(4) Å for the molybdenum compound, values close to those observed for the cobalt environment in the polyanion $[As_4Co_2W_{40}O_{140}(H_2O)_2]^{24-}$,[5] in which As–O distances are equal to 3.43 and 3.06 Å. However, the reaction of cobalt with compound **1** did not lead to the expected result but yielded a compound based on an Anderson structure. The reaction is quite clean:

$$Co^{2+} + 2[As_3Mo_3O_{15}]^{3-} \rightarrow [As_6CoMo_6O_{30}]^{4-}$$

Let us point out that the Anderson type tellurium-containing structure shows that an excess of tellurium occurred, since $Te(OH)_6$ neutral groups are present in the crystal. Similarly, an excess of cobalt was needed to crystallize our compound **3** and $[Co(H_2O)_6]^{2+}$ is associated in the crystal structure as a cation.

Some Anderson type compounds have a crown of six $MO_6$ groups in which the internal octahedral site is void. All sides of the crown tetrahedrons then are fixed. One can attach two $AsO_4$ groups, two $MoO_4$ groups, or two $AsO_3CH_3$ groups.[11] In compound **3**, a rather unique situation is observed. The internal octahedral site is filled up with cobalt, and also two tripod *cyclo*-triarsenate(III) groups, one on each side, are fixed.

As a conclusion, we have prepared and crystallized $M_3O_{13}$, the building block of many polyanions. It is actually stabilized by a chain triarsenate(III), making $[As_3Mo_3O_{15}]^{3-}$. When reacted with cobalt(II), it yields a unique Anderson structure with a cobalt-filled internal octahedral site and two caps made of two *cyclo*-triarsenate(III), $[As_6CoMo_6O_{30}]^{4-}$.

**Supplementary Material Available:** Full listings of crystal data for the three compounds **1–3** and tables of the main distances and angles for compound **2** and anisotropic thermal parameters for the three compounds (5 pages); tables of observed and calculated structure factors for the three compounds (20 pages). Ordering information is given on any current masthead page.

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# Ligand and Alkali Metal Cation Control on the Molecular Complexity of Anionic Chromium(II) Aryloxides. Preparation and Crystal Structure of Dimeric $(PhO)_{10}Cr_2Li_6(THF)_6$ and $(2,6\text{-}Me_2C_6H_3O)_6Cr_2Li_2(THF)_4$ and Trimeric $(GuO)_{14}Cr_3Na_9Cl$ [GuO = $(o\text{-}CH_3O)C_6H_4O$] with an Encapsulated Chloride Ion

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Two new anionic, dimeric chromium(II) alkoxides, $(PhO)_{10}Cr_2Li_6(THF)_6$ (**3**) and $(2,6\text{-}Me_2C_6H_3O)_6Cr_2Li_2(THF)_4$ (**4**), have been prepared and characterized by X-ray structure determination. The two complexes possess similar $Cr_2(OR)_2$ cores with a fairly long Cr–Cr distance [Cr···Cr′ = 3.149 (2) and 3.091 (1) Å for **3** and **4**, respectively]. In complex **3**, the unit $Cr_2(OPh)_2$ is incorporated into two separated $(PhO)_4Li_3(THF)_3$ polyhedra, while in complex **4** the same core is attached to two $(RO)Li(THF)_2$ units with an overall linear arrangement of the Li–Cr–Cr–Li backbone. Replacement with TMEDA of the four THF molecules attached to lithium cleaved the dimeric structure of **3** and **4**, forming the monomeric $(RO)_4CrLi_2(TMEDA)_2$ [R = Ph (**5a**), $2,6\text{-}Me_2C_6H_3O$ (**5b**)]. Reaction of $CrCl_2(THF)_2$ with 2 equiv of GuONa [GuO = $(o\text{-}CH_3O)C_6H_4O$] led to the formation of the polymeric $[(GuO)_2Cr]_n$ as an insoluble, pyrophoric solid. Further reaction with an excess of (GuO)Na formed the trinuclear $(GuO)_{14}Cr_3Na_9Cl$ (**6**). Treatment of **6** with 18-crown-6 led to the disruption of the trinuclear arrangement and formation of the polymeric $[(GuO)_2Cr]_n$ species. Crystal data for **3**, **4**, and **6** are as follows. **3** is triclinic, space group $P\bar{1}$, with $a$ = 12.511 (1) Å, $b$ = 13.145 (1) Å, $c$ = 15.260 (2) Å, $\alpha$ = 98.77 (1)°, $\beta$ = 106.27 (1)°, $\gamma$ = 117.18 (1)°, $V$ = 2024.2 (3) Å$^3$, and $Z$ = 1; **4** is monoclinic, space group $C2/c$, with $a$ = 15.318 (4) Å, $b$ = 18.245 (4) Å, $c$ = 22.113 (6) Å, $\beta$ = 100.90 (2)°, $V$ = 6069 (3) Å$^3$, and $Z$ = 4; **6** is orthorhombic, space group $Pba2$, with $a$ = 26.720 (1) Å, $b$ = 26.916 (2) Å, $c$ = 15.670 (2) Å, $V$ = 11269.8 (17) Å$^3$, and $Z$ = 4.

## Introduction

A recent revival of interest in the literature of group 1 metals has shown that, among the properties of these metals, the Lewis acidity is responsible for several important features including the (i) high degree of nuclearity observed in the solid-state structures of these compounds,[1] (ii) strong interactions with unsaturated organic systems,[2,3] and (iii) $\sigma$-acceptor interactions with transition metals.[3]

A very important ancillary role of the alkali-metal cation has been recognized in the stabilization and reactivity of anionic transition metalates.[5,6] However, the molecular geometry of these species seems to be determined mainly by the electronic configuration of the transition metal and by the nature of the ligand. By contrast, recent results in the chemistry of tetravalent zirconium[7] and divalent chromium[8,9] have shown that alkali-metal cations are capable of playing a preeminent role in determining the molecular complexity (monomeric versus di-, oligo-, and

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polymeric). In the case of Cr(II) anionic alkoxides $(RO)_8Cr_2Na_4(THF)_4$,[8] the Lewis acidity of sodium was shown, among the properties of the alkali-metal cation, to be able to hold together the same molecular frame of the quadruply bonded $R_8Cr_2Li_4(THF)_4$[10] in the absence of a Cr–Cr bond and to be responsible for the polymeric aggregation observed in the solid-state structure of $[(\eta^1\text{-}2,5\text{-}Me_2C_4H_2N)_4CrNa_2(THF)_2(Et_2O)]_n$.[9] Since minor modifications introduced into the coordination sphere of the alkali-metal cation are causing major electronic and geometrical reorganization around the transition metal,[8c] we were interested to study how factors intrinsic in both the alkali-metal cation (dimension, coordination environment) and the ligand (steric hindrance, presence of additional donor atoms) may be able to affect the overall molecular geometry of anionic alkoxochromates(II).

Herein we describe the unexpected structural features of some novel anionic chromium(II) phenoxides, resulting from the replacement of sodium by the smaller lithium, the modification of the lithium coordination sphere, and the functionalization of the phenoxide aromatic ring.

## Experimental Part

All operations were performed under an inert atmosphere ($N_2$ or Ar) with standard Schlenk techniques or in a nitrogen-filled drybox (Braun MB-200). $CrCl_2(THF)_2$ was prepared according to published procedures.[11] TMEDA was chromatographed over $Al_2O_3$ and distilled from melted potassium. Infrared spectra were recorded on a Perkin-Elmer 283 instrument from Nujol mulls prepared in a drybox. Elemental analyses were carried out at the Microanalytical Department of the Chemistry Department of the State University of Groningen. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with a microanalytical balance and sealed into a specially designed Teflon capsule. Data were recorded at variable temperatures in the range 100–298 K by using a Faraday balance (Oxford Instruments) interfaced with an Apple II Computer. Plots of $1/\chi_g$ against $T$ (K) were in satisfactory agreement with the Curie–Weiss law in all cases. Magnetic moments were calculated by following standard methods[12] and corrections for underlying diamagnetism were applied to the data.[13]

**$(PhO)_{10}Cr_2Li_6(THF)_6$ (3).** $CrCl_2(THF)_2$ (1.05 g, 3.9 mmol) was added to a solution of PhOLi (23.8 mmol) in THF (50 mL). After being stirred for 3 h, the color of the mixture was deep blue. The solvent was evaporated in vacuo, and the residual solid was recrystallized from boiling heptane (40 mL) containing 5 mL of THF. Deep blue crystals of **3** separated upon cooling at 0 °C. Yield: 1.62 g (1.07 mmol, 55%). Anal. Calcd (found) for $C_{84}H_{98}O_{16}Li_6Cr_2$: C, 66.85 (66.51); H, 6.54 (6.52); Li, 2.76 (2.00); Cr, 6.89 (6.99). IR (Nujol mull, KBr; $cm^{-1}$): $\nu$ 1580 (s), 1480 (s), 1295 (s), 1280 (m), 1250 (s), 1155 (s), 1140 (m), 1060 (m), 1035 (s), 1000 (w), 980 (s), 900 (w), 880 (w), 865 (m), 840 (s), 820 (m), 760 (s), 690 (s), 605 (w). ($\mu_{eff} = 2.55\mu_B$.)

**$(2,6\text{-}Me_2C_6H_3O)_6Cr_2Li_2(THF)_4$ (4). Method A.** A solution of *n*-BuLi in hexane (7.9 mL, 2.5 N, 19.7 mmol) was added dropwise to a cooled (−30 °C) solution of $2,6\text{-}Me_2C_6H_3OH$ (2.41 g, 19.7 mmol) in THF (40 mL). After 20 min of stirring, $CrCl_2(THF)_2$ (1.75 g, 6.5 mmol) was added to the resulting solution. The color turned purple, and the stirring was continued for 10 h. After solvent evaporation in vacuo, the residual solid was redissolved in ether (20 mL) and light purple crystals of **4** were obtained upon cooling at −30 °C (2.14 g, 1.89 mmol, 58%). Anal. Calcd (found) for $C_{64}H_{86}O_{10}Cr_2Li_2$: C, 67.83 (66.82); H, 7.65 (7.60); Cr, 9.18 (9.06); Li, 1.22 (1.32). IR (Nujol mull, KBr; $cm^{-1}$): $\nu$ 1585 (s), 1380 (s), 1220 (m), 1210 (m), 1080 (s), 1040 (s), 970 (w), 940 (w), 910 (m), 890 (m), 845 (s), 745 (s), 715 (m), 695 (s), 590 (w), 580 (m), 530 (s), 495 (w), 460 (m). ($\mu_{eff} = 3.24\ \mu_B$.)

**Method B.** Solid $[(2,6\text{-}Me_2C_6H_3O)_2Cr]_n$[8] (2.0 g, 6.8 mmol) was added to a solution of $2,6\text{-}Me_2C_6H_3OLi$ prepared by treatment of a cooled solution (−30 °C) of $2,6\text{-}Me_2C_6H_3OH$ (0.83 g, 6.8 mmol) in THF (30 mL) with *n*-BuLi (2.7 mL, 2.5 N, 6.8 mmol) in hexane. After stirring of the resulting mixture for 10 h, the solvent was removed in vacuo and the residual solid redissolved in ether (15 mL). Purple crystalline **4** was obtained upon cooling at −30 °C (2.83 g, 2.5 mmol, 73% yield).

**$(PhO)_4CrLi_2(TMEDA)_2$ (5a).** A solution of **3** (1.32 g, 0.88 mmol) in toluene (75 mL) containing TMEDA (20 mL) was refluxed for 1.5 h. The color turned purple, and after solvent removal in vacuo the solid residue was redissolved in hexane (70 mL). The resulting slurry was boiled and filtered to remove the white solid and allowed to cool at room temperature. Large pink-purple crystals separated upon standing at room temperature overnight (1.13 g, 1.7 mmol, 96%). Anal. Calcd (found) for $C_{36}H_{52}O_4N_4CrLi_2$: C, 64.47 (64.13); H, 7.75 (7.64); Li, 2.09 (1.86); N, 8.35 (8.14); Cr, 7.76 (7.57). IR (Nujol mull, KBr; $cm^{-1}$): $\nu$ 1585 (s), 1355 (m), 1275 (s), 1185 (w), 1160 (s), 1135 (m), 1100 (w), 1065 (s), 1040 (m), 1025 (s), 995 (m), 950 (s), 880 (m), 845 (s), 830 (m), 795 (w), 760 (s), 690 (s), 610 (w), 590 (s), 5109 (s), 500 (w).

**$(2,6\text{-}Me_2C_6H_3O)_4CrLi_2(TMEDA)_2$ (5b). Method A.** A solution of *n*-BuLi (3.3 mL, 2.5 N, 8.3 mmol) was added dropwise to a cooled solution (−30 °C) of $2,6\text{-}Me_2C_6H_3OH$ (1.02 g, 8.4 mmol) in THF (30 mL). The resulting purple mixture, obtained upon addition of $CrCl_2(THF)_2$ (0.60 g, 2.2 mmol), was stirred 10 h and evaporated in vacuo, and the residual solid was redissolved in ether (10 mL) containing TMEDA (1 mL). Large purple crystals of **5** were obtained upon cooling at −30 °C (1.26 g, 1.6 mmol, 73% yield). Anal. Calcd (found) for $C_{44}H_{68}O_4N_4CrLi_2$: C, 67.50 (67.53); H, 8.75 (8.84); Li, 1.77 (1.26); N, 7.16 (7.14); Cr, 6.65 (6.57). IR (Nujol mull, KBr; $cm^{-1}$): $\nu$ 1580 (s), 1420 (m), 1370 (w), 1350 (w), 1120 (s), 1170 (w), 1160 (w), 1120 (w), 1090 (s), 1070 (w), 1030 (m), 1010 (m), 970 (w), 950 (s), 910 (w), 840 (s), 780 (m), 740 (s), 690 (s), 585 (s), 570 (w), 530 (s), 460 (m), 430 (w). ($\mu_{eff} = 4.64\mu_B$.)

**Method B.** A solution of $(2,6\text{-}Me_2C_6H_3O)_6Cr_2Li_2(THF)_4$ (2.73 g, 2.4 mmol) in toluene (25 mL) containing TMEDA (3 mL) was refluxed for 30 min. After the mixture was cooled at −30 °C, purple crystals of **5** separated. Yield: 0.97 g (1.2 mmol, 26% based on Cr). The remaining mother liquor was allowed to stand at room temperature for 2 days, whereupon a blue-purple amorphous solid separated. Elemental analysis and IR spectroscopy identified the solid as $[2,6\text{-}Me_2C_6H_3O)_2Cr]_n$[8a] (0.53 g, 1.6 mmol, 33% based on Cr).

**$(GuO)_{14}Na_9Cr_3Cl\cdot 2C_7H_8$ (6).** NaH (0.73 g, 30 mmol) was slowly added to a stirred solution of guaiacol (3.86 g, 31 mmol) in THF (100 mL). The addition of $CrCl_2(THF)_2$ (2.87 g, 10.7 mmol) slowly turned the color purple. The mixture was refluxed for 30 min and stirred for additional 20 h. After evaporation of the solvent in vacuo, the residual solid was recrystallized from boiling toluene (30 mL) containing 20 mL of THF. Purple crystals of **6** were obtained upon cooling at −30 °C. Yield: 2.29 g, 1.04 mmol, 29%. Anal. Calcd (found) for $C_{112}H_{114}O_{28}Na_9Cr_3Cl$: C, 58.28 (57.60); H, 4.94 (4.93); Cl, 1.53 (1.67); Na, 8.97 (8.68); Cr, 6.77 (6.76). IR (Nujol mull, KBr; $cm^{-1}$): $\nu$ 1740 (m), 1590 (s), 1580 (s), 1495 (s), 1460 (s), 1385 (m), 1320 (s), 1300 (s), 1270 (s), 1215 (s), 1180 (s), 1110 (s), 1050 (m), 1020 (s), 910 (s), 855 (s), 750 (s), 700 (s), 605 (s), 580 (m), 555 (m), 480 (m), 420 (s). ($\mu_{eff} = 3.24\ \mu_B$.)

**Reaction of $(GuO)_{14}Na_9Cr_3Cl$ with 18-Crown-6.** Anhydrous 18-crown-6 (1.74 g, 6.6 mmol) was added to a solution of **6** (1.21 g, 0.55 mmol) in THF (40 mL). The resulting mixture was heated at 60 °C for 40 min, upon which a blue-gray precipitate formed. The product was identified by elemental analysis and IR spectroscopy as $[(GuO)_2Cr]_n$. Yield: 0.21 g, 0.70 mmol, 42%. Anal. Calcd (found) for $C_{14}H_{14}O_4Cr$:

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**Table I.** Crystal Data and Structural Analysis Results

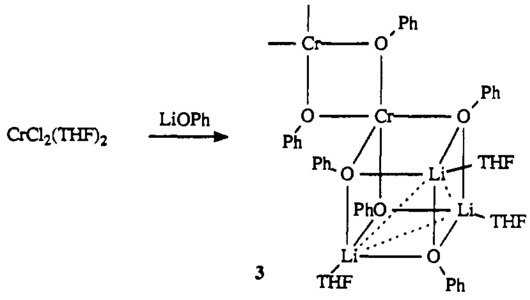
| | complex | | |
|---|---|---|---|
| | 3 | 4 | 6 |
| formula | $C_{84}H_{98}O_{16}Cr_2Li_6$ | $C_{64}H_{86}O_{10}Cr_2Li_2$ | $C_{112}H_{114}O_{28}Na_9Cr_3Cl$ |
| space group | $P\bar{1}$ | $C2/c$ | *Pba*2 |
| cryst system | triclinic | monoclinic | orthorhombic |
| *Z* | 1 | 4 | 4 |
| *a*, Å | 12.511 (1) | 15.318 (4) | 26.720 (1) |
| *b*, Å | 13.145 (1) | 18.245 (4) | 26.916 (2) |
| *c*, Å | 15.260 (1) | 22.113 (6) | 15.670 (2) |
| $\alpha$, deg | 98.77 (1) | | |
| $\beta$, deg | 106.27 (1) | 100.90 (2) | |
| $\gamma$, deg | 117.18 (1) | | |
| *V*, Å$^3$ | 2024.2 (3) | 6069 (3) | 11269.8 (17) |
| $D_{calcd}$, g cm$^{-3}$ | 1.24 | 1.240 | 1.359 |
| $\mu_{calcd}$, cm$^{-1}$ | 3.22 | 4.0 | 4.0 |
| radiation (Mo K$\alpha$), Å | 0.71073 | 0.71073 | 0.71073 |
| *T*, K | 298 | 130 | 100 |
| $R_F$ | 0.052 | 0.068 | 0.055 |
| $R_w$ | 0.059 | 0.063 | 0.037 |

C, 56.37 (56.30); H, 4.69 (4.70); Cr, 17.44 (17.33). IR (Nujol mull, KBr; cm$^{-1}$): $\nu$ 1590 (s), 1580 (m), 1490 (s), 1325 (s), 1285 (s), 1260 (s), 1210 (s), 1170 (s), 1110 (s), 1040 (w), 1030 (s), 920 (m), 850 (s), 760 (m), 735 (s), 610 (s), 430 (s).

**X-ray Crystallography. Complex 3.** A light blue rectangular-shaped crystal of approximate dimensions 0.4 × 0.3 × 0.15 mm was mounted in a Lindemann capillary, in a drybox under nitrogen atmosphere. Accurate unit cell parameters and an orientation matrix were obtained by least-squares refinement of 34 well-centered reflections. Crystal data and details on data collection and refinement are listed in Table I. Data were collected at room temperature on a four-circle Huber diffractometer. A $\theta/2\theta$ scan mode was used to collect one hemisphere of data ($+h,\pm k,\pm l$) with the maximum $2\theta$ of 45°, with Mo K$\alpha$ radiation. Three standard reflections were monitored for every 97 reflections collected and showed no significant variations throughout the data set collection. After data reduction and Lorentz–polarization corrections, a $\psi$-scan procedure was used for empirical absorption correction. From a total of 5291 data points, 2557 with intensities greater than $3\sigma$ were used in the structure analysis. The structure was solved in the triclinic space group $P\bar{1}$ (No. 2) by conventional heavy-atom methods. The position of the chromium atom was determined by a Patterson map, while the remaining non-hydrogen atom positions were located from subsequent difference-Fourier maps. This procedure was followed by several cycles of full-matrix least-squares refinement. Idealized hydrogen atom positions were calculated with C–H = 0.95 Å. Neither the positions nor the temperature factors were refined for the hydrogen atoms. Most of the THF carbon atoms refined with large temperature factors indicating partial disorder. This not uncommon feature (THF appears to be planar at room temperature, in contrast to the normal puckered conformation)[14] indicates the superposition of two or more nonplanar conformers. Convergence resulted in final agreement factors of $R = 0.052$ and $R_w = 0.059$. All calculations were performed on a VAX 11/750 computer (Department of Chemistry and Biochemistry, University of California, Los Angeles, CA).[15a] Pertinent numerical data on structure determination and refinement are given in Table I. Final atomic coordinates are given in Table II.

**Complex 4.** The crystal (a fragment cleaved from a larger crystal) was glued on the top of a glass fiber and transferred into the cold nitrogen stream of the low-temperature unit mounted on a Enraf-Nonius CAD-4F diffractometer interfaced with a PDP-11/23 computer. Precise lattice parameters and their standard deviation were derived from the angular setting of 22 reflections in the range $7.73 < \theta < 14.36°$. Reduced cell calculations did not indicate any higher lattice symmetry.[16] Crystal and/or instrumental instability were monitored by the intensity of two reference reflections measured every 3 h of X-ray exposure time. The net intensities of the data were corrected for the scale variation and Lorentz and polarization effects but not for absorption. Due to the weak scattering power of the crystals, only the reflections with $I < 2.0\sigma(I)$ were considered unobserved and therefore not used in the analysis. Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance of the two reference reflections,[17] resulting in 3427 reflections that satisfy the $I \geq 2.0\sigma(I)$ criterion of observability. Pertinent numerical data on structure determination and refinement are given in Table I. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86).[18] Refinement using anisotropic thermal parameters followed by Fourier syntheses resulted in the location of all the non-THF hydrogen atoms; the remaining hydrogen atoms were initially placed at their idealized positions and introduced in the final refinement. Refinement on *F* by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and an overall temperature factor for the hydrogen atoms converged at $R = 0.068$ ($R_w = 0.063$). Scattering factors were taken from Cromer and Mann.[19] Anomalous dispersion factors were taken from Cromer and Liberman.[20] A final difference Fourier map did not show any significant residual feature. Final atomic coordinates are given in Table III; relevant bond distances and angles are given in Table V. Extensive lists of values on molecular geometry and tables of observed and calculated structure factors are given as supplementary material. All calculations were carried out on the CDC-Cyber 170/760 computer at the University of Groningen with the program packages XTAL,[21] EUCLID[22] (calculation on geometric data), and a locally modified version of the program PLUTO[23] (preparation of illustrations).

**Scheme I**



3

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(15) (a) The program used in this work included modified versions of the following programs: REDUCE (Broach, Coppens, Becker, Blessing), peak profile analysis, Lorentz and polarization corrections; MULTAN (Main), package of programs including direct methods, structure factor normalization, Fourier transform, and peak search; ORFLS (Busing, Martin, Levy), structure factors calculation and full-matrix least-squares refinement; ORFFE (Busing, Edwards, Hamilton), distance, angle, and error calculationh; HYDROGEN (Trueblood), calculation of hydrogen atomic position; ORTEP (Johnson) figure plotting; PUBLIST (Hoel), structure factor listing. Scattering factors and corrections for anomalous dispersion components were taken from ref 15b. (b) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

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**Table II.** Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **3**

| atom | $x$ | $y$ | $z$ | $U_{eq}$,[a] Å$^2$ |
|---|---|---|---|---|
| Cr(1) | 0.1237 (1) | 0.0390 (1) | 0.0924 (1) | 0.051 (1) |
| Li(1) | 0.382 (1) | 0.126 (1) | 0.2401 (9) | 0.06 (1) |
| Li(2) | 0.189 (1) | −0.041 (1) | 0.2697 (9) | 0.07 (1) |
| Li(3) | 0.232 (1) | 0.177 (1) | 0.3053 (9) | 0.06 (1) |
| O(1) | −0.0230 (4) | −0.1052 (4) | −0.0219 (3) | 0.058 (6) |
| O(2) | 0.2801 (4) | 0.2005 (4) | 0.1942 (3) | 0.054 (5) |
| O(3) | 0.2274 (4) | −0.0348 (4) | 0.1516 (3) | 0.054 (6) |
| O(4) | 0.0757 (4) | 0.0235 (4) | 0.2308 (3) | 0.060 (6) |
| O(5) | 0.3453 (5) | 0.1110 (4) | 0.3539 (3) | 0.069 (6) |
| C(10) | −0.0452 (7) | −0.2204 (6) | −0.0505 (5) | 0.05 (1) |
| C(11) | −0.0007 (8) | −0.2512 (7) | −0.1154 (6) | 0.08 (1) |
| C(12) | −0.019 (1) | −0.3664 (9) | −0.1402 (7) | 0.10 (1) |
| C(13) | −0.085 (1) | −0.4485 (8) | −0.1010 (8) | 0.10 (1) |
| C(14) | −0.130 (1) | −0.4189 (8) | −0.0360 (6) | 0.10 (1) |
| C(15) | −0.1131 (8) | −0.3028 (7) | −0.0108 (5) | 0.07 (1) |
| C(20) | 0.3573 (6) | 0.3028 (6) | 0.1789 (5) | 0.05 (1) |
| C(21) | 0.4015 (7) | 0.4152 (6) | 0.2424 (5) | 0.06 (1) |
| C(22) | 0.4854 (9) | 0.5208 (7) | 0.2283 (7) | 0.09 (1) |
| C(23) | 0.5246 (9) | 0.5161 (8) | 0.1531 (7) | 0.09 (1) |
| C(24) | 0.4797 (8) | 0.4054 (9) | 0.0903 (6) | 0.08 (1) |
| C(25) | 0.3955 (8) | 0.2986 (6) | 0.1025 (5) | 0.07 (1) |
| C(30) | 0.2711 (6) | −0.0957 (6) | 0.1086 (5) | 0.05 (1) |
| C(31) | 0.2830 (7) | −0.1840 (7) | 0.1416 (5) | 0.06 (1) |
| C(32) | 0.3329 (9) | −0.2444 (7) | 0.0991 (7) | 0.09 (1) |
| C(33) | 0.3694 (9) | −0.2185 (9) | 0.0251 (8) | 0.09 (1) |
| C(34) | 0.3599 (8) | −0.1277 (9) | −0.0069 (6) | 0.09 (1) |
| C(35) | 0.3091 (7) | −0.0688 (7) | 0.0341 (5) | 0.07 (1) |
| C(40) | −0.0350 (8) | −0.0205 (6) | 0.2443 (6) | 0.06 (1) |
| C(41) | −0.0357 (9) | −0.0197 (8) | 0.3365 (6) | 0.09 (1) |
| C(42) | −0.152 (1) | −0.068 (1) | 0.3489 (9) | 0.12 (2) |
| C(43) | −0.269 (1) | −0.1151 (9) | 0.273 (1) | 0.11 (2) |
| C(44) | −0.2702 (9) | −0.1153 (8) | 0.1828 (8) | 0.10 (1) |
| C(45) | −0.1533 (8) | −0.0664 (7) | 0.1689 (6) | 0.07 (1) |
| C(50) | 0.4297 (7) | 0.1647 (7) | 0.4399 (6) | 0.06 (1) |
| C(51) | 0.5270 (9) | 0.2890 (8) | 0.4752 (6) | 0.09 (1) |
| C(52) | 0.6156 (9) | 0.3491 (8) | 0.5713 (7) | 0.10 (1) |
| C(53) | 0.612 (1) | 0.289 (1) | 0.6366 (7) | 0.11 (1) |
| C(54) | 0.520 (1) | 0.169 (1) | 0.6062 (7) | 0.11 (1) |
| C(55) | 0.4309 (8) | 0.1078 (7) | 0.5100 (7) | 0.09 (1) |
| O(6) | 0.5571 (5) | 0.1788 (5) | 0.2517 (4) | 0.08 (1) |
| C(60) | 0.6620 (9) | 0.2951 (8) | 0.2681 (7) | 0.10 (1) |
| C(61) | 0.779 (1) | 0.300 (1) | 0.319 (1) | 0.17 (2) |
| C(62) | 0.748 (1) | 0.182 (1) | 0.319 (1) | 0.16 (2) |
| C(63) | 0.6085 (9) | 0.1059 (8) | 0.2791 (8) | 0.11 (1) |
| O(7) | 0.2259 (6) | 0.2890 (5) | 0.4015 (4) | 0.08 (1) |
| C(70) | 0.118 (1) | 0.3068 (8) | 0.3770 (7) | 0.10 (1) |
| C(71) | 0.117 (1) | 0.356 (1) | 0.4692 (9) | 0.19 (2) |
| C(72) | 0.217 (1) | 0.364 (1) | 0.5429 (8) | 0.16 (2) |
| C(73) | 0.288 (1) | 0.327 (1) | 0.5028 (7) | 0.13 (2) |
| O(8) | 0.1080 (6) | −0.1914 (5) | 0.2996 (4) | 0.09 (1) |
| C(80) | 0.133 (1) | −0.2266 (8) | 0.3807 (7) | 0.11 (1) |
| C(81) | 0.049 (1) | −0.361 (1) | 0.3454 (9) | 0.13 (1) |
| C(82) | −0.061 (1) | −0.391 (1) | 0.2593 (9) | 0.13 (2) |
| C(83) | −0.019 (1) | −0.285 (1) | 0.2323 (9) | 0.18 (2) |

[a] $U_{eq} = [1/(6\pi^2)]\sum\sum\beta_{ij}a_ia_j$.

**Table III.** Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H atoms of **4**, with Their Esd's in Parentheses

| | $x$ | $y$ | $z$ | $U_{eq}$,[a] Å$^2$ |
|---|---|---|---|---|
| Cr(1) | 0.39737 (5) | 0.34227 (4) | 0.23327 (4) | 0.0181 (2) |
| O(1) | 0.2869 (1) | 0.3467 (1) | 0.2679 (1) | 0.025 (1) |
| O(2) | 0.5036 (1) | 0.3292 (1) | 0.1935 (1) | 0.024 (1) |
| O(3) | 0.3135 (1) | 0.3668 (1) | 0.1558 (1) | 0.021 (1) |
| O(4) | 0.1492 (2) | 0.2536 (1) | 0.1699 (1) | 0.038 (1) |
| O(5) | 0.1120 (2) | 0.4160 (1) | 0.1643 (1) | 0.039 (1) |
| C(1) | 0.2603 (3) | 0.3246 (3) | 0.3197 (2) | 0.032 (1) |
| C(2) | 0.2182 (3) | 0.3757 (4) | 0.3535 (2) | 0.042 (2) |
| C(3) | 0.1903 (4) | 0.3482 (5) | 0.4051 (3) | 0.081 (3) |
| C(4) | 0.2044 (4) | 0.2810 (5) | 0.4272 (3) | 0.096 (4) |
| C(5) | 0.2446 (4) | 0.2335 (4) | 0.3938 (3) | 0.066 (3) |
| C(6) | 0.2726 (3) | 0.2522 (3) | 0.3404 (3) | 0.041 (2) |
| C(7) | 0.2025 (4) | 0.4513 (4) | 0.3307 (3) | 0.063 (3) |
| C(8) | 0.3130 (4) | 0.1981 (3) | 0.3036 (3) | 0.051 (3) |
| C(9) | 0.5026 (3) | 0.3071 (3) | 0.1335 (2) | 0.023 (1) |
| C(10) | 0.4723 (3) | 0.2371 (3) | 0.1156 (2) | 0.026 (1) |
| C(11) | 0.4758 (3) | 0.2132 (3) | 0.0560 (2) | 0.033 (1) |
| C(12) | 0.5067 (4) | 0.2595 (3) | 0.0155 (2) | 0.038 (2) |
| C(13) | 0.5322 (3) | 0.3296 (3) | 0.0333 (2) | 0.032 (1) |
| C(14) | 0.5297 (3) | 0.3559 (3) | 0.0918 (2) | 0.025 (1) |
| C(15) | 0.4369 (4) | 0.1871 (3) | 0.1581 (3) | 0.039 (1) |
| C(16) | 0.5550 (3) | 0.4319 (3) | 0.1100 (2) | 0.033 (1) |
| C(17) | 0.3159 (3) | 0.4227 (3) | 0.1163 (2) | 0.025 (1) |
| C(18) | 0.2892 (3) | 0.4102 (3) | 0.0527 (2) | 0.031 (1) |
| C(19) | 0.2888 (4) | 0.4693 (3) | 0.0131 (3) | 0.046 (2) |
| C(20) | 0.3124 (4) | 0.5376 (3) | 0.0328 (3) | 0.054 (2) |
| C(21) | 0.3395 (3) | 0.5488 (3) | 0.0945 (3) | 0.052 (2) |
| C(22) | 0.3416 (3) | 0.4933 (3) | 0.1378 (2) | 0.031 (1) |
| C(23) | 0.2634 (4) | 0.3357 (4) | 0.0313 (2) | 0.048 (2) |
| C(24) | 0.3691 (3) | 0.5082 (3) | 0.2046 (3) | 0.044 (2) |
| C(25) | 0.1631 (4) | 0.1963 (3) | 0.1285 (3) | 0.050 (2) |
| C(26) | 0.1029 (6) | 0.1357 (4) | 0.1405 (3) | 0.081 (3) |
| C(27) | 0.0340 (4) | 0.1711 (4) | 0.1681 (3) | 0.076 (3) |
| C(28) | 0.0834 (4) | 0.2307 (3) | 0.2040 (3) | 0.049 (3) |
| C(29) | 0.1186 (4) | 0.4953 (4) | 0.1642 (3) | 0.060 (3) |
| C(30) | 0.0891 (4) | 0.5177 (4) | 0.0988 (4) | 0.070 (3) |
| C(31) | 0.0199 (5) | 0.4630 (4) | 0.0748 (4) | 0.090 (4) |
| C(32) | 0.0417 (5) | 0.3997 (4) | 0.1169 (4) | 0.100 (4) |
| Li(1) | 0.2100 (5) | 0.3480 (5) | 0.1871 (4) | 0.032 (3) |

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_ia_ja_i\cdot a_j$.

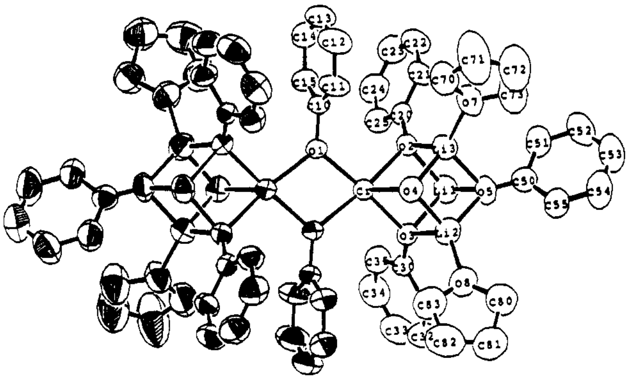

**Figure 1.** ORTEP plot of 3. Thermal ellipsoids are drawn at the 50% probability level. The aromatic ring attached to O(4) and THF molecules attached to Li have been left out for clarity reasons.

**Complex 6.** X-ray data were collected at 100 K for a blue, block-shaped crystal covered with a layer of paraffin oil and mounted on a glass fiber. Unit cell parameters were calculated from the SET4 setting angles[24] for 25 reflections in the range $9 < \theta < 15°$. The space group was derived from the observed systematic absence as either *Pba*2 or *Pbam*. The first one resulted in a satisfactory refinement. The intensity of 10817 reflections [of which 6963 with $I > 2.5\sigma(I)$] were corrected for *Lp* but not for absorption. The structure was solved with standard Patterson and Fourier methods (SHELX-86)[18] and refined on *F* by full-matrix least-squares (SHELX-76)[25] with anisotropic thermal parameters for the non-hydrogen atoms with the exception of the carbon atoms (in order to keep the reflection to parameters ratio at an acceptable value). Hydrogen atoms were introduced at calculated positions and refined with fixed geometry with respect to their carrier atoms, with two common isotropic thermal parameters. Refinement of the inverted structure resulted in slightly higher *R* values. Crystal data and numerical details on the structure determination and refinement are given in Table I. Final atomic coordinates are given in Table IV. Relevant bond distances and angles are given in Table V. Scattering factors were obtained from ref 17 and corrected for anomalous dispersion.[20] The calculation of the geometrical data and the preparation of the thermal motion ellipsoid plot were carried out with the program PLATON of the EUCLID package.[22] All calculations were carried out on Micro VAX-II cluster.

## Results and Discussion

The reaction of an excess of LiOPh with $CrCl_2(THF)_2$ proceeds in THF, forming deep blue solutions from which dark blue crystals

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**Table IV.** Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **6**

| atom | $x$ | $y$ | $z$ | $U_{eq}$, Å$^2$ | atom | $x$ | $y$ | $z$ | $U_{eq}$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| Cr(1) | 0.5 | 0.5 | 0.3104 | 0.0161 (6) | C(48) | 0.1543 (3) | 0.3991 (3) | 0.2170 (6) | 0.030 (2) |
| Cr(2) | 0.52712 (5) | 0.58882 (5) | 0.0299 (1) | 0.0187 (5) | C(49) | 0.0747 (3) | 0.6792 (3) | 0.2437 (6) | 0.037 (3) |
| Cr(3) | 0.03393 (5) | 0.41634 (5) | 0.5003 (1) | 0.0195 (5) | C(51) | 0.3736 (3) | 0.3690 (3) | 0.4560 (5) | 0.023 (2) |
| Cr(4) | 0 | 0.5 | 0.7833 (2) | 0.0187 (7) | C(52) | 0.3094 (3) | 0.3294 (3) | 0.1781 (6) | 0.038 (3) |
| Cl(1) | 0 | 0 | 0.1247 (2) | 0.022 (1) | C(53) | 0.3653 (3) | 0.4374 (3) | −0.2503 (6) | 0.029 (2) |
| Cl(2) | 0.5 | 0 | 0.5971 (2) | 0.021 (1) | C(54) | 0.3962 (3) | 0.6381 (3) | −0.2161 (6) | 0.032 (2) |
| Na(1) | 0.4774 (1) | 0.3914 (1) | 0.2345 (2) | 0.021 (1) | C(55) | 0.4504 (3) | 0.7569 (3) | 0.1722 (5) | 0.023 (2) |
| Na(2) | 0.3947 (1) | 0.4745 (1) | 0.1924 (2) | 0.027 (1) | C(56) | 0.3759 (3) | 0.6162 (3) | 0.4673 (5) | 0.029 (2) |
| Na(3) | 0.4078 (1) | 0.5313 (1) | 0.0062 (2) | 0.027 (1) | C(57) | 0.2578 (3) | 0.6191 (3) | 0.0666 (5) | 0.035 (2) |
| Na(4) | 0.5 | 0.5 | −0.1070 (3) | 0.026 (2) | C(58) | 0.1558 (3) | 0.4493 (3) | 0.2301 (5) | 0.027 (2) |
| Na(5) | 0.4112 (1) | 0.5999 (1) | 0.1884 (2) | 0.024 (1) | C(59) | 0.0442 (3) | 0.6405 (3) | 0.2162 (6) | 0.028 (2) |
| Na(6) | 0.0957 (1) | 0.5375 (1) | 0.4580 (2) | 0.030 (1) | C(61) | 0.4012 (3) | 0.3877 (3) | 0.3895 (5) | 0.019 (2) |
| Na(7) | 0 | 0.5 | 0.3530 (3) | 0.026 (2) | C(62) | 0.3429 (3) | 0.3687 (3) | 0.1733 (6) | 0.026 (2) |
| Na(8) | 0.0359 (1) | 0.3936 (1) | 0.7043 (2) | 0.023 (1) | C(63) | 0.3987 (3) | 0.4548 (3) | −0.1894 (5) | 0.024 (2) |
| Na(9) | 0.0763 (1) | 0.6060 (1) | 0.6605 (2) | 0.026 (1) | C(64) | 0.4091 (3) | 0.6088 (3) | −0.1480 (6) | 0.027 (2) |
| Na(10) | 0.1036 (1) | 0.4884 (1) | 0.6553 (2) | 0.025 (1) | C(65) | 0.4623 (3) | 0.7070 (3) | 0.1746 (5) | 0.023 (2) |
| O(11) | 0.4386 (2) | 0.4549 (2) | 0.3138 (3) | 0.017 (2) | C(66) | 0.3944 (3) | 0.6011 (3) | 0.3873 (6) | 0.026 (2) |
| O(12) | 0.4180 (2) | 0.4033 (2) | 0.1190 (3) | 0.024 (2) | C(67) | 0.3044 (3) | 0.6035 (3) | 0.0956 (5) | 0.020 (2) |
| O(13) | 0.4307 (2) | 0.4560 (2) | −0.0453 (3) | 0.020 (2) | C(68) | 0.1289 (3) | 0.4687 (3) | 0.2992 (5) | 0.021 (2) |
| O(14) | 0.4702 (2) | 0.5764 (2) | −0.0527 (3) | 0.023 (2) | C(69) | 0.0274 (3) | 0.6043 (3) | 0.2731 (5) | 0.020 (2) |
| O(15) | 0.4814 (2) | 0.6299 (2) | 0.1071 (3) | 0.020 (2) | C(71) | 0.4119 (3) | 0.3048 (3) | 0.3319 (6) | 0.032 (2) |
| O(16) | 0.4566 (2) | 0.5620 (2) | 0.3026 (3) | 0.020 (2) | C(72) | 0.2929 (3) | 0.4198 (4) | 0.2657 (7) | 0.050 (3) |
| O(17) | 0.3641 (2) | 0.5401 (2) | 0.1272 (3) | 0.022 (2) | C(73) | 0.4353 (3) | 0.5126 (3) | −0.2884 (6) | 0.046 (3) |
| O(18) | 0.0761 (2) | 0.4584 (2) | 0.4202 (3) | 0.020 (2) | C(74) | 0.3252 (3) | 0.5787 (3) | −0.1292 (6) | 0.039 (3) |
| O(19) | 0.0232 (2) | 0.5737 (2) | 0.4164 (3) | 0.020 (2) | C(75) | 0.4595 (3) | 0.7060 (3) | 0.3291 (5) | 0.033 (2) |
| O(21) | 0.4230 (2) | 0.3577 (2) | 0.3283 (3) | 0.026 (2) | C(76) | 0.3155 (3) | 0.6184 (3) | 0.3223 (7) | 0.049 (3) |
| O(22) | 0.3350 (2) | 0.4142 (2) | 0.2098 (4) | 0.036 (2) | C(77) | 0.3312 (3) | 0.6879 (3) | 0.1118 (7) | 0.049 (3) |
| O(23) | 0.4367 (2) | 0.4883 (2) | −0.2065 (3) | 0.035 (2) | C(78) | 0.1510 (3) | 0.5517 (3) | 0.2644 (6) | 0.048 (3) |
| O(24) | 0.3760 (2) | 0.5810 (2) | −0.1001 (4) | 0.034 (2) | C(79) | −0.0231 (3) | 0.5638 (3) | 0.1688 (5) | 0.033 (2) |
| O(25) | 0.4684 (2) | 0.6801 (2) | 0.2496 (3) | 0.027 (2) | C(81) | 0.2173 (3) | 0.2201 (3) | 0.4980 (6) | 0.039 (3) |
| O(26) | 0.3662 (2) | 0.6021 (2) | 0.3139 (4) | 0.038 (2) | C(82) | 0.2045 (4) | 0.2589 (4) | 0.4407 (7) | 0.070 (4) |
| O(27) | 0.3415 (2) | 0.6366 (2) | 0.1179 (4) | 0.028 (2) | C(83) | 0.2356 (4) | 0.2579 (4) | 0.3705 (7) | 0.068 (4) |
| O(28) | 0.1267 (2) | 0.5187 (2) | 0.3194 (4) | 0.032 (2) | C(84) | 0.2709 (4) | 0.2258 (4) | 0.3499 (8) | 0.080 (4) |
| O(29) | 0.0007 (2) | 0.5631 (2) | 0.2509 (3) | 0.024 (2) | C(85) | 0.2827 (4) | 0.1883 (4) | 0.4076 (7) | 0.063 (3) |
| O(110) | 0.0078 (2) | 0.6292 (2) | 0.5767 (3) | 0.021 (2) | C(86) | 0.2539 (3) | 0.1855 (3) | 0.4824 (6) | 0.041 (3) |
| O(111) | 0.0890 (2) | 0.4126 (2) | 0.5896 (3) | 0.019 (2) | C(87) | 0.1868 (4) | 0.2185 (5) | 0.5813 (8) | 0.096 (4) |
| O(112) | 0.1283 (2) | 0.5572 (2) | 0.5836 (3) | 0.018 (2) | C(88) | 0.2953 (6) | 0.2537 (6) | 0.854 (1) | 0.117 (5) |
| O(113) | 0.0321 (2) | 0.5684 (2) | 0.7749 (3) | 0.020 (2) | C(89) | 0.2710 (6) | 0.2700 (5) | 0.923 (1) | 0.119 (6) |
| O(114) | 0.0671 (2) | 0.4658 (2) | 0.7802 (3) | 0.023 (2) | C(90) | 0.2234 (6) | 0.2669 (6) | 0.947 (1) | 0.146 (7) |
| O(210) | 0.0903 (2) | 0.6833 (2) | 0.6000 (4) | 0.025 (2) | C(91) | 0.1964 (5) | 0.2382 (5) | 0.8875 (9) | 0.095 (5) |
| O(211) | 0.1095 (2) | 0.3510 (2) | 0.7166 (4) | 0.026 (2) | C(92) | 0.2181 (5) | 0.2227 (5) | 0.8143 (9) | 0.088 (4) |
| O(212) | 0.1593 (2) | 0.6034 (2) | 0.7231 (4) | 0.039 (2) | C(93) | 0.2662 (5) | 0.2322 (4) | 0.7849 (9) | 0.100 (5) |
| O(213) | 0.0172 (2) | 0.6651 (2) | 0.7780 (4) | 0.029 (2) | C(94) | 0.3464 (5) | 0.2649 (6) | 0.823 (1) | 0.197 (8) |
| O(214) | 0.1653 (2) | 0.4712 (2) | 0.7540 (4) | 0.026 (2) | C(110) | 0.0052 (3) | 0.6784 (3) | 0.5641 (5) | 0.016 (2) |
| C(11) | 0.4102 (3) | 0.4393 (3) | 0.3784 (5) | 0.018 (2) | C(111) | 0.1343 (3) | 0.3907 (3) | 0.5914 (6) | 0.021 (2) |
| C(12) | 0.3869 (3) | 0.3643 (3) | 0.1254 (5) | 0.022 (2) | C(112) | 0.1767 (3) | 0.5638 (3) | 0.5930 (6) | 0.022 (2) |
| C(13) | 0.3962 (3) | 0.4399 (3) | −0.1023 (6) | 0.025 (2) | C(113) | 0.0459 (3) | 0.5923 (3) | 0.8464 (5) | 0.021 (2) |
| C(14) | 0.4597 (3) | 0.6042 (3) | −0.1208 (5) | 0.023 (2) | C(114) | 0.0974 (3) | 0.4491 (3) | 0.8424 (5) | 0.019 (2) |
| C(15) | 0.4693 (3) | 0.6781 (3) | 0.0988 (5) | 0.021 (2) | C(210) | −0.0397 (3) | 0.7024 (3) | 0.5426 (5) | 0.021 (2) |
| C(16) | 0.4416 (3) | 0.5797 (3) | 0.3794 (5) | 0.020 (2) | C(211) | 0.1710 (3) | 0.4027 (3) | 0.5319 (6) | 0.028 (2) |
| C(17) | 0.3181 (3) | 0.5526 (3) | 0.1017 (5) | 0.021 (2) | C(212) | 0.2119 (3) | 0.5471 (3) | 0.5333 (5) | 0.024 (2) |
| C(18) | 0.1011 (3) | 0.4380 (3) | 0.3548 (5) | 0.023 (2) | C(213) | 0.0664 (3) | 0.5687 (3) | 0.9175 (5) | 0.024 (2) |
| C(19) | 0.0401 (3) | 0.6081 (3) | 0.3610 (5) | 0.022 (2) | C(214) | 0.0800 (3) | 0.4298 (3) | 0.9188 (5) | 0.026 (2) |
| C(21) | 0.3890 (3) | 0.4701 (3) | 0.4393 (5) | 0.022 (2) | C(310) | −0.0409 (3) | 0.7536 (3) | 0.5320 (5) | 0.029 (2) |
| C(22) | 0.3972 (3) | 0.3185 (3) | 0.0863 (5) | 0.028 (2) | C(311) | 0.2180 (3) | 0.3805 (3) | 0.5369 (6) | 0.035 (2) |
| C(23) | 0.3581 (3) | 0.4081 (3) | −0.0805 (6) | 0.032 (2) | C(312) | 0.2636 (3) | 0.5532 (3) | 0.5486 (5) | 0.027 (2) |
| C(24) | 0.4954 (3) | 0.6297 (3) | −0.1681 (5) | 0.023 (2) | C(313) | 0.0807 (3) | 0.5967 (3) | 0.9889 (6) | 0.027 (2) |
| C(25) | 0.4625 (3) | 0.7026 (3) | 0.0215 (5) | 0.028 (2) | C(314) | 0.1116 (3) | 0.4123 (3) | 0.9805 (6) | 0.031 (2) |
| C(26) | 0.4714 (3) | 0.5763 (3) | 0.4531 (5) | 0.019 (2) | C(410) | 0.0018 (3) | 0.7823 (3) | 0.5430 (5) | 0.029 (2) |
| C(27) | 0.2809 (3) | 0.5174 (3) | 0.0788 (5) | 0.031 (2) | C(411) | 0.2299 (3) | 0.3487 (3) | 0.6030 (6) | 0.033 (2) |
| C(28) | 0.1023 (3) | 0.3873 (3) | 0.3391 (5) | 0.025 (2) | C(412) | 0.2804 (3) | 0.5756 (3) | 0.6207 (5) | 0.031 (2) |
| C(29) | 0.0711 (3) | 0.6466 (3) | 0.3870 (5) | 0.023 (2) | C(413) | 0.0759 (3) | 0.6476 (3) | 0.9902 (6) | 0.028 (2) |
| C(31) | 0.3611 (3) | 0.4525 (3) | 0.5053 (6) | 0.032 (2) | C(414) | 0.1623 (3) | 0.4127 (3) | 0.9676 (6) | 0.033 (2) |
| C(32) | 0.3638 (3) | 0.2785 (3) | 0.0959 (6) | 0.038 (3) | C(510) | 0.0463 (3) | 0.7604 (3) | 0.5649 (5) | 0.027 (2) |
| C(33) | 0.3233 (3) | 0.3906 (3) | −0.1401 (6) | 0.042 (3) | C(511) | 0.1933 (3) | 0.3382 (3) | 0.6628 (6) | 0.029 (2) |
| C(34) | 0.4815 (3) | 0.6591 (3) | −0.2379 (5) | 0.027 (2) | C(512) | 0.2467 (3) | 0.5941 (3) | 0.6801 (5) | 0.027 (2) |
| C(35) | 0.4490 (3) | 0.7521 (3) | 0.0198 (6) | 0.034 (2) | C(513) | 0.0557 (3) | 0.6719 (3) | 0.9207 (5) | 0.026 (2) |
| C(36) | 0.4534 (3) | 0.5923 (3) | 0.5312 (6) | 0.029 (2) | C(514) | 0.1813 (3) | 0.4319 (3) | 0.8915 (6) | 0.031 (2) |
| C(37) | 0.2225 (3) | 0.5814 (3) | 0.0449 (6) | 0.038 (3) | C(610) | 0.0480 (3) | 0.7085 (3) | 0.5767 (5) | 0.023 (2) |
| C(38) | 0.1288 (3) | 0.3668 (3) | 0.2690 (6) | 0.034 (2) | C(611) | 0.1471 (3) | 0.3593 (3) | 0.6577 (5) | 0.023 (2) |
| C(39) | 0.0888 (3) | 0.6821 (3) | 0.3292 (6) | 0.028 (2) | C(612) | 0.1963 (3) | 0.5878 (3) | 0.6665 (5) | 0.025 (2) |
| C(41) | 0.3532 (3) | 0.4019 (3) | 0.5164 (5) | 0.024 (2) | C(613) | 0.0394 (3) | 0.6442 (3) | 0.8512 (5) | 0.020 (2) |
| C(42) | 0.3201 (3) | 0.2843 (3) | 0.1408 (6) | 0.042 (3) | C(614) | 0.1499 (3) | 0.4511 (3) | 0.8298 (5) | 0.018 (2) |
| C(43) | 0.3287 (3) | 0.4045 (3) | −0.2250 (6) | 0.035 (2) | C(710) | 0.1360 (3) | 0.7094 (3) | 0.5972 (7) | 0.051 (3) |
| C(44) | 0.4324 (3) | 0.6639 (3) | −0.2593 (6) | 0.032 (2) | C(711) | 0.1215 (3) | 0.3215 (3) | 0.7888 (6) | 0.038 (3) |
| C(45) | 0.4433 (3) | 0.7796 (3) | 0.0929 (6) | 0.036 (2) | C(712) | 0.1759 (4) | 0.6099 (4) | 0.8116 (6) | 0.051 (3) |
| C(46) | 0.4067 (3) | 0.6116 (3) | 0.5377 (6) | 0.029 (2) | C(713) | 0.0098 (3) | 0.7178 (3) | 0.7775 (6) | 0.030 (2) |
| C(47) | 0.2347 (3) | 0.5330 (3) | 0.0497 (6) | 0.040 (3) | C(714) | 0.2174 (3) | 0.4669 (3) | 0.7347 (5) | 0.029 (2) |

of $(PhO)_{10}Cr_2Li_6(THF)_6$ (3) were isolated upon recrystallization from heptane/THF mixtures (Scheme I).

The structure of 3 has been clarified by X-ray diffraction analysis, the overall geometry of the molecule being shown in

**Table V.** Selected Bond Distances (Å) and Angles (deg)

| 3 | | 4 | | 6 | |
|---|---|---|---|---|---|
| Cr(1)–Cr(1′) | 3.149 (2) | Cr(1)–O(2) | 2.004 (3) | Cr(1)–O(11) | 2.040 (5) |
| Cr(1)–O(1) | 2.006 (4) | Cr(1)–O(1) | 1.987 (3) | Cr(2)–O(12) | 2.037 (5) |
| Cr(1)–O(1′) | 2.007 (4) | Cr(1)–O(3) | 1.988 (3) | Cr(2)–O(13) | 2.028 (5) |
| Cr(1)–O(2) | 2.061 (4) | Li(1)–O(1) | 1.946 (9) | Na(1)–O(11) | 2.353 (6) |
| Cr(1)–O(3) | 2.050 (4) | Li(1)–O(6) | 1.917 (13) | Cr(1)···Cl(1) | 2.910 (3) |
| Cr(1)–O(4) | 2.365 (5) | Cr(1)–Cr(1′) | 3.091 (1) | Cr(2)···Cl(1) | 2.906 (2) |
| Cr(1)–Li(1) | 2.929 (11) | Cr(1)–O(2)–Cr(1′) | 100.6 (1) | Cr(1)–O(16) | 2.036 (5) |
| Li(1)–Li(2) | 2.628 (17) | O(2)–Cr(1)–O(2′) | 77.8 (1) | Cr(1)···Cr(2) | 5.055 (2) |
| Li(1)–O(2) | 1.976 (13) | O(2)–Cr(1)–O(3) | 95.4 (1) | Cr(1)···Cr(2b) | 4.996 (2) |
| Li(1)–O(3) | 1.995 (12) | O(1)–Cr(1)–O(2) | 174.3 (1) | Cr(1)···Cr(2b) | 5.055 (2) |
| Li(1)–O(5) | 1.933 (15) | O(1)–Cr(1)–O(3) | 82.2 (1) | O(11)–Cr(1)–O(16b) | 88.4 (2) |
| O(1)–Cr(1)–O(1′) | 76.6 (2) | | | | |
| Cr(1)–O(1)–Cr(1′) | 103.4 (2) | | | | |
| O(1)–Cr(1)–O(2) | 171.0 (2) | | | | |
| O(1)–Cr(1)–O(3) | 99.9 (2) | | | | |
| O(1)–Cr(1)–O(4) | 108.9 (2) | | | | |
| O(2)–Cr(1)–O(4) | 79.3 (2) | | | | |

Figure 1. The structure consists of discrete dimeric units composed of two identical fragments related to each other by an inversion center placed between the two chromium atoms. The linkage between the two fragments is obtained through two $\eta^2$-OPh groups, which bridge the two pentacoordinated Cr atoms with a fairly long Cr···Cr distance [Cr···Cr = 3.149 (2) Å]. Each Cr atom is also part of a coordination polyhedron formed by four alkoxide groups and three tetracoordinated Li cations. One molecule of coordinated THF is borne by each Li atom. The geometry of each of the two identical polyhedra can be described in terms of two interpenetrating $Li_3Cr$ and $(PhO)_4$ tetrahedra, resulting in an overall pseudocubane structure. The structure of the two polyhedra may also be regarded in terms of the regular cubane structure, often observed with lithium derivatives,[26] of an hypothetical tetrameric $(LiOR)_4$, where a LiOR fragment has been replaced by a $Cr(OPh)_2$ unit. The size of the $CrLi_3$ tetrahedron [Li–Li = 2.626 (3) Å; Cr–Li = 3.048 (3) Å] is similar to that of the $Li_4$ unit found in $(MeLi)_4$[27] and $(LiC{\equiv}CPh)_4$.[28] Remarkably enough, the very short Li···Li distances observed in complex **3** [average Li···Li = 2.626 Å] are shorter than the unquestionable "bonding" values of the $Li_2$ molecule (2.67 Å) and metallic Li (3.04 Å). While the Li···Li interactions are unlikely essential for the aggregation observed in complex **3**, the skeletal cubane bonding may be explained in terms of 12 2-center electron-pair Li–O and Cr–O bonds (and no Li–Li bonds), if each oxygen atom were to act as a 6-electron ligand. The two $\eta^2$-OR groups and two others sited on the corners of the plane Cr–O(2)–O(3) of the polyhedron are coplanar with chromium showing nearly equal Cr–O distances [average Cr–O = 2.029 (3) Å]. Conversely, the fifth OR group bonded to chromium, which lies on the corner of the cubane unit in a position perpendicular to the O(1)–O(1)′–O(2)–O(3)–Cr plane, shows a remarkably longer Cr–O distance [Cr–O(4) = 2.365 (3) Å]. Therefore, the overall geometry around the Cr atom is square-based pyramidal.

The square-pyramidal geometry observed around the chromium atom is reminiscent of the mononuclear fragments that are the building blocks of the well-known quadruply bonded dichromium complexes bridged by three-center chelating ligands,[29] although the presence of Cr–Cr bond is ruled out in complex **3** by the long Cr···Cr distance [3.149 (2) Å]. A comparable Cr···Cr distance has been found in the sterically encumbered $\{[(t\text{-Bu})_3CO]Cr[\mu\text{-}OCH(t\text{-Bu})_2]\}_2$ complex[30] with a similar $Cr_2X_2$ core, which indicates that in this case the organic moiety of the alkoxo group has only minor influence on the value of the intermetallic separation.

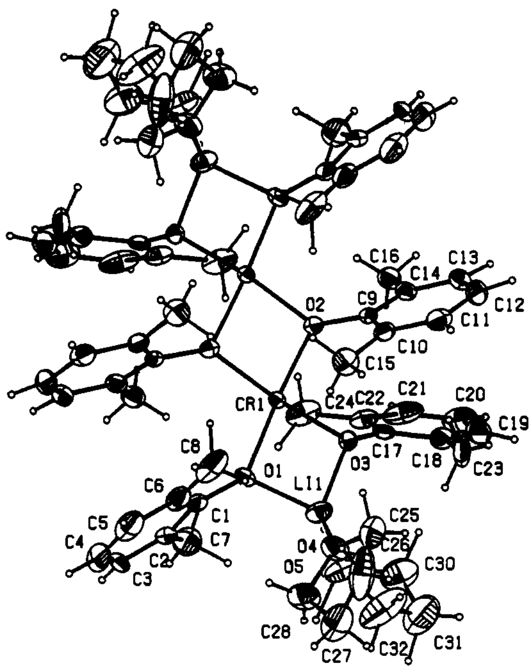
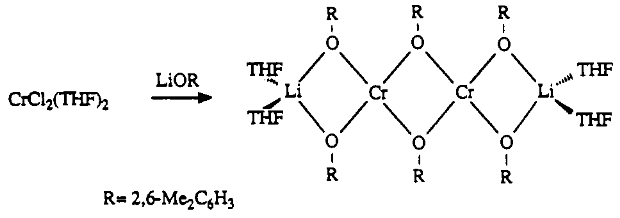


**Figure 2.** ORTEP plot of **4**. Thermal ellipsoids are drawn at the 50% probability level.

**Scheme II**



**4**

The value of the magnetic moment of **3** ($\mu_{eff}$ = 2.55 $\mu_B$) is only slightly lower than expected for a low-spin $d^4$ electronic configuration ($\mu_{eff}$ = 2.83 $\mu_B$ spin only)[12] and comparable with those of monomeric $(pyrrolyl)_2Cr(py)_3$[9] and $(Py)Cr[C_6H_4(o\text{-}CH_2NMe_3)]_2$[31] possessing similar coordination geometry.

The introduction of two methyl groups at the ortho positions of the phenyl ring significantly increases the steric hindrance and

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(26) See for example: (a) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 79. (b) Bogdanovic, B.; Kruger, C.; Wermeckes, B. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 817.

(27) Köster, K.; Thoennes, D.; Weiss, E. *J. Organomet. Chem.* **1978**, *160*, 1.

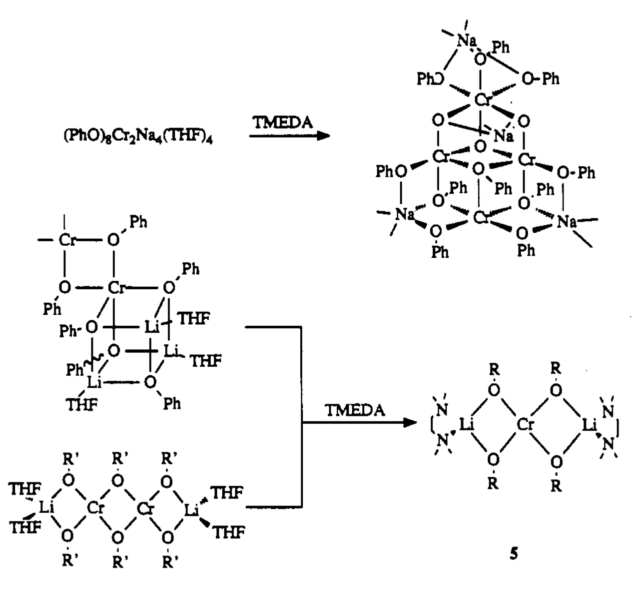
(28) Schubert, B.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 496.

(29) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982, and references cited therein.

(30) (a) Hvoslef, J.; Hope, H.; Murray, B. D.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1983**, *1438*. (b) Murray, B. D.; Hope, H.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 169.

(31) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; Spek, A. L. Manuscript in preparation.

**Scheme III**



R = Ph (**5a**); 2,6-$Me_2C_6H_3$ (**5b**)

precludes the dimeric aggregation in the case of the Na derivative $(2,6\text{-}Me_2C_6H_3O)_4CrNa_2(L)_4$.[8a] Conversely, the reaction of $CrCl_2(THF)_2$ with an excess of 2,6-$Me_2C_6H_3OLi$ led instead to the formation of a linear dimeric complex with six bridging aryloxide groups, $(RO)_6Cr_2Li_2(THF)_4$ (**4**) (Scheme II).

The structure of **4**, as demonstrated by an X-ray diffraction analysis, consists of two identical $(RO)_3CrLi(THF)_2$ moieties connected via bridging $\mu$-OR groups, in an overall linear arrangement of the Li–Cr–Cr–Li core (Figure 2). The values of the Cr–O and Li–O distances formed by the six bridging aryloxide groups [average Cr–O = 1.993 (3) Å, Li–O = 1.911 (9) Å] compare well with those observed for **3**. The coordination geometry around each chromium atom is square planar, with the transition metal lying in the center of a plane bound by four oxygen atoms of four aryloxo groups. The oxygen atoms engaged in the formation of the bridges Cr–O–Cr and Cr–O–Li are however remarkably different. A trigonal arrangement has been observed for the two oxygen atoms bridging the two chromium, possibly suggesting some extent of O → Cr $\pi$ interaction, while the usual pyramidal geometry has been observed for the other two oxygens that bridge lithium and chromium (distance of C17 from the plane Cr1–O3–Li1 = 0.734 Å). In spite of this noticeable difference, the Cr–O bonding distances are quite similar. The value of the Cr···Cr distance [Cr(1)···Cr(1a) = 3.091 (1) Å], although shorter than in **3**, is not in agreement with the existence of a Cr–Cr bond. The long Cr···Li nonbonding distance [Cr···Li = 2.861 (8) Å] excludes a direct Cr–Li $\sigma$ interaction.

The value of the magnetic moment of **4** ($\mu_{eff}$ = 3.22 $\mu_B$) is intermediate between those expected for a high- and low-spin $d^4$ electronic configuration (4.90 and 2.83 $\mu_B$, respectively). The linear dependence of the magnetic susceptibility on the reciprocal of the temperature ($1/T$), found in agreement with the Curie–Weiss law in the range 50–298 K, showed a largely negative value of $\Theta$ ($\Theta$ = –45 K), which suggests antiferromagnetic coupling as a possible cause for lowering the value of $\mu_{eff}$.[12]

The introduction of TMEDA in the coordination sphere of sodium affords several unexpected transformation of $(RO)_8Cr_2Na_4L_4$ including cleavage of the dimeric structure[8a,b] or disproportionation and major molecular reorganization,[8c] depending on the nature of both the Lewis base coordinated to the alkali-metal cation and the aryloxide organic moiety (Scheme III). Similar treatment of the lithium derivatives **3** and **4** with TMEDA (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) cleaved the dimeric core forming purple crystals of the monomeric $(RO)_4CrLi_2(TMEDA)_2$ [R = Ph (**5a**), 2,6-$Me_2C_6H_3O$ (**5b**)]. There was no indication of oxidation in the reaction of **3** with TMEDA, as it might be expected on the basis of the behavior of $(PhO)_8Cr_2Na_4(THF)_4$.[8c] In the case of **4**, it was possible to isolate and characterize the polymeric $[(RO)_2Cr]_n$ (**6**) as a reaction byproduct.

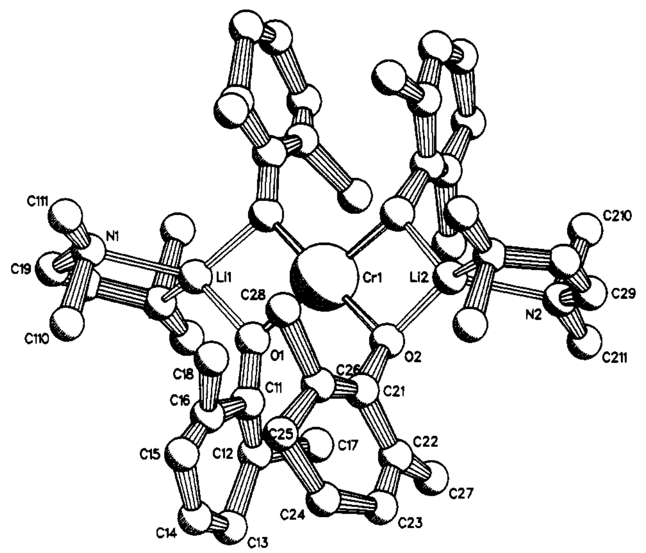
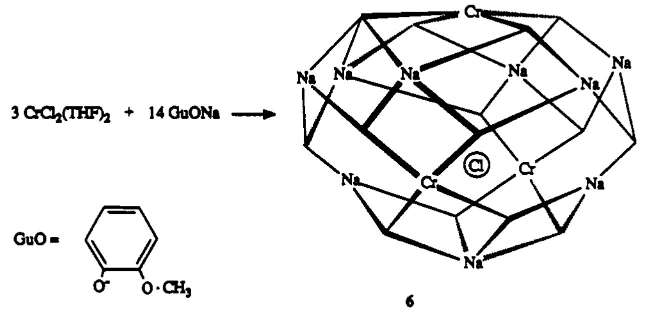


**Figure 3.** ORTEP plot of **5**. Thermal ellipsoids are drawn at the 50% probability level. Aromatic rings and TMEDA molecules attached to the Li atoms have been deleted for clarity reasons.

**Scheme IV**



The monomeric nature of **5** is suggested by the analytical data and the similarities of the magnetic and spectroscopic properties with those of the previously reported $[(2,6\text{-}Me_2C_6H_3O)_4CrNa_2(TMEDA)_2]$,[8a] and it has been confirmed by preliminary X-ray diffraction analysis carried out on a single crystal of **5b**.[32] In addition to the poor diffraction pattern, extensive disorder problems did not allow a reasonable convergence to acceptable values of *R*. However, the monomeric nature of the molecule remains demonstrated (Figure 3) and closely resembles the previously reported $(RO)_4CrNa_2(TMEDA)_2$ ($R$ = 2,6-$Me_2C_6H_3$).[8a]

The functionalization of the phenyl ring ortho position with a methoxy group, such as in the guaiacolate, caused a significant modification of the molecular structure. The reaction of $CrCl_2(THF)_2$ with stoichiometric amounts of GuONa (GuO = $(o\text{-}CH_3O)C_6H_4O$] proceeded forming the polymeric $[(GuO)_2Cr]_n$. Further reaction with GuONa required the use of a large excess (6 equiv) in order to achieve the complete dissolution of the insoluble starting material. Light violet crystals of $(GuO)_{14}Cr_3Na_9Cl$ (**6**) were isolated in good yield from the resulting purple solutions (Scheme IV).

The rather complex structure of **6** was clarified by an X-ray diffraction analysis and is shown in Figures 4 and 5. The molecule possesses a trinuclear core with the three chromium atoms symmetrically placed around a chlorine atom in a planar arrangement. However, the Cr···Cr [average Cr···Cr = 5.030 (2) Å] and Cr···Cl distances [average Cr···Cl = 2.908 (3) Å] are too long to provide significant bonding, and these interactions are not likely able to

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[32] Crystal data for **5**: monoclinic, *C2/c*, *a* = 13.325 (3) Å, *b* = 22.047 (3) Å, *c* = 17.059 (5) Å, $\beta$ = 108.40 (1)°, *V* = 4595 Å$^3$, *Z* = 4. Edema, J. J. H.; Gambarotta, S.; Bensimon, C. Unpublished results.

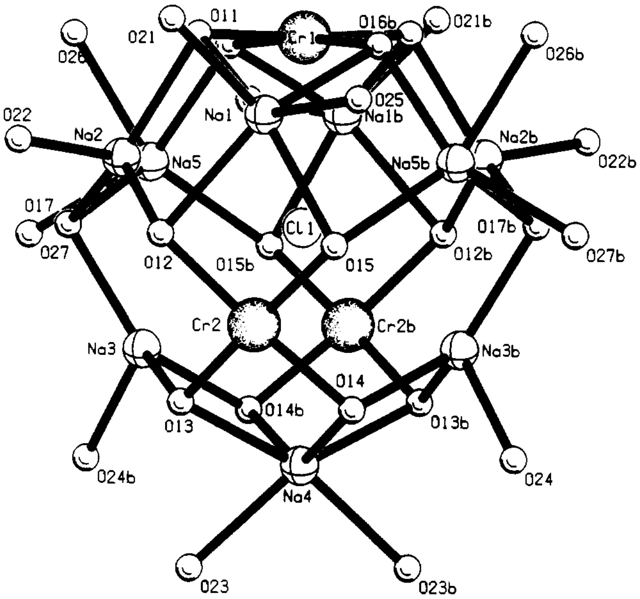

**Figure 4.** Core of **6** drawn with adopted numbering scheme. Aromatic carbon atoms have been left out for clarity reasons.

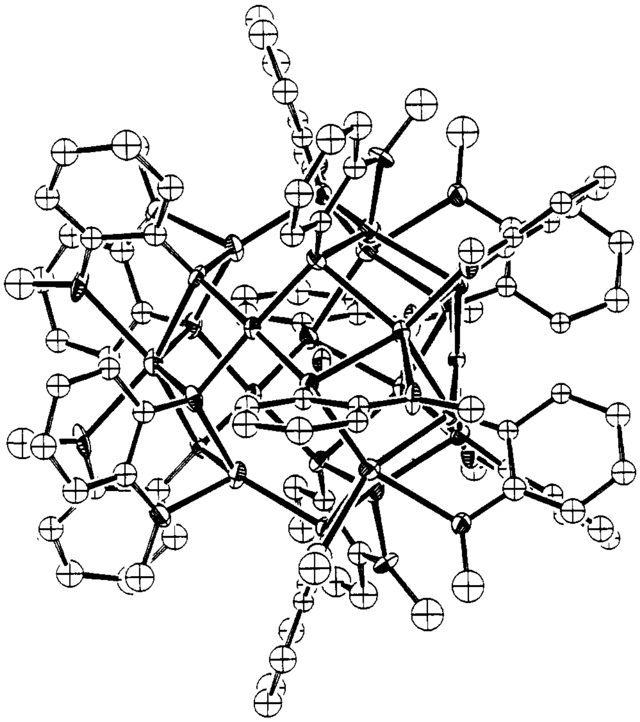

**Figure 5.** Thermal motion ellipsoid plot for **6** drawn at the 30% probability level.

hold together the molecular frame. Conversely, the bonding of the molecule is provided to the molecule by a network of bridges realized between the chromium atoms with nine sodium and twelve oxygen atoms from the fourteen guaiacolate molecules. Three Na atoms are coplanar with the three chromium atoms and chlorine, while the remaining six are symmetrically placed on the two sides of the $Na_3Cr_3Cl$ plane. Due to the fact that the shortest Na···Cl distance (ranging from 3.198 to 3.722 Å) excludes a direct Cl → Na bonding interaction, the molecular structure can be regarded as one of the rare cases of encapsulation of chlorine sometimes encountered in the cluster chemistry of the electron-rich late transition metals.[33] The coordination geometry around each chromium atom is the quite usual square planar, with chromium placed in the center of the plane defined by four oxygen atoms from four different molecules of guaiacol. The Cr–O distances [average Cr–O = 2.034 (5) Å] compare well with those of the other chromium(II) alkoxides.[8,30] The deviation of chromium from the basal plane is almost insignificant. The three sodium atoms coplanar with chromium are hexacoordinated (trigonal prismatic), while the remaining ones are tetra- (Na3, Na3b, Na2, Na2b) and pentacoordinated (Na5, Na5b), with slightly different values of the Na–O distances (ranging from 2.198 to 2.548 Å).

The encapsulated Cl atom and a Na countercation cannot be removed from the molecular core without having a complete destruction of the molecular polyhedron. Treatment of **6** with 18-crown-6 (excess) resulted in fact in the formation of the polymeric $[(GuO)_2Cr]_n$ as a gray, pyrophoric solid. The same polymeric complex is exclusively formed in the reaction of $CrCl_2(THF)_2$ with 2 equiv of either lithium or potassium guaiacolate. While an excess of the potassium salt did not modify the result, a large excess of lithium guaiacolate gave only brown intractable oil.

In conclusion, the alkali-metal cation has a preeminent role in assembling the dimeric or even oligomeric structures of anionic chromium(II) alkoxides. The unpredictable structure of **6**, the facile cleavage of **3** and **4** (Scheme IV), and the considerable structural differences between lithium and sodium alkoxo chromates suggest in fact that the alkali metal provides a delicate balance of factors (Lewis acidity, dimension, preferential coordination number), which results in the final degree of molecular aggregation. While there is no doubt that the modification of the coordination sphere of Li is the driving force of the cleavage of the $Cr_2(OR)_2$ core of **3** and **4** (Scheme IV), it remains unclear why simple replacement of THF with TMEDA in the coordination sphere of Li is able to strongly modify the molecular structure. Although a rationalization of this remarkable behavior is not possible so far, the fundamental role of the alkali-metal cation in determining the bonding and the nuclearity of chromium(II) alkoxo chromates remains ascertained.

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**Supplementary Material Available:** For each complex, tables of thermal parameters, hydrogen atom positional parameters, and extensive bond distances and angles (33 pages); lists of observed and calculated structure factors (95 pages). Ordering information is given on any current masthead page.

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[33] (a) Birker, P. J. M. *J. Chem. Soc., Chem. Commun.* **1980**, 946. (b) Birker, P. J. M. *Inorg. Chem.* **1981**, *20*, 2877.