

Binuclear Chromium(III) Complexes with *N,N'*-Bis(2-pyridylmethyl)-1,2-propanediamine. Circular Dichroism and Stereochemical and Magnetic Properties

KIRSTEN MICHELSEN and ERIK PEDERSEN

Chemistry Department I (Inorganic Chemistry), University of Copenhagen, H.C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

The synthesis, stereochemical and magnetic properties of binuclear di- μ -hydroxo complexes of the type $[(C_{15}H_{20}N_4)Cr(OH)_2Cr(C_{15}H_{20}N_4)]^{4+}$ with the racemic and optically active tetradentate ligand *N,N'*-bis(2-pyridylmethyl)-1,2-propanediamine are reported. Where the title complex is prepared from racemic ligand, three racemic pairs of complexes are obtained, each resolvable into catoptric forms, two of which are identical with the complexes prepared from *N,N'*-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine. The structures of the complexes are deduced from the decompositions to parentage mononuclear *cis*- α -dichloro complexes of established structures.

The circular dichroism spectra of the optically active di- μ -hydroxo complexes as well as the μ -hydroxo- μ -oxo and di- μ -oxo complexes are reported. Only the first ones (vis. region) can be used in assigning the absolute configurations unambiguously. The magnetic susceptibilities of four of the di- μ -hydroxo complexes indicate antiferromagnetic exchange coupling giving rise to singlet-triplet separations between 44 and 50 cm^{-1} . A fit of the data to a model assuming independent triplet, quintet and septet energies is almost consistent with the Heisenberg model corrected for biquadratic exchange.

Binuclear chromium(III) complexes with one or two bridging hydroxo groups, the so-called monools and diols, have recently received much attention because of their spectroscopic, structural and magnetic properties.¹⁻³¹

In previous works from this laboratory we have reported the synthesis, resolution and properties of diols of chromium(III) with pyridyl substituted

bidentate ligands such as (2-pyridyl)methylamine (abbrev. pic),¹⁴ 1-(2-pyridyl)ethylamine (mepic)²¹ and the tetradentate ligand *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen).¹⁷ This work deals with the corresponding compounds of the related ligand *N,N'*-bis(2-pyridylmethyl)-1,2-propanediamine (bispicpn), Fig. 1.

While the structure of our dimeric compound with mepic has been shown by X-ray analysis to be a diol,²⁵ we have not yet proved that the dimeric complexes with bispicen and bispicpn are diols of the formula $[ACr(OH)_2CrA](ClO_4)_4 \cdot 4 H_2O$ and not aquahydroxo monools of the formula $[(H_2O)ACr(OH)CrA(OH)](ClO_4)_4 \cdot 3 H_2O$. The latter possibility cannot be entirely excluded after the discovery of a relatively fast equilibrium in solution between a corresponding diol and monool with 1,2-ethanediamine.³²⁻³⁵ Thus, for example, thermogravimetry showed that our compounds were totally dehydrated below 140 °C. It was not possible, however, to distinguish between crystal and complex-bound water. No other physical measurements gave a final answer to this problem although our magnetic and spectroscopic measurements strongly indicate the presence of diols in the solid state and in the solutions, respectively.

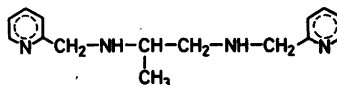


Fig. 1. *N,N'*-Bis(2-pyridylmethyl)-1,2-propanediamine, bispicpn, $C_{15}H_{20}N_4$.

EXPERIMENTAL

Reagents. Pyridine-2-carboxaldehyde was purchased from Merk-Schuchardt. 1,2-Propanediamine was resolved following the method of Dwyer *et al.*³⁶ SP-Sephadex C-25 was purchased from Pharmacia, Uppsala, Sweden. All other compounds 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 and a Cary Model 118 spectrophotometer. The spectra are characterized by their maxima and minima (ϵ , λ), where the molar extinction coefficient ϵ is in units of $l\ mol^{-1}\ cm^{-1}$ and λ is in nm. Circular dichroism was measured on Roussel-Jouan Dichrographe III in the region 650–200 nm. The extrema are given below as $(\Delta\epsilon, \lambda) = [(\epsilon_l - \epsilon_r), \lambda]$. $[Co(en)_3]Cl_3 \cdot 1/2NaCl \cdot 3H_2O$ was used as a standard with $(\Delta\epsilon, \lambda) = (1.92, 489)$. The compounds were dissolved in 0.1 M hydrochloric acid, 0.01 M sodium hydroxide + 1 M sodium chloride, 4 M sodium hydroxide and a solution of lithium methoxide in ethanol (*vis. region only*). The different media were chosen in order to obtain spectra of the di- μ -hydroxo ion, the μ -hydroxo- μ -oxo ion and the di- μ -oxo ion. The acid dissociation constant K_{a1} of the di- μ -hydroxo ion with *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen) was roughly determined by Ole Mønsted. A more detailed description of the potentiometric method and of the equipment is published elsewhere.³⁷ The preliminary result is $pK_{a1} = 9.3$, $\mu = 1$ M, 25 °C. Judging from spectral measurements the acid dissociation constants for the corresponding diols with *N,N'*-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine {bispic(-pn)} have values of the same magnitude. Optical rotation was measured on a Perkin Elmer Model 141 polarimeter. The magnetic susceptibilities of powdered samples were measured by the Faraday method in the temperature range 4–270 K at a field strength of 12.000 Oe. The magnetic field was calibrated with $Hg[Co(NCS)_4]$.³⁸ A more detailed description of the equipment is published elsewhere.^{7,20} Thermogravimetry was performed on an instrument, which has been described previously.³⁹

Preparations. 1. *N,N'*-Bis(2-pyridylmethyl)-1,2-propanediamine, $C_{15}H_{20}N_4$ (abbrev. bispicpn) and *N,N'*-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine, $(-)_D-C_{15}H_{20}N_4$ (abbrev. bis-

pic(-pn)). The ligands were prepared from pyridine-2-carboxaldehyde and 1,2-propanediamine or $(-)_D-1,2(R)$ -propanediamine following mainly the principles of Goodwin and Lions.⁴⁰ The crude amines were purified *via* the hydrochlorides as described for *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine.¹⁷ The pure hydrochlorides normally crystallized with 2 mol of crystal water.

2. Di- μ -hydroxobis[{*N,N'*-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine}chromium(III)] perchlorate, $(+)_D-[\{bispic(-pn)\}Cr(OH)_2Cr\{bispic(-pn)\}](ClO_4)_4 \cdot 3H_2O$ and $(-)_D-[\{bispic(-pn)\}Cr(OH)_2Cr\{bispic(-pn)\}](ClO_4)_4 \cdot 3H_2O$. A crude product from which we isolated two different red compounds was prepared using in principle the general method developed in our laboratory for the preparation of diols with pyridyl-substituted amine ligands.^{14,17,21} $[CrBr_2(H_2O)_4]Br \cdot 2H_2O$ (1.00 g, 2.50 mmol) was dissolved in water (1 ml). 2-Methoxyethanol (2 ml), a spatula of zinc dust and bispic(-pn) (0.8 ml 2.50 mmol) were stirred in. Filtering from zinc dust after 10 min was followed by precipitation with ethanol and ether. The red precipitate was dissolved in water (400 ml) and transferred to a column of SP-Sephadex C 25 ($l \sim 22$ cm, diam. ~ 4 cm). The compounds were eluted with a phosphate solution (0.1 M NaH_2PO_4 – 0.1 M Na_2HPO_4). Two red bands presumed to contain binuclear complexes were recognized. The first band, called 1, was very weak. The second band, called 2, was very distinct and large. The eluates were both diluted four times with water and adsorbed to short columns, where sodium and phosphate ions were eluted with 0.1 M hydrochloric acid, and the complexes afterwards with 4 M hydrochloric acid. The chlorides were precipitated with ethanol and ether from the ice-cooled solutions. Afterwards they were converted to the corresponding perchlorates by the addition of saturated solutions of sodium perchlorate to hot water solutions of the compounds in question. Cooling on ice, filtering and washing with ethanol followed. Recrystallizations from boiling water normally gave losses of about 25 %.

Band 1. The yields were very small (<1 %). Therefore the eluates from several syntheses were collected and treated at one time.

Anal. $(+)_D-[\{Cr\{R\}-C_{15}H_{20}N_4\}(OH)]_2(ClO_4)_4 \cdot 3H_2O$: Cr, C, N, H, Cl.
 $(\epsilon, \lambda)_{max}$: (220, 533), (148, 384),
 $(\epsilon, \lambda)_{min}$: (36.8, 437), (82.6, 350.5).
 $(\Delta\epsilon, \lambda)_{ex}$: (+4.47, 521), (-0.73, 377).

When the perchlorate was left for a week with conc. hydrochloric acid in a stoppered flask, red-violet crystals appeared. They were identified by their absorption and circular dichroism spectra as

(+)_D-*cis-α*-[Cr{bispic(-pn)}Cl₂]ClO₄.⁴¹

(ϵ , λ)_{max}: (103, 542.5), (101, 406).

(ϵ , λ)_{min}: (25.8, 462), (10.4, 353).

($\Delta\epsilon$, λ)_{ex}: (-1.05, 576), (+1.14, 508).

Band 2. The yields varied from 680 mg to 1030 mg (49%–75%) and were most frequently 840 mg (61%).

Anal. (-)_D-[Cr{(R)-C₁₅H₂₀N₄}(OH)]₂(ClO₄)₄·3H₂O: Cr, C, N, H, Cl.

In other cases the compound crystallized with 4 mol of crystal water.

(ϵ , λ)_{max}: (173, 529), (147, 386)

(ϵ , λ)_{min}: (34.6, 439), (74.0, 350)

($\Delta\epsilon$, λ)_{ex}: (-5.86, 522), (+1.48, 381).

When the perchlorate was left for one week with conc. hydrochloric acid in a stoppered flask, blue-violet crystals appeared. They were identified by their absorption and circular dichroism spectra as

(-)_D-*cis-α*-[Cr{bispic(-pn)}Cl₂]ClO₄.⁴¹

(ϵ , λ)_{max}: (96.5, 553), (90.9, 410).

(ϵ , λ)_{min}: (22.4, 468), (5.3, 355).

($\Delta\epsilon$, λ)_{ex}: (+1.23, 595), (-1.65, 522).

Two violet bands were left on the original column. They were later isolated and investigated.

3. Di- μ -hydroxobis[*N,N'*-bis(2-pyridylmethyl)-1,2-propanediamine]chromium(III) perchlorate, [bispicpn]Cr(OH)₂Cr{bispicpn}(ClO₄)₄·4H₂O, three isomers. When the optically active amine was replaced by racemic amine, bispicpn, in the synthesis described above, we obtained three different red bands on the Sephadex column. The first band, called 11, was very weak. The next band, called 12, was of considerable size, and the last band, called 22, was the largest. From the bands three red compounds were isolated as perchlorates as described above.

Band 11: The yield of this compound was normally less than 1%. Therefore the eluates from several syntheses were collected and treated at one time.

Anal. [Cr(C₁₅H₂₀N₄)(OH)]₂(ClO₄)₄·4H₂O: Cr

(ϵ , λ)_{max}: (222, 533), (147, 384).

(ϵ , λ)_{min}: (35.2, 436.5), (81.1, 350.5).

As the absorption spectrum of the compound is identical with that of the compound from band 1, this compound must be the corresponding racemate.

Band 12: The yield was normally about 290 mg (21%). In a single experiment it was 30%.

Anal. [Cr(C₁₅H₂₀N₄)(OH)]₂(ClO₄)₄·4H₂O: Cr, C, N, H, Cl.

Sometimes the compound crystallized with 3 mol of crystal water.

(ϵ , λ)_{max}: (198, 532), (149, 384).

(ϵ , λ)_{min}: (34.1, 431), (77.8, 350).

When the chloride salt was left for 14 days in a

stoppered flask with conc. hydrochloric acid, large blue-violet crystals separated. They were identified by their absorption spectrum as one of the two possible *cis-α*-dichloro complexes, *cis-α*₂-[Cr{bispicpn}Cl₂]Cl·3H₂O.⁴¹

(ϵ , λ)_{max}: (95.6, 553), (91.1, 409).

(ϵ , λ)_{min}: (22.3, 468), (7.1, 356).

To the filtrate from these crystals were added ethanol and ether. The precipitated chloride salt was converted to an iodide by redissolution in water and precipitation by the addition of sodium iodide. The lavender-coloured compound was identified by its absorption spectrum as the second of the two possible *cis-α*-dichloro complexes, *cis-α*₁-[Cr{bispicpn}Cl₂]I.⁴¹

(ϵ , λ)_{max}: (102, 543), (101, 407).

(ϵ , λ)_{min}: (27.4, 463), (23.9, 353).

The resolution of this racemic dinuclear compound into its catoptromers was performed and will be published later.

Band 22. The yields varied from 490 mg to 602 mg (35%–43%). Anal. [Cr(C₁₅H₂₀N₄)(OH)]₂(ClO₄)₄·4H₂O: Cr, C, N, H, Cl. Sometimes the compound crystallized with 3 mol of crystal water.

(ϵ , λ)_{max}: (172, 529), (147, 386).

(ϵ , λ)_{min}: (33.7, 439), (74.0, 350).

The absorption spectrum of the compound is identical with that of the compound isolated from band 2. Add to this that a resolution of the iodide salt following the same method as described for the resolution of [bispicpn]Cr(OH)₂Cr{bispicpn}I₄¹⁷ gave (-)_D-[bispicpn]Cr(OH)₂Cr{bispicpn}I₂(SbOtar)₂·9H₂O with the following data:

(ϵ , λ)_{max}: (172, 529), (150, 386).

(ϵ , λ)_{min}: (36.2, 440), (79.2, 350).

($\Delta\epsilon$, λ)_{ex}: (-5.84, 521), (+1.45, 380).

Therefore the compound must be the racemate corresponding to the compound from band 2. When the perchlorate was left for one week in a stoppered flask with conc. hydrochloric acid, blue-violet crystals appeared. They were identified by the absorption spectrum as one of the *cis-α*-dichloro complexes,

*cis-α*₂-[Cr{bispicpn}Cl₂]ClO₄.⁴¹

(ϵ , λ)_{max}: (95.5, 553), (89.7, 409).

(ϵ , λ)_{min}: (24.7, 468), (9.8, 356).

Two violet bands were left on the original column. They were later isolated and investigated.

RESULTS AND DISCUSSION

Synthesis and resolution. We have earlier discovered,^{14,17,21} that binuclear hydroxobridged chromium(III) complexes with pyridyl substituted ligands could be obtained by the reaction of

chromium(III) bromide hexahydrate and the amine in question in the presence of zinc dust or chromium(II). In the present case the method worked equally well, and we got two optically active diols with bispic(-pn), the corresponding two *racemic* diols with bispicpn and an extra *racemic* diol with bispicpn. The separation of the isomers was accomplished by column chromatography. Two of the *racemic* compounds (bands 12 and 22) were resolved with sodium antimonyl (+)_D-tartrate as a resolving agent. In both cases the (-)_D-isomer formed the less soluble diastereoisomer. The yields of the third *racemic* compound (band 11) were too small to allow a resolution.

The compounds mentioned above all had the same red colour. We could also isolate blue-violet compounds. The results from their investigation will be published later.

While heating at 140 °C for 1 h of solid aquahydroxo monool and solid *racemic* diol with 1,2-ethanediamine resulted in conversion to *meso* diol of 95 and 20 % respectively,³⁵ similar reactions did not seem to take place in our case, as absorption as well as circular dichroism spectra remained unchanged after the compounds had undergone the same treatment.

Stereochemistry of the compounds. In a previous work on *cis*-dichloro complexes of chromium(III) with *N,N'*-bis(2-pyridylmethyl)-1,2-propanediamine, bispic(-pn),⁴¹ we have isolated and investigated the two possible *cis-α*-isomers, Δ -*cis-α*-[Cr{bispic(-pn)}Cl₂]⁺, { $\Delta(\alpha)(R)$ } and Λ -*cis-α*-[Cr{bispic(-pn)}Cl₂]⁺, { $\Lambda(\alpha)(R)$ }, Figs. 2a and 2b. (R=bispic(-pn)). The structure of one of the compounds has later been confirmed by an

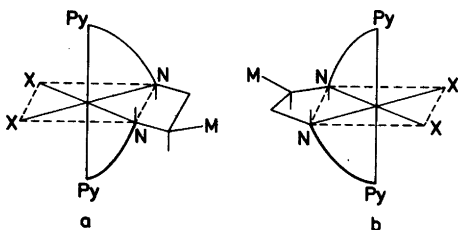


Fig. 2.

a, Δ -*cis-α*-[Cr{bispic((-pn)}Cl₂]⁺, { $\Delta(\alpha)(R)$ }.
b, Λ -*cis-α*-[Cr{bispic(-pn)}Cl₂]⁺, { $\Lambda(\alpha)(R)$ }.
Bispic(-pn) = *N,N'*-bis(2-pyridylmethyl)-1,2(R)-propanediamine. Py symbolizes the pyridine nitrogen, M the methyl group and X the chloride.

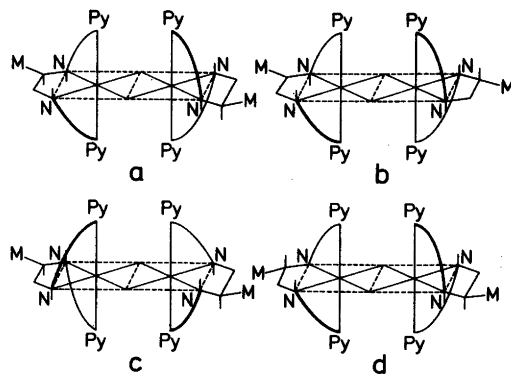


Fig. 3. Some of the different isomers of $[\{\text{bispic}(-\text{pn})\}\text{Cr}(\text{OH})_2\text{Cr}\{\text{bispic}(-\text{pn})\}]^{4+}$
a, $\{\Lambda(\alpha)(R)\Lambda(\alpha)(R)\}$. b, $\{\Lambda(\alpha)(R)\Lambda(\alpha)(R)\}$.
c, $\{\Delta(\alpha)(R)\Delta(\alpha)(R)\}$. d, $\{\Lambda(\alpha)(R)\Lambda(\alpha)(S)\}$.

X-ray structure analysis carried out by Hata *et al.*⁴²

When the diol prepared from bispic(-pn) and isolated from band 1 was decomposed by conc. hydrochloric acid, Λ -*cis-α*-[Cr{bispic(-pn)}Cl₂]⁺ was formed. On the assumption that the acid cleavage reaction proceeds with the retention of configuration, the diol in question, (+)_D-[{\text{bispic}(-\text{pn})\}\text{Cr}(\text{OH})_2\text{Cr}\{\text{bispic}(-\text{pn})\}]^{4+}, therefore has one of the structures { $\Lambda(\alpha)(R)\Lambda(\alpha)(R)$ } that are illustrated in Figs. 3a and 3b (methyl group isomers). The diol isolated from band 11 constituted the corresponding *racemic* compound, { $\Lambda(\alpha)(R)\Lambda(\alpha)(R)$, $\Delta(\alpha)(S)\Delta(\alpha)(S)$ }.

Similarly the optically active diol isolated from band 2, (-)_D-[{\text{bispic}(-\text{pn})\}\text{Cr}(\text{OH})_2\text{Cr}\{\text{bispic}(-\text{pn})\}]^{4+}, was decomposed to Δ -*cis-α*-[Cr{bispic(-pn)}Cl₂]⁺. One of the methyl group isomers of the structure { $\Delta(\alpha)(R)\Delta(\alpha)(R)$ } is pictured in Fig. 3c. From band 22 the corresponding *racemic* compound { $\Delta(\alpha)(R)\Delta(\alpha)(R)$, $\Lambda(\alpha)(S)\Lambda(\alpha)(S)$ } was isolated.

The diol that was isolated from band 12 decomposed when treated with conc. hydrochloric acid to both possible *racemic cis-α*-dichloro complexes, { $\Lambda(\alpha)(R)$, $\Delta(\alpha)(S)$ } and { $\Lambda(\alpha)(S)$, $\Delta(\alpha)(R)$ }. These *cis-α*-skeletons may be combined to form two different types of resolvable diols, namely { $\Lambda(\alpha)(R)\Lambda(\alpha)(S)$, $\Delta(\alpha)(R)\Delta(\alpha)(S)$ } and { $\Lambda(\alpha)(R)\Delta(\alpha)(R)$, $\Lambda(\alpha)(S)\Delta(\alpha)(S)$ }. Among these possibilities, the first one, Fig. 3d (the methyl group is omitted) is

the most probable because the above-mentioned diol had many properties in common with the two other diols of the similar structure, and because we did not get a third red compound (of the structure $\{\Lambda(\alpha)(R)\Delta(\alpha)(R)\}$) from the synthesis with bispic(-pn).

Electronic spectra. The absorption spectra of the three different racemic compounds dissolved in different media are presented in Figs. 4–8 and in Tables 1–3.

We presume that the spectra of the compounds dissolved in 0.1 M hydrochloric acid represent the spectra of di- μ -hydroxobis[$\{N,N'$ -bis-(2-pyridylmethyl)-1,2-propanediamine}chromium-(III) ions (diols). The absorption spectra in the vis. region, Figs. 4–6, Table 1, are slightly different from the corresponding spectra of the diols with 2-pyridyl-methylamine¹⁴ and 1-(2-pyridyl)ethylamine,¹⁷ the intensities of the second bands being 16–17 % higher, and the positions of both bands being shifted 6–10 nm. The spectra of the compounds dissolved in water

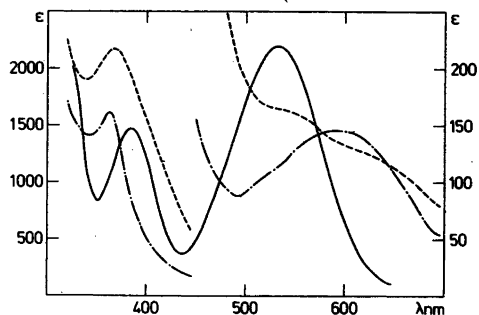


Fig. 4. The absorption spectra of $[\{\text{bispicpn}\}\text{Cr}(\text{OH})_2\text{Cr}\{\text{bispicpn}\}]^{4+}$, bands 1 and 11 in 0.1 M HCl (di- μ -hydroxo), (—), in 0.01 M NaOH+1 M NaCl (μ -hydroxo- μ -oxo), (---) and in 4 M NaOH (di- μ -oxo), (- - -). Vis. region.

and in 0.1 M hydrochloric acid are identical. When 4 M hydrochloric acid is used as a solvent, the only noticeable change is a shifting of the first

Table 1. Electronic spectral parameters for di- μ -hydroxocomplexes of chromium(III) with N,N' -bis(2-pyridylmethyl)-1,2-propanediamine (bispicpn) and N,N' -bis(2-pyridylmethyl)-1,2(R)-(propanediamine (bispic(-pn)) in 0.1 M HCl. Region 700–300 nm.

Ligand A	Ion, presumed to be dominant: [ACr(OH) ₂ CrA] ⁴⁺	(ϵ , λ) _{max}
bispicpn bispic(-pn)	band 11. $\Delta S \Delta S, ARAR$ band 1. $ARAR$	(222, 533), (147, 384)
bispicpn	band 12. $\Delta S \Delta R, ARAS$	(198, 532), (149, 384)
bispicpn bispic(-pn)	band 22. $\Delta R \Delta R, ASAS$ band 2. $\Delta R \Delta R$	(172, 529), (147, 386)

Table 2. Electronic spectral parameters for di- μ -hydroxocomplexes of chromium(III) with N,N' -bis(2-pyridylmethyl)-1,2-propanediamine (bispicpn) and N,N' -bis(2-pyridylmethyl)-1,2(R)-(propanediamine (bispic(-pn)) in 0.01 M NaOH, 1 M NaCl. Region 700–300 nm.

Ligand A	Ion, presumed to be dominant: [ACr(OH)(O)CrA] ³⁺	(ϵ , λ) _{max}
bispicpn bispic(-pn)	band 11. $\Delta S \Delta S, ARAR$ band 1. $ARAR$	(145, 590), (1618, 363)
bispicpn	band 12. $\Delta S \Delta R, ARAS$	(130, 590), (1553, 365)
bispicpn bispic(-pn)	band 22. $\Delta R \Delta R, ASAS$ band 2. $\Delta R \Delta R$	(113, 585), (1397, 365)

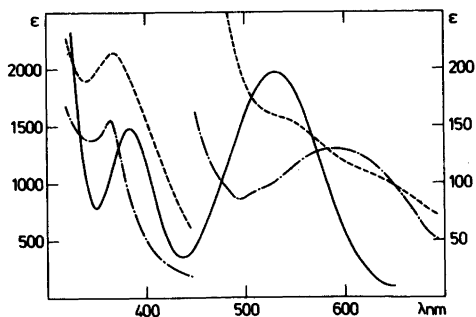


Fig. 5. The absorption spectra of $[\{\text{bispicpn}\}\text{Cr}(\text{OH})_2\text{Cr}\{\text{bispicpn}\}]^{4+}$, band 12 in 0.1 M HCl (di- μ -hydroxo), (—), in 0.01 M NaOH+1 M NaCl (μ -hydroxo- μ -oxo), (- - -) and in 4 M NaOH (di- μ -oxo), (- · -). Vis. region.

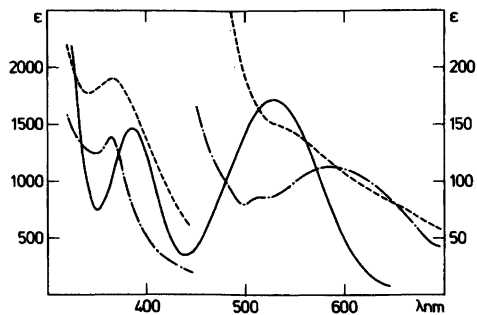


Fig. 6. The absorption spectra of $[\{\text{bispicpn}\}\text{Cr}(\text{OH})_2\text{Cr}\{\text{bispicpn}\}]^{4+}$, bands 2 and 22 in 0.1 M HCl (di- μ -hydroxo), (—), in 0.01 M NaOH+1 M NaCl (μ -hydroxo- μ -oxo), (- - -) and in 4 M NaOH (di- μ -oxo), (- · -). Vis. region.

band on 1.5 nm. If the compounds therefore, contrary to all expectations, should be aquahydroxo monools, then the corresponding diaqua monools must be remarkably strong acids. In the case of diols of 1,2-ethanediamine the spectrum changed with time due to the rapid equilibrium between the diol and the aquahydroxo monool.³⁵ We did not recognize similar changes of the spectra within reasonable time (8 h).

Based on rough and preliminary determinations of the acidity constants for the diols, we also presume, that each of the bluish solutions of the diols in 0.01 M sodium hydroxide +1 M sodium chloride contains one species only, namely a μ -hydroxo- μ -oxobis[$\{N,N'$ -bis(2-pyridylmethyl)-1,2-propanediamine}chromium(III)] ion. The spectra, Figs. 4-6 and Table 2, did not change within 8 h, and they are utterly different from the spectrum of the dihydroxo monool of chro-

mium(III) with 1,2-ethanediamine³⁵ but resemble the spectrum of the μ -hydroxo- μ -oxo bis[$\{1$ -(2-pyridyl)ethylamine}chromium(III)] ion.³⁰

To obtain the spectra of the di- μ -oxobis[$\{N,N'$ -bis(2-pyridylmethyl)-1,2-propanediamine}chromium(III)] ions we dissolved the complexes in 4 M sodium hydroxide. These solutions are yellow, just as the compounds of the formula $[\text{Cr}\{\text{bispicpn}\}\text{O}]_2(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ which we can isolate from them. The first absorption bands, Figs. 4-6 and Table 3, show a splitting appearing as two shoulders. The bands at approx. 365 nm have the same high intensities as we observed in the case of the corresponding μ -hydroxo- μ -oxo complexes.

In Fig. 7 the spectra of the three different complexes are united to illustrate the systematic variation that manifested already in the different rates of migration on the column.

Table 3. Electronic spectral parameters for di- μ -hydroxocomplexes of chromium(III) with N,N' -bis(2-pyridylmethyl)-1,2-propanediamine (bispicpn) and N,N' -bis(2-pyridylmethyl)-1,2(R)-propanediamine (bispic(-pn)) in 4 M NaOH. Region 700-300 nm.

Ligand A	Ion, presumed to be dominant: $[\text{ACr}(\text{O})_2\text{CrA}]^{2+}$	$(\epsilon, \lambda)_{\text{max}}$
bispicpn bispic(-pn)	band 11. $\Delta\text{SAS}, \Delta\text{RAR}$ band 1. ARAR	$(129, 610)_{\text{sh}}, (164, 535)_{\text{sh}}, (2164, 365)$
bispicpn	band 12. $\Delta\text{SAR}, \text{ARAS}$	$(114, 610)_{\text{sh}}, (158, 535)_{\text{sh}}, (2154, 367)$
bispicpn bispic(-pn)	band 22. $\Delta\text{RAR}, \text{ASAS}$ band 2. ΔRAR	$(96, 615)_{\text{sh}}, (149, 535)_{\text{sh}}, (1906, 365)$

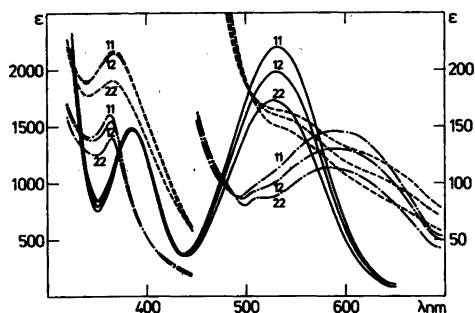


Fig. 7. The united spectra of the compounds isolated from bands 11, 12 and 22 illustrate the systematic variation in the spectroscopic properties.

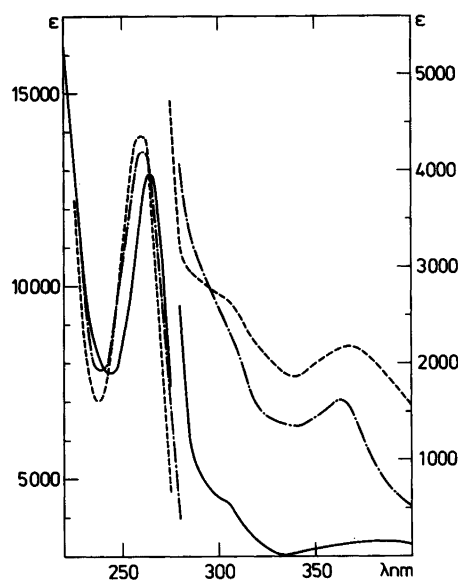


Fig. 8. The absorption spectra of $[\{\text{bispicpn}\}\text{Cr}(\text{OH})_2\text{Cr}\{\text{bispicpn}\}]^{4+}$, band 1 in 0.1 M HCl (di- μ -hydroxo), (—), in 0.01 M NaOH+1 M NaCl (μ -hydroxo- μ -oxo), (---) and in 4 M NaOH (di- μ -oxo), (- - -). UV region.

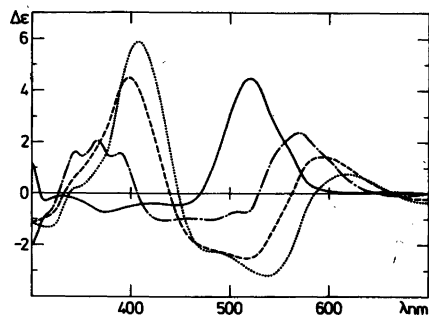


Fig. 9. The circular dichroism spectra of $\Lambda\Lambda$ - $(+)\text{D}$ - $[\{\text{bispic}(-\text{pn})\}\text{Cr}(\text{OH})_2\text{Cr}\{\text{bispic}(-\text{pn})\}]^{4+}$, band 1, in 0.1 M HCl (di- μ -hydroxo), (—), in 0.01 M NaOH+1 M NaCl (μ -hydroxo- μ -oxo), (---), in 4 M NaOH (di- μ -oxo), (- - -) and in LiOMe-ethanol (di- μ -oxo), (...). Vis. region.

The spectra in the UV region are presented by the spectra of one of the complexes, Fig. 8, as they are very similar with a relatively sharp ligand band at 260 nm and a shoulder at about 300 nm.

Circular dichroism spectra. The interesting circular dichroism spectra of the two different optically active compounds dissolved in the same different media as used for the absorption spectra are presented in Figs. 9–12 and in Tables 4–7.

The spectra in 0.1 M hydrochloric acid in the vis. region, Figs. 9–10 and Table 4, resemble those of the corresponding diols with 2-pyridylmethylamine¹⁴ and 1-(2-pyridyl)ethylamine,¹⁷ although some small differences can be noticed, for instance regarding the position of the first dominant band and the shape of the second. As mentioned above, the diol isolated from band 1, Fig. 9, has the structure $\{\Lambda(\alpha)(R)\Lambda(\alpha)(R)\}$ and the diol isolated from band 2, Fig. 10, the structure $\{\Delta(\alpha)(R)\Delta(\alpha)(R)\}$. This agrees with the empirical rule that relates the sign of the dominant CD-band in the region of the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ $d-d$ absorption of the chromium(III) ion to the

Table 4. CD-spectral parameters for di- μ -hydroxocomplexes of chromium(III) with N,N' -bis(2-pyridylmethyl)-1,2(R)-propanediamine (bispic(-pn)) in 0.1 M HCl. Region 700–300 nm.

Ligand	Ion, presumed to be dominant: $[\text{ACr}(\text{OH})_2\text{CrA}]^{4+}$	$(\Delta\epsilon, \lambda)_{\text{ex}}$
bispic(-pn)	band 1 $(+)\text{D}$ -ARAR	(+4.47, 521), (-0.73, 377)
bispic(-pn)	band 2 $(-)\text{D}$ - Δ RAR	(-5.86, 522), (+1.48, 381)

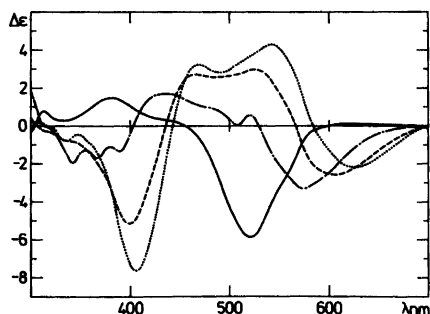


Fig. 10. The circular dichroism spectra of $\Delta\Delta(-)_D$ -[$\{\text{bispic}(-\text{pn})\}\text{Cr}(\text{OH})_2\text{Cr}\{\text{bispic}(-\text{pn})\}\}^{4+}$, band 2, in 0.1 M HCl (di- μ -hydroxo), (—), in 0.01 M NaOH+1 M NaCl (μ -hydroxo- μ -oxo), (---), in 4 M NaOH (---) and in LiOMe-ethanol (di- μ -oxo), (...). Vis. region.

configuration around the metal atom.⁴³ The application of this rule, however, becomes more dubious regarding the spectra of the strongly basic solutions.

The spectra of the μ -hydroxo- μ -oxo complexes in the vis. region, Figs. 9–10 and Table 5, are specially interesting because of their fine structure. Unfortunately we are still not able to utilize all the information they offer because of their complexity. They are characterized by a lot of common features which we recognize from the μ -oxo- μ -hydroxo complex with 1-(2-pyridyl)ethylamine.³⁰

The same resemblance is found between the spectra of the di- μ -oxo complexes, in the vis. region, Figs. 9–10 and Table 6, and the corresponding complex with 1-(2-pyridyl)ethylamine.³⁰ They are nearly identical in shape with the spectra of the compounds dissolved in lithium methoxide in ethanol, Figs. 9–10 and Table 7.

The less interesting circular dichroism spectra in the UV region are presented in Figs. 11 and 12.

Magnetic Properties. The average magnetic susceptibilities and effective moments as functions of temperature were determined for the two optically active compounds, band 1 and band 2,

Table 5. CD-spectral parameters for di- μ -hydroxocomplexes of chromium(III) with *N,N'*-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine (bispic(-pn)) in 0.01 M NaOH, 1 M NaCl. Region 700–300 nm.

Ligand A	Ion, presumed to be dominant: [ACr(OH)(O)CrA] ³⁺	($\Delta\epsilon$, λ) _{ex}
bispic(-pn)	band 1. (+) _D -ARAR	(-0.10, 681), (+2.36, 569), (-0.75, 517), (-1.06, 480) (-1.06, 432), (+1.55, 390), (+2.05, 368), (+1.61, 344).
bispic(-pn)	band 2. (-) _D - Δ R Δ R	(-3.22, 574), (+0.56, 520), (+1.05, 472) (+1.69, 439), (-1.33, 389), (-1.68, 367), (-1.95, 343).

Table 6. CD-spectral parameters for di- μ -hydroxocomplexes of chromium(III) with *N,N'*-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine (bispic(-pn)) in 4 M NaOH. Region 700–300 nm.

Ligand A	Ion, presumed to be dominant: [ACr(O) ₂ CrA] ²⁺	($\Delta\epsilon$, λ) _{ex}
bispic(-pn)	band 1 (+) _D -ARAR	(+1.42, 594), (-2.52, 519), (-2.24, 488), (+4.50, 399), (-0.92, 317)
bispic(-pn)	band 2 (-) _D - Δ R Δ R	(-2.61, 606), (+2.97, 524), (+2.69, 466), (-5.14, 399), (-0.80, 336).

Table 7. CD-spectral parameters for di- μ -hydroxocomplexes of chromium(III) with N,N' -bis(2-pyridylmethyl)-1,2(R)-propanediamine (bispic(-pn)) in LiOCH_3 , $\text{C}_2\text{H}_5\text{OH}$. Region 700–300 nm.

Ligand A	Ion, presumed to be dominant: [ACr(O) ₂ CrA] ²⁺	($\Delta\epsilon$, λ) _{ex}
bispic(-pn)	band 1 (+) _D - $\Lambda R \Lambda R$	(+0.77, 619), (-3.19, 539), (-2.26, 487), (+5.88, 407), (+0.25, 345), (-1.32, 315).
bispic(-pn)	band 2 (-) _D - $\Delta R \Delta R$	(-2.16, 630), (+4.32, 542), (+3.23, 470), (-7.64, 407), (-0.79, 335), (+0.24, 309).

and for the two abundant racemic compounds, band 12 and band 22. As an example, the results for band 12 are shown in Fig. 13. The susceptibility data were fitted to the expression

$$\chi_A' = -(N/H) \frac{\sum_i \left(\frac{\partial E_i}{\partial H} \right) e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} \quad (1)$$

where E_i are the energies of the 16 components of the ground state manifold by minimization of

$$\sum_i (\chi_i^{\text{obs}} - \chi_A')^2 / \left\{ \sigma^2(\chi) + \left(\frac{\partial \chi}{\partial T} \right)^2 \sigma^2(T) \right\} \quad (2)$$

The estimated standard deviations $\sigma(\chi)$ and $\sigma(T)$ are reported elsewhere.²² The fitting was accomplished by application of three different models for the exchange Hamiltonian. Model 1 assumed the simple Heisenberg Hamiltonian

$$\mathcal{H} = \vec{S}_1 \cdot \vec{S}_2 \quad (3)$$

Model 2 included a biquadratic exchange term according to

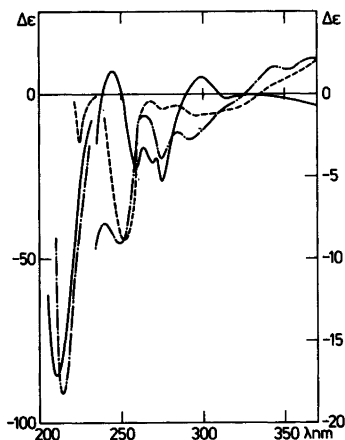


Fig. 11. The circular dichroism spectra of $\Lambda\Lambda$ -(+)_D-[$\{\text{bispic}(-\text{pn})\}\text{Cr}(\text{OH})_2\text{-Cr}\{\text{bispic}(-\text{pn})\}\}^{4+}$, band 1, in 0.1 M HCl (di- μ -hydroxo), (—), in 0.01 M NaOH+1 M NaCl (μ -hydroxo- μ -oxo), (---) and in 4 M NaOH (di- μ -oxo), (- - -). UV region.

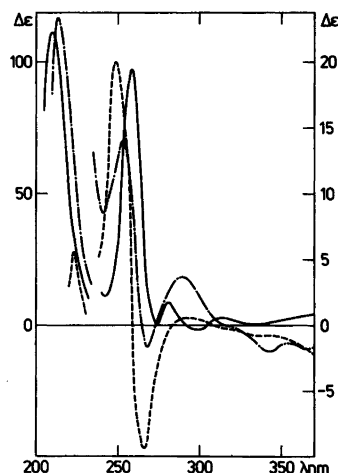


Fig. 12. The circular dichroism spectra of $\Lambda\Lambda$ -(-)_D-[$\{\text{bispic}(-\text{pn})\}\text{Cr}(\text{OH})_2\text{-Cr}\{\text{bispic}(-\text{pn})\}\}^{4+}$, band 2, in 0.1 M HCl (di- μ -hydroxo), (—), in 0.01 M NaOH+1 M NaCl (μ -hydroxo- μ -oxo), (---) and in 4 M NaOH (di- μ -oxo), (- - -). UV region.

Table 8. Parameters derived from magnetic susceptibility data for di- μ -hydroxo complexes of chromium(III) with N,N' -bis(2-pyridylmethyl)-1,2-propanediamine (bands 12 and 22) and N,N' -bis(2-pyridylmethyl)-1,2-(*R*)-propanediamine (bands 1 and 2).

	Band 1 ΔRAR		Band 12 $\Delta SAR, \Delta RAS$		Band 2 ΔRAR		Band 22 $\Delta RAR, \Delta SAS$	
	Model 1 ^a	Model 3	Model 1	Model 3	Model 1	Model 3	Model 1	Model 3
J (cm^{-1})	49.81(7)	-	44.44(6)	-	47.88(5)	-	44.79(7)	-
$E(1)$ (cm^{-1})	49.81(7) ^b	49.20(3)	44.44(6) ^b	43.75(2)	47.88(5) ^b	47.50(2)	44.79(7) ^b	43.92(5)
$E(2)$ (cm^{-1})	149.4(2) ^b	137.7(1)	133.3(2) ^b	126.7(1)	143.6(2) ^b	136.2(1)	134.4(2) ^b	125.0(3)
$E(3)$ (cm^{-1})	298.9(4) ^b	263.4(4)	266.6(4) ^b	237.4(4)	287.3(4) ^b	261.6(2)	268.7(4) ^b	234.5(8)
g	2.002(5)	1.979(3)	2.008(5)	1.981(3)	2.021(3)	1.983(1)	2.009(6)	1.981(5)
% monomer	0.033(1)	0.005(6)	0.030(1)	0.007(6)	0.015(1)	0.006(1)	0.029(1)	-0.0009(9) ^c
var/f^d	19.1	0.83	14.0	1.04	17.5	0.47	16.8	1.86
f	426	424	395	393	453	451	366	364

^a See text for description of the models. ^b Calculated from the derived J values. ^c A negative value of this parameter is, of course, a pure artifact of our fitting procedure. Note that the value is only one standard deviation away from zero. ^d Variance per degree of freedom.

$$\mathcal{H} = \mathcal{S}_1 \cdot \mathcal{S}_2 + j(\mathcal{S}_1 \cdot \mathcal{S}_2)^2 \quad (4)$$

Finally, model 3 assumed independent energies of the triplet, quintet and septet states; and it merely assumed, as do the earlier models, absence of any zero-field splitting within these levels and an isotropic Zeeman effect. Further details of the fitting procedure can be found elsewhere.²¹

Some of the results of the data fittings are displayed in Table 8 and an example of one set of measurements is shown in Fig. 13. It is obvious that within the estimated experimental uncertainties the data are not sufficiently well described by the simple Heisenberg Hamiltonian (model 1). Inclusion of the biquadratic exchange term (model 2) markedly improves the fits, lowering the variance per degree of freedom (var/f) from approx. 20 to approx. 3. Moreover, inclusion of the additional variable in model 3 in most cases leads to a further small but significant improvement, var/f being reduced to approx 1. In no case, however, did the calculated triplet energy change by more than 0.6 cm^{-1} by going from model 1 to model 2 and no more than 0.1 cm^{-1} by going from model 2 to model 3. As a common feature, it was found that within models 2 and 3 the septet energy was estimated to be approx. 30 cm^{-1} lower in energy than within model 1.

It is apparent from all these models that all four of these five isomers described herein have singlet ground states with triplet states lying approx. 45 cm^{-1} higher in energy. These results should be compared with the singlet-triplet separations ranging from 32 to 37 cm^{-1} as found in a related series of di- μ -hydroxo complexes of 1-(2-pyridyl)-ethylamine²¹ one of which has been structurally characterized,²⁵ namely di- μ -hydroxobis[bis((*S*)-1-(2-pyridyl)ethylamine)-chromium(III)] dithionate dihydrate. Since this compound has the hydrogens of the μ -hydroxo groups in the bridging plane, maximum exchange coupling for the given geometry of the bridging system is expected. The present series of complexes show even slightly larger coupling constants. It is, therefore, very unlikely that they should be aquahydroxo monools where only one superexchange path is possible which is expected to lead to smaller coupling constants. These arguments are based on the Glerup-Hodgson-Pedersen GHP model⁴⁴ for magnetic exchange in such systems. This model also predicts only small

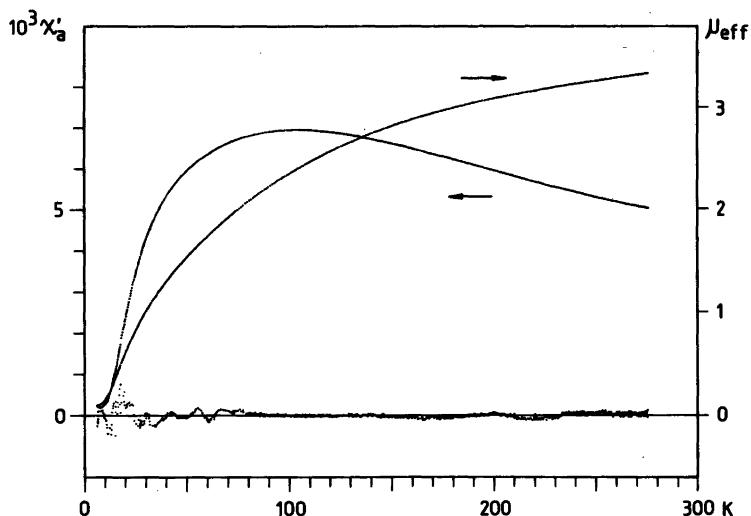


Fig. 13. Magnetic susceptibility (left scale in c.g.s. units) and effective magnetic moment (right scale in Bohr magnetons) of $\Delta\Delta(-)_D$ -[bis(pic(-pn))Cr(OH)₂Cr{bis(pic(-pn))}(ClO₄)₄·4 H₂O]. The lower set of points indicates $50 \times (\chi_{\text{obs}} - \chi_{\text{calc}})$, as obtained from fitting of the results to model 3, cf. Table 8.

differences between the geometries of the bridging systems in the aforementioned complex dithionate²⁵ and the present series. The verification of this conclusion must, however, await the results of ongoing X-ray structural investigations.

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