

## Synthesis and Characterization of the Dimeric Chromium(III) Complex Di- $\mu$ -hydroxobis[ $\{N,N'$ -bis(2-pyridylmethyl)-1,3-propanediamine}chromium(III)] Perchlorate, $[(\text{bispictn})\text{Cr}(\text{OH})_2](\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$

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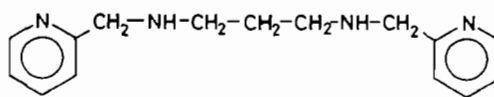
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The synthesis and spectroscopic properties of two isomers of the complex  $[(\text{bispictn})\text{Cr}(\text{OH})_2]^{4+}$ , where  $\text{bispictn} = N,N'$ -bis(2-pyridylmethyl)-1,3-propanediamine,  $\text{C}_{15}\text{H}_{20}\text{N}_4$ , are described. The crystal structure of the perchlorate salt trihydrate of the violet isomer has been determined from 3-dimensional counter X-ray data. The complex crystallizes in the monoclinic space group  $C2/c$  with eight dinuclear formula units in a cell of dimensions  $a = 38.323(11)$ ,  $b = 14.458(7)$ ,  $c = 17.027(7)$  Å,  $\beta = 106.24(3)^\circ$ . The structure has been refined to a final R-factor of 0.065 based on 3710 independent intensities. The crystals contain a racemic mixture, but in any given molecule the configurations at both chromium centers are the same ( $\Delta\Delta$  or  $\Lambda\Lambda$ ). Both ligands bind in the cis- $\beta$  form, the configurations at all four secondary nitrogen atoms being the same, so the complex is best described as a racemic mixture of the  $\{\Lambda(\beta)(RR')\Lambda(\beta)(RR')\}$  and  $\{\Delta(\beta)(SS')\Delta(\beta)(SS')\}$  isomers. The six-membered chelate rings form a chair conformation at one metal and a skew-boat at the other. The magnetic susceptibility of the complex indicates antiferromagnetic coupling between the chromium centers, the triplet state lying approximately  $32.5 \text{ cm}^{-1}$  higher in energy than the ground state singlet.

### Introduction

The spectroscopic, magnetic, and structural properties of dimeric chromium(III) complexes bridged by one or two hydroxo groups are being studied by several groups [1–16]. One of the reasons for this continued interest is the emergence of models which attempt to quantify the relationship between the isotropic magnetic exchange coupling constant,  $J$ , and the structure of the bridging unit for a variety of different dimeric systems [7, 8, 15, 17–22].

In some of our earlier publications [13, 16, 23–26] we have reported the synthesis and characterization of di- $\mu$ -hydroxochromium(III) complexes with a series of pyridyl-substituted bidentate and tetradentate ligands. We here introduce the first fully characterized dimeric complex of the ligand  $N,N'$ -bis(2-pyridylmethyl)-1,3-propanediamine,  $\text{bispictn}$  (I), which is one of the numerous possible isomers of



(I)

the complex cation di- $\mu$ -hydroxobis[ $\{N,N'$ -bis(2-pyridylmethyl)-1,3-propanediamine}chromium(III)],  $[(\text{bispictn})\text{Cr}(\text{OH})_2]^{4+}$ .

### Experimental

#### Reagents

Pyridine-2-carboxaldehyde was purchased from Merck-Schuchardt. 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 the H.C. Ørsted 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 ( $\epsilon$ ,  $\lambda$ ), where the molar

extinction coefficient  $\epsilon$  is in units of  $l \text{ mol}^{-1} \text{ cm}^{-1}$  and  $\lambda$  is in nm. The compounds were dissolved in 0.1 M hydrochloric acid. The magnetic susceptibilities of powdered samples were measured by the Faraday method in the temperature range 3.72–272 K at a field strength of 12,000 Oe. The magnetic field was calibrated with  $\text{Hg}[\text{Co}(\text{NCS})_4]$  [27]. A more detailed description of the equipment is published elsewhere [28, 29].

### Synthetic

#### *N,N'*-Bis(2-pyridylmethyl)-1,3-propanediamine, $\text{C}_{15}\text{H}_{20}\text{N}_4$ (abbrev. *bispictn*)

The ligand was prepared from pyridine-2-carboxaldehyde and 1,3-propanediamine following mainly the procedure of Goodwin and Lions [30]. The crude amine was purified via the hydrochloride as described for *N,N'*-bis-(2-pyridylmethyl)-1,2-ethanediamine [24]. The pure hydrochloride crystallizes with two mol of water.

#### Three oligomeric complexes of chromium(III) and *bispictn*

A crude product from which we isolated two different binuclear di- $\mu$ -hydroxo complexes and one tetranuclear complex was prepared using in principle the general method developed in our laboratories for the preparation of diols with pyridyl-substituted amine ligands [23–25].  $[\text{Cr}(\text{H}_2\text{O})_4\text{Br}_2]\text{Br}\cdot 2\text{H}_2\text{O}$  (2.00 g, 5.00 mmol) was dissolved in water (2 ml). A spatula of zinc dust and *bispictn* (1.2 ml, >5 mmol) were stirred in. A red precipitate immediately formed in the red solution. After 30 min the precipitate was redissolved by the addition of more water. The solution was filtered to remove excess zinc, diluted to 400 ml and transferred to a column of SP-Sephadex C-25 (1 = 10 cm, diam. ~4 cm). The compounds were eluted with a solution of sodium sulfate (24 g in 1 L). Three distinct bands presumed to contain oligomeric complexes appeared. The first band, called 1, had the same characteristic red colour as the red form of  $[\text{bispicrCr}(\text{OH})_2\text{Crbispicr}](\text{ClO}_4)_4\cdot 3\text{H}_2\text{O}$  [24]. The band passed through the column very quickly. A second small band, called 2, was violet with a brownish tint, perhaps not completely pure, and passed through the column rather slowly. The third band, called 3, was violet and was eluted from the original column with 4 M hydrochloric acid, when the other two bands had passed. The eluates were diluted four times with water and adsorbed on short columns, where sodium and sulfate 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. After cooling on ice, the solids were filtered and washed with ethanol. Recrystallizations from boiling water normally gave losses of about 30% to 40%.

**Band 1** Di- $\mu$ -hydroxobis[*N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine]chromium(III) perchlorate, red form,  $[(\text{C}_{15}\text{H}_{20}\text{N}_4)\text{Cr}(\text{OH})_2\text{Cr}(\text{C}_{15}\text{H}_{20}\text{N}_4)](\text{ClO}_4)_4\cdot 4\text{H}_2\text{O}$ . The yields varied from 0.36 g to 0.76 g (13%–27%). Found: Cr 9.44; C 32.27; N 9.97; H 4.28; Cl 12.80. Calc. for  $[\text{Cr}(\text{C}_{15}\text{H}_{20}\text{N}_4)(\text{OH})_2](\text{ClO}_4)_4\cdot 4\text{H}_2\text{O}$ : Cr 9.28; C 32.16; N 10.00; H 4.50; Cl 12.66. ( $\epsilon$ ,  $\lambda$ )<sub>max</sub>: (167, 535), (111, 383). ( $\epsilon$ ,  $\lambda$ )<sub>min</sub>: (27.8, 441), (56.1, 350.5).

**Band 2** The compound is presumed to be tris[di- $\mu$ -hydroxo[*N,N'*-bis-(2-pyridylmethyl)-1,3-propanediamine]chromium(III)]chromium(III) perchlorate,  $[\text{Cr}\{\text{Cr}(\text{C}_{15}\text{H}_{20}\text{N}_4)(\text{OH})_2\}_3](\text{ClO}_4)_6\cdot 4\text{H}_2\text{O}$ . The yields were very small, 0.13 g to 0.15 g (6%–7%). Found: Cr 12.04; C 30.92; N 9.68; H 4.62; Cl 12.19. Calc. for  $\text{Cr}_4\text{C}_{45}\text{H}_{66}\text{N}_{12}\text{O}_{30}\text{Cl}_6\cdot 4\text{H}_2\text{O}$ : Cr 11.90; C 30.92; N 9.62; H 4.27; Cl 12.17. ( $\epsilon$ ,  $\lambda$ )<sub>max</sub>: (259, 509), (210, 375). ( $\epsilon$ ,  $\lambda$ )<sub>min</sub>: (66.7, 431), (156, 347).

**Band 3** Di- $\mu$ -hydroxobis[*N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine]chromium(III) perchlorate, violet form,  $[(\text{C}_{15}\text{H}_{20}\text{N}_4)\text{Cr}(\text{OH})_2\text{Cr}(\text{C}_{15}\text{H}_{20}\text{N}_4)](\text{ClO}_4)_4\cdot 3\text{H}_2\text{O}$ . The yields varied from 0.38 g to 0.40 g (14%–15%). Found: Cr 9.46; C 32.61; N 10.14; H 4.23; Cl 12.94. Calc. for  $\text{Cr}_2\text{C}_{30}\text{H}_{42}\text{N}_8\text{O}_{18}\text{Cl}_4\cdot 3\text{H}_2\text{O}$ : Cr 9.43; C 32.68; N 10.16; H 4.39; Cl 12.86. ( $\epsilon$ ,  $\lambda$ )<sub>max</sub>: (197, 541), (147, 387). ( $\epsilon$ ,  $\lambda$ )<sub>min</sub>: (38.0, 444), (69.4, 351).

#### Conversion of the red diol (band 1) to the violet diol (band 3)

A solution of  $[\text{bispictnCr}(\text{OH})_2\text{Crbispictn}](\text{ClO}_4)_4\cdot 4\text{H}_2\text{O}$ , red form, (0.52 g, 0.46 mmol in 60 ml) was left in a stoppered flask for two months. Then the solution was diluted to 400 ml and transferred to a column of SP-Sephadex C-25 (1 ~ 10 cm, diam. ~4 cm). Elution with a solution of sodium sulfate (24 g in 1 l) gave three bands, a weak, orange band, presumably a monomeric diaqua complex, a red band containing the starting material, and a large, intense blue-violet band. A determination of the chromium content in the red eluate revealed that only 9–10% of the starting material was untransformed. After the elution of the first two bands, the blue-violet band was eluted with hydrochloric acid (4 M). The eluate was diluted 20 times with water and transferred to a new short column, where residual sodium and sulfate ions were eluted with hydrochloric acid (0.1 M). The complex was eluted afterwards with hydrochloric acid (4 M), and the chloride was precipitated from the ice-cooled solution by the

addition of ethanol and ether. Yield: 0.25 g (58%). The compound was identified by means of the absorption spectrum.

### Crystallographic Measurements

The data were collected and reduced in the standard manner [31] using an Enraf-Nonius diffractometer. The cell constants and data collection parameters are listed in Table I.

TABLE I. Crystallographic and Data Collection Parameters.

Formula: Cr <sub>2</sub> C <sub>30</sub> H <sub>48</sub> Cl <sub>4</sub> N <sub>8</sub> O <sub>21</sub>	$D_o = 1.58 \text{ g cm}^{-3}$
$a = 38.323(11) \text{ \AA}$	$Z = 8$
$b = 14.458(7) \text{ \AA}$	$D_c = 1.617 \text{ g cm}^{-3}$
$c = 17.027(7) \text{ \AA}$	Space group: C2/c
$\beta = 106.24(3)^\circ$	$\mu = 7.88 \text{ cm}^{-1}$
$V = 9057.7 \text{ \AA}^3$	Data range: $2^\circ < \theta < 25^\circ$
NO = 3710 [ $I > 3\sigma(I)$ ]	

The structure was solved by the heavy-atom method. The positions of the two independent chromium atoms were deduced from a three-dimensional Patterson function, and the remaining non-hydrogen atoms were located in subsequent difference Fourier maps. It was soon apparent that one of the four independent perchlorate anions occupied two special positions on the twofold axis, and moreover that in one of these two positions there was disorder around the twofold. The problem, therefore, involved 68 independent atomic positions. Consequently, we decided to conduct the least-squares refinement in two separable blocks, one containing the inner sphere at Cr(1) plus its associated ligands and some perchlorate groups and the other the inner sphere at Cr(2), its associated ligands and the remaining perchlorate and water atoms. The Cr<sub>2</sub>O<sub>2</sub> bridging unit was refined in both blocks. Hence, the number of variables in a block was 306, the number of data available being 3710. In the final least-squares cycles no parameter underwent a shift of more than  $0.55\sigma$ , which is taken as evidence of convergence. The final values of the conventional R-factors R<sub>1</sub> and R<sub>2</sub> were 0.066 and 0.065. Attempts to locate the hydrogen atoms were unsuccessful, and a final difference Fourier contained peaks of about  $0.5 \text{ e\AA}^{-3}$  in chemically meaningless locations.

The final atomic positional parameters are given in Table II, and listings of thermal parameters and observed and calculated structure amplitudes are available.

## Results and Discussion

### Stereochemistry of the Complexes

In a previous article [16] on dimeric complexes with the related ligand bispicen, we discussed the

TABLE II. Positional Parameters for [(bispicn)Cr(OH)]<sub>2</sub>·(ClO<sub>4</sub>)<sub>4</sub>·3H<sub>2</sub>O.

Atom	x	y	z
Cr(1)	0.8917(1)	0.3272(1)	0.3699(1)
Cr(2)	0.8637(1)	0.1432(1)	0.2883(1)
Cl(1)	0.8295(1)	-0.1604(2)	0.1268(2)
Cl(2)	0.7401(1)	0.0849(2)	0.9169(2)
Cl(3)	0.9296(1)	0.3871(2)	0.0436(3)
Cl(4)	0.0	0.1603(3)	0.25
Cl(5)	0.5	0.3096(3)	0.25
O(1)	0.8726(1)	0.2720(3)	0.2607(3)
O(2)	0.8882(1)	0.1961(3)	0.3961(3)
O(3)	0.8138(2)	-0.0903(5)	0.1602(5)
O(4)	0.8058(3)	-0.2199(7)	0.0798(7)
O(5)	0.8565(4)	-0.1941(8)	0.1793(7)
O(6)	0.8424(3)	-0.1167(9)	0.0671(7)
O(7)	0.7128(2)	0.0242(6)	0.8683(5)
O(8)	0.7695(2)	0.0315(5)	0.9649(5)
O(9)	0.7504(2)	0.1470(6)	0.8688(6)
O(10)	0.7230(2)	0.1315(6)	0.9699(5)
O(11)	0.9341(2)	0.2986(6)	0.0275(8)
O(12)	0.9522(3)	0.4432(7)	0.0125(8)
O(13)	0.8937(2)	0.4190(5)	0.0102(5)
O(14)	0.9396(5)	0.4026(12)	0.1178(9)
O(15)	-0.0322(2)	0.2163(5)	0.2372(5)
O(16)	-0.0012(3)	0.1133(8)	0.1744(8)
O(17)	0.5	0.2132(7)	0.25
O(18)	0.5346(12)	0.3391(22)	0.2694(37)
O(19)	0.5098(19)	0.3338(19)	0.1717(36)
O(20)	0.5245(20)	0.3513(31)	0.3098(48)
OW(1)	0.5927(2)	0.4049(5)	0.4706(4)
OW(2)	0.8551(2)	0.3783(6)	0.1312(5)
OW(3)	0.5243(3)	0.4681(9)	0.4431(7)
N(1)A	0.8992(2)	0.4592(5)	0.3275(4)
N(2)A	0.9459(2)	0.3157(5)	0.3689(4)
C(2)A	0.9319(3)	0.4764(7)	0.3170(5)
C(3)A	0.9411(3)	0.5580(8)	0.2884(7)
C(4)A	0.9152(4)	0.6267(8)	0.2705(7)
C(5)A	0.8820(4)	0.6119(7)	0.2788(7)
C(6)A	0.8743(3)	0.5268(7)	0.3089(6)
C(7)A	0.9591(3)	0.4005(8)	0.3383(7)
C(8)A	0.9719(3)	0.2775(7)	0.4434(7)
C(9)A	0.9733(3)	0.3348(8)	0.5196(7)
N(1)B	0.8412(2)	0.3634(4)	0.3840(5)
N(2)B	0.9069(2)	0.3692(4)	0.4901(4)
C(2)B	0.8410(3)	0.3783(5)	0.4614(6)
C(3)B	0.8103(3)	0.4055(7)	0.4781(6)
C(4)B	0.7791(3)	0.4171(7)	0.4176(9)
C(5)B	0.7789(3)	0.4031(6)	0.3367(7)
C(6)B	0.8101(3)	0.3759(6)	0.3217(5)
C(7)B	0.8758(3)	0.3591(6)	0.5245(5)
C(8)B	0.9397(3)	0.3298(7)	0.5496(6)
N(1)C	0.8640(2)	0.0067(4)	0.3334(4)
N(2)C	0.9115(2)	0.0905(4)	0.2694(4)
C(2)C	0.8966(3)	-0.0336(6)	0.3502(5)
C(3)C	0.9014(3)	-0.1235(8)	0.3839(6)
C(4)C	0.8726(3)	-0.1705(7)	0.3996(6)
C(5)C	0.8397(3)	-0.1291(7)	0.3806(6)
C(6)C	0.8361(3)	-0.0405(6)	0.3476(5)
C(7)C	0.9270(2)	0.0241(6)	0.3373(5)

(continued overleaf)

TABLE II (continued)

Atom	x	y	z
C(8)C	0.9068(2)	0.0447(6)	0.1874(6)
C(9)C	0.8895(3)	0.1130(7)	0.1191(5)
N(1)D	0.8120(2)	0.1614(4)	0.2983(5)
N(2)D	0.8339(2)	0.1113(4)	0.1692(4)
C(2)D	0.7851(3)	0.1580(5)	0.2266(6)
C(3)D	0.7487(3)	0.1608(7)	0.2258(7)
C(4)D	0.7404(3)	0.1669(7)	0.2988(8)
C(5)D	0.7666(3)	0.1686(7)	0.3697(7)
C(6)D	0.8024(2)	0.1647(5)	0.3693(5)
C(7)D	0.7979(3)	0.1551(6)	0.1512(6)
C(8)D	0.8496(3)	0.1273(6)	0.0994(5)

different isomers which can occur among the monomeric *cis* diaqua complexes which may be regarded as the building blocks of our dinuclear species. There are three enantiomeric pairs, namely  $\Lambda$ -*cis*( $\alpha$ ){SS},  $\Lambda$ -*cis*( $\beta$ ){RR'}, and  $\Lambda$ -*cis*( $\beta$ ){SR'} and their  $\Delta$  enantiomers [32]. These *cis*-complexes could be combined to form three different dinuclear species containing two  $\alpha$ -skeletons and eight containing one  $\alpha$ - and one  $\beta$ -skeleton. We did not at that time discuss the possible  $\beta,\beta$  isomers since we had observed none of these. There are, however, twenty, because in addition to the configurational possibilities at each chromium atom [ $\Lambda$  or  $\Delta$ ] and at the two equatorial nitrogen atoms [R or S], we have the possibility of *cis* or *trans* forms because of the asymmetry of the ligand. This concept is demonstrated in Fig. 1, where we adopt the convention of naming the *cis*-isomer that one in which both axial pyridine groups are on the same side of the  $\text{Cr}_2\text{O}_2$  plane, and the *trans*-isomer the one in which the axial pyridine groups are on opposite sides. If we focus our attention on those complexes which have the same configuration at both metal centers, since we have seen no isomers containing one  $\Lambda$  and one  $\Delta$  skeleton, there are nine enantiomeric pairs, two of which [the red { $\Lambda(\alpha)$ (SS) $\Lambda(\alpha)$ (SS)} and the blue-violet { $\Lambda(\alpha)$ (SS) $\Lambda(\beta)$ (RR')}] we have isolated and characterized [16, 24]. In the case of bispictn, the number of possible isomers is the same; in both

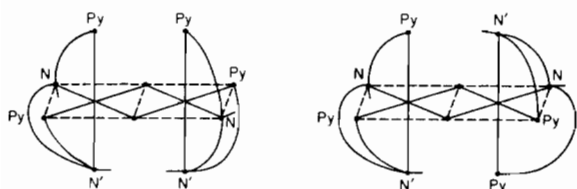


Fig. 1. Examples of a *cis* (left) and a *trans* (right) form of a  $\beta,\beta$  isomer. The secondary nitrogen atoms are labelled N and N', the latter being *cis* to both bridging atoms, while pyridine nitrogen atoms are labelled Py. The isomers shown here are (a) *cis*-{ $\Lambda(\beta)$ (RR') $\Lambda(\beta)$ (RR')} and (b) *trans*-{ $\Lambda(\beta)$ (RR') $\Lambda(\beta)$ (RR')}.

cases we neglect the conformational isomerism possible in the five-membered en ring ( $\delta$  or  $\lambda$ ) or the six-membered tn ring (chair or skew boat). In this case, we assume that the red complex which we reported above is the { $\Lambda(\alpha)$ (SS) $\Lambda(\alpha)$ (SS)} plus its enantiomer analogous to that seen in the red bispicen complex. As we shall demonstrate (*vide infra*), the violet complex is one of the  $\beta,\beta$  racemates.

#### Electronic Spectra

The absorption spectra of the two diols (vis. region) are shown in Fig. 2. The lower symmetry of the violet diol is manifested by the broader absorption band, the difference in the half-widths of the first bands being about  $400\text{ cm}^{-1}$ .

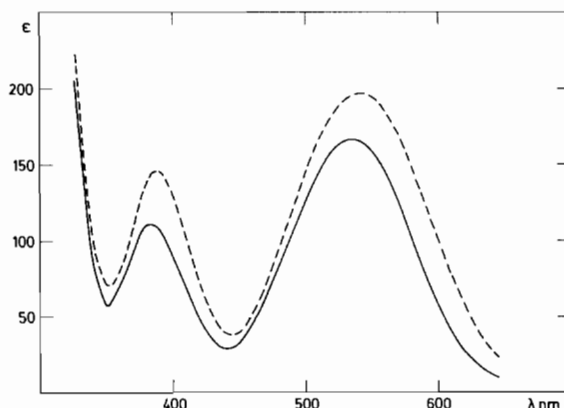


Fig. 2. The absorption spectra of [bispictnCr(OH)<sub>2</sub>Crbispictn]<sup>4+</sup>, red form, { $\Lambda(\alpha)$ (SS) $\Lambda(\alpha)$ (SS),  $\Delta(\alpha)$ (RR) $\Delta(\alpha)$ (RR)} (—) and of [bispictnCr(OH)<sub>2</sub>Crbispictn]<sup>4+</sup>, blue-violet form, { $\Lambda(\beta)$ (RR') $\Lambda(\beta)$ (RR'),  $\Delta(\beta)$ (SS') $\Delta(\beta)$ (SS')} (---) in 0.1 M HCl. Vis. region.

#### Description of the Structure

The structure consists of binuclear [(bispictn)Cr(OH)<sub>2</sub>]<sup>4+</sup> cations, perchlorate anions, and water molecules. The geometry of the cation is shown in Fig. 3, and the principal bond lengths and bond angles in the cation are presented in Tables III and IV.

The geometry at each chromium center is approximately octahedral, the ligating atoms being the four nitrogen atoms of the bispictn ligand and the oxygen atoms of the two bridging hydroxo moieties. The isomer isolated here is the  $\beta,\beta$  form, in which the pyridine nitrogen atoms are mutually *cis* at both chromium centers. It is noteworthy that in the related complex [(bispicen)Cr(OH)<sub>2</sub>]<sup>4+</sup> the isomer isolated under similar conditions was the  $\alpha,\beta$  isomer [16]. The configuration at the two metal centers is the same, being  $\Lambda\Lambda$  in the cation shown in Fig. 3, although in this centrosymmetric space group there is an equal number of  $\Delta\Delta$  isomers. The six-membered chelate rings have different conformations. The ring

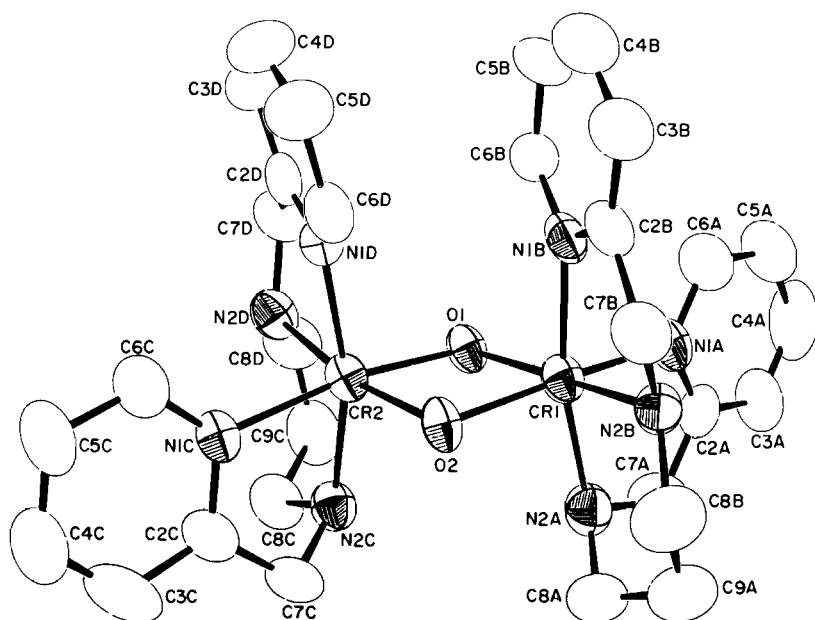


Fig. 3. View of the  $[(\text{bispictn})\text{Cr}(\text{OH})_2]^{4+}$  cation. The isomer shown here is the  $\text{cis}\{-\Lambda(\beta)(\text{RR}')\Lambda(\beta)(\text{RR}')\}$  form, but in this centrosymmetric space group there is an equal number of  $\text{cis}\{-\Delta(\beta)(\text{SS}')\Delta(\beta)(\text{SS}')\}$  isomers. Hydrogen atoms are omitted for clarity.

TABLE III. Internuclear Distances (Å) in  $[(\text{bispictn})\text{Cr}(\text{OH})_2]^{4+}$ .

Atoms	Distance	Atoms	Distance
Cr(1)–O(1)	1.966(5)	Cr(2)–O(1)	1.973(5)
Cr(1)–O(2)	1.962(5)	Cr(2)–O(2)	1.967(5)
Cr(1)–N(1)A	2.088(7)	Cr(2)–N(1)C	2.116(6)
Cr(1)–N(2)A	2.090(7)	Cr(2)–N(2)C	2.089(6)
Cr(1)–N(1)B	2.084(7)	Cr(2)–N(1)D	2.053(6)
Cr(1)–N(2)B	2.058(7)	Cr(2)–N(2)D	2.082(6)
N(1)A–C(2)A	1.336(10)	N(1)C–C(2)C	1.336(9)
C(2)A–C(3)A	1.361(12)	C(2)C–C(3)C	1.412(12)
C(3)A–C(4)A	1.378(15)	C(3)C–C(4)C	1.385(13)
C(4)A–C(5)A	1.339(14)	C(4)C–C(5)C	1.352(12)
C(5)A–C(6)A	1.396(13)	C(5)C–C(6)C	1.390(11)
C(6)A–N(1)A	1.342(11)	C(6)C–N(1)C	1.347(10)
C(2)A–C(7)A	1.487(12)	C(2)C–C(7)C	1.498(11)
C(7)A–N(2)A	1.476(11)	C(7)C–N(2)C	1.492(10)
N(2)A–C(8)A	1.484(11)	N(2)C–C(8)C	1.510(10)
C(8)A–C(9)A	1.528(13)	C(8)C–C(9)C	1.529(12)
C(9)A–C(8)B	1.511(13)	C(9)C–C(8)D	1.487(12)
N(1)B–C(2)B	1.338(10)	N(1)D–C(2)D	1.359(10)
C(2)B–C(3)B	1.344(12)	C(2)D–C(3)D	1.390(12)
C(3)B–C(4)B	1.350(13)	C(3)D–C(4)D	1.371(13)
C(4)B–C(5)B	1.390(13)	C(4)D–C(5)D	1.339(12)
C(5)B–C(6)B	1.351(12)	C(5)D–C(6)D	1.375(12)
C(6)B–N(1)B	1.365(10)	C(6)D–N(1)D	1.359(9)
C(2)B–C(7)B	1.488(11)	C(2)D–C(7)D	1.497(12)
C(7)B–N(2)B	1.474(10)	C(7)D–N(2)D	1.472(10)
N(2)B–C(8)B	1.489(11)	N(2)D–C(8)D	1.494(10)
Cr(1)–Cr(2)	3.054(2)		

at Cr(1), formed by Cr(1), N(2)A, C(8)A, C(9)A, C(8)B, N(2)B, adopts the classical chair conforma-

tion; thus, atoms N(2)A, C(8)A, C(8)B, N(2)B are roughly coplanar [maximum deviation 0.03 Å], while Cr(1) sits 0.78 Å above this plane and C(9)A lies 0.70 Å below it. The ring at Cr(2) is a skew boat, the conformation shown in Fig. 3 being  $\lambda$ .

The five-membered ring subtended by the A ring [*i.e.* Cr(1), N(1)A, C(2)A, C(7)A, N(2)A] is planar, with no atom deviating from the least-squares plane by more than 0.01 Å. The other five-membered rings are distinctly non-planar, however, and can all be viewed as envelope forms in which the four atoms Cr, N(1), C(2), C(7), are coplanar [maximum deviations 0.03 Å (B), 0.01 Å (C), 0.05 Å (D)] while atom N(2) lies out of the plane by 0.51 Å, 0.68 Å, and 0.49 Å in the B, C, and D rings, respectively.

The configuration at all secondary nitrogen atoms [N(2)A, N(2)B, N(2)C, N(2)D] is the same, being R [33] in the enantiomer shown in Fig. 3. The pyridine rings are *cis* (see Fig. 1), so the enantiomer depicted in Fig. 3 is the  $\text{cis}\{-\Lambda(\beta)(\text{RR}')\Lambda(\beta)(\text{RR}')\}$  form, and the crystals contain a racemic mixture of the isomer and its enantiomer  $\text{cis}\{-\Delta(\beta)(\text{SS}')\Delta(\beta)(\text{SS}')\}$ .

At Cr(1) the *trans* angles lie in the narrow range of 168.3(3)–170.9(2)°, while those at Cr(2) show a greater deviation of 165.3(2) to 169.5(2)°. The *cis* chelate bond angles fall, as anticipated, into two groups: the N(1)X–Cr–N(2)X [X = A, B, C, D] angles subtended at the metal by the five-membered rings all fall in the narrow range of 78.5(3) to 80.6(3)° with an average value of 79.8(9)°; the N(2)X–Cr–N(2)Y angles subtended by the six-membered rings formed by the triethylenediamine moieties are larger, at 91.4(3) and 92.0(3) or an average of 91.7(4)°. The non-chelate *cis* angles N(1)X–Cr–N(1)Y

TABLE IV. Principal Bond Angles (deg) in  $[\text{Cr}(\text{bispictn})\text{OH}]_2^{4+}$ .

O(1)–Cr(1)–O(2)	78.0(2)	O(1)–Cr(2)–O(2)	77.7(2)
O(1)–Cr(1)–N(1)A	95.5(2)	O(1)–Cr(2)–N(1)C	169.3(2)
O(1)–Cr(1)–N(2)A	93.9(2)	O(1)–Cr(2)–N(2)C	95.2(2)
O(1)–Cr(1)–N(1)B	95.7(3)	O(1)–Cr(2)–N(1)D	97.6(2)
O(1)–Cr(1)–N(2)B	170.9(2)	O(1)–Cr(2)–N(2)D	93.5(2)
O(2)–Cr(1)–N(1)A	170.7(3)	O(2)–Cr(2)–N(1)C	94.1(2)
O(2)–Cr(1)–N(2)A	93.2(3)	O(2)–Cr(2)–N(2)C	94.4(2)
O(2)–Cr(1)–N(1)B	95.2(2)	O(2)–Cr(2)–N(1)D	95.3(2)
O(2)–Cr(1)–N(2)B	94.4(2)	O(2)–Cr(2)–N(2)D	169.5(2)
N(1)A–Cr(1)–N(2)A	80.6(3)	N(1)C–Cr(2)–N(2)C	78.5(3)
N(1)A–Cr(1)–N(1)B	91.9(3)	N(1)C–Cr(2)–N(1)D	89.8(3)
N(1)A–Cr(1)–N(2)B	92.7(3)	N(1)C–Cr(2)–N(2)D	95.3(2)
N(2)A–Cr(1)–N(1)B	168.3(3)	N(2)C–Cr(2)–N(1)D	165.3(2)
N(2)A–Cr(1)–N(2)B	91.4(3)	N(2)C–Cr(2)–N(2)D	92.0(3)
N(1)B–Cr(1)–N(2)B	79.9(3)	N(1)D–Cr(2)–N(2)D	80.2(3)
Cr(1)–O(1)–Cr(2)	101.7(2)	Cr(1)–O(2)–Cr(2)	102.0(2)

and  $\text{N}(1)\text{X}–\text{Cr}–\text{N}(2)\text{Y}$  are in the range of 89.8(3) to 95.3(2)°.

The eight independent Cr–N distances are in the range 2.053(6) to 2.116(6) Å, there being no discernible systematic difference between distances involving pyridine nitrogen atoms  $[\text{N}(1)\text{X}]$  and those involving amine nitrogen atoms  $[\text{N}(2)\text{X}]$ . At Cr(1) the shortest bond is Cr(1)–N(2)B [2.058(7) Å] which is *trans* to a bridging hydroxo group; at Cr(2), however, the shortest bond [Cr(2)–N(1)D, 2.053(6) Å] is *trans* to an amine nitrogen atom. These Cr–N bond lengths are all within the ranges observed for related complexes [1, 2, 4–6, 13, 14, 16].

The bridging  $\text{Cr}_2\text{O}_2$  unit is not strictly planar, the chromium atoms lying 0.05 Å above the unweighted least-squares plane while the oxygen atoms lie 0.05 Å below it. Consequently, the dimer can be viewed as what Kahn and coworkers have called a ‘roof-shaped’ species [34, 35]; in the present complex the angle  $\delta$  defined as the dihedral angle between the planes Cr(1), O(1), O(2) and Cr(2), O(1), O(2) is 172.0°, which is not expected to have a significant impact on the magnetic properties of the complex [35]. The bridging Cr–O–Cr angles are 101.65(22)° and 102.03(23)°, with an average value of  $\phi = 101.8(3)$ °. The Cr(1)–Cr(2) separation is 3.054(2) Å and the O(1)–Cr–O(2) angles are 78.0(2) and 77.7(2)°. The bridging Cr–O distances are in the range 1.962(5)–1.973(5) Å with an average value of  $R = 1.967(5)$  Å. These values are within the ranges reported for other di- $\mu$ -hydroxo dimers of chromium(III). Since we were unable to locate the hydrogen atoms on the bridge, we are unable to calculate the dihedral angle  $\theta$ . While there is evidently extensive hydrogen bonding in the crystals, our inability to locate the hydrogen atoms in the structure renders any discussion unjustified.

The ordered perchlorates [one of which sits on a twofold axis] exhibit normal distorted tetrahedral

geometries, with Cl–O distances in the range 1.234(14) to 1.444(10) Å with an average of 1.376(66) Å. Similarly, the angles O–Cl–O range from 99.9(7) to 117.4(8)° with an average of 110(5)°. These ranges and averages are similar to those reported for other complexes, [16, 36–39]. The disordered perchlorate group, which also sits on a twofold axis, shows a range of Cl–O distances from 1.32(5) to 1.52(3) Å with angles ranging from 100(1) to 119(2)°.

#### Magnetic Properties

Plots of the temperature dependence of average magnetic susceptibility and the effective magnetic moment of a polycrystalline sample of  $[(\text{bispictn})\text{Cr}(\text{OH})]_2(\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$  are displayed in Fig. 4. The observed susceptibility data were fitted as described elsewhere [5, 10, 16] using three distinct models for

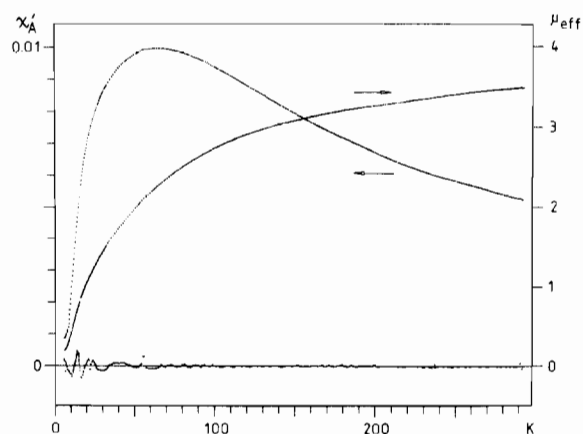


Fig. 4. Temperature variation of magnetic susceptibility per chromium (left scale, cgs units) and effective magnetic moment (right scale, Bohr magnetons) or  $[(\text{bispictn})\text{Cr}(\text{OH})]_2(\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$ . The lower, almost random distribution of dots around the abscissa represents  $(\chi_{\text{obs}} - \chi_{\text{calc}}) \times 50$ , where  $\chi_{\text{calc}}$  is based on Model 3 in Table V.

the exchange Hamiltonian. Model 1 is based on the simple Van Vleck Hamiltonian

$$H = JS_1 \cdot S_2 + g\mu_B M_S'$$

in which the only exchange variable is  $J$  and the triplet, quintet, and septet energies are simply  $J$ ,  $3J$ , and  $6J$ , respectively. In Model 2 the Hamiltonian was expanded to include a second-order term ('biquadratic exchange')

$$H = JS_1 \cdot S_2 - j(S_1 \cdot S_2)^2 + g\mu_B M_S'$$

which leads to energies of  $(J + 6.5j)$ ,  $(3J + 13.5j)$ , and  $(6J + 9.0j)$  for the triplet, quintet, and septet, respectively. Finally, in Model 3 we allow the energies of these three states to vary independently by writing the generalized Hamiltonian

$$H = E(S') + g\mu_B M_S'$$

where  $S'$  is the total spin of the state and  $E(S')$  is its energy [e.g.  $E(1)$  is the triplet state energy, *etc.*]. All models neglect zero field splitting and assume isotropic Zeeman effects. In addition to the one, two, or three exchange variables in models 1, 2 or 3, respectively, we refined the isotropic  $g$  value, a temperature-independent susceptibility term, and the percentage of monomeric impurity (assumed to obey the Curie Law) present in the sample. Thus, the number of variables in model  $N$  is given by  $(3 + N)$ .

The results of the fits using these three models are presented in Table V. It is apparent that the data fit all three models very well, although the improvements in the variance per degree of freedom ( $\text{var}/f$ ) on going from model 1 to model 2 and from model 2 to model 3 are all statistically significant. The best fit, obtained with model 3, gives values of  $g = 1.981(3)$ ,  $E(1) = 32.56(3) \text{ cm}^{-1}$ ,  $E(2) = 96.3(1) \text{ cm}^{-1}$ , and  $E(3) = 195.5(4) \text{ cm}^{-1}$ .

Since the structure analysis did not produce a value of the dihedral angle  $\theta$  we are unable to calcu-

late a value for  $J$  using our GHP model [15] for  $J$  in terms of the structural parameters  $R$ ,  $\theta$ , and  $\phi$ . However, it is of interest to note that with values of  $R = 1.967 \text{ \AA}$  and  $\phi = 101.8^\circ$ , there is no value of  $\theta$  which corresponds to  $J = 32.56 \text{ cm}^{-1}$ ; with these  $R$  and  $\phi$  values, the maximum value of  $J$  calculated is  $19.0 \text{ cm}^{-1}$  (at  $\theta = 0^\circ$ ). In this parameter range, the value of  $J$  is extremely sensitive to small changes in  $R$  and insensitive to relatively large changes in  $\theta$  and  $\phi$ . Thus, with  $R = 1.94 \text{ \AA}$  and  $\phi = 101.8^\circ$ , we calculate  $J$  to be  $32.6 \text{ cm}^{-1}$  at  $\theta = 0^\circ$  and  $24.6 \text{ cm}^{-1}$  at  $\theta = 30^\circ$ . Similarly, increasing  $\phi$  by  $4^\circ$  increases the calculated value of  $J$  by only  $0.5 \text{ cm}^{-1}$ . Clearly, the present model is in only fair agreement with the observed structural and magnetic data, but it should be noted that this may merely be due to an inadequate value of the parameter  $a$  in the expression [15]

$$J = \exp(-ar)\{bJ_{AF} - cJ_F\},$$

where  $J_{AF}$  and  $J_F$  are the angularly-dependent anti-ferromagnetic and ferromagnetic contributions to  $J$ , rather than to any conceptual error in the model's approach. The parameters  $a$ ,  $b$ ,  $c$  will be refined further when additional precise structural and magnetic data become available. At the present stage, however, it must be concluded that the model is not yet sufficiently refined to serve as a predictor of precise structural parameters on the basis of magnetic measurements alone.

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TABLE V. Magnetic Results Derived from Susceptibility Data.

Parameter	Model 1 <sup>a</sup>	Model 2 <sup>a</sup>	Model 3 <sup>a</sup>
$J$ ( $\text{cm}^{-1}$ )	32.40(2)	32.31(10)	—
$j$ ( $\text{cm}^{-1}$ )	—	0.01(1)	—
$E(1)$ ( $\text{cm}^{-1}$ )	32.40(2) <sup>b</sup>	32.4(1) <sup>b</sup>	32.56(2)
$E(2)$ ( $\text{cm}^{-1}$ )	97.20(6) <sup>b</sup>	97.1(3) <sup>b</sup>	96.3(1)
$E(3)$ ( $\text{cm}^{-1}$ )	194.4(1) <sup>b</sup>	194.0(6) <sup>b</sup>	195.5(4)
$g$	1.990(1)	1.987(3)	1.981(3)
NO <sup>c</sup>	500	500	500
$\text{var}/f^d$	1.73	1.64	1.46
% monomer	0.466(3)	0.464(3)	0.454(3)

<sup>a</sup>See text. <sup>b</sup>Calculated from the derived parameters for comparison with other models. <sup>c</sup>The number of susceptibility data. <sup>d</sup>See text. The number of degrees of freedom ( $f$ ) is NO(500) minus the number of variables.

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