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Synthesis and Characterization of the Chromium(III) Dimer Bis(μ -hydroxo)bis[[N,N' -bis(2-pyridylmethyl)-1,2-ethanediamine]chromium(III)] Perchlorate, [(bispicen)Cr(OH)]₂(ClO₄)₄·H₂O

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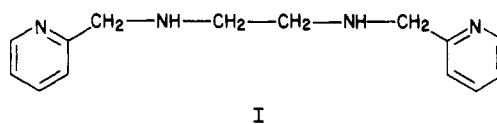
A new blue-violet isomer of the dinuclear chromium(III) complex cation bis(μ -hydroxo)bis[[N,N' -bis(2-pyridylmethyl)-1,2-ethanediamine]chromium(III)], [Cr(C₁₄H₁₈N₄)OH]₂⁴⁺ or [(bispicen)Cr(OH)]₂⁴⁺, has been synthesized. The complex forms from either the racemic or any optically active red isomer on standing in aqueous solution for an extended period. The crystal structure of the perchlorate salt, [(bispicen)Cr(OH)]₂(ClO₄)₄·H₂O, has been determined by using counter X-ray data. The complex crystallizes in the monoclinic space group $P2_1/n$ with 4 dinuclear formula units in a cell of dimensions $a = 12.434$ (2) Å, $b = 21.449$ (7) Å, $c = 15.495$ (4) Å, and $\beta = 98.63$ (2)°. The structure has been refined by full-matrix least-squares methods to a final value of the weighted R factor of 0.067 on the basis of 2366 independent intensities. The dinuclear cation contains one α -cis skeleton and one β -cis skeleton, the configuration at both centers being the same ($\Delta\Delta$ or $\Lambda\Lambda$). The configurations at the secondary nitrogen atoms in the β skeleton are the same, so the complex isolated may be described as a racemic mixture of $\Lambda(\alpha)$ -SS- $\Lambda(\beta)$ -RR' and $\Delta(\alpha)$ -RR- $\Delta(\beta)$ -SS' forms. This enantiomeric pair is one of four possible pairs that can be formed from one cis- α and one cis- β skeleton. The magnetic susceptibility of the complex indicates antiferromagnetic coupling. The susceptibility data were fitted to a model that assumes independent triplet, quintet, and septet energies, but the results are almost consistent with the Landé rule derived from the Van Vleck expression. The triplet energy is 23.79 (5) cm⁻¹. The structural parameters derived from the crystallographic experiment have been used to calculate the triplet energy on the basis of the semiempirical Glerup-Hodgson-Pedersen model and lead to a calculated value of 25.9 cm⁻¹, which is in remarkable agreement with the observed value.

Introduction

The investigation of the spectroscopic, structural, and magnetic properties of dinuclear chromium(III) complexes continues to be an area of intense research activity,²⁻¹⁷ with particular emphasis on attempts to correlate the spectral and magnetic properties of these complexes with specific structural features. For the bis(μ -hydroxo) complexes, most of which have been of the symmetric forms [L₂Cr(OH)]₂ⁿ⁺ or [A₄Cr(OH)]₂ⁿ⁺ (where L is a bidentate and A is a monodentate ligand), it is generally agreed that the isotropic magnetic coupling constant, J , is determined by the geometry of the Cr₂O₂ bridging unit. Thus, the importance of the Cr—O—Cr angle, ϕ , and the Cr—O bond length, R , have been noted by several groups.^{2,4,12,14} More recently, both we^{3,5,7,18,19} and others¹⁵ have noted the significance of the dihedral angle θ between the O—H vector and the Cr₂O₂ plane, and we have now derived a quantitative relationship between J and these three structural parameters for this class of complexes.⁶

As was noted above, however, the only dimers that have been

structurally characterized predominantly possess rigorous C_1 but nearly C_{2h} symmetry^{5,9-11,13} although a few have approximated D_2 symmetry.^{8,20} Our recent synthesis²¹ of the complex [(bispicen)Cr(OH)]₂⁴⁺, where bispicen is N,N' -bis(2-pyridylmethyl)-1,2-ethanediamine (I), a tetradentate ligand, provided



I

us with an opportunity to investigate the effect of gross deviations from C_{2h} and/or D_2 symmetry on the magnetic exchange parameter J . Presumably, if a highly unsymmetric isomer fits into the general Glerup-Hodgson-Pedersen (GHP) formulation⁶ we can be confident that the local symmetry at each chromium center plays an insignificant role in determining J ; this is not the case for the four-coordinate copper(II) analogues, [CuLOH]₂ⁿ⁺.²²

In our earlier work²¹ we described the synthesis and resolution of a red racemic complex to which we assigned the formula [(bispicen)Cr(OH)]₂I₄·3H₂O on the basis of its chemical and spectroscopic properties. Since we have not yet obtained a suitable sample for crystallographic analysis, we are admittedly unable to totally exclude the possibility that the complex is not a singly bridged complex of the type [(H₂O)(bispicen)Cr(OH)Cr(bispicen)(OH)]I₄·2H₂O in view of the discovery of an equilibrium in solution between the analogous singly and doubly bridged ethanediamine complexes.²³⁻²⁵ It is noteworthy, however, that recent magnetic measurements on this red complex also support the assignment as a doubly bridged form in the solid state, just as the spec-

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troscopic data indicate that form in solution.

In solution the red dimer can be transformed to another dinuclear species, which is the main subject of the present paper. This new blue-violet complex has now been examined by spectroscopic, magnetic, and crystallographic techniques and is shown to be a doubly bridged complex. We here report the results of our studies of this isomer of the complex [(bispicen)Cr(OH)]₂(ClO₄)₄·H₂O. Numerous isomers of this formulation can exist, at least theoretically, because of both the chirality associated with the ligand coordination and the availability of both α and β configurations. The stereochemistry of complexes of this type is discussed in detail.

Experimental Section

Reagents. Pyridine-2-carboxaldehyde was purchased from Merck-Schuchardt. *N,N'*-Bis(2-pyridylmethyl)-1,2-ethanediamine was prepared following mainly the method described by Goodwin and Lions,²⁶ but with the modification published before.²¹ 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 (ϵ , λ), where the molar extinction coefficient ϵ is in units of L mol⁻¹ cm⁻¹ and λ 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 4.0–298 K at a field strength of 12 000 Oe. The magnetic field was calibrated with Hg[Co(NCS)₄].²⁷ A more detailed description of the equipment is published elsewhere.^{18,28}

Syntheses. **Bis(μ -hydroxo)bis[*N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine]chromium(III) Iodide, Red Form,** [(C₁₄H₁₈N₄)Cr(OH)₂Cr(C₁₄H₁₈N₄)]₂·3H₂O (1). The compound was prepared as described before.²¹ In some samples the content of crystal water was 4 mol.

(-)-Bis(μ -hydroxo)bis[*N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine]chromium(III) Iodide, Red Form, D-(-)-[(C₁₄H₁₈N₄)Cr(OH)₂Cr(C₁₄H₁₈N₄)]₂·3H₂O (2). The racemic red dimer was resolved with sodium antimonyl D-(+)-tartrate as described before.²¹

Bis(μ -hydroxo)bis[*N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine]chromium(III) Perchlorate, Blue-Violet Form, [(C₁₄H₁₈N₄)Cr(OH)₂Cr(C₁₄H₁₈N₄)](ClO₄)₄·H₂O (3). Compound 1 (0.59 g, 0.55 mmol) was dissolved in water (60 mL), and the solution was left in a stoppered flask. After 5 weeks the solution was diluted 10 times and transferred to a column of SP-Sephadex C-25 (length ~10 cm, diameter ~4 cm). Elution with a solution of sodium sulfate (0.15 M) gave three bands, a very weak, orange band, presumably a monomer 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 11–12% 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 immediately diluted 20 times and transferred to a new column (length ~10 cm, diameter ~2.5 cm), where residual sodium and sulfate ions were eluted with 0.1 M hydrochloric acid. The complex was eluted afterwards with 4 M hydrochloric acid. The chloride was precipitated with ethanol (99%) and ether from the ice-cooled solution. When ether and ethanol had evaporated from the sticky solid (the next day), the chloride was converted to the corresponding perchlorate by the addition of a saturated solution of sodium perchlorate (4 g) to its hot water solution (15 mL). Cooling on ice, filtering, and washing with ethanol (95%) left 0.31 g of glistening, blue-violet, practically pure crystals (61%). Recrystallization from boiling water normally resulted in an additional loss of 15–17%. Anal. Calcd for [Cr(C₁₄H₁₈N₄)(OH)]₂(ClO₄)₄·H₂O: Cr, 10.01; C, 32.39; N, 10.79; H, 4.27; Cl, 13.52. Found: Cr, 10.02; C, 32.25; N, 10.67; H, 3.91; Cl, 13.65. In other cases the compound crystallized

with 0 or 2 mol of crystal water. UV: ϵ (λ_{\max}) 231 (540), 127 (384); ϵ (λ_{\min}) 45.4 (441), 78.7 (352). The synthetic procedure was repeated several times but with the optically active, red dimer, compound 2, as the starting material. The yield, however, always consisted of the optically inactive blue-violet dimer described above.

X-ray Data Collection. The data were collected and reduced in the manner described by Graves and Hodgson.²⁹ No preliminary X-ray photographs were taken. A prismatic crystal was mounted on a glass fiber in an arbitrary orientation and placed on an Enraf-Nonius CAD-4 automatic diffractometer. Accurate cell constants, obtained by least-squares refinement of the diffractometer settings of 25 reflections, were $a = 12.434$ (2) Å, $b = 21.449$ (7) Å, $c = 15.495$ (4) Å, and $\beta = 98.63$ (2)°; the observations were made at 20 °C with an assumed wavelength of 0.709 26 Å. ω scans of several axial reflections indicated that the crystal was of acceptable quality. The observed systematic absences were $k = 2n + 1$ for $0k0$ and $h + l = 2n + 1$ for $h0l$, which are consistent only with the monoclinic space group $P2_1/n$, a nonstandard setting of $P2_1/c$ ($C2_h$, No. 14). The measured density of 1.66 g cm⁻³ is in good agreement with the value of 1.688 g cm⁻³ calculated for 4 binuclear formula units per cell; consequently, in space group $P2_1/n$ no crystallographic symmetry is imposed on the dimers.

Diffraction data were collected on the CAD-4 diffractometer with Mo radiation [$\lambda(\text{Mo K}\alpha_1) = 0.709 26$ Å] and a graphite monochromator. A unique set of data (hkl) in the range $2^\circ \leq 2\theta \leq 45^\circ$ was collected by the θ - 2θ scan technique. Intensity checks on three standard reflections were made after every 3 h of X-ray exposure time, and orientation checks on three different standard reflections were made after every 300 reflections. No systematic variation in these standards was encountered throughout data collection.

A small data set to be used for the empirical absorption correction was also collected. These consisted of ϕ scans for seven reflections with $\chi \geq 80^\circ$. For each reflection, scans were started at $\psi = 0^\circ$ and continue at 10° intervals so that a total of 37 scans was taken.

Data reduction was carried out in the usual fashion. The intensities were assigned standard deviations according to the formula of Ibers and co-workers,³⁰ and the intensities and their standard deviations were then corrected for Lorentz-polarization effects. The absorption coefficient for this compound with Mo K α radiation is 8.66 cm⁻¹, and examination of the ψ -scan data suggested that no correction for absorption was necessary in the present case. A total of 5556 independent intensities were collected, of which only 2366 had $l > 3\sigma(l)$; only these latter data were used in the refinement of the structure.

Structure Solution and Refinement. The structure was solved by the heavy-atom technique. The positions of the two independent chromium atoms were determined from a three-dimensional Patterson function. All other non-hydrogen atoms were located in subsequent difference Fourier maps. Isotropic least-squares refinement of these positions gave values of the usual agreement factors $R = \sum |F_o| - |F_c| / \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$ of 0.125 and 0.133, respectively. All least-squares calculations were carried out on F , the function minimized being $\sum w(|F_o| - |F_c|)^2$. All programs used were those provided in the CAD4/SDP package; atomic scattering factors are taken from ref 31.

Because of the potentially large number of variables involved, we elected to refine anisotropically only the Cr, Cl, O, and N atoms, i.e. the C atoms were refined isotropically. The locations of 36 of the 40 hydrogen atoms could be calculated on the basis of expected geometries at C or N, based on C-H and N-H distances of 0.95 and 0.90 Å, respectively. The H atoms on the bridging hydroxo groups were located in a difference Fourier map, but attempts to refine these positions were unsuccessful. We were unable to locate the hydrogen atoms on the water molecule. Indeed, the oxygen atom of the water molecule showed such a marked tendency to oscillate that eventually we were forced to fix its atomic positional parameter to those obtained from a difference Fourier map. Consequently, the final least-squares calculation included anisotropic refinement of the 33 atoms and isotropic refinement of the 28 carbon atoms, for a total of 407 variables and 2366 reflections. The contributions to F_c of the 38 hydrogen atoms

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Table I. Positional Parameters in $[(\text{bispicen})\text{Cr}(\text{OH})]_2(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$

atom	x	y	z
Cr(1)	0.1931 (2)	0.1368 (1)	0.2504 (1)
Cr(2)	-0.0479 (2)	0.1697 (1)	0.2223 (1)
Cl(1)	0.5408 (3)	0.3169 (2)	0.0374 (2)
Cl(2)	0.1865 (3)	0.3612 (2)	0.3830 (2)
Cl(3)	0.5914 (3)	0.0762 (2)	0.3522 (3)
Cl(4)	0.5992 (4)	0.3437 (3)	0.4152 (3)
O(1)	0.0800 (6)	0.1722 (4)	0.3107 (5)
O(2)	0.0625 (6)	0.1374 (4)	0.1603 (5)
O(11)	0.5269 (8)	0.2991 (5)	0.1229 (6)
O(12)	0.5982 (10)	0.2798 (5)	-0.0053 (8)
O(13)	0.4285 (12)	0.3111 (6)	-0.0103 (9)
O(14)	0.5633 (10)	0.3782 (5)	0.0263 (7)
O(21)	0.0997 (9)	0.3777 (6)	0.4233 (8)
O(22)	0.1592 (10)	0.3151 (6)	0.3210 (8)
O(23)	0.2698 (11)	0.3370 (6)	0.4410 (7)
O(24)	0.2275 (13)	0.4079 (7)	0.3463 (12)
O(31)	0.5340 (9)	0.1202 (6)	0.2953 (8)
O(32)	0.5329 (10)	0.0600 (7)	0.4158 (8)
O(33)	0.6214 (12)	0.0282 (7)	0.3037 (12)
O(34)	0.6908 (11)	0.1080 (8)	0.3878 (10)
O(41)	0.5549 (17)	0.3669 (11)	0.4661 (15)
O(42)	0.5515 (15)	0.3509 (9)	0.3346 (9)
O(43)	0.6990 (12)	0.3646 (8)	0.4202 (12)
O(44)	0.6035 (21)	0.2828 (9)	0.4441 (12)
OW	0.0640	0.0340	0.0390
N(1)A	0.2977 (8)	0.1125 (4)	0.1669 (6)
N(2)A	0.2602 (8)	0.2235 (5)	0.2263 (7)
N(1)B	0.1778 (8)	0.0476 (5)	0.3002 (7)
N(2)B	0.3155 (8)	0.1370 (5)	0.3549 (7)
N(1)C	-0.0330 (8)	0.2618 (5)	0.1796 (6)
N(2)C	-0.1601 (8)	0.2166 (5)	0.2847 (7)
N(1)D	-0.0937 (8)	0.0827 (5)	0.2617 (6)
N(2)D	-0.1821 (9)	0.1489 (5)	0.1294 (7)
C(2)A	0.333 (1)	0.1599 (6)	0.1202 (8)
C(3)A	0.404 (1)	0.1510 (7)	0.0604 (9)
C(4)A	0.437 (1)	0.0918 (7)	0.0476 (9)
C(5)A	0.404 (1)	0.0428 (7)	0.0928 (10)
C(6)A	0.335 (1)	0.0557 (7)	0.1538 (9)
C(2)B	0.228 (1)	0.0408 (7)	0.3837 (9)
C(3)B	0.226 (1)	-0.0163 (7)	0.4263 (10)
C(4)B	0.176 (1)	-0.0646 (8)	0.3813 (11)
C(5)B	0.127 (1)	-0.0601 (7)	0.3004 (10)
C(6)B	0.129 (1)	-0.0018 (7)	0.2556 (8)
C(2)C	-0.072 (1)	0.3023 (7)	0.2342 (9)
C(3)C	-0.062 (1)	0.3672 (8)	0.2123 (10)
C(4)C	-0.014 (1)	0.3817 (8)	0.1438 (10)
C(5)C	0.028 (1)	0.3417 (7)	0.0922 (10)
C(6)C	0.015 (1)	0.2791 (7)	0.1133 (9)
C(2)D	-0.150 (1)	0.0480 (7)	0.1967 (9)
C(3)D	-0.177 (1)	-0.0137 (7)	0.2126 (9)
C(4)D	-0.150 (1)	-0.0362 (7)	0.2947 (9)
C(5)D	-0.098 (1)	-0.0016 (7)	0.3606 (9)
C(6)D	-0.068 (1)	0.0595 (6)	0.3421 (8)
C(7)A	0.289 (1)	0.2210 (7)	0.1373 (9)
C(8)A	0.358 (1)	0.2346 (7)	0.2934 (9)
C(7)B	0.281 (1)	0.0973 (7)	0.4240 (9)
C(8)B	0.342 (1)	0.2038 (7)	0.3774 (9)
C(7)C	-0.119 (1)	0.2800 (7)	0.3073 (10)
C(8)C	-0.266 (1)	0.2180 (8)	0.2254 (11)
C(7)D	-0.178 (1)	0.0810 (7)	0.1141 (10)
C(8)D	-0.281 (1)	0.1651 (8)	0.1655 (10)
H(1)	0.104	0.193	0.355
H(2)	0.082	0.109	0.117

were included in the calculation, but no hydrogen atom parameter was varied. The final values of R and R_w were 0.077 and 0.067, respectively. The atomic positional parameters are presented in Table I, and listings of thermal parameters and observed and calculated structure amplitudes are available.

Results and Discussion

Stereochemistry of the Compounds. The binuclear ion $[(\text{bispicen})\text{Cr}(\text{OH})_2\text{Cr}(\text{bispicen})]^{4+}$ in principle exists in several isomeric forms. The isomerism becomes easier to grasp, when we start looking at the stereochemistry of the cis skeletons that

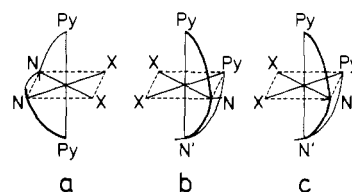


Figure 1. *cis*- α - and *cis*- β - $[\text{Cr}(\text{bispicen})\text{X}_2]^+$ (bispicen = *N,N'*-bis-(2-pyridylmethyl)-1,2-ethanediamine, $\text{C}_{14}\text{H}_{18}\text{N}_4$; py = the pyridine nitrogen): (a) Λ -*cis*- α -SS [$\Lambda(\alpha)$ -SS]; (b) Λ -*cis*- β -RR' [$\Lambda(\beta)$ -RR']; (c) Λ -*cis*- β -SR' [$\Lambda(\beta)$ -SR']. *R* and *S* refer to the absolute configuration of the coordinated secondary nitrogen atoms following the rules of Cahn et al.³⁵ In order to distinguish between the secondary nitrogen atoms, the atom that is in *cis* position to both the atoms X is denoted *N'*.

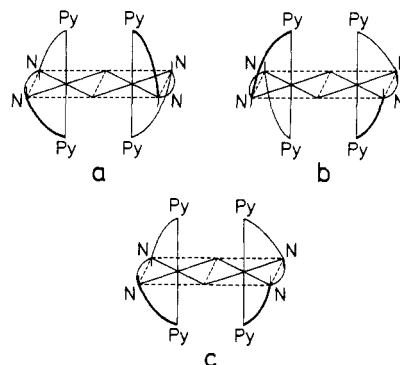


Figure 2. $[(\text{bispicen})\text{Cr}(\text{OH})_2\text{Cr}(\text{bispicen})]^{4+}$ isomers that can be constructed from two *cis*- α skeletons: (a) $\Lambda(\alpha)$ -SS- $\Lambda(\alpha)$ -SS; (b) $\Delta(\alpha)$ -RR- $\Delta(\alpha)$ -RR; (c) $\Lambda(\alpha)$ -SS- $\Delta(\alpha)$ -RR.

are the building blocks from which the dimers can be constructed.

The general formula *cis*- $[\text{Cr}(\text{bispicen})\text{X}_2]^+$ includes two types of geometrical isomers, namely isomers with the symmetrical *cis*- α configuration (Λ -*cis*- α and Δ -*cis*- α) represented in Figure 1a by the enantiomer with the configuration Λ around the central atom³² and isomers with the unsymmetrical *cis*- β configuration (Λ -*cis*- β and Δ -*cis*- β) represented in Figure 1b,c by the enantiomers with the configuration Λ around the central atom.

Sargeson and Searle³³ drew attention to the fact that one of the secondary nitrogen atoms in the *cis*- β - $[\text{Co}(\text{trien})\text{X}_2]^+$ ion (trien is the tetradentate ligand triethylenetetramine) can coordinate in two different ways while the other secondary nitrogen atom is bound in a fixed position. In the case of the *cis*- α - $[\text{Co}(\text{trien})\text{X}_2]^+$ ion both secondary nitrogen atoms are forced to take up fixed positions. Similarly the asymmetry of the coordinated secondary nitrogen atoms in the *cis*- β - $[\text{Cr}(\text{bispicen})\text{X}_2]^+$ ion creates two pairs of enantiomers: Λ -*vis*- β -RR' (Figure 1b) (and the enantiomer Δ -*cis*- β -SS') and Λ -*cis*- β -SR' (Figure 1c) (and the enantiomer Δ -*cis*- β -RS').³⁴ Only one enantiomer pair is probable for the *cis*- α - $[\text{Cr}(\text{bispicen})\text{X}_2]^+$ ion, namely Λ -*cis*- α -SS (Figure 1a) and Δ -*cis*- α -RR.

Returning now to the dimeric compounds, we find that two *cis*- α skeletons may be combined to form three different

(32) The nomenclature Λ and Δ is defined in: *Inorg. Chem.* **1970**, *9*, 1. For its application to bridged dimers, see: Thewalt, U.; Jensen, K. A.; Schäffer, C. E. *Inorg. Chem.* **1972**, *11*, 2129.

(33) Sargeson, A. M.; Searle, G. H. *Inorg. Chem.* **1967**, *6*, 787.

(34) *R* and *S* refer to the absolute configuration of the coordinated nitrogen atoms following the rules of Cahn et al.³⁵ In order to distinguish between the secondary nitrogen atoms, the atom which is in *cis* position to both the atoms X is denoted *N'*.

(35) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

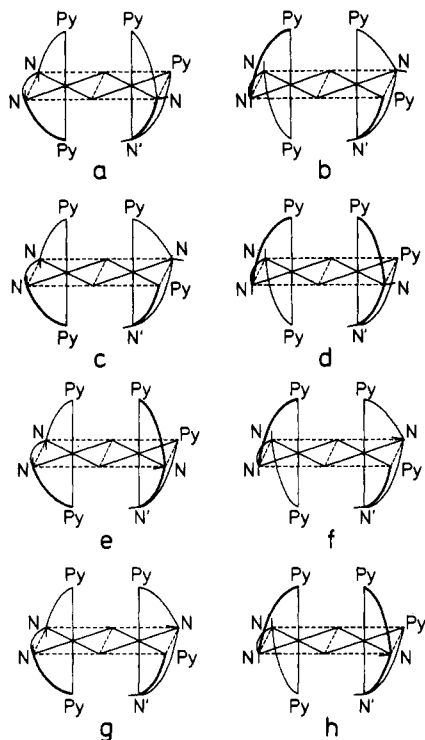
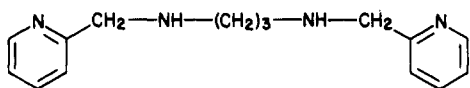


Figure 3. [(bispicen)Cr(OH)]₂Cr(bispicen)]⁴⁺ isomers that can be constructed from a cis- α and a cis- β skeleton (compounds are pairwise enantiomers): (a) $\Delta(\alpha)$ -SS- $\Delta(\beta)$ -RR'; (b) $\Delta(\alpha)$ -RR- $\Delta(\beta)$ -SS'; (c) $\Delta(\alpha)$ -SS- $\Delta(\beta)$ -SS'; (d) $\Delta(\alpha)$ -RR- $\Delta(\beta)$ -RR'; (e) $\Delta(\alpha)$ -SS- $\Delta(\beta)$ -SR'; (f) $\Delta(\alpha)$ -RR- $\Delta(\beta)$ -RS'; (g) $\Delta(\alpha)$ -SS- $\Delta(\beta)$ -RS'; (h) $\Delta(\alpha)$ -RR- $\Delta(\beta)$ -SR'.

isomeric dimers (Figure 2). In the first work on bis(μ -hydroxo) complexes with bispicen²¹ we described the preparation and resolution of a red compound, namely a racemate of the two enantiomers $\Delta(\alpha)$ -SS- $\Delta(\alpha)$ -SS and $\Delta(\alpha)$ -RR- $\Delta(\alpha)$ -RR (Figure 2a,b). We thought at that time that the existence of any other isomer could be excluded because of steric hindrances. In that respect we were wrong, as we shall demonstrate here (vide infra) that the present blue-violet isomer consists of one of the four pairs of enantiomers that can be constructed from one cis- α and one cis- β skeleton (see Figure 3). We have not yet observed any of the numerous isomeric dimers of this complex which can be constructed from two cis- β skeletons, but it is noteworthy that with the closely related ligand bispicen (II) we have structurally characterized a dimer of this kind.³⁶



II

As is demonstrated by the structural analysis (vide infra) in water solution the red, symmetric ion (Figure 2a,b) is transformed to an isomeric blue-violet, unsymmetric form (Figure 3a,b). The transformation evidently involves a racemization, and the interesting mechanism will be studied in greater detail by following the analogous transformation of the parent *cis*- α -diaqua[*N,N'*-bis-(2-pyridylmethyl)-1,2-ethanediamine]chromium(III) ion to a *cis*- β isomer. Although the blue-violet diol is a racemate, we have not yet accomplished its resolution.

The absorption spectra of the two dimers (visible region) are shown in Figure 4, and a comparison of the spectral data

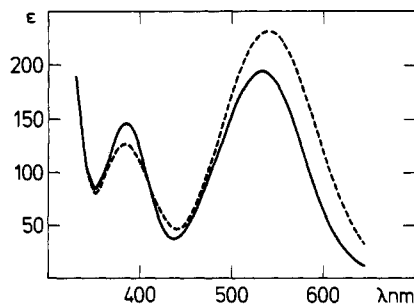


Figure 4. Absorption spectra (0.1 M HCl; visible region): [(bispicen)Cr(OH)]₂Cr(bispicen)]⁴⁺, red forms, $\Delta(\alpha)$ -SS- $\Delta(\alpha)$ -SS, $\Delta(\alpha)$ -RR- $\Delta(\alpha)$ -RR (—); [(bispicen)Cr(OH)]₂Cr(bispicen)]⁴⁺, blue-violet form, $\Delta(\alpha)$ -SS- $\Delta(\beta)$ -RR', $\Delta(\alpha)$ -RR- $\Delta(\beta)$ -SS' (---).

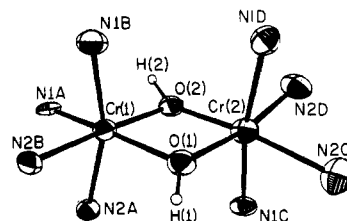


Figure 5. View of the inner coordination sphere in [(bispicen)Cr(OH)]₂(ClO₄)₄·H₂O. Hydrogen atoms are shown as open spheres of arbitrary size, but other ellipsoids are drawn at the 40% probability level. Atoms N(1)A etc. are pyridine nitrogen atoms while N(2)A etc. are ethylenediamine nitrogen atoms.

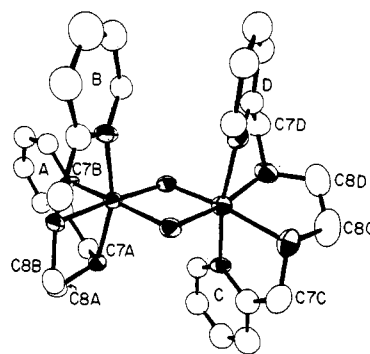


Figure 6. View of the cation in [(bispicen)Cr(OH)]₂(ClO₄)₄·H₂O. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 40% probability level. The dimer shown here has the $\Delta\Delta\delta\lambda$ conformation, but in this centrosymmetric space group there are an equal number of $\Delta\Delta\lambda\delta$ forms.

Table II. Electronic Spectral Parameters for Bis(μ -hydroxo) Complexes of Chromium(III) with *N,N'*-Bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen) in 0.1 M HCl (Region 700–300 nm)

compd	ϵ (λ_{max} , nm)	half-width (δ), cm^{-1}
[Cr(bispicen)(OH)] ₂ ⁴⁺ , red form	198 (534), 151 (385)	3914
[Cr(bispicen)(OH)] ₂ ⁴⁺ , blue-violet form	231 (540), 127 (384)	4208

appears in Table II. As might have been expected the asymmetry of the blue-violet dimer is reflected in the broader absorption bands; for example, the difference in the half-widths of the first bands is about 300 cm^{-1} .

Description of the Structure. The structure consists of binuclear [(bispicen)Cr(OH)]₂⁴⁺ cations that are hydrogen bonded to perchlorate anions and the water molecule. A view of the inner coordination sphere of the cation is given in Figure

(36) Fischer, H. R.; Hodgson, D. J.; Michelsen, K.; Pedersen, E. *Inorg. Chim. Acta*, in press.

Table III. Internuclear Separations (Å) in [(bispicen)Cr(OH)]₂(ClO₄)₄·H₂O

		Inner Coordination Sphere			
Cr(1)–O(1)	1.955 (5)	Cr(2)–O(1)	1.938 (5)		
Cr(1)–O(2)	1.976 (5)	Cr(2)–O(2)	1.918 (5)		
Cr(1)–N(1)A	2.035 (7)	Cr(2)–N(1)C	2.101 (7)		
Cr(1)–N(2)A	2.096 (7)	Cr(2)–N(2)C	2.074 (7)		
Cr(1)–N(1)B	2.081 (7)	Cr(2)–N(1)D	2.070 (7)		
Cr(1)–N(2)B	2.049 (7)	Cr(2)–N(2)D	2.081 (7)		
Cr(1)–Cr(2)	3.046 (2)				
		Ligands			
	A	B	C	D	av
N(1)–C(2)	1.358 (10)	1.358 (10)	1.352 (11)	1.357 (10)	1.356 (3)
C(2)–C(3)	1.384 (11)	1.394 (12)	1.442 (13)	1.398 (11)	1.404 (26)
C(3)–C(4)	1.360 (12)	1.351 (12)	1.332 (12)	1.357 (12)	1.350 (13)
C(4)–C(5)	1.361 (12)	1.310 (11)	1.332 (12)	1.346 (12)	1.337 (19)
C(5)–C(6)	1.395 (11)	1.431 (11)	1.396 (11)	1.402 (12)	1.406 (17)
C(6)–N(1)	1.331 (10)	1.359 (10)	1.317 (10)	1.335 (10)	1.336 (17)
C(2)–C(7)	1.462 (11)	1.469 (11)	1.435 (13)	1.458 (12)	1.456 (15)
C(7)–N(2)	1.474 (10)	1.484 (10)	1.475 (12)	1.479 (12)	1.478 (5)
N(2)–C(8)	1.499 (10)	1.500 (11)	1.486 (12)	1.472 (12)	1.489 (13)
C(8)–C(8)'	1.502		1.461		
		Anions			
		X			
	1	2	3	4	
Cl(X)–O(X1)	1.413 (6)	1.372 (7)	1.409 (8)	1.141 (16)	
Cl(X)–O(X2)	1.314 (7)	1.385 (8)	1.354 (8)	1.310 (10)	
Cl(X)–O(X3)	1.484 (10)	1.368 (9)	1.361 (10)	1.310 (10)	
Cl(X)–O(X4)	1.361 (7)	1.295 (9)	1.446 (11)	1.379 (17)	
	av Cl–O = 1.356 (77)				

5, and the whole cation is shown in Figure 6. The bond lengths around the two chromium(III) centers and those in the ligands and the anions are tabulated in Table III. The bond angles in the cation and anions are given in Table IV.

The geometry about each chromium center is roughly octahedral. At Cr(1) the trans angles range from 160.5 (3) to 172.9 (3)°, the greatest distortion from linearity being the intraligand angle N(1)B–Cr–N(2)A. At Cr(2) the angular distortions are less severe, the trans angles lying in the narrow range 169.1 (3)–172.1 (3)°. The chelate-bond angles formed by the 2-(aminomethyl)pyridine portions of the ligands [i.e., N(1)A–Cr(1)–N(2)A, N(1)B–Cr(1)–N(2)B, etc.] fall in the narrow range of 77.5 (3)–78.9 (3)°, with an average value of 78.2 (7)°. The chelate angles formed by the ethylenediamine moieties [i.e., N(2)A–Cr(1)–N(2)B and N(2)C–Cr(2)–N(2)D], however, are larger, with values of 82.6 (3) and 84.3 (3)°. The bond lengths associated with the two chromium centers show surprising differences. Thus, the Cr(2)–O distances of 1.938 (5) and 1.918 (5) Å are considerably shorter than the Cr(1)–O separations of 1.955 (5) and 1.976 (5) Å. Indeed, while all of these distances fall within the range of 1.91–1.980 Å previously reported for bis(μ -hydroxo) dimers of chromium(III),^{5,6} the Cr(2)–O(2) value of 1.918 (5) Å falls at the lower extreme while the Cr(1)–O(2) length of 1.976 (5) Å is near the upper limit; it is noteworthy that the Cr–N bonds trans to Cr–O show the opposite trend, i.e. the in-plane Cr(2)–N distances of 2.074 (7) and 2.081 (7) Å are longer than the Cr(1)–N values of 2.035 (7) and 2.049 (7) Å.

The apparent reason for this striking difference is evident from an examination of Figure 6, which shows that the present complex contains one α -cis skeleton [at Cr(2)] and one β -cis skeleton [Cr(1)]. The configuration at both centers shown in Figure 6 is Δ , but in this centrosymmetric space group there is an equal number of $\Lambda\Lambda$ isomers. Moreover, it is evident from the figure that the configurations at the two secondary nitrogen atoms on Cr(1), namely N(2)A and N(2)B, are both the same and are *S* in the enantiomer shown in the figure. Thus, the enantiomer depicted in Figure 6 corresponds to that in Figure 3b, and hence the present complex is a racemate of

the two enantiomers $\Lambda(\alpha)$ -SS- $\Lambda(\beta)$ -RR' and $\Delta(\alpha)$ -RR- $\Delta(\beta)$ -SS' (Figure 3a,b).

The bridging Cr₂O₂ unit is very nearly planar, with no atom deviating by more than 0.015 (8) Å from the unweighted least-squares plane. The bridging Cr(1)–O(1)–Cr(2) and Cr(1)–O(2)–Cr(2) angles are 102.9 (4) and 103.1 (3)°, leading to an average value of ϕ of 103.0 (4)°; the O(1)–Cr(1)–O(2) and O(2)–Cr(2)–O(1) angles are 76.2 (2) and 77.9 (2)°, and the Cr(1)–Cr(2) separation is 3.046 (2) Å. The Cr–O–Cr angles in the present structure are among the largest values reported for dimers of this kind, falling just inside the range of 97.6 (1)–103.4 (1)° previously observed.^{10,37} The hydrogen atoms on the bridging hydroxo groups, H(1) and H(2), lie out of the bridging plane, H(1) sitting 0.29 Å above the plane while H(2) is 0.26 Å below it. These displacements correspond to dihedral angles $\theta(1)$ and $\theta(2)$ of 20.4 and 16.0°, respectively, and an average value θ of 18 (3)°. Since the hydrogen atom parameters were not refined, this estimate of θ is necessarily imprecise.

The four independent pyridine rings in the bispicen ligands are all planar within the limits of the precision of this experiment, no atom deviating by more than 1.3 σ from the six-atom least-squares plane. The intraligand distances are apparently normal. In the dimer shown in Figure 6 the ethylenediamine ring conformation is δ at Cr(1) [N(2)A–C(8)A–C(8)B–N(2)B–Cr(1)] and λ at Cr(2) [N(2)C–C(8)C–C(8)D–N(2)D–Cr(2)], so that the dimer shown is $\Delta\Delta\delta\lambda$, but in this centrosymmetric space group there are an equal number of enantiomeric $\Lambda\Lambda\lambda\delta$ conformers.

There is extensive hydrogen bonding in the crystals, with all potential donor atoms participating. The bridging hydroxo groups O(1)–H(1) and O(2)–H(2) form hydrogen bonds to perchlorate anions, the O(1)···O(12) and O(1)–H(1)···O(12) distance and angle being 3.008 (10) Å and 151° while the O(2)···O(41) and O(2)–H(2)···O(41) values are 3.00 (3) Å and 123°, respectively. The O(2)–H(2) hydrogen bonding

(37) Kaas, K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1976, 32, 2021.

Table IV. Internuclear Angles (deg) in [(bispicen)Cr(OH)]₂(ClO₄)₄·H₂O

	Cation				
O(1)-Cr(1)-O(2)	76.2 (2)	O(1)-Cr(2)-O(2)	77.9 (2)		
O(1)-Cr(1)-N(1)A	167.8 (3)	O(1)-Cr(2)-N(1)C	95.4 (3)		
O(1)-Cr(1)-N(2)A	94.3 (3)	O(1)-Cr(2)-N(2)C	101.2 (3)		
O(1)-Cr(1)-N(1)B	93.9 (3)	O(1)-Cr(2)-N(1)D	92.8 (3)		
O(1)-Cr(1)-N(2)B	97.1 (3)	O(1)-Cr(2)-N(2)D	169.2 (3)		
O(2)-Cr(1)-N(1)A	95.1 (2)	O(2)-Cr(2)-N(1)C	94.5 (3)		
O(2)-Cr(1)-N(2)A	100.1 (2)	O(2)-Cr(2)-N(2)C	172.1 (3)		
O(2)-Cr(1)-N(1)B	99.1 (3)	O(2)-Cr(2)-N(1)D	94.1 (3)		
O(2)-Cr(1)-N(2)B	172.9 (3)	O(2)-Cr(2)-N(2)D	97.9 (3)		
N(1)A-Cr(1)-N(2)A	78.7 (3)	N(1)C-Cr(2)-N(2)C	77.7 (3)		
N(1)A-Cr(1)-N(1)B	96.0 (3)	N(1)C-Cr(2)-N(1)D	169.1 (3)		
N(1)A-Cr(1)-N(2)B	91.9 (3)	N(1)C-Cr(2)-N(2)D	94.8 (3)		
N(2)A-Cr(1)-N(1)B	160.5 (3)	N(2)C-Cr(2)-N(1)D	93.8 (3)		
N(2)A-Cr(1)-N(2)B	82.6 (3)	N(2)C-Cr(2)-N(2)D	84.3 (3)		
N(1)B-Cr(1)-N(2)B	78.9 (3)	N(1)D-Cr(2)-N(2)D	77.5 (3)		
Cr(1)-O(1)-Cr(2)	102.9 (4)	Cr(1)-O(2)-Cr(2)	103.1 (3)		
Ligands					
	A	B	C	D	av
Cr-N(1)-C(2)	115.9 (5)	113.4 (5)	110.5 (5)	114.1 (5)	113.5 (22)
Cr-N(1)-C(6)	127.0 (5)	126.0 (5)	125.7 (5)	125.0 (5)	125.9 (8)
C(2)-N(1)-C(6)	117.1 (8)	120.5 (8)	123.6 (8)	120.8 (8)	120.5 (27)
Cr-N(2)-C(7)	107.0 (5)	107.8 (5)	109.0 (5)	106.0 (6)	107.5 (13)
Cr-N(2)-C(8)	108.8 (5)	107.2 (5)	108.3 (5)	108.6 (5)	108.2 (7)
C(7)-N(2)-C(8)	111.7 (8)	117.2 (8)	111.7 (8)	110.4 (8)	112.8 (30)
N(1)-C(2)-C(3)	122.9 (9)	120.5 (9)	115.0 (9)	120.0 (9)	119.6 (33)
N(1)-C(2)-C(7)	114.4 (8)	115.4 (8)	120.5 (8)	114.4 (8)	116.2 (29)
C(3)-C(2)-C(7)	122.8 (9)	124.1 (9)	124.6 (9)	125.6 (9)	124.3 (12)
C(2)-C(3)-C(4)	117.7 (9)	118.0 (9)	118.5 (9)	117.9 (9)	118.0 (3)
C(3)-C(4)-C(5)	121.6 (9)	123.2 (9)	126.2 (9)	122.7 (9)	123.4 (20)
C(4)-C(5)-C(6)	117.4 (9)	119.5 (9)	114.1 (9)	118.1 (9)	117.3 (23)
C(5)-C(6)-N(1)	123.3 (8)	118.2 (8)	122.4 (8)	120.3 (8)	121.1 (23)
C(2)-C(7)-N(2)	110.6 (8)	108.9 (8)	106.8 (9)	110.2 (8)	109.1 (17)
N(2)-C(8)-C(8')	109.1 (8)	105.7 (8)	113.5 (8)	112.6 (8)	110.1 (36)
Anions					
	X				
	1	2	3	4	
O(X1)-Cl(X)-O(X2)	117.4 (6)	111.9 (6)	110.6 (6)	114.3 (16)	
O(X1)-Cl(X)-O(X3)	101.9 (5)	111.7 (6)	108.4 (8)	111.2 (16)	
O(X1)-Cl(X)-O(X4)	115.9 (5)	112.8 (7)	104.3 (6)	100.9 (16)	
O(X2)-Cl(X)-O(X3)	103.9 (6)	105.5 (6)	115.4 (7)	107.8 (9)	
O(X2)-Cl(X)-O(X4)	112.6 (6)	108.7 (9)	111.4 (7)	114.3 (10)	
O(X3)-Cl(X)-O(X4)	102.4 (5)	105.8 (8)	106.1 (7)	108.3 (13)	
av O-Cl-O = 109.3 (47)					

may be bifurcated, involving both the interaction above and an interaction with the water molecule with associated O(2)···O_w and O(2)-H(2)···O_w parameters of 2.91 Å and 155°. The four ethylenediamine nitrogen atoms all form hydrogen bonds to the anions, although the interaction involving N(2)C is apparently very weak while N(2)B may form a bifurcated hydrogen bond to two oxygen atoms from the same perchlorate group. The probable hydrogen bonding is tabulated in Table V. Since we were unable to locate the hydrogen atoms on the water molecule O_w, it is impossible to assess the potential donor hydrogen bonds involving O_w.

The perchlorate groups are all approximately tetrahedral; the Cl(4)-O(41) distance of 1.14 (2) Å is significantly shorter than the other 15 values of 1.295 (9)-1.446 (11) Å and may be in error because of the proximity of O(41) and the unrefined water molecule, O_w. The other 15 distances have an average value of 1.37 (5) Å, which is similar to that found in other perchlorate complexes.³⁸ Similarly, the 24 independent O-Cl-O angles show a normal range of 101 (2)-117.4 (6)°, with an average value of 109 (5)°; these angles are again unremarkable. The metrical parameters in the four anions are summarized in Tables III and IV.

Table V. Probable A-H···B Hydrogen Bonds

A	H	B	A-B, Å	H-B, Å	A-H···B, deg
O(1)	H(1)	O(12)	3.008 (10)	2.24	151
O(2)	H(2)	O(41)	3.00 (3)	2.37	123
O(2)	H(2)	OW	2.91	2.01	155
N(2)A	HN2A	O(22)	2.85 (1)	2.11	138
N(2)B	HN2B	O(31)	3.02 (1)	2.17	155
N(2)B	HN2B	O(32)	3.19 (1)	2.44	139
N(2)C	HN2C	O(13)	3.26 (1)	2.51	136
N(2)D	HN2D	O(23)	2.91 (1)	2.16	138

Magnetic Properties. The average magnetic susceptibility and effective magnetic moment of a polycrystalline sample of the complex as functions of temperature are shown in Figure 7. The susceptibilities were fitted as described elsewhere³ to the expression

$$\chi_A' = -\frac{N}{H} \frac{\sum_i (\partial E_i / \partial H) \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)}$$

where the quantities E_i are the energies of the sixteen components of the ground-state manifold. The fit was accomplished by using three separate models for the exchange

(38) Haddad, M. S.; Wilson, S. R.; Hodgson, D. J.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1981**, *103*, 384 and references therein.

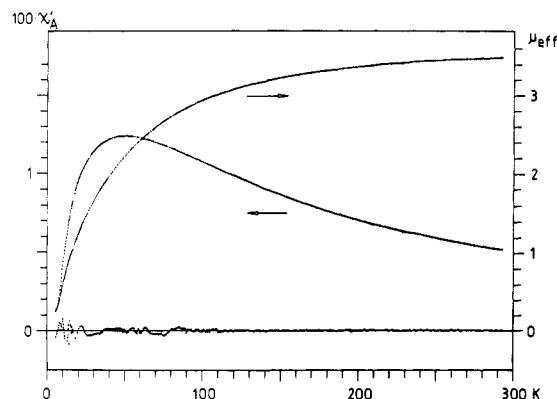


Figure 7. Magnetic susceptibility per chromium atom (left scale, cgsu) and effective magnetic moment (right scale, μ_B) of $[(\text{bispicen})\text{Cr}(\text{OH})_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}]$. The lower, almost random, distribution of dots around the abscissa gives $50(\chi_{\text{obsd}} - \chi_{\text{calcd}})$ where χ_{calcd} is obtained from the parameters of model 3 in Table VI.

Hamiltonian. Model 1 was based on the Van Vleck Hamiltonian

$$H = JS_1 \cdot S_2$$

in which the triplet, quintet, and septet energies are defined as J , $3J$, and $6J$, respectively, with a single exchange variable J . Model 2 involved the same Hamiltonian expanded to include a biquadratic exchange term³⁹

$$H = JS_1 \cdot S_2 - j(S_1 \cdot S_2)^2$$

that allows two variable exchange parameters (J and j) and in which the triplet, quintet, and septet energies are $J + 6.5j$, $3J + 13.5j$, and $6J + 9.0j$, respectively. In model 3 we used the entirely generalized Hamiltonian

$$H = E(S') + g\mu_B M_{S'}$$

where $S' (=S_1 + S_2)$ can have the values 0–3 in the case of two $S = 3/2$ nuclei. In this form of the Hamiltonian the energies $E(1)$, $E(2)$, and $E(3)$ of the triplet, quintet, and septet states, respectively, are independent magnetic variables. The model neglects any zero-field splitting within these levels and assumes (as do the other models) an isotropic Zeeman effect. In addition to the exchange variables, in all three cases we also refined the isotropic g value, a temperature-independent contribution to the susceptibility, and a parameter that corrects the susceptibilities for the assumed presence of a small quantity of monomeric impurity (assumed to obey the Curie law).

The results of the data fitting are shown in Table VI. It is apparent that the observed susceptibility data are reasonably

Table VI. Parameters Derived from Magnetic Susceptibility Data^a

parameter	model 1	model 2	model 3
J , cm^{-1}	23.42 (3)	22.90 (15)	
j , cm^{-1}		0.070 (19)	
$E(1)$, cm^{-1}	23.42 (3) ^b	23.35 (15) ^b	23.79 (5)
$E(2)$, cm^{-1}	70.26 (9) ^b	69.6 (5) ^b	69.3 (2)
$E(3)$, cm^{-1}	140.5 (2) ^b	138.0 (9) ^b	142.4 (8)
g	1.991 (3)	1.993 (6)	1.981 (6)
f^c	396	395	394
var/ f^d	5.52	5.37	1.12
% monomer	0.026 (5)	0.024 (7)	0.026 (7)

^a See text for a description of the three models. ^b Calculated from the derived parameter(s) for comparison with results from other models. ^c The number of degrees of freedom in the calculation; this is simply the number of data (400) minus the number of variables. ^d Variance/degree of freedom.

well described by all three models. Inclusion of the biquadratic term in model 2 leads to little improvement over model 1, the variance/degree of freedom falling only from 5.52 to 5.37. Application of model 3 gives significant improvement, variance/degree of freedom falling to 1.12. Necessarily, as shown in Table VI, all three models lead to approximately the same derived results, the best fit (model 3) yielding $g = 1.981$ (6), $E(1) = 23.79$ (5) cm^{-1} , $E(2) = 69.3$ (2) cm^{-1} , and $E(3) = 142.4$ (8) cm^{-1} .

The results here can be compared with those that we have previously obtained for other dimeric species of this general type. Using the average values of the Cr–O bridge distances (R), the Cr–O–Cr angles (ϕ), and the dihedral angles (θ) of 1.947 Å, 103.0°, and 18° determined here, we calculate by using the GHP model that we have described elsewhere⁶ a value of 25.9 cm^{-1} for J . With these particular structural parameters, the calculated value of J is more sensitive to small variations in R than in θ or ϕ . This calculated J value is, of course, very similar to the value of 23.8 cm^{-1} observed here and may serve to confirm the validity of the model.

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Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, and observed and calculated structure amplitudes (22 pages). Ordering information is given on any current masthead page.

(39) Regrettably, the form of this Hamiltonian is incorrectly given in some of our earlier papers (e.g., eq 3 in ref 3), but all derived parameters in those papers are correct.