Evolution of the Structural Parameters and Magnetic Properties in a Series of Di(μ-hydroxy)bis(nitrilotriacetato)dichromium(III) Complexes

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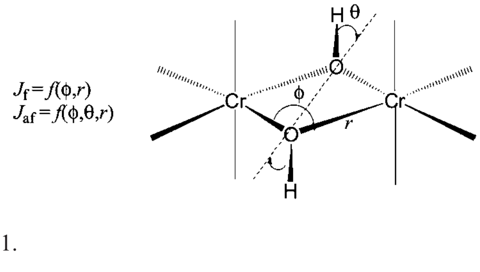
Dedicated to Prof. André E. Merbach (EPFL, Lausanne, Switzerland) on the occasion of 65th birthday

Keywords: Chromium / Alkaline earth metals / N,O ligands / Magnetic properties

Four heterometallic complexes $\{Mg(H_2O)_6\}[Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot 4H_2O$ (**I**), $\{Ca(H_2O)_3\}[Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot 3H_2O$ (**II**), $\{Sr(H_2O)_3\}[Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot 3H_2O$ (**III**) and $\{Ba(H_2O)_3\text{-}dmso\}[Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot 2H_2O$ (**IV**) containing dinuclear *bis*(μ-hydroxo) chromium(III) complex ions, where *nta* is the nitrilotriacetate ligand and *dmso* is dimethyl sulfoxide, have been prepared and crystallographically characterised. Compound **I** displays an ionic type structure, **II** and **III** are 3D coordination polymers and **IV** behaves like a 2D coordination polymer. In these compounds, the chromium(III) dimeric unit exhibits different structural features. It forms a polymeric structure by coordination of alkaline earth metal ions and/or formation of hydrogen-bonding interactions. The temperature dependencies of the magnetic susceptibilities of **I**–**IV** were fitted on the basis of the expression derived from the isotropic Hamiltonian including a biquadratic exchange term, $\hat{H} = -2J(\vec{S}_1\,\vec{S}_2) - j(\vec{S}_1\,\vec{S}_2)^2$. The values of the coupling interaction (J) range from $-17.38\ cm^{-1}$ to $-5.80\ cm^{-1}$ and the biquadratic terms (j) from $+0.71$ to $2.02\ cm^{-1}$. The experimental and theoretical values of J (calculated, using the Glerup–Hodgson–Pedersen model) have been discussed.

Introduction

The magnetic interactions between the unpaired electrons located at different metal atoms in polynuclear compounds are an important characteristic of magnetic materials.[1] The interest in this arises from the essential contribution of the exchange coupling constant to the magnetic properties of compounds containing coupled paramagnetic centres.[2] Among the transition-metal binuclear complexes known, many bridged complexes of transition metals with a wide variety of bridging ligands such as mono-cyanide[3] (CN^-, $S\text{–}CN^-$, $O\text{–}CN^-$), chloro,[4] azido,[5] oxo,[6,7] hydroxo,[8] oxalato[9] or even more complex bridges have been already described. The magnetic behaviour of these compounds depends on the ligand nature, the metal coordination number and the geometrical structure of the bridge. For closely related complexes such as alkoxo- and hydroxo-bridged $V^{II}O$[10] or oxo-bridged dimers,[11] magneto-structural correlations have been established. Many[12] studies have been devoted to chromium(III) dimers $[Cr_2(\mu\text{-}OH)_2L_x]^y$ with a *bis*(μ-hydroxo) bridge, where L are bidentate or polydentate ligands. For these types of dimer, Hoffmann and coworkers[12a] have characterised the exchange coupling constant J as the sum of ferromagnetic (J_f) and antiferromagnetic (J_{af}) terms where $J = J_{af} + J_f$. The two contributions J_f and J_{af} can be correlated to structural parameters: the metal-oxygen distance r, the in plane bridge angle φ as well as the out-of-plane distortions θ of the hydroxide ligand (Scheme 1).[12]



Scheme 1.

In the development of this correlation, Pedersen and coworkers[12b,12c] demonstrated that the magnetic exchange is highly sensitive to both θ and r or to the hybridisation state of the bridging oxygen atom.

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In this paper, we report the synthesis, structures and magnetic characterisation of four chromium(III) alkaline earth heterometallic complexes: $\{Mg(H_2O)_6\}[Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot 4H_2O$, (**I**), $\{Ca(H_2O)_3\}[Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot 3H_2O$ (**II**), $\{Sr(H_2O)_3\}[Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot 3H_2O$ (**III**) and $\{Ba(H_2O)_3\text{-}dmso\}[Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot 2H_2O$ (**IV**) where *nta* is the nitrilotriacetate ligand and *dmso* is dimethyl sulfoxide.

Results and Discussion

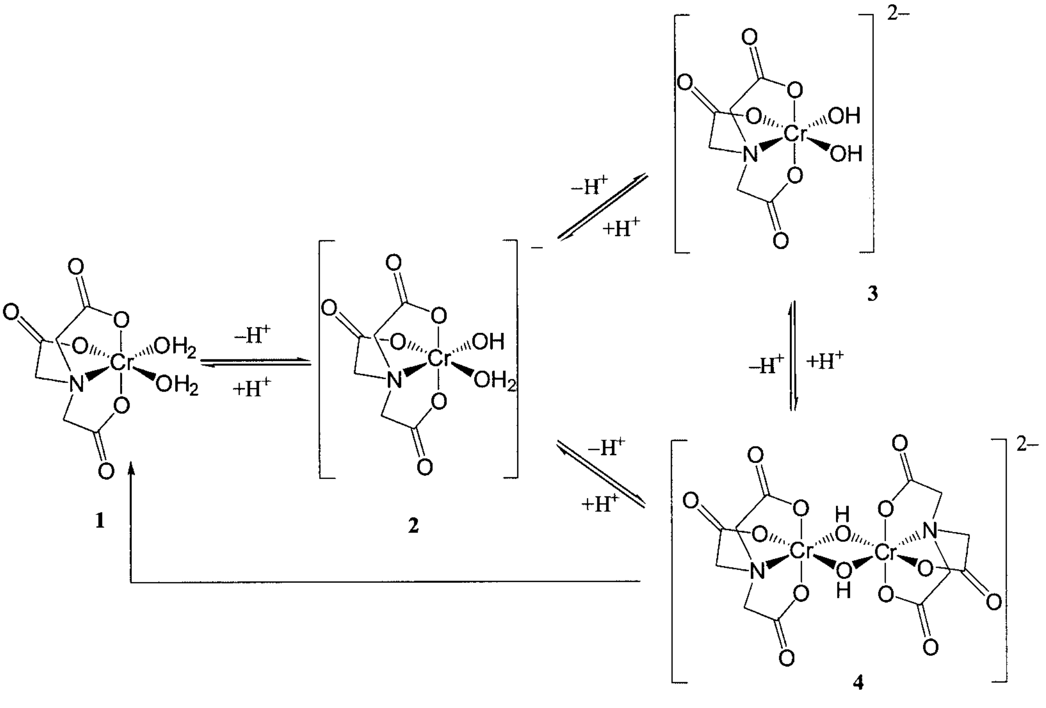
Synthesis and Characterisation of the Complexes

The heterometallic complexes **I**–**IV** containing dinuclear bis(μ-hydroxo)chromium(III) complex ions were prepared by the interaction of $CrCl_3\cdot 6H_2O$ and $M_3(nta)_2$ (where M = Ca^{2+}, Sr^{2+} or Ba^{2+}). The reactions proceed in aqueous solutions and the pH was adjusted with a solution of $M(OH)_2$. $M_3(nta)_2$ was previously obtained by an exchange reaction between MCO_3 and nitrilotriacetic acid (H_3nta). As usual, the formation of the dinuclear complex ion (**4**) (Scheme 2) results from a hydrolysis reaction which is characteristic of chromium(III) ions.[13] The reversibility of the protolytic reaction between **1** and **2** and also between **2** and **3** has already been demonstrated byspectroscopic (UV/Vis, ^{2}H NMR) and pH-metric investigations of different Co^{III} and Cr^{III}-*nta* complexes.[14]

This work reveals that the dimeric ions (**4**) are broken in an irreversible protonation step to form diaqua complexes (**1**). The very slow dimerisation steps **2**↔**4** and **3**↔**4** proceed over several days.[15] Compound **I** was obtained by an exchange reaction between the barium compound **IV** and $MgSO_4$.

In order to establish the coordination modes of the carboxylic groups of the nitrilotriacetate ligands, the IR absorption spectra of **I**–**IV** were determined. In the IR spectra, the difference between the asymmetric and the symmetric stretching frequencies [$\Delta = \nu_{as}(COO^-) - \nu_s(COO^-)$] characterises the coordination modes of the carboxylic groups.[15] In the IR spectrum of **I**, three intensive bands were found, namely one at ca. 1623 cm^{-1} related to $\nu_{as}(COO^-)$ and two at 1363 and 1335 cm^{-1} attributable to $\nu_s(COO^-)$. The differences between the asymmetric and symmetric frequencies are equal to 260 and 287 cm^{-1}. Differences higher than 250 cm^{-1} indicate two different monodentate modes of coordination for the carboxylate groups. In the IR spectra of compounds **II** and **III**, three intense bands corresponding to carboxylate moieties do exist: for **II** they are $\nu_{as}(COO^-) = 1596$ cm^{-1} and $\nu_s(COO^-) = 1385$ and 1345 cm^{-1} whereas for complex **III** these bands appear at 1597, 1386 and 1345 cm^{-1}. The related frequency differences $\Delta = 252$ cm^{-1} and 211 cm^{-1} support the presence of monodentate and bidentate bridging modes of coordination, respectively. The similarities of the values for complexes **II** and **III** suggest isostructural arrangements for the nitrilotriacetate ligands. Two coordination modes are also present in **IV**: monodentate ($\Delta = 255$ cm^{-1}) and bridging or chelating ($\Delta = 231$ cm^{-1}).

The electronic spectra of complexes **I**–**IV** in aqueous solution (in the 300–1100 nm range) show two bands $\nu_1(^4A_{2g}\rightarrow{}^4T_{2g}) = 17069$ cm^{-1} (ε = 40 L mol^{-1} cm^{-1}) and $\nu_2[^4A_{2g}\rightarrow{}^4T_{1g}(F)] = 24510$ cm^{-1} (ε = 63 L mol^{-1} cm^{-1}), characteristic for an $\{NO_5\}$ octahedral environment for chromium(III) with ligand field parameters $10Dq = 17069$ cm^{-1} and $B = 745$ cm^{-1}.[16] The configuration interaction (x) between



Scheme 2.

the $^4T_{1g}(F)$ and $^4T_{1g}(P)$ states of the same symmetry is 6214 cm^{-1}. The similarities in the wave numbers for **I**–**IV** indicate that the complexes dissociate in solution, keeping the dianionic dichromium structure unchanged.

Structures

A perspective view of the centrosymmetric dinuclear complex anion **I** is shown in Figure 1. A similar $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$ unit is present in the four complexes **I**–**IV** as well as in the $Cs_2[M_2(\mu\text{-}OH)_2(nta)_2]\cdot 4H_2O$ entities already reported (M = Cr, Co).[14a,14b] In compounds **II**–**IV**, the asymmetric part of the unit-cell contains two crystallographically independent nitrilotriacetate molecules which generate two different centrosymmetric dimeric anions (named **A** and **B** hereafter) (Figure 2).The octahedral coordination of the chromium atoms implies four donor atoms from the nta^{3-} ligands (N,O,O,O) and two bridging OH groups. For **I**–**IV**, the average Cr–N bond length is 2.060 Å [from 2.052(3) to 2.069(2) Å, Table 1] while a more significant dispersion is observed for the Cr–O bonds [from 1.952(1) to 2.015(2) Å]. The nta^{3-} ligand forms three five-membered ring chelates with the central atom. According to ref.[17] these rings can be classified as one *R* ring {N(1) CrO(6)C(6)C(5)N(1)} and two *G* rings (Figure 1). For complexes **I**–**IV**, the sums of the endocyclic angles vary in the ranges 537.5–540.0° and 524.9–536.2° for the *R* and *G* rings, respectively. Two oxygen atoms from hydroxy groups act as bridges in the $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$ anion (Figure 1 and Figure 2).The Cr–(μ-OH) bond lengths are in the range 1.942(3)–1.979(1) Å, as in the previously published $Cr_2(\mu\text{-}OH)_2$ fragments.[12,14a,14b,18b] Slight differences characterise the Cr–O(1)–Cr* angles (*φ*) [96.0(1)–101.2(8)°] (Table 1). As a consequence, the Cr–Cr distances vary from 2.928(1) to 3.014(1) Å. Significant differences can also be observed for the angles defined by the O–H and O(1)–O(1)* vectors (*θ* angles in Scheme 1 and Table 1). These angles are essential for differentiating the dimeric units and are 51(2)° (dimer **A**) and 8(3)° (dimer **B**) in compound **II.**

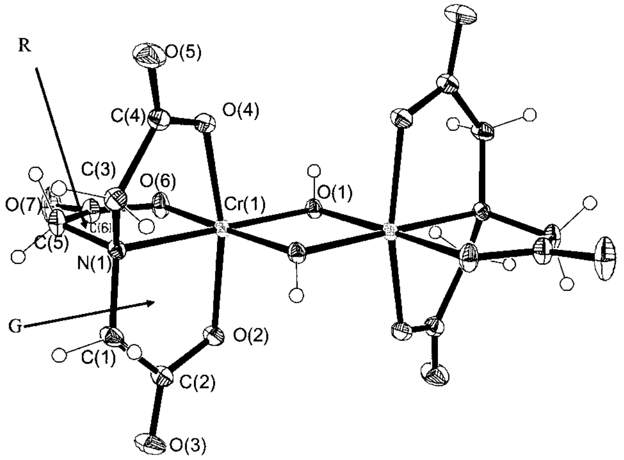


Figure 1. Perspective view of $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$ with the numbering scheme for **I**. Thermal ellipsoids are drawn at the 30% probability level.

The sizes of the alkaline earth metal ions from Mg^{2+} (0.72 Å) to Ba^{2+} (1.35 Å)[18a] lead to a change in the coordi-

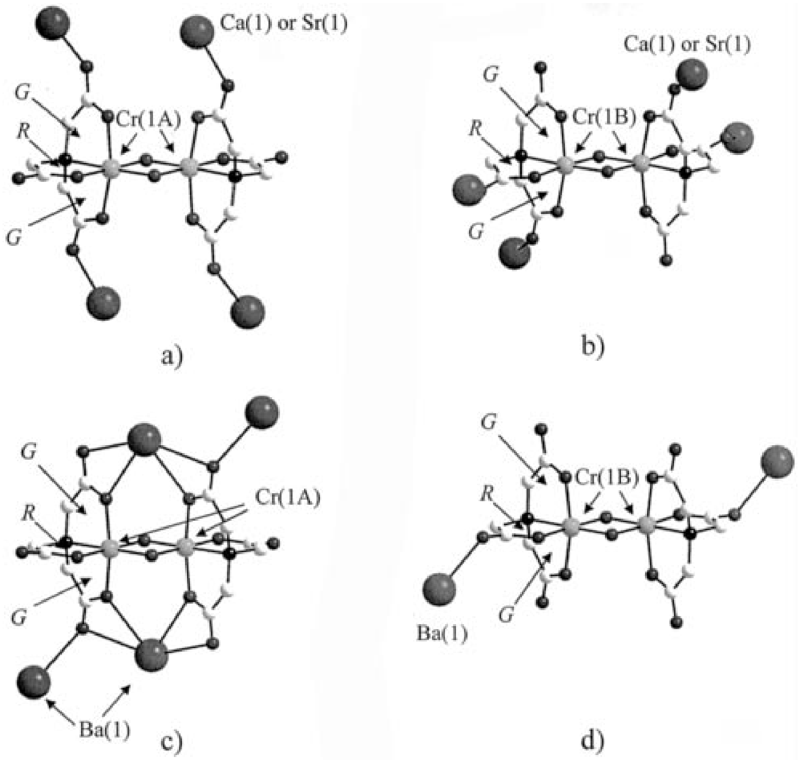


Figure 2. Ball and stick representations of the **A** and **B** type chromium(III) dimers in **II**–**IV**. a) **IIA** or **IIIA**, b) **IIB** or **IIIB**, c) **IVA** and d) **IVB**.

Table 1. Selected bond lengths [Å] and angles [°] in the $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$ dimers in **I**–**IV**.

	I	**II**		**III**		**IV**	
		A[a]	B	A	B	A	B
Cr–O(1)	1.966(1)	1.950(2)	1.950(2)	1.950(2)	1.942(3)	1.961(2)	1.943(2)
Cr–O(1)*	1.979(1)	1.958(2)	1.951(2)	1.949(2)	1.954(3)	1.978(2)	1.948(2)
Cr–O(2)	1.995(1)	1.989(2)	1.993(2)	1.999(2)	1.970(3)	1.959(2)	1.975(2)
Cr–O(4)	1.993(1)	1.987(2)	2.015(2)	1.975(2)	2.007(2)	1.976(2)	2.003(2)
Cr–O(6)	1.952(1)	1.983(2)	1.965(2)	1.965(2)	1.963(2)	1.953(2)	1.967(2)
Cr–N(1)	2.060(1)	2.065(2)	2.069(2)	2.063(3)	2.064(3)	2.052(3)	2.058(3)
Cr···Cr	2.985(1)	2.935(1)	3.014(1)	2.919(1)	2.993(1)	2.928(1)	2.929(1)
O(1)–Cr–O(2)	97.53(5)	98.43(7)	97.19(8)	100.3(1)	96.1(1)	96.9(1)	97.5(1)
O(1)–Cr–O(4)	99.10(5)	97.94(7)	101.43(8)	96.7(1)	101.7(1)	96.7(1)	99.4(1)
O(1)–Cr–N(1)	179.36(4)	179.76(7)	177.66(8)	178.3(1)	177.1(1)	178.8(2)	178.9(1)
O(1)*–Cr–O(2)	90.69(5)	91.77(8)	91.67(9)	91.8(1)	91.7(1)	89.8(1)	91.2(1)
O(1)*–Cr–O(4)	88.81(5)	88.92(8)	91.44(8)	88.3(1)	90.4(1)	87.6(1)	89.1(1)
O(1)*–Cr–N(1)	98.94(4)	97.12(7)	100.45(7)	97.1(1)	99.7(1)	97.3(1)	98.6(1)
O(2)–Cr–O(4)	163.11(4)	163.57(7)	161.38(7)	162.9(1)	162.2(1)	165.8(1)	163.0(1)
O(2)–Cr–O(6)	89.67(6)	89.46(8)	90.20(8)	89.3(1)	91.7(1)	90.4(1)	89.8(1)
O(2)–Cr–N(1)	82.72(5)	81.57(7)	80.59(8)	81.4(1)	81.1(1)	83.3(1)	82.0(1)
O(4)–Cr–N(1)	80.68(5)	82.05(7)	80.79(8)	81.6(1)	81.2(1)	83.2(1)	81.1(1)
O(6)–Cr–O(1)	94.77(4)	95.85(7)	95.99(7)	94.9(1)	96.1(1)	94.6(1)	93.6(1)
O(6)–Cr–O(1)*	176.43(4)	178.18(6)	174.65(7)	177.8(1)	174.8(1)	178.6(1)	175.9(1)
O(6)–Cr–O(4)	91.88(6)	90.28(8)	88.38(7)	91.2(1)	87.7(1)	92.5(1)	91.1(1)
O(6)–Cr–N(1)	84.63(4)	84.39(7)	84.80(7)	84.9(1)	84.8(1)	84.2(2)	85.5(1)
Cr–O(1)–Cr (φ)	98.34(4)	97.36(7)	101.20(8)	96.9(1)	100.4(1)	96.0(1)	97.7(1)
θ [°]	50(2)	51(2)	8(3)	50(4)	28(4)	50(3)	37(4)
Symm. transf. for *	*–x*, *–y* + 1, *–z*	*–x* + 1, *–y* + 1, *–z*	*–x* + 3, *–y*, *–z* + 1	*–x* + 1, *–y* + 1, *–z*	*x* + 3, *–y*, *–z* + 1	*–x* + 1, *–y* + 1, *–z* + 1	*–x* + 2, *–y* + 1, *–z*

[a] Two crystallographically independent *nta* molecules are named as **A** and **B**.

nation polyhedron and induce different assemblies of the dinuclear units in the polymer networks. In **I** the Mg^{2+} ion is surrounded by six water molecules and has an octahedral coordination geometry. The Mg–O distances vary between 2.049(1) Å and 2.072(2) Å, with the O–Mg–O angles close to 90°. Distances and bond angles (Table S2) are similar to those found in other $[Mg(H_2O)_6]^{2+}$ containing compounds.[18] Multiple hydrogen bonds involving coordinated and solvated water molecules link the $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$ anions with the $[Mg(H_2O)_6]^{2+}$ cations in a 3D network (Figure S1).

The isostructural compounds **II** and **III** are 3D coordination polymers (Figure 3). In this framework, four bridging carboxylic groups (η^1:η^1:μ_2) arising from four *G* rings from the **A** type dimers form bonds with seven-coordinate Ca or Sr ions (see a in Figure 2). On the other hand, two *G* and two *R* rings are used for the **B** type dimers (see b in Figure 2). The coordination polyhedron of Ca^{2+} is completed by four carboxylate oxygen atoms belonging to four Cr dimers with Ca–O lengths ranging from 2.395(2) to 2.431(2) Å and by three water molecules with bond lengths ranging from 2.410(2) to 2.427(2) Å (Figure 3). The corresponding bond lengths to the Sr centres in **III** increase with the ionic radius of Sr^{2+}. The Sr–O(*w*) bond lengths are in the range of 2.526(2)–2.573(2) Å and the Sr–O_{carb} distances vary from 2.507(2) to 2.561(2) Å. The 3D structure is stabilised by O–H···O hydrogen bonds (Table S1). The increase in the Sr–O bond lengths in comparison with the Ca–O distances leads to small modifications in the orientations of some of the H-bonds.

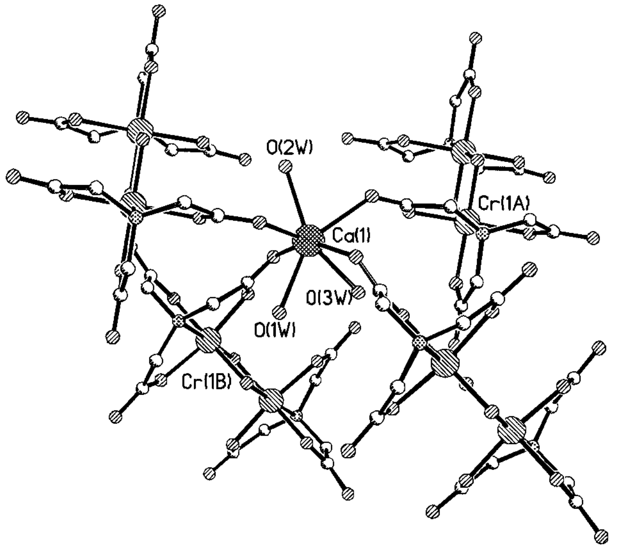


Figure 3. Coordination environment of Ca^{2+} in the 3D network of compound **II**.

In compound **IV**, the **A** type dimers have four *G* carboxylic groups chelating the ten- coordinate Ba^{2+} ions (see c in Figure 2). In **IV-A**, the carboxylic groups exhibit different bridging functions: two are tridentate bridging groups (η^2:η^1:μ_2) whereas the other two are tetradentate (η^2:η^2:μ_2). In contrast, only two *trans* (*R*) carboxylic bridging groups (η^1:η^1:μ_2) are bound to the Ba^{2+} ions in the **B** type dimers, (see d in Figure 2). The coordination sphere of barium is composed of six oxygen atoms from two nta^{3-} ligands [dis-

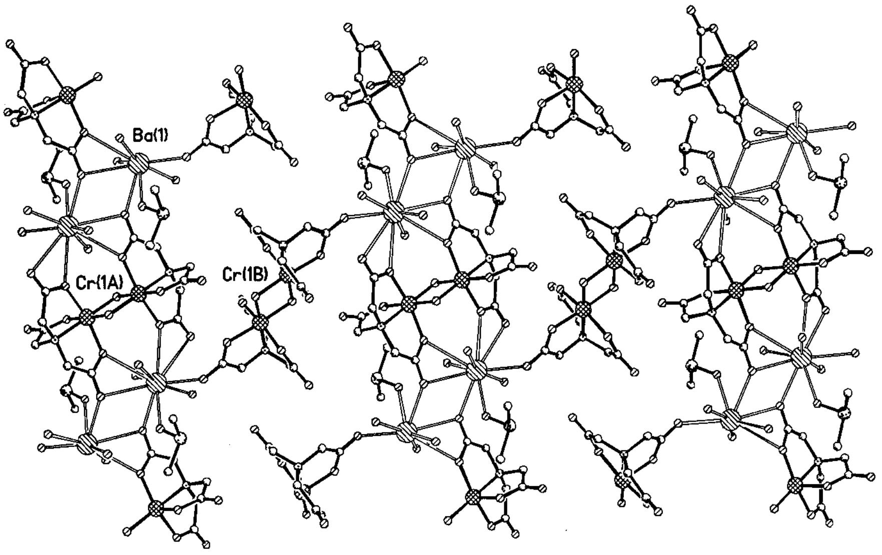


Figure 4. View of the 2D polymeric layer in compound **IV**. Hydrogen atoms and solvated water molecules have been omitted for clarity.

tances: 2.697(2)–3.094(3) Å], one dimethyl sulfoxide molecule [Ba(1)–O(1S) = 2.751(3) Å] and three H_2O molecules [2.786(3)–2.813(3) Å]. A centrosymmetric dimer **B** joins two atoms [Ba(1) and Ba(1*)] through two oxygen atoms [Ba(1)–O(7B) = 2.697(2) Å] whereas the second dimer (**A**) has five short contacts [2.827(2)–3.094(3) Å] with Ba(1). Furthermore, the carboxylate oxygen atoms O(5A) form a bridge between two centrosymmetric Ba^{2+} ions yielding dimers with Ba···Ba distances of 4.691(1) Å (Figure 4). Decadentate chelate-bridging dimeric anions enable the formation of chains with alternating of Cr(1A) and Ba(1) dimers along the *b* axis while Cr(1B)-dimers join the adjacent chains to give 2D polymeric layers (Figure 4). The layers are held together by hydrogen bonds (Table S1).

Magnetic Studies

The magnetic behaviour of compounds **I**–**IV** has been studied in the 2–300 K temperature range. As an example, the magnetic behaviour of **II** is shown in Figure 5 in the form of the thermal variation of χ_M, where χ_M is the molar susceptibility corrected for diamagnetism. At 300 K, χ_M is equal to 1.1×10^{-2} cm^{3}mol^{-1} which corresponds to the expected value for two uncoupled metal ($S = {}^3/_2$) ions both in the $^4A_{2g}$ ground state. As usual, the appropriate model for obtaining a fairly good agreement between the theoretical and experimental data may include a biquadratic exchange term [Equation (1)]. The resultant Hamiltonian is:[11e,11f,19]

$$\hat{H} = -2J(\vec{S}_1 \cdot \vec{S}_2) - j(\vec{S}_1 \cdot \vec{S}_2)^2 \tag{1}$$

and this leads to the following expression [Equation (2)].

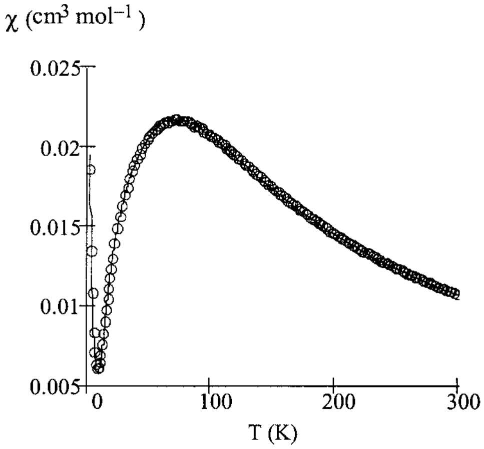


Figure 5. Magnetic susceptibility data for **II**. The solid line corresponds to the best fit for a pair of exchange-coupled $S = {}^3/_2$ spins including biquadratic exchange.

where the variable magnetic parameters *J* and *j* determine triplet, quintet and septet electronic ground states $E(^3A_2'') = -2J + 6.5j$, $E(^5A_1') = -6J + 13.5j$ and $E(^7A_2'') = -12J + 9j$, respectively (Scheme S1). C_{pi} represents the paramagnetic impurity factor. Least-squares fittings of the experimental data lead to the parameters collected in Table 2 with the agreement factors defined by $R = \Sigma(\chi_{calc} - \chi_{obs})^2/\Sigma(\chi_{obs})^2$. The negative *J* value indicates that the main exchange interaction in the dimeric building block fragments is antiferromagnetic. On the contrary, however, the biquadratic exchange *j* is positive but of lower amplitude with a

$$\chi_m = \frac{2Ng^2\mu_B^2(1-C_{pi})}{kT}\cdot\frac{\exp\left[{(2J-6{,}5j)}/{kT}\right]+5\exp\left[{(6J-13{,}5j)}/{kT}\right]+14\exp\left[{(12J-9j)}/{kT}\right]}{1+3\exp\left[{(2J-6{,}5j)}/{kT}\right]+5\exp\left[{(6J-13{,}5j)}/{kT}\right]+7\exp\left[{(12J-9j)}/{kT}\right]} \tag{2}$$

$j/2J$ ratio equal to 0.05.[20] In our complexes, a parallel evolution of J and j can be observed, with an increase of $|J|$ occurring as $|j|$ increases and a ratio varying from 0.05 to 0.06.

Table 2. Best parameters obtained from magnetic susceptibility data fitting.

Parameters	I	II	III	IV
J	–5.80(1)	–12.59(1)	–13.85(1)	–17.38(1)
j	0.71(2)	1.29(2)	1.31(2)	2.02(2)
Cp	–0.006	–0.039	–0.012	–0.0063
R	7×10^{-5}	7×10^{-5}	9×10^{-7}	9×10^{-7}

The exchange interaction in chromium(III) dimers with $S = 0, 1, 2$ and 3 concerns two coupled $(^4A_{2g})a(^4A_{2g})b$ states derived from the $|t_{2g}{}^3(a)t_{2g}{}^3(b)>$ configuration where $^4A_{2g}$ and $t_{2g}{}^3$ characterise two d^3-metal centres a and b. The chromium(III) t_{2g} orbitals containing the unpaired electrons and the p orbitals of the bridging OH-ligands are both involved in the superexchange interactions. In this pathway, the magnetic interactions also depend upon the orientation of the oxygen atom orbitals which determine the dominant contributions between the two paramagnetic centres. The resultant expression for J in the Heisenberg's Hamiltonian may be calculated using the Glerup–Hodgson–Pedersen model [Equation (3)].[12]

$$J = J_{af} - J_f = e^{-a(r-1.8)}\left[\frac{b\cdot\cos^4\theta}{\left\{(1-\sin^2\theta)\big/\tan^2(\phi/2)\right\}^2} - \frac{c\cdot\sin\phi}{(1-\cos\phi)^2}\right] \quad (3)$$

where r, φ and θ are defined as represented in Scheme 1. The calculated J values with $a = 19$ Å^{-1}, $b = 611$ cm^{-1} and $c = 172$ cm^{-1} [12b] and the experimental ones for **I**–**IV** are presented in Figure 6. Theoretical J values with their standard deviations were calculated using distances and angles obtained from X-ray experiments. For compound **I** and for **II-A** and **III-A** type dimers, experimental and theoretical estimations of J values are in fair agreement. For dimers **II-B** and **III-B**, the theoretical values are overestimated compared with the experimental measurements. This difference may be explained by a supplementary interaction between dimers through Ca or Sr ions. Indeed, the carboxylate groups bridge Cr and Ca or Sr ions in a *syn-anti* conformation for dimers **A** and in an *anti-anti* conformation for dimers **B**.

The Hamiltonian used in our calculations assumes that the chromium dimers are well isolated from each other. A look at the structural determinations indicates that this assumption is only true for complex **I**. In complexes **II**–**IV**, the Ca, Sr and Ba ions bridge these dinuclear units but we have no experimental evidence to suggest that such bridges are able to transmit magnetic interactions. On the contrary, the quality of the fits obtained for the entire set of complexes agrees with the accuracy of the retained Hamiltonian and the absence of magnetic interactions through the alkaline-earth metal ions.

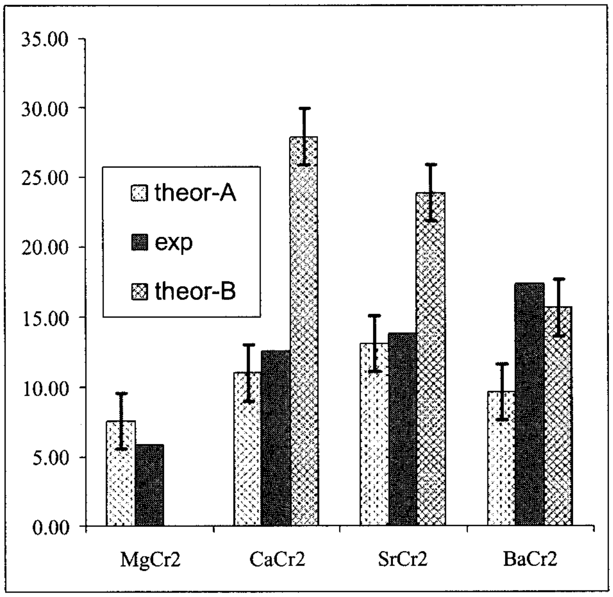


Figure 6. Experimental (best fit of Eq. 2) and theoretical (Glerup–Hodgson–Pedersen model, Eq. 3) J values for compounds **I**–**IV** (**theor-A** and **theor-B** correspond to the values calculated with the crystallographic data of the **A** and **B** dimers).

Conclusion

Four new heterometallic chromium nitrilotriacetate complexes have been synthesized and structurally characterised by X-ray analysis. The dinuclear di-(μ-hydroxo) chromium anion $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$ is present in each complex. Thus, the effect of substitution of one alkaline earth metal with another, while preserving the basic composition and inducing a variation in the number of solvated water molecules, affords dramatic alterations in the molecular structures which range from an ionic type in compound **I** to coordination polymers in **II**–**IV**. This is predetermined by the coordination function of $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$ and its binding to give 2D or 3D coordination polymers.

The IR spectra confirm, with help of the Δ parameters [$\Delta = \nu_{as}(COO^-) - \nu_s(COO^-)$], that monodentate, bidentate bridging or chelating coordination modes of the carboxylate groups are present. This is consistent with the structural features of the studied complexes.

The magnetic properties of this series of di-μ-hydroxo bridged chromium(III) complexes containing the nitrilotriacetic ligand include antiferromagnetic coupling interactions with J values ranging from –5.80 to –17.38 cm^{-1}. A comparison of the best fit magnetic parameters with theoretical values calculated using the Glerup–Hodgson–Pedersen model clearly shows a fair correlation with the structural parameters of the dinuclear units, with only a minute influence from the hydrogen bonds and the alkaline earth metal bridges.

Experimental Section

Materials: All starting materials and solvents were purchased from Aldrich and were used without further purification. Elemental analyses (C, H, N) were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse.

Syntheses: Calcium [Di-μ-hydroxy-bis(nitrilotriacetato)dichromium(III)] Hexahydrate $\{Ca(H_2O)_3\}[Cr_2(\mu\text{-}OH)_2(\mathit{nta})_2]\cdot 3H_2O$ (II): Water (100 mL) was added to a mixture of $H_3\mathit{nta}$ (0.76 g, 4 mmol) and dispersed $CaCO_3$ (0.6 g, 6 mmol). The resultant solution was warmed to 95 °C. After complete dissolution of $CaCO_3$, $CrCl_3\cdot 6H_2O$ (1.07 g, 4 mmol) in water (50 mL) was added to the initial solution (the temperature was maintained at about 95 °C). Heating was stopped after 1 h and a saturated solution of $Ca(OH)_2$ was added dropwise in order to raise the pH value to 6.5–7.0. As a result, the solution changed from violet to navy blue-green. The reaction mixture was filtered and concentrated to 30 mL. After 24 h, the crystals which appeared were separated by filtration, washed with cold water, ethanol and diethyl ether. Yield 70%. $C_{12}H_{26}CaCr_2N_2O_{20}$: calcd. C 21.76, H 3.96, N 4.23; found C 21.63, H 4.03, N 4.21.IR (KBr): $\tilde{\nu}$ = 3318 (br,m) ν(OH), 1596 (vs) $\nu_{as}(CO_2)$, 1455 (w) 1429 (w) $\delta(CH_2)$, 1385 (s) 1345 (s) $\nu_s(CO_2)$, 1272 (m) 1216 (m) $\rho_\omega(CH_2)$, 1098 (m) 1010 (m) ν(CN), 974 (w) ρ_r, 953 (m) 941 (m) ν(CC), 748 (s) $\delta(CO_2)$, 624 (s) $\rho_\omega(CO_2)$ cm^{-1}.

Strontium [Di-μ-hydroxy-bis(nitrilotriacetato)dichromium(III)] Hexahydrate $\{Sr(H_2O)_3\}[Cr_2(\mu\text{-}OH)_2(\mathit{nta})_2]\cdot 3H_2O$ (III)andBarium [Di-μ-hydroxy-bis(nitrilotriaacetato)dichromium(III)] Dimethyl Sulfoxide Pentahydrate $\{Ba(H_2O)_3\mathit{dmso}\}[Cr_2(\mu\text{-}OH)_2(\mathit{nta})_2]\cdot 2H_2O$ (IV): The syntheses were analogous to that of **II** except for neutralisation of the reaction mixture (pH = 6.5–7) that was carried out with concentrated NH_4OH.Compound **IV** was recrystallised from dimethyl sulfoxide. $\{Sr(H_2O)_3\}[Cr_2(\mu\text{-}OH)_2(\mathit{nta})_2]\cdot 3H_2O$ (**III**) Yield 65%. $C_{12}H_{26}Cr_2N_2O_{20}Sr$: calcd. C 20.30, H 3.69, N 3.95; found C 20.35, H 3.89, N 3.71. IR (KBr): $\tilde{\nu}$ = 3319 (m, br) ν(OH), 1597 (vs) $\nu_{as}(CO_2)$, 1455 (w) 1430 (w) $\delta(CH_2)$, 1386 (s) 1345 (s) $\nu_s(CO_2)$, 1274 (m) $\rho_\omega(CH_2)$, 1100 (m) 1011 (m) ν(CN), 941 (m) ν(CC), 744 (s) $\delta(CO_2)$, 621 (s) $\rho_\omega(CO_2)$ cm^{-1}.$\{Ba(H_2O)_3\mathit{dmso}\}[Cr_2(\mu\text{-}OH)_2(\mathit{nta})_2]\cdot 2H_2O$(**IV**) Yield 55%. $C_{14}H_{30}BaCr_2N_2O_{20}S$: calcd. C 20.51, H 3.69, N 3.42; found C 20.50, H 3.42, N 3.48. IR (KBr): $\tilde{\nu}$ = 3421 (s, br) ν(OH), 1653 (vs) 1617 (vs) $\nu_{as}(CO_2)$, 1456 (w) $\delta(CH_2)$, 1386 (vs) $\nu_s(CO_2)$, 1268 (m) 1212 (w) $\rho_\omega(CH_2)$, 1104 1093 (w) ν(CN), 951 (m) ν(CC), 754 (s) $\delta(CO_2)$, 621 (m) $\rho_\omega(CO_2)$ cm^{-1}.

Magnesium [Di-μ-hydroxy-bis(nitrilotriacetato)dichromium(III)] Decahydrate$\{Mg(H_2O)_6\}[Cr_2(\mu\text{-}OH)_2(\mathit{nta})_2]\cdot 4H_2O$ (I): $MgSO_4\cdot 7H_2O$ (0.25 g, 1 mmol) was dissolved in water (50 mL) and the crystalline complex **IV** (0.74 g, 1 mmol) was added. The mixture was stirred for 2 h at 70°C. The solution was then filtered and concentrated to a volume of 20 mL. A substance crystallised from the navy blue-green solution over 24 h and this was separated by filtration. The crystals obtained were washed with cold water, alcohol and eventually with acetone and were dried at room temperature. Yield 67%. $C_{12}H_{34}Cr_2MgN_2O_{24}$: calcd. C 20.05, H 4.78, N 3.89; found C 20.91, H 4.56, N 4.05. IR (KBr): $\tilde{\nu}$ = 3356 (s, br) ν(OH), 1623 (vs) $\nu_{as}(CO_2)$, 1457 (w) 1420 (w) $\delta(CH_2)$, 1363 (s) 1335 (s) $\nu_s(CO_2)$, 1268 (m) 1220 (m) $\rho_\omega(CH_2)$, 1107 (m) 1092 (m) ν(CN), 934 (m) ν(CC), 746 (s) $\delta(CO_2)$, 620 (s) $\rho_\omega(CO_2)$ cm^{-1}.

The substances **I–IV** are soluble in water, slightly soluble in DMSO and DMF but insoluble in ethanol and acetone.

Physical Measurements: TheIR spectra (KBr pellets) were recorded on a GX system 2000 Perkin–Elmer spectrophotometer. Electronic absorption spectra were recorded on a Perkin–Elmer UV/Vis-NIR-

Table 3. Crystal data and details of structural determinations.

	I	**II**	**III**	**IV**
Empirical formula	$C_{12}H_{34}Cr_2MgN_2O_{24}$	$C_{12}H_{26}CaCr_2N_2O_{20}$	$C_{12}H_{26}Cr_2N_2O_{20}Sr$	$C_{14}H_{30}BaCr_2N_2O_{20}S$
Formula mass	718.72	662.43	709.97	819.80
Temperature (K)	293	293	180	293
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	6.555(1)	9.711(2)	9.761(3)	9.787(2)
b [Å]	10.144(2)	10.576(2)	10.587(3)	10.974(2)
c [Å]	11.430(2)	13.041(3)	13.076(4)	12.876(3)
α [°]	111.52(3)	88.68(3)	89.05(2)	99.02(3)
β [°]	101.26(3)	75.03(3)	76.28(2)	90.96(3)
γ [°]	91.94(3)	64.23(3)	64.01(3)	102.45(3)
V [Å^3]	688.8(2)	1159.1(4)	1174.2(6)	1331.9(5)
D_{calc} [Mg m^{-3}]	1.733	1.898	2.008	2.044
Z	1	2	2	2
μ [mm^{-1}]	0.915	1.258	3.271	2.434
F(000)	372	680	716	816
Crystal size [mm]	0.35 × 0.35 × 0.3	0.40 × 0.20 × 0.07	0.37 × 0.15 × 0.12	0.40 × 0.2 × 0.2
θ range for data collection[°]	3.652–9.50	3.712–9.93	3.213–2.14	2.893–2.03
Limiting indices	$-8 \le h \le 6$, $-13 \le k \le 13$, $-15 \le l \le 15$	$-13 \le h \le 13$, $-8 \le k \le 14$, $-17 \le l \le 17$	$-12 \le h \le 14$, $-15 \le k \le 15$, $-18 \le l \le 19$	$-14 \le h \le 12$, $-15 \le k \le 15$, $-18 \le l \le 18$
Reflections collected	6581 [R_{int} = 0.0156]	14862 [R_{int} = 0.0239]	12499[R_{int} = 0.0474]	14140[R_{int} = 0.0367]
Completeness to θ	90.1%	88.7%	90.0%	90.4%
Data/restraints/parameters	3449/0/255	5961/19/426	7478/20/378	8402/16/417
Goodness-of-fit on F^2	1.070	1.059	0.850	0.982
T_{max} and T_{min}	0.809 and 0.737	0.805 and 0.698	0.988 and 0.559	0.980 and 0.705
R_1, wR_2 [$I > 2\sigma(I)$]	0.0270, 0.0715	0.0378, 0.0982	0.0466, 0.0879	0.0399, 0.0890
R_1, wR_2 (all data)	0.0292, 0.0733	0.0428, 0.1025	0.0790, 0.0962	0.0550, 0.0965
Largest diff. peak and hole (e Å^{-3})	0.321 and –0.496	0.684 and –0.695	1.760 and –1.207	1.727 and –1.331

Lambda-19 spectrophotometer. Magnetic susceptibility data (2–300 K) were collected on powdered samples using a SQUID-based sample magnetometer on a Quantum Design model MPMS instrument in an applied magnetic field of 0.1 T. All data were corrected for the diamagnetism of the ligands as estimated from Pascal's constants.[21]

Single-Crystal X-ray Analyses: X-ray diffraction data were collected with a KUMA KM4CCD-κ-axis diffractometer for compounds **I** and **II**, anOxford-Diffraction XCALIBUR CCD instrument for **III** and a Stoe Imaging Plate Diffractometer System (IPDS)[22a] for **IV** using graphite-monochromated Mo-K_α radiation. Absorption corrections were introduced for **I**–**IV** using semi-empirical methods from symmetry equivalent reflections.[22b,22c] Crystal data, details of data collections and refinements for **I**–**IV** are given in Table 3. The structures were solved by direct methods with SHELXS-97[22d] and refined on F^2 with SHELXL-97[22e] with an anisotropic approach for non-hydrogen atoms. In the crystal structure of **IV**, two water molecules O(2*w*) and O(4*w*) are disordered over two positions in the unit cell. The ratios of the site occupancy factors of the major and minor components *sof* O(2*w*)/*sof* O(2*w**) and *sof* O(4*w*)/*sof* O(4*w**) are 3:1. The positional parameters for the hydrogen atoms of bridging OH groups in **I**–**IV** were located objectively from the difference syntheses of electronic density and were refined in isotropic approximation. The accuracy of the determinations of H-atom coordinates guarantees that the estimated standard deviations of O–H bonds are no more than 0.05 Å and those of the bond angles no more than 4° (these data are used for interpretation of magnetic properties, see above). Other hydrogen atoms were also located from the difference syntheses of electronic density, except for the H-atoms of the minor components water molecules O(2*w**) and O(4*w**) for **IV**. H-atoms were refined in an isotropic approximation for **I** and **II**, except for the H-atoms of the H_2O molecules of **II**. In all other cases the positions of H atoms were allowed to ride on a pivot atom with isotropic displacement parameters fixed at $1.5 \times U_{eq}$ for H_2O and CH_3, and $1.2 \times U_{eq}$ for CH_2 groups where U_{eq} is the equivalent isotropic displacement parameter for the pivot atom.

CCDC-244108, -244109, -244110 and -244111 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information Available: Figure S1. Packing diagram of compound **I**. Hydrogen atoms are omitted for the sake of clarity and hydrogen bonds are indicated by dotted lines. Figure S2. Magnetic susceptibility data for **I**, **III** and **IV**. Table S1. Hydrogen bonding interactions in the crystal structures of **I**–**IV**. Table S2. Bond lengths [Å] in coordination polyhedra of the alkaline-earth metals in structures **I**–**IV**. Scheme S1. Energy level diagram for di(μ-hydroxo)chromium(III) dimers ($S = {}^3/_2$).

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