Synthesis, structure, magnetic and catalytic properties of new dinuclear chromium(III) complexes with oxazoline alcoholate ligands†

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The dinuclear chromium complexes $[Cr_2(N,O)_3Cl_3]$ (**6**) (N,O = 4,4-dimethyl-2-oxazolylmethanolate), $[Cr_2(N,O^{Me2})_2(EtOH)_2Cl_4]$ (**7**) and $[Cr_2(N,O^{Me2})_2(H_2O)_2Cl_4]$ (**8**) (N,O^{Me2} = 4,4-dimethyl-2-oxazolyldimethylmethanolate) have been prepared and characterized, including by single-crystal X-ray diffraction. Complex **6** is unsymmetrical, with two chloride ligands terminally bound to one Cr atom, whereas **7** and **8** (in $\mathbf{8}\cdot C_4H_8O$) which contain two molecules of coordinated ethanol or water, respectively, are centrosymmetric. These chromium complexes are paramagnetic, and the magnetic properties of **6** and **7** in the solid state correspond to antiferromagnetic behaviour, which was confirmed by DFT calculations of their electronic structures. Complexes **6**–**8** were evaluated in the catalytic oligomerization and/or polymerization of ethylene with different aluminium-based cocatalysts, and MMAO proved to be the most effective one. In the presence of MMAO, the influence of different reaction parameters, such as the Al/Cr molar ratio, reaction temperature and ethylene pressure, was investigated. Complex **7** showed the highest activity for ethylene polymerization at both 1 atm and 10 atm of ethylene pressure, up to 620 000 g mol^{-1}(Cr) h^{-1} in the latter case.

Introduction

While the Cr/SiO$_2$ Phillips catalyst, including its gas-phase Union Carbide UNIPOL version, is used to produce more than one-third of the polyethylene sold worldwide,[1] significant improvements in activities for non-metallocene homogeneous transition-metal olefin oligomerization and polymerization catalysts have recently been achieved.[2] In recent years, Cp-free chromium complexes have attracted much attention as efficient and selective homogeneous catalysts, with the expectation that variation of their ligands could further improve their performances.[3] In particular, various diphosphinoamine ligands with different substituents on both the N and P atoms have led to highly active and selective chromium precatalysts for the trimerization[4] and, more recently, tetramerization[5] of ethylene.

Transition metal complexes with chelating P,N bidentate or N,P,N tridentate ligands containing oxazoline heterocycles, of *e.g.* Ru(II), Ni(II) and Pd(II), are efficient precatalysts in a number of reactions.[6] Nickel complexes bearing bidentate NOP-type or tridentate NOPON-type ligands (see below) are very active for the dimerisation of ethylene in the presence of small amounts of cocatalyst (2 or 6 equiv. of AlEtCl$_2$).[7] Hexacoordinated dinuclear nickel complexes containing the chelating oxazoline alcohol ligands (N,OH) are also active for ethylene oligomerization with MAO or AlEtCl$_2$ as cocatalyst.[8] In contrast, cobalt complexes with NOP- or NOPON-type ligands were found to have moderate activity for ethylene oligomerization.[9] It appeared to us interesting to prepare and study chromium complexes containing such NOP- or NOPON-type ligands for the catalytic oligomerization and/or polymerization of ethylene. Although our initial objective was hampered by P–O bond cleavage during the preparation or re-crystallization of the complexes, the resulting dinuclear chromium complexes with anionic N,O oxazoline alcoholate are of great interest and we could subsequently prepare them directly from the corresponding oxazoline alcohol.

Results and discussion

Synthesis and characterization

The oxazoline alcohols **1** and **2**,[10] the (4,4-dimethyl-2-oxazolylmethanoxy)diphenylphosphine ligand **3** (NOP)[11] and the bis(oxazolinyl)phenylphosphonite ligands **4** (NOPON) and **5** (NOPON^{Me2})[12] were prepared according to the literature (Scheme 1).

The reactions of $[CrCl_3(THF)_3]$ with ligand **3** (NOP) or ligand **4** (NOPON) in dichloromethane produced the same green powder and the corresponding green single crystals (see below) were analyzed by X-ray diffraction.† This indicated that cleavage of P–O bond(s) had taken place to yield a new, unsymmetrical dinuclear complex **6** [eqn (1)]. The latter was then prepared in high yield in a more rational way by reaction of the oxazoline alcoholate derived from **1** with $[CrCl_3(THF)_3]$ in THF [eqn (1)]. The infrared ν(C=N) stretching bands of complex **6** at 1653, 1646 and 1624 cm^{-1} correspond to three different C=N bonds, and these values are

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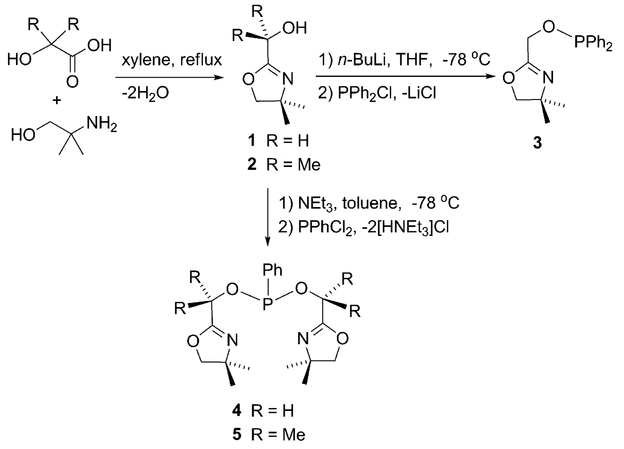
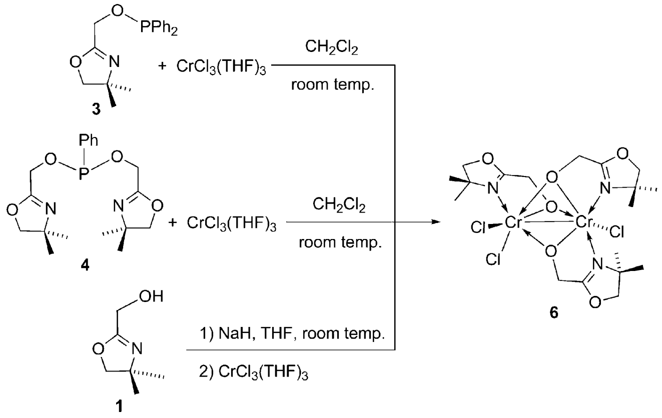


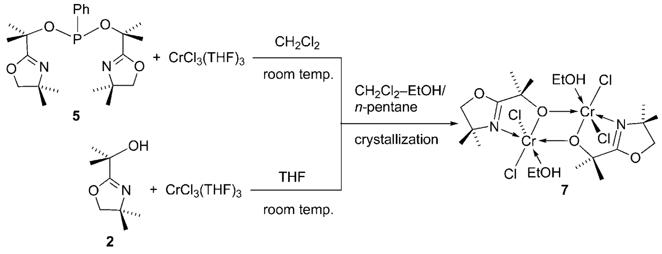
Scheme 1 Synthesis of the ligands.

shifted to lower wavenumbers when compared to that for the free oxazoline alcohol **1** (1673 cm^{-1}).



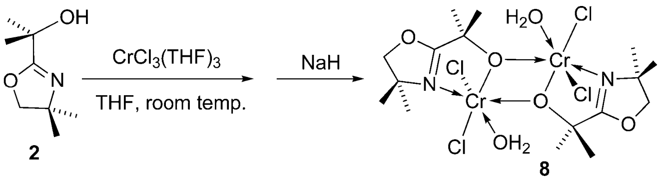
(1)

A similar behaviour was observed in the reaction between ligand **5** (NOPON^{Me2}) and [CrCl$_3$(THF)$_3$] with the scission of the P–O bonds. The purple crystals obtained by layering a CH$_2$Cl$_2$–EtOH solution containing 2–5 vol% EtOH with *n*-pentane were shown by X-ray diffraction to correspond to a centrosymmetric dinuclear complex **7**, in which an ethanol molecule is coordinated to each chromium centre [eqn (2)]. Details of the crystal structure are given below. An alternative synthesis consisting in the reaction of the oxazoline alcohol **2** with [CrCl$_3$(THF)$_3$] in THF afforded a green powder, of which the green solution in the CH$_2$Cl$_2$–EtOH mixture, layered with *n*-pentane, yielded purple crystals of **7** after a few days. The infrared stretching vibration bands for ν(O–H) from ethanol and ν(C=N) for complex **7** were clearly observed at 3142 and 1645 cm^{-1} respectively (shift from 1655 cm^{-1} for the free oxazoline alcohol **2**).



(2)

Addition of NaH to the mixture containing the oxazoline alcohol **2** and [CrCl$_3$(THF)$_3$] in THF resulted in the disappearance of the initial green precipitate and a dramatic color change from green to purple. After filtration and concentration of the filtrate under reduced pressure, the residue was treated with diethyl ether to give a gray–purple powder and a blue–purple solution. A purple solid was obtained after placing the blue–purple solution at a lower temperature; it was redissolved in dichloromethane and slow diffusion of *n*-pentane into this solution afforded purple crystals of **8**·THF [eqn (3)]. An X-ray structure determination established the presence of a water molecule coordinated to each chromium centre in the dinuclear complex **8**. The infrared absorptions at 3260 and 1644 cm^{-1} correspond to the stretching vibration bands of ν(O–H) from water and ν(C=N) respectively.



(3)

The single-crystal X-ray structures of complexes **6**–**8** in the solid state are shown in Fig. 1–3 and selected bond lengths and angles are collected in Tables 1–3.

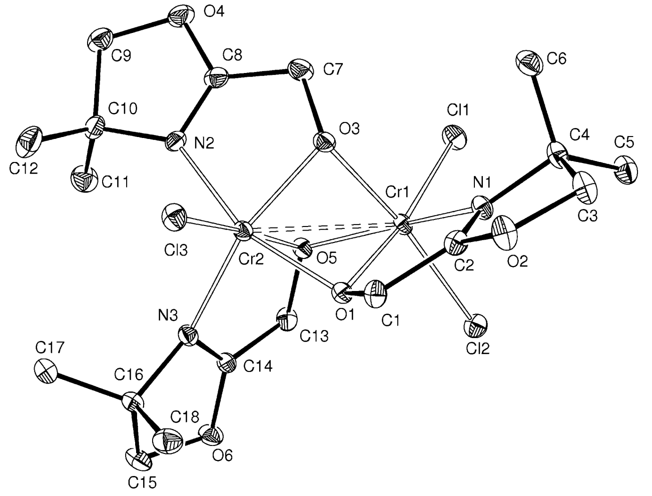


Fig. 1 ORTEP view of the molecular structure of complex **6** with thermal ellipsoids drawn at the 50% probability level. H atoms omitted for clarity.

Complex **6** (Fig. 1) crystallized in the non-centrosymmetric space group $P2_12_12_1$. Its asymmetric dinuclear molecular structure shows three alcoholate ligands, one chelating on Cr1 and two on Cr2. Their oxygen atoms (O1, O3 and O5) further symmetrically bridge the metal centres and define the face shared by the two distorted coordination octahedra. The aminoalcoholates thus feature a μ-$\kappa^1(O)$:$\kappa^2(N,O)$ bonding mode, rather rare in chromium complexes.[13] Dichromium compounds bridged by three alcoholate ligands are also rather rare.[14] The coordination around the metal centres is completed by two terminal chlorides for Cr1 and one for Cr2. To minimize the steric repulsion between the methyl groups in the α position to the nitrogen, the two O, Cr, N chelation planes on Cr2 form a dihedral angle of 84.23(8)°. The six Cr–O bonds, three Cr–N bonds and three Cr–Cl bonds have similar lengths,

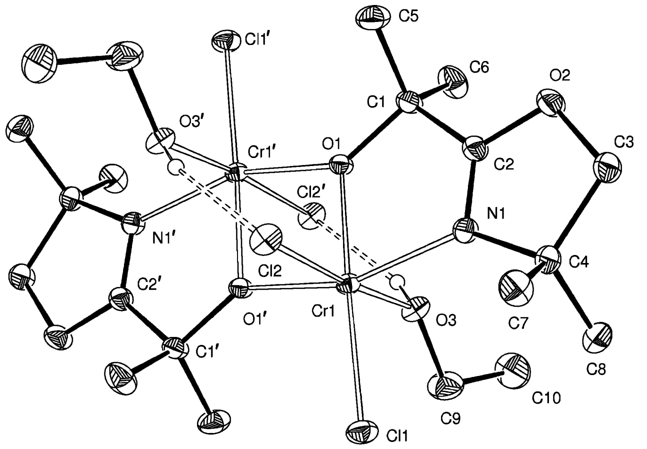


Fig. 2 ORTEP view of the molecular structure of complex **7** with thermal ellipsoids drawn at the 50% probability level. H atoms omitted for clarity, except the OH protons. Selected bond distances and angles are reported in Table 2. Symmetry operations generating equivalent atoms (′): –*x*, –*y*, –*z*.

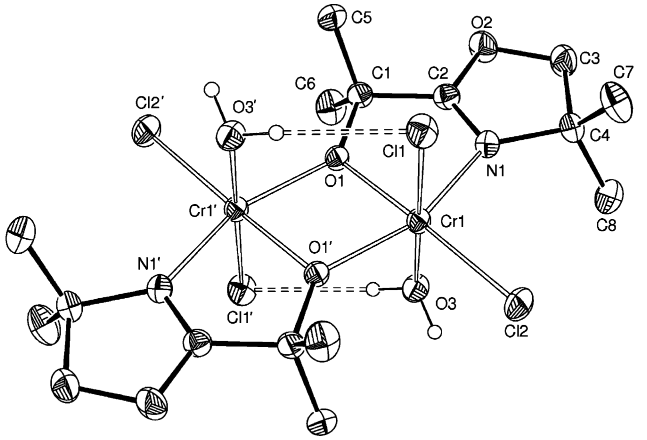


Fig. 3 ORTEP plot of the molecular structure of centrosymmetric molecule A of complex **8** in **8**·C_4H_8O with thermal ellipsoids drawn at the 50% probability level. H atoms omitted for clarity, except the water protons. Selected bond distances (Å) and angles (°) are reported in Table 3. Independent molecule B shows analogous bond lengths and angles. Symmetry operations generating equivalent atoms (′): –*x*, –*y*, –*z*.

respectively, which are in good agreement with the values typically found for Cr(III) species. The geometrical constrains due to the chelating and bridging coordination modes [mean chelation N–Cr–O angle: 81.4(1)°, mean O–Cr–O angle: 78.47(9)°] result, as mentioned above, in a significantly distorted octahedral geometry for both metal centres [with the largest deviation of the axial angle from the ideal 180° being for N1–Cr1–O5, 157.74(9)°]. The three C=N bonds in the oxazoline heterocycles retain a typical double-bond character with an average bond length of 1.278(4) Å. The Cr–Cr distance of 2.7388(6) Å is short enough to be consistent with a bonding interaction between the metals. Chromium complexes with short Cr–Cr contacts have been reported in the literature,[15] the shortest bond being 1.749(2) Å.[15g]

At variance with the chelates featured in **6**, the N,O ligands in complexes **7** and **8** contain two methyl groups on the carbon atom α to the alcoholate oxygen atom. These dinuclear, centrosymmetric complexes (Fig. 2 and 3) are similar, differing only in the nature of the coordinated solvent molecules (ethanol in **7** and water in **8**).

Table 1 Selected bond lengths (Å) and bond angles (°) in complex **6**

Bond lengths			
Cr1–O1	2.008(2)	Cr2–O1	1.999(2)
Cr1–O3	2.032(2)	Cr2–O3	1.978(2)
Cr1–O5	2.005(2)	Cr2–O5	1.999(2)
Cr1–N1	2.044(3)	Cr2–N2	2.056(3)
Cr1–Cl1	2.3066(8)	Cr2–N3	2.056(3)
Cr1–Cl2	2.3003(9)	Cr2–Cl3	2.3091(8)
N1–C2	1.278(4)	N3–C14	1.282(4)
N2–C8	1.274(4)	Cr1–Cr2	2.7388(6)
Bond angles			
O1–Cr1–O3	77.80(7)		
O1–Cr1–O5	78.13(7)	O1–Cr2–O3	79.27(8)
O3–Cr1–O5	77.74(8)	O1–Cr2–O5	78.45(9)
N1–Cr1–O1	81.308)	N2–Cr2–O3	78.46(7)
Cl1–Cr1–Cl2	92.75(3)	N3–Cr2–O5	81.75(9)
Cr1–O1–Cr2	86.24(7)	Cr1–O5–Cr2	86.32(7)
Cr1–O3–Cr2	86.13(8)		

Table 2 Selected bond lengths (Å) and bond angles (°) in complex **7**. Symmetry operations generating equivalent atoms (′): –*x*, –*y*, –*z*

Bond lengths			
Cr1–N1	2.039(2)	Cr1–Cl1	2.2916(5)
Cr1–O1	1.974(1)	Cr1–Cl2	2.3393(6)
Cr1–O1′	1.984(1)	N1–C2	1.271(2)
Cr1–O3	2.049(2)	Cr1 · · · Cr1′	3.0867(5)
Bond angles			
O1–Cr1–O1′	77.52(5)	Cl1–Cr1–Cl2	92.68(2)
O1–Cr1–N1	80.11(6)	Cl2–Cr1–O3	175.50(4)
O1′–Cr1–N1	157.55(6)	Cr1–O1–Cr1′	102.48(5)
Cl1–Cr1–O1	175.58(4)		

Table 3 Selected bond lengths (Å) and bond angles (°) in complex **8** in **8**·THF. Symmetry operations generating equivalent atoms (′): –*x*, –*y*, –*z*

Bond lengths			
Cr1A–N1A	2.044(2)	Cr1B–N1B	2.042(3)
Cr1A–O1A	1.966(2)	Cr1B–O1B	1.967(2)
Cr1A–O1A′	1.986(2)	Cr1B–O1B′	1.983(2)
Cr1A–O3WA	2.037(2)	Cr1B–O3WB	2.051(2)
Cr1A–Cl1A	2.286(1)	Cr1B–Cl1B	2.2890(9)
Cr1A–Cl2A	2.352(1)	Cr1B–Cl2B	2.3473(8)
N1A–C2A	1.273(4)	N1B–C2B	1.267(4)
Cr1A · · · Cr1A′	3.0894(6)	Cr1B · · · Cr1B′	3.0876(6)
Bond angles			
O1A–Cr1A–O1A′	77.16(9)	O1B–Cr1B–O1B′	77.16(9)
O1A–Cr1A–N1A	80.28(9)	O1B–Cr1B–N1B	80.25(9)
Cl2A–Cr1A–O3wA	178.05(8)	Cl2B–Cr1B–O3wB	178.30(8)
Cl1A–Cr1A–Cl2A	92.39(4)	Cl1B—Cr1B–Cl2B	93.29(3)
Cr1A–O1A–Cr1A′	102.84(9)	Cr1B–O1B–Cr1B′	102.84(9)

In view of the structural similarity between **7** and **8** (see Tables 2 and 3), only the first will be described in some detail.

In the dinuclear centrosymmetric crystal structure of **7**, each metal centre is N,O chelated by an alcoholate ligand. The oxygen atoms further bridge the chromium atoms in such a way that a planar $Cr_2(\mu\text{-}O)_2$ group is formed. Two mutually *cis* terminal chlorides and an ethanol molecule complete the distorted octahedral coordination of each metal, the two octahedra sharing one edge. The smallest angles at the metals are, as in the case of **6**, the chelation and the O–Cr–O angles. The Cr–N and Cr–O bond distances are close to those found in **6** and similar to those found in mononuclear and dinuclear Cr(III) aminoalcoholate and picolinate complexes.[16,17] The Cr1–Cl2 bond distance is only slightly longer than Cr1–Cl1, while the Cr–Cr distance of 3.0867(6) Å is longer than that in **6**. The C2–N1 bond in the oxazoline ring has the typical double-bond character with a length of 1.271(2) Å. The O1, Cr1, N1, C1, C2, C3, C4, O2, Cl1 atoms together with their centrosymmetric counterparts are almost coplanar [maximum deviation from the mean plane defined by the aforementioned atoms: 0.061(1) Å (Cl1)], as a result of the equatorial chelation of the alcoholates (if the solvent molecules and Cl2 are considered as axial ligands). In both structures two intramolecular centrosymmetric hydrogen bonds are established between the solvents and the axial chlorides (H···O distances: 2.31(3) Å in **7** and 2.29(4) Å for molecule B in **8**).

Magnetic properties

The magnetic properties of **6** and **7** in the solid state were investigated in the temperature range of 300–1.8 K with an applied field of 5 kOe. The Curie constants C = 4.2(1) emu K mol^{-1} and C = 3.8(1) emu K mol^{-1} for **6** and **7** respectively were determined from a fit of the $1/\chi$ *versus* T curve to the Curie–Weiss law in the high-temperature region (150–300 K) (see Fig. 4). They are in very good agreement with the expected value for two Cr(III) ions.[18]

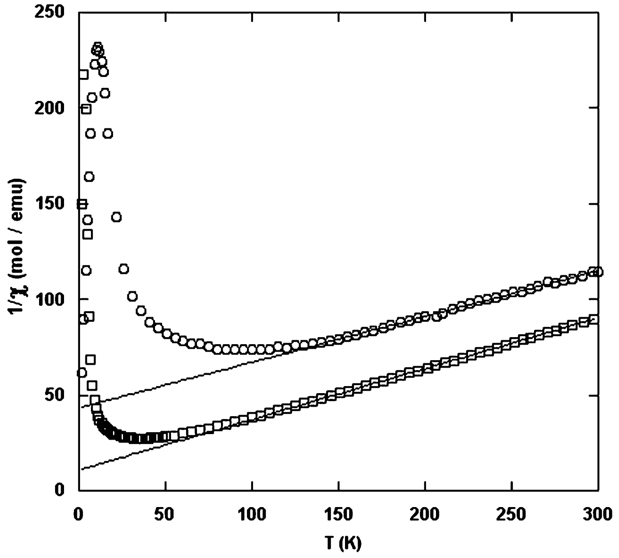


Fig. 4 Experimental $1/\chi$ = f(T) curves for **6** (○) and **7** (☐) and best fits (full lines) using the Curie–Weiss law above 150 K.

For both compounds, the room temperature value for the χT product (2.6 and 3.3 emu K mol^{-1} for **6** and **7**) is below the expected value for two uncoupled Cr(III) ions (3.75 emu K mol^{-1} considering g = 2.0). The χT product decreases continuously down to almost 0 emu K mol^{-1} upon decreasing the temperature down to 1.8 K, indicating the occurrence of an intramolecular antiferromagnetic interaction, in agreement with the negative sign of the Weiss temperature (−181(1) and −41(1) K for **6** and **7** respectively).

The fitting of the χ = f(T) curves (Fig. 5) was done by using the following spin Hamiltonian where all parameters have their usual meaning and the spin operator S is defined as $S = S_{\text{Cr1}} + S_{\text{Cr2}}$:[19]

$$\hat{\mathscr{H}} = -JS_{Cr1}S_{Cr2} + g\beta HS$$

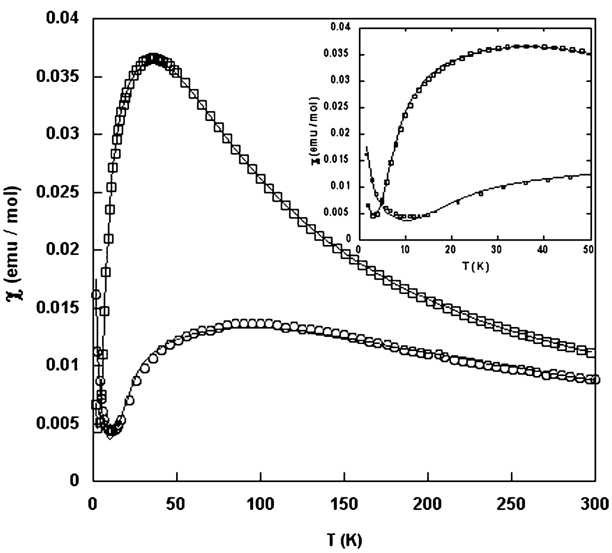


Fig. 5 Experimental χ = f(T) curves for **6** (○) and **7** (☐) and best fits (full lines) (see text). Insert : zoom on the low-temperature region.

To reproduce the data satisfactorily we had to consider a certain amount ρ of paramagnetic impurity ($S_{\text{impur}} = 3/2$).

The fits leads to the following values: J = −43.6(1) cm^{-1}, g = 1.95(1) and ρ = 0.9(1)% ($R = 8.6 \times 10^{-4}$) for **6** and J = −16.4(1) cm^{-1}, g = 1.98(1) and ρ = 0.3(1)% ($R = 2.8 \times 10^{-5}$) for **7**.[20] The nature and magnitude of the magnetic interaction is perfectly in line with the previously published magneto-structural correlations in hydroxo- or alkoxo-bridged Cr(III) binuclear complexes.[16,21] For instance, the structural features of the core of complex **7** are very similar to those of the core of [Cr(pic)$_2$OH]$_2$ (pic = 2-carboxypyridine)[16] (Cr–O bond lengths range from 1.974(1) to 1.984(1) Å in **7** and from 1.934 to 1.980 Å in [Cr(pic)$_2$OH]$_2$; the Cr–Cr distance is 3.0867(5) Å in **7** and 2.999 Å in [Cr(pic)$_2$OH]$_2$ and the Cr–O–Cr angle is 102.48(5)° in **7** and ranges from 99.0 to 101.6° in [Cr(pic)$_2$OH]$_2$) and the magnetic coupling constants are thus logically very similar (J = −16.4 cm^{-1} for **7** and J = −16.04 cm^{-1} for [Cr(pic)$_2$OH]$_2$).[16]

The magnitude of the antiferromagnetic coupling in **6** deserves a comment. The Cr–O–Cr bridges are more bent in **6** (mean value 86.2(7)°) than in **7** but the Cr–Cr distance is much shorter. Therefore, the fact that a Cr–O–Cr angle close to 90° would tend to reinforce the ferromagnetic contribution to the overall exchange coupling[22] is counter-balanced by the shortness of the Cr–Cr distance which leads to a direct overlap of the magnetic orbitals, bringing in that way a relatively strong antiferromagnetic contribution.

In order to estimate the magnetic exchange coupling in these two complexes from first-principles calculations and to clarify the influence of the different number of bridging ions (three O

Table 4 Energy difference (hartree) between the ferromagnetic and symmetry-broken antiferromagnetic DFT solution for a model Cr-dimer as a function of the Cr–Cr distance (Å) ($\Delta E < 0$ = antiferromagnetic behaviour, $\Delta E > 0$ = ferromagnetic behaviour)

Cr–Cr/Å	1.5	2	2.5	2.74	3	3.08
ΔE/hartree	–0.156	0.067	0.151	0.162	0.189	0.192

bridges in **6** and only two in **7**) we performed density functional theory (DFT)[23] calculations at the all-electron level with the Gaussian-orbital-based NRLMOL code[24] using the Perdew–Burke–Ernzerhof (PBE) generalized-gradient approximation for the exchange and correlation functional.[25]

The DFT calculations of the electronic structures of **6** and **7** confirmed the experimental results. Both molecules show an overall antiferromagnetic behaviour, however the magnitude of the exchange coupling obtained from DFT is larger compared to the experimental values ($J = -57$ cm^{-1} for **6** and $J = -37$ cm^{-1} for **7**), which is usually the case for J values obtained from PBE.[26] This can be attributed to a general failure of DFT because standard DFT functionals are not localizing the d-states strongly enough. In order to elucidate in detail the influence of the different Cr–Cr distance (shorter Cr–Cr distance in **6**) on the overall coupling strength, we carried out a series of model calculations based on a Cr(III) dimer varying the Cr–Cr distances.

As shown in Table 4 the ferromagnetic coupling increases with increasing distance. This behaviour can be explained by the Hay–Thibeault–Hoffmann model.[27] It describes weakly interacting metal centres in terms of pairwise interaction of molecular orbitals. On the basis of configuration interaction of molecular orbitals, one finds for small interactions that the difference of squares of orbital energies becomes a measure of the singlet–triplet energy splitting. If the orbitals carrying the spins have the same energy, then antiferromagnetic interactions vanish and ferromagnetic coupling is predicted. By increasing the Cr–Cr distance the interaction of the two ions and therefore the splitting of the d-orbitals is reduced, which leads consequently to a reduced singlet–triplet splitting. Therefore, the ferromagnetic interaction becomes stronger. This behaviour suggest a smaller overall antiferromagnetic coupling for complex **7** with larger Cr–Cr distance. However, the number of bridging ligands may also play a role, since a larger number of bridges may lead to an increased antiferromagnetic coupling. This would influence the total J value in the correct direction, because complex **6** with three bridging atoms shows stronger antiferromagnetic coupling. Nevertheless, this increase may not be as strong as one might expect due to a decreased electronic density at each bridge in the case of three bridging ligands compared to only two bridging ligands. It seems that there exists a mixture of several effects which result in an overall antiferromagnetic coupling.

Catalytic oligomerization and/or polymerization of ethylene

Complexes **6–8** were evaluated as precatalysts in the oligomerization and/or polymerization of ethylene in order to examine the influence of coordinated ligands and solvent molecules on the catalytic performances of the complexes. Different reaction conditions, such as the nature of the cocatalyst, the Al/Cr molar ratio, the reaction temperature and ethylene pressure, were investigated and the catalytic results were summarized in Table 5. Under most of the conditions employed, each complex yielded predominantly polyethylene and 1-butene as the main oligomeric products with negligible amounts of C_6 oligomers and no C_{8+} oligomers were detected.

Various aluminium-based cocatalysts were used with complex **6** to identify the most effective one at 20 °C and 1 atm of ethylene pressure. When triethylaluminium or diethylaluminium chloride was used as cocatalyst only 1-butene was observed but the activity for ethylene oligomerization was low or very low respectively. In the presence of MAO or MMAO, complex **6** led mostly to polyethylene with a small amount of butenes with moderate activities. Very small amount of 1-butene were formed with MAO (A_o < 100 g mol^{-1}(Cr) h^{-1}) but a higher activity for ethylene dimerization was found with MMAO, although both MAO and MMAO led to comparable activities for ethylene polymerization. In view of our interest for ethylene oligomerization products, MMAO was therefore chosen in the subsequent investigations.

Table 5 Ethylene oligomerization and/or polymerization with precatalysts **6–8**[a]

					Oligomers	Polymers	
	Co-catalyst	Al/Cr	T^b/°C	P^c/atm	A_o/g mol^{-1}(Cr) h^{-1}	A_p/g mol^{-1}(Cr) h^{-1}	$T_m{}^d$/°C
6	$AlEt_3$	500	20	1	3080	—	—
6	Et_2AlCl	200	20	1	310	—	—
6	MAO	500	20	1	<100	14 000	n.d.
6	MMAO	100	20	1	350	6800	n.d.
6	MMAO	300	20	1	700	12 500	n.d.
6	MMAO	500	20	1	960	15 400	n.d.
6	MMAO	1000	20	1	2720	16 100	n.d.
6	MMAO	1000	0	1	1630	27300	135.6
6	MMAO	1000	40	1	3120	5100	n.d.
6	MMAO	1000	60	1	2280	1400	n.d.
7	MMAO	1000	0	1	1960	37 900	135.6
8	MMAO	1000	0	1	1650	23 600	134.6
6	MMAO	1000	25	10	36 000	140 000	134.9
7	MMAO	1000	25	10	24 700	620 000	134.0
8	MMAO	1000	25	10	23 700	234 000	132.0

[a] General conditions: 5.0 µmol of precatalyst; 30 mL of toluene at 1 atm; 100 mL of toluene at 10 atm; reaction time = 30 min. [b] Reaction temperature. [c] Ethylene pressure. [d] Determined by DSC.

On treatment with MMAO, both oligomerization and polymerization activities of complex **6** increased along with increasing the Al/Cr molar ratio from 100, 300, 500 to 1000 and the best catalytic result was obtained with a Al/Cr molar ratio of 1000. The reaction temperature also significantly affected the catalytic activity. Lower temperatures were more favorable for ethylene polymerization and the polymerization activity greatly decreased when the reaction temperature was increased. When the temperature was increased from 0 to 40 °C, the oligomerization activity went up gradually; however, at 60 °C, the amount of both oligomers and polymer declined.

Complexes **6–8** were also investigated at 0 °C in the presence of MMAO (Al/Cr = 1000). Under similar conditions, these three complexes showed comparable oligomerization activities, whereas complex **7** produced mostly polyethylene. The difference of catalytic properties between **6** and **7** can be ascribed to different structures and the introduction of the *gem*-dimethyl groups on the carbon atom α to the oxazoline ring for **7**. The presence of different solvent molecules (ethanol or water) coordinated to the chromium centres resulted in different catalytic activities between **7** and **8**.

The catalytic experiments performed under 10 atm of ethylene pressure indicated that ethylene pressure significantly affected the catalytic behaviour (Table 5). Each complex gave much higher catalytic activity and complex **7** was most active for ethylene polymerization among these three precatalysts. The highest polymerization activity reached was 620 000 g mol^{-1}(Cr) h^{-1}.

The melting points (T_m) of the polyethylenes obtained with complexes **6–8** were determined by differential scanning calorimetry analysis (DSC). For the different precatalysts, the melting points at 1 atm were very similar (**6–8**: 135.6, 135.6 and 134.6 °C respectively) and the increase in ethylene pressure led to a slightly lower melting points of the polyethylenes (range from 132.0 to 134.9 °C). The melting points around 135 °C were consistent with linear polyethylenes.[1c] All the PE samples obtained showed intense bands at *ca.* 2918 cm^{-1} ($\nu_{as}CH_2$) and 2850 cm^{-1} ($\nu_{s}CH_2$) in the FT-IR spectra. The peaks around 1473–1464 cm^{-1} and 730–718 cm^{-1} were assigned, respectively, to scissoring and rocking vibrations of sequential methylene groups in the solid state. Additional bands include a weak peak at *ca.* 1641 cm^{-1} attributed to stretching vibration absorption band of C=C double bond, a weak peak at 1386 cm^{-1} due to the methyl symmetrical deformation mode and a weak peak at 909 cm^{-1} corresponds to the methyl rocking band due to the chain-terminating methyl groups.[28]

Conclusion

The dinuclear chromium(III) complexes **6–8**, containing anionic, *N,O*-oxazoline-alcoholate ligands, have been prepared by different methods and characterized by infrared spectroscopy and elemental analysis. Their structures in the solid state were established by single-crystal X-ray diffraction analysis.† Complex **6** has an unsymmetrical dinuclear structure, whereas **7** and **8**, which contain coordinated ethanol or water molecules respectively, are centrosymmetric molecules. The magnetic properties of the paramagnetic, Cr(III) complexes **6** and **7** show intramolecular antiferromagnetic interactions which were confirmed by DFT calculations of their electronic structures. Complexes **6–8** were used as precatalysts in the dimerization and/or polymerization of ethylene in the presence of aluminium-based cocatalysts and MMAO was found to be the most effective cocatalyst. On treatment with MMAO, complexes **6–8** mainly produced linear polyethylenes. Complex **7** was the most active for ethylene polymerization at both 1 and 10 atm of ethylene pressure, with activities up to 620 000 g mol^{-1}(Cr) h^{-1} in the latter case.

Experimental

General considerations

All manipulations were carried out under an inert-gas atmosphere using standard Schlenk techniques. IR spectra in the range 4000–650 cm^{-1} were recorded on a Thermo Nicolet 6700 instrument, equipped with SMART Orbit Diamond ATR accessory. Elemental C, H, N analyses were performed on a Flash EA 1112 microanalyzer. GC analyses were performed with a Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.2 mm i.d., 0.25 μm film thickness) CP-Sil 5 CB capillary column. The yield of oligomers was calculated by referencing to the mass of solvent on the basis of the prerequisite that the mass of each fraction was approximately proportional to its integrated area in the GC trace. DSC traces and melting points of polyethylenes were obtained from the second scanning run on a Perkin-Elmer DSC-7 instrument, which was initially calibrated for the melting point of an indium standard at a heating rate of 10 °C min^{-1}.

All solvents were dried and distilled using common techniques unless otherwise stated. The compounds 4,4-dimethyl-2-oxazolylmethanol (**1**),[29] 4,4-dimethyl-2-oxazolyldimethyl methanol (**2**),[4] (4,4-dimethyl-2-oxazolylmethoxy)diphenylphosphine (**3**),[30] bis(4,4-dimethyl-2-oxazolylmethoxy)phenylphosphine (NOPON, **4**), bis(4,4-dimethyl-2-oxazolyldimethylmethoxy)phenylphosphine (NOPON^{Me2}, **5**)[31] and [$CrCl_3(THF)_3$][32] were prepared according to the literature methods. Methylaluminoxane (MAO, 1.46 mol L^{-1} in toluene) and modified-methylaluminoxane (MMAO-3A, 7% aluminium in heptane solution) were purchased from Akzo Corp (USA). Trimethylaluminium (2 mol L^{-1} in toluene) and diethylaluminium chloride (Et_2AlCl, 1 mol L^{-1} in hexane) were purchased from Acros Chemicals. Other chemicals were commercially available and used without further purification unless otherwise stated.

Synthesis of [$Cr_2(N,O)_3Cl_3$] (6)

Method A. To a stirred solution of the phosphinito-oxazoline ligand **3** (0.504 g, 1.61 mmol) in 15 mL of dichloromethane was added under nitrogen 0.8 equiv. of solid [$CrCl_3(THF)_3$] (0.482 g, 1.29 mmol) and the colour of the solution immediately changed from colourless to green. The reaction mixture was stirred for 16 h at room temperature. After evaporation of the solvent under reduced pressure, the residue was washed with diethyl ether (3 × 15 mL) and pentane (15 mL) and dried under vacuum to afford a green powder (0.650 g). This green powder was recrystallized to give green crystals of **6** (0.258 g, 67% yield).

Method B. To a stirred solution of the bis(oxazoline)-phenylphosphonite NOPON ligand **4** (0.275 g, 0.76 mmol) in 20 mL of dichloromethane was added under nitrogen 0.8 equiv. of solid [$CrCl_3(THF)_3$] (0.254 g, 0.68 mmol), and the colour of the solution changed to blue–green and then green. The reaction mixture was stirred for 15 h at room temperature. After the solvent was evaporated under reduced pressure, the residue was washed with diethyl ether (2 × 30 mL) and dried in vacuum to yield a green powder (0.315 g), which was recrystallized to give green crystals of **6** (0.111 g, 55% yield).

Method C. To a solution of the oxazoline alcohol **1** (0.215 g, 1.66 mmol) in 30 mL of THF was added NaH (0.100 g, 2.5 mmol, 60% in oil) and the mixture was stirred at room temperature for 4 h. After removing the excess NaH by filtration, solid [$CrCl_3(THF)_3$] (0.370 g, 0.99 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 18 h. The NaCl formed was removed by filtration and the solution was evaporated under reduced pressure, the solid residue washed with diethyl ether and dried under vacuum to give a green powder (0.277 g, 93% yield). The powder obtained was dissolved in dichloromethane and the solution was layered with *n*-pentane for several days to give green crystals of **6**. FT-IR: 1653, 1646, 1624 cm^{-1} (ν(C=N)). Anal. calcd for $C_{18}H_{30}Cl_3Cr_2N_2O_6$ (594.8): C, 36.35; H, 5.08; N, 7.06. Found: C, 36.64; H, 5.43; N, 6.64.

Synthesis of [$Cr_2(N,O^{Me2})_2(EtOH)_2Cl_4$] (7)

Method A. To a solution of the bis(oxazoline)phenylphosphonite NOPON^{Me2} ligand **5** (0.194 g, 0.46 mmol) in 15 mL of dichloromethane, was added under nitrogen 0.9 equiv. of solid [$CrCl_3(THF)_3$] (0.158 g, 0.42 mmol) and the colour of the solution changed from purple to green. The reaction mixture was stirred for 18 h at room temperature. After the dichloromethane was evaporated under reduced pressure, the residue was washed with diethyl ether (3 × 20 mL) and dried under vacuum to yield a gray–green powder (0.155 g) which was recrystallized to give purple crystals of **7** (0.074 g, 54% yield).

Method B. The oxazoline alcohol **2** (0.252 g, 1.60 mmol) and solid [$CrCl_3(THF)_3$] (0.375 g, 1.00 mmol) were mixed in a Schlenk tube and 30 mL of THF were added. The mixture was stirred at room temperature for 16 h, affording a green precipitate and a green solution. After partial evaporation of the THF, diethyl ether was added and the product was collected by filtration, washed with diethyl ether and dried under vacuum, to give a green powder (0.360 g). This green powder could be transformed into purple crystals of **7** (0.165 g, 51% yield).

The powders obtained by these two methods were dissolved in a mixture of dichloromethane–ethanol (2–5 vol% ethanol) which was layered with *n*-pentane for several days to produce **7** as purple crystals. FT-IR: 3142 cm^{-1} (ν(O–H) from ethanol), 1645 cm^{-1} (ν(C=N)). Anal. calcd for $C_{20}H_{40}Cl_4Cr_2N_2O_6$ (650.35): C, 36.94; H, 6.20; N, 4.31. Found: C, 36.55; H, 6.27; N, 4.05.

Synthesis of [$Cr_2(N,O^{Me2})_2(H_2O)_2Cl_4$] (8)

The oxazoline alcohol **2** (0.252 g, 1.60 mmol) and solid [$CrCl_3(THF)_3$] (0.375 g, 1.00 mmol) were mixed in a Schlenk tube and 30 mL of THF were added. The mixture was stirred at room temperature for 15 h to form a green precipitate and a green solution. NaH (0.06 g, 1.5 mmol, 60% in oil) was then added and some bubbles were produced and the green precipitate disappeared gradually to generate a purple solution. The mixture was stirred at room temperature for another 3 h and filtered. The filtrate was concentrated under reduced pressure to a very small volume, and addition of diethyl ether produced a precipitate and a blue–purple solution. The precipitate was filtered, washed with diethyl ether and dried under vacuum to give a gray–purple powder (0.261 g, 88% yield). The blue–purple solution was placed in the fridge overnight and a purple solid was obtained, which was redissolved in dichloromethane and layering of the solution with *n*-pentane afforded purple crystals of **8**·THF suitable for X-ray diffraction. FT-IR: 3260 cm^{-1} (ν(O–H) from H_2O), 1644 cm^{-1} (ν(C=N)). Anal. calcd for $C_{16}H_{32}Cl_4Cr_2N_2O_6$ (594.24): C, 32.34; H, 5.43; N, 4.71. Found: C, 32.39; H, 5.84; N, 4.38.

Oligomerization and polymerization of ethylene

At 1 atm of ethylene pressure. A flame-dried three-neck flask was loaded with the precatalyst then evacuated and filled three times with nitrogen. Then ethylene was charged together with freshly distilled toluene and stirred for 10 min under 1 atm of ethylene pressure. The reaction temperature was controlled by the water bath and a certain quantity of cocatalyst was injected *via* a syringe. The reaction mixture was stirred for 30 min and the mixture was cooled with an ice bath. Then an aliquot amount of the solution was collected with a syringe and quenched by the addition of 5% aqueous hydrogen chloride for GC analysis. The contents and distribution of oligomers were determined by GC. The residual solution was quenched with 5% hydrochloric acid ethanol. The precipitated polymers were collected by filtration, washed with ethanol, dried under vacuum at 60 °C to constant weight.

At 10 atm of ethylene pressure. A 250 mL stainless steel autoclave reactor equipped with a mechanical stirrer and a temperature controller was heated *in vacuo* for at least 2 h above 80 °C, allowed to cool to the required reaction temperature under ethylene atmosphere, and then charged with toluene, the desired amount of cocatalyst, and a toluene solution of precatalyst; the total volume of the reaction mixture was 100 mL. At the reaction temperature, the reactor was sealed and pressurized to 10 atm with ethylene, and the ethylene pressure was maintained by feeding of ethylene. After the reaction was carried out for 30 min, the pressure was released and a small amount of the reaction solution was collected and 5% aqueous hydrogen chloride was added for GC analysis. The residual reaction solution was quenched with 5% hydrochloric acid in ethanol, the polymers were filtered, washed with ethanol and dried under vacuum at 60 °C to constant weight.

Magnetic measurements

Magnetic measurements were performed using a Quantum Design MPMS-XL SQUID magnetometer. The susceptibility measurement was performed in the 300–1.8 K temperature range with an applied field of 5 kOe. Magnetization measurements at different fields at a given temperature confirm the absence of ferromagnetic impurities. Data were corrected for the sample holder and diamagnetism was estimated from Pascal constants.

X-Ray structure determinations

Diffraction data of complexes **6**, **7** and **8** in **8**·THF were collected on a Kappa CCD diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å).[33]

Table 6 Crystallographic data for complexes **6**, **7** and **8**·C_4H_8O

	6	**7**	**8**·C_4H_8O
Formula	$C_{18}H_{30}Cl_3Cr_2N_3O_6$	$C_{20}H_{40}Cl_4Cr_2N_2O_6$	$C_{16}H_{32}Cl_4Cr_2N_2O_6\cdot C_4H_8O$
Formula weight	594.80	650.34	666.34
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_12_12_1$	$C2/c$	$P\bar{1}$
a/Å	8.7526(2)	19.4810(7)	10.3470(4)
b/Å	14.4126(5)	9.5507(3)	10.8770(4)
c/Å	19.5866(6)	16.9528(7)	14.7240(7)
α/°	90.00	90.00	98.425(2)
β/°	90.00	113.479(2)	102.112(3)
γ/°	90.00	90.00	109.096(2)
V/Å^3	2470.8(1)	2893.0(2)	1489.0(1)
Z	4	4	2
Color	Green	Purple	Violet
Crystal size/mm	0.06 × 0.05 × 0.05	0.1 × 0.08 × 0.08	0.10 × 0.05 × 0.05
D_{calc}/g cm^{-3}	1.599	1.493	1.486
μ/mm^{-1}	1.242	1.156	1.127
Max. 2θ	27.49	30.03	27.42
$F(000)$	1224	1352	692
Measured refl.	18 007	12 332	12 878
Observed refl. $[I > 2\sigma(I)]$	4813	3321	4481
Parameters	296	163	340
R_{int}	0.0545	0.0434	0.0492
R_1 $[I > 2\sigma(I)]$	0.0364	0.0374	0.0478
wR_2 $[I > 2\sigma(I)]$	0.0696	0.0949	0.1074
wR_2 (all data)	0.0736	0.1022	0.1249
S	1.011	1.066	1.023
Largest diff. peak, hole/e Å^{-3}	0.264, –0.491	0.417, –0.734	0.385, –0.644
Flack parameter	0.003(17)	—	—

Crystallographic and experimental details are summarized in Table 6. The structures were solved by direct methods (SHELXS-97)[34] and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97) with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined riding on the corresponding parent atoms, with refined torsion angles for the methyl groups. The water and ethanol protons in **7** and **8**·THF, respectively, were found in the ΔF maps and refined unconstrained. Crystallographic data for all of the structures in this paper can be found in the ESI.†

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