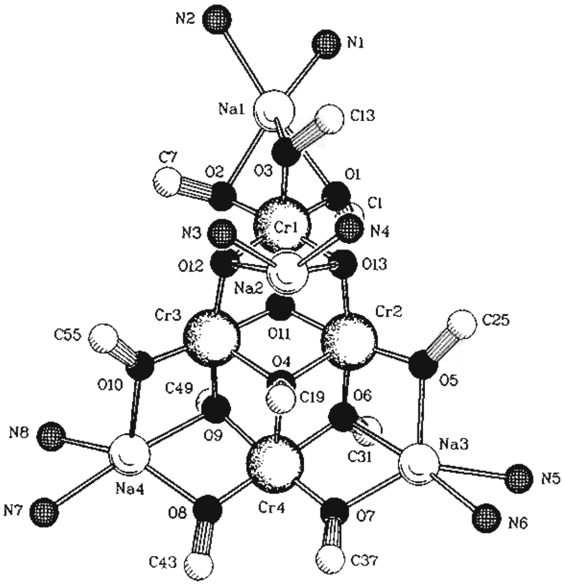


Figure 3. Plot of the core of 2 with adopted numbering scheme; aromatic and carbon atoms of the TMEDA molecule have been left out.

The structure of 2 has been demonstrated by X-ray analysis, the overall geometry being reported in Figures 2 and 3. The tetrameric unit can be regarded as constituted by three different fragments linked together by bridging alkoxides and μ_3-O oxo groups. The geometry of the monomeric $(PhO)_4CrNa_2(TMEDA)_2$ unit at the bottom of the molecule is planar and closely resembles the previously reported $(2,6\text{-}Me_2C_6H_3O)_4CrNa_2(TMEDA)$.[20] A second planar and dimer fragment is parallel to the first, while the last monomeric group lies on top of the coordination polyhedron. One of the μ_3-OPh groups, which links the three chromium atoms of the first two fragments, occupies the vertices of the three square pyramids based on the three chromium atoms (average deviation of Cr from the plane 0.05 Å) and reaches considerably longer Cr–O distances (average Cr–O = 2.336 Å). The Cr atom of the last monomeric fragment displays a regular octahedral coordination geometry with comparable values of the Cr–O bond distance (average Cr–O = 1.993 Å). The Cr···Cr nonbonding distances of the $(PhO)_3Cr_3(\mu_3\text{-}O)_3$ core are quite comparable (average Cr···Cr = 3.313 Å) and exclude the presence of Cr–Cr bonds. Finally, three of the four Na atoms display a normal pentacoordination, while the sodium atom bonded to two μ_3-O groups is tetracoordinated distored square planar. The C–O bond of a μ_3-OPh group is placed on the formal fifth coordination site of the ideal square pyramid centered on Na, reaching a fairly short nonbonding distance [O4···Na2 = 3.046 (4) Å; C19···Na2 = 2.963 (6) Å]. A combination of steric factors and Lewis acidity of the sodium atom is probably responsible for this unusual coordination geometry of sodium, since the coordination geometry of O4 is only slightly distorted tetrahedral and the C–O distance is quite normal [O4–C19 = 1.328 (7) Å].

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Supplementary Material Available: For 1 and 2, tables of bond distances, bond angles, thermal parameters, hydrogen atom positional parameters, and crystal data and a table of torsion angles and a labeled structure of 2 (23 pages); lists of structure factors for 1 and 2 (98 pages). Ordering information is given on any current masthead page.

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(45) (a) Evans, W. J.; Sollberger, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 6095. (b) Poncelet, O.; Sartain, W. J.; Hubert-Pfalzgraf, H. L.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 263.

(46) Caulton, K. G. Personal communication.