Chromium(II) Alkoxides: Synthesis and Crystal Structure of the Monomeric [(RO)₄Cr][Na(TMEDA)]₂ (R = 2,6-Dimethylphenyl) and Dimeric [(RO)₈Cr₂][NaL]₄ (R = Phenyl; L = THF, Pyridine) without a Cr–Cr Bond. An Insight into the Question of Cr–Cr Quadruple Bond Formation

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Received August 10, 1988

Abstract: Chromium(II) alkoxides have been synthesized by reaction of CrCl₂THF₂ with RONa [R = Ph (a), 2,6-dimethylphenyl (b), β-C₁₀H₇ (c), *i*-Pr (d)]. The reaction products are highly insoluble, pyrophoric, and probably polymeric [(RO)₂Cr]ₙ (1). In the case of the sterically demanding alkoxide R = 2,6-(*t*-Bu)₂-4-MePh, the highly soluble and monomeric (RO)₂Cr(THF)₂ has been obtained in crystalline form. Less bulky ligands allow a fast reaction with an excess of RONa leading to the formation of the purple [(RO)₄Cr][Na(THF)₂]₂ (2). In the case of R = 2,6-dimethylphenyl, a stable crystalline compound has been isolated upon treatment with *N,N,N′,N′*-tetramethylethylenediamine (TMEDA). The crystal data of [(2,6-Me₂C₆H₃O)₄Cr][Na(TMEDA)]₂ (2b) [Mo Kα (λ = 0.710 73 Å)] at 130 K are as follows: *a* = 13.882 (4), *b* = 14.189 (3), *c* = 15.700 (7) Å; α = 66.47 (3), β = 67.99 (2), γ = 87.33 (2)°; *Z* = 2; triclinic space group *P*1̄. Solvent removal in vacuo allows the dimerization of 2 [R = Ph (a), β-C₁₀H₇ (c), *i*-Pr (d)] with formation of the green [(RO)₈Cr₂][Na(L)]₄ (L = THF, py) (3). The structure of the phenyl derivative has been demonstrated by X-ray analysis. Crystal data for [(PhO)₈Cr₂]-[Na(py)]₄·C₆H₅CH₃ (3a″) [Mo Kα (λ = 0.710 73 Å)] are as follows: *a* = 13.672 (1), *b* = 22.561 (1), *c* = 23.013 (1) Å; *Z* = 4; orthorhombic space group *Pccn*. The long Cr···Cr distance in the complex 3a″ (3.634 (1) Å) rules out the presence of a Cr–Cr bond. Na abstraction from 2 and 3 by reaction with 18-crown-6 leads to the formation of polymeric 1.

Amongst the metal atoms known to form compounds with multiple M–M bonds, those of the group VI elements (Cr, Mo, and W) are most common.[1] In the coordination chemistry of di- and trivalent tungsten and molybdenum, these bonds are especially robust and favor the formation of polynuclear compounds even in the absence of bridging ligands.[2–4] In the chemistry of chromium, the formation of metal–metal bonds seems more restricted to oxidation state II (no triply bonded Cr₂X₆-type molecule has yet been identified) where the d⁴ electronic configuration allows the formation of an unusually short Cr–Cr quadruple bond, the so-called "supershort".[5]

Interesting questions arise about the degree of stability introduced in the molecule by the Cr–Cr multiple bond, the identification of the factors that promote or inhibit its formation, and the possible implications for the chemical reactivity. In a series of reports, Cotton has clarified the relationship between the occurrence of this abnormally short Cr–Cr distance and the presence of ligands alongside the intermetallic axis.[1b,5b] There are several arguments against the idea that the particular geometry of the ligands employed in these systems constrains the metal atoms to such a short distance.[6] However, the experimental results show that the occurrence of a Cr–Cr supershort bond is strictly limited (as a rule with only two exceptions[7–9]) to the special geometry of the bridging three-atom chelating ligands, which form five-membered rings with the two chromium atoms. The nature of the donor atom (oxygen, carbon, nitrogen) seems to have no influence in this respect.[1b,10]
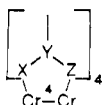
In contrast to the experimental evidence, theoretical calculations carried out on Cr₂(O₂CR)₄ and on [X₈Cr₂]⁴⁻ surprisingly predicted that a Cr–Cr quadruple bond will have a little contribution to the ground state,[11–13] if any at all.[14,15] In accordance with the the-

oretical prediction that the Cr–Cr supershort bond is relatively weak, its cleavage is easy. Simple coordination with ligands such

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as ammonia,[16] α,α'-bipyridine,[17] or phosphine[18] is sufficient to elongate the intermetallic distance up to 2.5 Å[19] or to break the multiple bond, forming monomeric and paramagnetic complexes. Finally, any attempt to modify the geometry of the three-center chelating ligands invariably leads to mononuclear paramagnetic species (either low-spin or high-spin), probably with square-planar coordination geometry of the metal center.[18] On the other hand, due to the extreme paucity of Cr(II) chemistry (except for the Cotton systems and the cyclopentadienyl derivatives), any attempt to generalize the behavior of chromium in this respect is quite unrealistic. A literature search yielded only one bulky monomeric Cr(II) amide,[20] two bulky alkoxides (both monomeric and dimeric),[21] one monomeric tetradentate Schiff base complex,[22] the monomeric $(CH_3)_2Cr(dmpe)_2$,[23a] and $Cr[H_2B(pz)_2]_2$.[23b]

For these reasons, following our interest in the chemistry of low-valent early-transition-metal alkoxides,[24] we have focused our attention on the synthesis of chromium(II) alkoxides. This report deals with the synthesis, structural characterization, and reactivity of new Cr(II) compounds and includes results with respect to the occurrence of the metal–metal bond.

Experimental Part

All the operations were performed under dry nitrogen with use of standard Schlenk techniques or in a nitrogen-filled drybox (Braun MB-200). $CrCl_2THF_2$[25] and $Mes_2Cr(THF)_3$[26] have been prepared according to published methods. Solvents were dried and distilled according to standard procedures. Infrared spectra were recorded on a Unicam SP3-300 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 determined on an MB 4 Oxford Gouy balance interfaced with an Apple II computer. Calculations of the μ_{eff} value were carried out by standard methods.

$[(PhO)_2Cr(THF)]_n$ (1a). Method a. $Mes_2Cr(THF)_3$ (1.24 g, 2.44 mmol) was dissolved in 20 mL of THF. The resulting purple solution was treated with 0.47 g of phenol (5.00 mmol). The color immediately turned blue, and a blue amorphous solid precipitated (0.41 g, 1.3 mmol, 54% yield). Anal. Calcd for $C_{16}H_{18}O_3Cr$ (found): C, 61.98 (61.60); H, 5.80 (5.70); Cr, 16.77 (16.60). IR (Nujol mull, KBr, cm^{-1}): 1590 (s), 1490 (s), 1290 (w), 1275 (w), 1250 (s), 1170 (w), 1080 (w), 1035 (w), 1005 (w), 885 (w), 850 (s), 830 (w), 775 (w), 760 (w), 700 (s), 600 (w).

Method b. A suspension of NaOPh was obtained by reacting NaH (0.17 g, 6.96 mmol) with phenol (0.65 g, 7.0 mmol) in 30 mL of THF. Further reaction with $CrCl_2THF_2$ (0.92 g, 3.45 mmol) led to the rapid formation of deep blue amorphous solid within a few minutes (0.58 g, 1.9 mmol, 54% yield). The product has been identified by IR spectroscopy and elemental analysis.

$[(2,6\text{-}Me_2C_6H_3O)_2Cr]_n$ (1b). Amounts and procedures were as above, yielding 57% of a red-purple solid. Anal. Calcd for $C_{16}H_{18}O_2Cr$ (found): C, 64.27 (64.31); H, 6.32 (6.12); Cr, 17.14 (17.69). IR (Nujol mull, KBr, cm^{-1}): 1580 (w), 1420 (m), 1250 (s), 1195 (s), 1090 (m), 830 (s), 775 (w), 750 (s), 745 (w), 690 (m), 586 (m).

$[(\beta\text{-}C_{10}H_7O)_2Cr]_n$ (1c). Amounts and procedures were as above, yielding 72% of a brown-green solid. Anal. Calcd for $C_{20}H_{14}O_2Cr$

(found): C, 71.01 (71.07); H, 4.14 (4.26); Cr, 15.08 (14.97). IR (Nujol mull, KBr, cm^{-1}): 1610 (s), 1580 (s), 1490 (m), 1350 (m), 1230 (s), 1205 (s), 1165 (s), 1105 (m), 1110 (w), 950 (m), 900 (m), 830 (m), 730 (s), 620 (w), 550 (m), 500 (w), 460 (m).

$[(i\text{-}PrO)_2Cr]_n$ (1d). Amounts and procedures were as above, yielding 72% of a purple-red solid. Anal. Calcd for $C_6H_{14}O_2Cr$ (found): C, 41.93 (42.05); H, 8.15 (8.24); Cr, 28.82 (28.89). IR (Nujol mull, KBr, cm^{-1}): 1335 (m), 1150 (m), 1120 (s), 950 (s), 815 (m), 580 (s).

$[(2,6\text{-}(t\text{-}Bu)_2\text{-}4\text{-}MeC_6H_2O)_2Cr(THF)_2]$ (1e). Method a. Neat 2,6-$(t\text{-}Bu)_2$-4-MeC_6H_2OH (0.66 g, 3.01 mmol) was added to a solution of 0.77 g of Mes_2CrTHF_3 (1.51 mmol) in 20 mL of THF. The resulting solution was gently heated until the color changed to blue. After 12 h of stirring, the mixture was evaporated to dryness and the residual blue solid recrystallized from heptane, yielding 0.92 g of blue crystalline solid (1.4 mmol, 91% yield). Anal. Calcd for $C_{38}H_{62}O_4Cr$ (found): C, 71.90 (71.95); H, 9.80 (10.00); Cr, 8.20 (7.98). IR (Nujol mull, KBr, cm^{-1}): 1405 (s), 1350 (w), 1260 (s), 1250 (m), 1225 (w), 1210 (w), 1190 (w), 1150 (w), 1105 (w), 1005 (s), 905 (w), 870 (w), 855 (m), 825 (m), 800 (w), 585 (w), 710 (w), 535 (s). ($\mu_{eff} = 4.68$ μ_B.)

Method b. The suspension obtained by reaction of 2,6-$(t\text{-}Bu)_2$-4-MeC_6H_2OH (3.89 g, 17.7 mmol) with NaH (0.42 g, 17.6 mmol) in THF (30 mL) was allowed to react with 2.30 g of $CrCl_2THF_2$ (8.6 mmol). The resulting blue mixture was stirred over 20 h, filtered, and evaporated to dryness, and the residual blue solid was recrystallized from toluene. Blue crystals of 1e were obtained on cooling at -20 °C (3.47 g, 5.2 mmol, 60% yield). The product has been identified by IR spectroscopy and elemental analysis.

$[(2,6\text{-}Me_2C_6H_3O)_4Cr][Na(TMEDA)]_2\cdot C_6H_5CH_3$ (2b). Method a. The suspension prepared by reaction of NaH (0.23 g, 9.60 mmol) with 2,6-$Me_2C_6H_3OH$ (1.19 g, 9.76 mmol) in 20 mL of THF was allowed to react with $CrCl_2THF_2$ (1.30 g, 4.87 mmol). After 20 min of stirring, the resulting purple mixture was evaporated to dryness. The residual purple solid, which does not change color in vacuo, was recrystallized from 10 mL of toluene containing 4 mL of TMEDA. Purple crystals separated (1.97 g, 2.2 mmol, 45% yield) on standing for 2 days at room temperature. Anal. Calcd for $C_{51}H_{76}O_4N_4Na_2Cr$ (found): C, 67.55 (67.41); H, 8.39 (8.41); Cr, 5.71 (5.74); N, 6.18 (6.11); Na, 5.08 (5.19). IR (Nujol mull, KBr, cm^{-1}): 1585 (s), 1405 (s), 1260 (m), 1250 (m), 1210 (m), 1185 (m), 1160 (w), 1150 (w), 1110 (w), 1070 (s), 1020 (w), 1005 (s), 925 (m), 825 (s), 725 (s), 670 (s), 585 (m), 510 (s), 450 (m). ($\mu_{eff} = 3.45$ μ_B.)

Method b. The suspension obtained by reaction of 2,6-$Me_2C_6H_3OH$ (0.25 g, 2.1 mmol) with NaH (0.053 g, 2.2 mmol) in THF (10 mL) was allowed to react with 1b (0.3 g, 1.0 mmol). The solid dissolved, yielding a purple solution. After evaporation to dryness, the resulting purple solid was recrystallized from toluene containing 1 ml of TMEDA. Purple crystals of 2b separated on cooling (0.42 g, 0.46 mmol, 46% yield). The product has been identified by IR spectroscopy and elemental analysis.

$[(PhO)_8Cr_2][Na(THF)]_4$ (3a'). Method a. $CrCl_2THF_2$ (2.20 g, 8.24 mmol) was added to a suspension of PhONa in THF (15 mL), obtained by reaction of 0.80 g of NaH (33.3 mmol) with 3.14 g of phenol (33.4 mmol). The resulting purple mixture was stirred for 1.5 h, filtered, and cooled at -30 °C. The well-formed purple crystals were pumped in vacuo, yielding a green pyrophoric solid. Recrystallization from 20 mL of toluene containing 5 mL of THF yielded green crystals upon cooling at -20 °C (3.74 g, 3.0 mmol, 74% yield). Anal. Calcd for $C_{64}H_{72}O_{12}Cr_2Na_4$ (found): C, 61.99 (62.02); H, 6.45 (6.39); Cr, 8.38 (8.24); Na, 7.42 (7.40). IR (Nujol mull, KBr, cm^{-1}): 1590 (s), 1485 (s), 1270 (s), 1160 (m), 1050 (m), 990 (w), 840 (m), 835 (w), 760 (s), 695 (s), 885 (s). ($\mu_{eff} = 2.84$ μ_B.)

Method b. A suspension of 1a (0.51 g, 1.65 mmol) in THF (10 mL) was treated with NaOPh (0.39 g, 3.36 mmol). The resulting purple mixture was stirred for 1 h. After solvent evaporation and recrystallization from toluene (10 mL) containing 3 mL of THF, green crystals were obtained (0.78 g, 0.63 mmol, 76% yield). The complex has been identified by IR spectroscopy and elemental analysis.

$[(PhO)_8Cr_2][Na(py)]_4\cdot C_6H_5CH_3$ (3a''). Dry pyridine (5 mL) was added to a solution of 3a' (2.50 g, 2.0 mmol) in 15 mL of toluene. After cooling the resulting solution at -10 °C, green crystals separated (2.22 g, 1.6 mmol, yield 82%). Anal. Calcd for $C_{75}H_{68}O_8N_4Cr_2Na_4$ (found): C, 66.72 (66.65); H, 5.04 (5.15); N, 4.15 (4.21); Cr, 7.70 (7.36); Na, 6.81 (6.58). IR (Nujol mull, KBr, cm^{-1}): 1585 (s), 1475 (s), 1435 (w), 1275 (s), 1160 (m), 1140 (w), 1080 (w), 1030 (w), 1010 (w), 990 (m), 875 (w), 865 (m), 825 (w), 750 (s), 740 (m), 725 (w), 695 (m), 685 (s), 590 (s). ($\mu_{eff} = 3.46$ μ_B.)

$[(\beta\text{-}C_{10}H_7O)_8Cr_2][Na(THF)]_4\cdot C_6H_5CH_3$ (3c). Method a. A THF suspension (15 mL), obtained upon reaction of β-$C_{10}H_7OH$ (2.40 g, 16.7 mmol) with NaH (0.4 g, 16.6 mmol), was allowed to react with $CrCl_2$-THF_2 (1.11 g, 4.1 mmol). The resulting mixture was stirred overnight. After evaporation to dryness, the resulting green solid was recrystallized from toluene (2.75 g, 1.6 mmol, 78% yield). Anal. Calcd for $C_{103}H_{91}$-

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Table I

	Crystal Data	
	2b	**3a″**
formula	$C_{51}H_{76}O_4N_4CrNa_2$	$C_{75}H_{68}O_8N_4CrNa_4$
cryst syst	triclinic	orthorhombic
space gp	$P\bar{1}$	$Pccn$
Z	2	4
F(000)	976	2808
a, Å	13.882 (4)	13.672 (1)
b, Å	14.189 (3)	22.561 (1)
c, Å	15.700 (7)	23.013 (1)
α, deg	66.47 (3)	
β, deg	67.99 (2)	
γ, deg	87.33 (2)	
V, Å³	2609.3 (8)	7098.5 (7)
$\mu_{Mo K\alpha}$, cm⁻¹	2.71	3.8
D_{calc}, g·cm⁻³	1.155	1.263
cryst size, mm	0.75 × 0.40 × 0.25	0.5 × 0.5 × 0.5
	Data Collection	
temp, K	130	298
radiatn (λ = 0.710 73 Å)	Mo Kα (graphite-monochromatized)	Mo Kα (Zr-filtered)
θ, (min–max), deg	1.0, 24	0.9 22.0
ω/2θ scan, deg	0.95 + 0.35 tan θ	0.60 + 0.35 tan θ
data set (h,k,l)	0:-15, -16:+16, -17:-17	0:14, 0:23, -24:24
total data, unique data	8130, 8130	9492, 4346
obs data [I > 2.5σ(I)]	6659	2268
	Refinement	
R, R_w, S	0.059, 0.071, 1.65	0.055, 0.021, 1.84
N_{par}	696	425
max shift/error	0.55	0.50
max residual density, e·Å⁻³	0.42	-0.40, 0.66
weighting scheme	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$

$Cr_2O_{12}Na_4$ (found): C, 71.85 (71.83); H, 5.69 (5.70); Cr, 5.30 (5.38); Na, 5.34 (5.38). IR (Nujol mull, KBr, cm⁻¹): 1620 (s), 1590 (s), 1570 (w), 1490 (s), 1330 (s), 1270 (s), 1255 (m), 1215 (s), 1170 (s), 1110 (m), 1030 (m), 950 (m), 910 (m), 840 (m), 800 (m), 750 (s). (μ_{eff} = 2.83 μ_B.)

Method b. Quantities and procedure as for **3a′**, yield 47%.

[(i-PrO)₈Cr₂][Na(THF)]₄ (3d). Method a. NaH (0.88 g, 36.7 mmol) in 25 mL of THF was reacted with i-PrOH (2.80 mL, 37 mmol). The green slurry formed after treatment with 1.93 g of CrCl₂THF₂ (7.2 mmol) was stirred for 3 h. The mixture was evaporated to dryness and the residual solid recrystallized from a small volume of toluene (15 mL). Light yellow crystals were obtained on cooling the resulting solution at -30 °C (2.72 g, 2.8 mmol, 79% yield). Anal. Calcd for $C_{40}H_{88}O_{12}$-Cr₂Na₄ (found): C, 50.21 (50.17); H, 9.20 (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. Procedure and quantities as for **3a′**, yield 27%.

Reaction of [(PhO)₈Cr₂][Na(THF)]₄ with 18-Crown-6. In a standard experiment, a THF solution (15 mL) of **3a′** (0.83 g, 0.67 mmol) was reacted with 0.78 g of dried 18-crown-6 (3 mmol). The blue **1a**, immediately separated, was collected and identified by IR spectroscopy and elemental analysis.

X-ray Crystallographic Studies. All X-ray data were collected on an Enraf-Nonius CAD-4F fully automatic diffractometer equipped with a locally modified low-temperature device. Further details on crystal data and refinement are reported in Table I.

Structure Solution and Refinement (2b). All the calculations were carried out using the SDP/PDP (Enraf-Nonius) program system. The atomic form factors, including anomalous scattering, were from *International Tables of Crystallography*.[27] A purple, single crystal of **2b** was attached to a glass fiber inside a drybox and immediately placed in the low-temperature nitrogen stream (130 K). Final lattice parameters were determined by a least-squares treatment using the setting angles of 25 reflections in the range 7.9° ≤ θ ≤ 15.2°. The intensities of 3 standard reflections, measured every 3 h, were used to monitor the drift in the primary beam, in the counting system, and also an eventual decrease of the crystal quality. From a total of 8130 reflections in the range 1° ≤ θ ≤ 24°, 6659 reflections were used in the refinement. Scaling factors, Lorentz and polarization corrections, were applied to the data. The linear

absorption coefficient was 2.71 cm⁻¹ with no absorption corrections applied. The structure was partly solved by direct methods. The positions of the remaining atoms could be revealed from successive Fourier difference maps. Block-diagonal least-squares of *F* with unit weights, converged to a final value of R = 0.059 and R_w = 0.071, using anisotropic temperature factors for the non-hydrogen atoms and fixed isotropic temperature factors for the hydrogen atoms. The hydrogen atoms were included in the refinement with a C–H distance of 0.96 Å. In spite of the disorder observed in the ring (C17–C22), the atoms involved were refined with an occupancy of 1. Table II contains the final atomic coordinates of **2b**.

Structure Solution and Refinement (3a″). An emerald-green crystal of **3a″** was sealed in a Lindemann capillary. Unit cell parameters were derived from the SET4 setting angles for 25 reflections in the range 9–13°. The space group was derived from the observed systematic absences. Two reference reflections showed a small decay of 1.5% during data collection. The data were corrected for Lorentz–Polarization and for the small decay but not for absorption (in the view of a variation less than 3% in the intensity of a 360° ψ scan) and averaged in a unique set of reflections (R_{av} = 4.5%). The resolution of the data set was poor, reflecting the disorder of the solvent molecule. The structure was solved with Patterson and Fourier techniques (SHELXS-86)[28] and refined on *F* by full-matrix least-squares methods on a microVax-II with SHELX-76.[29] Hydrogen atoms were introduced at calculated positions (C–H = 0.98 Å) and refined with fixed geometry. The atoms of the solvent molecule (toluene) are located on a 2-fold crystallographic axis and exhibit large anisotropic thermal motions. Refinement was carried out with slack constraints, in order to avoid unsatisfactory toluene ring geometry. The refined parameter set included a scale factor, the coordinates of the non-hydrogen atoms, anisotropic thermal parameters, and two separate isotropic thermal motion parameters for the H atoms. Final positional parameters for the non-hydrogen atoms are listed in Table III. Scattering factors were taken from ref 30 and corrected for anomalous dispersion.[31] The calculation of geometrical data and the preparation of the thermal motion ellipsoids plot were carried out with the program PLATON of the EUCLID package.[32]
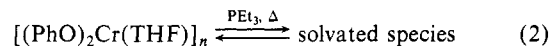
Discussion and Results

According to eq 1, Mes₂Cr(THF)₃ (Mes = 2,4,6-mesityl) reacts with 2 equiv of several aromatic and aliphatic alcohols in THF to form the homoleptic [(OR)₂Cr]ₙ (1) [R = Ph (a), 2,6-dimethylphenyl (b), β-C₁₀H₇ (c), i-Pr (d)]. The color of these

$$Mes_2Cr(THF)_3 + 2ROH \rightarrow [(RO)_2Cr]_n \quad (1)$$
$$\mathbf{1}$$
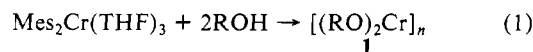
R = Ph (a), 2,6-dimethylphenyl (b), β-C₁₀H₇ (c), i-Pr (d)

pyrophoric, insoluble, and probably polymeric species[33] is remarkably affected by the nature of the alkoxo ligand. An anomalous behavior has been observed in the case of the very bulky substituent R = 2,6-(t-Bu)₂-4-MePh, which allows the isolation of the highly soluble (OR)₂Cr(THF)₂ in crystalline form. The monomeric structure in this case has been demonstrated by an X-ray diffraction analysis.[34b] The magnetic moment (μ_{eff} = 4.68 μ_B) is consistent with a high-spin d⁴ electronic configuration of chromium. Compounds **1**, containing variable amounts of NaCl, have also been obtained by reacting CrCl₂(THF)₂ with 2 equiv of the corresponding NaOR. Any attempt to break the polymeric structure failed. Only in the case of [(PhO)₂Cr(THF)]ₙ (**1a**), can the blue solid be solubilized in boiling toluene, upon addition of an excess of Et₃P. However, on standing at room temperature, phosphine-free amorphous **1** separates, suggesting the presence of dissociation/association equilibria in solution (eq 2). Polymeric

$$[(PhO)_2Cr(THF)]_n \underset{}{\overset{PEt_3, \Delta}{\rightleftharpoons}} \text{solvated species} \quad (2)$$

chromium alkoxides and phenoxides react with an excess of the

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Chromium(II) Alkoxides

J. Am. Chem. Soc., Vol. 111, No. 6, 1989 2145

Table II. Positional Parameters and Their Estimated Standard Deviations (**2b**)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Cr	0.35051 (6)	0.12780 (6)	0.24629 (6)	0.81 (2)	C21	0.4244 (6)	−0.2708 (7)	0.3259 (9)	5.8 (4)
Na1	0.1669 (2)	−0.0190 (2)	0.2564 (2)	2.04 (8)	C22	0.4105 (5)	−0.1658 (6)	0.2612 (7)	3.3 (3)
Na2	0.5376 (2)	0.2816 (2)	0.2195 (2)	1.82 (7)	C23	0.4554 (6)	−0.1196 (8)	0.1495 (8)	5.8 (4)
O1	0.3723 (3)	0.2737 (3)	0.2286 (3)	1.3 (1)	C24	0.2404 (6)	−0.0883 (7)	0.4724 (6)	4.3 (3)
O2	0.4937 (3)	0.1179 (3)	0.2487 (3)	1.4 (1)	C25	0.1708 (4)	0.2173 (4)	0.1855 (4)	1.1 (2)
O3	0.3276 (3)	−0.0156 (3)	0.2598 (3)	1.4 (1)	C26	0.2110 (4)	0.2503 (4)	0.0800 (4)	1.5 (2)
O4	0.2080 (3)	0.1403 (3)	0.2428 (3)	1.5 (1)	C27	0.1671 (5)	0.3270 (5)	0.0227 (5)	1.9 (2)
N1	0.0135 (4)	−0.0080 (4)	0.2078 (4)	2.5 (2)	C28	0.0841 (5)	0.3723 (5)	0.0681 (5)	2.3 (2)
N2	0.0927 (4)	−0.2010 (4)	0.3173 (4)	1.5 (1)	C29	0.0447 (4)	0.3407 (5)	0.1708 (5)	2.0 (2)
N3	0.7305 (4)	0.3045 (4)	0.1653 (4)	2.1 (2)	C30	0.0864 (4)	0.2634 (4)	0.2311 (4)	1.4 (2)
N4	0.5714 (4)	0.4259 (4)	0.2584 (4)	2.0 (2)	C31	0.0426 (5)	0.2285 (5)	0.3436 (5)	2.3 (2)
C1	0.3123 (4)	0.3335 (4)	0.2689 (4)	1.2 (2)	C32	0.3014 (5)	0.2024 (5)	0.0292 (5)	2.6 (2)
C2	0.2682 (4)	0.3047 (4)	0.3735 (4)	1.5 (2)	C33	0.0851 (6)	−0.2780 (5)	0.4174 (5)	2.7 (2)
C3	0.2127 (5)	0.3724 (5)	0.4120 (5)	2.1 (2)	C34	0.1671 (5)	−0.2325 (5)	0.2391 (5)	2.5 (2)
C4	0.1994 (5)	0.4697 (5)	0.3484 (5)	2.5 (2)	C35	−0.0118 (5)	−0.2001 (5)	0.3146 (5)	1.9 (2)
C5	0.2424 (5)	0.4978 (5)	0.2456 (5)	2.2 (2)	C36	−0.0171 (5)	−0.1123 (5)	0.2186 (5)	2.3 (2)
C6	0.2980 (4)	0.4320 (4)	0.2043 (5)	1.6 (2)	C37	−0.0639 (6)	0.0177 (6)	0.2896 (7)	3.6 (3)
C7	0.3433 (5)	0.4627 (5)	0.0924 (5)	2.2 (2)	C38	0.0186 (6)	0.0683 (6)	0.1087 (7)	4.2 (3)
C8	0.2819 (5)	0.2000 (5)	0.4431 (5)	2.4 (2)	C39	0.8028 (5)	0.3003 (6)	0.0705 (6)	3.5 (3)
C9	0.5704 (4)	0.0647 (4)	0.2137 (4)	1.3 (2)	C40	0.7416 (6)	0.2167 (5)	0.2529 (6)	3.6 (3)
C10	0.6010 (4)	−0.0178 (4)	0.2818 (5)	1.6 (2)	C41	0.7563 (5)	0.4053 (5)	0.1635 (5)	2.2 (2)
C11	0.6817 (5)	−0.0702 (5)	0.2435 (5)	2.3 (2)	C42	0.6803 (5)	0.4251 (5)	0.2528 (5)	2.5 (2)
C12	0.7328 (5)	−0.0431 (5)	0.1422 (5)	2.4 (2)	C43	0.5602 (5)	0.5218 (5)	0.1792 (6)	2.9 (2)
C13	0.7047 (5)	0.0400 (5)	0.0750 (5)	2.3 (2)	C44	0.5010 (6)	0.4206 (7)	0.3585 (6)	3.7 (3)
C14	0.6245 (4)	0.0945 (5)	0.1091 (5)	1.7 (2)	C45	0.6761 (6)	0.6276 (6)	0.3949 (6)	3.5 (3)
C15	0.5944 (5)	0.1855 (6)	0.0365 (5)	2.8 (2)	C46	0.7828 (5)	0.6101 (5)	0.3326 (5)	2.5 (2)
C16	0.5475 (5)	−0.0463 (5)	0.3929 (5)	2.6 (2)	C47	0.8364 (5)	0.5318 (5)	0.3772 (5)	2.5 (2)
C17	0.3496 (5)	−0.1085 (4)	0.3123 (5)	1.7 (2)	C48	0.9347 (6)	0.5169 (5)	0.3186 (6)	3.3 (3)
C18	0.3050 (6)	−0.1510 (6)	0.4191 (6)	3.2 (2)	C49	0.9819 (6)	0.5788 (6)	0.2141 (6)	3.4 (3)
C19	0.3196 (8)	−0.2488 (6)	0.4747 (7)	5.3 (3)	C50	0.9283 (6)	0.6562 (6)	0.1704 (6)	3.2 (2)
C20	0.3755 (8)	−0.3046 (6)	0.4305 (8)	6.1 (4)	C51	0.8300 (5)	0.6728 (5)	0.2272 (5)	2.3 (2)

Table III. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for **3a″**

atom	x	y	z	U_{eq},^{a} Å^2	atom	x	y	z	U_{eq},^{a} Å^2
Cr1	−0.07077 (6)	−0.06619 (4)	−0.01597 (4)	0.0585 (3)	C34	−0.3692 (5)	−0.0962 (3)	0.1503 (3)	0.091 (4)
Na1	−0.1611 (1)	0.05593 (9)	0.03329 (8)	0.0660 (9)	C35	−0.3618 (5)	−0.1039 (3)	0.0915 (3)	0.084 (3)
Na2	0.0335 (1)	−0.03636 (8)	0.10681 (8)	0.0632 (9)	C36	−0.2802 (5)	−0.0868 (3)	0.0619 (2)	0.065 (3)
O10	−0.0030 (2)	−0.0654 (2)	−0.0917 (1)	0.062 (2)	C41	0.0334 (6)	−0.1578 (3)	0.0528 (2)	0.052 (3)
O20	−0.1649 (3)	−0.0077 (1)	−0.0474 (1)	0.059 (2)	C42	0.1148 (5)	−0.1795 (3)	0.0807 (3)	0.074 (3)
O30	−0.1195 (3)	−0.0464 (2)	0.0627 (1)	0.062 (2)	C43	0.1083 (6)	−0.2297 (4)	0.1150 (3)	0.108 (4)
O40	0.0403 (2)	−0.1086 (1)	0.0210 (1)	0.060 (1)	C44	0.0216 (7)	−0.2588 (3)	0.1214 (3)	0.102 (4)
N51	0.0597 (5)	−0.0787 (3)	0.1996 (2)	0.071 (3)	C45	−0.0593 (6)	−0.2385 (3)	0.0937 (3)	0.091 (4)
N61	−0.3194 (4)	0.1007 (3)	0.0439 (2)	0.073 (3)	C46	−0.0534 (5)	−0.1883 (3)	0.0598 (3)	0.071 (3)
C11	0.0356 (4)	−0.1056 (3)	−0.1274 (3)	0.049 (3)	C52	0.1336 (5)	−0.0616 (3)	0.2322 (3)	0.085 (3)
C12	0.0412 (4)	−0.0943 (3)	−0.1864 (3)	0.075 (3)	C53	0.1594 (5)	−0.0888 (4)	0.2828 (3)	0.106 (4)
C13	0.0834 (5)	−0.1340 (3)	−0.2237 (3)	0.092 (3)	C54	0.1080 (7)	−0.1368 (4)	0.3003 (3)	0.107 (5)
C14	0.1195 (5)	−0.1869 (3)	−0.2049 (3)	0.090 (4)	C55	0.0322 (6)	−0.1554 (3)	0.2674 (4)	0.095 (4)
C15	0.1154 (5)	−0.1991 (3)	−0.1470 (3)	0.086 (3)	C56	0.0100 (5)	−0.1255 (3)	0.2175 (3)	0.082 (3)
C16	0.0729 (4)	−0.1597 (3)	−0.1085 (3)	0.068 (3)	C62	−0.3371 (6)	0.1567 (4)	0.0317 (3)	0.082 (4)
C21	−0.2330 (4)	−0.0140 (3)	−0.0887 (2)	0.050 (3)	C63	−0.4281 (9)	0.1811 (3)	0.0308 (3)	0.100 (4)
C22	−0.2983 (5)	0.0317 (3)	−0.0997 (3)	0.070 (3)	C64	−0.5046 (7)	0.1461 (5)	0.0437 (4)	0.113 (5)
C23	−0.3674 (5)	0.0259 (3)	−0.1430 (3)	0.093 (4)	C65	−0.4898 (7)	0.0882 (4)	0.0554 (3)	0.100 (4)
C24	−0.3740 (5)	−0.0244 (4)	−0.1758 (3)	0.099 (4)	C66	−0.3970 (7)	0.0674 (3)	0.0558 (3)	0.085 (3)
C25	−0.3110 (5)	−0.0700 (3)	−0.1646 (3)	0.089 (4)	C71	0.25	0.25	0.2526 (9)	0.41 (2)
C26	−0.2412 (4)	−0.0655 (3)	−0.1218 (3)	0.069 (3)	C72	0.2500 (9)	0.2500 (6)	0.207 (1)	0.41 (6)
C31	−0.2003 (4)	−0.0627 (3)	0.0899 (3)	0.051 (3)	C73	0.1799 (9)	0.2250 (6)	0.1729 (5)	0.202 (9)
C32	−0.2090 (4)	−0.0539 (3)	0.1495 (3)	0.074 (3)	C74	0.1717 (7)	0.2310 (3)	0.1139 (5)	0.31 (2)
C33	−0.2915 (6)	−0.0713 (3)	0.1792 (3)	0.093 (3)	C75	0.25	0.25	0.0789 (7)	0.21 (1)

$^a U_{eq} = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^* a_i a_j$.

corresponding NaOR to generate purple solutions, which, when cooled, produced well-formed purple crystals of [(RO)$_4$CrNa$_2$-(THF)$_4$] (**2**) (eq 3). Regrettably, product instability prevented

$$[(RO)_2Cr]_n \xrightarrow[\text{2NaOR}]{\text{18-crown-6}}$$

1
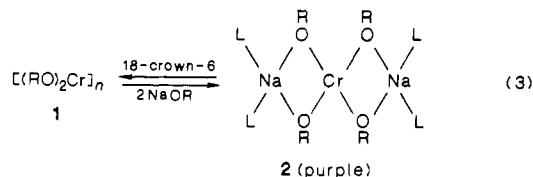
2 (purple)

R = Ph (a), 2,6-dimethylphenyl (b), β-C$_{10}$H$_7$ (c); L = THF, ½ TMEDA

either reproducible analytical determination or structural char-

acterization by X-ray analysis. However, in one case (R = 2,6-dimethylphenyl) the purple crystalline material does not change color in vacuo. Stable crystals of [(RO)$_4$Cr][Na(TMEDA)]$_2$ (**2b**), suitable for single-crystal X-ray diffraction analysis, have been obtained upon treatment with 2 equiv of N,N,N',N'-tetramethylethylenediamine (TMEDA). The unit cell of **2b** contains two centrosymmetric monomers and two molecules of disordered toluene. The molecule consists of a [(RO)$_4$Cr]$^{2-}$ dianion, which chelates the two Na cations using the oxygen atoms of the alkoxide groups (Figure 1). All the atoms in the molecule's core (O1, O2, O3, O4, Cr, Na1, Na2) lie in the same plane. The two molecules of coordinated TMEDA give an unusually flattened tetrahedral geometry (O3–Na1–N1 = 166.1 (2)°; N1–Na1–N2 = 74.2 (2)°; O3–Na1–O4 = 73.1 (2)°) to the Na atoms. The aromatic rings

Table IV. Selected Bond Distances (Å) and Angles (deg) for **2b**

Bond Angles			
Na1–Cr–Na2	176.05 (7)	O3–Na1–N2	109.8 (2)
O1–Cr–O2	85.2 (2)	O4–Na1–N1	106.6 (2)
O1–Cr–O3	178.1 (2)	O4–Na1–N2	165.0 (2)
O1–Cr–O4	93.9 (2)	N1–Na1–N2	74.2 (2)
O2–Cr–O3	96.0 (2)	Cr–O1–Na2	100.3 (2)
O2–Cr–O4	179.0 (2)	Cr–O2–Na2	100.3 (2)
O3–Cr–O4	84.9 (2)	Cr–O3–Na1	101.3 (2)
O3–Na1–O4	73.1 (2)	Cr–O4–Na1	100.7 (2)
O3–Na1–N1	166.1 (2)		

Bond Distances			
Cr–Na1	3.284 (3)	Na1–N1	2.496 (8)
Cr–Na2	3.265 (3)	Na1–N2	2.487 (5)
Cr–O1	1.997 (4)	Na2–O1	2.251 (5)
Cr–O2	2.000 (4)	Na2–O2	2.247 (5)
Cr–O3	1.988 (4)	Na2–N3	2.480 (6)
Cr–O4	1.997 (4)	Na2–N4	2.468 (7)
Na1–O3	2.255 (5)	O1–C1	1.335 (7)
Na1–O4	2.263 (5)		

Table V. Selected Bond Distances (Å) and Angles (deg) for **3a″** [a]

Bond Angles			
O10–Cr1–O20	88.7 (1)	Na1′–O10–Na2′	98.4 (1)
O10–Cr1–O30	164.4 (1)	Cr1–O20–Na1	96.0 (2)
O10–Cr1–O40	91.4 (1)	Cr1–O20–Na2′	89.8 (2)
O20–Cr1–O30	88.0 (2)	Na1–O20–Na2′	100.2 (1)
O20–Cr1–O40	167.0 (2)	Cr1–O30–Na1	92.2 (1)
O30–Cr1–O40	88.5 (2)	Cr1–O30–Na2	96.8 (2)
Cr1–O10–Na1′	87.1 (1)	Na1–O30–Na2	103.6 (2)
Cr1–O10–Na2′	93.2 (1)	C41–O40–Cr1	125.6 (4)

Bond Distances			
Cr1–O10	1.974 (3)	Na1–O40′	2.388 (4)
Cr1–O20	1.981 (4)	Na1–N61	2.400 (6)
Cr1–O30	1.981 (3)	Na2–O10′	2.360 (4)
Cr1–O40	1.987 (3)	Na2–O20′	2.467 (4)
Na1–O10′	2.625 (3)	Na2–O30	2.336 (4)
Na1–O20	2.347 (4)	Na2–O40	2.562 (4)
Na1–O30	2.472 (4)	Na2–N51	2.367 (5)
		Cr1···Cr1′	3.634 (1)

[a] Primed atoms are related by the symmetry operation $-x$, $-y$, $-z$.
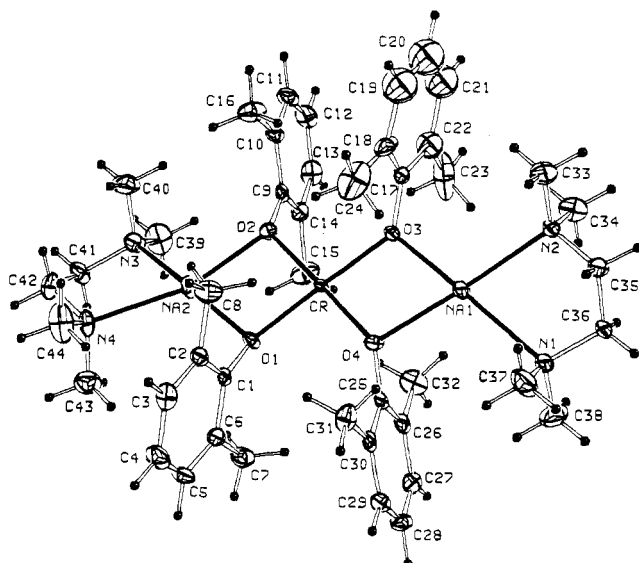
Figure 1. Thermal motion ellipsoid plot for [(2,6-Me$_2$C$_6$H$_3$O)$_4$Cr][Na-(TMEDA)]$_2$ (**2b**) drawn at the 50% probability level.

are almost parallel and perpendicular to the molecular plane. One of the two methyl groups in the ortho position of each phenyl ring is directed toward the fifth coordination site of one Na atom, reaching the near vicinity (3.4 Å). Probably, the presence of these methyl groups precludes the Na atoms from achieving the usual pentacoordinated geometry. The Cr–O distances [ranging between

1.997 (4) and 2.000 (4) Å] are quite similar to the value observed for [{Cr(μ-OCH-t-Bu$_2$)(OC-t-Bu$_3$)}$_2$].[21] However, the tricoordinated oxygen atoms of the bridging alkoxide groups in the complex **2b** are pyramidal and not trigonal, presumably indicating the absence of π-bonding character between oxygen and chromium.

Sodium phenoxide can be removed from the coordination sphere by simple treatment with a crown ether (18-crown-6), forming the blue insoluble and polymeric **1** (eq 3).

The values of the magnetic susceptibility of **2b** showed a linear dependence on the temperature in the range 4.3–298 K in agreement with the Curie law. Strangely, the value of the magnetic moment (μ_{eff} = 3.45 μ_B) is significantly higher than expected for a tetracoordinated square-planar geometry of Cr having low-spin d^4 electronic configuration (μ_B/Cr calculated spin only for a low-spin d^4 μ_{eff} = 2.83 μ_B).

As previously mentioned, the purple **2a**, **2c**, and **2d** release solvent spontaneously, forming greenish gray pyrophoric materials. These solids can be redissolved in toluene in the presence of small amounts of THF (larger amounts of THF form the starting purple **2**). The resulting emerald-green solutions precipitate, on cooling, stable, large, green crystals in good yield (eq 4). In all cases the

R = Ph (a), β–C$_{10}$H$_7$ (c), i–Pr (d); L = THF (single prime), py (double prime)
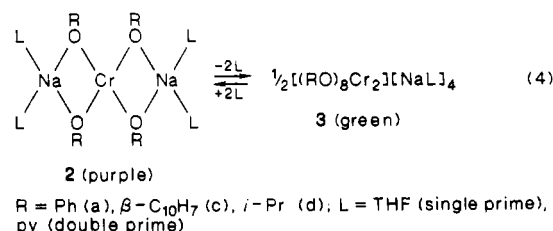
analytical data are consistent with the formulation [(RO)$_8$Cr$_2$][Na(THF)]$_4$ (**3**). All attempts to obtain a similar transformation for the 2,6-dimethylphenyl derivative failed. When small amounts of pyridine were used to solubilize the green solids in boiling toluene, no appreciable color change was observed, and the crystalline materials, which separated on cooling, showed analytical data consistent with the formulation [(RO)$_8$Cr$_2$][Na-(py)]$_4$·C$_6$H$_5$CH$_3$. In the case of **3a′**, **3a″**, and **3d**, the structures have been determined by X-ray diffraction studies.[34]

Complex **3a″** crystallizes in the orthorhombic space group *Pccn*. The unit cell consists of four discrete dimeric, centrosymmetric molecules of [(PhO)$_8$Cr$_2$][Na(py)]$_4$ and four molecules of disordered toluene. The geometry can be described as a distorted coordination octahedron with two Cr atoms occupying the apical positions and four Na atoms that lie in the equatorial plane (Figure 2). The eight aryloxide groups cover the eight faces of the octahedron with η^3-O atoms [Cr–O = 1.974 (3)–1.987 (3) Å, Na–O = 2.336 (4)–2.625 (3) Å]. The Cr atoms are slightly outside the plane bounded by the four oxygen atoms [distance from the plane 0.245 (2) Å], and the geometry around the transition metal is slightly distorted square planar. The Na atoms are pentacoordinated, the fifth coordination site being occupied by one molecule of pyridine. The long Cr···Cr nonbonding distance [3.634 (1)Å] rules out the presence of a Cr–Cr bond.

The three isostructural complexes **3a′**,[34] **3a″**, and **3d**[34b] showed a remarkable discrepancy in their magnetic properties. Linear dependence of 1/χ_{eff} on the temperature (50–298 K), in agreement with the Curie–Weiss law, has been found in all cases. However, whereas the values of the magnetic moment for **3a′** and **3c** (μ_{eff} = 2.84 and 2.83 μ_B, respectively) suggest a d^4 low-spin electronic configuration, in the case of **3a″** and **3d**, much higher values (μ_{eff} = 3.46 and 3.25 μ_B, respectively) have been observed. In all the cases, the large negative values of θ indicate the presence of a strong direct antiferromagnetic exchange possibly responsible for the lowering of the μ_{eff} values.[35] However, the small structural differences, including the values of the Cr···Cr distances in the three complexes (3.622, 3.634, and 3.739 Å for **3a′**, **3a″**, and **3d**

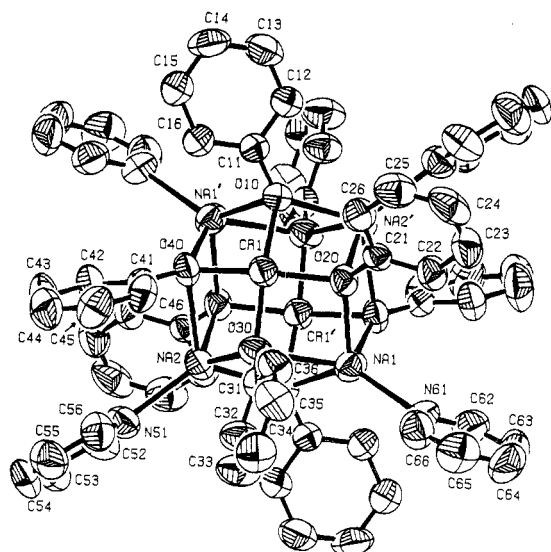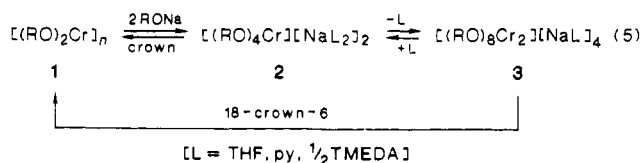(35) Mabbs, F. E.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973.

Chromium(II) Alkoxides

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Figure 2. Thermal motion ellipsoid plot for $[(PhO)_8Cr_2][Na(py)]_4$ (**3a''**) drawn at the 50% probability level.

respectively), cannot in any case justify these discrepancies. We believe that a significant extent of ligand-mediated superexchange contributes to the final values of the magnetic properties, as indicated by the strong influence of the nature of the ligands.

The Lewis acidity of Na seems to be the driving force for the formation of the dimeric unit **3**. In fact, reaction of **3** with a crown ether (18-crown-6) leads again to the formation of the original polymeric material **1**, while treatment with an excess of coordinating solvent generates the purple **2** (eq 5). The steric hindrance

$$[(RO)_2Cr]_n \underset{crown}{\overset{2\,RONa}{\rightleftharpoons}} [(RO)_4Cr][NaL_2]_2 \underset{+L}{\overset{-L}{\rightleftharpoons}} [(RO)_8Cr_2][NaL]_4 \quad (5)$$

$$\underset{\textbf{1}}{} \qquad \underset{\textbf{2}}{} \qquad \underset{\textbf{3}}{}$$

$$\vert\underline{}_{18-crown-6}\underline{}\vert$$

$$[L = THF, py, \tfrac{1}{2}TMEDA]$$

of the organic moiety of the alkoxo ligand plays a quite fundamental role in this chemistry. In fact, whereas attempts to convert the purple **2** into the green **3** were unsuccessful in the case of 2,6-dimethylphenoxide, in the case of the smaller isopropoxide group the reaction goes directly to the formation of **3d**. Finally, as already mentioned, no further aggregation with RONa is possible for the monomeric $(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2O)_2Cr(THF)_2$ where the size of the alkyl groups in the ortho positions of the phenyl rings hinders polymeric aggregation.

The absence of a Cr–Cr bond in the complexes **3** is surprising in view of the fact that, in the isostructural $[R_8Cr_2][Li(THF)]_4$ complexes,[8,9] a very short Cr–Cr quadruple bond (1.98 Å) has been found. Furthermore, in $[R_8Cr_2][Li(THF)]_4$, the two Cr atoms are slightly intruded into the coordination polyhedron at the plane described by the four η^3-CH$_3$ ligands (Figure 3). For this reason one can argue that the distortion is caused by the tendency of chromium to form a quadruple bond, and this is the driving force for the formation of dinuclear species. In contrast, the two Cr atoms in complexes **3** are slightly extruded from the polyhedron with slight distortion from the square-planar geometry. Calculations carried out on the basis of purely geometrical con-

$[Me_8Cr_2][LiL]_4$ $\qquad\qquad$ $[(RO)_8Cr_2][NaL]_4$
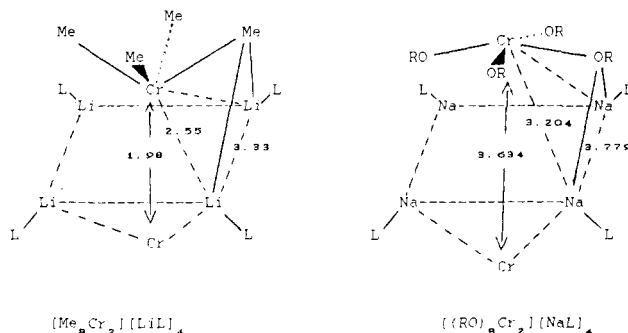
For clarity reasons the ligands have been partly omitted

Figure 3.

siderations exclude as unrealistic the possibility of ascribing this remarkable difference to the different sizes of the alkali-metal cations.[36] In our opinion, the different nature of the donor atom, used by the η^3-bonded alkoxo ligands (oxygen instead of carbon), is more responsible for this unexpected discrepancy. We believe that the electronic configuration of the complexes $[(RO)_8Cr_2]^{4-}$ (**3**) should be somewhat between $[Cl_8Cr_2]^{4-}$ and $[Me_8Cr_2]^{4-}$, which represent the two extreme cases of nonbonding $[(\sigma)^2(\delta)^2(\delta^*)^2(\sigma^*)^2]$ and bonding $[(\sigma)^2(\pi)^4(\delta)^2]$ configurations.[11b,15] In analogy to the case of $[Cl_8Cr_2]^{4-}$, a small separation is expected between the two electronic states, corresponding to the bonding and nonbonding levels (a gap of only 17 kcal/mol has been calculated for $[Cl_8Cr_2]^{4-}$). In that case, a simple thermal depopulation of the bonding state to the benefit of the nonbonding state might explain the absence of Cr–Cr bond. In other words, the different nature of the donor atom (carbon, oxygen, chlorine) may drastically affect the relative energies of the various configurations that mix with the nonbonding configurations, thus modifying their relative proportions in the ground state.

The suggestion (at this stage not conclusive) that emerges from our results is that the formation of Cr–Cr quadruple bonds is mainly driven by two factors, both intrinsic to the nature of the ligand: (a) the geometry, which is able to shorten or to elongate the intermetallic distance and which seems to be the dominating factor; (b) the nature of the donor atom, which modifies the relative populations of the bonding and nonbonding configurations in the ground state.

Further work to verify this hypothesis is under way, together with a study of the factors that influence the degree of molecular aggregation and Cr–Cr interaction (alkali-metal cation, donor atom).

Supplementary Material Available: Tables of temperature factors, torsion angles, bond angles and distances, thermal parameters, and hydrogen atom positional parameters (17 pages); lists of structure factors for **2b** and **3a''** (53 pages). Ordering information is given on any current masthead page.

(36) Pauling, L. *The Chemical Bond*; Cornell University Press: Ithaca, NY, 1967.