A Double-bridged Binuclear Chromium(III) Complex with 1-(2-Pyridyl)ethylamine. Stereochemical and Magnetic Properties of Di-μ-hydroxobis [bis{1-(2-pyridyl)ethylamine}-chromium(III)] Ions

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

The synthesis, resolution and stereochemical and magnetic properties of binuclear complexes of the double-bridged type $[(C_7H_{10}N_2)_2Cr(OH)_2Cr(C_7H_{10}N_2)_2]^{4+}$, where the bidentate ligand $C_7H_{10}N_2$ is 1-(2-pyridyl)ethylamine, are reported for the first time. The ligand apparently chelates stereospecifically in this type of complexes. In the case when the title complex is prepared from racemic ligand, one obtains only one racemic pair of complexes, resolvable into catoptric forms, that are identical with the complexes prepared from $(+)_D$- and $(-)_D$-{1-(2-pyridyl)ethylamine}, respectively.

Based on the circular dichroism in the visible range the $(-)_D$-$[\{(R)(+)_D$-$C_7H_{10}N_2\}_2Cr(OH)_2Cr\{(R)(+)_D$-$C_7H_{10}N_2\}_2]^{4+}$ ion is assigned the absolute configuration $\Delta\Delta$. The preliminary results from an X-ray analysis support this assignment.

The magnetic susceptibility of powdered samples of $\Lambda\Lambda(+)_D$-$[\{(S)(-)_D$-$C_7H_{10}N_2\}_2Cr(OH)_2Cr\{(S)(-)_D$-$C_7H_{10}N_2\}_2](S_2O_6)_2.2H_2O$ has been examined in the temperature range $4.5-287$ K. The dimer exhibits an antiferromagnetic exchange interaction. The data were fitted to a model assuming independent triplet, quintet and septet energies. The results were almost consistent with the Van Vleck equation and with a triplet energy of $32.95(9)$ cm^{-1}. The susceptibilities of other active and racemic bromide, dithionate and perchlorate salts were measured in the range $45-300$ K. Singlet–triplet splittings were in all cases in the range $31-37$ cm^{-1}.

Dimeric chromium(III) complexes with two hydroxo groups as bridging ligands, the so-called diols, have recently received much attention because of their spectroscopic,[1–6] structural and magnetic properties.[7–21]

In a recent paper from this laboratory the synthesis, resolution and properties of the binuclear ion $[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]^{4+}$, where the bidentate ligand $C_6H_8N_2 = (2\text{-pyridyl})$methylamine (Fig. 1a), were reported.[5] The present work deals with the corresponding compounds of the closely related amine $C_7H_{10}N_2 = 1$-(2-pyridyl)ethylamine (Fig. 1b). We described the preparation and resolution of this ligand in an earlier work,[22] and the absolute chirality of the $(-)_D$-form was found by X-ray analysis to be S.[23]

For the di-μ-hydroxo complexes of copper(II), several groups of workers have noted apparently simple correlations between the structural and
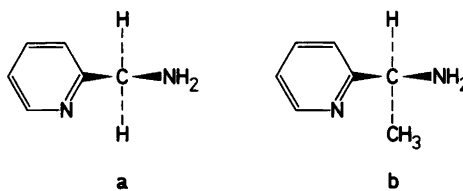

Fig. 1. a. (2-Pyridyl)methylamine, $C_6H_8N_2$.
b. 1-(2-Pyridyl)ethylamine, $C_7H_{10}N_2$.

magnetic properties.[21,24] The magnetic interactions seem to be determined essentially by the geometry of the bridging system. A more complex behaviour has been observed for the chromium(III) complexes. It must be born in mind, however, that only a few complexes are known, in which the geometry of the entire bridging systems, including the hydrogen atoms, has been well determined from X-ray diffraction.

We have, therefore, continued such studies on chromium(III) dimers. We here report the magnetic properties of $\Lambda\Lambda(+)_D$-$[\{(S)(-)_D$-$C_7H_{10}N_2\}_2$Cr-$(OH)_2Cr\{(S)(-)_D$-$C_7H_{10}N_2\}_2](S_2O_6)_2.2H_2O$ and the corresponding active and racemic salts in relation to the preliminary results of a determination of the crystal and molecular structure of the optically active salt.[19]

EXPERIMENTAL

Reagents. Racemic 1-(2-pyridyl)ethylamine was prepared and resolved as described before. SP-Sephadex C 25 was purchased from Pharmacia, Uppsala, Sweden. All other chemicals were of reagent grade and were used without further purifications.

Analyses. The chromium analyses were performed on a Perkin Elmer 403 Atomic Absorption Spectrophotometer. The microanalytical laboratory of this institute carried out the carbon, nitrogen, hydrogen and halogen analyses by standard methods.

Physical measurements. Absorption spectra were recorded on a Cary Model 14 spectrophotometer. The spectra are characterized by their maxima and minima (ε,λ), where the molar extinction coefficient ε is in units of 1 mol^{-1} cm^{-1} and λ is in nm. Circular dichroism was measured on a Roussel-Jouan Dichrographe I in the region $650-350$ nm, on a Roussel-Jouan Dichrographe III in the region $350-200$ nm. The maxima are given below as $(\Delta\varepsilon,\lambda)=[(\varepsilon_l-\varepsilon_r),\lambda]$. Optical rotation was measured on a Perkin Elmer Model 141 polarimeter. In all cases the solvent was 0.1 M hydrochloric acid. The magnetic susceptibility of powdered samples was measured by the Faraday method in the temperature range $4.2-300$ K at a field strength of 12 000 G. The magnetic field was calibrated with Hg[Co-(NCS)$_4$].[25] A more detailed description of the equipment is published elsewhere.[18,26]

Preparations

1. Racemic ligand complexes. 1 a. Di-μ-hydroxobis[bis{1-(2-pyridyl)ethylamine}chromium(III)] bromide, $[(C_7H_{10}N_2)_2Cr(OH)_2Cr(C_7H_{10}N_2)_2]$-

Br$_4$.3H$_2$O. 1.00 g $[CrBr_2(H_2O)_4]Br.2H_2O$ (2.50 mmol) was dissolved in $2-3$ ml 2-methoxyethanol, and a spatula of zinc powder and 0.6 ml racemic 1-(2-pyridyl)ethylamine (~ 5 mmol) were stirred in. Red crystals immediately precipitated. They were filtered after 15 min and washed with 2-methoxyethanol and ethanol. This crude product was always contaminated with metallic zinc and a zinc compound (perhaps a tetrabromozincate). Pure zinc-free diol could be obtained by conversion to a perchlorate (1 b) or an iodide (1 c) or, as in this case, by ion exchange. A filtered solution of the crude product was absorbed on a short column (length 5 cm, diameter 2.5 cm) of an SP-Sephadex C-25 cation exchanger. Elution with 0.1 M sodium bromide (250 ml) and 0.1 M hydrobromic acid (100 ml) removed the unwanted ions. Finally, the diol was eluted with 1 M hydrobromic acid and precipitated with ethanol and ether. Yield: 0.370 g (30 %). In other experiments, yields ranging from 26 to 35 % were obtained. Recrystallization from boiling water (2 ml) with the addition of lithium bromide (0.5 g), ethanol (40 ml) and ether (20 ml) yielded 0.339 g. Anal. $[Cr(C_7H_{10}N_2)_2OH]_2Br_4$.-3H$_2$O: Cr, C, N, H, Br. In other experiments the complex crystallized with 4 or 5 mol of crystal water. $(\varepsilon,\lambda)_{max}$: (200, 535.5), (119, 378). $(\varepsilon,\lambda)_{min}$: (26, 435), (65, 350).

1 b. Di-μ-hydroxobis[bis{1-(2-pyridyl)ethylamine}chromium(III)] perchlorate, $[(C_7H_{10}N_2)_2$-$Cr(OH)_2Cr(C_7H_{10}N_2)_2](ClO_4)_4.3H_2O$. The crude product, prepared from 1.00 g $[CrBr_2(H_2O)_4]Br.$-$2H_2O$ (see 1 a), was dissolved in boiling water (6 ml), and a solution of sodium perchlorate (2 g) in water (1 ml) was added to the filtrate. Cooling on ice. Filtering and washing with ethanol. Yield: 0.599 g (22 %). The compound was recrystallized from boiling water (6 ml). The loss was 25 %. Anal. $[Cr(C_7H_{10}N_2)_2OH]_2(ClO_4)_4.3H_2O$: Cr, C, N, H, Cl. In other experiments the compound crystallized with 2 mol of crystal water. $(\varepsilon,\lambda)_{max}$: (202, 535.5), (119, 378). $(\varepsilon,\lambda)_{min}$: (26, 435), (67, 350).

1 c. Di-μ-hydroxobis[bis{1-(2-pyridyl)ethylamine}chromium(III)] iodide, $[(C_7H_{10}N_2)_2Cr$-$(OH)_2Cr(C_7H_{10}N_2)_2]I_4.3H_2O$. The crude product prepared from 1.00 g $[CrBr_2(H_2O)_4]Br.2H_2O$ (see 1 a) was dissolved in boiling water (6 ml), and a solution of sodium iodide (1 g) in water (1 ml) was added to the filtrate. Cooling on ice. Filtering and washing with ethanol. Yield: 0.501 g (34 %). The compound was recrystallized from boiling water with 70 % recovery. Anal. $[Cr(C_7H_{10}N_2)_2OH]_2I_4.$-$3H_2O$: Cr, C, N, H, I. $(\varepsilon,\lambda)_{max}$: (201, 535.5), 122, 378). $(\varepsilon,\lambda)_{min}$: (28, 434), (71, 350).

2. Resolution of racemic ligand complexes. 2 a. $(-)_D$-Di-μ-hydroxobis[bis{1-(2-pyridyl)ethylamine}chromium(III)] diantimonyl $(+)_D$-tartrate dibromide, $(-)_D$-$[(C_7H_{10}N_2)_2Cr(OH)_2Cr(C_7H_{10}$-

$N_2)_2]\{(+)_D$-$SbOC_4H_4O_6\}_2Br_2.7H_2O$. Compound 1 a (2.20 g, 2.2 mmol) was dissolved in hot water (6−7 ml, 70 °C). Sodium antimonyl $(+)_D$-tartrate (2.6 g, 8.4 mmol) was dissolved in hot water (5 ml, 70 °C). These solutions were mixed, gently heated for a moment and then left at room temperature for 1 h. Filtering and washing with ethanol−water (1:1) and ethanol. Yield: 1.36 g (42 %). Anal. $[Cr(C_7H_{10}N_2)_2OH]_2(SbOC_4H_4O_6)_2Br_2.7H_2O$: Cr, C, N, H, Br. $(\varepsilon,\lambda)_{max}$: (202, 535.5), (122, 378). $(\varepsilon,\lambda)_{min}$: (29, 435), (68, 350). $(\Delta\varepsilon,\lambda)_{max}$: (−5.44, 504.5), (+1.70, 374).

2 b. $(-)_D$-Di-μ-hydroxobis[bis{1-(2-pyridyl)ethyl-amine}chromium(III)] bromide, $(-)_D$-$[(C_7H_{10}N_2)_2$-$Cr(OH)_2Cr(C_7H_{10}N_2)_2]Br_4.3H_2O$. Compound 2 a (1.10 g, 0.74 mmol) was dissolved in 3−4 ml 1 M sodium hydroxide. Ethanol (80 ml) was added to precipitate sodium antimonyl $(+)_D$-tartrate. The filtrate was acidified with conc. hydrobromic acid, and by the addition of lithium bromide (5 g), ethanol and ether, violet crystals of the active bromide separated. Yield: 0.699 g (94 %). The compound was recrystallized as described for 1 a. Anal. $[Cr(C_7H_{10}N_2)_2OH]_2Br_4.3H_2O$: Cr, C, N, H, Br. $(\varepsilon,\lambda)_{max}$: (199, 535.5), (120, 378). $(\varepsilon,\lambda)_{min}$: (27, 435), (65, 350). $(\Delta\varepsilon,\lambda)_{max}$: (−5.40, 504.5), (+1.67, 374).

2 c. $(-)_D$-Di-μ-hydroxobis[bis{1-(2-pyridyl)ethyl-amine}chromium(III)] perchlorate, $(-)_D$-$[(C_7H_{10}$-$N_2)_2Cr(OH)_2Cr(C_7H_{10}N_2)_2](ClO_4)_4.2H_2O$. Compound 2 a (0.250 g, 0.17 mmol) was dissolved in boiling water (5 ml). A solution of sodium perchlorate (1 g, 1 ml) was added, and fluffy crystals separated. Filtering and washing with 1 M sodium perchlorate and with ethanol. Yield: 0.135 g (75 %). Anal. $[Cr(C_7H_{10}N_2)_2OH]_2(ClO_4)_4.2H_2O$: Cr, C, N, H, Cl. $(\varepsilon,\lambda)_{max}$: (199, 535.5), (121, 378). $(\varepsilon,\lambda)_{min}$: (27, 435), (68, 350). $(\Delta\varepsilon,\lambda)_{max}$: (−5.43, 504.5), (+1.66, 374).

3. Active ligand complexes. 3 a. $(+)_D$-Di-μ-hydroxobis[bis{$(-)_D$-1-(2-pyridyl)ethylamine}chro-mium(III)] bromide, $(+)_D$-$[\{(-)_D$-$C_7H_{10}N_2\}_2Cr$-$(OH)_2Cr\{(-)_D$-$C_7H_{10}N_2\}_2]Br_4.3H_2O$. The compound was prepared as 1a except that the racemic ligand was replaced by $(-)_D$-1-(2-pyridyl)ethyl-amine. The yield was normally 30 %. Anal. $[Cr-(C_7H_{10}N_2)_2OH]_2Br_4.3H_2O$: Cr, C, N, H, Br. $(\varepsilon,\lambda)_{max}$: (199, 535.5), (120, 378). $(\varepsilon,\lambda)_{min}$: (28, 434), (67, 350). $(\Delta\varepsilon,\lambda)_{max}$: (5.41, 504), (−1.71, 375).

3 b. $(+)_D$-Di-μ-hydroxobis[bis{$(-)_D$-1-(2-pyridyl)-ethylamine}chromium(III)] dithionate, $(+)_D$-$[\{(-)_D$-$C_7H_{10}N_2\}_2Cr(OH)_2Cr\{(-)_D$-$C_7H_{10}N_2\}_2]$-$(S_2O_6)_2.5H_2O$. Compound 3a (0.122 g, 0.122 mmol) was dissolved in boiling water (2 ml). Sodium dithionate (0.1 g) was added and dissolved by gentle heating. A few minutes later red, needle-shaped crystals separated. Washing with ice-cold water. Yield: 0.111 g (91 %). Anal. $[Cr(C_7H_{10}N_2)_2$-$OH]_2(S_2O_6)_2.5H_2O$: Cr, C, N, H. In other experi-

ments the complex crystallized with 2, 3 or 4 mol of crystal water. $(\varepsilon,\lambda)_{max}$: (203, 535.5), (120, 378). $(\varepsilon,\lambda)_{min}$: (27, 434), (66, 350).

3 c. $(-)_D$-Di-μ-hydroxo[bis{$(+)_D$-1-(2-pyridyl)-ethylamine}chromium(III)] perchlorate, $(-)_D$-$[\{(+)_D$-$C_7H_{10}N_2\}_2Cr(OH)_2Cr\{(+)_D$-$C_7H_{10}N_2\}_2]$-$(ClO_4)_4.2H_2O$. The compound was prepared as 1b except that the racemic ligand was replaced by $(+)_D$-1-(2-pyridyl)ethylamine. The yields varied from 30 to 35 %. Anal. $[Cr(C_7H_{10}N_2)_2OH]_2(ClO_4)_4.2$-$H_2O$: Cr, C, N, H, Cl. $(\varepsilon,\lambda)_{max}$: (200, 535.5), (122, 378). $(\varepsilon,\lambda)_{min}$: (28, 434), (70, 350). $(\Delta\varepsilon,\lambda)_{max}$: (−5.41, 504.5), (+1.73, 374).

3 d. $(+)_D$-Di-μ-hydroxobis[bis{$(-)_D$-1-(2-pyridyl)-ethylamine}chromium(III)] perchlorate, $(+)_D$-$[\{(-)_D$-$C_7H_{10}N_2\}_2Cr(OH)_2\{(-)_D$-$C_7H_{10}N_2\}_2]$-$(ClO_4)_4.2H_2O$. The compound was prepared as 1b except that the racemic ligand was replaced by $(-)_D$-1-(2-pyridyl)ethylamine. Yields as above. Anal. $[Cr(C_7H_{10}N_2)_2OH]_2(ClO_4)_4.2H_2O$: Cr, C, N, H, Cl. $(\varepsilon,\lambda)_{max}$: (201, 535.5), (121, 378). $(\varepsilon,\lambda)_{min}$: (27, 434), (67, 350). $(\Delta\varepsilon,\lambda)_{max}$: (+5.40, 504.5), (−1.66, 374).

RESULTS AND DISCUSSION

Synthesis and resolution. We have earlier found [5,6] that di-μ-hydroxo complexes of chromium(III) with the related ligands (2-pyridyl)methylamine and 1,6-bis-(2'-pyridyl)-2,5-diazahexane could be obtained by the reaction of chromium(III) bromide hexa-hydrate, with the amine in question in the presence of zinc dust. The same method could be used here, but the yields never exceeded 40 %. The byproducts, as revealed by column chromatography, consisted partly of several lavender-coloured polymeric com-pounds containing ions of a higher charge than four, and partly of a small amount of a monomeric compound. Only one diol-band appeared on the column, just as it was impossible to isolate more than one diol-isomer from the reaction mixture, no matter whether racemic or optically active amine had been used in the preparation. We cannot, however, preclude the existence of other isomers, because they could have evaded our detection if they were formed in sufficiently small amounts.

Like the corresponding diols with (2-pyridyl)-methylamine,[5] 1,6-bis-(2'-pyridyl)-2,5-diazahexane,[6] 1,10-phenanthroline and 2,2'-bipyridine,[3] the diol prepared from racemic 1-(2-pyridyl)ethylamine could be resolved with sodium antimonyl $(+)_D$-tartrate as a resolving agent. The less soluble diastereoisomer was converted into a perchlorate that turned out to be identical with the diol-per-
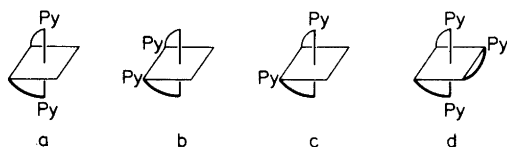
Fig. 2. a, b, c. Geometrical isomers of *cis*-complexes of (2-pyridyl)methylamine with chromium(III). Py symbolizes the pyridine nitrogen. The ligand configurations around the central atoms on the figures are all Λ. a. α-*cis* (Λα). b. α'-*cis* (Λα'). c. β-*cis* (Λβ). d. A meridional isomer of a *tris*-complex of 1-(2-pyridyl)ethylamine with cobalt(III) or chromium-(III), *mer*-Λ.

chlorate prepared direct from (R)(+)$_D$-{1-(2-pyridyl)ethylamine}.

Stereochemistry of the di-μ-hydroxobis[bis{1-(2-pyridyl)ethylamine}chromium(III) ion. The binuclear ion [(C$_7$H$_{10}$N$_2$)$_2$Cr(OH)$_2$Cr(C$_7$H$_{10}$N$_2$)$_2$]$^{4+}$ could in principle exist in several isomeric forms. The isomerism becomes easier to grasp when at first we ignore the methyl group in the amine and consider the isomerism of diols formed with the closely related ligand, (2-pyridyl)methylamine (Fig. 1). This ligand is unsymmetrical, and consequently three geometrical isomers of *cis*-complexes of chromium(III) may occur (Fig. 2 a−c). These *cis*-skeletons are the building stones from which twenty-four diols can be constructed as shown below. From two α-*cis*-skeletons, for instance, we can build up three different isomers (Fig. 3 a−c). Correspondingly we obtain three isomers from two α'-*cis*-skeletons. Two β-*cis*-skeletons result in six isomers. The combination of an α-*cis* and an α'-*cis*-skeleton gives four isomers as do the combinations of α-*cis* and β-*cis*-skeletons and of α'-*cis* and β-*cis* skeletons, respectively.

Molecular models indicate, however, that all compounds containing an α'-*cis* or a β-*cis* skeleton as well as all *meso*-isomers are hindered sterically.
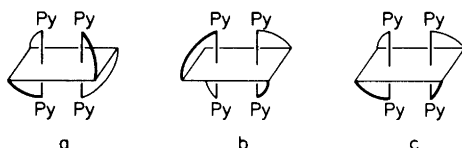

Fig. 3. [(C$_6$H$_8$N$_2$)$_2$Cr(OH)$_2$Cr(C$_6$H$_8$N$_2$)$_2$]$^{4+}$. a−c are the three isomers that can be constructed from two α-*cis*-skeletons. a. ΛαΛα. b. ΔαΔα. c. ΛαΔα.
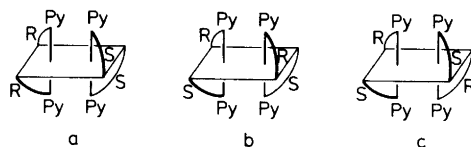
Fig. 4. ΛΛ-[(C$_7$H$_{10}$N$_2$)$_2$Cr(OH)$_2$Cr(C$_7$H$_{10}$N$_2$)$_2$]$^{4+}$. a, b and c show the three different ΛΛ isomers containing two R-amines and two S-amines. a. ΛRR ΛSS. b. ΛRS ΛRS. c. ΛRS ΛSR.

That leaves us with the possibility of finding two isomers only, namely the catoptromers ΛαΛα and ΔαΔα shown in Fig. 3 a and b.

Returning now to 1-(2-pyridyl)ethylamine we find that geometrical isomerism caused by the methyl-groups makes the simplified picture complicated again. Instead of one ΛΛ isomer and one ΔΔ isomer we get the theoretical possibility of seven ΛΛ isomers and seven ΔΔ isomers, namely:

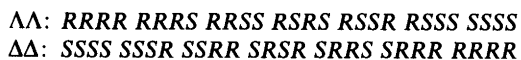ΛΛ: *RRRR RRRS RRSS RSRS RSSR RSSS SSSS*

ΔΔ: *SSSS SSSR SSRR SRSR SRRS SRRR RRRR*

Fig. 4 shows how the combination of two R-amines and two S-amines necessarily results in three different complexes with the configuration ΛΛ.

In the case when [(C$_7$H$_{10}$N$_2$)$_2$Cr(OH)$_2$Cr-(C$_7$H$_{10}$N$_2$)$_2$]$^{4+}$ was prepared from (S)(−)$_D$-{1-(2-pyridyl)ethylamine} only one optically active complex, namely ΛΛ-(+)$_D$-[{(−)$_D$-C$_7$H$_{10}$N$_2$}$_2$Cr(OH)$_2$-Cr{(−)$_D$-C$_7$H$_{10}$N$_2$}$_2$]$^{4+}$ (abbrev. ΛΛS$_4$) was obtained. The expected ΔΔS$_4$ isomer was never detected. When racemic amine was used as a starting material, we were able to find one racemate only, instead of seven as expected. This racemate was resolved, and, as mentioned above, the identity of one of the isolated species proved that we had been dealing with a racemate of ΔΔR$_4$ and ΛΛS$_4$.

Results from an earlier work on *tris*-complexes of (S)(−)$_D$-{1-(2-pyridyl)ethylamine} and cobalt-(III)[22] support this evidence of stereospecific coordination. The existence of two meridional isomers, namely *mer*-Λ(+)$_D$-[Co{(S)(−)$_D$-C$_7$H$_{10}$N$_2$}$_3$]$^{3+}$ (abbrev. ΛS$_3$) and *mer*-Δ(−)$_D$-[Co{(S)(−)$_D$-C$_7$H$_{10}$N$_2$}$_3$]$^{3+}$ (abbrev. ΔS$_3$) was expected at that time, but we found only one, namely the ΛS$_3$ isomer.

Recognizing that both a meridional *tris*-complex (Fig. 2 d) and a di-μ-hydroxo complex (Fig. 3 a and b) contain an α-*cis*-skeleton (Fig. 2 a), it is an
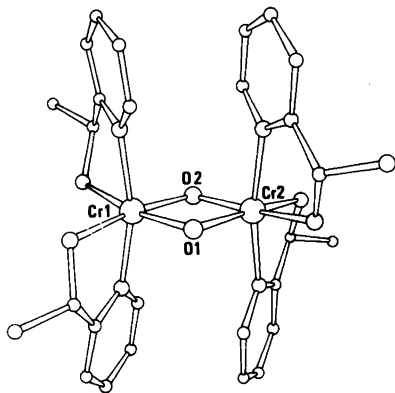
Fig. 5. View of cation in $\Lambda\Lambda(+)_D$-$[\{(S)(-)_D$-$C_7H_{10}N_2\}_2Cr(OH)_2Cr\{(S)(-)_D$-$C_7H_{10}N_2\}_2]$-$(S_2O_6)_2$·$2H_2O$. Hydrogen atoms are omitted for clarity. Refer to the text for details of distances and angles.

Fig. 6. The absorption spectrum (top) and the circular dichroism (bottom) of $(-)_D$-$[\{(R)(+)_D$-$C_7H_{10}N_2\}_2Cr(OH)_2Cr\{(R)(+)_D$-$C_7H_{10}N_2\}_2]^{4+}$. Region $620-300$ nm.

obvious thought that the possible stereospecificity is linked to the α-*cis*-skeleton, and that investigations on α-*cis*-complexes of chromium(III) and cobalt(III) with 1-(2-pyridyl)ethylamine might throw light on the problem.

Configuration and optical activity. The preliminary results from an X-ray analysis of $(+)_D$-$[\{(S)(-)_D$-$C_7H_{10}N_2\}_2Cr(OH)_2Cr\{(S)(-)_D$-$C_7H_{10}N_2\}_2]$-$(S_2O_6)_2$·$2H_2O^{19}$ (Fig. 5) prove that this compound has the configuration $\Lambda\Lambda$. The catoptromer, $(-)_D$-$[\{(R)(+)_D$-$C_7H_{10}N_2\}_2Cr(OH)_2Cr\{(R)(+)_D$-$C_7H_{10}N_2\}_2]^{4+}$, whose absorption and circular dichroism spectra (vis. region) are shown in Fig. 6, consequently has the configuration $\Delta\Delta$. This is in agreement with the empirical rule that relates a
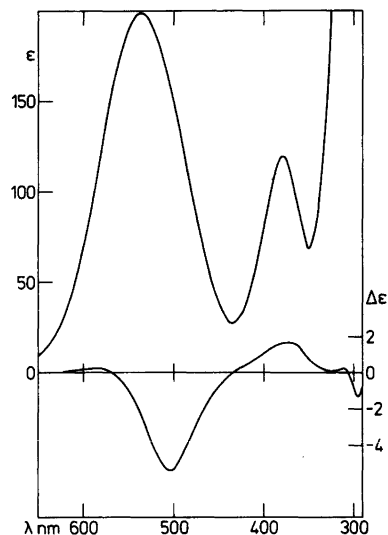
dominant negative CD-band in the region of the cubic $^4A_{2g}\rightarrow{}^4T_{2g}$ $d-d$ absorption of the chromium-(III) ion to a $\Delta\Delta$ configuration.[27] A comparison with spectral data for related compounds is presented in Table 1.

From the X-ray analysis it also appears that $(S)(-)_D$-$\{1$-$(2$-pyridyl)ethylamine$\}$ chelates with the conformation δ, thus preferring the conformation in which the methyl group is equatorial. The same amine conformation was earlier found in *fac*-Λ-$[Co\{(S)(-)_D$-$C_7H_{10}N_2\}_3]^{3+}$.[23]

Table 1. CD-spectral parameters for some di-μ-hydroxo complexes of chromium(III) with (2-pyridyl)-methylamine $(C_6H_8N_2)$, 1-(2-pyridyl)ethylamine $(C_7H_{10}N_2)$, 1,6-bis(2′-pyridyl)-2,5-diazahexane $(C_{14}H_{18}N_4)$, 1,10-phenanthroline $(C_{12}H_8N_2)$ and 2,2′-bipyridine $(C_{10}H_8N_2)$.

Compound	$\lambda_{ex}(1)$ nm	$\Delta\varepsilon_{ex}(1)$	$\lambda_{ex}(2)$ nm	$\Delta\varepsilon_{ex}(2)$	$\lambda_{ex}(3)$ nm	$\Delta\varepsilon_{ex}(3)$	Ref.
$(-)_D$-$[Cr(C_6H_8N_2)_2OH]_2^{4+}$	588	$+0.37$	508	-5.55	376	$+1.62$	5
$(-)_D$-$[Cr\{(R)(+)_D$-$C_7H_{10}N_2\}_2OH]_2^{4+}$	~585	~$+0.22$	504.5	-5.41	374	$+1.73$	
$(+)_D$-$[Cr\{(S)(-)_D$-$C_7H_{10}N_2\}_2OH]_2^{4+}$	~583	~-0.23	504.5	$+5.40$	374	-1.66	
$(-)_D$-$[Cr(C_7H_{10}N_2)_2OH]_2^{4+}$ (2c)	~583	~$+0.23$	504.5	-5.43	374	$+1.66$	
$(-)_D$-$[Cr(C_{14}H_{18}N_4)OH]_2^{4+}$			520	-5.30	382	$+1.10$	6
$(+)_D$-$[Cr(C_{14}H_{18}N_4)OH]_2^{4+}$			520	$+5.42$	383	-1.13	6
$(-)_D$-$[Cr(C_{12}H_8N_2)_2OH]_2^{4+}$			~520	~-6.2	~400	~$+2.6$	3
$(-)_D$-$[Cr(C_{10}H_8N_2)_2OH]_2^{4+}$	615	$+0.18$	518	-6.62	402	$+0.79$	28
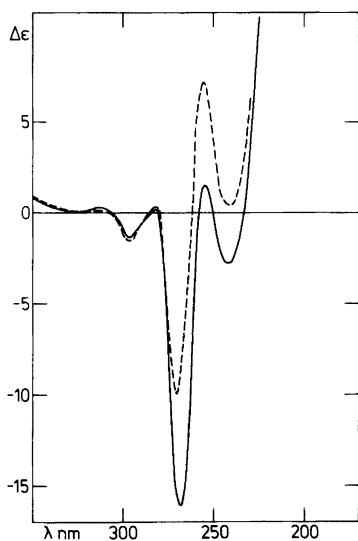
Fig. 7. The circular dichroism spectra of $(-)_D$-$[\{(R)(+)_D\text{-}C_7H_{10}N_2\}_2Cr(OH)_2Cr\{(R)(+)_D\text{-}C_7H_{10}N_2\}_2]^{4+}$ (———) and of $(-)_D$-$[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]^{4+}$ (———). Region 350—220 nm.

The CD-spectra of $(-)_D$-$[\{(R)(+)_D\text{-}C_7H_{10}N_2\}_2Cr(OH)_2Cr\{(R)(+)_D\text{-}C_7H_{10}N_2\}_2]^{4+}$ and $(-)_D$-$[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]^{4+}$ in the region

350—220 nm are shown in Fig. 7. The CD-spectrum of the di-μ-hydroxo complex with (2-pyridyl)methyl-amine is included for comparison. It is not possible to interpret the spectra at the present time, but we find it worthwhile to draw attention to the small, sharp peaks in the region 320—280 nm. Apparently they are closely linked to the binuclear structure of the di-μ-hydroxo complexes, as they were never detected in the corresponding mononuclear *cis*-complexes.

Magnetic and structural properties. The average magnetic susceptibility and effective moment of a powdered sample of $(+)_D$-$[\{(S)(-)_D\text{-}C_7H_{10}N_2\}_2Cr(OH)_2Cr\{(S)(-)_D\text{-}C_7H_{10}N_2\}_2](S_2O_6)_2.2H_2O$ as functions of temperature are shown in Fig. 8. Similar results were obtained for the related bromide, dithionate and perchlorate salts with the important difference, however, that the magnetic properties of these salts were measured only in the interval 45—300 K. The susceptibility data were fitted to the expression

$$\chi'_A = -\frac{N}{H}\frac{\sum_i\left(\dfrac{\partial E_i}{\partial H}\right)e^{-(E_i/kT)}}{\sum_i e^{-(E_i/kT)}} \tag{1}$$

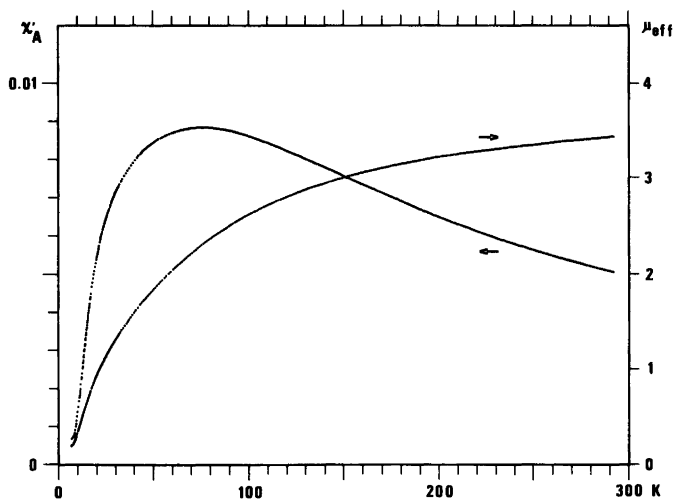where E_i refers to the energies of the sixteen components of the ground states, by minimization[29] of

Fig. 8. Magnetic susceptibility (left scale in c.g.s. units) and effective magnetic moment (right scale in Bohr magnetons) of $\Lambda\Lambda(+)_D$-$[\{(S)(-)_D\text{-}C_7H_{10}N_2\}_2Cr(OH)_2Cr\{(S)(-)_D\text{-}C_7H_{10}N_2\}_2](S_2O_6)_2.2H_2O$. The dots represent 330 measurements. The theoretical values corresponding to the parameters in Table 2 fall within the areas of the dots.

$$\sum_{i} (\chi_i^{obs} - \chi_A')^2 / \left\{ \sigma^2(\chi) + \left(\frac{\partial \chi}{\partial T} \right)^2 \sigma^2(T) \right\} \qquad (2)$$

We assumed the Hamiltonian

$$\mathcal{H} = E(S') + g\beta H M_{S'} \qquad (3)$$

where $\mathbf{S}' = \mathbf{S}_1 + \mathbf{S}_2$. Since $S_1 = S_2 = 3/2$, S' takes the values 0,1,2 and 3. Eqn. (3) implies independent energies of the singlet, triplet, quintet and septet levels, absence of zero-field splittings within these and furthermore an isotropic Zeeman effect. This is a generalized version of the Van Vleck Hamiltonian which in some cases has been expanded with a biquadratic exchange term according to

$$\mathcal{H} = J\mathbf{S}_1\mathbf{S}_2 + j(\mathbf{S}_1\mathbf{S}_2)^2 \qquad (4)$$

The relations between $E(S')$, J and j restricted by eqn. (4) are given by

$$\begin{aligned} E(1) - E(0) &= J - 13/2\,j \\ E(2) - E(0) &= 3J - 27/2\,j \\ E(3) - E(0) &= 6J - 9j \end{aligned} \qquad (5)$$

where the J-terms follow the Landé rule.

The results of fitting the susceptibility of the $(+)_D$-dithionate to eqns. (1) and (3) are shown in Table 2. We assumed a normal distribution of errors of each measurement corresponding to standard deviations of the susceptibilities of 0.05 % and of the temperature of 0.05 K plus 0.05 % of the deviation of the actual temperature from that of boiling nitrogen which was used as a reference. The estimated standard deviations of our suscepti-bility measurements are thus a factor of ten smaller

than the accuracy of the standard[25] used for calibration of $H\partial H/\partial x$. This calibration constant, the molecular weight assumed, and the g-factors obtained from our fitting procedure are strongly correlated, g^2 being proportional to the molecular weight and roughly inversely proportional to $H\partial H/\partial x$. The calculated standard deviations of the g-factors as obtained from the fitting procedure and as shown in Table 2 do therefore not reflect the absolute accuracy, estimated to be 0.3 %. The $E(S')$ values, however, are determined from the shape of the susceptibility vs. temperature and not cor-related with the molecular weight and $H\partial H/\partial x$.

The ratio between the variance and the degrees of freedom indicates good agreement with the model expressed in eqn. (3) according to the estimates of a χ^2-test. This ratio was 1.5 when the data were fitted to eqn. (4). For the other salts for which the low-temperature data are missing the data were fitted to eqn. (4) with and without j fixed to zero. It was found in all cases that zero was within the range of the estimated j-values plus/minus two standard deviations.

The parameters obtained from the $(+)_D$-dithio-nate are close to the predictions of the simple Van Vleck Hamiltonian although small deviations do occur. In terms of the super-exchange model by Anderson[30] as later clarified by Glerup[20] for interacting d^3-configurations the antiferromagnet-ism of compounds of the present type can be accounted for[15] in terms of configuration interac-tion between the $t_2^3 \times t_2^3$ ground states and excited transfer states of the types $t_2^2 \times t_2^4$. In the limiting case of small energy separations in the charge trans-fer states relative to the excitation energy, the

Table 2. Results of the digital fitting procedure for susceptibilities. $E(1)$, $E(2)$, and $E(3)$ refer to the triplet, quintet, and septet energies, respectively. Other parameters in the procedure were a temperature inde-pendent susceptibility term besides the standard diamagnetic corrections (results $30-120 \times 10^{-6}$ c.g.s. units) and monomeric impurities (results $0-0.3$ mol %).

Compound	$E(1)$ cm^{-1}	$E(2)$ cm^{-1}	$E(3)$ cm^{-1}	Degrees of freedom (f)	Variance per f	g
rac-$[Cr(C_7H_{10}N_2)_2OH]_2Br_4.3H_2O$	35.64(4)	3E(1)	6E(1)	327	0.4	1.979(2)
$(-)_D$-$[Cr\{(R)(+)_D$-$C_7H_{10}N_2\}_2OH]_2Br_4.3H_2O$	31.6(1)	3E(1)	6E(1)	309	0.2	1.961(4)
rac-$[Cr(C_7H_{10}N_2)_2OH]_2(ClO_4)_4.3H_2O$	30.53(4)	3E(1)	6E(1)	330	0.9	2.000(2)
$(+)_D$-$[Cr\{(S)(-)_D$-$C_7H_{10}N_2\}_2OH]_2$-$(ClO_4)_4.2\frac{1}{2}H_2O$	33.79(6)	3E(1)	6E(1)	343	0.2	1.989(2)
rac-$[Cr(C_7H_{10}N_2)_2OH]_2(S_2O_6)_2.5H_2O$	36.85(3)	3E(1)	6E(1)	396	0.4	1.976(1)
$(+)_D$-$[Cr\{(S)(-)_D$-$C_7H_{10}N_2\}_2OH]_2$-$(S_2O_6)_2.2H_2O$	32.95(9)	101.2(4)	200(1)	324	1.3	1.993(8)

Table 3. Geometry of the chromium-oxygen ring system and the singlet-triplet splitting for di-μ-hydroxo complexes of chromium(III) with 1,10-phenanthroline $(C_{12}H_8N_2)$, 1,2-ethanediamine $(C_2H_8N_2)$ and $(S)(-)_D$-{1-(2-pyridyl)ethylamine}$(C_7H_{10}N_2)$. Average values are given for $Cr-O$ and $Cr-O-Cr$.

| | $[Cr(C_{12}H_8N_2)_2OH]_2^{4+}$ | | $[Cr(C_2H_8N_2)_2OH]_2^{4+}$ | | $(+)_D$-$[Cr\{(S)(-)_D$- |
	Chloride	Iodide	Dithionate	Dichloride Diperchlorate	$C_7H_{10}N_2\}_2OH]_2^{4+}$ Dithionate
Cr−Cr (Å)	3.008	2.986	3.032	3.059	3.019
Cr−O (Å)	1.927	1.920	1.979	1.949	1.938
Cr−O−Cr (°)	102.7	102.1	100.0	103.4	102.3
Triplet energy (cm^{-1})	55	53.6	3.68	28[a]	32.95
Ref.	9	11	14	31	19

[a] For the corresponding bromide and perchlorate salts the triplet energies are 24 cm^{-1} and 27 cm^{-1}, respectively.

consequence of such an interaction for the ground states is antiferromagnetism according to the Van Vleck equation. We feel at the present stage that it is too early to correlate the small deviations from the Van Vleck equation with energy separations in the charge transfer states.

The singlet-triplet splittings found for the present compounds are within the range of values observed in other chromium(III) diols. For comparison, average values of known distances and angles as well as of singlet-triplet splittings are given in Table 3, and the view of the $\Lambda\Lambda$-$(+)_D$-$[\{(S)(-)_D$-$C_7H_{10}N_2\}_2Cr(OH)_2Cr\{(S)(-)_D$-$C_7H_{10}N_2\}_2]^{4+}$ cation as found in the dithionate salt[19] is shown in Fig. 5. The positions of the hydrogen atoms on the bridging oxygen atoms have not been determined for the phenanthroline complexes.[9,11] For the other complexes mentioned in Table 3 the hydrogen atoms are at the expected distances from the oxygen atoms, and they are within 5° from the almost planar arrangement of bridging oxygen and chromium atoms, except for the magnetically anomalous ethylenediamine complex dithionate where they are approximately 60° out of the plane. These hydrogen positions appear to be determined by formation of hydrogen bonds to the anions or water molecules. On this basis we expect hydrogen positions close to the bridging plane in the phenanthroline complexes.

According to simple considerations concerning "super-exchange pathways" in systems with two coupled d^3-configurations[15,20] the largest antiferromagnetic couplings in di-μ-hydroxobridged systems are expected when the hydrogen atoms on the bridges are in the bridging plane. This leaves a p_z-orbital perpendicular to this plane available for maximum overlap with the d_{zx}- and d_{yz}-orbitals on the metal atoms.[15]

The magnetic interaction in the ethylenediamine complex dithionate is remarkably small, and this compound has the longest $Cr-O$ distances, and hydrogen positions in the bridging system far away from the bridging plane. Only variations with 3° of the $Cr-O-Cr$ angles are observed.

A simple pattern seems to emerge from these considerations. All data presently available are consistent with the interpretations that out-of-plane positions of the hydrogens lead to reduced π-overlaps between the metals and the bridging oxygen atoms, and consequently small magnetic interactions, and increased metal-to-oxygen distances, the driving force being unpredictable hydrogen bonding effects in the lattice.

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