Syntheses, Structures and Magnetic Properties of Fluoro-Bridged Di- and Tetranuclear Chromium(III) Complexes with Tetrahydrosalen and Substituted Tetrahydrosalen Derivatives as Ligands. Crystal Structure of an Ethoxo-Fluoro-Bridged Dichromium(III) Complex and a Tetrafluoro-Bridged Tetrachromium(III) Complex

Arnd Böttcher,[a] Horst Elias,[a] Jørgen Glerup,[b] Markus Neuburger,[c] Carl Erik Olsen,[e] Helmut Paulus,[d] Johan Springborg[†,e] and Margareta Zehnder[c]

[a]Anorganische Chemie III, Eduard-Zintl-Institut, Technische Hochschule Darmstadt, Hochschulstrasse 10, D-64289 Darmstadt, Germany, [b]Chemistry Laboratory, H.C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark, [c]Institut für Anorganische Chemie der Universität Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland, [d]Strukturforschung, Fachbereich Materialwissenschaft, Technische Hochschule Darmstadt, Petersenstr. 20, D-64287 Darmstadt, Germany and [e]Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark

Böttcher, A., Elias, H., Glerup, J., Neuburger, M., Olsen, C. E., Paulus, H., Springborg, J. and Zehnder, M., 1994. Syntheses, Structures and Magnetic Properties of Fluoro-bridged Di- and Tetranuclear Chromium(III) Complexes with Tetrahydrosalen and Substituted Tetrahydrosalen Derivatives as Ligands. Crystal Structure of an Ethoxo-Fluoro-Bridged Dichromium(III) Complex and a Tetrafluoro-Bridged Tetrachromium(III) Complex. – Acta Chem. Scand. 48: 967–980 © Acta Chemica Scandinavica 1994.

A series of novel fluoro-bridged di- and tetranuclear chromium(III) complexes have been synthesized by the reaction of trans-$[Cr(py)_4F_2]ClO_4$ in organic solvents with tetrahydrosalen and substituted tetrahydrosalen derivatives L^1–L^6 (L^i denotes divalent anions of H_2L^i).

The ligands H_2L^1 and H_2L^2 have been described previously and the syntheses of the new tetrahydrogenated substituted derivatives of $H_2[H_4]$salen: H_2L^3, H_2L^4, H_2L^5 and H_2L^6, and the parent diimines are given in the present study (H_2L^1 = N,N'-bis(2-hydroxybenzyl)-1,2-ethanediamine, H_2L^2 = N,N'-bis(3-tert-butyl-2-hydroxy-5-methylbenzyl)-1,2-ethanediamine, H_2L^3 = N,N'-bis(2-hydroxy-benzyl)-trans-(S,S)-1,2-cyclohexanediamine, H_2L^4 = N,N'-bis(2-hydroxybenzyl)-cis-1,2-cyclohexanediamine, H_2L^5 = N,N'-bis(3-tert-butyl-2-hydroxy-5-methylbenz-yl)-trans-(S,S)-1,2-cyclohexanediamine, H_2L^6 = N,N'-bis(3-tert-butyl-2-hydroxy-5-methylbenzyl)-cis-1,2-cyclohexanediamine).

Four new fluoro-bridged complexes with the stoichiometric formulae $[CrLF]_q$ (L = L^1, L^2, L^3 and L^6) were obtained from the reaction of trans-$[Cr(py)_4F_2]ClO_4$ and L in 2-methoxyethanol. The complex $[(CrL^5)_2(F)(CH_3CH_2O)]\cdot H_2O$ was obtained similarly using ethanol as solvent.

The crystal structures of two of these complexes have been solved: $[(CrL^5)_2(F)(CH_3CH_2O)]\cdot H_2O$ and $[CrL^1F]_4$. For $[(CrL^5)_2(F)(CH_3CH_2O)]\cdot H_2O$ the crystal system is monoclinic, the lattice constants are $a = 25.274(2)$, $b = 9.009(1)$, $c = 18.182(2)$ Å, $\beta = 128.024(9)°$, the volume of the unit cell is $3261.93(65)$ Å^3. The space group is C2. The refinement of 353 variables includes 2585 of the 3620 independent reflections. The final residual is 5.03%.

The dinuclear molecule consists of two slightly distorted octahedrally cis-coordinated chromium(III) atoms bound together by a fluoride bridge and an ethoxo bridge. The Cr–F–Cr angle is 103.9° and the Cr–O–Cr angle is 101.3°. The corresponding Cr–F and Cr–O distances are 1.975 and 2.009 Å, respectively. The molecule is optically active, and it is shown that the absolute configuration of the dinuclear molecule is Δ(S,S),Δ(S,S), where Δ refers to the two chiral centers of the cyclohexane ring.

[†] To whom correspondence should be addressed.

For $[CrL^1F]_4$ the crystal system is monoclinic, the lattice constants are $a = 18.292(5)$, $b = 18.599(5)$, $c = 17.974(5)$ Å, $\beta = 95.34(1)°$, the volume of the unit cell is 6088.36 Å^3. The space group is $C2/c$. The refinement of 397 variables includes 3979 of the 4289 independent reflections. The final residual is 6.59%. The tetranuclear molecule consists of a Cr_4F_4 ring in which the chromium(III) atoms are linked by fluoride bridges, which have Cr–F–Cr angles of 148.0 and 150.5° and Cr–F distances of 1.925–1.945 Å. The coordination geometry around each chromium(III) atom is a slightly distorted octahedron with *cis* configuration and the chelate is alternating Δ and Λ, so the molecule may be described (ignoring lattice induced distortions) as a *meso*-$\Delta,\Lambda,\Delta,\Lambda$ isomer.

From the magnetic susceptibility of these compounds it is concluded that they are weakly coupled antiferromagnetic or ferromagnetic polynuclear species. The susceptibility data for the complex $[(CrL^5)_2(F)(C_2H_5O)]$ are indicative of a weak antiferromagnetic coupling. The susceptibility data for the complexes $[CrL^2F]_2$ and $[CrL^6F]_2$ are very similar and suggest that they are weakly ferromagnetically coupled, which is rather unusual for polynuclear chromium(III) complexes. The magnetic susceptibilities of $[CrL^1F]_4$ and $[CrL^3F]_4$ (measured in the temperature range 3–400 K) are very similar and show the expected behaviour characteristic for weakly antiferromagnetically coupled tetranuclear chromium(III) complexes.

A very large number of coordination compounds with the diimine ligand H$_2$salen and its substituted derivatives have been reported[1,2] (ligand abbreviations are shown in the Appendix, see also Scheme 2). We are currently investigating the much less studied coordination compounds of the corresponding tetrahydrogenated ligand H$_2$[H$_4$]salen and its derivatives. Recently we have reported the synthesis, crystal structures and properties of a series of nickel(II),[3,4] iron(III),[5] copper(II)[6] and cobalt-(II)[6] complexes with the tetrahydrogenated ligands L^1 and L^2 shown in Scheme 2. These complexes exhibit structural properties and chemical behaviour different from those of to the corresponding salen complexes. This might be due to a different ligand field strength exerted by these ligands and to an increased flexibility (sp^3 hybridized N-donor atoms) of the ligand tetrahydrosalen, which also allows non-planar coordination geometries.

For example, nickel(II) tetrahydrosalen complexes with a specific substitution pattern on the benzene rings of the ligands activate O$_2$ under very mild conditions, which finally leads to the oxidative dehydrogenation of one C–N bond.[3] These complexes are monomeric and show a higher distortion of the NiN$_2$O$_2$ coordination plane than the corresponding nickel(II)salen complexes.[7] In the case of iron(III) complexes the flexibility of tetrahydrosalen and its derivatives is demonstrated by the formation of dihydroxo or dimethoxo bridged dimers,[5,8] in contrast to the tendency of iron(III) salen complexes to form oxo bridged species, such as $[(Fe(salen))_2O]$.[9,10]

As a continuation of this study an investigation of the corresponding chromium(III) tetrahydrosalen complexes has been initiated. Only few chromium(III) complexes with salen^{2-} or its substituted derivatives have been reported,[11,12] and to our knowledge only one chromium(III) complex with tetrahydrogenated salen has been published,[13] but the structure of this complex was not established.

Chromium(III) has a strong tendency to form oligomeric complexes with bridging ligands such as HO$^-$, RO$^-$ and RCOO$^-$.[14–16] In the present case, it was therefore anticipated that chromium(III) with tetrahydrosalen, like iron(III) as mentioned above, would form
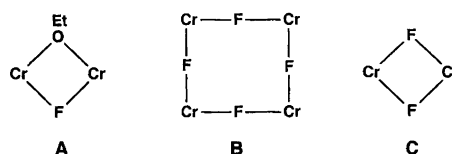
Scheme 1.

oligomeric rather than monomeric species. 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 with increasing bulkiness has been investigated. We here report our results for the reactions of *trans*-$[Cr(py)_4F_2]^+$ with these tetrahydrosalen ligands, which were found to give di- and tetranuclear fluoro-bridged complexes of the type shown in Scheme 1. Five new chromium(III) complexes with the ligands L^1, L^2, L^3, L^5 and L^6 described and the crystal structures of two of these complexes have been established: $[(CrL^5)_2(F)(CH_3CH_2O)]\cdot H_2O$ and $[CrL^1F]_4$.

The synthesis of the new substituted derivatives of H$_2$[H$_4$]salen: H$_2$L^3, H$_2$L^4, H$_2$L^5 and H$_2$L^6, and the parent diimines are given (L^i denotes divalent anions of H$_2$L^i).

Experimental

Materials. The compounds H$_2$L^1,[17] H$_2$L^2,[3] *trans*-(S,S)-1,2-cyclohexanediammonium di((+)-$_D$-hydrogentartrate),[18] *cis*-1,2-cyclohexanediammonium sulfate,[19] 3-*tert*-butyl-5-methylsalicylaldehyde[20] and *trans*-$[Cr(py)_4F_4]ClO_4$[21] were obtained from methods given in the literature. All other chemicals were of analytical grade.

Analyses. C, H, N and Cl analyses were made by Preben Hansen at the Microanalytical Laboratory at the H.C. Ørsted Institute, Copenhagen. F analyses were carried out by Mikroanalytisches Labor Pascher, Remagen, Germany.

IR spectra. IR spectra were recorded on a Perkin Elmer System 2000 FTIR spectrometer.

UV–VIS absorption spectra. UV–VIS absorption spectra were obtained using a Cary 3 spectrophotometer.

Mass spectra. FD mass spectra were obtained using a Varian MAT 311 A mass spectrometer. 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 for chromium(III) complexes and fragments are for the center of the isotope clusters.

^1H NMR spectra. ^{1}H NMR spectra were measured at 5.87 T on a Bruker AC 250 NMR spectrometer equipped with a 5 mm probe for ^{1}H NMR measurement. ^{1}H chemical shift values (δ) are reported in ppm relative TMS in CDCl$_3$.

Magnetic measurements. The magnetic moments have been measured with a Faraday balance described elsewhere.[22] The measurements were performed at a field strength of 1.3 T. The data have been corrected for diamagnetism using Pascal's constants.

EPR measurements. 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. For the synthesis of the ligands given in the following (preparation nos. 1–8) the yields of the salen-type ligands are all 80–90% and the yields of the tetrahydrosalen-type ligands are all 50–70%. The purity of each of the ligands was estimated to be greater than 98% based on ^{1}H NMR spectra. For the ligand abbreviations see the Appendix and Scheme 2.

1. H$_2$sal-trans-(S,S)-1,2-chxn. To a solution of *trans*(S,S)-1,2-cyclohexanediammonium-di-((+)$_D$-hydrogentartrate) (20.7 g, 0.05 mol) in 4 M NaOH (50 ml) salicylaldehyde (12.2 g, 0.1 mol) was added slowly at 50°C with constant stirring. Then the yellow mixture was boiled for 10 min. The crude product that separated as a viscous yellow oil solidified on slow cooling, was collected on a filter, washed several times with cold water and recrystallized from chloroform/cyclohexane (1:2) to give yellows crystals. ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 1.4–1.5$ (m, 4 H; CH$_2$), 1.7–1.9 (m, 4 H; CH$_2$), 3.3 [t, ^3J(H,H) = 2 Hz, 2 H; CH], 6.7–7.2 (m, 8 H; aryl-H), 8.3 (s, 2 H; CH), 13.3 (s, 2 H; OH). IR(cm^{-1}): 1620 (C = N).

2. H$_2$L^3 = H$_2$[H$_4$]sal-trans-(S,S)-1,2-chxn. H$_2$sal-trans-(S,S)-1,2-chxn (8 g, 0.025 mol) was dissolved in methanol (80 ml) with heating to about 60°C and stirring. Then sodium borohydride (2.85 g, 0.075 mol) was added portionwise within 1 h. During this time the yellow colour disappeared, and at the end of the reaction the solution was colourless.

Then 20 ml of water were added and the colourless mixture was boiled for 10 min. After cooling the solvent was partially evaporated *in vacuo* at room temperature using a rotary evaporator. Colourless crystals precipitated and were filtered off, washed with small amounts of methanol, dried in air and recrystallized from chloroform/cyclohexane (1:2). ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 1.2$

H$_2$L^1

H$_2$L^2

H$_2$L^3

H$_2$L^4

H$_2$L^5

H$_2$L^6
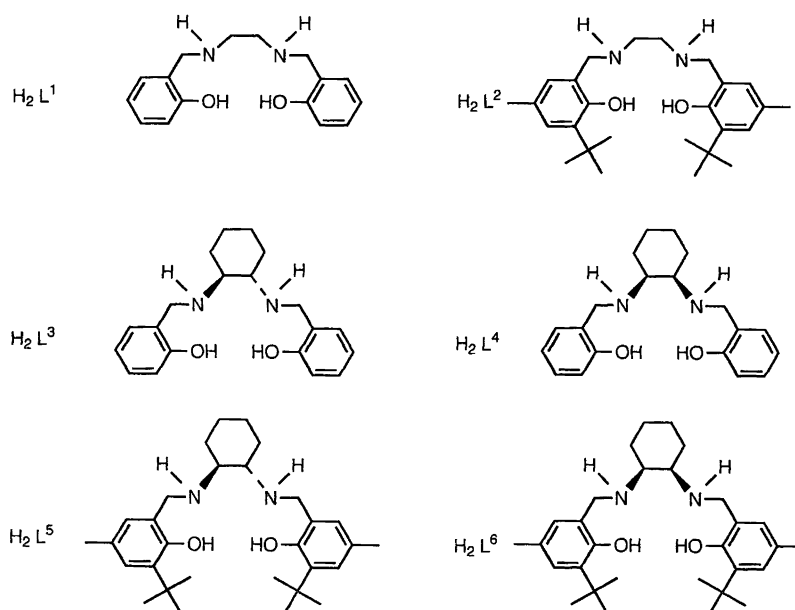
Scheme 2.

(m, 4 H; CH_2), 1.7 (m, 2 H; CH_2), 2.1 (m, 2 H; CH_2), 2.4 [t, ^3J(H,H) = 2 Hz, 2 H; CH], 3.9 [dd, ^2J(H,H) = 6 Hz, 4 H; CH_2], 5.8 (br. s, 2 H, NH), 6.7–7.2 (m, 8 H; aryl-H). IR(cm^{-1}): 3300 (N–H).

3. H_2sal-cis-1,2-chxn. Salicylaldehyde (6.1 g, 0.05 mol) was added slowly to a solution of *cis*-1,2-cyclohexanedi-ammonium sulfate (5.3 g, 0.025 mol) in 4 M NaOH (12.5 ml). The mixture was stirred and heated for 30 min to about 80°C and then cooled in an ice bath. The yellow crystals that formed were filtered off, washed with water and recrystallized from chloroform/cyclohexane (1:2). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.5–1.8 (m, 4 H; CH_2), 1.9–2.0 (m, 4 H; CH_2), 3.5 (m, 2 H; CH), 6.8–7.3 (m, 8 H, aryl-H), 8.3 (s, 2 H; CH), 13.5 (s, 2 H; OH). IR(cm^{-1}): 1620 (C = N).

4. $H_2L^4 = H_2[H_4]$sal-cis-1,2-chxn. Reduction of H$_2$sal-*cis*-1,2-chxn with sodium borohydride (using 3 mol of sodium borohydride per mol ligand) in methanol according to the procedure described in preparation no. 2 gave co-lourless crystals of H$_2$L^4. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.5–1.8 (m, 8 H; CH_2), 2.7 (m, 2 H; CH), 3.7 (m, 4 H; CH_2), 6.5–7.0 (m, 8 H; aryl-H). IR(cm^{-1}): 3300 (N–H), weak.

5. H_2tBuMesal-trans-(S,S)-1,2-chxn. A solution of 3-*tert*-butyl-5-methylsalicylaldehyde (8 g, 0.0417 mol) in methanol (50 ml) was added slowly to a solution of *trans*-(S,S)-1,2-cyclohexanediammonium di((+)$_D$-hydrogentar-trate) (8.625 g, 0.0209 mol) in 2 M NaOH (42 ml). The yellow mixture was stirred and heated to about 65 °C for 15 min and then cooled in an ice bath. The partially crystalline product was filtered off, washed with cold water and recrystallized from ethanol to give pure yellow crystals. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.4 (s, 18 H; tBu), 1.3–1.5 (m, 4 H; CH_2), 1.7–1.9 (m, 4 H; CH_2), 2.2 (s, 6 H; CH_3), 3.3 [t, ^3J(H,H) = 2 Hz, 2 H; CH], 6.7–7.0 (m, 4 H; aryl-H), 8.2 (s, 2 H; CH), 13.6 (s, 2 H; OH). IR(cm^{-1}): 1620 (C = N).

6. $H_2L^5 = H_2$tBuMe[H_4]sal-trans-(S,S)-1,2-chxn. H$_2$tBu-Mesal-*trans*-(S,S)-1,2-chxn (5 g, 0.011 mol) was dissolved in hot methanol (300 ml, about 60°C). NaBH$_4$ (1.23 g, 0.033 mol) was added portionwise to the hot solution within 1 h. During this time the intense yellow colour of the salen ligand disappeared; at the end of the reaction the solution was light yellow. An insoluble yellow by-product was filtered off. Then the solution was boiled and concentrated to 100 ml and finally cooled. The colourless precipitate that formed was filtered off and washed with water and dried in air. The ligand was re-crystallized from ethanol. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.4 (s, 18 H; tBu), 1.3–1.5 (m, 4 H; CH_2), 1.6–1.7 (m, 2 H; CH_2), 2.1 (m, 2 H; CH_2), 2.15 (s, 6 H; CH_3), 2.4 [t, ^3J(H,H) = 3 Hz, 2 H; CH], 3.9 [dd, ^2J(H,H) = 6 Hz, 4 H; CH_2], 6.7–7.0 (m, 4 H; aryl-H), 10.7 (br. s, 2 H; OH). IR(cm^{-1}): 3300 (N–H).

7. H_2tBuMesal-cis-1,2-chxn. 3-*tert*-Butyl-5-methylsali-cylaldehyde was reacted with *cis*-1,2-cyclohexanediam-monium sulfate as described in preparation no. 3 to give yellow crystals. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.4 (s, 18 H; tBu), 1.4–2.0 (m, 8 H; CH_2), 2.2 (s, 6 H; CH_3), 3.5 (t, 2 H; CH), 6.9–7.1 (m, 4 H; aryl-H), 8.3 (s, 2 H; CH), 13.7 (s, 2 H; OH). IR(cm^{-1}): 1620 (C = N).

8. $H_2L^6 = H_2$tBuMe[H_4]sal-cis-1,2-chxn. H$_2$tBuMesal-*cis*-1,2-chxn was reduced with sodium borohydride (1:3) in methanol as described in preparation no. 2. Recrystallization of the crude product from ethanol gave co-lourless crystals of pure H$_2$L^6. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.4 (s, 18 H; tBu), 1.3–1.8 (m, 8 H; CH_2), 2.2 (s, 6 H; CH_3), 2.8 (t, 2 H; CH), 3.9 [dd, ^2J(H,H) = 6 Hz, 4 H; CH_2], 6.7–7.0 (m, 4 H; aryl-H), 10.6 (br. s, 2 H; OH). IR(cm^{-1}): 3300 (N–H).

9. [CrL^{1}F]$_4$. A solution of H$_2$L^1 (1.36 g, 5 mmol) and *trans*-[Cr(py)$_4$F$_2$]ClO$_4$ (2.525 g, 5 mmol) in 2-methoxy-ethanol (20 ml) was boiled under reflux for 1 h. During this time a purple precipitate was formed, which was filtered off after cooling, washed with water, ethanol, and diethyl ether and dried in air. This gave 990 mg of a purple powder (57%). Larger crystals of the complex were prepared according to the same procedure, with the modification that the reaction was carried out at only 80°C for 24 h and the reaction mixture was cooled very slowly afterwards. Yield: 390 mg (22%). Analytical data: Calculated for C$_{16}$H$_{18}$N$_2$O$_2$CrF: C, 56.30; H, 5.32; N, 8.20; F, 5.57. Found: C, 55.89; H, 5.46; N, 8.06; F, 5.4. FDMS *m/z*: 322 ([CrL^1]). FABMS *m/z*: 1365 (M = [CrL^{1}F]$_4$, 1345 (M–HF). The complex is soluble in hot 4 M perchloric acid.

10. [CrL^{2}F]$_2$·H$_2$O. A solution of H$_2$L^2 (1.03 g, 2.5 mmol) and *trans*-[(Cr(py)$_4$F$_2$]ClO$_4$ (1.263 g, 2.5 mmol) in 2-methoxyethanol (30 ml) was heated under reflux. After 2 h the mixture was allowed to cool and to stand overnight. Small, blue crystals were separated and filtered off, washed twice with ethanol and with diethyl ether and dried in air. Yield: 870 mg (71%). Larger crystals were prepared according to the same procedure, with the modification that the reaction was carried out for 48 h at 80°C and the reaction mixture was cooled very slowly. Yield: 550 mg (45%). Analytical data: Calculated for C$_{26}$H$_{38}$N$_2$O$_2$CrF·0.5H$_2$O:C, 63.65; H, 8.01; N, 5.71; F, 3.87. Found: C, 63.75; H, 8.01; N, 5.89: F, 5.09. FDMS *m/z* = 962 (M = [CrL^{2}F]$_2$). FABMS *m/z* = 962 (M), 943 (M–F). The complex is soluble in glacial acetic acid, in DMF, in pyridine and very poorly soluble in DMSO and chloroform.

11. [CrL^{3}F]$_4$·2H$_2$O. A solution of H$_2$L^3 (652 mg, 2 mmol) and *trans*-[(Cr(py)$_4$F$_2$]ClO$_4$ (1.010 g, 2 mmol) in 2-methoxyethanol (30 ml) was heated for 72 h at 80°C and then cooled very slowly to 20°C. The purple crystals that formed were filtered off and washed with

water, ethanol and diethyl ether and dried in air. Yield: 514 mg (63%). Analytical data: Calculated for $C_{20}H_{24}N_2O_2CrF \cdot 0.5H_2O$: C, 59.4; H, 6.23; N, 6.92; F, 4.70. Found: C, 58.71; H, 6.24; N 6.63; F, 5.79. FDMS $m/z = 376$ [CrL^3], 771 [CrL^{3}FCrL^3]. FABMS $m/z = 1581$ (M = [CrL^{3}F]$_4$), 1561 (M–HF). The complex is almost insoluble in aqueous and organic solvents.

12. [(CrL^5)$_2$(F)(CH$_3$CH$_2$O)]·H$_2$O. Preparation using 2-methoxyethanol as solvent. A solution of *trans*-[Cr(py)$_4$F$_2$]ClO$_4$ (1.010 g, 2 mmol) and H$_2$L^5 (932 mg, 2 mmol) in 2-methoxyethanol (40 ml) and 99.9% ethanol (ca. 1 ml) was heated to 80°C for 48 h. Then the solution was cooled slowly to room temperature and finally kept at 5°C for 2 d. The light-green crystals that separated were filtered off, washed with water, ethanol and diethyl ether and dried in air. Yield: 160 mg (15%). Analytical data: Calculated for $C_{62}H_{95}N_4O_6Cr_2F$: C, 66.76; H, 8.58; N, 5.02; F, 1.70. Found: C, 66.50; H, 8.66; N, 5.06; F, 1.94. FDMS $m/z = 1096$ (M = [(CrL^5)$_2$(F)(CH$_3$CH$_2$O)]. FABMS $m/z = 1096$ (M), 1051 (M–CH$_3$CH$_2$O), 516 ([CrL^5]). The complex is soluble in DMF, glacial acetic acid, chloroform and pyridine. When the synthesis was carried out under the same conditions, but without addition of ethanol no crystals were formed.

Preparation using ethanol as solvent H$_2$L^5 (800 mg, 1.7 mmol) was dissolved in hot 99.9% ethanol (50 ml, 75°C). [Cr(py)$_4$F$_2$]ClO$_4$ (870 mg, 1.7 mmol), dissolved in hot 99.9% ethanol (50 ml), was added in one portion. The mixture was heated in an oil bath at 75°C for 24 h. During this time dark-green crystals began to precipitate. The heating was continued for another 24 h, then the mixture was allowed to cool slowly and was kept at 5°C for 2 d. Then the crystals were filtered off, washed with ethanol and several times with water and dried over CaCl$_2$. Yield: 690 mg (74%). Analytical data: Calculated for $C_{62}H_{95}N_4O_6Cr_2F$: C, 66.76; H, 8.58; N, 5.02. Found C, 67.25; H, 8.58; N, 5.06. FDMS $m/z = 1096$ ([(CrL^5)$_2$(F)(CH$_3$CH$_2$O)]). IR spectra and X-ray powder diffraction diagrams showed that this complex is identical to the one obtained using 2-methoxyethanol as solvent. This result was confirmed by the results obtained from the determination of the cell parameters of one single crystal of this complex, which led to the same values as those of the X-ray structure determination of a crystal obtained from the reaction in 2-methoxyethanol.

13. [CrL^{6}F]$_2$·H$_2$O. A solution of H$_2$L^6 (932 mg, 2 mmol) and *trans*-[Cr(py)$_4$F$_2$]ClO$_4$ (1.010 g, 2 mmol) in 2-methoxyethanol (30 ml) was heated for 48 h at 80°C. Then the solvent was reduced to half of the volume by boiling the mixture for 10 min. The solution was kept at 5°C for 10 d, during which time a blue product precipitated. The product was filtered off, washed with several portions of ethanol, then with diethyl ether and dried in air. Yield: 110 mg (11%). Analytical data: Calculated for $C_{30}H_{44}N_2O_2CrF \cdot 0.5H_2O$: C, 66.15; H, 8.33; N, 5.14; F,

3.49. Found: C, 65.91; H, 8.58; N, 5.01; F, 3.28. FDMS $m/z = 1070$ (M = [CrL^{6}F]$_2$), 535 (M/2). FABMS $m/z = 1070$ (M), 1051 (M–F). The product is soluble in chloroform.

X-Ray structure determination

Crystal structure of [CrL^{1}F]$_4$. Dark-blue needle-shaped crystals were grown as described above (preparation no. 9, 80°C). Crystal data and parameters of the data collection are compiled in Table 1. Intensities were measured on a four-cycle diffractometer (Stoe-Stadi-4) using graphite-monochromatized MoK$_\alpha$ radiation ($\lambda = 0.710$ 69 Å, scan $2\theta:\omega = 1:1$). Cell constants were determined by the least-squares method from the 2θ angles of 42 reflections measured ($T = 297$ K) on the same instrument. LP and background corrections and a numerical absorption correction (SHELX-76)[23] were applied. The structure was solved by direct methods with SHELXS-86[23] and refined by least squares to the R-values given in Table 1. Hydrogen atoms were positioned geometrically (C–H distances 0.96 Å) and not refined. An empirical extinction correction was applied. Scattering factors were taken from the literature.[24] The final positional parameters are given in Table 2. Selected bond lengths and angles are given in Table 3. A list of calculated and observed structure factors as well as anisotropic temperature factors is available from the authors.

Crystal structure of [(CrL^5)$_2$(F)(CH$_3$CH$_2$O)]·H$_2$O. Green crystals were obtained by the preparation using 2-methoxyethanol as solvent (preparation no. 12). Crystal data and parameters of the data collection are compiled in

Table 1. Crystal data and a summary of data reduction and structure refinement for Δ,Λ,Δ,Λ-[CrL^{1}F]$_4$.

Compound	[CrL^{1}F]$_4$
Formula	[C$_{16}$H$_{18}$N$_2$O$_2$CrF]$_4$
Formula mass	1365.28 g mol^{-1}
Space group	C2/c (No. 15)
Wavelength (MoKα)	0.710 69 Å
Crystal system	Monoclinic
Temperature /K	297
a/Å	18.292(5)
B/Å	18.599(5)
c/Å	17.974(5)
β/°	95.34(1)
V/Å^3	6088.36
Z	4
F(000)	4064
D_c/g cm^{-3}	1.49
μ(MoKα)/cm^{-1}	7.50
Crystal size/mm	0.2×0.25×1.5
Scan mode	2θ:ω = 1:1, "learnt profile"
2θ-range/°	3–45
Weights	2.84/σ^2(F)
No. of independent reflections	4289
No. of observed reflections	3979
No. of variables	397
R	0.0659
R_w	0.0519

Table 2. Positional parameters and equivalent isotropic thermal parameters for $[Cr(L^1)F]_4$.

Atom	x/a	y/b	z/c	$U_{eq}/\text{Å}^2$
Cr(1)	0.09252(4)	0.36208(4)	0.36981(4)	0.0476(5)
F(1)	0.08798(15)	0.37477(14)	0.26204(13)	0.0568(18)
O(1)	0.06236(17)	0.46057(17)	0.37902(17)	0.0494(21)
C(1)	0.09894(29)	0.51625(28)	0.35519(25)	0.0496(35)
C(2)	0.06255(30)	0.57684(31)	0.32955(30)	0.0694(41)
C(3)	0.09864(39)	0.63673(37)	0.306616(37)	0.1006(57)
C(4)	0.17383(42)	0.63748(43)	0.30721(37)	0.0975(60)
C(5)	0.21073(37)	0.57910(44)	0.33213(38)	0.0936(57)
C(6)	0.17560(33)	0.51822(35)	0.35777(36)	0.0762(47)
C(7)	0.21861(34)	0.45497(41)	0.38774(62)	0.2193(109)
N(1)	0.19972(22)	0.38736(26)	0.37566(25)	0.0670(32)
C(8)	0.24123(37)	0.32527(38)	0.39702(50)	0.1424(76)
C(9)	0.21206(34)	0.25903(37)	0.37926(39)	0.0981(57)
N(2)	0.13273(25)	0.25892(22)	0.35980(23)	0.0617(31)
C(10)	0.09264(31)	0.20478(28)	0.39857(28)	0.0681(40)
C(11)	0.08342(26)	0.21953(29)	0.48046(28)	0.0521(35)
C(12)	0.06859(30)	0.16176(33)	0.52417(34)	0.0752(45)
C(13)	0.05776(37)	0.16864(39)	0.59793(38)	0.1050(60)
C5 14)	0.06224539)	0.23510(41)	0.62806(37)	0.1129(62)
C(15)	0.07757(32)	0.29433(34)	0.58783(30)	0.0771(44)
C(16)	0.08726(26)	0.28832(30)	0.51262(27)	0.0511(35)
O(2)	0.10037(19)	0.34863(18)	0.47611(17)	0.0609(24)
Cr(2)	0.10989(4)	0.33701(4)	0.16638(4)	0.0467(5)
F(2)	0.00559(14)	0.32456(13)	0.13963(14)	0.0563(18)
O(3)	0.11921(19)	0.23940(17)	0.20302(17)	0.0595(23)
C(17)	0.10914(26)	0.17888(26)	0.16267(28)	0.0508(34)
C(18)	0.08477(31)	0.11723(29)	0.19618(34)	0.0734(42)
C(19)	0.07377(34)	0.05443(32)	0.15661(43)	0.0877(52)
C(20)	0.08657(35)	0.05092(34)	0.08357(40)	0.0839(52)
C(21)	0.11178(34)	0.11050(34)	0.05027(34)	0.0819(48)
C(22)	0.12374(30)	0.17509(29)	0.08818(29)	0.0596(38)
C(23)	0.15699(39)	0.23829(34)	0.05209(34)	0.1082(58)
N(3)	0.12154(29)	0.30277(25)	0.05977(24)	0.0840(37)
C(24)	0.14344(34)	0.36515(30)	0.01597(29)	0.0829(45)
C(25)	0.09555(29)	0.42812(29)	0.03449(27)	0.0653(39)
N(4)	0.09849(21)	0.43719(21)	0.11630(21)	0.0519(27)
C(26)	0.15258(28)	0.49202(25)	0.14799(30)	0.0630(38)
C(27)	0.23179(29)	0.46954(31)	0.14655(31)	0.0610(39)
C(28)	0.28186(37)	0.51903(32)	0.12292(36)	0.0844(49)
C(29)	0.35520(40)	0.50158(39)	0.12749(42)	0.0989(59)
C(30)	0.37860(36)	0.43593(42)	0.15345(42)	0.1001(58)
C(31)	0.33076(34)	0.38641(35)	0.17419(38)	0.0890(51)
C(32)	0.25576(32)	0.40151(33)	0.17173(35)	0.0716(45)
O(4)	0.21099(20)	0.35106(21)	0.19342(26)	0.0902(32)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \, a_j).$$

Table 4. Unit-cell parameters were determined by accurate centering of 25 strong independent reflections by the least-squares method. Reflection intensities were collected at 298 K on an Enraf-Nonius CAD4 four-circle diffractometer equipped with a graphite monochromator and using CuK_α radiation. Three standard reflections monitored every hour during data collection showed no intensity loss. The usual corrections were applied. Diffraction absorption correction has been determined by Ψ-scans. The structure was solved by the Patterson method using the program SHELXS-86.[23] Anisotropic least-squares refinement was carried out on all non-H-atoms except for the water of crystallization using the program CRYSTALS.[25] Positions of H-atoms were calculated except those bonded to the nitrogen atoms which

have been refined isotropically restraining the N–H distances to 1 Å. The absolute configuration of the structure was known from the syntheses and has been confirmed by refining the enantiopole parameter [0.062(5)].[26] Scattering factors were taken from the literature.[24] The final positional parameters are given in Table 5 and selected bond lengths and angles are given in Table 6. A list of calculated and observed structure factors as well as anisotropic temperature factors is available from the authors.

Results and discussion

Syntheses. A series of new di- and tetranuclear chromium(III) complexes with the ligands $L = L^1$, L^2, L^3, L^5

Table 3. Selected bond lengths and distances (in Å) and angles (in °) for $[Cr(L^1)F]_4$.

Cr(1)–F(1)	1.945(2)	Cr(2)–F(1)	1.934(3)
Cr(1)–F(2)*	1.925(1)	Cr(2)–F(2)	1.930(3)
Cr(1)–O(1)	1.925(3)	Cr(2)–O(3)	1.933(3)
Cr(1)–O(2)	1.919(3)	Cr(2)–O(4)	1.886(4)
Cr(1)–N(1)	2.010(4)	Cr(2)–N(3)	2.049(4)
Cr(1)–N(2)	2.069(4)	Cr(2)–N(4)	2.071(4)
Cr(1)–Cr(2)	3.729(4)	Cr(2)–Cr(1)*	3.728(4)
Cr(1)–Cr(1)*	5.226(6)	Cr(2)–Cr(2)*	5.239(6)
F(1)–F(2)	2.711(4)	F(1)–F(2)*	2.741(4)
F(1)–F(1)*	3.207(6)	F(2)–F(2)*	3.995(6)
F(1)–Cr(1)–F(2)*	90.2(1)	F(2)–Cr(2)–F(1)	89.1(1)
F(1)–Cr(1)–O(1)	89.1(1)	F(2)–Cr(2)–O(3)	91.5(1)
F(1)–CR(1)–O(2)	178.1(1)	F(2)–Cr(2)–O(4)	178.8(2)
F(1)–Cr(1)–N(1)	88.6(2)	F(2)–Cr(2)–N(3)	85.1(1)
F(1)–Cr(1)–N(2)	90.5(1)	F(2)–Cr(2)–N(4)	86.7(1)
O(1)–Cr(1)–O(2)	91.9(1)	O(3)–Cr(2)–O(4)	89.4(2)
N(1)–Cr(1)–N(2)	82.4(2)	N(3)–Cr(2)–N(4)	83.6(2)
O(1)–Cr(1)–N(1)	93.4(2)	O(3)–Cr(2)–N(3)	90.8(2)
O(1)–Cr(1)–N(2)	175.8(2)	O(3)–Cr(2)–N(4)	174.2(1)
O(2)–Cr(1)–N(1)	89.8(2)	O(4)–Cr(2)–N(3)	95.7(2)
O(2)–Cr(1)–N(2)	88.4(2)	O(4)–Cr(2)–N(4)	92.5(2)
Cr(1)–F(1)–Cr(2)	148.0(1)	Cr(2)–F(2)–Cr(1)*	150.1(1)

* Asteriks indicate symmetry-related atoms (operator $-x$, y, $-z+0.5$).

Table 4. Crystal data and a summary of data reduction and structure refinement for $\Delta(S,S),\Delta(S,S)-[(CrL^5)_2(F)(CH_3CH_2O)] \cdot H_2O$.

Compound	$[(CrL^5)_2(F)(CH_3CH_2O)] \cdot H_2O$
Formula	$C_{62}H_{95}N_4O_6Cr_2F$
Formula mass	1115.454
Space group	$C2$ (No. 5)
Wavelength (CuKα)/Å	1.54178
Crystal system	Monoclinic
Temperature/K	298
a/Å	25.274(2)
b/Å	9.009(1)
c/Å	18.182(2)
β/°	128.024(9)
V/Å$_3$	3261.93(65)
Z	2
F(000)	1200
D_c/g cm^{-3}	1.136
μ(CuKα)/cm^{-1}	31.739
Crystal size/mm	0.10×0.15×0.45
Scan mode	$\omega/2\theta$
θ_{max}/°	77.5
Weights	wght$\times[1-(\Delta F/6\sigma F)^2]^2$ (Tukey & Prince)
No. of independent reflections	3620
No. of observed reflections	2585
No. of varialbes	353
R	5.03
R_w	5.53

Table 5. Positional and equivalent isotropic thermal parameters for $\Delta(S,S),\Delta(S,S)-[(CrL^5)_2(F)(CH_3CH_2O)] \cdot H_2O$.

Atom	x/a	y/b	z/c	U (iso)
CR(1)	0.06503(3)	0.0119(3)	0.10301(4)	0.0335
O(1)	0.1207(2)	0.1469(5)	0.2061(2)	0.0436
C(1)	0.1250(2)	0.1649(6)	0.2836(3)	0.0418
C(2)	0.1871(3)	0.1993(6)	0.3714(3)	0.0496
C(3)	0.2517(3)	0.2259(7)	0.3817(4)	0.0593
C(4)	0.3134(3)	0.254(1)	0.4838(5)	0.0862
C(5)	0.2675(4)	0.0856(9)	0.3497(5)	0.0789
C(6)	0.2418(3)	0.3600(9)	0.3246(5)	0.0725
C(7)	0.1861(3)	0.2165(8)	0.4466(4)	0.0609
C(8)	0.1310(3)	0.1966(7)	0.4433(4)	0.0575
C(9)	0.1340(4)	0.211(1)	0.5288(4)	0.0775
C(10)	0.0702(3)	0.1656(6)	0.3571(3)	0.0504
C(11)	0.0674(3)	0.1500(6)	0.2777(3)	0.0448
C(12)	0.0011(3)	0.1213(6)	0.1857(3)	0.0415
N(1)	0.0026(2)	−0.0154(5)	0.1413(2)	0.0369
C(13)	0.0226(2)	−0.1491(6)	0.2011(4)	0.0413
C(14)	−0.0348(3)	−0.2171(7)	0.1954(4)	0.0582
C(15)	−0.0093(4)	−0.3481(8)	0.2624(5)	0.0690
C(16)	0.0262(4)	−0.4611(6)	0.2444(5)	0.0682
C(17)	0.0827(3)	−0.3922(7)	0.2479(4)	0.0576
C(18)	0.0566(2)	−0.2602(6)	0.1808(3)	0.à423
N(2)	0.1094(2)	−0.1809(5)	0.1826(3)	0.0380
C(19)	0.1372(3)	−0.2712(7)	0.1449(4)	0.0522
C(20)	0.1941(2)	−0.1934(7)	0.1560(3)	0.0471
C(21)	0.2574(3)	−0.2594(8)	0.2086(4)	0.0543
C(22)	0.3106(3)	−0.194(1)	0.2174(4)	0.0609
C(23)	0.3790(3)	−0.265(1)	0.2751(5)	0.0855
C(24)	0.2982(3)	−0.0595(9)	0.1713(4)	0.0601
C(25)	0.2361(2)	0.011(1)	0.1173(3)	0.0538
C(26)	0.2268(3)	0.1580(9)	0.0669(5)	0.0644
C(27)	0.1715(4)	0.140(1)	−0.0359(5)	0.0828
C(28)	0.2901(4)	0.200(1)	0.0750(7)	0.1013
C(29)	0.2107(7)	0.282(1)	0.1036(9)	0.1138
C(30)	0.1826(2)	−0.0548(6)	0.1110(3)	0.0438
O(2)	0.1214(1)	0.0070(6)	0.0634(2)	0.0439
F(1)	0.0000	−0.1232(5)	0.0000	0.0365
O(3)^a	0.0023	0.1531(5)	−0.0016	0.0292
C(31)^a	−0.0158(6)	0.3029(9)	−0.008(2)	0.0565
C(32)^a	0.0391(8)	0.403(2)	0.028(1)	0.0983
O(41)^b	0.4949	0.1989	0.5025	0.1765
O(42)^b	0.5005	0.0646	0.4993	0.1779
O(43)^b	0.5452	0.3120	0.5785	0.1586
O(44)^b	0.4996	0.4147	0.5048	0.1811

^{a} Occupancies of the ethoxo-bridge=0.5 (caused by disorder). ^{b} Sum of the occupancies of the water of crystallization=1.

and L^6 has been synthesized. The ligands L^1–L^6 are shown in Scheme 2. The ligands L^1 and L^2 have been described previously,[3,17] and the new ligands L^3, L^4, L^5 and L^6 were obtained by reaction of two moles of the parent aromatic aldehydes with 1 mol of either cis-1,2-cyclohexanediamine or trans-(S,S)-1,2-cyclohexanedi-

amine, respectively, followed by reduction with borohydride (see Experimental).

Fluoro complexes with the stoichiometry $[CrLF]_q$ ($L = L^1$, L^2, L^3 and L^6) were obtained from the reaction of trans-$[Cr(py)_4F_2]ClO_4$ and L in 2-methoxyethanol at 124°C and were isolated in high yields [50–70%, with the exception of the L^6 complex (10–15%)]. Reaction with L^5 using the same conditions did not produce well defined products, but when ethanol was used as solvent the complex $[(CrL^5)_2(F)(CH_3CH_2O)]$ was obtained in a high yield (74%). The same product could be obtained from 2-methoxyethanol with a small amount of ethanol added, but the yield was low (14%). Attempts to isolate complexes with the ligand L^4 failed for unknown reasons.

Table 6. Selected bond lengths and distances (in Å) and angles (in °) for $\Delta(S,S),\Delta(S,S)-[CrL^5)_2(F)(C_2H_5O)]$.

Cr(1)–O(1)	1.930(4)	Cr(1)–F(1)	1.975(3)
Cr(1)–N(1)	2.094(4)	Cr(1)*–F(1)	1.975(3)
Cr(1)–N(2)	2.090(5)	Cr(1)–O(3)	2.009(3)
Cr(1)–O(2)	1.954(3)	Cr(1)*–O(3)	2.011(3)
Cr(1)–Cr(1)*	3.109(1)		
N(2)–Cr(1)–O(1)	95.3(2)	O(3)–Cr(1)–O(1)	101.4(2)
N(2)–Cr(1)–N(1)	82.3(2)	O(3)–Cr(1)–N(1)	94.2(1)
O(2)–Cr(1)–O(1)	96.4(2)	O(3)–Cr(1)–N(2)	162.9(7)
O(2)–Cr(1)–N(1)	171.8(2)	O(3)–Cr(1)–O(2)	89.7(1)
O(2)–Cr(1)–N(2)	91.9(2)	O(3)–Cr(1)–F(1)	77.4(1)
F(1)–Cr(1)–O(1)	173.2(1)	O(3)–Cr(1)*–F(1)	77.3(1)
F(1)–Cr(1)–N(1)	83.4(1)	Cr(1)–F(1)–Cr(1)*	103.9(2)
F(1)–Cr(1)–N(2)	85.6(2)	Cr(1)–O(3)–Cr(1)*	101.3(2)
F(1)–Cr(1)–O(2)	90.4(1)		

* Atoms with asterisks are symmetry-generated (operator $-x$, y, $-z$).

The stoichiometry of the new complexes indicates that they are neutral, so-called inner-complexes, and it is therefore not surprising that they all are insoluble or sparingly soluble in aqueous solutions and in most other hydrophilic solvents. Most of the compounds are slightly soluble in organic solvents such as chloroform or DMF, while the compounds $[CrL^1F]_4$ and $[CrL^3F]_4$ were found to be insoluble in all solvents studied. The low solubility made it in practice impossible to characterize and study these new complexes by the classical methods such as pH studies. Data for the visible absorption spectra are given in Table 7, which also include the infrared (N–H) stretching vibrations and the coupling constants J calculated from measurements of the magnetic susceptibilities (see below).

Descriptions of the two crystal structures

[CrL¹F]₄ The complex $[CrL^1F]_4$ crystallizes in the monoclinic space group $C2/c$ with 4 formula units (16 Cr atoms) per unit cell. The numbering scheme is given in Fig. 1. Figure 2 gives a view of the coordination geometry and Fig. 3 shows a projection of the unit cell along [010]. The crystal structure of $[CrL^1F]_4$ consists of discrete tetranuclear units of four chromium atoms linked by four fluoride bridges. The Cr centers are octahedrally coordinated by the tetradentate ligand $[H_4]salen^{2-}$ and two fluoride ions in *cis* configuration.

Each fluoride ion connects two $[CrL^1]^+$ cores. As a result, an eight-membered ring with alternating Cr and F
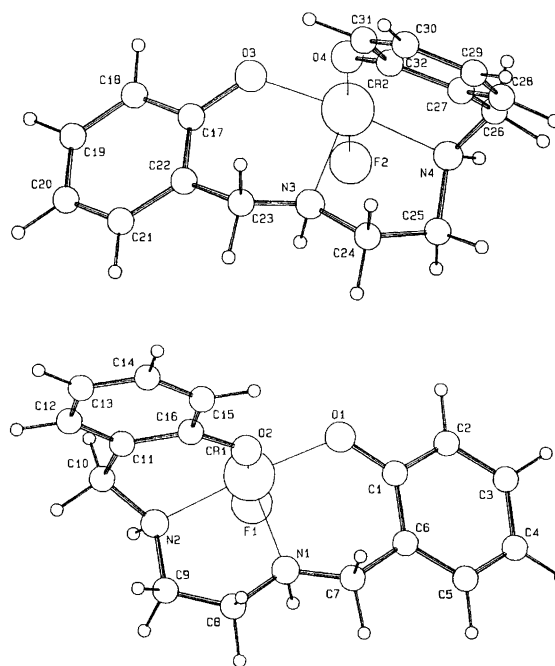

Fig. 1. Structural view and numbering scheme for the two different chromium(III) sites Cr(1) and Cr(2) of the tetranuclear molecule $\Delta,\Lambda,\Delta,\Lambda-[CrL^1F]_4$.

atoms is formed. From the point of symmetry, opposite $[CrL^1]^+$ cores and F atoms, respectively, are related by a two-fold rotation axis running through the geometrical centre of the eight-membered ring. Cr atoms are displaced by 0.23 Å and F atoms by 0.47 Å from the least-squares plane through Cr(1), Cr(2), Cr(1)* and Cr(2)* (Cr and Cr* means opposite and identical chromium centres). The arrangement of the N_2O_2 chelate around the chromium centres is $\Delta,\Lambda,\Delta,\Lambda$ so that opposite chromium centres have the same configuration (Λ and Δ refer to the configuration of the two N,O chelates of the L^1 ligand around each chromium centre). The crystal therefore consists of a racemic mixture with two identical pairs of enantiomers in the unit cell: $\Delta Cr(1),\Lambda Cr(2),\Delta Cr(1)^*$, $\Lambda Cr(2)^*$ and $\Lambda Cr(1),\Delta Cr(2),\Lambda Cr(1)^*,\Delta Cr(2)^*$. The minor difference in conformation between the Cr(1) and Cr(2) centres of the same chirality is probably due to lattice forces. Ignoring these small differences, which will not persist in solution, the molecule is therefore best described as a *meso*-$\Delta,\Lambda,\Delta,\Lambda$ isomer (Fig. 4).

Table 7. Spectroscopic and magnetic data.

Compound	Colour of solid complex	$(\varepsilon,\lambda)^a$		v_{NH}/cm^{-1}	g	J/cm^{-1}	J'/cm^{-1}
$[(CrL^5)_2(F)(C_2H_5O)] \cdot H_2O$	Green	$(202,600)_{max}$	$(98,454)_{max}^c$	3133	1.97	2.91	–
$[CrL^2F]_2 \cdot H_2O$	Blue	$(221,600)_{max}$	$(128,420)_{sh}^c$	3266, 3167	–	–	–
$[CrL^6F]_2 \cdot H_2O$	Blue	$(207,596)_{max}$	$(136,420)_{sh}^c$	3254, 3163	1.98	-3.39	–
$[CrL^1F]_4$	Purple	$-^b$		3222, 3090	1.99	9.7	3.2
$[CrL^3F]_4 \cdot 2H_2O$	Purple	$-^b$		3231, 3060	1.98	11.1	2.6

^{a} All molar absorbancies are given in L (mol Cr(III))$^{-1}$ cm^{-1}. ^{b} Insoluble. ^{c} Chloroform.
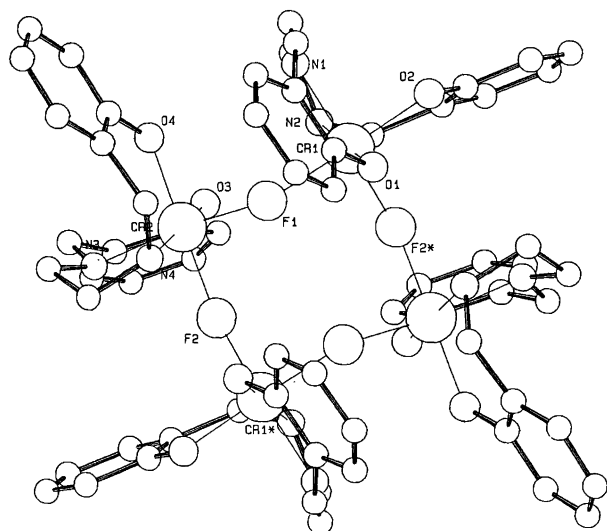
Fig. 2. View of the coordination geometry in the complex Δ,Λ,Δ,Λ-[CrL¹F]₄.

Selected bond lengths and angles are listed in Table 3. The angles given show that the octahedron around the chromium centre is slightly distorted. The Cr–F distances are found to be in the range 1.925–1.945 Å and differ only slightly, whereas the Cr–N distances (2.010–2.071 Å) and Cr–O distances (1.886–1.933 Å) differ significantly. The mean bridging Cr–F–Cr angle is 149.2°, and the mean F–Cr–F angle is 89.7°. The shortest intramolecular Cr–Cr distance is 3.728 Å, the average separation of opposite Cr atoms in the ring is 5.223 Å. The observed anomalously high temperature factors of C(7) and C(8) might be due to a partial disorder of these atoms. The tetranuclear units are well separated from each other (the closest Cr–Cr distance between neighbouring tetramers is 7.71 Å).
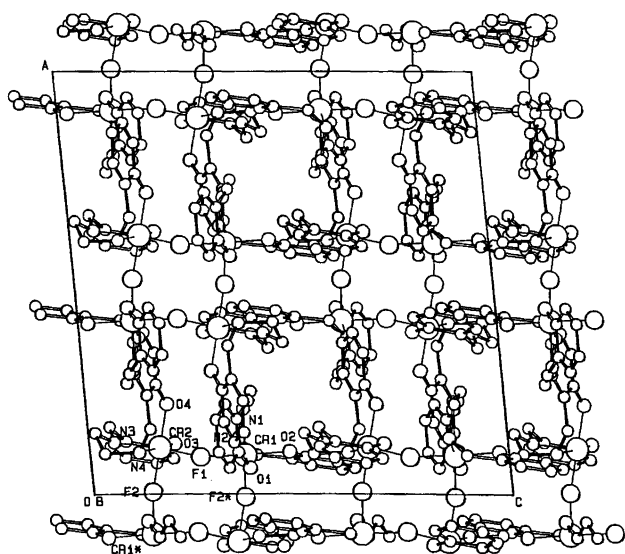

Fig. 4. Schematic drawing of the coordination geometry of Δ,Λ,Δ,Λ-[CrL¹F]₄ illustrating the configurations Δ and Λ around the chromium(III) centres (Δ and Λ are defined with respect to the N,O chelates).

[(CrL⁵)₂(F)(C₂H₅O)]·H₂O. The complex crystallizes in the monoclinic space group C2. This space group has two independent two-fold axes. The dimeric molecule is lying across a two-fold axis. Figure 5 shows a view along the two-fold axis; Fig. 6 shows the molecule rotated by 90°. The geometry of the salen ligand covers completely one bridging site and leaves the other free. The two bridging ligands reflect this fact. One is small and in the centre of the molecule (F⁻), the other is bigger and therefore found in the uncovered outside bridging site (CH₃CH₂O⁻). The structure shows two disordered parts, which are both found near the two-fold axes. One is the water of crystallization, which is located around the two-fold axis in 0.5, y, 0.5. It is observed in the difference map as four peaks of spare electron density and was therefore not refined. The other disordered part is the ethoxo bridge, which is located on the other two-fold axis in 0, y, 0. Restraints for distances, angles and temperature parameters have been used to refine this part of the structure. For clarity, only one of the two possible positions of the ethoxo bridge has been plotted in the figures. The molecule is optically active and the crystal contains only one isomer with the absolute configuration Δ(S,S),Δ(S,S),

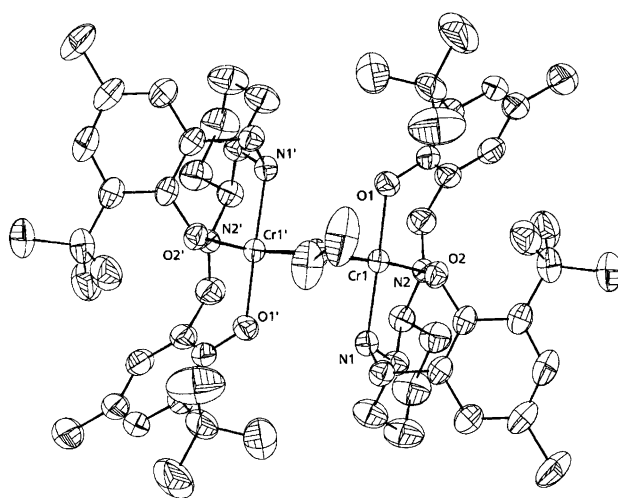*Fig. 3.* Projection of the unit cell of the complex Δ,Λ,Δ,Λ-[CrL¹F]₄ along [0 1 0].

Fig. 5. View along the two-fold axis of the coordination geometry in the complex Δ(S,S),Δ(S,S)-[(CrL⁵)₂(F)CH₃CH₂O)]·H₂O.
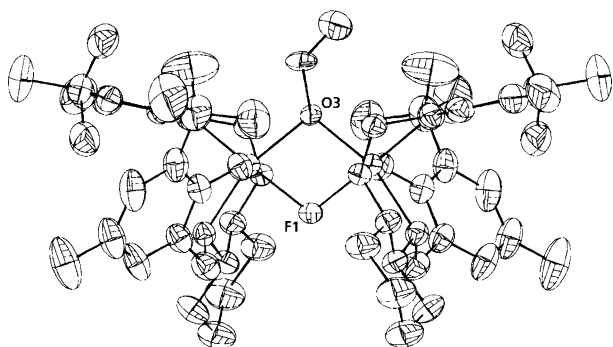
Fig. 6. View of the coordination geometry in the complex $\Delta(S,S),\Delta(S,S)$-[(CrL^5)$_2$(F)(CH$_3$CH$_2$O)]·H$_2$O.

where S refers to the chiral centers of the cyclohexane group [e.g. C(13)] and Δ refers to the configuration of the two N,O chelates of the tetrahydrosalen ligand. The conformation of the N–C–C–N chelate is δ. The numbering scheme is shown in Fig. 7. A schematic drawing of the coordination geometry is shown in Fig. 8.

The angles around the Cr center show a distortion of the octahedral coordination geometry. The Cr–F distances are 1.975 Å, the distances between the Cr atoms and the bridging O atoms are found to be 2.009 and 2.012 Å, respectively. The Cr–N distances (2.090 and 2.094 A) and the distances between the Cr atoms and the phenolic O atoms (1.930 and 1.954 Å) differ slightly. The Cr–Cr distance amounts to 3.111 Å. The Cr–F–Cr bridging angle is 103.9° and the average O(bridge)–Cr–F angle is 77.35°.

Structure assignments of the remaining complexes. The bridging skeletons discussed in this paragraph are shown in Scheme 1. The dinuclear structure with two different bridging groups (A in Scheme 1) was unambiguously shown for the complex [(CrL^5)$_4$(F)(CH$_3$CH$_2$O)], while the tetranuclear structure was shown for the complex [CrL^{1}F]$_4$ (B in Scheme 1). In the following an assign-
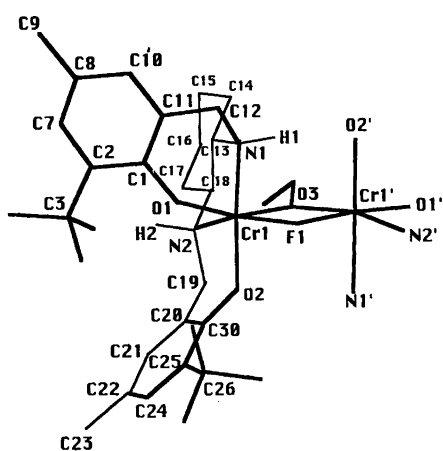

Fig. 7. Numbering scheme for the structure of $\Delta(S,S),\Delta(S,S)$, [(CrL^5)$_2$(F)(CH$_3$CH$_2$O)]·H$_2$O.
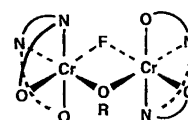

Fig. 8. Schematic drawing of the coordination geometry of $\Delta(S,S),\Delta(S,S)$-[(CrL^5)$_2$(F)(CH$_3$CH$_2$O)]·H$_2$O illustrating the configurations Δ and Λ around the chromium(III) centres (Δ and Λ are defined with respect to the N,O chelates).

ment of the bridging skeletons of the remaining three complexes is attempted primarily based upon the FD and FAB mass spectra (see Experimental), the EPR spectra and the magnetic properties (vide infra).

FD and FAB mass spectrometry give reliable results for the present type of complexes, as illustrated by the results for the di- and tetranuclear species, [(CrL^5)$_2$(F)(CH$_3$CH$_2$O)] and [CrL^{1}F]$_4$, whose structures have been established by X-ray studies. The FD spectrum of the dinuclear species clearly established its molecular formula by the presence of a dominant cluster peak centred at $m/z = 1096$. Only very little fragmentation was observed. The FABMS data gave a similar result and also intense clusters for the fragments [(CrL^5)$_2$F] and [CrL^5]. The FABMS data of the tetranuclear species gave an intense cluster for the species [CrL^{1}F]$_4$ and also a cluster for the fragment [Cr$_4$(L^1)$_4$F$_3$]. The maximum m/z limit for the FD equipment used in this study was 1200, and we were therefore not able to test for FD signals corresponding to the tetranuclear entity using this technique. For the remaining species FABMS and FDMS (except in one other case with $M_w > 1200$, L^3) similarly gave clusters for the molecular species, as discussed in the following.

The similarity of the complexes with L^2 and L^6 indicates that they have a common bridging skeleton. The color in the solid state (blue) and the maxima of the visible absorption spectra (600 and 596 nm) are similar for the two species. The magnetic properties clearly show that both complexes are oligomeric (di- or tetranuclear), although the nuclearity was not established. The FDMS for the L^2 and L^6 species, respectively, gave an intense cluster with m/z values corresponding to the [CrL^{i}F]$_2$ species. Very little fragmentation was observed. The FABMS similarly gave peaks which indicated a dinuclear structure, although the fragmentation was more pronounced (see Experimental). It is therefore concluded that both complexes have a dinuclear structure, and since the other reactions discussed in this study have lead to formation of fluoro bridges, we tentatively suggest that these dinuclear species contain two fluoro bridges as shown in Scheme 1 (C). However, the notion that the phenoxide ligands could act as bridging ligands can not be excluded.

The L^1 and L^3 complexes are both purple in the solid state. The FABMS data of the L^3 complex gave an intense cluster for the species [CrL^{3}F]$_4$ and also a cluster for the fragment [Cr$_4$(L^3)$_4$F$_3$], which indicates that this

complex is tetranuclear like the L^1 complex. It is therefore concluded that the L^3 complex without doubt has a tetranuclear structure as shown in Scheme 1 (B). This conclusion is substantiated by the magnetic properties, which strongly suggest that the two species have the same tetranuclear structure.

Magnetic susceptibility. The magnetic susceptibility data indicate that these compounds are weakly coupled antiferromagnetic or ferromagnetic polynuclear species.

The susceptibility data for the complex $[(CrL^5)_2(F)(C_2H_5O)] \cdot H_2O$ have a maximum at 10.4 K, and the magnetic moment decreases from $5.4\mu_B$ to $2\mu_B$ on cooling from room temperature to 4 K. This is indicative of a weak antiferromagnetic coupling.

The susceptibility data for the complexes $[CrL^2F]_2$ and $[CrL^6F]_2$ are almost identical. The magnetic moment increases from $5.45\mu_B$ to $5.55\mu_B$ on cooling from room temperature to 25 K and shows on further cooling a maximum of $6.02\mu_B$ at 6.5 K, which is indicative of a weak ferromagnetic coupling. To prove that the increase in magnetic moment is a genuine ferromagnetic coupling, the compound $[CrL^6F]_2$ was measured mixed with 10% silicone grease to prevent reorientation of the crystals. This measurement gave almost the same result as that without added grease and is shown in Fig. 9. The compound $[CrL^2F]_2$ has not been measured in grease, and therefore we have not attempted to estimate the parameters for this compound.

The temperature dependence of the magnetic susceptibility of $[CrL^1F]_4$ and $[CrL^3F]_4$ was measured in the temperature range 4–300 K. The results, which are almost identical for the two species, are shown for $[CrL^1F]_4$ in Fig. 10. The susceptibility shows a maximum at approximately 25 K, and the effective magnetic mo-
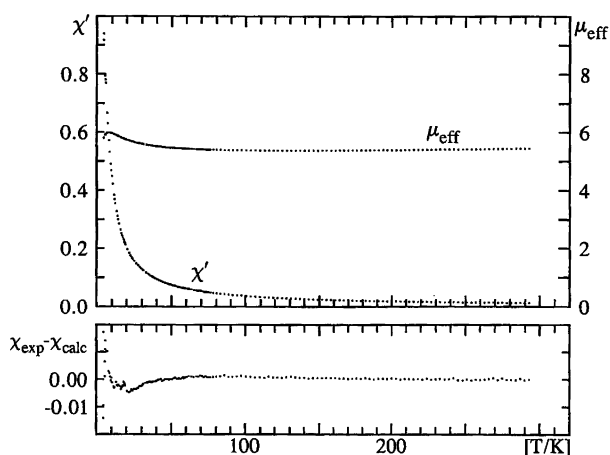

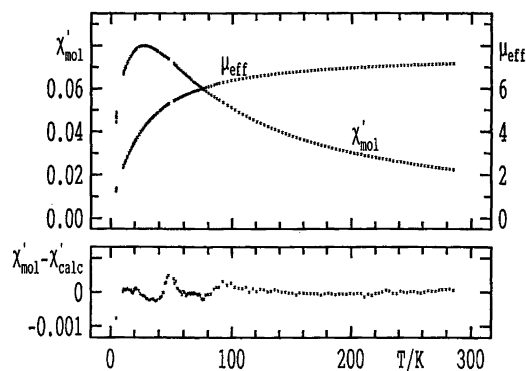Fig. 10. The magnetic susceptibility (in c.g.s. units) and the effective magnetic moment as function of temperature of $[CrL^1F]_4$. The lower graph gives the difference between the measured and calculated susceptibilities.

ment declines from $7.1\mu_B$ at room temperature to $1\mu_B$ at 4 K. This is the expected behaviour characteristic of weakly antiferromagnetically coupled tetranuclear chromium(III) complexes. For an uncoupled tetranuclear chromium(III) complex with $g = 2$ the expected magnetic moment is $7.75\mu_B$. The magnetism of tetranuclear chromium(III) complexes where the metals are arranged in almost a square have been discussed elsewhere.[27]

The temperature dependence of the magnetic susceptibilities $\chi'_{mol,exp}$ was approximated by eqn. (1):

$$\chi'_{mol,exp} \approx \chi'_{mol,calc}$$

$$= -\frac{N}{H} \frac{\sum_i \frac{\partial E_i}{\partial H} \exp\left(-E_i/kT\right)}{\sum_i \exp\left(-E_i/kT\right)} + K + C/T \quad (1)$$

by minimization of the expression in eqn. (2)

$$\sum_t \frac{[\chi'_{mol,exp}(T) - \chi'_{mol,calc}(T)]^2}{\sigma^2(\chi') + \left(\frac{\partial\chi}{\partial T}\right)^2 \sigma^2(T)} \quad (2)$$

within the framework of nonlinear regression analysis. $\sigma(\chi')$ and $\sigma(T)$ are the estimated standard deviations of the measured magnetic susceptibility and temperature, respectively. In eqn. (1) the ratio C/T accounts for paramagnetic impurities and K accounts for temperature-independent paramagnetism and minor deviations in the correction for diamagnetism. Values calculated for C/T and K were always very small. For the tetranuclear complexes the energies E_i of the 256 components of the ground state manifold were obtained by means of the isotropic spin Hamiltonian operator, eqn. (3)

$$\hat{H} = \sum_{i=1}^{4} g\mu_B \hat{S}_i \cdot \hat{H} + J \sum_{i=1}^{4} \hat{S}_i \cdot \hat{S}_{(i+1)mod4}$$

$$+ J' \sum_{i=1}^{2} \hat{S}_i \cdot \hat{S}_{i+2} \quad (3)$$

Fig. 9. The magnetic susceptibility (in c.g.s. units) and the effective magnetic moments as function of temperature of $[CrL^6F]_2$. The fitting was accomplished with the operators in eqns. (4) and (5) and gave $J = -3.39$ cm^{-1}, $D_1 = D_2 = 0.014$ cm^{-1} and $g = 1.98$. The lower graph gives the difference between the measured and calculated susceptibilities.

where it is assumed that the g values for the four chromium atoms are identical. The second term in eqn. (3) accounts for interactions between neighbouring chromium atoms, and the last term accounts for the interaction between opposed chromium atoms. For the dinuclear complexes the energies of the 16 components of the ground-state manifold were obtained by means of the isotropic spin Hamiltonian operator in eqn. (4):

$$\hat{H} = \sum_{i=1}^{2} g\mu_B \hat{S}_i \cdot \hat{H} + J\hat{S}_i \cdot \hat{S}_2 \qquad (4)$$

Also in this case it was assumed that the g values for the two chromium atoms are identical. The parameters obtained by the minimization are given in Table 7.

The magnetic parameters for the dinuclear compound $[(CrL^5)_2(F)(C_2H_5O)]$ were calculated as described above for the dinuclear model (Table 7).

The magnetic data for the complexes $[CrL^2F]_2$ and $[CrL^6F]_2$ are almost identical. The data for these complexes show that they are weakly ferromagnetically coupled, and this is rather unusual for polynuclear chromium(III) complexes. For dihydroxo-bridges dichromium(III) complexes the condition for ferromagnetic coupling has been discussed as a function of the structure parameters.[28] When fitting parameters to data from ferromagnetically coupled complexes, it is essential to use an expression like eqn. (1), which can handle the different populations at low temperatures of the ground levels (different populations of the different M_s values). This phenomenon is generally called magnetic saturation and results in the observed maximum in the measured magnetic moments. To obtain a good fit a monoatomic zero field splitting has been introduced by complementing the Hamilton operator in eqn. (4) with expression (5):

$$\sum_{i=1}^{2} D_i \left\{ \hat{S}_{iz}^2 - \frac{1}{3} S_i (S_i + 1) \right\} \qquad (5)$$

For the tetranuclear complexes, $[CrL^1F]_4$ and $[CrL^3F]_4$, it is seen (Table 7) that the interaction between neighbouring chromium atoms is more important, as expected, than the interaction between opposed chromium atoms.[27] It is noted that calculations using a model for dinuclear species did not give well defined parameters.

EPR spectra. To avoid broad and uncharacteristic EPR spectra it is generally required that the compound can be diluted in some way, e.g. dissolved in a diamagnetic host or in a frozen glass, or that the magnetic states can be sufficiently depopulated by cooling. The present complexes have a low solubility in most solvents and the magnetic interactions are so small that cooling even to 4 K is not sufficient to dilute these compounds magnetically. Therefore the EPR spectra have only been obtained in a few cases.

The compounds $[(CrL^5)_2(F)(C_2H_5O)] \cdot H_2O$, $[CrL^6F]_2$ and $[CrL^2F]_2$ have solid-state EPR spectra which are typical for dinuclear complexes. The spectrum of

$[(CrL^5)_2(F)(C_2H_5O)] \cdot H_2O$ given in Fig. 11 has been recorded at 4 K. This is a typical spectrum from the quintet state which emerges as a result of the antiferromagnetic coupling of the two chromium(III) ions.

The spectra of the tetranuclear complexes contain a broad line centred around $g = 2$. This can be explained by consulting Fig. 8 in Ref. 27, where the energy levels of some tetranuclear chromium(III) complexes have been given as a function of J and J'. Owing to the density of states, and thereby the large number of transitions between the energy levels, it is expected that all these lines will collapse to one broad signal.

Comparison with other compounds. Only one single example of a fluoro-bridged Werner-type complex has been reported previously, viz. the trifluoro-bridged dinuclear anion $Cr_2F_9^{3-}$.[29] The di- and tetranuclear coordination compounds in the present study therefore add a novel feature to the very large body of structural chemistry already established within this field. The fluoride ligand acts in many respects like the hydroxide ligand. Both ligands have nearly the same ligand field parameters Δ_σ and Δ_π, although the values for fluoride are somewhat smaller than those for hydroxide.[30] The coordinated hydroxide ion may be protonated, and the same is true for the coordinated fluoride ion, although it normally requires more acid conditions to protonate the latter.

The hydroxo-bridged chromium(III) complexes and also chromium(III) complexes with other bridges, such as carboxylate, normally undergo bridge cleavage in acidic or basic aqueous solutions. The rates by which these cleavage reactions occur varies considerably with the nature of the non-bridging ligands and of course with the bridging ligand, and half-lives from months and days to milliseconds have been reported.[15,16,31–33] The present fluoro-bridged complexes are insoluble in water, and a study of the thermodynamic and kinetic properties similar to those reported for many of the hydroxo-bridged species, is hampered. From preliminary qualitative experiments it can be concluded that all these new fluoro-bridged species undergo acid-catalyzed bridge cleavage. As a typical reaction the cleavage of $[CrL^1F]_2$ in 4 M

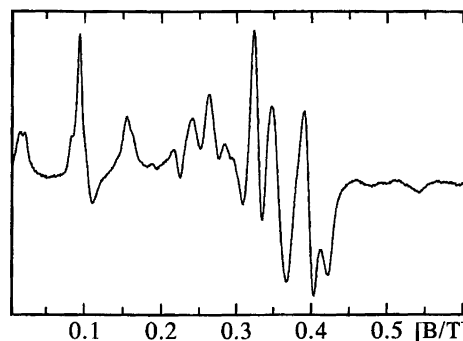*Fig. 11.* The EPR spectrum of solid $\Delta(S,S)$-$\Delta(S,S)$-$[(CrL^5)_2(F)(CH_3CH_2O)] \cdot H_2O$ measured at 4 K and at 9.39 GHz.

$HClO_4$ could be mentioned. The purple complex is insoluble in water, but dissolves in hot 4 M $HClO_4$ to give a red solution probably containing a mixture of monomeric cis-disqua, cis-fluoroaqua and cis-difluoro species. The apparent inertness probably reflects the low solubility even in acidic solution rather than inertness of the fluoro-bridged species. In fact, the fluoro-bridged species are expected to be less stable in aqueous solution than their hydroxo-bridged analogues (cf. the greater base strength of Cr–OH compared to Cr–F), but we have no experimental evidence for this proposal.

The published[34–36] Cr–F distances for terminally coordinated fluoride are all in the region 1.84–1.91 Å and the hitherto longest reported bond length is for terminally coordinated fluoride in the trinuclear complex $[C(NH_2)_3]_2[Cr_3O(OOCCH_2H_5)_6F_3]$ (1.909 and 1.914 Å). These distances are shorter than the reported[37,38] distances for terminally coordinated hydroxide (1.926–1.930 Å). The present fluoro-bridged complexes L^1 and L^5 have both significantly longer Cr–F (bridge) distances than reported for the mononuclear complexes, and furthermore these distances are even longer than the Cr–O(bridge) distances (1.944–1.949 Å) in the cases where the protons on the hydroxide ligands are approximately in the Cr–O–Cr planes.[28]

The Cr–F (bridge) distance, 1.975 Å, found for the dinuclear complex, $[(CrL^5)(F)(C_2H_5O)]\cdot H_2O$, is comparable with the bond length (1.993 Å) reported for the trifluoro-bridged complex $[(CH_3)_4N]_3$ $[F_3Cr(F)_3CrF_3]$.[29] To our knowledge the latter complex is the only previously reported example of a well characterized fluoro-bridged complex. However, the Cr–F–Cr entity has been established in the solid state of salts such as $KCrF_4$ and $MnCrF_5$. The crystallographic data for these salts showed Cr–F–Cr angles from 140 to 150° and Cr–F distances from 1.87 to 1.93 Å,[39,40] which are similar to the values found for the tetranuclear complex (148–150.5° and 1.925–1.945 Å).

The bridging skeleton of the two fluoro-bridged complexes (A and C in Scheme 1) is analogous to that of the corresponding dihydroxo-bridged analogues, the so-called 'diols'. The latter have been studied in detail for many years and a large number of crystallographic studies has been reported.[15,16] The ethoxofluoro-bridged complex (with L^5) is also related to methoxohydroxo- and diethoxo-bridged chromium(III)-compounds.[41] In the diols the Cr–O–Cr angles vary from 99.9 to 103.4°. Similar angles are found in alkoxo complexes (101.0–101.8°).[41] The corresponding angles in the present complex are 101.3° [CrO(Et)–Cr] and 103.9° (Cr–F–Cr).

Tetranuclear complexes of chromium(III) are well known, and have in many cases been characterized by crystal structures. Most of the known tetranuclear compounds are hydroxo- and/or oxo-bridged.[14–16] In addition to the well-known classical 'rhodoso' structure[42,43] a chromium(III) analogue to the so-called 'Werners Brown Salt'[44,45–47] and a chain-like[48] tetranuclear complex have been described. Recently also cubane- and adamantane-

like structures have been reported.[49–53] The tetranuclear cyclic $(CrX)_4$ bridging skeleton reported here is the first example of this type of structure within chromium(III) chemistry, and to our knowledge similar structures have not been reported for other metal ions, such as cobalt-(III), iron(III) manganese(II,III,IV) etc., which are known to form polynuclear species of the types discussed here.

Comparison of the antiferromagnetic coupling in the fluoro-bridged complexes with the hydroxo-bridges complexes shows that the hydroxo bridge is more efficient for transmitting the antiferromagnetic interaction than the fluoro bridge. The J-values for monohydroxo-bridged complexes vary from 20–35 cm^{-1}, while the fluoro-bridged complexes have J-values around 10 cm^{-1}. The antiferromagnetic interaction between the two metal atoms takes place through π-bonds between the t_2-orbitals on each metal atom and the p-orbitals on the bridging ligands. Because of the approximately right angles between the two metal bonds at the bridging ligands there is only one p-orbital on the bridging fluoride available for the π-interactions and the same is true for the hydroxide ligand when the proton on the oxygen atom is in the Cr–O–Cr plane. The antiferromagnetic interactions in dihydroxo-bridged complexes as a function of the geometry of the hydroxo-bridge has previously been discussed thouroughly.[28] Because of the shorter bridging ligand distances for the Cr–O (bridge) bonds compared with the Cr–F (bridge) bonds the π-interactions are stronger for the hydroxo-bridge than for the fluoro-bridge. This results in a stronger antiferromagnetic interaction for the hydroxo-bridge than for the fluoro-bridge.

Appendix

The following ligand abbreviations have been used (see also Scheme 2):

cis-chxn = cis-1,2-cyclohexanediamine

trans-(S,S)-chxn = trans-(S,S)-1,2-cyclohexanediamine

H_2salen = N,N′-bis(2-hydroxybenzylidene)-1,2-ethanediamine

H_2sal-trans-(S,S)-1,2-chxn = N,N′-bis(2-hydroxybenzylidene)-trans-(S,S)-1,2-cyclohexanediamine

H_2tBuMesal-trans-(S,S)-1,2-chxn = N,N′-bis(3-tert-butyl-2-hydroxy-5-methylbenzylidene)-trans-(S,S)-1,2-cyclohexanediamine

H_2sal-cis-1,2-chxn = N,N′-bis(2-hydroxybenzylidene)-cis-1,2-cyclohexanediamine

H_2tBuMesal-cis-1,2-chxn = N,N′-bis(3-tert-butyl-2-hydroxy-5-methylbenzylidene)-cis-1,2-cyclohexanediamine

H_2L^1 = tetrahydrosalen = $H_2[H_4]$salen = N,N'-bis(2-hydroxybenzyl)-1,2-ethanediamine

H_2L^2 = N,N'-bis(3-*tert*-butyl-2-hydroxy-5-methyl-benzyl)-1,2-ethanediamine

H_2L^3 = N,N'-bis(2-hydroxybenzyl)-*trans*-(S,S)-1,2-cyclohexanediamine

H_2L^4 = N,N'-bis(2-hydroxybenzyl)-*cis*-1,2-cyclohexanediamine

H_2L^5 = N,N'-bis(3-*tert*-butyl-2-hydroxy-5-methyl-benzyl)-*trans*-(S,S)-1,2-cyclohexanediamine

H_2L^6 = N,N'-bis(3-*tert*-2-hydroxy-5-methylbenzyl)-*cis*-1,2-cyclohexanediamine.

References

1. Hobday, M. D. and Smith, T. D. *Coord. Chem. Rev. 9* (1972–73) 331.
2. Holm, R. H., Everett, G. W. and Chakravorty, A. *Progr. Inorg. Chem. 7* (1966) 83.
3. Böttcher, A., Elias, H., Müller, L. and Paulus, H. *Angew. Chem. 104* (1992) 635; *Angew. Chem. Int. Ed. Engl. 31* (1992) 623.
4. Böttcher, A., Eisenmann, B., Elias, H., Hilms, E., Huber, A., Kniep, R., Neuburger, M., Röhr, C., Springborg, J. and Zehnder, M. *Z. Naturforsch., Teil B49* (1994) 1089.
5. Baran, P., Böttcher, A., Elias, H., Haase, W., Hüber, M., Fuess, H. and Paulus, H. *Z. Naturforsch., Teil B 47* (1992) 1681.
6. Böttcher, A., Elias, H., Jäger, E.-G., Langfelderova, H., Mazur, M., Müller, L., Paulus, H., Pelikan, P., Rudolph, M. and Valko, M. *Inorg. Chem. 32* (1993) 4131.
7. Gaetani Manfredotti, A. and Guastini, C. *Acta Crystallogr., Sect. C 39* (1983) 863.
8. Borer, L., Thalken, L., Ceccarelli, C., Glick, M., Zhang, J. H. and Reiff, W. M. *Inorg. Chem. 22* (1983) 1719.
9. Kurtz, D. M. *Chem. Rev. 90* (1990) 585.
10. Lewis, J., Mabbs, F. E. and Richards, A. *J. Chem. Soc. A* (1967) 1014.
11. Coggon, P., Mc Phail, A. T., Mabbs, F. E., Richards, A. and Thornley, A. S. *J. Chem. Soc. A* (1970) 3296.
12. Yamada, S. and Iwasaki, K. *Inorg. Chim. Acta 5* (1971) 3.
13. Ainscough, E. W., Bingham, A. G., Brodie, A. M., Husbands, J. M. and Plowman, J. E. *J. Chem. Soc., Dalton Trans.* (1981) 1701.
14. Sykes, A. G. and Weil, J. A. *Progr. Inorg. Chem. 13* (1970) 1.
15. Springborg, J. In: A. G. Sykes, Ed., *Advances in Inorganic Chemistry*, Academic Press, San Diego 1988, Vol. 32, p. 55.
16. Andersen, P. *Coord. Chem. Rev. 94* (1989) 47.
17. Amundsen, A. R., Whelan, J. and Bosnich, B. *J. Am. Chem. Soc. 99* (1977) 6730.
18. Galsbøl, F., Stenbøl, P. and Søndergaard Sørensen, B. *Acta Chem. Scand. 26* (1972) 3605.
19. Toftlund, H. and Laier, T. *Acta Chem. Scand., Sect. A 31* (1977) 651.
20. Berres, C. Deutsches Bundespatent DBP 952629 (1956).
21. Glerup, J., Josephsen, J., Michelsen, K., Pedersen, J. and Schäffer, C. E. *Acta Chem. Scand. 24* (1970) 247.
22. Josephsen, J. and Pedersen, E. *Inorg. Chem. 16* (1977) 2534.
23. Sheldrick, G. M. SHELXS-76, Universität Göttingen, 1976 and Sheldrick, G. M. SHELXS-86, Universität Göttingen, 1986.
24. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974; Vol. IV.
25. Watkin, D. *Crystals*, Issue 9, Chemical Crystallography Laboratory, Oxford 1990.
26. Flack, H. *Acta Crystallogr., Sect. A 39* (1983) 876.
27. Glerup, J., Hazell, A. and Michelsen, K. *Acta Chem. Scand. 45* (1991) 1025.
28. Glerup, J., Hodgson, D. J. and Pedersen, E. *Acta Chem. Scand., Sect. A 37* (1983) 161.
29. Kiriazis, L. and Mattes, R. *Z. Anorg. Allg. Chem. 593* (1991) 90.
30. Glerup, J., Mønsted, O. and Schäffer, C. E. *Inorg. Chem. 15* (1976) 1399.
31. Kaas, K., Nielsen, B. and Springborg, J. *Acta Chem. Scand. 43* (1989) 233.
32. Springborg, J. *Acta Chem. Scand. 46* (1992) 906.
33. Springborg, J. *Acta Chem. Scand. 46* (1992) 1047.
34. Bianchini, R. J., Geiser, U., Place, HK, Kaizaki, S., Morita, Y. and Legg, I. *Inorg. Chem. 25* (1986) 2129.
35. Solans, X., Font-Altaba, M., Montfort, M. and Ribas, J. *Acta Crystallogr., Sect. B 38* (1982) 2899.
36. Anson, C. E., Chai-sa'ard, N., Bourke, J. P., Cannon, R. D., Jayasooriya, U. A. and Powell, A. K. *Inorg. Chem. 32* (1993) 1502.
37. Larsen, S., Nielsen, K. B. and Trabjerg, I. *Acta Chem. Scand., Sect. A 37* (1983) 833.
38. Hodgson, D. J. and Pedersen, E. *Inorg. Chem. 19* (1980) 3116.
39. Dewan, J. C. and Edwards, A. J. *J. Chem. Soc., Chem. Commun.* (1977) 533.
40. Ferey, G., de Pape, R., Poulain, M., Grandjean, D. and Hardy, A. *Acta Crystallogr., Sect. B 34* (1978) 1084.
41. Fischer, H. R., Glerup, J., Hodgson, D. J. and Pedersen, E. *Inorg. Chem. 21* (1982) 3063.
42. Bang, E. *Acta Chem. Scand., Sect. A 38* (1984) 419.
43. Flood, M. T., Marsh, R. E. and Gray, H. B. *J. Am. Chem. Soc. 91* (1969) 193.
44. Andersen, P. and Berg, T. *Acta Chem. Scand., Sect. A 32* (1978) 989.
45. Andersen, P., Damhus, T., Pedersen, E. and Petersen, A. *Acta Chem. Scand., Sect. A 38* (1984) 359.
46. Andersen, P. and Bang, E. *Acta Chem. Scand., Sect. A 40* (1986) 476.
47. Andersen, P. and Berg, T. *J. Chem. Soc., Chem. Commun.* (1974) 600.
48. Damhus, T. and Pedersen, E. *Inorg. Chem. 23* (1984) 695.
49. Glerup, J., Weihe, H., Goodson, P. A. and Hodgson, D. J. *Inorg. Chim. Acta 212* (1983) 281.
50. Akhter, L., Clegg, W., Collison, D. and Garner, C. D. *Inorg. Chem. 24* (1985) 1725.
51. Wormsbäcker, D., Nicholas, K. M. and Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* (1985) 721.
52. Bottomley, F., Paez, D. E. and White, P. S. *J. Am. Chem. Soc. 104* (1982) 5651.
53. Glerup, J., Hazell, A., Michelsen, K. and Weihe, H. *Acta Chem. Scand. 48* (1994) 618.