# Synthesis, Crystal Structure, and Magnetic Properties of a Ferromagnetically Coupled Difluoro-Bridged Dinuclear Chromium(III) Complex with a Substituted Tetrahydrosalen Derivative as Ligand[†]

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A novel difluoro-bridged dinuclear chromium(III) complex has been synthesized by the reaction of *trans*-[Cr-(py)$_4$F$_2$]ClO$_4$ in 2-methoxyethanol with a substituted tetrahydrosalen derivative L$^8$ (L$^8$ means the negatively charged ligand obtained by dissociation of two protons from H$_2$L$^8$ = *N*,*N'*-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)-1,2-ethanediamine). The crystal structure of [CrL$^8$F]$_2$·2C$_3$H$_8$O$_2$ has been determined. The crystal system is triclinic, and the lattice constants are $a$ = 9.604(2) Å, $b$ = 13.346(2) Å, $c$ = 15.751(2) Å, $\alpha$ = 74.00(1)°, $\beta$ = 87.94(1)°, and $\gamma$ = 70.55(1)°. $Z$ = 1 and the volume of the unit cell is 1826.40(49) Å$^3$. The space group is $\bar{P}1$ (No. 2). The refinement of 456 variables includes 6279 of the 7631 independent reflections. The final residual is 4.08%. The centrosymmetric dinuclear molecule consists of two slightly distorted octahedrally *cis* coordinated chromium centers bound together by two fluoride bridges. The Cr−F−Cr angle is 100.90(4)°, and the Cr−F(bridge) distances are 2.0172(8) and 1.9754(9) Å, and the Cr−Cr distance is 3.0787(4) Å. The configuration of the dinuclear molecule is *cis,cis*-O,O'-Δ,Λ, where *cis* refers to the position of the two oxygen donors and Δ and Λ refer to the configuration of the two N,O chelates of the tetradentate ligand L$^8$ at each of the two chromium(III) centers. The two chromium-(III) centers in the complex are ferromagnetically coupled. On basis of measurements of the field-dependent magnetization and the magnetic susceptibility, respectively, it has been shown unambiguously that the ground state is a septet state. It has not been possible to determine the monoatomic zero field splitting parameter $D$ from the magnetic susceptibility measurements, but the parameter has been determined from the EPR spectra measured at 4 and 21 K. From simulation of the EPR spectra the following parameters have been obtained: $J$ = −1.4 cm$^{-1}$, $D_e$ = 0.008 cm$^{-1}$, $E_e$ = −0.015 cm$^{-1}$, $D_a$ = $D_b$ = −0.658 cm$^{-1}$, $E_a$ = $E_b$ = 0.133 cm$^{-1}$, $g_{xa}$ = $g_{xb}$ = $g_{ya}$ = $g_{yb}$ = 1.98, and $g_{za}$ = $g_{zb}$ = 2.00.

## Introduction

As a continuation of our current studies[1−18] on thermodynamic, kinetic, magnetic, and electronic properties of di-, tri-, and tetranuclear complexes, we initiated[19,20] an investigation of oligomeric chromium(III) compounds with the tetrahydrogenated ligand H$_2$[H$_4$]salen and its derivatives. We and others have for many years studied transition metal complexes of these ligands,[21−33] but only few chromium(III) complexes with salen$^{2−}$

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[†] Ligand abbreviations (see also Chart 1): H$_2$L$^1$ = tetrahydrosalen = H$_2$[H$_4$]salen = *N*,*N'*-bis(2-hydroxybenzyl)-1,2-diaminoethane; H$_2$L$^2$ = *N*,*N'*-bis(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)-1,2-diaminoethane; H$_2$L$^3$ = *N*,*N'*-bis(2-hydroxybenzyl)-*trans*-(*S*,*S*)-1,2-cyclohexanediamine; H$_2$L$^4$ = *N*,*N'*-bis(2-hydroxybenzyl)-*cis*-1,2-cyclohexanediamine; H$_2$L$^5$ = *N*,*N'*-bis(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)-*trans*-(*S*,*S*)-1,2-cyclohexanediamine; H$_2$L$^6$ = *N*,*N'*-bis(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)-*cis*-1,2-cyclohexanediamine; H$_2$L$^7$ = *N*-(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)-*N'*-(1-(2-pyridyl)-ethyl)-1,1-dimethyl-1,2-ethanediamine; H$_2$L$^8$ = *N*,*N'*-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)-1,2-ethanediamine.
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or its substituted derivatives have been reported,[28–31] and only one chromium(III) complex with tetrahydrogenated salen has been published[32] prior to our recent studies.[19,20] In order to study the possible steric effects of substituents on the [H$_4$]salen$^{2-}$ backbone upon the stereochemistry and nuclearity of the complexes a series of ligands (L$^1$ to L$^7$ in Chart 1) with increasing bulkiness were investigated. The result was that minor changes in the ligand structure result in drastic changes in products. The ligands L$^1$ and L$^3$, respectively, were found to give tetranuclear chromium(III) species with a novel bridging skeleton, shown by a crystal structure of the [CrL$^1$]$_4$ complex, as schematically shown in Chart 2A. The ligands L$^2$ and L$^6$, respectively, gave dinuclear complexes assumed to have a difluoro-bridged structure as shown in Chart 2B. In this context it is noted that the crystal structure of another tetranuclear chromium(III) complex has been reported recently.[34] In the latter case the bridging skeleton is similar to that shown in Chart 2A, but with an additional fluoro-bridge between two opposed chromium(III) centers. With the ligand L$^5$ a dinuclear complex with an ethoxo and fluoro bridge was formed as shown by its crystal structure (Chart 2C). In all the above-mentioned experiments the compound *trans*-[Cr(py)$_4$F$_2$]ClO$_4$ was used as starting material. Using *trans*-[Cr(py)$_4$Cl$_2$]ClO$_4$ as starting
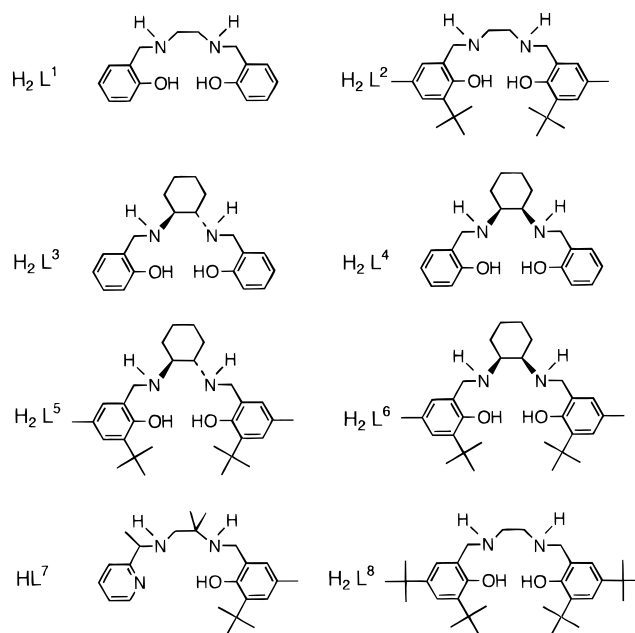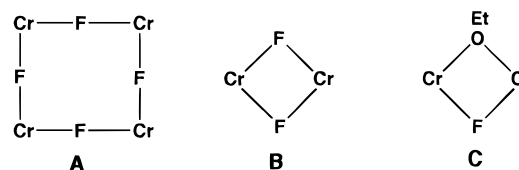
**Chart 1**



**Chart 2**



material, phenoxo-bridged complexes were formed and one of these has been characterized by an X-ray structure analysis.[20]

The proposed difluoro-bridged complexes (with L$^2$ and L$^6$) were shown to exhibit a ferromagnetic coupling between the two chromium(III) centers. This is a rather unusual situation for chromium(III), and it was therefore desirable to further characterize these compounds. Unfortunately we were unable to grow crystals suitable for X-ray structure determination, so that the proposed structures remained uncertain until now. In this work we describe our successful attempt to synthesize an analogue to the supposedly difluoro-bridged complexes reported previously and a crystal structure determination of the complex. Having successfully characterized the structure of this new difluoro-bridged compound it was an obvious candidate for a more detailed study of the magnetic and electronic interactions between the two metal centers using magnetic measurements and EPR spectroscopy. When the sample is cooled to very low temperatures (4 K), the increase in intensity of certain lines within the septet EPR spectrum proves that these lines are transitions from the lowest energy levels. On the basis of these facts we have been able to determine the absolute value of the zero field splitting (zfs) of the individual metal atoms.

## Experimental Section

The compound *trans*-[Cr(py)$_4$F$_2$]ClO$_4$ was prepared by published methods.[12,35] All other chemicals were of analytical grade. C, H, and N analyses were made by Preben Hansen at the Microanalytical Laboratory at the H. C. Ørsted Institute, Copenhagen. UV–vis absorption spectra were obtained using a Cary 3, or a Hewlett-Packard, 8451A, diode array spectrophotometer.

Proton NMR spectra were recorded on a Varian EM 360 L (60 MHz) spectrometer and chemical shift values ($\delta$) are reported in ppm relative to TMS in CDCl$_3$.

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Positive ion FAB mass spectra were obtained on a Jeol AX505W mass spectrometer using NBA (3-nitrobenzylalcohol) as matrix. The $m/z$ values given in the following are for the center of the isotope clusters.

Field dependent magnetization measurements at 3.5 K were performed by a Faraday system consisting of an Oxford Instrument superconducting magnet with a main field up to 8 T, and a maximum gradient field of 10 T m$^{-1}$. The system is equipped with a Cahn D200 microbalance with a resolution of 0.1 $\mu$g. HgCo(SCN)$_4$ was used as a calibrant. The sample was constituted of crystals contained in an aluminium container. The effect of the container was determined independently.

The magnetic susceptibility (cgs units) of powdered samples was measured with a Faraday balance, described elsewhere,[37] in the temperature range 2−300 K at field strengths of 0.26, 0.52, 0.78, 1.04, and 1.3 T. The measurements have also been performed on a mixture of the complex with 10% silicone grease to see if reorientation of the crystallites was of importance. The susceptibility data have been corrected for diamagnetism by Pascal's constants.

The EPR spectra have been measured with a Bruker ESP 300 equipped with an Oxford flow-cryostat ESP 900 (EPR frequency 9.39 GHz, modulation frequency 100 kHz, and modulation amplitude 0.5 mT).

**Syntheses.** *N,N′*-**Bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)-1,2-ethanediamine (H$_2$L$^8$).** 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde was prepared according to a published procedure.[36]

A solution of 23.43 g (0.1 mol) of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde in 200 mL of ethanol was heated to 70 °C and 3.01 g (0.05 mol) of 1,2-ethanediamine was added dropwise with stirring. The solution was then allowed to cool to room temperature. The yellow salen ligand was filtered off and washed with cold ethanol. Yield: 20.9 g (85%).

The salen ligand was reduced to the tetrahydrosalen ligand by the following method. To a stirred suspension of 9.86 g (0.02 mol) of salen ligand in 40 mL glacial acetic acid was added 3.77 g (0.06 mol) of solid NaBH$_3$CN within 2 h, whereupon the salen ligand dissolved and the solution became colorless. Then 60 mL of water was added and the pH was adjusted to approximately 7 by addition of concentrated NaOH. The mixture was extracted with 3 × 80 mL of CH$_2$Cl$_2$. The organic extract was washed with Na$_2$CO$_3$ solution and dried over anhydrous Na$_2$SO$_4$, and the solvent was evaporated in vacuo. The colorless residue was recrystallized from chloroform/petroleum ether to yield colorless needles of the pure compound. Yield: 6.96 g (70%). Melting point: 187 °C. IR data (KBr): $\nu$(N−H) 3300, 3340 cm$^{-1}$. $^1$H-NMR data (60 MHz, CDCl$_3$): $\delta$ = 1.3 (s, 18H; tBu), 1.4 (s, 18H; tBu), 2.9 (s, 4H; CH$_2$), 4.0 (s, 4H; CH$_2$), 6.9−7.4 (m, 4H; aryl-H).

**[CrL$^8$F]$_2$·2C$_3$H$_8$O$_2$.** A mixture of H$_2$L$^8$ (1.242 g, 2.5 mmol), *trans*-[Cr(py)$_4$F$_2$]ClO$_4$ (1.265 g, 2.5 mmol), and 2-methoxyethanol (60 mL) placed in a conical flask equipped with a condenser was stirred at 70 °C for approximately 15 min, during which time all solid dissolved. The solution was then kept without stirring at 70 °C for 3 days. Dark black-green crystals separated. The mixture was slowly cooled to room temperature and then kept for 2 days at 5 °C. The crystals were filtered off, washed with three 10-mL portions of 96% ethanol and then with diethyl ether, and dried in the air. Yield: 0.83 g (52%). Anal. Calcd for C$_{32}$H$_{50}$N$_2$O$_2$CrF·C$_3$H$_8$O$_2$: C, 65.50; H, 9.11; N, 4.36. Found: C, 65.35; H, 9.15; N, 4.42. FABMS $m/z$: 1130 (M = [CrL$^8$F]$_2$). The product is soluble in chloroform (green-blue), acetone (blue), hot dmso (purple), hot dmf (bluish purple), and hot nitromethane (blue). It is insoluble in acidic, neutral, and basic aqueous solutions.

UV−vis data: ($\epsilon$/(L (mol of Cr(III))$^{-1}$ cm$^{-1}$), $\lambda$/nm)$_{max}$ (189, 596, and 12450, 290, and 12600, 246); ($\epsilon$/(L(mol Cr(III))$^{-1}$ cm$^{-1}$), $\lambda$/nm)$_{shoulder}$ 199, 406. Solvent: chloroform.

**X-ray Structure Determination.** Crystal data and parameters of the data collection are compiled in Table 1. Unit-cell parameters were determined by accurate centring of 25 strong independent reflections with 17.93° ≤ $\theta$ ≤ 50.55° by the least-squares method. Reflection intensities were collected at 298 K on a four-cycle diffractometer Enraf-Nonius CAD4 equipped with a graphite monochromator and using

**Table 1.** Crystallographic data for [CrL$^8$F]$_2$·2C$_3$H$_8$O$_2$[a]

| chem formula | [C$_{32}$H$_{50}$O$_2$N$_2$FCr]$_2$·2C$_3$H$_8$O$_2$ |
| --- | --- |
| fw | 1283.706 |
| $a$/Å | 9.604(2) |
| $b$/Å | 13.346(2) |
| $c$/Å | 15.751(2) |
| $\alpha$/deg | 74.00(1) |
| $\beta$/deg | 87.94(1) |
| $\gamma$/deg | 70.55(1) |
| $V$/Å$^3$ | 1826.40(49) |
| Z | 1 |
| space group | $P\bar{1}$ (No. 2) |
| $T$/K | 298 |
| wavelength (Cu K$\alpha$)/Å | 1.54178 |
| $D_c$/gcm$^{-3}$ | 1.167 |
| $\mu$(CuK$_\alpha$)/cm$^{-1}$ | 29.315 |
| $R$ % | 4.08 |
| $R_w$ % | 4.47 |

[a] See also description of the crystal structure concerning the number of variables. $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = (\sum w||F_o| - |F_c|^2/\sum w|F_o|^2)^{1/2}$.

CuK$\alpha$ radiation. Three standard reflections monitored every hour showed no intensity loss. The usual corrections were applied. Diffraction absorption correction has been determined by $\psi$-scans. The structure was solved by the Patterson method using the program SHELXS-86.[38] Anisotropic least-squares refinement was carried out on all non-H-atoms using the program CRYSTALS.[39] Positions of H atoms have been calculated except those bonded to N or O atoms which have been refined isotropically restraining their bond lengths to 1 Å. Scattering factors were taken from the literature.[40] Final positional parameters for non-hydrogen atoms are given in Table 2, and selected bond lengths and angles are given in Table 3.

## Results and Discussion

**Synthesis.** A new dinuclear chromium(III) complex with the ligand L$^8$ (Chart 1) has been synthesized. The ligands L$^1$−L$^7$ shown in Chart 1 refer to previously[19,20] studied di- and tetranuclear species with chromium(III) as mentioned above. A novel fluoro-bridged complex with the stoichiometry [CrL$^8$F]$_2$·2C$_3$H$_8$O$_2$ was obtained from the reaction of *trans*-[Cr(py)$_4$ F$_2$]ClO$_4$ and L$^8$ in 2-methoxyethanol at 70 °C and was isolated in high yield (52%) as black-green crystals. The stoichiometry of the new complex, obtained from elemental analysis and FABMS, strongly indicated that it is a dinuclear neutral, so-called inner complex, and it is therefore not surprising that it is insoluble in acidic, neutral, and basic aqueous solvents. It is soluble in several organic solvents. The general low solubility of this new species made it in practice impossible to characterize and study it by the classical methods such as pH studies. The visible absorption spectrum (see Experimental Section) is similar to those reported[19] for the two supposedly difluoro-bridged complexes with the ligands L$^2$ and L$^6$.

**X-ray Crystal Structure of [CrL$^8$F]$_2$·2C$_3$H$_8$O$_2$.** The crystals of [CrL$^8$F]$_2$·2C$_3$H$_8$O$_2$ were thin, yellow-green plates. The sample chosen for the X-ray experiment had the dimensions of 0.10 × 0.14 × 0.38 mm (Table 1). The dimeric molecule crystallizes in the triclinic space group $P\bar{1}$ (No. 2). The structure is shown in Figure 1. The space between the ball-shaped molecules is filled with solvent molecules (2-methoxyethanol) from the reaction. The arrangement in the unit cell is shown in Figure 2, and the numbering of the atoms is shown in Figure 3. The center of symmetry falls together with the centroid of

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**Table 2.** Positional Parameters and Equivalent Isotropic Thermal Parameters for [CrL⁸F]₂·2C₃H₈O₂

| atom | x/a | y/b | z/c | U(eq) |
|------|------|------|------|------|
| Cr(1) | −0.09119(3) | 0.03301(2) | 0.07642(1) | 0.0274 |
| F(1) | −0.10483(9) | −0.02224(7) | −0.02893(5) | 0.0340 |
| O(1) | −0.0719(1) | 0.09685(9) | 0.16674(7) | 0.0373 |
| C(1) | −0.1165(2) | 0.2035(1) | 0.1679(1) | 0.0349 |
| C(2) | −0.1426(2) | 0.2305(1) | 0.2499(1) | 0.0384 |
| C(3) | −0.1435(2) | 0.1435(2) | 0.3368(1) | 0.0449 |
| C(4) | 0.0073(3) | 0.0537(2) | 0.3609(1) | 0.0674 |
| C(5) | −0.1845(3) | 0.1945(2) | 0.4145(1) | 0.0578 |
| C(6) | −0.2593(3) | 0.0907(2) | 0.3277(1) | 0.0639 |
| C(7) | −0.1705(2) | 0.3402(1) | 0.2481(1) | 0.0425 |
| C(8) | −0.1803(2) | 0.4261(1) | 0.1715(1) | 0.0421 |
| C(9) | −0.2076(2) | 0.5440(1) | 0.1770(1) | 0.0526 |
| C(10) | −0.3549(3) | 0.5848(2) | 0.2176(2) | 0.0689 |
| C(11) | −0.0850(4) | 0.5445(3) | 0.2333(3) | 0.0818 |
| C(12) | −0.2195(4) | 0.6264(2) | 0.0840(2) | 0.0723 |
| (C(110)) | −0.197(2) | 0.5436(8) | 0.2745(6) | 0.0744) |
| (C(111)) | −0.093(1) | 0.5877(9) | 0.1271(9) | 0.0587) |
| (C(112)) | −0.358(1) | 0.6168(8) | 0.136(1) | 0.0968) |
| C(13) | −0.1652(2) | 0.3984(1) | 0.0923(1) | 0.0426 |
| C(14) | −0.1341(2) | 0.2896(1) | 0.0896(1) | 0.0385 |
| C(15) | −0.1116(2) | 0.2672(1) | 0.0005(1) | 0.0403 |
| N(1) | −0.1808(2) | 0.1880(1) | −0.01177(8) | 0.0366 |
| C(16) | −0.3445(2) | 0.2246(1) | −0.0090(1) | 0.0461 |
| C(17) | −0.3949(2) | 0.1247(2) | 0.0174(1) | 0.0447 |
| N(2) | −0.3067(1) | 0.0498(1) | 0.10027(9) | 0.0378 |
| C(18) | −0.3258(2) | −0.0600(1) | 0.1333(1) | 0.0433 |
| C(19) | −0.2366(2) | −0.1252(1) | 0.2199(1) | 0.0378 |
| C(20) | −0.3071(2) | −0.1555(2) | 0.2971(1) | 0.0441 |
| C(21) | −0.2270(2) | −0.2157(2) | 0.3773(1) | 0.0456 |
| C(22) | −0.3040(2) | −0.2463(2) | 0.4634(1) | 0.0594 |
| C(23) | −0.3872(8) | −0.3200(6) | 0.4528(3) | 0.0831 |
| C(24) | −0.407(1) | −0.1472(5) | 0.4831(5) | 0.1119 |
| C(25) | −0.1901(6) | −0.3162(7) | 0.5439(3) | 0.0890 |
| (C(123)) | −0.283(1) | −0.3636(6) | 0.4898(6) | 0.1046) |
| (C(124)) | −0.4683(7) | −0.1797(9) | 0.4499(5) | 0.0895) |
| (C(125)) | −0.2411(9) | −0.2141(9) | 0.5344(4) | 0.0804) |
| C(26) | −0.0736(2) | −0.2481(2) | 0.3761(1) | 0.0437 |
| C(27) | 0.0036(2) | −0.2220(1) | 0.3011(1) | 0.0372 |
| C(28) | 0.1733(2) | −0.2700(1) | 0.3040(1) | 0.0426 |
| C(29) | 0.2150(2) | −0.3509(2) | 0.2471(1) | 0.0532 |
| C(30) | 0.2422(3) | −0.3363(2) | 0.3977(1) | 0.0618 |
| C(31) | 0.2449(2) | −0.1805(2) | 0.2695(2) | 0.0563 |
| C(32) | −0.0817(2) | −0.1545(1) | 0.2216(1) | 0.0336 |
| O(2) | −0.0181(1) | −0.11936(9) | 0.14700(7) | 0.0355 |
| O(40) | −0.2930(3) | 0.8947(2) | −0.1075(2) | 0.0967 |
| C(41) | −0.2821(4) | 0.8742(3) | −0.1883(2) | 0.0959 |
| C(42) | −0.2783(4) | 0.7619(3) | −0.1860(2) | 0.0945 |
| O(43) | −0.4161(2) | 0.7483(2) | −0.1627(2) | 0.0918 |
| C(44) | −0.4216(5) | 0.6450(4) | −0.1655(3) | 0.1211 |

*a* Rows in parentheses refer to the less frequent of the disordered forms, see text. The isotropic equivalent displacement parameter is defined as one-third of the trace of the orthogonalized **U**ᵢⱼ tensor.

**Table 3.** Selected Distances (Å) and Angles (deg)

| | | | |
|------|------|------|------|
| Cr(1)−Cr(1)* | 3.0787(4) | Cr(1)−N(1) | 2.065(1) |
| Cr(1)−F(1) | 2.0172(8) | Cr(1)−N(2) | 2.039(1) |
| Cr(1)−F(1)* | 1.9754(9) | Cr(1)−O(2) | 1.929(1) |
| Cr(1)−O(1) | 1.891(1) | | |
| | | | |
| F(1)−Cr(1)−F(1)* | 79.10(4) | N(2)−Cr(1)−O(1) | 92.37(5) |
| O(1)−Cr(1)−F(1) | 173.80(4) | N(2)−Cr(1)−N(1) | 83.84(5) |
| O(1)−Cr(1)−F(1)* | 96.96(5) | O(2)−Cr(1)−F(1) | 88.00(4) |
| N(1)−Cr(1)−F(1) | 84.38(4) | O(2)−Cr(1)−F(1)* | 91.44(4) |
| N(1)−Cr(1)−F(1)* | 89.74(5) | O(2)−Cr(1)−O(1) | 96.93(5) |
| N(1)−Cr(1)−O(1) | 90.85(5) | O(2)−Cr(1)−N(1) | 171.93(5) |
| N(2)−Cr(1)−F(1) | 91.06(5) | O(2)−Cr(1)−N(2) | 93.66(5) |
| N(2)−Cr(1)−F(1)* | 168.76(4) | Cr(1)−F(1)−Cr(1)* | 100.90(4) |

the four-membered ring formed by the two chromium and the two fluorine atoms.

Two of the four *tert*-butyl groups of the hydrogenated salen ligand are disordered. They are rotating around the bond to
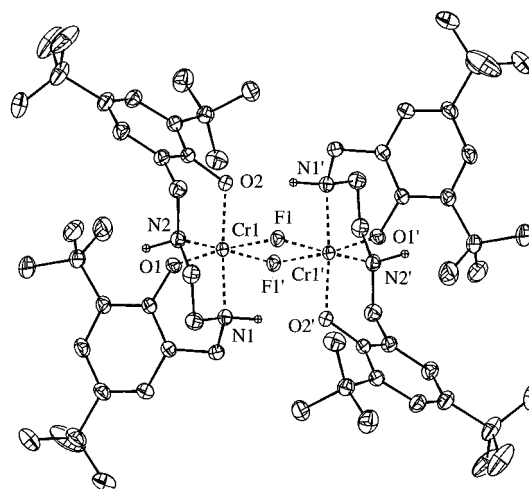


**Figure 1.** Structural view of the coordination geometry of [CrL⁸F]₂.

the phenyl ring. They have been refined using a disorder model. The occupancies of the two contributors have been refined holding their sum equal to 1. This procedure led to acceptable anisotropic temperature parameters but of course augmented the number of refined parameters theoretically expected. For one group we found a ratio of frequency of 84% to 16%, for the second one, the ratio was 58% to 42%. In Table 2 the values concerning the less frequent form are given in parentheses. For clarity, only the more frequent form is shown in Figures 1 and 2. The configuration of the dinuclear molecule is *cis,cis*-O,O′-Δ,Λ, where *cis* refers to the position of the two oxygen donors and Δ and Λ refer to the configuration of the two N,O chelates of the tetradentate ligand L⁸ at each of the two chromium(III) centers as shown in Figure 4. The same *cis,cis*-O,O′ configuration has been reported for the dinuclear (L⁵) and tetranuclear (L¹) complexes mentioned above.[19]

The octahedral coordination polyhedra around the two Cr centers are distorted and all angles deviate significantly from 90°. Whereas the Cr−N distances differ only slightly (2.065 and 2.039 Å) the differences in the Cr−F distances (2.017 and 1.975 Å) and the Cr−O distances (1.891 and 1.929 Å), respectively, are more pronounced. The F−Cr−F angle is 79.10° and the Cr−F−Cr angle is 100.90°. The Cr−Cr distance is 3.0787 Å.

**Magnetization Measurements.** In order to obtain evidence for the septet ground state, magnetization measurements were performed. A plot of the field dependent magnetization measurement at 3.5 K is presented in Figure 5, where the magnetization is plotted versus the magnetic field $B$ (T). The experimental data approach saturation, following the behavior of a Brillouin function[41] of a $S = 3$ spin system. The theoretical expressions (eqs 1−3) were applied for calculation. The best

$$M = Ng\,\mu_B S B_S(\eta) \tag{1}$$

$$B_S(\eta) = \frac{1}{S}\left[\left(S + \frac{1}{2}\right)\coth\left(S + \frac{1}{2}\right)\eta - \frac{1}{2}\coth\frac{\eta}{2}\right] \tag{2}$$

$$\eta = \frac{g\mu_B B_0}{kT} \tag{3}$$

fit, represented in Figure 5 as a solid line, was obtained with $g = 1.92(3)$. The calculated $g$ value is in good agreement with that obtained from magnetic susceptibility measurements. However, it has to be considered that from magnetization

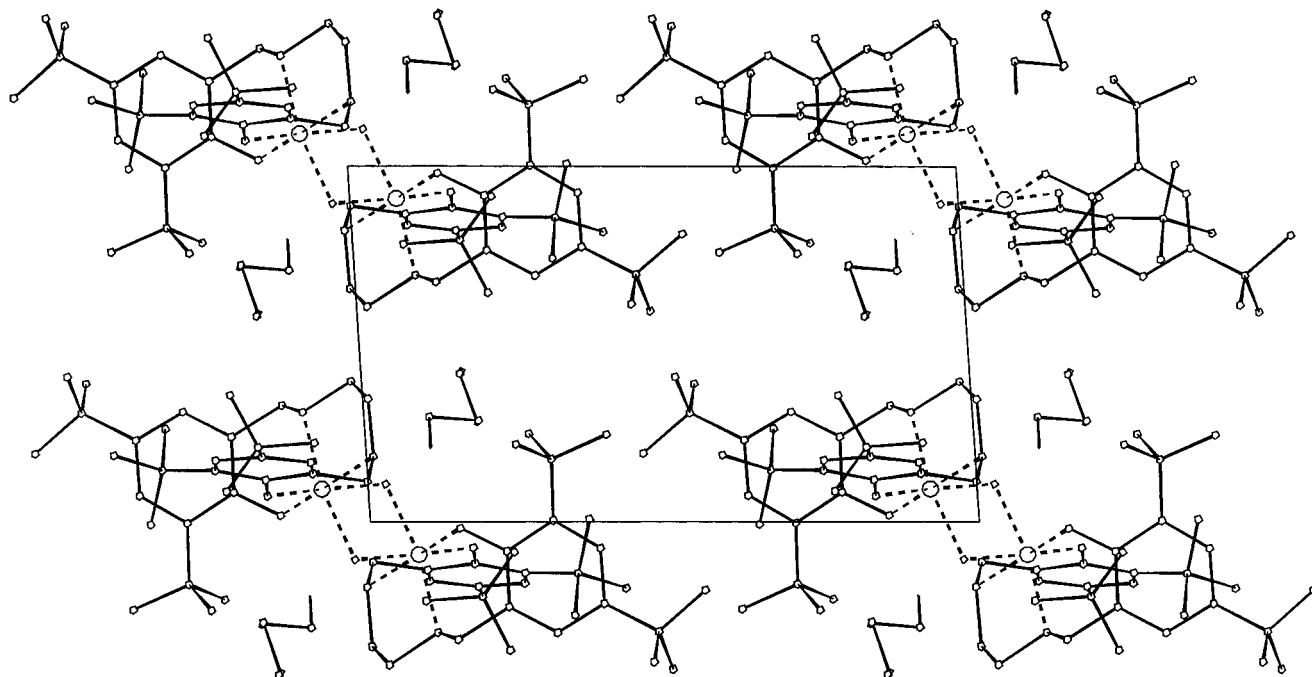(41) Carlin, R. L. *Magnetochemistry*; Springer Verlag: Berlin, 1986; p 333.

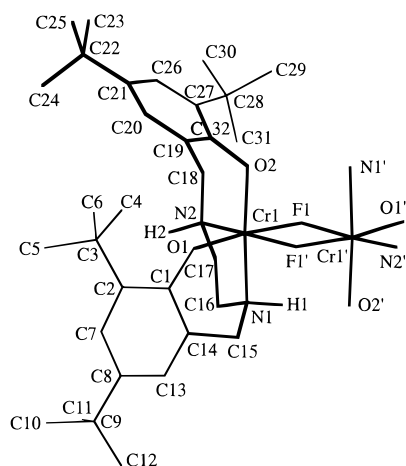**Figure 2.** Unit cell viewed along the crystallographic *b*-axis.
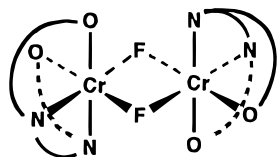


**Figure 3.** Numbering scheme for [CrL$^8$F]$_2$.



**Figure 4.** Schematical drawing of the coordination geometry of *cis,-cis*-O,O′-Δ,Λ-[CrL$^8$F]$_2$ illustrating the configuration of the dinuclear molecule, where *cis* refers to the position of the two oxygen donors and Δ and Λ refer to the configuration of the two N,O chelates of the tetradentate L$^8$ at each of the two chromium(III) centers.



**Figure 5.** Plot of the magnetization per molecule vs. magnetic field strength *B/T*. Experimental data (●) and calculated graph (—) of the Brillouin equation with *T* = 3.5 K, S = 3, g = 1.92.



**Figure 6.** The magnetic susceptibility (cgs units) and the effective magnetic moment of *cis,cis*-O,O′-Δ,Λ-[CrL$^8$F]$_2$·2C$_3$H$_8$O$_2$.

measurements only information about the ground state is obtained. Exchange coupling, intercluster interaction as well as zero-field splitting of the ground state lead to reduced magnetization data, which are disregarded using the Brillouin expression. Hence lower g values are obtained.[42]

**Magnetic Susceptibility.** The magnetic moment measured at 1.3 T increases from 5.25 $\mu_B$ at room temperature to a maximum of 6 $\mu_B$ at 4 K and then decreases slightly at 2 K. At 1.3 T there is a distinct maximum while at 0.26 T there is no
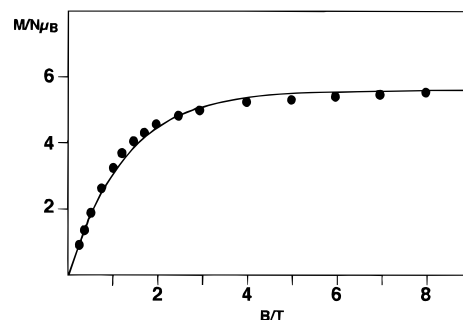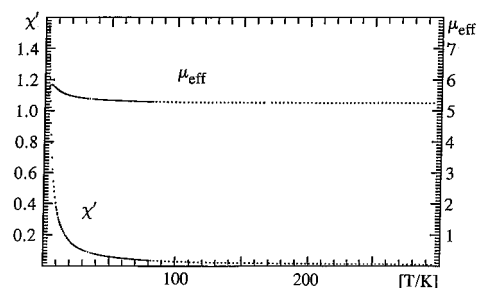
maximum above 2 K (Figure 6). The susceptibility is slightly field dependent between 2 and 5 K. This behavior is in accordance with a small ferromagnetic interaction and the decrease in magnetic moment between 4 and 2 K is caused by saturation effects. To assure that the ferromagnetic interaction is not caused by reorientation of small anisotropic crystallites in the magnetic field the susceptibility has been measured having mixed the compound with 10% grease, and it is concluded that the ferromagnetic coupling is genuine. Because of the saturation effects it is mandatory to calculate the magnetic susceptibility of a ferromagnetically coupled complex from eq 4 and not from the Van-Vleck equation.

(42) Brown, D. B.; Crawford, V. H.; Wittall, J.; Hatfield, W. E. *J. Phys. Chem.* **1977**, *81*, 1303.

$$\chi' = \frac{1}{3}\sum_{j=x,y,z} - \frac{N}{B_0}\frac{\sum_i \dfrac{\partial E_{ij}}{B_0}\exp(-E_{ij}/kT)}{\sum_i \exp(-E_{ij}/kT)} + \frac{C}{T} + K \quad (4)$$

The $E_{ij}$ values were calculated by means of the operator in eq 5. From the EPR spectra discussed below it is concluded

$$E_{ij} = J\hat{S}_a\cdot\hat{S}_b + \sum_{i=a,b}D_i[\hat{S}_{iz}^2 - {}^1\!/_3 S(S+1)] \quad (5)$$

that the monoatomic zfs parameter $D$ in the septet state is negative and of the same order of magnitude as the $J$ value, *vide supra.* We have therefore tried to determine the monoatomic zfs parameter as well as the $J$ value from the susceptibility data. The $g$ values and $D_i$ values for the two metal atoms are assumed to be equal in accordance with the crystal structure. However, the $D$ value and the $J$ value are strongly correlated, so that minimization of the expression in eq 6 failed to give

$$\sum_T \frac{[\chi_{\text{mol,exp}(T)} - \chi_{\text{mol,calc}(T)}]^2}{\sigma^2(\chi') + \left(\dfrac{\partial\chi'}{\partial T}\right)^2\sigma^2(T)} \quad (6)$$

well-defined values for these parameters. The following parameters were obtained: $J = -1.5(7)$ cm$^{-1}$, $|D| = 1(1)$ cm$^{-1}$ where the $g$ values have been fixed at 1.98.

**EPR Spectra.** A large number of EPR studies of dinuclear Cr(III) compounds have been published,[11,15−20,43,44] and in all cases the two chromium(III) centers have been antiferromagnetically coupled with $J$ values ranging from 5 to 147 cm$^{-1}$. These spectra are dominated by transitions within the quintet state. Only in a few cases it has been possible to assign lines in the spectra to the triplet[17,43] or septet[16,43] states. It is difficult to determine all the parameters of the spin Hamilton operator from the powder EPR spectrum of a dimeric chromium complex alone. Measurements on single crystals have previously been used for this purpose.[43] It has also been possible to obtain the monomeric parameters $D_a$, $D_b$, $E_a$, $E_b$ and the $g$ values from powder spectra of a similar dinuclear complex, in which one of the two Cr(III) ions is substituted by a diamagnetic metal ion, e.g. Co(III).[16,17] In the present study, it has been possible only to obtain measurements on powder. Generally EPR spectra have to be recorded using diluted samples in order to obtain narrow lines. However, the large bulky ligand L$^8$ insures a sufficient large distance between the ferromagnetically coupled dinuclear units, making intermolecular magnetic interaction negligible.

X-band EPR-spectra of a powdered sample of [CrL$^8$F]$_2$·2C$_3$H$_8$O$_2$ measured at 4 and 21 K are shown in Figure 7. The EPR spectra were simulated by means of the spin Hamilton operator given in eq 7. $H_{\text{ex}}$ is given by eq 8 and $H_a$ by eq 9

$$\hat{H} = \hat{H}_{\text{ex}} + \hat{H}_a + \hat{H}_b \quad (7)$$

$$\hat{H}_{\text{ex}} = J\hat{S}_a\cdot\hat{S}_a + D_e(2\hat{S}_{az}\hat{S}_{bz} - \hat{S}_{ax}\hat{S}_{bx} - \hat{S}_{ay}\hat{S}_{by}) + \\ E_e(\hat{S}_{ax}S_{bx} - \hat{S}_{ay}\hat{S}_{by}) \quad (8)$$

$$\hat{H}_a = \bar{g}_a\mu_B\hat{B}\cdot\hat{S}_a + D_a\left[\hat{S}_{az}^2 - \frac{1}{3}S_a(S_a+1)\right] + E_a(\hat{S}_{ax}^2 - \hat{S}_{ay}^2) \quad (9)$$
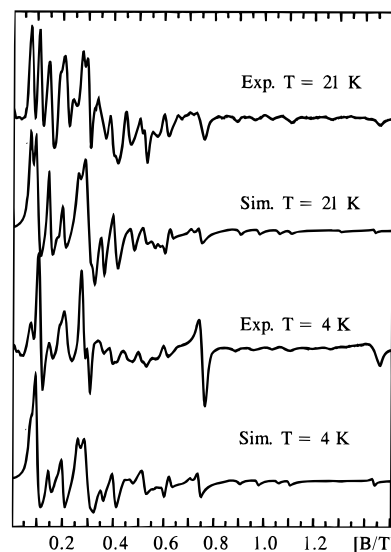


**Figure 7.** Experimental and simulated EPR spectra at 21 and 4 K. The intensities of the simulated spectra are Boltzmann weighted.

with a similar operator for $H_b$. $H_{\text{ex}}$ describes the interaction between the two chromium ions, while $H_a$ and $H_b$ are monomeric operators.

The coupling of the two Cr(III) ($S = {}^3\!/_2$) ions results in states with $S = 0$, 1, 2, and 3 with energies 0, $J$, $3J$, and $6J$, respectively. The negative sign of $J$ (*vide infra*) indicating ferromagnetic coupling, implies that the septet has the lowest energy. All the lines in the experimental spectra can be assigned to transitions within either the septet or the quintet states. From the temperature variation of the intensities, it is concluded that the lines at 0.1, 0.28, 0.75, and 1.45 T belong to the septet and those at 0.07, 0.15, and 0.3 T to the quintet.

Because of the crystallographic equivalence of the two chromium ions in the dimeric unit, corresponding monomeric parameters are equal. That is, $D_a = D_b$, $E_a = E_b$, and $g_{qa} = g_{qb}$ ($q = x$, $y$, $z$). In this case the energy matrix of dimension 16 can be transformed into two matrices of dimensions 6 and 10, respectively. The first of these matrices contains the singlet and quintet part of the energy matrix, while the latter contains the triplet and septet part.[15] The use of an effective spin Hamiltonian[41] was not justified due to the low value of $J$.

The low numerical value of $J$ in the present case means that both the septet and the quintet states are sufficiently populated to be represented in the EPR spectrum even at 4 K. From these two parts of the spectrum it has been possible to determine all the spin Hamilton parameters.

The parameters $D_a$, $D_b$, and $D_e$ occur in a constant ratio in the septet part of the spin Hamilton matrix, and likewise for the parameters $E_a$, $E_b$, and $E_e$. From the septet part of the spectrum it is only possible to determine an effective $D$ parameter ($D_{\text{septet}} = {}^9\!/_{10}D_e + {}^1\!/_5 D_a + {}^1\!/_5 D_b$) and an effective $E$ parameter ($E_{\text{septet}} = 3E_e + 2E_a + 2E_b$). The quintet spectrum is mainly determined from $D_e$ and $E_e$, while $D_a$, $D_b$, $E_a$, and $E_b$ only have second-order influence through the matrix elements between the singlet and the quintet. From the quintet spectrum it is therefore possible to determine only approximate values for the monomeric parameters.

For these reasons, the simulations were carried out by first simulating the septet spectrum alone with the parameters $D_e$ and $E_e$ set to zero. A trial and error approach with systematic variation of the monomeric $D$ and $E$ parameters was used. A

(43) Kremer, S. *Inorg. Chem.* **1985**, *24*, 887.
(44) Andersen, P.; Døssing, A.; Larsen, S.; Pedersen, E. *Acta Chem. Scand.* **1987**, *A41*, 381.
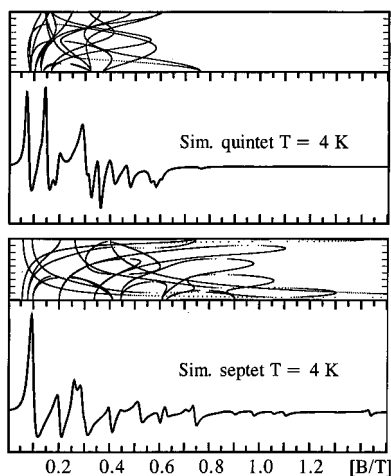
**Figure 8.** Simulated quintet (top) and septet (bottom) EPR spectra. The top boxes show the angular dependencies of the transitions.
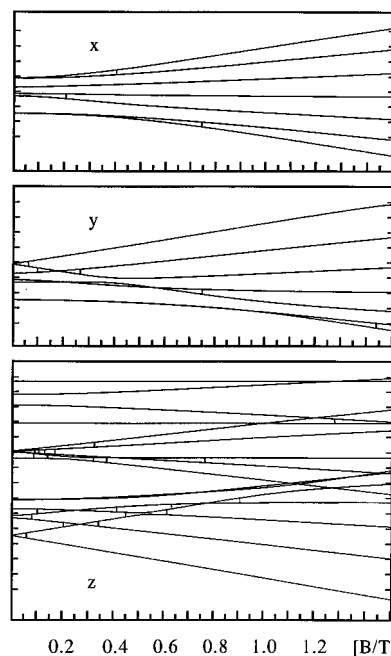


**Figure 9.** Plot of the energy levels as a function of the magnetic field. The three boxes show the magnetic field parallel to the magnetic x axis (top), y axis (middle) and z axis (bottom) of the dimeric molecule. For the x-axis and y-axis only the energy levels for the septet state are shown, while for the z-axis the energy levels for all states are shown.

negative value of the monomeric zero field splitting parameters $D_a$ and $D_b$ was chosen, since this implies that the transitions observed at 0.75 and 1.45 T are from the ground levels at these magnetic fields (see Figure 8). This is in accordance with the observed increase of the intensities of these transitions with decreasing temperature. When a satisfying septet spectrum was obtained (Figure 8, bottom), quintet spectra with different values for $D$, $D_e$, $E$, $E_e$, and $J$ were simulated with $D_{septet}$ and $E_{septet}$ held constant (Figure 8, top). In the simulated spectra in Figures 7 and 8, the intensities of all transitions were weighted with their Boltzmann population at the given temperatures.

Since the value of $J$ could not be determined accurately from the measurements of the magnetic susceptibility (see above), these parameters have been estimated by including $J$ as a variable in the simulations.

The final results are shown in Figures 7–9, which have been obtained using the following parameters: $J = -1.4$ cm$^{-1}$, $D_e = 0.008$ cm$^{-1}$, $E_e = -0.015$ cm$^{-1}$, $D_a = D_b = -0.658$ cm$^{-1}$, $E_a = E_b = 0.133$ cm$^{-1}$, $g_{xa} = g_{xb} = g_{ya} = g_{yb} = 1.98$, and $g_{za} = g_{zb} = 2.00$.

The antiferromagnetic coupling in dihydroxo-bridged chromium(III) complexes has been explained in a semiquantitative angular overlap model, which relates the magnitude of the coupling to the Cr−O−Cr angle, Cr−O bond length, and the angle $\theta$ between the bridging plane and the OH vector of the bridging group.[13] The crystallographic data for the bridging angles and distances in the present difluoro-bridged complex and in the dihydroxo-bridged complexes (with a small antiferromagnetic coupling) are very similar[1] and therefore do not provide a basis for an explanation of the different magnetic behavior.

**Summary.** The previously proposed difluoro-bridged structure of the complexes with L$^2$ and L$^6$ was essentially based upon FABMS data. The present results confirm these assignments in that the properties of the present complex with L$^8$ are very similar to those reported for the L$^2$ and L$^6$ complexes. From the present data and our previous studies[19,20] it is found that the ligands which afford dinuclear fluoro-bridged complexes (L$^2$, L$^5$, L$^6$, and L$^8$; fluoro-bridged complexes have not been obtained with L$^4$ and L$^7$) are those which have bulky groups in position 3 of the aromatic ring system, whereas the tetranuclear species have been obtained with the less bulky ligands L$^1$ and L$^3$. It is possible that repulsion between the tertiary butyl groups belonging to adjacent chromium(III) centers favor dinuclear species, but at present it can not be excluded that different solubilities of the species play an important role. On basis of the magnetic measurements, it has been shown unambiguously that the ground state of the difluoro-bridged compound is the septet state. It has not been possible to determine the monoatomic zfs parameter D from the magnetic measurements, but this parameter has successfully been determined from the EPR spectra.

**Supporting Information Available:** Tables of crystallographic data, atomic parameters, complete bond lengths and bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (7 pages). Ordering information is given on any current masthead page.

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