



# Synthesis and molecular structure of the tetranuclear $\mu_4$ -oxo-centered chromium complex $[\text{Cr}_4(\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_4(\mu_4\text{-O})(\mu\text{-Cl})_6]$

Franco Ossola \*, Franco Benetollo

*Istituto di Chimica e Tecnologie Inorganiche e dei Materiali Avanzati, Area della Ricerca del CNR, Corso Stati Uniti 4, I-35127 Padova, Italy*

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## Abstract

The complex  $[\text{CrCl}_3(\text{THF})_3]$  reacts with  $\text{Li}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)$  in THF at room temperature (r.t.) to form the tetranuclear complex  $[\text{Cr}_4(\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_4(\mu_4\text{-O})(\mu\text{-Cl})_6]$  (**1**) where each chromium atom has a distorted octahedral coordination geometry with an oxygen atom shared among the four metal ions. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

We are involved in the synthesis of organochromium derivatives having alkyl ligands with terminal Lewis basic group, as 3-(dimethylamino)propyl [1]. These groups can behave as bidentate ligands and allow intramolecular coordinative saturation for the metal, with nitrogen as electron donor, increasing the stability of the complex [2].

Recently we found that  $[\text{CrCl}_3(\text{THF})_3]$  reacted with the tetranuclear Grignard reagent  $[\text{LMg}_2\text{Cl}_3(\text{THF})_2]_2$  (**2**) ( $\text{L} = \text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$ ) affording the trinuclear mixed-metal compound  $[\{\text{L}_2\text{Cr}(\mu\text{-Cl})_2\}_2\text{Mg}]$  (**3**) [1]. The molecular structure of **3** showed an unusual Cr–Mg–Cr core where the central Mg atom was chloride-bridged to two  $\text{L}_2\text{Cr}(\mu\text{-Cl})_2$  fragments in opposite positions. The stability of this core, and ease of formation of **3**, seems to preclude the use of **2** in the synthesis of other different 3-(dimethylamino)propyl chromium derivatives not containing Mg [3]. Consequently we decided to replace **2** with the corresponding [3-(dimethylamino)propyl]lithium salt LiL [4]. The reaction of  $[\text{CrCl}_3(\text{THF})_3]$  with LiL gives the tetranuclear

$\mu_4$ -oxo-centered complex  $[\text{Cr}_4(\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_4(\mu_4\text{-O})(\mu\text{-Cl})_6]$  (**1**), whose synthesis and molecular structure are reported here.

## 2. Results and discussion

The reaction between  $[\text{CrCl}_3(\text{THF})_3]$  and LiL in THF at r.t. gave the compound **1**. Compound **1** crystallizes from THF/hexane solutions in the form of emerald green prisms. Its molecular structure is depicted in Fig. 1. The molecule has 2-fold crystallographic symmetry and appears as a cage built around the central  $\mu_4$ -oxygen, which lies on the crystallographic  $C_2$  axis and exhibits a distorted tetrahedral geometry being linked to four chromium atoms ( $\text{Cr}(1)\text{--O--Cr}(2)$   $106.7(1)^\circ$ ,  $\text{Cr}(2)\text{--O--Cr}(1^{(a)})$   $130.8(1)^\circ$  and  $\text{Cr}(1)\text{--O--Cr}(1^{(a)})$   $93.6(1)^\circ$ ; (a) at  $1-x, -y, z$ ).

The cage defined by Cr and Cl atoms is a distorted quadratic antiprism formed by the two rectangular faces  $\text{Cr}(\mu\text{-Cl})_2\text{Cr}$ . In both rectangles each chlorine is asymmetrically bridged to the corresponding metal center ( $\text{Cr}(1)\cdots\text{Cl}(1)$  and  $\text{Cr}(2)\cdots\text{Cl}(3)$ ), while the Cr–Cl bond distances involving the chlorine bridging the two rectangular faces of the antiprism have equal distances

\* Corresponding author. Fax: +39-49-8702911.

(Cr(1)···Cl(2) 2.383(3) and Cr(2)···Cl(2) 2.385(3) Å, respectively).

Each metal atom has a distorted octahedral coordination geometry formed by the central oxygen, three chlorine atoms and one bidentate L ligand.

To our knowledge, only two other structurally characterized examples of oxo-centered tetranuclear chromium complexes exist: the organometallic Cr(II) compound  $[\text{Cr}_4(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)_4(\text{O}_2\text{CCH}_3)_2\text{O}]$  [5], where the oxo-ligand connects two Cr–Cr bonded fragments, and the inorganic Cr(III) derivative  $[\text{Ph}_4\text{P}]_3[\text{Cr}_4\text{O}(\mu_3\text{-SO}_4)_2(\mu\text{-Cl})_5\text{Cl}_4]\cdot\text{MeCN}$  [6]. The Cr–O bonds of **1** have a mean length of 2.026(8) comparable to the averaged value of 2.001(1) Å found in  $[\text{Cr}_4(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)_4(\text{O}_2\text{CCH}_3)_2\text{O}]$  for the  $\mu_4\text{-O}$  moiety and to the 1.987(2) and 2.004(8) Å values found in  $[\text{Ph}_4\text{P}]_3[\text{Cr}_4\text{O}(\mu_3\text{-SO}_4)_2(\mu\text{-Cl})_5\text{Cl}_4]\cdot\text{MeCN}$ . The symmetric distances Cr–Cl of **1** (averaged values 2.384(3) Å) compare to the average value of 2.388(5) Å reported for the bridging chlorine in the latter complex.

At first sight, the most plausible source of the unexpected  $\mu_4\text{-O}$  could be inadvertent admission of moisture or hydroxide ions, but we have to consider that all the procedures have been carried out under strictly anaerobic conditions and synthesis is reproducible, consequently it is improbable that oxygen incorporation could derive from atmospheric moisture; moreover, oxygen-containing impurities in  $[\text{CrCl}_3(\text{THF})_3]$  and LiL are very low (see Section 3). A possible source of oxygen could be THF, in fact, reactions with oxygenated impurities present in the solvent, not eliminable by standard purification procedures, and reactions with THF leading to oxygen incorporation are possible [7–9]. However, at this stage, the source of

the unexpected  $\mu_4\text{-O}$  can be only matter of speculation.

Compound **1** shows a remarkable stability. Crystals can be treated with acidic solutions without any sign of decomposition. In addition, thermogravimetric studies shows **1** is stable in air up to 220°C; an exothermic decomposition follows (225 and 375°C) giving stable  $\text{Cr}_2\text{O}_3$  at 450°C (weight loss = 61.15%; calc. for  $\text{Cr}_2\text{O}_3$  61.08%).

Reactions of LiL with  $[\text{CrCl}_3(\text{THF})_3]$  and  $[\text{Cr}(\text{CH}_3)\text{Cl}_2(\text{THF})_3]$ , with a LiL:[Cr-reagent] ratio 2:1 have been carried out, but elemental analysis showed that in no case were the isolated products simple  $\text{CrL}_2\text{X}$ -type complexes (X = Cl,  $\text{CH}_3$ ).

### 3. Experimental

#### 3.1. General comments

All operations were carried out in nitrogen-filled glove boxes with the rigorous exclusion of oxygen and moisture. Solvents were purified by standard methods (THF by sodium-potassium/benzophenone procedure) and used immediately after distillation [10]. 3-(Dimethylamino)propyl chloride was obtained from the commercially available HCl salt by treatment with sodium hydroxide solution and extraction and dried over potassium carbonate. The complex  $[\text{Cr}(\text{CH}_3)\text{Cl}_2(\text{THF})_3]$  was synthesized following the procedure of Ref. [11]. Thermogravimetric data in air were obtained on a Netzsch STA 429 thermoanalytical equipment (flux rate  $200\text{ cm}^3\text{ min}^{-1}$ ) reference material  $\text{Al}_2\text{O}_3$ . C, H, N and O elemental analyses were performed with a Fisons EA 1108 (CHNS-O version) elemental analyzer.

Since commercial  $[\text{CrCl}_3(\text{THF})_3]$  was not pure and the samples of  $[\text{CrCl}_3(\text{THF})_3]$  we obtained according to literature procedures [12] were contaminated by a black decomposition product generated during the high-temperature extraction, we slightly modified the synthesis reported [12]. In fact, we found that zinc-catalyzed conversion of anhydrous chromium trichloride into its tetrahydrofuranate also occurs at r.t. After 4 days of stirring a dry-THF suspension of anhydrous  $\text{CrCl}_3$  (99%) and zinc dust (ca. 50:1), the conversion to  $[\text{CrCl}_3(\text{THF})_3]$  was complete. Filtration of the solution from zinc and evaporation of THF gave  $[\text{CrCl}_3(\text{THF})_3]$ .

LiL was synthesized by reaction of lithium powder with 3-(dimethylamino)propyl chloride according to Ref. [4]. Purification by double recrystallization from hexane-cooled solutions was performed (Anal. Calc. for  $\text{C}_5\text{H}_{12}\text{NLi}$ : C, 64.52; H, 12.90; N, 15.05. Found: C, 64.13; H, 12.74; N, 14.83%; oxygen determination was also carried out in order to exclude the presence of

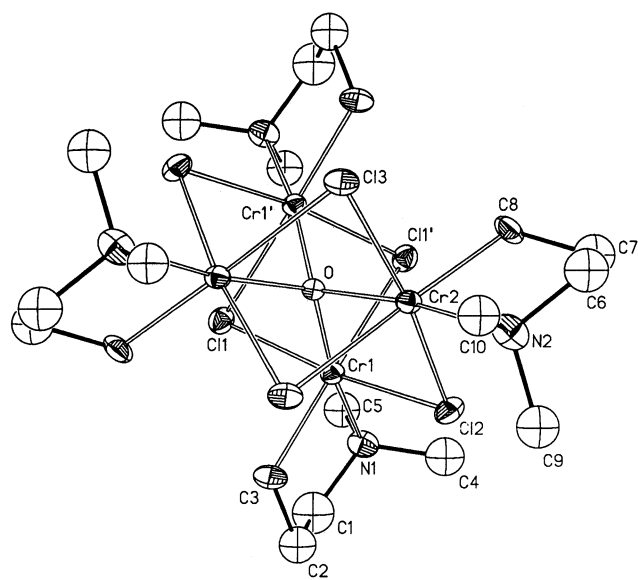


Fig. 1. Molecular structure and atomic labelling scheme for  $[\text{Cr}_4(\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_4(\mu_4\text{-O})(\mu\text{-Cl})_6]$ . The hydrogen atoms have been omitted for clarity.

O-containing species in LiL, no oxygen was found). The compound was found pure on NMR grade.

### 3.2. Synthesis of **1**

A solution of LiL (317 mg, 3.41 mmol) in 10 ml of THF was added dropwise at r.t. to a solution of  $[\text{CrCl}_3(\text{THF})_3]$  (1258 mg, 3.36 mmol) in 30 ml of THF while stirring. The resulting solution was stirred for 24 h. Emerald green crystals of **1** slowly grew (ca. 2 weeks) on the walls of the vessel by repeatedly placing thin layers of hexane over the THF solution and allowing the layers to mix by slow diffusion. Crystals were separated from the deep green solution and analyzed (156 mg, 0.20 mmol, yield 24%; significant amounts of **1** and increases in yield can be obtained by further recrystallizations). Compound **1** decomposes at 220°C.

IR (KBr pellets): 1634(m), 1468(s), 1168(m), 1008(m), 964(m), 774(m), 563(m), 530(s)  $\text{cm}^{-1}$ . Vis  $\lambda_{\text{max}}$  (THF): 651, 453 nm.

Anal. Calc. for  $\text{C}_{20}\text{H}_{48}\text{N}_4\text{OCl}_6\text{Cr}_4$ : C, 30.73; H, 6.15; N, 7.17; Cl, 27.27%. Found: C, 31.54; H, 6.42; N, 7.10; Cl, 27.35%.

### 3.3. Crystal data and structure determination

$[\text{Cr}_4(\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_4(\mu_4\text{-O})(\mu\text{-Cl})_6]$ ,  $\text{C}_{20}\text{H}_{48}\text{N}_4\text{OCl}_6\text{Cr}_4$ ,  $M_r = 781.3$ , green prism ( $0.44 \times 0.48 \times 0.20$  mm) orthorhombic, space group  $Aba2$ ,  $a = 12.949$  (3),  $b = 12.507$  (3),  $c = 20.269$  (5) Å,  $\mu(\text{Mo-K}\alpha) = 18.0$   $\text{cm}^{-1}$ ,  $F(000) = 1608$ ,  $T = 293$  K.

A prismatic crystal was lodged in a Lindemann glass capillary inside a drybox and centered on a four-circle Philips PW1100 (Febo System) [13]. The orientation matrix and cell dimensions were determined by least squares refinement of the angular positions of 30 reflections. Three standard reflections were monitored every 200 reflections. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects and for absorption as described by North et al. [14].

The structure was solved by direct methods [15]. Refinement was carried out by full-matrix least-squares; the function minimized was  $\sum w(F_o^2 - F_c^2)^2$ , with weighting scheme  $w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 29.23P]$ , where  $P = \max(F_o^2 + 2F_c^2)/3$ . The atoms linked to chromium were refined anisotropically while the remaining non-hydrogen atoms were refined isotropically due to the disordering of the attached carbons atoms, (the N–C bond distances were refined with restriction). In the final difference map two residuals of 0.8 ( $\text{e Å}^{-3}$ ) were detected in the proximity of heavy atoms. The H-atoms were placed in calculated positions with fixed, isotropic thermal parameters (1.2  $\text{U}_{\text{equivalents}}$  of the parent carbon atom). Structure refinement was carried out

Table 1  
Selected bond lengths (Å) and angles (°) for  $[\text{Cr}_4(\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_4(\mu_4\text{-O})(\mu\text{-Cl})_6]$

Bond lengths			
Cr(1)–Cl(1)	2.385(3)	Cr(1)–Cl(1) <sup>a</sup>	2.609(3)
Cr(1)–Cl(2)	2.383(3)	Cr(2)–Cl(2)	2.385(3)
Cr(2)–Cl(3)	2.388(3)	Cr(2)–Cl(3) <sup>a</sup>	2.613(3)
Cr(1)–O	2.020(8)	Cr(2)–O	2.033(8)
Cr(1)–N(1)	2.19(1)	Cr(1)–C(3)	2.09(1)
Cr(2)–N(2)	2.20(1)	Cr(2)–C(8)	2.08(1)
Bond angles			
N(1)–Cr(1)–C(3)	83.3(4)	O–Cr(1)–C(3)	105.8(3)
O–Cr(1)–N(1)	170.9(3)	Cl(2)–Cr(1)–C(3)	90.0(3)
Cl(2)–Cr(1)–N(1)	95.9(3)	Cl(2)–Cr(1)–O	83.8(1)
Cl(1)–Cr(1)–C(3)	94.2(3)	Cl(1)–Cr(1)–N(1)	93.7(3)
Cl(1)–Cr(1)–O	86.3(1)	Cl(1)–Cr(1)–Cl(2)	169.9(1)
N(2)–Cr(2)–C(8)	82.3(4)	O–Cr(2)–C(8)	106.0(4)
O–Cr(2)–N(2)	171.6(3)	Cl(3)–Cr(2)–C(8)	94.4(3)
Cl(3)–Cr(2)–N(2)	94.3(3)	Cl(3)–Cr(2)–O	86.4(1)
Cl(2)–Cr(2)–C(8)	89.6(3)	Cl(2)–Cr(2)–N(2)	95.5(3)
Cl(2)–Cr(2)–O	83.5(1)	Cl(2)–Cr(2)–Cl(3)	169.8(1)
Cr(1)–Cl(2)–Cr(2)	86.0(1)	Cr(1)–Cl(1)–Cr(1) <sup>a</sup>	72.1(1)
Cr(2)–Cl(3)–Cr(2) <sup>a</sup>	72.3(1)	Cr(1)–O–Cr(2)	106.7(1)
Cr(1)–O–Cr(2) <sup>a</sup>	130.8(1)	Cr(1)–O–Cr(1) <sup>a</sup>	93.6(1)

<sup>a</sup> At 1–x, –y, z.

with SHELXL-93 [16]; drawings were produced using ORTEP II [17]. Selected bond lengths and angles are given in Table 1.

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- [3] In fact, Cl-substitution with the (dimethylamino)propyl ligand does not proceed further: the reaction of **3** with **2** (with a 3:2 ratio = 1:2) does not occur, even in refluxing THF and, analogously, the reaction of  $[\text{CrCl}_3(\text{THF})_3]$  with **2** ( $[\text{CrCl}_3(\text{THF})_3]:\mathbf{2}$  ratio = 1:4) in THF produces **3** (91% yield based on  $[\text{CrCl}_3(\text{THF})_3]$ ). In both cases trisubstitution is not achieved. Furthermore, the reaction of  $[\text{Cr}(\text{CH}_3)_2\text{Cl}_2(\text{THF})_3]$  with **2** ( $[\text{Cr}(\text{CH}_3)_2\text{Cl}_2(\text{THF})_3]:\mathbf{2}$  ratio = 1:0.5) in THF at –40°C affords **3**.
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