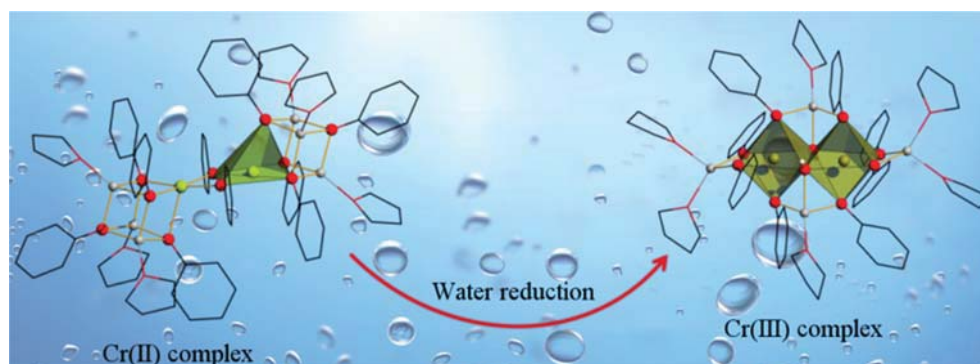


Mixed Metal Multinuclear Cr(III) Cage Compounds and Coordination Polymers Based on Unsubstituted Phenolate: Design, Synthesis, Mechanism, and Properties

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ABSTRACT: Oxidative substitution reactions of chromium(II) chloride with lithium phenoxide in the presence of water give access to new polynuclear chromium(III) aryloxy complexes and coordination polymers. While a one-dimensional coordination polymer based on chromium(III), $[\text{Cr}_2(\mu_3\text{-OPh})_2(\mu\text{-OPh})_6(\mu\text{-OH})(\mu_3\text{-Li})_4(\mu_3\text{-Cl})_2\text{Li}(\text{THF})_6]_n$, is first obtained by serendipity, the controlled addition of water to the initial Cr(II) complex as well as variation of the stoichiometry lead to three new discrete chromium(III) aggregates, namely, $[\text{Cr}(\text{OPh})_4(\mu\text{-OH})\text{Li}_2(\text{THF})_3]_2$, $[\text{Cr}_3\text{Li}_3(\text{OPh})_9(\mu_3\text{-OH})(\mu_3\text{-O})(\text{THF})_6]$, and $[\text{Cr}_4(\mu\text{-OPh})_8(\mu_3\text{-OH})_6(\mu\text{-OH})_2\text{Cl}_2\text{Li}_6(\text{THF})_6] \cdot 2\text{THF}$. The use of deuterated species allowed confirmation of the oxidation based on the addition of water by detection of H_2 , HD, and D_2 . During these investigations, we have also identified a THF-adduct of chromium(II) chloride, $[\text{CrCl}_2(\text{THF})_2]$, used in the literature as a precursor in numerous syntheses, but with a hitherto unknown structure.

INTRODUCTION

A mixed metal compound is a general term to define, e.g., oxides, salts, and complexes containing at least two different metal species. Mixed metal alkoxide compounds of, e.g., d-block elements with alkali,¹ alkaline earth,² lanthanide,³ and actinide⁴ metal ions, are an attractive field of research due to their large panel of applications. Indeed, as a function of the metal ions and ligands, mixed metal compounds can be used in catalysis,^{5,6} magnetism,^{7,8} optoelectronics,^{9,10} luminescence,^{11–15} energy storage (battery),^{1,16–18} or fuel cells.^{19–21} The properties of such polymetallic compounds depend on (a) the types and proportions of metallic species, and (b) the use of ligands allowing the tuning of the properties. Indeed, depending of the ligand, we obtained a different configuration of complex which in the case of the bridging ligand, changes angles and distances between metals ions. The bulkiness of the ligand has a major role in the case where accessibility of metal center is necessary, e.g., in catalysis.^{5,6}

In our group, we have investigated alkali and alkaline earth metal compounds in order to study their behavior in nonaqueous solvents, their analogy to transition metals, and

possible applications in oxide materials.^{2,22–43} We have previously shown that group 2 metal halides may act as starting materials for both homometallic alkaline earth and mixed-metal alkali and alkaline earth aryl and alkoxide cage compounds obtained from (partial) abstraction of halide.^{2,38,39,42–44} Depending on the bulk of the R group on the alkoxide or aryloxy reagent and the nature of the alkali metal and the solvent of crystallization, different structures were achieved.^{36,37,43,44} In this context, we have also used calixarenes, which can be understood as cyclic polyphenols, to obtain lithium polyaryloxides.^{22,23,37,40} This straightforward access to mixed metal aryl- and alkoxides inspired us to use this approach, replacing alkaline earth metal halides by chromium dihalides as starting compounds due to their better solubility and in spite of the sensitivity of such compounds to humidity.⁴⁵

Very similar to a compound described by us, $[\text{Ca}(\text{OPh})_8\text{Li}_6(\text{THF})_6]$,⁴² the literature reports on a Cr(II) compound,



namely, $[\text{Cr}(\text{OPh})_5\text{Li}_3(\text{THF})_3]_2$, **A** (Figure 1), described by Edema et al.⁴⁶

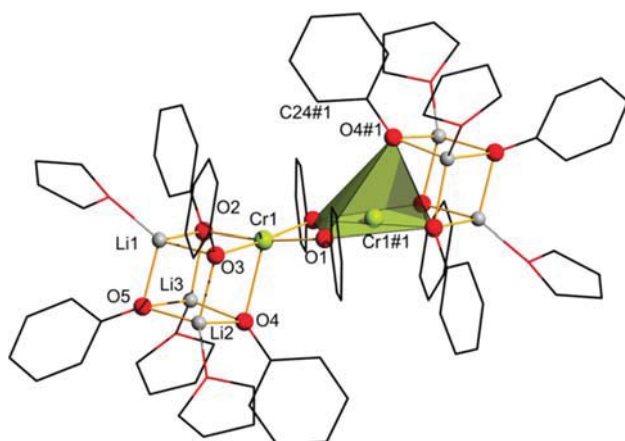


Figure 1. Molecular structure of chromium(II) complex (**A**) measured at 150 K.⁴⁷

We were intrigued by this structure, expecting it to be easily oxidized yielding new Cr(III) species which are otherwise not available by direct synthesis from Cr(III) salts and reactions with phenolates. Indeed, the known species of Cr(III) clusters and aryloxy ligands are based on substituted phenolates,^{46,48–53} while unsubstituted Cr(III) phenolates are unknown to the best of our knowledge.

In this contribution, we will introduce a new access to synthesize a series of unsubstituted phenoxides of Cr(III) by systematically increasing the number of chromium ions in the aggregate upon modifying the ratio of CrCl_2 to LiOPh and the amount of water and/or LiOH in the reaction mixture. We can thus obtain dinuclear, trinuclear, tetranuclear, mixed metallic Cr(III) compounds as well as coordination polymers. The oxidation process is investigated in detail with deuterated reagents, and the magnetic properties of one compound will be discussed.

RESULTS AND DISCUSSION

The Starting Material $[\text{CrCl}_2(\text{THF})_2]_n$. Cr(II) chloride is often used as the starting material because it is quite soluble in THF,^{25,27,29,54,55} yet its structure was unknown. $[\text{CrCl}_2(\text{THF})_2]$ (**1**) was obtained by crystallization of dry chromium(II) chloride in dry THF and crystallizes in the triclinic space group $P\bar{1}$ (No. 2, Table S1). The asymmetric unit of **1** consists of half of one-half Cr(II) ion, one THF molecule, and one chloride ion. In **1**, the chromium ion is surrounded in a square planar arrangement by two chloride anions and two THF molecules in trans positions to each other (Figure 2). The chromium ion is furthermore surrounded by two additional chloride ions, one from each neighbor entity in a one-dimensional (1-D) chain structure. Two chloride ions Cl1 and Cl1#1 are thus acting as bridging anions, directly connecting to the next metal ions in a chain (Figure 2), yielding a bond valence sum (BVS)⁵⁶ of 1.87. This low value confirms the sensitivity of **1** toward air and humidity, which immediately leads to the decomposition of the light green crystals into a pink powder.

The distance Cr1–O1 is 2.067(1) Å, the distances Cr1–Cl are 2.4131(5) Å and 2.8923(5) Å for Cl1 and Cl1#2. The angle O1–Cr1–Cl is close to 90°, while the angles Cl1–Cr1–Cl1#2

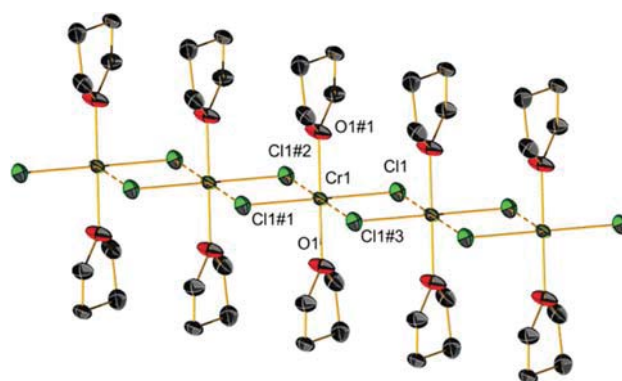


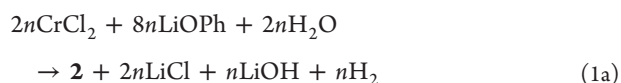
Figure 2. View of the molecular structure of **1** in a chain; 90% of probability, H atoms are omitted for clarity; #1: $2 - x, -y, 2 - z$; #2: $x - 1, y, z$; #3: $3 - x, -y, 2 - z$.

(96.29(1)°) and Cl1–Cr1–Cl1#3 (83.71(1)°) are far away from the ideal value for an octahedron. Cr(II) is known to have a Jahn–Teller effect,^{57–65} and in the case of **1**, the distortion along the Cr...Cl1#1 bond corresponds to the Jahn–Teller distortion $T\otimes e_g$.

The packing of the compound aligned along the *a*-axis (Figure 3) shows no interactions between the chains. Compared to pure CrCl_2 , with a Cr–Cl distance of 2.374 Å, in **1**, the Cr–Cl bonds are longer due to the coordination by THF. This can be conceived as a “cutting out” process using THF as scissors on CrCl_2 (as previously described by us for BaI_2).^{66,67} Indeed, during the solvation, the short contacts between the polymeric chains are replaced by coordination with THF, and this loss of short contacts increases the distance between the chains, as highlighted in a comparison in Figure 3.

Reaction of the solution of **1** with LiOPh under extremely dry conditions yields the expected blue solution from which single crystals of **A** were obtained and confirmed by measuring the single crystal structure at 150 K,⁴⁷ essentially confirming Edema et al.⁴⁶ In the following, we studied the reaction outcomes using different ratios of CrCl_2 to LiOPh and water and/or LiOH.

A First Coordination Polymer $[\text{Cr}_2(\mu_3\text{-OPh})_2(\mu\text{-OPh})_6(\mu\text{-OH})(\mu_3\text{-Li})_4(\mu_3\text{-Cl})_2\text{Li}(\text{THF})_6]_n$. Upon reaction of CrCl_2 with 4 equiv of LiOPh and water, a 1-D coordination polymer $[\text{Cr}_2(\mu_3\text{-OPh})_2(\mu\text{-OPh})_6(\mu\text{-OH})(\mu_3\text{-Li})_4(\mu_3\text{-Cl})_2\text{Li}(\text{THF})_6]_n$ (**2**) was obtained. A possible second reaction equation (eq 1b) leads to in a first step the formation of **A** as a nonisolated intermediate compound. Both reaction schemes are in principle possible as LiCl is slightly soluble under the given conditions, while the experimental observation shows the initial formation of a blue solution, indicating the formation of **A**. The solution turns green to yield **1** only upon contact with water when filtering through a nondried frit. The contact with water was short, and the substitution of chloride by phenoxide was incomplete.



Compound **2** crystallizes in the monoclinic space group $P2_1/n$, and its monomeric building block is composed of

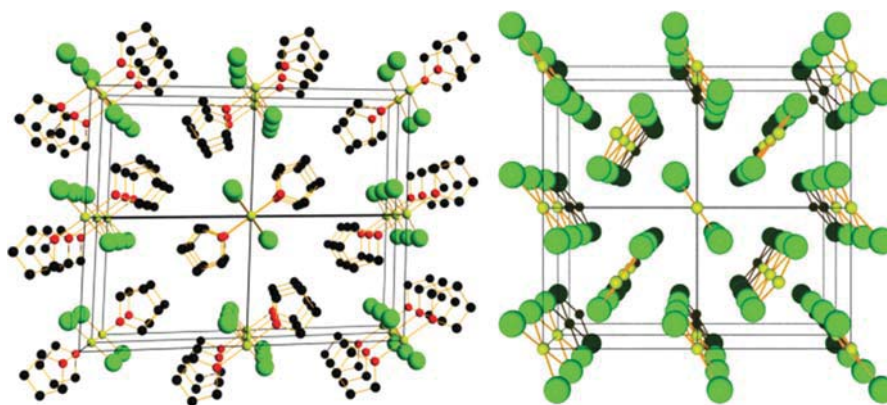


Figure 3. View of the molecular structures of **2** along the *a*-axis; H atoms are omitted for clarity (left) and pure CrCl_2 along the *c*-axis (right)⁶⁷ (color code: light green: Cr, green: Cl, red: O, black: C).

$(\text{THF})_6\text{Li}_5\text{Cr}_2(\text{OPh})_8(\text{OH})\text{Cl}_2$ units, which are connected via chloride atoms (Cl1 and Cl2#2) by the bridging lithium ions Li5 and its symmetry equivalent (Figure 4). The coordination

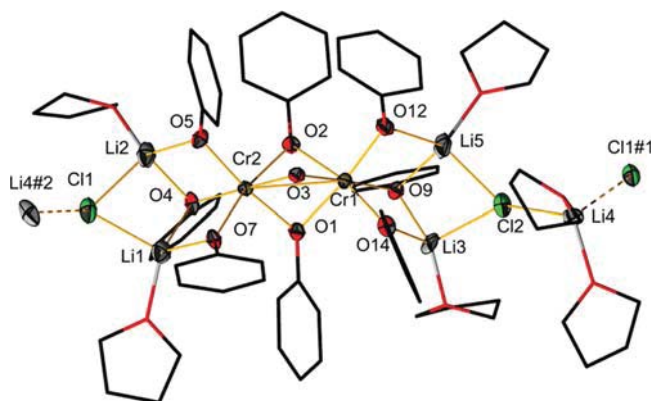


Figure 4. Molecular view of monomeric unit of **2**, 50% of probability, #1 = $x - 0.5, 0.5 - y, z - 0.5$; #2 = $0.5 + x, 0.5 - y, 0.5 + z$; H atoms are omitted for clarity.

sphere of Li5 is completed by two THF molecules. In the monomer, two chromium ions are connected by two bridging phenoxides with O1 and O2 and an oxygen atom O3 of a hydroxide ligand. Compared to **A**, in which only two OPh-groups bridge the two chromium ions, there are three bridging ligands in **2**. Each chromium atom is also connected to three

phenoxides O4, O5, and O6 for Cr1 and O7, O8, and O9 for Cr2, which act as bridging ligands to two lithium ions, in a way that each lithium ion connects with two phenoxides. In this way, Cr1, Li1, Li2 and O4, O5, O6 as well as Cl1 on one side, and Cr2, Li2, Li3, O7, O8, O9, and Cl2 on the other side, form an open heterocubane structure as compared to the complete cubane moieties observed in the structure of **A**. The “missing” lithium ion Li5 has formally “folded out” of the heterocubane and acts as bridging link between the monomers, yielding a 1-D motif. In total, comparing **2** to **A**, an incomplete substitution as well as an oxidation reaction has occurred in **2**.

The distance between the two chromium ions is $2.757(2)$ Å, and the octahedra around the chromium ions are connected via a common face. The metal–metal distance falls into typical values for a Cr–Cr contact (graph S1, CSD version 5.36 (November 2014), 91 entries between 2.751 and 2.80 Å on 1060 answers), and a Fourier map of **2** confirms this, showing electron density between the two Cr(III) ions (Figure S11). The BVS method gives value of 3.01 and 2.98. These two values indicate clearly the oxidation state +III, which were validated also by XPS analysis (Figure S2). The length of a monomeric unit is ca. 11.5 Å.

There are two face-sharing octahedra around the chromium ions (confirming the metal–metal bond), which are fused via an edge to the tetrahedra around the lithium ions Li1 and Li2, respectively Li3 and Li4. The two tetrahedra around the lithium ions Li1 and Li2 are also linked via a common edge, as is the case for Li3 and Li4. The 1-D strand representation further

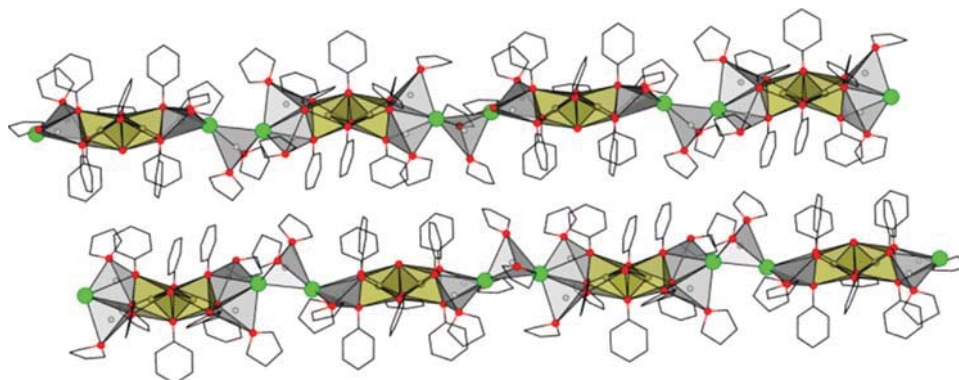
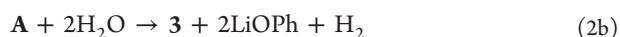
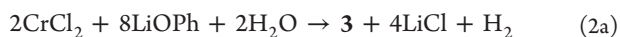


Figure 5. Molecular view of **2** in polyhedral mode; C-bound H atoms are omitted for clarity. (Color codes: green: Cl, yellow: Cr, gray: Li, red: O, black: C.)

illustrates that the individual chains are slightly polar in that the chloride ions and the tetrahedra around Li5 all point to the same side of the polymer chain. This is however compensated by the orientation of the neighbor chains as shown in Figure 5.

This first result of an unprecedented Cr(III) coordination polymer initiated us to investigate the substitution process of chloride by phenoxide in more detail, especially since the structure of compound 2 seemed to us as an intermediate structure to simpler cluster compounds with complete chloride substitution. Indeed, the stoichiometric ratio of 1:4 between CrCl_2 and LiOPh should be sufficient for complete anion substitution. We therefore repeated the reaction by adding 2 equiv of water on purpose in the reaction mixture.

The Dinuclear Chromium Compound $[\text{Cr}(\text{OPh})_4(\mu\text{-OH})\text{Li}_2(\text{THF})_3]_2$. The reaction of CrCl_2 with 4 equiv of LiOPh yields first **A** in a blue solution, and upon addition of 2 equiv of water, the green Cr(III) compound is obtained as $[\text{Cr}(\text{OPh})_4(\mu\text{-OH})\text{Li}_2(\text{THF})_3]_2$ (**3**). In addition, 4 equiv of LiCl are immediately precipitated as white-gray powder, as determined by gravimetry and IR.



In contrast to **2**, compound **3** is a finite, dinuclear chromium complex in which all chloride ions have been substituted. Each transition metal ion is surrounded by four phenoxide and two hydroxide ligands in an octahedral fashion (Figure 6). In

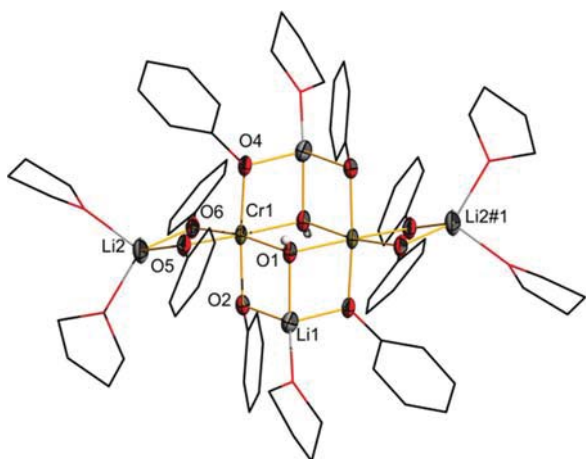


Figure 6. Molecular view of complex **3**; 50% of probability; #1 = $-x, -y, 1 - z$; H atoms except for OH groups are omitted for clarity.

comparison to **2**, the distance between the two chromium ions is much longer with ca. 3.18 Å. Indeed, the two chromium atoms are now connected via a common edge, formed by the two hydroxyl groups, and not via a common face as in **2**. For each chromium ion in **3**, the two phenoxide units lying in the equatorial plane together with the OH-groups are connecting further to a lithium ion, whose coordination sphere is completed by two THF molecules. The axial phenoxide ligands are also connecting each to a lithium ion. The coordination sphere of the latter is completed by one of the hydroxide moieties and one terminally bound THF molecule. Alternatively, the core structure of **3** can be described as based on two incomplete heterocubane units made of one lithium and two chromium ions as well as four O atoms on the corners, and

fused via a common Cr_2O_2 face. The BVS confirms the oxidation state of +III with 2.92.

The heterocubane moieties in **3** resemble the ones in **2**, except that the chloride ion has been replaced by OPh. The structural motif with two chromium ions bridged by hydroxide ligands is reminiscent of the condensation reactions of chromium hydrate hydroxide complexes from which water molecules are eliminated.

In order to better understand the oxidation of Cr(II) to Cr(III) and to verify the formation of hydrogen, we decided to investigate this mechanism in more detail.

Study of the Oxidation Process of Chromium(II). Cr^{2+} is in principle able to promote the dissociation of water in H^+ and OH^- due to its Lewis acidic properties. On the basis of its redox potential ($\text{Cr}^{3+}/\text{Cr}^{2+} -0.407 \text{ V vs ENH}$), Cr(II) is able to reduce protons following the reaction: $2\text{Cr}^{2+} + 2\text{H}^+ \rightarrow 2\text{Cr}^{3+} + \text{H}_2$. Yet, under exclusion of oxygen, Cr(II) can be produced in water by reduction with zinc and is kinetically stable in the gray-blue solution over several hours if not days.⁶⁸ In our experiments, the reactions are carried out in THF, and if the redox process takes place in THF with water present, hydrogen production should be observed. In order to observe the gas production, the following experiment was carried out: The solution of chromium(II)-complex **A** is introduced into a three-necked Schlenk flask equipped with a long needle to introduce a mixture of water and THF (Figure 7). Furthermore, an NMR

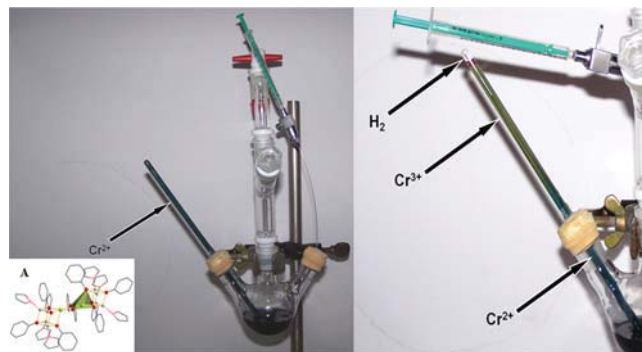


Figure 7. (Left) Assembly for the detection of gas production, before the addition of water; (right) after addition of water and THF into the tube, the solution turns green and a gas is produced.

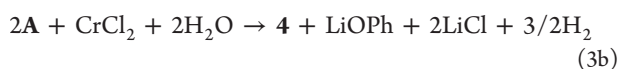
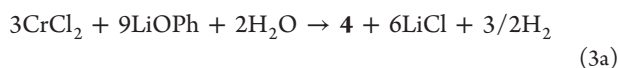
tube to collect the formed gas is connected to the glassware and plunges into the solution such as to be filled completely with the solution. The setup was tested for its joints maintaining good vacuum and good gas protection to avoid oxidation from other sources such as air. The injection of water is made via the syringe directly into the NMR tube at its closed end part. Apparition of gas bubbles and a color change of the solution, starting from the top and migrating down, are consequently observed (Figure 7, right). The mass spectrometric analysis of the collected gas showed that hydrogen was indeed formed. Determination of gas volume is however impossible due to the solubility of H_2 in THF.⁶⁹ The measured volume corresponded thus only to ca. 1/3 of the expected volume. The repeat experiment with deuterated water, only showed the formation of hydrogen even after heating, and no deuterium was found. We therefore tested a second hypothesis for the oxidation of chromium involving THF. We prepared the Cr(II) solution in deuterated THF and added water with a syringe. The mass analysis of the formed gas showed again only the formation of

hydrogen gas. This leads to the assumption that THF is not producing the gas in the oxidation progress since no deuterium could be observed. A third hypothesis proposes a participation of the hydrogen atoms of phenol as the last hydrogen source in the system. Indeed, the solid state structure of complex **A** shows some possible interactions between the square pyramidally coordinated Cr(II) ions and a hydrogen atom of a phenyl ring pointing over the vacant coordination site of the cation. In order to verify this hypothesis, LiOPh-*d*₅ was prepared by lithiation of phenol-*d*₆ with *n*-butyl lithium, showing no signals for aromatic H atoms in ¹H NMR. This compound was then added to chromium(II) chloride for the formation of the deuterated complex. Upon addition of water, the mass analysis of the formed gas showed again only the formation of hydrogen gas. This leads to the conclusion that phenoxide alone is also not responsible for hydrogen formation in the oxidation progress since no deuterated gas could be observed. The last hypothesis is thus a cumulative participation of THF, phenoxide, and water by scrambling of H/D atoms. We prepared two samples of **A** with LiOPh-*d*₅ in solution in THF-*d*₈ and added to the first sample water and to the second one deuterated water. For both samples, the mass analysis of the formed gas showed the presence of H₂, HD, and D₂. The detection of H₂ and HD in the second experiment can be due to the sample preparation of LiOPh-*d*₅. Indeed, LiOPh-*d*₅ was prepared in nondeuterated THF, isolated by drying and subsequent redissolving in THF-*d*₈. The NMR spectrum of the LiOPh-*d*₅ in THF-*d*₈ did not show any proton signals, but given the sensitivity of the method, the presence of hydrogen cannot be excluded. Finally, the hypothesis of aromatic hydrogen exchange is validated by the ¹H NMR spectrum of the fully deuterated complex **A** (Supporting Information). Indeed, on the spectrum taken after addition of water to the THF-*d*₈ solution of the deuterated complex **A**, a signal at 6.36 ppm (CD₂Cl₂ as solvent) appears. Indeed, the clues obtained with these spectra point all toward the participation of the hydrogen atom in para position of the phenoxide.

One should also mention that it is possible that samples inside the mass spectrometer can exchange D with H by interactions with the instrument walls, hence leading to hydrogen detection when only deuterium is expected.

In order to study the influences of the relative amounts of reactants and the formation of further possible cluster compounds, reactions were carried out in different ratios of Cr(II) to LiOPh.

The Trinuclear Chromium Complex [Cr₃Li₃(OPh)₉(μ₃-OH)(μ₃-O)(THF)₆]. Reacting CrCl₂ with LiOPh in a ratio 1:3 and with a substoichiometric amount of water (eq 3a), the trinuclear Cr(III)-compound [Cr₃Li₃(OPh)₉(μ₃-OH)(μ₃-O)(THF)₆] (**4**) was obtained. The reaction path can also be described via the formation of **A** (eq 3b). Again, a precipitate of LiCl indicated that the reaction took place.



4 is again a molecular compound with no remaining chloride ligands and crystallizes in the cubic space group *I*-43*d*. The compound core is composed of three chromium ions in triangle arrangement connected to each other via edge-bridging phenoxide ligands and by two face-bridging oxygen atoms,

one of which stems from an oxide, the other from a hydroxide. To each chromium ion, a lithium ion is connected via two bridging phenoxide moieties, resulting in a distorted octahedral coordination of the transition metal cations. The tetrahedral coordination sphere of the lithium ions is completed by two THF molecules. The chromium ions are separated by 2.743(1) Å, and their coordination octahedra are connected two by two via a common face, both facts indicating metal–metal bonds. All three octahedra are connected by a common edge (O1–O7) (Figure 8). For compound **4**, the BVS method gives a

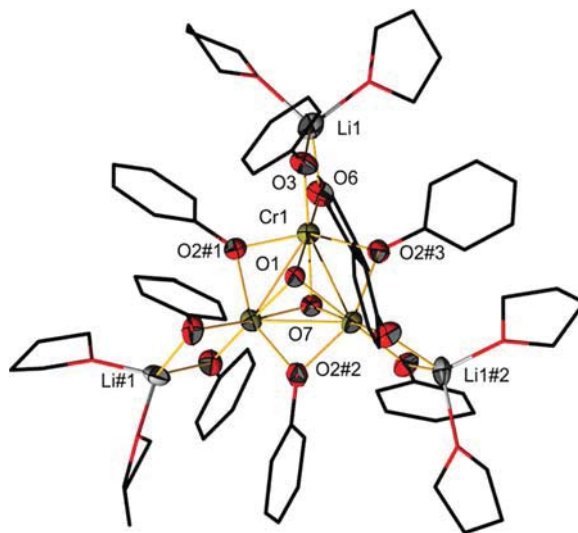


Figure 8. Molecular view of the complex **4**; 50% of probability, #1 = *z* – 0.5, 0.5 – *x*, 1 – *y*; #2 = 0.5 – *y*, 1 – *z*, 0.5 + *x*; some H atoms are omitted for clarity.

value of 3.03 for each transition metal ion, showing once again that oxidation to Cr(III) occurred. Thus, O1 and O7 are not identical, since we need a total charge of –3 for both oxygen atoms. That implies the presence of one hydroxide and one oxide as bridging ligands. As no hydrogen atoms are visible in the X-ray structure, in order to elucidate this problem, a detailed analysis of bond lengths and the geometry of the structure gives a clue to the identity of each, oxide and hydroxide. Thus, comparing the distances between the oxygen atoms and the centroids of the closest phenyl groups (4 Å for O1 and 4.2 Å for O7), the distances between the oxygen atoms and the centroids of the second phenyl group (5 Å for O1 and 5.4 Å for O7) and the angle O–O(Ph)–centroid (88° for O1 and 93° for O7), the phenyl groups around O1 are pointing toward O1. This inclination of the phenoxides toward the central oxygen atom O1 indicates the presence of a hydrogen atom. Furthermore, the distances Cr1–O1 of 2.033(4) Å are significantly longer than Cr1–O7 with 1.930(4) Å, underlining the assumption that O1 belongs to the hydroxide and O7 to the oxide.

This experiment, yielding compound **4**, showed the influence of water content relative to CrCl₂. If this ratio is such that Cr(II) is in excess, both hydrogen atoms of one water molecule are apparently abstracted to give the oxide anion. This is again similar to the condensation reactions observed on the way between Cr(OH)₃ and Cr₂O₃.⁷⁰

At this point of our investigations, we suspected the origin of the hydroxide groups being maybe also due to the presence of LiOH in the lithium phenoxide solution. In the following, we

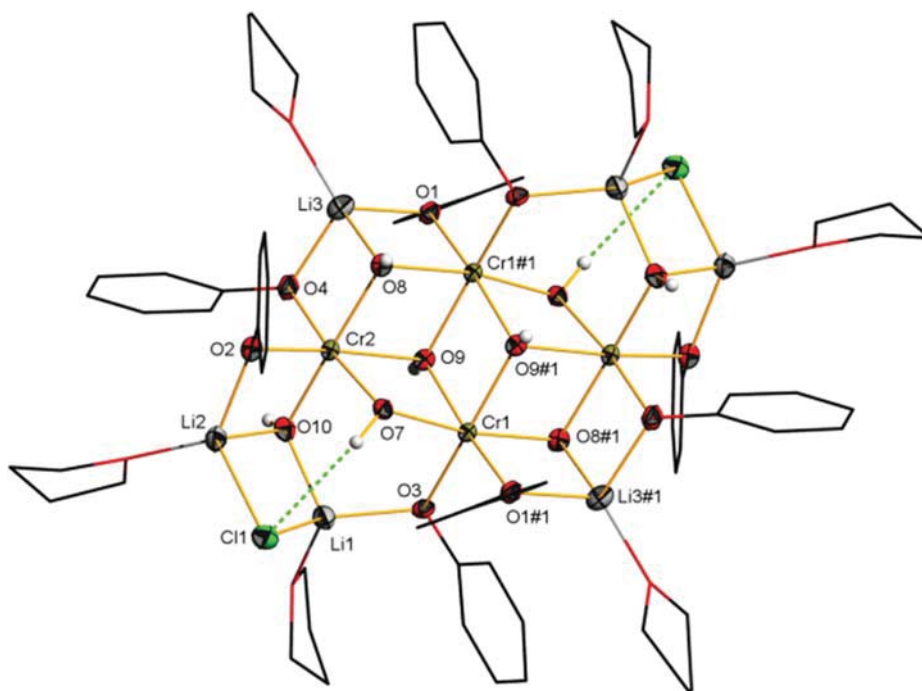
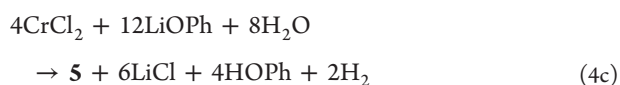
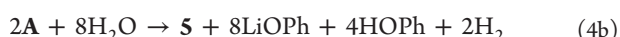
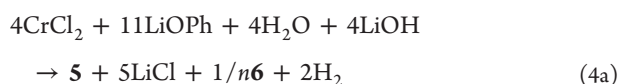


Figure 9. Molecular view of complex **5**; 50% of probability, #1 = 1 - *x*, 1 - *y*, 1 - *z*; H atoms except for OH, and THF molecules are omitted for clarity.

therefore carried out reactions by adding LiOH on purpose in addition to water. Although that LiOH is insoluble in THF, the next reaction yielded a new product rich in hydroxide groups.

The Tetranuclear Chromium $[\text{Cr}_4(\mu\text{-OPh})_8(\mu_3\text{-OH})_6(\mu\text{-OH})_2\text{Cl}_2\text{Li}_6(\text{THF})_6]\cdot 2\text{THF}$. The compound $[\text{Cr}_4(\mu\text{-OPh})_8(\mu_3\text{-OH})_6(\mu\text{-OH})_2\text{Cl}_2\text{Li}_6(\text{THF})_6]\cdot 2\text{THF}$ (**5**) is obtained when CrCl_2 is reacted with an excess of LiOPh and in the presence of LiOH and water. The reaction is best described by eq 4a, yet reaction pathways following eqs 4b and 4c are also proposed. We will see later why pathways 4b and 4c are less probable in the described case.



Compound **5** crystallizes in the triclinic space group $P\bar{1}$, the core consisting of four chromium(III) ions bridged by six hydroxide groups to give two face-sharing open heterocubane moieties similar as in **3**, but all with three chromium ions and four oxygen atoms on the corners (Figure 9). As water and CrCl_2 are used in equal molar amounts (in contrast to **4**), only hydroxide groups, but no oxide are observed. To each open cubane unit, one other open heterocubane is fused, forming each a LiCr_2O_4 unit. Such heterocubane type motifs are typical for condensation reactions in, e.g., hydroxides of octahedrally coordinated M(III) cations such as Al^{3+} and Cr^{3+} .^{71,72}

The chromium atoms are octahedrally coordinated by six oxygen atoms, four of which stem from hydroxide and two from phenoxide groups. The phenoxide groups as well as the hydroxide groups O7, O8, and O10 coordinate further to lithium ions, the latter of which are also coordinated by one

THF for Li3, and additionally by one chloride for Li1 and Li2. The hydroxide groups O9 and O9#1 form H-bonds to free THF, thus closing the outer shell of the structure and probably preventing further aggregation or condensation. Further, an intramolecular short contact between H7 and Cl1 of 2.5490(8) Å could be found. Cr1 is separated from Cr2 by 3.1496(6) Å, which is longer than in **4** as their octahedra are connected by one edge instead of a common face. Accordingly, Cr1#1 and Cr2 are distant by 3.0969(7) Å and are also connected by one edge like the octahedra of Cr1 and Cr1#1, in which the two chromium ions are separated by 3.1551(9) Å. The oxidation of the metal ion is validated by the BVS values of Cr1 and Cr2, which 2.96 and 2.95, respectively.

In a complex obtained by Edema, $[(\text{PhO})_{10}\text{Cr}_4\text{O}_3\text{Na}_4(\text{TMEDA})_4]$, only O^{2-} and no halide ions are found in the structure, yet the core $\text{Cr}_4\text{O}_3(\text{OPh})_{10}$ is similar to the core $\text{Cr}_4(\text{OPh})_8(\text{OH})_8$ of **6**, but less symmetric (Scheme 1).⁴⁶

As it can be seen from reaction scheme described in eq 4a, a second product can be isolated from this reaction, which is not possible following the reaction paths eqs 4b or 4c.

$[\{\text{Li}(\text{THF})\}_4(\text{OPh})_3\text{Cl}]_n$ - A Side-Product of the Synthesis of **5.** The compound $[\{\text{Li}(\text{THF})\}_4(\text{OPh})_3\text{Cl}]_n$, **6**, (Figure 10) has been obtained during our investigations as a side product to compound **5**. It also formed when we tried to resynthesize compound **7**, or more generally, when LiOPh was used in large excess with respect to the transition metal halide. In the case of **5**, its formation can be accounted for in eq 4a. Examples of lithium phenoxide complexes with THF are limited to the best of our knowledge to two structures, one cubane⁷³ and one hexameric structure.⁷⁴ A third example of a possible side-product structure is the open cubane structure characterized by Pink in 1994.⁷⁵

Compound **6** crystallizes in the triclinic space group $P1$, forming a 1-D coordination polymer composed of a distorted heterocubane core formed by four lithium ions, three phenoxide ligands, and one chloride ion. Three of the four

Scheme 1. Comparison of the Cores of $[(\text{PhO})_{10}\text{Cr}_4\text{O}_3\text{Na}_4\text{TMEDA}]_4$ ⁴⁶ (Top Left) and **Compound 5**

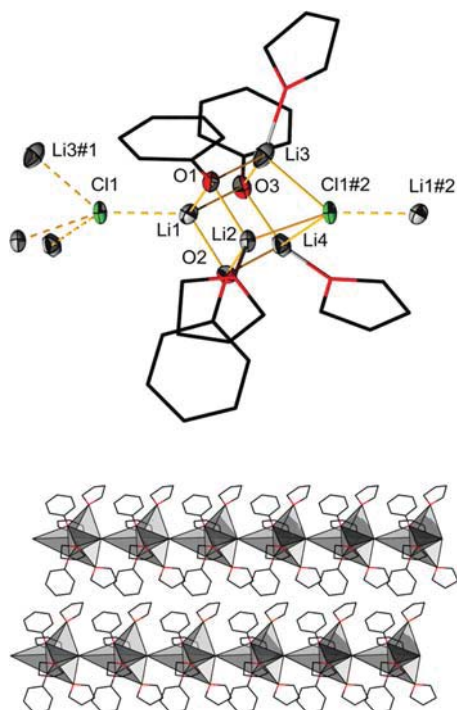
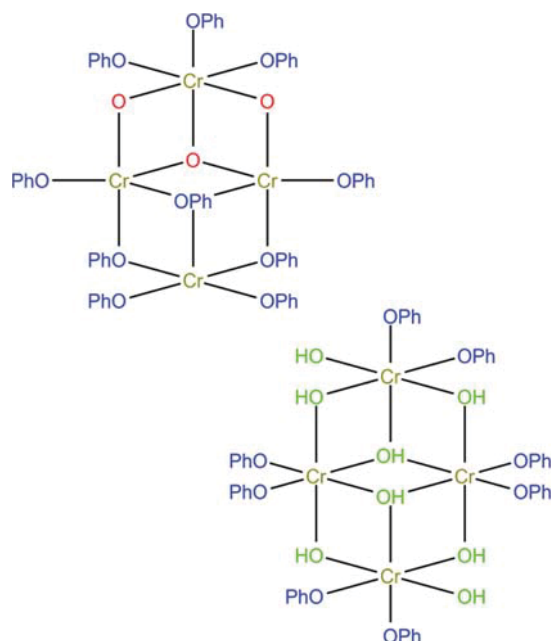


Figure 10. Molecular view of the complex **6**; 50% of probability, #1 = $x - 1, y, z$; #2 = $x + 1, y, z$; (top); molecular view of **6** in polyhedral mode (bottom); H atoms are omitted for clarity.

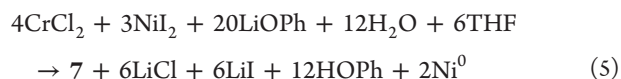
lithium ions are connected to two phenoxide ligands (Li2–O1 1.90(1) Å, Li2–O2 1.97(2) Å, Li3–O1 1.91(1) Å, Li3–O3 1.93(2) Å, Li4–O2 1.95(1) and Li4–O3 1.92(1) Å) and to the chloride ion (Li2–Cl1#2 2.42(1) Å, Li3–Cl1#2 2.43(1) Å, Li4–Cl1#2 2.48(2) Å), their coordination sphere being completed by one THF molecule (Li2–O4 1.90(1) Å, Li3–O5 1.90(1) Å, Li4–O6 1.89(1) Å). The last lithium ion is coordinated to three phenoxide moieties (Li1–O1 1.91(2) Å,

Li1–O2 and Li1–O3 1.94(1) Å) and to the chloride ion of the next cubane unit (Li1–Cl1 2.42(1) Å). This latter bond produces the polymeric chain structure of **3**. The cubane core is distorted on the chloride position with Li–Cl1#1–Li angles of 69.3(5)°, 69.2(5)°, and 71.0(5)°.

These crystals were sensitive to moisture, and we are not able to handle them for further analysis without decomposition.

Motivated by the different Li–Cr compounds which we obtained so far, we challenged the trimetallic reaction in the following.

The Trimetallic Compound $[\text{NiCr}_4(\mu\text{-OPh})_{12}(\mu_3\text{-OH})_8\text{Li}_6\text{Cl}_2(\text{THF})_6]\cdot 2\text{THF}$. In order to achieve a trimetallic complex, we reacted CrCl_2 and NiI_2 in THF with an excess LiOPh in the presence of water (eq 5). Indicated already by the standard redox potentials of the two transition metal ions, a redox process occurs immediately also in THF, leading to the precipitation of metallic nickel, while the Cr(II) is oxidized to Cr(III) . Despite these circumstances, one single crystal of $[\text{NiCr}_4(\mu\text{-OPh})_{12}(\mu_3\text{-OH})_8\text{Li}_6\text{Cl}_2(\text{THF})_6]\cdot 2\text{THF}$ (**7**) could be found in the mother liquor—a reaction which we unfortunately could not reproduce to date. Nevertheless, we wish to share the crystal structure of this exciting compound, which crystallizes in the triclinic space group $P\bar{1}$ (Figure 11).



The structure of **7** is built up around one central nickel ion Ni1 surrounded by six hydroxide moieties O1, O2, O3 and their symmetry equivalents. Connected to this core are two units similar to **3**, one of which is represented in purple on Figure 11 (bottom). These two entities are connected by the Ni1 , Li1, Cl1 and their symmetry equivalents. Cl1 connects the two units by coordination to the outer lithium ions of each moiety, namely, Li2 and Li4. This Cl1 is also connected to Li1, which connects the two units by binding with O1, O1#1 of the two hydroxide and O5 and O10#1 of the two phenoxide units, resulting in a pentacoordination for Li1.

Similar as in **3**, each chromium ions is surrounded by three phenoxides (O5, O6, O7 for Cr1 and O8, O9, O10 for Cr2) and three hydroxide ligands (O1, O2, and O4 for Cr1 and O2, O3, and O4 for Cr2) forming an octahedron. The two chromium atoms are connected with a common edge, the latter bridging two octahedra. For each chromium ion, two phenoxides are in the equatorial plane, both are connected to a lithium ion, whose coordination sphere is completed by one THF molecules and Cl1 (or Cl1#1). The equatorial coordination sites of the two chromium ions are completed by two bridging hydroxide anions. The axial phenoxides O7 and O8 are also connected to Li3, which completes its coordination sphere with one of the hydroxide moiety O4 and one THF molecule. The three hydroxides O1 to O3 are connected to Ni1. The four chromium and the nickel ions possess octahedral coordination, the lithium Li2, Li3, and Li4 are tetrahedrally coordinated, Li1 is pentacoordinated, and all these polyhedra are connected together by edges.

Magnetic Properties. While all compounds, in particular **7**, are interesting from a point of view of magnetism, we could only obtain compound **4** in sufficient amounts and purity to obtain a meaningful result. An interesting characteristic of this compound **4** is the C3 axis passing through the oxide and the hydroxide ions, dividing the compound into three equivalent parts. Paramagnetic Cr(III) ions are able to couple anti-

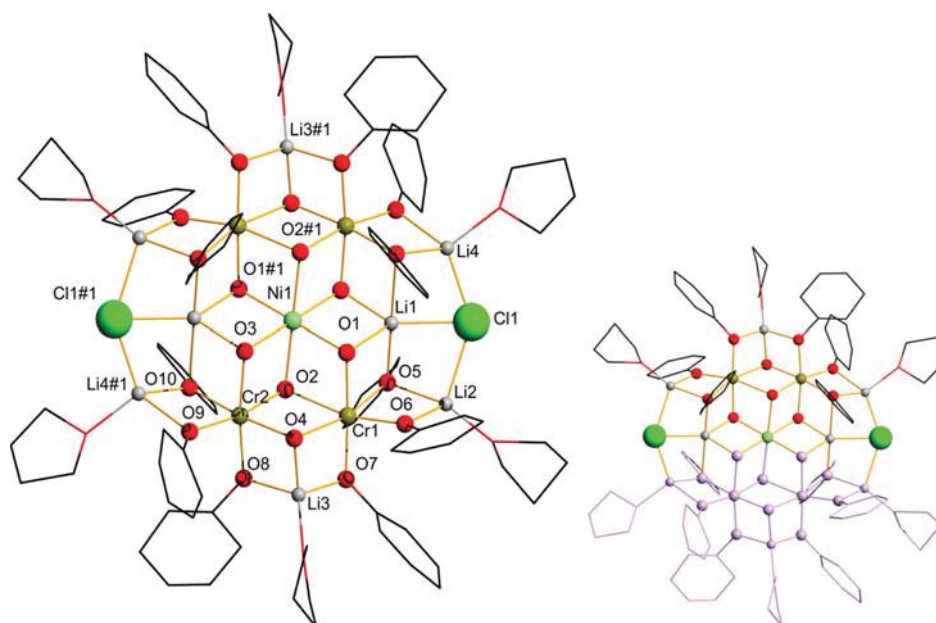


Figure 11. Molecular view of $7 \#1 = 1 - x, 1 - y, 1 - z$ (left); with in purple the skeleton similar to **3** (right); H atoms and free THF are omitted for clarity.

ferromagnetically.^{76,77} The question, which arose thus for compound **4**, is if there is a spin frustration between the three ions, leading to molecular magnetism.

Magnetic measurements have been performed in collaboration with Prof. Karl Wiegart and Prof. Dr. Phalguni Chaudhuri at the Max Plank Institute from Mülheim an der Ruhr. Compound **4** was measured in a SQUID magnetometer with a 1 T external field at varying temperature. Figure 12

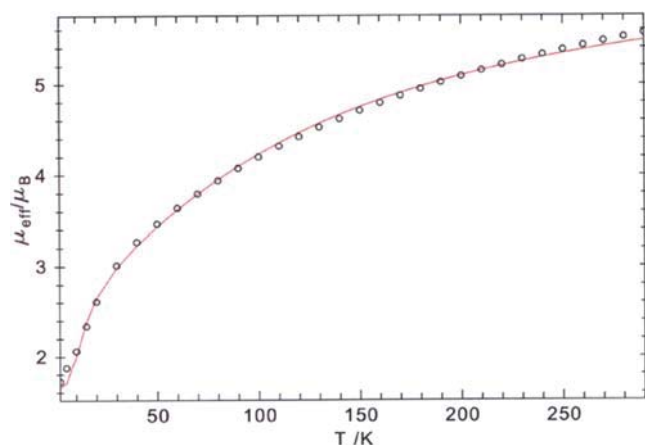


Figure 12. Magnetic measurement of complex **4**.

shows the result of this measurement with a break in the curve at ca. 30 K. The fitting of this measurement gave us a two “J”-model to describe the exchange pathways. The spin Hamiltonian used is

$$H = -2J_{12}(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_1 \cdot \vec{S}_3) - 2J_{23}(\vec{S}_2 \cdot \vec{S}_3)$$

with J_{12} and J_{13} equal to -11.8 cm^{-1} and J_{23} to -19.3 cm^{-1} for g_1, g_2 , and g_3 equal to 1.95. Hence, we do not observe the same J for all of the chromium(III) ions present in **4**. We hypothesize that a breakdown of the symmetry occurs at low temperature with a loss of the C3. Indeed, such a case has been described for

another “triangular” Cr-structure, namely, $[\text{Cr}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]\text{Cl}$ (**B**), which Figgis and Robertson characterized by X-ray structure determination in 1965.⁷⁸ In 1972, Dubicki and Day studied and published the electronic spectrum of **B**,⁷⁹ the absorption spectrum was measured at 4.2 and 295 K, and the conclusion was made that **B** loses its C3 axis at low temperature. A similar phenomenon was found with a copper(II) triangle. In this case, a Jahn–Teller distortion occurs, and at very low temperature, the unpaired electron orbital is found to localize on only one of the three nuclei of the Cu_3 -trimer, with concomitant loss of the 3-fold symmetry.^{79,80} These two examples found in the literature reinforce the idea that the breakdown on the magnetism curve can be due to the loss of the 3-fold rotation axis at low temperature.

CONCLUSIONS

In conclusion, we identified the crystal structure of the starting material using CrCl_2 in THF. Its reaction with the unsubstituted LiOPh in the presence of water gave easy access to mixed-metal Li–Cr aggregates and one coordination polymer and oxidation of Cr(II) to Cr(III). The coordination polymer **2** was obtained as an intermediate on the way to the dinuclear chromium compound **3**. Variation of the ratio of CrCl_2 to LiOPh while using the same molar amounts of water with respect to chromium led to the coordination polymer, the dinuclear, and the tetranuclear compounds **2**, **3**, and **5**. The trinuclear species was obtained when water was used in a substoichiometric ratio with respect to CrCl_2 . This led to a full deprotonation of one of the water molecules in **4**. This approach also allowed the isolation of a trimetallic pentanuclear compound, **7**.

Metal–metal bonds are found in the coordination polymer **2** and the “triangular” complex **4**, based on face-sharing coordination octahedra around the Cr(III) ions. The other structures possess edge-sharing polyhedra and do not afford metal–metal bonds.

We have determined the crystal structure of a classical starting compound for chromium complexes and shown that

the synthesis of a new class of chromium(III) complexes is possible by using the reactivity of a chromium(II) complex versus water. The process of the chromium oxidation is not yet completely understood, but participation of the full complex is definitely necessary for this reaction, and we have shown that water is reduced to hydrogen during this process. This production of gas has been demonstrated by visual and analytical methods. We have also identified a new side-product of metal aryloxide complex; this compound is the first example of lithium phenoxide compound containing chloride ion.

All in all, the results show that multinuclear complexes of Cr(III) with unsubstituted phenoxide ligands can easily form during oxidative substitution reactions with LiOPh. We are currently exploring the reactivity of other transition metal halides with aryloxides and alkylloxides and the possibility to form mixed-metal cage compounds and to form the corresponding oxides from the latter.

METHODS

All experiments were carried out under an inert argon atmosphere, using the Schlenk technique.⁸¹ THF was dried in a drying unit under argon and stocked on molecular sieve; other solvents were bought dried and stocked on molecular sieve. The BVS calculations were performed with Valist⁸² or on a web application.⁸³

For single-crystal measurements, a Stoe IPDS IIT, equipped with monochromated Mo K α radiation (0.71073 Å) was used. IR and NMR spectra were recorded on a Bruker Tensor 27 and on a Bruker AM360, respectively. Magnetic measurement was conducted on a SQUID magnetometer (Quantum Design) with a 1.0 T external field by Prof. Dr. Karl Wieghardt and Prof. Dr. Phalguni Chaudhuri from the MPI für Bioanorganische Chemie, Mülheim an der Ruhr (Germany). XPS measurements were performed by Prof. Philipp Aebi and Dr. Gunnar Garnier from the University of Fribourg.

[Cr(μ -OPh)(μ_3 -OPh)₄Li₃(THF)₃]₂ **A**: CrCl₂ (0.5 g, 4 mmol) was dried under a vacuum at 400 °C during 1 h and added to a solution of PhOLi (24 mmol) in THF (24 mL, 1.0 M). After the solution was stirred for 30 min under reflux, the color of the mixture was deep blue. The solvent was concentrated in a vacuum; afterward the solution was kept at -24 °C. Deep blue crystals of **A** were obtained as described in the literature.²⁵ Our single crystal analysis at 150 K gives $a = 12.410(2)$ Å, $b = 12.994(2)$ Å, $c = 15.053(2)$ Å, $\alpha = 98.43(1)^\circ$, $\beta = 106.211(9)^\circ$, $\gamma = 116.731(8)^\circ$, $P1$.²⁶

[CrCl₂(THF)₂] **1**: CrCl₂ (0.10 g, 0.8 mmol) was dried for 1 h under a vacuum at 350 °C and then dissolved in 30 mL of dried THF, heating to reflux under magnetic stirring during 1 h. Afterward the solution was filtered under argon, and the solution was concentrated and kept at room temperature. Green single crystals of **1** suitable for X-ray analysis grew in 2 weeks with a yield of 10%. No IR or elemental analysis were possible due to the extreme sensitivity of the compound.

[Cr₂(μ_3 -OPh)₂(μ -OPh)₆(μ -OH)(μ_3 -Li)₄(μ_3 -Cl)₂Li(THF)₆]_n **2**: CrCl₂ (0.51 g, 4.17 mmol) was dried for 2 h under a vacuum at 300 °C and then dissolved in 50 mL of THF, heating to reflux under magnetic stirring during 1 h. Afterward 27 mL (6.5 equiv) of a solution of lithium phenoxide 1.0 M in THF was added slowly, and the mixture was heated to reflux under magnetic stirring during 30 min. The solution was filtrated, concentrated, and 20 mL of heptane was added, and the mixture was left at room temperature. Green single crystals of **2** suitable for X-ray analysis grew in a few weeks. ¹H NMR: (360 MHz, THF-*d*₈): 6.91 ppm (s, 2H, OPh), 6.58 (br, 2H, OPh), 6.37 (br, 1H, OPh), 3.58 (s, THF OCH₂), 1.73 (THF CH₂); ¹³C NMR (360 MHz, THF-*d*₈): 129.65 (OPh), 119.29 (OPh), 115.24 (OPh), 68.41 (THF), 26.16 (THF); XPS: $E_{B(Cr)} = 577.95$ eV (Cr 2p_{3/2}).⁸⁴

[Cr(OPh)₄(μ_3 -OH)Li(THF)₃]₂ **3**: CrCl₂ (0.51 g, 4.17 mmol) was dried for 2 h under a vacuum at 300 °C and then dissolved in 50 mL of THF, heating to reflux under magnetic stirring during 1 h. Afterward 27 mL (6.5 equiv) of a solution of lithium phenoxide 1.0 M in THF was added slowly, and the mixture was heated to reflux under magnetic stirring during 30 min. The solution was filtrated, concentrated, and 20

mL of heptane was added, and the mixture was left at room temperature. Green single crystals of **3** suitable for X-ray analysis grew in a few weeks.

[Cr₃(μ_3 -OH)(μ_3 -O)(OPh)₉Li₃(THF)₆] **4**: CrCl₂ (0.51 g, 4.17 mmol) was dried for 2 h under vacuum at 300 °C and then dissolved in 50 mL of THF, heating to reflux under magnetic stirring during 1 h. Afterward 25 mL (6 equiv) of a solution of lithium phenoxide 1.0 M in THF was added slowly, and the mixture was heated to reflux under magnetic stirring during 30 min. The solution was filtrated, concentrated, and 20 mL of heptane was added, and the mixture was left at room temperature. Green single crystals of **4** suitable for X-ray analysis grow in some weeks.

[Cr₄(μ -OPh)₈(μ_3 -OH)₆(μ -OH)₂Cl₂Li₆(THF)₆]₂THF **5** and [Li(THF)]₄(OPh)₃Cl]_n **6**: CrCl₂ (0.2 g, 1.6 mmol) was dried for 2 h under a vacuum at 300 °C and then dissolved in 50 mL of THF, heating to reflux under magnetic stirring during 1 h. Afterward 18 mL (ca. 12 equiv) of a solution of lithium phenoxide 1.0 M saturated in solid LiOH in THF was added slowly, and the mixture was heated to reflux under magnetic stirring during 30 min. The solution was filtrated, concentrated, and 20 mL of heptane was added, and the mixture was left at room temperature. Green single crystals of **5** and colorless crystals of **6** suitable for X-ray analysis grew in a few weeks. Compound **6** was also identified as a coproduct in many reactions in which we used LiOPh in large excess versus the metal halide.

[NiCr₄(μ -OPh)₈(μ_3 -OH)₁₂Cl₂Li₆(THF)₆]₂THF **7**: CrCl₂ (0.16 g, 1.3 mmol) and NiI₂ (0.33g, 1.05 mmol) were dried for 1 h under a vacuum at 300 °C and then dissolved in 20 mL of THF, heating to reflux under magnetic stirring during 1 h. Afterward 25 mL (~10.5 equiv) of a solution of lithium phenoxide 1.0 M in THF was added slowly, and the mixture was heated to reflux under magnetic stirring during 30 min. The solution was filtrated, concentrated, and 20 mL of heptane was added, and the mixture was left at room temperature. Green single crystals of **7** suitable for X-ray analysis grew in a few weeks.

Oxidation Tests. **A** in THF-*d*₈: **A** was dried under a vacuum at 150 °C during 1 h and redissolved in THF-*d*₈ (99.5% and dried over molecular sieves).

A with OPh-*d*₅: phenol-*d*₆ (99%, 1 g, 1 mmol) was dried under a vacuum at 120 °C during 2 h and put in suspension in hexane. *n*-BuLi on solution in hexane was slowly added at -70 °C (1 mmol) at kept on stirring for 2 h. Afterward hexane was removed and LiOPh-*d*₅ was put on solution in dry THF. CrCl₂ (21 mg, 0.17 mmol) was dried under a vacuum at 400 °C during 1 h and added to a solution of LiPhO-*d*₅.

A with OPh-*d*₅ in THF-*d*₈: **A** with OPh-*d*₅ was dried under a vacuum at 150 °C during 1 h and redissolved in THF-*d*₈ (99.5% and dried over molecular sieves).

X-ray Crystallography. All crystals were mounted on a loop, and all geometric and intensity data were taken from this crystal. Data collection using Mo-K α radiation ($\lambda = 0.71073$ Å) was performed at 150 K on a STOE IPDS-IIT diffractometer equipped with an Oxford Cryosystem open flow cryostat.⁸⁵ Absorption correction was partially integrated in the data reduction procedure.⁸⁶ The structure was solved by SIR 2004 and refined using full-matrix least-squares on F^2 with the SHELX-97 package.^{87,88} All heavy atoms could be refined anisotropically. Hydrogen atoms were introduced as fixed contributors when a residual electronic density was observed near their expected positions.

Crystal data: (1) C₈H₁₆Cl₂CrO₂, $M = 267.11$ g·mol⁻¹, triclinic, $P1$ (No. 2), $a = 3.9645(2)$; $b = 7.2398(4)$; $c = 9.2813(5)$ Å; $\alpha = 86.918(4)^\circ$; $\beta = 79.841(4)^\circ$; $\gamma = 87.105(4)^\circ$; $V = 261.61(2)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.695$ Mg m⁻³, $F(000) = 138$, $T = 150$ K, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 0.120$ mm⁻¹, $2.2^\circ < \theta < 25^\circ$, 1703 reflections of which 924 unique and 924 observed, 61 parameters refined, GOF (on F^2) = 0.937, $R_1 = \Sigma|F_o| - F_c|/\Sigma F_o = 0.0404$, $wR_2 = 0.1363$ for $I > 2\sigma(I)$.

(2) C₇₂H₈₉Cl₂Cr₂Li₅O₁₅, $M = 1404.02$ g·mol⁻¹, monoclinic, $P2_1/n$ (No. 14), $a = 14.0733(3)$; $b = 19.2260(5)$; $c = 26.8165(7)$ Å, $\beta = 90.716(2)^\circ$; $V = 7255.3(3)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.285$ Mg m⁻³, $F(000) = 2948$, $T = 150$ K, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 0.120$ mm⁻¹, $1.3^\circ < \theta < 23.6^\circ$, 39649 reflections of which 10 556 unique and 5837 observed,

733 parameters refined, GOF (on F^2) = 1.06, $R_1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.0946$, $wR_2 = 0.2525$ for $I > 2\sigma(I)$.

(3) $C_{72}H_{90}Cr_2Li_4O_{16}$, $M = 1342.32$ g·mol⁻¹, monoclinic, $P2_1/n$ (No. 14), $a = 15.3093(5)$; $b = 13.7569(3)$; $c = 17.2503(6)$ Å; $\beta = 106.529(3)^\circ$; $V = 3482.93(18)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.280$ Mg m⁻³, $F(000) = 1420$, $T = 200$ K, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 0.120$ mm⁻¹, $2.46^\circ < \theta < 22.50^\circ$, 4489 reflections of which 16749 unique and 5515 observed, 395 parameters refined, GOF (on F^2) = 0.92, $R_1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.0788$, $wR_2 = 0.2262$ for $I > 2\sigma(I)$.

(4) $C_{78}H_{93}Cr_3Li_3O_{17}$, $M = 1479.34$ g·mol⁻¹, cubic, $I-43d$ (No. 220), $a = 31.8702(5)$ Å; $V = 32370.9(9)$ Å³, $Z = 16$, $\rho_{\text{calcd}} = 1.214$ Mg m⁻³, $F(000) = 12448$, $T = 200$ K, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 0.120$ mm⁻¹, $1.8^\circ < \theta < 22.70^\circ$, 114 902 reflections of which 3596 unique and 3096 observed, 305 parameters refined, GOF (on F^2) = 1.21, $R_1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.0809$, $wR_2 = 0.1619$ for $I > 2\sigma(I)$.

(5) $C_{80}H_{112}Cl_2Cr_4Li_6O_{24}$, $M = 1778.29$ g·mol⁻¹, triclinic, $P\bar{1}$ (No. 2), $a = 13.6390(3)$; $b = 14.4630(3)$; $c = 14.3910(3)$ Å; $\alpha = 98.203(2)^\circ$; $\beta = 109.422(1)^\circ$; $\gamma = 115.869(1)^\circ$; $V = 2266.22(8)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.303$ Mg m⁻³, $F(000) = 932$, $T = 150$ K, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 0.120$ mm⁻¹, $2.5^\circ < \theta < 25.0^\circ$, 78195 reflections of which 7833 unique and 6514 observed, 454 parameters refined, GOF (on F^2) = 1.09, $R_1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.0789$, $wR_2 = 0.1872$ for $I > 2\sigma(I)$.

(6) $C_{30}H_{39}ClLi_4O_6$, $M = 558.82$ g·mol⁻¹, triclinic, $P1$ (No. 1), $a = 6.2669(3)$; $b = 11.7767(8)$; $c = 11.9650(7)$ Å; $\alpha = 66.479(5)^\circ$; $\beta = 76.664(4)^\circ$; $\gamma = 77.411(5)^\circ$; $V = 779.97(8)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.190$ Mg m⁻³, $F(000) = 296$, $T = 200$ K, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 0.120$ mm⁻¹, $2.13^\circ < \theta < 25.00^\circ$, 27 734 reflections of which 5294 unique and 2603 observed, 370 parameters refined, GOF (on F^2) = 0.963, $R_1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.0981$, $wR_2 = 0.1078$, Flack parameter $-0.1(1)$.

(7) $C_{104}H_{132}Cl_2Cr_4Li_8NiO_{28}$, $M = 2223.23$ g·mol⁻¹, triclinic, $P\bar{1}$ (No. 2), $a = 14.410(2)$; $b = 15.240(2)$; $c = 17.062(3)$ Å; $\alpha = 65.919(11)^\circ$; $\beta = 76.997(13)^\circ$; $\gamma = 72.015(12)^\circ$; $V = 3232.6(9)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.142$ Mg m⁻³, $F(000) = 1154$, $T = 200$ K, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 0.120$ mm⁻¹, $1.51^\circ < \theta < 20.00^\circ$, 54 511 reflections of which 5451 unique and 1077 observed, 196 parameters refined, GOF (on F^2) = 0.81, $R_1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.1489$ (degradation of crystal during manipulation due to moisture sensitivity), $wR_2 = 0.3089$.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained on quoting the depositing numbers CCDC-865128 (A), 812531 (1), 812534 (2), 812532 (3), 812536 (4), 812535 (5), 865080 (6), and 812533 (7) (Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.cgd.5b01084](https://doi.org/10.1021/acs.cgd.5b01084).

Crystallographic information files (ZIP)

Cr–Cr bond distances graph, electron density map of compound 1, XPS analysis of compound 1, NMR-data and table of X-ray data with important bond distances and bond valence sums (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. A.C. did most of the synthetic work for compounds 1–7. J.P.B. contributed to the elucidation of the oxidation mechanism.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

BVS = bond valence sum; THF = tetrahydrofuran

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